

# SYMPOSIUM K

## K: Functional Organic Materials and Devices

December 1 - 5, 2003

### Chairs

**Ghassan E. Jabbour**

Optical Sciences Center  
University of Arizona  
Tucson, AZ 85721  
520-626-8324

**Cherie R. Kagan**

IBM T. J. Watson Research Center  
P.O. Box 218  
Yorktown Heights, NY 10598  
914-945-3003

**Vladimir Bulovic**

Dept. of Electrical Engr. & Computer Science  
Massachusetts Institute of Technology  
Cambridge, MA 02139  
617-253-7012

**Mary E. Galvin**

Dept. of Materials Science & Engr.  
University of Delaware  
301 Spencer Laboratory  
Newark, NJ 19716-3106  
302-831-0873

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\* Invited paper

**8:30 AM \*K1.1**

**Application Driven Organic Electronics.** Charles G. Sodini and Vladimir Bulovic; EECS, MIT, Cambridge, Massachusetts.

Over the last decade, enormous strides have been made in the field of organic electronics. A first generation of visible organic light emitting devices has been commercialized. Photodetectors with collection efficiencies as high as 75 percent, and solar cells with power conversion efficiencies as high as 3 percent have been reported. Printed organic thin film transistor circuits containing hundreds of active gates have been operated at frequencies exceeding 1 kHz. As a whole, this work represents an extraordinary technological achievement on an entirely new materials platform, but it is just a beginning of what is to come. With the advent of techniques for manipulating materials at the nanoscale and development of manufacturing methods for devising large area nanostructures, further advancements are envisioned. At present, there is a strong need to identify the dominant technological drivers for development of commercially viable products using organic electronic technologies. This presentation will summarize the findings of the workshop aimed at answering that question. Specific application concepts and philosophies leading towards commercialization will be presented. Workshop participants were from both industry and academia and included Marc Baldo (M.I.T.), Gary Baldwin (U.C. Berkeley), Zhenan Bao (Lucent Technologies), Hugo DeMan (I.M.E.C.), Mark Horowitz (Stanford University), Michael Kane (Sarnoff Corporation), Tommie Kelley (3-M), John Kymissis (M.I.T.), Robert Mertens (I.M.E.C.), Peter Peumans (Princeton University), Robert Reuss (DARPA), Vivek Subramanian (U.C. Berkeley), Someya Takao (University of Tokyo), and Ching Tang (Kodak).

**9:00 AM K1.2**

**High-Efficiency Tandem Organic Light-Emitting Diodes.** Liang-Sheng Liao, Kevin P Klubek and Ching W Tang; Display Technology Lab, R&D, Eastman Kodak Company, Rochester, New York.

Novel organic light-emitting diodes (OLEDs) capable of producing extraordinarily high luminance have been achieved using a tandem device structure. Based on a stack of transparent electroluminescent (EL) units connected electrically in series, the tandem structure is operable with a reduced current density and an increased driving voltage, both by a factor proportional to the number of EL units in the stack. The resulting luminous efficiency (cd/A), i.e., luminance output (cd/m<sup>2</sup>) per unit of current density (A/m<sup>2</sup>), can be substantially increased, along with the operational lifetime. Using an optically transparent doped organic "p-n" junction as the connecting unit between adjacent EL units, excellent light out-coupling has been achieved with negligible attenuation due to the tandem structure. Efficient carrier regeneration at the "p-n" junction connection unit is achieved without significant additional voltage, thus the power conversion efficiency is conserved or even enhanced. The luminous efficiency is found to scale almost linearly with the number of EL units in the stack, giving values as high as 30 cd/A or 135 cd/A for 3-unit tandem OLEDs using a fluorescent or phosphorescent emitter, respectively.

**9:15 AM K1.3**

**CO<sub>2</sub>-Processible Poly(fluorene)s for LEDs.** Andrew B Holmes, Klaus Kahle and Khai-Leok Chan; Chemistry, University of Cambridge, Cambridge, United Kingdom.

Poly(fluorene) derivatives are the most popular materials for the emissive layer in polymer-based light emitting devices. Much progress has been realized in the ink-jet printing of red, green and blue materials for full color displays, but there are various restrictions on the choice of solvent for this purpose. We have recently demonstrated that dense carbon dioxide can be used for the patterned deposition of polymer materials on a silicon wafer. In this presentation we also report on the controlled synthesis of oligomeric and polymeric poly(9,9-dialkyl)fluorene derivatives which are CO<sub>2</sub>-soluble blue luminescent materials. The paper will describe the synthesis and properties of these novel materials as well as the subtle influences that the CO<sub>2</sub>-philic substituents exert on their optoelectronic properties.

**9:30 AM \*K1.4**

**Charge transport in polymeric opto-electronic devices.** Paul W.M. Blom, Teunis van Woudenberg, Cristina Tanase, Valentin Mihailetchi and Bert de Boer; Materials Science Centre, University of Groningen, Groningen, Netherlands.

Charge transport properties of conjugated polymers are relevant for their application in light-emitting diodes, transistors and solar cells.

The experimental hole mobilities extracted from diodes and transistors, based on the same polymeric semiconductor, can differ by three orders of magnitude. We resolve this apparent discrepancy in the charge transport description by considering that the hole mobility depends strongly on the charge carrier density in disordered semiconducting polymers. In solar cells the polymeric semiconductors are blended with acceptor molecules which might also change their charge transport properties. The dependence of the charge transport on the different device geometries is determined and its relevance for device performance is discussed.

**10:30 AM K1.5**

**Chemical Architecture in PPV copolymers – Effect on electroluminescence.** Subramanian Vaidyanathan and Mary E Galvin; Materials Science & Engineering, University of Delaware, Newark, Delaware.

We have synthesized and characterized a series of copolymers of a poly(phenylene vinylene) derivative (PPV) with an oxadiazole containing PPV derivative (OxaPPV) for use in polymeric light emitting diodes. Our investigation has focused on a systematic study of the chain architecture and its role in luminescence, thus we have studied alternating, statistical and block copolymers of PPV and OxaPPV in addition to their blends. While the alternating copolymer and the blends show an enhancement of up to a factor of two in luminescence efficiency compared to the PPV homopolymer, the best EL performance was observed in statistical copolymers, which showed over 50% improvement in luminescence efficiency as compared to the alternating copolymer. Also these statistical copolymers showed very good compositional tolerance, with little degradation in performance through a wide compositional range (30% to 70% PPV). These and our recent results from a multi-block PPV-OxaPPV copolymer will be discussed.

**10:45 AM K1.6**

**Temperature Dependence of injection in Organic Materials.** Ambily Santha, Yulong Shen and George G. Malliaras; Materials Science & Engineering, Cornell University, Ithaca, New York.

Understanding of the basic transport mechanism in organic materials is not only of fundamental academic interest, but also has technical relevance which may help for the better device performance of organic light emitting diode displays (OLED), organic thin film field effect transistors (OTFT) and photovoltaic cells. The charge injection and transport mechanism in organic materials is not well understood like in inorganic semiconductors. The injection and charge transport through TPD:PC is investigated by measuring the current-voltage (I-V) characteristics as a function of temperature on Pt/TPD:PC/Ag and Au/TPD:PC/Ag geometries. From the I-V characteristics at different temperatures we have done a detailed analysis of efficiency, dependence of mobility on electric field and temperature.

**11:00 AM \*K1.7**

Laine

(Abstract Not Available)

**11:30 AM K1.8**

**Solution processable hybrid semiconducting polymer/inorganic optoelectronic devices.** Eyal Aharon<sup>1</sup>, Kieran J Reynolds<sup>2</sup>, Richard H Friend<sup>2</sup> and Gitti L Frey<sup>1</sup>; <sup>1</sup>Materials Engineering, Technion, Haifa, Israel; <sup>2</sup>Physics, University of Cambridge, Cambridge, United Kingdom.

Room temperature solution-processing of conductors and semiconductors provides the means to fabricate large area optoelectronic devices at very low cost. Conjugated polymers have exemplified this, with applications to light-emitting diodes, photovoltaic devices and field-effect transistors. Processing inorganic materials from solution, on the other hand, is less developed. In this work we demonstrate the integration of solution-processed inorganic films in polymer light-emitting diodes and photovoltaic devices to form fully solution processed multilayer hybrid devices. The layered structure of the metal dichalcogenides, MX<sub>2</sub> (M = Mo, W, Nb, Ta, Sn; X = S, Se), enables the deposition of thin films through Li intercalation and exfoliation. These inorganic materials are metallic, semiconducting or insulating. Both polymeric and inorganic materials in the devices are selected based on their electronic and morphological properties. The energy levels offset at the polymer/inorganic heterojunctions are designed to enhance charge recombination or charge separation in light-emitting diodes and photovoltaic devices, respectively. Furthermore, the inorganic films are also used as charge injecting or charge blocking layers and absorbers in the devices. Tailoring the polymer/inorganic heterojunction and utilizing functional inorganic layers, thus emphasizing the organic/inorganic synergism, results in improved device performance and enhanced device efficiencies.

11:45 AM **K1.9**

**Excited State Localization, Red-Shifted Emission and Energy Transfer Processes Involving Chemical Defects in Poly-fluorene Based Materials.** Egbert Zojer<sup>1,2</sup>, Alexander

Pogantsch<sup>2</sup>, Herbert Wiesenhofer<sup>2</sup>, Stephan Rentenberger<sup>2</sup>, Lorenz Romaner<sup>1,2,3</sup>, Emmanuelle Hennebicq<sup>4</sup>, David Beljonne<sup>5</sup>, Gernot Trattning<sup>2</sup>, Georg Heimel<sup>2,1</sup>, Gregor Langer<sup>5</sup>, Wolfgang Kern<sup>5</sup>, Patricia Scandiucci de Freitas<sup>6</sup>, Ulrich Scherf<sup>6</sup>, Emil J.W. List<sup>3</sup> and Jean-Luc Bredas<sup>1</sup>; <sup>1</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Institut fuer Festkoerperphysik, Technische Universitaet Graz, Graz, Austria; <sup>3</sup>Christian Doppler Laboratory Advanced Functional Materials, Technische Universitaet Graz, Institute of Nanostructured Materials and Photonics, Graz, Austria; <sup>4</sup>Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut, Mons, Belgium; <sup>5</sup>Institut fuer Chemische Technologie Organischer Stoffe, Technische Universitaet Graz, Graz, Austria; <sup>6</sup>Makromolekulare Chemie, Fachbereich Chemie, Bergische Universitaet Wuppertal, Wuppertal, Germany.

Poly-fluorene (PF) is one of the most commonly used blue emitters in polymer based LEDs. It has been shown recently that the red-shifted emission frequently observed in degraded PF devices is largely due to the formation of chemical defects (ketone groups at the 9-carbon of fluorene) and not directly related to aggregation or excimer formation. In this contribution we present a quantum-mechanical characterization of the excited states in poly-fluorenes bearing ketonic defects. The state responsible for the yellow-green emission is identified as an optically weakly allowed charge-transfer  $\text{Pi-Pi}^*$  state, which is localized at the fluorenone unit. The transition energy to that state is several tenths of an eV below the delocalized  $\text{Pi-Pi}^*$  excited state, which is also found in defect free polyfluorene. The appearance of two excited states near the band gap results in several channels for excitation energy transfer to the defects, which we model on the basis of the distributed monopole method. The quantum-chemical studies are confirmed by spectroscopic investigations on well defined fluorene-fluorenone co-polymers as well as on photochemically degraded poly(fluorene). Additionally, we show that exposing PF films with ketonic defects to gaseous chemical reagents can result either in a shift or a disappearance of the fluorenone-based emission. For the case of hydrazine + UV light, we, e.g., find a blue-shift of the defect emission by 0.2, which, according to the quantum-mechanical modeling, can be attributed to a conversion of the ketonic to hydrazone defects. A comparable blue-shift is also found both experimentally as well as theoretically for ladder-type PPP chains.

SESSION K2: Light Emitters II

Chair: Michael Weaver

Monday Afternoon, December 1, 2003

Back Bay C (Sheraton)

1:30 PM **K2.1**

**Exciton-phonon coupling in conjugated organic molecules.**

Georg Heimel<sup>1,2</sup>, Alexander Pogantsch<sup>1</sup>, Jean-Luc Bredas<sup>2</sup> and Egbert Zojer<sup>2</sup>; <sup>1</sup>Institute of Solid State Physics, Graz University of Technology, Graz, Austria; <sup>2</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Conjugated organic molecules are successfully used as laser dyes and in light emitting electro-optical devices. Their lowest energy singlet excited state  $S_1$  is highly dipole allowed and can thus account for the high fluorescence quantum yield that is required for these applications. The nature of  $S_1$  is essentially electron-hole like. In order to devise an adequate description of this excitation one generally needs to take into account correlation effects and thus leave the independent particle picture. The local change in the electronic configuration due to the presence of this bound electron-hole pair induces a local relaxation of the nuclei towards new equilibrium positions prior to the emission process. This strong exciton-phonon coupling gives rise to exciton self localization, a large Stokes Shift, and a pronounced vibronic progression in the optical spectra of many conjugated, organic molecules. In a crystalline environment, the exciton is mostly localized onto a single molecule and so is the accompanying geometry distortion. Taking this relaxation into account leads to a redistribution of oscillator strength into the lower, otherwise forbidden Davydov component. In the present study we want to address several of above mentioned consequences of this excited state geometry relaxation. Particular emphasis will be put on the Franck-Condon activity of highly anharmonic librations. Correlated quantum chemical methods are applied in order to study the oligo(*para*-phenylenes) as an example for the important class of rod like,  $\pi$ -conjugated, organic molecules.

1:45 PM **\*K2.2**

**Polymer-polymer heterostructures for semiconductor devices.**

Peter Ho<sup>1,2</sup>, Lay-Lay Chua<sup>1</sup>, Natasha Conway<sup>2</sup>, Jeremy H. Burroughes<sup>2</sup> and Richard H. Friend<sup>1,2</sup>; <sup>1</sup>Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Cambridge Display Technology, Cambridge, United Kingdom.

The characteristics of polymer semiconductor devices depend crucially on incorporating appropriate high-quality polymer-polymer heterostructures. Such heterostructures may perform key functions in charge-carrier confinement, exciton-confinement, and/or photon confinement in the device. Up till now however the ability to fabricate polymer multilayers has been limited, ironically, by the key processing advantage of organic polymers - their common solubility in organic solvent systems. Solution deposition of the subsequent polymer layer then destroys the integrity of the previous layer. This restricts the accessible heterostructures either to those from precursor-route polymers or polymers that are mutually incompatible and hence processable in different solvents, or to techniques involving "float-off", or the layer-by-layer polyelectrolyte assembly. Here we report a simple and general route to crosslink a wide range of conjugated polymer films post-deposition. We show that semiconducting polymer films can be insolubilized over a range of thickness from 1 nm to 500 nm. This allows one to build any desired number of semiconductor polymer layers and opens up new avenues for the photopatterning of these polymer films. More crucially we demonstrate that the crosslinking can be implemented for a range of polymers without introducing deep localization potential that trap charge-carriers or excitons. Therefore the process is compatible with state-of-the-art devices. We are then able to access and study the properties of a number of practical polymer-polymer heterostructures in devices. For example, we will show that with an appropriate hole injection heterostructure, external quantum efficiencies of 5 % photon/electron can be obtained from a fluorene-benzothiadiazole copolymer at low drive voltages (5 V) and high brightness (10,000 cd/m<sup>2</sup>).

2:15 PM **K2.3**

**Ultra-wide Energy Gap Hosts (UGHs) for High Efficiency, Deep Blue Phosphorescent Organic Light Emitting Diodes.**

Xiaofan Ren<sup>1</sup>, Russell J Holmes<sup>2</sup>, Jian Li<sup>1</sup>, Peter I Djurovich<sup>1</sup>, Stephen R Forrest<sup>2</sup> and Mark E Thompson<sup>1</sup>; <sup>1</sup>Chemistry, University of Southern California, Los Angeles, California; <sup>2</sup>Electrical Engineering, University of Princeton, Princeton, New Jersey.

Device efficiencies close to the theoretical limit of 100% (internal) have been achieved for red and green phosphorescent organic light emitting diodes (OLEDs), however, the efficiencies of blue phosphorescent devices are well below this level. Due to the high energies associated with the excitons in blue OLEDs, a number quenching mechanisms could become accessible, which are not present in lower energy green or red emitting OLEDs, resulting in exciton quenching being a key factor limiting the performance of blue OLEDs. Among them, two quenching mechanisms, energy transfer between the triplet energy levels of the host and phosphorescence guest materials, and the emission/exciton quenching by polarons in the emissive layer, are believed to play a significant role in lowering blue device efficiencies. Here, we introduce the concept of Ultra-wide Energy Gap Hosts (UGHs). The materials that we have focused on for this application have a high aromatic content, but are not conjugated. The structure motif gives the material a energy gap, ca. 4-5 eV, provides good compatibility with the phosphorescent dopants which often have a high aromatic content and give them high thermal stability. Furthermore, the deep HOMOs and high LUMOs associated with UGHs deter the injection of holes and electrons into the host, significantly lowering the density of non-dopant localized polarons in the emissive layer. With deep blue iridium(III) bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate, Fir6, as the dopant, and UGH1 (Si(phenyl)2(meta-tolyl)2) as the host, deep blue electrophosphorescence device with a 8.8% maximum (external) quantum efficiency and 11 Lm/W luminous power efficiency has been achieved. It represents a significant increase in performance over traditional deep blue electrophosphorescence guest-host system. Moreover, it demonstrates that efficient device can be realized even when the all of the charge in the emissive layer is carried by the dopant and none by the host. In my talk I will discuss the properties of this blue device and the use of other UGH materials in high energy electrophosphorescent devices.

2:30 PM **K2.4**

**Polymer Phase Separation For White Light Lighting**

**Applications.** Gao Liu, Steve Johnson and John B Kerr; Lawrence Berkeley National Laboratory, Berkeley, California.

We report synthesis of light emitting, hydrophilic derivatives of PPV and polyfluorene (PF) polymers. When these polymers are mixed with conventional MEH-PPV or 9,9-dihexylpolyfluorene polymers, they phase separate. By changing substrate structure, polymer concentration and ratio, solvent and spin speed, we can adjust the phase separation properties of the freshly made composite polymer

thin films. Because of the different solvation properties of these polymers, domain structures can be further adjusted by selective solvent annealing. The successive annealing provides a variety of film structures including PF spheres in PPV, PPV spheres in PF, lamellar shapes, etc. The photoluminescent properties of these films not only change with the ratio of the PF and PPV but also change according to the annealing time and film morphology. With small domain structures, the excitons migrate out of the PF domain and trap in the PPV resulting in an emission pattern identical to pure PPV film. However with increasing domain size after annealing, the two polymers start to behave independently to give white light from mixing multiple emissions.

### 3:15 PM \*K2.5

#### High performance phosphorescent OLEDs.

Michael Stuart Weaver, Raymond C Kwong and Julie J Brown; Universal Display Corp., Ewing, New Jersey.

Some of the very latest developments in the field of phosphorescent organic light emitting devices (PHOLEDs) will be presented. For example a new green device containing a phosphorescent dopant showing a peak emission wavelength of 520nm with CIE co-ordinates of (0.30, 0.60) will be discussed. A peak luminance efficiency of  $>27\text{cd/A}$  (7.5% external quantum efficiency (EQE)) is observed at  $600\text{cd/m}^2$  and the efficiency remains relatively flat from 50 to  $2000\text{cd/m}^2$  i.e. the region in which an active matrix display would operate. This material is also highly suitable for passive matrix drive applications. At  $20,000\text{cd/m}^2$  the luminance efficiency is still high at  $20\text{cd/A}$ . This particular dopant also shows excellent device stability. Under constant dc current lifetest at room temperature from a starting luminance of  $600\text{cd/m}^2$ , the PHOLED had decayed by only 4% to  $576\text{cd/m}^2$  after 2000 hours of operation. Also presented in this paper will be the latest developments in blue and red PHOLEDs. For example a red PHOLED with peak a luminance efficiency of  $>14\text{cd/A}$  at  $300\text{cd/m}^2$  with CIE co-ordinates of (0.65, 0.35) will be discussed. At  $10,000\text{cd/m}^2$  the efficiency is  $8.5\text{cd/A}$ . The lifetime of this material is  $>15,000$  hours from a starting luminance of  $300\text{cd/m}^2$ . A red/orange PHOLED with peak a luminance efficiency of  $>24\text{cd/A}$  at  $300\text{cd/m}^2$  at (0.61, 0.38) with a lifetime of  $>10,000$  hours will also be presented. Acknowledgements We would like to gratefully acknowledge the efforts of the entire technical team at UDC and PPG Industries. We would also like to thank Professor Mark Thompson at University of Southern California and Professor Stephen Forrest at Princeton University.

### 3:45 PM K2.6

#### Neutron Reflectivity Studies of Surface Segregation Effects in Polymer Light Emitting Diode Structures.

Simon John Martin<sup>1</sup>, Mark Geoghegan<sup>1</sup>, Ilaria Grizzi<sup>2</sup>, Anthony M. Higgins<sup>1</sup>, Richard A. L. Jones<sup>1</sup> and Paul C. Jukes<sup>1</sup>; <sup>1</sup>Department of Physics and Astronomy, University of Sheffield, Sheffield, South Yorkshire, United Kingdom; <sup>2</sup>CDT Ltd, Cambridge, Cambridgeshire, United Kingdom.

The field of all-polymer electronics has seen rapid growth in the academic world and the technology is now approaching commercialization. All-polymer devices include polymer light emitting diodes, microcavity LEDs, photodiodes and field effect transistors. The long term success of all-polymer devices in the market place is dependant on the development of the understanding and control of the failure mechanisms at play. An important part of the all-polymer device technology are the conducting polymers used as charge injection layers or electrodes; the material of choice is a blend of the conducting polymer poly(3,4-ethylene dioxythiophene) (PEDT) with poly(4-styrene sulphonate) (PSS). Such PSS/PEDT blends are produced commercially by Bayer GmbH under the name Baytron P. It can be processed in aqueous form by techniques such as spin casting and inkjet printing to form transparent electrodes. Because PSS/PEDT is a polymer blend we should expect its composition to be different at a surface or an interface than it is in the bulk. In the case of the PSS/PEDT blend, the PSS effectively dopes the PEDT, which means that surface or interface segregation will alter the charge transport characteristics of that interface. We report here on our recent work using neutron reflectivity to study segregation effects in these blends. First, we show that we can control the surface composition of PSS/PEDT blends by heat treatment. We have been able to deduce the surface excess of PSS and the concentration profile of the PSS induced in spin cast films annealed at temperatures up to 200 C. PSS is observed to preferentially segregate to the air/vacuum interface, which means that there is a gradual monotonic increase in the composition of PEDT with depth into the sample, which is likely to affect, for example, hole injection when using Baytron P as an anode or as a coating for an indium tin oxide anode. We will also discuss neutron reflectivity measurements of light emitting diode structures that include PSS/PEDT charge injection layers. We have found that the degree of segregation of the PSS to the PSS/PEDT-light emitting polymer interface increases with the amount of time that the device has been run for. We will compare this current induced segregation with our results for thermal annealing

and discuss its implications for device operation.

### 4:00 PM K2.7

#### High work function Indium tin oxide films for organic light emitting diode applications.

Tsung-Hsin Chen<sup>1</sup>, Yung Liou<sup>2</sup> and Tadahiro Ohmi<sup>1</sup>; <sup>1</sup>New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan; <sup>2</sup>Institute of Physics, Academia Sinica, Taipei, Taiwan.

Doping the indium tin oxide (ITO) films with Hf to increase the work function has been successfully fabricated by reactive magnetron sputtering. Compared with the typical work function of ITO films of 4.7 eV without doping, the work function has been increased by doping with Hf. The highest work function of the doped ITO films was 5.45 eV with the Hf concentration about 1 atm% in this study. We have made a new organic light emitting diode (OLED) by inserting this doped ITO film in between the original hole transport layer and the existing ITO anode. Good surface roughness ( $<1\text{nm}$ ), low sheet resistance ( $<10\text{ ohms per square}$ ) and highly transparency ( $>85\%$ ) have still been achieved. Both the turn-on voltage and the luminescence of the new OLED have been improved comparing with the device without the doped ITO film that has shown the potential applications. The effect of the film thickness, the work function, the crystal structure and orientation of the doped ITO films has been investigated. Secondary ion mass spectrometry (SIMS) has been used to determine the dopant concentration. X-ray diffraction (XRD) was used to characterize the film crystal structure and orientation. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to characterize the film surface morphology and surface roughness. 4-point probe was used to measure the sheet resistance. Optical transmittance of the doped film on the regular ITO glass was also measured.

### 4:15 PM K2.8

#### Improved Thermal Management in Small-area Polymer Light Emitting Diodes Revealed by Scanning Thermal Microscopy.

David George Lidzey<sup>1</sup>, Farhad Boroumand<sup>2</sup> and Azzedine Hammiche<sup>2</sup>; <sup>1</sup>Department of Physics and Astronomy, University of Sheffield, Sheffield, United Kingdom; <sup>2</sup>Department of Physics, University of Lancaster, Lancaster, United Kingdom.

We have used scanning thermal microscopy (SThM) to directly image the heat generated in a conjugated polymer light emitting diode (LED) during operation. To our knowledge, this is the first time that this technique has been used to study a working organic electronic device. Previous device studies have highlighted that organic LEDs operating at elevated temperatures have reduced operational lifetimes. It has also been shown that Joule heating within an LED is itself a significant cause of heating. Such internally generated heat may particularly be problematic in polymeric LEDs due to the relatively poor thermal conductivity of disordered organic materials. It is thus important to quantify the heat generation in such devices and develop methods to mitigate it. The devices that we have studied have used a blend of polyfluorene polymers as the charge transporting and active emissive layers. For comparison, we have studied LEDs deposited in two different formats. Our standard-area LEDs are defined by the overlap of the cathode and anode stripes, and have an active size of  $1.5 \times 3\text{ mm}$ . Small-area LEDs were fabricated using standard photolithography techniques. A 50 micrometer hole was opened in a resistive silicon nitride film deposited on to an ITO anode. By coating the patterned silicon nitride substrate with a polymer film, we created a series of 50 micrometer diameter LED pixels. The SThM was positioned above the centre of an LED, and the temperature rise during operation was measured. The temperature of the standard area device cathodes increased by around 15 degrees centigrade in approximately 4 seconds. For an equivalent power input, the temperature rise that was observed in the small area devices was one order of magnitude less than that observed in the standard-area devices. The significantly improved thermal management in the small area devices occurs as a direct result of it being effectively surrounded by a large thermal reservoir that acts as an efficient heat sink. We show that this improved thermal management allows the LEDs to operate at a very much higher current densities and luminances before failure. Pulsed measurements demonstrate that small area LEDs can emit electroluminescence with a brightness in excess of  $6.5\text{ Mcd / m}^2$ . Using the SThM we explore the temperature distribution across a small-area and standard-area LEDs. We identify a weak temperature gradient across the small-area LEDs, and image the flow of heat into the surrounding heat-sink. In the standard-area LED we find that the polymer film surrounding the device becomes warm, with temperature rises of 5 degrees centigrade observed more than 1.5 mm away from the device. Our measurements confirm that significant temperature rises might be expected in displays composed of many densely integrated devices operating at high brightness.

### 4:30 PM K2.9

#### High Performance Organic Light-emitting Diodes Based on

**ITO Thin Films Grown by Ion-Assisted Deposition at Room Temperature.** Yu Yang<sup>1</sup>, Qinglan Huang<sup>1</sup>, Tobin J. Marks<sup>1</sup>, Mark E. Madsen<sup>2</sup>, Antonio DiVenere<sup>2</sup> and Seng-Tiong Ho<sup>2</sup>; <sup>1</sup>Chemistry Department, Northwestern University, Evanston, Illinois; <sup>2</sup>Phosistor Technologies, Inc., Evanston, Illinois.

ITO thin films were deposited on glass and PET substrates by Ion-assisted deposition (IAD) at room temperature. The optical and electrical properties of these films were studied as a function of O<sub>2</sub> partial pressure and ion energies. ITO thin films with a root mean square (RMS) roughness of 0.9 nm and 3.6 nm on glass and PET, respectively, over a range of 5 μm × 5 μm, with a conductivity of ~1500 S/cm, and optical transmittance of > 80% in the visible range, were obtained and used as the anode in OLEDs. The turn-on voltage of the IAD-ITO OLED on PET is 3.8 V, which is slightly lower than 4.6 V of commercial ITO-based control. A maximum luminance of 36,900 cd/m<sup>2</sup> and external forward quantum efficiency of 2.0 % have been achieved on IAD-derived ITO glass OLED. A maximum luminance of 12,000 cd/m<sup>2</sup> and external forward quantum efficiency of 1.6 % have been achieved on the plastic device at much lower driving voltages vs. that of the control.

#### 4:45 PM K2.10

**Iridium oxide coated anode for organic light emitting diodes.** Soo Young Kim<sup>1</sup>, Ki-Beom Kim<sup>2</sup>, Yoon-Heung Tak<sup>2</sup> and Jong-Lam Lee<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Kyungbuk, South Korea; <sup>2</sup>LG Electronics Inc., Kumi, Kyungbuk, South Korea.

Since Tang and Van Slyke have developed multilayer organic light emitting diodes (OLEDs), many efforts have been made to improve the device performance. It was recognized that the external quantum efficiency of OLEDs depends on the carrier injection efficiency and the carrier recombination efficiency. It is reported that iridium oxide (IrO<sub>x</sub>) has high work function (> 5eV), high transparency, and low electrical resistivity. In order to enhance the hole injections in OLEDs, an ultrathin layer of IrO<sub>x</sub> was inserted as a hole injection layer (HIL) between the indium tin oxide (ITO) anode and 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α-NPD). The device structure is glass|ITO (1500 Å)|HIL|α-NPD (500 Å)|tris(8-hydroxyquinoline) aluminum (600 Å)|LiF (40 Å)|Al (1000 Å). Copper phthalocyanine, Ir, or IrO<sub>x</sub> was used as HIL material. The effect of the layer thickness of HIL upon the device performance has also been investigated. A low turn-on voltage was observed for the device with IrO<sub>x</sub> on ITO. Furthermore, the life time increased for the IrO<sub>x</sub> based device. Synchrotron radiation photoelectron spectroscopy results showed that the secondary electron emission peak of IrO<sub>x</sub> shifted toward higher kinetic energy about 1 eV after depositing the IrO<sub>x</sub> on ITO, indicating that the relative work function increased. Thus, the barrier height between α-NPD and ITO anode lowered, resulting in the reduction of the turn-on voltage of OLEDs as well as the enhancement of the life time.

SESSION K3: Light Emitters III and Printing  
Chairs: John Rogers and Yang Yang  
Tuesday Morning, December 2, 2003  
Back Bay C (Sheraton)

#### 8:30 AM \*K3.1

**Semiconducting Polymer Blends for Broadband, Low-threshold Polymer Lasers.** Ruidong Xia, George Heliotis, Mariano Campoy-Quiles, Pablo Etchegeoin and Donal D. C. Bradley; Ultrafast Photonics Collaboration, Experimental Solid State Group & Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2BZ, United Kingdom.

Following the successful demonstration of optically pumped conjugated polymers lasers, considerable efforts are currently being made to improve the intrinsic carrier mobilities in these materials and lower their lasing thresholds in order to develop electrically pumped polymer laser diodes. Such organic laser sources may eventually compete with inorganic semiconductor lasers in a number of fields, especially if the benefits of low-cost, low-temperature, high throughput manufacture on a variety of substrates can be attained. Here, we report a detailed investigation of the optical gain properties of fluorene-based conjugated polymer blends comprising different ratios of Poly(9,9-dioctylfluorene-co-benzothiadiazole) [F8BT] and a Dow proprietary copolymer, known as Dow Red F. The photoluminescence (PL) quantum efficiency was increased from 40% in pure Dow Red F to 53% in the optimised blends through a decrease in concentration quenching. In addition, there was a corresponding increase in the PL decay time from 2.72 ns to 3.10 ns. Deep red (λ ≥ 680 nm) amplified spontaneous emission (ASE) was observed at very

low excitation energies (≥ 45 nJ for 10 ns, 10 Hz pulses) in planar asymmetric waveguides. The spectral location of the maximum waveguide amplification was widely tuned (654 nm to 686 nm, i.e. Δλ ≥ 30 nm) by controlling the fraction of Dow Red F. The net gain and loss characteristics of the polymer waveguides as a function of the Red F concentration are reported together with the ellipsometrically determined optical constants. Finally, we present the characteristics of optically pumped distributed feedback (DFB) lasers fabricated with the same blends. The lasing wavelength was systematically tuned over a very broad spectral range ≤ 73 nm (627 nm to 700 nm) and the lasing thresholds were found to be as low as 0.55 nJ per pulse (10 ns, 10 Hz). Our observations highlight the broadband gain that is accessible with F8BT/Dow Red F blends and demonstrate the opportunities available for materials optimisation to further reduce lasing thresholds.

#### 9:00 AM K3.2

**Polariton Emission from a Resonant Cavity Organic Light Emitting Device Containing J-Aggregates.**

Jonathan R. Tischler<sup>1</sup>, Jung Hoon Song<sup>2</sup>, Arto V. Nurmikko<sup>2</sup> and Vladimir Bulovic<sup>1</sup>; <sup>1</sup>Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; <sup>2</sup>Division of Engineering, Brown University, Providence, Rhode Island.

We present the first demonstration of polariton emission from an electrically pumped structure. Our demonstration is enabled by the high absorption constant (~10<sup>6</sup> cm<sup>-1</sup>), and narrow absorption spectra (λ<sub>max</sub> = 590 nm, FWHM = 20 nm) of ordered J-Aggregate monolayers inserted into a planar microcavity. The strong coupling between the J-Aggregate excitons and the optical modes of the microcavity drastically alters the light-matter interaction, giving rise to the polariton emission. The angularly resolved EL spectrum exhibits the characteristic anti-crossing of polariton energy bands, and we observe Rabi-splitting in excess of 100 meV, corresponding to a Rabi frequency of more than 24 THz. Due to the large Rabi-splitting (an order of magnitude larger than for any inorganic system) polariton emission peaks are pronounced even at room temperature. This all-organic active device is the first to enable electrical pumping of polaritons in any material system. A typical layered structure contains a 4 to 10 monolayers thick film of J-Aggregates of the cyanine dye 5,6-Dichloro-2-[3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-benzimidazolylidene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide sodium salt, sandwiched between hole and electron transporting layers with metallic and/or DBR reflective mirrors forming the microcavity. Although the quality factor of the microcavity is less than 100, polariton emission is still observed because of the high oscillator strength of the J-Aggregate monolayers. This demonstration could enable practical implementations of previously proposed polariton based optoelectronic devices such as low threshold polariton lasers and sub-picosecond optical clocks.

#### 9:15 AM K3.3

**Probing Electrochemical Models for Organic Light-Emitting Diodes with Quinacridone Dendrimers and Near-IR Dopants.**

Ware H. Flora, Adrian Ortiz, Dominic V. McGrath and Neal R. Armstrong; Department of Chemistry, University of Arizona, Tucson, Arizona.

Organic light-emitting diodes (OLEDs) typically incorporate a guest dye that is believed to harvest energy from the host dye by Förster energy transfer. Recent work in our group and others suggests that charge trapping by these guest dopants occurs in the condensed phase device environment through processes that are analogous to, and predicted by, solution redox processes. These charge transfer events are an important component of energy harvesting by the guest dye, and a thorough understanding of these processes will assist in the design of more efficient OLED materials. This talk will focus on two related subjects: A) We discuss the use of near-IR emitting guest dyes in single layer OLED materials which provide for unique electroluminescence responses of the OLED, and a means of quantitating the degree to which charge transfer events contribute to device emission. The relative guest emission intensity in the OLED has a logarithmic dependence on the thermodynamic driving force for charge transfer, as predicted by Marcus theory for similar redox processes for these molecules in solution. B) A series of quinacridone dendrimer guest dyes (visible emitters) were synthesized and characterized by solution electrochemistry, spectroscopy, and by their electroluminescence response in Alq3/PVK-based OLEDs. Although electron transfer rates for redox processes in solution decrease an order of magnitude from G0 to G3, in single-layer OLEDs, quinacridone emission due to charge transfer events is not inhibited, presumably due to rapid charge transfer between these dendrimerized quinacridones and the hole transporting polymer (PVK) and/or the host (Alq3) emitters.

#### 9:30 AM K3.4

**Synthesis and Characterization of Conductive Branched Star**

**Poly(Ester-Thiophene)S.** Leeyih Wang<sup>1</sup>, Chih-Fu Yeh<sup>2</sup> and S-P Rei<sup>2</sup>; <sup>1</sup>Ctr Condensed Matter Sci, National Taiwan University, Taipei, Taiwan; <sup>2</sup>Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei, Taiwan.

Multi-armed conductive coreshell-like copolymers were constructed by the use of poly( $\epsilon$ -caprolactones) and poly(3-alkylthiophene) as the core and shell materials, respectively. The synthetic strategy based on divergent route includes the formation of starburst poly( $\epsilon$ -caprolactones) via living ring-opening polymerization and then the growth of 3-alkylthiophene segments via oxidative polymerization using FeCl<sub>3</sub> as an oxidant. Various spectroscopic methods and gel permeation chromatography were utilized to study the chemical structure and molecular weight characteristics of these copolymers. All of the data indicated a narrow distribution on both the arm-length and the degree of branching. The UV-Vis spectra of the star copolymers revealed apparent red shift due to the attachment of the thiophene chains. Importantly, these new materials exhibited high solubility in common organic solvents and good film-formation properties. The chemical structure, molecular weight characteristics, and electronic properties of these novel conductive polymers will be presented and discussed.

9:45 AM **K3.5**

**Phosphorescence Quenching by Host Materials in Phosphor-doped Organic Light Emitting Devices.** Sudhakar Madhusoodhanan, Peter I Djurovich, Thico E Hogen-Esch and Mark E Thompson; Chemistry, University of Southern California, Los Angeles, California.

Thermal, photoluminescence, and electrochemical properties are considered important for the host materials in phosphor doped organic light emitting devices (OLED). However, phosphor quenching by the triplet of the host is typically not evaluated. In order to understand the energy transfer process between phosphors and conjugated polymeric host materials, we have used two oligomers as models of common wide-gap conjugated polymers, i.e. a fluorene trimer (F<sub>3</sub>) for polyfluorene and a phenylene tetramer (SC-5) for polyphenylene. Both F<sub>3</sub> and SC-5 have high singlet energies (3.2 eV and 3.4 eV respectively). Phosphorescence is not observed, but we expect their triplet energies to be higher than the analogous polymers, considering the higher singlet energies for the model compounds than the polymers. Phosphor quenching by a small molecule host material, meta N,N'-di(4,7-dimethylcarbazolyl)benzene, (mCP\*) was also studied for comparison. Cyclometallated iridium complexes with blue (FP), green (PPY), yellow (BT), orange (PQ) and red (BTP) emission spectra were the phosphors used for this study. mCP\* did not quench emission from any of the phosphors, consistent with its high triplet energy ca. 3.0 eV. In case of F<sub>3</sub>, quenching of FP and PPY emission was exothermic while for BT, PQ, and BTP the quenching process was endothermic. For SC-5, quenching was significant only for FP and negligible for the other phosphors. Based on above results, triplet energy of F<sub>3</sub> and SC-5 is estimated to be below 2.3 eV and 2.5 eV respectively which is close to their predicted values in the literature. Conjugated polymers, having a lower triplet energy compared to an oligomer, should quench emission more efficiently in phosphor doped OLEDs resulting in devices with low quantum efficiencies. Our study highlights an important criterion that needs to be considered when designing phosphor doped OLEDs. In order to fabricate highly efficient phosphor doped OLEDs, host materials with high triplet energy need to be used.

10:30 AM **\*K3.6**

**Carbon Nanotube Transistors Formed by Soft Contact Lamination.** John Rogers<sup>1</sup>, Anshu Gaur<sup>1</sup>, Matthew Meitl<sup>1</sup>, Graciela Blanchet<sup>2</sup> and Curt Fincher<sup>2</sup>; <sup>1</sup>University of Illinois, Urbana, Illinois; <sup>2</sup>Central Research and Development, DuPont, Wilmington, Delaware.

High resolution metal electrodes that are supported by elastomeric layers can be physically laminated against electroactive organics to form high quality electrical contacts. In this talk we demonstrate that this soft contact lamination approach can yield carbon nanotube transistors with good performance characteristics. These devices and the methods used to construct them may be important for future organic optoelectronic systems.

11:00 AM **K3.7**

**Polymer thin-film transistor arrays for display backplanes patterned by stamping.** Alberto Salleo, William Wong, Kateri E Paul, Michael L Chabiny, Raj Apte and Robert Street; Palo Alto Research Center, Palo Alto, California.

Recent progresses in polymer thin-film transistors (TFTs) have led to the fabrication of devices with carrier mobilities up to 0.1 cm<sup>2</sup>/Vsec and good sub-threshold swing (~1V/dec on 100 nm SiO<sub>2</sub>). The next step towards commercial application of polymer TFTs in large-area electronics consists in the ability to efficiently fabricate arrays of

TFTs at low cost. Array fabrication must include patterning of the semiconductor in order to isolate adjacent devices and minimize leakage. Semiconducting polymers enable the use of solution-based techniques, such as ink-jet printing. It is desirable to develop other patterning techniques compatible with roll-to-roll processing. We have developed a process similar to relief printing that allows us to stamp semiconducting polymer on a variety of surfaces. The stamp is molded from polydimethylsiloxane (PDMS) against a master. The polymer forms a patterned film under the areas of the stamp that remain in conformal contact with the substrate. We obtained patterns with edge definition of the order of a few microns. The stamping process was successfully used to pattern two polymer semiconductors: a poly(fluorene) (F8T2) and a high-performance regioregular polythiophene. 1-D and 2-D thin film patterns were created over ~cm<sup>2</sup> areas on a variety of substrates (oxidized Si wafers, glass, kapton, parylene-coated Si wafers). Patterning the polymers on arrays of predefined electrodes allowed to fabricate by hand full TFT arrays on glass in seconds. The TFT island separation (~few tens of microns) was designed to be appropriate for the fabrication of TFT arrays and minimize registration requirements. The stamped devices showed good electrical characteristics, comparable to those obtained by spin coating.

11:15 AM **\*K3.8**

**Reactive Inkjet Printing For Structures And Devices.**

Paul Calvert<sup>2,1</sup>, Ghassan Jabbour<sup>1</sup> and Yuka Yoshioka<sup>1</sup>; <sup>1</sup>MSE Dept., University of Arizona, Tucson, Arizona; <sup>2</sup>University of Massachusetts, Dartmouth, Massachusetts.

Inkjet printing is familiar as a method for forming 2-dimensional patterns. With a typical ink and substrate, a dried droplet has a diameter of 50-100 microns and a thickness of 100 nm. Much thicker layers can be formed by overlapping drops to form lines, lines to form layers and then multiple layers to form thick films. The small thickness of each layer allows rapid mixing of materials if two different inks are superimposed. As a result it is possible to carry out chemical reactions between layers. Examples will be given including building thick layers of conducting polymer, forming insoluble gels by from epoxy and amine inks or from self-assembling cationic and anionic polymers and patterning conducting polymer using an etching ink. One can also form inorganic layers from combinations of powders and bonding agents. In addition to building multilayer, multimaterial structures, it is also possible to envisage strategies to enhance the resolution through suitable combinations of materials.

11:45 AM **K3.9**

**Organic Field-Effect Transistors by Ultra-Fine Screen-Printing with Resolution of 20  $\mu$ m.** Takao Someya<sup>1</sup>,

Masatoshi Kitamura<sup>2</sup>, Yasuhiko Arakawa<sup>2</sup> and Yasushi Sano<sup>3</sup>; <sup>1</sup>Quantum Phase Electronics Center, University of Tokyo, Tokyo, Japan; <sup>2</sup>Research Center for Advanced Science and Technology, University of Tokyo, Tokyo, Japan; <sup>3</sup>SP-Solution Co. Ltd., Chiba, Japan.

We have successfully fabricated high-quality organic field-effect transistors by ultra-fine screen-printing techniques with resolution of 20  $\mu$ m, which is in the important range (from a few to a few tens of  $\mu$ m) for many practical applications of organic transistors. Fine electrode patterns were formed from silver pastes by a screen-printing machine (MT-320, Micro-Tec Co., Ltd., Japan). The substrates were 10 cm squares of ITO/glasses or 4'' heavily doped silicon wafers, both of which were capped with 300 nm thick SiO<sub>2</sub> layers. We used 500 ppi screen meshes (Tokyo Process Service Co. Ltd., Japan) consisting of stainless steel wires with diameter of 18  $\mu$ m. The attack angle of the squeegee, a rubbery tool to press pastes through screen meshes, was precisely controlled to be 70° so that fine patterns could be obtained reproducibly and uniformly for large area. Pattered electrodes on the substrates were kept at 120 °C for 30 min to evaporate solvents in silver pastes. Note here that the temperature is compatible with a process using PET sheets and other plastic substrates. A fine electrode pattern could be obtained and the channel length, the spacing between source and drain electrodes, was as small as 20  $\mu$ m. Finally, 30 nm thick film of pentacene was deposited on the substrates with fine patterns in the vacuum sublimation system at the ambient substrate temperature. FET characteristics were measured with a semiconductor parameter analyzer. On/off ratio of drain current was as high as 10<sup>4</sup> and hole mobility was calculated to be 0.03 cm<sup>2</sup>/Vs. The present technique is easily scaled up to 1 m with the larger printing machines, which are commercially available for 65'' PDP applications, and therefore we believe that our approach is promising for ultra-low cost process to make large area circuits with organic transistors.

SESSION K4: Photovoltaics I  
Chairs: Rene Janssen and Peter Peumans  
Tuesday Afternoon, December 2, 2003

**1:30 PM \*K4.1****Nanostructured Materials For Polymer Photovoltaics.**

Rene A.J. Janssen, Martijn M. Wienk, Jeroen K.J. van Duren and Waldo J.E. Beek; Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands.

Motivated by a demand for inexpensive renewable energy sources there is a considerable interest for organic, polymer, and organic-inorganic solid-state photovoltaic cells. A particular encouraging approach to polymer solar cells is the so-called bulk-heterojunction solar cell, that consists of a nanoscopic phase-segregated composite film of a p-type conjugated polymer and a n-type fullerene derivative or inorganic semiconductor. The rate of formation and the longevity of photoinduced charges in the solid state are key-factors for the ultimate performance of thin film solar cells. To address these issues we studied the temporal evolution of photoinduced energy and electron transfer reactions that occur in these materials and in covalently bound oligomer-fullerene molecules in solution and in the solid state. New materials for polymer/fullerene solar cells will be presented that improve light absorption and that provide energy conversion efficiencies over 3% under standardized AM1.5 conditions. Using a combination of ultrafast spectroscopic (fluorescence and pump-probe) and morphological studies (AFM, TEM, and SIMS) it will be shown that the morphology of the active layer has a crucial role in determining the overall energy conversion efficiency. For hybrid solar cells, new methods will be described that allow mixing of conjugated polymers with metal oxides into nanostructured films that show promising behavior when used in a photovoltaic device.

**2:00 PM \*K4.2****Nanostructured Oxide / Conjugated Polymer Composite Photovoltaic Devices.**

Sean Eric Shaheen<sup>1</sup>, Renee B. Peterson<sup>2</sup>, Kathryn E. Brown<sup>1</sup>, Clark L. Fields<sup>2</sup>, Maikel van Hest<sup>1</sup>, Alexander Miedaner<sup>1</sup>, Garry Rumbles<sup>1</sup>, Brian A. Gregg<sup>1</sup> and David S. Ginley<sup>1</sup>; <sup>1</sup>National Renewable Energy Laboratory, Golden, Colorado; <sup>2</sup>Chemistry, University of Northern Colorado, Greeley, Colorado.

Photovoltaic devices based on a bulk heterojunction blend of a conjugated polymer with an electron acceptor species have now achieved power conversion efficiencies exceeding 3% under solar illumination. One of the factors limiting the performance of these devices is the recombination of holes and electrons to the ground state prior to being transported to the electrodes. This imposes limitations on how thick the devices can be made, and thus how much light is absorbed. A possible solution to this problem is the use of semiconducting metal oxide nanostructures as substrates for these devices. Here we discuss low temperature, solution-based fabrication of mesoporous tin oxide nanostructures and zinc oxide carpets in which nanofibers are grown vertically from the surface of the substrate. We demonstrate that the electronic properties of the surface of these materials can be significantly altered by chemisorption of various electron acceptor species and that the energetics of charge transfer at the oxide / polymer interface can be enhanced. Finally, we discuss the fabrication of prototype nanostructured oxide / conjugated polymer composite photovoltaic devices.

**2:30 PM K4.3****Controlled Assembly of Photovoltaic Nanocrystal/Polymer Composites.**

Ilan Gur<sup>1,3,2</sup>, Delia Milliron<sup>2,3</sup> and A Paul Alivisatos<sup>2,3</sup>; <sup>1</sup>Materials Science and Engineering, University of California, Berkeley, Berkeley, California; <sup>2</sup>Chemistry, University of California, Berkeley, Berkeley, California; <sup>3</sup>Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

While dispersed heterojunctions offer great potential for enhancing charge separation and collection in organic solar cells, current designs are highly limited by a lack of control over composite film morphology. We have developed a new approach for assembly of dispersed nanocrystal/polymer heterojunctions, whereby well-characterized ordered composites can be produced with control over nanocrystal dispersion. Ordered composites of cadmium telluride nanocrystals and poly(3-hexylthiophene) were assembled on both gold and indium tin oxide substrates via stepwise solution deposition. Modification of substrates with bi-functional linker molecules allowed for self-assembly of bound nanocrystal monolayers. Polymer was then spincast from a good solvent, filling gaps in the nanocrystal monolayer and yielding the final composite film. We have found that nanocrystal dispersion in such films is governed by the coverage of the original nanocrystal monolayer, which can be controlled via choice of linker molecule and deposition parameters. Another degree of control arises from the ability to vary the thickness of the polymer layer that is deposited within the interstices of the nanocrystal array. Assembled

films incorporated tetrapod-shaped cadmium telluride nanocrystals based on a previously reported synthesis, which allows for independent control of particle size and band-gap. This material is ideal for photovoltaic applications as it offers broadband absorption that is well matched to the solar spectrum. In addition, the branched tetrapod structure ensures a direct pathway for electron transport through the blend device.

**3:15 PM K4.4****Efficient small molecular weight bulk heterojunction solar cells by phase separation in a confined geometry.**

Peter Peumans<sup>2</sup>, Soichi Uchida<sup>2</sup> and Stephen R. Forrest<sup>2</sup>; <sup>1</sup>Electrical Engineering, Princeton University, Princeton, New Jersey; <sup>2</sup>Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, New Jersey.

The demonstration [1,2] and optimization [3] of the bulk heterojunction (BH) has led to impressive progress in the power conversion efficiency ( $\eta_P$ ) of polymer photovoltaic (PV) cells. The BH solves the exciton diffusion bottleneck of organic PV cells using an interpenetrating network of the donor and acceptor materials obtained by controlled phase separation of a blend of both materials. However, the realization of small molecular weight BH PV cells has been elusive because phase separation of a solid-state donor-acceptor (DA) binary mixture is accompanied by surface roughening, leading to incomplete contact formation and short-circuited devices. Here, we demonstrate a method for the realization of bulk heterojunction photovoltaic cells based on annealing-induced phase separation in confined mixtures of the small molecular weight materials copper phthalocyanine (CuPc) and 3,4,9,10-perylene tetracarboxylic bis-benzimidazole (PTCBI). To prevent surface-roughening during phase segregation, the solid-state mixed films are confined by a 100nm-thick Ag cap during annealing. While this cap prevents the development of surface roughness, it does not prevent phase segregation in the bulk of the mixture, leading to an interpenetrating network of  $\sim 20$ nm-diameter, pure, crystalline domains after annealing at 550K, as evidenced by electron microscopy, X-Ray diffraction and computer models. The resulting DA networks exhibit  $>30$ -fold improvements in external quantum efficiency ( $\eta_{EQE}$ ) over the non-annealed films after annealing at 540K. To undo degradation of the Ag metal contact during annealing, the Ag film is peeled-off and replaced with an exciton-blocking-layer/Ag contact. Contact replacement and a second anneal at 460K result in devices with a peak  $\eta_{EQE}$  of 28% and  $\eta_P$  of (1.42 $\pm$ 0.07)%. The peak  $\eta_{EQE}$  and  $\eta_P$  of an optimized bilayer device are 14% and (1.1 $\pm$ 0.1)%, respectively. Our results are the highest efficiencies reported for CuPc/PTCBI "Tang" PV cells [4]. References [1] J. J. M. Halls and C.A. Walsh and N.C. Greenham and E.A. Marseglia, R.H. Friend, S. Moratti and A.B. Holmes, Nature 376, 498 (1995). [2] G. Yu, J. Gao, J. Hummelen, F. Wudl and A.J. Heeger, Science 270, 1789 (1995). [3] F. Padinger, R.S. Rittberger and Sariciftci, Adv. Funct. Mater. 13, 85-88 (2003). [4] P. Peumans, A. Yakimov and S.R. Forrest, J. Appl. Phys. 93, 3693-3723 (2003).

**3:30 PM \*K4.5****Electronic Integration of Photosynthetic complexes.**

Julie Norville<sup>1</sup>, Marc Baldo<sup>1</sup>, Patrick Kiley<sup>2</sup>, Shuguang Zhang<sup>2</sup>, Francesco Stellacci<sup>3</sup> and Barry Bruce<sup>4</sup>; <sup>1</sup>Department of Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; <sup>2</sup>Center for Biomedical Engineering, MIT, Cambridge, Massachusetts; <sup>3</sup>Department of Materials Science, MIT, Cambridge, Massachusetts; <sup>4</sup>Department of Biology, University of Tennessee, Knoxville, Tennessee.

Biological photosynthetic protein-molecular complexes are archetype molecular circuits. Optimized by evolution, photosynthetic complexes have quantum efficiencies approaching 100%, making them attractive components for inclusion in photovoltaic devices. We describe electronic devices containing the complex Photosystem I (PSI), obtained from spinach. In addition, we characterize the self-assembly of oriented monolayers of PSI and discuss the potential for repairable electronics based on the reversible assembly and exchange of biological protein complexes.

**4:00 PM K4.6****Dye sensitized photovoltaic devices using solid-state**

**polyelectrolyte thin films.** Hiroaki Tokuhisa, Geoffrey Lowman and Paula T. Hammond; Chemical Engineering, MIT, Cambridge, Massachusetts.

We report photovoltaic devices consisting of TiO<sub>2</sub>, organic dyes and polyelectrolyte layer-by-layer (LBL) composite films. The devices exhibit 2~3% efficiency with unfiltered Xe lamp as a light source. A LBL assembled 1-alkyl-3-methylimidazolium iodide film was fabricated by alternating exposure to dilute aqueous solutions of linear polyethyleneimine (LPEI) or polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA), followed by post-assembly permeation of 1-alkyl-3-methylimidazolium iodide. The LBL

polyelectrolyte films act as a good polymer matrix and spacer material for dye sensitized photovoltaic devices. Specific performance metrics of dye sensitized photovoltaic devices constructed with the LBL / 1-alkyl-3-methylimidazolium iodide composite films, TiO<sub>2</sub> and organic dyes will be reported.

#### 4:15 PM \*K4.7

**Effect of Temperature and Illumination on the Electrical Characteristics of Polymer-Fullerene Bulk Heterojunction Solar Cells.** Vladimir Dyakonov, Ingo Riedel and Zivayi Chiguvare; University of Oldenburg, Oldenburg, Germany.

Easily processable conjugated polymers for optoelectronics, in general, and for photovoltaic energy conversion, in particular, is an attractive research field, in which the combined efforts of material science, device engineers, and spectroscopists are welcomed. To improve the efficiency of polymer solar cells, currently within the range of 2.0 and 3.0%, it is vital to understand which mechanisms control the current-voltage characteristics of a given device. Temperature and light intensity dependence of the main solar cell parameters is very informative for analysing losses. Firstly, temperature studies of Voc clearly show a linear increase towards thermodynamic values given by the HOMO-LUMO gap of the donor and acceptor. The open circuit voltage in the range 0.92V-0.97V was measured with a new DPM-12 acceptor. It is at least 100mV higher than the expected value, whereas the electron affinity is not much different from the widely used PCBM. The Jsc(T) was found to be controlled by a monomolecular recombination on the traps with the activation energy of 34meV. The second aspect is the manner in which electrical contact to the polymer or fullerene is created. The current flow across the ITO/P3HT/Al device is limited by hole injection at the Al/P3HT interface at T<240K when the device is reverse biased. Above this temperature, the bulk transport properties control the electrical characteristics. For the forward bias case, the ITO/P3HT contact does not limit the current, instead a space charge accumulates due to the low hole mobility in the polymer. A criterion will be discussed that allows for the determination of the field at which the charge injection through thermionic emission equals that of field emission for a given temperature, and interface potential barrier height.

#### 4:45 PM K4.8

**Photoconductivity of individual single-wall carbon nanotubes.** Marcus Freitag<sup>1,2</sup>, Yves Martin<sup>2</sup>, James A. Misewich<sup>2</sup>, Richard Martel<sup>2</sup> and Phaedon Avouris<sup>2</sup>; <sup>1</sup>Carbon Nanotechnologies, Inc., Houston, Texas; <sup>2</sup>IBM, Yorktown Heights, New York.

We have observed photoconductivity in single carbon nanotubes incorporated as the channel of ambipolar field-effect transistors. The nanotube molecule - only about 1.3 nm in diameter - acts as a polarized, wavelength-sensitive photodetector in the near infrared and has an estimated quantum efficiency of >10%. Hot electron-hole pairs are generated in the carbon nanotube mainly through transitions between its second van-Hove singularities. The carriers are separated by an applied electric field, leading to the photocurrent. The inherent selectivity due to the one-dimensional band structure lets individual laser-grown nanotubes detect radiation at specific wavelengths between 830 nm and >980 nm. The polarization maximum occurs along the direction of the carbon nanotube. Even without applied bias, some devices generate a photocurrent due to an asymmetric band bending in the contact regions. This photovoltaic effect is indicative of Schottky barriers of unequal height.

SESSION K5: Joint Session with V5: Interface Properties in Organic LEDs and Solar Cells I  
Chairs: Michael Gratzel and Neil Greenham  
Wednesday Morning, December 3, 2003  
Back Bay C (Sheraton)

#### 8:30 AM \*K5.1

**The Role of ITO Surface Pre-treatments in OLED and PV Performance: Control of Electronically Active Surface Area and Enhancement of Charge Injection Rates.**

Neal R. Armstrong, Chet Carter, Adam Simmonds and Carrie Donley; Chemistry, University of Arizona, Tucson, Arizona.

Commercially prepared indium-tin oxide (ITO), and related transparent conductive oxides (TCOs) are the anodes of choice for both organic light emitting diode (OLED) and organic photovoltaic (PV) devices, and are also the substrate of choice for many emerging chemical and biosensor technologies. The performance of these thin film devices, however, has been shown to be critically dependent upon the surface pretreatments of these materials, and a wide range of pretreatment protocols have been developed to enhance their work functions, provide chemical stability, and optimize charge injection rates. We show here that many of the problems inherent to the use of

ITO and related TCOs arise in the tendency toward hydrolysis of these oxides, as soon as they see even trace levels of atmospheric water, rendering up to 60-80% of the oxide surface electronically (electrochemically) inactive. Plasma etching, followed by simple chemisorption of dipolar molecules can be used to alter surface work functions, and greatly enhance electrochemically determined solution charge transfer rates of probe molecules. We also show strong correlations between the enhancement of these solution charge transfer rates, and device performance, in simple OLED and PV platforms.

#### 9:00 AM K5.2

**Transparent Conducting Oxide-Organic Transport Medium Interfaces. Tuning OLED Charge Injection and Interfacial Cohesion at the Molecular Level.** Tobin J. Marks, Chemistry, Northwestern U., Evanston, Illinois.

Small molecule and polymer based light emitting diodes typically consist of a transparent conducting oxide (TCO) anode, hole transporting layers (HTLs), emissive layers (EMLs), electron transporting layers (ETLs), and a low work function cathode. Although the fundamental physics of those factors influencing charge injection and electron-hole recombination and how these influence luminous efficiency are reasonably well understood, this is not true of those chemical and materials factors which govern luminescence, nanostructural integrity, and durability. We report here synthetic and physical studies focused on the consequences of: 1) Anode functionalization via molecular self-assembly, 2) Controlling the microstructure of the TCO-HTL interface, hence interfacial stability and hole injection fluence, 3) Substituting ITO with other TCOs having differing chemical and physical properties.

#### 9:15 AM K5.3

**Polymer Composite Light-emitting Devices with White Light Emission.** Cheng Huang<sup>1</sup>, Gang Huang<sup>2</sup>, C. Yin<sup>3</sup> and C.Z. Yang<sup>3</sup>;

<sup>1</sup>Materials Research Institute and Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania;

<sup>2</sup>Electronic Materials and Thin Film Devices Division, Physics Department, Suzhou University, Suzhou, Jiangsu, China;

<sup>3</sup>Department of Polymer Science and Engineering, Nanjing University, Nanjing, Jiangsu, China.

Recently composite organic light-emitting devices (COLEDs) such as polymer/dyes LEDs, polymer/quantum-dots LEDs, and polymer/polymer LEDs, have attracted attention mainly due to interfacial energy transfer, recombination, and excitation at the molecular level or on the nanoscale from the smart polymer composites, which could lead to improved performance or unique functionality in organic thin-film optoelectronic devices, such as color tunability, high energy conversion efficiency and easy single-layer fabrication. In this paper we demonstrate novel white-light-emitting single-layer alternating-current (ac) devices fabricated using the conjugated polymer composites. The new devices consist of a single emissive layer of polymer blends of conjugated electroluminescent polymers and sulfonated polyethylene oxide polyurethane single-ion conductors, sandwiched between two electrodes. The introduction of the single-ion polymer solid-state conductors modifies the charge injection characteristics, and this configuration enables the devices to work under both forward and reverse dc bias as well as in ac modes. A color-shifting phenomenon was observed in these devices, the EL spectra were greatly blue-shifted and extended, and thus the emission became white. The single-ion conductor based on sulfonated ionomers is capable of modifying the emission properties of emissive polymer at the molecular-scale interface such that the device emits the different color of lights than the bulk does. These color-shifting effects provide a new approach to achieve different emitting colors from limited luminescent polymers and are meaningful for the investigation on molecular-scale interface control and interaction between the electronic and ionic carriers in these devices. Also, these white light-emitting ac devices provide a novel approach to the fabrication of white and white generated R-G-B multicolor light emitting devices.

#### 9:30 AM \*K5.4

**Electron Transfer at Molecular-Semiconductor Interfaces.**

Gerald John Meyer, Chemistry, Johns Hopkins, Baltimore, Maryland.

It is well known that the energetic position of the conduction band edge, Ecb, of single crystal metal oxide semiconductors can be tuned with pH in aqueous solution. Much less is known about conduction band tuning in non-aqueous solution or with nanocrystalline materials. We have developed methods for tuning Ecb in anatase nanocrystals (with pH and other potential determining cations) relative to the formal reduction potentials of Ru(II), Os(II), and Re(I) polypyridyl metal-to-ligand charge transfer (MLCT) sensitizers. These studies are important in the development of mechanistic models of dye-sensitization and may provide a general approach for optimization of power conversion efficiencies in regenerative solar cells. Photoinduced electron transfer studies at these sensitized semiconductor interfaces



will be presented.

#### 10:30 AM \*K5.5

**Aromatic Amines as Co-Sensitizers in Dye Sensitized, Low Temperature Sintered Titania Solar Cells.** Russell Gaudiana, Savvas Hadjikyriacou, Jin-An He, David Waller and Zhengguo Zhu; Konarka Technologies, Inc., Lowell, Massachusetts.

Solar cells based on titania require the use of sensitizing dyes in order to make the absorption band coincident with the solar spectrum. The most successful sensitizing dyes are based on Ru-bipyridyls and are chosen for their absorption and redox characteristics. In addition to absorbing visible light, the sensitizing dye injects an electron from its excited state into the band gap of the titania. The injected electron must be conducted through the titania to an electrode upon which the titania is coated. One of the energy wasting pathways available to the injected electron is back transfer to an oxidized dye species on the surface of the titania. We have discovered a simple means of alleviating this energy wasting pathway by anchoring aromatic amines, i.e., co-sensitizers, at low concentration along with the Ru-based bipyridyl sensitizing dye to the surface of titania nanoparticles. Our results indicate that there is a significant increase in cell efficiency (~15% @AM 1.5, area > 1cm<sup>2</sup>) due to an increase in current when these species are present on the surface in combination with the dyes. We will report our preliminary results on a series of co-sensitizers, and we will compare these to literature findings which use similar compounds as either co-adsorbed species on titania or as substituents on the sensitizing dye molecule itself.

#### 11:00 AM K5.6

**Dye-sensitized TiO<sub>2</sub> solar cells on flexible substrates using laser based techniques.** Heungsoo Kim<sup>1</sup>, Gary P. Kushto<sup>2</sup>, Craig B. Arnold<sup>3</sup>, Alberto Pique<sup>1</sup> and Zakya H. Kafafi<sup>2</sup>; <sup>1</sup>Materials Science and Technology Division, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Optical Science Division, Naval Research Laboratory, Washington, District of Columbia; <sup>3</sup>Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey.

Laser direct-write (LDW) has been used to deposit mesoporous semiconducting TiO<sub>2</sub> nanoparticles for use in dye-sensitized solar cells. LDW enables the fabrication of conformal structures containing metals, ceramics, polymers and composites on rigid and flexible substrates without the use of masks or additional patterning techniques. The transferred material maintains a porous, high surface area structure that is ideally suited for dye-sensitized solar cells. In this experiment, a pulsed UV laser (355nm) is used to forward transfer the TiO<sub>2</sub> nanoparticle inks onto transparent conducting electrodes on flexible (polyethylene terephthalate (PET)) and rigid (glass) substrates. For the cells based on flexible PET substrates, the transferred TiO<sub>2</sub> layers were sintered using an in-situ laser to improve electron paths without damaging PET substrates. The interface and crystal structure of the processed TiO<sub>2</sub> layers were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). In our preliminary results, the solar cells fabricated with the laser processed TiO<sub>2</sub> on glass showed improved efficiencies than the device based on TiO<sub>2</sub> layer coated on glass using a conventional blading technique. We will present our experimental results for the optimization of laser processing conditions and interface properties for the deposition of TiO<sub>2</sub> on glass and PET substrates as a function of open circuit voltage, short circuit current, fill factor, and conversion efficiency.

#### 11:15 AM K5.7

**Charge Transport of Iodide/Tri-iodide Redox Couple in Ion Gels and Application to Dye-sensitized Solar Cells.**

Ryuji Kawano<sup>1</sup>, Masayoshi Watanabe<sup>1</sup>, Hiroshi Matsui<sup>2</sup> and Nobuo Tanabe<sup>2</sup>; <sup>1</sup>Department of Chemistry and Biotechnology, Yokohama Nat. Univ., Yokohama, Kanagawa, Japan; <sup>2</sup>Electronics Material Department, Material technology Laboratory, Fujikura Ltd., Koto-ku, Tokyo, Japan.

While dye-sensitized solar cells (DSSCs) offer cheap solar cells with reasonably high energy conversion efficiencies, the practical application requires solution of the fabrication problems and improvement of the long-term stability. The main problem is encapsulation of the cell with a volatile organic solvent electrolyte. Ionic liquids (room temperature molten salts: ILs) have unique properties such as non-volatility, non-flammability, high ionic conductivity and gel-forming property with polymers, and have been applied to the solar cells. We previously reported<sup>1</sup>) that equilibrium potentials and charge transport of an iodide/tri-iodide redox couple in an ionic liquid can be revealed by using microelectrode technique, where the anomaly of the charge transport at high concentrations of the redox couple with increasing of tri-iodide concentration can be attributed to the exchange reaction of I<sup>-</sup> + I<sub>3</sub><sup>-</sup> to I<sub>3</sub><sup>-</sup> + I<sup>-</sup>. So far, polymer electrolytes for DSSCs were mainly physical gels, because of the difficulty of chemical cross-linking reaction in the presence of

iodine molecules. We prepared chemical gels containing of iodide by using urethane-forming reaction. The charge transport mechanisms in the ion gels were analyzed by the electrochemical measurements using microelectrodes similar to the ionic liquids. Application of the ion gels to the DSSCs will also be reported. 1) R. Kawano and M. Watanabe, Chem., Commun., 2003, 330.

#### 11:30 AM K5.8

**Enhancement of Photoelectric Effect in Organic Dye Thin Film Cells by Surface Plasmon Excitation.** Keizo Kato<sup>1,2</sup>, Masaru Hirano<sup>3</sup>, Kazunari Shinbo<sup>1,2</sup>, Futao Kaneko<sup>1,2</sup> and Takashi Wakamatsu<sup>4</sup>; <sup>1</sup>Department of Electrical and Electronic Engineering, Niigata University, Niigata, Japan; <sup>2</sup>Center for Transdisciplinary Research, Niigata University, Niigata, Japan; <sup>3</sup>Graduate School of Science and Technology, Niigata University, Niigata, Japan; <sup>4</sup>Department of Electrical Engineering, Ibaraki National College of Technology, Hitachinaka, Japan.

Photoelectric properties have been investigated for the organic dye thin film cells utilizing surface plasmon (SP) excitation. The cells fabricated in this work had a prism/Al thin film/organic dye thin film/Ag thin film structure, which was the Kretschmann configuration in the attenuated total reflection (ATR) method. If the organic dye thin film exhibits p-type conduction, the Schottky and Ohmic contacts can be obtained at the interfaces between the organic dye and Al thin films and between the organic dye and Ag thin films, respectively, and the cells used in this work show photoelectric properties. The ATR properties were calculated for the cells using various parameters of the organic dye thin films and the prisms. It was found that the SP could be resonantly excited at the interface between Ag thin film and air using a prism with a low refractive index. On the contrary, it was found that the SP could be resonantly excited at both interfaces between Ag thin film and air and between Al and organic dye thin films using a prism with a high refractive index. It has been also estimated that the electric fields and optical absorptions in the organic dye thin films could be enhanced by the excitations of SP in the ATR configuration. The ATR and short-circuit photocurrent properties have been simultaneously measured as a function of the incident angles of the laser beams. The experimental and calculated results of the ATR and short-circuit photocurrent properties and the optical absorptions of the organic dye layers were discussed. It was found that the photoelectric effect in the organic dye thin film cells the Kretschmann configuration was enhanced by the SP excitation.

#### 11:45 AM K5.9

**The Organic/Inorganic Interface in Micro and Nano Composite Materials.** Zhexiong Tang, Hui Wan, Sze C Yang and Bruno M Vittimberga; Chemistry, University of Rhode Island, Kingston, Rhode Island.

Organic/inorganic composite particles provide an interesting material for studying the organic/inorganic interfaces relevant to that of thin film heterostructure devices. Due to the high percentage of interfacial material in a micro or nano composite, the chemical and spectroscopic evidences for interfacial interaction is not easily obscured by the bulk materials not at the interfacial region. We are interested in using the synthesis and the characterization of micro and nano composites to provide reference data for understanding the thin film interfaces in organic thin film devices. We report composite particles with an inorganic core and an organic shell with linear dimension in the micrometer and nano meter range. The inorganic core used in this study includes metal and ceramic particles with a wide range of electronic conductivity and proton affinity. The organic shell includes the intrinsic conducting polymers and organic dye molecules. Several methods of chemical synthesis and physical adsorption are used to assemble the organic/inorganic interfaces. The differences in the chemical and spectroscopic signatures of the composites of the synthesized material are characterized. The strategies for forming organic/inorganic junction with good electronic contact will be discussed.

SESSION K6: Joint Session with V6: Interface Properties in Organic LEDs and Solar Cells II

Chair: Sue A. Carter

Wednesday Afternoon, December 3, 2003  
Back Bay C (Sheraton)

#### 1:30 PM \*K6.1

**Modeling Of Polymer Photovoltaic Devices.** James A. Baker, Catherine M. Ramsdale, Baoquan Sun, Henry J. Snaith and Neil C. Greenham; Department of Physics, University of Cambridge, Cambridge, United Kingdom.

In this talk, I will present models which show how microscopic transport and recombination processes determine the current-voltage characteristics of polymer photovoltaic devices. Numerical solution of

the drift-diffusion-recombination equations allows us to predict current-voltage curves as a function of intensity, taking into account space-charge effects. In bilayer donor-acceptor devices, carriers are generated at the internal heterojunction, producing a diffusion current away from the heterojunction. At open circuit, this current must be balanced by a drift current produced by an internal electric field, which gives rise to additional contribution to the open-circuit voltage which depends logarithmically on intensity. Away from open-circuit conditions, the efficiency of the device is determined by the rate of dissociation of the bound polaron pairs which are produced by photoinduced charge transfer at the heterojunction. I will also discuss how these models may be extended to describe the performance of more complex structures such as polymer blends.

#### 2:00 PM K6.2

**Ultralight, Flexible and All-Solid-State Polymer Solar Cells.** Krishna C. Mandal, Michael K. Choi, Anton G. Smirnov, Rochelle B. Jones, Alan B. Kon, Fei Wang, D. Peramunage and R. David Rauh; Research & Development, EIC Laboratories, Inc., Norwood, Massachusetts.

This paper describes our research on new type of solar cells with very high specific power densities (1000-5000 kW/kg) for generating power in a new generation of ultralight space payloads. Several large area solar cells have been fabricated based on emerging concepts of interpenetrating network donor-acceptor composites and on dye-sensitized nanoporous TiO<sub>2</sub>, both types on thin, ultralight polymer substrates using low temperature processing conditions. High charge mobilities, processible conjugated organic polymers with a unique dendritic "star" structure developed at EIC Laboratories have been successfully utilized as an active component for the first time. Under solar simulator AM0 illumination, conversion efficiency > 2%, an extended lifetime with minimal efficiency loss, and a capability to operate under high vacuum have been demonstrated. These solar cells are highly promising because of their exceptionally low manufacturing cost and good prospects for stability in the space environment over a broad temperature range. These integrated polymer cells will enable inflatable solar arrays and sails that incorporate electronic components and also electrochromic layers for thermal or photon momentum control.

#### 2:15 PM K6.3

**Controlling Conjugated Polymer Thin Film Morphology.** Alison J. Breeze<sup>1</sup>, G. Rumbles<sup>1</sup>, B. A. Gregg<sup>1</sup> and D. S. Ginley<sup>2</sup>; <sup>1</sup>Basic Sciences, National Renewable Energy Laboratory, Golden, Colorado; <sup>2</sup>National Center for Photovoltaics, National Renewable Energy Laboratory, Golden, Colorado.

We have explored methods to control the morphology of photoactive conjugated polymer thin films. The polymers studied, poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylene vinylene) (OC<sub>1</sub>C<sub>10</sub>-PPV) and regioregular poly(3-hexylthiophene) (P3HT), are commonly utilized in organic optoelectronic devices such as photovoltaics, light-emitting diodes, and thin film transistors. Understanding and controlling the factors which affect the film morphology is vital for optimizing device performance. Through analysis of the absorption characteristics of the films, we have found that the substrate influences the film such that there is an increased degree of order of the polymer chains close to the substrate / film interface. The rate of solvent evaporation from a spin-cast film, controlled through both solvent choice and processing conditions, also strongly affects the degree of order in the film: fast drying films display a lower degree of order than films which dry more slowly. Device performance for polymer-based solar cells constructed under various processing conditions will be presented.

#### 2:30 PM K6.4

**Temperature Dependent Study on PPV-based Polymer Hybrid Photovoltaic Devices.** Yuko K Nakazawa<sup>1</sup>, Sue A Carter<sup>1</sup>, H. H Hoerhold<sup>2</sup> and H. Tillmann<sup>2</sup>; <sup>1</sup>Dept. of Physics, Univ. of California Santa Cruz, Santa Cruz, California; <sup>2</sup>Institute of Organic Chemistry and Macromolecular Chemistry, Univ. of Jena, Jena, Germany.

Results on the temperature dependent I-V characteristics of polymer hybrid photovoltaic devices based on PPV copolymers are presented. We modified device architectures by blending [6,6]-phenyl-C<sub>61</sub> butyric acid methyl ester (PCBM) or cyano (CN)-ether-PPV in the active layer of the PPV copolymer. The polymer photovoltaic devices consist of patterned ITO, a spun cast sintered TiO<sub>x</sub> sol-gel layer, a spun cast polymer layer, and an evaporated Au electrode. The PPV/TiO<sub>x</sub> interface serves as the electronic dissociating surface, with PPV serving as the hole-transporter and TiO<sub>x</sub> as the electron transporter. The addition of CN-ether-PPV and PCBM results in improvements in the device performance due to increase in the number of dissociation sites. The photo generated current-voltage relationships are measured in a temperature controlled OXFORD cryostat operating between

200K to 400K using a 5w xenon lamp as the light source. We also measure the temperature dependence of the dark current to extract the zero field hole mobility using space charge limited current analysis. These measurements will be analyzed to determine how changes in the carrier mobility affect device performance for different hybrid structures. Comparisons will also be made between structures consisting of TiO<sub>x</sub>/Au interfaces and PEDOT:PSS/LiF interfaces. Finally, an analytical model will be proposed for describing the effect of charge transport on polymer-based photovoltaics.

#### 2:45 PM K6.5

**Photovoltaic Cells Based on Semiconducting Polymers in Self-Assembled Mesoporous Titania.** Michael David McGehee and Kevin Michael Coakley; Materials Science and Engineering, Stanford University, Stanford, California.

We have developed a technique for making high-quality thin films of titania with well ordered arrays of pores that have a diameter in the range of 4-10 nm using a titania sol-gel precursor and a structure-directing amphiphilic block copolymer. We have filled the pores with regioregular poly(3-hexyl thiophene) by spin casting the polymer on top of the titania and then heating the polymer at temperatures between 100 and 200 degrees C. We find that 32 % of the volume of the film can be filled with polymer in just a few minutes at 200 degrees C. At lower temperatures, the infiltration process takes longer and the amount of polymer that can be incorporated is less. We hypothesize that the polymer coats the walls of the pores and that the coating is thicker when the polymer is incorporated at higher temperatures. Using absorption and photoluminescence spectroscopy we have determined that the polymer chains take on a coiled conformation in the pores and that there is little or no polymer crystallization. The photoluminescence measurements also show that photoinduced electron transfer takes place from the polymer to the titania, but that not all of the excitons are quenched by electron transfer. Since the pores are less than 10 nm in diameter and excitons can diffuse over this distance before emitting a photon in a spin cast polymer film, we think that exciton diffusion is hindered inside the pores. We attribute this to the coiled polymer chain morphology. Modifying the titania surface with an organic monolayer improves the morphology of the polymer, enabling more effective exciton diffusion and electron transfer to the titania. We will present the effect that these titania surface modifiers have on the performance of photovoltaic cells made with polymers in mesoporous titania.

#### 3:30 PM \*K6.6

**Application of Printing Techniques in Modifying Interfacial Properties in Organic Electronics and Optoelectronics.** Ghassan E. Jabbour, Y. Yoshioka and P. Calvert; Optical Sciences Center, University of Arizona, Tucson, Arizona.

Organic based electronics and optoelectronics materials and devices have been progressing at a rapid rate in the last few years. The active layers in these devices can range from few monolayers to several tens of nanometers in thickness. Devices based on such layers are greatly influenced by the interfaces between them. In this talk we will focus on how to modify the electrical sheet resistivity of conducting polymers using inkjet printing. This technique allows for the creation of grey-scale electrical interfaces that have direct application in many areas including the fabrication of low cost light-emitting structures.

#### 4:00 PM K6.7

**Organic Light Emitting Devices with Laminated Top Contacts.** Dan Bernards<sup>1</sup>, Tom Biegala<sup>1</sup>, Jason Slinker<sup>1</sup>, Alon Gorodetsky<sup>1</sup>, Sara Parker<sup>1</sup>, Samuel Flores-Torres<sup>2</sup>, Hector Abruna<sup>2</sup> and George G Malliaras<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

It is known that top contact evaporation damages organic thin films. To address this problem, lamination techniques have been developed as a non-impact methods for top contact deposition. OLEDs with both evaporated and laminated contacts have been fabricated and tested to assess the impact of evaporation on organic films. Differences in performance of these devices will be discussed.

#### 4:15 PM K6.8

**Solvent Processible Composite Carbon Nanotube Cathode for Polymer LED Applications.** Gao Liu, Steve Johnson and John B Kerr; Lawrence Berkeley National Laboratory, Berkeley, California.

We report the first successful application of polymer and single wall carbon nanotube (SWCN) composite materials as an electron injection cathode to fabricate LED devices with MEH-PPV and polyfluorene as light emitting layers. The polymer and SWCN composite electrode is solvent processible and readily applied onto the light emitting material using printing or other solvent-casting techniques. The turn-on voltage for these devices is as low as 5 V. The

emission spectra are similar to metal cathode based devices. The SWCN are aggregated in the polymer matrix resulting in a textured light output. The SWCN aggregation also improves the conductivity of the composite cathode. The properties of the light emitting polymer and cathode polymer host affect the intensity and efficiency of the polymer LED device. This study is focused on "composite polymer - SWCN - light emitting polymer" interfaces in this system. By adjusting the polymer host structure, concentration of SWCN in the polymer host and light emitting polymer structure, the SWCN are organized at the surface of the light emitting polymer to achieve higher efficiency through improved LED polymer and SWCN contact.

#### 4:30 PM \*K6.9

**Printable Optoelectronics: Light-Emitting Displays And Photovoltaics On Flexible Substrates.** Melissa Ann Kreger<sup>1,2</sup>, S. A. Carter<sup>2</sup>, M. Wilkinson<sup>1</sup>, Y. Nakazawa<sup>2</sup>, J. J. Breeden<sup>1</sup>, E. Jones<sup>1</sup>, M. Hendricks<sup>1</sup>, H. H. Horhold<sup>3</sup> and H. Tillmann<sup>3</sup>; <sup>1</sup>Add-Vision, Inc., Scotts Valley, California; <sup>2</sup>Physics Department, University of California-Santa Cruz, Santa Cruz, California; <sup>3</sup>Institute for Organic and Macromolecular Chemistry, University of Jena, Jena.

The objective of this research was to explore the screen-printing process to fabricate inexpensive optoelectronic devices. We have fabricated light-emitting displays and polymer based photovoltaics on flexible PET substrates. Various device structures are discussed with reference to cost effective construction, optimum performance and stability. The processing conditions associated with patterning substrates, ink formulation, printing active layers, and encapsulation will be presented. We are continually interested in the durability of the polymer inks, the electroluminescence uniformity, the luminance output, the quantum efficiency, and the stability of the displays in both dry nitrogen and air atmospheres. Results for light-emitting polymer devices created by a fully screen-printed process including J-V-L characteristics, external quantum efficiency and lifetimes are presented. We will also report our work on hybrid inorganic/organic photovoltaics. Plastic solar cells provide an opportunity for inexpensive solar energy conversion. The viability of screen-printing a low cost, large area solid state device consisting of a titanium oxide sol gel or nanoparticle anode, a photoactive polymer layer and a silver cathode has been investigated. Effective exciton dissociation, charge transport and collection are discussed with respect to interfacial morphology at the titanium oxide/polymer boundary and polymer layer thickness. Lifetime measurements, complimented by microscopy images suggest the primary degradation mechanisms are affiliated with impurities or insoluble material in the charge transport or emissive layers, delamination of electrodes, or chemical reaction with air and water.

#### SESSION K7: Poster Session: Physical Properties and Synthesis of Materials

Chairs: Mary Galvin and George Malliaras  
Wednesday Evening, December 3, 2003

8:00 PM  
Exhibition Hall D (Hynes)

#### K7.1

**Synthesis and Characterization of Novel Conductive Fullerene-Based Star Polymers Containing PAA/PANI Arms.** Chih-Chien Chu<sup>1,2</sup>, Tong-In Ho<sup>1</sup> and Leeyih Wang<sup>2,3</sup>; <sup>1</sup>Chemistry, National Taiwan University, Taipei, Taiwan; <sup>2</sup>Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; <sup>3</sup>Institute of Polymer Sciences and Technology, National Taiwan University, Taipei, Taiwan.

Synthesis and characterization of Novel C60-based starburst polymer complex comprising conjugated moieties will be demonstrated. The synthetic strategy involves: 1) design and synthesis of multifunctional fullerene as core molecule, 2) preparation of star-like poly(acrylic acid) (PAA) via the arm-first and core-first methods, 3) formation of conducting complexes at each polymer arm via PAA-guided synthesis of polyaniline (PANI). The analysis of molecular weight distribution provides clear evidences for the formation of starburst polymer complexes. These Novel materials also exhibit excellent stability in aqueous solution. In addition, the results from the star polymer complex of PSS/PEDOT will be presented and discussed.

#### K7.2

**Standard and Non-Standard Techniques for Phthalocyanine Preparation.** Boris Ildusovich Kharisov<sup>1</sup>, Luis Angel Garza Rodriguez<sup>1</sup>, Miguel Angel Mendez Rojas<sup>2</sup>, Ubaldo Ortiz Mendez<sup>1</sup> and Leonor Maria Blanco Jerez<sup>1</sup>; <sup>1</sup>Facultad de Ciencias Quimicas, Universidad Autonoma de Nuevo Leon, San Nicolas de los Garza, Nuevo Leon, Mexico; <sup>2</sup>Department of Chemistry, Universidad de Las Americas, Puebla, Puebla, Mexico.

Several standard and non-standard techniques for the synthesis of metal-free phthalocyanine (PcH<sub>2</sub>) and metal phthalocyanines ("PcM<sup>n</sup>") from urea and phthalic anhydride, phthalimide, 1,3-diiminoisindoline (1,3-D) and phthalonitrile have been generalized. The results show that the nature of the solvent is the most important factor in the conventional chemical and direct electrochemical synthesis of the final products. Different routes for phthalocyanine preparation are discussed, in particular, use of activated pyroforic and Rieke metals, "sacrificial" metal anodes, and ultraviolet irradiation of the reaction system.

#### K7.3

**The Preparation of Tripodal Hybrid Hyperbranched Polymers.** Tae Sung Si, Bum-Je Cho and Sang Man Koo; Chemical engineering, School of engineering, Hanyang University, Seoul, South Korea.

Novel tripodal hybrid hyperbranched polymers based on organosilanes and organic groups were prepared using hydrosilylation with following conditions: reaction temperature of 90 °C, polymerization time of 18 hrs, and Pt(dvs) as a catalyst. The products were characterized by IR and <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR and showed amber-colored resin in room temperature. From the GPC result, it was founded that the degree of polymerization was rather low with the molecular weight of 1500 g/mol. The thermal analysis showed that the hyperbranched polymers exhibited low T<sub>g</sub> ranging from -114 to -83 °C. They decomposed at the temperature ranging from 462 to 492 °C and converted to ceramic material at 800 °C with the char yield of 16-47%. The UV-visible-NIR spectra of the polymers showed broad absorptions in the 300~320 nm region, which is red shifted, compared to phenyl group (260 nm), due to the conjugation effect. The conductivity and fluorescence properties of hyperbranched polymer were also investigated.

#### K7.4

**Novel polymeric thin film deposition based on PECVD process.** Mario J. Cazeca<sup>1</sup>, Changshu Kuo<sup>1</sup> and Jayant Kumar<sup>2</sup>; <sup>1</sup>AST Products, Inc., Billerica, Massachusetts; <sup>2</sup>Physics Department, University of Massachusetts Lowell, Lowell, Massachusetts.

We have developed a polymeric thin film deposition process, where a plasma enhanced chemical vapor deposition reactor is equipped with a gas monomer injector apparatus composed of a micro-pump and a small heated chamber. Monomer reagents injected by the micro-pump inside the heated chamber are transformed to the vapor state and delivered to the plasma chamber. This system allows thin film deposition from monomers with high boiling point; over 160C. Thin films deposited by this system are pinhole free and uniform over an 8 inch diameter substrate. This system also renders the deposition of novel polymer films in multilayers with different characteristics or gradient compositions for waveguiding and related applications. Photoelectric polymer thin films constructed by thiophene families or other reagents have also been prepared with simultaneous dopant deposition. Characterization of films prepared by these processes will be presented.

#### K7.5

**Synthesis and Electrochemical Properties of Bithiophene-containing Cyclobutadiene Cp Cobalt Complexes.** Paul Byrne, Dongwhan Lee and Timothy M Swager; Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

An emerging trend in the design and synthesis of new conducting polymers concerns enhancing delocalization of charge carriers within the polymer. In an approach to develop new synthetic strategies for the synthesis of such electroactive materials, a cobalt-stabilized cyclobutadiene moiety was incorporated into a prototypical conducting polymer, polythiophene. It was expected that the inherent antiaromaticity of the cyclobutadiene system would promote charge delocalization in the polymer, rendering unique electrochemical properties. The [2+2] cycloaddition of alkynes mediated by CpCo(CO)<sub>2</sub> was utilized to synthesize several bithiophene-containing cobalt complexes. These compounds were electrochemically polymerized to give the desired thiophene-cyclobutadiene metallopolymers. The electrochemical properties of these materials were studied using various techniques including in situ conductivity measurements and spectroelectrochemistry. The effect of the stereochemistry of the monomers on the electrochemistry of the resulting polymers was also investigated.

#### K7.6

**Ambipolar Carrier Transport In Bithiazole Oligomers.** Woong Sang Jahng<sup>1</sup>, Hyunsik Moon<sup>2</sup>, Anthony H. Francis<sup>1</sup> and M. David Curtis<sup>1,2</sup>; <sup>1</sup>Chemistry, University of Michigan, Ann Arbor, Michigan; <sup>2</sup>Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Most organic semiconducting materials that have been studied over the last decade can be described as p-type semiconductors in which holes are the major charge carriers. Only very few materials were found to function as air stable n-type semiconductors, although ambipolar transport materials would be ideal for many applications. For electron transport, materials should be designed such that radical anion may be stabilized. In this respect, electron deficient heterocyclic ring systems such as thiazole are favorable to facilitate electron conduction. We report ambipolar carrier transport in thin films of bithiazole oligomers, characterized by both time-of-flight (TOF) technique and space charge limited current (SCLC) spectroscopy. Electron and hole mobilities, measured by the TOF technique on Au (200 nm)/Si wafer/4,4'-dibutyl 2,2'-bithiazole (BBT) dimer (0.85 mm)/Au (20 nm), were found to be  $2.6 \times 10^{-4} \text{ cm}^2/\text{Vs}$  and  $1.9 \times 10^{-4} \text{ cm}^2/\text{Vs}$ , respectively. The comparable mobilities were obtained in SCLC spectroscopy. Film morphology, temperature dependence of mobility and thereby transport mechanism will be discussed.

#### K7.7

##### **Electro-Driven Polypyrrole Actuators Working in Air.**

Hideori Okuzaki, Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Kofu, Japan.

The combination of electrical and hygroscopic nature of conducting polymers provides an insight into the development of a new class of electro-driven actuators or artificial muscle systems that work in ambient air. We have previously reported that electrochemically synthesized polypyrrole films undergo quick and intensive bending in air as a result of a dimensional change due to the sorption of water vapor from one side of the film. Furthermore, we have found that an application of electric field causes contraction of this film in air. Under isometric conditions, the film generates contractile stress in response to the RH change and/or electric field. When dc 2V is applied to the film under the thermostatic conditions (RT, 50% RH), the film generates contractile stress repeatedly in response to the applied voltage. The stress reaches 6.1 MPa, corresponding to an equivalent contractile force of 93 gf, which is 4 orders of magnitude larger than its own weight (7.6 mg) and is nearly 20 times that of skeletal muscle in animals (0.3 MPa). The mechanism can be explained in terms of the electrically induced dehydration of the conducting polymer film caused by the local Joule heating. Unlike in the conducting polymers based on the electrochemical doping, this system can serve as a new type of electrically driven muscle that works in air without using an electrolyte solution or counter and reference electrodes, where the electric field is capable of controlling the sorption equilibrium to desorb water vapor from the film. Furthermore, various conducting polymers that undergo dimensional changes due to the sorption of water vapor can be employed on the same principle.

#### K7.8

##### **Design and Assembly of Iron Oxide Nanoparticles for Sensor Application.**

Lingyan Wang<sup>1</sup>, Li Han<sup>1</sup>, Jin Luo<sup>1</sup>, Masato Tominaga<sup>2</sup> and Chuan-Jian Zhong<sup>1</sup>, <sup>1</sup>Chemistry, SUNY-Binghamton, Binghamton, New York; <sup>2</sup>Kumamoto University College of Medical Science, Kumamoto, Japan.

Metal and oxide nanoparticles offer intriguing opportunities for designing chemically sensitive interfacial materials because of novel electronic and magnetic properties emerging at the nanoscale. This presentation describes recent results of two approaches towards the preparation of iron oxide nanoparticles. In the first approach, iron-storage ferritin was utilized for the preparation of iron oxide nanoparticles. The preparation involves thermal removal of the protein shell from ferritin. In the second approach, iron pentacarbonyl compounds are used for the preparation of iron oxide nanoparticles by thermal decomposition at controlled temperatures and under different capping agents. Iron oxide nanoparticles with a range of core sizes, different surface compositions, and high monodispersity have been prepared. The structure and morphology have been characterized using TEM, AFM, UV-Vis, and FTIR techniques. The assembly of the nanoparticles on chemoresistor and piezoelectric devices is studied for detecting volatile organic vapors.

#### K7.9

##### **Electrical Transport Through Self-Assembled Multilayers of a Mercaptoalkanoic Acid in a Self-Aligned Structure for Low Parasitic Leakage.**

Troy Graves-Abe<sup>1</sup>, Zhenan Bao<sup>2</sup> and J C Sturm<sup>1</sup>, <sup>1</sup>Center for Photonics and Optoelectronic Materials, Dept. of Electrical Engineering, Princeton University, Princeton, New Jersey; <sup>2</sup>Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey.

Molecular-scale electronics, in which critical device dimensions are defined by the length of a molecule, represent a fundamental scaling limit. One approach to fabricate such devices involves self-assembly of organic monolayers, and charge transport in the metal-monolayer

junctions formed in these systems has been studied [1]. If the devices are to be used in traditional logic circuits, it will be necessary to employ a transistor geometry in which a third terminal gates the junction to control its gain. Although most work to date has focused on short molecules (< 3 nm), longer molecules are necessary in a 3-terminal device to allow penetration of the gate field into the molecular layer [2]. However, long semiconducting molecules (> 5 nm) do not self-assemble well [3]. Therefore, we have examined an alternative approach [4], in which multiple layers of HS(CH<sub>2</sub>)<sub>10</sub>COOH (MUA) are self-assembled to obtain organic films that are 4 - 11 nm thick. We integrate these layers into a novel structure for minimizing electrical defects in self-assembled organic layers and report on the first current-voltage characteristics of MUA multilayers. Multiple layers of MUA were grown on gold by alternating immersions of a gold-coated substrate into solutions containing first MUA then Cu(CIO<sub>4</sub>)<sub>2</sub>. Each immersion in the first solution increased the thickness of the MUA multilayer by 1.5 nm, as confirmed by ellipsometry. Films of 3 to 7 layers (4 - 11 nm) were grown in this manner. To measure electrical characteristics, a second gold electrode was then deposited on top of the organic layer by thermal evaporation. However, it was found that large-area (> 10 μm<sup>2</sup>) devices were frequently shorted due to the high possibility of penetration of the evaporated gold through the thin MUA film. Minimal-area devices were fabricated by first etching into a silicon wafer to define pillars. A thin gold film and a layer of SiO<sub>x</sub> were then deposited vertically onto the structure so that the SiO<sub>x</sub> covered the top of the gold film, but not its side (defined by the pillar edge). MUA layers were then grown on the exposed sides of the gold. Finally, a second layer of gold was deposited at a shallow angle and reduced substrate temperature to contact the organic film. This structure ensures a small device area (only along the pillar edge) because SiO<sub>x</sub> separates the gold layers on the top of the pillar. Devices having contact areas less than 10 x 0.03 μm<sup>2</sup> and yields greater than 90% were obtained. Devices were insulating for both positive and negative bias and remained stable over multiple scans. Currents decreased and breakdown voltages increased as the MUA layer increased from 4 - 11 nm in thickness. Qualitative description of the results will be presented. [1] J. K. N. Mbindyo et al, J Am Chem Soc 124, 4020 (2002). [2] C. R. Kagan et al, Nano Lett 3, 119 (2003). [3] J. M. Tour, Acc Chem Res 33, 791 (2000). [4] S.D. Evans et al, J Am Chem Soc 113, 5866 (1991).

#### K7.10

##### **Self-Assembly in Liquid Crystals.**

Yue Zhao, Steve Leclair, Xia Tong and Yves Dory, Chemistry, University of Sherbrooke, Sherbrooke, Quebec, Canada.

Liquid crystals were used as self-assembly medium to generate new structures and new functional materials. On the one hand, self-assembly of a cyclic peptide in a nematic liquid crystal results in the formation of micrometer-sized hexagonal tubes organized by nanotubes of the peptide, as a result of a hierarchical and self-similar growth process. On the other hand, gelation of a cholesteric liquid crystal by a gelling compound (gelator) containing azobenzene chromophore gives rise to nanometer-sized fibrous aggregates of the gelator in the liquid crystal. Such self-assembled liquid crystal gels can display scattering-based electrooptical switching and be used to prepare electrically switchable diffraction grating due to a light-induced reorganization process.

#### K7.11

##### **Electro-Optical Properties of P(VDF-TrFE) Based Terpolymer and its Application for a Tunable Fabry-Perot Interferometer.**

Daeyong Jeong<sup>1</sup>, Yong-Hong Ye<sup>2</sup> and Qiming Zhang<sup>1,2</sup>, <sup>1</sup>Materials Research Institute, University Park, Pennsylvania; <sup>2</sup>Electrical Engineering, University Park, Pennsylvania.

With the high electrostrictive strain, high energy irradiated poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer has attracted much attention in actuation technologies, recently, we found that PVDF based terpolymer, which is obtained by randomly inserting a bulky monomer into copolymer chain, also shows relaxor behavior and possesses large strain up to ~7%. Furthermore, this terpolymer is promising for microdevice fabrication with the easiness of thin film process. In P(VDF-TrFE) based polymers, it is known that large strain is associated with the molecular conformation change. This structural change may also induce the large reflective index change. In this presentation, the electro-optic (E-O) effects of P(VDF-TrFE) based terpolymers will be investigated. P(VDF-TrFE) polymer has high transparency from the visible to Near-IR range. In order to characterize E-O coefficients, Mach-Zender interferometry method was employed. In addition, tunable Fabry-Perot interferometer will be fabricated using the E-O properties and/or the electromechanical properties of P(VDF-TrFE) terpolymer.

#### K7.12

##### **Switchable Bragg Gratings Based on Liquid Crystal Infiltrated Polyelectrolyte Multilayer System.**

Lei Zhai<sup>1,2</sup>,

Hyunku Ahn<sup>1,2</sup>, Aleks J White<sup>1</sup>, Tom Wang<sup>1,2</sup>, Michael F Rubner<sup>1</sup> and Robert E Cohen<sup>2</sup>; <sup>1</sup>Department of Materials and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Electrically switchable Bragg gratings have numerous potential applications in optical communications. Polyelectrolyte multilayer Bragg stacks with alternating solid and porous blocks have been built using poly(acrylic acid) (PAA), poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (SPS). The porous blocks were developed through the formation of nanosize pores in the PAA/PAH blocks upon immersion of the assembled films into a pH 2.3 bath for 60 seconds followed by 60 s rinse with deionized water. The PAA/PAH blocks were capable of undergoing a reversible, pH-gated nanoporosity transition while the SPS/PAH blocks remained unchanged under low pH conditions. Liquid crystal E7 was successfully loaded into the nanoporous blocks by capillary forces to form a Bragg stack with alternating blocks of tunable refractive index. We are currently exploring electric-field-switchable Bragg gratings using this system.

#### **K7.13**

##### **Synthesis of New Two-Photon Absorbing C60 Derivatives.**

Prashant A Padmawar<sup>1</sup>, Taizoon Canteenwala<sup>1</sup>, Sarika Verma<sup>1</sup>, Long Y Chiang<sup>1</sup> and Loon-Seng Tan<sup>2</sup>; <sup>1</sup>Department of Chemistry, Institute of Nanoscience and Engineering, University of Massachusetts Lowell, Lowell, Massachusetts; <sup>2</sup>Polymer Branch, AFRL/MLBP, Air Force Research Laboratory, Wright-Patterson Air Force Base, Dayton, Ohio.

Novel covalently linked C60-diphenylaminofluorene dyads 7-(1,2-dihydro-1,2-methanofulleren[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene and 7-(1,2-dihydro-1,2-methanofulleren[60]-61-{1,1-dicyanoethylene})-9,9-diethyl-2-diphenyl aminofluorene were synthesized. Synthetic method involved cyclopropanation of C60 with a key synthon 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene to yield 7-(1,2-dihydro-1,2-methanofulleren[60]-61-carbonyl)-9,9-diethyl-2-diphenylamino fluorene which on further introduction of dicyanoethylene group at C-62 afforded 7-(1,2-dihydro-1,2-methanofulleren[60]-61-{1,1-dicyanoethylene})-9,9-diethyl-2-diphenylamino fluorene. Synthesis of key synthon 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene was achieved by a three-steps procedure starting from commercially available 2-bromofluorene via diethylation at C-9 of fluorene, Buchwald-Hartwig protocol for attachment of diphenylamino group at C-2 of fluorene, and further Friedel Craft acetylation to get bromoacetyl group at C-7 of fluorene moiety. These novel C60-diphenylaminofluorene derivatives were fully characterized, using conventional spectroscopic studies including <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, MS, absorption and emission spectra and X-ray crystallography. Its fluorescence spectrum shows strong quenching of the fluorene fluorescence by the attached C60 cage. Target compounds are potentially useful fluorophores in two-photon fluorescence microscopy as their UV-vis spectra display desirable absorption in the range of interest suitable for two-photon excitation. Preliminary measurements indicated these derivatives exhibiting high two-photon cross-sections. Detailed results will be discussed.

#### **K7.14**

##### **The Synthesis and Properties of Novel Hybrid Organic-Inorganic Non-Linear Optical (NLO) Materials.**

Inna Perepichka, Mireille Ellaya, Le H. Dao, Nathalie Perret and Jean-Claud Kieffer; INRS-Energy, Materials and Telecommunications, University of Quebec, Varennes, Quebec, Canada.

For the last two decades, a considerable interest has been developed to organic NLO materials, for applications in telecommunications and relevant fields. In contrast to commercialized inorganic materials such as LiNbO<sub>3</sub>, organic NLO materials have a much faster response and potentially a much lower cost of production. Their properties can also be fine tuned through a rational structural design. The typical organic NLO chromophores are highly polarizable push-pull molecules of D- $\pi$ -A type. Usually these NLO-active compounds are blended with a processible polymer and the individual NLO molecules are aligned in the polymer matrix by electrical field poling to produce working NLO devices[1]. A typical problem in this fabrication method is the high tendency of NLO chromophores to form crystalline domains, often with a centrosymmetric structure. To overcome this problem, a covalent linkage of NLO molecules to polymer chains has been employed. The most significant recent advance in this technology is the use of organosilicone polymers as a matrix for NLO chromophores (which are also covalently linked to the polymer)[2,3]. This approach allows for facile low-cost fabrication of the NLO materials via sol-gel chemistry, and the materials benefit from the exceptionally high thermal stability and perfect transparency of organosilicates. However, the majority of the studies of these hybrid organic-inorganic NLO materials employed rather simple NLO chromophores, which

have moderate NLO activities, and the engineering environment of this research paid little attention to the chemical side of the problem[4,5,6]. We report here the design and synthesis of different NLO chromophores, their attachment to silicon-based prepolymer, polymerization via sol-gel hydrolytic process, materials characterization by various methods (IR, UV, etc) and studies of NLO activity in second harmonic generation (SHG) experiments. More specifically, we will present (i) the synthesis of NLO D- $\pi$ -A chromophores (D = dialkylamino group,  $\pi$  = azobenzene, bithiophene, or dithienof[3,2-b:2',3'-d]thiophene, and A = nitro, tricyanoethylene, or diphenylthiobarbituric), (ii) the attachment of the NLO chromophores to the silicone chain by an improved *catalytic* epoxide-alcohol or isocyanate-alcohol reactions under mild conditions, and (iii) the influence of these improvements on the NLO properties of the new hybrid organic-inorganic NLO materials. -----  
References [1] Dao, L.H.; Parbhakar, K.; Nguyen, M.H.; Jin, J.M.; Sun, Y.; Beaudoin, Y.; Dittus, H.; Eigenbrod, C. Acta Astronautica, 2002, 51, 699 [2] Sekkat, Z.; Wood, J.; Geerts, Y.; Knoll W. Langmuir 1996, 12, 2976. [3] Delaire, J. A.; Nakatani, K. Chem. Rev. 2000, 100, 1817. [4] Hsiue, G.-H.; Lee, R.-H.; Jeng, R.-J. Chem. Mater. 1997, 9, 883. [5] Lebeau, B.; Brasselet, S.; Zyss, J.; Sanchez, C. Chem. Mater. 1997, 9, 1012. [6] Rojo, G.; Martin, G.; Agullo-Lopez, F.; Chem. Mater. 2000, 12, 3603.

#### **K7.15**

##### **Dynamically Tunable Optical Shutters Based on Molecularely-Assembled Polymeric Microstructures.**

Hyunku Ahn<sup>1,2</sup>, Lei Zhai<sup>1,2</sup>, Alex J. White<sup>1</sup>, Adam J. Nolte<sup>2</sup>, Tom Wang<sup>2</sup>, Robert E. Cohen<sup>2</sup> and Michael F. Rubner<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Layer by layer assembly has received much attention recently as a simple, versatile technique for building various thin film optoelectronic devices. We have previously found that multilayer films composed of the weak polyelectrolytes poly (acrylic acid) (PAA) and poly (allylamine hydrochloride) (PAH) can undergo a transition to a 3-D interconnected microporous network in a bath of low-pH water. These microporous structures were characterized by atomic force microscopy and scanning electron microscopy. In this work, the birefringent nematic liquid crystal E7 was successfully loaded into the microporous multilayers by capillary forces to create tunable light scattering centers. Electrically tunable optical shutters based on these molecularely-assembled polymeric microstructures were fabricated. When an electric field is applied, the refractive index of the aligned LC along the direction of the electric field and the polymer matrix was matched, which caused the device to change from an opaque to a transparent state. The optical characterization and the electrical properties of the devices were investigated. Transmission measurements showed reversible switching and an optical contrast ratio of approximately 2.7 under application of an electric field strength  $E=7V/\mu m$ .

#### **K7.16**

**Abstract Withdrawn**

#### **K7.17**

##### **Electrochemical Study of Tetra-15-Crown-5-Phthalocyanine and Its Copper and Cobalt Complexes.**

Boris Ildusovich Kharisov<sup>1</sup>, Jose Fernando Garcia Martinez<sup>1</sup>, Leonor Maria Blanco Jerez<sup>1</sup>, Yulia Germanovna Gorbunova<sup>2</sup>, Aslan Yusupovich Tsivadze<sup>2</sup> and Ubaldo Ortiz Mendez<sup>1</sup>; <sup>1</sup>Facultad de Ciencias Quimicas, Universidad Autonoma de Nuevo Leon, San Nicolas de los Garza, Nuevo Leon, Mexico; <sup>2</sup>Institute of Physical Chemistry, Moscow, Russian Federation.

The electrochemical study of tetra-15-crown-5-phthalocyanine and its copper and cobalt complexes was carried out using linear and cyclic voltamperometry in order to establish the comparative electrochemical behavior of the ligand and its complexes and offer the mechanism of electrochemical reactions in solution for these compounds.

#### **K7.18**

**Simple microfluidic systems for reaction engineering using functional polymers.** Suresh Valiyaveetil, Basheer Chanbasha and Hian Kee Lee; Chemistry, National University of Singapore, Singapore, Singapore.

Microfluidic devices use the integrated circuit (IC) technology and silicon or glass as substrate for fabrication. These technologies require specialized set of equipments and expertise. Here we propose to develop a simple microfluidic system using capillary tubes and functional polymers. The talk will focus on our design criteria and preliminary results from Suzuki coupling, a well known reaction for aromatic C-C bond formation.

### **K7.19**

#### **Preparation and Electrochemical Characterization of Porphyrin Polymers on Silicon Surfaces for Hybrid Molecular Information Storage Devices.** Zhiming Liu<sup>1</sup>, Amir A Yasser<sup>1</sup>,

Lingyun Wei<sup>1</sup>, Jonathan S Lindsey<sup>2</sup> and David F Bocian<sup>1</sup>;

<sup>1</sup>Chemistry, University of California, Riverside, Riverside, California;

<sup>2</sup>Chemistry, North Carolina State University, Raleigh, North Carolina.

We have been working to construct hybrid molecular information storage devices. In the basic design, an electroactive molecule such as a porphyrin is covalently attached to a conductive surface such as Au or Si. The molecules can be oxidized to a cationic state upon application of an applied potential. When the potential is removed, the molecules store charge for extended periods; this forms the basis of the memory storage device. As the feature size of a memory cell shrinks to nanoscale dimensions, fewer and fewer molecules will occupy the cell feature. Accordingly, it will be increasingly difficult to detect the stored charge. One solution to this problem is to stack molecules in the Z-dimension. We have found that porphyrins bearing two (or more) ethynyl groups can be made to polymerize under the conditions that we typically employ for forming monolayers on Si surfaces. The porphyrin polymers have been characterized by cyclic voltammetry and open-circuit amperometry. It was found that the porphyrin polymers are electrochemically robust and exhibit charge-retention times that are comparable (or longer) than those of monolayers of similar molecules. However, the magnitude of the charge stored in the polymers is much larger than for monolayers, thereby facilitating detection of the charge.

### **K7.20**

#### **Octaphenylsilsesquioxane as a platform for functional nanoparticles.** Chad Michael Brick<sup>1</sup>, Kaoru Adachi<sup>1</sup>, Mark Roll<sup>3</sup>, Michael Asuncion<sup>3</sup> and Richard Laine<sup>2,3</sup>; <sup>1</sup>Chemistry, University of Michigan, Ann Arbor, Michigan; <sup>2</sup>Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; <sup>3</sup>Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Octaphenylsilsesquioxane (OPS) was successfully modified by Friedel-Crafts alkylation using  $\text{AlCl}_3$  and a variety of linear and branched alkyl bromides. High yields were obtained without Si-C bond cleavage despite the known propensity of  $\text{AlCl}_3$  to promote this reaction. The resulting materials were characterized by standard techniques and found to offer a core-shell structure consisting of a hard, inorganic silica core (0.53 nm) coupled to rigid phenyl groups (0.4 nm) making an inner core 1.3 nm in diameter and a flexible outer shell (1-2 nm) of aliphatic chains. The resulting hairy nanoparticles have high thermal stability ( $>400^\circ\text{C}$ ) and melting points as low as  $56^\circ\text{C}$ , which offer potential as high temperature lubricants. The bromination of OPS was also studied, with several well-controlled products with differing degrees of products developed. These materials were subjected to Heck chemistry with a variety of compounds in order to produce photoluminescent and dendritic hybrid nanomaterials.

### **K7.21**

#### **Cu Nuclei Substitution on Fluorocarbon Surface with Single Shot of ArF laser Irradiation.** Tatsuya Mochizuki and Masataka Murahara; Electrical Engineering, Tokai Univ., Hiratsuka, Kanagawa, Japan.

Cu nuclei were grown on a fluorocarbon surface with only 10-nanosecond laser irradiation. The electric circuit printed board have been generally produced the copper foil by electro-less plating after making the rough sample and Pt or Pd sticking, such as a catalyst core. However, this method generated a high frequency noise due to roughness of the sample surface. In our previous studies, metal atoms were directly combined atoms composing plastics, forming the copper foil by using a photochemistry-technique with ArF laser, this method needed not surface rough on catalysis. However, Cu atoms substitution on the fluorocarbon surface required more than 3000 shot of ArF laser irradiation in the presence of copper sulfate water solution. On the other hand, the polyimide (PI) could be substituted with Cu atoms by only single shot of ArF laser irradiation. Then the Cu atoms substitution on the photo-oxidized fluorocarbon was demonstrated with only single shot of ArF laser as same as PI substitution. A fused silica glass was placed on the sample surface, and the sulfate water solution was poured into the gap between the glass and sample, to form a thin layer of the sulfate water solution. Then the circuit patterned ArF laser light was irradiated vertically on the sample surface. By this treatment, Cu nuclei were substituted on the fluorocarbon surface. The modified sample was immersed in the electro-less plating solution, at 60 degrees Celsius for 10 minutes; the copper thin film of about  $15\mu\text{m}$  was grown on the modified surface at the laser fluence of  $20\text{ mJ}/\text{cm}^2$  with the shot number of 4. In conclusion, the ideal electric circuit printed board to be used for high frequency reasons was demonstrated.

### **K7.22**

#### **Novel malic acid-zinc hydrogels.** Norifumi Azuma, <sup>1</sup>NIMS, Tsukuba, Japan; <sup>2</sup>Okayama univ., Okayama, Japan.

Hydrogels of malic acid and zinc (Zn-MA gels) in which the carboxyl and hydroxyl groups directly bonded together via  $\text{Zn}^{2+}$  ions were prepared at room temperature. The concentration of MA in the starting solutions was fixed to be 0.5 mol/l while the molar ratio of Zn/MA was varied; 0.8:1.0 and 1.0:1.0. The pH values of the solutions were controlled by the addition of 1 M NaOH solution. Glassy hydrogels were obtained in a narrow region of pH7.2-7.4. They were 20~90% transparent. Not only the storage ( $G'$ ) and loss ( $G''$ ) moduli were measured at frequency of 1.0Hz and 1.0 Pa stress strain but also yield stress was measured as a function of the amount of the NaOH solution. The yield stress for the Zn-MA gels showed a maximum value near 7.0 in pH. The maximum values of  $G'$ ,  $G''$  and yield stress for the Zn-MA gel with 0.8 in Zn/MA were 9.20(S.D.,1.34)kPa, 4.95(0.64)kPa and 0.09(0.03)kPa at pH6.8, respectively. They were smaller than those of the Zn-MA gel with 1.0 in Zn/MA [354(17.7)kPa and 136(4.36) kPa and 0.57(0.02)kPa]. These differences were attributed to the greater density of crosslinking in the latter gel due to larger relative Zn ion content. Fourier transform Raman spectroscopies for the glassy hydrogels showed red shifts of the peaks assigned to (-COO) and (-OH) from the commonly observed position 1333 to 1324  $\text{cm}^{-1}$ . Also observed was a similar red shift from 1087 to 1080  $\text{cm}^{-1}$  of the (-C-OH) peak due to the hydroxyl groups of MA. It is thus concluded that Zn ions are bonded to both carboxyl and hydroxyl groups of MA.

### **K7.23**

#### **Utilization of the Internal Free Volume of Iptycene-Based Molecular Scaffolds Towards the Insulation of Conducting Polymers.** John P. Amara and Timothy M. Swager; Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The development of a method by which the charge carriers in conducting polymers can be completely isolated, and therefore, insulated from counter-ions, oxygen and moisture infiltration, and even proximal conducting polymer strands is of great interest to our research group. A possible approach towards the insulation of a conducting polymer is to locate the charge carrier conduction pathway of the polymer within the bounds of the internal free volume excluded by an iptycene scaffold. If the scaffold is large enough, the conducting polymer will dwell in this "vacuum" of internal free volume and the outside environment; air, moisture, counter-ions, etc., would be prevented from approaching close enough to react with the conducting polymer. The targeted polymer incorporates large iptycene ribs as an insulating sheath, which serves to shroud the conducting polymer backbone. An important element of the target design is that, as the monomers combine to form the polymer, each iptycene scaffold should adopt a conformation, in order to minimize steric repulsion, where it is splayed in a direction opposite the direction of the adjacent subunits. Thus, the iptycene insulation should serve to shroud the conducting polymer backbone from every direction. Such insulated conducting polymers may lead to the development of new organic polymer displays which would never bleach, and possibly, a step could be made toward novel organic superconducting materials. Such a method may also be applied to the development of a "molecular wire" which bridges two terminals and allows the fundamental properties of molecular conduction to be probed.

### **K7.24 TRANSFERRED TO K9.9**

### **K7.25**

#### **Ionic Liquid Electrolytes The Elixir of Life for Electrofunctional Devices.** Gordon George Wallace, IPRI, University of Wollongong, Wollongong, New South Wales, Australia.

This presentation reviews our work on ionic liquid electrolytes for use with inherently conducting polymer (ICP) based devices. Selected ionic liquids have been shown to interact strongly with ICPs resulting in improvements in mechanical properties and highly efficient electrochemical switching. These factors coupled with high electrochemical and environmental stability make them very attractive electrolytes. These properties have been put to use in the development of new artificial muscles and photoelectrochemical cells based on ICPs.

### **K7.26**

#### **Metallo-Supramolecular Polymers: New functional Materials with controlled Nanostructures via self-assembly processes.** Ulrich S Schubert, Schmatloch Stefan, Abdelkrim El-ghayoury and Harald Hofmeier; Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands.

The design and synthesis of complex functional macromolecular architectures represents one of the main challenges in present research. In particular the introduction of "non-covalent" interactions into tailor-made macromolecules seems to be highly promising [1]. In this contribution, we report on the synthesis and characterization of linear metallo-supramolecular polymers by the self-organization of terpyridine-modified macromolecules with ruthenium(II) ions [2]. Different reaction conditions (solvent, concentration) were used in order to obtain well-soluble high molecular weight polymers, which were characterized by UV-vis and NMR spectroscopy as well as GPC. The latter case represents the first reported investigation of extended metallo-supramolecular polymers. The morphology of the polymers was studied by AFM, revealing highly organized nanostructures. The non-covalent polymerization could be reversed applying external stimuli, such as pH, temperature, redox processes or strong chelating agents [3]. Moreover, the combination with covalent cross-linking entities allowed an even more sophisticated design of functional nanomaterials. In this case the construction of "smart" or "intelligent" materials is now possible. [4]. [1] J.-M. Lehn, *Macromol. Chem., Macromol. Symp.* 1993, 69, 1; U.S. Schubert, C. Eschbaumer, *Angew. Chem. Int. Ed.* 2002, 41, 2892. [2] U.S. Schubert, O. Hien, C. Eschbaumer, *Macromol. Rapid Commun.* 2000, 21, 1156; U.S. Schubert, C. Eschbaumer, *Macromol. Symp.* 2001, 163, 177; U.S. Schubert, S. Schmatloch, A.A. Precup, *Design. Monom. Polym.* 2002, 5, 211; U.S. Schubert, H. Hofmeier, *Macromol. Rapid Commun.* 2002, 23, 561; S. Schmatloch, U.S. Schubert, *Macromol. Symp.* 2003, in press. [3] S. Schmatloch, U.S. Schubert, *Macromol. Rapid Commun.* 2002, 23, 957. [4] A. El-ghayoury, H. Hofmeier, B. de Ruiter, U.S. Schubert, *Macromolecules* 2003, 36, 3955.

SESSION K8: Photovoltaics II and FETs I  
Chairs: Marc Baldo and Ghassan Jabbour  
Thursday Morning, December 4, 2003  
Back Bay C (Sheraton)

#### 8:30 AM \*K8.1

##### Nanostructure-Property Relations In Conjugated Polymer/Fullerene Bulk-Heterojunction Solar Cells.

Harald Hoppe<sup>1</sup>, M. Niggemann<sup>2</sup>, C. Winder<sup>1</sup>, J. Kraut<sup>3</sup>, R. Hiesgen<sup>3</sup>, A. Hinsch<sup>2</sup>, D. Meissner<sup>1,4</sup> and N. S. Sariciftci<sup>1</sup>; <sup>1</sup>Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University Linz, Linz, Austria; <sup>2</sup>Fraunhofer Institute for Solar Energy Systems (ISE), Freiburg, Germany; <sup>3</sup>University of Applied Sciences Esslingen, Esslingen, Germany; <sup>4</sup>University of Applied Sciences UA Wels, Wels, Austria.

Thin film organic solar cells based on conjugated polymer/fullerene blends are subject of increasing research interest within the past few years [1-3]. One main progress in terms of solar energy conversion efficiency has been achieved by introducing the bulk heterojunction concept [4-6] instead of the bilayer structure [7-10]. This can be understood as a result of a highly increased interface between electron and hole conducting phases. The photoinduced charge generation occurs at this interface through a charge transfer process. The control of the nanoscale-morphology of the photoactive layer of this bulk-heterojunction solar cell provides the possibility for improving its solar energy conversion efficiency. We report comparative studies on atomic force microscopy (AFM) and scanning electron microscopy (SEM) to visualize the underlying nanomorphology of a solid blend of MDMO-PPV (3,7 - dimethyloctyloxy methyloxy poly(paraphenylene vinylene) and the fullerene C<sub>60</sub>-derivative PCBM (1-(3-methoxycarbonyl) propyl-1-phenyl [6,6]C<sub>61</sub>) in the photoactive film. In addition, photoluminescence measurements on the pristine materials as well as on the blend films are discussed. Furthermore the device parameters of solar cells with varying mixing ratios are discussed and conclusions to the conditions in the casting solution are drawn. References: [1] C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, *Adv. Funct. Mater.* 2001, 11, 15 [2] V. Dyakonov, *PhysicaE* 2002, 14, 53 [3] C.J. Brabec, V. Dyakonov, J. Parisi and N. S. Sariciftci, *Organic Photovoltaics*, Springer Series in Materials Science 2003, Vol. 60 [4] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* 1995, 270, 1789 [5] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature* 1995, 376, 498 [6] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, *Appl. Phys. Lett.* 2001, 78, 841 [7] C. W. Tang, *Appl. Phys. Lett.* 1986, 48, 183 [8] N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky, and F. Wudl, *Appl. Phys. Lett.* 1993, 62, 585 [9] J. J. M. Halls, K. Pichler, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Appl. Phys. Lett.* 1996, 68, 3120 [10] L. A. A. Petterson, L. S. Roman, O. Inganäs, *J. Appl. Phys.* 1999, 86, 487

#### 9:00 AM K8.2

Polymer brushes for polymer electronics. Wilhelm Huck<sup>1</sup>, Henning Sirringhaus<sup>2</sup>, Greg Whiting<sup>1</sup>, Henry Snaith<sup>2</sup> and Richard

Friend<sup>2</sup>; <sup>1</sup>University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

Polymers are ubiquitous in device fabrication and as active components in polymeric devices. Current fabrication methods however, offer little control over the ordering at the molecular level of these polymers. Strategies that improve control should also offer opportunities to improve device performance. Polymer brushes grown from patterned surfaces not only amplify the initial pattern to make it more chemically and mechanically robust, but at the same time introduce useful chemical and physical properties to the surface. Our synthetic route to such polymer brushes allows full control over the thickness, density and composition of the polymer films. At the same time the synthesis of (patterned) brushes is compatible with substrates that are used in polymeric devices. All polymer chains are tethered to the substrate, which leads to films that are well-ordered at the molecular level. We will present results on the use of brushes in a number of different device-related situations. Controlled-growth of brushes can be used for making e-beam resists, whereas similar brushes can be used as dielectric layers. We also synthesized arylamine-containing brushes in photovoltaic devices which outperform polymer blend devices. These examples demonstrate that polymer brushes offer a new level of control over all components in polymeric devices at the nanometer level.

#### 9:15 AM K8.3

##### A Hybrid Organic-Inorganic Thin-Film Photodiode.

Evan L. Williams<sup>1</sup>, Qi Wang<sup>2</sup>, Sean E. Shaheen<sup>2</sup> and Ghassan E. Jabbour<sup>1</sup>; <sup>1</sup>Optical Sciences Center, Univ. of Arizona, Tucson, Arizona; <sup>2</sup>National Renewable Energy Laboratory, Golden, Colorado.

An organic-inorganic hybrid photodiode has been fabricated using poly(N-vinylcarbazole) (PVK) and hydrogenated amorphous silicon (a-Si:H) for the respective layers. The a-Si:H was deposited via hot-wire chemical vapor deposition (HWCVD). The substrate temperature ((140°C) utilized in this method allowed for minimal damage to the underlying, spin-cast PVK layer. The characteristics of these materials and their interface gave rise to the following device characteristics: a photosensitivity of nearly 700, a photogain of over 100, and a moderately fast response time of 500 μs.

#### 9:30 AM \*K8.4

##### Diels-Alder Adducts of Pentacene as Precursors For Solution Processed Fabrication of Organic Thin Film Transistors.

A. Afzali, C. D. Dimitrakopoulos, C. R. Kagan and T. O. Graham; IBM T.J. Watson Research Center, Yorktown Heights, New York.

Among organic semiconductors, pentacene has emerged as the most promising material for use in organic thin film transistors and their applications in various electronic devices. However, in order to exploit the advantages of organic molecules, such as ease of processing, fabrication of integrated circuits must entail a continuous, solution processing of organic materials. In this talk, we present a simple approach for high yield synthesis of soluble pentacene precursors. The structure-property relationship of several precursors will be discussed and their effect on mobility and environmental stability of pentacene TFTs will be presented.

#### 10:30 AM K8.5

##### Effect of Molecular Weight on the Chain Packing and Mobility of Regioregular Polythiophene.

Michael David McGehee<sup>1</sup>, R. Joe Kline<sup>1</sup>, Ekaterina N. Kadnikova<sup>2</sup>, Jinsong Liu<sup>2</sup> and Jean M.J. Frechet<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, Stanford University, Stanford, California; <sup>2</sup>Chemistry, University of California at Berkeley, Berkeley, California.

Regioregular poly (3-hexylthiophene) (P3HT) has one of the highest field-effect mobilities of any semiconducting polymer and is one of the leading candidates to replace amorphous silicon as the active layer of low-cost thin-film transistors. We have discovered that the field-effect mobility of this polymer increases by four orders of magnitude as the molecular weight is increased from 3.2 kD to 36.5 kD. To determine the mechanisms underlying this surprising trend, we have characterized the structure of the films with atomic force microscopy, x-ray diffraction, UV-vis absorption spectroscopy and photoluminescence spectroscopy. Collectively, the results of these experiments show that low-molecular-weight samples form highly crystalline nanorods that are poorly connected to each other, while high-molecular-weight samples form less ordered structures. They suggest that the high molecular weight films have higher mobility since polymer chains are better connected to each other. Control experiments rule out other explanations for the mobility versus molecular weight trend, such as end group trapping, chemical defects, polydispersity effects and regioregularity effects. This study points out the importance of optimizing the molecular weight of regioregular P3HT for making high-mobility transistors and sheds light on how

charge moves through this polymer. Ideas for obtaining record mobilities with polymers will be presented.

#### 10:45 AM **K8.6**

**Morphology of Pentacene Films on Styrenic Polymer Substrates.** G. Nunes Jr., J. S. Meth and Michael Lefenfeld; Central Research & Development, DuPont, Wilmington, Delaware.

Polymer dielectric materials will play a key role in the fabrication of flexible electronic circuits based on organic semiconductors. While such dielectrics will provide passivation, encapsulation, and insulation of wire crossings, their most critical function will be to serve as the gate insulator in thin film transistors. In the case of transistors based on vapor-deposited pentacene, the polymer dielectric also serves as the substrate for the nucleation and growth of the semiconductor film. One can therefore expect this layer to have a profound influence on the structure and morphology of the pentacene, and therefore an effect on its electronic transport properties. In this paper we will discuss our atomic force microscopy investigations of the grain size and morphology of pentacene films grown on a variety of styrenic polymer surfaces. The choice of styrenic polymers was based on reports that pentacene shows a high mobility when grown on polyhydroxystyrene (PHS) substrates.<sup>1</sup> Solutions of several polymers, including PHS as a control, were spin-coated onto quartz discs. Pentacene was deposited simultaneously onto all the substrates at room temperature using a deposition rate of .02 nm/sec. Tapping mode AFM revealed that the typical grain size ranged from  $\sim 4 \mu\text{m}$  on PHS down to about  $.1 \mu\text{m}$  on polystyrene. AFM studies of the bare polymer surfaces showed them all to be similarly smooth and flat, suggesting that chemical interactions between the polymer and the pentacene control the density of nucleation sites and subsequent film growth.<sup>1</sup> H. Klauk et al., Appl. Phys. Lett. **82**, 4175 (2003).

#### 11:00 AM **\*K8.7**

**Interface Effects In Organic Field Effect Transistors.** Janos Veres, Simon Ogier, Giles Lloyd, Stephen Leeming, Domenico Cupertino and Soad Mohialdin Khaffaf; Electronic Materials, AVECIA, Manchester, United Kingdom.

Disorder is an important property of organic semiconductors. We have studied the behaviour of a number of polymeric materials in field effect devices (FETs), among them amorphous organic polymers. In particular, bulk transport properties were compared to that of interface transport in FETs. It was found that disorder could be increased by a polar gate insulator interface, while the material remained essentially amorphous. We attributed this to the modulation of site energies in the material due to local polarisation effects. Evidence of enhanced carrier localisation was found, for example, in the increased temperature activation of the carrier mobility. These findings led to much improved field effect devices by using low-k gate insulators quite contrary to the existing trend to use high permittivity layers. It also made it possible to obtain meaningful mobilities from field effect devices that are close to the bulk mobility of the material. The range of compounds studied with different gate dielectrics is being continuously extended and new results are reported relating the change of threshold voltage due to the interface. The interface effects discussed here are unique and are the result of carrier localisation being characteristic in organic materials. A number of related observations appearing in the literature are reviewed. The underlying physics is compared to the case of band-like semiconductors.

#### 11:30 AM **\*K8.8**

**Poly(3-hexylthiophene) Field-Effect Transistors with High Dielectric Constant Gate Insulator.** Guangming Wang<sup>1</sup>, Daniel Moses<sup>1</sup>, Alan J. Heeger<sup>1</sup>, Hong-Mei Zhang<sup>2</sup>, Mux Narasimhan<sup>2</sup> and R. E. Demaray<sup>2</sup>; <sup>1</sup>Institute for Polymers and Organic Solids, Univ of California-Santa Barbara, Santa Barbara, California; <sup>2</sup>Symmorphix, Inc., Santa Clara, California.

High dielectric constant ( $\kappa = 41$ ) titanium oxide ( $\text{TiO}_2$ ) was used as the gate insulator in field-effect transistors (FETs) with regioregular poly(3-hexylthiophene) (RR-P3HT) as the electronically active semiconductor. Good FET characteristics were obtained with saturation at relatively low drive voltages ( $\approx 2\text{V}$ ) and with carrier mobilities of  $1.3 \times 10^{-2} \text{ cm}^2/\text{Vs}$ . Deposition of a thin layer of  $\text{SiO}_2$  (thicknesses of 3 and 17 nm) on top of the  $\text{TiO}_2$  (97 nm) gate insulator resulted in a reduced effective dielectric constant  $\kappa_{eff} = 31$  for 3 nm of  $\text{SiO}_2$  and ( $\kappa_{eff} = 19$  for 17 nm  $\text{SiO}_2$ ), but with significant improvement in the FET characteristics; the field-effect mobility increased by an order of magnitude to  $5.4 \times 10^{-2} \text{ cm}^2/\text{Vs}$ , the on/off ratio increased from  $10^2$  to  $6 \times 10^4$ , and the leakage current decreased by a factor of approximately  $10^2$ . The importance of the thin  $\text{SiO}_2$  layer was confirmed using aluminum oxide ( $\text{Al}_2\text{O}_3$ ) ( $\kappa = 8.4$ ) as the gate insulator in RR-P3HT FETs.

#### 1:30 PM **K9.1**

**Synthesis and Transistor Performance of Oligofluorene and Polyacene Derivatives.** Hyunsik Moon<sup>1,2</sup>, Andrew J. Lovinger<sup>1</sup> and Zhenan Bao<sup>1</sup>; <sup>1</sup>Bell laboratories, Lucent Technologies, Murray Hill, New Jersey; <sup>2</sup>University of Michigan, Ann Arbor, Michigan.

Organic electroactive materials are now being considered as the active materials in displays, electronic circuits, solar cells, chemical and biological sensors, actuators, lasers, memory elements, and fuel cells. The flexibility of their molecular design and synthesis makes it possible to fine-tune the physical properties and material structure of organic solids to meet the requirements of technologically significant applications. Organic semiconductors with high field effect mobility and high on/off ratio are crucial for yielding high performance organic transistors for the above potential applications. Our recent effort has been focused on designing materials with optimized thin film morphology through solution or vapor phase deposition. In addition, these semiconductors are designed to be stable towards photo-oxidation so that their transistor devices will have improved stability. Specifically, we have synthesized new oligofluorene and polyacene derivatives which show promising transistor performance. The synthesis, film morphological characterization and transistor performance of these materials will be presented.

#### 1:45 PM **K9.2**

**Synthesis of Novel Semiconducting Liquid Crystalline Materials and Their Performance in Organic Field Effect Transistor Devices.** Mark Giles, Martin Heeney, Clare Bailey, David Graham, Maxim Shkunov, David Sparrowe, Steve Tierney, Weimin Zhang and Iain McCulloch; NB-C UK, Merck Chemicals Ltd, Southampton, Hampshire, United Kingdom.

As the area of organic electronics advances, the performance of the semiconducting component in organic field effect transistors (OFET's) has become of key importance. New semiconductors, which can be solution processed, possess high mobility, and are stable in ambient conditions are required. This work describes the development of solution processible small molecule polymerisable liquid crystalline semiconductors, referred to as reactive mesogens. The design, synthesis, and performance in transistor devices of these materials are discussed. The relationship between liquid crystal molecular structure, its corresponding phase behaviour and electrical performance is examined. Molecular design methodology was employed to control the liquid crystalline morphology and therefore optimise organisation and packing. Alignment of the molecules in large homeotropic domains was achieved through surface treatment techniques, and the highly ordered mesophase was preserved by polymerisation of the reactive end groups, creating a crosslinked network.

#### 2:00 PM **K9.3**

**Contact Effects in Pentacene Transistors.** Paul Pesavento, Reid Chesterfield, Chris Newman, Kanan Puntambekar and C Daniel Frisbie; Chemical Engineering and Materials Science, University of Minnesota - Twin Cities, Minneapolis, Minnesota.

We describe 4-terminal measurements designed to probe voltage drops at source and drain electrodes in pentacene field effect transistors. Film and contact resistances are extracted from the measured potential drops. The devices consist of conventional source and drain electrodes contacting a pentacene film deposited on a dielectric/gate electrode assembly. Voltage sensing leads penetrate into the source-drain channel and are used to monitor potentials in the pentacene film while it is passing current during drain voltage (VD) or gate voltage (VG) sweeps. We have investigated film and channel resistances as a function of VD, VG, temperature, contact metallurgy, and film thickness. We will report on these results with an emphasis on the effect of the metal type (e.g., Ag, Au, Pt) for the source and drain electrodes and the effect of the contact geometry (top or bottom contacts). The four terminal measurements also allow us to extract field effect mobilities for pentacene films that are corrected for voltage drops at the contacts.

#### 2:15 PM **\*K9.4**

**Realizing the Amplification of Molecular Wire Sensors: Isolated Nanoscopic Conduction Pathways.** Timothy M Swager, Chemistry, MIT, Cambridge, Massachusetts.

The ability of electronic polymers (molecular wires) to amplify sensory signals has been well documented in both optical and electrical transduction schemes. In resistivity-based sensors the ultimate gain is realized when the carriers are constrained to nanoscopic pathways. In this architecture the carriers are forced to traverse any barriers that



are erected as a result of a molecular recognition event. Without restricted nanoscopic pathways the carriers can simply go around the barrier and while the resistivity will be increased, the full potential of the gain is not realized. In this lecture I will describe systems that for fill the desired restrictions in carrier transport and present analysis that supports our assertion that molecular wires are excellent amplifiers. Sensory materials will be described that are designed to recognize and respond to ions, neutral organic molecules, and gases.

#### 2:45 PM **K9.5**

##### **New Functional Pi-Systems for Photo-redox Switching.**

Martin Robert Bryce, Changsheng Wang, Igor Perepichka and Andrew Beeby; Chemistry, University of Durham, Durham, DH1 3LE, United Kingdom.

The development of new organic pi-systems which can reversibly switch between two or more read-out states is a central theme in contemporary molecular electronics research. We will present our latest results on the synthesis and properties of a range of functional pi-systems which are designed to act as photo-redox switches, i.e. molecules for which fluorescence can be turned ON or OFF by varying the electrochemical potential of the system [1]. The materials currently under investigation in our laboratory in this context include derivatives of phtalocyanine, tetrathiafulvalene, diaryloxadiazole and metal-phenanthroline complexes. Their synthesis, electrochemical and photophysical properties will be discussed. [1] Bryce, M. R. et al, J. Org. Chem. 2002, 67, 9130.

#### 3:30 PM \***K9.6**

##### **A Systems Approach to Molecular Electronics.** James R. Heath, Chemistry Department, Caltech, Pasadena, California.

Molecular electronics is an area of research in which molecules are employed to yield the active (switches) and passive device components (diodes, resistors) of an electronic circuit or integrated circuit. In this presentation, I will cover issues related to scaling molecular electronics circuitry to device densities approaching 10<sup>11</sup>/cm<sup>2</sup>, including multiplexing methods for interfacing those circuits to the outside world, experiments aimed at understanding active and passive molecular electronics devices and mechanisms, as well as the molecular/electrode interface.

#### 4:00 PM **K9.7**

##### **A solid-state Sensor Diode Based on the Combination of a Molecular Switch and a Conjugated Polymer.** Magnus Berggren and Peter Andersson; ITN, Linköping University, Norrköping, Sweden.

Here we report on a solid-state sensor & detector diode. The organic layer consists of a combination of a molecular switch and a conjugated polymer, here PPV. Upon exposing the diode to external stimuli, in this case light, the molecular switch changes its electrical performance. This switch of the molecule is read out as a change in the diode characteristics. The molecular switching characteristics is bistable to its nature. In the sensor diode this offer a detection function that has a memory effect. This means that the detection event can be decoupled from the read-out event. The read-out signal is nearly linear vs the dose of the light exposed. The novel sensor concept opens up for new solutions regarding the design of electronic sensor & detector matrices.

#### 4:15 PM **K9.8**

##### **Nanostructuring Cu Surfaces Using Custom Designed Molecular Molds** Nanostructuring Cu Surfaces Using Custom Designed Molecular Molds. Federico Rosei<sup>1,2</sup>, Roberto Otero<sup>2</sup>, Peter Thoststrup<sup>2</sup>, Yoshitaka Naitoh<sup>2</sup>, Erik Laegsgaard<sup>2</sup>, Ivan Stensgaard<sup>2</sup>, Flemming Besenbacher<sup>2</sup>, Ping Jiang<sup>3</sup>, Andre Gourdon<sup>3</sup> and Christian Joachim<sup>3</sup>; <sup>1</sup>EMT, INRS, Varennes, Quebec, Canada; <sup>2</sup>Physics, University of Aarhus, Aarhus, Denmark; <sup>3</sup>CEMES, CNRS, Toulouse, France.

Large organic molecules have recently attracted interest from a fundamental point of view and for prospective applications in nanoelectronics, since they are the basic building blocks for molecular electronics devices [1,2]. Here we report the design from first principles and the demonstration of a nanoscale molecular template. In particular, we describe the adsorption of C104H108 (called Violet Lander (VL) molecule) on a Cu(110) surface in the temperature range 100-300 K. Molecules from the Lander family have a central polyaromatic molecular "wire", terminated by a fluoranthene group, and four Tbp substituents that act as spacer legs. In previous work [3] we observed that in the case of the simpler Single Lander (SL) molecule, the shape conferred by the legs to the molecule, together with the strong interaction of the wire with the Cu substrate, enables it to act as an atomic scale template. The VL was then designed similarly to the SL, but with a longer molecular board (2.5 nm vs 1.7 nm). As described in the following, the molding action induced by the VL is related to the one induced by the SL in the same way as the

board of the VL relates to the board of the SL [4]. This demonstrates that surface reconstructions can be controlled by appropriately designing the molecular structure. These results point to the exploitation of such phenomena for surface engineering at the nanometer scale with applications ranging from molecular electronics to asymmetric catalysis. References. [1] C. Joachim et al., Nature 408, 541 (2000). [2] F. Rosei, M. Schunack, Y. Naitoh, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, Ch. Joachim, F. Besenbacher, Properties of large organic molecules on metal surfaces, Prog. Surf. Sci. 71, 95 (2002). [3] F. Rosei et al., Organic molecules acting as templates on Metal Surfaces, Science 296, 328 (2002). [4] R. Otero et al., in preparation.

#### 4:30 PM **K9.9**

##### **The First Genuine Covalent TTF-TCNQ Diad: Extremely Low HOMO - LUMO Gap And High Quality Langmuir Blodgett Films.** Dmitrii F Perepichka<sup>1,2</sup>, Martin R Bryce<sup>2</sup>,

Christopher Pearson<sup>3</sup>, Michael C Petty<sup>3</sup>, Eric J. L. McInnes<sup>4</sup> and Jing P Zhao<sup>4</sup>; <sup>1</sup>INRS-Energy, Materials and Telecommunications, University of Quebec, Varennes, Quebec, Canada; <sup>2</sup>Department of Chemistry, University of Durham, Durham, United Kingdom; <sup>3</sup>School of Engineering, University of Durham, Durham, United Kingdom; <sup>4</sup>EPSC EPR Service, Department of Chemistry, University of Manchester, Manchester, United Kingdom.

The challenge of covalent linking a tetrathiafulvalene (TTF) to 7,7,8,8-tetracyanoquinodimethane (TCNQ) moiety was laid down by Aviram and Ratner,[1] shortly after the first report of metallic conductivity in the intermolecular TTF:TCNQ complex.[2] It was proposed that a single donor-σ-acceptor molecule could rectify electric current, opening the era of molecular electronics. Since then numerous attempts to synthesise TTF-TCNQ hybrids have been undertaken. However, the only two reports claiming covalent linkage of TTF and TCNQ described syntheses of "EPR-active products", which were difficult to purify, and the structures of which were not convincingly established.[3,4] It soon became apparent that coupling any strong π-electron donor to a strong acceptor is extremely difficult task, although many moderate acceptors have been attached to TTF.[5] We will report the synthesis of the first well characterized analytically pure TTF-σ-TCNQ diad {5-methyl-4',5'-dipentylTTF-1-methyl 2-TCNQ-propanoate **1**} by coupling of a TCNQ acid chloride to a lithium salt of TTF alcohol at -100 °C. Due to a rigid linker, **1** can exist in a head-to-tail complexed and linear conformations, the properties of which have been accurately predicted by DFT calculations. The very strong electron donor/acceptor properties of the TTF and TCNQ moieties of this molecule provide the lowest HOMO-LUMO gap ever reported for closed shell organic molecules (0.16 eV, by electrochemistry). This low gap allows the first observation of a thermoexcited electron transfer in organic donor-acceptor diad. The compound is zwitter-ionic in the solid state, but is essentially neutral in solution (radical concentration 1.4%). High stability of all five possible redox states (**1**<sup>0</sup>, **1**<sup>+</sup>, **1**<sup>2+</sup>, **1**<sup>-</sup>, **1**<sup>2-</sup>) offers a potential application of **1** as an electrochromic material for Vis-NIR region. Compound **1** forms well-organized Langmuir-Blodgett films of very high quality, the structural and conductive properties of which will be discussed in the light of application in molecular electronics.

References: [1] Aviram, A.; Ratner, M. A. Chem. Phys. Lett. 1974, 29, 277. [2] Ferraris, J.; Cowan, D. O.; Walatka, V. V.; Perlstein, J. H. J. Am. Chem. Soc. 1973, 95, 948. [3] Hertzler, W. R. J. Org. Chem. 1976, 41, 1412. [4] Panetta, C. A.; Baghdadchi, J.; Metzger, R. M. Mol. Cryst. Liq. Cryst. 1984, 107, 103. [5] Bryce, M. R. Adv. Mater. 1999, 11, 11; Segura, J. L.; Martín, N. Angew. Chem. Int. Ed. 2001, 40, 1372.

#### 4:45 PM **K9.10**

##### **Polysilicon based nanoscale vertical structures with redox-active monolayers.** Qian Zhao, Shyam Surthi, Qiliang Li, Srivardhan Gowda, Guru Mathur and Veena Misra; Electrical & Computer Engineering, North Carolina State University, Raleigh, North Carolina.

Molecular-based devices are proving to be a promising alternative to the next generation electronic devices, with scaling possible down to the molecular level. Of this class, the hybrid silicon-molecular approach affords the advantage of integrating the charge storage molecules with the existing silicon technology. Here we report on the fabrication and characterization of capacitor structures containing redox-active monolayers on polysilicon surfaces. With optimized attachment process, self-assembled monolayers (SAMs) of redox-active ferrocene and porphyrin molecules were achieved with appropriate linkers. The test structures of electrolyte-molecule-polysilicon (EMP) capacitors were characterized using conventional cyclic voltammetry and impedance spectroscopy (C-V and G-V) techniques. Peaks due to the charging and discharging currents associated with redox process were observed in cyclic voltammetry. The impedance measurements also showed corresponding peaks in capacitance and conductance

at low voltages. Using traditional lithography technique on a stack of nitride/polysilicon/nitride on silicon, we have successfully fabricated EMP capacitor structures by forming monolayers of these molecules on the sidewall of the polysilicon layer (50-100 nm). The electrical characterization of the SAMs on the nanoscale polysilicon structures showed that the molecules could be attached to nanoscale areas with approximately the same density ( $\sim 10^{14}$  cm<sup>-2</sup> for ferrocene and  $\sim 10^{13}$  cm<sup>-2</sup> for porphyrin) as larger areas. This indicates that polysilicon could be a good candidate for future nanoscale microelectronic devices based on hybrid silicon-molecular approach. The inherent scalability and good stability of the SAMs derived from the polysilicon sidewall capacitors shows that this type of structure may be used for exploring the concept of vertical device.

SESSION K10: Poster Session: Devices and Structures  
Chairs: Vladimir Bulovic and Michael McGehee  
Thursday Evening, December 4, 2003  
8:00 PM  
Exhibition Hall D (Hynes)

#### **K10.1**

**The Electrical Characteristics of Nanoscale Conjugated Polymer Field-Effect Transistors.** Liang Wang<sup>1</sup>, Taeho Jung<sup>1</sup>, Daniel Fine<sup>1</sup>, Saiful I Khondaker<sup>2</sup>, Zhen Yao<sup>2</sup>, Heinz von Seggern<sup>3</sup> and Ananth Dodabalapur<sup>1</sup>; <sup>1</sup>Microelectronics Research Center, University of Texas at Austin, Austin, Texas; <sup>2</sup>Department of Physics, University of Texas at Austin, Austin, Texas; <sup>3</sup>Inst. of Materials Science, Technical University of Darmstadt, Darmstadt, Germany.

Regioregular polythiophene has been successfully used in large-area FET's on account of its excellent self-assembly properties. In this work, regioregular poly(3-hexylthiophene) is used as the active semiconductor in field effect transistors with channel lengths from several micrometers down to 4nm. Nanometer scale gaps between Au electrodes are formed by a combination of electron beam lithography and electrostatic trapping of Au nanoparticles followed by electromigration processes. To suppress the spreading current effects due to the small channel width/length ratios in these nanoscale gaps, we employed a pair of guarding electrodes near the two sides of the channel. The true responses of the nanometer scale FET's exhibit pronounced short-channel behaviors. The impact of gap geometry and the mechanisms of charge transport will be discussed. Our home-developed numerical model simulated the behavior of a 5nm channel FET which is in good agreement with the experimental data. Strategies to overcome the short-channel effects and achieve single-macromolecule type transistor operation will be discussed.

#### **K10.2**

**Abstract Withdrawn**

#### **K10.3**

**Solvent Effect on Chain Behaviors in Conjugated Polymer-based Light-emitting Diodes.** Hanpeng Dong<sup>1</sup> and Mary E. Galvin<sup>2</sup>; <sup>1</sup>Eastman Kodak Company, Rochester, New York; <sup>2</sup>Materials Science and Engineering, University of Delaware, Newark, Delaware.

This study reports the effects of solvent properties on conjugated polymer chain behaviors and the polymer light emitting diode (PLED) device performance. Oxadiazole-containing PPV (C8L) exhibits very different chain morphologies in solvents such as THF, 1,1,2,2-tetrachloroethane (TCE) and the mixture of the two. It is found that the polymer chains are more extended in TCE, which dissolves the side alkoxy chains better. The addition of THF into TCE disrupts the chain packing and enhances PL in film. The use of a mixed solvent system is seen to result in better device performance, probably due to a chain morphology, which better balances charge transport and EL. This study shows the possibility of optimizing device performance by engineering chain morphologies through solvent selection.

#### **K10.4**

**Electroluminescent Devices Based on Transition Metal Complexes.** Jason Slinker<sup>1</sup>, Alon Gorodetsky<sup>1</sup>, Sara Parker<sup>1</sup>, Dan Bernards<sup>1</sup>, Samuel Flores-Torres<sup>2</sup>, Keon Woo Lee<sup>2</sup>, Hector D Abruna<sup>2</sup>, Paul A Houston<sup>2</sup>, Stefan Bernhard<sup>3</sup>, Michael J Winokur<sup>4</sup> and George G Malliaras<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York; <sup>3</sup>Department of Chemistry, Princeton University, Princeton, New Jersey; <sup>4</sup>Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin.

Transition metal complexes, such as ruthenium tris-bipyridine, [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, have recently prompted extensive photophysical and

electrochemical study. Motivated by their high photoluminescence efficiencies in solution, light-emitting devices based on transition metal complexes have been developed as potential candidates for flat-panel display and lighting applications. Their device characteristics are dominated by the presence of mobile ions that redistribute under an applied field and assist charge injection. These devices have been shown to be among the most efficient devices produced from organic compounds, with external quantum efficiencies in excess of 5%. Through a collaborative effort, we have investigated the electrochemical, spectroscopic, and electroluminescent properties of ruthenium, iridium, osmium, and rhodium complexes. We have examined the connections between the photophysical properties of these materials and the device performance by changing the film thickness, exploring the temperature dependence of the photoluminescence and electroluminescence, and varying the complex ligands. We have probed the ohmicity of the device contacts by systematically varying the cathodes and anodes of light-emitting devices based on [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>. We have addressed device performance parameters such as the limits of their efficiency, the availability of multiple colors, their response time and their operational lifetime.

#### **K10.5**

**Monodisperse Glassy Nematic Oligo(fluorene)s for Efficient and Stable Linearly Polarized Blue Emission.**

Sean W Culligan<sup>1</sup>, Yanhou Geng<sup>1</sup>, Shaw H Chen<sup>1</sup>, Kevin Klubek<sup>2</sup>, Kathleen M Vaeth<sup>3</sup> and Ching W Tang<sup>2</sup>; <sup>1</sup>Department of Chemical Engineering, University of Rochester, Rochester, New York; <sup>2</sup>Hard Copy and Display Technology Division, Eastman Kodak Company, Rochester, New York; <sup>3</sup>Polymer Science and Technology Laboratory, Eastman Kodak Company, Rochester, New York.

Linearly polarized light-emitting diodes have been intensely pursued in recent years. The interest stems from the technological relevance to the realization of liquid crystal displays with much improved power efficiency. Several different approaches have been explored to produce uniaxially oriented chromophores, such as mechanical stretching, Langmuir-Blodgett deposition, and mediation by nematic liquid crystal mesomorphism. The most straightforward approach is the use of nematic liquid crystalline light-emitters by taking advantage of self-organization into monodomain films. Poly(fluorene)s appear to be promising for linearly polarized electroluminescence because of their capability for nematic mesomorphism and high thin film quantum yield blue emission. However, the requirement of thermal annealing at an elevated temperature with accompanying problems remains a hurdle to practical application. Therefore, we have designed and synthesized monodisperse oligo(fluorene)s with a number of repeat units ranging from 5 to 12 to elucidate the effects of chain length and pendant structure on thermotropic and optical properties. Through optimization of molecular structure, novel materials with elevated glass transition and nematic-to-isotropic transition temperatures have been successfully prepared. As a result of solubility and ease of purification, chemical purity, structural uniformity, and low viscosity, defect-free glassy nematic films were readily prepared by spin casting with subsequent thermal annealing at about 10 °C above a glass transition of 90 to 150 °C depending primarily on chain length. Both the absorption and fluorescence dichroic ratios of monodomain thin films were found to increase with molecular aspect ratio. With a buffered conductive alignment layer comprised of PEDOT/PSS, highly efficient and deep blue linearly polarized organic light-emitting diodes with an emission dichroic ratio up to 30 have been demonstrated.

#### **K10.6**

**Optical Anisotropy in Organic / Inorganic Composites.**

Brian P Gorman<sup>1</sup>, Arup Neogi<sup>1</sup>, Terry Golding<sup>1</sup>, Seokhyun Yoon<sup>2</sup>, Angelo Mascarenhas<sup>2</sup> and Teruya Ishihara<sup>3</sup>; <sup>1</sup>Dept. of Physics, University of North Texas, Denton, Texas; <sup>2</sup>National Renewable Energy Laboratory, Golden, Colorado; <sup>3</sup>Frontier Research Systems, Hiroswa, Japan.

Organic / inorganic perovskite structured dielectric quantum wells have been shown to give a range of excitonic binding energies by changing the chemistries of the organic barrier and, to a lesser extent, the inorganic well layers. In addition, these materials have the added benefit of self-organizing into multiple quantum well structures, eliminating the need for non-equilibrium growth techniques. In this study, bis-phenethyl-ammonium lead iodide (PEPI; (C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>) layers spin-coated on glass substrates were studied in order to determine their optical and structural properties. Variable angle spectroscopic ellipsometry (VASE) and polarization dependent absorption measurements were used in order to determine the anisotropy of n and k with respect to the crystal axes. The excitonic absorption energy (2.37 eV) coincides well with photoluminescence and electroreflectance data. No change in n or k is observed in these films with respect to their axes parallel to the substrate. However, a significant change in k is observed in the direction perpendicular to the substrate due to the texturing of the

film perpendicular to the substrate, as evidenced by X-ray diffraction. These results illustrate that excitonic absorption due to dielectric confinement dominates perpendicular to the substrate.

#### **K10.7**

**Abstract Withdrawn**

#### **K10.8**

##### **Transient Electroluminescent Characteristics of Polymer Light-Emitting Diodes with LiF/Al Electrode.** You-Tae Won<sup>1</sup>,

Jin Jang<sup>1</sup> and Dong Young Kim<sup>2</sup>; <sup>1</sup>Dept. of Physics and TFT-LCD National Lab., Kyung Hee University, Seoul, South Korea; <sup>2</sup>Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

The balanced charge injection is one of the most important parameters to improve the quantum efficiency of organic light-emitting diodes (OLEDs) in the viewpoint of device physics. Recently, an inserted LiF layer improves significantly the quantum efficiency of OLEDs with an Al electrode. The mechanism behind this enhancement has been proposed in various aspects. [1-3] such as tunneling, longer electron attenuation of the barrier height to electron injection, and dissociation of the LiF to form a low work function contact. In this work, the device of ITO/MEHPPV/LiF(10Å)/Al was characterized in terms of transient electroluminescent and I-V-L characteristics at different temperatures to investigate the effect of a LiF layer. The external quantum efficiency of an Al-only device was 0.002% photons per an electron. LiF/Al device improved the quantum efficiency up to 0.12%. The drift hole mobility of MEHPPV was  $4.38 \times 10^{-5} \text{ cm}^2/\text{Vs}$  and  $1.03 \times 10^{-5} \text{ cm}^2/\text{Vs}$  at 295K and 190 K from the delaytime in transient EL profile. The emission efficiency of the Al-only device was  $5.52 \times 10^{-3} \text{ cd/A}$  at 295K and  $4.82 \times 10^{-2} \text{ cd/A}$  at 190K, respectively. The efficiency evaluated at 190K increased by 8 times compared to that at 295K. However, the emission efficiency of LiF/Al device at 190K increased less than a factor of 2 as 0.31 cd/A at 295K and 0.56 cd/A at 190K, respectively. The temperature dependence of light emission characteristics strongly decreased with LiF/Al cathode. The LiF layer enhanced the electron injection process by lowering the tunneling barrier. [1] T.M. Brown, R.H. Friend, I.S. Millard, D.J. Lacey, J.H. Burroughes, and F. Cacialli, *Appl. Phys. Lett.* 77, 3096 (2000) [2] L.S. Hung, C.W. Tang, and M.G. Mason, *Appl. Phys. Lett.* 70, 152 (1997) [3] G.E. Jabbour, Y. Kawabe, S.E. Shaheen, J.F. Wang, M.M. Morrell, B. Kippenlen, and N. Peyghambarian, *Appl. Phys. Lett.* 71, 1762 (1997) [4] S.Y. Park, C.H. Lee, W.J. Song, and C. Seoul, *Current Appl. Phys.* 1, 116-120 (2001)

#### **K10.9**

##### **Organic Light Emitting Diodes Based on a Blend of MEH-PPV and a New Electron Transporting Material.**

Jin Hyung Ahn<sup>1</sup>, Changsheng Wang<sup>2</sup>, Christopher Pearson<sup>1</sup>, Martin R Bryce<sup>2</sup> and Michael C Petty<sup>1</sup>; <sup>1</sup>School of Engineering and Centre for Molecular and Nanoscale Electronics, University of Durham, Durham, United Kingdom; <sup>2</sup>Department of Chemistry and Centre for Molecular and Nanoscale Electronics, University of Durham, Durham, United Kingdom.

Organic light emitting diodes (OLEDs) containing a blend of poly[2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV) and a new electron transporting material, 2,7-bis[2-(4-tert-butylphenyl)-1,3,5-oxadiazol-5-yl]-9,9-dihexylfluorene have been fabricated. Indium-tin-oxide-coated glass served as the anode electrode and the blend was spin-coated on top of this. The device structure was completed by evaporated aluminium. The external quantum efficiencies of the OLEDs containing the electron transport compound were increased significantly over those obtained for devices based only on MEH-PPV. For example, the external quantum efficiency for a device incorporating 95% of electron transport compound was two orders of magnitude greater than the value for a non-blended device. Further improvements in the electrical characteristics of the OLEDs were obtained by the insertion of a hole transporting layer - poly(3,4-ethylene dioxythiophene) (PEDOT) - between the anode and the blended polymer. The highest external quantum efficiency obtained was 0.3%. In all our investigations the electroluminescence (orange/yellow emission) originated from the MEH-PPV material, even for very high concentrations (>90%) of the electron transport layer. This suggests a high efficiency for charge transfer between the electron transport material (itself a blue emitter) and the MEH-PPV. A detailed discussion of the operating characteristics of the blended layer OLEDs will be presented.

#### **K10.10**

##### **Directly Imprinted Laser Feedback Structures In Electroactive Conjugated Polymers Using Soft Lithography.**

Martin Gaal<sup>2,3</sup>, Christoph Gadermaier<sup>2,3</sup>, Harald Plank<sup>2,3</sup>, Alexander Pogantsch<sup>1</sup>, Erik Moderegger<sup>4</sup>, Guether Leising<sup>4</sup> and Emil J.W. List<sup>2,3,1</sup>; <sup>1</sup>Institute of Solid State Physics, University of Technology Graz, Graz, Austria; <sup>2</sup>Christian Doppler Laboratory

Advanced Functional Materials, University of Technology Graz, Graz, Austria; <sup>3</sup>Christian Doppler Laboratory Advanced Functional Materials, Joanneum Reserach, Weiz, Austria; <sup>4</sup>Science & Technology Scientific, AT&S AG, Leoben, Austria.

In the last decade, highly luminescent conjugated polymers became more and more attractive for the realisation of an organic injection laser diode. Up to now, conjugated polymers have been used in a multitude of applications, especially in electronic and optoelectronic devices. It is well known that the photoluminescence from polymer films shows a strong spectral line narrowing under high optical excitation intensities, which has been ascribed to amplified spontaneous emission (ASE) occurring in the polymer film. Furthermore, the understanding and fabrication of distributed feedback (DFB) structures is an essential step for laser action. This feedback may either be produced in the substrate or directly in the active polymer layer. Moreover, when focusing the pump beam on the imprinted DFB grating, the fluorescence and ASE spectrum collapses into a single narrow laser line. We present a new approach combining two typical techniques from the large field of soft lithography, liquid embossing and micromolding in capillaries. Soft lithography is the collective name for a set of accomplished non-lithographic, inexpensive and versatile techniques, and is a serious competitor to the conventional photolithography. The key element is the use of elastomeric stamps in order to achieve features as small as 10 nm. By means of this approach optical feedback structures were directly imprinted into a conjugated polymer and thus optically pumped laser arrays were obtained and characterized.

#### **K10.11**

##### **Study of Electron Injection in Organic Electroluminescent Devices.** Chimed Ganzorig and Masamichi Fujihira; Department of Biomolecular Engineering, Tokyo Institute of Technology, Yokohama, Japan.

Device performance is critically dependent on the efficient injection of electrons from the cathode into organic semiconductors. A well-known way to enhance electron injection is to use of low-work-function alkali or alkaline earth metals. These metals have high reactivity with oxygen and moisture, and thus tend to give unstable cathodes. The search for better electrode materials to replace these air sensitive metals has led to the discovery of bilayer cathodes by introducing a thin layer of lithium salts of fluoride [1] and carboxylates [2] as an electron injection layer. The mechanisms for enhanced electron injection are still under investigation. Recently, we found by X-ray photoelectron spectroscopy (XPS) data that mixture of alkali metal and its carboxylates was deposited during vapor deposition of alkali metal carboxylates [3]. We report here the effects of sodium carboxylates such as formate, acetate, and benzoate at tris(8-hydroxyquinoline)aluminum (Alq3)/Al interface on the performance of organic electroluminescent (EL) devices. Study of electron injection in more detail and the experimental results in the device characteristics will be reported at the symposium. [1] L. S. Hung, C. W. Tang, and M. G. Tang, *Appl. Phys. Lett.* 70, 152 (1997). [2] C. Ganzorig and M. Fujihira, *Jpn. J. Appl. Phys.* 38, L1348 (1999). [3] Y. Matsuda, C. Ganzorig, K. Suga, and M. Fujihira, Abstracts of Spring Meeting of Japanese Society of Applied Physics, 2003.

#### **K10.12**

##### **Characterization of Adhesives for OLED Encapsulation Using a Modified Ca-Spot Test Method.** Volker J. Hagemann<sup>2</sup>, Dirk Hertel<sup>1</sup>, Thomas Frank<sup>1</sup>, Joern Pommerehne<sup>1</sup>, Simone Leu<sup>1</sup> and Matthias Koehler<sup>1</sup>; <sup>1</sup>Luminescence Technology, SCHOTT Spezialglas GmbH, Mainz, Germany; <sup>2</sup>Product Development Optoelectronics, SCHOTT Glas, Mainz, Germany.

Organic Light Emitting Diodes (OLEDs) are being commercialised as an emissive technology for display applications and are becoming increasingly attractive for lighting. Among the key issues for their market success are shelf lifetime and reliability. The light emitting polymers as well as the highly reactive cathode materials are easily degraded by water and oxygen. Therefore highly impermeable substrates, seals and covers are needed to meet the lifetime requirements. To enable the measurement of the specified water vapour transmission rates that are as low as  $10^{-6} \text{ g/cm}^2/\text{day}$ , a new test method, the Ca-spot test is used. In brief, a thin Ca film ( $\approx 100 \text{ nm}$ ) instead of an OLED is deposited onto the substrate and encapsulated thereafter. Water vapour or oxygen that penetrates into the encapsulated area reacts with the Ca and the semitransparent metal film will turn transparent. The transmission increase is a measure for the permeability of the encapsulation. This test is increasingly used for permeability measurements of barriers on plastic substrates. In this work we focus on the permeability of the glue line seal that ties the cover to the substrate. It provides the only channel of permeation if intrinsically impermeable glass substrates and covers are used. To adapt the Ca-spot test to our needs, tests were also performed on fully sealed Ca-spots. With this sample design the water

vapour that penetrates through the adhesive film degrades the edges of the Ca-spot rather than decreasing the metal film thickness homogeneously. The speed of edge degradation and the lag time are measured to derive the permeability  $P$  and the Diffusion coefficient  $D$ , respectively. Using these methods the initial water content, the diffusion coefficient  $D$ , the partition coefficient  $H$  and the permeability  $P=DH$  is measured for a variety of adhesives under various climatic conditions to further improve the encapsulation.

#### **K10.13**

**Photochemical Patterning for Multicolor Polymer LEDs.** Alexander Pogantsch<sup>1</sup>, Stephan Rentenberger<sup>1</sup>, Gernot Trattng<sup>1</sup>, Gregor Langer<sup>2</sup>, Juergen Keplinger<sup>2</sup>, Wolfgang Kern<sup>2</sup>, Hartwig Tillmann<sup>3</sup>, Hans-Heinrich Hoerhold<sup>3</sup>, Ulrich Scherf<sup>4</sup> and Egbert Zojer<sup>1,5</sup>; <sup>1</sup>Institut fuer Festkoerperphysik, Technische Universitaet Graz, Graz, Austria; <sup>2</sup>Institut fuer Chemische Technologie Organischer Stoffe, Technische Universitaet Graz, Graz, Austria; <sup>3</sup>Institut fuer Organische Chemie und Makromolekulare Chemie, Universitaet Jena, Jena, Germany; <sup>4</sup>Makromolekulare Chemie, Fachbereich Chemie, Bergische Universitaet Wuppertal, Wuppertal, Germany; <sup>5</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

In this contribution we present photo-lithographic techniques to laterally structure the emission color of polymer light emitting devices (PLEDs). The discussed approaches rely on single-layer structures in which the active layer is an energy-transfer system consisting of several components. As host polymer we choose poly-fluorene as a blue emitter and as guests various vinylene containing materials emitting in the green to red spectral region. The concentration of the guest molecules is chosen so that in the pristine devices the emission color is determined by the guest system with the lowest energy-gap. Using chemically reducing agents like hydrazine (N<sub>2</sub>H<sub>4</sub>) or components undergoing a photo-addition to the C=C double bonds (propanethiol (C<sub>3</sub>H<sub>7</sub>-SH) as gaseous reactant or dodecanethiol as an additional component in the polymer blend) we selectively reduce the conjugation of the vinylene-containing polymer(s) and thus the energy-transfer efficiency to the guests. This provides a simple and efficient way to realize multicolor emission from a single substrate as well as multicolor light-emitting logos with common anodes and cathodes. The reactants are chosen in a way that neither the quantum-efficiency nor the lifetime of the devices is deteriorated and due to the single active layer, the emission color is independent of the applied bias voltage. The photochemical bleaching of the guests is achieved within seconds, which makes the discussed approach possibly attractive for industrial applications. In addition, the effect of the gaseous agents on the color-stability of the poly-fluorene host will be discussed.

#### **K10.14**

**Interfacial phenomenon in organic light emitting diodes using photoemission.** Seyed Tadayyon, Chem., The University of Western Ontario, London, Ontario, Canada.

The interfacial properties are of vital importance in polymer and organic light emitting diodes (LEDs) since the charge carriers injection process and, hence, the quantum efficiency of devices depend largely on electronic structure of the contact. The interfaces between ITO anode, NPB, and tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) are investigated for samples made in UHV and is compared with the samples made in a controlled ambient of H<sub>2</sub>O and O<sub>2</sub>. The interface properties are investigated using x-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), and atomic force microscopy (AFM). The samples were obtained by thermal evaporation of the organics on to ITO substrates without breaking the vacuum. The base pressure of the chamber was kept <10<sup>-8</sup> torr during the evaporation. The interfaces are also investigated for possible reaction which definitely influence the performance of the device. It is critical to know whether interdiffusion occurs at the interface between cathode and Alq<sub>3</sub> forming an interfacial zone and if it happens whether it protects the Alq<sub>3</sub> layer from further movement of cathode material. In the latter case it can be determined at what conditions we can build a cathodic layer such that the formation of the interfacial layer occurs upon deposition. The energy alignment at the interfaces was measured using UPS. This measurement allows for measuring the energy barrier to charge injection at anode and cathode interfaces as well as energy barrier to charge transfer at organic/organic interface.

#### **K10.15**

**Abstract Withdrawn**

#### **K10.16**

**Voltage distribution of Organic Bistable Devices and three-terminal organic memory device.** Jun He, Liping Ma and Yang Yang; Department of Materials Science and Engineering, UCLA, Los Angeles, California.

In this presentation, we report the electrical study of organic bistable devices that have an organic/metal nano-structure/organic triple layer structure sandwiched between two metal electrodes. When the biased voltage on such device is larger than a critical voltage, the device switches from high impedance state (Off state) to low impedance state (On state). This transition is nonvolatile, and it cannot be erased until a negative voltage is applied. Ideal application of this device is for nonvolatile memory devices. When a voltage is applied between two electrodes, the potential drop across the top/bottom organic layer is monitored. We found that although the bottom and the top organic layers have the same thickness (consequently, this is a symmetrical device structure), the potential drop across the device is asymmetric. Almost all the biased voltage on the device drops on the bottom organic layer, even more so when the device is at off state. And the potential drop across the top organic layer increases sharply when the devices switch from Off state to On state. This decreasing in the impedance of the organic layers, especially the bottom organic layer, is regarded as the main reason for switching behavior of organic bistable devices. Studying the asymmetric distribution of voltage is very helpful in understanding the mechanism of organic bistable devices. In addition, we demonstrated that this device can be operated as a three terminal device.

#### **K10.17**

**Structure-property Investigation of Asymmetrically Functionalized Polyparaphenylenes.** Suresh Valiyaveetil<sup>1</sup>, Renu Ravindranath<sup>1</sup> and Vetrichelvan Muthalagu<sup>2</sup>; <sup>1</sup>Chemistry, National University of Singapore, Singapore, Singapore; <sup>2</sup>Molecular Engineering of Biological and Chemical Systems, Singapore-MIT Alliance, Singapore, Singapore.

Conducting polymers are interesting group of polymers owing to their potential use in many emerging technologies. There have been many reports dealing with interesting structure and properties of such polymers in the literature. Our group at the National University of Singapore is focussed on developing asymmetrically functionalized polyparaphenylenes and fine-tuning their optical properties using various external stimuli. Recently we published the synthesis of a few polymers in this area in which intramolecular hydrogen bonding and alkyl chain crystallization facilitated the lamella-type organization of individual chains inside the polymer lattice. This presentation will highlight our strategy, synthesis, structure-property investigation of a series of such polymers incorporated with hydrogen bond donor-acceptor groups as well as metal ion binding functional groups.

#### **K10.18**

**Separate-coating and layer-by-layer deposition of polymer semiconductors by the spray deposition technique.** Katsuhiko Fujita, Takamasa Ishikawa and Tetsuo Tsutsui; Graduate School of Engineering Sciences, Kyushu university, Kasuga, Fukuoka, Japan.

We have reported a new type of polymer ultra-thin film preparation method, the spray deposition, and the application for organic optoelectronic devices such as an organic light emitting diode (OLED). In this method, a highly diluted solution of an organic material is nebulized into air and concentrated under a controlled evaporation condition. The resulting aerosol is transported by a carrier gas and deposited onto a solid substrate. This method has substantial advantages that an almost insoluble and non-evaporative material can be fabricated into a thin film, and that a separate-coating and layer-by-layer structure of polymers can be performed. An OLED was prepared from highly diluted THF solutions, below 1 ppm, of two poly-phenylenevinylene derivatives. One shows red emission and the other green. The red polymer was deposited on an ITO electrode through a shadow mask with 10-20 micrometer line width to result a fine separate-coating and the green one was deposited onto the patterned film. An Al anode was deposited on the polymer film in a vacuum evaporator. The fabricated OLED showed a patterned emission at around 10 V. This method will be a powerful tool for optoelectronic studies of materials of very low solubility or pyrolytic organic materials.

#### **K10.19**

**Effects of Chelating Agent Additives in Light-Emitting Polymer Diodes.** Kuo Yu Chen, Chi-Shen Tuan, Wan-Jung Teng and Hsin-Chen Chang; Opto Electronic Chemical R&D Division, Union Chemical Laboratories / Industrial Technology Research Institute, Hsinchu, Taiwan.

The purity of conjugated polymer is very important for the opto-electrical properties of light-emitting polymer diodes. However, it is difficult to purify conjugated polymer, especially for metal ions deriving from raw materials, container and environmental contamination. The residual metal ions will increase current leakage and reduce the stability of devices. In this paper, a series of chelating agents were added to chelate residual metal ions in

poly(2,3-dibutyloxy-1,4-phenylene vinylene) and poly(9,9-dioctylfluorene). The effects of various chelating agents addition on the opto-electrical properties of devices were investigated. The devices with chelating agents exhibited a lower turn-on voltage and higher rectification ratio than those without chelating agents. The results support the idea that the addition of chelating agent can decrease the current leakage of light-emitting polymer diodes.

#### **K10.20**

##### **Color Saturated Quantum Efficient**

##### **Poly(p-phenylene-ethynylene) (PPE) Blue OLEDs.**

Craig Alan Breen<sup>1</sup>, Yaakov R Tischler<sup>2</sup>, Vladimir Bulovic<sup>2</sup> and

Timothy M Swager<sup>1</sup>; <sup>1</sup>Chemistry, MIT, Cambridge, Massachusetts; <sup>2</sup>Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts.

Poly(p-phenylene ethynylene) (PPE) based OLEDs have the potential to meet the current OLED industry challenge to develop efficient, saturated, blue emitting devices that have long-term stability. PPE luminescence is tunable between 420 nm and 490 nm with an average FWHM of 25 nm due to the rigidity of the ethynylene linkage in the conjugated system. By grafting polystyrene to the PPE, we can isolate the individual polymer backbones and eliminate aggregation phenomena, resulting in high thin film photoluminescent quantum yields of 60% – 70%. This synthetic modification also increases the stability of the PPEs by preventing oxidative damage typically associated with aggregation phenomena. Under photoexcitation in an ambient air atmosphere with 0.4 W/cm<sup>2</sup> of 408 nm CW laser-light, the luminescent efficiency decreases to 20% of the initial value after 7 hours of exposure. This is more than an order of magnitude more stable to photooxidation than a typical OLED emitter such as Alq<sub>3</sub> or Ir(ppy)<sub>3</sub>. The best external quantum efficiencies of grafted PPE OLEDs are greater than 1%, with luminescent efficiency of 0.18 lm/W and 0.43 cd/A at 25 cd/m<sup>2</sup> and drive voltage of 7.6 V. EL spectra match PL thin film emission with CIE coordinates ranging from (x,y) = (0.176, 0.093) to (0.173, 0.293) for different PPE derivatives.

#### **K10.21**

##### **Memory Effect from Charge Trapping in Layered Organic Structures.**

Sung Hoon Kang<sup>1,2</sup>, Todd Crisp<sup>1</sup>, Ioannis Kymissis<sup>1,3</sup> and Vladimir Bulovic<sup>1,3</sup>; <sup>1</sup>Laboratory of Organic Optics and Electronics, MIT, Cambridge, Massachusetts; <sup>2</sup>Materials Science and Engineering, MIT, Cambridge, Massachusetts; <sup>3</sup>Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts.

We demonstrate that charge trapping in organic hetero-junction structures results in two distinct phenomena that both manifest as a memory behavior. Trapped charge can (1) increase the carrier mobility in organic structures; (2) generate current during the de-trapping process. We independently demonstrate the two processes in electrically active structures that contain molecular thin films with an inserted trap layer. The trap layer is a 10 nm thick film consisting of either organic molecules (Alq<sub>3</sub> or TPD doped with laser dye DCM2) or clustered metal. Analysis of the energy band structures indicates that both DCM2 sites and the metal clusters can trap charge, consistent with the measured current-voltage characteristics. For DCM2 doped devices we observe quenching of DCM2 photoluminescent (PL) upon charging, which allows us to quantify the trapped charge density as 10<sup>18</sup> cm<sup>-3</sup>, or approximately 10% of the inserted trap sites. We also demonstrate that the trapping layers can be incorporated within an OLED structure in a manner that does not affect forward bias I-V characteristics, but allows storage of information on the OLED by applying reverse bias on the device. In such manner, OLED display pixel arrays can be used as memory arrays that, for example, store information when the display is dormant.

#### **K10.22**

##### **Abstract Withdrawn**

#### **K10.23**

##### **Emissive Chemical Defects In Ladder-Type**

**Poly(Para-Phenylene)s.** Lorenz Romaner<sup>2,3,4</sup>, Georg Heimel<sup>1</sup>, Herbert Wiesenhofer<sup>1</sup>, Patricia Scanducci de Freitas<sup>5</sup>, Roland Guentner<sup>5</sup>, Ullrich Scherf<sup>6</sup>, Jean Luc Bredas<sup>1</sup>, Egbert Zojer<sup>1,4</sup> and Emil J.W. List<sup>2,3,1</sup>; <sup>1</sup>Institute of Solid State Physics, University of Technology Graz, Graz, Austria; <sup>2</sup>Christian Doppler Laboratory "Advanced Functional Materials", Graz University of Technology, Graz, Austria; <sup>3</sup>Christian Doppler Laboratory "Advanced Functional Materials", Institute of Nanostructured Materials and Photonics, Weiz, Austria; <sup>4</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; <sup>5</sup>Makromolekulare Chemie, Fachbereich Chemie, Bergische Universitaet Wuppertal, Wuppertal, Germany.

Bridged poly(para-phenylene)-type polymers have been extensively

studied over the last ten years. Good processability, high quantum efficiency of fluorescence, and the blue emission colour make this class of materials promising candidates for high-efficiency polymer electroluminescent devices. One of the encountered difficulties is that the devices turn out to be unstable during operation, gradually revealing a low-energy emission band in the range from 2.0-2.5 eV. This turns the desired blue colour of EL into a greenish emission. The unwanted emission band has been attributed to excimer or aggregate formation. However, for polyfluorene, another representative of the class of poly(para-phenylene)-type polymers, it has recently been shown that this change in emission colour is rather related to oxidative degradation processes, giving rise to emissive on-chain defects. In this work, we present results extending this finding to ladder-type poly(para-phenylene). We have studied two different types of ladder-type polymers by UV/VIS and infrared spectroscopy in annealing experiments and complemented the experimental studies with quantum-chemical calculations. The chemical stability of the polymers (as derived from the change in the infrared spectra) can be correlated with the relative intensity of the low-energy emission band. A closer inspection of the signature of the C=O stretching mode suggests the presence of several types of ketonic defects. The excitation energies, oscillator strengths and vibrational eigenmodes of the two chemically most plausible defect-types have then been calculated with correlated quantum chemical techniques. These studies reveal that only certain defect species give rise to low energy emission, while others merely result in a quenching of the luminescence.

#### **K10.24**

##### **Defect States Management in Organic and Inorganic**

**Conducting Polymer Films and Devices.** Marian Tzolov<sup>1,2,3</sup>, W. Bruetting<sup>2</sup>, P. W. Cyr<sup>3</sup>, M. Schwoerer<sup>2</sup>, E. H. Sargent<sup>3</sup> and I. Manners<sup>3</sup>; <sup>1</sup>Brown University, Providence, Rhode Island; <sup>2</sup>University of Bayreuth, Bayreuth, Germany; <sup>3</sup>University of Toronto, Toronto, Ontario, Canada.

The conducting polymers are well established as electronic material. However, the presence of electronic defects/traps in most of the cases has been pointed out as serious drawback for the device applications. Here we report direct experimental observation of defect states in thin films and in device structures and we demonstrate methods to manage the defect state formation. Our approach has been applied to several PPV derivatives as well as to the metal atom containing polymer polyferrocenylmethylphenylsilane (PFMPS). We studied PPV films made from precursor route and from soluble derivatives, the latter showing very good performance in light emitting devices [1]. The ground state has been investigated by using photothermal deflection spectroscopy. Several characteristic features have been identified below the absorption edge, some of them appearing in all types of PPV derivatives. All subgap features were observed in the photocurrent spectra of precursor route PPV based devices confirming the direct involvement of the corresponding electronic states in the electronic processes. Further confirmation of this finding was gained from the investigation of Al/PPV/ITO structures by two types of photocurrent measurements - time resolved and optical quenching - in various executions. These data together with photocapacitance measurements allow to conclude that a space charge builds up upon illumination leading to redistribution of the electric field in the device. The experimental data have been explained within a model assuming dissociation of the photogenerated excitons on the defect states. Further support of our findings was gained from the measurement of the photoluminescence quantum efficiency and from the photomodulation spectroscopy of thin films and from current-voltage, capacitance-voltage, and impedance- frequency measurements on device structures. The PFMPS is inorganic polymer with high resistivity, little or no photoconductivity and very efficient quenching of the photoluminescence. We invented a photooxidation process increasing the conductivity by several orders of magnitude and leading to the appearance of photoconductivity. The treated films retain their properties over months at ambient conditions. The photooxidation process was studied and we show that it is reversible and the neutral polymer can be regenerated. The photocurrent spectrum of the treated films mimics that of the absorption indicating that the photooxidized material is not a mechanical mixture of oxidized and unoxidized polymer units. Photomodulation spectroscopy revealed the existence of long-lived photoexcited states with a lifetime in the millisecond range. They have been interpreted as trapped excitons at the polymer chain defects created during the photooxidation process. The dissociation of the trapped excitons serves the photocurrent generation. [1] H. Becker et al., Adv. Mat. **12** 42 (2000).

#### **K10.25**

##### **High Performance Organic Light Emitting Transistors.**

Hiroyuki Endoh<sup>1,4</sup>, Yuko Sakai<sup>1</sup>, Atsushi Oda<sup>2,4</sup>, Kenji Nakamura<sup>4</sup>, Masatoshi Sakai<sup>3,4</sup>, Masakazu Nakamura<sup>3</sup> and Kazuhiro Kudo<sup>3,4</sup>; <sup>1</sup>NEC Corporation, Kawasaki, Japan; <sup>2</sup>Research Institute for Organic Electronics, yonezawa, Japan; <sup>3</sup>Chiba University, Chiba, Japan; <sup>4</sup>Optoelectronic Industry and Technology Development Association,

tokyo, Japan.

Optoelectronic elements using organic materials show promise for low-cost, large-area and flexible devices. We have fabricated organic light-emitting-transistors (OLET)<sup>(1)</sup> combining static induction transistor (SIT)<sup>(2)</sup> with organic light-emitting-diode (OLED) and investigated static and dynamic characteristics. All layers were fabricated on indium-tin-oxide (ITO) coated glass substrate using vacuum evaporation technique at approximately  $10^{-5}$  Torr. We have used 4,4'-bis[N-(1-naphthyl)-N-phenyl- amino] biphenyl ( $\alpha$ -NPD) for the organic semi-conductive layer. The luminescence layer was formed by tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) or organic amino-compounds. The OLET has a grid-type Al gate electrode that was formed using a shadow evaporation mask in the hole transporting layers. The effective electrode area of OLET is approximately 4 mm<sup>2</sup>. In fabricating the organic OLET, the controllability of the shape and thickness of grid-type Al gate electrode and organic layers are important. By optimizing the device structure, high performance of OLETs was obtained. The drain - source current ( $I_{DS}$ ) at a constant drain - source voltage ( $V_{DS}$ ) decreases with increasing the gate voltage ( $V_G$ ). The current is controlled by relatively small  $V_G$  (-1 V) and a typical SIT characteristic is obtained in the OLET. The luminescence also varies corresponding to the I-V characteristics. The maximum current and luminance values were approximately 10 mA and 10,000 cd/m<sup>2</sup>, respectively. The results obtained here demonstrate that the OLET is a suitable element for flexible sheet displays. (1) K.Kudo et al., Thin Solid Films, 327-329, 792 (1998) (2) K.Kudo et al., Synthetic Metal, 111-112, 11 (2000)

#### K10.26

**Molecular doping between two planar-stacking organic compounds: PTCDA and BTQBT.** Jiangeng Xue<sup>1,2</sup> and Stephen R. Forrest<sup>1,2</sup>; <sup>1</sup>Center for Photonics and Optoelectronic Materials (POEM), Princeton University, Princeton, New Jersey; <sup>2</sup>Dept of Electrical Engineering, Princeton University, Princeton, New Jersey.

Doping in organic materials to increase conductivity has received considerable interest in recent years, and it has been demonstrated that organic light-emitting devices incorporating doped hole and electron transport layers have lower drive voltages and higher luminance efficiencies than devices with undoped hole/electron transport layers [1,2]. The ionization potentials of two planar-stacking small molecular weight organic compounds, bis(1,2,5-thiadiazolo)-*p*-quinobis(1,3-dithiole) (BTQBT) and 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA), are reported to be 4.6 eV [3] and 6.7 eV [4], respectively. As the optical gap of both molecules is 2.2 eV, this indicates the LUMO of PTCDA is nearly at the same energy as the HOMO of BTQBT, which may lead to efficient electron transfer from a BTQBT molecule to a nearby PTCDA molecule. As a result, BTQBT may act as a donor in PTCDA, and conversely PTCDA may act as an acceptor in BTQBT. Due to similarities in molecular size and crystal structure, it is possible to achieve both n- and p-type doping using these two materials. Ultraviolet photoemission spectroscopy (UPS) measurements are first performed on heterojunctions between PTCDA and BTQBT grown by ultrahigh vacuum organic molecular beam deposition at room temperature. The Fermi level in a BTQBT film shifts from midgap to  $0.2 \pm 0.1$  eV above the HOMO after a 60 Å thick PTCDA overlayer is deposited on the BTQBT film, whereas the Fermi level in PTCDA shifts to  $2.1 \pm 0.1$  eV above the HOMO (or 0.1 eV below the LUMO) after a 70 Å thick BTQBT overlayer is deposited, which confirms the charge transfer between these two materials. Doped films are grown by co-evaporating two materials at different ratios. UPS, scanning electron microscopy, x-ray diffraction, UV-visible spectroscopy, and current-voltage measurements over a wide temperature range are used to characterize the structural, optical and electronic properties of the doped films. [1] X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, and K. Leo, Appl. Phys. Lett. 78, 410 (2001). [2] M. Pfeiffer, S. R. Forrest, K. Leo, and M. E. Thompson, Adv. Mater. 14, 1633 (2002). [3] H. Fujimoto, K. Kamiya, S. Tanaka, T. Mori, Y. Yamashita, H. Inokuchi, and K. Seki, Chem. Phys. 165, 135 (1992). [4] I. G. Hill, D. Milliron, J. Schwartz, and A. Kahn, Appl. Surf. Sci. 166, 354 (2000).

#### K10.27

**Green Emissive Ketone Type Chemical Defects - In Poly-Phenylene Based Conjugated Polymers.** Emil J.W. List<sup>2,3,1</sup>, Lorenz Romaner<sup>2,3</sup>, Christoph Gadermaier<sup>2,3</sup>, Martin Gaal<sup>2,3</sup>, Alexander Pogantsch<sup>1</sup>, Egbert Zojer<sup>1</sup>, Roland Guentner<sup>4</sup>, Patricia Scandiucci de Freitas<sup>4</sup> and Ullrich Scherf<sup>4</sup>; <sup>1</sup>Institute of Solid State Physics, University of Technology Graz, Graz, Austria; <sup>2</sup>Christian Doppler Laboratory Advanced Functional Materials, University of Technology Graz, Graz, Austria; <sup>3</sup>Christian Doppler Laboratory Advanced Functional Materials, Joanneum Research, Weiz, Austria; <sup>4</sup>Makromolekulare Chemie, Fachbereich Chemie, Bergische Universitaet Wuppertal, Wuppertal, Germany.

For future display applications of conjugated polymers the currently most challenging topic is the realization of colour stable blue light emission. All available poly(para-phenylene) type materials (PPP), which are the most promising family of blue light emitters, are prone to degradation resulting in an unwanted change in colour due to the emerging of a lower energetic greenish emission peak. This band has been mostly been attributed to aggregate and/or excimer formation in the material. However, as we show, both excimer and aggregate formation are very unlikely to be the origins of the low energy emission band in poly-fluorene based conjugated polymers. Instead all experimental observations show fluorescence from an on-chain oxidative defect to be the source of this emission band. In this context, using UV-VIS, PL emission and infrared spectroscopy we will present spectroscopic evidence for the formation of keto defect sites i.e. fluorenone molecules in different types of different PPP-type polymers as a consequence of different ongoing degradation processes. It will be demonstrated that keto defects can be generated in the material directly during polymer synthesis, photo- or electrooxidative degradation processes and thermal treatment in ambient atmosphere. In addition the low emission band at 2.2-2.3 eV in poly-fluorene based conjugated materials is studied by various spectroscopic methods on defined co-polymers of 9-9'-difarnesyl-fluorene with 9-fluorenone which can be seen as a model compound for degraded poly-fluorenes. Absorption, electroluminescence, and photoluminescence in the film (temperature dependent) and solution (room temperature) reveal the optical properties of the low emission band at 2.2-2.3 eV emerging in polyfluorene type polymers upon degradation. All the experimental evidences presented yield direct evidence against excimer or aggregate formation as the primary source of the low emission band. Instead keto defect sites i.e. fluorenone molecules incorporated in the polymer backbone can be shown to be responsible for the emissive defect. E.J.W. List et al. Advanced Materials, 14, 374-378 (2002). U. Scherf, E. J. W. List, Advanced Materials 14, 477 (2002). L. Romaner et al. Advanced Functional Materials, 13, xxx (2003).

#### K10.28

**Applications of Confocal Microscopy and Near-Field Optical Microscopy to Organic Light-Emitting Electrochemical Cells and Field-Effect Transistors.** Melissa Summers<sup>1</sup>, Ludvig Edman<sup>2</sup>, Marc Pauchard<sup>2</sup>, Alan J. Heeger<sup>2</sup> and Steven K. Buratto<sup>1</sup>; <sup>1</sup>Chemistry, University of California, Santa Barbara, Santa Barbara, California; <sup>2</sup>Physics, University of California, Santa Barbara, Santa Barbara, California.

We demonstrate the practical use of laser scanning confocal microscopy (LSCM) and near-field scanning optical microscopy (NSOM) to characterize the optical properties of functional organic devices. We obtain high resolution electroluminescence images of the p-n junction of a lithium salt doped polymer light-emitting electrochemical cell (LEC) in a planar configuration, using a simple vacuum chamber to eliminate the effects of photo-oxidation. The charge carrier balance is determined based on the position of the electroluminescent region within the planar LEC channel. The in-situ photoluminescence obtained from the same sample correlates to the electroluminescence, demonstrating that PL is an effective predictor of EL behavior in these devices. We also characterize these devices using NSOM to probe the relationship between film morphology and photoluminescence. In addition to LECs, we also study organic field-effect transistors. Polarization modulation in combination with our confocal technique reveals the extent of molecular alignment at the organic-dielectric interface in a FET, which has important implications about the carrier mobilities for these devices. Novel applications of NSOM to the characterization of functional transistors will also be discussed.

#### K10.29

**Design and Development of Novel Materials Based on 1,2,4,5-Tetra Arylenevinylene Substituted Benzene for Optoelectronic Applications.** Zuhra Ishmuratova Niazimbetova and Mary E. Galvin; Materials Science & Engineering, University of Delaware, Newark, Delaware.

It is known that intermolecular interaction in conjugated polymers can quench the luminescence, but at the same time may increase wave function overlap of the p-electrons and hence benefit charge transport. In this presentation we will focus on the preparation and investigation of model compounds, oligo-(arylenevinylenes), to study charge delocalization through the central benzene ring, as well as the effect of steric hindrance and incorporation of electron-transporting moieties. It is found that the tetra-substituted oligomer (1,2,4,5-) exhibited strong interactions between the pair of para substituted arms and high photoluminescence efficiency. X-Ray diffraction (XRD), microscopy (TEM) and photophysical studies show that some of the oligomers studied are capable of periodic  $\pi$ - $\pi$  stacking to form ordered-layered structures, which may be suitable for field-effect transistor (FET) and photovoltaics (PV). Liquid crystalline ordering

is supported by polarized light microscopy studies. We also present results from single layer light emitting diodes (LED) made out of the oligomers and blends of the oligomers with poly(p-phenylenevinylene) (PPV) as well as preliminary PV device characterization.

#### **K10.30**

**Efficient Long-Lived Alq<sub>3</sub>-Based Oleds Via Hole-Current Modulation.** Mathew Mathai<sup>1</sup>, Fotios Papadimitrakopoulos<sup>1</sup> and Bing Hsieh<sup>2</sup>; <sup>1</sup>Department of Chemistry, Polymer Program, Nanomaterials Optoelectronics, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan.

In the case of organic light emitting diodes (OLEDs) based on Aluminum tris-(8-hydroxyquinoline) or Alq<sub>3</sub>, it has been shown that excessive injection of holes into the active light-emitting Alq<sub>3</sub> layer results in oxidative degradation due to the formation of cationic species. While it is difficult to control bipolar charge transport in a multi-layer OLED solely by means of charge injecting mechanisms, the variable conductivity (between 10<sup>-8</sup> and 10<sup>-6</sup> S/cm) of a salt containing, hole transporting polymer layer (oxidized transport layer or OTL) can be utilized to fine tune the number of holes being injected into Alq<sub>3</sub>. By means of this technique we demonstrate that there is an optimum extent of hole injection for Alq<sub>3</sub> based OLEDs in order for them to operate with a maximum quantum efficiency of 1.75% and long operating lifetimes exceeding 1000 hours under a continuous DC current of 10 mA/cm<sup>2</sup>. In addition, due to minimized interfacial energy barriers in the OTL modified devices, we can analyze them based on the variation of electric field across active layers and charge transport through the polymer layer. Based on a finite electron-hole recombination cross section for Alq<sub>3</sub>, we are able to predict the modulated hole current required in order to operate these devices with minimal oxidative chemical degradation.

#### **K10.31**

**Morphological Studies of Aluminum tris-(quinoline-8-olate) by <sup>27</sup>Al Solid State NMR.** Magesh Nandagopal<sup>1</sup>, Mathew Mathai<sup>1</sup>, Fotios Papadimitrakopoulos<sup>1,2</sup> and Marcel Utz<sup>1,3</sup>; <sup>1</sup>Institute of Materials Science, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Department of Chemistry, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Department of Physics, University of Connecticut, Storrs, Connecticut.

Solid state <sup>27</sup>Al NMR has been used to study different crystal polymorphs of aluminum tris-(quinoline-8-olate) (Alq<sub>3</sub>), which is the most widely used electron transport material for organic light emitting diodes (OLEDs). A variety of crystal polymorphs of Alq<sub>3</sub> have been grown, of which the recently discovered  $\delta$  phase has generated considerable interest due to its blue shifted emission. Our studies enable us to assign the facial isomeric form of Alq<sub>3</sub> to the  $\delta$  phase and the meridional isomer to the other crystal polymorphs. Systematic analysis of samples prepared by thermal evaporation under various conditions indicates that <sup>27</sup>Al NMR holds great promise to characterize structural disorder at the molecular scale. The correlation of film growth parameters to both structural disorder and crystalline polymorph composition could ultimately enable us to better understand the charge transport properties and long-term performance of Alq<sub>3</sub>-based OLEDs.

#### **K10.32**

**Abstract Withdrawn**

#### **K10.33**

**Electrical and Luminescent Properties of Conducting Polymer-based Composites Containing PbS Nanocrystals with Different Capping Ligands.** Luda Bakueva, Gerasimos Konstantatos, Larissa Levina, Sergei Musikhin and Edward H. Sargent; Electrical and computer engineering, University of Toronto, Toronto, Ontario, Canada.

PbS quantum dot nanoparticles embedded in conducting polymers have been recently reported [1] as promising materials for photo- and electroluminescence in the spectral range 1 - 1.6 microns of interest in fibre-optic communications and biological assays. High luminescence efficiency in these structures is to a great extent determined by the optimal choice of a capping material, which creates a molecular layer covering the nanocrystals to suppress surface recombination and prevent their aggregation. We present the results of a systematic comparison of the role of 12-carbon vs. 18-carbon amine chain capping groups. We observe a significant increase in both photo- and electroluminescence as a result of the use of the longer capping group. The results are explained with reference to a surface dipole layer created by strongly polarized capping molecules, which is additionally confirmed by a strong asymmetry of electrical characteristics not observed in [1]. [1] L. Bakueva, S. Musikhin, M.A.Hines, T.-W.F. Chang, M. Tsolov, G. D.Scholes, E.H.Sargent, Appl. Phys. Lett. 82, 2895 (2003)

#### **K10.34**

**Abstract Withdrawn**

#### **K10.35**

**Thin Doped Channels in Polymer Thin film Transistors and Evidence of Conduction.** Munira Raja<sup>1</sup>, Naser Sedghi<sup>1</sup>, Bill Eccleston<sup>1</sup>, Sameer Badriya<sup>2</sup> and Simon J Higgins<sup>2</sup>; <sup>1</sup>Electrical Engineering & Electronics, University of Liverpool, Liverpool, UK; <sup>2</sup>Chemistry, University of Liverpool, Liverpool, UK.

Doped channels in polymer TFTs promise to minimize the channel shortening and therefore enhance the circuit performance of such devices. It is also known that hole drift mobility is strongly dependent on the dopant concentration in the bulk of a polymer film and that the field effect mobility is approximately two orders of magnitude higher than in the bulk [1-2]. It is important to ascertain whether it is the dopant or free hole concentration that is physically the most significant. In order to minimize various forms of instability, it is advisable to use thin polymer layers. This minimizes the migration of dopant through the polymer and hence reduces the gate leakage and threshold voltage shift. When the film approaches sub-nanometer dimensions an additional mechanism comes into play that substantially reduces the field effect mobility. Successively TFTs have been fabricated with thinned poly(3-hexylthiophene) films, with close to 100% regioregularity, and a background doping level of  $1 \times 10^{16} \text{cm}^{-3}$  (or less) doped with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [3]. The devices have inverted structure with a high-K gate dielectric (alumina). The threshold voltage is -1.23 V which is a consequence of using this gate material. It is consistent with  $V_{DD}$  of -10V: an important factor if power dissipation is to be minimized. It is demonstrated that the doping level rather than the hole concentration is the critical factor. This leads to the conclusion that the increase in mobility is not a result of the filling of band edge states by carriers, at least in these pure materials of high regioregularity. A tentative model is proposed that depends on the hopping of carriers between small clusters of dopant. It is qualitatively consistent with the strong dependence of mobility on doping level and a Poole-Frenkel type of behaviour. [1] A. R. Brown, D. M. de Leeuw, E. E. Havinga and A. Pomp, Synth. Met. 68, pp. 65, 1994. [2] C. P. Jarrett, R. H. Friend, A. R. Brown and D. M. de Leeuw, J. Appl. Phys. 77 (12), pp. 6289, 1995. [3] M. Raja, G. C. R. Lloyd, N. Sedghi, W. Eccleston, R. Di Lucrezia and S. J. Higgins, J. Appl. Phys. 92 (3), pp. 1441, 2002.

#### **K10.36**

**Electronic characteristics of polymer electrochemical devices on paper or plastic substrate.** Nathaniel D. Robinson<sup>1</sup>, Per-Olof Svensson<sup>1</sup>, David Nilsson<sup>1</sup>, Jessica Hall<sup>1</sup>, Robert Forchheimer<sup>2</sup> and Magnus Berggren<sup>1</sup>; <sup>1</sup>Dept. of Science and Technology, Linköping University, Norrköping, Sweden; <sup>2</sup>Dept. of Electrical Engineering (ISY), Linköping University, Linköping, Sweden.

With recent reports of devices unique to electrochemical polymers such as specialized sensors and displays and components which mimic the electronic behavior of their field-effect counterparts such as diodes and transistors, a description of the fundamental physical phenomena behind their performance is timely. Specifically, what modulates the current in these devices? Although such components are often geometrically complex, they are all constructed from three fundamental structures employing three basic materials: conducting electrochemically active polymer (such as PEDOT:PSS), electrolyte (liquid, gel or solid) and insulating substrate (paper or plastic). This paper presents experimental measurements on and within these structures and compares them to theoretical predictions based on fundamental physics. The model and experiments relate device performance to material properties (mobilities, etc.) and the structure's geometry. The electronic behavior of each of the three fundamental structures is governed by different transport phenomena. Structure 1, in which a potential is applied along a stripe of polymer and a region between the contacts is covered with electrolyte, responds based on changes in the electronic conductivity of the polymer caused by the applied electric field. Structure 2 is a secondary battery (or display cell) with 2 polymer electrodes connected by electrolyte. For structure 2, the ion mobility in the electrolyte or across the electrolyte-polymer interface governs the rate at which the device responds to changes in voltage applied between the two polymer electrodes. Structure 3 is constructed by adding an "island" of polymer in the electrolyte separating the two electrodes in structure 2. This area is addressed only when a voltage drop exists in the electrolyte surrounding the island (an ionic current must exist). The polymer response to an electric field is analogous to the response of a structure 1 device except that there is no electronic current flowing through the island once the polymer has adjusted to a new field. This structure is strongly affected by changes in the ionic conductivity of the electrolyte and the electronic conductivity and redox reaction rate of the polymer. Given this view of the operation of

the three structures, significant improvements have been made in our electrochemical devices. Further, it has enabled the development of new technologies for "electrochemical logic" and measurement components.

#### **K10.37**

**Characteristics of pentacene field effect transistors fabricated on ultra flat sapphire substrate.** Jun Yamaguchi<sup>1</sup>, Kenji Itaka<sup>1,2</sup> and Hideomi Koinuma<sup>1,2</sup>, <sup>1</sup>Materials & Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; <sup>2</sup>JST-CREST, Kawaguchi, Saitama, Japan.

Field effect transistors (FETs) using organic semiconductors attract much interest with the improvement of their mobility exceeding to that of amorphous silicon. In particular, pentacene is a promising material as active layer due to its high mobility. We have investigated the relationship among the surface morphology of gate dielectric layer, the grain size of pentacene and the field effect mobility. Inverted staggered FETs with different dimensions of pentacene active layers and gate dielectric layers were fabricated by using patterned shadow masks. It was found that FET characteristics is remarkably sensitive to the atomic scale flatness of sapphire substrate. To obtain a flat surface of gate structure, sapphire(0001) substrate was made to have steps and terraces structure by annealing in air at 1000°C. Alumina films as gate dielectric layer was deposited by rf magnetron sputtering and ITO gate electrodes were deposited by pulsed laser deposition. AFM images showed that the morphology of both alumina and ITO films were sensitive to substrate temperature. In particular, ITO films deposited at room temperature exhibited steps and terraces structure transcribed from the morphology of sapphire substrate. Pentacene thin films were thermally evaporated at 0.9nm/min on the gate structure. The grain size of pentacene films being strongly dependent on the morphology of gate dielectric layer ranged from 0.2 $\mu$ m to 2 $\mu$ m. With the improvement of flatness of dielectric layer, the mobility of FET increased to exceed 1.0cm<sup>2</sup>/V·s

#### **K10.38**

**Hole Transport Properties in Amorphous Thin Films of Spiro-linked Compounds.** Tobat Saragi, Thomas Fuhrmann and Josef Salbeck; Macromolecular Chemistry and Molecular Materials, Department of Natural Sciences, University of Kassel, Kassel, Germany.

Organic semiconducting materials are promising candidates for low cost device application such as organic light emitting diodes, organic solar cells and organic transistors. recent results in organic transistors based on organic single crystal or polycrystalline samples have shown a very good performance. However, there is still a problem with the presence of grain boundaries limiting the reproducibility of the devices. In our experiments, we have fabricated organic transistors based on amorphous molecular glasses. Morphologically stable materials with high glass transition temperature (T<sub>g</sub>) and high charge carriers mobilities are required for the above mentioned application. We measured the hole mobility for high-T<sub>g</sub> molecular glasses 2,2',7,7'-tetrakis(dipheylamino)-9,9'-spirobifluorene (Spiro-TAD) and 2,2',7,7'-tetra-(3-methyldipheylamino)-9,9'-spirobifluorene (Spiro-TPD) by field-effect transistor method. The film morphology, the influence of oxidizing atmospheres, the temperature and field dependence have been studied as well.

#### **K10.39**

**Abstract Withdrawn**

#### **K10.40**

**Organic Transistors as Biosensors.** Jeff Mason<sup>1</sup>, Zhengtao Zhu<sup>1</sup>, Sanjay Aggarwal<sup>1</sup>, Jamie Schnapp<sup>1</sup>, George Malliaras<sup>1</sup>, Antje Baeumner<sup>2</sup>, Nate Cady<sup>3</sup>, Carl Batt<sup>3</sup> and Brian Ray<sup>4</sup>, <sup>1</sup>Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Biological and Environmental Engineering, Cornell University, Ithaca, New York; <sup>3</sup>Food Science, Cornell University, Ithaca, New York; <sup>4</sup>Agave BioSystems, Ithaca, New York.

There is a great deal of interest in developing new biosensors due to their importance in a wide range of areas, including food safety, environmental monitoring, medical diagnostics, and defense. These new sensors should be small, easily portable, inexpensive, fast, and capable of detecting low concentrations of specific analytes with high sensitivity and high selectivity. Devices based on organic semiconductors have the potential to satisfy these criteria. Such devices can be easily and inexpensively fabricated on a variety of substrates, and the semiconducting molecules can be chemically synthesized or modified for specific applications. In the current work, we demonstrate the applicability of organic thin film transistors (OTFTs) for detecting biological species in aqueous environments. Pentacene OTFTs were fabricated on Si substrates with SiO<sub>2</sub> as the gate dielectric, and poly(dimethyl siloxane) (PDMS) microfluidic

channels were used to expose the active regions of the transistors to aqueous solutions with different ionic strengths and pH as well as buffer solutions containing rat basophilic leukemia (RBL) cells. We will also discuss unusual field-effect transistors based on the doped conducting polymer poly(ethylenedioxy-thiophene)-polystyrenesulphonate (PEDOT:PSS) and the application of these transistors to DNA sensing.

#### **K10.41**

**Degradation Mechanisms of Organic Thin Film Transistors under Ambient Conditions.** Yong Hoon Kim, Sung Kyu Park, Jeong In Han, Dae Gyu Moon and Won Keun Kim; Korea Electronics Technology Institute, Pyungtaek, Kyunggi, South Korea.

Recent reports on active-matrix liquid crystal displays (AM-LCDs) driven by organic thin-film transistors (OTFTs) have increased interest in organic-material based electronic devices, such as flexible displays and flexible integrated circuits (ICs). However, commonly used organic semiconductor materials are very vulnerable to oxygen and water vapor molecules, thus in order to prevent the degradation of organic materials by these molecules, oxygen and water vapor passivation layers must be adopted. In this report, to investigate the effects of oxygen and water vapor molecules on the performance of organic semiconductors, transistor characteristics such as on/off currents, threshold voltage and field effect mobility changes under various conditions were observed. As a reference, organic transistors were kept under vacuum or dry N<sub>2</sub> atmosphere and the electrical properties were measured. Also, to investigate the oxygen and water vapor effects on the electrical properties, samples were measured under O<sub>2</sub> and wet N<sub>2</sub> atmosphere as a function of time of exposure. The on current, threshold voltage and the field effect mobility were greatly affected by the environment condition, typically in water vapor environment and it suggests that a proper passivation layer is a prerequisite. We applied various oxide layers and organic materials as a passivation layer and analyzed their passivation properties. As an organic semiconductor material, poly(3-hexylthiophene) with head-to-tail regioregularity of 98.5% was used. The organic transistors were fabricated on glass substrates instead of plastic substrates, since the oxygen and water vapor transmission rates of plastic substrates are very high relative to glass substrates and oxygen and water vapor may penetrate through the substrate and may affect the electrical performance.

#### **K10.42**

**Water-induced Electronic Effects on Device Operation of Polythiophene-based Field-effect Transistors.** Satoshi Hoshino, Manabu Yoshida, Sei Uemura, Takehito Kodzasa, Toshihide Kamata and Kiyoshi Yase; Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan.

We investigated influence of moisture on device characteristics of a polythiophene-based field-effect transistor (FET) to gain a deep understanding behind the mechanism of the air susceptibility of device operation generally found in this kind of devices. Our regioregular poly(3-*n*-hexylthiophene) (P3HT)-based FET with top-contact source and drain electrodes showed an output profile including effective field-effect modulation and a saturation behavior in the output current when they operated in absolute N<sub>2</sub> and O<sub>2</sub> at ambient pressure as well as in a vacuum. By contrast, the device operation was significantly influenced by a marked increase in the conductivity of the active layer if the FET was exposed to N<sub>2</sub> humidified with water, and the operation characteristics were quite similar to that found in ambient atmosphere in such aspects of the distortion in the output profile as a deterioration in the saturation behavior in the current and enlarged off-state conduction. We attributed the dominant factor of the air susceptibility to an electronic perturbation originating from atmospheric water rather than O<sub>2</sub>, whose *p*-type doping activity to P3HT caused only a small increase in the conductivity of the active layer and slight decrease in the field-effect mobility for the exposure at ambient pressure. We discussed the mechanism of the water-induced electronic perturbation based on the difference in the response of the device characteristics to the exposure between water and O<sub>2</sub>. We concluded that water molecules affected the device operation through highly exoergic adsorption onto the P3HT layer and an accumulation of charge carriers induced by their large dipole momentum in the vicinity of the active layer surface. We estimated that the majority of the carrier conduction occurred in the surface region where the charge density was raised by the water adsorption, consequently observing the significant distortion of the output profile.

#### **K10.43**

**Abstract Withdrawn**

#### **K10.44**

**Abstract Withdrawn**



#### **K10.45**

##### **Bias stress effects and anomalous temperature dependence of charge transport in polymer thin-film transistors.**

**Alberto Salleo**, Michael L Chabinye, Kateri E Paul, William S Wong, Raj B Apte and Robert A Street; Palo Alto Research Center, Palo Alto, California.

Most recent studies on polymer TFTs have focused on characterizing device performance in terms of carrier mobility, on-off ratio, threshold voltage and sub-threshold slope. As these figures of merit improve, circuits built with polymer TFTs become feasible. Along with appropriate electrical performance however, stability is required in order to realize such circuits. In particular, bias stress (i.e. the progressive shift of the threshold voltage as the device is operated) causes polymer TFT circuits to fail. In this work we characterize non-ideal behavior of polymer thin film transistors (TFTs). We studied a high-performance regioregular polythiophene (PT) and poly(9,9-dioctyl-fluorene co-biothiophene) (F8T2) with mobility in the range  $10^{-2}$ - $10^{-1}$  cm<sup>2</sup>/Vsec. Bias stress is a property of the semiconductor rather than the dielectric or the dielectric/semiconductor interface. F8T2 devices relaxed slowly and recovered under band-gap illumination, suggesting that the stress mechanism involves charge trapping in the semiconductor. The PT devices on the other hand recovered within a few seconds in the dark at room temperature. We also observed an anomalous temperature dependence of the mobility in PT: between 240K and 170K the mobility appears to increase with decreasing temperature. The magnitude of the stress effect is proportional to the square of the hole concentration, and propose that the physical mechanism is the formation of bipolarons. Under this hypothesis, the differences in bias-stress kinetics can be related to the relative bipolaron stability in the two polymers. Because the onset of bias-stress is related to the hole concentration in the channel, its consequences on device design and operation will be discussed. The surprising temperature anomaly in PT can also be successfully modeled by taking into account the formation of bipolarons.

#### **K10.46**

##### **Receptor - Mediated Chemical Sensing with Organic FETs.**

**Daniel Hayes Fine**<sup>1</sup>, David F. Cauble<sup>2</sup>, Taeho Jung<sup>1</sup>, Liang Wang<sup>1</sup>, Heinz von Seggern<sup>1</sup>, Michael J. Krische<sup>2</sup> and Ananth Dodabalapur<sup>1</sup>; <sup>1</sup>Micro Electronics Research Center, The University of Texas at Austin, Austin, Texas; <sup>2</sup>Chemistry and Biochemistry, Organic Division, The University of Texas at Austin, Austin, Texas.

Organic field-effect transistors (FETs) have been shown to be effective chemical vapor sensors. Their sensitivity can be modified, and even substantially enhanced, through the use of small molecule receptors. These receptors functionalize the grain boundaries of the semiconductor, making the sensor more sensitive to some types of chemical species. Our data indicates that the response to analytes with and without receptors are markedly different, from a positive change in transistor drain current (where the analyte appears to dope the semiconductor), to a sharp decrease in current (where the analyte appears to create trap centers in the semiconductor). The data also show that in the case of a negative response, the original electrical performance of the device can be recovered after exposure to the analyte by reverse biasing. We have also looked at the reliability of these sensor devices as well as how the devices' responses to analytes scale with device dimensions, including devices with channel lengths as small as 4 nm. Results on chemical and biological sensing in aqueous ambients will also be reported.

#### **K10.47**

##### **Analysis of Bending Stresses in Polymer TFT incorporated with Encapsulation Layer.**

**Jun Baek Park**<sup>1</sup>, Dae Shik Seo<sup>1</sup>, Yong Hoon Kim<sup>2</sup>, Sung Kyu Park<sup>2</sup>, Dae Gyu Moon<sup>2</sup> and Jeong In Han<sup>2</sup>; <sup>1</sup>Department of Electrical & Electronic Engineering, Yonsei University, Seoul, South Korea; <sup>2</sup>Information Display Research Center, Korea Electronics Technology Institute, Pyungtaek, Kyunggi, South Korea.

This experiment gives the basic understanding about bending stress of plastic-based electronics incorporated with encapsulation layers. From the experiments about position-dependent stress distribution of patterned indium-tin-oxide (ITO) array, it is noted that when external bending force applied, the more cracks occurs corresponding to the higher stress intensity as moves from edge position toward center position. Moreover, using six different sandwich structures varying encapsulation or buffer layer materials (SiO<sub>2</sub>, PI) and their thickness, both external bending stress and residual stress of triple-layer structure (substrate-ITO-encapsulation or substrate-buffer-ITO) can be quantified and numerically analyzed corresponding to crack distributions (farthest cracked island position). Based on the experiments, we applied this mechanism to plastic-based polymer thin film transistors (TFTs) array and measured their electrical variation regarding position and encapsulation materials of the polymer TFTs

array after imposing external bending force. Consequently, it should be noted that sandwich structure with larger coefficient of thermal expansion and more elastic encapsulation material favors for the stable operation of the devices when they were externally bent.

#### **K10.48**

##### **Doped Polymer Field-Effect Transistors.**

**Satoki Ashizawa**<sup>1</sup>, Ryoike Horikawa<sup>2</sup> and Hidenori Okuzaki<sup>1</sup>; <sup>1</sup>Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Kofu, Japan; <sup>2</sup>Faculty of Engineering, University of Yamanashi, Kofu, Japan.

Flexible and transparent all-polymer field-effect transistors (FETs) using a doped conducting polymer, poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT/PSS), as a channel material were fabricated by the line patterning method without exploiting photolithography, vacuum deposition, or printing of conductive inks. The pattern of source-drain electrodes is printed by laser printer and then coated with the PEDOT/PSS aqueous solution and dried with a hot air gun. The printed toner was removed by ultrasonication in toluene for about 10 seconds, leaving the conducting pattern on the substrate. The PVP, used as an insulating layer, is spin-coated from isopropanol solution, and finally, a PEDOT/PSS gate electrode overlapping the channel is spin-coated. It is noted the FET has a conducting channel made of PEDOT/PSS instead of the semiconductors. An "on" state of the FET is when no voltage is applied between the gate and source electrodes ( $V_g = 0V$ ) because the conducting channel, made of PEDOT/PSS, is already built in between the source and drain electrodes but not be induce by the gate voltage, i.e., the device is "normally on". The FET operates both in the depletion and enhancement modes in response to the positive and negative gate voltages, respectively.

#### **K10.49**

##### **Oligo(2,6-Anthrylene)s: Acene-Oligomer Approach for Organic Field-Effect Transistors.**

**Kaname Ito**<sup>1</sup>, Toshiyasu Suzuki<sup>1</sup>, Youji Inoue<sup>2</sup> and Shizuo Tokito<sup>2</sup>; <sup>1</sup>Institute for Molecular Science, Okazaki, Japan; <sup>2</sup>NHK Science and Technical Research Laboratories, Tokyo, Japan.

Oligo(2,6-anthrylene)s (2A and 3A) and their dihexyl derivatives (DH-2A and DH-3A) have been synthesized by the Suzuki coupling using palladium catalysts. Organic field-effect transistors (OFETs) of these anthracene oligomers were fabricated on SiO<sub>2</sub>/Si substrates by high-vacuum evaporation. OFETs with 2A exhibited FET activity, and the hole mobilities ranged from 0.0031 to 0.013 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The oligomer 3A showed even higher mobilities (0.064-0.072 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>). Field-effect mobilities of DH-2A were greater than 0.1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The highest mobilities (0.18 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) were observed in DH-3A OFETs. X-ray diffraction studies on the films indicated a high degree of lamellar ordering and crystallinity.

#### **K10.50**

##### **A study on molecular alignment in organic field effect transistors using epitaxially grown platinum(II) octaethyl porphyrin films.**

**Yong-Young Noh**<sup>1</sup>, Dong-Yu Kim<sup>1</sup>, Jang-Joo Kim<sup>1</sup>, Kiyoshi Yase<sup>2</sup>, Yuji Yoshida<sup>2</sup> and Torsten Fritsch<sup>3</sup>; <sup>1</sup>Department of Materials Science and Engineering, Kwangju Institute of Science and Technology(K-JIST), Gwangju, South Korea; <sup>2</sup>Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; <sup>3</sup>Institut für Angewante Photophysik, TU Dresden, Dresden, Germany.

Organic field effect transistors (OFETs) have attracted a great deal of interest for use in application such as thin film transistors for active matrix liquid crystal displays or organic light emitting displays as well as low end data storage. Electron or hole mobility has been improved via the production of highly ordered organic films.[1] To obtain the highly ordered organic thin films, OFETs were fabricated using organic epitaxy films deposited on potassium bromide (KBr) single crystals.[2] Molecular alignment of platinum(II) octaethyl porphyrin (PtOEP) crystals evaporated on KBr can be readily changed from perpendicular to parallel by changing the substrate temperature (Ts). OFETs using epitaxially grown PtOEP films were demonstrated by a wet transferring process from KBr to SiO<sub>2</sub> substrate. The field effect mobility of the film aligned perpendicular to the substrate was 100 times higher than that of the film aligned parallel. We will also discuss the reason why the PtOEP films show the different alignments as Ts via scanning tunneling microscopy (STM) studies and potential energy (PE) calculation of the monolayer of PtOEP films on KBr and Au(111). [1] C.D. Dimitrakopoulos et al., Adv.Mater.,2002,14,99. [2] Y.-Y. Noh et al., Adv.Mater.,2003,15,699.

#### **K10.51**

##### **The Stilbene Polymers for Organic Field-Effect Transistors.**

**Yoshikazu Akiyama**, Toshiya Sagisaka, Masafumi Torii, Takashi

Okada, Yoshinobu Nakayama and Masaomi Sasaki; R&D Center, RICOH, Yokohama, Japan.

The organic field-effect transistors (OFETs) are promised to be widely useful, because the film is easy to fabricate in large scale with low-cost by solution process. The characteristics of some OFETs have been intensively investigated, however the materials such as polythiophenes used in the OFETs have various problems. We synthesize stilbene polymers that have the triarylamine structure, and examine their OFETs' properties, because the structure will have high hole-transport ability. The stilbene polymers are synthesized by Wittig - Horner reaction. The number average molecular weight is approximately 20,000. Typical value of the time of flight mobility of these materials is  $4.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at the field intensity of 25 MV/m. The value is higher than that of the usual molecular-doped organic photo-conductor (OPC) materials in 2 order. The gradient of the mobility shown by a square root rule of the field intensity is the same as OPCs' one, and this becomes suitable in the transistor action. The OFETs that have a top contact structure are made on Si wafer. The contact electrode made of Au with the size of 35  $\mu\text{m}(\text{L}) \times 10000 \mu\text{m}(\text{W})$ . The active layer is fabricated by spin coating. A toluene solvent in which the polymer concentration is 1 wt% is used. The properties of OFETs using the stilbene polymers are examined. The OFET shows the FET mobility of  $1.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  under the condition of gate voltage  $V_G$  and drain-source voltage  $V_{DS}$  are 20V, respectively, and on current  $I_{ON}$  is  $6 \times 10^{-7} \text{ A}$  and off current  $I_{OFF}$  is  $4 \times 10^{-10} \text{ A}$ . From these data, it is estimated that the family of stilbene polymers will have a potential to become promising candidates for OFETs' material.

#### **K10.52**

##### **Perfluorinated Oligothiophenes and Pentacene as n-Type Semiconductors for Organic Field-Effect Transistors.**

Toshiyasu Suzuki<sup>1</sup>, Sakamoto Youichi<sup>1</sup>, Youji Inoue<sup>2</sup> and Shizuo Tokito<sup>2</sup>; <sup>1</sup>Institute for Molecular Science, Okazaki, Japan; <sup>2</sup>NHKK Science and Technical Research Laboratories, Tokyo, Japan.

Organic semiconductors have attained much attention because of the recent progress of organic light-emitting diodes (OLEDs) and field-effect transistors (OFETs). We reported that perfluorinated oligo(p-phenylene)s, such as perfluoro-p-sexiphenyl (C36F26), were efficient n-type semiconductors for the electron-transport layer of OLEDs [1]. Molecular design of organic semiconductors for FETs should be different from that for OLEDs. A FET requires planar and crystalline materials for high carrier mobility. On the other hand, an OLED prefers non-planar and amorphous materials. We designed perfluorinated oligothiophenes and pentacene as potential n-type semiconductors for OFETs because of the following reasons: (1) These perfluorinated molecules are expected to be planar. (2) Oligothiophenes and pentacene are excellent p-type semiconductors with high hole mobility. (3) Perfluorination is an effective way to convert a p-type organic semiconductor to n-type one. We report herein the syntheses and properties of perfluorinated oligothiophenes up to the octamer and perfluorinated pentacene (C22F14). OFETs with these new n-type semiconductors will be also presented. [1] (a) Heidenhain, S. B.; Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Mori, T.; Tokito, S.; Taga, Y. *J. Am. Chem. Soc.* 2000, 122, 10240-10241. (b) Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Tokito, S.; Taga, Y. *J. Am. Chem. Soc.* 2000, 122, 1832-1833.

#### **K10.53**

##### **Effect Of Dip Coating On Regioregular Poly(3-hexylthiophene) Field-Effect Transistors.**

Guangming Wang, Takashi Hirasa, Daniel Moses and Alan J Heeger; Institute for Polymers and Organic Solids, Mitsubishi Chemical Center for Advanced Materials, University of California at Santa Barbara, Santa Barbara, California.

It has been known that dip coating is very effective for increasing the field-effect mobility of regioregular poly(3-hexylthiophene) (RR-P3HT) based on our previous results. In this paper we report influence of dip-coating speed and concentration of polymer solution on characteristics of RR-P3HT field-effect transistors (FETs) with top-contact structure. It was found that the field-effect mobility increased with decrease of the dip coating speed from the low concentration of solution, and it did change a little when the dip-coating speed lowered to a value, such as 500  $\mu\text{m}/\text{min}$  that we obtained from concentration of solution (0.5~0.8 mg/ml) with chloroform as solvent. From the higher concentration solution, the mobility increased with decreasing dip coating speed just in the range of high dip-coating speed. However, if the dip coating speed was down to a value, such as 1,000  $\mu\text{m}/\text{min}$  obtained, the mobility decreased. But all on/off ratios increased with raising the dip coating speed (<10,000 $\mu\text{m}/\text{min}$ ).

#### **K10.54**

##### **Polyimide Gate Insulator for Organic Thin Film Transistors.**

Mi Hye Yi<sup>1</sup>, Sung Mook Choi<sup>1</sup>, Moo Yeol Lee<sup>1</sup>, Jae Heung Lee<sup>1</sup>, Lee-Mi Do<sup>2</sup>, Yong Suk Yang<sup>2</sup> and Jeong Ik Lee<sup>2</sup>; <sup>1</sup>Advanced Materials Division, Korea Research Institute of Chemical Technology, Taejeon, South Korea; <sup>2</sup>ETRI, Taejeon, South Korea.

In this study, a series of polyimide(PI) precursors was synthesized from various tetracarboxylic acid dianhydrides (PMDA, BTDA, CBDA) and novel aromatic diamine with polar substituents, which can be used for organic gate insulator in pentacene organic thin film transistors (TFT). The obtained polyamic acid solution was spin-coated and cured at 250 °C for 1hr. We had investigated a relationship between field effect mobility of pentacene TFTs using 0.3 $\mu\text{m}$  thick gate insulators and properties of the obtained polyimides such as dielectric constant, breakdown voltage, chemical resistance and photosensitivity. Further, surface roughness of the polyimide thin films was examined by Atomic Force Microscopy (AFM) and surface tension was also determined, which was ranged from 0.2~20 nm and 40~50 dyne/cm, respectively. We have also studied effects of surface properties of polyimide thin films on field effect mobility of pentacene TFTs using organic insulator, which was compared them those of organic TFTs previous reported.

#### **K10.55**

##### **Polymer insulator layer in organic field effect transistors.**

Henrik G O Sandberg, Tomas Backlund, Ronald Osterbacka and Henrik Stubbs; Department of Physics, Abo Akademi University, ABO, Finland.

Organic field effect transistors often refer to the semiconducting layer of the device. However, true organic devices also incorporate organic materials as gate insulator and electrode materials. For flexibility a plastic or paper substrate can be used as a mechanical support. Said substrate materials are also well suited for device manufacture by a printing process and there is much activity in optimizing printing techniques for electronic device manufacture. Plastic substrates often show better device characteristics than devices prepared on standard glass slides. This observation may be denoted to better chemical compatibility with the organic materials or purity of the plastic substrate. Surface roughness may also play a role. Even so the polymer insulator layer, on the other hand, may degrade device characteristics compared to traditional inorganic insulator materials. Current leakage is seen with many insulator materials in device configuration. Some frequently used polymeric insulator materials have been studied and the impact on device characteristics has been investigated in various environments and as a function of material preparation. Procedures for cross-linking of the gate insulator layer are investigated in order to improve device characteristics and layer integrity during subsequent manufacturing steps. It is shown that the device performance is directly influenced by the properties of the insulating layer as it is prepared in various ways. The processes that occur in the insulator layer can be rather complex and interaction with neighboring layers may occur during device operation. As a semiconducting polymer poly(3-hexylthiophene) is used in the devices.

#### **K10.56**

**Advantage of the pseudo vertical configuration for organic FETs.** Manabu Yoshida, Sei Uemura, Satoshi Hoshino, Takehito Kodzasa and Toshihide Kamata; Organic Semiconductor Device Research Group, National Institute of Advanced Science and Technology, Tsukuba, Ibaraki, Japan.

Using organic semiconductors is an attractive way for developing flexible, lightweight, and low-cost devices. In order to fully attract the abilities of organic semiconductors, we have created a new pseudo vertical structure for organic field-effect transistors (OFETs) for developing high performance, large-area, and flexible organic devices. In this structure, a drain electrode (bottom), an active layer, and a source electrode (top) are deposited layer-by-layer on the gate insulator surface. Since this device includes both top- and bottom-contact portions between the electrodes and the active layer, this is called top and bottom contact (TBC) structure. The active layer is vertically sandwiched by the drain and source electrodes, and then the channel region forms between the top electrode and the edge of the bottom electrode. Therefore, the channel length is flexibly controlled by varying the active layer thickness for various applications. Namely, very short channel length can be easily fabricated not using any photolithography and related micro patterning processes. We have actually fabricated a pentacene TBCFET with a 0.5- $\mu\text{m}$  channel length using only simple layer-by-layer process. In the TBCFET, a large current density (40  $\mu\text{A}/\text{mm}$ ) and the effective gate-modulation were observed even under the low applied voltage (at  $V_{DS} = 5\text{V}$ ). Due to the unique structure, the ordinary model of gate-modulation for the planar-type FET would not be applicable to the TBCFET. In the case of TBCFET, the gate modulation of the drain current  $I_D$  does not result from the channel conductivity change on applying a gate voltage ( $V_G$ ) unlike the ordinary planar-type FET. To understand their operation mechanism,

we have suggested the novel model of gate modulation that is applicable to TBCFET. The experimental results show that the  $I_D$  non-linearly depends on the drain source voltage ( $V_{DS}$ ), and then the exponent of  $V_{DS}$  is changed from 6.8 to 3.5 by increasing  $V_G$  negatively. This behavior completely deviates from the model for the ordinary planar-type FET. According to the change of the exponent, the carrier conduction mechanism is changed from the trapped charge limited (TCL) type to the space charge limited (SCL) type by increasing  $V_G$  negatively. As a result, it has been concluded that the gate modulation of TBCFET is governed by the change of the carrier conduction mechanism rather than the change of the channel conductivity. Applications and practicalizations of the TBCFET will be discussed.

#### **K10.57**

##### **Fabrication of Organic Static Induction Transistors with Higher Order Nanostructures by Spontaneous Formation.**

Joseph Chennemkeril Mathew, Naoki Hirashima, Masakazu Nakamura, Masaaki Iizuka and Kazuhiro Kudo; Department of Electronics and Mechanical Engineering, Chiba University, Chiba, Japan.

Organic transistors find many future applications as they are the driving component for flexible displays. Static induction transistors (SITs) are suitable candidates for high current applications [1]. Low noise, low distortion and high power capability makes them useful in high power transistors. Phthalocyanines (Pc) have potential as the active material for these devices due to their low cost, high stability and low toxicity. To improve performance of organic devices based on Pc, we have tried higher order nanostructures in the active region. The electronic properties of organic SITs strongly depend upon their internal microscopic structures. Here a wet process was used for the preparation of the nanostructures. For the wet process, we have employed polystyrene (PS) nanospheres as the masks for the fabrication of bottom drain electrode. The gate electrode and the active region were patterned by a selective mechanical exfoliation using ultrasonic wave apart from the conventional nanolithographic process. The modulation of the drain current by the gate voltage was confirmed as obtained from the static characteristics. In the present work, the cross-sectional structure and the device characteristics of these nano SITs will be discussed. Reference: [1] K.Kudo, D.X.Wang, M.Iizuka, S.Kuniyoshi and K.Tanaka, Thin Solid Films 331 (1998) 51.

#### **K10.58**

##### **Double layer structured polymer gate dielectric for organic field effect transistor.** Sei Uemura, Manabu Yoshida, Satoshi Hoshino, Takehito Kodzasa and Toshihide Kamata; National Institute of Advanced Science and Technology, Ibaraki, Japan.

Polymer materials are promising materials for flexible and low-cost fabrication such as spin coating, spray coating, and printing. Recently, the use of polymer dielectric gate materials such as poly(methyl-methacrylate) (PMMA) has been reported for the organic FET. However, there are still a lot of problem to use a polymer as a gate dielectric. One of the serious problems is in the cause of the hysteresis in the transfer characteristics. It has been considered that such hysteresis behavior is caused by mobile ions because it can be penetrated into the semiconductor layer and then affected considerably the drain current. However, it is difficult not easy to remove completely the mobile ion from polymer because the ion is entangle with the polymer chain. In addition, the use is limited the choice of the semiconductor layer. When the device is fabricated with wet-process, the PMMA layer is fused the major polymer semiconductor such as polythiophene and polyfluorene derivatives because PMMA is soluble to organic solvent such as chloroform or toluene, which is solvent for polymer semiconductor. The fusion between polymer insulator and semiconductor layer limits the choice of the material for the device fabrication. In order to remove the influence of the mobile ion and to improve the adaptability for device fabrication, we designed a double layer structure of the gate dielectric insulator. Namely, the surface of the PMMA layer is modified with another insulator layer that prevents the diffusion of the mobile ions in the device films. For that purpose, clay mineral seems to be a good candidate for the modifier of the PMMA surface. Clay minerals composed of superimposed crystalline aluminosilicate layers have anionically charged interlayer and the surface. The positively-charged molecules such as organic molecules cation and metal ion are intercalated in their interlayer spaces or adsorbed at the surface. Therefore, some kind of clay mineral would be useful to block the diffusion of a mobile ion on the polymer surface. A pentacene FET was fabricated with PMMA gate dielectric modified the surface with a clay mineral, to begin with. In its FET properties, the hysteresis was disappeared due to adsorbing the ion at the surface of the INT layer and its interlayer. However, since the surface roughness of the insulator layer is increased by the clay modification, the mobility and on/off ratio is lower than that reported by several researchers. Therefore, it is important to decrease the surface roughness. For that

purpose, clay dispersed PVA was used as a modification layer. We a fabricated with poly(3-hexylthiophene) FET and PMMA modified the surface with the clay dispersed PVA by wet-processes. The polymer FET showed the stable FET behavior.

#### **K10.59**

##### **Carrier Mobility and Radiation Effects In Pentacene Based Field Effect Transistors.** Gregory Theriot<sup>1</sup>, Joseph W Tringe<sup>1</sup>,

Roderick A Devine<sup>1</sup>, Lisong Zhou<sup>2</sup>, Thomas N Jackson<sup>2</sup> and Erik Brandon<sup>3</sup>; <sup>1</sup>VSSE, AFRL-Kirtland AF Base, Albuquerque, New Mexico; <sup>2</sup>Electrical Engineering, Pennsylvania State University, University Park, Pennsylvania; <sup>3</sup>Materials and Device technology, NASA Jet Propulsion Laboratory, Pasadena, California.

Carrier mobility measurements have been made on pentacene based field effect transistors having channel lengths in the range 20 to 5  $\mu\text{m}$  and channel widths of 100  $\mu\text{m}$ . Consistent with other authors we observe an effective channel length dependent mobility which might be attributed to contact resistance at the source and drain electrodes. In devices where an asymmetry in the electrode structure ('flagging' effect) is observed by atomic force microscopy we measure an effective channel mobility whose magnitude depends upon the current direction during measurement. For 20  $\mu\text{m}$  devices with the source contact on the flagged electrode and the drain contact on an unflagged electrode the mobility is repeatedly found to be  $\sim 30\%$  larger than when the drain contact is made on the flagged electrode. The magnitude of this difference decreases as the channel length decreases and in 5  $\mu\text{m}$  devices no anisotropy was found even though evidence for flagging was observed by atomic force microscopy. Close examination of the morphology of the pentacene film at the edges of flagged and unflagged electrodes shows clear differences except for the smallest channel length devices. It is suggested that this result is inconsistent with a purely contact resistance model. Preliminary radiation sensitivity measurements of the transistor structures are in progress and results will be presented in detail at the conference.

#### **K10.60**

##### **Characterization of Polymer Dielectric Thin Films for Organic Thin Film Transistors.** Lee-Mi Do<sup>1</sup>, Mi-Hye Yi<sup>2</sup>, Jong-ik Lee<sup>1</sup>, Young-Suk Yang<sup>1</sup>, Sung-Mook Choi<sup>2</sup>, Moo-Yeol Lee<sup>2</sup>, Sun-Ki Kwon<sup>3</sup> and Hong-Ku Shim<sup>4</sup>;

<sup>1</sup>Basic Research Laboratory, Electronics and Telecommunications Research Institute, Taejeon, South Korea; <sup>2</sup>Advanced Materials Division, Korea Research Institute of Chemical Technology, Taejeon, South Korea; <sup>3</sup>Department of Chemistry, Kyung Sang National University, Jin-Ju, South Korea; <sup>4</sup>Center for Advanced Functional Polymers, Department of Chemistry and School of Molecular Science, Korea Advanced Institute of Science and Technology, Taejeon, South Korea.

Low-cost and high-volume manufacturing process is envisioned for low temperature processable organic electronics and flexible display fabrication. The use of polymeric insulator thin film devices has become increasingly interest due to simple process in organic thin film transistor. The mobility of polymeric thin film transistor is affected by surface properties, wettability and/or thickness of polymeric insulators. In this study, we characterized photosensitive polyimides insulator with polymeric semiconductor layer. We obtained that the mobility of pentacene with photosensitive polyimides dielectric layer is about  $10^7 \text{ cm}^2/\text{Vs}$ . Characterization of various photosensitive polyimids will be presented in detail.

#### **K10.61**

##### **Characterization of Vapor Deposited Semiconducting Layer for Organic Thin Film Transistors.** Lee-Mi Do<sup>1</sup>, Young-Suk Yang<sup>1</sup>, Jong-ik Lee<sup>1</sup>, Ji-Ho Youk<sup>1</sup>, Hyung-Sun Kim<sup>2</sup>, Yun-Hi Kim<sup>2</sup>,

Sun-Ki Kwon<sup>2</sup>, Mi-Hye Yi<sup>3</sup> and Hong-Ku Shim<sup>4</sup>;

<sup>1</sup>Basic Research Institute, Electronics and Telecommunications Research Institute, Taejeon, South Korea; <sup>2</sup>Department of Chemistry, Kyung Sang National University, Jinju, South Korea; <sup>3</sup>Advanced Materials Division, Korea Research Institute of Chemical Technology, Taejeon, South Korea; <sup>4</sup>Center for Advanced Functional Polymers, Department of Chemistry and School of Molecular Science, Korea Advanced Institute of Science and Technology, Taejeon, South Korea.

Organic electronic devices have made very rapid progress in the last several years. Specially, organic materials have been of interest for conductive and semiconductor applications for flexible display. We fabricated organic thin film transistor using thiophene oligomer as active area. The mobility of derivatives of thiophene oligomer (4T23) is affected by not only surface morphology but also interface properties between insulator and semiconductor active layer. The measured organic thin-film transistors using tetrathiophene oligomer have shown as large as  $0.02 \text{ cm}^2/\text{Vs}$ . The electrical and chemical characterization of interface using between insulator layer and semiconductor layer will be presented in detail. Furthermore, increasing the on/off ratio and the device performance approach method will be also proposed.

#### **K10.62**

**Supramolecular Memory-Switching Elements Using Organic Supramolecular Structures.** Anirban Bandyopadhyay<sup>1</sup> and Amlan J. Pal<sup>2</sup>; <sup>1</sup>Solid State Physics, Indian Association for the cultivation of Science, Kolkata, West Bengal, India; <sup>2</sup>Solid State Physics, Indian Association for the Cultivation of Science., Kolkata, India.

We have observed large conductance switching in devices based on acceptor-rich organic molecules. We have shown that electroreduction of the molecules results in high-conducting state of the devices. By varying functional groups in the same molecular backbone, we have tuned the leakage current and hence the ON/OFF ratio (from 104 to 4). We have used three different kind of redox active molecule namely Rose Bengal, DDQ, TAPA to understand solid state redox switching phenomena. Furthermore, the molecules in the reduced state have inherent memory, which enabled the devices for RAM (continuous transition between the binary 1 and 0 states) and ROM (remembering 1 or 0 state) applications. When the active switching molecules were self-assembled in supramolecular matrices via electrostatic self-assembly (ESA), structural peculiarities have enabled us to control the leakage current by two orders in magnitude. Molecular rotation and oxidation-reduction of asymmetric double planer molecules is a simultaneous event and we have shown that by varying the structural peculiarities of the host polymer matrix, we can allow both mechanism to play one reverse to another (PAH/RB) and one independent of each other (PPV/RB). When both the mechanism opposes each other then Rose Bengal based supramolecule shows reproducible transition between 1 and 0 states due to oxidation and reduction in the lower voltage range (2-4V). Double plane of the molecule rotates in the matrix to give off plane non-conjugation (0) and in plane conjugation (1) in the higher voltage region (4-6V), which is equivalent to NOT operation in a single switching element. By changing supramolecular structure we can allow both the mechanism to play independent of each other and then a single element shows reversible switching between (0,0), (0,1), (1,0), (1,1) states.

#### **K10.63**

**A Simplified, Low Switching Voltage Organic-on-Inorganic Diode Memory Element Utilizing a Conductive Polymer Fuse on a Doped Si Substrate.** Shawn Smith, Barry Rand and Stephen R. Forrest; Princeton University, Princeton, New Jersey.

A non-volatile, write-once-read-many-times (WORM) memory device utilizing an organic-on-inorganic (OI) diode with one side of the diode as a conductive polymer fuse is presented. The conductive polymer, polyethylenedioxythiophene:polyesterene sulfonic acid (PEDOT:PSS), switches in a fuse-like manner, while the nonlinearity of the OI heterojunction provides for a passive matrix memory configuration. This configuration is a significant simplification from past demonstrations of WORM memories in that the underlying Si p-n junction is simply replaced by a doped Si wafer [1]. The device switches at ~4 V for polymer films with thickness of ~50 nm. This is significantly lower than the switching voltage used in PEDOT:PSS/p-n Si memory elements. The switching results in a permanent reduction of forward-bias current of approximately 2-3 orders of magnitude. We also demonstrate the effect of etching the PEDOT:PSS that surrounds the devices. This results in a reduction in dark current of >3 orders of magnitude and increased rectification ratio. These results demonstrate a simple device structure for low-cost passive matrix WORM memories for archival storage applications. [1] S. Moller, S. R. Forrest, C. Perlov, W. Jackson and C. Taussig, submitted for publication (2003), and MRS 2003 Fall Meeting, Boston.

#### **K10.64**

**Efficient Solid-State Dye-Sensitized Solar Cells.** Matthew Thomas Lloyd<sup>1</sup>, Shawn Scully<sup>1</sup>, Rafael Herrera<sup>2</sup>, Emmanuel Giannelis<sup>1</sup> and George Malliaras<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York.

Dye-sensitized nanocrystalline photoelectrochemical solar cells have high power conversion efficiencies, long service lives, and low fabrication costs, making them competitive with traditional inorganic photovoltaics. Without sacrificing performance, a solid-state component is needed to replace the liquid electrolyte layer of the cell in order to further reduce manufacturing costs and increase the lifetime of the cell. We introduced an ion conducting polymeric gel, PVDF-co-HFP (poly(vinylidene fluoride-hexafluoropropylene), blended with an iodide based redox couple as a semi-solid hole transporting layer and compared the performance to standard liquid based cells. We also tested the addition of ~5% (vol.) clay nanoparticles to increase the solvent retention and mechanical robustness of the PVDF-HFP. We showed that the polymer electrolyte suitably replaced the liquid electrolyte and that the nanoparticles increased the mechanical resiliency of the cells.

#### **K10.65**

**Self-organizing Discotic Phthalocyanines: Processing into Thin Film with Promising OFET and Organic PV behavior.** Wei Xia, Carrie L. Donley, Britt A. Minch, SeungHyup Yoo, Chet Carter, Benoit Domercq, Bernard Kippelen, and Neal R. Armstrong, Optical Science Center, University of Arizona, Tucson, AZ; Department of Chemistry, University of Arizona, Tucson AZ. Wei Xia, chemistry, University of Arizona, Tucson, Arizona.

Octa-substituted phthalocyanines, with either a) benzyloxyethoxy side chains or b) benzyloxyethylsulfanyl side chains self-organize into columnar aggregates which can be transferred as LB thin films of rod-like aggregates, lying parallel to the substrate plane. Thio- vs. alkoxy-linking of the side chains to the Pc core induces a more distinct transition in DSC to the LC mesophase, and at a higher transition temperature. The high degree of anisotropy in dark and photo-conductivity in these films (parallel vs. perpendicular to the rod axis) has made them interesting candidates for organic field effect transistors materials. Recent X-ray reflectivity and AFM studies of these films show a significant change in ordering of these layers, as a function of surface modification and annealing. In order to produce new organic PV layers from these materials it has been necessary to induce the same degree of rod-like aggregate formation in spin-cast films, but with the rod axis perpendicular to the substrate plane. XRD and AFM studies show that a significant reorganization of such surfaces occurs as a result of annealing, with a transition to ordered structures approaching those desired for optimum PV activity. PV cells with the configuration ITO(PEDOT/PSS)/Pc/C60/Al were evaluated, and it was determined that the reorganization of the Pc films led to a 3.5X increase in the short-circuit current density and a significant reduction in the series resistance. Photovoltages were limited by pinholes formed in the highly structured Pc films, arising from some dewetting of the Pc from the substrate during annealing.

#### **K10.66**

**Exciton Diffusion and Dissociation in Conjugated Polymer/Fullerene Heterostructures.** Denis E. Markov and Paul W. M. Blom; Materials Science Centre, University of Groningen, Groningen, Netherlands.

Compositions of conjugated polymers and fullerene molecules are very promising for solar cells applications. After photoexcitation excitons created in the polymer diffuse to the polymer/fullerene heterojunction where efficient charge separation takes place. An important parameter is the exciton diffusion length which determines the maximum size of the polymer phase in a polymer/fullerene blend. As a model system bilayers of evaporated C<sub>60</sub> and various poly(p-phenylene vinylene) (PPV) derivatives have been systematically investigated. The diffusion of excitons and the subsequent quenching of the luminescence at the C<sub>60</sub>/PPV have been monitored using steady-state as well as pico- and subpicosecond time-resolved luminescence measurements. The time-resolved luminescence was numerically simulated in an exciton diffusion model with quenching at the heterojunction by electron transfer from the PPV to the C<sub>60</sub> molecules. Depending on the PPV-derivative exciton diffusion lengths of up to several tens of nanometers have been found which indicate the optimum domain size in conjugated polymer based photovoltaic devices.

#### **K10.67**

**Novel Two-Dimensional Oligomers for Electroactive Device Applications.** Hermona Yirmeyah Christian, Zukhra I Niazimbetova and Mary E Galvin; Department of Materials Science and Engineering, University of Delaware, Newark, Delaware.

In recent years, the development of efficient organic-based electroactive devices (PLEDs, PVs and TFTs) has been a widely studied area of research. However, difficulties associated with interchain transport of charge carriers have proven to be a barrier to improving the device efficiency. A polymer with charge delocalization over two dimensions should allow for facile carrier transport thereby improving device performance. Imbalance in charge injection and transport of electrons and holes have also presented a challenge in improving device operation. Our group has recently synthesized and characterized 2-dimensional conjugated poly(phenylene vinylene) (PPV) oligomers. One oligomer of interest contained oxadiazole units situated in a para- position relative to each other. The introduction of the electron deficient oxadiazole unit into the hole transporting PPV backbone serves to improve the electron injection and transport. The present work focuses on the synthesis and characterization of a 2-D PPV oligomer that has the oxadiazole moieties in an ortho- position with respect to each other. Preliminary studies show that these materials may have PLED as well photovoltaic applications. Synthesis, optical and thermal properties, and PLED and PV device characterization will be reported.

#### **K10.68**

**Pentacene as a Hole-Conductor in Sensitized Nanocrystalline Solar Cells.** Alex Christopher Mayer<sup>1,2</sup>, Shawn Scully<sup>3,2,1</sup>, Matthew Lloyd<sup>1</sup>, George Malliaras<sup>1</sup>, Ricardo Ruiz<sup>1</sup> and Brian O'Regan<sup>2</sup>;  
<sup>1</sup>Cornell University, Ithaca, New York; <sup>2</sup>ECN, Petten, Netherlands;  
<sup>3</sup>Stanford, Palo Alto, California.

Dye sensitized solar cells (DSSC) with a liquid electrolyte have progressed significantly in the last decade. Complications with the electrolyte such as sealing and degradation motivated studies of solid-state organic semiconductors as replacements. Due to the promise shown by pentacene in thin-film transistors (TFT), we explore the incorporation of pentacene versus other hole conductors in DSSCs.

#### **K10.69**

**Self-Assembly and Optoelectronic Properties of Oligo(Phenylene Vinylene) Triblock Amphiphiles.** James F. Hulvat<sup>1</sup>, Keisuke Tajima<sup>2</sup>, Marina Sofos<sup>1</sup> and Samuel I. Stupp<sup>1,2,3</sup>. <sup>1</sup>Materials Science & Engineering, Northwestern University, Evanston, Illinois; <sup>2</sup>Chemistry, Northwestern University, Evanston, Illinois; <sup>3</sup>Feinberg School of Medicine, Northwestern University, Chicago, Illinois.

Functionalized oligo(phenylene vinylene) (OPV) molecules have received significant attention for application in optoelectronic devices, due to the high efficiency and stability of the phenylene vinylene chromophore. Molecular self-assembly provides the capability to direct and control the aggregation of OPV molecules within an ordered nanostructure, altering its electronic and optical properties. We have synthesized a series of novel, tri-block amphiphiles consisting of a phenylene vinylene trimer or tetramer asymmetrically end-substituted with an oligo(ethylene oxide) block and an alkyl block. The amphiphilic nature of these molecules induces them to self-organize into a variety of ordered nanostructures, exhibiting both thermotropic and lyotropic liquid crystalline phases. Tuning the length of the alkyl tail and the hydrophilic head group controls the structure and solubility of the molecule. OPV amphiphiles have been prepared that are water soluble, forming strongly fluorescent, lyotropic liquid crystalline gels. Other OPV amphiphiles form ordered, self-supporting gels in polar organic solvents. The structure of these materials has been characterized using a variety of techniques, including small angle x-ray scattering (SAXS), differential scanning calorimetry (DSC), and fluorescence microscopy. Photoluminescence shows a strong dependence on the structure of the material. Increased luminescence was observed in the liquid crystalline state, possibly due to confinement and isolation of the OPV segments within the two-dimensional layers of a lamellar, liquid crystalline phase. These OPV-amphiphiles have potential application as polarized emission layers in organic LEDs, as well as for functional organic templates for inorganic phases, such as silica and CdSe. This approach could lead to hybrid solar cell devices in which the ordered OPV nanostructure acts as a charge collecting, hole transport layer. Using molecular self-assembly to control the organization of nanostructured OPV should significantly improve the performance of these materials in optoelectronic devices.

#### **K10.70**

**Polymer photovoltaic cells based on the random copolymers of 2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene and thiophene.** Yongfang Li, Jianhui Hou, Chunhe Yang and Jing Qiao; Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

The random copolymers of 2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PV) and thiophene were synthesized by Gilch method, and were characterized by absorption spectra, photoluminescent (PL) spectra and cyclic voltammetry. The absorption characteristics of the copolymers were regulated by changing the ratio of thiophene to MEH-PV units in the copolymers. With the increase of the thiophene ratio, the absorption spectra of the copolymers were broadened and red shifted in comparison with that of MEH-PPV. Although the PL intensity and PL life time of the copolymers were obviously decreased with the copolymerization of thiophene, the PL lifetime of the copolymer is still two orders higher than that of Copolymer/C60 system. Electrochemical p-doping potential of the copolymers decreased a little, indicating a higher HOMO energy level and a better hole transporting ability. Photovoltaic (PV) cells based on the copolymers/C60 (1:2 wt/wt) system were fabricated and characterized by I-V and IPCE (input photon to converted current efficiency) measurements. Energy conversion efficiency of the PV cells based on the copolymer/C60 system was improved by the random copolymerization of thiophene into MEH-PPV. The best result was obtained for the PV cell based on the copolymer with 10% thiophene in the copolymer with a 38% increase of the energy conversion efficiency in comparison with that of the PV cell based on MEH-PPV.

#### **K10.71**

**Electrical properties of DNA characterized by conducting-atomic force microscopy.** Claude Nogues<sup>1</sup>, Ron Naaman<sup>1</sup>, Shirley Daube<sup>2</sup>, Sidney Cohen<sup>2</sup>, Hezy Cohen<sup>3</sup> and Danny Porath<sup>3</sup>; <sup>1</sup>Dept of Chemistry Physics, Weizmann Institut of Science, Rehovot, Israel; <sup>2</sup>Chemical Services Dept, Weizmann Institut of Science, Rehovot, Israel; <sup>3</sup>Dept of Physical Chemistry, Hebrew University, Jerusalem, Israel.

Miniaturization of electronic devices below the sub-micro range is a natural next goal in developing faster, denser and smaller devices. As nanometer level dimensions are approached molecules have been suggested as 'electronic devices'. Several key challenges remain before these molecular devices can be used in practical circuits. Among the most important one is the need for methods that can be used to assemble molecules as wires on surfaces, preferably in a deterministic manner. While the primary biological function of DNA involves information storage and transduction, its unique structural properties can be exploited to make a molecular wire. Especially the interaction between its complementary sequences is specific and reversible. It can be easily synthesized in different lengths and can be modified with different functional groups that allow attachment on different surfaces. Unfortunately the electrical properties of DNA are not well characterized yet. This information is essential for building a molecular device with DNA. Therefore, we applied conducting-atomic force microscopy (cAFM) for investigating the electrical properties of well characterized self-assembled layer of DNA on gold substrate. A thiolated single strand DNA can form well packed monolayer on gold, depending on the adsorption conditions. Thus, different adsorption strategies were used in order to obtain the best packed and reproducible DNA self-assembled monolayer (SAM) on gold surfaces. In a similar way, it is possible to form monolayer of DNA on gold nanoparticles. Using the complementary strand to the one used for the SAM on the flat gold, one is able to hybridize the two complementary strands and to form nanoparticle-DNA-gold surface system. Here, the double strand DNA may act as molecular wire connecting two gold electrodes, the substrate and the gold nanoparticles. Results on the characterization of the DNA monolayers will be presented as well as results on the conductivity measurements performed on the well characterized system.

#### **K10.72**

**Dielectric Spectroscopy of Altitudinal Dipolar Molecular Rotors.** Laura Clarke<sup>1</sup>, Mary Beth Mulcahy<sup>2</sup>, Robert Horansky<sup>1</sup>, Dominik Horinek<sup>2</sup>, Xiaolai Zheng<sup>2</sup>, Thomas Magnera<sup>2</sup>, Josef Michl<sup>2</sup> and John Price<sup>1</sup>; <sup>1</sup>Physics, University of Colorado, Boulder, Colorado; <sup>2</sup>Chemistry, University of Colorado, Boulder, Colorado.

We study two dimensional monolayer collections of molecules synthetically designed to have a single rotational degree of freedom when surface mounted. Because the rotary portion of the molecules is dipolar, we can utilize an external electric field to both manipulate and observe their orientation and dynamics. With such a system, custom dielectric materials could potentially be designed to possess a variety of response times, permanent and induced dipole moments, and degrees of ordering. Previously, our collaboration presented dielectric spectroscopy results on "azimuthal" surface mounted rotors with a rotational axis perpendicular to the surface. [1] Here, we discuss a rotor consisting of two stands supporting a dipolar "paddlewheel" between them. These "altitudinal" rotors can be probed with electric fields either along or perpendicular to the substrate plane and can be mounted on both gold and fused silica substrates. Paddlewheels mounted on gold are predicted to have a low barrier for 360 degree rotation: such structures could have applications to enhancing fluid flow at surfaces. Thin film samples of the paddlewheel rotors on fused silica show a dielectric response consistent with barrier heights predicted from molecular mechanics. In keeping with the surface mounted nature of the molecule, we find that the observed rotor response can be suppressed when adsorbates are present on the surface. We discuss recent results. [1] L.I. Clarke et. al., Nanotechnology 13(4), 533 (2002).

#### **K10.73**

**Electric Field - Induced Orientation of Nanowires in Ultra-thin Films of Block Copolymers Containing Regioregular Poly(3-hexylthiophene).** Shijun Jia<sup>1</sup>, Rui Zhang<sup>1</sup>, Tomasz Kowalewski<sup>1</sup>, Bo Li<sup>2</sup> and David N. Lambeth<sup>2</sup>; <sup>1</sup>Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania; <sup>2</sup>Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania.

(Semi)conducting polymers are believed to hold considerable promise as materials for inexpensive electronics, sensors and actuators and even molecular electronics. One of the outstanding challenges with these materials is control of polymer morphology and, in particular, fabrication of uniform, well defined nanostructures. It is expected that achievement of these goals will lead to better understanding of

electrical properties of (semi)conducting polymers and will facilitate the improvement of their performance in devices. We have demonstrated recently [*Angewandte Chemie*, **2002**, *41*, 329], that in the case of regioregular poly(alkylthiophenes), block copolymerization with immiscible segments, such as polystyrene or poly(methyl acrylate) yields materials which under favorable kinetic conditions form very well defined nanoribbons (or nanowires). This effect has been attributed to the synergistic combination of nanoscale phase separation and crystallization of polythiophene segments. This presentation will describe the achievement of a uniform alignment of these nanostructures by solvent casting between micropatterned electrodes. This effect is based on the well-known fact that in the presence of electric field (EF), the interfaces between two dielectrics tend to align along the EF. In the past, this phenomenon has been demonstrated to lead to the uniform orientation of cylindrical domains in microphase separated block copolymers of polystyrene and poly(methylmethacrylate) [*Science*, **1996**, *273*, 931; *Science*, **2000**, *290*, 2126]. The orientation was achieved when copolymer melts were placed between electrodes in the presence of the EF. In contrast with mentioned past work, which required prolonged ( $\sim 24$  hrs) annealing above the glass transition temperature of both segments, the method described herein utilizes solvent casting, where the oriented nanostructures form within seconds during evaporation of the solvent. The experiments were carried out with 100 nm tall gold microelectrodes spaced by 4  $\mu\text{m}$ , which were patterned on a Si wafer using standard techniques. Microdroplets of solution of poly(3-hexylthiophene)-b-polystyrene in toluene were placed on the patterned substrate in the presence of the EF and were allowed to freely evaporate. Tapping mode AFM observations of such prepared samples revealed the presence of characteristic "nanowires" similar to those observed in our earlier work. Remarkably, nanowires deposited between the electrodes exhibited strong alignment along the EF direction. No preferential orientation was observed for nanostructures deposited on top of gold electrodes. In addition to the role of processing conditions necessary for the achievement of the uniform alignment of block copolymer nanowires, the impact of the orientation on the characteristics of devices fabricated from such nanostructures will be also discussed.

#### K10.74

**Design, synthesis and evaluation of photoactuating and photorheological polymers with photo-responsive groups in the side chain.** M Moniruzzaman<sup>1</sup>, C Sabey<sup>1</sup>, G Fernando<sup>1</sup>, R Badcock<sup>1</sup>, J D Talbot<sup>1</sup>, D Winter<sup>1</sup>, A Bandara<sup>2</sup>, E Kronfli<sup>3</sup> and J Akhavan<sup>3</sup>; <sup>1</sup>Centre for Photo-Analysis and Photo-Manipulation, Cranfield University, Swindon, Wiltshire, United Kingdom; <sup>2</sup>School of Chemical and Pharmaceutical Sciences, Kingston University, Kingston-upon-Thames, Surrey, United Kingdom; <sup>3</sup>Department of Environmental and Ordnance Systems, Cranfield University, Swindon, Wiltshire, United Kingdom.

This paper reports on the design, synthesis, and evaluation of polymeric systems that exhibit photo-actuation and photorheological phenomena when subjected to UV irradiation. Previous investigations of photorheological behaviour have been conducted on photoresponsive backbone polymers and/or responsive groups attached with a hydrophilic system. Other researchers have not examined the photoactuation effect of polymer liquids. Therefore, we focused our attention on the design of molecules having azobenzene with no substituent and spiroyrans in the side chain and their photoactuation and photorheological phenomena were investigated using *in-situ* techniques. Azo- and spiro-based monomers and co-polymers were designed, synthesised and characterised using conventional analysis techniques such as NMR and UV-Visible spectroscopy. Spacer molecules were also introduced into the main chain of the polymer in order to assess the mechanism of the photoactuation and rheology effect. *In-situ* photorheological and photoactuation characterisation of the monomers and polymers were carried out using a custom-modified cone and plate rheometer and a bulb and capillary apparatus with image analysis respectively. The photoactuation phenomena of solid films of physical blended and chemically connected spiroyrans with polymethylmethacrylate (PMMA) were measured using an *in-situ* optical fibre interferometry technique. Some of the conclusions reached are: (i) Azobenzene and spiropyran based monomers and their copolymers with methylmethacrylate (MMA) have been successfully synthesised. (ii) The photo induced trans-cis isomerisation was quantified by NMR and found to be 73% within  $\pm 1\%$  and showed excellent agreement with UV-Visible spectroscopic measurements. (iii) Co-polymers of trans-4-methacryloyloxyazobenzene and methylmethacrylate exhibited a 73% reduction in specific viscosity upon UV irradiation in a reproducible and repeatable process (iv) Spiropyran based polymer films exhibited  $\sim 4\%$  reversible photo-actuation due to photochemical ring opening of the spiropyran chromophores. (v) Photo-induced trans to cis- isomerisation and/or ring opening reaction caused a small, but detectable, photoactuation effect in polymer liquids upon UV irradiation.

#### K10.75

**Chromogenic Gel Networks - Novel Functional Polymer Materials.** Arno Seeboth, Detlef Loetzsch and Joerg Kriwanek; Fraunhofer Institute for Applied Polymer Research, Berlin, Germany.

The preparation and characterization of gels with chromogenic properties has met with growing interest in the last years [1]. A novel chromogenic gel network was obtained by adding small amounts of a polyalkoxide to a thermochromic Phenol Red containing PVA/borax/surfactant hydrogel [2]. A thermotropic behavior based on a phase separation process was found to appear already at a polyalkoxide content of 0.8 wt.%. Moreover, the concentration dependence of the zwitterionic sulfobetaine surfactant on the thermochromic and thermotropic behavior was investigated. For this purpose a hydrogel containing 1.1 wt.% polyalkoxide was chosen to which sulfobetaine concentrations below and above the critical micelle concentration ( $\text{cmc} = 3.8 \times 10^{-3} \text{ mol kg}^{-1}$ ) were added. The UV/Vis absorption spectra of these hydrogels are investigated. Two absorption bands are detected. The first one with a  $\lambda_{\text{max}} \approx 440 \text{ nm}$  which corresponds to the phenol form of Phenol Red and the second one with a  $\lambda_{\text{max}} \approx 563 \text{ nm}$  which corresponds to the phenolate form of Phenol Red. With increasing sulfobetaine concentration a decrease of the intensity of both UV/Vis absorption bands occur. It is well known that above the cmc surfactants can influence the UV/Vis absorption behavior of water soluble dyes. However, here this effect takes place already at the lowest sulfobetaine concentration of  $2.5 \times 10^{-3} \text{ mol kg}^{-1}$ , which is significant below the cmc. To characterize the thermotropic behavior the transparency of the gels were measured as a function of temperature. Again even below the critical micelle concentration (cmc) a significant influence of the surfactant concentration on the thermotropic properties is observed. To explain this behavior the formation of complexes between dye molecules and aggregates of sulfobetaine, or as an alternative model an interaction of the dye with single sulfobetaine molecules are discussed. References 1. Peter Bamfield, chromogenic phenomena, The Royal Society of Chemistry 2001 2. Kriwanek, J.; Vetter, R.; Loetzsch, D.; Seeboth, A. *Polymers for Advanced Technologies* 2003 (14) 79

#### K10.76

**Photosensitive Polymeric Materials for Two-Photon 3-D High Density Optical Data Storage.** Kevin D Belfield<sup>1</sup>, Katherine J Schafer<sup>1</sup>, Lawino Kagumba<sup>2</sup> and Norman Rice<sup>2</sup>; <sup>1</sup>Chemistry, University of Central Florida, Orlando, Florida; <sup>2</sup>Triton Systems, Inc., Chelmsford, Massachusetts.

Photoinduced modulation of optical properties of a polymeric medium are employed to develop a multi-layer, three-dimensional write-once read-many (WORM) data storage medium with two-photon fluorescence readout. Both image writing and reading is accomplished via two-photon excitation of polymer films containing an acid-sensitive fluorophore and photoacid generator (PAG). Photosensitive polymeric materials are described as is demonstration of multilayer, three-dimensional data storage.

#### K10.77

**Abstract Withdrawn**

#### K10.78

**Intramolecular Charge Transfer Materials based on Fluorene Electron Acceptors.** Igor F Perepichka<sup>1,2</sup>, Dmitrii F. Perepichka<sup>1,4</sup>, Nikolai I. Sokolov<sup>3</sup>, Martin R. Bryce<sup>2</sup> and Dmitrii D. Mysyk<sup>5</sup>; <sup>1</sup>Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk, Ukraine; <sup>2</sup>Department of Chemistry, University of Durham, Durham, United Kingdom; <sup>3</sup>Laboratory of Holography, Natural Faculty, University "Kyivo-Mogylyans'ka Academy", Kyiv, Ukraine; <sup>4</sup>INRS-Energy, Materials and Telecommunications, University of Quebec, Varennes, Quebec, Canada; <sup>5</sup>Department of Chemistry, Donetsk Technical University, Donetsk, Ukraine.

High photoconductivity and excellent rheological properties of thin films of poly(2,3-epoxypropyl)carbazole (PEPK) and related carbazole-containing polymers make them cost-efficient materials for optical data storage, particularly for hologram recording. Doping these films with electron acceptors of the fluorene series enable to increase substantially the level of PEPK photoconductivity and to shift it to visible region of the spectrum. We present our results on synthesis and properties of electron acceptors of the fluorene series, in which introduction of a donor moiety results in pronounced intramolecular charge transfer (ICT) whereas the molecule keeps its high electron affinity for intermolecular charge transfer interaction with polymer matrix. As a result such materials show increased photoconductivity in their ICT region, which can be tuned by structural changes in a donor and an acceptor parts of D- $\pi$ -A molecule. We demonstrate that the photoconductivity and spectral response of PEPK films can be controlled through well-balanced

electron affinity, ICT energy and rheology of electron acceptor dopants. We also present some our results on a potential of this type of materials in related applications: non-linear optics, photovoltaics, etc. and discuss their perspectives as multifunctional materials.

#### **K10.79**

##### **Novel Strategy to Apply Polymeric Hole Transport Layers to Indium-Tin-Oxide Anode by Covalent Binding.**

Qinglan Huang<sup>1,2</sup> and Tobin J Marks<sup>1,2</sup>; <sup>1</sup>Chemistry, Northwestern University, Evanston, Illinois; <sup>2</sup>Materials Research Center, Northwestern University, Evanston, Illinois.

Multilayer polymer-based light-emitting diodes (PLEDs) are desirable due to the generally superior device performance vs. single-layer counterparts. However, spin-casting, a standard method to fabricate layered PLED structures can partially dissolve the previous layer while depositing the next one, and results in deteriorated device performance. A different methodology is demonstrated here to deposit a polysiloxane hole transport material onto a triarylamine trichlorosilane-functionalized indium-tin-oxide (ITO) anode via a simple dipping, washing, and drying process. The so-obtained polymeric hole transport layer has been characterized by AFM, UV-vis spectroscopy, X-ray reflectivity, and cyclic voltammetry, revealing a uniform, smooth, and charge transport-active layer for PLEDs. Its resistance to common organic solvents such as toluene, tetrahydrofuran, etc. allows a wide range of polymers to be spin-coated onto it without dissolving the layer beneath. Multilayer PLEDs using the above hole transport layer and polyfluorene as the emissive layer give luminance and efficiencies comparable to standard PLEDs having structure: ITO/PEDOT/polyfluorene/Ca/Al. Also, this hole transport layer can be used in small molecule OLEDs in which a multilayer structure is fabricated via thermal evaporation. Up to 14,000 cd/m<sup>2</sup> luminance and 0.7 % external forward quantum efficiency are achieved. Compared to other non-spin casting methods to deposit polymers, including electrostatic self-assembly, post-deposition cross-linking or polymerization, the present strategy affords a facile and simple alternative.

#### **K10.80**

##### **Luminiscence of Photopolymerized Liquid Crystal**

**Diacrylates.** Pedro L. Saez and Carlos Aguilera; Universidad de Concepcion, Concepcion, Chile.

Light emitting diodes(LEDs) of organic materials have especially been expected to be devices for large flexible panel displays. On important development of these field was the discovers of main chain polymer that combine the optical and electronic properties of semiconductors. However, the characteristic of conjugated polymer is that present random distributed defects , which lead to a statistical distribution of conjugated lengths. In the context , the synthesis and characterization of materials based at monomers direactives which containing a fluorene core were described. They exhibit an efficient fluorescence and have liquid crystalline behavior. Thin films have been prepared by in-situ photopolymerization technique order to produce polarized light emitting films for photo and electroluminescence.

#### **K10.81**

##### **Sputter-deposited transparent cathode for top emitting**

**OLED.** Choong-Heui Chung, Young Wook Ko, Yong Soon Park, Choong-Yong Sohn, Yong-Hae Kim, Hae Yong Chu and Jin Ho Lee; Basic research Lab, ETRI, Daejeon, South Korea.

Sputter-deposited electron injecting electrode can improve the efficiency and reliability of organic light emitting diode (OLED) as compared to a vacuum heat deposited electrode. Commercial application of top emitting OLED has been hampered by a low ITO deposition rate (~0.3 nm/min) because sputtered particles having high kinetic energy may damage underlying organic layers during the sputtering. Faster deposition of ITO is essential for the practical realization of top emitting OLED. We have developed sputter deposition technique both to eliminate damage by sputtered particles and to increase deposition rate of ITO. The devices with the structure of flexible substrate/ anode (100nm)/ CuPc(10nm)/ NPB(50nm)/ Alq3(60nm)/ LiF(0.5nm)/ buffer layer/ ITO(100-80nm) were successfully fabricated for top emitting OLED.

#### **K10.82**

##### **Al cathode based transparent organic light emitting diode on flexible substrate.**

Young Wook Ko, Choong-Heui Chung, Yong Soon Park, Choong-Yong Sohn, Yong-Hae Kim, Hae Yong Chu and Jin Ho Lee; ETRI, Taejeon, South Korea.

Al based semi-transparent cathode electrode was studied for high efficient transparent organic light emission diode on flexible substrate. Optical transmittance, reflectance, I-V-L, and electrical resistance of device were measured as a function of the thicknesses of Al and deposition conditions of ITO to understand the relationship between

the device efficiency and deposition parameters. The organic devices were fabricated by conventional thermal evaporation and ITO cover electrode was deposited by radio frequency (RF) sputtering with high deposition rate. A typical white OLED device structure with high efficient and transparent characteristics is as follows: PES flexible substrate/ ITO(100nm)/ TPD(50nm)/ SAIq:DCJTb (30nm, 0.5%)/ Alq3(20nm)/ organic buffer layer/ LiF(0.5nm)/ Al based transparent cathode electrode. The maximum brightness and quantum efficiency of the device show about 3000cd/m<sup>2</sup> and 2.0%, respectively.

#### **K10.83**

##### **Color Tuning of Cyclometalated Iridium Complexes in the Blue - Red Range through Modification of Phenylpyrazole Derivatives based on DFT Calculations.**

Tae-Hyuk Kwon<sup>1,2</sup>, Su Jin Park<sup>2</sup>, Kwan Hee Lee<sup>2</sup> and Jong-In Hong<sup>1,2</sup>; <sup>1</sup>Department of Chemistry, Seoul National University, Seoul, South Korea; <sup>2</sup>Corporate R&D Center, Samsung SDI, Yongin, South Korea.

In this study, we investigate how the emission wavelength of Iridium complexes can be tuned through structural modification of the main ligand. We report the photophysics of a new cyclometalated iridium complexes where phenylpyrazole derivatives serve as the main ligand and isoquinolinecarboxylic acid serves as the ancillary ligand. Our initial approach is to calculate the theoretical energy band gap via Density Functional Theory (DFT) Calculations, and then to tune the emission wavelength of the photoluminescent iridium complexes through structural modification of the ligand. Our results provide the potential for the synthesis of iridium complexes with different emission wavelength through modification of the ligand. These modifications include placing a different group (such as a methyl substituent) at various positions on the main ligand. Different  $\lambda_{max}$ 's are also generated by using different ancillary ligands such as 1-isoquinolinecarboxylic acid and 3-isoquinolinecarboxylic acid.

#### **K10.84**

##### **Electrochromic Devices based on the Layer by Layer Polymer**

**Thin Film Assembly Process.** Nicole Zacharia and Paula Hammond; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Electrochromism has been the subject of much recent research, and is the basis of a number of newly available commercial devices. Materials such as transition metal oxides, conducting polymers, and small organic molecules (e.g. viologens) have all shown electrochromic properties. Metal oxides such as WO<sub>3</sub> or TiO<sub>2</sub> show some of the best contrast changes upon coloration, but have relatively slow switching speeds. Since the coloration occurs upon the intercalation of small anions (Li<sup>+</sup>, H<sup>+</sup>) into the metal oxide surface, using nanoparticles helps to improve coloration times. The layer by layer assembly technique, by which a substrate is sequentially exposed to oppositely charged solutions of polyions, is a method for constructing homogeneous thin films from multiple components. Not only polyions, but other components such as colloids or metal nanoparticles can also be incorporated into these films. Transition metal oxides are interesting in that they not only possess electrochromic properties but can be used as gas sensors as well. By creating composite polymer/nanoparticle films, we can control the environment around the nanoparticles in order to enhance these properties. We have synthesized water based colloidal suspensions of TiO<sub>2</sub> and WO<sub>3</sub> particles by hydrolysis reactions. These suspensions were imaged with TEM. These suspensions and TiO<sub>2</sub> colloid commercially obtained were incorporated into layer by layer structures. UV-vis and profilometry confirm that the structures are layer-by-layer, and incorporate metal oxide nanoparticles. These films show electrochromism, and color relatively quickly (order of 30 seconds). They change from a clear, "bleached," state to a dark blue state.

#### **K10.85**

##### **Synthesis, Characterization and DFT studies of bis- and tris-cyclometalated Ir(III) complexes having 2-(2,4-difluorophenyl)-4-methylpyridine : Lowest-lying Excited State-dependent Emission Colors.**

Jae Il Kim<sup>1</sup>, Su-Jin Park<sup>2</sup>, Kwan-Hee Lee<sup>2</sup> and Jin-Kyu Lee<sup>1</sup>; <sup>1</sup>School of Chemistry and Molecular Engineering, Seoul National University, Seoul, South Korea; <sup>2</sup>Corporate R&D Center, Samsung SDI Co., Ltd., Giheung, Gyeonggi, South Korea.

Octahedral Ir(III) complexes having the general formula C<sub>N</sub>2Ir(LX) (where C<sub>N</sub> is a monoanionic cyclometalating ligands and LX is a bidentate, monoanionic ligands) have been reported.  $\mu$ -chloro-bridged dimers of formula fpmp2Ir( $\mu$ -Cl)2Irfpmp2 have prepared from IrCl<sub>3</sub>·#8729;3H<sub>2</sub>O with excess cyclometalating 2-(2,4-difluorophenyl)-4-methylpyridine (fpmpH) and been converted into neutral, monomeric bischelate Ir(III) complexes with excess LX ligand. Reaction with excess fpmpH ligand gave neutral, monomeric trischelate Irfpmp3 complex, having facial and meridional configurations. Thermal, photophysical, electrochemical properties

have been studied for Ir(III) complexes prepared in this study. Thermal and electrochemical properties of homoleptic trischelate Ir(III) complexes have been studied with TGA and CV (Cyclic Voltammetry), respectively. Ligand exchange dynamics of bischelate CN<sub>2</sub>Ir(LX) complexes have been studied with time-course photoluminescence and NMR spectroscopy to study the effect of LX ligand on the chemical stability. The crystal structures of these complexes were obtained by X-ray crystallography. Theoretical studies using Density Functional Theory (DFT) Calculations have been performed to evaluate the photophysical characteristics, showing a good agreement with the experimental results.

#### **K10.86**

**Lifetime Improvement of Light Emitting Devices based on Ru(II) complex.** Nobuaki Takane<sup>1</sup>, Andrew Magyer<sup>2</sup>, Whitney Gaynor<sup>1</sup> and Michael F Rubner<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Physics and Computer Science, Hamilton College, Clinton, New York.

We have been exploring solid-state light emitting thin film devices based on the tris(2,2'-bipyridyl) ruthenium(II) complex [Ru(bpy)<sub>3</sub>]. In a previous study, by dispersing the Ru(II) complex in poly(methyl methacrylate) (PMMA) matrix, the film quality was improved and an increase in the photoluminescent and electroluminescent efficiency was observed. In addition, the ionic conductivity of Ru(II) complex devices can be increased by changing the chemical structure of the complex itself or by decreasing the size of the mobile counter-ion with a simple ion exchange. In this paper, we will report that the half-life of devices strongly depends on the thickness of the emitting layer, the matrix polymer and the cathode structure. First, the maximum external efficiency is observed at a thickness of 150nm in the range of 80 to 200nm. The optimized thickness gives the longest half-life when the half-life is compared at different thicknesses and at the same luminance. Second, by using polystyrene instead of PMMA, it is observed that the half-life at the same luminance in the glove box is more than twice as long. The effects of polymers that have different hydrophobic, electrical and thermal properties will be discussed. We also found that the half-life of new aluminum stacked silver cathode device is more than twice as long as Ag-only devices. It is assumed that the stacked thick aluminum layer prevents moisture and O<sub>2</sub> penetration. We also found that packaging procedures affect the lifetime in the atmosphere. Packaging materials and procedures will be presented.

#### **K10.87**

**Photogenerated Carrier Profile Determination in Polymeric Light-Emitting Diodes By Steady State and Transient Photocurrent Measurements.** Lucas Fugikawa Santos<sup>1</sup>, Rodrigo Fernando Bianchi<sup>1</sup>, Roberto Mendonca Faria<sup>1</sup> and Sergio Mergulhao<sup>2</sup>; <sup>1</sup>DFCM, Instituto de Fisica de Sao Carlos, Sao Carlos, SP, Brazil; <sup>2</sup>DF, Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil.

Photogenerated charge carrier profiles in poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH-PPV, and poly(2-methoxy-5-(2'-hexyloxy)-1,4-phenylene vinylene), MH-PPV, light-emitting diodes were determined from steady-state photocurrent spectra and transient photocurrent decay measurements. The observation that the photocurrent spectra behavior is strongly dependent on the bias polarity and amplitude suggests the existence of an intrinsic electric field, determined by the difference in the work function of the metallic electrodes, as well as a field dependence on the free charge carrier generation rates. The obtained results reveal built-in voltages of -0.2 V and +0.6 V for Au and Al electrodes, respectively. A simple model, taking into account the carrier mobility (determined by transient measurements), the carriers trapping distributions and the optical absorption coefficient is proposed to determine the photogeneration profile in the polymeric layer. (Acknowledgments to Fapesp - Brazil)

#### **K10.88**

**Photoluminescence properties of MEH-PPV films prepared by slow solvent evaporation.** Sergei Anatolii Arnautov<sup>1</sup>, Dmitry Yu. Paraschuk<sup>2</sup>, Elena M. Nechvolodova<sup>1</sup>, Klavdija N. Ryzhkova<sup>1</sup>, Nina V. Zhidkova<sup>1</sup>, Alexander A. Bakulin<sup>2</sup>, Alexander N. Khodarev<sup>2</sup> and Dmitry S. Martyanov<sup>2</sup>; <sup>1</sup>Polymers, Institute of Chemical Physics RAS, Moscow, Russian Federation; <sup>2</sup>International Laser Center, Moscow State University, Moscow, Russian Federation.

Conjugated polymers are very attractive for a wide variety of photonics applications. Soluble phenylene-based conjugated polymers are in the focus of research activity mainly because of their luminescent properties and simple processability. It is well known that solution-prepared polymers films demonstrate a wide distribution of intramolecular conformations and intermolecular interactions. The latter are generally considered to be detrimental, for example, to

LED applications as they favour formation of non-emissive or weakly emissive states. In this work, we show that efficient interchain interactions can be compatible with intensive luminescence. Using poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), we prepared polymer films by two different methods - by dip-coating and by an original method based on slow solvent evaporation (SSE) from the solution, and reported their photoluminescence properties. MEH-PPV with molecular weight ca. 125 000 g/mol from Sigma-Aldrich was dissolved in toluene or chlorobenzene under stirring for 60-90 min at 50°C to give 0.5-2% (w/v) solutions. Films were prepared on glass substrates by dip-coating and by slow evaporation of large amount of solution. The SSE films show a broader main absorption peak at ~500 nm compared with the dip-coated films indicating a wider distribution of conjugation lengths. At the same time, the PL spectra of SSE films are not wider than that of the dip-coated films and show a ~15 nm red shift. Such a red shift is about that of the dip-coated films compared with the MEH-PPV solution. Furthermore, the measured PL quantum yield for the SSE films is no less than that of the dip-coated films and is about 10%. We discuss the observed optical features of the SSE films as a manifestation of enhanced interchain organization leading to effective energy funneling to the emissive species.

#### **K10.89**

**Polymer Electrochromic Devices for Fast Switching Windows and Displays.** Avni Anil Argun, Ali Cirpan, Mathieu Berard and John R. Reynolds; Chemistry, University of Florida, Gainesville, Florida.

Research into polymer-based electrochromic devices (ECDs) shows their potential for a variety of useful applications such as multi-colored displays, switchable mirrors, and smart windows. Our work is directed to new polymer electrochromic materials that exhibit high optical contrasts, sub-second switching times, ease of processability, and long term switching properties. We have developed a family of dioxathiophene based polymers with modified electronic properties and enhanced solution processability. By utilizing the outstanding electrochromic properties of these electroactive polymers, several different ECD designs including absorptive/transmissive, reflective, and lateral devices were built and characterized. Here, we present the concept of using spray-coated polymer films in window type ECDs utilizing complimentary coloring polymers. These devices exhibit especially high coloration efficiencies (4,800 cm<sup>2</sup>/C) with remarkably fast switching times (0.3 sec). ECDs based on this concept are also constructed using gold-coated porous polymer substrates. We have observed high reflectance contrast values both in the visible (ΔR = 55%) and the NIR region (ΔR = 75%). Using these metallized membranes, we have also constructed lateral ECDs comprised of patterned electrodes where we can independently address specific regions on a device and create high contrast switchable surfaces. These display devices operate at low voltages (+/- 1V) and require low power to switch (0.6 mW/cm<sup>2</sup>).

#### **K10.90**

**A Study On A Polyamic Acids Prepared From Functional Diamines Containing n-Alkyl Succinimide Moiety for Vertically Aligned LCD Devices.** Mi Hye Yi, Yong-Woon Kim, Yoon Jung Lee, Jong Chan Won and Kil-Yeong Choi; Advanced Materials Division, Korea Research Institute of Chemical Technology, Taejeon, South Korea.

Polyimides can be widely used as a material for electro-optic devices on their own advantages such as excellent thermal property, good mechanical property and electrical property, etc. In this study, a series of polyimides were synthesized from functional diamines having n-alkyl succinimide moiety and alicyclic dianhydride like cyclobutane-1,2,3,4-tetracarboxylic dianhydride [CBDA] or 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride [DOCDA]. All polyamic acids were imidized at high temperature on hot plate. Thermal properties, transparency as well as surface tension of resulting polyimides thin layer were determined. We have also investigated electro-optic properties of LCD cell fabricated with the polyimides, which showed very high pretilt angle above 88 degree even after rubbing process. Further, we will discuss relationship of the pretilt angle with chemical structure of polyimides., which can be used for vertically aligned liquid crystal alignment. It was shown that pretilt angles were affected by length and contents of alkyl side chains of functional diamines.

#### **K10.91**

**Polymer Solar Cells Based on TiO<sub>2</sub> and Polyalkylthiophenes Prepared by the In-Situ Polymerization Method.** Yi-Jun Lin<sup>1</sup>, Leeyih Wang<sup>2,3</sup> and Wen-Yen Chiu<sup>1,3</sup>; <sup>1</sup>Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan; <sup>2</sup>Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; <sup>3</sup>Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan.



A new TiO<sub>2</sub>/polyalkylthiophene (PAT) photovoltaic cell was fabricated by the electrochemical polymerization of alkylthiophene monomers and the deposition of the in-situ formed PAT on the nanoporous TiO<sub>2</sub>-coated ITO glass. The mechanism of electrodeposition and growth of the PAT films were investigated by means of chronoamperometry and cyclic voltammetry. The surface morphology and the distribution of phases of these hybrid materials were extensively examined by XPS, SEM-EDX and SPM instruments. A great increase in the interface between the PAT phase (electron donor) and TiO<sub>2</sub> phase (electron acceptor) was observed. This is caused by the higher accessibility to small pores for thiophene monomer than for the PAT chain. The effects of the size of TiO<sub>2</sub> and the chain-length of alkyl group in PATs on the photophysical and photovoltaic properties of the solar cells will be presented and discussed.

#### **K10.92**

**Multi-Layer Solar Cells Based on Nanoporous TiO<sub>2</sub> and a Fluorene-Thiophene Copolymer.** Punniamorthy Ravirajan<sup>1,3</sup>, Saif Haque<sup>2</sup>, James Durrant<sup>2</sup>, Donal Bradley<sup>1</sup> and Jenny Nelson<sup>1</sup>; <sup>1</sup>Centre for Electronic Materials and Devices, Department of Physics, Imperial College London, London, England, United Kingdom; <sup>2</sup>Centre for Electronic Materials and Devices, Department of Chemistry, Imperial College London, London, England, United Kingdom; <sup>3</sup>Department of Physics, University of Jaffna, Jaffna, Northern Province, Sri Lanka.

Hybrid solar cells containing TiO<sub>2</sub> and a hole conducting polymer, which acts as both light absorber and hole-conductor, are of interest for low cost solar energy conversion. However, the efficiency of such devices is limited by the poor hole-mobility of the polymer, the poor penetration of the polymer into the porous TiO<sub>2</sub> and the limited optical absorption range typical of conjugated polymers. In this study, we focus on a system consisting of a high hole-mobility poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) polymer in contact with thin nanoporous TiO<sub>2</sub> films. We report a fabrication methodology and cell design for TiO<sub>2</sub>/polymer multilayer device where efficient polymer penetration into highly structured TiO<sub>2</sub> networks is observed. Photoinduced charge transfer yield and recombination kinetics were measured using nanosecond – millisecond transient optical spectroscopy. These measurements show that polymer penetration into the pores is improved by a dip coating step and that charge separation occurs very close to the TiO<sub>2</sub> nanocrystal-polymer interface. The recombination time between positive polarons in the polymer and electrons in the TiO<sub>2</sub> is around 100 microseconds, which compares well with the best polymer solar cells. Photovoltaic performance under AM1.5 equivalent illumination was studied as a function of the TiO<sub>2</sub>/polymer device design. The fill factor is increased from 0.24 to 0.44 by dip coating the TiO<sub>2</sub> electrode with polymer before spin coating a second polymer layer. The open circuit voltage also increases and the power conversion efficiency is doubled. The device performance is further improved by introducing a PEDOT layer between the polymer and the top Au electrode. This improved multilayer device produced a short circuit current density of 0.6 mAcm<sup>-2</sup>, a fill factor of 0.44 and an open circuit voltage of 0.7 V under AM1.5 illumination. The power conversion efficiency of this multilayer device is three times greater than the device without either the dip coated polymer layer or PEDOT.

#### **K10.93**

**Designing and Developing New Two-Dimensional Oligomers with Cyano Substituents for application in Electroactive Devices.** Yashpal Bhandari, Zukhra Niazimbetova and Mary E Galvin; Materials Sc and Engg, University of Delaware, Newark, Delaware.

The last two decades have seen a growing interest in the field of Organic Semiconductors specifically for applications in PLEDs, TFTs, and Photovoltaics. While there has been significant progress there is still a need to improve carrier mobility, specifically electron mobility.  $\pi$ -stacking in some crystalline semiconducting polymers and oligomers, induces a 2-dimensional delocalization of charge and increases carrier mobility by decreasing the activation energy for interchain carrier hopping. In addition to carrier mobility, PLED efficiency depends on charge injection, which in turn depends on the barriers between the energy levels of the polymer (HOMO for hole injection and LUMO for electron injection) and the work function of the contact metal electrodes. The smaller the barrier the greater the charge injection. We have developed an oligomer with an electron withdrawing cyano substituent which has the potential for stacking, 2-dimensional delocalization of charge and improved charge injection. The synthesis, characterization and application of this molecule in PLEDs and PVs will be presented.

#### **K10.94**

**Abstract Withdrawn**

#### **K10.95**

**Preparation and investigation of TiO<sub>2</sub> blocking layer in solid-state, dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells.** Hans-Werner Schmidt<sup>1</sup>, Bin Peng<sup>1</sup>, Gert Jungmann<sup>1</sup>, Mukundan Thelakkat<sup>1</sup>, Claus Jaeger<sup>2</sup> and Dietrich Haarer<sup>2</sup>; <sup>1</sup>Makromolekulare Chemie I, Universitaet Bayreuth, Bayreuth, Germany; <sup>2</sup>Experimentalphysik IV, Universitaet Bayreuth, Bayreuth, Germany.

The preparation steps of solid-state dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells are optimized with respect to the blocking TiO<sub>2</sub> layer which is one of the important layers in such a multi-layer solar cell. By varying the number of spraying cycles in the preparation of the blocking TiO<sub>2</sub> films, a series of samples with increasing blocking layer thicknesses has been prepared. Influence of the increasing blocking TiO<sub>2</sub> layer thickness on the surface morphology was examined using scanning electron microscope (SEM). The thickness and refractive index of the blocking layers were also investigated with ellipsometry measurements. A linear increase in TiO<sub>2</sub> layer thickness with the number of spraying cycles was observed for repetitive spraying cycles between 6 and 30. To characterize the rectifying behavior of the blocking layer, cells with the structure, FTO/blocking TiO<sub>2</sub>/hole conductor/Au, were prepared and their current (I)-voltage (U) properties were investigated. Solid state solar cells were also prepared with different blocking layer thicknesses and their photovoltaic properties were investigated in order to study the influence of the blocking layer thickness on solar cell performance. From the results, an optimum number of ten spraying cycles (corresponding to a film thickness of 150 nm) for the preparation of blocking TiO<sub>2</sub> is suggested to obtain the best rectifying behavior and best photovoltaic properties of the corresponding solar cells. The automated procedure of preparing the blocking layer guarantees reproducibility in obtaining constant thickness and quality of this crucial layer as seen in the current-voltage characteristics of the solar cells.

#### **K10.96**

**Injection and Transport in PC/TMTPD with Varied Charge Density.** Man Hoi Wong<sup>1</sup>, Yulong Shen<sup>1</sup>, Ahmad R. Hosseini<sup>1</sup>, Bing R. Hsieh<sup>2</sup>, David H. Dunlap<sup>3</sup> and George G. Malliaras<sup>1</sup>; <sup>1</sup>Cornell University, Ithaca, New York; <sup>2</sup>Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan; <sup>3</sup>Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico.

A study is done to understand the dependence of injection and transport on the degree of doping of an organic semiconductor. A model organic semiconductor, tetra-methyl triphenyl diamine doped polycarbonate (PC:TMTPD) was used for these experiments. By substituting TMTPD molecules with a TMTPD+SbF<sub>6</sub><sup>-</sup> salt, the degree of charge density in the organic semiconductor was systematically varied. The conductivity of the material was measured and changes in the electrical characteristics of devices with various electrodes were analyzed to yield the dependence of injection on the degree of doping. This provided a better understanding of how doping, and electrode spacing affect device performance.

#### **K10.97**

**New Electro-Optic Materials Based on Conjugated Polymer - Liquid Crystal Solutions.** Evgueni E. Nesterov and Timothy M. Swager; Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The efficient photoexcitation energy migration through the polymer chain is a basis for various applications of conjugated polymers in electro-optical devices and sensors. The ability to control the energy transfer by using external stimuli is important not only for design of new molecular devices but may also improve our understanding of the overall mechanism of this process. Here we report a novel approach to design of the electro-optic organic materials based on the solution of end-capped conjugated polymers in nematic liquid crystals. In such systems, the electro-optic response results from the dynamic control of the intramolecular energy transfer. As an example, we report anthracene-capped poly-(p-phenylene-ethynylenes) (PPEs). The anthracene units act as band gap lowering energy traps facilitating the efficient excitation energy funneling from PPE chain towards the termini. This causes, upon photoirradiation, the fluorescent emission both from the PPE chain and from the anthracene units. Dissolving of the polymer in common nematic liquid crystals (LCs) enhances the efficiency of the energy migration due to improving polymer alignment and increasing overall intra-chain conjugation, thus leading to increased emission from the terminal groups. However, applying an external electric field to the system may cause conformational changes which disrupt such a high conjugation. Depending on frequency of the external electric field, the extent of the energy migration towards the end groups can be finely tuned, which results in a substantial change in the ratio of emission from the PPE chain and anthracene termini. Possible modifications of the materials structure to enhance the electro-optic response as well as photophysical study of these systems

will be discussed.

#### **K10.98**

**Modeling energy transfer processes in conjugated polymers - the role of chemical defects.** Herbert Wiesenhofer<sup>1,2</sup>, Emmanuelle Hennebicq<sup>2,3</sup>, David Beljonne<sup>3</sup>, Jean-Luc Bredas<sup>2,4</sup> and Egbert Zojer<sup>1,2,4</sup>; <sup>1</sup>Institute of Solid State Physics, Graz University of Technology, Graz, Austria; <sup>2</sup>Department of Chemistry, University of Arizona, Tucson, Arizona; <sup>3</sup>Chemistry of Novel Materials, University of Mons-Hainaut, Mons, Belgium; <sup>4</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Energy transfer is a key process in a number of organic optoelectronic devices. It can be applied for instance to tune the emission color of polymer blends to realize multicolor or white LEDs. On the other hand, undesired effects, such as quenching of excitons at defects or at charged and neutral quasi-particles, also involve energy transfer. In this contribution, we investigate when the simple point-dipole approximation (Foerster transfer) can be applied to describe energy transfer in organic thin films. Within this approximation, the Coulombic contribution to the transfer rate is described on the basis of transition dipoles, which are assumed to be localized at the centers of the donor and acceptor molecules. However, it has been shown that for inter-molecular distances comparable to the size of the molecules, the actual molecular structure plays a significant role. To study the relevance of such molecular-structure effects in conjugated polymers, we have chosen as a test case to describe the energy-transfer process to ketonic defects in bridged poly(para-phenylene)-type systems. In addition to their practical relevance, these are ideal models because of the occurrence of two low-lying excited states with sizable oscillator strength. One of these states is localized on the repeat unit bearing a ketonic defect while the other is delocalized, which results in two different energy-transfer channels. The major result is that significant deviations appear between the point-dipole approximation and more sophisticated models. This is explained on the basis of the different shapes of the transition densities contributing to the transition dipoles. Moreover, we find that for head-to-tail configurations of the donor and acceptor units, the point-dipole approximation strongly underestimates the transfer efficiency, while the opposite is true for co-facial configurations.

#### **K10.99**

**Charge Transporting Property of Paramagnetic Organic Stable Radicals in Amorphous State.** Takashi Kurata<sup>1</sup>, Yong-Jin Pu<sup>1</sup>, Hiroyuki Nishide<sup>1</sup> and Junji Kido<sup>2</sup>; <sup>1</sup>Applied Chemistry, Waseda University, Tokyo, Japan; <sup>2</sup>Polymer Science and Engineering, Yamagata University, Yonezawa, Japan.

Charge-transport of an open-shell molecule itself in amorphous state is unknown and interesting to the correlative properties of electricity and magnetism, such as spin-polarized current, magnetoresistance, or ferromagnetic semiconductivity. We prepared three organic stable radicals, tris(*p*-bromophenyl)aminium hexachloroantimonate (TBAHA), Yangs biradical (YB), and di-*p*-anisyl nitroxide radical (DANO), and investigated their charge transporting property in amorphous state. Their current density was extremely small because of the very low mobility of the localized charge. To improve the hole mobility of the nitroxide-radical, we synthesized triarylamine-substituted nitroxide radicals, 4-(*N*-*t*-butyl-*N*-oxylamino)-4', 4'-dimethoxytriphenylamine and 4, 4'-dimethoxy-4<sup>n</sup>-(1-oxyl-3-oxide-4, 4, 5, 5-tetramethylimidazole-2-yl)triphenylamine. The magnetic and charge transporting property of these radicals will be also discussed.

#### **K10.100**

**Structure and VOC Gas Sensing Properties of Plasma Polymerized Polypyrrole Films.** Kouta Hosono, Ichiro Matsubara, Norimitsu Murayama, Woosuck Shin and Noriya Izu; AIST(Advanced Industrial Science and Technology, Nagoya, Japan.

Polypyrrole (PPy) is one of the typical conducting polymers, and applicable to electrical devices and chemical sensors. Although the plasma polymerization can form dense and pinhole-free PPy thin films, the lack of conductivity is regarded as a problem to be solved. Only iodine doped PPy films have been synthesized so far by the plasma polymerization process, yet the conductivity of the films is not sufficient. An attempt has been made to study the structural and electrical properties of plasma polymerized and 4-ethylbenzenesulfonic acid (EBSA)-doped PPy thin films. The conductivity of the EBSA doped PPy films is more than three orders of magnitude larger than that of the iodine doped PPy films. Comparative studies on the infrared spectroscopy, elemental analysis, and UV-VIS spectroscopy give information that the some pyrrole rings are remained in the plasma polymerized pyrrole (PPPy) films prepared with a low discharge power, whereas almost all the pyrrole rings are cleaved in the PPPy films prepared with a high discharge power and the three-dimensional crosslinked structure seems to be formed. We have

evaluated the VOC gas sensing properties for the EBSA doped PPPy films. The EBSA doped PPPy films exhibit higher sensitivities to polar analytes such as formaldehyde and acetaldehyde, whereas it showed a little response to toluene and benzene.

#### **K10.101**

**Surface potential variation in a molecularly doped polymer system observed by high sensitivity electric force microscopy.** William Richard Silveira, Erik Muller, Neil Jenkins, Brian To and John Marohn; Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

We are trying to gain a more microscopic understanding of interface properties and charge trapping by making careful and quantitative electric force microscopy (EFM) measurements. Since organic conductors are often unavoidably disordered, electric force microscopy is well suited for testing microscopic theories. We have used variable temperature electric force microscopy to study and image the surface potential in films of the hopping conductor triphenylamine-doped polycarbonate (TPD-PC), a molecularly doped polymer system used in xerography. In 100 nm thick films with a surface roughness less than 1 nm, we find a 60-80 mV variation in surface potential on a 100-200 nm length scale. We have varied substrates, degree of dipole doping, film thickness, TPD concentration, and temperature. The results tentatively indicate the spatial variation of an interface dipole. Finally, we have incorporated ultra-soft silicon microcantilevers into our microscope to dramatically increase sensitivity. We find that the resonance frequency and quality factor of the cantilevers are a very sensitive function of voltage, distance, and the underlying sample. Such electromechanical dissipation measurements hold promise for quantifying and imaging in-plane conductivity in thin organic films.

#### **K10.102**

**Charge-Transfer and High-Dielectric-Constant in Organic and Polymeric Solids.** Cheng Huang and Qiming Zhang; Materials Research Institute and Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania.

Mixed-valence systems are characterized by at least two redox sites with different oxidation states or combining at least an acceptor and a donor group linked by a bridge that mediates the transfer of charge (electrons) from one site to the other because of an intramolecular electron-transfer (IET) process, different from an intermolecular electron-transfer process-hopping of electrons-which has been widely studied in doped organic or polymer conductors. Such an IET process takes place in response to different external stimuli, which shows unique physical properties. It was found that some purely organic and polymeric solids exhibit extremely high dielectric constant due to collective electronic phenomena in charge-transfer systems. These radicals are electroactive species that in addition to being quite synthetically accessible, display a high thermal and chemical stability. The synthesis and characterization of mixed-valence organic systems act as examples to study intramolecular electron-transfer phenomena with organic molecules. It is more interesting that the mixed-valence systems can be extended to alternating polymer materials. In this paper, by using a simplified model we analyzed the main characteristics of mixed-valence organic systems. Two kinds of organic polymer solids were synthesized and characterized: 1) phthalocyanine oligomers (PolyCuPc) and polymers, and 2) polyacene quinone radical (PAQR) mixed-valence ladder-type polymers. High dielectric constant phenomena, charge-transfer and interfacial polarization will be investigated. This study provides not only suitable tools to describe, understand, and analyze organic and polymeric mixed-valence systems with unique performance, but also helpful guides to design and synthesize such systems as high-dielectric-constant polymer actuator materials.

#### **K10.103**

**Charge Transport In Doped Organic Semiconductor.** Yulong Shen<sup>1</sup>, Kenneth Diest<sup>1</sup>, Man Hoi Wong<sup>1</sup>, Bing R. Hsieh<sup>2</sup>, David H. Dunlap<sup>3</sup> and George G. Malliaras<sup>1</sup>; <sup>1</sup>Cornell University, Ithaca, New York; <sup>2</sup>Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan; <sup>3</sup>Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico.

The effect of doping on the conductivity of the organic semiconductor N,N,N',N'-tetra-*p*-tolyl-4,4'-biphenyldiamine dispersed polycarbonate (PC:TMTDP) was investigated. Doping was performed in a controlled manner by replacing a fraction of the TMTDP molecules with their salt TMTDP + :SbF<sub>6</sub><sup>-</sup>, while keeping the distance between the TMTDP molecules constant. The conductivity was found to be thermally activated and exhibited two regimes: When less than 1% of the TMTDP molecules was doped, the conductivity increased with doping in a nearly linear fashion, having an activation energy of 0.2 eV. At higher doping levels the conductivity increased superlinearly

with doping, while at the same time the activation energy decreased, reaching a low of 0.12 eV when every TMTPD molecule was oxidized. This behavior can be understood in terms of transport manifold filling, Coulombic trapping of charge, and broadening of the transport manifold due to dipolar disorder induced by the dopants.

#### **K10.104**

**Development of Multifunctional Polymer Systems for Surface Molecular Imprinting Technology.** Abdiaziz A Farah<sup>1</sup>, Raluca Voicu<sup>1</sup>, Pascal Lecuyer<sup>2</sup>, Farid Bensebaa<sup>2</sup> and Karim Faid<sup>1</sup>;  
<sup>1</sup>Institute of Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario, Canada; <sup>2</sup>Institute of Chemical Processing environmental & Technology, National Research Council of Canada, Ottawa, Ontario, Canada.

Molecularly imprinted polymers (MIPs) have recently emerged as a new research domain both in academia and in industry. A large variety of molecularly imprinted polymer systems have been reported in the literature for use in chemical separations and catalysis as well in biochemical and pharmaceutical applications. A new paradigm of molecular imprinting using surface characterization techniques in conjunction with a nanotemplating methodology will be presented. A surface-attached moiety is used as a stamp, and is contacted with a variety of functional monomers. Following the selective removal of the stamps, recognition cavities are created on a substrate surface and are found to be selective towards the moiety of interest. In this contribution, we report on the synthesis and characterization of a number of multi-functional polymers (i.e. poly(methacrylates) with both specific recognition sites and surface-attachable groups) that are used to incorporate a target molecules and form an artificial recognition cavity. Upon the transfer and attachment to a defined substrate, these artificial recognition cavities are used to selectively rebind the target molecules. Comprehensive solution and solid-state characterizations of the multi-functional polymers as well as the surface-anchored polymer nano-template will be presented, including 1H-NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), gel permeation chromatography (GPC), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared reflection-absorption spectroscopy (FT-IRRAS) and Scanning Probe Microscopy (SPM).

#### **K10.105**

**Morphology Evolution in Nano-Scale Light-Emitting Domains in MEH-PPV/PMMA Blends.** Nisha Ananthakrishnan, Benjamin Harrison, Randolph S Duran, Kirk S Schanze and John R Reynolds; Chemistry, University of Florida, Gainesville, Florida.

The effect of polymer blend composition and morphology on light emitting characteristics of MEH-PPV/PMMA blend films was investigated. The evolution of the microstructure from isolated light-emitting domains ranging in diameter from 300-900 nm and 100 nm thickness to a continuous light emitting material was seen as the composition of MEH-PPV in the blend film was increased. The 5 wt% compositional study was used to demonstrate stability of morphology, as identical structures were observed for the blend film dried in air, vacuum dried at room temperature and vacuum dried at 80 degC. A "phase inversion" is observed at approximately 50 wt% MEH-PPV where a bi-continuous network of the two polymers is observed. Results of AFM (topographic and phase images), bright field, fluorescence microscopy and the emission from LEDs using the bright field in fluorescence microscope are used to illustrate this morphological evolution. This study also demonstrated that the highest efficiency devices were obtained at 75 wt% MEH-PPV where a continuous light-emitting polymer structure surrounds isolated domains of PMMA.

SESSION K11: Optically Active Materials and Electronic Memories

Chairs: John Reynolds and Gordon Wallace  
Friday Morning, December 5, 2003  
Back Bay C (Sheraton)

#### **8:30 AM \*K11.1**

**Patterning Of Dioxythiophene Based Polymer Electrochromic Devices.** John R Reynolds, Avni Argun, Pierre Henri Aubert, Mathieu Berard, Ali Cirpan, Carleton Gaupp, Christophe Grenier, Jessica Hancock, Benjamin Reeves and Irina Schwendeman; Chemistry, Univ. of Florida, Gainesville, Florida.

By controlling the electron-rich character and degree of pi-overlap along a conjugated polymer chain, a family of multi-colored electrochromic polymers has been developed. Within this, low band gap polymers provide cathodically coloring materials, while high band gap polymers provide anodically coloring materials. A broad spectral variation is accomplished via copolymer composition yielding films

whose colors range through yellow-orange-red-purple-blue, while controlled conductivity changes allow for infrared electrochromism. When complementary anodically and cathodically coloring polymer pairs are utilized in absorption-transmission configured electrochromic devices, large changes in visible light transmission can be rapidly modulated (sub-second switching). Patterned electrodes allow the construction of laterally configured electrochromic devices in which the reflectivity from metal surfaces can be modulated across a broad spectrum. Thin metal films as electrode contacts have been prepared using a combination of metal vapor deposition and line patterning methods yielding highly flexible electrochromic devices. Application of commercially available PEDOT/PSS as an electrode material has yielded the first truly all-polymer electrochromic devices. By careful control of polymerization conditions, electrochromic polymers prepared using commercially available monomers can be incorporated into relatively long-lived devices.

#### **9:00 AM K11.2**

**Planar Polymer Light-Emitting Devices with Extremely Large Inter-electrode Spacing.** Justin Dane and Jun Gao; Physics, Queen, Kingston, Ontario, Canada.

A polymer light-emitting electrochemical cell (LEC) offers an alternative approach to achieving electroluminescence (EL) from conjugated polymers. Unlike a polymer light-emitting diode (PLED), the operation of a LEC involves in situ electrochemical doping and the formation of a dynamic p-i-n junction. A LEC is relatively insensitive to the variations in device thickness (anode-to-cathode spacing). As a result, planar LECs (pLECs) have been demonstrated on pre-patterned substrates with micrometer inter-electrode spacing, and yet still have the same low turn-on voltage as a regular sandwich LEC only a few hundred nanometers thick. This suggests exploring the possibility of making pLECs with even larger inter-electrode spacing. Here we report pLECs with inter-electrode spacing up to 2 mm, nearly 100 times larger than previously demonstrated. These large pLECs offer a unique and, arguably, the most direct approach for polymer device research. High-resolution imaging of EL using only a digital camera reveals an extremely wide emission zone, indicative of a surprisingly inefficient recombination process in these polymer devices with balanced charge injection. Imaging under UV excitation reveals an electrochromic effect due to p-doping of the polymer film. The p-doped region migrates towards the cathode unevenly during operation, causing the emission zone at its frontier to shift and giving rise to its irregular shape.

#### **9:15 AM K11.3**

**Electric field visualization within electrolytes using electrically isolated electrochromic polymer islands.**

Nathanial D. Robinson, Elias Said, David Nilsson, Per-Olof Svensson, Jessica Hall and Magnus Berggren; Dept. of Science and Technology (ITN), Linköping University, Norrköping, Sweden.

The electric field within a 2-dimensional electrolyte can be visualized by applying the electrolyte over an array of dots of electrochromic polymer material (such as PEDOT:PSS) on a plastic foil and observing the color change within each polymer dot. The result is a vector-field analogous to that obtained by placing an array of iron pins in a magnetic field, except that this measurement also allows for the magnitude, as well as the direction, of the field to be measured at each location. The devices studied were created by etching

PEDOT:PSS on AGFA Orgacon<sup>TM</sup> foil leaving an array of small circles. Any method and reversibly electrochromic polymer could have been used. The electrolyte was then applied as a thin film on top of the foil. The measurement requires that an electric field be present within the electrolyte, which generally means that there is an ionic current. In the experiments presented here, a constant voltage was applied between an anode and a cathode while the field was visualized between the two. The visualization is based on the color change associated with the doping/de-doping within each electrochromic polymer dot in response to the voltage drop across the island. The whole device is then rasterized using a standard flatbed scanner and the resulting image analyzed. This device has direct applications as a method for electrolyte evaluation, but is also applicable in bio-analytical measurements and separations such as electrophoresis.

#### **9:30 AM K11.4**

**Polythiophene Based Thermochromic Pigments: Control of Reversibility.** Brett L Lucht, Yu Wang, Adrienne Marold, Nadia Archambault and William Euler; Chemistry, University of Rhode Island, Kingston, Rhode Island.

Thermochromic materials are used to provide a rapid, visual assessment of temperature. Currently available, commercially used reversible thermochromics are based on either liquid crystal technology or acid-base reactions. Both of these technologies have a variety of disadvantages including high cost, poor thermal and light stability, large particle size, and extractability. We report on the

development of new thermochromic pigments based on polythiophenes. There have been numerous investigations of the structure and organization of polythiophene films and the structural changes that occur during the thermochromic transition. The investigations have primarily focused on the behavior of these materials as pure films or in solution. However, the utilization of conjugated polymers as thermochromic pigments requires them to be dispersed in a host polymer matrix. There have been few investigations on the thermochromic properties of polythiophenes in host polymers. In this article we discuss an investigation of the structure, organization, and thermochromism of substituted polythiophenes as pure solids and as dispersions in host polymers. The host polymers of most interest include polystyrene, polycarbonate, and polyolefins. The generally accepted mechanism for the thermochromic transition is based on a two-step process. At low temperature the conjugated repeat units are in a planar conformation and the substituents of the polythiophene chain ordered into a lattice. As the temperature is raised, the side chain lattice melts and the resulting disorder allows the main chain repeat units to twist away from planarity. The twisting of the polythiophene units increases the band gap, resulting in a blue shift of the optical absorption. The melting of the sidechains causes a zipper effect, which results in a sharp thermochromic transition. However, the role of intramolecular aggregation in the thermochromic transition is unclear. We will discuss the investigation of the thermochromic properties of poly(3-alkylthiophene)s with reversible and controlled reversible thermochromic transitions. The investigation of the materials as both pure solids and as dispersions in commodity plastics has been conducted. The temperature of the thermochromic transition and reversibility of the transition is dependent upon the alkyl substituents but largely independent of host polymer. Poly(3-alkylthiophene)s with sharp thermochromic transitions between 40 and 140 °C have been prepared and investigated. The controlled reversibility of poly(3-alkylthiophene)s allows the reversible thermal marking. We will propose a mechanism for the observed controlled reversibility of poly(3-alkylthiophene)s.

#### 10:15 AM K11.5

**Carbon Nanotube Biofibres.** Gordon George Wallace<sup>1</sup>, Joseph Barisci<sup>1</sup>, Simon Moulton<sup>1</sup>, May Tahhan<sup>1</sup>, Philippe Poulin<sup>2</sup>, Stephane Badaire<sup>2</sup>, Thibaud Vaugien<sup>2</sup> and Maryse Maugey<sup>2</sup>; <sup>1</sup>IPRI, University of Wollongong, Wollongong, New South Wales, Australia; <sup>2</sup>Centre de Recherche Paul Pascal, CNRS, Pessac, France.

The assembly of fibres with appropriate mechanical and electronic properties combined with biofunctionality will impact on areas such as biosensors, bioseparations and new platforms for cell culturing and stimulation. In this work we present an exciting new development wherein biomolecules (e.g. DNA) have proven to be exceptional dispersants for single wall carbon nanotubes. These dispersants can subsequently be spun into a coagulation bath to produce CNT fibres with exceptional mechanical attributes as well as acceptable electronic and electrochemical properties. Our recent studies into the use of other biomolecules for fibre spinning will also be presented.

#### 10:30 AM \*K11.6

**Electric-Field Effect Devices Based on Doped Conducting Polymers.** Arthur J Epstein<sup>1,2</sup>, Fang-Chi Hsu<sup>1</sup>, Nan-Rong Chiou<sup>3</sup>, Oliver Waldmann<sup>1</sup>, June Hyoung Park<sup>1</sup>, Youngmin Kim<sup>1</sup> and Vladimir N Prigodin<sup>1</sup>; <sup>1</sup>Physics, The Ohio State University, Columbus, Ohio; <sup>2</sup>Chemistry, The Ohio State University, Columbus, Ohio; <sup>3</sup>Chemical Engineering, The Ohio State University, Columbus, Ohio.

The field effect devices prepared using active channels fabricated from doped conducting polymers, such as PEDOT/PSS (polyethylenedioxythiophene/poly(styrene sulfonic acid)), polypyrrole Cl<sub>1</sub> and polyaniline with various dopants are reported. Normally in the "on" state, the devices have a sharp switch off at a small gate voltage. The current ratio Ion/Ioff/ can exceed 10<sup>4</sup> at room temperature. The temperature dependence of the dc conductivity of the PEDOT/PSS follows the variable range hopping law both before and after application of the gate voltage. The activation energy, T<sub>0</sub>, increases even for on/off ratios as small as 1.07 demonstrating that the electric field effect has changed the bulk charge transport in the active channel despite the expected screening due to mobile charge carriers. Based on these transport and optical studies we propose that the conducting polymer is near the metal-insulator transition and that the field effect in the transistor is related with electric field modulating this transition in the region underneath of gate through field induced ion motion. The time dynamics of current with the gate modulation strongly supports our proposal. We demonstrate fabrication of inverter, amplifier and nonvolatile memory circuits based on these field effect devices. Application of the Doped Polymer Field Effect Devices (DPFEDs) to memory, amplifier and other devices will be discussed. Supported in part by Office of Naval Research.

#### 11:00 AM K11.7

**Conductive Electrochromic Polymers as Electrochemical Fuses for Hybrid Inorganic/Organic Semiconductor Memories.** Sven Moller<sup>1</sup>, Stephen Forrest<sup>1</sup>, Craig Perlov<sup>2</sup>, Warren Jackson<sup>2</sup> and Carl Taussig<sup>2</sup>; <sup>1</sup>Princeton University, Princeton, New Jersey; <sup>2</sup>Hewlett-Packard Labs, Palo Alto, California.

We demonstrate a non-volatile, write-once-read-many-times (WORM) memory device employing a thin film silicon diode on a flexible substrate integrated in series with a conductive polymer fuse. The nonlinearity of the silicon diode enables a large scale passive matrix memory configuration, while the conductive polyethylenedioxythiophene:polystyrene sulfonic acid (PEDT:PSS) polymer acts as a switch with fuse-like behavior for data storage. The polymer can be switched within 2 microsec, resulting in a permanent increase of resistivity of the memory pixel up to a factor of 1000. We analyze the switching mechanism and find that while it is primarily due to current-induced redox reactions in the polymer, it also depends on electric field and thermal activation of the conductivity switching process. The switching effect performance is highly reliable in its operation, and the fuses do not degrade after many thousand read cycles in ambient at room temperature. To our knowledge, this reports the first demonstration of permanent non-destructive conductivity switching in a conductive polymer. Given these results, very high performance, low cost, lightweight archival hybrid inorganic/organic WORM memories for video image and other archival storage applications are feasible.

#### 11:15 AM \*K11.8

**High Performance Organic Memory Device.** Yang Yang, Jianhua Wu, Jun He, Liping Ma and Qianfei Xu; Materials Sci. & Eng., UCLA, Los Angeles, California.

In this presentation, we present our latest study of high performance organic memory device and its theoretical modeling. The device structure is organic/metal/organic tri-layer sandwiched between two metal electrodes. When the metal nano-particle layer is presented within the organic layer, the density-of-states (DOS) has a dramatical change. For pure organic material, the DOS is mainly located near the LUMO and HOMO levels. Hence, the probably for charge transmission from the Al electrode into the organic layer is small, due to the mis-match of Al Fermi level and the DOS of organics. However, the DOS of the nano-particle layer is located in the mid-gap state. When the nano-particle layer is charged, the charge transmission probability enhanced several orders of magnitude. As a result, the device conductivity also enhances several orders of magnitudes. This study clearly explains the importance of the nano-particle layer and device operating mechanism. 9/9/03 Changed from invited to oral per Symposium Organizer, G. Jabbour.

#### 11:45 AM K11.9

**A Low-Voltage Rewritable, Spincast Organic Memory Device.** Ronald C.G. Naber<sup>1</sup>, Paul W.M. Blom<sup>1</sup> and Alwin W. Marsman<sup>2</sup>; <sup>1</sup>Materials Science Centre, University of Groningen, Groningen, Netherlands; <sup>2</sup>Philips Research Laboratories, Eindhoven, Netherlands.

Ferroelectric copolymer films of poly(vinylidene fluoride/trifluoroethylene) are used for many applications such as microphones and actuators. Another interesting use is to integrate the material into a field effect transistor to make a nonvolatile memory device. By combining current efforts to make patterned PEDOT:PSS electrodes and to find high-performance polymer semiconductors, one could conceivably make an all-organic NVRAM by spincasting only. The major problem with the applicability of P(VDF/TrFE) is the high voltage needed to switch the remanent polarization. This voltage can be lowered by using very thin films (<100 nm), but reported results on thin films gave an inferior ferroelectric response so far. In dissimilar capacitor devices, with active layer thicknesses of only a few tens of nanometers, we were able to reduce the switching voltages down to 2 Volts and still maintain a remanent polarization only slightly less than the bulk value (~40 mC/m<sup>2</sup> for the 50/50 copolymer).

SESSION K12: Active Materials  
Chairs: Vladimir Bulovic and Aimee Rose  
Friday Afternoon, December 5, 2003  
Back Bay C (Sheraton)

#### 1:30 PM K12.1

**Chemosensing Lasing Action In Conjugated Polymers.** Aimee Rose<sup>1,2</sup>, Zhengguo Zhu<sup>1</sup>, Conor Madigan<sup>2</sup>, Timothy Swager<sup>1</sup> and Vladimir Bulovic<sup>2</sup>; <sup>1</sup>Chemistry, MIT, Cambridge, Massachusetts; <sup>2</sup>Laboratory for Organic Optoelectronics, MIT, Cambridge, Massachusetts; <sup>3</sup>MIT, Brookline, Massachusetts.

Previous work in our group has demonstrated the bright fluorescence

of electron rich conjugated polymers is significantly attenuated upon exposure to electron deficient aromatic analytes such as trinitrotoluene (TNT). The mechanism responsible is most likely an electron transfer event from the excited state of the polymer to the lowest unoccupied molecular orbital (LUMO) of the particular analyte. Hence, electrostatics dictate to which compounds a particular polymer will respond. With careful design of novel fluorescent conjugated polymers, responses to attograms of TNT can be measured. It has also been well established that conjugated polymers can exhibit stimulated emission when optically pumped with high energy excitation. Stimulated emission is very sensitive to any type of competitive process; non-radiative decay of excited states can increase the threshold for observation of stimulated emission and even prevent it entirely. Because sensitivity of these materials to TNT results from induced non-radiative decay, exposure to TNT near threshold should therefore prevent stimulated emission at that input energy. This approach to detecting TNT and other electron-deficient analytes offers unprecedented enhancement in sensitivity. Stimulated emission is a non-linear process therefore output intensity increases exponentially with input power once lasing threshold has been reached. Attenuation of this signal when compared to the spontaneous (linear) emission response is inherently more sensitive since signal-to-noise of the emission measurements can be improved by orders of magnitude. In addition, we have demonstrated that stimulated modes of emission are more significantly attenuated upon analyte exposure than their spontaneous counterparts. This enhanced quenching coupled with improved emission intensity signal-to-noise provides a significant and novel enhancement in sensitivity over what is observed below lasing threshold. \*Presenting/ Contact Author Aimee Rose Physical Science Inc 20 New England Business Center Andover MA 01810 Ph. 987.689.0003 Fax 987.689.3232 arose@alum.mit.edu

#### 1:45 PM K12.2

**Design of Organic Star-shaped Electro-optic chromophores: Synthesis and Correlation of Guest-host Morphology with Electro-optic Activity.** Padma Gopalan, Howard Edan Katz and David J McGee; Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey.

Azo-benzene based push-pull chromophores with dendritic architecture were synthesized as active materials for electro-optic applications. These chromophores were synthesized in 6 to 7 synthetic steps with an average yield of 60-80% per step and high purity. STEM analysis of the blends of chromophores with polymer host enabled the correlation of the activity of these large chromophores with the blend morphology. Amorphous polycarbonate host effectively disperses the chromophores in 2–20 nm aggregates in the active materials. However, macrophase separation into 200–500 nm aggregates was observed in the methacrylate host matrix. UV-Vis spectroscopy showed significant influence of the transient dipole moment to the observed  $r_{33}$  values. These chromophores were stable to photochemical oxidation in ambient light and air. The electrical poling conditions were optimized for each chromophore as the  $T_g$  of the composite material varied significantly. The highest EO coefficient achieved was 22–25 pm/V at 1550 nm wavelength.

#### 2:00 PM K12.3

**The study on new organometallic complex crystals with high second- and third- nonlinear effects.** Dong Xu<sup>1</sup>, Guang hui Zhang<sup>1,2</sup>, Xin qiang Wang<sup>1</sup>, Yak tak Chow<sup>2</sup>, Xie ning Jiang<sup>1</sup>, Meng kai Lv<sup>1</sup> and Duo rong Yuan<sup>1</sup>; <sup>1</sup>State Key Lab. of Crystal materials, Shandong University, Jinan, Shandong, China; <sup>2</sup>Optoelectronics Research Centre, City University of Hong Kong, Hong Kong, China.

In this paper New Organometallic complex crystals using for doubling of diode laser or all optical switch is reported. Over 10 mw violet at 404 nm has been achieved by ZCTC crystal; Some of ET derivatives may possess much higher nonlinear coefficient than that of organic materials. Previous studies with respect to nonlinear optical material have mainly focused on inorganic oxide or conjugated organic molecular system, while on the contrary, our attention has been paid to organo-metallic complex compounds, which structures not only have coordinating polyhedron in geometry like in oxide crystals, but also possess conjugated planar molecules or radicals like in organic crystals. The structural characteristic may make organometallic complex crystals improving and adjusting some properties of inorganic or organic crystals. The efforts on organic semiconductor with non-central symmetrical structure and high mobility is very important for exploring new nonlinear optical materials used in many application of photo-electronic devices with fast response. ZnCd(SCN)<sub>4</sub> (abbreviated as ZCTC) crystal, one of bimetallic thiocyanate complex crystals with ABTC structure type, is chiefly nonlinear optical material for realizing blue-violet light output by laser diode frequency-doubling. Main parameters of ZCTC and various common crystals were shown in Table.1. The decomposing temperature is up to 234<sup>o</sup> C , UV cutoff is 290 nm, the factor of merit is higher than that of KTP, BBO crystal. The growth morphology and mechanism have

also been investigated by AFM, the defects are mainly caused by liquid inclusions, which are formed due to instability of step bunches and macro-steps in ZCTC crystals, and hole bunches oriented along b-axis direction have also discovered. The results are useful to guide the practical crystal growth process. Another kinds of organometallic nonlinear materials is several derivatives of BEDT-TTE (abbreviated as ET). The design, synthesis, growth and characterization of some nonlinear optical materials chosen have been paid into large attention and in process. The structural features resulted in fact that nonlinear coefficient, especially Third-order effects, may be much higher than that of organic or polymer materials. Table 1. Main Parameters of ZCTC and Various Common Crystals

#### 2:15 PM K12.4

**Azo Polymers Containing Two Types of Main Chain Units for Thick Holographic Media.** Jiro Minabe, Tatsuya Maruyama, Katsunori Kawano, Shin Yasuda, Kazuhiro Hayashi and Yasuhiro Ogasawara; Corporate Research Lab., Fuji Xerox Co., Ltd., Kanagawa, Japan.

Polymers with azobenzene side groups have attracted much attention as materials for holographic storage. Optically induced birefringence in the azo polymer films contributes to formation of holograms. Volume holographic storage requires thick media (> 200  $\mu$ m) to achieve high storage density. However, it is difficult to fabricate the thick azo polymer films compatible with low-scattering noise, high photosensitivity and high stability of data. In general, amorphous polymers exhibit low-scattering noise, but magnitude and stability of the birefringence leave room for improvement. On the other hand, semicrystalline polymers have the large and stable birefringence, but they have high-scattering nature. To utilize the advantages of both types of polymers, we controlled crystallinity of azo polyester by changing the copolymerization ratio of two types of main chain monomers: The polyesters were synthesized with 6,6'- (4,4'-oxydiphenylenedioxy) dihexanol (OPOH), 6,6'- (4,4'-sulfonyldiphenylenedioxy) dihexanol and diethyl isophthalate containing a side chain unit. The polyesters with OPOH of 0 mol% and 100 mol% are amorphous and semicrystalline, respectively. Among six kinds of the polyesters with various OPOH ratios, the polyester with OPOH of 90 mol% exhibited the best performance: (i) The optically induced birefringence was maximized. (ii) The birefringence relaxation after the recording was 5 %. It was one eighth of that for the amorphous polyester with 0 mol%. (iii) A low-scattering film of 250  $\mu$ m in thickness was easily prepared by heating and quenching processes, while the film of the semicrystalline polyester with 100 mol% was not. (iv) The exposure energy for the diffraction efficiency of 20 % was 20 J/cm<sup>2</sup>. It was one sixth of that for the film of the amorphous polyester with 0 mol%. Thus, the copolymerization with two kinds of main chain monomers is an effective method of designing the azo polymer film for volume holographic storage.

#### 2:30 PM K12.5

**Fabrication of a Urea Sensor on a Biologically Derived Plastic.** Terri Wilson<sup>1</sup>, Emmanuel P Giannelis<sup>2</sup>, Carl A Batt<sup>3</sup>, Nuttawee Niamsin<sup>3</sup>, K V Madanagopal<sup>4</sup> and Scott J Stelick<sup>4</sup>; <sup>1</sup>Chemical & Biomolecular Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Materials Science & Engineering, Cornell University, Ithaca, New York; <sup>3</sup>Food Science, Cornell University, Ithaca, New York; <sup>4</sup>Alliance for Nanomedical Technologies, Ithaca, New York.

A novel class of nanofabricated biosensors on a biodegradable platform is being developed. They consist of interdigitated microelectrodes, with a gap size and electrode width of 50 micrometers, evaporated onto polyhydroxybutyrate, a biologically derived plastic film, which is also biocompatible. The target analyte, urea or glucose, is detected conductimetrically by monitoring the change in conductance during their enzymatic hydrolysis. The functionalization of the microelectrodes is accomplished by either immobilization of the enzyme in a sol-gel matrix or direct attachment using appropriate surface chemistry. A microfluidic device has been integrated with the sensor containing microfluidic channels made of a polydimethylsiloxane/polyhydroxybutyrate hybrid. In this talk we will present the fabrication methods, miniaturization efforts including developing a hand-held device, and the biosensor's application to the conductimetric detection of glucose and urea.

#### 2:45 PM K12.6

**Photoaddressable Block Copolymers for Holographic Data Storage - Synthesis Properties and Applications.** Hans-Werner Schmidt<sup>1</sup>, Carsten Frenz<sup>1</sup>, Thomas Breiner<sup>1</sup>, Ulrich Theissen<sup>2</sup> and Dietrich Haarer<sup>2</sup>; <sup>1</sup>Makromolekulare Chemie I, Universitaet Bayreuth, Bayreuth, Germany; <sup>2</sup>Experimental Physik IV, Universitaet Bayreuth, Bayreuth, Germany.

Light-induced reorientation of azobenzene chromophores in polymers has been subject of intense chemical and physical research in the past 20 years. For example the materials properties and their orientation

dynamics were investigated as a function of spacer length, content and nature of the azo-chromophore. Our study is based on an additional concept, the geometrical constraint imposed by introducing the azobenzene sidegroups into microphase-separated domains of a block copolymer. First examples of such block copolymers are described by Mao et al., [1] who attached azo sidegroups to an isoprene backbone in a block copolymer with polystyrene as matrix. We present in this contribution several homopolymers and block copolymers synthesized by living anionic polymerization. As a strategy to obtain the final homopolymers and block copolymers an optimized polymeranalogous reaction was applied. For example, in one series block copolymers based on poly(styrene)-block-poly(butadiene) with a high degree of 1,2-polydiene content were synthesized. The polymerization was carried out in analogy to the procedure developed by Saenger et al. [2] The polydiene-block was functionalized by a hydroboration reaction to generate a poly(1-butene-4-ol) block which was suitable for the further polymeranalogous reactions. Another block copolymer system consists of poly(methylmethacrylate)-block-poly(hydroxyethyl-methacrylate) which was synthesized by sequential anionic polymerization. T-butyl-dimethyl-silyl as a rather stable protection group [3]-for HEMA was selected [4]. Various azobenzene chromophores with reactive acid chloride groups were synthesized and attached to the backbone. The resulting polymers were characterized by DSC, TGA and SEC measurements. The morphologies were investigated by TEM and AFM measurements. Thin films (1 mm to 20 mm) and thick samples (500 mm to 1 mm) were prepared and investigated by means of transmission holography. The holograms are written with a wavelength slightly higher than  $\lambda_{max}$  of the absorption band (488 nm or 532 nm) and read out at a wavelength outside of the absorption band (685 nm). The writing beams induced a reorientation of the chromophores resulting in an anisotropy of the refractive index which is detected by the reading beam. We measured the evolution time of the refractive index within thin and thick samples focusing on the orientation and relaxation dynamics of the chromophores within different morphologies. For thick samples we achieved an angular multiplexing with a resolution down to 0.2 degree. [1] G. Mao, J. Wang, C. K. Ober, J. T. Chen, E. L. Thomas et. al., *Macromolecules* 30 (1997) 2556 [2] J. Saenger, C. Tefehne, R. Lay, W. Gronski, *Polymer Bulletin* 36 (1996) 19 [3] A. Hirao, H. Kato, K. Yamaguchi, S. Nakahama, *Macromolecules* 19 (1986) 1294 [4] T. Breiner, H.-W. Schmidt, A.H.E. Mueller, *e-Polymers* No. 22 (2002)

#### 3:30 PM \*K12.7

**Electronic Transport Properties of Molecular Structures from Mixed-Valence Model Compounds to Single Molecules and Beyond.** Marcel Mayor, Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Karlsruhe, Germany.

Electron transport through molecular structures is investigated in detail by different methods, and correlations between molecular structures and transport properties are the focus of the presentation. The potential of rigid  $\pi$ -systems to act as molecular wires was explored. Reducible units (polythiophenylbenzenes) were connected by the structural motives of question and the resulting dimer-like structures were investigated by electrochemical methods. To examine the potential of the most promising molecular wire motive the diacetylene connector in further detail, longer rigid-rod like structures and cyclic compounds consisting of diacetylene connected poly-thiophenyl substituted benzenes were synthesized as model compounds and studied by electrochemical and optical methods. While para diacetylene substituted benzenes are communication active connectors, meta diacetylene substituted benzenes turned out to be passive ones. The resulting molecular structure vs. knowledge of electron transport properties allowed to synthesize tailor-made rod-like structures to be investigated as bridging molecules between two electrodes. Comparison of the I/V characteristics with the symmetry of the studied molecules provided first indications, that single molecules can be immobilized and studied between two gold electrodes. Further work was focused on tuning the resistance of the set-up by varying the molecular structure. For instance, the potential of a platinum(II) complex as single molecule insulator could be shown. Finally, the above gathered electronic skills of molecular structures allow the design of new nano-scale objects with tailor-made physical properties. As a first example, a giant cyclic molecule is designed and synthesized that fulfills all requirements to observe persistent currents in molecular structures.

#### 4:00 PM K12.8

**Computer Designed, Molecularly Assembled Rugate Filters.** Adam J Nolte<sup>1</sup>, Michael F Rubner<sup>1</sup> and Robert E Cohen<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Earlier work has confirmed the possibility of using the polyelectrolyte multilayer (PEM) deposition technique with subsequent in situ nanoparticle synthesis to create optical interference coatings. Such

coatings are generally based on alternating layers of quarterwave optical thickness, and demonstrate interesting optical characteristics, such as tunable reflection and pass bands. The desire to extend this technique to filters possessing arbitrary variations in refractive index (rugate filters) is motivated by the ability to enhance the optical filter performance. Such enhancements can include the narrowing of reflection bands and the elimination of higher order reflectance lobes. This talk will discuss the unique way PEMs are suited to creating rugate filters through "digitization" of the continuous index profile design, whereby the sequential thickness control of numerous discrete high index and low index layers is used to approximate a smooth refractive index profile. Spectroscopic results obtained following the construction of a PEM-based apodized rugate filter confirm the presence of a high reflection band with minimal sidelobe reflectances, while cross-sectional TEM reveals the enabling microstructure and highlights the precise nanoscale control that PEM-templated nanoparticle synthesis offers the materials designer.

#### 4:15 PM K12.9

**Carbon Nanotube Actuators and Sensors.** Alan Dalton, Steve Collins, Edgar Munoz, Ali Aliev, Dong-Seok Suh, Joselito M Razal, Mike Koslov, Satish Karsala, Anvar A Zakhidov and Ray H Baughman; NanoTech Institute, University of Texas @ Dallas, Richardson, Texas.

Porous single wall carbon nanotube arrays have been fabricated in the form of sheets and fibers. Utilizing this porosity and the high surface area of carbon nanotubes, we find that these assemblies can act as smart noses or tongues that respond to chemicals by actuating like muscles. We use this chemically induced actuation to make cantilever actuators which use the differential expansion of opposite sides of film strips to cause actuation by sheet bending. Electron microscopy, Raman scattering and x-ray diffraction are used to characterize the actuating assemblies. The origin of this phenomenon is discussed in relation to charge injection, interfacial stresses and overall growth of the nano-fiber diameter as a consequence of adsorption of a chemical on the surfaces of nanotube bundles. Possible applications are discussed.

#### 4:30 PM K12.10

**Integration of visible and IR-active semiconductor nanocrystals with optical lithographic processing.**

Vikram Sundar<sup>1</sup>, Ylva Olsson<sup>1</sup>, jonathan steckel<sup>2</sup>, moungi g bawendi<sup>2</sup>, ron rapaport<sup>1</sup>, dan fuchs<sup>1</sup> and gang chen<sup>1</sup>; <sup>1</sup>bell laboratories, lucent.technologies, Hoboken, New Jersey; <sup>2</sup>chemistry, massachusetts institute of technology, cambridge, Massachusetts.

Semiconductor nanocrystals have garnered much interest recently for potential applications ranging from active media in lasers to biological tagging. While some of this potential has been realized in the case of biological labeling, their use in optical applications, however, has been hindered by the inability to integrate these nanocrystals with standard optical lithography techniques. We present the first results of incorporating these quantum dots within fluorinated polymers that form low-loss waveguides in the near IR and are amenable to optical lithography. Engineering the surface of the quantum dots with suitable surfactants is shown to be critical in stabilizing these nanocrystals in low-loss polymers. Subsequent patterning of these polymers using optical lithographic techniques is demonstrated with the construction of ridge waveguides with low surface roughness. We also construct multi-color layered waveguide structures that could be useful for highly parallel multiplexing applications. By careful choice of the size as well as the composition of the nanocrystals we are able to create waveguides that are luminescent in the visible as well as the IR regions of the optical spectrum. Optical, linear and non-linear, characteristics of these hybrid nanocrystals/polymer waveguides are also presented.