

# SYMPOSIUM BB

## Organic Optoelectronic Materials, Processing, and Devices

November 25 – 30, 2001

### Chairs

**Zhenan Bao**

Bell Labs  
Lucent Technologies  
Rm 1 A261  
Murray Hill, NJ 07974  
908-582-4716

**Vladimir Bulovic**

Dept of Electrical Engr  
MIT  
Rm 13-3138  
Cambridge, MA 02139  
617-253-7012

**Susan P. Ermer**

Lockheed Martin Adv Tech Ctr  
O/L9-21 B/204  
Palo Alto, CA 94304  
650-424-3131

**Alex K-Y. Jen**

Dept of MS&E  
Univ of Washington  
Box 352120  
Seattle, WA 98195-2120  
206-543-2626

**George G. Malliaras**

Dept of MS&E  
Cornell Univ  
Ithaca, NY 14853-1501  
607-255-1956

**Michael D. McGehee**

Dept of MS&E  
Stanford Univ  
MC 2205  
Stanford, CA 94305-2205  
650-736-0307

### Symposium Support

Lumera Corporation  
†MMR Technologies, Inc.  
Universal Display Corporation

†2001 Fall Exhibitor

Proceedings to be published in both book form and online

(see *ONLINE PUBLICATIONS* at [www.mrs.org](http://www.mrs.org))

as Volume 708

of the Materials Research Society  
Symposium Proceedings Series

\* Invited paper

## TUTORIAL

**FT BB: ORGANIC ELECTRONICS:  
CONCEPTS, MATERIALS AND DEVICES**  
Sunday, November 25, 2001  
2:00 p.m. - 5:00 p.m.  
Room 200 (Hynes)

This tutorial short course will introduce the basic opportunities and approaches to modern organic electronic devices. The extremely rapid advances in organic materials for use in photonics and electronics have given birth to a large community of researchers who are exploring ways to make the early decades of the 21st century the era of organic electronics. Chief among the devices currently moving toward commercialization are organic light-emitting displays, solar cells and low cost transistor circuits. This tutorial will consider the opportunities and challenges confronting this field, starting with basic physics and chemistry issues. Then we will discuss many unique aspects of materials science related to making high-performance organic optoelectronic components. We will conclude with an in-depth discussion of several organic devices including organic light emitting devices, photodetectors, thin film transistors, and solar cells.

### Instructors:

**Steve R. Forrest**, Princeton University  
**Mark E. Thompson**, University of Southern California

SESSION BB1: ELECTRONIC STRUCTURE AND  
OPTICAL PROPERTIES OF ORGANIC SOLIDS  
Chair: Vladimir Bulovic  
Monday Morning, November 26, 2001  
Constitution A (Sheraton)

### NOTE EARLY START

**8:15 AM \*BB1.1**  
PHOTOPHYSICS OF SEMICONDUCTING POLYMERS.  
A.J. Heeger, D. Moses and P. Miranda, Institute for Polymers and Organic Solids, UCSB, Santa Barbara, CA.

Ultrafast photoinduced absorption by the infrared-active vibrational (IRAV) modes is used to detect charged photo-excitations (polarons) in semiconducting polymers. The experiments, carried out in zero applied electric field, demonstrate ultrafast photogeneration of polarons (within 100 fs) with quantum efficiencies of approx. 10%. The ultrafast photoinduced IRAV mode absorption indicates that both charged polarons and neutral excitons are independently generated even at the earliest times. Similar results are obtained from conjugated chains in solution. Transient photoconductivity results are fully consistent with the charge generation data obtained from the photoinduced absorption by the IRAV modes. The weak pump-wavelength dependence of the polaron density implies that the exciton binding energy is small and that the lowest energy optical absorption results from an interband transition. High resolution studies of field induced ionization of the neutral excitons gives approx. 60 meV for the exciton binding energy.

**8:45 AM BB1.2**  
NON-RADIATIVE LOSSES AND THE PROSPECTS FOR  
ELECTRICALLY-PUMPED ORGANIC LASERS. M.A. Baldo, R.J. Holmes and S.R. Forrest, Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, NJ.

The photoluminescence efficiency of a typical crystalline semiconductor laser material such as GaAs is approximately 100%, and relatively independent of excitation strength. Organic light emitting devices (OLEDs) have also demonstrated a maximum internal efficiency approaching 100%. However, the highest efficiency organic electroluminescence is typically realized at very low current densities since non-radiative losses typically increase with excitation strength. We examine the effects of non-radiative losses on the quantum efficiency of fluorescent organic electroluminescent devices, and find that non-radiative energy transfer to triplets and electrically injected polarons is the dominant loss mechanism for singlet excitons. At the very high current densities required to induce gain and lasing, the density of polarons and triplets must be minimized by careful selection of the organic material. In particular, we show that weak intermolecular overlap in amorphous organic materials reduces charge mobility and triplet-triplet annihilation, thereby impeding the realization of electrically-pumped lasing. We quantify the major loss mechanisms in archetype molecular organic electroluminescent films, and calculate the charge transport mobility required for lasing in a film that employs Forster energy transfer to a luminescent dye.

Furthermore, recent work on tetracene lasers reported by Schon, et al [1] will be considered in this context. Finally, we discuss techniques for alleviating both polaron and triplet losses.

[1] Schon JH, Kloc C, Dodabalapur A, Batlogg B. Science. 289, 599 (2000).

**9:00 AM BB1.3**  
EXCITED STATE DYNAMICS IN POLY-PHENYLENEVINYLENE (PPV) OLIGOMERS: A THEORETICAL STUDY. Sergei Tretiak, Richard L. Martin, Avadh Saxena and Alan R. Bishop, Los Alamos National Laboratory, Los Alamos, NM.

A new method for the simulation of excited state molecular dynamics in extended molecular systems is applied to compute and analyze electronic structure and excited states adiabatic potentials of poly-phenylenevinylene (PPV) oligomers. This approach combines the Random Phase Approximation with AM1 and PM3 semiempirical models generated by MOPAC. The excited-state molecular dynamics algorithm is based on the adiabatic propagation of the ground-state and transition single-electron density matrices along the trajectory. Calculated excited states parameters, linear absorption and fluorescence spectra agree well with available experimental data. Complementary two-dimensional analysis of corresponding transition density matrices provides an efficient way for tracing the origin of various optical transitions by identifying the underlying changes in charge densities and bond-orders. This approach is inexpensive and numerically efficient method of computing molecular excited state adiabatic surfaces and modeling femto-to-pico second time-dependent dynamics along these trajectories.

**9:15 AM \*BB1.4**  
RELATIONSHIP BETWEEN MORPHOLOGY AND  
PHOTOPHYSICS OF CONJUGATED POLYMERS. Rachel Jakubiak, Chris Collison, Varaporn Treemanekarn, Pei Wang, Christine Liberatore, Lewis Rothberg, University of Rochester, Rochester, NY.

We study the effects of polymer morphology on optical properties of phenylenevinylens by comparing samples in different solvents and in thin film form. Structural measurements from magnetic resonance lead us to speculate that aggregation leads to sterically induced increases in conjugation length. All of our optical results from solutions (absorption, photoluminescence, luminescence excitation and time-resolved photoluminescence) are consistent with the approximation that there are only two types of conjugation segments. Those in well-packed regions of the polymer are rigid and have low photoluminescence quantum yield while more flexible segments are highly fluorescent. While we find that reducing pi-stacking does inhibit excimer formation, we show that interchain polaron pair formation is an intrinsic process with high yield for aggregated chains that serves to decrease the quantum yield even without pi-stacking. The reduction of luminescence in packed regions is not accompanied by a substantial change in exciton lifetime. We make time-resolved measurements to try to understand how this is possible. In films, we believe that the polaron pair formation is very rapid and this explains both reduced quantum yield and subpicosecond charged species formation observed by others. We will present an analysis of the contributions of this pathway to the long-lived photoluminescence in phenylenevinylene polymers.

**10:15 AM \*BB1.5**  
IMAGING OF OPTOELECTRONIC PROCESSES IN NANO-METER-SCALE STRUCTURES AND COMPOSITES. David Adams, Department of Chemistry, Columbia University, New York, NY.

There is growing interest in the underlying physical processes in optoelectronic devices based on composites of organic and inorganic electronic materials, including low-cost large-area solid-state solar cell and light emitting devices, photodetectors, and optical memories. Such devices are often thin-film multilayer structures involving nanostructured polymeric and/or crystalline organic layers and inorganic layers supported on conducting/transparent indium tin oxide glass electrodes. The unique electrooptic behavior of these devices and essential physical processes such as charge injection/separation at interfaces, charge and exciton mobilities, exciton decay processes, and exciton/charge-carrier interactions are often intimately controlled by the detailed nanostructured morphologies of the system. There is a need for experimental tools that allow for imaging (spatial resolution) of the physical properties and processes associated with nanometer scale structures. Ideally, simultaneous imaging of the layer morphology and physical processes would ultimately allow for a direct correlation of morphology and device physics in a functional device, device prototype, or isolated nanostructure. Nanometer scale structures are expected to impact broad areas of electronics and optics technology. The realization of the technological applications requires a greater understanding of how nanostructures are synthesized and fabricated and importantly

requires a greater understanding of the intrinsic and potentially unique physical properties of nanostructures. Here we present recent results where two complimentary new methods are used to spatially and temporally resolve optoelectronic properties and processes in nanostructured thin films. Electric field modulated near-field scanning optical microscopy (NSOM) and light-modulated scanning electrostatic potential microscopy (SEPM) are used to investigate self-organizing liquid crystalline molecular semiconductors and photoconductors, and inorganic semiconductor particle/conducting polymer nanocomposites.

#### 10:45 AM **BB1.6**

FIELD INDUCED CHARGE GENERATION IN POLY(9,9-DIOCTYLFLUORENE) (PFO). T. Virgili, Department of Physics and Astronomy, The University of Sheffield, Sheffield, UNITED KINGDOM; D.D.C. Bradley Centre for Electronic Materials and Devices, The Blackett Laboratory, Imperial College, London, UNITED KINGDOM; G. Lanzani, G. Cerullo, C. Gadermaier, S. De Silvestri, Dipartimento di Fisica-INFN, CEQSE-CNR, Politecnico di Milano, Milan, ITALY.

We report femtosecond electric-field-assisted pump-probe measurements on organic light-emitting devices based on poly(9,9-dioctylfluorene) [PFO]. Many of the elementary processes taking place in LEDs can be directly probed via this technique in both the temporal and spectral domains. Here we present results for studies of field-induced polaron generation (monitored at 2.14 eV) and the build-up of a triplet exciton population, following polaron-polaron fusion (monitored at 1.51 eV). The potential benefits of this new approach for the study of device physics will be discussed. We thank the Dow Chemical Company for provision of the PFO samples used in this study.

We also acknowledge financial support from the Dow Chemical Company, the Commission of the European Community (TMR Network EUROLED).

#### 11:00 AM **BB1.7**

NEAR FIELD SCANNING OPTICAL MICROSCOPY (NSOM) INVESTIGATION OF GENERATION, DRIFT, AND DIFFUSION OF INDIVIDUAL CARRIERS IN ORGANIC SEMICONDUCTORS. Jason McNeill, Paul F. Barbara, Univ Texas Austin, Dept of Chemistry, Austin, TX.

NSOM is used to probe carrier generation, drift, and diffusion on the nanometer length scale in organic semiconductor materials such as conjugated polymers and amorphous and crystalline organic semiconductors. The migration of charge carriers in response to a pulsed electric field was determined on the 100-nm length scale and microsecond time scale employing photoluminescence detection and near field optical excitation. A metal coating on the near field probe which defines the sub-wavelength aperture serves as a  $\sim 100$  nm diameter electrode which acts to either collect or repel majority charge carriers, depending on the sign of the applied voltage. The transient response of the local carrier density is determined by carrier-induced photoluminescence quenching. A model including carrier drift and carrier diffusion describes the transient response. The role of oxygen in photoinduced carrier generation, exciton quenching, and charge trapping is also investigated. We report fluctuations in the photoluminescence which indicate motion of individual polarons in an organic semiconductor.

#### 11:15 AM **BB1.8**

SPATIALLY RESOLVED SPECTROSCOPY OF ORGANIC THIN FILMS. Ji Yu, Dong Hee Son, Jason McNeill, and Paul Barbara, University of Texas, Austin, TX.

Fluorescence detected ultrafast two pulse correlation spectroscopy of various thin-film samples in a confocal microscope will be described. For conjugated polymer samples and nanostructured aromatic materials ultrafast dynamics due to exciton annihilation is the dominant mechanism for ultrafast dynamics. Finally, results of experiments in progress to observe ultrafast dynamics for single molecules will be presented. We gratefully acknowledge the National Science Foundation for support of our research.

#### 11:30 AM **\*BB1.9**

NEAR-FIELD SCANNING OPTICAL MICROSCOPY (NSOM) STUDIES OF INTERCHAIN INTERACTIONS IN FILMS OF CONJUGATE POLYMERS. Benjamin J. Schwartz, Thuc-Quyen Nguyen, UCLA, Dept of Chem & Biochem, Los Angeles, CA; Richard D. Schaller, Justin C. Johnson, Lynn F. Lee, Louis H. Haber, Richard J. Saykally, UC Berkeley, Dept Chem, Berkeley, CA.

We present the results of near-field scanning optical microscopy (NSOM) experiments examining films of MEH-PPV that were prepared in different ways. The spatially-resolved photoluminescence (SRPL) collected on top of nanometer-scale topographical features

(“bumps”) exhibited by spin-cast MEH-PPV films show an enhancement of the red portion of the emission relative to spectra collected from flat regions of the film. Moreover, photo-oxidative damage (signified by a red-shift and drop in quantum yield of the SRPL) occurs more quickly in the flat regions of the films than on the bumps. Taken together, these observations suggest that the bumps on the films correspond to regions in which the chains are packed more tightly: the red-shifted emission results from increased interchain interactions, while the decreased photodamage rate results from the poorer penetration of oxygen between the tightly packed polymer chains. We also find that the spatial homogeneity of MEH-PPV films can be improved by thermal annealing: heating above the polymers glass transition temperature removes the topographic features, producing a uniform, weak and red-shifted SRPL due to increased interchain interactions. We also use NSOM to measure the solvatochromism of the emissive interchain species at the surface of the annealed films placed into contact with drops of various polar liquids. We find that the majority ( $\sim 95\%$ ) of film regions show a blue-shift of the SRPL with increasing liquid polarity, indicative of “excimer-like” interchain species with little excited-state charge separation. In a few localized film regions ( $\sim 5\%$ ), however, the SRPL red-shifts with increasing liquid polarity, suggestive of an interchain species with a high degree of charge separation, such as a “polaron pair”. The presence of fabrication history-dependent multiple interchain electronic species in films of conjugated polymers has important implications for the optimization of optoelectronic devices based on these materials.

### SESSION BB2: METAL/ORGANIC INTERFACES-ELECTRONIC STRUCTURE AND CHARGE INJECTION

Chair: Marc Baldo  
Monday Afternoon, November 26, 2001  
Constitution A (Sheraton)

#### 1:30 PM **\*BB2.1**

POSSIBLE BAND BENDING AND RELATED PHENOMENA AT ORGANIC/METAL INTERFACES PROBED BY KELVIN PROBE AND OTHER METHODS. Kazuhiko Seki, Nagoya Univ., Research Center for Materials Science, Nagoya, JAPAN; Naoki Hayashi, Yuuki Washizu, Noritaka Matsue, Kazuma Tsuboi, Yukio Ouchi, Nagoya Univ., Graduate School of Science, Nagoya, JAPAN; Tohru Araki, Saitama Univ., Faculty of Science, Saitama, JAPAN; Eisuke Ito, Institute for Physical and Chemical Research, Wako, JAPAN; Hisao Ishii, Nagoya Univ., Graduate School of Science, Nagoya, JAPAN.

Recent extensive studies of organic interfaces by many groups revealed rich phenomena at organic/metal, metal/organic, and organic/organic interfaces, e.g. dipole layer formation right at the interface, possible chemical reaction and interdiffusion, and possible band bending leading to Fermi level alignment. In this talk, we focus our attention examining such possible band bending at interfaces formed by depositing a layer of undoped molecular material onto clean metal surface under ultrahigh vacuum (UHV) condition using Kelvin probe method. With this method, we can probe the change of the work function of the system, or the relative energy of the vacuum level relative to the Fermi level of the substrate, up to thickness of the order of 100 nm. In contrast, photoemission spectroscopy using conventional light source can not be applied to such thick molecular film without charging problems. We have already examined the interfaces formed by depositing TPD (N,N-bis(3-methylphenyl)-N,N-diphenyl-[1,1-biphenyl]-4,4-diamine) molecule on various metals, where we found the lack of band bending leading to Fermi level alignment [1]. In this talk, we report on the extension of such studies to C60 on metals. The deposition on clean Ag, Au, and Cu films (prepared by UHV-deposition) showed (1) initial steep drop of work function corresponding to dipole layer formation leading to similar work function, and then (2) slow change leading to rather similar value of work function. The conclusion (1) is different from that by Ohno, Weaver and others [2] reporting the Fermi level alignment at such small thickness of C60 [2]. The finding (2) is in contrast to the case of TPD, suggesting possible band bending in C60 leading to Fermi level alignment. This might be induced by impurities remaining in C60, leading to similar situation with the recent observation of band bending by Leo et al. [3], where another organic material was intendedly doped. Examination of Alq3 (tris(8-hydroxyquinolino) aluminum) and further studies of TPD will be also presented. [1] N. Hayashi et al., Synth. Metals, 121, 1717 (2001). [2] T. Ohno et al., Phys. Rev. B 44, 113474 (1991). [3] K. Leo, private communication.

#### 2:00 PM **\*BB2.2**

PHOTOELECTRON SPECTROSCOPY OF INTERFACES IN

POLYMER-BASED ELECTRONIC DEVICES. W.R. Salaneck, M. Fahlman, and G. Greczynski, Department of Physics, Linköping University, Linköping, SWEDEN.

The newest polymer devices involve current injection, with entirely different requirements on the metal (and often optically transparent indium tin oxide) electrodes. In models of charge injection, both at the cathode and at the anode, a simple abrupt picture of the polymer-metal interface is used in most cases. In general, a detailed knowledge of the metal-on-polymer or polymer-on-metal interface is necessary for a complete understanding of device characteristics. In this contribution, some of the issues surrounding polymer-metal interfaces will be presented. Then the results of several studies of polymer-metal interfaces will be reviewed, in order to illustrate the type of details that may be important in determining device behavior. Without the loss of generality, some specific materials systems will be discussed with in the review of general interface properties.

#### 2:30 PM **BB2.3**

A PHOTOEMISSION AND INVERSE PHOTOEMISSION SPECTROSCOPIC STUDY OF INTERFACE FORMATION IN ORGANIC THIN FILM TRANSISTORS. N.J. Watkins, Li Yan, S. Zorba, and Yongli Gao, Univ of Rochester, Dept of Physics and Astronomy, Rochester, NY.

Pentacene, perylene, and sexithiophene are all materials being used in organic thin film transistors due to their relatively large mobilities. It has been suggested that the functional behavior in organic thin film transistors occurs within the first few molecular layers of the device at the interfaces between the organic and the metals and dielectrics used in fabrication of the thin film transistors. This makes understanding the electronic behavior of the interfaces involved in these devices critical. In order to better understand these interfaces we investigated the interface formation using photoemission spectroscopy and inverse photoemission spectroscopy to examine layer by layer growth of pentacene, perylene, and sexithiophene on conductors, dielectrics, and charge transfer agents and vice versa. We observed indications of dipole formation at the interfaces between the metals and organics for organic on metal deposition. There appears to be a linear relation between the interface dipole and metal workfunction with the observed dipoles ranging from a 1 eV dipole at the interface between sexithiophene and gold to a -0.46 eV dipole at the interface between pentacene and calcium. On the other hand, more complex material intermixing takes place during metal on organic deposition and as a result, the electronic structure of the interface differs from that of organic on metal deposition. Possible charge transfer, dipole formation and energy level bending at these interfaces will be discussed.

#### 2:45 PM **BB2.4**

INTERACTION AND ENERGY LEVEL ALIGNMENT AT INTERFACES BETWEEN PENTACENE AND LOW WORK FUNCTION METALS. Norbert Koch, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ; Jacques Ghijsen, Namur Univ, LISE, Namur, BELGIUM; Ricardo Ruiz, Vanderbilt Univ, Dept of Physics, Nashville, TN; Jens Pflaum, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ; Robert L. Johnson, Hamburg Univ, II. Inst f. Experimentalphysik, Hamburg, GERMANY; Jean-Jacques Pireaux, Namur Univ, LISE, Namur, BELGIUM; Jeffrey Schwartz, Princeton Univ, Dept of Chemistry, Princeton, NJ; Antoine Kahn, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ.

A number of low workfunction metals (samarium, alkali metals) were deposited onto vacuum sublimed thin films of pentacene. The change in the valence electronic structure of the organic material was studied by in situ ultraviolet photoemission spectroscopy (UPS). Alkali metal intercalation leads to the appearance of a new photoemission feature within the pentacene energy gap, due to a charge transfer from the alkali atoms to the lowest unoccupied molecular orbital (LUMO) of the organic material. The energy spacing between this emission feature and the relaxed highest occupied molecular orbital (HOMO) of the pristine molecule is 1 eV. From X-ray photoemission spectroscopy core level analysis, we estimate a concentration ratio of two alkali metal atoms per pentacene molecule at maximum intercalation level, leading to a complete filling of the LUMO. This is consistent with the results from UPS that the new emission is always observed below the Fermi-level. Samarium is found to exhibit a more subtle interaction with pentacene: the molecular orbitals remain almost unperturbed upon Sm deposition. The resulting energy level alignment at this interface seems to be very favorable for the injection of electrons from Sm into pentacene, as the HOMO-onset is found at 1.8 eV below the metal Fermi edge. This value is close to the 2.2 eV HOMO-LUMO gap of pentacene measured by UPS and inverse photoemission spectroscopy, thus corresponding to a small electron injection barrier.

#### 3:30 PM **\*BB2.5**

CARRIER INJECTION IN METAL/ORGANIC/METAL STRUCTURES: DEPENDENCE ON INTERFACE ELECTRONIC

STRUCTURE, MORPHOLOGY AND CHEMISTRY. Chongfei Shen, Antoine Kahn, Dept. of Electrical Engineering, Princeton University, Princeton, NJ.

We examine the relationship between chemical reaction, interdiffusion, electronic structure and current injection at interfaces between metals and thin films of  $\pi$ -conjugated molecules. The analysis is based on a series of interface spectroscopy and in-situ current-voltage measurements performed in ultra-high vacuum. Interfaces formed by deposition of a metal on an organic film are generally found to be broader than interfaces formed by reverse deposition sequence. Metal atoms diffuse and/or react in the organic layer, acting as electrically active dopant and altering the electronic properties and the structure deep into the molecular film. These interactions have a profound impact on the injection and transport of charge carriers across organic interfaces. We present a comprehensive investigation of these effects performed on a series of metal/organic/metal structures. The organic compounds are Alq<sub>3</sub> (tris-(8-hydroxyquinolino) aluminum) and F<sub>16</sub>CuPc (copper hexadecafluorophthalocyanine), and the metals are Mg, Al and Au. Combinations of structures including permutations of Al and Au as top and bottom contacts, and ultra-thin metal layers inserted into the bulk of the organic film, are used to investigate the effects. Key results are: 1. the predominant role of chemistry-derived electronic gap states, which lead to identical metal/organic barriers for Mg(Al)-on-Alq<sub>3</sub> and Alq<sub>3</sub>-on-Mg(Al); 2. the p-type doping induced by Au atoms diffused into organic films like Alq<sub>3</sub> and F<sub>16</sub>CuPc, making metal-on-organic and organic-on-metal interfaces electrically inequivalent; and 3. the structural disruption of the F<sub>16</sub>CuPc molecular stacks resulting from chemical reaction with Al, leading to considerable decrease in electron mobility through the material. Work supported by the MRSEC program of the National Science Foundation (DMR-9809483) and the NJCOE.

#### 4:00 PM **BB2.6**

PHOTOELECTRON SPECTROSCOPICAL STUDY OF THE RELEVANT ENERGY LEVELS IN CONJUGATED POLYMER FILMS AND DEVICES. S.C. Veenstra, A. Heeres, U. Stalmach, J. Wildeman, G. Hadziioannou, G.A. Sawatzky, H.T. Jonkman Materials Science Center, University of Groningen, Groningen, THE NETHERLANDS.

Semi-conducting conjugated oligomers and polymers form an interesting class of materials. Their electrical properties range from insulating to super-conducting. Their optical properties may be tuned by chemically modifying the parent polymer resulting in highly luminescent materials spanning the optical spectrum from the blue to the red. The above mentioned properties combined with their ease to process make these materials interesting candidates for commercial applications like field effect transistors and photovoltaic devices; light emitting diodes based on polymers already reached the commercial stage. In order to get a better insight in the electronic structure of these carbon-based semi-conducting materials we studied in a systematic way the electronic structure development, starting from the monomer (fragments) up to the polymer. We studied the electronic structure of isolated molecules in a combined experimental (using electron spectroscopy) and theoretical approach (using a simple tight binding model). By using an effective dielectric constant we can use the same method for determination of the energy levels in a solid. Further we studied the influence of interfaces on the electronic structure, especially the donor-acceptor interface (present in conjugated polymer-C60 based photovoltaic devices) and the organic-metal interface (representing the electrode-semiconductor interface). At these interfaces we found strong deviations from the bulk properties due to strong local electric fields. Presently we study, by combining spectroscopic and electrical transport measurements, the influence of these interface effects on the device properties of light emitting diodes and photovoltaic devices.

#### 4:15 PM **BB2.7**

FABRICATION AND CHARACTERIZATION OF METAL-MOLECULE-METAL JUNCTIONS BY CONDUCTING PROBE ATOMIC FORCE MICROSCOPY. Jeremy Beebe, Vince Engelkes, Larry L. Miller, C. Daniel Frisbie, Depts of Chemistry and Chemical Engr and Mattis Sci, Univ of Minnesota, Minneapolis, MN.

Molecular junctions are formed by contacting self-assembled monolayers (SAMs) of thiol- or isocyanide-containing molecules with a metal-coated atomic force microscope tip. This method of junction formation has the following salient features: (1) the junctions are easy to assemble; (2) the contact areas are small, on the order of 10 nm<sup>2</sup> so that a small number of molecules are involved; (3) the I-V characteristics can be measured as a function of load applied to the tip-SAM contact. We describe measurements of the junction resistance as a function of SAM thickness and applied load. By extrapolating plots of resistance versus SAM thickness to zero thickness we obtain an estimate of the metal-molecule contact resistance. We have investigated the contact resistance as a function of probe radius,

applied load, type of metal coating, and the nature of the chemical contact (thiol versus isonitrile). We demonstrate that this conducting probe atomic force microscopy (CP-AFM) approach is a convenient method for measuring fundamental properties of molecular junctions.

#### 4:30 PM BB2.8

**ENGINEERING ORGANIC/INORGANIC INTERFACES IN POLYMER LEDS.** Kieran Reynolds, Gitti Frey, Richard Friend, Univ of Cambridge, Dept of Physics, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

To improve efficiency and light emission from polymer light emitting diodes (PLEDs) carrier injection and balancing must be optimised. This is currently achieved using multilayer devices. However, the electrode/polymer interfaces are difficult to control and critically influence device performance. In this work PLEDs were fabricated with charge injecting layers and charge blocking layers consisting of fully solution processable inorganic materials, namely transition metal dichalcogenides (TMDCs) and their corresponding oxides (TMOs) respectively. Typically the device configuration was ITO/TMDC/TMO/emissive layer/Ca/Al. The organic emissive layer was a polyfluorene blend. Devices including TMDC/TMO injecting and blocking layers gave high luminous efficiencies (in excess of 10 Lm/W) and high brightness (greater than 50 000 Cd/m<sup>2</sup>). The performance of these devices was improved with respect to ITO only devices and comparable to devices fabricated using poly(3,4-ethylene dioxothiophene):poly(styrenesulphonate) (PEDOT:PSS) as a hole injecting layer. The TMDC layers showed extremely good hole injection, approaching an ohmic contact at the anode, due to their high work function and dangling-bond free surfaces. A variety of TMDCs were used and the effect of the TMO blocking layers thickness on device performance was investigated. Both the TMDC and the organic material show advantageous device properties resulting in excellent device performance, which points towards organic/inorganic synergism.

#### 4:45 PM BB2.9

**MODIFICATION OF INDIUM TIN OXIDE FOR IMPROVED HOLE INJECTION IN ORGANIC LIGHT EMITTING DIODES.** Yulong Shen, Man Hoi Wong, Ken Diest, George Malliaras, MS&E, Cornell Univ; G. Koley, Michael G. Spencer, School of Electrical & Computer Engineering, Cornell Univ, Ithaca, NY.

Indium Tin Oxide is the most commonly used anode electrode in organic light emitting diodes (OLEDs). A critical parameter for charge injection is its workfunction, varies between 4.5 and 5.1 eV, depending on the sample preparation and cleaning procedure. These large variations in the workfunction translate to even larger variations in the injected current, which is a major issue for the fabrication of efficient OLEDs. We demonstrate a way to treat ITO and get a contact with good injection characteristics, regardless of the ITO preparation procedure. We have carried out direct measurements of the injection efficiency at the ITO/TPD contact (TPD is N-N'-diphenyl-N-N'-bis(3-methylphenyl)-1-1-biphenyl-4,4'-diamine, a commonly used hole transport layer). The contact is found to be current-limiting, supplying TPD only with 1% of the space charge limited current. By introducing a thin layer of Pt, the injection efficiency approaches 100%, i.e. the contact becomes Ohmic. The performance of the contact shows little sensitivity to the details of the ITO preparation. A mechanism for this improvement is proposed.

#### SESSION BB3: POSTER SESSION

Chairs: Lewis J. Rothberg and William R. Salaneck

Monday Evening, November 26, 2001

8:00 PM

Exhibition Hall D (Hynes)

#### BB3.1

**THE ENERGY GAP LAW FOR TRIPLET STATES IN PT-CONTAINING PHENYLENE ETHYNYLENE POLYMERS AND MONOMERS.** Joanne S. Wilson, Nazia Chawdhury, Amana L.T. Khan, Anna Köhler, Richard Friend, Univ of Cambridge, Cavendish Lab, UNITED KINGDOM; Muna R.A. Al-Mandhary, Muhammad S. Khan, Dept of Chemistry, College of Science, Sultan Qaboos Univ, SULTANATE OF OMAN; Mohammed Younus, Paul R. Raithby, Dept of Chemistry, Univ of Cambridge, UNITED KINGDOM.

The energy gap law established for aromatic hydrocarbons and rare earth ions relates the non-radiative decay rate to the energy gap of a transition. We show that this energy gap law can be applied to the phosphorescence of a series of Pt-containing conjugated phenylene ethynylene polymers and monomers. The non-radiative decay rate of the phosphorescence increases exponentially with decreasing T<sub>1</sub>-S<sub>0</sub> gap for the polymers and monomers at 300 and 20 K. We compare the values we find for the non-radiative and radiative decay rates to those

typically found for organic conjugated molecules. We then discuss the multi-phonon emission process by which non-radiative decay occurs in these phenylene ethynylenes. Using a Franck-Condon analysis we compare the phosphorescence spectra of deuterated and non-deuterated compounds to determine the main phonon modes that contribute to the non-radiative decay. Comparison of the non-radiative decay of polymers with that of their corresponding monomers highlights the role of electron-lattice coupling

#### BB3.2

**LOCAL ORDER IN AMORPHOUS ORGANIC MOLECULAR THIN FILMS: THE EFFECT OF DIPOLAR CORRELATIONS ON LUMINESCENT RED SHIFTS, CONCENTRATION QUENCHING OF EMISSION AND ELECTRON TRANSPORT.** M.A. Baldo, Z.G. Soos\* and S.R. Forrest, Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, NJ, \*Department of Chemistry, Princeton University, Princeton, NJ.

Thin films of many molecular materials are considered 'amorphous' because they possess no detectable long-range order. However, we show that the fluorescence spectrum of polar molecules may shift due to the formation of ordered polar domains within an otherwise amorphous film matrix. This so-called "solid state solvation effect"[1] appears to be a general feature of most luminescent amorphous thin films, where the lumophore or the host molecular matrix have permanent electrostatic multipoles. We derive a model to explain this shift and the associated quenching of luminescence as domains are formed and grow. We demonstrate that the inclusion of dipole-dipole intermolecular correlations has a significant effect on calculations of the electronic properties of organic amorphous thin films. In particular, the presence of the dipoles leads to a broadening of the electronic density of states in the films, which affects the carrier mobility and other transport characteristics of the materials. In this talk, we will discuss both experimentally and analytically the effects that dipolar correlations have on the performance of organic light emitting devices.

[1] V. Bulovic, A. Shoustikov, M.A. Baldo, E. Bose, V.G. Kozlov, M.E. Thompson and S.R. Forrest, Chem. Phys. Lett., 287, 455 (1998).

#### BB3.3

**THEORETICAL FUNDAMENTATION OF THE LUMINESCENCE EFFECTS IN TRINUCLEAR SILVER ORGANOMETALLIC COMPOUNDS.** Roberto Salcedo, L. Enrique Sansores, Ana Martinez, Instituto de Investigaciones en Materiales, UNAM, Ciudad Universitaria, Coyoacan, Mexico D.F., MEXICO.

The trimeric organometallic compound [Ag(CH<sub>3</sub>NCOCH<sub>3</sub>)<sub>3</sub>] is solvoluminescent, to explain this phenomenon we have carried out theoretical calculations of the complex in gas phase and in solution at B3LYP level. Calculations about the presence of triplet states were also carried out by mean of configuration interaction schemes, an exciton was found in these calculations, the nature of the exciton is studied in order to found a fundamentation of the luminescence effect. Some features about the very symmetric molecule and the crystal package are also discussed.

#### BB3.4

**ABSORPTION AND LUMINESCENCE PROPERTIES OF OLIGOPHENYL AGGREGATES.** Sylke Blumstengel, Francesco Meinardi, Alessandro Borghesi, Riccardo Tubino, Univ of Milano-Bicocca, Dept of Materials Science and INFM, Milan, ITALY.

Photophysical properties of thin films of p-quaterphenyl (P4) and p-hexaphenyl (P6) grown by organic molecular beam deposition technique have been investigated. Depending on the deposition conditions, structure and morphology of the grown films can be modified which allows establishing a relationship between the supermolecular organization of the oligomer chains in the thin film and the resulting optical properties. Comparison with absorption and emission properties of the isolated molecules obtained by inclusion of P4 and P6 in a proper matrix as well as of nanoaggregates precipitated from solution lead us to the conclusion that excited state interactions strongly modify the electronic structure of oligophenyls in the solid state. The absorption and luminescence properties of oligophenyls in thin films and nanoaggregates will be discussed in the frame of the molecular exciton theory.

#### BB3.5

**A MODEL HAMILTONIAN FOR THE DESCRIPTION OF THE ELECTRONIC PROPERTIES OF OLIGOMERS AND POLYMERS.** H.T. Jonkman, S.C. Veenstra, R. Telesca, J. Snijders and G.A. Sawatzky, Material Science Center, University of Groningen, Groningen, THE NETHERLANDS.

A simple tight binding two band model Hamiltonian has been constructed, which gives an good description of the excited and

ionised state properties of oligomers such as PT, PPP and PPV. First principle estimates of the parameters were obtained from (time dependent) density functional calculations on the lower oligomers. We show that electron correlation plays an important role in these systems and that most of the optical spectral weight is carried by a Frenkel type singlet excitonic like state, the corresponding triplet excitons are even more tightly bound than the singlets.

**BB3.6**  
OPTOELECTRONIC JUNCTION DEVICES BASED ON ORGANIC/INORGANIC HETERO-PAIRED SEMICONDUCTORS. Raoul Schroeder, Bowling Green State Univ., Center for Materials Science, Dept of Physics and Astronomy, Bowling Green, OH and Virginia Tech, Dept of Physics, Blacksburg, VA; Bruno Ullrich, Bowling Green State Univ., Center for Materials Science, Dept of Physics and Astronomy, Bowling Green, OH.

The use of hybrid devices consisting of organic and inorganic semiconductors provides many advantages for optoelectronic applications, such as combining the high charge carrier mobilities in anorganic crystalline thin films and high photo-sensitivity, luminescence quantum yields, and ease of deposition of conjugated molecules. In this paper, thin film hybrid structures based on organic conjugated polymers and II-VI inorganic semiconductors were fabricated using spin-coating and pulsed laser deposition. A promising hetero-pairing is CdS and poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diy) (PF2/6) due to the electron carrier majority in the former and the higher hole mobility in the latter with the potential to form p-n junctions. Varying the deposition techniques alters the quality of the interface between CdS and PF2/6 and results in different efficiencies of charge collection and recombination in the device. The charge carrier dynamics were studied using modulated photocurrent measurements and the electron-hole pair separation was monitored by detecting the photoluminescence excited by single photon absorption, as well as two-photon absorption by means of cw and femtosecond lasers, respectively.

**BB3.7**  
RESONANT TUNNELING AND THE SUBSTITUENT EFFECT ON NEGATIVE DIFFERENTIAL RESISTANCE IN A MOLECULAR JUNCTION. Nikita Matsunaga, Department of Chemistry and Biochemistry, Long Island University, Brooklyn, NY; and Karl Sohlberg, Department of Chemistry, Drexel University, Philadelphia, PA.

Recently there has been an explosion of interest in the potential use of individual molecules as electronic device elements. The electrical characteristics of molecular junctions, individual molecules spanning the gap between two metal electrodes, have been reported and certain molecular species have been found to exhibit highly nonlinear current versus applied-voltage ( $I/V$ ) properties. Intriguingly, these nonlinearities (pronounced peaks) in the  $I/V$  behavior are extremely sensitive to the functionalization of the molecule forming the junction. The substitution of a single functional group can completely eliminate the nonlinear behavior. Many have suggested that resonant tunneling could lead to the observed nonlinearities. Resonant tunneling requires a double potential barrier along the electron transfer coordinate. We propose a possible physical origin for such a double potential barrier and support the model with first principles electronic structure calculations. Next we apply a quantum mechanical tunneling model for electron transport through the double potential barrier. The model not only gives insight into the origin of nonlinear  $I/V$  behavior in molecular junctions, but also explains the effect of substituent functional groups on the junction molecule.

**BB3.8**  
THEORETICAL APPROACH TO DYNAMICS AND FUNCTION OF MOLECULAR SYSTEMS. Thomas Frauenheim, Thomas Niehaus, Marcus Elstner, Gotthard Seifert University of Paderborn, GERMANY; Aldo Di Carlo, Jörg Widany, Marieta Gheorghie, Paolo Lugli, University Tor Vergata, Rome, ITALY.

Here we show how a density-functional based method (DFTB) can contribute to the understanding of large-scale organic materials. Recent theoretical developments are presented which allow to efficiently calculate excited state properties (1), examine laser induced ultrafast dynamics (2) and predict tunneling currents (3). (1) We calculated the optical spectra of several oligothiophenes. Results show that the absorption maximum may be tailored via changes in chainlength and chemical substitution. Furthermore the experimentally found enhancement of photoluminescence efficiency via inter-ring bridging is examined. (2) Interaction of molecules with fs-laserpulses leads to coherent vibrational excitation. Our simulations show a strong mode selectivity for high intensity pulses and illustrate the interplay between displacive and Raman-type excitation mechanisms. (3) We have developed a simulation tool to study the current transport in molecular structures. In our approach the system

is described via DFTB while boundary conditions to account for current carrying states are accounted via Green function techniques. Thermal average of transport properties are obtained by performing Molecular Dynamics simulations. The developed tool has been applied to nanotubes, DNA and organic/inorganic heterojunctions.

**BB3.9**  
PHOTOSENSITIZED REACTION OF POLY(L-LACTIC ACID) VIA TWO-PHOTON IONIZATION OF DOPANT. Wataru Sakai, Kosuke Wakabayashi, Hiroshi Nishinaka, Hiroki Kawamoto, Motoi Kinoshita, Naoto Tsutsumi, Dept of Polymer Science & Engineering, Kyoto Institute of Technology, Kyoto, JAPAN.

To understand the role of electron in the matrix polymer is not only of fundamental interest, but also is critically important to polymer application. We here studied the photosensitized reaction of poly(L-lactic acid) (PLA) via an anionic reaction process using spectrophotometry, ESR, GPC measurements, and semiempirical molecular orbital calculation. PLA film doped with TMPD was irradiated at 77 K using UV light. The light cannot directly excite PLA matrix itself. After that, we observed a new broad absorption band over the original spectrum. The signal was due to  $\text{TMPD}^{\bullet+}$  which was produced by the two-photon ionization. The ESR spectrum of the irradiated sample also indicated the presence of the  $\text{TMPD}^{\bullet+}$  and, furthermore, main chain scission radical of PLA. During the thermal annealing at 0°C, the latter radical changed to another radical species by dehydrogenation of the  $\alpha$ -hydrogen of PLA main chain.  $\text{TMPD}^{\bullet+}$  was extremely stable at room temperature for several days. However, by thermal annealing at 40°C, all the radicals decayed due to the enhanced molecular motions near  $T_g$  of PLA (58.7°C). Spectral simulation for the obtained ESR spectra revealed the relative amounts. Quantitative changes of radicals were compared. GPC measurements clearly indicated a decrease in the molecular weight of PLA after irradiation. The semiempirical molecular orbital calculation was used to compare the relative differences of activation energies for several different reaction processes.

**BB3.10**  
AB INITIO STUDY ON VIBRATIONAL ANHARMONIC COUPLING EFFECTS IN OLIGO(PARA-PHENYLENES). G. Heime<sup>a</sup>, D. Somitsch<sup>b</sup>, P. Knoll<sup>b</sup> and E. Zojer<sup>a</sup>; <sup>a</sup>Inst. of Solid State Physics, Graz University of Technology, Graz, AUSTRIA; <sup>b</sup>Inst. for Experimental Physics, University of Graz, Graz, AUSTRIA.

In this study we present a theoretical approach to simulate vibrational anharmonic coupling effects seen in the Raman spectra of oligo(*para-phenylenes*). Quantum chemical ab initio methods are applied to determine third order force constants and energy corrections on the vibrational frequencies of the isolated molecules. Semiempirical methods are applied to compute Raman intensities of fundamentals and combination bands. This methodology is then used to characterize the previously unassigned Fermi resonance in oligo(*para-phenylenes*) around 1600 $\text{cm}^{-1}$ . The precise origin of this Fermi dyad is deduced from a similar phenomenon in benzene with the help of a detailed normal coordinate analysis. A quantitative explanation for the energetic positions and the intensities of the two components of the Fermi dyad is given. The evolution of this quantum mechanical resonance with oligomer length is described. Our predictions compare well to experimental Raman spectra measured for the series of oligo(*para-phenylenes*) containing two to six phenyl rings. We show that this Fermi doublet is extremely sensitive on chemical modifications such as deuteration or substitution. Furthermore it yields information on the structural conformation of this class of molecules. It can also be used to characterize excited states of the molecules as well as charged species.

**BB3.11**  
SIMULATION OF CHIRALLY-INDUCED EXCITONIC OPTICAL EFFECTS IN BISCYANINE DYE WITH SHIFF BASE (OPTICAL AND MOLECULAR STRUCTURE SIMULATIONS). C. Andraud, Ecole Normale Supérieure de Lyon, Lyon, FRANCE; K.J. Plucinski, Mil. Univ. of Technology, Warsaw, POLAND; I.V. Kityk, Institute of Physics, WSP Czestochowa, POLAND.

Since the discovery of chirally-induced optical effects [1], there have been various studies carried out into the optical properties of chiral molecules. Up till now interpretation of optical properties has been based on non-empirical coupled oscillator and group polarizability approaches. Molecular dynamics geometry optimization have not normally been carried out, and for this reason, such a relevant parameter as molecular geometry has not been adequately taken into account. There have also been no investigations focusing on a self-consistent quantum chemical description of the phenomena observed. The main goals of the present paper are: - to investigate the influence of particular molecular parameters on the optical spectra; - to determine the dependence of the exciton splitting on p-conjugated bond length and charges of particular chromophore groups. An earlier

semi-empirical theoretical study [2] established that circular dichroism (CD) and rotational strength (RS) are sensitive to the  $p$ -conjugated length, distance between the chromophores, and to the inter-chromophore angle. Traditional methods for quantum chemical calculation of electronic properties for such molecules are predominantly based on semi-empirical approaches fitted by experimental RS. We applied restricted Hartree-Fock (RHF) and density functional theory (DFT) models to carry out structural geometry optimization and simulation of space dispersion optical effects. For our investigations, we chose biscyanine dye with a Schiff base (BDSB) molecule [2]. The BDSB family has received considerable attention due to the possibility of varying cationic substitution, together with stereochemistry variation. These parameters determine biexciton coupling. Comparison of theoretical and experimental results for biscyanine dye with a Schiff base showed a sufficiently good level of agreement. We found that the DFT approach gives substantially better agreement than the RHF. We have found that the molecules investigated may be used as effective chromophores of laser irradiation. The quantum efficiency of these molecules was at least one order higher than that of well-known tetrathiafulvalene. We decided to prepare the film in a form of oriented materials which have aligned chemical bonds. These bonds are photodestructed and may be involved in a creation of the typically new quantum electronics devices.

#### References:

1. E.U. Condon, Rev.Mod.Phys., 9, 432 (1937); E.U. Condon, W. Altar, and H. Eyring, J.Chem.Phys., 5, 753 (1937).
2. N. Berova and K. Nakanishi, in Circular Dichroism: Principles and Applications, Second Edition, Ed. by N. Berova, K. Nakanishi, and R.W. Woody, John Wiley & Sons, 2000, p. 337.

#### BB3.12

A COMPUTATIONAL INVESTIGATION OF CONJUGATED ORGANICS FOR ELECTRONICS NEAR THE SINGLE MOLECULE SCALE. Ari B. Silver and Karl Sohlberg, Department of Chemistry, Drexel University, Philadelphia, PA.

In the search for higher transistor densities in electronic components, a significant advance could be achieved by employing individual molecules as device elements. Conjugated molecules have been identified as strong potential candidates for single molecule electronic devices. For example, thin films of the conjugated species, 1-cyano-3-phenyl urea (PUN), exhibit an electrical conductance change that may be manipulated on the sub-nanometer scale, which is near the single molecule level [App. Phys. Lett. **73**, 3303, (1998)]. It has been proposed, based on experimental infrared absorbance spectra, that this conductance change results from polymerization in the film via an opening of the C≡N bond. A significant shift is observed in the C≡N stretching frequency coincident with the conductance change. We have conducted a computational investigation of the structure and energetics for PUN monomer and  $n$ -mer species. An extensive conformational search was carried out using a novel search procedure to identify the energetically preferred forms of the monomer and dimer. Subsequent calculations based on these structures indicate that the vibrational frequency of the nitrile group drops by approximately 200 wave numbers upon polymerization, consistent with the experimental values and confirming the polymerization mechanism.

#### BB3.13

THIN FILM STUDIES OF CONDUCTING POLYMERS ON MANGANITE OXIDE SUBSTRATES. Mchele Sumstine, Robert Carpick, Mark Rzechowski, Lei Wang, Michael Winokur, University of Wisconsin, Depts. of Physics and Engineering Physics, Madison, WI.

Spin-polarized injection of carriers into conducting polymers is a new and promising approach for improving luminescence by tailoring the carriers spin states. The feasibility of using thin LaCaMnO<sub>3</sub> and LaSrMnO<sub>3</sub> magnetic oxide surfaces as a source for spin polarized hole injection into organic thin films is investigated. Thin films of both  $\sigma$  and  $\pi$  conjugated polymers [polydiakylsilanes and poly(2-methoxy, 5-(2/ethyl)-hexyloxy- $p$ -phenylene), 2MEH-PPV, respectively] have been prepared by spin coating on both oxide and silicon wafer substrates. The optical properties of the polymer films have been characterized by photoluminescence and UV-vis absorption. The surface morphology and structure are characterized with atomic force microscopy. LED devices have been fabricated and the electroluminescence monitored.

#### BB3.14

EFFECT OF THERMAL DISORDER ON ELECTRON-PHONON COUPLING IN POLY( $P$ -PHENYLENE VINYLENE). C.A.M. Borges, A. Marletta, R.M. Faria and F.E.G. Guimarães, Universidade de São Paulo, Instituto de Física de São Carlos, São Carlos, São Carlos, BRAZIL.

We studied experimentally and theoretically the dependence of

temperature on electron-phonon coupling in the emission spectra of poly( $p$ -phenylene vinylene), PPV. The PPV films were prepared joining a novel self-assembly methodology and a low temperature conversion process. The main advantage of this SA procedure is that thermal conversion may be performed at considerably lower temperatures (80-100 °C) in a few minutes, producing high conjugated PPV films with incredibly sharp and well-resolved vibronic structures in the photoluminescence. Site selective luminescence spectroscopy was employed to better resolve the fine structures of different vibrational modes. Using Franck-Condon analysis, the experimental vibronic progressions of PPV can be well described through three effective, inhomogeneous broadened vibrational modes with energies at 330, 1163 and 1550 cm<sup>-1</sup>. As the temperature increases the electron-phonon coupling for the 1550 cm<sup>-1</sup> mode remains constant while, for the other two modes, the coupling increases. This trend is consistent with the result that high-energy vibrational modes are strongly localized with respect to the size of the effective conjugation length and, therefore, less sensitive to the thermal disorder.

#### BB3.15

LIGHT-INDUCED DEEP GAP STATES IN ORGANIC POLYMER LIGHT EMITTING MATERIALS. Shu-Jen Lee<sup>1,2</sup>, Carleton H. Seager<sup>3</sup>, Yongtaek Hong<sup>1</sup>, and Jerzy Kanicki<sup>1</sup>. <sup>1</sup>Solid-State Electronics Laboratory, Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, MI; <sup>2</sup>Macromolecular Science and Engineering Program, University of Michigan, Ann Arbor, MI. <sup>3</sup>Sandia National Laboratories, Albuquerque, NM.

Light-induced deep gap states could lead to the decrease in the quantum efficiency of the organic polymer light-emitting devices (OP-LEDs). We have used combination of the light-induced electron spin resonance (LESr) and the photo-thermal deflection spectroscopy (PDS) to study the nature of the point defects (deep gap states) in the fluorene based co-polymers before, during and after UV-illumination. We have found that both the LESr and PDS signals (at low photon energies) increased with the increasing UV-illumination time. We have observed that the light induced spin density increased from  $\sim 1.50 \times 10^{15}$  to  $\sim 1.16 \times 10^{16}$  spin/gr after 30 minutes of UV-illumination. While the  $g$ -value ( $g \sim 2.004$ ) and the peak-to-peak width ( $\Delta H_{pp}$ ) did not change significantly with the UV-illumination. The polymer absorption coefficients deduced from PDS spectrum at  $\lambda = 1000$  nm have also increased from  $\sim 9$  to  $\sim 11$  cm<sup>-1</sup> after 30 minutes of UV-illumination. The results indicate that both the increase in the sub-band gap absorption (measured by PDS) and electron spin resonance has the same origin. We think that the deep gap states are due to carbon radicals induced by UV-illumination. We have further investigated the time evolution of the photo-luminescence (PL) spectra with UV-illumination and established that the PL peak intensity decreased to  $\sim 10\%$  of its initial dark peak intensity value after 30 minutes of UV-illumination. This result strongly suggests that the light-induced deep gap states, e.g. carbon radicals, are the non-radiative recombination centers, which are responsible for photoluminescence quenching.

#### BB3.16

TIME-RESOLVED SPECTRAL MEASUREMENT OF DENDRIMER MOLECULAR FILMS WITH A RHODAMINE B CORE. Minniu Zhou, Akira Otomo, Shiyoshi Yokoyama, Shinro Mashiko, Kansai Advanced Research Center, Communications Research Laboratory, JAPAN.

Toward the development of new optical functional device, organic materials have attracted increasing amount of attentions in recent years. We have focused our attention on molecular thin films fabricated using novel organic materials such as dendrimer with various types of dye core. In this report, the photon energy transfer caused by the interaction of dendrimer molecules, has been measured as a term of absorbance. A pump-probe measurement was carried out for a ultrafast time-resolved spectroscopy with a time resolution of approximately 100 fs. The wavelength of the pump light was 550 nm and a white continuum light spanning from 450 nm to 750 nm was used as a probe light. A spin-coated molecular film made of a Rhodamine B cored dendrimer (molecular weight was 4,885) has a relatively high molecular-number density of  $6.68 \times 10^{14}$  (mol/cm<sup>-2</sup>). A strong stimulated emission at a wavelength 612 nm was measured and a fast decay is assumed as caused by intermolecular action between Rhodamine B cored molecules. The detail of the fast decay is under investigation. The lifetime of the excited state was measured to be as small as approximately 10 ps, it would be possible to be fabricated as a high repetition-rate optical functional element. We will compare several types of molecular films with different molecular densities, and will discuss about the transfer efficiency of the photon energy.

#### BB3.17

NEAR-FIELD PHOTOCONDUCTIVITY AND FLUORESCENCE IMAGING ON BLENDS OF CONJUGATED POLYMERS. R. Riehn,

R. Stevenson, J.J.M. Halls, Cavendish Lab, University of Cambridge, Cambridge, UNITED KINGDOM; D.-J. Kang, Dept of Materials Science, University of Cambridge, Cambridge, UNITED KINGDOM; D.R. Richards, Dept of Physics, Kings College London, London, UNITED KINGDOM; F. Cacialli, Dept of Physics and Astronomy, University College London, London, UNITED KINGDOM.

We report simultaneous photoconductivity and fluorescence imaging in thin films of phase-separated conjugated polymer blends on silica substrates. We used polyfluorene-based polymers and a near-field optical probe at 488 nm for excitation. For this we employed a SNOM system which we have especially designed for reliably locating and observing small features embedded in large samples. The near-field probes were etched optical fibres, coated with a 100 nm thick Al film, having apertures obtained by focused ion beam (FIB) milling. Measurements were carried out at field strengths up to 12 kV/cm. The field was applied between gold electrodes thermally evaporated on top of the polymer film, and spaced approximately 150 micrometers. The chosen wavelength excites only one of the phase-separated polymers, thus leading to high photoconductivity and photoluminescence in areas rich in that polymer. We find good correlation of topographic, photoluminescence and photoconductivity images.

### **BB3.18**

**SINGLE MOLECULE STUDIES OF INTERFACIAL ELECTRON TRANSFER.** Michael W. Holman, Benjamin J. Gross, David M. Adams, Columbia University, Department of Chemistry, New York, NY.

The near-field scanning optical microscope (NSOM) enables us to study single molecules in the spatial, energetic, and temporal domains: we can determine the three-dimensional orientation of single molecules, collect fluorescence spectra, and observe how fluorescence intensity varies with time. It is thus possible to use fluorescence to study the kinetics of electron transfer from a single molecule to a metal or semiconductor electrode in an applied electric field, and to relate this process to molecular orientation and dynamics and to the electronic structure of the molecule. Understanding these effects on electron transfer will be important for understanding and designing molecular electronic devices. Towards this end, single molecules of a perylene dye on glass have been investigated with the NSOM; these results, along models for future experiments, are presented here.

### **BB3.19**

**NEAR FIELD SCANNING OPTICAL MICROSCOPY (NSOM) OF ENERGY TRANSFER AND EXCITON/POLARON INTERACTIONS IN MOLECULAR CRYSTALS.** Zhonghua Yu, Jason McNeill, Doo Young Kim, Paul Barbara, University of Texas, Austin, TX.

NSOM is used to locally excite single crystals of organic molecular materials including pentacene and tetracene. Far field imaging using energy transfer to an emitting layer and a triplet detector monitors the spatial extent of triplet energy transfer. Other experiments using a biased NSOM tip monitor exciton/polaron interactions using the field-induced fluorescence modulation technique developed by the authors. Related experiments using ultrafast pulses will also be described.

We gratefully acknowledge the National Science Foundation for support of our research.

### **BB3.20**

**SURFACE POTENTIAL IMAGING OF ORGANIC THIN FILMS ON METALS IN VACUUM.** Kei Kobayashi, International Innovation Center, Kyoto University, Kyoto, JAPAN; Keiichi Umeda, Kenji Ishida, Toshihisa Horiuchi, Hirofumi Yamada, Kazumi Matsushige, Department of Electronic Science and Engineering, Kyoto University, Kyoto, JAPAN; Shu Hotta, Advanced Technology Research Laboratories, Matsushita Electric Industrial Co., Ltd., Kawasaki, JAPAN.

Organic thin films on metals have recently attracted widespread interests in terms of molecular electronics. However, the electronic structures of the molecules on metallic substrates have not been well understood. So that we are studying electronic properties of organic thin films on metallic substrates by using Kelvin Force Microscopy (KFM). In this study, surface potential (SP) of organic thin films on metallic substrates was mapped two-dimensionally by KFM. We operated KFM both in an ambient condition and in a vacuum environment and we irradiates the samples with UV light while acquiring SP images. Moreover, we investigated the dependence of the photoinduced SP on the wavelength of UV light. Thus we could obtain information on the electronic properties such as charge transfer or induced dipole at the interface between the organic thin films and the metallic substrates. The molecules we used was oligothiophene molecule, dimethylequinqueithiophene (DM5T). The molecule shows various unique electrical and optical properties due to their

$\pi$ -conjugated systems where the electrons are delocalized inside the individual molecules. Monolayer films and films with a few molecular layers was prepared on metallic substrates by a vacuum deposition method. The SP of a DM5T island on the Pt substrate appeared higher than the substrate while that on the Ta substrate appeared lower than the Ta substrate. The polarity of the SP of DM5T islands depended on the work function of the substrate metals. However, when we irradiated the samples with UV light, SP of DM5T islands became lower than before for both films. Furthermore, when we irradiated the samples with UV light with the wavelength of 400 nm, the SP abruptly became lower than before for both films.

### **BB3.21**

**IMPROVEMENT OF POWER EFFICIENCY IN ORGANIC ELECTROLUMINESCENT DEVICES.** Chimed Ganzorig, Masamichi Fujihira, Tokyo Institute of Technology, Dept of Biomolecular Engineering, Yokohama, JAPAN.

In order to improve power efficiency of organic electroluminescent (EL) devices, i.e., ITO/HTL/ETL/M, enhanced electron and hole injection at ETL/M and ITO/HTL interface, respectively, was attempted by designing proper charge injection at these interfaces. Here, ITO, HTL, ETL, and M are abbreviations for indium-tin-oxide, hole transport layer, electron transport layer, and Al cathode. Enhanced electron injection by introducing a thin layer of Li salts of fluoride, acetate, and benzoate between the Al and tris(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>) ETL was described. We found that Li benzoate exhibited the best device performance of all the electron-injection materials studied. We also described the effect of alkali metal acetates and found that the electron injection was enhanced in the order of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> and Cs salt was the best EL performance. The devices based on a bare ITO usually exhibited inefficient hole injection due to insufficient high work function and required high drive voltages. Thus, chemical modification of ITO surfaces has been attempted to tuning the work function of the ITO in order to reduce hole injection barrier height. We have demonstrated the EL characteristics of the devices with ITO chemically modified with H-, Cl-, and CF<sub>3</sub>-terminated benzoyl chlorides. By using of reactive -COCl groups, ITO surfaces were covered quickly and work function of ITO changed widely depending upon permanent dipole moments introduced in  $\rho$ -position of benzoyl chloride. Correlation between change in the work function of ITO and EL characteristics was examined. Possible working mechanisms for reducing the drive voltages and increasing EL efficiency by enhanced charge injection at interfaces have been discussed in detail.

### **BB3.22**

**CHEMICAL MODIFICATION OF INDIUM TIN OXIDE ELECTRODES BY SURFACE MOLECULAR DESIGN.** Chimed Ganzorig, Yuukou Matsuda and Masamichi Fujihira, Tokyo Institute of Technology, Department of Biomolecular Engineering, Yokohama, JAPAN.

Indium-tin-oxide (ITO) is the most widely used material as a transparent electrode due to its excellent transparency and high conductivity. The devices based on a bare ITO, however, exhibited inefficient hole injection due to insufficient high work function and required high drive voltages. Thus, various surface treatments of ITO have been attempted to change the work function of ITO in order to reduce the hole injection barrier height. EL characteristics of devices were improved dramatically using ITO chemically modified with H-, Cl-, and CF<sub>3</sub>-terminated benzoyl chlorides. By the use of reactive -COCl groups, ITO surfaces were modified quickly and the work function of the modified ITO was changed widely depending upon the permanent dipole moments introduced in  $\rho$ -position of benzoyl chloride. We also compared the performance of the EL devices with ITO modified with different binding groups (-SO<sub>2</sub>Cl, -COCl, and -PO<sub>2</sub>Cl<sub>2</sub>) of  $\rho$ -chlorobenzene derivatives. Finally, we examined the correlation between the change in the work function and the performance of the EL devices by the chemical modification and found that the enormous increase in ITO work function up to 0.9 eV is possible using phenylphosphoryl dichloride with a CF<sub>3</sub>-terminal group in  $\rho$ -position.

### **BB3.23**

**ENERGY LEVEL ALIGNMENT AT METAL/CuPc AND CuPc/METAL INTERFACES INVESTIGATED BY PHOTOEMISSION SPECTROSCOPY.** Li Yan, Univ of Rochester, Dept of Physics and Astronomy, Rochester, NY; C.W. Tang, Eastman Kodak, Co. Rochester, NY; N.J. Watkins, S. Zorba and Yongli Gao, Univ of Rochester, Dept of Physics and Astronomy, Rochester, NY.

We have investigated the electronic structure and chemistry of interfaces formed between copper phthalocyanine (CuPc) and Au or Cs using x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS). Both metal/CuPc and CuPc/metal interfaces are formed by a layer-by-layer approach with the spectra taken at selected steps to

monitor the energy level changes during the processes. Charge transfer is observed in both Cs/CuPc and CuPc/Cs interfaces, illustrated by the formation of a new feature in the previously forbidden energy gap. In these interfaces, the highest occupied molecular orbital (HOMO) and other molecular orbitals of CuPc shift about 1 eV to the lower kinetic energy. As a result, the lowest unoccupied molecular orbital (LUMO) of CuPc is pinned at the Fermi level, which is observed directly with inverse photoemission spectroscopy (IPES). The electron injection barrier at the interface is estimated to be less than 0.2 eV. These results can explain the observed electron injection enhancement when a CuPc layer doped with a group IA metal is inserted between the cathode and the active organic material. In the Au/CuPc and CuPc/Au interfaces, neither charge transfer nor chemical reaction is observed during the interface formation. We estimate that a significant electron injection barrier of about 0.9 eV exist at the interfaces.

#### **BB3.24**

**EFFECTS OF SURFACE MORPHOLOGY OF THE ITO THIN FILM ON THE INSTABILITY OF ORGANIC LIGHT EMITTING DIODE.** Ki-Beom Kim, Jae-Hoon Jung and Hyung-Guen Park, OEL Development Gr., PDP Division, LG Electronics, Kyungbuk, KOREA; Kwang-Ho Lee and Jong-Lam Lee, Dept. of Material Science and Engineering, POSTECH, Pohang, Kyungbuk, KOREA.

Organic light emitting devices (OLEDs) receive considerable attention due to highly attractive low-cost and large area displays. But, the weak point in the commercialization is the short lifetime of OLED. It was reported that uneven surface morphology of indium-tin-oxide (ITO) provides the reason of point defect and the decrease of brightness. In this work, the relationship between surface roughness of ITO and electrical characteristic of OLED was systematically examined to clarify the effect of surface roughness of ITO electrode on the driving characteristics of OLED. Several types of ITO substrates with different surface morphology were prepared. The surface roughness of ITO was measured using atomic force microscope (AFM), and the existence of spike was checked. The OLED devices were fabricated on those substrates and their electro-optical properties were measured by I-V-L system. The number of dark spot was counted before and after the I-V-L measurements. The increase in the number of dark spot on ITO electrode by the electrical stress was counted. The forward I-V characteristics of OLED were independent of the peak-to-valley roughness (Rpv), but the reverse leakage current was increased with the increase of Rpv. After electrical stressing for 1000 hrs under the forward bias, a number of dark spots were produced at the vicinity of the spike. The chemical analysis using electron dispersive spectroscopy showed that the spot is mainly composed of indium atoms. From these results, degradation mechanism of OLED is discussed.

#### **BB3.25**

**INTERACTION AT ORGANIC/METAL INTERFACES STUDIED BY ELECTRON SPECTROSCOPIES AND OTHER TECHNIQUES.** Hisao Ishii, Takahiro Yokoyama, Yoko Sakurai, Noritaka Mitsuie, Yukio Ouchi, Nagoya Univ, Graduate School of Science, Nagoya, JAPAN; Eisuke Ito, Institute for Physical and Chemical Research, Wako, JAPAN; Tohru Araki, Saitama Univ, Faculty of Science, Saitama, JAPAN; Kazunori Umishita, Kazuhiko Seki, Nagoya Univ, Research Center for Materials Science, Nagoya, JAPAN.

Interfaces between a functional-organic material and an electrode often play an important role in organic devices. Especially, cathode metals with low work function often induce reactive interfaces with organic layer. For example, charge transfer nature was reported at K-Alq<sub>3</sub> interface, while "destructive interaction" was proposed at Al-Alq<sub>3</sub> system [1]. Such reactive interfaces have been investigated mainly by photoemission spectroscopy and the nature of the interaction at the interface is not yet well understood. To clarify this point, the combined measurements with other techniques are highly desired. In this study, reactive organic-metal mixed system such as K-sexiphenyl(6P), K-fullerene, K-Alq<sub>3</sub>, Al-Alq<sub>3</sub>, and Ca-TPD were investigated by UV photoemission spectroscopy (UPS), X-ray photoemission spectroscopy (XPS), and metastable atom electron spectroscopy (MAES). For K-mixed systems, new state appeared above the original highest occupied molecular orbital (HOMO) of the organic materials as other alkaline metal-organic systems reported in literatures. For Al-Alq<sub>3</sub> and Ca-TPD systems, in addition to the emergence of new state, spectral broadening of the whole region of the UPS was observed as reported for Al-Alq<sub>3</sub> interface in ref.1. For K-Alq<sub>3</sub> and Al-Alq<sub>3</sub>, X-ray absorption spectroscopy (NEXAFS) and infrared reflection absorption spectroscopy (IRAS) were also performed to get further information on the interfaces. The former probes unoccupied state of the interface, and the latter can give information on the change of the molecular structure. In the conference, we will report the detailed results and discuss the interaction at such metal-organic system.

[1] G. Mason et.al., J. Appl. Phys., vol.89, 2756, (2001).

#### **BB3.26**

**NANO-STRUCTURE CONTROL OF CATHODE BUFFER-LAYERS AND LUMINESCENT PROPERTIES OF ORGANIC ELECTROLUMINESCENT DEVICE.** Kazunari Shinbo, Eigo Sakai, Futao Kaneko, Keizo Kato, Takahiro Kawakami, Niigata Univ, Dept of Electrical and Electronic Engineering, Niigata, JAPAN; and Toyoyasu Tadokoro, Nippon Seiki Co., Ltd., Nagaoka, JAPAN.

Recently, it is well known that buffer layers, that is, electron and/or hole injection layers are very useful for improving characteristics of organic light emitting diodes (OLEDs). In this study, OLEDs with cathode buffer layers of nano-meter thicknesses were fabricated and the electrical and luminescent properties were observed. The OLEDs have structures of ITO anode / CuPc (20 nm) / TPD (70 nm) / Alq<sub>3</sub> (70 nm) / cathode buffer-layer / Al cathode (150 nm). CuPc layers were deposited as anode buffer-layers. Bilayers of aluminum and Alq<sub>3</sub> thin films were deposited on the Alq<sub>3</sub> emitting layer as the cathode buffer-layers. All the films on ITO electrodes were deposited sequentially without exposure to air. The current vs. voltage (I-V) characteristics of the devices were improved with inserting one bilayer of Al and Alq<sub>3</sub> as the cathode buffer-layer. The thickness of the Al film for the buffer-layer was varied from 0.35 to 1.40 nm, while that of the Alq<sub>3</sub> layer was constant 0.35 nm. It was considered that there was an optimum thickness for the Al layer. Electroluminescences from Alq<sub>3</sub> were observed for all the fabricated devices. The luminances of the devices with buffer-layers were also larger than those of the device without the layers and the luminance depends on the thickness of the Al layer. The changes of the characteristics were considered to be due to modulation of barrier at the interface between the Alq<sub>3</sub> layer and the Al cathode. Moreover, stabilities were improved for the devices with several bilayers of the buffer-layer. The buffer-layers fabricated in this study are very useful for improving the OLEDs.

#### **BB3.27**

**CONTROLLED INJECTION OF HOLES INTO Alq<sub>3</sub>-BASED OLEDs BY MEANS OF AN OXIDIZED TRANSPORT LAYER.** Mathew Mathai, Keith Higginson, Fotios Papadimitrakopoulos\*, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT; Bing Hsieh, Canon R&D Center Americas, Inc., San Jose, CA.

Improved lifetimes in excess of 5000 hours of stable operation have been achieved by minimizing the intrinsic degradation mechanism due to the presence of excess holes in Alq<sub>3</sub> based Organic Light Emitting Diodes (OLEDs). This is achieved by modifying the ITO anode with an oxidized transport layer (OTL) comprising a hole transporting polycarbonate (PC-TPB-DEG) doped with various concentrations of antimonium hexafluoride salt of N,N,N',N'-tetra-p-tolyl-4,4'-biphenyldiamine (TMTPD<sup>+</sup> SbF<sub>6</sub><sup>-</sup>). The variation in the conductivity of the OTL allows the controlled injection of just enough holes into the Alq<sub>3</sub> layer in order to form excitons and thus prevent the formation of device degrading cationic species of Alq<sub>3</sub>. This is in contrast to the use of hole blocking layers, which do not afford such controlled hole injection. The stable operating characteristics of these devices clearly indicates the improved lifetimes of the device with optimized hole injection. The presence of the OTL also provides passivation of ITO surface and its planarization. The analysis of hole and electron current variations in these devices is discussed.

#### **BB3.28**

**STM AND STS INVESTIGATION OF ULTRATHIN COPPER PHTHALOCYANINE LAYERS DEPOSITED ON Au(111).** M.S. Xu, J.B. Xu, K. Xue, J.Z. He, I.H. Wilson, Dept of Electronic Engineering, Material Science and Technology Research Centre, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, P.R. CHINA.

Copper phthalocyanine (CuPc) buffer layers built in organic light-emitting diodes greatly improve the device properties. But the underlying charge injection and transport in CuPc are still unclear. CuPc ultrathin films deposited on Au(111) surface were investigated by scanning tunneling microscopy (STM) and spectroscopy (STS). The molecular resolution STM images reveal that the CuPc molecules form highly ordered films and various domains are clearly observed. From STS, the charge injection into the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of CuPc allows us to determine the energy band gap at appropriate tunneling parameters. The measured band gap value of approximate 2.0 eV are compared to those by optical absorption measurements. The effect of tunneling resistance on STS will also be discussed.

#### **BB3.29**

**MULTI-LAYER CONTACTS FOR ORGANIC LIGHT-EMITTING DIODES WITH ENHANCED INJECTION EFFICIENCY.** Ludmila Bakueva, Sergei Musikhin, Edward H. Sargent, Alexander Shik, University of Toronto, Dept of Electrical and Computer Engineering, Toronto, Ontario, CANADA.

A low level of electron injection is one of the major obstacles to achieving high-efficiency organic light-emitting diodes (OLED). To improve the injection characteristics, multi-layer contacts for OLED containing tunnel-transparent dielectric layer of nanometer thickness were fabricated and investigated. The voltage drop at this layer shifts the metal Fermi level relative to the polymer molecular orbitals responsible for the carrier transport, increasing noticeably the injection efficiency. To investigate this phenomenon more thoroughly, two different polymers, PPV and CN-PPP, having different HOMO-LUMO gaps and different dielectrics, particularly,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , LiF, were employed. Polymer layers were prepared by the spin-coating method and dielectric and metallic contact layers grown by vacuum deposition. Both n- and p-injecting contacts characterised by different parameters and metal material were investigated. The introduction of a suitably-chosen dielectric layer results in an increase in the injection efficiency by up to a factor of several tens. Recently, a similar phenomenon has been observed in another polymer with CsF dielectric film and attributed to the Cs doping [1]. Our results show that the effect has a universal character connected with the engineering of tunnelling injection with the adequate explanation mentioned above.

Further sophistication of the injecting contacts consists in creating additional intermediate thin metallic layer playing the role of the third, base electrode, similar to hot-electron transistors with metallic base [2]. Additional bias applied to the base electrode permits variable injection efficiency and quantum yield over a wide range.

1. P. Piroreun et al - Appl. Phys. Lett. 77, 2403 (2000).
2. J. Lindmayer. - Proc. IEEE 52, 1751 (1964).

### **BB3.30**

**EFFECTS OF SURFACE TREATMENT OF ITO THIN FILM ON THE ELECTRICAL PROPERTIES OF ORGANIC LIGHT EMITTING DIODE.** Kwang-Ho Lee, Dept of Material Science and Engineering, POSTECH, Pohang, Kyungbuk, KOREA; Ki-Beom Kim, Jae-Hoon Jung and Hyoung-Guen Park, LG Electronics, OLED Development Gr., PDP Division, Kumi, KOREA; Jong-Lam Lee, POSTECH, Dept of Material Science and Engineering, Pohang, Kyungbuk, KOREA.

Organic light emitting devices (OLEDs) receive considerable attention due to highly attractive low-cost and large area displays. The surface treatments of ITO using UV exposure followed by plasma treatment was effective in improving electrical properties of OLED device. For the plasma treatment, DC and RF power sources were used. Such plasma treatment could cause the production of defects on the surface of ITO. The plasma source of inductively coupled plasma (ICP) has advantages such as high density of plasma and low defect creation. No results have been reported on the effect of such ICP treatment on the improvement of electrical properties of OLED. The surface of ITO substrate was treated with ICP using several gases such as  $\text{O}_2$ ,  $\text{N}_2$ , and Ar before depositing organic layers. Flow rates of gases were 10 sccm and plasma power was changed from 50 to 200 W. The atomic composition and atomic binding energies of each bond were characterized with X-ray photoemission spectroscopy and the results were used to interpret the electrical properties of OLEDs. The forward I-V characteristics of OLED were dramatically improved with the surface treatment using  $\text{O}_2$  plasma. The forward bias corresponding to  $750 \text{ mA/cm}^2$  reduced to 10V by the treatment. The atomic ratio of Sn/In decreased by 18.3%, but that of O/In increased by 22%. The binding energies of Sn-O and In-O bonds were respectively increased by 0.5 and 0.4 eV. These results show that production of oxygen vacancies were enhanced by the treatment using the ICP treatment. From this, the mechanism in the improvement of OLED by the  $\text{O}_2$  ICP is proposed.

### **BB3.31**

**NEW EFFICIENT YELLOW-EMITTING DEVICES BASED ON A COPOLYMER DERIVATED FROM FLUORENE.** Sophie Panozzo, Yann Kervella, Jean-Claude Vial and Olivier Stéphan, Université Joseph Fourier and CNRS (UMR 5588), Spectrométrie Physique, Grenoble, FRANCE.

Poly(alkylfluorene)s are promising polymeric materials for light emitting diodes because of their high photoluminescence quantum efficiency and thermal stability. Nevertheless, it's now well established that in the solid state such materials exhibit changes in their structural and optical properties upon annealing or electrical excitation. This leads generally to an uncontrolled red-shifted fluorescence with reduced intensity by excitons migration and relaxation through excimers. We present here promising results using a new fluorene copolymer. In order to favour  $\pi$ -stacking, a fluorene monomeric unit bearing planar side group has been used, as co-monomer, with the more classical 9,9-di-n-nonylfluorene unit. As expected with fluorene-based material, when excited at 370 nm, the corresponding dilute copolymer solution photoluminescence spectra shows a peak centered at 450 nm (blue emission). However, in the

solid state, immediate organisation of the layer occurs leading to a red-shifted emission centered at 550 nm (yellow emission). As a result, it is noteworthy that OLEDs based on this new material exhibit no spectral evolution upon device operation. However, whereas the red-shift leads to a quenching of luminescence for regular poly(alkylfluorene), this leads in our case to higher photo- and electro-luminescence efficiency. Indeed, the luminescence quantum efficiency is twenty times greater for the copolymer than for the corresponding alkylfluorene homopolymer. Even for a low planar co-monomer content, i.e. 10% mol, the  $i(v)$  characteristics show an increase both in the efficiency of recombination of the carriers and in the quantum efficiency ( $1300 \text{ Cd/m}^2$  at 10 V bias).

### **BB3.32**

Abstract Withdrawn.

### **BB3.33**

**RED-EMITTING DEVICE USING CARBOXAMIDE-BIPYRIDINE RUTHENIUM (II) COMPLEXES.** Jessie Jouve, Jean-Claude Vial, Univ. J. Fourier, Spectrométrie Physique; Alain Deronzier, Jean-Claude Leprêtre, Univ. J. Fourier, LEOPR; Olivier Stéphan, Univ. J. Fourier, Spectrométrie Physique, FRANCE.

The discovery of organic light emitting electrochemical cells (OLECs) has opened new directions for organic light emitting devices based on luminescent materials. In this field, (2,2'-bipyridine) Ruthenium complexes have received most interest used as former material or blended with a solid ionic electrolyte. In contrast with OLEDs, the polymer-electrode interfaces behave as ohmic contacts and thus there is no limitation to carrier injection due to band offset between the Fermi levels of electrodes and the HOMO and LUMO of the luminescent material. Nevertheless, side reactions associated with electrochemical reduction of the ligands lead to a strong decrease of the luminescence within few hours. Thus, the obvious advantages of OLECs in terms of operating voltage (close to the electrochemical gap of the material) and electroluminescence efficiency are strong incentives to investigate species exhibiting enhanced stability towards reduction. One elegant procedure is to tune the ruthenium complex redox potentials so that the "n" doping region is shifted towards positive values. With this aim in view, we report promising results based on the use of a bipyridine complex bearing hexyl carboxamide side groups. Due to the electron-withdrawing effect of the carboxamide groups the electroactivity window is reduced when compared to regular tris-bipyridine Ru(II) complex, leading to a red emission centered at 654 nm.

### **BB3.34**

**LINE SHAPE ANALYSIS OF PHOTOLUMINESCENCE SPECTRA ON SOLUTIONS OF MD-PPV.** Flávia Maria Marconi, Rodrigo Fernando Bianchi, Alexandre Marletta, Lucas Fugigawa Santos, Luiz Antonio de Oliveira Nunes, Roberto Mendonça Faria, Débora Terezia Balogh, Universidade de São Paulo, Instituto de Física de São Carlos, São Carlos, BRAZIL.

In this work we study the strong effect that solvents used in the preparation of thin films of poly(3-methoxy-5-dodecoxy-*p*-phenylene-vinylene) (MD-PPV) has in the absorption and emission spectra. We carried out absorption UV-Vis region and photoluminescence (PL) measurements of MD-PPV solutions in several solvents at room temperature. UV-Vis measurements show a solvatochromic effect, shifting the maximum absorbance to higher energy as the value of the solvent solubility parameter ( $\delta_H$ ) increases. PL measurements, on the other hand, show an exciton peak at 558 nm, which tends to increase in intensity as ( $\delta_H$ ) increases, while an electron-phonon peak at 590 nm decreases. The polymer-solvent interactions were interpreted making use of a Franck-Condon model, which assumes a Gaussian distribution of conjugated segments along the molecular chain and takes into account the conformational disorder and torsion motion of the polymer chain. We observed that lower is ( $\delta_H$ ) value higher is the Huang-Rhys parameter.

This work was sponsored by Fapesp - Brazil.

### **BB3.35**

**HIGHLY EFFICIENT BLUE ELECTROLUMINESCENCE FROM NEW SPIROBIFLUORENE DERIVATIVES HAVING ALKOXY SUBSTITUTES.** Hyoyoung Lee, Jiyoung Oh, Hye Yong Chu, Jeong-Ik Lee, Seong Hyun Kim, Yong Suk Yang, Lee-Mi Do, Taehyoung Zyung, Telecommunication Basic Research Lab., ETRI, Taejeon, KOREA.

We report the synthesis and characterization of new alkoxy substituted spirobifluorene derivatives. The spirobifluorene compounds having alkoxy hydrocarbon chains were readily soluble in common organic solvents, having improved film-forming properties and had a significantly reduced tendency to crystallize, resulting in increasing their service lifetime. The optical and electroluminescent spectra were characterized. Electroluminescence (EL) properties of

three-layer light emitting diodes (LED) of ITO/TPD/spiro-bifluorene/Alq<sub>3</sub>/LiF/Al as the active layer were characterized. Blue emission peaking of the EL spectrum of the three-layer device at 402 nm and a luminance of 3,125 cd/m<sup>2</sup> were achieved at a drive voltage 12.8 V. The luminous efficiency was obtained to be 1.7 lm/W. The color coordinate in CIE chromaticity is (0.16, 0.09), which is in a pure blue region. The external quantum efficiency was obtained to be 2.0%. The results indicate that the spirobifluorene compounds having alkoxy hydrocarbon chains are strongly potential blue emitters for LED applications.

### **BB3.36**

**NOVEL POLYMER HETEROSTRUCTURES FOR PHOTONIC AND ELECTRONIC HETEROSTRUCTURES VIA MOLECULAR LAYER-BY-LAYER ASSEMBLY.** Jeri'Ann King, Jonas Mendelsohn, Michael F. Rubner, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA; Michael Ramey, John R. Reynolds, Department of Chemistry, University of Florida, Gainesville, FL.

The central theme of this work is the creation of electrostatically-driven layer-by-layer assembled polymers heterostructures for photonic and opto-electronic applications. The high level of molecular control that is achieved makes this a very attractive processing technique. Previously, our group has demonstrated light emitting devices (LEDs) of poly(phenylene vinylene) (PPV)-based multilayers as well as interface-modified heterostructure LED systems with improved performance. We now demonstrate enhanced performance of PPV-based LED heterostructures into which 20-35nm SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles are incorporated. Light output is increased by up to 60% and external quantum efficiencies improve by more than a factor of 2. We take advantage of the architectural control provided by this layer-by-layer assembly and create heterostructures in which the nanoparticles are precisely placed at varying positions throughout the active region of the LED. We demonstrate that the device performance is enhanced by the placement of the nanoparticle-polymer composite at the center of the multilayer system or in contact with the metal electrode. Conversely, the device performance is degraded by placement of the nanoparticle-polymer composite in contact with the indium tin oxide electrode. We have also explored polyelectrolyte multilayer systems for the creation of modulated index of refraction heterostructures consisting of high and low index of refraction(n) components. For the latter we have successfully created highly uniform fluorocarbon-based polyelectrolyte multilayers with n as low as 1.39 at 633nm. These multilayers are rich in the fluorocarbon component relative to the polycation used in assembly. Metal and nanoparticle-incorporated polyelectrolyte multilayers are currently being explored as high index of refraction components for layer-by-layer assembled photonic systems such as 1-dimensional photonic band gap structures and microcavity-LEDs.

### **BB3.37**

**A NOVEL SERIES OF EFFICIENT NAPHTHALENE-BASED LIGHT-EMITTING CONJUGATED POLYMERS.** Wei-Ling Wang, Yee-Hing Lai, Department of Chemistry, Faculty of Science, National University of Singapore, SINGAPORE.

Conjugated polymers offer many advantages as materials for use in light-emitting diodes (LEDs). A critical element in designing and fabricating such materials is the control of their emission wavelength. A novel series of soluble 1,4- and 1,5-conjugated naphthalene-based thiophene copolymers have been chemically synthesized and characterized. Their structures are consistent with that expected as indicated by NMR, FTIR and Elemental Analysis. The polymers with 1,4-disubstituted naphthalene demonstrate efficient blue-green light emission, while polymers with 1,5-disubstituted naphthalene demonstrate efficient blue light emission. The change in glass transition temperature, UV-vis spectra, fluorescence spectra and conductivity with different linkage of polymer backbone has been observed and discussed. The structure-property relationship of the polymer backbone has also been studied.

### **BB3.38**

**ELECTROPHOSPHORESCENT LIGHT EMITTING DEVICES USING MIXED LIGAND Ir(III) COMPLEXES.** Hae Won Lee, R.R. Das, Jang-Joo Kim, Kwang-ju Institute of Science and Technology, Dept of Material Science and Engineering, Kwang-ju, KOREA.

We have fabricated phosphorescent light emitting devices using mixed ligand orthometalated Ir(III) complexes. Ir(III) is coordinated to a common orthometalating ligand (ppy) and different non-orthometalating,  $\delta$ -accepting ligands. These materials can be compiled to the device demanding energy transfer, since the luminescent excited states of both the complexes are assigned as metal-to-ligand charge-transfer (MLCT) to the ppy ligand. The metal centered (MC) excited states in these complexes are moved to very high energies by the strong  $\sigma$ -bonding effect of ppy negating the possibility of emission

from these states. The complexes have different emission energy at room temperature. This can be ascribed to the less p-accepting ability of the ligands other than 2-phenylpyridines. The influence of these characteristics of the ligands not only controls the photophysical behavior of the complexes but is also manifested in the electroluminescence properties. In this presentation, we will report the strength of the  $\delta$ -accepting and electron delocalizing abilities of non-orthometalating ligands coordinated to Ir(III). The lifetimes, external quantum yields, and luminescence power efficiencies of the devices were studied and compared.

### **BB3.39**

**POLYMER ELECTROPHOSPHORESCENT LIGHT EMITTING DEVICES USING NEW IRIDIUM(III) COMPLEXES.** Rupasree Ragini Das, Chang-Lyool Lee, Jang-Joo Kim, Kwangju Institute of Science and Technology, Department of Materials Science and Engineering, Kwangju, KOREA.

Ir(III) complexes coordinated to orthometalating ligands like phenylpyridine have been the focus of recent research for useful applications in high-efficiency electrophosphorescence organic light emitting devices (OLEDs) because of their effective emission from the <sup>3</sup>MLCT states. The maximal performance of the device is not only dependent on the optimal conditions but also controlled by the coordinating ligands to Ir(III). In this paper we investigate the effect of the fine-tuning brought in by the introduction of a methyl substituent in the pyridine ring of 2-phenylpyridine on the HOMO and emitting <sup>3</sup>MLCT states of its Ir(III) complex and the subsequent impact on the energy transfer from the host to the guest in OLEDs. We have synthesized a new green emitting Ir(III) complex with 3-methyl-2-phenylpyridine, Ir(mpp)<sub>3</sub> and fabricated polymer based electrophosphorescence devices furnishing good quantum yield. Again, the emissive state, emissive states lifetime, quantum yield of emission and subsequent performance of the device are greatly influenced by a decrease in the number of the orthometalating ligand and introduction of nonorthometalating uninegative bidentate ligands. We have investigated these effects in mixed ligand complexes utilising 3-methyl-2-phenyl pyridine along with other uninegative bidentate ligands.

### **BB3.40**

**EFFECT OF HOST POLYMERS ON ENERGY TRANSFER AND CHARGE CONFINEMENT IN PHOSPHORESCENCE DYE DOPED POLYMER LIGHT EMITTING DEVICES.** Yong-Young Noh, Chang-Lyool Lee, Jang-Joo Kim, Department of Material Science and Engineering, Kwangju Institute of Science and Technology, Kwangju, SOUTH KOREA; In-Wook Hwang, and Yong-Rok Kim, Department of Chemistry, Yonsei University, Seoul, SOUTH KOREA.

We have investigated the effect of host polymer for electrophosphorescent light emitting devices (EPLEDs) doped with fac-tri(2-phenylpyridine) iridium (Ir(ppy)<sub>3</sub>). We selected host materials of poly(N-vinylcarbazol) (PVK), poly(2-vinylnaphthalene) (PVN), polyacenaphthalene (PAN), and polyfluorene derivative poly[9,9'-di-n-hexyl-2,7-fluorene-alt-1,4-(2,5-di-n-hexylo-xy)phenylene] (PFHP), which have almost same spectrum overlaps for efficient Forster energy transfer. However, the PL spectra of these films were remarkably different for different host materials. PVK, PAN and PVN films showed PL from Ir(ppy)<sub>3</sub>, but PFHP showed emission only from PFHP with little emission from Ir(ppy)<sub>3</sub> even with high doping concentrations when host polymers are excited. Time resolve PL exhibited that host polymers having longer lifetime than the rate of energy transfer from singlet to MLCT<sup>1</sup> show the efficient energy transfer. Shorter excited state lifetime than the energy transfer rate gives little emission from guest. This is the reasonable result as photo-physical kinetics, however, unusual behavior as the theory of Forster energy transfer. The EL spectra from devices showed almost the same characteristics for different polymer hosts. The device with PVK host showed more intense emission in EL from Ir(ppy)<sub>3</sub> than in PL at the same concentrations. PFHP device also showed emission from Ir(ppy)<sub>3</sub>, which is significantly different from PL. The differences in EL and PL for different host polymers will be discussed based on the energy levels, I-V-L curves, and time resolved PL and EL characteristics for various concentrations of the dopant. Contributions from energy transfers and charge confinement effects will also be discussed.

### **BB3.41**

**NEW SPIROBIFLUORENE DERIVATIVES FOR ELECTROLUMINESCENCE APPLICATIONS.** Jiyoung Oh, Hyoyoung Lee, Hye Yong Chu, Jeong-Ik Lee, Seong Hyun Kim, Yong Suk Yang, Lee-Mi Do, Taehyung Zyung, ETRI, Telecommunications Basic Research Lab., Taejeon, KOREA.

A series of spirobifluorene derivatives with alkoxy substituents at one side of spirobifluorene and phenylene substituents at the other side has been prepared and characterized in order to understand the effect

of phenylene substituents. These materials are soluble in customary organic solvents and have good thermal stability especially if number of phenyl group at phenylene substituents is increased. The results of photoluminescence (PL) and electroluminescence (EL) indicate that spirobifluorene derivatives should be regarded as a promising candidate in electroluminescence applications.

#### BB3.42

##### LIQUID STATE NMR STUDY ON LIGAND EXCHANGE DYNAMICS IN $Alq_3$ . Changqing Chen and Fotios

Papadimitrakopoulos\*, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT; Marcel Utz\*. \*Department of Physics, and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT.

Tris-8-(hydroxyquinoline) aluminum ( $Alq_3$ ) complexes have been extensively used as electron-transporting and emitting layers in organic light-emitting diodes (LEDs). The three quinoline ligands in the  $Alq_3$  complex are not symmetry-equivalent. We report our recent results on the exchange dynamics of the three inequivalent ligands in  $Alq_3$  complexes from two-dimensional liquid state Nuclear Magnetic Resonance (NMR) spectroscopy. These findings may shed light onto the physical-aging-assisted device degradation behavior of  $Alq_3$ -based organic light-emitting devices.

#### BB3.43

DIRECT EVIDENCE FOR ANNIHILATION OF SINGLET EXCITONS BY TRIPLET EXCITONS IN PL-CONJUGATED POLYMERS. E.J.W. List<sup>a,b</sup>, U. Scherf<sup>c</sup>, K. Müllen<sup>d</sup>, W. Graupner<sup>e,\*</sup>, C.-H. Kim<sup>f</sup> and J. Shinar<sup>b,f</sup>. <sup>a</sup>Institut für Festkörperphysik, Technische Universität Graz, Graz, AUSTRIA; <sup>b</sup>Ames Laboratory - USDOE, <sup>†</sup>Iowa State University, Ames, IA; <sup>c</sup>Institut für Physikalische und Theoretische Chemie, Universität Potsdam, Golm, GERMANY; <sup>d</sup>Max-Planck-Institut für Polymerforschung, Mainz, GERMANY; <sup>e</sup>Department of Physics, Virginia Tech, Blacksburg, VA; <sup>f</sup>Department of Physics and Astronomy, Iowa State University, Ames, IA. \*Present address: eMagin Corporation, Hopewell Junction, NY. <sup>†</sup>Ames Laboratory is operated by Iowa State University for the USDOE under Contract W-7405-Eng-82.

We provide the first direct evidence for nonradiative quenching of singlet excitons (SE's) by triplet excitons (TE's) in conjugated polymers and an estimate of the strength of this interaction. The elucidation of this issue is highly desirable since in polymer light emitting devices injected carriers form TE's with a yield of up to 75%. Moreover, as a result of the dipole forbidden transition of TE's to the ground state, the lifetime of the TE is extremely long relative to that of the SE's. This results in a high steady state TE density and hence a high probability for interacting with other species, such as quenching SE's. For this study a blend of two conjugated polymers which consists of the blue-emitting methyl-substituted poly(*para*-phenylene)-type LPPP host and the orange-emitting poly(perylene-co-diethynylbenzene) guest was studied by photoinduced absorption (PA) and photoluminescence (PL)-detected magnetic resonance. The guest was chosen because both its PL and its TE half-field-for-resonance at  $g \gg 4$  are distinct from those of the host. Hence we could alter the population of the TE spin sublevels of each of the two polymers separately and simultaneously monitor its effect on the decay of SE's in each of the polymers. From the latter we find that a reduction of TE's on either of the two polymers enhances the SE decay on both polymers nearly identically. The PA results rule out other possible mechanisms to yield this signal, except one: a long range SE-TE annihilation due to a dipole-dipole transfer mechanism. Based on this finding, we calculate the transfer radius and quantify the annihilation process for the presented system and for other conjugated polymers such as poly(*p*-phenylene vinylene) and polyfluorene.

#### BB3.44

NOVEL PHOTOLUMINESCENT MATERIALS BASED ON 3,4-ETHYLENEDIOXYTHIOPHENE AND POLYPHENYLENEVINYLENE. Richard V. Gregory, Paul E. Pitman, Michael F. Pepitone, Stephen Hardaker, School of Materials Science and Engineering, Clemson University, Clemson, SC.

Poly(3,4-ethylenedioxythiophene) is a conducting polymer of considerable interest due to its low band gap (1.6 eV), moderate conductivity (100 S/cm) and remarkable stability. Recently, new electron-rich bis-heterocycle substituted arylene derivatives of 3,4-ethylenedioxythiophene (EDOT) monomers have been synthesized that exhibit strong luminescence. In order to take advantage of the luminescent behavior of these recently developed EDOT derivatives as well as other luminescent oligomers, and to avoid difficulties due to poor solubility, these moieties are being appended to polymers with acceptable solution behavior. Appended moieties include 3-alkylthiophenes, cyanovinyls and 1,3,4-oxadiazole. These

substructures lead to greater luminescent behavior as well as begin to improve the solubility in common organic solvents, a crucial issue for processing any highly conjugated material. Additionally, novel poly-phenylenevinylene (PPV) derivatives are being synthesized. Instead of varying ring substituents to alter solubility and luminescent properties, conjugation length and chain morphology within the polymer is being controlled by the introduction of meta linkages in order to ascertain the effect and desirability of chain defects that have been introduced in a controlled fashion. This evolving technology may form the basis for "tunable" emissive polymeric materials.

#### BB3.45

Abstract Withdrawn.

#### BB3.46

HIGH GLASS-TRANSITION SPIRO-TERFLUORENES AS STABLE FLUORESCENT MATERIALS. Yanhou Geng, Dimitris Katsis, Sean Culligan, Jane J. Ou, Shaw H. Chen, Lewis Rothberg, University of Rochester, Departments of Chemical Engineering and Chemistry, Laboratory for Laser Energetics, Rochester, NY.

A series of fully spiro-configured oligo(fluorene)s were synthesized and characterized to be amorphous materials showing a glass transition temperature of 296°C with dendritic aromatic pendants, the highest value ever reported for organic molecular systems. X-ray single crystal analysis of key structural moieties indicated nearly perpendicular orientations at all spiro-links. The UV-Vis absorption spectroscopy of solid film versus dilute solution suggested absence of aggregates in the ground state and no increase in torsion angle with an increasing volume of the aromatic pendant. All these conformational characteristics are consistent with molecular mechanics simulation. Fluorescence spectra showed a 10 to 14 nm red-shift of solid film from dilute solution, presumably due to energy migration to more planar fluorene chromophores in the excited state. Upon prolonged heating under argon, blue emission was found to persist, while the emission intensity was found to decrease with a phenyl pendant but to increase with a dendritic pendant. The effect of thermal annealing on emission intensity was quantified with the measurement of fluorescence quantum yield. The opposite trend in the blue emission as a consequence of thermal annealing was interpreted in terms of the extent of interchromophoric interactions dictated by the aromatic pendant.

#### BB3.47

NEAR-INFRARED ELECTROLUMINESCENCE FROM LN(TPP)ACAC BASED CONJUGATED POLYMER BLENDS. Mohamed Bouguettaya, Benjamin S. Harrison, Timothy J. Foley, James M. Boncella, Kirk S. Schanze and John R. Reynolds, University of Florida, Dept of Chemistry and Center for Macromolecular Science and Engineering; Joonbo Shim, Paul H. Holloway, University of Florida, Dept of MS&E; G. Padmanaban, S. Ramakrishnan, Indian Institute of Science, Dept of Inorganic and Physical Chemistry, Bangalore, INDIA.

In the present communication, we report near-IR photoluminescence (PL) and electroluminescence (EL) from blends of MEH-PPV and a dialkoxy functionalized poly(*p*-phenylene) (PPP-OR11) with Yb(TPP)acac and Er(TPP)acac (TPP = 5,10,15,20-tetraphenylporphyrin, acac = acetylacetonate). This process is believed to involve sensitization of the lanthanide-TPP complex by the conjugated polymer, via Förster energy transfer and leads to the narrow bandwidth emission derived from the Yb  $^2F_{5/2} \rightarrow ^2F_{7/2}$  (977 nm) and Er  $^4I_{13/2} \rightarrow ^4I_{15/2}$  (1560 nm) transitions. Near-IR electroluminescent devices were constructed using the Ln(TPP)acac complexes where Ln = Yb3 (5 mol %) and Er3 (5 mol %). The spectral data show that the visible emission of the conjugated polymer is strongly suppressed, and the device emission is dominated by the near-IR output of the Ln complexes. The data shows also that the narrow bandwidth characteristic of the lanthanide emission is preserved in the EL devices. The recorded i-V and quantitative light output characteristics for a device show that the turn-on voltage (4 V) is low compared to devices constructed with neat lanthanide complexes.

#### BB3.48

HIGHLY EFFICIENT PHOTOLUMINESCENT AND ELECTROLUMINESCENT PROPERTIES OF STRUCTURALLY DEFINED FLUORENE BASED COPOLYMERS. Petra Herguth, Xuezhong S. Jiang, Michelle S. Liu, Alex K.-Y. Jen, University of Washington, Department of Materials Science and Engineering, Seattle, WA.

Color emission of fluorene-based copolymers can be tuned by using various low band gap monomers in the polymerization. It has been shown that the incorporation of benzothiadiazole (BTD) into the polymer chain results in a bright green emission at 540 nm with much higher quantum efficiencies than observed in the homo polymer of

fluorene. However, there is very little information exists in explaining the effect of polymer structures on their properties. Most of the polymers synthesized are based on a random incorporation of monomers into the polymer chain. In our study, several random or structurally well-defined polymers based on fluorene have been synthesized via the Suzuki-coupling reaction to investigate these properties. Two or three different monomers were used in this study. Monomer ratios were varied to study the effect of concentration on their properties. The spectroscopic data suggest that the formation of blocks that are rich in BTB. It explains for the strong green emission observed at 540nm. This may be due to efficient energy transfer from fluorene-containing segments to these blocks and result in no emission at other wavelengths. These polymers were incorporated into double-layer devices (ITO/BTPD-PFCB/Polymer/Ca/Ag). Low turn-on voltages (below 4V) and high external quantum efficiencies (4-9%) were obtained in all cases.

**BB3.49**  
LUMINESCENT POLYSTYRENE COMPOSITION CHARACTERISTICS STABILITY TECHNOLOGIC FORECASTING. Artem Yu Borisenko, Vitalij G. Senchishin, Institute for Single Crystals, Kharkov, UKRAINE.

This paper is devoted to the investigation of luminescent polystyrene composition characteristics stability. Luminescent polystyrene compositions obtained by means of bulk polymerization and injection molding methods were studied. The influence of polystyrene composition production regimes on their characteristics stability were studied. The influence of thermo- and radiative aging on composition properties was explored by means of accelerated tests. The optimal conditions of polystyrene composition using, such as predicted working time, acceptable dose and dose rate of irradiation were determined. On the base of performed investigation the optimal production scheme of polystyrene composition with high luminescent characteristics was established.

**BB3.50**  
POLYMER BLENDS FOR LIGHT EMITTING DIODES (PLEDS): OPTIMIZATION OF MIXING RATIOS AND PREPARATION CONDITIONS FOR HIGH EFFICIENT DEVICES. Joerg Blaessing, Jan Birnstock, Karsten Heuser, Matthias Stoessel, Georg Wittmann, Marcus Scheffel, Arvid Hunze, Siemens AG, Erlangen, GERMANY; Albrecht Winnacker, Institut fuer Werkstoffwissenschaften VI, Universitaet Erlangen-Nuernberg, GERMANY.

Emitting layers for polymer light emitting diodes (PLEDs) can either consist of polymer blends or copolymers. Polymer blends are well known to exhibit phase separation which can influence the diode characteristics. We prepare polymer blends with different concentrations of electron and hole transport materials, e.g. Poly-(9-vinylcarbazole), PVK, in Poly-(p-phenylenevinylene), PPV as emitting material and investigate the influence of the mixing ratio and the surface morphology on the efficiencies and lifetimes of PLEDs. The diode consists of a glass substrate covered with ITO as anode, a film of Poly(3,4-ethylenedioxythiophene), PEDOT as planarization and barrier layer, the polymer blend and on top of the device calcium/silver or barium/silver as cathode. We prepare the functional polymer layers from solution by spin coating. First, we change the concentration of the electron or hole transport material in PPV to find the ideal mixing ratio concerning device efficiencies. The mixing ratio has also a strong impact on the surface structure of the polymer blend film. The analysis is done with an Atomic Force Microscope (AFM) and a Scanning Near-field Optical Microscope (SNOM). In a second step, we vary several preparation parameters (e.g. drying conditions, solvents) and investigate the influence on the diode characteristics and the phase separation of the polymer blend. The stage of the phase separation affect the morphology (e.g. surface roughness, peak-valley distance) of the functional polymer layer. In some cases we find a peak-valley distance in the range of the half layer thickness. A high surface roughness can promote shorts in the diode and thus decrease their lifetime. But the film roughness can be reduced by the variation of the drying condition.

**BB3.51**  
WHITE ORGANIC ELECTROLUMINESCENT DEVICES USING THE DIRECT INK-JET PRINTING METHOD. Ryuichi Satoh, Shigeki Naka, Miki Shibata, Hiroyuki Okada, Hiroyoshi Onnagawa, Toyama Univ., Dept. of Electric and Electronic Engineering, Toyama, JAPAN; Takeshi Miyabayashi, Brother Industries, Ltd., Nagoya, JAPAN.

The ink-jet printing method for organic electroluminescent device fabrication have been extensively studied.[1,2,3] We had proposed the *direct ink-jet printing* (D-IJP) method which is simply directly printing method utilizing a mixture of hole transport, electron transport, and emission materials.[4] In this time, we have studied white organic electroluminescent devices using D-IJP. The mixture of

a host polymer of poly(N-vinylcarbazole) (PVCz), electron transport material of 2,5-Bis(1-naphthyl)-1,3,4-oxadiazole (BND), dyes of coumarin 6 (C6), and 4-(Dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) is dissolved in 1,2-Dichloroethane. This mixture is directly printed on a glass substrate with indium tin oxide (ITO). The ratio of PVCz: BND: C6: DCM is 64:16:1:4 and the solution of 1 wt% mixture is used. The printer head used for the ink-jet printing is made of ceramic in order to tolerate the organic solvents and has a piezoelectric device. Cathode electrode of LiF(1nm)/Al was subsequently evaporated. To date, maximum luminance of 1,820 cd/m<sup>2</sup> is obtained. The emission spectrum shows three peaks of 450, 488, and 553 nm, which derived from PVCz, C6, and DCM and clear white emission is obtained. A spectrum shift of voltage dependence is smaller and the shift of CIE color coordinates is  $x = 0.011$  and  $y = 0.015$ .

[1] T. Shimoda, S. Miyashita, and H. Kiguchi, Patent Gazette of Japan, 10-12377, (1998).  
[2] T.R. Hebner, C.C. Wu, D. Marcy, M.H. Lu, and J.C. Strum, *Appl. Phys. Lett.*, **72**(5), 519 (1998).  
[3] J. Bharathan and Y. Yang, *Appl. Phys. Lett.*, **72**(21), 2660 (1998).  
[4] K. Yoshimori, S. Naka, M. Shibata, H. Okada, and H. Onnagawa, *Ext. Abst. 18th Intl. Display Res. Conf. (Asia Display '98)*, 213 (1998).

**BB3.52**  
STRUCTURAL DEPENDENCE AND DYNAMICS OF WHITE LUMINESCENCE IN MULTILAYER STRUCTURES FOR WHITE ORGANIC LIGHT EMITTING DEVICES. Shizuo Fujita, Kyoto Univ, Int Innovation Center, Kyoto, JAPAN; Ken-ichi Uesaka, Shigeo Fujita, Kyoto Univ, Dept of Electron Sci Eng, Kyoto, JAPAN.

White luminescence from organic materials is generally obtained by overlapping of multi-colors emitted from different luminescent layers, e.g., of blue, green, and red lines from three different luminescent layers. Therefore, the control of intensity and spectrum of each of the luminescence lines is important for the chromaticity of white luminescence. In this paper, the white luminescence spectra are carefully investigated in terms of the multilayer structures and a rule for designing the white luminescence is discussed. The first investigation was for the simplest structure which consisted of 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (PPCP) and tris(8-hydroxyquinoline)-aluminum (Alq) emitting blue and green luminescence, respectively, as emission and electron transport layers combined with diamine (TPD) as a hole transport layer. Mixing of PPCP and Alq resulted in green luminescence completely from Alq upto its concentration of 5% due to fast and effective energy transfer from excited PPCP to Alq, which was confirmed by time-resolved photoluminescence dynamics study. On the other hand, the stack of PPCP and Alq resulted in white luminescence if the thickness of each layer was appropriately chosen. The luminescence efficiency was higher in Alq, and therefore one of the structures effectively emitting white luminescence was designed as PPCP(40nm)/Alq(10nm), which was proposed based on the luminescence dynamics investigated and microscopic structural characterization. The 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) was further added to the PPCP/Alq structure intending to enhance the red luminescence. We propose the structure where the DCM layer is excited by the blue and green luminescence from PPCP and Alq, because it was effective to obtain the red luminescence rather than electrical injection. It was also effective, compared to the PPCP/Alq/DCM stacking structure, in avoiding increase of the operating voltage. The detailed investigation of luminescence dynamics is also conducted and will be presented at the symposium.

**BB3.53**  
HIGH EFFICIENCY BLUE ORGANIC LIGHT EMITTING DEVICES WITH A BUFFER LAYER. Hye Yong Chu, Hoyoung Lee, Jiyoung Oh, Jeong-Ik Lee, Sung Hyun Kim, Yong Suk Yang, Lee-Mi Do, Taehyoung Zyung, ETRI, Taejeon, TAIWAN.

We report the blue electroluminescent properties of organic light emitting devices (OLEDs) with a buffer layer between hole transport layer (HTL) and spirofluorene emissive layer (EML). The OLEDs consists of ITO/TPD/buffer layer/spirofluorene/Alq<sub>3</sub>/LiF/Al. The buffer layer is co-deposited with HTL and EML materials at various molar ratios for efficient carrier injection into EML. The turn-on voltage of the devices having a buffer layer was reduced about 2V in comparison of the OLED without a buffer layer. The external quantum efficiency was estimated to be 3.5%. The luminous efficiency was obtained to be 2.0 lm/W. We will discuss the effects of buffer layers on blue OLEDs.

**BB3.54**  
FABRICATION OF FULL COLOUR POLYMER LEDs BY PIEZO INK-JET PRINTING. Steve Yeates, Neil Tallant, Avecia Research Center, Manchester, UNITED KINGDOM; S. Heun, Covion Organic Semiconductors GmbH, Frankfurt, GERMANY.

We report recent progress in the use of drop on demand piezo ink-jet printing in the fabrication of full colour polymer LED's. The manufacturing steps that may be replaced, the limitations and concerns associated with PLED ink-jet technology, and the technical benefits of the approach will be explained.

#### **BB3.55**

**INCORPORATION OF A HYDROGEL "PEN" WITH POLYELECTROLYTES FOR DEPOSITION OF POLYMERIC MULTILAYERS.** Christophe J. Lefaux, Patrick T. Mather, University of Connecticut, Polymer Program and Chemical Engineering Dept., Storrs, CT; Jeffrey W. Baur, Air Force Research Laboratory, Wright Patterson AFB, OH.

Optimization and discovery of organic materials for use in photovoltaic devices is needed for timely transition of new materials in this important area of energy technologies. Hydrogel contact deposition offers one approach to enable this goal by providing a rapid processing tool for discrete polymeric multilayer islands that allows screening of thin polymer devices. Our specific implementation of this idea combines aspects of both electrostatic self-assembly (ESA) with localized contact stamping. For the present study, we are investigating the pore size of different cross-linking density hydrogel applicators of polyhydroxyethylacrylate (PHEA), as the pore size has been found to control the incorporation of free polymer. We have studied the swelling response and the loading of the hydrogel pens by two different polyelectrolyte solutions namely, poly(sodium acrylate) and poly(allylamine hydrochloride). It is observed that the swelling response is a function of both the crosslink density and the nature of the polyelectrolyte solution. In particular, we find that increasing concentration of poly(sodium acrylate) significantly enhances swelling into PHEA gels relative to pure water, while the opposite is true for poly(allylamine hydrochloride) solutions. Using the polyelectrolyte-incorporated gels, we have investigated the controlled growth of patterned multilayers processed from these two polymers by cyclic contact deposition upon a silicon substrate using UV-Vis absorption, ellipsometry, and AFM as characterization methods. We will present a high level of control over multilayer growth on the nanometer scale with simultaneous micron-scale control over lateral dimensions.

#### **BB3.56**

**NOVEL PHOTOPHYSICS IN A HIGHLY CRYSTALLINE PPV DERIVATIVE.** Marc Sims, University of Sheffield, Dept of Physics and Astronomy, Sheffield, UNITED KINGDOM; Donal Bradley, Centre for Electronic Materials and Devices, Imperial College, London, UNITED KINGDOM; Paul Burn, Dyson Perrins Laboratory, University of Oxford, Oxford, UNITED KINGDOM.

We report the photoluminescence quantum efficiency as a function of temperature for a novel PPV derivative with an unprecedented degree of crystallinity: XRD studies conducted on the polymer reveal a series of six well defined Bragg lines with a full width half maxima corresponding to a domain size in the order of 0.1 $\mu$ m. On cooling to 5K, we observe a 50% increase in the PLQE relative to the room temperature value followed by an up to five fold drop within an hour of constant exposure to the 325nm line of a HeCd laser. Upon increase of the temperature, the PLQE reverts back to the original value, which emphasises the physical nature of the fatigue effect. The 50% rise in PLQE, but not the subsequent fatigue, are observed by exposure to the 354nm line. The phenomena responsible for this dramatic effect have been probed by a variety of spectroscopic measurements and the results of these investigations will be presented.

### **SESSION BB4: PHOTONIC/NONLINEAR OPTICAL MATERIALS AND DEVICES**

Chair: Susan P. Ermer  
Tuesday Morning, November 27, 2001  
Constitution A (Sheraton)

#### **NOTE EARLY START**

#### **8:15 AM \*BB4.1**

**RATIONAL DESIGN OF ORGANIC ELECTRO-OPTIC MATERIALS.** Larry Dalton, Bruce Robinson, Robert Neilsen, Alex Jen, Univ of Washington, Dept of Chemistry, Seattle, WA.

Equilibrium and kinetic Monte Carlo calculations are used to guide the design of electro-optic chromophores and the choice of processing conditions to translate these chromophores into stable electro-optic materials. The relationship of chromophore molecular structure and processing conditions to electro-optic activity, optical loss, thermal stability, photochemical stability, and processability is discussed. This design paradigm has permitted materials competitive with lithium niobate to be prepared and even to be processed into sophisticated

3-D architectures. A variety of prototype device structures are reviewed.

#### **8:45 AM BB4.2**

**HIGHLY EFFICIENT PERFLUOROCYCLOBUTANE-CONTAINING THERMOSET POLYMERS AND DENDRIMERS FOR HIGH-SPEED ELECTRO-OPTIC DEVICES.** Alex K.-Y. Jen, Hong Ma, Takafumi Sassa, Baoquan Chen, and Sen Liu, Department of Materials Science and Engineering, University of Washington, Seattle, WA; Larry R. Dalton, Department of Chemistry, University of Washington, Seattle, WA.

A new and efficient approach for synthesizing novel second-order NLO perfluorocyclobutane (PFCB) polymers and dendrimers has been developed by utilizing the crosslinking reaction between the di(trifluorovinylether)-containing NLO chromophores and the in solid state at 180-200°C. The radical-mediated, stepwise cycloaddition reaction offers great tolerance to very sensitive functional groups (even for the tricyanovinyl acceptor). The resulting NLO PFCB materials exhibited excellent processability, low optical loss, and very good thermal, nonlinear optical and mechanical properties. Incorporation of the 3-D shape, phenyl-tetracyanobutadienyl(Ph-TCBD)-containing NLO chromophores into double-end cross-linkable dendrimers further enhanced macroscopic optical nonlinearity (above 60 pm/V at 1550 nm) and reduced optical loss.

#### **9:00 AM BB4.3**

**HIGHLY PROCESSABLE AND PROPERTY TUNABLE PERFLUOROCYCLOBUTYL (PFCB) COPOLYMERS FOR LOW LOSS OPTICAL WAVEGUIDING.** Dennis Smith, Suresh Kumar, Shengrong Chen, Jianyong Jin, Clark Ligon, Clemson Univ, Dept of Chemistry, Clemson, SC; John Ballato, Steve Foulger, Dept of MS&E, Clemson Univ, Clemson, SC.

Organic polymers are increasingly attractive alternatives to inorganic components in telecommunication devices. Polymers offer flexibility, low cost fabrication and connection, high transparency in the visible and near-infrared spectra, and versatility in structure, properties, and grades for task specific integration such as local-area-network applications. Halogenated polymers in particular show negligible transmission losses in the range desired and fluoropolymers represent the lowest loss examples of organic polymers to date. However, commercial perfluoropolymers in general are limited by poor processability, difficult refractive index matching, and they typically do not exhibit the thermal and thermomechanical stability required for some commercial processes and extreme environment in-use applications. Our strategy has focused on the thermal cyclo-polymerization of trifunctional and bifunctional aryl trifluorovinyl ether monomers to perfluorocyclobutane (PFCB) copolymers. PFCB polymers and copolymers enjoy a unique combination of properties well suited for optical applications such as, high temperature stability, precisely controlled refractive index, low moisture absorption, excellent melt and solution processability, a high thermo-optic coefficient, and low transmission loss at 1350 and 1550 nm. Copolymerization reactions offer tailored thermal and optical properties by simple choice of comonomer. PFCB polymers can be solution or melt microfabricated via standard methods and can also be processed by soft-lithography techniques as well as new simplified procedures to give sub-micron diffractive elements. Processing parameters and characterization including thermal properties ( $T_g = 160-350^\circ\text{C}$ ), optical loss ( $< 0.2$  at 1550nm), dn/dT relationships, and device performance will be presented.

#### **9:15 AM BB4.4**

**NOVEL POLAR SELF-ASSEMBLED MULTILAYERS FOR SECOND-ORDER NONLINEAR OPTICS.** P.J. Neyman, C. Brands, J.R. Heflin, Virginia Tech, Department of Physics; M.T. Guzy, S.M. Shah, R.M. Davis, K.E. Van Cott, Virginia Tech, Department of Chemical Engineering; H. Wang, H.W. Gibson, Virginia Tech, Department of Chemistry.

Ionically self-assembled monolayer (ISAM) films have been recently shown to spontaneously produce noncentrosymmetric ordering that gives rise to a substantial second order nonlinear optical (NLO) response. Typically, ISAM films for NLO response are an assemblage of bilayers of oppositely charged polymers whose NLO response can be improved through variation of pH and ionic strength of the immersion solutions. So far, this optimization has focused on the NLO-active anion. We have found that the chromophores at the layer interfaces, where the ionic bonds order the NLO dipoles, are the main contributor to NLO response. More recently, we have examined the effects of using three different NLO-inactive polycations at two different pH values and have observed dramatic variation in bilayer thickness and  $\chi^{(2)}$ . While significant improvements in  $\chi^{(2)}$  have resulted from optimization of the pH and ionic strength, the full potential of ISAM films has not yet been realized. The formation of ISAM films from polymers results in a significant degree of

cancellation due to chromophores oriented towards both the preceding and following layers. We will describe several approaches using monomeric chromophores that allow a much higher degree of net polar alignment. These include dianionic chromophores with different  $pK_a$  values on opposite ends, chromophores with different numbers of ionic groups on opposite ends, and hybrid mechanisms in which one end is ionic and the other is covalently attached into the film. We will also discuss approaches incorporating cyclodextrin inclusion-complexes as well as clay platelets.

#### 9:30 AM **BB4.5**

SECOND ORDER NONLINEAR OPTICAL FILMS BY ALTERNATING POLYELECTROLYTE DEPOSITION WITH ENABLING NEW POLYMERS. M. Joseph Roberts, Geoff Lindsay, Naval Air Warfare Center Weapons Division, Materials and Chemistry Branch, China Lake, CA; Warren N. Herman, Naval Air Warfare Center Aircraft Division, Electro-Optic Sensors Branch, Patuxent River; Michael Therien, University of Pennsylvania, PA.

Alternating polyelectrolyte aqueous solution deposition technique (APD) may be used to process nonlinear optical polymers (NLOP) into noncentrosymmetric ordered films near room temperature. In this study, second-order NLOP APD films were prepared by alternately dipping a substrate into aqueous solutions of new polymers with improved chromophores compared to those used previously. Evidence for uniform layer to layer deposition includes a linear increase of UV-Visible absorbance and quadratic increase of second harmonic generated light intensity as a function of film thickness. An optical interference technique is used to establish the orientation of the chromophores. Thermal stability of polar order in these films is measured during slow temperature ramping of  $1\text{ }^\circ\text{C}/\text{min}$ . Films are further characterized by AFM. Work is in progress to deposit thicker optical quality films with improved NLO figures of merit.

#### 10:00 AM \***BB4.6**

THE CHEMISTRY OF TWO-PHOTON ABSORBING MATERIALS. Christina A. Bauer, Kevin Braun, David Carrig, Stephen M. Kuebler, Seth R. Marder, Timo Meyer-Friedrichsen, Christopher Ober\*, Joseph W. Perry, Stephanie J.K. Pond, Mariacristina Rumi, Francesco Stellacci, Wim Wenseleers, Tianyue Yu\*, Ya-dong Zhang, Wenhui Zhou, University of Arizona, Department of Chemistry, Tucson, AZ. \*Cornell University, Materials Science and Engineering, Ithaca, NY.

Two-photon absorption (TPA) provides a method to excite molecules with three-dimensional spatial resolution. In the past, we have developed molecules with exceptionally large TPA cross sections. Here, we will describe new systems that have large TPA cross sections and other properties that make them useful for microfabricating complex three-dimensional objects. In particular, we will describe our attempt to synthesize very efficient radical and photoacid generators based upon bis(styryl)benzene molecules.

#### 10:30 AM **BB4.7**

FABRICATION OF REFRACTIVE INDEX AND RELIEF GRATINGS IN POLYMER FILMS FOR DFB LASERS. Thomas Kavc, Gregor Langer, Wolfgang Kern, Graz Univ. of Technology, ICTOS, AUSTRIA; Gerald Kranzelbinder, Eric Toussaere, ENS Cachan, LPQM, FRANCE; Graham A. Turnbull, Ifor D.W. Samuel, Univ. of St. Andrews, School of Physics and Astronomy, UNITED KINGDOM; Kurt F. Iskra, Theo Neger, Graz Univ. of Technology, Institute for Exp. Physics, AUSTRIA.

Gratings in polymer films are important for optoelectronics and for the setup of organic lasers based upon distributed feedback (DFB). In addition, the recording of holograms is achieved by engraving phase and relief gratings in thin films. Our investigation was focused on photosensitive polymers which form refractive index and/or relief gratings upon patterned deep UV irradiation. We investigated the photoreactions of polymers bearing SCN groups, e.g. poly(4-vinylbenzyl thiocyanate) (PVBT) and poly(styrene-co-4-vinylbenzyl thiocyanate) (PST-co-VBT). Upon UV irradiation (254 nm), the SCN groups undergo a photoisomerization to the corresponding isothiocyanates (NCS). The refractive index  $n$  of PVBT increased from 1.629 to 1.660 after UV irradiation,  $n$  of (PST-co-VBT) increased from 1.616 to 1.630. Subsequent modification with gaseous amines (ammonia ( $\text{NH}_3$ ), propylamine (PA), ethylene diamine (ED) and hydrazine ( $\text{N}_2\text{H}_4$ )) yielded thiourea groups in the irradiated areas. Gas phase reaction with  $\text{NH}_3$ , ED and  $\text{N}_2\text{H}_4$  increased the refractive index of the polymer film ( $\Delta n = 0.010$ ;  $0.006$  and  $0.012$ ), while the refractive index was lowered after reaction with PA ( $\Delta n = -0.008$ ). The gas phase reaction also caused an increase of the film thickness:  $\text{NH}_3$  +4%;  $\text{N}_2\text{H}_4$  +4%; PA and ED +17%. A NdYAG-Laser (266 nm) was used for holographic illumination of PST-co-VBT films doped with 2 wt.-% DCM. The illuminated films ( $d = 400\text{ nm}$ ) were treated with the amines mentioned above and gave surface and relief gratings with a grating period of ca. 400 nm. The depths of the gratings were between 10 and 40 nm. These devices showed DFB

laser-activity when pumped with a NdYAG-Laser (532 nm). The laser emission had a spectral line width below 1 nm and was fully polarized parallel to the grating (threshold near  $1\text{ }\mu\text{J cm}^{-2}$ ). Work with conjugated polymers for the setup of DFB lasers is in progress.

#### 10:45 AM **BB4.8**

LOW-LOSS POLYMER OPTICAL WAVEGUIDES WITH HIGH THERMAL STABILITY. Jae-Wook Kang, Jae-Pil Kim, Won-Young Lee, Joon-Sung Kim, Jae-Suk Lee, Jang-Joo Kim, K-JIST, Dept of Material Sciences and Engineering, Kwangju, KOREA.

We synthesized new cross-linkable fluorinated poly(arylene ether sulfides) (FPAESI) for optical waveguides applications, which have high thermal stability, high optical transparency in the infrared communication region, and much smaller birefringence than other thermally stable fluorinated polyimides. Sulfide group in the polymer was introduced to improve the adhesion to Si substrates. To increase the solvent resistance during the multiplayer overcoating, we introduced the 3-ethynylphenol (EP) in fluorinated poly(arylene ether sulfides) as a cross-linkable end-capper. The refractive index of the material can be easily controlled from 1.52 to 1.53 by changing of fluorine content in the materials. The birefringence,  $\Delta n = n_T - n_{TM}$ , of the cured polymers were  $0.0044 \sim 0.0047$  at the wavelength of 1550 nm. This is much lower than those of fluorinated polyimides for optical waveguides. The refractive index of FPAESI after being stored at  $100^\circ\text{C}$  for 1000 h remains almost constant demonstrating the thermal stability. The propagation loss of the channel waveguides fabricated using reactive ion etching was less than  $0.42\text{ dB/cm}$  and  $0.4\text{ dB/cm}$  at the wavelength of 1550 nm for TE and TM polarizations, respectively.

#### 11:00 AM \***BB4.9**

SELF-ASSEMBLY APPROACHES TO THE FABRICATION OF PHOTONIC DEVICES. Younan Xia, Byron Gates, University of Washington, Seattle, WA.

We are developing new approaches based on self-assembly to the fabrication of photonic devices such as two-dimensional arrays of microlenses and three-dimensional photonic crystals. In all these approaches, monodispersed spherical colloids (polymer beads or silica spheres) were used as the building blocks, from which two- and three-dimensionally ordered lattices were formed through self-induced or template-directed assembly. In this presentation, I will discuss the procedures and potential applications of these methods, with focus on the demonstration of functional microphotonic devices.

#### 11:30 AM \***BB4.10**

MULTIPOLAR MOLECULAR ENGINEERING FOR HIGH BIT-RATE OPTICAL SIGNAL PROCESSING. Isabelle Ledoux, Sophie Brasselet, Joseph Zyss Laboratoire de Photonique Quantique et Moleculaire - Ecole Normale Supérieure de Cachan, Cedex, FRANCE.

The emergence of polymer-based electro-optics (EO) devices with huge bandwidth acceptance and low modulation voltage is the result of two decades of intense molecular and material engineering studies, combined with a more recent technological maturation of fabrication processes. We will first discuss the optimization of the so-called "factor of merit" for EO applications, as a result of an adequate trade-off between the nonlinear response of the active dye molecules and other essential parameters such as transparency in the near-infrared, thermal stability during the whole elaboration process, or limitation of the dye aggregation process. Molecules currently used as active units in EO polymeric are based on 1-D rod-like intramolecular charge transfer structures that are suitable for DC electric field poling, resulting in a strongly dipolar and anisotropic nonlinear response which would require additional efforts to fulfill specific requirements of optical communications systems in terms of polarization-independence of the device response. More recently, the demonstrated relevance of 2-D and 3-D multipolar structures has considerably widened the choice of candidate molecules for NLO applications. Octupolar molecular engineering for nonlinear optics will be discussed in terms of the synthetic implementation of general 2-D and 3-D point charge templates made-up of alternating charges at the edges of a cube. The full exploitation of the tensorial character of the hyperpolarizability permits to considerably broaden the pool of candidate molecular structures, with specific advantages in terms of linear isotropy and transparency-efficiency trade-off. We will present various examples of design strategies for 2-D and 3-D octupolar structures, whereby metal complexes provide particularly appealing assets in terms of built-in chirality in conjunction with hyperpolarizability. For all these systems, experimental values mainly based on polarized harmonic light scattering will be presented and discussed in the light of a quantum molecular modelling by a  $n$ -level model and a transparency-efficiency figure of merit. As octupolar molecules cannot be ordered using the classical electric-field poling techniques currently used for dipolar systems, the question of octupolar ordering will be discussed. A "crystalline engineering" aiming at the

optimization of the molecular packing in crystalline structures made of octupolar molecules has been recently developed. All-optical poling techniques are now being used to induce a permanent octupolar order within polymeric materials containing photoisomerizable octupolar molecules. Such extension of the dimensionality at the molecular and material levels opens new perspectives for the elaboration of polarization-independent materials and devices.

#### SESSION BB5: DESIGN AND SYNTHESIS OF ELECTROLUMINESCENT MATERIALS

Chair: Michael D. McGehee

Tuesday Afternoon, November 27, 2001

Constitution A (Sheraton)

##### 1:30 PM \*BB5.1

DEVELOPMENT OF HIGH-PERFORMANCE ORGANIC ELECTROLUMINESCENT DEVICES USING NOVEL AMORPHOUS MOLECULAR MATERIALS. Yasuhiko Shirota, Motoi Kinoshita, Kenji Okumoto, and Hidekaru Doi, Department of Applied Chemistry, Faculty of Engineering, Osaka University, Osaka, JAPAN.

The performance of organic electroluminescent (EL) devices depends on materials functioning in various specialized roles, including charge-transporting, charge-blocking and emitting materials. Amorphous molecular materials that form uniform amorphous thin films have been found to be well suited for use in organic EL devices. We have been created novel classes of hole-transporting amorphous molecular materials with high glass-transition temperatures, hole-blocking amorphous molecular materials that permit the fabrication of blue-violet-emitting organic EL devices, and emitting amorphous molecular materials as bipolar radical formants. We report here the synthesis and properties of these new materials and the performance of organic EL devices using the synthesized materials.

##### 2:00 PM \*BB5.2

DESIGN OF LUMINESCENT POLYMERS FOR LEDs. Ian D. Rees, Takeshi Sano, Rainer E. Martin, Yuguang Ma, Andrew B. Holmes, Univ. Cambridge, Melville Laboratory, Cambridge, UNITED KINGDOM; Shuang Fang Lim, Franco Cacialli and Richard H. Friend, Univ. Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

Light emitting polymers have emerged as very promising materials for the active layer in light emitting devices owing to their color tunability, stability and potential for cheap processing over large areas. Materials based on poly(1,4-phenylene vinylene)s were the early candidates, but more recently attention has been directed to polyaromatics and their heterocyclic counterparts. One very promising class of fluorescent materials is the poly(9,9-dialkyl-2,7-fluorene)s. However, a recognised complication is the tendency for these materials to undergo aggregation and produce unwanted longer wavelength emission. In this paper we describe a number of approaches to minimize these unwanted features by introduction of comonomers designed to interfere with aggregate formation.

##### 2:30 PM BB5.3

THIN FILM LIGHT-EMITTING DEVICES BASED ON RUTHENIUM (II) COMPLEXES. Hartmut Rudmann, Satoru Shimada, Michael F. Rubner, Massachusetts Institute of Technology, Dept of MS&E, Cambridge, MA.

Recently we showed that it is possible to fabricate simple, single layer light-emitting devices comprised of a thin film of blends of tris(2,2'-bipyridyl) ruthenium(II) hexafluorophosphate [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and a glassy polymer sandwiched between an ITO anode and an aluminum cathode. Due to the electrochemical nature of the device operation, a high external quantum efficiency at a low operating voltage can be achieved. Such devices exhibit external quantum efficiencies in the range of 2 - 2.5% at luminance levels of 100 - 300 cd/m<sup>2</sup> and a half-life greater than 1000 hours continuous operation. We now achieved external quantum efficiencies as high as 5% at luminance levels of 30 - 100 cd/m<sup>2</sup>. This increase in performance is the result of two advances. First, we found that the aluminum cathode is not chemically stable and damages the device over time. By switching to cathode materials like silver or gold, this problem is greatly alleviated. The use of such high work function metals is only possible with electrochemically driven devices. Second, we designed and synthesized a number of new Ru (II) complexes with different alkyl-substituents on the bipyridyl ligands. Devices containing these new Ru (II) complexes show a higher electroluminescence efficiency than devices made of the unmodified Ru(bpy)<sub>3</sub><sup>2+</sup> complex. In addition, these devices show a shorter transient time to reach a steady luminance level due to the increased free volume and, therefore, higher ion mobility. The ion mobility can be further increased by switching to smaller counter-ions

such as BF<sub>4</sub>. As a result, devices that contain the new Ru (II) complexes with BF<sub>4</sub> counter-ions emit light almost instantaneously (< 1 second) after the operating voltage has been applied.

##### 2:45 PM BB5.4

NOVEL LANTHANIDE ORGANOMETALLIC COMPLEXES FOR IR LIGHT SOURCES (LASERS AND OPTICAL AMPLIFIERS). Sylke Blumstengel, Francesco Meinardi, Riccardo Tubino, Università Milano-Bicocca, Dipartimento di Scienza dei Materiali, Milano, ITALY; Nataly Colombi, Silvia Destri, Istituto di Chimica delle Macromolecole-CNR, Milano, ITALY.

In the field of organic IR emitters, stable rare earth ion complexes bearing conjugated ligands are receiving increasing attention since they combine the advantages of the organic ligands (high absorption cross section, solubility etc.) with those of the inorganic component (IR emission, long lifetime). To obtain optically pumped LASERS and amplifiers with a suitable efficiency based on organometallic complexes, beside an efficient population of the ligand excited state followed by short range (Dexter) energy transfer to the rare earth ion, it is also necessary that the organic ligand can be excited at an energy as low as possible. In this work, novel Er<sup>3+</sup> crown-ethers with the absorption edge in the low energy tail of the visible spectrum are presented. Both solutions and films of these complexes have been prepared and in all samples a 1.5 μm luminescence excited with an Ar<sup>+</sup> laser is demonstrated. Finally the PL efficiency of our compounds is discussed in relation with that of other common organometallic compound as Er(Q)<sub>3</sub>.

##### 3:30 PM \*BB5.5

POLYMERS FOR LEDs. Mary Galvin, University of Delaware, Department of MS&E, Newark, DE.

Polymeric light-emitting diodes (PLEDs) have the potential for significant commercial applications in the display industry. While scientists have been able to increase the efficiencies and lifetimes of these devices, much remains to be done. We are still lacking a comprehensive knowledge of the fundamental structure/property relationships in this class of polymers. There is also a need for polymers with more balanced electron and hole transport. This talk will focus on some recent results in these areas.

##### 4:00 PM \*BB5.6

SMALL MOLECULE AND POLYMERIC LUMINESCENT SOLIDS. Hieu Duong, Fred Wudl, Qichun Zhang, Rebecca M. Vestall, University of California, Department of Chemistry and Biochemistry and Exotic Materials Institute, Los Angeles, CA.

The design and synthesis of novel fluorescent molecules with luminescence ranging from blue to red will be presented. The incorporation of a luminescent chromophore into a standard polymer backbone for the preparation of blue luminescent fibers and films will also be presented. The design and synthesis of small molecule electron-transport molecules will also be communicated.

##### 4:30 PM BB5.7

EFFICIENT BLUE LIGHT EMITTING POLYMERS. Qibing Pei, Shun-chi Chang\*, Yang Yang\*, SRI International, Menlo Park, CA; \* Department of Materials Science and Engineering, UCLA, Los Angeles, CA.

Blue light emitting polymers are still the bottleneck for the development of polymer displays. Poly(paraphenylenes) and their close relatives, poly(fluorenes), have been among the most promising. However, several drawbacks, including low semiconductivity and thermal instability, have limited the performance of blue polymer LEDs. We will present a series of new poly(paraphenylenes) exhibiting both high luminescent efficiency and thermal stability. LEDs have been demonstrated with 4.2cd/A and 360cd/m<sup>2</sup> at 8V.

##### 4:45 PM BB5.8

NEW MOLECULAR AND POLYMERIC ELECTRON-TRANSPORT MATERIALS FOR LIGHT-EMITTING DEVICES. Martin R. Bryce, Changsheng Wang, Dept of Chemistry, University of Durham, Durham, ENGLAND; Gun-Young Jung, Yulin Hua, Michael C. Petty, School of Engineering, University of Durham, ENGLAND.

We will describe the design, synthesis and structural properties (including X-ray crystal analysis) of new pyridine- and 1,3,4-oxadiazole- containing oligomers and polymers. We have fabricated LEDs using MEH-PPV as the emissive material with an additional layer of these materials, either thermally evaporated or spin coated, acting as an efficient electron-injection/hole-blocking layer to improve device performance. We will discuss the characteristics of these bilayer LEDs, and devices with additional buffer layers which further improve their stability and lifetimes. The effects of processing conditions: notably deposition rate, thickness of

the thermally evaporated Al top electrode and annealing processes, will be presented. We will also discuss work on new polymeric diaryloxadiazole systems in this context.

For references to our recent work on these systems see:

C. Wang, M.R. Bryce et al, *Adv. Mater.*, 2000, 12, 217; C. Wang, M.R. Bryce et al, *Chem. Mater.*, 2001, 13, 1167; C. Wang, M.R. Bryce et al, *Adv. Funct. Mater.*, 2001, 11, 47; G.Y. Jung, C. Wang, M.R. Bryce, et al, *SPIE Proceedings*, 2001, 4105, 307; G.Y. Jung, C. Wang, C. Pea, C. Pearson, M.R. Bryce, M.C. Petty, *J. Appl. Phys.*, submitted.

#### SESSION BB6: APPLICATIONS IN DISPLAYS

Chair: George G. Malliaras  
Wednesday Morning, November 28, 2001  
Constitution A (Sheraton)

#### NOTE EARLY START

##### 8:15 AM \*BB6.1

NANOPRECISE SELF-ASSEMBLY OF MOLECULE-BASED OPTOELECTRONIC STRUCTURES. ELECTRO-OPTIC AND ELECTROLUMINESCENT ARRAYS. Tobin J. Marks, Dept. of Chemistry and the Materials Research Center, Northwestern U., Evanston, IL.

Self-limiting chemisorptive siloxane condensation chemistry offers the attractive possibility of constructing, with sub-nanometer precision, robust, conformally adherent, optically functional, interlinked assemblies composed of designed, microstructurally and photo-physically well-defined building blocks. We discuss here the implementation of such strategies for the fabrication and soft lithographic patterning of organic electro-optic and emissive structures. In the electro-optic area, we report: i) efficient, automatable routes to very large electro-optic response self-assembled superlattices, ii) a new way to tune the refractive indices of such materials, iii) the fabrication and properties of the first self-assembled electro-optic modulator. In the LED area, we report: i) electrode passivation and charge injection balance control, ii) elucidation of matrix order vs. disorder effects on charge transport, iii) control of interfacial electrode-organic cohesion effects on charge injection, iv) the fabrication of emissive nanodiodes having dimensions less than 50 nm, v) superior device characteristics of high-work function anode alternatives to ITO.

##### 8:45 AM BB6.2

BRIGHT WHITE ELECTROPHOSPHORESCENT TRIPLE-EMISSIVE LAYER ORGANIC LIGHT EMITTING DEVICE. Brian D'Andrade, Stephen Forrest, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ; Mark Thompson, Univ of Southern California, Dept of Chemistry, Los Angeles, CA; Yeh-Jiun Tung, Universal Display Corp, Ewing, NJ.

Efficient organic light emitting devices (OLEDs) based on fluorescent molecular organic materials have been used extensively in full color flat panel displays. Several fluorescent materials have been previously combined[1] in a single OLED for white light emission for backlighting applications. However, the efficiency of fluorescent emitters is limited by a 0.33 singlet-to triplet exciton formation ratio, where only the singlet states radiate light. Since blue, green and red phosphor-doped OLEDs have been previously shown to have external quantum efficiencies ( $\eta_{ext}$ ) of nearly 20% due to their ability to harness triplet emissive states[2,3], these dopants present the possibility of realizing extremely high efficiency white light sources for LCD backlights, room lighting and other applications. In this work, we show that by doping an emissive layer sequentially (starting from the hole transport layer/doped electron transporting emissive layer interface) with the blue phosphor, iridium(III)bis(4,6-di-fluorophenyl)-pyridinato- $N,C^2$ ) picolinate (FIrpic), followed by the red phosphor bis(2-(2'-benzo[4,5-a]thienyl)pyridinato- $N,C^3$ )iridium(acetylacetonate) (Btp<sub>2</sub>Ir(acac)), and the green phosphor fac tris(2-phenylpyridine)iridium (Ir(ppy)<sub>3</sub>) into spatially distant bands of a 4,4'-N,N'-dicarbazole-biphenyl (CBP), efficient white light electrophosphorescence is observed. The thickness and positions of the doped bands relative to the hole and electron injection layers were adjusted to maximize efficiency and optimize color balance. White light with Commission Internationale de l'Eclairage coordinates of (0.31, 0.35), an  $\eta_{ext}$  of (3.9 ± 0.4)% corresponding to 7 cd/A and a maximum luminance of (36,000 ± 4,000) cd/m<sup>2</sup> at 15.8 V were obtained. By controlling diffusion through the doped CBP layers using exciton blocking layers, the  $\eta_{ext}$  can be increased to (5.0 ± 0.5)%.

1. X. Jiang, Z. Zhang, W. Zhao, W. Zhu, B. Zhang and S. Xu, *J. Phys. D: Appl. Phys.* **33**, 473 (2000).
2. Chihaya Adachi, Marc A. Baldo, Mark E. Thompson and Stephen R. Forrest submitted to *J. Appl. Phys.*
3. Yasunori Taga and Masamichi Ikai, presented at the Materials Research Society Spring Meeting, San Francisco, CA, 2001 (unpub).

##### 9:00 AM BB6.3

N-TYPE ORGANIC THIN FILM TRANSISTOR BASED ON N,N'DIALKYL 3,4,9,10-PERYLENE TETRACARBOXYLIC DIIMIDE DERIVATIVES. Patrick R.L. Malenfant, Christos D. Dimitrakopoulos, Jeffrey D. Gelorme, Laura L Kosbar, Teresita O. Graham, IBM Corporation T.J. Watson Research Center, Yorktown Heights, NY; Alessandro Curioni, Wanda Andreoni, IBM Research Division Zurich Research Laboratory, Saumerstrasse 4 Rueschlikon, SWITZERLAND.

We are currently fabricating organic n-type field effect transistors for the purpose of making complimentary circuits. The organic channel materials are N,N'-dialkyl-3,4,9,10-perylene tetracarboxylic diimide derivatives. Devices have been prepared where various surface treatments have been explored as well as different device configurations (i.e. bottom vs top contact devices). Mobilities up to 0.6 cm<sup>2</sup>/Vs and current on/off ratios up to 1E5 have been obtained.

##### 9:15 AM BB6.4

HIGHLY EFFICIENT BLUE ORGANIC LIGHT-EMITTING DIODES USING PYRENE-ADAMANTANE DERIVATIVES. H. Fujikawa, T. Mori, H. Tanaka, H. Takeuchi and Y. Taga, TOYOTA Central Research & Development Laboratories, Inc., Nagakute, Aichi, JAPAN.

Organic light-emitting diodes (OLEDs) are promising candidates for the next generation full-color, flat panel displays. Recently, multi-color displays using the OLEDs have been commercialized. However, further research and development are required to improve the lifetime and the color tunability. Material developments are especially important. In this paper, we show the electroluminescent (EL) properties of OLEDs with new emitting materials, pyrene-adamantane derivatives. We synthesized a new blue emissive material, adamantane derivative which has two pyrene units (PY-AD). The PY-AD exhibits strong blue photoluminescence in a solid state, which is due to pyrene moiety. The PY-AD has a high glass transition temperature of 181°C, which is attributed to the rigid adamantane unit. In addition, the excellent morphological stability was confirmed in the thin films prepared by vacuum deposition. Using the PY-AD, the OLEDs were fabricated and the EL properties were investigated. Blue emission with a peak at 467 nm was observed and a high efficiency of 1.9 cd/A was obtained at a luminance of 300 cd/m<sup>2</sup>. The good stability was also achieved in a continuous operation at room temperature and high temperatures. Our results suggest that the adamantane derivatives are promising materials for highly efficient blue emission.

##### 9:30 AM \*BB6.5

'PAPER LIKE' ELECTROPHORETIC DISPLAY TECHNOLOGY SUITABLE FOR MASS PRODUCTION. Georges Hadziioannou, Polymer Chemistry Laboratory, Groningen University, Groningen, THE NETHERLANDS; Papyron B.V. Zernike Science Park, Groningen, THE NETHERLANDS.

Desired properties of the future third generation displays include bistability of the active media, low power consumption, large viewing angle, flexibility and large area low cost manufacturability. Conventional paper shows most of these properties, however a once printed image can not be changed. For that reason scientists have been working on an electronic version of paper since the 1970's. A so called electrophoretic image display combines the advantages of paper with electronic addressing. If viewed from the front, a dye solution containing colored charged particles shows either the color of the dye or of the particles, depending on the polarity of an applied electric field. One of the challenges in this type of display is to prevent transverse particle migration. To overcome this problem the displays developed by Papyron are based on a thin perforated plastic film. The individual wells are arranged in a regular array and constitute single display pixels upon filling with an electrophoretic ink. There are a number of benefits of this approach compared with the microcapsules that others are using. One of them is the ability to fill different holes with different colors. An ink jet printing technique will be developed to achieve this goal. If a fluid with a very high room temperature viscosity, but low viscosity at elevated temperatures is used, the image can be addressed at high temperatures but will remain indefinitely without power consumption at room temperature, just like conventional paper.

##### 10:30 AM \*BB6.6

SPIN-DEPENDENT EXCITON FORMATION IN MOLECULAR AND POLYMERIC LIGHT-EMITTING DIODES. J.S. Wilson, A.S. Dhoot, A.J.A.B. Seeley, University of Cambridge, Cavendish Laboratory, UNITED KINGDOM; M.S. Khan, Sultan Qaboos Univ, Chemistry Dept., Sultanate of Oman; A. Köhler, R.H. Friend, University of Cambridge, Cavendish Laboratory, UNITED KINGDOM.

The ratio of spin singlet to spin triplet exciton formation following electron-hole capture in organic light-emitting diodes controls the efficiency of operation. We have studied a polymer containing platinum in the polymer chain, and a model monomer, which show both singlet and triplet luminescence. Comparison of the photo-excited emission with the electroluminescence allows direct measurement of the singlet:triplet formation ratio for electroluminescence. We find ratios close to 25% for the model monomer, but in excess of 50% for the polymer. We discuss models for spin-dependent electron-hole capture for the case of the polymer.

#### 11:00 AM **BB6.7**

##### PERFORMANCE OF LIGHT EMITTING POLYMER (LEP) DEVICES FABRICATED BY INK JET PRINTING.

N. Athanassopoulou, S.K. Heeks, J.C. Carter, P.J. Lyon, A. Wehrum, P. Montez, J.H. Burroughes, C.R. Towns and I. Grizzi, CDT Ltd, Cambridge, UNITED KINGDOM; M. de Kok, M. Buechel, S. de Winter, S. Vulto, K. Mutsaers, T. van den Biggelaar, I. Camps, P. Duineveld, J.E. Rubingh, E. Haskal, P. van de Weijer, Philips Research, Eindhoven, THE NETHERLANDS.

Ink jet printing has been shown to be a viable route for fabricating high resolution, active and passive matrix, full colour, LEP displays [1,2]. In order to ink jet print it is necessary to make modifications to the ink jet printer heads, the substrate and also the polymer solutions. The modifications of the polymers to inks, has been found to effect the electronic and photonic properties of the electroluminescent polymer layers in devices. We have formulated polymer inks with rheological properties optimised for ink jet printing together with substrates whose surface energies have been modified to preferentially wet the active area of the pixel. We will compare and contrast the properties of LEP devices prepared through ink jet printing and through traditional spin coating deposition techniques in terms of efficiency, lifetime and uniformity.

[1] S.K. Heeks, J.H. Burroughes, C. Towns, S. Cina, N. Baynes, N. Athanassopoulou, J.C. Carter, S. Miyashita, SID DIGEST, 518, 2001.

[2] E.I. Haskal, M. Buechel, S.K. Heeks, N. Athanassopoulou, J. O'Brien, D.J. Brennan, M. Fleuster and R.J. Visser, AD/IDW 2001(submitted).

#### 11:15 AM **BB6.8**

##### THREE-COLOR PASSIVE-MATRIX DISPLAY WITH DYE-DIFFUSION-PATTERNED POLYMER THIN-FILM AND A NOVEL TRI-LAYER STRUCTURE. Ke Long, Florian Pschenitzka and J.C. Sturm, Center for Photonics and Optoelectronic Materials (POEM), Dept of Electrical Engineering, Princeton University, Princeton, NJ.

Passive-matrix displays using organic light-emitting devices (OLEDs) have been of great interest for applications in light-weight, flexible flat panel displays. Polymers are attractive materials for OLED displays because they can be deposited by low-cost and high-throughput methods such as spin-coating. The emission colors of polymers can be controlled by adding a small amount of fluorescent dyes into the polymer film. In this work, we applied a solvent-enhanced dye diffusion method[1] to locally dope a previously spin-coated polymer film with different dyes, to fabricate side-by-side RGB subpixels for a full color display. First we spin-coated a blue dye-doped poly(9-vinylcarbazole)(PVK) polymer layer. Then green and red dyes in 300 microm wide stripes were added to the polymer layer from large-area patterned dye sources in two thermal transfer printing steps, followed by a room-temperature solvent-vapor annealing step to distribute dyes uniformly into the polymer film. 300 microm RGB color stripes by photoluminescence over a 3.5cm x 2.5cm area of excellent uniformity resulted. High leakage and low efficiency of the single-layer doped polymer LEDs limit their application in passive matrix displays. To reduce reverse leakage current and raise efficiency, a blanket tri-8-hydroxyquinoline aluminum(Alq) electron transport layer(ETL) was deposited over the polymer layer after the dye diffusion step, along with a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline(BCP) hole/exciton blocking layer between the Alq and the PVK to ensure all light emission occurred from the doped polymer and not from the Alq. Devices with this novel tri-layer structure have a higher external quantum efficiency (~1%) and an extremely low reverse leakage current (rectification ratio of 1,000,000 at +/- 10V). A three-color passive-matrix display with 300um x 1mm RGB subpixels was fabricated with this structure.

This work is supported by DARPA and NJCST.

Reference:

[1] F. Pschenitzka and J.C. Sturm, Appl Phys Lett 78 (17), 2584 (2001).

#### 11:30 AM **BB6.9**

##### INCREASED EXTERNAL QUANTUM EFFICIENCY OF OLEDs USING MICROLENS ARRAYS. S. Möller and S.R. Forrest, Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, NJ.

We have developed a technique to fabricate ordered arrays of plastic microlenses with diameters  $d \sim 10 \mu\text{m}$ , to increase the light output of organic light emitting devices (OLED). The lenses, which are much smaller and not aligned to the OLEDs positioned on the opposite surface of a glass substrate, outcouple light which is not emitted into the escape cone of the substrate. This technique increases the external OLED quantum-efficiency ( $\eta_{ext}$ ) by a factor of  $\sim 1.5$ , i.e. for state of the art devices<sup>1</sup>  $\eta_{ext} > 25\%$  (90lm/W) is anticipated. Our current results have shown that an electrophosphorescent device based on an Ir(ppy)<sub>3</sub> doped emitting layer has an efficiency increased from 8% using a flat substrate, to 12% using one with microlenses. In contrast to diffractive optical elements<sup>2</sup> (monolayers of silica spheres with  $d=550\text{nm}$ ) or alignment of single, large hemispherical lenses<sup>3</sup>, the microlens arrays allow for inexpensive, large area fabrication and need no alignment. The mold for the lens array was fabricated in a silicon wafer using a photolithographic process followed by selectively etching the silicon through a silicon nitride mask. After removing the etch mask, the mold is filled with the transparent elastomer PDMS (poly-di-methyl-siloxane). A glass substrate is placed on the PDMS which is cured at 340K for 2h. Due to the poor adhesion to silicon the lens sheet stays on the glass substrate, which subsequently is used to grow the OLEDs. Since the microlenses significantly increase OLED efficiency, they are expected to lead to extended device lifetime and power consumption.

<sup>1</sup> C. Adachi, M.A. Baldo, S.R. Forrest and M.E. Thompson, Appl. Phys. Lett. 77, 6 (2000).

<sup>2</sup> T. Yamasaki, K. Sumioka and T. Tsutsui, Appl. Phys. Lett. 76, 10 (2000).

<sup>3</sup> V. Bulovic V.B. Khalfin, G. Gu, P.E. Burrows, D.Z. Garbuzov and S.R. Forrest, Phys. Rev. B 58, 7 (1998).

#### 11:45 AM **BB6.10**

##### A 2" MONOCHROME 64x96 PASSIVE MATRIX POLYMER LED. J.N. Huiberts, M. Büchel, M.M. de Kok, S.I.E. Vulto, P. van de Weijer, E.A. Meulenkaamp and E. Haskal, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

Royal Philips Electronics has recently launched the first commercially available polymer LED, a 2" monochrome 64x96 passive-matrix display. The transition from a working laboratory prototype to a commercial product involved several non-trivial aspects. The integration of charge transport and photon generation in one type of PPV-material requires a fine-tuning of the device structure. In this presentation, a number of physical properties and observed phenomena will be discussed that must be taken into account during the selection of a polymer material and the choice of the device structure; for example, the color, the driving conditions, the initial electron and hole mobility, the polymer thickness, the electrodes, the lifetime and an important failure mode. The use of the pulsed driving scheme essential for a passive matrix configuration puts certain limitations on the active polymer but offers surprising advantages as well. One of these advantages is a substantial increase of the lifetime by nearly a factor 3 compared to DC driving (lifetime~40000 hour).

#### SESSION BB7: ELECTROCHROMIC POLYMERS/SENSORS

Chair: Alex K-Y. Jen

Wednesday Afternoon, November 28, 2001  
Constitution A (Sheraton)

#### 1:30 PM **\*BB7.1**

##### ELECTROLUMINESCENCE AND ELECTROCHROMISM BEYOND THE VISIBLE RANGE: NIR EMITTING PLED'S AND Ir ELECTROCHROMISM. John R. Reynolds, Benjamin S. Harrison, Timothy J. Foley, Joonbo Shim, Mohamed Bouguettaya, James M. Boncella, Paul H. Holloway, Kirk S. Schanze, David B. Tanner, Irina Schwendeman, and Jungseok Hwang, Departments of Chemistry, Physics, Materials Science and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL; S. Ramakrishnan and G. Padmanaban, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, Karnataka, INDIA.

This lecture provides an overview of a group effort on NIR electroluminescence and IR electrochromism. Significant advances continue to be made in developing visible light emitting PLEDs and electrochromic polymers with visible color responses. Less effort has been directed to longer wavelengths. Here, we report near-IR photoluminescence (PL) and electroluminescence (EL) from blends of MEH-PPV with Yb(TPP)acac and Er(TPP)acac (TPP = 5,10,15,20-tetraphenylporphyrin, acac = acetylacetonate). PL studies of films produced by blending 2 mol% Yb(TPP)acac with MEH-PPV shows the polymer fluorescence (589 nm) is quenched approximately 98% with appearance of the Yb emission at 977 nm in the near-IR. Analogous results are observed when Er(TPP)acac is blended into

MEH-PPV, but in this case the near-IR emission appears at 1560 nm. EL spectra of PLEDs fabricated using the Ln(TPP)acac complexes show that the visible emission of the MEH-PPV is strongly suppressed, and the device emission is dominated by the near-IR output of the Ln complex. A dialkoxy derivative of poly(p-phenylene) has also been employed demonstrating the generality of this method. Utilizing an outward facing electrochromic device design with a porous gold/Mylar top electrode, we have been able to modulate the reflectivity off of the gold surface throughout the visible, NIR and mid-IR regions utilizing the electrochromic response of the dimethyl derivative of poly(3,4-propylenedioxythiophene) (PProDOT-Me2). The surface changes from a deep blue when the polymer is in the reduced state to a reflective gold when the polymer is oxidatively doped due to the high transmissivity of PProDOT-Me2 to visible light. The inverse EC effect is observed throughout the infrared region as the neutral form of the PProDOT-Me2 is transmissive (the surface is IR reflective), while the doped and conducting form of the polymer (and thus the coated surface) is IR absorbing.

#### **2:00 PM BB7.2**

**PHOTOPHYSICS OF OLIGOETHER FUNCTIONALIZED POLY(PARA PHENYLENE) BASED MIXED IONIC ELECTRONIC CONDUCTORS.** Franz P. Wenzl, Gernot Mauthner, Emil J.W. List, Inst. fuer Festkoerperphysik, Technische Universitaet Graz, AUSTRIA; Christian Suess, Anja Haase, Georg Jakopic, Inst. fuer Nanostrukturierte Materialien und Photonik, Joanneum Research GmbH, Weiz, AUSTRIA; Dieter Somitsch, Peter Knoll, Inst. fuer Experimentalphysik, Universitaet Graz, AUSTRIA; M. Bouguettaya, John R. Reynolds, Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL; Guenther Leising, Institut fuer Nanostrukturierte Materialien und Photonik, Joanneum Research GmbH, Weiz, AUSTRIA, Science & Technology, AT&S AG, Leoben, AUSTRIA.

We report on investigations of the photophysics of different oligoethylene oxide functionalized poly(para phenylene) (PPP) based polymeric mixed ionic electronic conductors (PMIECs). In order to study the influence of ion complexation homopolymers and copolymers (PPP-ORX), consisting of a PPP backbone and oligoethylene oxide side-chains of varying chain length were synthesized to supply the polymers with an ion transporting functionality. These polymers were investigated in their pristine and ion-complexed form with a Li salt (lithium triflate, providing the ionic species) by means of UV/VIS/NIR absorption and steady state photoluminescence measurements and photoinduced absorption (PIA) spectroscopy. With infrared spectroscopy we determine the degree of ion dissociation. Spectroscopic ellipsometry delivered the optical parameters and atomic force microscopy (AFM) complemented this study with morphological aspects of the polymer system.

#### **2:15 PM BB7.3**

**SYNTHESIS OF NOVEL LIGHT EMITTING POLYMERS (LEPs) VIA RING-OPENING POLYMERISATION OF MACROCYCLIC PRECURSORS.** Steve Yeates, AVECIA, Manchester, UNITED KINGDOM; Richard Williams, Philip Hodge, Manchester University, Manchester, UNITED KINGDOM.

A number of challenges are associated with the application of high molecular weight rigid rod polymers in LEP structures, particularly regards their solution characteristics. They often yield high viscosity solutions even at high dilution which can give rise to difficulties, especially in the application of ink-jet printing. Classical precursor routes have been employed but concerns exist over poor device performance as a consequence of imperfect conjugation and retained impurities within the device structure. We have investigated the placement of suitable electroluminescent chromophores into precursor cyclic oligomers which upon heating will ring open to give high molecular weight polymer. The advantages of the approach in the production of complex multi-layer thin film devices include the very much lower initial viscosities of macrocyclic oligomers relative to the corresponding high molecular weight polymers, the complete absence of by-products, and the fact that ring-opening polymerisations of strain-free macrocycles are largely entropy-driven and thermally neutral. Results on the synthesis of this novel class of materials is presented, along with initial EL performance data.

#### **2:30 PM BB7.4**

**CONJUGATED POLYMERS FOR THIN FILM COATING PROCESS.** Zhexiong Tang, Wenguang Li, Cheryl Nowak, and Sze C. Yang, Univ of Rhode Island, Dept of Chemistry, Kingston, RI.

Conjugated polymers are used in light emitting diodes, thin film transistors, electrochromic devices and chemical sensors. The device performance is critically dependent on the quality of the thin film of the conjugated polymer coating on these devices. The chemical purity of the polymer, the film forming property, and the coating process are important for the quality of the thin film. It is often difficult to meet

all of these demands by chemically derivatizing the conjugated polymers. It is desirable to be able to optimize the film forming properties without compromising the opto-electronic properties. We report an approach for solving this problem by synthesizing a double-strand polymeric complex of the conjugated polymer. The first strand of the complex is the conjugated polymer that carries the appropriate optical or electronic properties. The second strand is a polymer that carries the properties necessary for thin film formation. Since the two strands of polymers are non-covalently bonded, the second strand can be functionalized without compromising the electro-optical properties of the conjugated polymer. The double-strand polymers were synthesized by a template-guided synthesis method. The double-strand polymer is dispersible in water or solvents. The molecular weight and the functional groups in the second strand can be selected for optimizing the film coating process. We will discuss the factors that influence the dispersibility of the polymeric complexes of polyaniline and polypyrrole with poly(acrylic acid). The influence of the molecular weight of the second strand, ranging from M.W. = 1,800 to 250,000, were studied. Other factors studied include the molar ratio of the first and the second strand, and the type of oxidants used for the polymerization reaction. The viscosity of the polymer solution was studied to understand the properties of the polymers.

#### **2:45 PM BB7.5**

**THE PRECURSOR POLYMER AND GRAFTING APPROACHES TOWARDS ULTRATHIN FILMS OF CONJUGATED POLYMERS PREPARED BY ELECTRODEPOSITION ON CONDUCTING SURFACES.** Rigoberto Advincola, Chuanjun Xia, Prasad Taraneekar, Suxiang Deng, Ken Ohnishi Department of Chemistry, University of Alabama at Birmingham Birmingham, AL.

In this talk, we report our results on the ultrathin film formation and electro-deposition of conjugated polymer films by a novel approach consisting of: 1) Synthesis of specialized "precursor" soluble oligomers and polymers 2) Electro-deposition of films from these polymers on specific sites of substrates and in specific sequences. This involves the formation of molecularly ordered cross-linked and network polymer systems primarily demonstrated in polythiophenes, polypyrroles, and polyfluorenes. We have investigated the properties of these films using AFM, SPS, ellipsometry, photoluminescence, XPS, and electrochemistry. Our results indicate that the overall optical and mechanical quality of these films are far superior compared to previously reported electropolymerized systems. This new approach will eventually allow us to fabricate patterned electrical and optical devices with fine resolution (ca 10 micron features) without using conventional spin casting and photolithographic techniques. The opportunity to prepare films of various optical, mechanical, and band-gap properties involves a rational design of the precursor polymer synthesis and the electrodeposition method. The electrical, electroluminescence, photoluminescence, and carrier mobility properties of these type of films are described.

#### **3:30 PM \*BB7.6**

**CONJUGATED POLYMERS AS SELF-AMPLIFYING SENSORY MATERIALS.** Timothy M. Swager, Dept. of Chemistry, Massachusetts Institute of Technology, Cambridge, MA.

We will discuss the design of conjugated organic polymers with chemically sensitive transport properties for the formation of ultra-high sensitivity chemical sensors. Amplification in these systems is derived from using multiple receptor sites for the target chemical species (analyte) to be detected. The analyte is designed to impede the transport of charged carriers or excited states (excitons) in the polymers. Alternatively the analyte can simply capture the carrier or exciton. A number of examples will be discussed including materials designed for the detection of explosives, chemical warfare agents, DNA, and ionic compounds.

#### **4:00 PM BB7.7**

**THE DEVELOPMENT OF MANUFACTURE ROUTES TO POLY-2,5-THIENYLENE VINYLENE (PTV) PRECURSOR, A SOLUTION PROCESSABLE ORGANIC SEMICONDUCTING MATERIAL.** Domenico Cupertino, Julie Fergus and Willi Kreuder, COVION Semi-conductors GmbH, Frankfurt, GERMANY; Albert van Bremen, Peter Herwig and Herman Schoo, TNO, Eindhoven, THE NETHERLANDS; Dago de Leeuw, Philips Research, Eindhoven, THE NETHERLANDS.

Semi-conducting organic materials are showing increasing potential as active components in electronic devices as they offer distinct advantages for the fabrication of low-cost and/or large area flexible electronic circuits. Although different types of organic materials have been investigated as the active component of electronic devices, many have proved to be unsuitable for such applications because they cannot readily be processed. For practical, commercial applications, the materials must be able to be deposited and patterned using

low-cost techniques such as printing/spin coating, rather than by high-cost vacuum deposition/photolithographical processes. The materials must also be accessible in sufficient quantity and purity to make any potential manufacture viable. In this work we report on progress that has been made towards developing processes suitable for the manufacture of a soluble PTV precursor polymer which can be coated from a solution phase and then converted to the active semiconductor layer in the device.

#### 4:15 PM **BB7.8**

**SYNTHESIS AND CHARACTERIZATION OF CONDUCTIVE STARBURST BLOCK COPOLYMERS.** Lee Y. Wang, Center for Condensed Matter Sciences, National Taiwan University, TAIWAN; Chih-Chian Chu, Jentaie Shiae, Department of Chemistry, National Sun Yat-Sen University, TAIWAN.

A series of novel star-like semiconductive block copolymers were synthesized by the use of hexacyclosulfated fullerene as central cores for anchoring multiple linear polyaniline-*b*-polyether chains. Chemical structure and molecular weight characteristics of these conductive stars were studied by various spectroscopic methods, gel permeation chromatography, and matrix assisted laser desorption/ionization mass spectrometry techniques. Mass spectra and GPC data clearly indicated a monodisperse structure in both degree of branching and arm length for the prepared star copolymers. Most significantly, these conjugated macromolecules not only showed excellent solubility in common organic solvents, such as THF, DMF, *m*-cresol and NMP, but also exhibited higher electrical conductivity than their parent arms. The effect of arm length and branching number on the electronic properties of materials will be also presented.

#### 4:30 PM **\*BB7.9**

**ELECTRICALLY ACTIVE ORGANIC/INORGANIC HYBRID MATERIALS.** Zhonghua Peng, Yongge Wei, Meng Lu, Bubin Xu, Chao Li, Calide Fung-Chi Cheung, Univ of Missouri-Kansas City, Dept of Chemistry, Kansas City, MO.

Polyoxometalates (POMs), clusters of early transition metal cations bridged by oxide anions, are a unique class of compounds with unmatched versatility, at least among inorganic systems, in terms of structural, electrochemical, and photophysical properties. Well defined, up to nanometer-size molecular chains, rings, and spheres, can be readily constructed. Their unique electronic, optical, and magnetic properties, as well as extreme thermal robustness, have made them extremely attractive in a number of applications ranging from catalysis and medicine to analysis and sensors. Among the many research areas on POMs, preparation of POM-based molecular materials has attracted significant interest. The prospect that the coexistence of organic delocalized *p*-electrons with localized *d* electrons may result in materials combining useful magnetic and electrical properties has stimulated intense research on POM/organic hybrid materials. The majority of such materials, however, are based on POM anion/organic cation salts. The weak intermolecular organic/inorganic contacts in these materials has prevented an effective interaction between the conducting *p*-electrons and localized *d* electrons. In this presentation, we report the synthesis of a novel new type of POM-based molecular material where POM clusters are covalently linked with organic conjugated segments in a variety of architectures. Such molecular hybrids are constructed via organic reactions using functionalized POM clusters as building blocks. This approach allows us to rationally design the structures and properties of the hybrid materials. It also allows a systematic study of structure-property relationships of POM clusters/organic conjugates. The detailed synthesis and optical properties of some novel POM/organic hybrid materials will be presented.

### SESSION BB8: ORGANIC TRANSISTORS

Chair: Hendrik Schön  
Thursday Morning, November 29, 2001  
Constitution A (Sheraton)

#### NOTE EARLY START

#### 8:15 AM **\*BB8.1**

**POLYMER TRANSISTOR CIRCUITS FABRICATED BY SOLUTION SELF-ASSEMBLY AND DIRECT INKJET PRINTING.** Henning Sirringhaus, Richard Friend, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM; Takeo Kawase, Chris Newsome, Epson Cambridge Laboratory, Cambridge UNITED KINGDOM; Devin MacKenzie, Plastic Logic Ltd., Cambridge, UNITED KINGDOM.

We have recently demonstrated fabrication of polymer transistor circuits by a combination of solution self-assembly and direct inkjet printing. Control over the morphology of the polymer semiconductor

and uniaxial alignment of polymer chains parallel to the direction of current flow in the device is obtained by making use of liquid crystalline self-organisation. Accurate definition of the transistor channel and other circuit components is achieved by direct inkjet printing combined with surface energy patterning. Here we discuss recent experiments investigating the resolution limits for this patterning technique as well as the application of this process to fabrication of integrated polymer logic circuits.

#### 8:45 AM **BB8.2**

**ORGANIC TRANSISTORS WITH SELF-ASSEMBLED MATERIALS AND NANO-SCALE CHANNELS.** Zhenan Bao, Hendrik Schön, Hong Meng, Joanna Slusky, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Organic thin film transistors (OFETs) are potentially interesting for low-cost large area flexible electronics. The performance of some reported OFETs is already similar to that of amorphous-Si devices. It is crucial that the organic semiconductor adopts preferred orientation to facilitate charge transport. Therefore, self-assembled materials play an extremely important role in OFETs. In this talk, we report our recent work on using self-assembled layers for both the dielectric and semiconducting layers. New device structures based on self-assembled materials resulted in unusually high transistor performance. The synthesis and performance of new self-assembled organic semiconductors will be presented. Finally new nanopatterning methods and transistors with electrodes separated in the nanometer scale will also be discussed.

#### 9:00 AM **BB8.3**

**PENTACENE CHANNEL THIN FILM TRANSISTORS BY ORGANIC VAPOR PHASE DEPOSITION.** Max Shtein<sup>1,2</sup>, Jay B. Benziger<sup>2</sup>, Stephen R. Forrest<sup>1,3</sup>. <sup>1</sup>Center for Photonics and Optoelectronic Materials (POEM). <sup>2</sup>Department of Chemical Engineering. <sup>3</sup>Department of Electrical Engineering; Princeton University, Princeton, NJ.

Thin film transistors (TFTs) based on crystalline organic materials have generated considerable interest recently, with performance characteristics approaching those of amorphous silicon TFTs. We use organic vapor phase deposition (OVPD), whereby the evaporated molecules are carried to the cooled substrate in an inert gas stream, to deposit pentacene-channel TFTs, which exhibit field-effect mobilities approaching  $1\text{cm}^2/\text{V}\cdot\text{s}$ , and on/off ratios exceeding  $10^5$ . By increasing the deposition chamber pressure and substrate temperature during the organic film growth, the average size of the pentacene channel may be increased to over  $5\mu\text{m}$ . The variation in the grain size is accompanied by a variation in the threshold voltage, on/off ratio, and effective channel hole mobility. A unique property of OVPD demonstrated in this work is the ability to control crystalline texture and grain size by varying chamber pressure and substrate temperature. Our experiments help identify processing windows for achieving optimal pentacene channel TFT performance.

#### 9:15 AM **BB8.4**

**MODELING OF CHANNEL FORMATION IN ORGANIC FIELD EFFECT TRANSISTORS.** T. Li and P.P. Ruden, University of Minnesota, Minneapolis, MN; I.H. Campbell and D.L. Smith, Los Alamos National Laboratory, Los Alamos, NM.

We present device model calculations for the channel formation in organic field effect transistors (OFETs). We consider transistor structures consisting of a gate electrode, a gate insulator, and a conjugated organic film with source and drain contacts either on top of the organic film (top contact structure) or between the gate insulator and the organic film (bottom contact structure). For both structures the formation of the channel at the interface between the gate insulator and the organic film is studied as a function of gate bias. We first consider the case in which the source and drain contacts are at the same potential and solve Poisson's equation in two dimensions, coupled with non-degenerate equilibrium statistics for the carrier density in the organic film. In the top contact structure, the carrier channel initially forms under the source and drain contacts if the source and drain contact metals have sufficiently large (*p*-channel) or sufficiently small (*n*-channel) work functions. If the contact metals do not satisfy this condition, channel formation near threshold may begin midway between the source and drain contacts. Similarly, in the bottom contact structure the carrier channel may initially form near the source and drain contacts or in the middle of the channel, depending on the contact materials. We study the carrier density profile and potential distribution in the organic material as a function of gate bias for different: source-drain metal work functions, gate electrode work function, gate insulator dielectric constant, and organic film thickness for both top and bottom contact structures. Both *n*- and *p*-channel device configurations are explored. The results demonstrate the role played by the source-drain and gate contact work functions in controlling the channel carrier density. Results of

the device model calculations are used to identify critical OFET design parameters.

#### 9:30 AM **BB8.5**

**p-TYPE ORGANIC THIN FILM TRANSISTOR BASED ON SOLUBLE PENTACENE AND ANTHRACENE DERIVATIVES.** Jeffrey D. Gelorme, Christos D. Dimitrakopoulos, Patrick R.L. Malenfant, Laura L. Kosbar, Ali Afzali, Teresita O.Graham, IBM Corporation, T.J. Watson Research Center, Yorktown Hts., NY.

We have been studying organic p-type materials made mainly from vacuum sublimed thin films of pentacene. In order to drive the cost of device manufacturing lower, solution cast films of p-type materials would be desirable. This is not possible with unmodified pentacene. In this talk we will discuss the preliminary results of the synthesis and characterization of several organic solvent soluble derivatives of pentacene and anthracene. These materials can also be vacuum deposited and have been shown to have  $10 \times 10^{-2}$  to  $10 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  field effect mobilities. We will compare the morphology of solution cast films versus films that are vacuum deposited, as well as the use of various underlayers and device configurations.

#### 10:15 AM **\*BB8.6**

**ORGANIC THIN FILM TRANSISTORS BASED ON PENTACENE CHANNELS.** C.D. Dimitrakopoulos, P.S. Andry, M.J. Farinelli, D.J. Frank, K.E. Fogel, T.O. Graham, L.L. Kosbar, F.R. Libsch, J.M. Shaw, P.M. Solomon, H.-S.P. Wong, IBM Corp., T.J. Watson Research Center, Yorktown Heights, NY.

In this talk, our work on the optimization of performance of organic thin film transistors (TFT) based on pentacene channels, will be presented. Furthermore, we will describe the development of a number of processing steps required for the future fabrication of organic circuits. Studies of pentacene device reliability under various conditions, which is an important parameter to take on account when contemplating organic TFT applications, will also be presented.

#### 10:45 AM **BB8.7**

**AIR STABLE, AMORPHOUS ORGANIC FILMS AND THEIR APPLICATIONS TO SOLUTION PROCESSABLE FLEXIBLE ELECTRONICS.** Janos Veres, Simon Ogier, Stephen Leeming, Beverley Brown, Domenico Cupertino, Avecia, Manchester, UNITED KINGDOM.

The rapidly expanding field of organic semiconductors for display and low-cost electronic applications requires materials which not only have high mobility but also benefit from solution processability and environmental stability. In this paper we present a new class of solution coatable organic materials with excellent stability to air and light. Spin-coated FET devices operate at ambient conditions without encapsulation and show p-type field-effect mobilities of  $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$  and on/off ratios greater than  $10^4$ . Thin films can be deposited from common organic solvents onto a variety of substrates. These films are mechanically robust and can withstand temperatures in excess of  $100^\circ\text{C}$  without significant changes in electrical performance. FET switching and transient characteristics at higher frequencies are also discussed. These types of materials should find applications in many areas of flexible electronics.

#### 11:00 AM **BB8.8**

**ORIENTATION OF PENTACENE FILMS USING SURFACE ALIGNMENT LAYERS AND ITS INFLUENCE ON THIN FILM TRANSISTOR CHARACTERISTICS.** M.L. Swiggers, G. Xia, J.D. Slinker, A.A. Gorodetsky, G.G. Malliaras, Materials Science and Engineering, Cornell University; R.L. Headrick, Cornell High Energy Synchrotron Source; B.T. Weslowski, R.N. Shashidhar, C.S. Dulcey, Center for Bio/Molecular Science & Engineering, Naval Research Laboratory.

We have investigated the effect of surface order on the orientation and mobility of pentacene. The surface order was created using monolayers and polymers that are normally used to align liquid crystals. Rubbed polyvinylalcohol layers were found to align approximately 27 percent of the pentacene grains within a 30 degrees range. When introduced in a thin film transistor, they were found to enhance the saturation current by a factor of 2.5. A mechanism for this enhancement is proposed.

#### 11:15 AM **BB8.9**

**ORGANIC THIN FILM TRANSISTORS USING THE NEARLY ISOTROPIC CONDUCTIVE PLANAR STACKING COMPOUND, BTQBT, GROWN BY ORGANIC MOLECULAR BEAM DEPOSITION.** Jianguo Xue, Stephen R. Forrest, Princeton Univ., Center for Photonics and Optoelectronic Materials (POEM) and Dept of Electrical Engineering, Princeton, NJ; Jingui Qin, Peter V. Bedworth, Karen Kustedjo, California Inst of Technology, Beckman

Inst, Pasadena, CA; Seth R.Marder, California Inst of Technology, Beckman Inst, Pasadena,CA, and Univ of Arizona, Dept of Chemistry, Tucson, AZ.

Organic materials with high carrier mobility are desirable for many electronic device applications, especially for thin film transistors (TFTs). Recently single crystals of the sulfur-containing bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole) (BTQBT) were found to have a Hall mobility of  $4 \text{ cm}^2/\text{V}\cdot\text{s}$  at room temperature [K. Imaeda et al., J. Mater. Chem. 2, 115 (1992)]. Also the lateral conductivity in this planar stacking material is about half of the conductivity along the stacking direction, giving this compound an unusually small anisotropy uncharacteristic of most molecular organic materials such as pentacene. Such properties make the planar stacking BTQBT particularly suited for organic electronic device applications. To fabricate high mobility TFTs, we began by investigating the conditions under which ordered thin films are achieved by the UHV process of organic molecular beam deposition (OMBD). Under the appropriate conditions, BTQBT thin films were grown into ordered structures independent of lattice matching with the underlying substrate, with higher growth rates favoring more ordered and uniform films. Unlike pentacene or  $\alpha$ -6T commonly used in TFT channels, planar BTQBT molecules stack on substrates with their stacking axis perpendicular to the substrate plane. The thin films retain the high conductivity and small anisotropy of the single crystal. The field-effect mobility of the OMBD grown films increases with deposition rate of the BTQBT layer, and reaches  $0.015 \text{ cm}^2/\text{V}\cdot\text{s}$  at  $2 \text{ \AA}/\text{s}$ . This is remarkable considering that the current in the BTQBT channel flows perpendicularly to the stacking direction where molecules have their strongest intermolecular interactions. In this talk, we will discuss the nature of transport in these planar stacking thin films, and will compare them to more conventional TFT materials.

#### 11:30 AM **BB8.10**

**INFLUENCE OF THE DIELECTRIC ON THE GROWTH AND PERFORMANCE OF PENTACENE THIN FILM TRANSISTORS.**

D. Knipp, R.A. Street, B. Krusor, R.B. Apte, Xerox Palto Alto Research Center, Palo Alto, CA; B.S. Ong, Xerox Research Center of Canada, Mississauga, ON, CANADA.

Electronic transport in evaporated pentacene thin film transistors (TFT) is related to the structural order of the polycrystalline films, which is very sensitive to the nature of the dielectric on which it is deposited. Most high mobility TFTs are deposited on thermally oxidized silicon wafers. However, since this substrate is not particularly interesting for device fabrication, alternative dielectrics consistent with thin film fabrication are of interest. A comparison of different dielectrics also helps identify the origin of the TFT parameters such as mobility, threshold voltage and sub-threshold slope, and their behavior under bias stress. We describe pentacene films evaporated on plasma-enhanced chemical-vapor deposited (PECVD) silicon oxide and silicon nitride, and on spin-cast bisbenzocyclobutene (BCB), as well as on thermally grown silicon oxide. Using atomic force microscopy, we observe a strong correlation between the surface topology/chemistry of the dielectric and the morphology of the pentacene films. Roughness of the PECVD deposited dielectrics inhibits the ordering of pentacene molecules on the surface. However, by optimizing the fabrication process of the dielectrics as well as the pentacene deposition conditions, we have achieved similar pentacene morphology on all the dielectrics, without employing self-assembled monolayers. High quality structural morphology is determined by x-ray diffraction measurements and crystallite sizes exceeding  $\sim 5 \mu\text{m}$ , with its characteristic herringbone structure. Measurements on TFT structures confirm the comparable quality of pentacene for each of the different dielectrics. In each case we find essentially the same mobility of  $\sim 0.5 \text{ cm}^2/\text{Vs}$  and on/off ratios higher than  $10^8$ . A detailed comparison of TFTs on thermal oxide and PECVD nitride also shows very similar characteristics in terms of threshold voltage and sub threshold slope. It is notable that we observe the similar bias stress effects on the threshold voltage, which suggests that this is a property of the pentacene film rather than the dielectric.

#### 11:45 AM **BB8.11**

**SYNTHESIS AND APPLICATION OF A NOVEL SOLUBLE PENTACENE PRECURSOR IN THIN FILM TRANSISTORS.**

Ali Afzali, Christos Dimitrakopoulos, Tricia L. Breen, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY.

Among organic semiconductors which have been studied and tested in thin film transistors and other electronic devices, pentacene has emerged as the best alternative to existing amorphous silicon based large-area electronics technology. Field-effect mobilities greater than 1 have been measured from vacuum-deposited thin films of pentacene. However, to be more cost competitive, pentacene or any other organic semiconductor must be processable by inexpensive solution deposition techniques such as printing, stamping or spin-coating. In this talk

high yield synthesis of a highly soluble pentacene precursor and its solid phase conversion to pentacene will be presented. Fabrication and testing of thin film transistors with active channels of pentacene obtained by thermal conversion of its precursor are also described in detail.

SESSION BB9: PHOTOVOLTAICS,  
PHOTODETECTORS/TRANSPORT IN BULK  
ORGANIC MATERIALS

Chair: Zhenan Bao  
Thursday Afternoon, November 29, 2001  
Constitution A (Sheraton)

**1:30 PM \*BB9.1**

Michael Graetzel, EPFL, Lausanne, SWITZERLAND.

ABSTRACT NOT AVAILABLE

**2:00 PM BB9.2**

VERY HIGH EFFICIENCY DOUBLE HETEROSTRUCTURE COPPER PHTHALOCYANINE/ $C_{60}$  PHOTOVOLTAIC CELLS. Peter Peumans, Aharon Yakimov, Stephen R. Forrest, Princeton University, Center for Photonics and Optoelectronic Materials (POEM), Dept of Electrical Engineering and the Princeton Materials Institute, Princeton, NJ.

We have demonstrated thin-film organic photovoltaic (PV) cells with power conversion efficiencies of  $(3.6 \pm 0.2)\%$  under one sun global AM1.5 simulated solar illumination of  $150 \text{ mW/cm}^2$  (1.5 suns). The cells are of the double heterostructure type<sup>1</sup>, with a vacuum deposited copper phthalocyanine donor and  $C_{60}$  acceptor film, and a bathocuproine exciton blocking layer (EBL)<sup>1</sup>. The results represent an improvement by a factor of two in efficiency over previously demonstrated thin-film EBL based PV cells<sup>1</sup> and are a substantial improvement over current state-of-the-art organic PV cells with demonstrated efficiencies of up to  $2.5\%$ <sup>2,3</sup>. This is a consequence of the long exciton diffusion length of  $C_{60}$ , demonstrating that materials choice is an important route to cell optimization. The photocarrier collection characteristics are influenced by the anode work function through the built-in electric field, allowing a degree of optimization. In contrast, the cell parameters are less sensitive to the cathode work function, which is attributed to cathode-induced defect states in the EBL energy gap. The presence of these defect states also explains the surprisingly low resistance of the EBL to electron transport for sufficiently thin ( $<150 \text{ \AA}$ ) films. Further improvements in power conversion efficiency (up to  $4.6\%$ ) have been achieved by employing the cells in a light trapping geometry. We will discuss our views on how to further improve the efficiency of organic PV cells.

<sup>1</sup>P. Peumans, V. Bulovic, and S.R. Forrest, Appl. Phys. Lett. 76, 2650 (2000).

<sup>2</sup>J.H. Schon, Ch. Kloc, and B. Batlogg, Appl. Phys. Lett. 77, 2473 (2000).

<sup>3</sup>S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromherz, and J.C. Hummelen, Appl. Phys. Lett. 78, 841 (2001).

**2:15 PM BB9.3**

ORGANIC SOLAR CELLS BASED ON EVAPORATED PLANAR AND BULK HETEROJUNCTIONS OF A PPV-PENTAMER AND  $C_{60}$ . Wim Geens, Tom Aernouts, Jef Poortmans, IMEC vzw, Leuven, BELGIUM; Georges Hadziioannou, University of Groningen, Dept of Polymer Chemistry and Materials Science Centre, Groningen, THE NETHERLANDS.

The technique of vacuum evaporation has been applied to deposit organic photovoltaic active layers. The five-ring PPV-type oligomer 2-methoxy-5-(2-ethylhexyloxy)-1,4-bis((4,4'-bisstyryl)styryl)benzene (MEH-OPV5) and  $C_{60}$  act as respectively donor and acceptor materials in planar heterojunction (MEH-OPV5/ $C_{60}$ ) and bulk heterojunction (MEH-OPV5: $C_{60}$ ) devices. These devices were fabricated with ITO/PEDOT bottom electrodes and Al top contacts. The performance of both solar cell configurations has been compared. It was found that under AM1.5 illumination the (MEH-OPV5/ $C_{60}$ ) cells exhibit a higher open-circuit voltage ( $\sim 0.97 \text{ V}$ ) than the (MEH-OPV5: $C_{60}$ ) devices ( $\sim 0.92 \text{ V}$ ). On the other hand, the limited exciton diffusion length in these materials was reflected in the lower short-circuit current density of the planar heterojunction cells as compared to the bulk heterojunction structures. Overall AM1.5 power conversion efficiencies above 2% are reported. Also the influence of the organic layer thickness and the substrate temperature during deposition on the device performance has been addressed. Thinner organic films generally resulted in higher short-circuit density values but affected the reproducibility of the solar cells. An elevated substrate temperature during deposition of the (MEH-OPV5: $C_{60}$ ) layers onto ITO/PEDOT led to the formation of nucleated islands of 100-150nm diameter with holes in between. As a result, no reliable

photovoltaic devices could be realized with such organic films. AFM analysis, spectral response measurements and dark IV characterization supported these findings.

**2:30 PM BB9.4**

ENHANCED PHOTOVOLTAIC RESPONSE IN IONICALLY SELF-ASSEMBLED MONOLAYER THIN-FILM DEVICES.

D. Marciu, M.B. Miller, C. Kozikowski, Luna Innovations, Inc., Blacksburg, VA; J.R. Heflin, S. Cho, B. Reid, K. Kuroda, W. Graupner, Department of Physics, Virginia Tech, Blacksburg, VA; H. Wang, H.W. Gibson, Department of Chemistry, Virginia Tech Blacksburg, VA; R.M. Davis, Department of Chemical Engineering, Virginia Tech, Blacksburg, VA.

We describe detailed studies of ionically self-assembled monolayer (ISAM) photovoltaic devices incorporating various electron acceptor materials: fullerenes, phthalocyanine and carbon nanotubes. The conducting polymer material generates electron/hole pairs when exposed to photons, and the electron acceptors aid in collecting these electrons before they can recombine with the holes, thus improving the efficiency of the PV process in the polymer. The ISAM technique allows the deposition of conducting polymer and fullerene materials in alternating layers of subnanometer thickness. This ensures that every photoexcited electron-hole pair is in proximity to a fullerene electron acceptor, thus minimizing electron-hole recombination and increasing the photocurrent. The individual thickness of each monolayer and the interpenetration of adjacent layers can be precisely controlled through the parameters of the electrolyte solutions. Using the ISAM technique, we demonstrated that it is possible to create ultrathin films (100 nm) of PV material that have performance on the order of that of silicon based photovoltaic devices.

**2:45 PM BB9.5**

PHOTOELECTRIC RESPONSE FROM NANOFIBROUS MEMBRANES. Kris Senecal, David Ziegler, US Army SBCCOM, Natick Soldier Center, Natick, MA; Jinan He, Ravi Mosurkal, Univ. Massachusetts, Dept of Chemistry, Lowell, MA; Heidi Schreuder-Gibson, Lynne Samuelson, US Army SBCCOM, Natick Soldier Center, Natick, MA.

Electrospinning has been used to prepare nanofibrous composite membranes of semi-conducting particles ( $\text{TiO}_2$ ) and photovoltaic dyes. Electrospinning is a relatively simple technique where electrical forces are used on polymeric solutions to produce nanoscale fibers. The resulting nanofibrous membranes have surface areas that are roughly one to two orders of magnitude higher than conventional thin films. It is believed that this higher surface will allow for more efficient light harvesting in photovoltaic devices. Our research has focused on the fabrication of organic/inorganic hybrid solar cells featuring dye sensitized nanocrystalline semiconductor particles using electrospinning. Phthalocyanine and N3 (cis-di(thiocyanato)bis(2,2'-bipyridyl)-4,4'-dicarboxylate) ruthenium(II) photoactive dyes were electrospun with semi-conductive  $\text{TiO}_2$  nanoparticles into a matrix polymer, polyacrylonitrile (PAN). Electron microscopy and elemental analysis of the electrospun membranes shows that each component is present and uniformly dispersed in the nanofibrous membranes. In general, the dye membranes electrospun with the  $\text{TiO}_2$  nanoparticles exhibited a greater photoelectric response than the membranes with dye only. The N3 dye membranes however showed the greatest photoresponse in comparison to the phthalocyanine dyes, with or without the  $\text{TiO}_2$  nanoparticles. Photoelectric responses on the order of 30 mA and 280 mV were achieved with dye-sensitized membranes and are believed to be the first demonstration of a photoelectric response from an electrospun nanofibrous membrane.

**3:00 PM BB9.6**

EFFICIENT NANOROD AND POLYMER PHOTOVOLTAICS VIA THERMAL TREATMENT. Wendy U. Huynh, Janke J. Dittmer and A. Paul Alivisatos, Dept of Chemistry, Univ of California, Berkeley, CA.

Highly efficient hybrid solar cells have been fabricated from blends of poly(3-hexylthiophene) and CdSe nanorods with aspect ratios of up to 20. Such devices reached external quantum efficiencies of up to 35% at 515nm corresponding to a monochromatic power conversion efficiency of 5%. Under AM1.5 conditions an efficiency of 1.6% was calculated. The highest performance was reached after thermal treatment of the nanorod/polymer blend films at  $120^\circ \text{C}$ . We present a detailed analysis of the mechanism behind this observation.

**3:45 PM \*BB9.7**

CHARGE TRANSPORT IN CRYSTALLINE ORGANIC SEMI-CONDUCTORS. Hendrik Schon, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

The charge transport in single crystals and polycrystalline thin films of organic semiconductors, such as pentacene, tetracene, or

oligothiophenes, is investigated. Coherent band-like motion is identified as intrinsic transport mechanism in these materials, however, disorder and grain boundaries lead to the observation of thermally activated transport. The electrical properties of single grain boundaries are investigated and the formation of a potential barrier due to trapped charge is verified. The consequences for thin film transistors will be discussed.

#### 4:15 PM **BB9.8**

##### THE EFFECT OF ENVIRONMENT AND SURFACE PREPARATION ON THE STRUCTURE AND ELECTRICAL TRANSPORT IN AN ORGANIC SEMICONDUCTOR.

Laura Kosbar, Christos Dimitrakopoulos, Teresita Graham, T.J. Watson Research Center, Yorktown Heights, NY; Debra Mascaro, MIT, Cambridge, MA.

Organic semiconductors offer promise for the future of low cost, flexible thin film transistors (TFTs). They can be deposited by low temperature techniques that are compatible with inexpensive flexible substrate materials such as plastics - thus expanding the possibilities for the manufacture of smartcards, RF identification tags, and light weight, flexible flat panel displays. While organic semiconductors have made impressive progress in the past decade, there is still need for improvement of both the performance and reproducibility of electrical transport properties in organic films. Understanding the effects of environmental factors on performance and reliability will be required for the majority of applications. Pentacene is considered to be relatively environmentally stable, however electrical performance may be highly susceptible to film morphology, interfaces at grain boundaries, and interactions at the surfaces of the gate dielectric and electrodes. We will review our work to date examining the effects of environmental factors on the ordering and performance of the organic semiconductor pentacene deposited on modified and unmodified substrates.

#### 4:30 PM **BB9.9**

##### CURRENT TRANSPORT MECHANISMS IN METAL-MOLECULE-METAL JUNCTIONS. Yongqiang Xue, Mark A.

Ratner, Department of Chemistry and Materials Research Center, Northwestern University, Evanston, IL.

Devices based on single molecules or molecular monolayers have received wide interests in recent years. Understanding current transport in these devices will provide the basis both for exploring new device concepts at the ultimate scaling limit and for realizing the full potential of molecule-based materials in device applications. Numerous interesting device characteristics, including molecular rectification and negative differential resistance, have been demonstrated. But the theoretical understanding of the transport mechanisms involved in these devices has not been achieved. In this talk, we present a theoretical investigation of the current transport mechanisms in metal-molecule-metal junctions using the self-consistent matrix Green's function method, which combines the non-equilibrium Green's function formalism of quantum transport with the density-functional theory of the molecular electronic structure. At the molecular scale, current transport is expected to be dominated by interface-related electronic processes such as tunneling and thermionic emission. The current-voltage characteristics of a given metal-molecule-metal junction will depend on details of the molecular electronic states under the applied electric field and the shape of the potential barrier at various bias voltages. In this work, we present such a microscopic description of the electron transport in metal-molecule-metal junctions by calculating the current- and conductance-voltage characteristics and showing its correlation with the modification of the molecular states, the change of the potential profile across the junction and the transmission characteristics at various applied bias voltages. We also show the dependence of the current-voltage characteristics on temperature, asymmetry of the contact, molecular structure and their microscopic foundations.

#### 4:45 PM **BB9.10**

TRANSPORT LEVELS IN PHOSPHORESCENT GUEST/ORGANIC HOST SYSTEMS MEASURED WITH PHOTO-ELECTRON SPECTROSCOPY. A.J. Mäkinen, Z.H. Kafafi, Optical Sciences Division, U.S. Naval Research Laboratory, Washington, DC; I.G. Hill, Sarnoff Corp., Princeton, NJ.

Using a combination of ultraviolet and x-ray photoelectron spectroscopy (UPS, XPS) we have studied the relative energy level alignment of two phosphorescent guest molecules, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum (PtOEP) and tris(2-phenylpyridine)iridium (Ir(ppy)<sub>3</sub>), doped in an electron transport host, tris(8-hydroxyquinolato) aluminum (III) (Alq<sub>3</sub>), and in a hole transport host, 4,4'-bis(carbazol-9-yl)biphenyl (CBP). In each of the guest-host systems, we find that the vacuum levels of the guest and the host molecules align, and that the position of the highest occupied molecular orbital (HOMO) of the phosphorescent

guests is independent of the guest molecule concentration (0.8-50% by mass) in the composite films. These results will be used to deduce the positions of the transport levels in the studied guest-host systems, relevant for organic light-emitting devices (OLEDs).

SESSION BB10: POSTER SESSION  
Chairs: Henning Sirringhaus and Christos D. Dimitrakopoulos  
Thursday Evening, November 29, 2001  
8:00 PM  
Exhibition Hall D (Hynes)

#### **BB10.1**

INVESTIGATION OF THE TEMPERATURE-DEPENDENT SURFACE MORPHOLOGY OF P-SEXIPHENYL THIN FILMS ON KCl(001). E.J. Kintzel, Jr., J.G. Skofronick, S.A. Safran, Departments of Physics and Chemistry, Florida State University, FL; E.S. Gillman, Thomas Jefferson National Accelerator Facility (TJNAF), D.-M. Smilgies, Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, NY.

Investigations of the temperature dependence of the morphology of thin films of p-sexiphenyl (p-6P) on KCl(001) were carried out by atomic force microscopy (AFM). AFM measurements were carried out in situ, at a base pressure of  $\sim 1 \times 10^{-6}$  mbar. Individual p-6P films were prepared by vacuum vapor deposition at a base pressure of  $\sim 1 \times 10^{-8}$  mbar onto a KCl(001) substrate which was maintained at 323 K. Analysis indicates similar morphologies for film temperatures maintained at 294 and 227 K, 264 and 157 K, and 188 and 128 K. AFM images for the first set of film temperatures indicates the presence of block-like islands of p-6P, with the edges of the islands aligned approximately along the KCl(110) direction. Peak heights and peak-to-peak distances are nearly equivalent at both temperatures. AFM images of the films in the second set indicate the presence of irregular islands of p-6P with no obvious preferential orientation. Comparison of these images shows peak heights and peak-to-peak distances have little variation. AFM images of the last set of film temperatures indicate the presence of triangular wedge-shaped structures of p-6P with the long leg of the triangle aligned in the direction of the KCl(110), and the short leg aligned approximately in the KCl(001) direction. A comparison of these wedge-shaped structures at the indicated film temperatures reveals that these features are rotated by approximately 180° with respect to each other. Subsequent images of the surface morphology taken again at 294 K, after the final 128 K temperature study was completed, revealed the original surface structure taken at the initial 294 K temperature study.

#### **BB10.2**

DESIGN OF CONJUGATED POLYMERS WITH 2-DIMENSIONAL CHARGE DELOCALIZATION FOR OPTOELECTRONIC APPLICATIONS. Zukhra I. Niazimbetova, Mary E. Galvin, Univ of Delaware, Dept of Materials Science and Engineering, Newark, DE.

Charge transport in conjugated polymers is usually 1-dimensional, with facile conduction and energy transfer occurring along the polymer chains. Mobility is limited by the necessity for chain-to-chain activated hopping transport. This motivated us to design and prepare 2-dimensional conjugated polymers that offer interesting possibilities for improvement of charge mobility and photophysical properties. In the present work, we report the preparation and study of conjugated oligomers, which contain a central aromatic ring for the potential of developing extended 2- or 3- dimensional polymer networks. Through a systematic study of these model compounds we aim to develop the ground rules for designing polymer networks with improved 2-dimensional charge delocalization and high 3-dimensional carrier mobility.

#### **BB10.3**

COMBINED PHOTOLUMINESCENCE AND PHOTO-ABSORPTION STUDIES OF POLY(DI-N-ALKYLSILANES) DURING THERMAL PROCESSING. Withoon Chunwachirasiri, David Sherlock, Robert West, Michael Winokur, University of Wisconsin, Depts of Physics and Chemistry, Madison, WI.

The influence of thermal processing history on the photophysics in semi-crystalline thin films of various ( $\sigma$ )-conjugated poly(di-n-alkylsilanes) (i.e, hexyl, octyl, decyl and dodecyl) has been investigated. Simultaneous measurements of the UV-Vis absorption and photoluminescence (PL) spectra reveal distinctive structural forms with significantly altered backbone conformations. Thermal quenching of these alkyl-substituted polysilanes is found to initiate a complex sequence of structural phase transitions with the formation of transient and metastable states. These results are in agreement with recent direct structural studies. In many instances thermal quenching is associated with the suppression of the alkyl side chain

ordering and significantly enhanced ( $\sigma$ )-conjugation. The PL is observed to be sensitive to the exact conformational form with, in some instance, strong suppression of the PL signal.

#### **BB10.4**

**OPTICAL AND ELECTRICAL PROPERTIES OF X-RAY AND ELECTRON BEAM-OLIGOMERIZED THIOPHENES.** Heejoon Ahn, James E. Whitten, Department of Chemistry and Center for Advanced Materials, The University of Massachusetts Lowell, Lowell, MA.

Oligomeric and polymeric thiophenes are an important class of materials with optoelectronic applications that include organic light-emitting diodes and field-effect transistors. Electron and X-ray irradiation of thiophene and substituted thiophene multilayers condensed on cryogenically cooled metal surfaces results in oligomerization/polymerization, as evidenced by the formation of a layer that does not desorb when the surface is warmed to room temperature. Electron bombardment of thick physisorbed layers can be used to form micron thick, fluorescent films. X-ray and ultraviolet photoelectron spectroscopy has been used to investigate the polymerization process as a function of electron beam energy, electron dose and substrate temperature, and comparison has been made to X-ray formed samples. Electrical and optical properties of the resulting films have been investigated. In the case of 5 keV electron bombardment of condensed 3-hexylthiophene, the organic film absorbs in the range of 300-600 nm, and excitation at 380 nm results in emission peaked at 520 nm. Comparison with photoluminescence spectra of chemically synthesized oligothiophenes indicates an average chain length of 4-5. The oligomeric nature of the film is consistent with the valence photoemission results. Possible device and nanotechnology applications of this procedure for forming conjugated oligomers will be discussed.

#### **BB10.5**

**SWITCHABLE CIRCULAR DICHROISM OF ACHIRAL CONJUGATED POLYMERS IN PROGRAMMED ELECTROSTATIC ASSEMBLIES.** Myunghwan Kim and Daniel J. Sandman, University of Massachusetts Lowell, Department of Chemistry, Center for Advanced Materials, Lowell, MA.

Achiral conjugated anionic polyelectrolytes (P3ATs, PDA) exhibit induced circular dichroism (ICD), when individual conjugated polymers are simply processed in programmed electrostatic assemblies with the polysaccharide chitosan. In addition, observation of ICD in those assemblies depends on whether or not the assemblies are treated with base or acid. The base and acid treatment of the assemblies (post-assembly-processing) is accompanied by significant shifts in the visible absorption spectra. For potential application of the post assembly processing property in sensor devices, the structural, morphological, and optical properties of assemblies are compared to those of the complex in solution and to those of a solid precipitate of the complex.

#### **BB10.6**

**VINYLENE-LINKED DONOR-ACCEPTOR POLYMERS.** Luis G. Madrigal, John R. Reynolds, University of Florida, Center for Macromolecular Science and Engineering, Gainesville, FL.

A family of vinylene-linked donor-acceptor polymers has been synthesized with the goals of producing materials with reduced electronic band gaps and accessible oxidative and reductive states. The Heck reaction was used to synthesize poly(pyridyl vinylene-1,4-n-alkoxy-phenylene vinylenes) (PPyr-V-P-V), poly(2,3-diphenyl [3,4-b]-pyridopyrazine vinylene-1,4-n-hexadecyloxy phenylene vinylene) (PPyrPyr(Ph)<sub>2</sub>-V-C16P-V), and poly(2,3-diphenyl-thienof[3,4-b]-pyrazine vinylene-1,4-n-hexadecyloxyphenylene vinylene (PThPyr(Ph)<sub>2</sub>-V-C16P-V). These polymers exhibit spectroscopically determined band gaps of 2.4, 2.0, and 1.6 eV respectively. Molecular weights for these soluble polymers range from 8,700 for PPyrPyr(Ph)<sub>2</sub>-V-C16P-V to 33,000 g/mol for PPyr-V-C16P-V as determined by GPC vs. PS. Doping of the polymers with antimony pentachloride shows the formation of new red-shifted optical absorption bands characteristic of charge transfer species.

#### **BB10.7**

**OPTICAL SPECTROSCOPIC STUDIES OF SOLUBLE FLUORENE-BASED CONJUGATED POLYMERS: A HYDROSTATIC PRESSURE AND TEMPERATURE STUDY.** C.M. Martin<sup>1</sup>, S. Guha<sup>2</sup>, J.D. Rice<sup>2</sup>, M. Chandrasekhar<sup>1</sup>, H.R. Chandrasekhar<sup>1</sup>, W. Graupner<sup>3,4</sup>, and U. Scherf<sup>5</sup>, <sup>1</sup>Dept. of Physics & Astronomy, University of Missouri-Columbia, MO; <sup>2</sup>Dept. of Physics, Astronomy & Materials Science, Southwest Missouri State University, Springfield, MO; <sup>3</sup>Dept. of Physics & Astronomy, Virginia Tech, Blacksburg, VA; <sup>4</sup>present address: eMagin Corporation, Hopewell Junction NY; <sup>5</sup>Physical and Theoretical Chemistry, Universitaet Potsdam, GERMANY.

Soluble fluorene-based conjugated polymers show the highest photoluminescence quantum yield (PLQY) of all conjugated polymers in the solid state.[1] Optical studies are presented as a function of temperature and hydrostatic pressure, using Raman scattering and photoluminescence from two polymers with distinct differences in their backbone conformation, namely, poly(9,9-bis-(2-ethylhexyl) fluorene-2,7-diyl) (PF) and ladder type poly(para-phenylene) (m-LPPP). PF has a substantially higher PLQY compared to m-LPPP and is also known to show phase transitions with changing temperatures.

Spectroscopic properties of conjugated polymers have varying degrees of sensitivity to backbone conformation. The key to understanding the fundamental differences between the two materials is the conformation of the backbone, namely the ribbon-type backbone in m-LPPP as opposed to single bond between two neighboring fluorene units in PF, which introduces a torsional degree of freedom. The consequences of this difference will be discussed in terms of the Huang Rlys factor as well as the mode Grueneisen parameters.

[1] A.W. Grice et al. Appl. Phys. Lett. 73, 629 (1998).

#### **BB10.8**

**OPTICAL ABSORPTION OF PHTHALOCYANINE DERIVATIVE ULTRATHIN FILMS ACCUMULATED BY LANGMUIR-BLODGETT METHOD.** Kouya Suzuki, Alsadoon Saliman, Takayuki Katoh, Nobuyuki Iwata, Hiroshi Yamamoto, Nihon Univ, College of Sci. & Tech., Chiba, JAPAN.

We have paid attentions to a phthalocyanine derivative as a noble chromogenic material of which the color is quickly changed by electric fields. The purposes of this work are to prepare the LB films with aligned Aluminium 1, 4, 8, 11, 15, 18, 22, 25 -octabutoxy-29H, 31H-phthalocyanine triethyl siloxide (AlPcTr) molecules and to investigate the optical absorption properties of the films. The LB films were prepared by a Kuhn type of apparatus with a moving barrier and a vertical dipping/lifting handler. The AlPcTr was dissolved in chloroform with an arachidic acid (AA) to stabilize a L-film on a water subphase. The optimized condition for the LB accumulation has been studied. The substrates used were glasses, ITO glasses or fused silica. It was confirmed from the result of X-ray diffraction that the obtained films had a Y-type of accumulated layers with the lattice spacing of about 5.3 nm. The surfaces of the LB films with accumulated 30 layers were very smooth with average roughness of less than 10nm. The optical absorption peaks of the obtained LB film were observed at 660nm and 750nm, and were blue-shifted by about 30nm comparing with those of AlPcTr in solution. The changes of absorption spectra of AlPcTr were discussed in relations to interactions between molecules.

#### **BB10.9**

**SURFACE STRUCTURE AND ELECTROCHEMICAL POLYMERIZATION OF MIXED, THIOPHENE-CAPPED MONOLAYERS.** Katherine Harrison, Jung F. Kang, S. Michael Kilbey, II, Clemson University, Department of Chemical Engineering, Clemson, SC.

Self-assembled monolayers (SAMs) containing constituents of conductive polymers are of interest because of their potential use as platforms for constructing sensors and electrooptic devices. We have been studying fundamental structure-property relationships of monolayers formed on indium tin-oxide (ITO) surfaces from mixtures of thiophene-capped and methyl-terminated alkyltrichlorosilanes. In addition to understanding how the assembly of mixed SAMs affects monolayer properties, we were interested in determining whether "good" monolayers could be made on ITO surfaces. Using external reflectance FTIR spectroscopy and XPS measurements we have found that the thiophene-capped alkyltrichlorosilanes do form upright, packed monolayers on ITO. Relative to the solution composition, the surface composition of mixed SAMs is enriched in the thiophene-capped component. By "diluting" the thiophene-capped component, we can affect the coupling of the thiophene head-groups along the SAM - when the surface density of thiophene-capped chains is high, the thiophene groups can be electrochemically polymerized to form a surface-tethered, conductive polythiophene. At low surface densities, the thiophene groups are too sparse to allow this to occur. We will discuss the implication of this phenomenon on creating surface-grown, tethered layers of conductive polymers.

#### **BB10.10**

**THE 'CHOLESTERIZATION' OF SWITCHABLE EMULSIONS.** Gianluca Di Profio, Jessica Lanzo, Fiore Pasquale Nicoletta, Giovanni De Filipo, Giuseppe Chidichimo Dipartimento di Chimica, Univ degli Studi della Calabria, Rende (CS), ITALY.

Switchable nematic emulsions, obtained by a fast cooling of isotropic mixture of nematic liquid crystal and monomers, show very low saturation fields but rather long relaxation times because of the bipolar configuration adopted by nematic directors. Such inconvenient

has prevented up to now use of switchable nematic emulsions as electro-optical devices. In order to obtain a good compromise between low saturation fields and fast relaxation times, we have experimentally studied the effect of 'cholesterization', i.e. the addition of chiral dopant, on the electro-optical properties of switchable nematic emulsions. The cholesterization results in a significant decrease of decay times, while the saturation fields are slightly affected by the addition of chiral molecules. Results are in a rather good agreement with a phenomenological model, which takes into account the increase of elastic energy due to the induced twist deformation.

**BB10.11**  
LIGHT INDUCED RE-ORIENTATION IN LIQUID CRYSTALLINE TRANS-STILBENE MOLECULES. Lucia Veltri, Bartolo Gabriele, Giovanni De Filipo, Fiore P. Nicoletta, Giuseppe Salerno, and Giuseppe Chidichimo, Dipartimento di Chimica, Univ degli Studi della Calabria, Rende (CS), ITALY.

Nematic liquid crystal monomers can be easily aligned by the application of an external field (electric or magnetic). At the same time, the irradiation of trans-stilbenes with a light of the adequate frequency can determine trans to cis isomerization (photo-induced process). In this work, we report the synthesis and the characterization of a series of liquid crystalline molecules bearing a trans-stilbene moiety, which can be photo-isomerized upon irradiation with visible light. The trans-cis conversion determines the phase transition from a liquid crystal to an isotropic phase. This process is thermally and photochemically reversible. We studied the reorientation properties of the mixtures formed by these molecules with low molecular weight liquid crystalline monomers, both upon exposure to light and after the application of an electric field.

**BB10.12**  
SYNTHESIS OF POLYANILINE USING ELECTROSTATICALLY LAYERED HEMATIN ASSEMBLIES. Bon-Cheol Ku, Soo-Hyoung Lee, Jayant Kumar, Center for Advanced Materials, Departments of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA; Ferdinando F. Bruno, Lynne A. Samuelson, Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

The enzyme, horseradish peroxidase has been recently used for the polymerization of water-soluble conductive polyaniline. Hematin, an iron-porphyrin molecule that catalyzes the oxidative polymerization of phenol and aniline, is a robust and inexpensive biomimetic alternative to horseradish peroxidase. The synthesis of conducting polyaniline, both onto surfaces and in solution, is presented using hematin (hydroxy-ferriporphyrin), multilayer assemblies prepared by electrostatic layer-by-layer assembly. Composite thin film assemblies were fabricated by electrostatic layer-by-layer alternate deposition of a polyelectrolyte, poly(dimethyl diallylammonium chloride), and hematin. These multilayer assemblies were then used for the polymerization of aniline in the presence of a polystyrene sulfonate template. It was found that the polymerization rate of aniline depends on both pH and on the concentration of hematin that is deposited. Detailed characterization of the hematin film fabrication and polyaniline synthesis will be presented.

**BB10.13**  
CONCENTRATION AND SOLVENT DEPENDENT VISIBLE SPECTRA OF POLY(TRICYANOVINYLDIMETHYLANILINE). Ik-Bum Kim, Daniel J. Sandman, University of Massachusetts Lowell, Department of Chemistry, Center for Advanced Materials, Lowell, MA.

This work presents unusual spectral behavior of poly(tricyanovinyl dimethylaniline) (1) in dilute solutions. A new conjugated polymer(1) was prepared from p-(tricyanovinyl)N,N-dimethylaniline via the use of a methylglucopyranoside reagent. It is observed that dilute solutions of 1 exhibit spectral features associated with aggregation. The associative interaction is studied by changing the salt concentration, such as LiBr, in DMF solution, by changing the concentration of 1, and by varying the solvents. The association modifies the visible spectra of 1 in dilute solutions. Electronic absorption spectra of 1 in DMF solution exhibit a maximum at 429 nm, with a shoulder at 510 nm. With increasing concentration, new absorption band arises between 480nm and 700nm. The salt dissociates the aggregate to decrease the additional spectral features. The visible spectra of 1 vary in different solvents. The associative interaction presumably arises from a dipole-dipole interaction among pendant side groups.

**BB10.14**  
NOVEL AMPHIPHILIC CONDUCTING POLYMERS: USE OF BACKBONE FUNCTIONALIZATION AND SELF-ASSEMBLY TO FINETUNE THE STRUCTURE-PROPERTY RELATIONSHIP.

Suresh Valiyaveetil, Baskar Chinnappan, Dept. of Chemistry, National University of Singapore, SINGAPORE.

During the last two decades, design and synthesis of conjugated polymers attracted attention due to their interesting optical, electrochemical, and electrical properties, which led to the fabrication of optoelectronic and electronic devices, photovoltaic cells and biosensors. Recently, we have designed and synthesized multifunctional poly(p-phenylene)s with free hydroxyl groups on the polymer backbone and explored the possibility of finetuning the optical properties by changing environmental conditions such as pH or presence of metal ions. In our design strategy, we explored the use of the hydroxyl groups incorporated on the polymer backbone as a hydrogen bonding functionality to planarize the backbone as well as potential ligand sites for complexation with metal ions. In this talk, we will focus on synthesis and characterization of a few novel polymers and discuss the optical properties in detail.

**BB10.15**  
NOVEL SQUARINE DYES WITH EXCELLENT SUBLIMATION ABILITY. Minquan Tian, Makoto Furuki, Izumi Iwasa, Yasuhiro Sato, Lyong Sun Pu, Fuji Xerox Co, Ltd, Corporate Research Center, Advanced Research Laboratory, Kanagawa, JAPAN; Satoshi Tatsuura, The Femtosecond Technology Research Association, Tsukuba, JAPAN.

Squaraine dyes are expected to have significant technological applications in many areas such as electrophotography, solar energy conversion, optical recording and nonlinear optics. For their practical applications, fabrication of thin films in high uniformity is very important. Although there have been some reports on the vacuum-sublimed thin films of squaraine dyes, we have found that vacuum deposition of pure dye films can not be expected using the known squaraine dyes because of their thermal decomposition in the process of sublimation. Therefore, we have synthesized novel squaraine dyes for thin film fabrication under vacuum. From investigations of these compounds by thermogravimetry and heating under vacuum, we found the effective structure of squaraine dye molecules for high sublimation ability. Furthermore, pure squaraine dye thin films, which could have been obtained only by solution coating so far, can be fabricated by vacuum deposition of those sublimable squaraine compounds.

The New Energy and Industrial Technology Development Organization (NEDO) supported this work within the framework of the Femtosecond Technology Research Project.

**BB10.16**  
NANOSTRUCTURED ULTRATHIN FILM ASSEMBLIES OF ELECTRO-OPTICALLY ACTIVE SOLUBLE OLIGO THIOPHENE DERIVATIVES: SYNTHESIS, ELECTROCHEMISTRY, AND DEPOSITION. Jason Locklin, Chuanjun Xia, Ji Ho Youk, Mi-kyoung Park, Rigoberto C. Advincula, Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL.

Oligothiophene derivatives with well-defined structures continue to attract attention because of their similarities to monodispersed polymer systems and their optical and electronic properties. These systems consist of well-defined structures, which lead to good charge transport properties and high carrier mobility. Our main objective with this work was to first synthesize linear, water-soluble sexithiophene bolaform amphiphiles that could be used for the fabrication of ultrathin films. We first investigated the solution properties of these bolaform amphiphiles and then used them in molecular assembly strategies involving alternate polyelectrolyte deposition with a variety of oppositely charged polyelectrolytes and conditions. The solution properties revealed unique aggregation behavior for Amphiphiles. The films were characterized using a variety of techniques, such as ellipsometry, surface plasmon spectroscopy, AFM, UV-Vis, XPS, TEM and polarized microscopy. Here we also report results for the different ultrathin film combinations prepared, e.g. ordering, multilayer formation, and their corresponding electro-optical properties. Patterning of these films is introduced.

**BB10.17**  
PHOTOPHYSICS OF NANOSTRUCTURED CHROMOPHORES IN CHANNEL FORMING COMPOUNDS. Riccardo Tubino, Univ. Milano Bicocca, Milano, ITALY; Chiara Botta, ICM-CNR Milano, ITALY; Gianni Bongiovanni, Andrea Mura, M. Antonietta Loi, Univ. Cagliari, Cagliari, ITALY; Giuseppe Di Silvestro, Univ. Milano, Milano ITALY.

Inclusion of strongly luminescent conjugated molecules in materials which form linear nanometric channels running along the length of the host microcrystal, allows the fabrication of organized, highly anisotropic structures of chromophores which mimic an important property of the natural antennae of the green plants. The role of the host compound, which acts as a template, is to prevent the

chromophore aggregation and to impose a specific supramolecular organization consisting of linear arrays of weakly interacting chromophore molecules which can act as nanometric waveguides. The optical (absorption and emission) properties of a variety of chromophores included in a channel forming host (the perhydro-triphenylene) will be presented and the data will be discussed in terms of the existing models describing the intermolecular excited state interactions.

#### **BB10.18**

Abstract Withdrawn.

#### **BB10.19**

**OPTICAL STUDIES OF ARTIFICIAL OPALS AS 3D PHOTONIC CRYSTALS.** D. Comoretto, G. Dellepiane INFM - Dipartimento di Chimica e Chimica Industriale, Università di Genova; R. Grassi, F. Marabelli, L.C. Andreani, INFM - Dipartimento di Fisica "A. Volta", Università di Pavia; C.J. Brabec, Christian Doppler Laboratory for Plastic Solar Cells, J. Kepler University Linz, AUSTRIA; A.A. Zakhidov, Honeywell International Inc., Research and Technology, Morristown, NJ.

Artificial opals films have been prepared by sedimentation of monodisperse silica and polystyrene spheres in water suspension. Atomic force microscope images show a triangular packing of the sphere at the surface of the deposited film. SEM images indicate a bulk fcc packing of the balls. The presence and the energy position of an optical pseudo gap in incidence-angle-dependent transmittance and reflectance spectra is accounted for by theoretical calculations of the photonic band structure based on the plane-wave expansion. These calculations indicate that this pseudo gap is due to the splitting of the photonic bands in the L point of the first Brillouin zone. The spectroscopic data show an additional loss structure due to the diffraction of the light from the regular surface of the sample which has been quantitatively accounted for by modeling the surface as a triangular lattice. The effect of the infiltration of opals with conjugated polymers is also reported.

#### **BB10.20**

**CRYSTAL ENGINEERING OF TWO DIMENSIONAL OCTUPOLES. 1,3,5-TRICYANO-2,4,6-TRIS(p-DIETHYLAMINOSTYRYL)BENZENE CRYSTAL WITH LARGE SECOND HARMONIC GENERATION.** Bong Rae Cho, Sang Hae Lee, Minhaeng Cho, and Seung-Joon Jeon, Dept of Chemistry, Korea Univ, KOREA; Kil Sik Min and Myunghyun Paik Suh, Dept of Chemistry, Seoul National Univ, Seoul, KOREA.

We report that 1,3,5-tricyano-2,4,6-tris(p-diethylaminostyryl)benzene (1) and its derivatives exhibit large first hyperpolarizability in CHCl<sub>3</sub> and significant second-harmonic generation (SHG) in the solid state. The origin of the powder SHG is crystallographically noncentrosymmetric crystal structure of 1. The X-ray structure reveals that the compound is planar. The important consequences of this planarity are (i) an increased beta value due to efficient charge transfer from the donors to the acceptors and (ii) a crystallographically noncentrosymmetric arrangement of the molecules induced by the enhanced inter-layer pi-pi stacking interactions. The three-dimensional arrangement of 1 in the crystal indicates that a unit cell is consisted of three molecules that are packed along the c axis with slight offset. It is noted that the strong pi-pi stacking interactions between the molecules in the neighboring layers, more specifically between the central phenyl group of 1 and a peripheral phenyl group of the nearest neighbor molecule, play a crucial role in the formation of the noncentrosymmetric crystal. There are also intermolecular herringbone pi-pi interactions between the phenyl groups in the side arms of the neighboring molecules. These pi-pi interactions induce all molecules to be oriented in the same direction in the crystal, and the molecular hyperpolarizabilities are accumulated to exhibit large SHG. This result provides a rational design strategy for the octupolar crystals with large SHG.

#### **BB10.21**

**RIGID NONLINEAR OPTICAL CHROMOPHORE: THE PHOTOPHYSICAL PROPERTY OF P-PHENYLENE BENZOBISTHIAZOLE DERIVATIVE.** S.-H. Lee, A. Otomo, T. Nakahama, T. Yamada, S. Yokoyama, S. Mashiko, Nano Technology Group, KARC, Communications Research Laboratory, Kobe, JAPAN.

We recently designed and synthesized a rigid and planar chromophore, p-phenylene benzobisthiazole unit with donor and acceptor groups, which expected to have a short cut-off of absorption on the longer wavelength side due to suppressed of distribution of the absorption band. The first hyperpolarizability ( $\beta$ ) of NLO chromophore was measured using HRS technique at 1064 nm in 1,1,1,3,3,3-hexafluoro-2-propanol. We applied the external reference method (ERM) to determine the  $\beta$  values and used p-nitroaniline (p-NA) as a reference solution. The  $\beta$  value of NLO chromophore is  $276 \times 10^{-30}$  esu, which

is ten times larger than the p-NA value. The chromophore showed good thermal stability up to 330°C in nitrogen atmosphere. The absorption and fluorescence spectrum indicated that NLO chromophore tends to form partial aggregates in the  $1 \times 10^{-4}$  M 1,1,1,3,3,3-hexafluoro-2-propanol solution of NLO chromophore. The  $\lambda_{max}$  and the shoulder structure of the absorption spectrum were observed at 370 and 470 nm, respectively. After a few days, the blue-shifted  $\lambda_{max}$  was observed at 355 nm and the shoulder becomes disappearing. It is supposed that the blue-shifted absorption spectrum is shown the characteristic of monomeric molecule. In order to clarify this partial aggregate phenomenon, this work is to investigate the photophysical properties of the chromophore characterized by optical absorption and emission spectroscopy, and so on. Also, the nonlinear property of the chromophore is studied.

#### **BB10.22**

**COLORATION EFFICIENCY MEASUREMENTS OF ELECTROCHROMIC POLYMERS BASED ON 3,4-ALKYLENE-DIOXYTHIOPHENES.** Carleton L. Gaupp, Dean M. Welsh, John R. Reynolds, University of Florida, Dept of Chemistry, Center for Macromolecular Science and Engineering, Gainesville, FL.

The effects of various alkylendioxy and discretely conjugated arylene units on the electrochromism and coloration efficiency (CE) of poly(3,4-alkylendioxythiophenes) (PXDOTs) were investigated. 3,4-Alkylendioxythiophenes were electropolymerized to yield polymeric films that were highly transmissive sky blue in their oxidized (doped) state and opaque blue in their charge-compensated (neutral) state. The CEs of such polymers were investigated to determine whether structural modifications in the monomer unit would result in changes in the amount of injected charge necessary to obtain a full color switch (oxidized - reduced) and to lay the ground work for a standard method with which to measure such a quantity by comparing the data to well-studied inorganic electrochromic materials (i.e. WO<sub>3</sub>). Polymers were deposited electrochemically onto ITO-coated glass slides to specified thicknesses to maximize the optical contrast (75%T for PProDOT-Me<sub>2</sub>) followed by switching the polymers using square-wave voltammetry, while simultaneously monitoring the UV-vis absorbance at  $\lambda_{max}$ . By increasing the substitution of the alkylendioxy bridge from ethylene (EDOT) to 2,2'-dimethylpropylene (ProDOT-Me<sub>2</sub>) the coloration efficiency increased markedly from 183 cm<sup>2</sup>/C to 375 cm<sup>2</sup>/C at 95% of full contrast, respectively. Such increases are attributed to an increase in the mean free volume in the polymer film where counterions have increased mobility between polymer chains.

#### **BB10.23**

**DUAL POLYMER DEVICES WITH VISIBLE AND INFRARED ELECTROCHROMIC PROPERTIES.** Irina Schwendeman, Roberta Hickman, Kyukwan Zong, Dean M. Welsh, John R. Reynolds, Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL; Jungseek Hwang, David B. Tanner, Department of Physics, University of Florida, Gainesville, FL.

Some of the most promising conducting polymers for use in electrochromic devices (ECDs) are poly(3,4-alkylendioxythiophenes) (PXDOTs), poly(3,4-alkylendioxyppyroles) (PXDOPs) and their derivatives. Here, we present two types of ECDs based on several PXDOP and PXDOT derivatives. An absorption/transmission window device containing PProDOT-Me<sub>2</sub> as the high contrast cathodically coloring layer, with PBEDOT-NMeCz or PProDOP-NPrS as anodically coloring complementary polymers has been used for light modulation. Changes in percent transmittance and relative luminance as high as 66% are obtained when the anodically coloring polymer is the high band gap PProDOP-NPrS. To broaden the absorption peak through the visible spectrum we use laminated cathodically coloring polymer layers (PEDOP/ PProDOT-Me<sub>2</sub>). A reflective device presented here consists of conducting polymers electrochemically deposited on gold/Mylar electrodes. This allows switching of the reflectivity of a metallic surface over a broad range of spectral energies. We have used it as a platform to study in-situ optical properties of various conducting polymers. For example, we show that PProDOT-Me<sub>2</sub> provides high electrochromic contrast in the visible (55%), NIR (90%) and mid-IR (60%) regions of the electromagnetic spectrum.

#### **BB10.24**

**PHOTO-ELECTRO-CHROMIC POLYMERIC FILM.** Giovanni De Filipo, Fiore P. Nicoletta, Marialuigia Macchione, Daniela Cupelli, and Giuseppe Chidichimo, Dipartimento di Chimica, Univ degli Studi della Calabria, Rende (CS), ITALY.

Methylene blue is a photo-active agent and its photo-reduction can occur in a polymeric film containing appropriate electron donor groups. In this work, we present our preliminary results concerning the optical properties of a photo-electro-chromic polymeric device

upon exposure to a red laser source. In fact, the device undergoes a transition from a blue state to a transparent one, which can be converted in the original colored state by application of an adequate DC electric field. We observe that the de-coloration times depend on the strength of electro donor molecules and, obviously, on the temperature. Results are in a rather well agreement with a simple theoretic model. We will show the potential applications of such polymeric materials for the fabrication of laser-write and electric-erase devices.

#### **BB10.25**

Abstract Withdrawn.

#### **BB10.26**

MIXED CONDUCTING POLYCARBAZOLES FOR ELECTROCHROMIC DEVICES. Francois Tran-Van, Thierry Henri, Juozas Vidas Grazulevicius, Claude Chevrot, Univ of Cergy-Pontoise, Cergy, Pontoise, FRANCE.

Polycarbazoles and poly (N-alkylcarbazole)s are conjugated polymers showing numerous potentialities specially for electrochromic devices [1-2]. However, like for others conducting polymers, the ionic conductivity is very low due to a weak mobility of the counter-ion in the film [1]. Consequently, the kinetic of the electrochemical reaction is limited which lead to an increase of the switching time of the device. On the other hand, electrochemical stability of polycarbazoles is limited to few hundred of cycles even for a material with a low polydispersity which tend to improve the stability of the material [2]. In order to improve the characteristics of an electrochromic cell based on polycarbazoles electrode (mobility of the counter-ion, switching time, lifetime) it is possible to use a conjugated polycarbazole backbone containing pendant solvating group such as oxyethylene units. Furthermore, their compatibility with an polyethyleneoxide based electrolyte could resolve interfacial problems in the all-solid state devices. So, we have synthesized several polycarbazoles having oxyethylene substituents. First of them is a N-substituted polycarbazole obtained as well from a dihalide monomer using zero valent nickel as a catalyst as from oxydative electropolymerization of unsubstituted monomer. Mobility of counter ion in this films is much higher than in polycarbazoles or poly(N-alkylcarbazole). Moreover, stability is largely increased when oxyethylene units are grafted on polycarbazole compared to alkyl substituents. Finally, in order to improve mechanical properties of carbazole films with oxyethylene units, we have also synthesized reticuled polycarbazoles from electropolymerization of a poly (N-epoxycarbazole) used as a monomer. Electrochemical characterization and comparison with linear polycarbazoles will be also presented.

[1] M.M. Verghese, M.K. Ram, H. Vardhan, B.D. Malthora, S.M. Ashraf, *Polymer*, **38**, 1997, 1625.

[2] C. Chevrot, S. Sadki, K. Kham, *Electrochim. Acta*, **46**, 2000, 759.

#### **BB10.27**

DUAL-MODE OPTICAL MOLECULAR SWITCHING SYSTEMS FOR ORGANIC MEMORIES. Douglas S. Galvao, Sheila F. Braga, Applied Physics Department, UNICAMP, Campinas, BRAZIL; Paulo M.V.B. Barone, Socrates O. Dantas, Physics Department, UFJF, Juiz de Fora, BRAZIL.

There is a great interest in molecular switching processes due to technological applications such as reversible optical storage and optical computing at molecular level. The design of functional devices has been object of intense theoretical and experimental research in the last years. Recently Feringa and collaborators have reported the synthesis of dual-mode optical molecular switches based on chiral helical-shaped alkenes for which chirality, fluorescence and UV/VIS spectra can be reversible modulated by light. Due to these remarkable properties these compounds are very promising building blocks for optical memory devices as well as model systems for theoretical investigations. In this work we report a theoretical study on the geometric and spectroscopic properties of these structures using the well known semi-empirical methods PM3 (Parametric Method 3) and ZINDO/S-CI (Zerner's Intermediate Neglect of Differential Overlap - Spectroscopic - Configuration Interaction). Our results show that there are two stable conformers very close in energy for each possible molecular helicity and with barrier for bond rotation along the main molecular axis of 40 kcal/mol. Under protonation these barrier significantly increase and might explain why the protonation leads to the blocking of the switching processes. We propose a model for the switching mechanism based on charge transfer and conformational changes during the isomer interconversion.

#### **BB10.28**

CHIRAL POLYALKYLTHIOPHENES FOR SECOND HARMONIC-GENERATION DEVICES AND POLARIZED OLED. France Lebon, Giovanna Longhi, Sergio Abbate, Dip. Scienze Biomediche Biotecnologie, Univ di Brescia and Istituto Nazionale di Fisica della Materia (INFN), Brescia, ITALY; Marinella Catellani,

Silvia Luzzati, Alberto Bolognesi, Ist. Chimica delle Macromolecole - CNR, Milano, ITALY; Feng Wang, Prasad L. Polavarapu, Dept. of Chemistry, Vanderbilt University, Nashville, TN.

Chiral polyalkylthiophenes are noncentrosymmetric organic material with electroluminescent properties, and can be used both in second harmonic-generation devices and in polarized light emitting diodes. The best experimental tool to ascertain the chirality of the material is the Circular Dichroism (CD). It has to be noted that the CD signals are very sensitive to the succession of thiophene units and that the regioregularity seems to be a crucial factor in the development of chiral structures. Recently [1] we have reported the characterization of polythiophenes with long bulky substituents for which we had good Vibrational Circular Dichroism (VCD) but poor Electronic CD data. This indicated that the chirality property was confined to the substituent group and had a weak influence on the conjugated polythiophene backbone. In this work we present the synthesis and the characterisation of a polyalkylthiophene with shorter alkyl group in which the chiral center is very close to the conjugated backbone: poly(3-[(S)-2-methylbutyl]-thiophene) (PMBT). The CD data are quite impressive: high solvatochromism is observed for solutions in mixed solvents and cast films have high CD as well. The strong Cotton effect can be associated to a highly ordered aggregated phase but the nature of this phase is not yet known. However, all this results indicate that PMBT is a good candidate for second harmonic-generation material, when appropriately treated. We also present the photo and electroluminescence characterization of single layer light emitting diode with the following configuration: ITO/PMBT/Al. [1] F. Lebon, G. Longhi, S. Abbate, M. Catellani, C. Zhao, P.L. Polavarapu, *Synthetic Metals*, **119**, 75 2001.

#### **BB10.29**

SPONTANEOUS SWITCHABLE GRATINGS FROM THE PHASE SEPARATION OF PHOTO-POLYMERIZABLE CHOLESTERIC MIXTURES. Giovanni De Filpo, Fiore P. Nicoletta, Roberta Cassano, Marialuigia Macchione, Daniela Cupelli, and Giuseppe Chidichimo Dipartimento di Chimica, Universita degli Studi della Calabria, Rende (CS), ITALY.

Permanent diffraction gratings can be built in polymer dispersed liquid crystals by using either photo-masks or crossed laser beams in order to modulate the light intensity across the film during the cure process. The intensity of light diffracted from these gratings can be controlled with an applied electric field. In this work we report our results on the formation of permanent gratings in photo-polymerizable mixtures composed of a cholesteric liquid crystal and liquid crystal monomer. Cells with a surface treatment, which allows a planar alignment, are filled with such homogeneous mixture. During the filling a phase separation between the cholesteric liquid crystal and the nematic monomer occurs. The phase separation is flow induced and results formed by parallel stripes of aligned monomer separated by planar domains of cholesteric liquid crystal. Such a situation can be gelated by U.V. irradiation of the samples and provides a long term stable diffraction gratings, whose efficiencies can be modulated by the application of an electric field. The grating structure has been investigated by optical and scanning electron microscopy. The advantages of using such techniques is also discussed.

#### **BB10.30**

THE ORIENTATION CONTROL OF LIQUID CRYSTAL DROPLETS DISPERSED IN A POLYMER MATRIX AND ITS APPLICATION IN ELECTRO-OPTICS. Fiore Nicoletta, Giovanni De Filpo, Daniela Cupelli, Marialuigia Macchione, Giuseppe Chidichimo, Dipartimento di Chimica, Univ degli Studi della Calabria, Rende (CS), ITALY.

The encapsulation of monomer molecules in liquid crystal droplets dispersed in a thermoplastic matrix provides a convenient method to control the orientation of liquid crystal directors. The imprint of droplet interfaces is obtained by photo-polymerization of monomer molecules by means of a polymerization induced phase separation process performed in a magnetic field. In such way a uniform orientation of liquid crystal directors can be achieved in cells without any surface treatment. The concentration of monomer molecules is an important parameter, which influence the final electro-optical properties of films. Some particular electro-optical applications are also shown.

#### **BB10.31**

NEW ORGANIC NONLINEAR OPTICAL MATERIALS: DITHIENYLETHYLENES. B. Sahaoui, Université d'Angers, K.J. Plucinski, Mil. Univ. of Technology, Warsaw, POLAND; I.V. Kityk, Inst. of Physics, WSP, Czestochowa, POLAND; B. Paci, CEA (LETI-Technologies Avancées), DEIN/SPE, Gif sur Yvette, FRANCE; P. Baldeck, Laboratoire de Spectrométrie Physique, Université J. Fourier, Saint Martin d'Hères, FRANCE, J.-M. Nunzi, CEA (LETI-Technologies Avancées), Gif sur Yvette, FRANCE, P.

Frère, J. Roncali, Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques, Université d'Angers, Angers, FRANCE.

An exciting area of research at present is the study of new optical materials which have great potential for use in non-linear optical devices. Due to their efficiency, chemical flexibility and high conjugated framework, organic compounds have received considerable attention as possible materials for non-linear optics. Organic conjugated molecules, in particular, are promising from the point of view of nonlinear optical applications. Considerable interest has emerged in recent years in materials which have optical limiting properties, making it possible to control the intensity or the pulse energy of laser beams for optical protection of eyes and photo-detectors. For this reason we looked for colorless materials which are transparent at low energy and absorb for the whole visible range for microjoule pulse energy. Materials with two-photon absorption satisfy the first requirement, but their nonlinear absorption is rather low. The above specifications were nearly reached in the nanosecond regime, although for a restricted wavelength range, by combining two-photon absorption with re-absorption toward excited states of higher energy. In this paper, we report on a systematic study of the third order nonlinear optical properties of two new dithienylethylenes: (a) (E)-1,2-bis[2-(3,4-dibutylthienyl)]ethylene, and (b) (E,E)-1,4-bis[2-(3,4-diHexylthienyl)buta-1,3-diene. The trans configuration of ethylenic units was established from NMR spectra for (b) and from X-ray structure for (a). The X-ray structure of (a) showed good planarity of the  $\pi$ -conjugated systems. The samples were studied in the form of solutions. These organic compounds were dissolved in chloroform. As expected, the chain extension led to a red - shift of the  $\lambda_{max}$ , and an increase in molecular absorption. We observed that both of the compounds investigated show a very weak linear absorption at wavelengths over 480 nm. Kerr ellipsometry measurements which allow the assignment of the non-linear absorption (excited state absorption) were also carried out in order to understand the origin of the optical nonlinearities. To measure the third-order susceptibilities of the organic compounds studied, we used a DFWM (degenerate four wave mixing) technique at  $\lambda=532$  nm in picosecond regime. The theoretical interpretation of DFWM is based on the Maxwell nonlinear propagation equations. The relevant quantum chemical calculations were carried out. The contributions of electronic and vibration subsystem, as well as the contribution of particular parts of each molecule to the output third-order non-linear optical response are given. On the basis of these measurements, we deduced the second order hyperpolarizability  $\gamma$  values, which are about  $10^3$  larger than the  $\gamma$  value of CS<sub>2</sub>. We also determined the optical power limiting properties of the compounds mentioned, using nanosecond laser pulses in the visible range.

#### **BB10.32**

**LINEAR AND NONLINEAR OPTICAL CHARACTERIZATION OF MULTIWALLED CARBON NANOTUBES.** Margaret Brennan, Takeyuki Kobayashi, Sean O'Flaherty, Jonathan N. Coleman, Werner J. Blau, Department of Physics, Trinity College Dublin, Dublin, IRELAND.

The optical properties of carbon nanotubes are of interest due to their unique quasi-one-dimensional structure and novel electronic properties. These non-planar carbon species are composed of concentric graphene cylinders several micrometers long and are closely related to the fullerenes. Such systems are predicted to have electronic structures dictated by their geometric structure and chirality. The one-dimensional spatial quantization in nanotubes is manifested as a series of sharp van Hove singularities in their electronic density of states. These regions of high concentration of electronic states create the potential for enhancement of optical transitions, which has important implications for the nonlinear optical properties of carbon nanotubes. We report on the observation of visible photoluminescence from multiwalled carbon nanotubes and graphite suspensions induced by excitation at 1064nm. In the case of multiwalled carbon nanotubes, the integrated photoluminescence intensities show a cubic power law dependence while graphite shows a linear dependence, which only becomes nonlinear above a threshold intensity. These results provide evidence for the enhancement of nonlinear optical behavior in multiwalled carbon nanotubes with respect to graphite. Multiphoton absorption is proposed as the dominant mechanism responsible for the photoluminescence from multiwalled carbon nanotubes. The nonlinear response in multiwalled carbon nanotubes has been further investigated by using degenerate four wave mixing. An ultrafast response is observed with a third order nonlinear susceptibility,  $\chi^{(3)}$  as high as  $10^{-10}$  esu. Blackbody radiation is observed in the near infrared region in both materials with multiwalled carbon nanotubes exhibiting lower blackbody temperatures than graphite under the same irradiation conditions.

#### **BB10.33**

**STRUCTURE TO PROPERTY RELATIONSHIPS FOR THE TWO-PHOTON ABSORPTION PROPERTIES OF CONJUGATED**

**ORGANIC MOLECULES.** Egbert Zojer<sup>a,b</sup>, Wim Wenseleers<sup>b</sup>, David Beljonne<sup>b,c</sup>, Zhigang Shuai<sup>c</sup>, Marcus Halikb, Cara Grassob, Seth Marder<sup>b</sup>, Joseph W. Perry<sup>b</sup>, and Jean-Luc Bredas<sup>b,c</sup>, <sup>a</sup>Advanced Materials Division, Institut für Festkörperphysik, Technische Universität Graz, Graz, AUSTRIA; <sup>b</sup>Department of Chemistry, The University of Arizona, Tucson, AZ; <sup>c</sup>Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Mons, BELGIUM.

The aim of our study is to establish a relationship between the chemical structure of a chromophore and its two-photon absorption (TPA) cross-section ( $\delta$ ). We apply various quantum chemical techniques to donor/acceptor substituted molecules, systematically varying the ground state polarization, the charge transfer distance and the nature of the conjugated backbone. In all investigated systems, we observe a maximum of the TPA cross-section to the lowest two-photon allowed state for a molecular conformation that is intermediate between the neutral and cyanine limits. This behavior is related to the evolution of the transition energies and matrix elements involving the lowest lying one- and two-photon allowed states. It is shown that the enhancement of  $\delta$  by donor and acceptor substitution and its collapse, when approaching the cyanine limit, are related to electron-correlation effects. A detailed analysis of the nature of involved electronic states reveals that a small TPA cross-section for the lowest lying TPA state coincides with a shift of oscillator strength to a higher lying state of Ag symmetry. The results of the theoretical simulations are compared to experimental studies on novel dyes substituted with boron containing heterocycles that display large  $\delta$ -values.

#### **BB10.34**

**CONTROL OF PHASE SEPARATION IN COMPOSITES OF NANOCRYSTALS AND POLYMER FOR USE IN SOLAR CELLS.** Janke J. Dittmer, Wendy U. Huynh, Delia Milliron, Gregory L. Whiting, William C. Libby and A. Paul Alivisatos, Department of Chemistry, University of California, Berkeley, CA.

A detailed study of the morphology-performance relationship in composites of CdSe nanocrystals and poly(3-hexylthiophene) is presented. We found that we can control the interaction of the inorganic and the organic component by modifying the surface as well as the shape of the nanoparticles. Furthermore, the inherent bulk phase separation can be reduced dramatically by varying the film thickness as well as the solvent employed for spin coating these materials. These morphological findings were used to understand the performance of photovoltaic devices made from the hybrid composites.

#### **BB10.35**

**NANOSCALE CONTROL OF THE POLYMER-FULLERENE INTERFACE IN PHOTOVOLTAIC DEVICES BY THERMALLY-INDUCED INTERDIFFUSION.** M. Drees, J.R. Heflin, W. Graupner, Virginia Tech, Department of Physics, Blacksburg, VA; D. Topasna, M.B. Miller, Luna Innovations, Blacksburg, VA; R.M. Davis, Virginia Tech, Department of Chemical Engineering, Blacksburg, VA.

Ultrafast photoinduced charge transfer from conjugated polymers to fullerenes has led to extensive studies of these systems as photovoltaic devices. The charge transfer process prevents radiative electron-hole recombination, resulting in free, mobile charges. A limiting factor is the exciton diffusion distance, which is of the order of 10 nm. If the fullerene is not within this distance of the optical excitation site, no charge separation will take place. The simplest system for such devices is a bilayer system in which a film of C60 is evaporated onto a spin-cast film of MEH-PPV, for example. If each film has a thickness of 100 nm, the active region for charge transfer is only a small volume at the interface. We describe studies in which the polymer is heated above the glass transition temperature in an inert environment, inducing an interdiffusion of the polymer and the fullerene layers. Cooling the polymer film below the glass transition temperature terminates the interdiffusion. With this process, a controlled, bulk, gradient heterojunction is created. Monitoring of the photoluminescence and the short circuit currents of the devices show a dramatic decrease in photoluminescence and concomitant increase in short circuit currents, demonstrating the improved interface. Initial studies with MEH-PPV and C60 have shown an increase in photocurrent of more than a factor of 6 compared to the unheated bilayer system. We will present systematic studies of the time/temperature profile of the interdiffusion process as correlated with photoluminescence quenching, increase of photocurrent, and the resultant nanostructured polymer-fullerene interface.

#### **BB10.36**

**SYNTHESIS AND PHOTOVOLTAIC CHARACTERIZATION OF FULLERENE-OLIGO(PHENYLENE ETHYNYLENE) HYBRIDS.** D. Tsamouras<sup>1</sup>, J.F. Nierengarten<sup>2</sup>, T. Gu<sup>2</sup>, V. Krasnikov<sup>1</sup>, G. Hadziioannou<sup>1</sup>. <sup>1</sup>Department of Polymer Chemistry and Materials Science Centre, University of Groningen, Groningen, THE

NETHERLANDS. <sup>2</sup>Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, Université Louis Pasteur et CNRS, Strasbourg, Cedex, FRANCE.

Asymmetrically substituted oligo(phenylene ethynylene) (OPE) derivatives have been prepared by a new iterative method and attached to C<sub>60</sub> molecules by a 1,3-dipolar cycloaddition of the azomethine ylides generated in situ from the corresponding aldehydes and sarcosine. The molecules obtained are suitable for the fabrication of photovoltaic devices based on interpenetrating networks of donors and acceptors, with a characteristic length scale of the network topology smaller than the exciton diffusion length. We have constructed a number of photovoltaic cells incorporating the OPEs as the active material between two energetically asymmetric electrode contacts. The device performance has been examined and functional characteristics have been determined too. These seem to depend systematically on the nature of the attached end-group and on the length of the donating moiety.

#### **BB10.37**

**BIOSENSORS FROM CONJUGATED POLYELECTROLYTES: ENERGY TRANSFER COMPLEXES.** Deli Wang, Guillermo C. Bazan, and Alan J. Heeger, University of California at Santa Barbara, Institute for Polymers and Organic Solids and Materials Department; Frauke Rininsland, David G. Whitten, Duncan W. McBranch, QTL Biosystems, LLC, Santa Fe, NM; Peter S. Heeger, Case Western Reserve University, Department of Medicine, Cleveland, OH; Wanlin Yu, National University of Singapore, Institute of Materials Research and Engineering, Republic of Singapore, SINGAPORE.

Complete Förster energy transfer from a blue emitting cationic conjugated polymer to an orange emitting anionic conjugated polymer was observed at a roughly 1:1 ratio (per repeat unit) of the two polymers. Photoluminescence (PL) from the energy transfer complex (ETC) can be quenched by both negatively charged and positively charged quenchers. Use of the ETC minimizes nonspecific interactions (which modify the PL) between conjugated polyelectrolytes and biopolymers. Quenching of the ETC PL by quencher-ligand conjugates has been observed. Initial experiments demonstrate recovery of the quenched PL when proteins exhibiting specific binding to the ligands are added to the quenched ETC.

#### **BB10.38**

**ROD-LIKE DINUCLEAR RUTHENIUM COMPLEXES FOR DYE-SENSITIZED PHOTOVOLTAICS.** Ravi Mosurkal, Jin-An He and Jayant Kumar, Center for Advanced Materials, University of Massachusetts, Lowell, MA; Lian Li, K.G. Chittibabu, Molecular Technologies Inc., Westford, MA; John Walker and Lynne Samuelson, Department of the Army, U.S. Army Soldier and Biological Chemical Command, Natick Soldier Center, Natick, MA.

Electron transfer from molecular dyes to wide bandgap semiconductors is of technological importance in photoelectrochemical energy conversion. Transition metal complexes are used as photosensitizers in nanocrystalline-titanium dioxide based dye-sensitized photovoltaic (DSPV) cells. Presently the most efficient and stable sensitizers are carboxylated Ru(II) polypyridyl complexes. However, most of these Ruthenium dyes are limited by small absorption coefficients at wavelengths above 650 nm. To improve the efficiency of such systems, an enhanced spectral response of the sensitizer in the red and near-IR region is required. Ruthenium complexes with tridentate terpyridine type ligands have many structural advantages over the complexes with bipyridine ligands. Polynuclear ruthenium complexes prepared using these terpyridine ligands bridged with phenylene rings show promising redox and photophysical properties. In this study, we have carried out synthesis, characterization and theoretical modeling of rigid, rod-like homometallic dinuclear ruthenium complexes using terpyridine ligands bridged with phenylene rings and bipyridine ligands. The photophysical and photovoltaic properties have been investigated. These supramolecular dyads are found to be efficient photosensitizers in DSPV cells when a liquid electrolyte is employed.

#### **BB10.39**

**PHOTOVOLTAIC EFFECTS BASED ON JUNCTIONS OF REGIOREGULAR POLY(3-ALKYLTHIOPHENE) FILMS AND AL.** Keiichi Kaneto, Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Izuka, Fukuoka, JAPAN; Koichi Rikitake, Graduate School of Computer Science and Systems Engineering, Kyushu Institute of Technology, Izuka, Fukuoka, JAPAN; Wataru Takashima, Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Izuka, Fukuoka, JAPAN.

Optoelectronic characteristics in the Schottky Junction of poly(3-alkylthiophene), PAT films with the structure of Au/PAT film/Al have been studied as the function of alkylchain length

(alkyl=butyl, hexyl, dodecyl and octadecyl), regioregularity, film thickness, temperature and treatment of Al surface. The junction at PAT/Al exhibits rectification with the ratio of more than 10<sup>5</sup> at +2.0 V and -2.0 V. The rectification ratio strongly depends on the treatment of Al surface. The fresh Al exposed to air for less than 5 min exhibits larger rectification ratio, however, the long exposure more than a day results in poor rectification ratio. The magnitude of photocurrent is larger for the PAT films with shorter alkylchain length and higher regioregularity (or head-tail coupled PATs). Light illumination to Al side results in the action spectra similar to the absorption spectra, which contrast to that light illumination to Au side. The facts indicate the carrier generation occurs at the interface of PAT/Al. Thickness of the junction or the depletion layer formed by the electron transfer from Al to PAT is estimated to be approximately 100 nm by means of the capacitance measurement. The magnitude of photocurrent was found to larger for thinner films (even less than 100 nm), when the light illuminated to Au side, indicating the carrier generation layer is much less than depletion layer. The result will be discussed taking the carrier generation and transport mechanisms into consideration.

#### **BB10.40**

**GENERATION AND TRANSPORT OF PHOTOCARRIERS IN HEAD-TAIL POLY(3-ALKYLTHIOPHENE) FILMS.** Koichi Rikitake, Graduate School of Computer Science and Systems Engineering, Kyushu Institute of Technology, Izuka, Fukuoka, JAPAN; Wataru Takashima, Keiichi Kaneto, Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Izuka, Fukuoka, JAPAN.

Among various kinds of conducting polymers consisting of  $\pi$ -electron systems, polythiophenes attract considerable interests for potential of the application to electronic devices, because of the processability and ambient stability. Poly(3-alkylthiophene)s, PATs which are substituted with alkyl groups at 3 position are soluble in common organic solvent and show even superconductivity by the gate induced electrons. In these years, photovoltaic effects in HT-PAT films as the function of regioregularity and alkyl chain length have been studied to elucidate the mechanisms of carrier generation and transport. It has been clarified that the photocarrier mobilities in regioregular HT-PAT films are considerably improved from those of non-regioregular PAT films by more than one or two orders of magnitude. In the PAT films/Al junction cells, current-voltage characteristics show excellent rectification due to formation of the Schottky type junction. By the light illumination to the cell, it is found that the carrier generation occurs at very thin PAT layer near the Al electrode with the assist of strong built-in field. However, it is still vague the detailed mechanism of carrier generation. In this paper, the studies of photocarrier generation and transport in HT-PAT film/Al junction at low temperatures will be reported. Schottky type cells of HT-PAT film/Al were fabricated by spin coating of HT-PAT chloroform solution followed by vacuum deposition of Al electrode. Photoaction spectra (AS) and current-voltage characteristics (CV) have been measured as the functions of temperature, light intensity and film thickness. It has been found that the photocurrent due to the photovoltaic effect increase with decreasing temperatures, then decreases with the maximum at around 270K. The AS at room temperature is similar to absorption spectra at room temperature, though the AS at lower temperature is blue shifted. The photocarrier generation and transport will be discussed taking the exciton dissociation though the interchain charge transfer under the built-in field by analyzing these results.

#### **BB10.41**

**THEORETICAL STUDY OF THE OPTIMAL MORPHOLOGY FOR ORGANIC/INORGANIC SOLAR CELLS.** V.M. Burlakov, G.A.D. Briggs and A.P. Sutton, Department of Materials, University of Oxford, UNITED KINGDOM.

The efficiency of organic/inorganic solar cells depends both on the parameters of the constituent materials, and on the organic/inorganic interface area of the composite. As the electron-hole pairs are produced at the interface, their total number photogenerated at some separation from the electrode is proportional to the differential interface area at this separation. The number of the carriers reaching the appropriate electrode, on the other hand, is restricted by the interface area they encounter on their way to the electrode, because of recombination at the interface. The interface area as a function of the separation from the electrodes can be optimized in a way that allows the maximum number of carriers to be generated and subsequently collected at the electrode. This problem allows a general analytical solution for steady state conditions (constant generation rate) and a random walk-like transport of the carriers giving the differential interface area  $S(x)$  in the form  $S(x) = S(0) / \sqrt{1 - R \cdot S(0) \cdot x}$ , where  $x$  is the separation from the electrode,  $R$  is the recombination rate per unit interface area, and  $S(0)$  is the differential interface area near the electrode. The result is applicable to both organic and inorganic phase, suggesting symmetric interface distribution with respect to the

middle plane of the solar cell. Possible practical realizations of the obtained distribution of  $S(x)$  are discussed.

#### **BB10.42**

Abstract Withdrawn.

#### **BB10.43**

**PHOTOELECTRIC CELLS OF MEROCYANINE LANGMUIR-BLODGETT FILMS UTILIZING SURFACE PLASMON EXCITATIONS.** Keizo Kato, Toshiharu Sato, Niigata University, Graduate School of Science and Technology, Niigata, JAPAN; Kazunari Shinbo, Futao Kaneko, Niigata University, Dept of Electrical and Electronic Engineering, Niigata, JAPAN; Takashi Wakamatsu, Ibaraki National College of Technology, Dept of Electrical Engineering, Ibaraki, JAPAN.

Short-circuit photocurrents due to surface plasmon excitations have been investigated for the photoelectric cells using Langmuir-Blodgett (LB) films of merocyanine (MC) dye. The MC dye exhibits p-type conduction, and the Schottky and Ohmic contacts are obtained at the interfaces between MC LB films and aluminum thin films and between MC LB films and silver thin films, respectively. Since the Schottky diodes show the photoelectric effects, the Schottky photoelectric cells have been constructed. The cells with two kinds of structures, that is, prism/aluminum/MC/silver (type I) and prism/magnesium fluoride/aluminum/MC/silver (type II), have been prepared. In the attenuated total reflection (ATR) method, the types I and II have the Kretschmann and Otto configurations, respectively. Surface plasmons have been resonantly excited at the interface between silver and air for the type I and at the interfaces between magnesium fluoride and aluminum and between silver and air for the type II. The ATR and the photocurrent properties have been simultaneously measured as a function of the incident angles of the laser beams. The peaks of the photocurrents have corresponded to the resonant angles of the ATR curves. The electric fields and optical absorptions in the cells have been also calculated using the dielectric constants and the film thicknesses obtained from the ATR measurements. The calculated absorptions in the MC layers as a function of the incident angles have corresponded to the results of photocurrents. The optical absorptions in the MC layers have been affected directly to the profiles of the photocurrents. It has been estimated that the photocurrents for both types I and II could be enhanced by the excitations of surface plasmons in the ATR configurations.

#### **BB10.44**

**HIGHLY SENSITIVE OPTICAL SENSORS USING ELECTROSPUN POLYMERIC NANOFIBROUS MEMBRANES.** Xianyan Wang, Soo-Hyoung Lee, Christopher Drew, Jayant Kumar, Center for Advanced Materials, Departments of Chemistry and Physics, University of Massachusetts Lowell, MA; Kris J. Senecal, Lynne A. Samuelson, Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

In recent years, polymer films have found an increasing role in sensors due to their unique characteristics. It is well known that the sensitivity of a polymer film is proportional to its surface area per unit mass. Recently, electrospinning has been used to generate polymeric thin films that have very large surface areas. Here, a polymer solution is exposed to a high static voltage, creating sub-micron or nanometer scale fibers that are then collected as a non-woven membrane. Electrospun nanofibrous membranes have surface areas approximately one to two orders of the magnitude higher than those found in continuous thin films and it is expected that their sensitivities in chemical sensors will be potentially as large. In this paper, the first use of an electrospun membrane as a highly responsive (on the order of less than 1 ppm to a few ppb) fluorescence quenching-based optical sensor is reported. A new polymer, polyacrylic acid - poly(pyrene methanol) (PAA-PM), was synthesized via covalent attachment of the fluorescent indicator, pyrene methanol (PM), onto polyacrylic acid (PAA). Optical chemical sensors were then fabricated by electrospinning PAA-PM and thermally crosslinkable polyurethane latex mixture solutions. The synthesis, characterization, electrospinning fabrication, and comparison of the sensitivities to analytes such as ferric ions, mercury, and 2,4-dinitrotoluene between the electrospun membranes and electrostatically layer-by-layer (ELBL) assembled films will be presented.

#### **BB10.45**

**DESIGN, SYNTHESIS AND ELECTROSPINNING OF A NOVEL FLUORESCENT POLYMER FOR OPTICAL SENSOR APPLICATIONS.** Soo-Hyoung Lee, Bon-Cheol Ku, X. Wang, J. Kumar, Center for Advanced Materials, Dept of Chemistry and Physics, Univ of Massachusetts Lowell, Lowell, MA; L.A. Samuelson, Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

This work describes the synthesis and electrospinning of new fluorescent polymers and their use for the fabrication of optical chemical sensors. New fluorescent monomers were first synthesized by coupling reactions between acryloyl chloride and pyrene derivatives, 1-pyrene methanol and 1-pyrene butanol. Fluorescent polymers containing pyrene molecules were then obtained by the copolymerization of these monomers with methylmethacrylate using 2,2'-azobisisobutyronitrile as the initiator. These polymers show distinct and well-defined fluorescence that is characteristic of the pyrene chromophores. Electrospinning was used to process these polymers into high surface area nanofibrous membranes for optical sensing. The resulting sensors show a high sensitivity to 2,4-dinitro toluene based on the fluorescence quenching of the pyrene chromophores. Fluorescence intensities decreased with increasing concentration of 2,4-dinitro toluene. The quenching behavior follows Stern-Volmer bimolecular quenching kinetics. The synthesis, characterization, electrospinning fabrication, and sensing capability of these polymers will be discussed.

#### **BB10.46**

**HOLE TRANSPORT IN SELF-ORGANIZED OLIGOSILANE THIN FILMS WITH HIGHLY ORDERED HOPPING SITES.** Hajime Okumoto, Tetsuo Yatabe, Andrew Richter, Masaki Shimomura, Akira Kaito, Nobutsugu Minami, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

Self-organized thin films of oligosilanes are a new class of fast hole transport materials due to their highly ordered structures characterized by a molecular orientation normal to substrates (i.e. parallel to the direction of carrier move) and a multi-layered structure with correlation length exceeding 10  $\mu\text{m}$ . In polycrystalline thin films of permethyldecasilane ( $\text{Me}(\text{SiMe}_2)_{10}\text{Me}$ ), the molecular order gave rise to quite a narrow distribution of hole mobility ( $> 1 \times 10^{-3} \text{ cm}^2/\text{Vs}$  at 300 K), showing a time-of-flight photocurrent transient with a clear plateau and a sharp decay. To clarify the carrier transport mechanism, we investigated hole transport for permethyloligosilanes ( $\text{Me}(\text{SiMe}_2)_n\text{Me}$ ) with different Si-chain length ( $n = 8 \sim 12$ ). The mobility systematically changed with the chain length. The longer chains gave higher mobilities because the smaller number of hopping at end of molecules was necessary for carriers to traverse a specific thickness of film. In addition, Si atoms' odd-even effect was observed for the mobility. This is explained by two different geometries of interdigitation of facing Me groups with even-numbered oligosilanes favoring the carrier transport. Thus the hole transport properties in self-organized oligosilanes are definitely characterized by highly ordered carrier hopping sites located at both ends of each aligned molecule. This fact suggests possible control of hole transport in oligosilane thin films by molecular design for hopping sites.

#### **BB10.47**

Abstract Withdrawn.

#### **BB10.48**

**STM-INDUCED PHOTON EMISSION FROM SELF-ASSEMBLED PORPHYRIN MOLECULES ON A Cu(100) SURFACE.** W. Deng<sup>1</sup>, Z. Xiao<sup>1</sup>, T. Ohgi<sup>1</sup>, D. Fujita<sup>1</sup>, H. Nejo<sup>1</sup>, N. Koguchi<sup>1</sup>, S. Yokoyama<sup>2</sup>, K. Kamikado<sup>2</sup>, S. Mashiko<sup>2</sup>. <sup>1</sup>National Institute for Materials Science, Tsukuba, Ibaraki, JAPAN. <sup>2</sup>Communication Research Laboratory, Iwaoka, JAPAN.

An ultrahigh-vacuum scanning tunneling microscope (STM) equipped a conductive optical fiber tip has been established to explore photon emission from a self-assembled monolayer (SAM) of M-tetra-[3,5-di-t-butylphenyl]porphyrin (M-TBPP, M = H<sub>2</sub>, Cu, Zn and Ni) molecules on a Cu(100) surface. In a few nanometer scale areas, photons emitted from molecules induced by tunneling electrons were collected within the near-field region through an apex of the conductive optical fiber tip. The photon emission can be attributed to the inelastic tunneling involving the optical fiber tip, the M-TBPP molecules and the Cu(100) surface. Photon emission spectra and the bias dependence of the photon intensity suggest the existence of two radiative processes, decay of local surface plasmon and molecular fluorescence, both of which are inelastic tunneling involving tip, molecules and substrate. The maximum quantum efficiency (QE) observed at sample bias +4.5V was  $\sim 8.0 \times 10^{-6}$  photons per tunneling electron. As for the excitation of local surface plasmons (tip-induced plasmons (TIP model)), the molecule is also excited by the inelastic scattering of tunneling electrons from the ground states to the excited states ( $\pi \rightarrow \pi^*$  transition). Quenching of molecular fluorescence by metal substrate is taken into consideration to be damped by decoupling of the porphyrin ring from the surface by the four di-t-butylphenyl (DBP) legs. The QE for molecular fluorescence at sample bias +3.0 V is approximately estimated to be  $\sim 3.0 \times 10^{-6}$  photons per tunneling electron. References 1. J. Lambe and S.L. McCarthy, Phys. Rev. Lett. 37, 923 (1976).

2. R. Berndt, J.K. Gimzewski and P. Johansson, Phys. Rev. Lett. 67, 3796(1991).  
 3. T.A. Jung, R.R. Schlittler and J.K. Gimzewski, Nature 386, 696(1997).

#### BB10.49

EVALUATION METHOD OF BULK TRAP DENSITY FOR ORGANIC MATERIALS. Satoshi Mizuo, Shigeru Tabatake, Shigeki Naka, Hiroyuki Okada, Hiroyoshi Onnagawa, Toyama Univ., Dept. of Electric and Electronic Engineering, Toyama, JAPAN.

We have studied a bulk trap density of organic materials, tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>), using the differential method[1] which method is used for the evaluation of the bulk trap density in amorphous-silicon (a-Si). Device structure of Al (400~Å) / LiF (10~Å) / Alq<sub>3</sub> (3000~Å) / LiF (10~Å) / Al(400~Å) was subsequently evaporated on glass substrate. Current density ( $J$ ) versus voltage ( $V$ ) characteristics was measured. Here, the Fermi level  $E_F$  was proportional to logarithm of the current density divided by the voltage. According to the differential method, the bulk trap density is expressed as %

$$N_T(E_F) = \frac{\epsilon_S \epsilon_0 \kappa_1 \kappa_2}{2d^2 kT} \frac{V}{m-1}$$

% where,  $m$  equals  $\partial(\ln J)/\partial(\ln V)$ ,  $k$  is the Boltzmann constant,  $T$  is the temperature,  $d$  is the thickness of the organic layer,  $\kappa_1$  is the average distance of injected charge from the anode ( $1 \leq \kappa_1 \leq 2$ ),  $\kappa_2$  is a ratio of carriers concentration at anode against injection carriers concentration. ( $1/2 \leq \kappa_2 \leq 1$ ),  $\kappa_1 \kappa_2$  products is assumed as unity, and relative dielectric constant  $\epsilon_S$  is three. The bulk trap density was about  $10^{16} \sim \text{cm}^{-3}$  under 0.45~0.60 eV below the lowest unoccupied molecular orbital (LUMO:  $E_C$ ) and was increased with increase in the Fermi energy. With increase in the Fermi energy, *i.e.*, decrease in the  $E_C - E_F$ , the bulk trap density increased exponentially. Density of state extracted to the LUMO was  $2 \times 10^{21} \sim \text{cm}^{-3}$ . This value is natural for the bulk trap density and also for the interface trap formation.[2] Activation energy of the current density estimated from temperature dependence was changed with the applied voltage. Thus, it is assumed that traps with various energy levels contribute conduction mechanism. At the temperature below 253~K, the effective trap density is underestimated because of carrier freezing. Shallow level trap under 0.55~eV below LUMO was also confirmed. [1] S. Nešpurek and J. Sworakowski, *J. Appl. Phys.*, **51**(4), 2098 (1980). [2] S. Naka, M. Tamekawa, T. Terashita, H. Okada, H.A. nada, and H. Onnagawa, *Synth. Met.*, **91**, 129 (1997).

#### BB10.50

PROBING STRUCTURE-MOBILITY RELATIONSHIPS IN THIN FILMS AND SINGLE CRYSTALS OF ORGANIC SEMICONDUCTORS. Reid J. Chesterfield, Paul V. Pesavento, C. Daniel Frisbie, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

The detailed connections between molecular structure, crystal packing, and charge carrier mobility in organic semiconductors remain to be elucidated, and understanding of these relationships is critically important to improvement of organic field effect transistors (OFETs). We describe experiments to explore the dependence of carrier mobility on ring-isomerism, packing motifs (herringbone versus pi-stack), and chemical substitution in a series of aromatic, fused ring compounds. Thin films and single crystals are grown from the vapor phase. Carrier mobilities are measured as a function of temperature by space charge limited current spectroscopy and field effect transistor measurements. The role of the metal-organic contacts in these experiments is also explored.

#### BB10.51

IMAGING CHARGE TRAPS IN ORGANIC THIN FILM TRANSISTORS. William R. Silveira, Chris Rickard, Neil Jenkins, James G. Kempf, and John A. Marohn, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY.

We are investigating organic thin film transistors by variable-temperature electric force microscopy (EFM). A long-standing question concerning the behavior of organic thin film transistors is the nature of interfacial charge traps and their relation to mobility in comparatively disordered material. In an organic thin-film transistor, charge is conducted within a few monolayers of the semiconductor dielectric interface. In many devices, this interface is rife with charge traps that must fill up before charge is conducted, and which may limit mobility. What is the chemical nature of these traps? Are they a property of the semiconductor, the dielectric, or both? What is the distribution of charge trap energies? Are the traps dynamic or static? Information about charge traps is usually inferred from analysis of bulk current-voltage measurements - few microscopic studies have been reported. In order to answer these questions we are constructing

a type of scanning electric force microscope with unique capabilities: it will work over a large temperature range and have exquisite sensitivity, yet employ a tip electric field small enough to not perturb charge in the sample. We will discuss ongoing work employing cryogenic electric force microscopy (cryo-EFM) to image charge traps in organic thin film transistors. First images from our variable temperature (4 to 350 K) atomic force microscope prove feasibility and sensitivity, and ongoing work to image and quantify charge energies and dynamics at single dopant sites by EFM will be detailed.

#### BB10.52

Transferred to BB6.3

#### BB10.53

CONTROLLED P-DOPING OF AN ORGANIC MOLECULAR SEMICONDUCTOR. Weiyang Gao, Calvin Chan and Antoine Kahn, Princeton Univ, Dept of Electrical Engr, Princeton, NJ.

Electrical doping is perceived as a key to enhance the performance and versatility of organic molecular devices [1]. Yet, few systematic investigations of the electronic structure of molecular films and interfaces doped with organic molecules have been published to date. We report a study of controlled p-doping of zinc phthalocyanine (ZnPc) co-evaporated on Au with a strong acceptor, tetrafluoro-tetracyano-quinodimethane (F<sub>4</sub>-TCNQ), using ultraviolet and inverse photoelectron spectroscopy (UPS, IPES) and current-voltage (I-V) measurements. This work builds on previous work by Leo et al [2]. We measure the electron affinity of F<sub>4</sub>-TCNQ to be 5.34eV, slightly larger than the ionization energy of ZnPc (5.28eV), suggesting an efficient host HOMO-to-guest LUMO charge transfer. Undoped ZnPc exhibits near mid-gap Fermi level ( $E_F$ ) and 'flat bands' away from the Au interface, indicative of quasi-intrinsic 'purity'. In ZnPc doped with ~3% (molar ratio) F<sub>4</sub>-TCNQ,  $E_F$  shifts toward the HOMO level by 0.72eV and reaches ~0.18 eV above the leading edge of the ZnPc HOMO. At the interface with Au, the ZnPc HOMO is 0.74 eV below  $E_F$ , leading to a depletion region with a 0.56eV 'band bending' away from the interface, consistent with the p-type character of the film. The width of the depletion region in doped ZnPc is measured at approximately 32Å, consistent with a simple electrostatic model based on the doping concentration and a dielectric constant  $\epsilon=3$ . In thick I-V measurements on diode structures with varying organic film thickness confirm efficient doping and suggest that the increase in the current is in part due to tunneling of holes through the narrow depletion region at the interface.

\*Work supported by the NSF (DMR-0097133).

1. Zhou et al., Appl. Phys. Lett., 78, 410 (2001).
2. K. Leo (private communication).

#### BB10.54

GROWTH AND DIFFUSION OF PENTACENE ON OXIDE SURFACES. Ricardo Ruiz, Leonard C. Feldman, Richard F. Haglund Jr., Vanderbilt University, Dept. of Physics and Astronomy, Nashville, TN; Rodney A. McKee, Oak Ridge National Laboratory, Oak Ridge, TN; Jens Pflaum, Norbert Koch, Giacinto Scoles, Antoine Kahn, Princeton University, Princeton Materials Institute, Princeton, NJ.

Molecular ordering in thin organic films deposited on oxide surfaces is important for devices such as organic-based field effect transistors. We report here a study of the growth of pentacene on SiO<sub>2</sub> as a function of substrate temperature (200K < T < 400K). The nominal layer thickness varies between 20Å and 150Å at a deposition rate of 1Å/min (base pressure of the UHV system: 10<sup>-10</sup>Torr). The measurements are carried out by Atomic Force Microscopy (AFM) and X-ray studies (NSLS, Brookhaven). To study molecular surface diffusion, the substrate is partially shielded from evaporation by metal clips. At low temperatures (T=210K) the film morphology corresponds to an almost completely closed layer. On top of this uniform layer, which is ~20Å thick, the growth becomes diffusion limited as indicated by the presence of islands having fractal geometry. The sharp transition of the organic film at the boundary of the shielded surface areas and the absence of molecules underneath the clips indicate that surface diffusion at low temperatures is strongly reduced. Pentacene thin films grown at room temperature follow the Vollmer-Weber mode (3D-structure). The island step height of 15.2Å measured by X-ray diffraction indicates that the long molecular axis is almost perpendicular to the SiO<sub>2</sub> surface. The observed thin film phase differs from the triclinic bulk phase. At elevated temperatures (~350K) the film morphology is determined by molecular patches having diameters of up to 4µm. Their meandering edges are higher than their center region. In the center of the patches, the terraces have single molecular steps consistent with an island-like growth mode. AFM measurements on samples grown above 375K show that most of the pentacene molecules are desorbed after impinging upon the surface due to the small sticking coefficient at this temperature. Additional data will be presented for pentacene grown on mica and BaTiO<sub>3</sub>.

#### **BB10.55**

NOVEL APPROACH FOR THE SYNTHESIS OF SYMMETRICAL OLIGO THIOPHENES: SYNTHESIS OF HIGHLY SOLUBLE SEXITHIOPHENE DERIVATIVE. Ali A. Afzali, Tricia L. Breen and Cherie R. Kagan, T.J. Watson Research Center, IBM Research Division, Yorktown Heights, NY.

In this talk, we report a new approach for the synthesis of symmetrical oligothiophenes based on a highly efficient palladium-catalyzed Ullmann coupling reaction. This synthetic route enables the simple preparation of substituted oligothiophenes with a wider range of functionalities and in higher yield compared to previously reported syntheses. We demonstrate our procedure by preparing a novel, highly soluble a,w-disubstituted sexithiophenes. Spectroscopic (UV/vis, NMR and DSC) characterization of the sexithiophene derivative will be presented. Thin film transistors (TFTs) fabricated by solution processing of the novel sexithiophene as the p-type semiconducting channel, and the effect of processing conditions on transport properties will be discussed in details

#### **BB10.56**

IMPROVED THIN-FILM TRANSISTOR (TFT) PERFORMANCE USING FRACTIONATED POLY(3-HEXYLTHIOPHENE) P3HT. Munira Raja, Giles Lloyd, Naser Sedghi, Bill Eccleston, Dept of Electrical Engineering and Electronics, Univ of Liverpool, Liverpool, UNITED KINGDOM; Rafaella Di Lucrezia, Simon Higgins, Dept of Chemistry, Univ of Liverpool, Liverpool, UNITED KINGDOM.

Conjugated polymers have increasingly been used as active layers in electronic devices such as thin-film transistors (TFTs). Currently, there is a drive to improve the speed and switching efficiency of TFTs for application in displays. The conjugated polymer regioregular poly(3-hexylthiophene) (P3HT) has attracted interest due to its high mobility compared to other organic semiconductors. Here, we have attempted to improve the electronic properties of P3HT processed in air. The P3HT was synthesised using the McCullough method which gives ~96% Head-Tail coupling of the alkylthiophenes. An improved fractional distillation (fractionation) process developed by Trznadel was performed on some P3HT samples to improve molecular mass (removing short chains) and regio-regularity. Head-Tail coupling for the fractionated polymer is estimated at ~100%. Long chains are thought to improve charge transport due to reduced inter-chain transfer and increased intra-chain transport. The fractions obtained contained traces of metals such as copper that could act as a dopant. Schottky diodes have been used to calculate the bulk mobility values and doping densities of both fractionated and non-fractionated P3HT. The forward current density of the non-fractionated P3HT was 10 times greater than the fractionated P3HT. The bulk mobility values were thus calculated to be  $2 \times 10^{-5} \text{ cm}^2/\text{Vs}$  and  $1 \times 10^{-6} \text{ cm}^2/\text{Vs}$  respectively. The high mobility for the non-fractionated P3HT may be due to the presence of the metal impurities. Using drift/diffusion theory and image force barrier lowering, the doping densities were calculated to be  $1.5 \times 10^{16} \text{ cm}^{-3}$  and  $2.6 \times 10^{16} \text{ cm}^{-3}$  for non-fractionated and fractionated P3HT respectively. The field effect mobility values obtained from the TFT measurements were  $1 \times 10^{-4} \text{ cm}^2/\text{Vs}$  and  $4 \times 10^{-5} \text{ cm}^2/\text{Vs}$  and on-off ratios of  $10^2$  and  $10^4$  were obtained for non-fractionated and fractionated P3HT respectively. The fractionated device shows a clearly defined sub-threshold region, which is of a much greater slope than the non-fractionated device.

#### **BB10.57**

INCREASING THE CARRIER MOBILITY IN P3HT BY DOPING FOR USE IN SCHOTTKY BARRIER TFTS. Munira Raja, Giles Lloyd, Naser Sedghi, Bill Eccleston, Dept of Electrical Engineering and Electronics, The Univ of Liverpool, Liverpool, UNITED KINGDOM; Rafaella Di Lucrezia, Simon J. Higgins, Dept of Chemistry, The Univ of Liverpool, Liverpool, UNITED KINGDOM.

All conjugated polymer TFTs investigated thus far have used gold as the source and drain electrodes. The Ohmic contact provided by gold does not restrict the bulk leakage currents of the device. This problem is particularly relevant due to the large amount of unintentional doping caused by oxygen. The potential barrier at the interface of Schottky contacts can be used to control this leakage current [1]. With increased doping, the depletion region width can be reduced allowing much smaller channels than with Ohmic contact devices. This allows the majority of the channel region to remain at the bulk potential and the gate electrode can control this region more effectively. Doping has also been observed to superlinearly increase carrier mobility and can therefore be used in a Schottky contact device to create a high mobility short channel TFT. Measurements and theory are presented examining the relationship between mobility and doping in poly(3-hexylthiophene) (P3HT). Schottky measurements have been used to calculate the doping density and bulk mobility of regioregular P3HT. Films doped with C60 and DDQ have also been studied. The carrier mobility in P3HT has been

observed to be proportional to *doping density*<sup>2.35</sup> with the coefficient of proportionality of the order of  $10^{-63}$ . These values show a greater rate of increase of mobility with doping density than other reported organic semiconductors. Field effect mobility of P3HT films was also calculated using TFT structures. The field effect mobility values were observed to be more than two orders of magnitude higher than bulk mobility values. The IV characteristics of P3HT films doped with C60 and DDQ show space-charge limited current behavior, indicating the creation of trap states in the doped material. However, the  $\mu\theta$  product of the material is still higher than the mobility of the undoped polymer. This indicates that the mobility is significantly increased despite the trapped charge on the dopant atoms.

[1] G. Lloyd and W. Eccleston, Mat. Res. Soc. Proc., Fall 2000, Vol. 660, JJ5.12.

#### **BB10.58**

KINETIC ROUGHENING STUDY OF PERYLENE ON Au AND GLASS SUBSTRATES. Serkan Zorba, Li yan, Neil J. Watkins and Yongli Gao, University of Rochester, Dept of Physics and Astronomy, Rochester, NY.

Perylene is one of the favorable organic semiconductors for organic thin film transistor (OTFT) and organic light emitting diode (OLED) applications. It is known to have high electron and hole mobilities. However mobility is largely dependent upon the morphology of the organic film. We studied the growth kinetics of perylene on Au and glass substrates deposited by vapor deposition. The films were grown with gradually increasing thickness which allowed us to examine both the spatial and temporal correlation of the surface roughness using atomic force microscopy. A roughness exponent of 0.82 is obtained for Au and 0.79 for glass. A growth exponent of 0.73 is obtained for Au and 0.21 for glass. From these values we conclude that perylene growth on Au is non-local growth, on the other hand perylene growth on glass is local growth. The result indicates the strong influence of the substrate on the film morphology and points possible ways to control and improve it.

#### **BB10.59**

CHARGE TRAPPING IN POLYFLUORENE COPOLYMER THIN-FILM TRANSISTORS. Richard J. Wilson, Lukas Bürgi, Henning Sirringhaus, Richard H. Friend, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM.

For many thin film transistor (TFT) applications the stability of the device threshold voltage, which is directly affected by charge trapping, is of crucial importance. We have fabricated conjugated polymer TFTs based on the hole transporting polyfluorene copolymer poly(9,9'-dioctylfluorene-co-N-(4-butylphenyl)diphenylamine) (TFB). Devices fabricated at room temperature exhibit low mobilities and large threshold voltage shifts. After annealing to temperatures of 200-250°C the threshold voltage stability improves markedly, and hole mobility of typically  $10^{-3} \text{ cm}^2/\text{Vs}$  in the saturated regime are achieved. This is surprising as TFB forms amorphous films, and no crystallization transition could be observed upon annealing. We have investigated the origin for this reduction of charge trapping by in-plane space-charge limited current and current transient measurements as a function of temperature. These measurements are combined with Kelvin probe atomic force microscopy which provides us with a potential map in the active channel region and at the injecting contacts of the device as well as with a local probe for trapped charges.

#### **BB10.60**

CRYSTALLINE ASSEMBLIES OF 2,5-DIHYDROXY-1,4-BENZOQUINONE. Fotios Papadimitrakopoulos, Ritesh Tipnis, Jeremiah Mwaura, Thomas Phely-Bobin, Mathew Mathai, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT; Faquir Jain, Nanomaterials Optoelectronics Laboratory, Department of Electrical and Systems Engineering, University of Connecticut, Storrs, CT.

The non-aqueous, layer-by-layer growth of metallorganic assemblies using coordination chemistry has shown an enormous potential in obtaining facile growth of highly ordered thin films, suitable for semiconductor applications. Although we had previously reported layer-by-layer growth of 8,8'-dihydroxy-5,5'-biquinoline (bisquinoline) with different zinc precursors, the assembled structure showed conformational diastereomerism which led to diminished crystallinity. In this paper we discuss the self-assembly of crystalline thin films of 2,5-dihydroxy-1,4-benzoquinone with zinc precursors. The film growth was monitored by a variety of spectroscopic techniques indicating a rapid and monotonic increase in film thickness. Wide angle x-ray diffraction characterization indicates that the films possess crystalline domains. The characteristics of these films in the device configuration of diodes and transistors are reported and the results correlated to their degree of crystallinity.

**BB10.61**

ANALYSIS OF THE POTENTIAL PROFILE IN AN ORGANIC FIELD-EFFECT TRANSISTOR USING SCANNING PROBE TECHNIQUES. Simon Ogier, Joe McMahon, Janos Veres, Avecia, Manchester, UNITED KINGDOM.

Organic field effect transistors (FET) have been investigated by atomic force microscopy techniques. Bottom gate FETs were prepared from a new class of solution-coatable, air and light stable organic semiconductor materials. Scanning electrical potential microscopy (SEPM) has been used to analyse the potential profile in the channel between the source and drain electrodes. This technique highlights areas where metal-semiconductor contacts are limiting the current flow and can also correlate topographical information (collected simultaneously) with potential data. High resolution mapping of the channel was possible at different gate and drain voltages helping the understanding of charge injection and transport in organic FET structures.

**BB10.62**

ENHANCED MAGNITUDE AND TEMPORAL RESPONSE OF ELECTROCHROMIC DEVICES FROM IONICALLY SELF-ASSEMBLED THIN FILMS. J.A. Janik, J.R. Heflin, Virginia Tech, Dept. of Physics, Blacksburg, VA; D. Marciu, M.B. Miller, Luna Innovations, Blacksburg, VA; R.M. Davis, Virginia Tech, Dept. of Chemical Engineering, Blacksburg, VA.

Ionically self-assembled monolayers (ISAMs), fabricated by alternate adsorption of cationic and anionic components, yield exceptionally homogeneous thin films with subnanometer control of the thickness and relative spatial location of the component materials. ISAM films were adsorbed onto indium tin-oxide coated glass substrates using electrochromic polymers, such as polyaniline(emeraldine base) (PANI) and poly-viologen, with the ionic conductor poly(2-acrylamido 2-methyl propane sulfonic acid) (PAMPS). Solid-state electrochromic devices, fabricated by sandwiching identical ISAM films with a conducting interlayer, exhibited large, reversible absorbance changes with application of 1.0 V. Devices in which PANI and PAMPS are placed in alternating layers showed larger magnitude absorbance changes and faster response times than those in which layers of PANI and poly(methacrylic acid) are followed by poly(allylamine hydrochloride) and PAMPS. Rise and fall times shorter than 50 milliseconds have been observed in the former devices. We describe systematic studies of the magnitude of the absorbance change and the switching speed as a function of nanoscale thickness and composition.

**BB10.63**

Abstract Withdrawn.

**BB10.64**

CONTROL AND ACTUATION OF MICRO-OPTICAL DEVICES BY ELECTROWETTING. Shu Yang, Tom Krupenkin, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

A phenomenon of electrowetting has been applied to the actuation of micro-optical devices. Both the surface and bulk properties of the materials are found important to control the device performance. Fundamental problems, such as stick-slip behavior and contact angle hysteresis associated with the surface roughness and surface contamination, are studied to optimize the choice of dielectric materials and their coatings. Some of the possible ways to control these phenomena are suggested. Several potential applications of the electrowetting actuated devices will be outlined.

**BB10.65**

LIGHT AMPLIFICATION IN LUMINESCENT POLYMER OPTICAL FIBERS. Takeyuki Kobayashi, Werner J. Blau, Department of Physics, Trinity College Dublin, Dublin, IRELAND; Hartwig Tillmann, Hans-Heinrich Hörhold, Friedrich-Schiller University, Institute for Organic Chemistry and Macromolecular Chemistry, Jena, GERMANY.

We report on fabrication of step index luminescent polymer optical fibers and observation of optical gain in the blue-green region. The polymer laser or amplifier in a fiber form is potentially important because of the possible penetration of plastic optical fibers into short-distance communication networks such as premise wiring and local area networks. The broad emission spectrum characteristic of luminescent polymers implies the possibility of generation and amplification of ultrashort optical pulses. Inexpensive, compact and tunable coherent light sources are appealing for such diverse applications as high-density data storage, spectroscopy and sensing. A novel green-emitting conjugated polymer, Thianthrene-MEH-PPV, and blue-emitting stilbenoid compounds, 1,2-bis(4-diphenylamino-phenyl)-ethylene and 1,4-bis(4-diphenylamino-styryl)-benzene, are specifically designed and synthesized for blue-green region of the

spectrum and have very high quantum yield and large Stokes shifts. Step index polymer optical fibers are fabricated by using the conjugated polymer and fluorescent stilbenoid compound-doped polymers as core materials. Significant spectral narrowing and superlinear increase of output intensity are observed under photoexcitation at 355 nm, which are indicative of occurrence of amplified spontaneous emission. By gain spectroscopy, a high gain coefficient of up to  $36 \text{ cm}^{-1}$  at 494 nm has been obtained for the 1,4-bis(4-diphenylamino-styryl)-benzene-doped fiber transversely photoexcited at  $12 \text{ mJ/cm}^2$ .

SESSION BB11/AA11: JOINT SESSION  
NOVEL PATTERNING SCHEMES

Chairs: Michael F. Rubner and Paula T. Hammond  
Friday Morning, November 30, 2001  
Constitution A (Sheraton)

**NOTE EARLY START****8:15 AM \*BB11.1/AA11.1**

THIN FILM PROCESSING SCHEMES FOR MANIPULATING ELECTRONICALLY ACTIVE ORGANICS. M.F. Rubner, Department of Materials Science and Engineering, MIT, Cambridge, MA.

In recent years, we have developed a number of simple strategies for manipulating electronically active polymers and small molecule light emitters into thin film devices. For example, we have utilized a layer-by-layer processing approach to form functionally active polyelectrolyte multilayers. Such films show promise as the active elements of light emitting devices, micro-phonic devices, thin film sensors and anti-reflection coatings. In addition, we have developed simple blending techniques that make it possible to fabricate high efficiency, red-orange light emitting thin films from the well known Ru(II) complex. Our best devices to date operate at low voltage (ca. 2.5 volts) with high external quantum efficiency (in the 4-5 % range), high brightness and good stability. These performance characteristics are obtained from a simple spin-coated blend system and by using stable electrode materials such as silver as the cathode. Recent developments in these two areas will be discussed.

**8:45 AM BB11.2/AA11.2**

NANOLITHOGRAPHIC PATTERNING OF ORGANIC ELECTRONIC DEVICES BY AN ADDITIVE METAL COLD WELDING PROCESS. Changsoon Kim and Stephen R. Forrest, Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, NJ.

We demonstrate a simple and high resolution patterning technique capable of creating submicrometer structures on organic thin film. Previously, we demonstrated that organic light emitting device cathodes could be quickly and easily patterned by locally removing metal film from the organic layers using a stamping process<sup>1</sup>. The new method described here differs from the earlier technique in that the metal film predeposited on a hard stamp is left behind on regions of the organic layers once stamp and organic layers come into contact. This metal-additive process has several advantages over the metal subtractive method reported earlier. For example, it uses a lower pressure which is independent of metal layer thickness. The process proceeds as follows: First, the metal film is deposited on a patterned stamp precoated with an anti-sticking layer such as Teflon, while a very thin ( $\sim 100 \text{ \AA}$ ) layer of the same metal is deposited across the entire surface of the organic film predeposited on a hard (e.g. Si) substrate. Selective cold welding is then induced between the metal films in the area defined by the raised features of the stamp by pressing the stamp onto the substrate. Upon separation of the stamp from the substrate, the metal film on the stamp is transferred to the substrate, resulting in a pattern defined by the shape of the stamp. Next, the thin metal film on the substrate between the patterned regions is removed by a brief exposure to a plasma or other dry etching process. This patterned metal film can be used as an etch mask or can serve as electrodes for electronic devices. We show that this process has a pattern resolution to  $\sim 10 \text{ nm}$  by fabricating a grating line pattern in a polymer where the individual lines are as small as  $80 \text{ nm}$ . Furthermore, using this additive transfer process, we demonstrate fabrication of pentacene thin film transistors where source and drain electrodes are added to the pentacene surface. A mobility of  $\sim 0.1 \text{ cm}^2/\text{Vs}$  and on/off ratio of  $\sim 10^6$  are obtained. Very short gate lengths are demonstrated.

[1] C. Kim, P.E. Burrows, S.R. Forrest, *Science* **288**, 831 (2000).

**9:00 AM BB11.3/AA11.3**

PHOTOPATTERNING OF PHENYLENE-VINYLENE BASED POLYMERS. Thomas Kavc, Gregor Langer, Wolfgang Kern, Kai

Mahler, Franz Stelzer, Gertraud Hayn, Robert Saf, Graz Univ. of Technology, ICTOS, AUSTRIA; Alexander Pogantsch, Emil J.W. List, Egbert Zojer, Graz Univ. of Technology, Institute of Solid State Physics, AUSTRIA; Kurt F. Iskra, Theo Neger, Graz Univ. of Technology, Institute of Experimental Physics, AUSTRIA; Hans-Heinrich Hörhold, Hartwig Tillmann, Univ. Jena, Institute of Organic Chemistry and Macromolecular Chemistry, GERMANY; Gerald Kranzelbinder, ENS Cachan, LPQM, FRANCE; Georg Jakopic, Joanneum Research, Weiz, AUSTRIA.

The patterning of conjugated materials is of general interest for controlling the emission properties of light emitting devices (LEDs). In addition, periodical structures are required for the realization of organic lasers based upon the principle of distributed feedback (DFB). We employed the photoreaction of gaseous hydrazine ( $N_2H_4$ ) with aromatic polymers to introduce patterns into films of polystyrene (PS), poly(2-vinylnaphthalene) (PVN) and phenylene-vinylene based polymers (PPV). Under UV irradiation in  $N_2H_4$  atmosphere the aromatic units in PS and PVN were partly transformed into aliphatic units (as evidenced by FTIR). This resulted in a decrease of the refractive index  $n$  by 0.04 (PS) and 0.11 (PVN). In the case of the PPV derivatives, the treatment first lead to a saturation of the vinylene units and subsequently to a conversion of the phenylene rings. The mechanisms of these reactions were investigated using model compounds. Spectroscopic studies showed that the photobleaching of the PPV derivatives resulted in a reduced conjugation (blue-shift of absorption spectra). The luminescence quantum yield, however, remained high during the initial stages of the photoreaction. This indicates that this process does not introduce quenching centers, which makes it promising for patterning the emission of luminescent devices. After prolonged UV irradiation under  $N_2H_4$  the energy gap of PPV was shifted to the far UV. Using interference lithography, gratings were enscribed in the PPV films resulting in a periodical modulation of the refractive index and the optical gain. The applicability of these structures for DFB lasing was investigated. As an alternative approach, PPV derivatives and laser dyes were incorporated into photosensitive polymers. Using poly(4-vinylbenzylthiocyanate-co-styrene) as matrix material, refractive index and surface relief gratings were obtained after patterned UV illumination. With these structures optically pumped DFB lasing was demonstrated.

#### 9:15 AM BB11.4/AA11.4

STUDY OF SURFACES PREPARED BY MICROCONTACT PRINTING METHODS USING CHEMICAL FORCE MICROSCOPY. Hiroki Okui, Fuminobu Sato, Uichi Akiba, Kosaku Suga, Masamichi Fujihira, Tokyo Institute of Technology, Department of Biomolecular Engineering, Yokohama, JAPAN.

In the present work, we applied chemical force microscopy (CFM) by mapping adhesive force using pulsed-force-mode atomic force microscopy (PFM-AFM) with chemically modified AFM tips to study mixing of two components in patterned self-assembled monolayers (SAMs). The patterned SAMs were prepared by two types of microcontact printing methods. One is the wet-inking method, in which inking of the stamp was done by placing a thiol ethanol solution on it and then removing the excess solution under a stream of nitrogen. The other is the contact-inking method, in which an inker pad made of polydimethylsiloxane (PDMS) was dipped in a thiol ethanol solution overnight, then the excess solution was removed by a stream of nitrogen, and finally the stamp was placed on the inker pad impregnated with the thiol solution. Contamination due to vapor phase transfer during stamping and defects in printed areas due to insufficient ink transfer were studied by the present CFM in water.

#### 9:30 AM BB11.5/AA11.5

TEMPLATING ORGANIC SEMICONDUCTORS VIA NANOSCALE SELF-ASSEMBLY. James F. Hulvat<sup>1</sup> and Samuel I. Stupp<sup>1,2,3</sup>, Department of Materials Science and Engineering<sup>1</sup>, Department of Chemistry<sup>2</sup>, and Medical School<sup>3</sup>, Northwestern University, Evanston, IL.

The science and technology of low cost organic electronics could be advanced significantly by utilizing aqueous, self-assembly processes to pattern and control the nanostructure of conducting polymers. This could simplify fabrication and improve efficiency of organic light emitting diodes (OLEDs), organic field effect transistors and other devices. Orientation and isolation of polymer chains enhances charge injection and reduce exciton quenching via interchain charge transfer. We report here a templating strategy utilizing nanoscale dielectric channels in liquid crystals to orient and isolate conducting, light-emissive polymers. The strategy involves confining monomeric precursors within the cylindrical hydrophobic core of a hexagonal lyotropic liquid crystal (LC). The amphiphilic molecule oligo(ethylene oxide)-oleyl ether forms a self-supporting gel in water with a hexagonal (H1) mesophase consisting of two nanometer cores. The hydrophobic nature of these cores allows high concentrations of

precursor molecules, such as 3,4-ethyldioxythiophene (EDOT), to be solubilized in an aqueous mesophase without disrupting the LC order. We have electropolymerized this monomer on gold and indium tin oxide (ITO) within the LC gel to form the conducting polymer poly(ethyldioxythiophene) (PEDOT). The PEDOT film produced here precisely mimics the orientation and domain texture of the LC template. When the LC template is removed, the PEDOT remaining on the electrode exhibits a birefringent texture commensurate with the original liquid crystal gel. EDOT electropolymerizes preferentially in LC domains oriented parallel to the applied potential. This novel result indicates the optical anisotropy of the LC mesophase is templated on the growing polymer. The PEDOT film formed is electrochromic, electrochemically dopable, and can be reversibly oxidized and reduced. This facile approach bridges the gap between conventional lithography and molecular self-assembly by confining polymers within a nanoscale liquid crystal template ordered over hundreds of microns. In this process, precursor monomers are isolated, oriented, polymerized and doped in a single step.

#### 9:45 AM BB11.6/AA11.6

MULTILAYER MICROCONTACT-PRINTING OF ELECTRODES FOR SEMICONDUCTING POLYMER DEVICES. M.M.J. Decré, J.B. Giesbers, M.H. Brees, R.J.M. Schroeders, P.P.J. van Eerd and G.H. Gelinck, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

Soft lithography has previously been reported for patterning source-drain electrodes of semiconducting polymer transistors, while other layers were relying on either low resolution at typically 50 micron alignments or else standard photolithography for designs requiring better alignment performance. It is however desirable to demonstrate that a single technology can offer solutions for all device layers, including alignment. In our work, both electrode layers are patterned using microcontact-printing, to within a layer-to-layer alignment of 5 micron. We realized electronic devices based on semiconducting polymers. The devices have a so-called "bottom-gate" design: the layers follow a substrate/gate/insulator/source-drain/semiconductor structure. Both electrode layers are made of gold on a thin titanium adhesion layer. Using a rubber stamp (Sylgard 184) impregnated with alkanethiols, we print each electrode with a patterned monolayer and then etch it. The in-layer registration and layer-to-layer alignment allow for a total alignment of 5 micron. The devices have 4 micron channel width and source-drain finger widths. We present results on transistors, ring oscillators and simple bit-encoding devices having a surface of several square-millimeter and tens of transistors. We will address the patterning of vias by soft lithography to offer a complete manufacturing approach.

#### 10:30 AM \*BB11.7/AA11.7

APPROACHES TO NONLITHOGRAPHIC ASSEMBLY: FROM POLYMER MULTILAYERS TO COLLOIDAL PARTICLES. Paula T. Hammond, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA.

Research directions in materials and polymer science include the development of surface-directed assembly that can guide the placement of molecular to micron-scale objects onto substrates in pre-determined arrangements for sensors, electrical and optical devices, MEMS, and 2-D photonic systems. Nonlithographic approaches to these goals such as nano to micronscale printing, molding, and templating, will be key to driving the technologies toward application and commercialization. In our group, we have demonstrated the ability to direct polymers to different regions of a surface based on both electrostatic and secondary interactions between the polymer and the surface. We have now established a set of rules that define the conditions required for selective deposition of different functionalized materials onto specific surface regions. We have successfully expanded this understanding of polyion-surface interactions to mesoscale systems, including functionalized colloidal systems and colloids. This concept of adsorption directed by chemistry is universal, and can be applied to dye molecules, polymers, and nanometer to micron sized functionalized particles. Incorporation of two or more different elements within a pattern or array is one of the challenges in this field. We have used these techniques to build up complex, laterally patterned microstructures on the surface, in which more than one materials system can be selectively placed on a surface. The use of polymer-on-polymer stamping as a means of patterning such materials onto plastic as well as glass and oxide surfaces will also be addressed.

#### 11:00 AM BB11.8/AA11.8

MICRON SCALE PATTERNING OF ORGANIC THIN FILMS VIA ORGANIC VAPOR PHASE DEPOSITION. Max Shtein<sup>1,2</sup>, Peter Peumans<sup>1,3</sup>, Anna Chwang<sup>4</sup>, Jay B. Benziger<sup>2</sup>, Stephen R. Forrest<sup>1,3</sup>; <sup>1</sup> Center for Photonics and Optoelectronic Materials (POEM), <sup>2</sup> Department of Chemical Engineering, <sup>3</sup> Department of Electrical

Engineering, Princeton University, Princeton, NJ; <sup>4</sup> Universal Display Corporation, Ewing, NJ.

Organic vapor phase deposition (OVPD) is attractive for fabrication of molecular organic devices due to low operation cost and ease of scale-up as compared to vacuum thermal evaporation. In OVPD, organic molecules are delivered from remote evaporation sources by an inert carrier gas (e.g. N<sub>2</sub>) into a hot wall reactor at pressures of from 10<sup>-2</sup> to 10 Torr, where selective deposition occurs on the cooled substrate. For many applications, such as in full color displays, it is often necessary to achieve selective area patterning the organic film on the substrate via deposition through a shadow mask. Using vacuum thermal evaporation, sharply defined pixels are readily achieved, since the molecular mean free path,  $\lambda$ , at 10<sup>-7</sup> Torr is  $\sim 1$  meter. However, OVPD typically proceeds at pressures  $\leq 10^{-2}$  Torr, with  $\lambda < 1$  cm, resulting in pixels with diffuse edges. In this work we show that OVPD growth of thin films with pattern definitions  $\sim 1\mu\text{m}$  can be achieved under the appropriate conditions of substrate temperature and reactor pressure. We describe Monte Carlo simulations (displayed in video) to determine the pixel pattern evolution in real time and its dependence upon the deposition pressure and the carrier flow rate. The simulations are then tested experimentally, and we find pattern definition as small as 1mm is readily achieved by OVPD growth through shadow masks. The results help identify useful processing conditions, and guide the design of future OVPD systems.

#### 11:15 AM BB11.9/AA11.9

EDGE TRANSFER LITHOGRAPHY. Oksana Cherniavsky, Karl Knutson, Aleksandar Adzic, Ling Zang, David M. Adams, Columbia University Dept of Chemistry, New York, NY.

A simple and general method, edge transfer lithography (ETL), has been developed for large-area patterning of self-assembled monolayers (SAMs) at nanometer resolution. ETL employs standard "ink" and "stamp" microcontact printing ( $\mu\text{CP}$ ) techniques and takes advantage of the intrinsic topographic character and discontinuous dewetting behavior of micropatterned elastomeric stamps to selectively apply ink solutions within the recesses of the stamp. A polydimethylsiloxane (PDMS) stamp is used to pattern alkyl silane SAMs on glass with 60-nanometer line width resolution. Molecules are controllably delivered from the stamp to a solid substrate of interest selectively along the edges of the stamp features. Four-way and higher order junctions can be created by multiple applications of the stamp. Patterned SAM surfaces allow for the guided assembly of molecular materials. ETL is a potentially useful method for creating large-area complex patterned nanoscale structures of other materials such as nanoparticles, with applications in nanotechnology, and the biological and surface sciences.

#### 11:30 AM BB11.10/AA11.10

ELECTROWETTING CONTROLLED TUNABLE LIQUID MICROLENS. Tom Krupenkin, Shu Yang, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Tunable liquid microlens capable of adjusting its focal length and lateral position is demonstrated. The microlens consists of a droplet of a transparent conductive liquid placed on a dielectric substrate with a hydrophobic coating. By varying the voltage applied to the structure, both the position and curvature of microlens can be changed. To improve the electrical and optical performance of the microlens, different conductive liquids, dielectric materials, and their surface coatings are studied. The influence of the bulk and surface properties of the materials on the microlens behavior is experimentally investigated and supported by theoretical calculation. Some of the potential physical and technological limitations of the microlens performance are outlined and possible ways to alleviate them are suggested. Several potential applications of the proposed microlens will also be discussed.

#### 11:45 AM BB11.11/AA11.11

MULTI-COLORED ELECTROCHROMIC CONJUGATED P- AND N-TYPE DOPABLE POLYMERS BASED ON ALTERNATING DIOXYTHIOPHENE DONORS AND PYRIDINE ACCEPTORS. C.J. DuBois, Jr., John R. Reynolds, University of Florida, Department of Chemistry and Center for Macromolecular Science and Engineering, Gainesville, FL.

This paper reports on a family of alternating donor-acceptor copolymers based on electron-rich 3,4-ethylenedioxythiophene (EDOT) and electron-poor pyridines, which exhibit low band-gaps and multi-colored redox states. The parent polymer, PBEDOT-Pyr, has a band gap of 1.9 eV and four readily accessible color states: neutral red, oxidized dark blue-purple, reduced purple, and protonated dark blue. Derivatization of the pyridine to enhance its acceptor strength has led to the synthesis of a group of aryl and alkyl derivatized pyridopyrazines (PyrPyr): specifically BEDOT-PyrPyr(Ph)<sub>2</sub> and BEDOT-PyrPyr(Hex)<sub>2</sub>. PBEDOT-PyrPyr(Ph)<sub>2</sub> has a band-gap of 1.2

eV and exhibits broad p-type doping electrochemistry centered at 1.1 V vs SCE. PBEDOT-PyrPyr(Ph)<sub>2</sub> also displays two distinct reduction peaks centered at -1.05 V and -1.70 V. Cyclic voltammetry, differential-pulse voltammetry, in-situ conductivity, colorimetry, and spectroelectrochemistry results will be discussed for this family.