SYMPOSIUM L

Organic and Polymeric Materials and Devices

April 22 – 25, 2003

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*Invited paper
SESSION 1: LIGHT-EMITTING DIODES  
Chair: Paul W.M. Blom  
Thursday Morning, 9-12, 1030  
Salon L-3 (Marriott)

8:30 AM *11.1  
POLYMER LEDS: RECENT PROGRESS  
Alan J. Heeger

I will summarize the results of a series of recent experiments directed toward improved performance in polymer LEDs. These include the following:  
1. Stabilization of the blue emission from polyfluorene using end-capping technique.  
2. Emission from thin films of the blue emission from polyfluorene using a novel electron injection layer.  
3. Enhanced performance from polymer LEDs through the use of a novel hole injection layer.  

9:00 AM L1.2  
THE EFFICIENCY OF POLYMER LEDS OVER A WIDE VOLTAGE RANGE  

Polymer LEDs show a strong dependence of the external efficiency on the applied voltage, or on the driving conditions. Generally, the efficiency increases rapidly above the built-in potential, followed by a slow decrease at higher voltage. The latter is particularly relevant for passive matrix (PM) operation of polymer LED displays, where high peak luminance and constant high driving voltages around 10 V are commonly used. It is well recognized that four factors can contribute to the observed voltage dependence: excitation formation probability, single to triplet excitation branching ratio, single photon fluorescence quantum efficiency $\eta_{\text{FP}}$, and photon escape probability or out-coupling efficiency $\eta_{\text{OC}}$. Here, the role of $\eta_{\text{FP}}$ and $\eta_{\text{OC}}$ is quantitatively determined by measurement of the photoluminescence yield under forward bias and of the angular dependence of the out-coupled light, respectively. It is found that $\eta_{\text{FP}}$ can be up to 75% lower under operating conditions similar to those used in PM driving, than at zero bias. The origin thereof is studied by variation of the polymer layer thickness, type of device (hole-only vs double-carrier), and bias (forward vs reverse). The roles of single-polaron quenching and excitation dissociation are discussed. The angular dependence of the light emission is used to locate the emission zone by means of optical model including forward and taking into account the orientation of the dipole emitters. With the location known, $\eta_{\text{OC}}$ can be evaluated. The methods described can also be used to extract external efficiencies of devices with different layout, e.g. with a different hole-injecting or electron-injecting layer.

9:15 AM L1.3  
ENHANCED LIGHT EMISSION THROUGH TRIPLET-TRIPLET ANHILATION IN ORGANIC ELECTROLUMINESCENT DEVICES  
M. Fujihira and C. Giannozzi, Department of Bioorganic Engineering, Tokyo Institute of Technology, Yokohama, JAPAN.

We demonstrate here that luminescence increased more than linearly with an increase in current density of tri{8-hydroquinolone} aluminates (Alq) doped electroluminescent (EL) devices and the EL efficiency reached the value of 1 mW/A or 25 mCd/A when electron hole injection was well balanced. The well balanced charge injection became possible by enhanced electron injection from Al cathode with an electron injection layer of alkali metal carboxylates [1] and hole injection by surface modification of ITO [2]. The luminescence curves were well fitted with a combination of a linear and a quadratic function of the current. The quadratic component can be attributed to additional singlet excited state [Alq] produced through triplet-triplet [T-T] annihilation of triplet excited states [Alq] produced signally with Alq. The requirement of the well-balanced charge injection implies that the long-lived $^{3}\text{Alq}^*$ was quenched efficiently by energy transfer to excess and colored $^{1}\text{Alq}^*$ anion or $^{1}\text{Alq}^*$ cation radicals in the emission zone when the charge injection was unbalanced. The short-lived $^{1}\text{Alq}^*$ was not quenched appreciably. This is the most important characteristic of Alq-doped EL devices. [1] C. Giannozzi and M. Fujihira, Jpn. J. Appl. Phys., 38, L3438 (1999) [2] C. Giannozzi, K.-J. Kwok, K. Yagi, and M. Fujihira, Appl. Phys. Lett., 79, 372 (2001).

9:30 AM *11.4  
HIGH EFFICIENCY ORGANIC EL DEVICES HAVING CHARGE GENERATION LAYER  
Junji Kido, Yamagata Univ, Graduate School of Science and Engineering, Yamagata, Yamagata, JAPAN; Takeshi Nakada, Jun Endo, Noritsu Kawanaga, Koshi Mori, Akira Yokoi, and Takashi Kikuchi, IMES Co., Ltd., Fujitsu, Kawasaki, JAPAN.

A new type of organic EL devices having charge generation layer (CGL) were developed. By applying voltage, holes and electrons are generated at CGL and injected to adjacent organic layers to reconcile with charge carriers with opposite sign. The quantum efficiency of EL devices is substantially improved. An external quantum efficiency of 10% was observed from a device, using fluorescent materials, having one CGL.

10:00 AM *11.5  
CHARGE INJECTION IN ORGANIC SEMICONDUCTORS  

The process of charge injection plays an important role in organic semiconductor devices. We studied the behavior of metal contacts with a host-guest organic semiconductor using a variety of techniques. These studies helped determine the dependence of the charge injection efficiency on parameters such as the mobility of the organic semiconductor, its carrier density (doping level) and thickness, and the energy barrier at the interface. We describe a theory that explains these experimental results and discusses similarities and differences in contacts of organic and inorganic semiconductors. The implications of our findings on the performance of organic light emitting diodes and thin film transistors will be discussed and guidelines and for forming Ohmic contacts will be presented.

11:00 AM *11.6  
EXCITONIC SINGLE-TRIPLET RATIOS IN MOLECULAR AND POLYMERIC ORGANIC SEMICONDUCTORS  
M. Bald, M. Segal, MIT, Dept. of Electrical Engineering and Computer Science, Cambridge, MA.

The ratio of singlet to triplet excitons is critical to the efficiency of fluorescent organic electroluminescent (EL) devices. Recent measurements have suggested that the formation statistics of excitons in polymeric semiconductors may favor fluorescent singlets over non-fluorescent triplet excitons. In some situations, fluorescent polymers may possess intrinsically higher EL efficiencies than low molecular weight fluorescent materials. We present a general technique for measuring the population, fluorescent efficiency of organic materials within EL devices. This allows us to determine the single fractions under EL conditions in archetype materials such as triis(8-hydroquinolone) aluminium (Alq3) and poly[2,5-isothiocyanato-5-[2-ethylhexyloxy]-1,4-phenylenevinylene] (MEH-PPV).

11:30 AM L1.7  
ELECTROCHEMICAL CHARACTERIZATION OF BLUE EMITTING POLYFLUORENE EL Devices  
Lidia Grzegorczyk, Clare Oden, Simon Goldmark, Carl Towns Cambridge Display Technology, Greenhouse House, Maltingly Rise, Cambridge, UNITED KINGDOM.

In an operating LED, electrons are injected into the polymer's LUMO level from the cathode and holes from the anode into the polymers HOMO level. The value of the electron affinity (EA) is usually inferred (often incorrectly) from the experimental HOMO level energy and value of the optical band gap. Using controlled devices under experimental conditions we can now directly access the EA position. Reduction events have been observed on poly(9,9-dioctyfluorene) (P8) and blue emitting polymers based on 9,9-dioctfluorene. This evidence is consistent and reversible. As predicted by theory, the LUMO level is entirely delocalized on P8 blocks. An EA of approx. -2.3 eV, equal to that of P8, is therefore a common feature of blue polymers containing sequences of 9,9-dioctfluorene. Blue emitting 9,9-dioctfluorene-triptycene blends of P8 with polymers containing either 4-acetylpropyl diphenylamine (TFB) or N,N'bis(4-ethylphenyl)-1,4-bis(phenylphenylenediamine (PF8) were characterized by an electron affinity of -2.1 eV. This result shows that the LUMO wave function in these systems is localized on the P8-P16-P8 units. In the case of P8 homopolymer the LUMO level is again localized, this time on the biphenyl unit at the junction of each 2 repeating units. The EA for this material is therefore lower than that of poly(9,9-dioctfluorene). As predicted by theory, these lower LUMO levels allow for more effective charge injection. This allows for easier access to the LUMO level and provides an understanding of the effects of the LUMO level on the efficiency of the EL device. This understanding is further supported by the modeling of the EL device, where the LUMO level is accurately predicted.
On-chip chemical defects in conjugated polymers have previously been associated with luminescence quenching. Recently, however, it was demonstrated that defective sites in conjugated polymers act as excitation traps and give rise to a broad emission red-shifted from the polymer backbone emission and characteristic of a fluorophore moiety. Using gated fluorescence spectroscopy this emission was clearly identified on isolated chains of pristine fluorophore polymers and oligomers, suggesting that the previous assignment to an intermolecular excited state is inappropriate (Lupton et al., APL 80, 4489 [2002]). Gated electroluminescence (EL) was also used to study the dynamics of charge trapping and delayed recombination on these defects (Lupton et al., PRB 65, 193392 [2002]). A further highly significant class of defects we have identified in conjugated polymers relate to metal impurities. We find that contamination of the polymer backbone with 80 ppm of closely bound palladium atoms is sufficient to enable efficient room temperature electrophosphorescence (Lupton et al., PRL 89, 107401 [2002]). The diffusion of triplets to these sites also gives rise to extremely fast phosphorescence observed under optical excitation, without modifying the electronic structure or inter-system crossing of the metastable state. Time resolved EL spectroscopy provides a tool to distinguish between delayed emission resulting from long lived defects and that from excitons formed by recombination in the internal field of the LED. We believe that the discovery of efficient triplet emission is of interest for LEDs but also for polymer lasers and single molecule devices, where triplets can easily be deactivated.

SESSION L2/K2.3

13:00 PM L2.1/K2.3

ORGANIC "MOLECULES" ON METAL SURFACES BY HIGH RESOLUTION STM


The adsorption of large organic molecules on surfaces plays a vital role in the emerging field of nanotechnology. Here we show how the unique resolving power of Scanning Tunnelling Microscopy yields new information on molecule diffusion and assembly by studying the surface diffusion of adsorbed molecules. Adsorbate motion across surfaces can be followed directly by time-resolved "STM movies". In the simplest picture of surface diffusion, the adsorbate jumps between nearest neighbor sites. Recent results suggest this is not necessarily true for complex molecules. By studying the diffusion of two related aromatic molecules, DC (C6H18) and DBC (C6H16), on Cu(110), we find that their diffusion is dominated by long jumps, spanning multiple lattice spacings. The DBC molecule has a core identical to DC, and six additional spacer legs, which increase its diffusion coefficient by four orders of magnitude with respect to DC. This ultimately demonstrates how molecules can be pre-designed to engineer their diffusion properties. Second, we describe the adsorption of the Lander molecule [2] (C10H18) on Cu(110) by STM in the temperature range 100-300 K. The Lander has a central polycyclic ring (conductive backbone) and four “spare legs” [3,5-disubstituted phenyl] for isolation from the substrate. Lander molecules are imaged as four separate lobes by STM, which may be arranged in three different conformations. Manipulation experiments with the STM at low temperatures on isolated Lander molecules adsorbed on step edges reveal a restructuring of Cu steps [4] when removed from a step, a nanostructure appears, two atomic rows in width (corresponding to the distance between the spacer legs within the molecule). Lander molecules were used as nanoscale templates, reshaping portions of step edges into characteristic nanostructures [1]. M. Schannek, T.R. Linderoth, F. Rosati et al., Phys. Rev. Lett. 88, 156102 (2002). [2] F. Rosati et al., Science 296, 328 (2002).

1:45 PM L2.2/K2.2

NANO-SCALE ORGANIC FIELD EFFECT TRANSISTORS AND SHORT CHANNEL EFFECTS.

W. Wagner, Universität Würzburg, Physikalisch-Technische Forschungsstelle, FB Physikalisches Institut, Würzburg, GERMANY (present address, International University Bremen, School of Eng. and Sci., Bremen, GERMANY); T. Muck, M. Leufgen, A. Leibl, M. Prem, T. Borzenko, G. Schmidt, L. Molenkamp, J. Geurs, Universität Würzburg, Physikalisch-Technisches Institut, EP III, Würzburg, GERMANY.

Down-scaling of organic thin film transistor on insulators (OFTETs) offers faster switching speeds as well as higher currents at present day technological limits. We report on the systematic reduction of the organic channel thickness down to 70 nm for OFETs using quarter thionaphene (4T) as active material. THF is used because of their possible high carrier mobility values. We use electron beam lithography to manufacture flexible polymer electronics on SiO2/Si substrates to fabricate OFETs within the common back-gate configuration. Deviations of the standard PET characteristics (short channel effects) are expected for channel lengths L comparable to junction width of the electrodes and/or to the gate insulator thickness. After deposition of the organic film by UVH evaporation long channel (L > 2 µm) devices exhibit standard characteristics at room temperature also used to nitrogen atmosphere. However, for SiO2 gate insulator of 200 nm thickness we found degradation of the saturation regime for L < 1 µm, while on/off ratios strongly deteriorate for channel lengths of 400 nm or below. The effects will be discussed in comparison with short channel effects on inorganic devices. Further, the observed drain current was found to increase by more than an order of magnitude for channel lengths L < 400 nm, which coincides with the average grain size in our organic layers. This indicates an important contribution of grain boundary scattering for the transport in the organic channel.

SESSION L2.

2:00 PM L2.2/K2.3

ELECTRICAL CONDUCTANCE OF SMALL ORGANIC MOLECULES

Norton D. Lang and Phaedon Avouris, IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY.

I will discuss a number of theoretical studies on carbon atomic wires and small organic molecules linking two or three electrodes, focusing particularly on the electrical conductance of these systems. I will consider such topics as the spatial distribution of the voltage drop in atomic wire, the oscillatory conductance of carbon wires as a function of length, the effect of unoccupied impurities on conductance, and the conductivity and density of electron states for a number of disubstituted benzenes, as well as pyrene and biphenyl.

SESSION L3.

3:00 PM L3.1

STRUCTURAL AND OPTOELECTRONIC PROPERTIES OF THE BLUE LUMINESCENT 4PHASE OF Alq3. M. Cille, J. Greiner, S. Forero, A. Mielk, W. Brütting*, Experimental Physics II, University of Bayreuth, Bayreuth, GERMANY; present address: University of Sussex, Electronics and Semiconductor Devices, Sussex, GERMANY.

Trio(8-hydroxyquinolinato)aluminum(III) (Alq3) stands as one of the most successful materials used in organic thin film electronic display applications. Although the partly monocristalline character of evaporated films used in these applications is known, so far comparatively few investigations have been devoted to the crystalline state of this organic material. This will be addressed through the occurence of the Alq3 molecules. It is well-known that depending on the mutual orientation of the hydroxyquinoline ligands, Alq3 can occur in two different stereoisomers: meridional and facial [1], however, until recently all existing phases (α, β and γ) have been found to consist of the meridional isomer [2]. In a previous work we have reported on a new crystalline phase of Alq3 (δ-Alq3) exhibiting strongly blue-shifted fluorescence [3]. Its significantly different optical properties have been tentatively ascribed to the occurrence of the γ-Alq3 molecule. Here we will present an in-depth characterization of the different phases of Alq3 by combining thermal, structural and vibrational analysis. These data provide unambiguous evidence for the existence of the facial isomer in the blue luminescent δ phase of Alq3. Furthermore, an efficient way to fabricate blue luminescent Alq3 in large amounts has been found. These results will be correlated with the optical properties of Alq3 and Alq3-substituted thin film electroluminescent devices [1]. A. Curioni et al. Chem. Phys. Lett. 294, 263 (1998); [2] M. Hennion et al. JACS 122, 5147 (2000); [3] M. Braun et al. J. Chem. Phys. 114, 9625 (2001).

3:30 PM L3.2

Research, Munich, GERMANY.

The performance of organic thin film transistors (TFTs) is determined primarily by the mobility of the charge carriers in the organic semiconductor, which often depends critically on the degree of molecular ordering in the material. A useful strategy for investigating the relationship between molecular structure and TFT performance is the systematic variation of the number of repeat units and substituents in a particular type of semiconductor. One particularly useful class of compounds for this type of investigation are the oligothiophenes, which differ in their degree of conjugation and the width of possible modifications in their chemical structure.

We examined a series of oligothiophenes with different chain lengths ranging from four to six units (dithiopyranyliithiophene, dicyclopentadienyliithiophene, and dicyclohexylthiophene) and with alkyl side chains ranging from 0 to 18 units (dicyclohexylthiophene, dicyclohexylthiophene, and dicyclohexylthiophene). We have fabricated test contact TFTs using solution-processed poly(3-hexylthiophene) and thermally evaporated active layers and found that the TFT performance depends critically on the length of the side chain and on the contact configuration (with mobilities ranging from 0.07 to 1.1 cm²/V s), which is relatively insensitive to the channel length.

We have also fabricated ring oscillators with dicyclohexylthiophene and measured a signal propagation delay of 30 ns per stage. In addition, we have fabricated substituted oligothiophene TFTs with ultra-thin, self-assembled monolayer (SAM) gate dielectrics, with the intent to evaluate if long alkyl side chains contribute usefully to the effective thickness of the SAM gate dielectric.

3:45 PM L.3.3 ENERGY LEVEL ALIGNMENT IN ORGANIC LIGHT EMITTING DEVICES. Paul E. Burrows, Kim F. Ferris, and Linda S. Sapochak, Pacific Northwest National Laboratory, Richland, WA.

The development of small molecule organic electroluminescence (EL) materials in organic light-emitting diodes (OLEDs) has proceeded rapidly since the report of efficient low voltage EL from aluminum tris(8-hydroquinoline) (Alq3). Further, reducing the operating voltage for small molecule OLEDs in a systematic manner is hindered by the fact that the device performance is known. In the case of the amorphous EL material, Alq3, the problem is complicated by the potential presence of two geometric isomers: a more polar and a less polar, which have different intrinsic and correspondingly different electronic states. We present some near-electronic-state calculations on Alq3 and the methyl-substituted materials, and the results are consistent with the experimental results.

4:00 PM L.3.4 IMAGING INDIVIDUAL CHAINS AND AGGREGATES ON CONJUGATED POLYMERS FILMS. J. van Duren, P. Jonkheijm, P. M. Koehnrad, R. A. J. Janssen, H. M. W. Salemink, and J. H. Wolter, Department of Applied Physics, Department of Chemistry, Eindhoven University of Technology, Eindhoven, THE NETHERLANDS.

The nano-scale spectroscopic properties of conjugated polymer films depend strongly on the local morphology. Therefore, the feasibility of conventional scanning probes to achieve sufficient resolution on bulk samples is a serious problem. We have developed a method to achieve molecular resolution on films of arbitrary thickness using a commercial atomic force microscope. The detection of the second harmonic image does not show any molecular resolution, as is usually the case on such samples, the simultaneously measured phase image clearly shows individual polymer chains. The observed phase contrast is explained to result from a strong van der Waals interaction between the metal-coated tip and the p-electrons in the conjugated backbone of the polymer. A simple but quantitative model is presented.

We have used our imaging technique to study the relationship between molecular structure and morphology of PPV derivatives. We found that the chains in the topmost layer of spin-coated films of the asymmetrically substituted polymer O1/OC10-PPV (or MDMO-PPV) are highly curved, with a typical radius of curvature of 5.7 nm. In contrast, the straight morphology of the substrate side of stripe-patterned O1/OC10-PPV shows straight individual chains, showing the residual relation between substitutional and morphology.

4:15 PM L.3.5 ENERGY LEVEL ALIGNMENT AT FULLERENE/PHANTHOLYCYANINE INTERFACE STUDIED BY ELECTRON SPECTROSCOPIC METHODS. Hisao Ishii, Tohoku University, Institute of Electrical Communication, Sendai, JAPAN, Atsushi Sato, Akira Kaken, Yutaka Onishi, Nagoya University, Graduate School of Science, Nagoya, JAPAN, Kazumori Umekita, Kanazawa University, Research Center for Materials Science, Nagoya, JAPAN.

Interfacial band offset and band bending of organic semiconductor are critical to understand and improve organic photovoltaic cells. In this study, the energy level alignment of fullerene/C60/PPV:PCBM interfaces which is one of the model interfaces of organic photovoltaic cells has been investigated using UV and X-ray photoelectron spectroscopy and metastable atom electron spectroscopy (MEAES). The interface which was formed by depositing metal-free phthalocyanine on C60 thin film (15 nm thick) was formed by depositing C60 on this thin film of 0.2 mm thickness in average. This result seems to indicate the interfacial dipole is different in polarity between the two interfaces. MAES is an extremely surface sensitive method and can probe interfacial surface selectively. MAES spectra reveal no significant interface dipole different in polarity between the two interfaces. This means that the possible doping of PC to C60 is not main origin of the observed energy shift. Alternative explanation of the energy shift will be discussed.


We have investigated the electronic, structural, and charge injection properties of interfaces formed between three electroactive conjugated organic materials, N,N-bis(1-naphthyl)-N,N'-diphenyl-1,4-phenylene diamine (NPD), pentacene, and a p-terphenyl derivative in contact to n-or p-doped poly(3,4-ethylenedioxythiophene) polystyrene sulfonate). The PEDOT/PSS. We studied the photoelectron spectroscopy of the hole injection barrier between the three organic materials using energy levels from PEDOT/PSS is lower than that of Au. A similar work function of the pristine electrode material surfaces (ca. 5 eV). This large difference is due to an effective change of the work function due to the deposition of organic materials, i.e., the decrease of the Au work function due to adsorption. Accordingly, model device structures built from NPD and pentacene on the other two different electrode materials show much higher currents densities (up to 10^5 A/cm²) for holes injection from PEDOT/PSS, while from Au. Hole injection from Au for n-PD and p-PD devices is independent of deposition sequence (i.e., n-PD-on Au vs. p-PD-on Au).
substrate [i.e., Au or PEDOT/PSS]. Pentacene devices exhibit significant asymmetries in that regard, due to a strong dependence of the measured molecular organization and mobility on the crystalline material on the substrate, as shown by atomic force microscopy and X-ray diffraction. Consequently, great care must be taken when modeling current-voltage characteristics of devices comprised of crystalline organic solids, especially when the influence of film thickness or different substrate materials is to be studied.

4:45 P.M. **L3.7**

PROBING CONDUCTING ORGANIC FILMS BY ELECTROMECHANICAL DISSIPATION AND ELECTRIC FORCE MICROSCOPY

John A. Marzol, William R. Sieheim, Jenna Harron, Brian Te, and Neil E. Jenkins, Dept. of Chemistry and Chemical Biology, Cornell University; Ithaca, NY; Erik M. Muller, Dept. of Physics, Cornell University; Ithaca, NY.

I will describe novel and highly sensitive variable-temperature and electric force microscope measurements on conducting organic thin films. The goal of these studies is to correlate work function, conductivity, and trap location with surface morphology in both thin films and in working organic field effect transistors. We are studying a number of systems including molecularly doped polymers (polyethylene-TPD), small molecule semiconductors (pentacene), and semiconducting polymers (polythiophene). We have custom fabricated silicon cantilevers that are ordered in a programmable manner more sensitive to forces than commercially available atomic force microscope cantilevers and have constructed an electric force microscope capable of operating at temperatures from 4.5 K.

L3.1

SESSION L4: POSTER SESSION
Chair: Neil C. Greenham
Tuesday Evening, April 23, 2003
8:00 PM - Salon 1-7 (Marriott)

**L4.1 REGENERATION OF ORMOSIL: A PROMISING ROUTE FOR TAILORING OPTICAL ABSORPTIONS.** Wei Liang, Yudong Zhang, Amir Faridz, NP Photonics Inc., Tucson, AZ.

Although inorganic glasses remain unsurpassed as optical transmission media, they are not universally suitable for fabrication of all ranges of integrated optical devices due to certain inherent limitations such as low flexibility, high brittleness and poor patterning. Polymer based optical materials also have several disadvantages such as low heat resistance, poor mechanical resistance and relatively poor adhesiveness. A solution for these contrasting problems may be provided by organic-inorganic approach through the sol-gel process. An attractive feature of the sol-gel process is that it enables the preparation of a variety of inorganic or organic-inorganic materials, which are either impossible or difficult being synthesized via other techniques. Inorganic solgel materials for integrated optic applications are mainly limited to the multi-step coating, conventional resist coating and photolithography. Employing the hybrid organic-inorganic materials alleviates these limitations. This family of materials has received an increasing attention owing to interesting chemical, mechanical, optical and physical properties that can be adjusted between organic and inorganic behaviors. However high concentration of CH gases, thus high vibration absorption in 1600-1800 nm ranges exacerbates the tail of absorption within 1550 nm window. This entails minimizing the number of CH in addition to OH in the sol-gel mixture in order to realize low loss optical devices. A possible way to achieve this goal is to promote the condensation and replace the CH bonds by CO bonds. In this paper, we report on a new class of silica substituted hybrid organic-inorganic materials with wide index and adhesion tunable properties for integrated optics. Material compositions and process parameters are optimized to achieve absorption <0.2dB/cm at 1550 nm. 1x16 Beam splitters are designed and fabricated which exhibit <1dB power uniformity and <3 dB coupling loss per interface.

**L4.2 ACTIVATED CATIONIC POLYMERIZATION OF 2,5-DIAZAL-3,4-ETHYLENEDIOL 1,10-TETRAHYDROXIDOPHENOL: CONDUCTING POLY[3,4-ETHYLENEDIOL 1,10-TETRAHYDROXIDOPHENOL].** Wonphil Bok, Jea Hoon Park, Youngnam Kim, Sung Kook Jeong, Myungji University, Dept of Chemistry, Yonin City, Kyungki Do, KOREA.

Among the several conducting polymers, poly[3,4-ethylenedioxythiophene] (PEDOT) is one of most promising material for practical applications because of the good thermal stability, high conductivity, and high transparency in the p-doped state. In addition, it is soluble in aqueous media, which is a necessary condition for the fabrication of optoelectronic devices. Therefore, a route to synthesizing PEDOT in organic and aqueous solutions has been highly desired. In this work, p-doped PEDOT was synthesized by chemical oxidative polymerization of 3,4-ethylenedioxythiophene both in organic and aqueous solutions, and it has been produced commercially by Bayer AG. Here we are reporting that PEDOTs with bandgaps of 1.5 eV were first synthesized by acid-promoted chemical oxidative polymerization of 3,4-ethylenedioxythiophene in aqueous solution. The cationic polycondensation was occurred via thiophenyl cation because of the high stability by strong electron-donating groups. The resulting conducting PEDOTs affect conductivity of Donor/Acceptor 1 (D/A 1) (pressed powder pellets) p-Doped of PEDOTs prepared by dihalo-EDOT with acid were treated with hydrazine in water to depoly the sample. After treatment of hydrazine for 24 h, the resulting polymers were soluble in NMP essentially the UV-spectrum were obtained. To the best our knowledge, PEDOT prepared by acid catalyzed cationic polycondensation is only one that is soluble in organic solvent to make the molecular weight and UV-absorbance.


We present a combined experimental and numerical study of current-voltage (I-V) and tip-height-voltage (z-V) spectroscopy by STM on conjugated polymer films with a thickness of several tens of nm. It is found that the sharpness of the STM tip crucially affects the potential distribution that determines both the I-V and z-V curves. An I-V (z-V) spectrum is measured by ramping the tip-sample bias through zero with the STM feedback system disabled (active). In the former case the varying current is measured, in the latter case the penetration of the tip into the layer, needed to keep the current constant, is measured. Our calculations proved that the single particle band gap of the polymer material can directly be extracted from z-V curves taken with a sharp (apex radius<100) tip, as was concluded earlier from experiments. Moreover, it is shown that z-V curves taken with a blunt tip (apex radius>100) directly reflect the potential distribution inside the polymer layer as it exists at the operational setpoint of the STM. In either case the agreement between the calculated and measured curves in good. I-V curves are calculated in four different regimes, namely injection or bulk limited transport for either a sharp or a blunt tip. Only for a blunt tip with bulk limited transport geometry effects where found to be negligible. In all other situations tip-geometry induced band bending resulted in currents that differ more than an order of magnitude from the predictions of the plane model that necessarily ignores this effect. For injection limited transport the current could be either unipolar or bipolar, depending on the tip radius. The model was used for simulating and solving the Poisson and transport equations in three dimensions. Both the electron and hole hopping injection at the contacts and their bulk transport are accounted for.


Poly[3,4-ethylenedioxythiophene]poly[styrene sulfonate] (PEDOT-PSS) is one of the most successful electronically conducting polymers available commercially. PEDOT-PSS can be used as a hole-injecting layer on ITO for polymeric electroluminescent devices. Such devices are shown to achieve good stability, lifetime and performance. However, de-doping of PEDOT-PSS largely degrades the polymer as a hole transporting material. In our study, we used X-ray photoemission spectroscopy to analyze the chemical nature of PEDOT-PSS/ITO surface and interface. The study sets the stage for improving the de-doping conditions and mechanisms. We found that de-doping of PEDOT-PSS occurred in the presence of both water and dissolved indium. The existence of water in PEDOT-PSS is due to its hydroscopic nature while the existence of indium in PEDOT-PSS is due to the etching effect of ITO by the acidic PEDOT-PSS.

**L4.5**

Abstract Withdrawn.
14.6 Abstract Withdrawn.

14.7 STRUCTURE-OPTICAL PROPERTY RELATIONSHIP STUDIES OF STYRYL PYRIMIDE DERIVATIVE FLUOREPHORES. Jeremy C. Conover, Aaron W. Harper, Donald P. and Katherine B. Loker Hydrocarbon Research Institute, University of Southern California, Department of Chemistry and the Loker Hydrocarbon Research Institute, Los Angeles, CA.

A set of six alkynamino-substituted styryl pyrimides have been designed, synthesized and characterized as chemically responsive fluorophores for the purpose of structure-property relationship studies. Various solvents, solutions, and solvents allow for the study of the absorption and emission properties of these fluorophores. Comparative analysis elucidated the roles of molecular symmetry, polarity, pimarity and cooperative and competitive intramolecular charge transfer interactions in the broad range of emission of these dyes. The perturbing effects of the solvent environment on UV/Vis spectra of these fluorophores are related to molecular polarization upon excitation and are the result of changes in intermolecular solute-solvent interactions such as Coulomb, inductive, dispersion, charge-transfer and hydrogen bonding forces. This set of styryl pyrimide includes both dipolar and quadrupolar environments and, common electronic and structural features are discussed. These fluorophores are based on well-known electron donor-acceptor pair chromophores and are expected to exhibit exceptional two-photon characteristics. Calculated second hyperpolarizabilities relating to the nonlinear index of refraction indicate comparable or greater two-photon activities than known two-photon molecules.

14.8 SYNTHESIS OF POLY(PHENYLENE VINYLENE) VIA RUTHENIUM-BASED ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION. Aaron W. Harper and Cory G. Miller, University of Southern California, Dept of Chemistry, Loker Hydrocarbon Research Inst, Los Angeles, CA.

Several new ruthenium-based metathesis catalysts have been developed for the ADMET polymerization of an electron rich, hindered alkynamino-substituted divinylbenzene monomer into PPV. The ligand substitution on the ruthenium atom is crucial for enhancing the overall activity of the catalyst to produce high molecular weight polymers. A nitrogen carbene ligand is required in the axial position to facilitate generation of the active ruthenium intermediate as well as stabilization of this intermediate. Variations in catalyst loading relative to monomer, as well as the activity of the catalyst itself, produces materials with different molecular weights and therefore different conjugation lengths. When molecular weights are large enough, this increase in conjugation decreases the singlet energy of the excited state and contracts the band gap.

14.9 AN INVESTIGATION OF THE OPTICAL AND ELECTRONIC PROPERTIES OF SOLUTION PROCESSED POLYCYCLOPENTADIENIONES THIN FILMS. Paolo Coppe and Michael L. Turner, Department of Chemistry, University of Sheffield, Sheffield, UNIKA DÖM, Sweden, weinentin, Department of Materials Science, University of California, Cupertino, Avesta Research Centre, Blackley, Manchester, UNITED KINGDOM.

Solution processable conjugated polymers are being extensively investigated as charge transport materials for use in electronic devices such as field effect transistors [1]. The mobility of charges in the materials is limited by the efficiency of hopping between localized states [2] and therefore close packing of adjacent chains in the solid state is essential for high charge mobilities. Recent studies using regioregular poly-3-alkylthiophenes have shown that the monomer structure and the polymer regiochemistry are critical parameters in achieving the correct thin film morphology [3]. We have recently reported the preparation and optical characterization of solution processable polycyclopentadienones. [4] These polymers are fused ring derivatives of the extensively studied poly-3-thiophenes and are structural analogues of the polythiophenes. This contribution describes an investigation of the structure/property relationships that govern solid state self-assembly of fused thiophene ring systems and examines the influence of polymer morphology in these systems on electronic properties such as field effect mobility. 1) Stringfellow, H.; Tessier, N.; Friend, R. H., Science, 1999, 580, 1741. 2) Cormil, J.; Beljonne, D.; Calvet, J.-P.; Bedn, J.-R., Adv. Mater., 2001, 13, 1053. 3) McCullough, R. D., Adv. Mater., 1998, 10, 02. 4) Coppe, P.; Cuperto, D. C.; Venteis, S. G.; Turner, M. L., J. Mater. Chem., 2002, 12, 2597.

14.10 PHOTOGRAPHIC PROPERTIES OF EUROPIUM III β-DIKETONE COMPLEXES THAT CAN BE EXCITED AT LOWER ENERGIES. Patrick J. Case, Aaron W. Harper, Donald P. and Katherine B. Loker Hydrocarbon Research Institute, Dept of Chemistry, University of Southern California, Los Angeles, CA.

In preliminary work performed in our lab, it was noticed that the ethylidene(2,4,4-trinitrophenyl)triphenylenzene(III) had an excitation maximum around 413 nm while its absorption maximum was around 373 nm. This sparked interest in seeing if lower energy polymers could be used for sensitization of lanthanide complexes. Because of promising results, an effort was made to create more emissive europium complexes that could be excited at around 410 nm. It was found that a series of novel β-diketone type ligands consisting of a naphthyl or phenanthrene unit on the C1 carbon and a thiophene ring on the C3 carbon have been synthesized. The photophysical parameters and quantum yields of the compounds containing 1,1-biphenyl as well as the effect of changing the heteroatom of the heterocyclic aliphatic ring from oxygen to sulfur will be presented. Also, effective triplet harvesting from a conjugated polymer will be shown.


Energy transfer from polypylene-type polymers to a series of organic dyes was studied. Two of the three polymers were synthesized via Suzuki coupling of 1,4-phenyleneboronic acid with 1,4-dihydrobenzene or 1,4-bis(dihydrobenzene), to obtain a polyphenylene with only para-linkages, as well as one with alternating para and meta linkages. The third polymer was a polyphenylene generated by a naphthyl-ended coupling of 2,5-dihydro-4-metilen Phenylene. The resulting polymers, having significant energy differences, were used as the energy donors. A variety of Coumarins were used as singlet acceptors, and several porphyrines were used in triplet acceptors. Photophysical data and energy transfer parameters will be presented.

14.12 OPTICAL PROPERTIES OF A TWITTERIONIC POLYPHENYlene DERIVATIVE CONTROLLED BY SELF-ASSEMBLY OF BIOMOLECULES. Peter Nilsson, Olle Inganäs, Linkoping Univ, Dept of Physics, Linkoping, SWEDEN.

A chiral, 3-substituted polythiophene with an amino acid function shows pH-dependent visible, emission and circular dichroism spectra in buffered aqueous solution. At pH equal to pI of the amino acid, the backbone adopts a non-planar right-handed helical conformation and the polymer chains are separated from each other. Increasing pH leads to a more planar conformation of the backbone and an aggregation of the polymer chains occurs. A lower pH will also lead to a more planar conformation of the backbone, but aggregation of the polymer chains appears to be absent. The aggregates are disrupted by increasingionic strength in alkaline buffer systems, indicating that hydrogen bonding is important for aggregation. On the other hand, ions containing an amino group and one or more hydroxyl groups induce a more planar conformation of the polymer backbone. The optical transitions of the synthetic derivative can be titrated by self-assembly of synthetic peptides and DNA-hybridization. This technique could be used as a platform for making novel biosensors and biomolecular switches.

14.13 ELECTROSYNTHESIS AND PROPERTIES OF POLYPHENYlene DERIVATIVE USING CO-SURFACTANT IN AQUEOUS MEDIA. Keith R. Beavenman and Philip M. Lessner, KEMET Electronics Corporation, Greenville, SC; Tourin, E.L., Meusel and Richard V. Gregory, School of Material Science and Engineering, Clemson Univ, Clemson, SC.

Using anionic surfactant in aqueous solution allows the increased EDOT solubility in water and produces an important change in the oxidation polymerization mechanism relative to neatotropic medium. We are currently concerned with the electrochemistry of poly(3,4-ethylenedioxythiophene) PEDOT doped with mixing anions from the electrolyte lithium tosylate co-surfactant sodium dodecyl sulphonate acid and sodium poly(styrene sulphonate acid). Strong electrochemical reduction occurs between EDOT oxidation, and a subsequent reductive step to form high quality polymer film with high conductivity, and good environmental stability. The films are synthesized by cyclic voltammetry and chronoamperometric methods, and characterized by UV-visible, and NMR spectroscopy.

14.14 VIBRATIONAL ANALYSIS OF COPPER PHTHALOCYanine THIN FILMS ON VARIOUS SUBSTRATES. Sixiong Wang, Xiang
Because of the importance of the structural properties of organic thin films for device performance, study of packing and orientation of the organic molecules on substrates is necessary. High-resolution electron energy loss spectroscopy (HREELS) measurements of copper phthalocyanine (CuPc) thin films on various substrates were performed. All the CuPc films were deposited in high vacuum at room temperature, and the vibrational excitations of monolayer, multilayer, and multilayer CuPc films have been studied step by step. The HREELS data show that CuPc films on HOPG and on hydrogen-terminated Si (111) surfaces suggest that CuPc molecules prefer to orient with their molecular planes parallel to the surface. Scanning electron microscopy show that CuPc molecules form isolated crystals on HOPG surface even with high thickness and X-ray diffraction results indicate the molecules are stacked straight along the surface normal. In contrast, continuous films of CuPc are grown on H-terminated Si (111) surface. On some common polycrystalline or amorphous substrates (polished molybdenum plate, ITO coated glass and non-H-terminated Si wafer), HREELS spectra indicate that the CuPc films arrange with random orientation due to the disordered nature of the substrate surfaces. The comparison between the HREELS spectra of monolayer and multilayer CuPc films will also be described.

**L4.15** ORGANIC LIGHT-EMITTING DIODES BASED ON ALUMINUM DOPED CHINONETUONG XU, F. L. H. Stewart, and M. Kenning Fung of, Chen Sing Lee**.

"Center of Super Diamond and Advanced Thin Films (CODAF) & Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, CHINA; Fraunhofer Institute for Thin Film and Surface Engineering (ILM), Freiburg, GERMANY.

Transparent conductive oxide (TCO) films, aluminum doped zinc oxide, were deposited on glass substrates by middle frequency magnetron sputtering. Aluminum-doped zinc was used as the sputtering target. By varying the sputtering conditions such as oxygen flow, sputtering power, target, substrate distance, deposition pressure, and the annealing temperature, ZnO:Al films with optimized film properties were obtained. Average optical transmission of 90% and sheet resistance of 6 ohm/square were achieved. Organic light-emitting diodes (OLEDs) were fabricated on the ZnO:Al films. To achieve 20%A/m^2 and 4000cd/m^2, less than 8V and 7V were required respectively. At 200mA/cm^2, a brightness of higher than 60000cd/m^2, corresponding to a power efficiency of higher than 1.5lm/W, was achieved. For comparison, only 0.9lm/W was achieved by the reference OLEDs fabricated on indium tin oxide (ITO) substrates.

**L4.16** POLYMER OPTICAL AMPLIFIERS. JUSTIN R. Lawrance, Graeme A. Burnham, M. Kenning Fung, and M. Kenning Fung of, Ultrafast Photonics Collaboration, School of Physics & Astronomy, University of St. Andrews, St. Andrews, UNITED KINGDOM.

In recent years, semiconducting conjugated polymers have received considerable interest as novel laser gain media. They exhibit optical gain over broad spectral ranges through the visible and are well suited to use in tunable lasers and have the potential to be used as broadband optical amplifiers. Such devices would be readily compatible with polymer optical fibres and integrated circuits. Polymer optical fibres are a favoured technology to relieve the telecommunications bottleneck in local area networks, and low-cost integrable optical amplifiers may increase the range and applicability of such systems. We demonstrate a compact, broadband optical amplifier using the conjugated polymer poly[3-methoxy-5-(3',7-dimethyl-1'-octyl)-1,4-phenylenevinylene] (OC: C62PM). Amplification was monitored using a modified dye laser system. Gains of 30-40 dB in a wavelength range of 575 to 640 nm, corresponding to a 50 THz bandwidth, are observed due to the broad luminescence spectrum and large cross-section for stimulated emission of the polymer. The variation in gain as a function of solution concentration is examined with 2 g/l being the optimum. The effect of different probe beam intensities on the gain is also examined. We observe a drop in gain at higher probe powers due to saturation effects and an increase in gain as the probe intensity decreases. Such behaviour is characteristic of optical amplifiers and can be modelled readily. For a 1 cm path length we measured a small signal gain of 44 dB, and deduce, a stimulated emission cross-section for OC: C62PM of 5 x 10^-19 cm^2. The experimental results for solid-state polymer optical amplifiers will be discussed.

**L4.17** Transferred to L4.3

- **L4.18** Abstract Withdrawn.
- **L4.19** Abstract Withdrawn.
- **L4.20** INFLUENCE OF ORGANIC FILM THICKNESS ON ORGANIC LIGHT-EMITTING DIODE PERFORMANCE. CHEN LII, CHUNG SHENG YU, SHENG KUN, ZHIGANG ZHOU, and CHING-CHE WANG of, Department of Electronic Science and Technology, National University of Science and Technology, Wuxi, CHINA.

For a given organic light-emitting diode (OLED), the change of organic layer thickness affects both electronic and optical performance of OLED. We detailed analyzed the whole lighting process, discussed every possible injection of carrier excited in OLED (be trapped, back flowing, leakage and recombination) and their affection to the electroluminescence efficiency through the influence of film thickness on those possibilities, we quantitatively analyzed the dependence of external quantum efficiency on organic thin film thickness. At the same time, combining current injection theory and recombination theory, we quantitatively simulated above phenomenon, which show how did the film thickness of different organic layer affect the external quantum efficiency. In addition, we quantitatively studied the dependence of threshold voltage, and operating lifetime on the film thickness. This work is helpful to optimize the design of OLED, and make it easy to model the performance of OLED by its process parameters.


To develop novel chromophores for photonic applications, we synthesized a series of transition metal-containing phenyl acetylide oligomers. These compounds have novel structural features, including attachment of a styryl-ethyne group and branching. The synthesis of these chromophores will be described, as well as optical characterization by spectrophotometry, fluorescence and flash photolysis experiments. Their properties will be compared with a base series of platinum acetylides we recently described in the literature (Rogers, J. E., et al. J. Phys. Chem. A 106: 10108-10115 (2002)).

**L4.22** INITIA- AND INTER-CHAIN ENERGY TRANSFER IN AN END-CAPPED CONJUGATED POLYMER. EMMANUELLE HENZBERG, DAVID BELJEM, JEAN-LUC BREDAS, Chemistry of Novel Materials, Mons, BELGIUM, and Department of Chemistry, Tuscon, AZ; GREG SCHOLES, Lash-Miller Chemical Laboratories, Toronto, CANADA.

We present a theoretical modeling of the energy-transfer processes taking place in covalently linked donor-acceptor systems, namely poly(phenylenevinylene) conjugated chains end-capped with a red-emitting phenylene derivative. The poly(phenylenevinylene) chains are formed by a statistical distribution of segments with different conjugation lengths and therefore different excitation energies. Upon photocexcitation, unidirectional long-range energy transfer processes thus occur towards lower energy sites, prior to final trapping of the excitations on the perylene derivatives. Both intra- and inter-molecular hopping processes involving different conjugated segments of the polymer chains and the perylene end-group are described in the framework of an improved Förster model based on the use of a monopole expansion of the transition moments. These calculations suggest that in solution, where molecular contacts are rare, exciton transport takes place through hopping along the conjugated chains, which is an intrinsically slow process. In contrast, interchain transport, dominating the energy transfer dynamics in the solid state, is found to be about one order of magnitude more efficient, as a result of larger electronic matrix elements between neighboring molecules. To account for the static disorder inherent to polymer materials (here associated with the presence of different conformers), random chains of increasing size (built from a distribution of conjugated segments with various lengths) were generated and average values of the energy transfer cross-sections extracted using Monte Carlo simulations. Finally, as a first step to account for the possibility of exciton delocalization over conjugated segments in close contacts, we have implemented a modified Fröhlich master equation for energy transfer between donor-acceptor states using a random combination of wavefunctions localized on single conjugated segments.

The design of an efficient, electro phosphorescent organic light emitting device (OLED) requires the selection of a host-guest materials combination that allows for exothermic energy transfer between the triplet energy levels of a conductive host and phosphorescent guest molecules. Exothermic refers to transfer from the host to a lower energy guest triplet state, liberating energy in the process. The exothermic energy transfer in blue electro phosphorescence lies in the lack of suitable high-energy hosts. Here, we demonstrate efficient blue electroluminescence using exothermic energy transfer from a host consisting of N,N-dicarbazolyl phenyl substituted iridium complex iridium (III)(1,10-diphenyl-10H-phenanthroline) (Ir(ppy))2 picoline (Pc)2. By examining the temperature dependence of the radiative lifetime and the photoluminescence of a film of mCP doped with Ir(ppy)2Pc, we confirm the presence of exothermic energy transfer. The maximum external electro luminescent quantum efficiency of devices employing mCP:Ir(ppy)2Pc is (7.5±0.8)%), with a luminous power efficiency of (8.9±0.5)lm/W, representing a significant increase in performance over previous, endothermic blue electroluminescent guest-host systems. 1


We have synthesized multichromatic chromophores based on spirobi fluorene (x-center), attaching donor and/or acceptor moieties, typically dipyridimino-p-phenyl and [3(p - ethylbutyl),3-coordinately]-benzyl at the ends: D-x-D (301), D-P-A (302) and A-x-A (303). We have investigated the properties of these chromophores in single and double layer devices consisting of ITO/PEDOT/P3HT/(A3Q)2/Mg:Ag. We were particularly interested in looking into the functional susceptibility of the redox-active moieties of chromophore toward incoming electrons and holes, and their influence on the LE properties. EL spectra of 301, 302 and 303 show the emission maxima at 540, 545 and 555 nm, respectively. The common feature throughout these devices is that their turn-on voltages are all less than 4 volts. The D/D and D/A pair chromophores, 301 and 302 show a remarkable increase of EL (ca.1000 and 400 cd/m2, respectively) in the presence of A3Q layer (as a double layer), compared to those (100 and 20 cd/m2, respectively) of respective single layers. A drastic change occurs with A/A pair chromophore, 303 by the presence of A3Q (double layer); the EL is decreased to 4 cd/m2 from 1000 cd/m2 of the single layer. Such a decrease is the consequence of a large excess electrons transferred to the emitting layer, serving as an excition quencher. Blending of 303 with PVK at 1:1 and 1.5 (303:PVK) to compensate the electron flow change of ITO/LE/Blue EL and the increased blue shift (65 nm) of emission band from that (555 nm) of pristine 303. However, the blend of 51 displays an entirely different EL spectrum that covers a broad wavelength (430 to 800 nm), emitting a white light.

L4.25 STRUCTURE AND MORPHOLOGY OF SOLUTION PROCESSED PENTACENE FILMS. Senior Rasing and Sigurd Wagner.

Organic thin films have attracted increasing interest for their potential use in electronic and optoelectronic devices. Solution processing presents benefits of low cost fabrication and large area compatibility, but is difficult to realize with poly cyclic

L4.26 1.54 MICRON EMISSION FROM ERQ BASED ORGANIC LIGHT-EMITTING DIODES. X. D. Feng and Z. H. Lu, Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, CANADA.

Organic light-emitting diodes (OLEDs) in visible spectrum are now commercialized, but it is still a challenge to extend the existing OLED technology to the area of optical communications aiming at 1.3 or 1.5 micron emission. We fabricated Er-doped oxyglinine Erbrism (Erq) based OLEDs, and 1.54 micron electroluminescence was observed at room temperature. The EL spectra is tunable by doping Erq structures. The physical mechanism behind them is discussed. An approach to further improvement on the quantum efficiency of 1.54 micron emission is also proposed.

L4.27 SYNTHESIS AND LIGHT-EMITTING PROPERTIES OF NEW POLYFLUORENE DERIVATIVES. Do-Hoon Hong, Kun-Ho Kim, National Institute of Technology, Dept. of Applied Chemistry, Kumi, KOREA, Ji-Hoon Lee, E-Polymer Ltd, Samsung Advanced Institute of Technology, Suwon, KOREA.

New polyfluorene derivatives, poly[9,9-bis[4-(4-tert-octylphenyl)] fluorene (POPOP-8) and poly[9,9-bis[4’-(2”’7”’-dimethylcyloxy)phenyl]] fluorene (POPOP-10) were synthesized through the Ni(0) mediated polymerization. The copolymers were characterized using FT-IR, spectroscopy, UV-vis spectroscopy, TGA, photoluminescence (PL) & electroluminescence (EL) spectroscopy, elemental analysis, and molecular weight studies. Interestingly no significant spectral change and formation of excimer emission were observed even after annealing the polymer film at 100°C for 2h. Light-emitting devices were fabricated in an ITO (indium-tin oxide) /PEDOT/polymer/Ca/Al configuration. Synthesis and EL properties of new polyfluorene derivatives will be presented.

L4.28 WHITE LIGHT-EMITTING DEVICES USING POLYMER BLENDS. Do-Hoon Hong, Dept. of Applied Chemistry, Kumho Naol Inst of Tech, Kumi, KOREA, Ji-Hoon Lee, E-Polymer Ltd, Samsung Advanced Inst of Tech, Suwon, KOREA; Jeong-Ik Lee, Basic Research Lab, ETRI, Taejon, KOREA; Chang-Hee Lee, Dept. of Physics, Inha Univ, Incheon, KOREA; Yong-Dae Kim, Dept. of Chemistry, Kon-Kuk Univ, Seoul, KOREA.

White light-emitting devices were fabricated using the blends of blue, green, red emissive polymers of poly[9,9-bis(3’-hexylphenyl) fluorene] (PEH), poly[9,9-dioctylfluorene-2,7-diyne] (POFV), poly[2,3’,7”,dimethylcyloxy]-1,4-phenylene-1,4-phenylenevinylene (CNPPV) and poly[2'(2’-ethylhexyl)-5’methoxy-1,4-phenylenevinylene] (MEl-PPF). Insensitive energy transfers between the blue polymer and the green and red polymer, which was observed in PL spectra of the blend films, provides a good advantage to get a white light emission due to better blend ratio controllability. The EL devices were fabricated with ITO/PEDOT/brazil/Ca/Al configuration and good white light-emission was obtained for a certain blend ratio. The light-emitting properties of polymer blends will be presented.

L4.29 OPTICAL PROPERTIES OF PPV/TiO2 NANOCOMPOSITE PREPARED BY USING A PARTICULATE SOL. Byung Duk Yang and Ki Ho Yoon, Yonsei Univ., Dept. of Ceramic Engineering, Seoul, KOREA.

The effect of particulate sol and nanopowder on conjugated polymer was investigated in terms of optical properties and chemical structure in PPV and PPV/TiO2 nanocomposites. TiO2 particulate sol did not
interact with PPV but made the stable nanocomposite. The enhancement of zero-phonon vibronic transition and the increase of vibronic splitting were observed in the photo-oxidation content were induced by the redox of rotational order. The PPV/ITO nanocomposite prepared by using a particulate sol had much better dispersion of nanoparticles than the composite prepared by a conventional method. In case of thermal conversion at 120°C, the conjugation length of PPV/ITO, a nanocomposite prepared by using a particulate sol was the longest while that of PPV was the shortest. The nanocomposites had slightly shorter conjugation length, compared with PPV when they were prepared under the same conditions at 200°C. The PPV/ITO nanocomposite prepared by using nanopowder showed the high vibronic splitting energy.

**L4.30**

**CARRIER DYNAMICS OF CONJUGATED OLIGOMERS.**
Jean-Chlaude Viai and Olivier Stéphan, J. Barrier Unir. CNRS, Lab Spectrometrie Physique, Grenoble, FRANCE; C. Andraud, Ecole Normale Supérieures-CNRS, Lyon, FRANCE; Lab Stereochim & Intéract Mol.

Time resolved photoluminescence experiments on conjugated structures (polymers, oligomers, gels) are not often performed. However they can provide rich information on the dynamics (radiative and non-radiative recombination, transport) of electronic carriers inside these materials. Indeed they can complement macroscopic information such as carrier mobility and they are more simple to perform because they avoid doping and electrical contacts. We want to demonstrate that on two particular cases. We have synthesized a whole set (from N=2 to 8) of alkylfluorene oligomers. They are studied in highly diluted solution at room temperature. In addition to the spectral behavior (seen in absorption and photoluminescence) which illustrate the classical red shift when N increase we also measured the quantum efficiency and the photoluminescence decay time in the picosecond range. These measurements are compared to those obtained on the polymer itself. Quantum efficiencies are stable and high (more than 80%) and the radiative rates increase with N. This is explained by an efficient dipole coupling between the monomers of the conjugated chain. This behavior contrasts with what we obtained on a set of regioirregular oligo-alkylfluorene in the same experimental conditions. Indeed in this case all oligomers are terminated by a chloride substitution. This hetero-atom localized the wave function and enhance the non-radiative recombination. We then measured a quantum efficiency smaller for small N going along with non radiative rates increasing as N decrease. We explain that by a localization of excitation (or carrier) on trap related to Chloride.

**L4.31**

**GREEN OLEDs: ELECTROLUMINESCENCE AND THE ELECTRICAL CARRIER TRANSPORT.**
L. Perez, R. Pustes, P. Loges, Departamento de Física, Universidad de A Coruña, A Coruña, PORTUGAL.

Organic Light Emitting Diodes (OLED) based on metal chelate complexes as emissive layer (Alq3) and a double hole transport layer of m-MTDATA / NPB have been fabricated. A complete characterization has been made in order to understand their optical and electrical properties. The electroluminescence (EL) shows a broad band peaked near 510 nm (green) and two small bands at near 425 nm (blue) and near 565 nm (orange). The result is a “white” EL. The origin of the orange and main green band is clearly the recombination inside the Alq3 layer while the blue band appears to be due to a recombination in a narrow layer in NPB/Alq3 interface. The electrical DC measurements have been performed in order to establish the nature of carrier transport and effectiveness. At low applied voltages, an injection of carriers through a small barrier (~0.2 V) control the current flow. After the transition to the bulk limited conduction, the results suggest that the electroluminescence (EL) takes place through a charge limited conduction (TCL) with characteristic trap energy near 0.13 eV controls the process. Some influence of metal-semiconductor interface and the bulk conduction are also discussed. The investigation of the efficiency dependence on the minority carriers reveals that the triple layer device with two hole transport layer can improve the EL (reduction of the driving voltage and therefore increase the stability), but also contributes to the widening of the EL band. The relationship between the electrical measurements and the electroluminescence spectrum is analysed. Finally, a general model is proposed based on the experimental results and energy band diagrams.

**L4.32**

**SYNTHESIS, PHOTO- AND ELECTRO-LUMINESCENT PROPERTIES OF NOVEL THIOPHENE BASED POLYMERS.**
George Vamvoukas, Yuning Li, Steven Holdcroft, Simon Fraser Univ, Dept of Chemistry, Burnaby, B.C., Canada; Hanry Aziz, Zoran D. Popovic, Xerox Research Center of Canada, Mississauga, Ontario, Canada

Derivatives of poly(thiophene)s are of interest for electronic and optoelectronic applications due to their good electrical properties, processability and stability. However, based on their poor solid state quantum efficiency, to due molecular aggregation, they are generally poor candidates as emitters for electro-photonic applications (e.g. OLEDs). In this presentation, the photostabilization effects of the post-functionalization of poly(thiophene)s towards the decrease of molecular aggregation, with the intent to improve the quantum yield of luminescence and color tunability will be discussed. To that end, it will be shown that by varying the mole ratio of electrophile and monomer, high photo- and electro-luminescence quantum efficiency as color tunability can be achieved. The synthesis, photophysical and electro-optical properties of polythiophenes will be presented and will demonstrate the potential of poly(thiophene)s as emitters in OLEDs.

**L4.33**

**STABILIZED BLUE EMISSION FROM POLYFLUORENE-BASED LIGHT EMITTING DIODES: ELIMINATION OF FLUORONE DEFECTS.**

Polyfluorene (PF) based light emitting diodes (LEDs) typically exhibit device degradation under operation with the emergence of a strong low energy emission band (at 2.2-2.4 eV). This longer wavelength band converts the desired blue emission into blue-green or even yellow. We have studied both the photoluminescence (PL) and electroluminescence (EL) of PFs with different molecular structures and found that the low energy emission band originates from fluorone defects which are introduced by photo-oxidation, thermal, or during device fabrication. XPS results show that the color-shifted EL on PF is strongly correlated to the fluorone defects. The fluorone defects generate a stronger contribution to the EL than to the PL. By utilization of a novel electron-transporting material as a buffer layer between the emissive PF and the Ca/Ag (Ba/Ag) cathode, the blue EL emission from the PF was stabilized.

**L4.34**

**SYNTHESIS OF NONDISPERSE CHIRAL OLIGOFLUORENE\[S] AND THEIR OPTICAL PROPERTIES IN NEAT FILMS.**
Yunhong Gong, Anita Trakolska, Sean W. Culligan, Dimitris Kouris, and Shane H. Chen, Univ. of Rochester, Dep of Chemical Engineering and Laboratory for Laser Energy, Center for Optoelectronics and Imaging, Rochester, NY.

Although various chiral-conjugated systems have been reported, the structural origins of the observed chiroptical properties have not successfully elucidated. Polychromes have been considered to be a prime candidate for optoelectronics due to their superior stability, high fluorescent quantum yield, and their potential for a spontaneous alignment mediated by liquid crystal mesomorphism. To facilitate the fabrication of defect-free glassy liquid-crystal films and increase structural alignment at the supramolecular level, we have synthesized and characterized the first series of non-dispersed chiral oligofluorene with a number of repeat units (n) up to 16. We have also examined the effects of chain length and geometry on both the planar and chiral properties of these films, and we have demonstrated that these materials are capable of achieving high optical activity. Finally, we have fabricated polarized polymerizable films, containing chiral oligofluorenes, which are capable of high spatial coherence in thin films. It was found that oligofluorenes with n > 5 are capable of cholesteric mesomorphism. Pristine spin-cast films, approximately 80 nm in thickness, were found to be amorphous while exhibiting pronounced circular dichroism and highly efficiently circularly polarized fluorescence. Nonamers capable of forming amorphous cholesteric films were prepared through optimization of the casting method. Variable angle spectroscopic ellipsometry was employed to determine the helical sense and pitch length of the cholesteric stack in thin films. It was also instrumental in the investigation of the resultant chiroptical properties. Furthermore, spatially circularly polarized light is highly efficient light-polarizing devices have been demonstrated with monodomain glassy cholesteric films.

**L4.35**

**OPTICAL SPECTRA OF PVK AND Alq3 UNDER HYDROSTATIC PRESSURE.**
Lin Ke, Soo Jin Chin, Lin Ke, Institute of Materials Research & Engineering, SINGAPORE; Zi Li Feng and Guo-Hua Li, National Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, P.R. CHINA.

Photoluminescence (PL) of poly[(phenylenevinylene) (PPV) and trifluorinated (fluorenone) aluminum complex (Alq3) under hydrostatic pressure up to 66 GPa is investigated. The excitation energies pressure coefficient is 55.8 meV GPa^-1 for PPV samples, while no obvious energy shift for Alq3 samples (pressure coefficient is -4.21 meV GPa^-1). We find that the details of crystalline arrangement crucially affects the optical properties. With increase of interchain distance in the Vatck
direction, leading to a richer exciton structure and an increase of radiative efficiency. This has implications for theoretical activity and optical processing of polymeric films. Our results indicate that polymers have an advantage over small molecules in OLED applications.

L4.36
Abstract Withdrawn.

L4.37
BALANCED CHARGE INJECTION AND SINGLE-EXCITON QUENCHING IN ORGANIC ELECTROLUMINESCENT DEVICES.
Chimed Ganorsoy, Masanichi Fujishira, Tokyo Inst of Tech, Dept of Biomolecular Eng, Yokohama, JAPAN.
We have recently reported that EL efficiency increased more than linearly with increase of current for tri(N-hydroxyquinoline) aluminum (Alq3)-based EL devices [1]. In particular, work function control of the aluminum plays a crucial role in the balanced EL processes at which holes and electrons are injected into a two-layer organic thin film with a heterojunction. In this work, we described well balanced electron and hole injections into organic layers of our improved devices [1,2] in order to maximize the EL efficiency. To clarify the balancing between electrons and holes, we also studied carefully using only single layer EL devices with different thicknesses. Moreover, our recent results have shown that the luminescence decreased less than linearly with an increase in current of Alq3-based devices with an Al cathode when electron injection was not improved significantly. We have not observed the improvement of the EL efficiency in these devices even for hole injection was enhanced [2,3]. The decrease in the EL efficiency was attributed to quenching of singlet excited state \( \text{Alq}^* \) by large excess cation \( \text{Alq}^+ \) radicals with increase in current due to partial overlap between fluorescence spectrum of \( \text{Alq}^* \) and absorption spectrum of \( \text{Alq}^+ \) radical ions, but not the corresponding singlet \( \text{Alq}^* \) radicals. [1] C. Ganorsoy and M. Fujishira, Appl. Phys. Lett. 81, 3137 (2002). [2] M. Fujishira and C. Ganorsoy, in Conjugated Polymer and Molecular Interfaces, A. Kahn, J.J. Premeau, W.R. Saltzberg, and K. Seki editors, (Marcel Dekker, Inc., 2002). p. 817. [3] C. Ganorsoy and M. Fujishira, Appl. Phys. Lett. 77, 421 (2000).

L4.38
PROCESS IN EFFICIENCY OF BLUE ORGANIC ELECTROLUMINESCENT DEVICES.
Yasuo Enbusa, Chime, Ganorsoy, Masanichi Fujishira, Tokyo Inst of Tech, Dept of Biomolecular Eng, Yokohama, JAPAN.
Compared with green organic electroluminescent (EL) devices, the EL characteristics of blue and red EL devices need to be improved particularly in terms of efficiency and color purity. The loss process in EL efficiency is related to the photoluminescence efficiency of organic materials, as well as additional losses due to exciton quenching mechanisms. We report here the EL characteristics of blue organic EL devices with hole transport layer as an emitter i.e ITO/NPD/DAM/Alq3/Al. Here, ITO, NPD, and Alq3 are abbreviations for an indium tin oxide electrode, a 4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]phenyl, a bathocuproine, and a tri(N-hydroxyquinoline) aluminum. Different types of molecule and cathode interface materials are used in this study [1]. In these devices modified by charge injection layer of the interface materials, we have never observed that the emission from NPD increased more than linearly with increase of current when holes and electron injection was well balanced [2]. Only we found that the EL efficiency decreases in curves with increase in current of all the devices studied. Our experimental results indicated that singlet excited states \( \text{NPD}^* \) was quenched efficiently by large excess cation \( \text{NPD}^+ \) radicals [3] accumulated new and in the emission zone due to large overlap between the fluorescence spectrum of \( \text{NPD}^* \) and absorption spectrum of \( \text{NPD}^+ \). In addition, \( \text{NPD}^* \) is also possible quenched by unbound \( \text{NPD}^+ \) radicals when large excess electron injection. The detailed investigation will be discussed at the symposium. [1] C. Ganorsoy, K. J. Kwan, Y. Yagi, and M. Fujishira, Appl. Phys. Lett. 79, 272 (2001). [2] C. Ganorsoy and M. Fujishira, Appl. Phys. Lett. 81, 3137 (2002). [3] C. Ganorsoy, K. Sugita, and M. Fujishira, Chem. Lett. 1192 (2000).

L4.39
PRESSURE- AND TEMPERATURE-INDUCED STRUCTURAL TRANSITIONS IN ORGANIC POLYCRYSTALLINE MATERIALS.
Sergey Borschuk, Griner, Iryna Khomskaya, Lingmin Liets, Tetyana Tetychynska, STC Institute for Single Crystals, NAS of Ukraine, Kharkiv, UKRAINE.
Pressure-compactd organic molecular polycrystals (e.g., stilbene, anthracene, p-terphenyl) are known to be a promising class of scintillator materials for radiation detectors. The use of such materials allows manufacturing of large-area scintillators of required shapes. However, their scintillation characteristics remain substantially inferior to those of standard single-crystalline scintillators made of the same material. Recently, it has been shown that under certain conditions of the combined action of pressure and promoting temperatures, structural transformations of the polycrystals could be substantially changed [1,2], and a theoretical model describing ordering processes in such systems has been proposed [3]. In this paper, we report our studies of the pressure/temperature effects on structural and scintillation properties of polycrystalline pellets made of crystalline powders of stilbene and p-terphenyl. Microscopic observations clearly show spontaneous formation of crystal alline regions, with subsequent solid-state reaction of crystal growth. Substantial improvement of scintillation properties is observed. Thus, for stilbene and p-terphenyl polycrystals, light outputs of up to 85-95% with respect to the corresponding single crystals was obtained. Possible mechanisms are proposed for the observed structural ordering and ways for optimization of the pressure/temperature parameters are discussed. In parallel experiments, we observed similar behavior with more complex substances (including those of biological origin), with marked effects due to specific features of supramolecular ordering. It is supposed that the methods of pressure and ordering procedures can be very promising for application, specifically, in radiation detectors, especially for detection of short-range ionizing particles, as well as fast neutrons. 1. B.V. Griner, S.V. Badzakaya, L.N. Lietski and V.D. Punkarskaya, Functional Materials V.1, No.1, p.156 (1994). 2. B.V. Griner, S.V. Badzakaya, L.N. Lietski, V.D. Punkarskaya and E.E. Lukan, Kristallofyrafl V.42, No.3, p.506 (1997). 3. S.V. Badzakaya, L.N. Lietski and P.P. Shafirany, In Abstracts of European Conference on Liquid Crystals. (Zakopane, Poland, 1997), p.122.

L4.40
Abstract Withdrawn.

L4.41
Abstract Withdrawn.

L4.42
NANOPARTICULAR SURFACES FOR CONTROLLED SELF-ASSEMBLY OF 1 D MOLECULAR NANOSTRUCTURES.
Federico Rosso*, Y. Naitoh, M. Schumack, E. Lepesgaard, I. Steengard, and P. Benshemcher, Physian Department and L-NANO, University of Aarhus, DENMARK, P. Jiang, A. Gourdon, and C. Jouciin, CESB/CNRS, Tours, FRANCE. *Present Address: INRS-EMT, Univ. du Quebec, Vertanes (QC) CANADA.
Organic molecular building blocks into a suitable architecture at the nanoscale is appealing for the development of future integrated nanoelectronics [1]. We used a large organic molecule called Lander [2] (C90H198), and investigated its electronic states at room temperature (RT) by Scanning Tunneling Microscopy (STM) and its Self-Assembly on Cu[110] by Scanning Tunneling Microscopy (STM). In recent work, the Lander was observed to act as a nanoscale mold, reshaping portions of step edges into characteristic nanostructures [2]. The Lander has a central polyaromatic molecular wire, and four spacer legs [3],[6]-ter-butylnaphthylene for isolation from the substrate. The four legs are imaged as four lobes with three different conformations by STM, two rhomboidal (chiral) shapes that are mirror symmetric to each other, and one rectangular shape. In order to create a suitable template for controlled molecular adsorption, the clean Cu[110] surface was exposed to oxygen to form the oxygen-induced [2,3] reconstruction. By dosing a proper amount of Oxygen at 350°C we can make Cu row domains along the [011] direction with 2-3 nm width between 2-3 domains. When Lander molecules are deposited on this template, they preferentially attach to bare Cu regions. By tuning molecular coverage in a controlled manner we obtain 1D molecular nanostructures. This type of directed self-assembly opens new possibilities for ordering organic molecules on surfaces. In a second set of experiments, spectra from isolated Lander molecules on Cu[110] terrace reveal two broad peaks observed at 0.5 V and 4.0 V. These can be tentatively associated with the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) states of the molecule at RT. References. [1] C. Jouciin, J.K. Ganorsoy and A. Aviram, Nature 418, 541 (2002). [2] F. Rosso et al., Organic molecules acting as templates on Metal Surfaces, Science 296, 338 (2002).

L4.43
Abstract Withdrawn.

L4.44
TRICYCLILIMINES CONNECTED VIA PHENYLENEEVPYLENE SUBUNITS. Hannes Denzer and Oleg Sosnovsky, Johannes Gutenberg University Mainz, Inst. of Organic Chemistry, Mainz, GERMANY.
The well-known hole transport properties of triarylhydrazines can be combined with the strong luminescence of stilbene chromophores. We present the synthesis of well soluble oligo(phenylevinylene)s with conjugation lengths of 2 to 6 styryl units, terminated by different
arylamines. The syntheses were performed via PO-activated dehalogenations and via PO-catalyzed allyl-N-coupling reactions. The fluorescence properties are primarily depending on the central stilbene segment. Cyclic volumetry reveals that the oxidation potential is nearly independent from the conjugated system, whereas the reduction is controlled by the stilbene segment.

**L4.45**

**THE SYNTHESIS, CONDENSATION, AND LUMINESCENCE OF OLIGOPHENYLE=NITRILE WITH ALKOXY SI-LANE END GROUPS**


Due to their strong fluorescence, stilbene oligomers are one of the preferred classes of luminescent organic materials for electrooptical applications. The good solubility of alkoxysubstituted OPVs is advantageous for the processing, but limits the fabrication of high-quality devices. Additionally, the stability of amorphous films is only poor. The concept to use the PMMA-OPV-PMA systems to form PO-catalyzed allyl-N-coupling reactions with terminal alkoxysilane moieties, to allow cross-linking via hydrolysis and formation of siloxane networks. The oxazoles are rigidly connected to the chromophores via Heck reaction or cross-methadition. Hydrolysis and condensation yields siloxane oligomers with pendant OPVs, thus greatly improving the film forming capability of these well-defined chromophores. The connection to cyclosiloxanes or silicone networks has a distinct influence on the electronic spectra of the OPVs in the solid film. Additionally, conjugated systems with high electron affinity like 2,5-dihydro-1.3.4-oxadiazole are functionalised with alkoxysilanes. These compounds are interesting for the preparation of inorganic-organic hybrid materials with luminescent units.

**L4.46**

**IN SITU DEVELOPMENT AND STUDY OF CONDUCTIVE POLYMER ELECTRODE FILMS ON PVDF SUBSTRATES FOR ELECTRO-AcouSTIC APPLICATION IN COCHLEAR IMPLANT.**

Arpitha Devi and Rodney Rosenme, Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH.

Sensorineural hearing loss (profound deafness) is a result of the inability of the transduction structures in the cochlea (organ of Corti) to convert the mechanical displacement of the basilar membrane to neural signals. A class of devices known as Cochlear Implants can significantly enhance the hearing ability in these patients. Fundamentally different from existing cochlear implant technology are the piezoelectric based devices we are developing which are totally implantable. The unit is completely self-contained, designed to work without any signal amplifiers or transmission elements, greatly simplifying the stimulation process, and enhancing the cosmetic appearance of the patient. These devices utilize the bending piezoelectric effect, which has been designed and consists of several elements of piezoelectric polymer film with conductive polymer electrode, embedded in a flexible and dielectric coated substrate. The incoming electrical energy (Pressure waves) into the cochlea generates electrical charge by virtue of the piezoelectric effect of the film. The generated charge is fed to electrical connections evaporated on the substrate and is used to stimulate surviving nerve fibers in the cochlea. In this concept, the amount of mechanical energy transferred to the cochlea is limited by size constraints and conducting liquid medium, the advantage of polymers over ceramics and metals, their flexibility, low acoustic impedance, and high sensitivity. However, in order to utilize these useful properties, the electrode materials are an important issue, since the conventionally used metal electrodes, have high acoustic impedance and also impose mechanical damping on the soft polymer which can significantly reduce the electromechanical efficiency of the transducer. Due to its flexibility, strong coherent interfaces, and significantly improved acoustic transparency, such an all-polymer electrode system is compared to metal-polymer system of similar design and also compared to the current technology.

**L4.47**

**THE CREATION OF A HYBRID PROTEIN/CONDUCTIVE POLYMER THERMOSENSOR.**

Lawrence L. Bray, Rajesh R. Naik, Markey O. Stone, Materials and Manufacturing Directorate, US Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

The use of thermal sensors and imaging devices has become so widespread that numerous applications ranging from military sensory to firefighting equipment rely heavily upon this technology. There is a desire, however, to improve the sensitivity of uncooled sensors while retaining the simplicity of their fabrication. Our research takes a biomimetic approach through the incorporation of thermosensitive proteins to enhance the properties of the infrared sensing device. By integrating these proteins into a matrix of poly(vinyl alcohol) doped with conductive polymer and phospholipids, we are able to achieve simple and reliable thermally sensitive chip can be fabricated. Here we describe our work in optimizing the polymer matrix formulation to maintain the thermal sensitivity of the chip while also controlling chip-to-chip uniformity and reducing external environmental effects. By tightly regulating the carbon black dispersion and through the application of a thin and transparent overcoat, uniform sensors can be fabricated with enhanced sensitivity and improved stability.

**L4.48**

**FIELD EFFECT CONDUCTANCE OF REGIOELECTRICAL POLY[3-HETHYLPHIOPHENE] NANOFIBERS.**

Jeffrey A. Merz and C. Daniel Frisbie, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

We are examining the electrical conductivity of nanofibers of regioelectrical poly(3-hexylphosphene) (RHPHNTI) as a part of a program to elucidate the role of microstructure on electrical transport in conducting polymer films. Nanofibers of RHPHNTI can be prepared by casting from dibutyl solutions of xylene or cyclohexanone. Analysis of the nanofibers by atomic force microscopy reveals fiber lengths of 5-10 µm, heights of 30-40 nm, and a random texture. Crystallinity and ordering within the nanofibers are determined by transmission electron microscopy (TEM) experiments. The electrical characterization setup consists of four electrodes and a capacitively coupled gate electrode. The four electrode setup is used to eliminate the effect of contacts on the measurements. Conductance measurements have yielded hole mobilities as high as 0.06 cm²/Vs and on/off ratios > 10⁵. Temperature studies reveal activation energies ranging from 60-115 meV depending on the substrate. Threshold voltage is found to increase in magnitude with decreasing temperature. The surface chemistry of the substrate affects the electrical properties of the nanofibers similar to thin films of RHPHNTI. Nanofibers were characterized on silicon dioxide and hexamethyldisilazane (HMD) treated silicon dioxide, alumina, and phosphonic acid treated alumina substrates. Probing transport in discrete conductance structures promised methods to address the role of microstructure in thin films. In particular, conductance measurements on RHPHNTI nanofibers allow separation of the effects on transport of the polymer-dielectric interface versus the semiconducting character of the films. ² J.J. Han, J. Moultou, and P. Smith, Journal of Polymer Science Part B: Polymer Physics 31, 735 (1993).

**L4.49**

**NANocrystalline SEMiconductor LEDs WITH SIMPLE STRUCTURE AND HIGH EFFICIENCY.**

Dietrich Bertram, Volker Wellner, Philips Research Laboratories, Aachen, GERMANY, Dimitri Tzahno, Horst Weiler, University of Hamburg, Hamburg, GERMANY.

Nanocrystalline semiconductor particles exhibit a size dependent band gap emission, due to size quantization effects. These particles are derived from solution chemistry and can be made monodisperse under the right synthesis conditions. Compared to organic materials, the inorganic nanoparticles show much higher stability against oxidation and degradation, which makes them an interesting candidate for LED and Ds based on semiconductor nanoparticles typically included low stability organic materials to provide charge injection. The talk will present a new class of nanoparticle LEDs, made without sensitive organic material. These LEDs show high efficiency throughout the red to green part of the visible spectrum and improved stability under ambient conditions without excessive encapsulation. Using high quality monosilicon suspensions, high color purity is achieved for the emission which gives the road to cheap, high quality displays based on inorganic semiconductor nanoparticles.

**SESSION L5: SPECTROSCOPY AND DEVICES**

Chair: George Mallinis

Wednesday Morning, April 23, 2018
Salon 1-3 (Marriott)

8:30 AM • L5.1

**CHARGE RECOMBINATION AND TRANSPORT STUDIES OF POLYMER/FULLERENE BLENDS AND PHOTOVOLTAIC DEVICES.**

A.P. Nagpure, S. V. Tenkar, S. R. Nakale, S. Cook, Y. Kim, J. Nelson, D.C. Bradley, L.B. Lajewski, Departments of Chemistry and Physics, Imperial College, London, UNITED KINGDOM; C. Winder, N.S. Sarrifi, Physical Chemistry, Johannes Kepler University, Linz, AUSTRIA; C. Baebe, Siemens AG, Erlangen, GERMANY.

Organic bulk heterojunctions are currently attracting attention for low cost plastic photoactive cells. Devices based on conjugated polymer / methanofullerene blended (MMD-PPV / PCBM) have been reported with energy conversion efficiencies of up to 2.5% [2]. A key issue in the development of such devices is the blending of the electron and hole transport materials on the nanometer scale. This
blending is essential to ensure efficient charge separation, with exciton diffusion lengths in such molecular materials being of the order of 10 nm. However, blending is that the carboxylic acid and carboxylate anions may not be well separated, resulting in recombination losses being a key factor limiting device performance. In this paper, we will address the kinetic competition between charge recombination and charge collection in polymer/fullerene nanocomposite films. These dynamics are studied by nanosecond to millisecond transient absorption spectroscopy and by time of flight studies of charge transport. Results will be presented for a range of polymer/fullerene systems as a function of temperature and temperature sweeping conditions (white light illumination, bias voltage etc.) [3-5].


9:00 AM L5.2

VOLTAGE-INDUCED INFRARED SPECTRA FROM FIELD-EFFECT TRANSISTORS FABRICATED WITH REGioregULAR POLY(3-ALKYLTHIOPHENE)8 Yuki Fukuraku, Hiroki Takano, Jun Yamamoto, Waseda Univ., Dept. of Chemistry, Tokyo, JAPAN.

We will demonstrate the usefulness of a combined use of infrared reflection-absorption spectroscopy and the FT-IR difference-spectrum method to study the charge carriers injected into the polymer layer in polymer field-effect transistors (FETs). We have fabricated FETs with regioregular poly(3-alkylthiophene) [alkyl: hexyl, octyl, and dodecyl]. Finger-shaped source and drain electrodes have been made. Each device measures about 0.36 mm by 0.18 mm with a channel length ca. 80 mm. A single reflection ATR accessory (Specac Golden Gate) has been used for infrared measurements. The upper plate of the accessory has been replaced by a home-made sample stage of a FET. Infrared light from an FT-IR spectrophotometer (Digilab FTS7000) is incident on the side of the finger-shaped source and drain electrodes with an incident angle of 45 degree. A half of the incident light can pass through the polymer layer. Voltage-induced infrared absorption spectra were measured by this method. We have observed a voltage-induced infrared spectrum from an FET based on regioregular poly(3-hexylthiophene) between the -10 V and the 45 V voltages applied to the gate electrode with respect to the source and drain electrodes. Positively observed bands are due to the species generated by the application of the bias of -10 V. The measured capacitance-voltage relation of the FET indicates that the positive carriers are induced in the polymer layer when a minus bias is applied to the gate electrode. The observed infrared spectrum is quite similar to that of a poly(3-hexylthiophene) film doped with ferric chloride. Thus, the observed infrared bands can be attributed to positive carriers (polaron) injected into the polymer layer by field effect in the positive direction of the gate bias. We will discuss the voltage-dependent shift of the peak position of the infrared spectra and the effect of the alkylic side chain on field-effect-induced infrared absorption.

9:15 AM L5.3

PHOTOLUMINESCENCE QUENCHING IN DOPED Alq3 ORGANIC LIGHT EMITTING DIODES. Terri Haskins, Arabinda Chowdhury, Ralph Young, and Lens Rothberg, Department of Chemistry, University of Rochester, Rochester, NY, Jerome Lenthart, Eastman Kodak Company, Rochester, NY.

Electroluminescent organic materials have recently made their way into display technology. There is considerable research underway to improve these materials to expand their utility. Alq3 [tris(8-quinolinoato)aluminum] is widely used in organic light emitting diodes (OLEDs) due to its excellent properties as a host for luminous dopants. Typically, the light output from an organic device is proportional to the injection current. However, in some important cases [1], the luminescence efficiency decreases with increasing current density. The resulting inefficient would make engineering a full panel organic display difficult. We report spectroscopic studies of the mechanism responsible for the decreased efficiency. We use in-situ Charge Modulation Spectroscopy (CMS) in both unipolar model devices of the structure (Alq3:IrPH3):Alq3 - insulator - cathode and bipolar transport devices which have an insulator layer. The dopant is the iridium dimer {Ir(tetramethyl-2,3-butadiene)Ir}(2) (IrPH3). The Alq3 is used as the host material and the photoluminescence quenching. In our studies we have observed the spectral signature of Alq3 cations (DCBT+) and Alq3 dianions (DCBT2-), evaluated the density of DCBT+ formed in the devices, and correlated its temporal behavior with the Alq3oluminescence. In our studies we have observed the optical properties of DCBT+ and DCBT2- formed in the devices, and correlated its temporal behavior with the Alq3oluminescence. This work is supported by the US Department of Energy, National Science Foundation, and the National Aeronautics and Space Administration.

10:30 AM L5.5

EXCITON CONFINEMENT AT POLYMER-POLYMER HETEROJUNCTIONS IN LEDS. Arne C. Mortensen, Anoop S. Dooot, Judson King, Conny Silva, and Richard H. Friend, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

Electro-hole-capture in LEDs can be arranged to take place at the heterojunctions formed between electron-transporting and hole-transporting semiconducting polymers. We find that the exciton formed by this process can be trapped at the heterojunction (exciplex), and that photon emission can occur either directly from this state or from the bandgap state if thermal excitation allows diffusion away from the heterojunction.

11:00 AM L5.6

CHARGE CARRIER GENERATION IN A CONJUGATED POLYMER STUDIED VIA SUB-20 FS PUMP-PUSH-PROBE EXPERIMENTS. Christoph Gadermaier, Emil J. W. List, Christian Doppler Laboratory for Advanced Functional Materials, Graz, AUSTRIA, Ugo Righini, Marco Versaci, Christian Mazor, Dipartimento di Fisica, Politecnico di Milano, ITALY, Ulrich Scherf, Mikromolekulare Chemie, Bergische Universitat, Wuppertal, GERMANY.

Ultrafast transient differential transmission (pump-probe) spectroscopy is a powerful tool to study the kinetics of dynamics of excited state processes. For a large variety of conjugated polymers pump-probe experiments have been performed by the delayed dynamics of singlet and triplet excitons as well as charge carriers. Charge carriers are essential in the electronic and optoelectronic properties one wants to exploit in the numerous upcoming applications of these materials. However, there is yet no comprehensive picture of the mechanisms that lead to their generation. Information about the charge carrier generation mechanisms can be obtained by monitoring their efficiency. We achieve such modulation via a modification of the pump-probe technology, which we call pump-push-probe. The first excited state Si is reexcited via a pump pulse towards a higher lying state Sn. The broadband probe reveals the dynamics of the relaxation of the excited state Sn as well as the kinetics of the states created from Sn. We find a number of simultaneously generated states (SE) and photoinduced absorption (PA) from the Si state as well as an increase of PA from the carriers. Hence the push pulse leads to an enhanced charge generation from a higher lying excited state Sn, which diminishes the SI population. The efficiency of this additional charge generation decreases rapidly with increasing pump-push delay, with a temporal behavior that hints towards both exciton energy migration and vibrational relaxation as the driving forces of the enhanced charge generation efficiency. The sub-20 fs pulse and probe durations allow the time-resolution of the ultrafast relaxation of the Sn state and enables us to untangle the contributions of the two mechanisms.

11:15 AM L5.7

THE EFFECT OF DOPING ON THE ENERGY DISTRIBUTION OF LOCALIZED STATES AND CARRIER TRANSPORT IN DISORDERED ORGANIC CONDUCTORS. Vladimir Archipov and Paul Heremans, IMEC, Leuven, BELGIUM; Eugenia Emelchenkov and Guy Adriaenssen, Semicond. Physics Lab., Univ. of Leuven,
BELGIUM. Heinz Bl"{a}sker, Inst. of Physical, Nuclear, and Macromolecular Chem., Philips Univ. of Marburg, GERMANY.

Charge carrier hopping within a positionally random and energetically disordered system of localized states was shown to be an adequate model for the description of both equilibrium and non-equilibrium conductivity in disordered organic semiconductors [1]. In a positionally random system, the energy disorder is to a large extent caused by Van der Waals and dipole-dipole interactions within a positionally and orientationally random system of molecules [2].

Hopping, i.e., the transition of a charge carrier from one site to another, is in addition to the distribution of dopant ions that will Coulombically interact with carriers localized in intrinsic hopping sites. This interaction further increases the energy disorder. This effect is especially important in view of a small value of the dielectric constant and, concomitantly, long range of the Coulomb interaction typical for molecular semiconductors. Increasing energy disorder with increasing dopant concentration will lead to broadening of the apparent density-of-states (DOS) distribution. Therefore, doping of a disordered organic semiconductor, on the other hand, increases the concentration of charge carriers and lifts up the Fermi level but, on the other hand, broadens the DOS distribution. While the former effect facilitates conductivity, the latter strongly suppresses the carrier hopping rate. The latter effect can dominate as some dopant concentrations such that doping appears to be even counterproductive as far as the carrier mobility is concerned. In the present work, an analytic model describing the DOS distribution and the carrier hopping mobility in doped organic materials is formulated. It is shown that doping shifts some intrinsic hopping sites to the deeper tail of the DOS distribution and, thus, creates additional deep traps for charge carriers. This leads to a decrease in the existing mobility and raises the dopant concentrations. At higher doping levels the filling of deep states takes over leading to steeply increasing mobility at high dopant concentrations.


11:30 AM L5.5
SURFACE-EMITTING DISTRIBUTED FEEDBACK LASERS BASED ON SEMICONDUCTING POLYFLUORENES.

George Hiltosis and Ruidong Xing, Ultrafast Photonics Collaboration, Experimetal Solid State Group and Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College, London, UNITED KINGDOM; Graham A. Turnbull, For D.W. Samuel, Organic Semiconductor Centre and Ultrafast Photonics Collaboration, School of Physics and Astronomy, University of St. Andrews, St. Andrews, UNITED KINGDOM; Piers Andrew, William L. Barnes, Thin Film Photonics Group, School of Physics, University of Exeter, Exeter, UNITED KINGDOM; Donal D.C. Bradley, Ultrafast Photonics Collaboration, Experimental Solid State Group and Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College, London, UNITED KINGDOM.

In recent years, semiconducting polymers have attracted considerable interest as novel gain media for devices such as lasers and optical amplifiers. In particular, an important target is the future realization of an electrically pumped solid-state polymer laser diode. Fluorine-containing polymer fluorophores are a particularly attractive class of semiconducting polymers for such applications because they show efficient charge transport properties, have low stimulated emission thresholds and are the only family of conjugated polymers that emit visible light over a wide visible spectrum. Hence, they offer great potential for the fabrication of low cost, compact, highly tunable solid-state lasers. Here, we report on the fabrication of optically pumped (355 nm pulses from a Q-switched Nd:YVO4 microchip laser) polymer distributed feedback (DFB) lasers utilizing two blue-emitting fluorophores as the gain medium. The lasers were made by deposition of thin layers of polymer on top of gratings that were etched into fused silica substrates. Distributed feedback was realized through the Bragg-scattering induced by the substrate corrugations. We demonstrate laser action in devices based on both polymers. The lasers operate in the blue, one at 455nm and the other at 465nm, and exhibit low threshold energies [3.3 nJ per pulse]. The wavelength, threshold energy, output power, and efficiency of the lasers are investigated. The shape and divergence of the output beams are measured and correlated with the internal lasing modes and the feedback mechanism present in the structures. Additional experiments were performed to investigate the effect of the grating structures on the polymer light emission. We show that the presence of the grating greatly modifies the emission characteristics of the polymer. This is observed through a photonic stop band around the Bragg wavelength. Lasing occurs at the band edge, as expected for an index-coupled DFB laser.

11:45 AM L5.9

We have determined the exciton binding energy Eb in stretched oriented films of poly(phenylene vinylene) to be about 80 meV, which is significantly smaller than that deduced by other researchers on the basis of measurements on disordered polymer films. It has been claimed that this magnitude of Eb is in contradiction with the operating fields in polymer-based light emitting diodes (OLEDs), which typically exceeds 105 V/cm. The claim has been that if indeed Eb were so small, this operating field would have dissipated the excitons due to the strong emission of the external field, thereby diminishing the light emission. In recent experiments we have clarified this issue and found that in contrast oriented PPV disordered polymer films generally exhibit higher threshold field for exciton quenching. We will present variety of data generated by photoco nductor action spectra as well as nanosecond excitation experiments and a discussion of the reasons for the higher Eb in disordered polymer films. The second topic of recent interest is related to the carrier recombination dynamics in conjugated polymers. Using transient photoco nductor experiments, we have recently found bi-molecular carrier recombination mechanisms operating in measurements that utilize very low light intensities. This is the first time such a mechanism has been found in a at time range of 1 ns in any polymer we have investigated. We will present the experimental, data analysis, and a discussion on the implications of these findings.

SESSION L6 TRANSISTORS
Chair: C. Daniel Frabie Wednesday Afternoon, April 23, 2003 Salon 1-3 (Marriott)


Polyfluorenes are a class of polyaromatic macromolecules that are characterized by an alternating backbone structure that consists of a 9,9-bis(alkylfluorene unit in combination with another aromatic group. The nature of the aromatic unit plays a key role in the electronic mobility, environment stability, and performance properties. For example, polyfluorenes which combine chromophoric and charge transporting aromatic units have received a great deal of attention over the last several years as the emissive layer in polymeric light emitting diodes [LUMAGION® Light-Emitting Polymers (LEPs)]. More recently, polyfluorenes have also been designed to perform as the organic semiconducting layer in polymeric field effect transistors (PFETs). This effort has led to a class of polymeric semiconductor materials with an excellent combination of charge mobility, environmental stability, and performance properties. One such polymer is the polyfluorene-based polymer on an alternating backbone of 9,9-bis(diocfluorenyl and 2,2′-bithiophene units. This material has been shown to have charge mobilities as high as 0.02 cm2/Vs with current on/off ratios of up to 106. The polyfluorene-bithiophene) is more resistant to doping by atmospheric oxygen than other polymeric semiconductors such as poly(3-hexylthiophene). Inks based on solutions of poly(fluorene-bithiophene) in xylene, mesitylene, and other solvents have also been prepared. The paper will focus on the recent advances in the synthesis, fabrication, and electrical characterization of polyfluorene-bithiophene. *Trademark of The Dow Chemical Company

1:45 PM L6.2 SOURCE/DRAIN CONTACTS IN ORGANIC POLYMER THIN FILM TRANSISTORS. Sondra Martin, Michael Hamilton, and Jennifer Kaslak, University of Michigan, Dept of Electrical Engineering and Computer Science, Ann Arbor, MI.

Although the electrical performances of most organic polymer thin-film transistors (OP-FTTs) were often limited by the polymer low conductivity, the source and drain contacts play a predominant role in the device operation. The devices used for our study of the role of the S/D contacts are gate-planarized thin-film transistors with a coplanar structure, i.e., source and drain contacts deposited before the organic polymer film. The devices use benzocyclobutene as gate planarization material, amorphous silicon nitride as gate insulator and ITO source and drain electrodes. The organic semiconductor in the transistor is a solution-based F8T2 [poly(9,9-dioctylfluorene-co-bithiophene). Typical performances of our devices are field-effect mobility about 6 x10−2 cm2/V·s, threshold voltage about 75 V, subthreshold swing about 1.5 V/dec and ON/OFF current ratio about 105. for
W/L = 116 µm/56 µm and gate insulator capacitance of 7.3 x 10⁻¹¹ F/cm². We observed, as expected, a significant channel length dependent effect. The TFT field-effect mobility, resulting from the non-negligible effect of the source and drain contacts. The role of the S/D contacts was initially investigated using a method developed for amorphous semiconductor thin-film transistors: the transverse line method. This method assumes channel layers of the S/D contact and access regions and models them by gate voltage dependent series resistance. High values of S/D series resistance, typically in the 10⁻¹¹ range for a (negative) gate voltage about 1 V above threshold, have already been described accurately the channel length dependence of our OP-TFT field-effect mobility. The OP-TFT intrinsic field-effect mobility and threshold voltage were also extracted. We have also observed the OP-TFT ID-VDS characteristics in the ON-state and with floating contacts. All transistors were examined with respect to the S/D contact current-voltage characteristics and we will present the results concerning ohmic and non-ohmic behaviors were observed. Results will be compared to typical data obtained on Si:H TFTs.

**2:00 PM L 6.3**
**NEW n-CHANNEL ORGANIC SEMICONDUCTORS FOR THIN FILM TRANSISTORS**
Reid J. Chesterfield and C. Daniel Frisbie, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN; Ted M. Pepeka, Kent R. Mann, and Larry L. Miller, Univ of Minnesota, Dept of Chemistry, Minneapolis, MN.

Organic semiconductors that function as p- or n-channel conductors in thin film transistors (TFTs) are an important class of materials because of the potential to realize large area, low cost, flexible, large-area TFT arrays. There are many examples of p-channel TFT conduktor, but reports of n-channel conductors have been rare. We are examining two families of materials based on quinoxaline/terthiophene or dibenzothiophene diimides for application as n-channel organic semiconductors in TFTs. The redox properties, crystal packing, and thin film microstructure of these materials can be tuned by varying the side chains. These compounds illustrate the elegance of using organic chemistry techniques to design semiconductors. Compounds in both the terthiophene and diimide family have shown n-channel room-temperature mobility as high as 0.2 cm²/Vs in vacuum evaporated TFTs. Key device parameters such as On/Off ratio, threshold voltage, and sub-threshold slope will also be reported. Trapping and activated transport have been investigated as a function of temperature and ambient environment. TFT performance has been measured in both top-contact and bottom-contact devices, surface chemistry of the dielectric, and contact metallurgy. There is a nice correlation between the solid state TFT behavior of these compounds and their solution redox properties, which offers a possible design criterion for TFTs.

**2:15 PM L 6.4**
**Abstract Withdrawn.**

**2:30 PM L 6.5**
**HIGH PERFORMANCE ORGANIC THIN FILM TRANSISTORS**
Tommy W. Kelley, Dawn V. Moyes, Paul F. Braude, Terry P. Smith, Thomas F. Kyser, and Robert M. Wiesler, Center for Magnetic Recording Research, Paul, MN; C. Daniel Frisbie and Paul Pesonen, University of Minnesota, Chemical Engineering and Materials Science, Minneapolis, MN.

We report here methods of surface modification and device construction which consistently result in high-blank pentacene-based TFTs and integrated circuits with mobilities as high as 1.7 cm²/Vs. Surface modifications include self-assembled monolayers (SAMs) and polymeric ultrathin films presenting a passivated interface on which the semiconductor can grow. High performance TFTs have been fabricated on a variety of dielectric materials, both organic and inorganic, and are currently being implemented in manufacturable constructions. Furthermore, the TFT field-effect mobility, resulting from the substituted pentacene materials and for a variety of organic semiconductors. Further experimental and theoretical analyses are underway to explain the elevated mobility in our samples, and efforts have been made to confirm these results through collaboration with the University of Minnesota.

**3:30 PM L 16.6**
**POLYCRYSTALLINE PENTACENE THIN FILM TRANSISTORS: MORPHOLOGY, STRUCTURAL PROPERTIES AND ELECTRONIC TRANSPORT**
Dieter Kippe, Palo Alto Research Center, Electronic Materials Laboratory, CA.

The structural and transport properties of evaporated pentacene organic thin film transistors (OTFT) are reported, showing the influence of the deposition conditions with different organic dielectrics. Dielectrics compatible with large area fabrication were explored to facilitate low cost electronics on glass or flexible plastic substrates. X-ray diffraction and atomic force microscopy show a clear correlation between the morphology and the structure of the highly polycrystalline films, for all dielectrics investigated. The roughness of the dielectric has a distinct influence on the morphology and the structural properties. Thus, on-chemically roughened oxides are in general highly ordered independent of the deposition conditions. The ordered films exhibit thin film and a bulk phase volume fraction increases with the deposition temperature and the film thickness. Careful control of the deposition conditions gives virtually identical films on thermal oxide and PECDV silicon nitride dielectrics. The electronic properties of inverted TFTs show that the TFT mobility is correlated with the morphology and structure of the films. The TFTs exhibit very similar mobilities of 0.2 cm²/Vs and on/off ratios of 10⁴ on thermal oxide and PECDV silicon nitride. The impact of the dielectric on the device parameters of mobility, threshold voltage and sub-threshold voltage slope is discussed. Temperature dependent measurements of the mobility were performed to study the influence of traps on the electronic transport and to gain understanding of the transport mechanisms of thermally evaporated pentacene TFTs.

**4:00 PM L 6.7**
**SYNTHESIS AND APPLICATION OF A PHOTOREACTIVE ORGANIC SEMICONDUCTOR IN THIN FILM TRANSISTORS**
A. Alers, C.D. Dimitrakopoulos, T.O. Graham, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY.

Organic semiconductors have received increasing attention during the past two decades due to potential low cost applications in electronic devices like OTFTs and OLEDs. However, the use of these materials is limited by the photochemical stability of the active layers. This have been addressed by using photoinitiator systems, which allow for the formation of photochemical bonds at specific locations. The use of photoreactive organic semiconductors in electronic devices, patterning by photolithographic methods, and fabrication of thin film transistors have been investigated. The results of these investigations have been discussed.

**4:15 PM L 6.8**
**PENTACENE TFTS WITH SUBMICRON CHANNEL LENGTHS**
A.G. Sizikov and P.R. Kagan, IBM Research, T.J. Watson Research Center, Yorktown Heights, NY.

We have investigated the characteristics of pentacene field effect devices fabricated with sub-micron channel length. The devices were fabricated under UV conditions that minimize the effect of ambient atmosphere before evaporation and on pentacene evaporation. The pentacene was evaporated to form the semiconducting channel of TFTs deposited onto thermally oxidized, highly doped Si wafers, which serve as the gate dielectric and electrode. The pentacene was patterned with a photolithography process, defining channel lengths ranging from 100 nm to 500 nm, to prepare bottom electrode geometry TFTs. Substrates cleaned by in situ annealing at 200 °C, produced polycrystalline pentacene thin films with grain sizes of 22 nm, larger than the electrode separations. The mobility and on/off ratios decreased with increasing channel length. TFTs with channel lengths of 450 nm have saturation mobilities as high as 0.1 cm²/Vs, a threshold voltage near zero, and current modulation of 10⁴. The influence of electrode material and surface derivatization with self-assembled monolayers and the dependence of channel length on transistor characteristics will be discussed.

**4:30 PM L 6.9**
**INTRA-GRAIN TOP CONTACT ORGANIC THIN FILM TRANSISTORS**
Christian Verklek, Stijn Noppe, Dimitri Janssen, Boudewijn Datta, Paul Verboeket van Denburg, Philips Research, Netherland, Leuven, BEELAND.

Transistors with channel lengths comparable to the diameter of a grain are a useful tool to study the charge-transport properties of organic polythiophene thin films, i.e. the intrinsic charge-transport inside one single-crystalline grain and the grain boundaries. Moreover, these transistors enable to probe single-channel device physics, which can be of importance for future applications. Submicron channel lengths normally require photolithographically defined source and drain contacts, defined before growth of the small molecule channel, resulting in so-called bottom-contact devices. Unfortunately, such bottom contacts influence the growth of the thin film, have limited compatibility with surface cleaning and treatments prior to growth, and possess a less favorable charge-injection geometry. Therefore, we have microcontacted a shadow mask which enables the deposition of contacts on top of the organic thin film, with channel lengths down to 1 µm. This
mask is successfully applied to make organic small-molecule thin-film transistors with small molecules such as pentacene. Both fabrication of the thin-film transistors and interpretation of the first transistor characteristics will be discussed.

4:45 PM L6.10
TRANSPORT MECHANISMS IN POLY(3-HETHYLTHIPHENOLE)
TRANSISTORS. D. Notokon and B. Hamadani, Rice University, Dept. of Physics and Astronomy, Houston, TX.

We observe a previously unreported transport mechanism in high quality poly(3-ethylthiphene) field effect transistors (FETs) of fixed aspect ratio with channel lengths from 50 µm to 200 nm. Over a large range of applied voltages, the drain current is considered a space-charge limited Poole-Frenkel (PF) hopping from source to drain. The prefactor to the PF electric field term is very strongly modulated by gate voltage and temperature. We discuss a model for this mechanism, as well as a departure from thermally driven PF hopping below 30 K.

SESSION L7: POSTER SESSION
Chair: Seniority
Wednesday Evening, April 23, 2003
8:00 PM
Salon L7 (Marriott)
L7.1

There is a great deal of interest in developing new chemical and biological sensors for use in a wide range of new applications, including food safety, environmental monitoring, medical diagnostics, and defense. These new sensors should be small, easily portable, inexpensive, fast, and capable of detecting low concentrations of specific analytes with high sensitivity and high selectivity. Devices based on organic semiconductors have the potential to satisfy these criteria. Such devices can be easily and inexpensively fabricated on a variety of substrates, and the semiconducting molecules can be chemically synthesized or modified for specific applications. In the current work, we demonstrate the applicability of organic thin film transistors (OTFTs) to both gas sensors and biosensors. We report on the characteristics of OTFTs when operated in a variety of well-controlled gaseous environments, and we use poly(dimethyl siloxane) (PDMS) microfluidic channels to expose the active regions of our devices to aqueous environments.

L7.2
MOLECULAR DESIGN, SYNTHESIS AND LUMINESCENT PROPERTIES OF NOVEL EBIRUIM[III]-ENCAPSULATED DENDRITIC SUPERMOLECULES BASED ON PORPHYRINS. Jeo Won Ko, Yaok-Jong Sun, Hyo-Joo Ko, Dong-In Kim, Hong-Kyu Kim, Center for Smart Light-Harvesting Materials and Department of Polymer Science & Engineering, Hanyang University, Daejeon, KOREA.

Recently, erbium-doped fiber amplifiers (EDFA) are widely used in the field of superhigh speed optical telecommunications. However, the amplification gain of current EDFA is not enough for amplifying the optical signals in small-photon devices, while the amplification gain is not a problem for long distance of several tens of meters. It is due to the poor solubility of erbium[III] ions in conventional inorganic media, limiting to 180-1000 ppm for Er,Yb-doped concentration on silica optic fiber. If higher than the limiting concentration is to be employed, Er,Yb ion interaction between themselves would cause non-radiative process (namely, cooperative processes) to occur, hence reducing the amplification gain. To solve this solubility problem and improve the luminescent properties, erbium[III] ions could be encapsulated by organic ligands. The ligands have to be designed such that it provides enough coordination sites to form a stable complex. Also, it should be considered as a photon antenna for energy transfer process from ligands to erbium[III] ions for getting a higher amplification gain.

To maximize the optical amplification efficiency, we have investigated the design and synthesis of the erbium[III]-encapsulated dendritic supramolecular supramolecule based on porphyrins. Present dendritic supramolecules consisted of an erbium[III]-chelated naphthalene [22 complex, porphyrins, and new ary ether type porphyrins. Functionalized naphthalene [22 complexes were easily prepared by condensation of aryl monothioaldehyde and tri(2-chloroethyl)amine hydrochloride in the presence of base. The reaction was carried out by high dilution reaction concentration at reflux temperature, giving a moderate to good yield. Also, we synthesized the porphyrins bearing phenyl and bromophenyl substituents at the meso-position from the corresponding aldehyde and pyrrole for the coupling with naphthalene, and, the dye-sensitized lanthanide porphyrins have been synthesized by coupling of a functionalized naphthalene [22 with functionalized porphyrins containing new ary ether type porphyrins. In this presentation, the synthetic routes and their luminescent properties of novel erbium[III]-encapsulated dendritic supramolecules will be discussed.

L7.3
MOLECULAR DESIGN, SYNTHESIS AND CHARACTERIZATION OF EBIRUIM-CORED SUPRAMOLECULAR COMPLEXES BASED ON NEW ARYL ETHER DENDRITIC PORPHYRINS FOR ELECTROCHEMICAL AMPLIFICATION. Kyung-Im Lim, Young, Jeo Won, Hyeon Kim, Center for Smart Light-Harvesting Materials and Department of Polymer Science & Engineering, Hanyang University, Daejeon, KOREA.

To achieve the super high speed telecommunication systems, the development of integrated planar waveguide amplifiers is extremely essential. At present, erbium-doped silica amplifiers are widely used. The Er°° ion shows an intra fshell transition from its first excited state (2H11/2) to the ground state (2H9/2), which takes place at a wavelength of 1.54 µm, one of the standard telecommunication wavelengths. However, lanthanide ion (Ln°°) has the poor solubility in conventional inorganic/organic media. So, if higher doping concentration was introduced to get the higher optical gain, clustered Ln°° species can be formed. These lanthanide ion aggregates cause the reduction of luminescent property through the cooperative energy transfer process. To circumvent the solubility and enhancement of the luminescent properties, we have designed and studied the erbium-cored supramolecular complexes based on porphyrins. We synthesized 5,10,15,20-tetraphenyl-2,6-(4-methoxy carbonylphenyl) porphin by the acid-catalyzed condensation of diphenylmethane and aldehyde. And then, we introduced the organic acid in light emitting bind site with lanthanide metal by hydrolysis. And, we also prepared the Zn inserted porphyrin as previously reported method. The structure of porphyrin ligands was identified by FTIR, 1HNMR, UV-Vis absorption and PL spectroscopies. And then, we have attempted several different synthetic methods to prepare Encored supramolecular complexes based on porphyrins and develop new synthetic route using model routes. The synthesized complexes were characterized by the FTIR, 1CP, EA, TGA, visible and near IR emission spectrosopies. Also, we have synthesized the Er-chelated complexes based on new ary ether dendritic porphyrins to enhance the luminescent property by energy transfer process. In this presentation, we will discuss the synthesis and luminescent properties of the erbium-cored supramolecular complexes based on new ary ether porphyrins.

L7.4
SPECTROSCOPIC PHOTOVOLTAGE CHARACTERIZATION OF PPV THIN FILMS SUITABLE FOR PLED APPLICATIONS. Girija Sinshar Samal, A.K. Bhowmik, Y.N. Mohapatra, Materials Science Programme and Samuel Center for Display Technologies, Indian Institute of Technology, Kharagpur, INDIA.

Opto-electronic characterization of active polymer materials to monitor photonic changes and radiative process has been intensively investigated in view of applications in light emitting and photovoltaic devices. In this paper we compare absorption, emission and photovoltage spectra in order to correlate creation, radiative recombination and separation of charge carriers in PPV. PPV films were spin coated on ITO/glass substrates. Photovoltage experiments were carried out using both conventional single layer LED structure (ITO/PPV/Al), and capacitance structure consisting of ITO/Mica/PPV/ITO in which a thin sheet of mica is pressed against the sample using an ITO glass substrate. The capacitance structure is appropriate for modulated surface photovoltage measurements. The absorption spectra and photoluminescence spectra obtained are as standard for PPV prepared by vacuum deposition methods. The temperature photovoltage spectra show features, which both complement and supplement the absorption and emission spectra. The photovoltage spectra for both types of devices have sharp features and are consistent with the inherent photo-physical properties indicating that the features observed are primarily due to PPV material itself. The photovoltage spectrum shows peaks and valleys corresponding to both absorption and emission features. In addition, we observe two sharp peaks with a separation of 0.17 eV in the extended range of 2.5-2.7 eV (i.e. a clear featureless region). The shape of the peaks strongly suggests that the peaks are most probably associated with photoionization of either excited state excitation or a defect-polaron complexes giving rise to non-radiative centers. A study of temperature dependence of photovoltage in the range of 50K-300K shows that the photovoltage decreases non-linearly with decrease in temperature and saturates at low temperature. The results are discussed in terms of temperature dependence of mobility and absorption co-efficients, and possible models for photoinitiation of quantum defects.

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L7.5 SYNTHESIS OF A ZERO-BIREFRINGENCE OPTICAL POLYMER BY THE BIREFRINGENT CRYSTAL DOPANT METHOD
Himori Okaishi a, b, Masaki Mutuk b, Akihiro Tagaya b and Yasuo Kokoi a, b
a Keio Univ, Yokohama, JAPAN, b 1ST ERATO, Kawasaki, JAPAN.

Birefringence induced by the orientation of polymer main chains during an injection-molding or extrusion process restricts the application of optical polymers to optical devices that require preserving the anisotropic phase of the crystalline structure. We propose two methods, the "random copolymerization method" and the "anisotropic molecule dopant method" to prepare transparent zero-birefringence optical polymers. However, heat resistant polymers generally exhibit optical orientation birefringence, which has not been eliminated yet by the two methods.

In this report, we propose a novel method, the "birefringent crystal dopant method" to compensate the positive birefringence of optical polymers by having birefringent needle-like crystals dispersed in the polymer matrix. We selected crystalline SrCoO crystals which have negative birefringence. In this method, the polymer particles at the opposite orientation birefringence to that of SrCoO crystals were selected for this method and prepared by reaction of a suspension of Sr(OH)2 with carbon tetrachloride, with a particle length of 100-300 nm and an aspect ratio of 2:5. Poly (MMA-c copolymer films with a composition MMA/MBA = 58/42 wt.%) was synthesized with a thickness of approximately 40 μm. The SrCoO particles were homogeneously doped into the copolymer films and the polymer doped films were uniaxially drawn at 130 ℃ and 4 mm/min. The positive birefringence of the drawn copolymer films at a wavelength of 655 nm was compensated at the SrCoO particles concentration of 0.5 wt.%. Transmission of the SrCoO particles doped copolymer films was 98.8% at a wavelength of 400 nm and the glass transition temperature of the films was 118.7 ℃. These results confirmed that the synthesized zero-birefringent polymer films have the same transparency and heat resistance as the blank copolymer films.

Therefore, we confirmed that the birefringent crystal dopant method was one of the promising candidates for obtaining heat resistant zero-birefringent optical polymers.

L7.6 MULTIFUNCTIONAL PHOTOVOLTAIC AND ELECTRO-LUMINESCENT DEVICES USING A STARBURST AMINE AS AN ELECTRON DONOR AND HOLE-TRANSPORTING MATERIAL.
Z.I. Hong, Center of Super-Diamond and Advanced Films (COSADF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, P.R. CHINA; and Changshun Institute of Optics, Fine Mechanics and Physics, Changshun, P.R. CHINA; C.S. Lee and S.T. Lee, COSADF and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, P.R. CHINA; W.L. Li, Changshun Institute of Optics, Fine Mechanics and Physics, Changshun, P.R. CHINA; Y. Shrota, Department of Applied Chemistry, Osaka University, Osaka, JAPAN.

Photovoltaic (PV) devices sensitive to near-ultraviolet light, using 4,4′,4′′-tris(2-methylphenylphenylamino)triphenylamine (m-MTDATA) as an electron donor and tri-(8-hydroxyquinoline)aluminum (Alq3) as an electron acceptor, were fabricated. Both the bilayer and trilayer devices (containing a thin layer of m-MTDATA and Alq3) showed PV and electroluminescent (EL) properties, suggesting their potential use as multifunction devices. Introduction of a thin mixing layer (5 nm) of m-MTDATA and Alq3 between the two organic layers of the original m-MTDATA/Alq3 bilayer device improved both the PV performance and the exciplex emission. The relationship between exciplex emission and PV effect of devices based on m-MTDATA was established. According to our results, increasing contact between electron donors and acceptors was an efficient way to improve the PV performance of organic molecular devices. It is considered that strong exciplex emission in an EL device is a good indicator for efficient charge transfer at organic interface, which is a basic requirement for good PV performance.

L7.7 TOWARDS SOLID STATE POLYMER LASERS ACROSS THE VISIBLE SPECTRUM. George Heliotis, Rudong Xue, Donald C. Bradley, Ultrafast Photonics Collaboration, Experimental Solid State Group and Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College, London, UNITED KINGDOM.

Semiconducting (conjugated) polymers are now attracting considerable interest as a new material class for use in electronics and optoelectronics. Currently there is increasing interest in developing these materials for use in novel gain media in devices such as lasers and optical amplifiers. Fluorocarbon-based polymers (polyfluorocarbons) are a very attractive class of conjugated polymers for such applications, due to their high photoluminescence and electroluminescence efficiencies, low stimulated emission thresholds, high stability in air and good properties as host materials for other emitters. Here, we report a systematic investigation of the properties of a new class of semiconducting polymers to establish their suitability as gain media for laser applications. We demonstrate light amplification in the blue, cyan and red parts of the spectrum via ultrashort-lightning amplified spontaneous emission (ASE) measurements on planar semiconductor waveguides. The gain characteristics of the gain waveguides (linewidth, intensity, threshold energy and peak wavelength) are measured as a function of excitation wavelength and intensity, film thickness and film morphology. The results are presented. Optical gain measurements at the various wavelengths revealed that the waveguides exhibit high net gain and low loss coefficients, making these materials attractive for tunable solid-state lasers with wavelengths that span the entire visible spectrum.

L7.8 ATTACHED EMITTING TWO-DIMENSIONAL DISTRIBUTED FEEDBACK LASER BASED ON A NOVEL FLUORESCENT COPOLYMER. Rudong Xue and George Heliotis, Ultrafast Photonics Collaboration, Experimental Solid State Group and Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College, London, UNITED KINGDOM; Graham A. Turner, D. W. Samuel, Organic Semiconductor Centre and Ultrafast Photonics Collaboration, School of Physics and Astronomy, University of St. Andrews, St. Andrews, UNITED KINGDOM; Piers Andrew and William L. Barnes, Tim Film Photonics Group, School of Physics, University of Exeter, Exeter, UNITED KINGDOM; Donald D.C. Bradley, Ultrafast Photonics Collaboration, Experimental Solid State Group and Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College, London, UNITED KINGDOM.

Semiconducting (conjugated) polymers are attractive candidates as the gain media for solid-state lasers due to, among other things, their high photoluminescence efficiency and low ASE threshold. It is expected that high gain factors can be obtained in these materials. Gain waveguides have the advantage that they offer a more compact and robust design compared to bulk waveguides and laser cavity. Furthermore, compared with conventional inorganic semiconductors, organic semiconductors offer potential advantages with respect to ease of processing, low cost and flexibility. Recent reports of lasing action in conjugated polymers have stimulated great interest in the development of lasers that may eventually compete with inorganic semiconductor structures. Here, we report the fabrication of a two-dimensional distributed feedback (DFB) laser using a novel fluorescent copolymer as the gain medium. The laser was made by depositing a thin polymer layer on top of a suitably nanopatterned substrate. The substrate comprised two crossed gratings etched at right angles into a fused silica plate. This structure provides a better optimised photonic mode density confinement compared with a single grating structure, which leads to reductions in the lasing threshold and increases in the output efficiency. Laser action was demonstrated by pumping the device with a compact diode-pumped, frequency doubled Nd:YVO4 laser operating at 532 nm. Lasing occurs at 680 nm and is located on the edge of the photonic stop band induced by the two-dimensional microstructure. The laser had a threshold of 4 J/m2 per pulse, and the output characteristics of the laser are described in detail and the shape and divergence of the output beam are correlated with the two-dimensional feedback mechanism.

L7.9 SPONTANEOUS ORIENTATION OF ALG3 MOLECULE IN EVAPORATED FILM AND ITS VANISHMENT BY LIGHT IRRADIATION. Keiji Sugi, Hsiao Ishii, Yusu Kimura, Michio Niimi, Tokyo University, Institute of Electro-Communication Engineering, Sendai, JAPAN; Naoki Higashi, Yukio Ouchi, Nagoya University, Graduate School of Science, Nagoya, JAPAN; Eiisuke Ito, Riken, Frontier Research System, Wako, JAPAN; Kazumitsu Saki, Nagoya University, Research Center for Materials Science, Nagoya, JAPAN.

Recently we found that high and persistent spontaneous buildup of the surface potential (SP) upon vacuum deposition of tris(8-hydroxyquinoline)aluminum [Alq3] on a substrate under dark conditions [38 V for 500 nm thick Alq3 film]. Such giant potential is removed by visible-light irradiation. Alq3 molecule has a permanent dipole and its spontaneous orientation is suggested as an origin of such giant SP [1]. Such properties suggest that Alq3 molecule has an ferroelectricity, and can open the possible application to various organic devices such as ferroelectric gate for memory FET. In this study, we focus on the mechanism of the removal of giant SP by visible-light and its possible ferroelectricity. The ratio of the decrease of SP was proportional to the logarithm of light irradiation time [1]. Numerical simulation for the decrease of SP was performed on the basis of a simple model where an oriented molecule becomes disoriented upon the absorption of an incident photon. This model well reproduced the observed logarithmic relation, suggesting that not photovoltaic effect but a rotation of the molecule by photoabsorption is plausible as the origin of the removal of the SP. As the ferroelectricity, the measurement of DE hysteresis will be reported. The examination of the retention time of such giant SP by Kelvin

L7.10

3D DIELECTRIC SCREENING AND QUANTUM MECHANICAL COHESION IN CONJUGATED POLYMERS. P. F. Plasser, J-J. van der Horst, P.A. Bobbert, M. A. J. Michelis, Polymer Physics Group, Dept. of Applied Physics and Dutch Polymer Institute, Eindhoven University of Technology, THE NETHERLANDS.

In many theoretical studies, the electronic and optical properties of conjugated polymers are treated in a single-chain picture. Here, we study the effects of 3D dielectric screening of the Coulomb interaction and 3D quantum mechanical coherence on the electronic and optical excitations in conjugated polymers. We perform a fully ab-initio calculation of the bandstructure and the excitonic spectrum of crystalline polythiophene and polyphenylenevinylene, using the GW approximation to the self-energy and including excitonic effects by solving the electron-hole Bethe-Salpeter equation. This calculation includes all effects of 3D screening and quantum mechanical coherence. We compare our results with calculations on a single polythiophene chain (no 3D screening and no 3D coherence) and polymer chains embedded in a dielectric medium (3D screening, but no 3D coherence). The calculated excitonic spectrum for polymer chains embedded in a dielectric medium generally agrees best with available experimental data. The calculation for a single chain leads to an unacceptably large (\(>1 \text{ eV}\)) exciton binding energy, whereas the crystalline calculations lead to too small exciton binding energies and optical gaps. Our conclusion is that in most experimental samples, 3D dielectric screening plays an important role, but quantum mechanical coherence between neighboring chains is absent. The absence of coherence is probably caused by the disordered nature of many polymers.

L7.11

THE CRYSTAL STRUCTURE OF ANTHRACENE UP TO 220 K: A X-RAY DIFFRACTION STUDY. Martin Oehsleh, Georg Heimel, Roland Reel, Graz University of Technology, Graz, AUSTRIA; Kerstin Hummer, Peter Puschmich, Claudia Amendola-Drexl, University of Graz, Graz, AUSTRIA; and Atsuko Nakayama, Advanced Carbon Center, AIST, Tsukuba, JAPAN.

This study concentrates on the crystal structure of anthracene under high pressure. Pressure was applied using the diamond anvil cell technique. In order to guarantee hydrostatic conditions within the sample chamber helium was used as pressure transmitting medium for the highest pressure region. To investigate the structural changes, single dispersive X-ray diffraction experiments using synchrotron radiation were carried out. The sample was polycrystalline anthracene powder of high purity. The measurements were performed in the Photon Factory beamline 18C optimized for high pressure X-ray experiments in Delye-Scherrer geometry. These data were analysed by Rietveld refinement methods to obtain the lattice constants under pressure and furthermore orientational parameters of the molecules within the unit cell. The data was collected under pressures up to 22 GPa and increased by 38%. As all changes in the crystal structure are gradual, no phase transition is observed in our X-ray measurements under hydrostatic conditions. The high quality of the measurements permitted to observe an increased overlap of the electron densities within the herringbone pattern under high pressure. This increased overlap has been previously investigated by density functional calculations.

L7.12

Abstract Withdrawn.

L7.13

FIELD EFFECT OF FULLERENE THIN FILM STUDIED BY DISPLACEMENT CURRENT MEASUREMENTS AND INFRARED ABSORPTION SPECTROSCOPY IN THE MULTIPLE REFLECTION TECNIque. Satoshi Ogura, Yutaka Kimura, Hsiao Ishii, and Michio Ninomi, Tohoku Univ. Research Institute of Electrical Communication, Sendai, JAPAN.

Recently, organic field effect transistors (OFETs) have attracted much attention. In spite of extensive studies, the mechanism of OFET is not yet well understood. Especially field effect doping is now under discussion after the observation of the data of Dr. Schön in Bell Laboratories. Here, we present two questions: one is whether field effect doping actually happens for organic semiconductors or not. Second is whether the accumulated carrier comes from in this study, we prepared a metal/insulator/semiconductor (MIS) structure as a prototype of FET structure. We used fullerene \(C_{60}\) as an organic semiconductor. By using a displacement current method we investigated the charge accumulation at the \(C_{60}/\text{insulator}\) interface due to applying electrical field. In-situ infrared absorption spectroscopy in the multiple internal reflection geometry was also performed for the MIS structure to examine the field effect doping. This technique enables us to investigate the degree of change of interface \(C_{60}\) layer under electric field. As a result, we observed electron injection from Au electrode to \(C_{60}\) followed by the decrease in an IR absorption peak due to fullerenes, which suggests that carrier injection is caused for carrier accumulation in the channel of OFET. The decrease of IR peak of \(C_{60}\) indicates the decrease of the amount of neutral \(C_{60}\) molecules, suggesting some doping effect induced by accumulated carriers. The detailed analysis of the observed spectral change due to electric field will be presented.

L7.14

ANALYSIS OF CHARACTERISTIC SHG FOR S8C AT THE AIR-WATER INTERFACE UNDER P-IN-P-OUT LASER CONFIGURATION. Chen-Xu Wu, Xiemin Univ. Dept. of Physics, Xiemen, P.R. CHINA; Hsing-Wei Peng, Inst. of Chemistry (CAS), The State Key Laboratory of Molecular Reaction Dynamics, Beijing, P.R. CHINA.

Second harmonic generation (SHG) technique is a very useful technique to investigate the physical and chemical properties of materials at interfaces. For monolayers at the air-water interface, it can probe the dynamics of molecules during monolayer compression. Investigations concerning SHG during monolayer compression have been reported. SHG signals depend on the configuration of input laser as well as the output laser direction detected. The SHG and surface pressure of 4-aminobiphenyl (4-ABP) monolayers at the air-water interface under different input-output configurations are measured during monolayer compression. Under p-in-p-out laser configuration, a characteristic peak of SHG density rather than a plateau under other laser configurations, is found. A theoretical analysis, which agrees well with experiments, is given for the special SHG characteristics of S8C monolayers under the p-in-p-out laser configuration.


L7.15


The occurrence of efficient photoinduced charge transfer in conjugated polymer doped with fullerene derivatives paves the road to fabrication of polymer-based photovoltaic devices. However, the mechanism of exciton dissociation in such systems is not yet fully understood. Recently, a model of on-chip hot exciton dissociation was suggested in order to explain the observed weak temperature dependence of photogeneration yield [1]. This model is based on the assumption that the effective temperature of an excited segment is higher than the ambient temperature due to intra- and inter-fragment dissociation of the excess photon energy. This approach cannot be directly applied to the dopant-assisted dissociation. Although some excess energy must be released upon carrier trapping it is not clear how this energy can be transferred to the twin carrier that occupies the polymer segment. In the present work, we suggest a model of exciton dissociation on charge transfer centers, which consists of conjugated segments and adjacent deep electron traps. The exciton carrier is delocalized within a polymer segment its minimum energy must also include the energy of zero-point oscillations within the chain potential well created by the charged trap. The latter effectively lowers the energy barrier for further separation. Therefore, facilitates exciton dissociation. At high dopant concentrations, exciton dissociation mostly occurs at the interface separating a photoactive polymer and dopant aggregates. We show that the fractional charge polarization of the polymer and dopant molecules at the interface substantially weakens the Coulomb interaction between elementary charges created after interfacial dissociation of excitons. This dipole layer strongly facilitates dissociation of interfacial geminate pairs into free carriers which can fully contribute to the observed high yield of photogeneration in conjugated polymer/fullerene blends. [1] V.I. Arkhipov, E.V. Emelino, and H. Biesele, Phys. Rev. Lett., 82, 1321 (1999).

L7.16

SOL-GEL NANOHYBRID MATERIALS INCORPORATING...
FUNCTIONAL THIACALIXARENES FOR NON LINEAR OPTICAL APPLICATIONS. Cedric Desroches, Stéphane Pauly, David Godts, Corinne Bolley, Laboratoire de Chimie Organique et Analytique, Université de Liège, Bâtiment des Sciences de la Matière, 4000 Liège, BELGIUM.

Optical Power Limitation (OPL) materials have been developed for the protection of light amplifying and emitting devices. Previous investigations evidenced that the optical limiting behaviour of a given molecule can be related to the de-localization of electrons and may be improved by the formation of heavy metal complexes. We have been investigating thiocalixarenes on the basis that they display delocalised electrons and can be selectively functionalized either on the upper rims or the lower rims. Moreover, the presence of electron donating sulfur bridges can play an important role regarding nonlinear optical properties and functional groups can be functionalized with ability to increase the electron delocalisation over the molecule and to form metal complexes. Thiocalixarenes bearing phenylthio, amino, imino or ethylenic groups on the lower rims were prepared and fully characterized. The formation of metal complexes was also investigated. They showed interesting optical properties. Optical limiting molecules need to be incorporated into an inorganic matrix in order to be useful for optical limiting devices. It is well known that the solgel route allows easy inclusion of organic dyes into an oxide network because of the low temperature of the process. Two major classes of the so-called organic-inorganic hybrids can be considered. In class I hybrids the organic molecules have weak chemical interactions with the inorganic network (Van der Waals hydrogen bonds). In class II hybrids the organic is strongly bonded to the inorganic network (covalent). Class I materials were found to be inhomogeneous and only low concentrations (c<1%) of thiocalixarenes could be reached in the final material. Class II hybrids were thus considered to permit the elaboration of highly concentrated and stable hybrids. A second functionalization (upper rims) with metal alkoxide groups had to be investigated in order to prepare the class II sol-gel hybrid materials incorporating the optically active molecule.

L7.17

Photovoltaic structures based on combination of electrically conductive polymers with inorganic semiconductors are currently intensely investigated with the aim to prepare photovoltaic devices. Conductive polymers attract interest due to the potential for producing low-cost, large-area and flexible photoelectrodes and solar cells. In this study, multilayer structures consisting of CuIn2S4 (CIS) and poly[3,4-ethylenedioxythiophene] (PEDOT) doped with polyaniline as a hole transport layer were prepared and investigated for photovoltaic applications. The polymer layer of p-type is considered as an alternative for the traditional buffer layer and window top layer on the CIS absorber layer in the cell structure. As the absorber layers are fabricated using a Co-In alloy, CIS films were synthesized directly on top of a layered structure on Cu tape substrate using a non-vacuum CSCuT technique. Thin PEDOT films doped with PSS were deposited onto RCN etched and vacuum annealed CIS films from an aqueous dispersion of PEDOT/PSS mixed with Nonemethylpyrrolidone, isopropanol, glycerin and epoxysilane additives using the spin-casting technique. In order to prepare stable PEDOT films of high quality with a good adherence to the surface of inorganic semiconductor CIS, the optimum parameters of spin-coating were selected experimentally. Average film thickness was determined microscopically and was about 1.5 μm for CIS and 0.5 μm for PEDOT films. Significant photovoltaic and photo-current of the fabricated CIS/PEDOT structures have been observed under standard light and white light illumination. Our deposition technique gives us an opportunity to prepare photovoltaic structures based on CIS and PEDOT thin films using relatively simple step-by-step method.

L7.18

Recent electrochromic experiments have shown the possibility of fine-tuning the emission spectrum of dipropylmethane dyes by chemical modification of specific subgroups. This property and the fact that they have a relatively small bandwidth makes these dyes good candidates for the development of full color polymer displays. We present the results of ab-initio (DFT-LDA) calculations in which we examined the energy level structures of various dipropylmethane oligomers and polymeric structures. Special attention will be paid to the comparison of the trends of the HOMO and LUMO energies. The calculated values for these energies will be compared with those obtained from cyclic voltammetry experiments. We also calculate the HOMO and LUMO energies for some polymers (e.g. PPV and polyfluorene) which are attractive from an industrial point of view to be used as a matrix for the dyes. The knowledge about these energies of the oligomeric or polymeric materials is necessary to estimate the efficiency of light conversion in these materials. We also wish to understand trapping of electrons, holes and excitons. Regarding the charge transport we can draw the following conclusions: We find that for the dyes in the PPV matrix it is favorable for the holes to stay on the polymer and the electrons to be trapped on the dye, although the energy gain is small. There are some experimental indications that indeed the electrons are trapped on the dye molecules. In the case of dyes in a polyfluorene matrix, it is favorable both for holes and electrons to go to the dye molecules. Again the remark should be made that the energy differences can be small (0.05-0.2 eV) and depend on the specific species of the dyes. Our study shows the feasibility to use ab-initio calculations as a predictive tool in this research area.

L7.19

The variation of the emissive properties of conjugated polymers is of immediate interest for the setup of organic light emitting devices (OLEDs). A novel strategy for a patterned modification of PPV films is presented. We employed the photoinitiated addition of thiols (R-SH) to the C=C double bonds in PPV in order to modify the emissive properties. This photoreaction, which is known under the name "Thiol-Ene Reaction", was found to be highly efficient and selective to various the enyne units in PPV. The reduction of the conjugation length lead to a dynamic change in the emissive properties and finally to a complete suppression of the emission. This technique can be employed for the generation of patterns in PPV films (blending). On the one hand, the reaction was carried out by UV illumination of PPV films in the presence of gaseous thiol (e.g. propynethiol). On the other hand, PPV films containing dodecanethiol were cast onto substrates and subjected to UV illumination. In both cases the photoinitiated Thiol-Ene addition was followed by real-time infrared spectroscopy (RTIR). An almost complete conversion of the C=C double bonds was achieved upon prolonged UV irradiation. We investigated the accelerating effect of free radical photoinitiators (e.g. benzoyl methyl ketone) on the addition reaction. An atmospheric pressure plasma ion beam treatment was used to deposit controlled amounts of the photoinitiator on PPV films. Subsequent UV illumination in the presence of gaseous thiols lead to a photodarkening predominantly in the areas containing the photoinitiator. The relationship between the deposited amount of photoinitiator, the UV illumination time and the resulting emissive properties of the PPV films was investigated. Applying this novel concept in combination with photomasks, laser-induced resolved photoprocessing of PPV was demonstrated.

L7.20
Abstract Withdrawn.

L7.21
THE CHARACTERIZATION OF A SILICOL-MAGNESIUM THIN FILM INTERFACE BY PHOTOELECTRON SPECTROSCOPY. A.J. Misikinen, Optical Sciences Division, Naval Research Laboratory, Washington, DC; M. Uchida, Chiono Corporation, Yokoha, JAPAN; Z.H. Kahali, Optical Sciences Division, Naval Research Laboratory, Washington, DC.

Photoelectron emission spectroscopy of an interface between Mg and a silicate derivative, 2,5-bis[(2,2'-dipyridyl)l-1,1-dimethyl-3,4-diphenyl silacyclopentane-P (PyPyPy)], shows the formation of two gap states both when metal is deposited onto an organic layer and when the organic is deposited onto the metal. The appearance of gap states is a result of electron transfer from the metal to the organic. Fermi level pinning occurs at the lowest unoccupied molecular orbital of PyPyPy, implying barrierless electron injection at the Mg/PyPyPy interface. This result is significant when employing a Mg electrode contact with PyPyPy in electronic, electrochemical and optoelectronic devices.
L7.22 HIGH PRESSURE STUDIES ON THE PACKING FORCES AND INTERMOLECULAR INTERACTION IN POLYPHENYLS. Georg Heimel, Martin Oehlert, Roland Resel, Inst. of Solid State Physics, Graz University of Technology, Graz, AUSTRIA; Peter Paschen, Kerstin Hammer, Claudia Ambrosch-Draxl, Inst. for Theoretical Chemistry, University of Graz, Koppellhuber-Bitschar, Inst. of Physical and Theoretical Chemistry, Graz University of Technology, Graz, AUSTRIA; Felix Porschen, Inst. of Mineralogy and Petrology, University of Bonn, Bonn, GERMANY.

In this work, we report on pressure induced structural changes in crystalline oligo(phenylene) containing two to six phenyl rings. The results are discussed with particular emphasis put on the implications these changes in intermolecular distances and molecular arrangement have on important bulk properties of this class of materials such as optical response and charge transport. We performed energy dispersive X-ray diffraction in a systematic study on polycrystalline films of highp, p-quaterphenyl, p-quaterphenyl p-quinquephenyl and p-sexiphenyl under hydrostatic pressure up to 60 kbar. Revisiting the crystal structures at ambient conditions reveals details in the packing principle. A linear relationship between the density at ambient conditions and the number of phenyl rings is found. High pressure investigations not only yield pressure dependent lattice parameters and hints towards pressure induced changes in the molecular arrangement but also allow for an analysis of the equations of state of these substances as a function of oligomer length. We report the previously unknown bulk modulus of p-quinquephenyl, p-quinquephenyl and p-sexiphenyl (\(B_0 = 83\) kbar, 83 kbar and 100 kbar respectively) and its pressure derivative (\(B_0 = 6.4, 7.5, 5.6\)). A linear dependence on the bulk modulus on the number of phenyl rings in the molecules and with that on their ambient conditions density is found.

L7.23 INDEX AND RELIEF GRATINGS IN POLYMERIC FILMS FOR ORGANIC DISTRIBUTED FEEDBACK LASERS. G. Longer, TU Graz, Inst. of Chemistry and Technology of Organic Materials, Graz, AUSTRIA; A. Pogorensen, TU Graz, Inst. of Chemistry and Technology of Organic Materials, Graz, AUSTRIA; D. Wright and J. Zys, ENS-Cachan, LPQM, Cachan, FRANCE; K.F. Iskra and T. Neger, TU Graz, Inst. of Chemistry and Technology of Organic Materials, Graz, AUSTRIA.

Gratings in polymer films are important for optoelectronics and for the setup of organic lasers based on the principle of distributed feedback (DFB). Our investigations were focused on a photosensitive polymer (poly(styrene-co-4-vinlybenzylchloroacrylate) / PST-co-VBT) which forms refractive index (by isomerization) and relief gratings (by laser ablation) upon deep UV irradiation. By gas phase modification with amines additional index changes as well as additional surface relief gratings were obtained with these polymers. Using interference illumination with the fourth harmonic of a Nd:YAG laser, 1D and 2D surface relief gratings were produced. DFB lasers were observed using excited dye (DMF) and charge-transfer dyes embedded into the photosensitive matrix. Also thin films of conjugated polymers cast onto the surface relief structures of PST-co-VBT show lasing action. The performance of these organic surface emitting laser devices and their spectral laser mode output were characterized. Strategies towards truly tunable DFB laser devices were investigated. A promising way is the functionalization of electroluminescent materials by responsive groups, e.g. CH2=CH2. This approach aims at elastic index and relief gratings with variable DFB emission wavelengths.

L7.24 Abstract Withdrawn.


In the quest for photocatalytic devices that are low cost, light weight and easy to produce, organic semiconducting solar cells (DSSCs) are good contenders. Overall solar light to electrical energy conversion efficiencies of 10% have been reported for devices based upon liquid electrolytes, (typically 12% in non-iridium). However there are a number of drawbacks associated with employing such liquid based electrolytes. For example problems with encapsulation of the liquid electrolyte and leakage of the solvent may seriously hinder the long-term stability of such devices. As a result, recently there have been heightened interest in the application of solid state versions of DSSCs, where the liquid based hole-conductor is replaced by a solid state hole-conductor. In this paper we present work on two hole-conductor systems: polymer electrolytes and p-type organic polymers, paying particular attention to the following points: 1) Development of small molecule [Example 1] and polymer based organic hole-conductors with ion solvating tetrathylenglycol side chains and their application in dye sensitised nanocrystalline solar cells. 2) The charge transfer processes that occur at the semiconductor / dye / hole conductor interface play an important role in controlling the overall efficiency of the device. Here we employ laser based transient absorption spectroscopy to study the charge transfer processes at the semiconductor / dye / hole conductor interface. In particular we highlight the importance of thermodynamic rather than kinetic control of the interfacial charge separation and the influence of energetic inhomogeneities upon the yield of charge separation. We also employ insulating metallic oxide barriers to retard the recombination interface and thereby enhance device performance. 3) The development of solid state dye sensitised on flexible plastic substrates. We report flexible DSSCs with overall efficiencies of ~3% (1Kmc2m2 solar light illumination) based upon polymer electrolytes.


The performance of optoelectronic devices made of conjugated polymers such as light-emitting diodes, photodetectors and lasers is determined by the properties of the excited state of the organic molecules. In particular the extent of electronic deactivation, the electron-lattice interaction and the inter- and intrachain coupling are presently investigated extensively. Typically, spectroscopic data on conjugated polymers are strongly affected by the broadening of the spectral features. The spectroscopy of single molecules avoids ensemble averaging and gives direct access to the optical properties of the individual molecule. Using single molecule spectroscopy we measure the line width by time resolved photoluminescence from a single conjugated polymer chain between 5 K and room temperature. We choose a ladder-type
poly(p-phenylene) as a model polymer system in this material exhibits a particularly low degree of inhomogeneous broadening together with a 
small amount of chemical shifts. At room temperature the spectrum of a single conjugated molecule nearly matches the bulk spectrum. At low temperature however, the single molecule spectrum shows a much smaller line width as compared to the bulk. This phenomenon calls for a dephasing time of T2 > 260 fs. In addition, the small line width allows the identification of various vibrational modes coupling to the electronic excitations. Employing a pulsed excitation source and guided wave detection to measure the single molecule photoluminescence spectrum with a time-resolution of 200 ps. The majority of the molecules investigated show a red-shift of the spectrum on a sub-ps timescale. This is a very direct observation of energy transfer between different conjugated segments located on the same polymer chain.

L7.28
Abstract Withdrawn.

L7.29
STRUCTURAL AND SPECTROSCOPIC STUDY OF LANGMUIR-SCHAFER FILMS OF Bis-Zethane-Bridged PORPHYRINS DIимер. G. Pannier, S. Conoci, S. Cofiga, Si Optoelectronics, Bios and Nano Systems, Corporate RD&D, ST. 
Microelectronics, Carin, ITALY, D. Pagnacco, S. Soratino, M. Maretta, Dipartimento di Scienze Chimiche, Universita di Carina, Catin, ITALY, L. Valli, Dipartimento Ingegneria dell’Illuminazione, Universita di Lecco, Lecco, ITALY, V.V. Borovkov and Y. Inoue, Institute of Photochromic Materials, URAST, JST, OSAKA, JAPAN.

Thin films of porphyrins and related compounds have attracted increasing attention in recent years being these molecules an extremely versatile source of compounds for a large variety of technological applications. Indeed, their potential employment in many fields of technological interest as photodetectors, optical antennas and switches as well as chemicals sensors has been extensively studied [1]. This work is dealing with the structural properties of bis-zethane-bridged porphyrin dimer (1) has shown unique temperature and solvent dependent syn-anti conformational switching properties in solution [2,3] making these compounds promising candidates for optical switches and sensors applications. In this work, we report on a structural and spectroscopic study of thin films. Monolayers of 1 have been first prepared at the air/water interface. The related surface-structure schematic curve showed that in dependence of the film pressure different condensed phases may occur in the monolayer. The inspection of the monolayer by Brewster Angle Microscopy (BAM) and UV-Vis spectroscopy lead to the observation of peculiar structures whose structural features and optical properties seemingly change upon film compression. Thin films [1-3 layers] of 1 have been then transferred on solid surfaces, by the Langmuir-Schäfer [LS] horizontal method. Either quartz slides or silicon oxide, previously hydrophobized with 1,1,1,3,3,3-hexanotetramine, have been used as substrates. Scanning Force Microscopy (SFM) images performed on these systems at different length scales, showed fractal networks constituted by nanoscopic supramolecular aggregates, whose size and shape depend again on the LS deposition surface pressure. UV-Vis spectroscopy measurements showed that the absorption is almost linearly related to the film thickness and directly connected to the surface pressure, led to the film morphology investigated by SFM [1]. [F. Kamps et al. Nature, 1980, 284, 49, N.A. Raskov et al. Nature 2000, 406, 710, [2] V.V. Borovkov et al., Chem. Phys. 2004, 305, 453, [3] V.V. Borovkov et al., J. Am. Chem. Soc., 2000, 122, 4403-4407].

L7.30
Abstract Withdrawn.

L7.31
EMISSION CHARACTERISTICS OF OLEDs ON PLANAR AND NON-PLANAR SUBSTRATES. M. Scheffel*1,b, A. Hunze*1,b, R. Pitschke*1,b, J. Birmstorck*1,b, W. Rögle*1,2, V. Vögler*, A. Winnacker*1,2.
*1Siemens AG, Erlangen, GERMANY, **1,2Institut für Werkstoffforschungen, Universität Erlangen, GERMANY; **1Lehrstuhl für Bildschirtechnik, Universität Stuttgart, GERMANY.

We report on the influence of different device architectures on the emissive behaviour of polymeric light emitting diodes. Goal of these investigations is an enhancement of external quantum efficiency. Planar substrates as well as substrates with modified surface morphologies have been used. On planar substrates, interference effects lead to a significant influence of film thicknesses on angular emission characteristics and on the extraction efficiency. The photon flux emitted from the devices was measured relative to the flux trapped within the substrate by waveguiding effects. The experimental data are compared to our modelling results of the emission of oriented dipoles embedded within a multilayer structure. For the processed devices, we find that a maximum increase of external quantum efficiency by nearly a factor of two can be expected by additional addition of waveguided light. As a consequence of this investigation, we modified the architecture of our devices and find in addition a significant increase. Introduction of light-enhancement elements between glass substrate and indium tin oxide anode results in the redirection of photon trajectories and thus a changed emission profile. Apart from optical effects, the modification of surface morphology gives rise to an altered electrical performance.

L7.32
PERIODICAL SELF ASSEMBLED PHOTONIC STRUCTURE IN POLYMER BLEND LIGHT EMITTING DIODES. G. Fischer, W.T.S. Huck, Melville Laboratory, Department of Chemistry, University of Cambridge, Cambridge, UK, N. Crichton, J. Z. Mackenzie, R.H. Friend, Cavendish Laboratory, Department of Physics, University of Cambridge, Cambridge, UNITED KINGDOM.

The light trapped inside organic light-emitting polymer diodes can be removed by scattering using a periodical structure introduced by pattern-directed phase separation. Self-assembled monolayers have been covalently bonded by microcontact printing to Poly-3,4-ethylenedioxythiophene (PEDOT) in order to create a periodical pattern with different surface energies. Phase separation of polyfluorenes follows the micron-scale pattern inducing a periodical photonic structure inside the device. These devices show a significant increase in external quantum efficiencies for thin films and bilayers devices. We find that these films show a strong angular dependence due to the scattering of the wave guided light trapped into the organic layers of the device. This effect is observed in both photoluminescence and electroluminescence.

L7.33

While organic molecular semiconductors are promising candidates for future electronics their intrinsic transport mechanisms are not yet fully understood. Here, we present theoretical ab-initio studies on low-temperature charge transport in terms of polaron bandwidth narrowing. Our approach of solving the Holstein-Peierls model for the electron-phonon interaction. It allows the calculation of the temperature dependence of the polaron bandwidths, including both local (Holstein) and nonlocal (Peierls) electron-phonon coupling. For dispersionless phonons, we derive an explicit analytical expression for the polaron bandwidths as a function of temperature which generalizes Holstein’s result of purely local coupling. As a first application of our method, we present model studies for oligo-ene crystals. The electron-phonon coupling constants are obtained combining the results from DFT-LDA calculations for the electronic bandstructure with a rigid-molecule approach for the intermolecular-phonon properties. This ab-initio approach allows a quantitative study of the bandwidth narrowing and provides novel microscopic insight into the relevance of the different coupling mechanisms (local vs. nonlocal) and the different behaviour of electrons and holes.

L7.34

We present studies of the Raman scattering from poly[(7-[9H-carbazole-9-y]fluorene) [PF2/6)] under hydrostatic pressures of 4-100 kbar at room temperature. We observe a Raman peak corresponding to the intra-ring C=C stretching mode at 1600 cm-1 and other peaks at 1582 cm-1, 1500 cm-1, and 1417 cm-1 which are studied as a function of pressure. All Raman peaks shift to higher energies with increasing pressure. Above 40 kbar they exhibit asymmetric and anisotropy line shapes. This is indicative of a strong electron-phonon interaction between the Raman phonons and the electrical continuum. The photoluminescence from bulk PF2/6 shows significant changes in the aggregate and defect related emissions increasing significantly above 40 kbar. Although the Raman spectra are excited with the 1.92 eV laser line, it appears that direct excitation of the aggregate or defect related emission occurs, causing real translations that interact with phonons to produce asymmetric line shapes. The line shift of the 1600 cm-1 Raman, due to the striking symmetry characteristic of a Breit-Wigner Fano (BWF) resonance. A detailed BWF line shape analysis for this peak as a
function of pressure shows that the asymmetry (1/4y) is relatively small up to about 35 kbar, with (1/4y) value between 0.005 and 0.1. Beyond this pressure, the asymmetry (1/4y) increases from 0.3 to 0.6. The linewidth increases as the square of pressure, while the frequency positions almost linearly with pressure.

L7.35

CHARGE TRANSPORT IN THIN POLYCRYSTALLINE FILMS OF ORGANIC SEMICONDUCTORS. Nishe Verhels, Vladimir Arkhipov, Paul Herecsei, Inse, Polymer and Molecular Electronics, Leuven, BELGIUM.

Thin films of thermally evaporated small-molecule materials, used in organic thin film transistors (OTFT), are generally polycrystalline with localized states concentrated within the amorphous phase separating crystalline grains. Therefore, one may expect that the grain boundaries will control charge transport in these materials and a grain boundary model offers an adequate approach to the conductivity in polycrystalline films. Charges, trapped in defects at the grain boundaries, create potential barriers and carrier jumps across these barriers are the rate-limiting step in the carrier transport. We assume a quasi-continuous energy distribution of localized states within grain boundaries rather than a constant interfacially trapped charge. Under such circumstances, the potential barrier height is self-consistently determined by filling of those states.

In terms of this model, we discuss the effects on the carrier mobility of dopant concentration, the lateral and vertical fields, i.e. drain voltage/channel length and gate voltage, as well as the limitations of this model and the differences with other models.

L7.36

ON THE ORIGIN OF GREEN EMISSION IN POLY-PHENYLENE BASED CONJUGATED POLYMERS. Everly J. Lue and Lorenz Romberg, Chairmen Laboratorium voor Polymeerfysische Materialen, Institute of Nanostructured Materials and Photonics, Joanneum Research, Wien, and Institute of Solid State Physics, Graz University of Technology, Graz, AUSTRIA, Alexander Poppitzsch, Institute of Solid State Physics, Graz University of Technology, Graz, Roland Guettner, Patrick Scanducci de Freitas, and Ulrich Scherf, Bergische Universität Wuppertal, Molekülphysik-Chemie, Fachbereich Chemie, Wuppertal, GERMANY.

For future display applications of conjugated polymers the currently most challenging topic is the realization of colour stable blue light emission. All available poly(paraphenylen type) materials (PPP) which are the most promising family of blue emitting polymers, are prone to degradation resulting in an unwanted change in colour due to the emerging of a lower energetic greenish emission peak. This band has been mostly been attributed to aggregate and/or excimer formation in the material. However, as we show, both excimer and aggregate formation are very unlikely to be the origins of the low energy emission band of PPP-type polymers. Instead all experimental observations suggest a radiative decay from the oxidized state to be the source of this emission band. In this context, using UV-VIS, PL, emission and infrared spectroscopy we will present spectroscopic evidence for the formation of keto defect sites in different types of different PPP-type polymers, as a consequence of different processes. It will be demonstrated that keto defects can be generated in the material directly during polymer synthesis, photo- or electrooxidative degradation processes and thermal treatment in ambient atmosphere.

In addition theoretical spectroscopic results are compared to results obtained for defined co-polymers of 9,9'-difluorenyl-fluorene with 9-fluorene. Studying such controlled fluorescences fluorene co-polymers model compounds a clear quantative correlation between the 9-fluorenyl content and the low-energy emission band intensity has been established.

L7.37

COLOR TUNING OF EMISSION OF IRIDIUM PHOSPHORS BY USING ANCILLARY LIGAND AND DEEP BLUE Iridium PHOSPHORS FOR OLEDs. Jian Li, Bert D. Al Fey, Vadim I. Adamovich, Peter I. Byrnes, Mark E. Thompson, Department of Chemistry, University of Southern California, Los Angeles, CA; Russell Holmes, Stephen R. Forrest, Department of Electrical Engineering, Princeton University, Princeton, NJ.

High efficiency organic light emitting devices (OLEDs) require the phosphorescent emitters. Due to the spin-orbit coupling of Ir atom, many cyclometalated Ir complexes are phosphorescent at room temperature, meaning these materials are candidates for dopant emitters in OLED applications. One method of modifying the emission energy, and hence the color, of Ir phosphors is to change the nature of cyclometalating ligand. For example, phenylpyridine-based Ir phosphors have green emission while Ir phosphors with phenylisocyanine will emit orange or red. (Ref. S. Limmack, et al., Inorg. Chem., 2001, 40, 1704-1711). This presentation will describe a new method of color tuning by employing high triplet energy ancillary ligands for Ir phosphors. Using a series of different ancillary ligands, i.e., a family of pyrazylcarbonyl, ppy, tetrakis(4-pyridyl)benzene (tpy), it is possible to vary the emission color of Ir phosphors over a wide range. For example, the emission colors of monolayer Ir(tpy) is orange (λmax = 550 nm) while multilayer Ir(tpy)2Cl2 is yellow (λmax = 545 nm). Electrochemical analysis of Ir(tpy), Ir(tpy)2, complexes shows that different ancillary ligands modify the emission energy by affecting the energy of the filled state (HOMO) while leaving the vacant states (LUMO) relatively unchanged.

L7.38

RUTHENIUM(II) ORGANOMETALLIC COMPLEXES AS NEW HOLE TRANSPORTING MATERIALS FOR OLEDS. Jian Li, Vadim I. Adamovich, Xiaofei Ren, Peter I. Byrnes, Mark E. Thompson, Department of Chemistry, University of Southern California, Los Angeles, CA.

Since the invention of the organic light emitting diodes (OLEDs) in 1987, the investigations into new hole transporting materials have typically focused on derivatives of tris(8-hydroxyquinolinato)aluminum, Alq3. Recently, our group has started to investigate organometallic complexes with reversible redox properties as hole-transporters for OLEDs. The present work describes a novel approach for hole transporting material design as well as introduces a new type of hole transporting material. Based on the Marcus electron transfer theory, a low energy barrier of electron exchange between bi(thiophene)[1-pyridyl]boron−ruthenium(II), Ru[P2(BH)2] and its cationic counterpart, Ru[P2(BH)2]2+, makes Ru[P2(BH)2]2+ a potentially good hole transporting material. The report demonstrates this by using one derivative of Ru[P2(BH)2]2+, bis[tetrakis(1-pyridyl)boron]ruthenium(II), Ru[P2(BH)2]2+ as hole transporting material, the device (ITO/Ru[P2(BH)2]2+/Alq3/NPD/Alq3/Ag) shows a low turn-on voltage around 5.5 V.

L7.39

LARGE OPTICAL AND NEAR INFRARED BIREFERENCE IN PHOTOADDRESSABLE POLYMERIC THIN FILMS. Beth L. Lasher*, Michael J.A. de Dood*, Albert Polman*, Harry A. Atwater*, California Institute of Technology, Watson Laboratory of Applied Physics, Pasadena, CA, *FOM Institute for Atomic and Molecular Physics, Amsterdam, NETHERLANDS.

Development of highly birefringent polymer materials is necessary for improving the capacity of data storage and is also potentially useful as a waveguide and active device material in integrated photonic devices. Photoaddressable polymers (PAPs) show considerable potential for these applications, with an unusually large birefringence of the order of 0.1 at 632 nm. We have characterized for the first time, via spectrophotometric ellipsometry, the birefringence of such PAP films from 630 to 1700 nm. Birefringence values measured indicate that the PAP is absorbing above 630 nm and maintains a very high birefringence (> 0.1) at wavelengths up to 1700 nm. We have also performed morphological characterization using optical and atomic force microscopy indicating that both cast spun and written 500 nm thick films are optically smooth but with topographic features of order 30 nm high. Absorption spectra of the PAP films indicate that it is strongly absorbing in the visible (400-680nm), so a 485nm Ar- laser beam was used for writing while birefringence and photo-birefringence was monitored with a 632nm HeNe laser. Writing was found to be the same for both the as-spun and the as-spun film was preferred to the polymer, leading to a strong in-plane birefringence due to the induced Zhoubene photonsimmonization cycle from the triss to cis configuration. This preferentially aligns the polymer side-chains perpendicular to the polarization direction. The effect of PAP birefringence on the plasma absorption of arrays of nanometer-scale metallic particles will also be presented.

L7.40

A NEW CLASS OF ORGANIC/INORGANIC HYBRID COMPLEXES AS PHOTOSENSITIZERS FOR NANOCRYSTALLINE TiO2 BASED DYE SENSITIZED PHOTOCATALYSTS. Ravi M. Krishna, Center for Advanced Materials, University of Massachusetts, Lowell, MA; Lynne J. Summck, Nati Solik Soldier, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

Currently, the investigation of efficient molecular photosensitizers for
the development of low cost dye-sensitized photovoltaic (DSPV) cells has been an area of tremendous interest. Transition metal complexes are used as dyes in photovoltaic devices based on nanoparticles of an inorganic conductor with a high absorption of visible light. However, the conversion efficiency of such devices is currently limited to around 3–5%.

**L7.41 CHARGE TRANSPORT DEPENDENCE ON CHARGE CONCENTRATION - EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF FIELD EFFECT TRANSISTORS**

Yasup Kimoto and Errik Leus, Dept of Electrical Engineering Department - Israel Institute of Technology, Haifa, ISRAEL, Shary Tal and Yosef Benjam, Dept of Chemistry, Technion, Israel Institute of Technology, Haifa, ISRAEL, Oren Tal and Yosi Rosenfeld, Dept of Physical Electronics, Faculty of Engineering, Tel Aviv University, ISRAEL.

Charge transport in conjugated polymers has been widely explored, in particular its dependence on the applied electric field and operation temperature. Previously, we calculated charge transport dependence on charge concentration in conjugated polymers. This theoretical model gave rise to two significant conclusions: 1) Mobility increases with charge concentration, and 2) V/μ ratio is higher than expected from the classical Einstein equation, kT/μ. In the current work, this prediction is examined in a charge concentration controlled device, i.e., polymer field effect transistor (PFET). In order to isolate extrinsic effects, we have examined the PFETs using several experimental methods, including DC characteristics, at different temperatures, atomic force microscope scans in both micro-Kelvin probe mode and force mode, and time-resolved reflectance and transmittance measurements. We use this set of measurements to extract the charge transport dependence on charge concentration and compare it to the theoretical predictions. This comparison allows us to reveal the role of the morphology and molecular weight in dictating the mobility dependence on the operation parameters.

**L7.42 SOLID STATE NMR INVESTIGATION OF THE STRUCTURE AND DYNAMICS OF ALUMINUM TRIS-(8-QUNOLINOLATE)**

Maghsoud Mardanmog, Mathew Mathai, Piotr Popovitch, Michael White, Institute of Materials Science, University of Connecticut, Storrs, CT.

Aluminum tris-(8-Qunolinolate) (Alaq) is the most widely used electron transport material for organic light-emitting diodes. Whereas the structure and dynamics of several of these compounds have been studied, there is currently a need for a better understanding of the molecular packing and dynamics in the device-relevant amorphous phase. We have applied advanced solid-state NMR methods, including both the spin-1/2 Carbon-13 and the spin-1/2 Aluminum-27 nuclei, in order to obtain structural and dynamic information from amorphous Alaq deposits. Comparison of the 2TA C spectra from amorphous Alaq to those obtained from crystalline polymorphs with known structure provides a direct experimental estimate of the ratio of facial to meridional isomer in the amorphous material. The molecular dynamics of Alaq molecules in both crystalline and amorphous forms was quantified using relaxation time measurements as well as 13C exchange spectroscopy.

**L7.43 FORMATION OF ONE-DIMENSIONAL CRYSTALLINE CHAINS IN PARA-SUBSTITUTED GROWTH ON MCA**

C. Tricht, G. Havaer, Dept of Physics, University of Leoben, Leoben, AUSTRIA.

A. Arendt, H. Sitter, Institute for Semiconductor and Solid State Physics, University Linz, Linz, AUSTRIA; G. Matt and N. S. Sicard, IF, Linz Inst. for Technical Physics, University Linz, Linz, AUSTRIA.

High-resolution atomic force microscopy is used to study the initial stage of growth of highly efficient Si-QEP photovoltaic cells. This stage is characterized by the nucleation of nanometer scale crystals and self-assembled crystalline chains with micrometer extension in one dimension [1]. These chains are well oriented and exhibit a very narrow bandgap, which is a crucial property for the high efficiency of solar cells when grown under these conditions. The self-assembly process requires the rearrangement of the crystals into entities, [1] A. Arendt, et al., Thin Solid Films, 418-419 (2002) 444.

**L7.44 ORGANIC LIGHT-EMITTING DIODES BASED ON MULTILAYER PHOTO-CROSSLINKABLE HOLE TRANSPORT COPOLYMERS**

Benoit Domergue, Richard D. Hreha, Chet Carter, Jose-Luis Malpaso, Joshua N. Hatfield, Christopher Schulz, Ysung Zhan, Seth R. McCall, and B. R. Kippelen, Optical Sciences Center, University of Arizona, Tucson, AZ. Department of Chemistry, University of Arizona, Tucson, AZ.

A series of soluble allylamine-based hole transporting polymers with various ionization potentials have been synthesized. The synthetic methodology allows for substitution of allyl groups on the amine with electron-donating and electron-withdrawing moieties which permits tuning of the redox potential of the polymer. The allylamine-based monomers had been copolymerized with cinnamone-based moieties to obtain photo-crosslinkable polymers. These materials can be crosslinked and patterned using a standard mask aligner designed for photolithography applications. The UV exposure conditions were optimized to obtain an insulating hole-transport layer with stable electroluminescent properties. Using a photolithographic mask, these materials have been patterned into 10 μm x 50 μm size features. These polymers have been used as hole transporting layers (HTLs) in multi-layer light-emitting diodes (ITO/HITL/AlQ3/MgAg) in which a HTL (ITO) was placed between the electron injection layer (AlQ3) and the emitting layer (tris[(8-hydroxyquinolinate)aluminum]). The electroluminescent properties have been evaluated and compared between devices made from polymers with different ionization potentials. The electroluminescent devices have been fabricated using a micropatterned spin-coated hole-transport layer to enhance the overall electroluminescent properties. Fully spin-coated devices have also been fabricated by spinning a blend of polystyrene and AlQ3 on top of a crosslinked hole-transport layer.

**L7.45 NITROGEN-6 FROM SELF-ASSEMBLING BLOCK COPOLYMERS**

Nael Schraga, Rafael Verduzco, Michael Kempe, Julian Kornfeld, California Institute of Technology, Department of Chemical Engineering, Pasadena, CA.

Block copolymers with long-side group liquid-crystalline midblocks (>800 kg/mol) and LC-photonic end-blocks form a physical network that swells readily in an analogous small molecule LC (see Figure) to form nematic gels. A range of side-group liquid-crystalline (LCLCP) block copolymers are used to produce the midblock to enable gelation at relatively low concentration. In contrast to nematic gels made by a photo-initiated polymerization, the present gels have exceptionally uniform optical properties. Under an applied strain, an initially unaligned, polymer-microgel aligns, creating a monodomain that is oriented well enough to generate clear birefringent figures. In addition, these gels are amenable to various processing strategies for printing large area displays, since the physical crosslinks are reversible by addition of solvent or by increasing temperature. The transition temperature can be tuned by the choice of the end-blocks. The material provide ideal model systems in which the molecular weight between crosslinks is well-defined and determined by the length of the polymer midblock. Using polymers of analogous synthesis we prepare SCLCPs with M up to 1,000,000 g/mol and Mw/Mn < 1.3. The synthesis and interactions of these SCLCPs with nLC-cholesterol are described first for homopolymers, examining the dramatic effects of molecular weight. At these higher molecular weights, we have measured a tumbling parameter less than negative one. We further describe the phase behavior and electrooptic response of nematic gel formed using ABA block-copolymers.

**L7.46 LAYER-BY-LAYER PHOTOELECTRIC DEVICES: NANO-PATTERNED TiO2 / ORGANIC DYE / POLYCELETROLYTE MULTILAYER COMPOSITES FOR PHOTOVOLTAIC DEVICES**

Hisashi Tanaka, Paul H. Hammond, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.
Large area photovoltaic and photoelectric devices are extremely desirable as a flexible means of energy production and storage. In particular, for the development of high performance thin films that can be applied to a broad range of surfaces. Further, the ability to pattern high refractive index inorganic compounds on such systems is of particular interest for the use of photonic and electronic devices. Both polymer and photoelectric materials will benefit from advances in processing. The fabrication of such devices is critical to the success of these technologies.

**L7.47**

**CHARGE CARRIER LIFETIMES IN A SUMERIC LIQUID CRYSTALLINE PHOTOCOVIDOR OF A 3-PHENYLPHTHALINE DERIVATIVE.** Hiroki Iino, Junichi Hana, Imaging Science and Engineering Lab., Tokyo Institute of Technology, Yokohama, JAPAN.

Recently, liquid crystals have been being recognized as a quality organic semiconductor, whose mobility exceeds $10^{-5}$ cm$^2$/V sec, since the electronic conduction was discovered in disordered and smectic liquid crystals. We have investigated the charge carrier lifetimes for electrons and holes in smectic mesophases of 3-phenylphthalamine derivative, 8-[[4-(octyloxy)phenyl]-2-dodecylphthalamine (8-APPN-012) by time-of-flight (TOF) measurement and found that the carrier transport for holes and electrons is quite different. For positive carrier, the well-defined non-dispersive transient photocurrents were observed within the thick cells over 500nm and at the applied electric field of 2x10$^4$ V/cm. On the other hand, we observed two transients for negative carriers in the cells of 5nm to 110nm, i.e., fast and slow transients that correspond to the mobility on the order of $10^{-5}$ cm$^2$/V sec and $10^{-4}$ cm$^2$/V sec in the SmA phase and $10^{-4}$ cm$^2$/V sec and $10^{-3}$ cm$^2$/V sec in the SmA phase, respectively. We deduced that the origin of the slow transient is due to drift of ionized chemical impurities generated by electron trapping. Thus, we could reveal that in the SmA phase and the electron lifetime trapping at the short times probably originated from a truce amount of impurity and expected to be $4x10^{-5}$ sec for SmA and SmB phases.

**L7.48**

**PULSED LASER DEPOSITION OF ALUMINUM TRIS-(8-HYDROXYQUINOLINE) THIN FILMS** Kenji Ebihara, PaikKyun Shin, Takao Ohshima, Tomoko Iseki, Kumamoto University, Department of Electrical and Computer Engineering, and Graduate School of Science and Technology, Kumamoto, JAPAN; Toshinari Yamaguchi, Takahisa Nakamura, Technology and Industry Foundation, Kumamoto, JAPAN.

Organic light emitting devices (OLED) have gained great interest due to their potential application as future flat panel display capable of low voltage operation. The Alq3 (aluminum tris-(8-hydroxyquinoline)) has attracted a great deal of interest as a material for OLED. This compound is one of the most reliable organic conducting and light emitting organic materials. The Alq3 (aluminum tris-8-hydroxyquinoline) has a long relaxed lifetime of 5x10$^4$ sec, and is a stable material for use in OLED devices. The PLD (Pulsed Laser Deposition) is used for depositing OLED materials such as organic thin films. ALD (Atomic Layer Deposition) is used for depositing OLED materials such as organic thin films. The PLD has advantages over other methods in terms of uniformity and high density deposition. The PLD process is carried out in a vacuum chamber under a high vacuum of 1x10$^{-6}$ Torr. The substrate is placed at a distance of 25 mm from the target and kept at room temperature. The PLD process was performed using a pulsed laser with a wavelength of 248 nm. The deposition was performed under a nitrogen atmosphere.

**L7.49**

**STUDY ON FIELD EFFECT CARRIER MOBILITY OF ORGANIC THIN FILM TRANSISTORS AT ULTRALOW TEMPERATURE.** Hiroki Tanaka, Eisei Fujwara, Mitsuaki Takenaka, Yoyo Yumen, Yoshihiro Yamasaki.

Much attention has recently been paid to carrier transport in organic thin film transistors (OFTETs). Electrical properties especially at low temperature are of great importance to the operation of OFTETs. We have studied the electron mobility of several organic materials including polythiophene and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (P3DT: PSS) at temperatures as low as 100K. The results showed that the electron mobility of the OFTETs at low temperatures is about 10$^{-5}$ cm$^2$/V sec, which is comparable to that of inorganic semiconductors. The results indicate that the OFTETs can be used as electronic devices at low temperatures.

**L7.50**

**BLUH LIGHT EMITTING DIODES USING ALKOXY SUBSTITUTED POLY[(SPHROFIUORENE)]S.** Jeong-Bee Lee, Hye Yong Chui, Hyo Young Lee, Joo Young Oh, Lee Mi Do, So Young Jung, Energy Research Lab., ETRI, Daejeon, KOREA; Jinmin Lee, Hong-Kyu Shin, Dept. of Chemistry, KAIST, Daejeon, KOREA.

Polyfluorene has attracted much research interest because of their possible application as light emitting material in polymeric light emitting devices (PLED). However, troublesome excimer formation upon passage of current was a major drawback for commercial applications. There have been several approaches to overcome excimer formation such as polymerization and end-capping, but they were not enough to suppress excimer completely. Introducing a sterically hindered spirofluorene into polymer backbone should be one possible method and here, we have synthesized spirofluorene monomer which has alkoy substituents to improve solubility as well as two nyl bromides for polymerization. Poly(3'-6'-alkoxy-9,9'-spirofluorene-2,7-diyl) and its copolymer were prepared through Ni I mediated polymerization. The photoluminescence (PL) spectra of the homopolymer and copolymer films have been measured with thermal annealing time at 150°C under an argon atmosphere and the development of excimer emission has not been observed. The photoluminescence (PL) spectra also exhibited pure blue light emission. The device performance was...
somewhat law and then we have prepared the copolymer of 4-n-butylphenyl-3(4'-formylphenyl)amine and the above spiroluxilines. The light and hence the device showed about 10 times higher efficiencies than the homopolymer while the CIE coordinate of the emission was almost same to that of the homopolymer. In this presentation, the detailed preparation method of polymer materials and the device characteristics will be discussed.

SESSION L8. MATERIALS
Chair: Christos D. Dimitrakopoulos
Thursday Morning, April 24, 2003
Salon I-3 [Merrill]

8:30 AM L8.1
THE ACES ROAD TO ORGANIC DEVICES. Hieu Duong, Q. Zhang, Hong-Ming, Izma Perepecij, Yang Yang and Fred... Chemistry and Biochemistry and Exotic Materials Institute, UCLA, Los Angeles, CA; Zhenan Bao, Theo Sigrist, Christain Kloc and Cheng-Hsun Chen, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

We will present our latest results of organic semiconductor devices with newly designed and synthesized molecules. These are members of the same family, including heterocenes, containing nitrogen heterocenes to provide stable electron transporting layers. We have synthesized tetrafluorostannic pentacene (substituents: methyl, methoxy, chloro) as well as unusual heterocenes.

9:00 AM L8.2
OLIGOMERIC AND POLYMERIC TRIPLET EMITTERS FOR LEDs. Alberts J. Sande, Nicholas R. Evans, Kay L. Robinson, Andrew B. Holmes, University of Cambridge, Melville Laboratory, Cambridge, UNITED KINGDOM; Anna Koehler, Richard H. Friend, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

In recent years the use of inorganic triplet emitters has raised the possibility of harnessing the full electroluminescence energy in organic light emitting diodes. This paper describes the synthesis and photophysical study of a series of solution-processable polymeric triplet emitters, which are hybrid copolymers based on a bis-cyclopentadienyl iridium(II)pyridylcyclopentadienyl complex (Irppy2) triplet emitter, and 9,9-diarylfluorene, which is the homopolymer. The objective of the study has been to develop efficient phosphorescent materials that are easily solution-processable. This was accomplished by the attachment of successive fluorenyl segments to the 4-position of the ligand of a bis-cyclopentadienyl iridium phosphor. It was shown that the stepwise addition of more fluorenyl repeat units to the phosphor gave rise to a gradual improvement in its performance as the emission layer in an OLED device structure. The polycyclic addition to the phosphor was further extended towards the development of a polyfluorenyl-phosphor hybrid system.

9:15 AM L8.3
NEW CONDUCTED MAIN CHAIN POLYMERIC SEMICONDUCTORS AND THEIR PERFORMANCE IN ORGANIC FIELD EFFECT TRANSISTOR DEVICES. Martin Heeney, Maxim Shkunov, Dave Spierw, Mark Giles, Marcus Thompson, Steve Tierney, Ian McCallum, Merck Chemicals, Chilworth, UNITED KINGDOM.

The performance of the semiconductor component in organic field effect transistors (OFET's), is a key parameter in the advancement of organic electronic devices. New conjugated main chain polymeric semiconductors, have been designed, synthesised and their performance in transistor devices evaluated. The relationship between polymer molecular structure, its corresponding macrostructure and transistor performance will be discussed. Molecular design methodology employed to control the semiconductor morphology, in an attempt to optimise main chain orientation with respect to the transistor channel. The thermal, optical and electrical behaviour of these polymers was characterised to reveal details of morphology, molecular orientation and oxidative stability. Both top and bottom gate transistor structures were fabricated, and device characterisation details will be presented and discussed.

9:30 AM L8.4
PORPHYRINS AS A NEW CLASS OF SOLUTION-PROCESSABLE ORGANIC SEMICONDUCTORS. Shinji Aramaki, Mitsubishi Chemical Corp., Yokohama, JAPAN; Nelson Uno, Ehime University, Dep. of Chemistry, Matsuyama, JAPAN.

Porphyrs have been widely studied because they have unique chemistry and they exist in biological system for special functions, related to its pi-electron system. Here, we report tetraphenylporphyrin can be used as a semiconductor for transistor applications. Furthermore, a thin film semiconductor can be formed with solution process. Soluble precursor compounds with brick layer structure forms a thin film by casting. The obtained film is amorphous and shows good film morphology. Then it is converted into an insulating crystaline semiconductor film quantitatively at elevated temperature of 150-210°C. Field effect transistors were fabricated by this method. FET operation appeared only after conversion of the precursor. Observed mobilities of the devices exceeded 10^3 cm^2/Vs with appropriate process and device structure.

9:45 AM L8.5
CONJUGATED WATER SOLUBLE CHROMOPHORES FOR BIOSENSING TECHNOLOGIES: A PRACTICAL METHOD OF AMPLIFIED DNA DETECTION. Brent S. Gaylord, Alan J. Heeger, and Guillermo C. Bazan, University of California at Santa Barbara, Materials Department, Santa Barbara, CA; Bin Liu, Shu Wang, and Chunhua Fan, University of California at Santa Barbara, Chemistry Department, Santa Barbara, CA.

Conjugated polymers are characterized by a de novo electronic structure and have shown the ability to serve as highly responsive optical reporters for chemical and biological targets. In this work we demonstrate the ability to use the light-harvesting properties of these unique materials for the purpose of highly specific and extremely sensitive DNA detection. Cationic polyfluorene and oligofluorene compounds were used as fluorescent donors in a novel energy transfer assay where signal transfer in aqueous media was controlled by specific electrostatic interactions. The advantage of this system is the capability to amplify the emission of commonly used small molecule dye acceptors which has enabled the detection of lower DNA target concentrations. Comparisons in sensitivity and simplicity will be made to recent DNA detection techniques to highlight some of the advantages of this new method. Experiments were also designed to examine the effect of single DNA base pair mismatches on sensor sensitivity to evaluate the utility of this assay in allele discrimination or in detecting SNPs (Single Nucleotide Polymorphisms).

10:30 AM L8.6
ORGANIC SEMICONDUCTING AND DIELECTRIC MATERIALS FOR PLASICT ELECTRONICS. Zhenan Bao, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Organic electronic materials are now being considered as the active materials in displays, electronic circuits, solar cells, chemical and biological sensors, actuators, lasers, memory elements, and fuel cells. The flexibility of their molecular design and synthesis makes it possible to fine-tune the physical properties and material structure of organic solids to meet the requirements of technologically significant applications. In this talk, the performance of several new organic semiconducting and dielectric materials will be presented. These materials are designed for high performance, low-temperature stability, and ease of fabrication.

11:00 AM L8.7

Polymer brushes have been widely used to tailor surface properties such as wettabillity, biocompatibility, corrosion resistance and friction. The advantage of polymer brushes over other surface modification methods (e.g. self-assembled monolayers) in their mechanical and chemical robustness, coupled with a high degree of synthetic flexibility towards the introduction of a variety of functionality. Ideally, the synthetic method to functional polymer brushes with polymer brushes, and should allow full control over the thickness, density and composition of the polymer films, while at the same time be compatible with substrates that are used in polymeric devices. Surface-initiated polymerization of polymer brushes (or grafting from method) has been very successful in this controlled growth and a variety of polymer brushes has been grown using different “living” polymerization conditions. We have now developed synthetic routes to grow brushes from PI/OT and other polymers. These brushes can be used to alter the surface properties of polymer substrates, but can also carry functional side chains which play an active role in the device. Our initial results on nanowires containing brushes in photovoltaic devices show the polymer brushes are fully compatible with device fabrication. This offers a new level of control over the active components in polymeric devices.

11:15 AM L8.8
A NOVEL STRATEGY FOR THE SOLID PHASE SYNTHESIS OF
ULTRA PURE ORGANIC SEMICONDUCTORS. David Turner and A. Spivey, Sheffield University, Department of Chemistry, UNITED KINGDOM. Domingo Baquero, Reni Aremany, Steve Yeates, Avecia Ltd., Manchester, UNITED KINGDOM

π-Conjugated heterocyclic oligomers are promising candidates for organic semiconductor devices. For their electronic properties, they are critical. Traditional approaches towards for example, regioregular oligo(3-alkylthiophenes) of well-defined length, rely on repetitive transition metal catalyzed cross-coupling of di-functional monomers in solution followed by careful purification of chromatographically similar intermediates after each successive iteration, a process which is time-consuming and inefficient. Recent publications applying solid phase synthesis [SPS] to the preparation of e.g. oligothiophenes demonstrate the route offers an attractive solution to some of the purification issues, however, the ultimate purity of the cleaned oligomer is critically dependent on the yields attained for each individual cross-coupling step. Incomplete cross-coupling results in depletion of the monomer to be substitution. We describe in this work the development of a novel and efficient strategy involving double-coupling, for the iterative solid phase preparation of oligo (3-alkylthiophenes) and other organic semiconductor materials of well-defined length and high purity. The method employs a germanium-based linker and exploits the orthogonal susceptibility of α-silyl and α-thiol substituted thiophene-derivatives towards nucleophilic ipso-protodemetalation. The germanium-based linker also allows for final cleavage by electrochemical ipso-degmerylation. Cleavage with acid will yield α-H terminated oligomers, whereas cleavage with halonium ions will yield α-halo terminated oligomers. Such α-differentiated tetelchic oligomers are valuable substrates for block copolymer preparation and for oligomer end-capping. The method additionally features a novel "backbone-free" Suzuki-type cross-coupling protocol.

11:30 AM #L8.9 HIGH PERFORMANCE p- AND n-CHANNEL POLYMER THIN FILM TRANSISTORS. Simon J. Jenks, Amit Babel, University of Washington, Department of Chemical Engineering and of Chemistry, Seattle, WA.

Availability of both p- and n-type polymer semiconductors having high carrier mobilities will facilitate the fabrication of all-polymer complementary integrated circuits for logic, memory and other plastic electronic applications. Most of the work on polymer thin-film transistors has to date focused on p-type semiconductors due to the scarcity of n-type conjugated polymers with sufficiently high electron affinity and ambient air stability. We are investigating conjugated ladder polymers as high carrier mobility semiconductors for thin film transistor applications. We have fabricated and studied n-channel field effect transistors based on n-type ladder conjugated polymers including poly(phenalennimine:polyphenothiazine). Field-effect mobility of electrons as high as 0.05 to 0.1 cm2/Vs range with on/off current ratios exceeding 100,000 has been observed in thin film transistors fabricated using spin coating. This represents the highest field-effect mobility of electrons yet found in conjugated polymer semiconductors. Atomic force microscopy of the ladder polymer thin films, processed under identical conditions as used for the FET fabrication, reveals nanoscale sheets that are randomly oriented within the film. Our results show that significant improvement in the performance of n-channel field effect transistors can be made by controlling the processing and morphology of this class of n-type conjugated polymers. High performance p-channel thin film transistors have also been achieved in a series of regioregular poly(alkylthiophenes) and their blends with various conjugated polymers, allowing the correlation of carrier mobility with structure and solid state morphology.

SESSION L9: LIGHT-EMITTING DIODES
Chair: Neil C. Greenham
Thursday Afternoon, April 24, 2003
Salon L3 (Marriott)

13:00 PM #L9.1 NANOSTRUCTURED MATERIALS IN ACTIVE ORGANIC DEVICES. Vladimir Bulovic, Electrical Engineering and Computer Science Department, Massachusetts Institute of Technology, Cambridge, MA.

Nanostructure integration of organic and inorganic materials into hybrid optoelectronic structures can enable development of active devices that combine the diversity of organic materials with the high performance and miniaturization and optical properties of inorganic nanocrystals. Optimization of such nanostructured electronic and optoelectronic devices ultimately depends upon the precise positioning of the constituent, functionally distinct nanoscale elements. This talk will describe our recent results of manufacturing through directed self-assembly, emphasizing the need for developing large area nanostructuring processes. Application of these methods to development of organic-inorganic hybrid LEDs and large-area phosphor-polymer light emitting devices will be described. Reproducibility and precision of our recent device work suggests a wide applicability of these new fabrication techniques.

2:00 PM L9.2 TRIPLET EXCIMER FORMATION IN AMORPHOUS THIN FILMS. Brian W. D’Andrade and Stephen R. Forrest, Princeton University, Dept. of Electrical Engineering, Princeton, NJ, Jason Brooks, Alex Alexander, Mark Thompson, Dept. of Chemistry, Univ. of Southern California, Los Angeles, CA.

Phosphorescent excimers have recently attracted attention for their use in white organic light emitting devices, because they can emit over a very broad range, have no absorption and are efficient. Devices made using this technique have recently shown to have a maximum power efficiency of 12% [W/ lm]. A single diode, a platinum[II]2,4,6-difluoro[2,2]pyridinidino-6-[2(1-acetylamino)benzene (mCP) host to efficiently produce white light based on triplet excimer and direct phosphorescence emission. Excimers have a broad spectral linewidth and no optical absorption because they have an unbound ground state [2]. The physics of excimer formation is therefore of much practical and scientific interest. The transient and steady state phospholuminescence and electroluminescence properties of mCP are used to understand the formation of triplet excimers and dimers in amorphous films grown by thermal evaporation. We find that the excimer and dimer have peak emission intensities at 2.07 eV and 1.83 eV, and have lifetimes of 1.69±0.3 ns and (800±80) ns at room temperature, respectively. When films are optically pumped, triplet excitons form on monomers and then diffuse via thermally activated hopping to nearby excimer sites with an activation energy of 374±4 meV. Further, excitation of triplet-aggregate states, or excimer-metal dimers via the association of cations and anions of electrically pumped PTP1 is achieved in an organic light-emitting device, which achieves a maximum external quantum efficiency of 2.4±0.3%.


Highly conductive organic semiconductors are important for many applications, including efficient low-voltage organic light emitting diodes (OLED). Although highly p-conducting materials are available, n-type doping is mostly limited to metallic doping which has major problems. We here present a new approach to stable n-type doping of organic matrices using organic dopants. In order to circumvent stability limitations of strong organic dopants, we produce the donor from a stable precursor compound in situ. As example, the cationic dye pyrrobin B chloride is dopant in 1,4,5,8-naphthalene tetracarbonyl diimidazole (NTCDI) yields conductivities of up to 1.9×10^-4 S/cm, two orders of magnitude higher than the conductivity of NTCDI doped with (bis[ethylenedithio]-tetrathiafulvalene [BEDT-TTF] as investigated previously [A. Nollas et al., J. Appl. Phys. 87, 4840 (2000)] and four orders of magnitude higher than similarly undoped NTCDI films. Field effect measurements are used to prove n-type conduction and to further study the doping effect. Combined FTR, VIS and mass spectrometry suggests the reduction of Pyrrobin B in the doping process. We also show that this doping mechanism can be generalized to other materials.
hydrophobic cores of a hexagonal liquid crystal formed in water by the amphiphilic oligo(ethylene oxide)poly(ethylene oxide) by polymerization. By allowing the monomer liquid crystal to self-assemble on an electrode surface, we can electropolymetrize PEDOT within these nanoscale hydrophobic cores to form conducting polymer films that precisely mimic the morphology and optical anisotropy of the liquid crystal template. Films of PEDOT, prepared in this manner, exhibit linear dichroism over domains hundreds of microns in size. The thickness and orientation of this domain is controlled by the orientation of the liquid crystal template relative to the applied electric field during polymerization. In contrast, otherwise thin films of PEDOT, these templated films are birefringent and exhibit linear dichroism in their optical absorption.

Conductivity and charge injection is improved due to alignment of the PEDOT chains. Organic light emitting diodes (OLEDs) prepared using these templated PEDOT films as hole injection layers display increased luminescence and higher injection efficiency. This approach bridges the gap between conventional lithography and molecular self-assembly by orienting polymers within a nanoscale liquid crystal template. The flexibility of this procedure provides considerable freedom to tailor the properties of these molecules. By controlling the process, precursor monomers can be isolated, oriented, polymerized, and doped in a single step. The molecular alignment locked-in during polymerization results in enhanced performance and novel anisotropic properties in organic electronic devices.

2:45 PM L10.5
HIGH PERFORMANCE ORGANIC DIODES. Liping Wu, Yang Yang.

High performance organic diodes have been fabricated by vacuum deposition method and post-treatment. The as-fabricated diode shows small rectification ratio, but after a proper post-treatment, the rectification ratio of the diodes enhanced tremendously. The rectification ratio of the devices after post-treatment can reach as high as 6 orders in magnitude. Most importantly, the respons speed of the devices to applied AC voltage is tremendously improved to megahertz range.

The current injection of the devices at 1.4 Volt forward voltage bias can reach 100 A/cm². In addition, the devices show high stability. To our knowledge, this device is the first organic diode which is high-speed, air stable (without encapsulation), and can handle high current density.

3:30 PM L10.6
THE USE OPTIL AND PT COMPLEXES TO ACHIEVE HIGH EFFICIENCIES IN MULTICOLOUR AND WHITE ORGANIC LIGHT EMITTING DIODES. Mark Thompson, Vidgin Adamovich, Jacques Brooks, Bert Alleyne, and Peter Djurovic, University of Southern California, Department of Chemistry, Los Angeles, CA; Stephen Forrest, Brian D’Andrade, and Russell Holmes, Princeton University, Department of Electrical Engineering, Princeton, NJ.

We have fabricated monochromatic organic light emitting diodes (OLEDs). These OLEDs can be fabricated in any color, ranging from blue to red. The key advance in our work is to efficiently utilize all of the excitons created in the electroluminescent process, giving OLEDs with efficiencies close to the theoretical limit of 100%. High efficiencies have been achieved by using phosphorescent based emitters, which eliminates inherent 25% upper limit of emission observed for traditional fluorescent based systems. The phosphorescence based OLEDs consist of materials containing organic metallic molecules (i.e. Pt, Ir) inside the metal complex in such systems. The high level of spin orbit coupling in these metal complexes gives efficient intersystem crossing, leading to strong emissive triplet excited states. We have recently demonstrated a unique light emission efficiency for OLEDs, simultaneous from monomer and dimer/eximer states of Ir and Pt dopants. This emission is a spectrum of visible, giving true white illumination. This white light emitting device gives excellent color rendering indices (i.e. 76-85) and high efficiencies (4-8%), 12 Lum/W. I will discuss our most recent advances in both monochromatic and white OLEDs.

4:00 PM L10.7
OPTIMISATION OF CONJUGATED POLYMERS AND PERFORMANCE IN ORGANIC DEVICES. Herman F.M. Schoo, Kornel T. Hoekstra, Jolanda J.A.M. Buitinga, Albert J.M. van Breezen, Ben M.W. Langeveld-Vos, John A.E.H. van Haren, Peter Herwig, Mieke Koeste, Nicole Kijgen, TNO Institute of Industrial Technology and Dutch Polymer Institute, Eindhoven, THE NETHERLANDS.

The performance of semiconductor devices like LEDs, LEC and photovoltaic cells is largely dependent on properties of the organic materials. This paper presents some examples of how properties of polymers, their synthetic route and reaction conditions may lead to differences in purity, chemical composition and defect structures. This can cause different processing behavior, morphology of polymer films and, ultimately, different device performances. Some examples of these relationships.

4:30 PM L10.8
ORIENTED SEMICONDUCTING POLYMER NANORODS. Michael D. Bawendi, Adhila Mehta, Pradeep Komar, Oak Ridge National Laboratory, Division of Chemical Sciences, Jie Zheng, and Robert M. Dickson, Georgia Institute of Technology, Dept. of Chemistry and Biochemistry.

We show that uniformly oriented rod-shaped nanostructures can be formed from isolated single chains of a common semiconductor polymer (MEH-PPV) by inkjet printing techniques. Electron microscopy images between the isolated nanorod particle and the coverage surface results in highly uniform orientation with the long axis perpendicular to the substrate. A combination of emission pattern imaging of fabrication studies and scanning probe microscopies showed that the structural, photophysical, and spectral properties of these materials are dramatically altered with respect to bulk or dilute thin-film preparations. Polarization microscopy measurements show that an extraordinary degree of intramolecular ordering of conjugated segments within individual particles. Spectroscopic studies of individual MEH-PPV nanoparticles show narrow [10 - 15 nm fwhm] emission spectra with a discrete distribution of center frequencies whose peaks can be correlated with excitonic traps of integer multiples of monomer conjugation lengths [8, 9, 10, and 11]. The observation of discrete emission characteristics in this important class of materials suggests exciting possibilities in photonics and molecular optoelectronics.

4:45 PM L10.9

A convenient photolithographic technique is described that provides for an efficient tuning of the emission color(s) of polymer based light emitting devices. The devices possess a single emissive layer based on a blend of conjugated polymers. In this blend, the lower bandgap material(s) contain(s) vinylene units (e.g. PPV), while the lower bandgap material is a derivative of polyfluorene. The photoinduced reaction to reduce the effective conjugation length of the blend’s lower bandgap component(s), the energy transfer efficiency from the higher bandgap component to the lower bandgap component(s) is diminished. In this way dual-color and red-green-blue emitting thin films are realized from a single spin-cast layer, without deteriorating the device characteristics. To achieve a photoinduced transformation of the vinylene units, we employ either hydrazine (H₂N - NH₃) or propylamine (C₃H₇NH₃) as reactive reagents or, alternatively, dodecanedithiol as an additional component in the polymer blend. While in the presence of N₂H₄, a photoinduced reduction preferentially of the vinylene units takes place, with the rest of the device properties maintained. In this context, the application of the “Thioli-Photoreaction” to conjugated polymers containing vinylene units (e.g. PPV) constitutes a novel approach for the phototunable tuning of the electrophoretic properties of the polymer materials. Since this process is compatible with regular film casting techniques, such as spin casting or doctor blading, it is a promising alternative to the more complex, traditional patterning approaches.

SESSION L10 POSTER SESSION
Chair: Christos D. Dimitrakopoulos Thursday Evening, April 23, 2003 8:00 PM

L10.1
IN SITU NANOSCALE OBSERVATION OF TEMPERATURE INDUCED SURFACE MORPHOLOGICAL EVOLUTION OF PBN THIN FILMS FOR DISPLAY APPLICATION. Mingshen Xu a, Jinhua Xu a, Jian An b, Ling He b, and Philip Christiano. aMaterials Science and Research Center, bDept of Physics, The Chinese University of Hong Kong, Shatin, NT, HONG KONG; Harry H.L. Kwok, Dept of Electrical & Computer Engineering, University of Victoria, Victoria, CANADA.

This paper reports an in situ study of N-doped (polymeric-1; 0.5-)N, N-diphenylamine-N'-diphenylamine-N'-phenylenediamine (PPN) film, at a hole transport layer having a glass transition temperature Tg at 95 °C and
generally used in Alq$_3$ based organic light-emitting diodes (OLEDs). The surface morphology evolution of the NPB thin film was visualized by atomic force microscopy (AFM). It was found that the morphology evolution starts at 60°C and proceeds until 150°C, and then the evolution remains stagnant until 250°C. This process is very similar to the characteristics of a glass transition. The surface morphology evolution occurs over a significant temperature range rather than in an abrupt alteration. Crystallization from the glass state swiftly takes place at 155°C, marked unambiguously by the dominant peaks in the micro-Raman spectrum. An unusual phenomenon was seen in the film, gradually melts and degrades, leaving completely the exposed underlying layer. The observation on the initial apparent surface glass transition temperature ($T_g$) provides in remarkable exploration of the present findings that the lifetime and luminance reduction is more than one order of magnitude shorter for OLEDs operated at 60 °C and 120 °C than that operated at room temperature. This is probably due to the fact that a small variation of morphology could be extremely crucial for charge injection and transport of the injected species over the orbital overlap distance of the molecules. The subsequent crystallization may facilitate a complete breakdown of OLEDs. It is suggested that the apparent surface glass transition temperature ($T_g$) be more technically helpful and significant than $T_g$ to gauge the temperature-dependent luminescence and lifetime of OLEDs.

L10.2 PYRIMETHENylene DOPED OPTICAL POLYMERS FOR AMPLIFIERS AND LASERS. M. Ramon, T. Bryden, T.S. Jones and D.D.C. Bradley, Ultrafast Photonics Collaboration, Dept. of Physics & Chemistry, Imperial College, London, UNITED KINGDOM

Polymeric, planar waveguides of pyromethene dyes-doped PMMA were prepared by spin coating (SC) and solution diffusion (SD) methods. Both techniques produce films that, under laser illumination, show strong spectral narrowing due to amplified spontaneous emission (ASE). Samples prepared by SD showed higher gain and lower losses than the SC films. The higher gain is due to the very high concentration used in the solution, while the very smooth surface of SD samples, reduced the scattering and therefore the losses. Ako due to the high concentration, SD samples were much more photostable (more than 100,000 pulses). Time resolved measurements indicate that SD films that show ASE are dominated by aggregates, which are normally thought to have a negative effect on gain. The SD method appears to offer a simple alternative for the production of planar waveguides for amplifier devices. We demonstrate amplification of green light via [ASE] measurements on optically pumped PM65FPMA planar waveguides. We report here studies of gain and loss, time-resolved photoluminescence and tunability of the lasing emission with the thickness of the waveguide.

L10.3 ELECTRICAL CHARACTERISTICS OF VACUUM-DEPOSITED AND SOLUTION PROCESSED DHIT THIN FILM TRANSISTORS. R. Chen, M. Ono, C. Lelik, T. Tsutsui, J.J. Molenkamp, Univ. Würzburg, EPFL, Würzburg, GERMANY; V. Wagner, International University Bremen, Bremen, GERMANY; H.L. Gomes, Universidade de Algare, Faro, PORTUGAL

Organic field-effect transistors (OFETs) show interesting possibilities like cheap processing or application as flexible devices [plastic electronics]. As active layer oligothiophenes e.g. tetrathien (4T) and tetracene and derivatives of interest for their conductivity and µ-electron systems. We present organic field-effect transistors with high mobility. The devices have been fabricated using different deposition techniques: vacuum deposition and solution processing. The mobility depends on several parameters like film thickness and structure, film quality and post treatment. The devices show field-effect mobility up to 10 cm$^2$/V·s. The transistors are fabricated using vacuum deposition and solution processing of OFETs on Si substrates. The former ones show typical LVC characteristics and higher currents. The temperature dependence measurements of drain-source current show significant variations of channel mobility which are very similar to the behaviour of a-GT (sechihinene). While negative gate voltage leads to a bias-stress of the device due to filling of traps in the accumulation layer, positive gate voltage improves the device behaviour. Therefore, the threshold voltage can be adjusted. We also observed a shift to higher negative voltages due to trapping of charges.

L10.4 PREPARATION OF NOVEL MACROSTRUCTURES BY ELECTROPOLYMERIZATION. P.A. Dyda and D.M. Taylor, Institute of Bioelectronics a Molecular Microsystems, University of Wales, Bangor, Gwynedd, UNITED KINGDOM; D. Lacey, Department of Chemistry, University of Hull, Hull, UNITED KINGDOM; C.J. Higgins, Department of Chemistry, University of Hull, Hull, UNITED KINGDOM

Electropolymerization is a powerful technique for electrochemically grafting insoluble, highly stable macroscopic films onto metal surfaces for a wide range of applications including sensors, displays and barrier layers. It is widely accepted that successful electrografting must be preceded by chemisorption of the monomer onto the metal; hence electrogating in the absence of electrogating reported in the literature. According to XPS, UPS and SERS measurements, the affinity of acrylic anhydride for gold, silver and copper differs greatly. It was found that polymeric films to gold while chemisorbing to silver and copper [2], [3]. Following a detailed study of the growing conditions, however, we have successfully electrografted films of polyacrylonitrile onto all three metals. In particular, we have focused on the kinetics of the grafting process and especially on the use of the potential injection method of the voltammogram as an indicator of film growth. A detailed characterisation of the grafted films has been undertaken using Raman microscopy, FTIR spectroscopy and Atomic Force Microscopy. This confirmed the preparation of smooth polymer films (max. roughness \pm 3 nm) with a molecular structure consistent with that expected for an electrografted layer. We are currently developing an in situ technique for monitoring polymer growth in a bid to fully understand the grafting process. In a parallel investigation we are attempting the electrografting of polyacrylonitrile films with [a] hydroxyl and (b) carboxyl moieties which can be used for the specific, chemical functionalisation of the deposited films. [1] Crispin, X. et al. J. Am. Chem. Soc., 1999, 121, 176187 [2] Parent, Ph. Lafon, C. Tourillon, G. J. Phys. Chem., 1999, 95, 5058-5066. [3] Xue, G.; Dong, J.; Zhang, J.; Sim, Y.; Polymer, 1994, 35, 723. [4] Crispin, X. et al., J. Electron Spectrosc. Relat. Phenom, 2001, 121, 57-74.


Conjugated polymers form an interesting class of materials for photovoltaic devices because of their photo-physical and charge transport properties. Polymer containing bulk heterojunction devices can be divided into three classes. Organic/inorganic hybrid cells, such as polymer/TiO$_2$ and polymer/CdSe composites, form one class. Another class may be defined by devices based on the use of polymers with small molecules, as for example blends of conjugated polymers with C$_60$ or perylene-diimide derivatives. The third class consists of two conjugated polymers. Here we report on recent progress on the development of these three types of organic photovoltaic devices with focus on polymer-polymer bulk heterojunction devices. The device characteristics, such as the external quantum efficiency (EQE) and the power conversion efficiency, are strongly related to the processing conditions. For the so-called ‘neat’ active blends of MDMO-PPV with a cyano-PPV derivative, the EQE increases from nearly 10% to 17% upon thermal anneal step. This thermal treatment is effective at temperatures higher than the highest glass transition temperature ($T_g$) of either polymer in the blend. This indicates that the morphology of the photoactive layer is one of the key aspects with respect to the efficiency of the polymer photovoltaic devices. Since for many substituted PPVs, the $T_g$ is close to the maximum operating temperature of the device (-80°C), these findings are also important for the development of stable polymer blend that can be used in practical situations.

L10.6 TETRASE AND 1.55µm QUANTUM DOT ORGANIC LIGHT EMITTING DEVICES. Seth Cee and Vladimir Bulović. Massachusetts Institute of Technology, Department of Electrical Engineering and Computer Science, Cambridge, MA.

We demonstrate efficient, tunable, and narrow-band electroluminescence from ordered inorganic quantum dot (QD) monolayers contacted by molecular organic thin films. The use of monolayers isolates the role of QDs in the LED light-emitting processes from their participation in charge conduction. The fabrication of QD monolayers is enabled by material phase segregation...
between the QD aliphatic capping groups and the aromatic organic materials. This fabrication technique is independent of QD size and material, allowing the change of the structural aspect ratio of the QDs without altering the device fabrication in any way. By varying the thickness of the insulting/passivating QD shell we show that the dominant mechanism for electroluminescence is Förster energy transfer from the organic molecules to the QDs. We have demonstrated color tunability in visible emitting Cs:QD-LEDs, as well as PGE QD-LEDs that emit at 1.55 μm.

L1.0.7 Abstract Withdrawn.

L1.0.8 HIGHLY RESPONSIVE OPTICAL SENSORS USING PYRENE SURFACE MODIFIED ELECTROSPUN MEMBRANES.
Xiuyun Wang, Zhihong Yang, Christopher Drew, and Jayant Kumar.
Center for Advanced Materials, Department of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA; and Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

To date, we have demonstrated that sensors fabricated by electrospinning a fluorophor containing polymer can have 2-3 orders of magnitude higher sensitivities than those from continuous thin films of the same sensing material. The sensitivity of these electrospun sensors was then increased to tens of parts-per-billion detection limits by adsorbing fluorescent conjugated polymers onto the surface of the electrospun nanofiber membrane using electrospraying layer-by-layer self-assembly. Here, we report yet further improvement of the sensitivity, reversibility and ease of fabrication of these sensors, by surface modification of electrospun nanofibers with a pyrene fluorophore. To fabricate the sensors, the fluorophor indicator, pyrenemethyl acid, was covalently attached onto the surface of poly [3-hexylthiophene-2,5-di-carboxylate] electrospun nanofibers membranes. This localization of the fluorescent tag to the surface of an already high surface area nanofiber membrane minimized the amount of inactive (embedded) fluorescent indicator, and resulted in significantly improved sensitivities and reversibility compared to similar systems in which the fluorescent polymer was dispersed throughout the electrospun nanofibers and allows for more direct control over the concentration of fluorophore used. The fluorescence of these films can be quenched by extremely low concentrations of quenching acceptor molecules. The use of these high sensitivity sensors that can be readily manufactured in large scale was demonstrated by monitoring the binding kinetics of a fluorphor using a quartz crystal microbalance.

L1.0.9 METAL OXIDE POLYMER NANOSTRUCTURES.
Christopher Drew, Xiuyun Wang, and Jayant Kumar.
Center for Advanced Materials, Department of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA; and Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

Polymer films with diameters in the range of 50-200 nm were electrospun from polycarbonate and collected as a fibrous membrane. Metal oxide coatings were subsequently applied by immersing the membranes into an aqueous liquid containing the metal-halogen salt and a halogen scavenger at room temperature for a number of hours. Adding multiple metal salts to the coating solution resulted in mixed metal oxide deposition. Coating solution stoichiometry was compared to metal oxide content in the final coating. Metal oxide coatings included titanium dioxide, tin dioxide, and zinc oxides. The coating thicknesses are highly variable. The novel, high surface-area, metal oxide nanostructures may find wide application as sensors, catalytic membranes and electrodes. Combinations of metal oxides result in different electronic band structures from the pure metal oxide, thereby offering the possibility of tuning the band gap for a particular application by stoichiometric control of the deposition solution.

L1.0.10 SELF-ASSEMBLY OPTICAL COMPONENTS.
Pavel Luzhnev, Michael Paskhno, Elena Sidorenko, Optivo, Inc., South San Francisco, CA.

Optivo has developed a unique Thin Crystal Film (TCF) technology enabling breakthrough optical components for a wide range of applications. TCF technology is based on innovative self-assembly methodologies that can be printed and then dry into a highly ordered crystalline film. TCFs are produced by deposition of water based isotropic liquid crystal formed by rod-like supramolecules of heterocyclic sulfonic acids. The supramolecules having a common structural unit, an aspect ratio of 1, form down to layers of order 10 nanometers thick. While drying, the layer crystallizes to a sub-micron thick semi-crystalline thin film functional layer with dichroic dye molecules aligned over the entire coated surface. The coatings exhibit properties of birefringent film polarizer. The thin anisotropy of reflection and absorption indices make TCFs attractive for LCD and OLED related applications. This presentation will provide an overview of TCF technology and will describe material structure, optical properties and characteristic, material processing and associated coating equipment.

L1.0.11 CONDUCTING POLYMERS BASED SUPERMOLECULAR FILMS FOR GAS SENSORS.
Macej Kumar Ram, Oles Duvvuru, Matt Aldiaski, Fractal Systems Inc., Safety Harbor, FL.

Gas sensors based on metal oxide sensing layers, and in particular SnO2 and WO3, are known to be widely used for the measurement of CO, CO2, aromatic hydrocarbon, NO2, but sensors do not primarily exhibit selectivity towards any of these species in general, and operates at a high temperature. Though a certain degree of selectivity is obtained by forming arrays of sensors but still lack selectivity at ambient humidity. To overcome stability, selectivity, portability and cost problems, we have initiated to develop gas sensors based on ordered ultrathin conducting polymers and nanocomposite films that the above problems can be proved to perform efficiently and selectively within seconds of exposure to gases. The present work focuses on the use of highly organized conducting polymer films with high conductivity, and for ultrathin films of conducting polymer/SnO2 nanoparticles composites, which will selectively recognize CO2 and NO2 gases with high sensitivity. The supramolecular approach will be utilized to fabricate films of conducting materials in the layer-by-layer self-assembly technique to emphasize sensitivity and selectivity issues that are otherwise unattainable with other fabrication methods or micronic. We have prepared and characterized several polymers, fabricated thin self-assembled films with different layer thickness in each of these in order to the study the effect of the number of layers on film properties relative to gas sensing. We have used several characterization techniques to prove feasibility of our approach, including conductivity, impedance, UV-Visible, FTIR, AFM and elemental analysis. With the expected high selectivity and low detection limit and versatility of the measurement procedure, our work will result into a miniaturized device.

L1.10 INFLUENCE OF LOCAL ORDER AND MOLECULAR DIPOLE STRENGTH ON THE DIRECTION OF EXCITON ENERGY IN ORGANIC THIN FILMS.
Cesar Mediguez, Vladimir Balaevich, Massachusetts Institute of Technology, Department of Electrical Engineering and Computer Science, Cambridge, MA.

It has been proposed that order in organic thin films should lead to dispersion of the molecular energy levels. We recently reported the direct measurement of this dispersion in excitonic energy levels for [3-methyl-6-[3,23,6,7-tetrahydro-1H,1H-benzof][1,3]quinoxalin-3-yl-ethyl]-4-hydroxy-4-ethylidene] propene-sulfonitrile (IP-CN), deposited in films of about 200 nm thick with low levels in organic thin film materials exists in the literature. In this presentation we apply our technique to a range of technologically important photoluminescent organic materials including [4-tert-butyl-1,1'-biphenyl]-4,4'-diamine (α-NPD), and N,N'-diphenyl-N,N'-bis[1-naphthyl]-1,1'-biphenyl-4,4'-diamine (TPD) to study the influence of molecular properties and molecular packing on solid state exciton energy distributions. We find that the two most important material parameters are the local ordering of molecules and the strength of the molecular electric dipole (i.e. the molecule’s polarity). Our data show that increasing local order decreases w_DOS, while increasing polarity increases w_DOS. Since highly polar molecules have a tendency to aggregate (and thereby locally order), some highly polar molecules can also yield films with small w_DOS. However, for non-polar molecules, we have found that w_DOS is negligible regardless of the degree of local order.
L10.13 CHARGE INJECTION IN DOPED ORGANIC SEMICONDUCTORS. Yulong Shen, Mei Hui Yang, and George G. Malliaras, Department of Materials Science & Engineering, Cornell University, Ithaca, NY; Bing Hsieh, Xerox Corporation; David Donahue, Department of Physics and Astronomy, University of New Mexico.

A study is done to understand the dependence of injection on the degree of doping of an organic semiconductor. A model organic semiconductor whose molecular structure is composed of methyl triphenylamine doped polycarbonate (PTCMA) was used for these experiments. By substituting the PTCMA molecules with a PTCMA-4-SF6 salt, the degree of doping in the organic semiconductor was systematically varied. Changes in the electrical characteristics of various devices with different concentrations of doped molecules were analyzed to yield the dependence of injection on the degree of doping. With increasing dopant concentration the temperature and distance between electrodes were varied. This provided a better understanding of how doping, temperature and electrode spacing affect device performance.

L10.14 PHOTOELECTRO OPTIC AND THEORETICAL STUDIES OF THE FRONTIER MOLECULAR ORBITALS OF QUINQUETHIOPHENE DERIVATIVES. Gary P. Kusko, Ian G. Hill, and Zakyan H. Hafifi, U.S. Naval Research Laboratory, Washington, DC; Ulrich Menzebier and Peter Blume, University Ulm, Ulm, GERMANY.

A thiophene oligomer represents a class of materials whose electronic properties can be tuned through control of the -conjugation length, side or main chain derivatization. The effect of substitution of the central thiophene ring by a furan, an oxazole or quinoline on the electronic properties of a series of quinque thiophene oligothiophenes is investigated using ultraviolet (UV) and x-ray (XPS) photoionization spectroscopies. ab initio and semiempirical calculations have been carried out to aid in the characterization of the electronic properties of these materials. These quinque thiophene derivatives are highly luminescent when dispersed in organic hosts. When incorporated as the active emissive layer in molecular organic light emitting devices (MOLEDs) they exhibit interesting carrier trapping effects as well. The results of the photoemission spectroscopic and ab initio studies conducted on these thiophene derivatives will be reported, and their relevance to the operational characteristics of MOLEDs based on them will be discussed.

L10.15 Abstract Withdrawn.

L10.16 ELECTRONIC PROPERTIES AND DEVICE APPLICATIONS OF CRYSTAL-ENGINEERED ACENES. John Anthony, Chai Landa, Marcia Payne, Susan Okain, University of Kentucky, Department of Chemistry, Lexington, KY.

The solid-state electronic properties of acenes such as pentacene have led to their successful use in numerous electronic devices. The demonstration that crystalline order in thin films was directly linked to improved device performance led us to investigate synthetically-modified acenes, in order to determine the effect of this functionalization on device performance. We have demonstrated that selective functionalization of acenes with simple, alkyney-containing groups leads to improved solubility and increased oxidative stability. By careful selection of substituents, the arrangement of the acenes in the solid state can be controlled to increase both the extent and dimensionality of pi-stacking between the aromatic units. Increasing pi-stacking leads to a significant increase in conductivity, and decrease in band-gap along the pi-stacking axis to well below 1 eV. Using a different set of substituents, pi-stacking in the solid can be totally eliminated, leading to the acene units being solvated in a crystalline shell of saturated hydrocarbon. The elimination of pi-stacking leads to highly fluorescent solids. The maintenance of crystalline order in evaporated thin films yields electroactive devices with greatly increased efficiencies compared with the pi-stacking unsubstituted acenes. Fine-tuning of the pi-stacking allows us to subtly alter the color of electroluminescence while maintaining essentially the same chromophore. Recent approaches to the synthesis and characterization of crystalline-derivatized higher acenes such as heptacene will also be presented.

L10.17 PHOTOEFFECT IN ORGANIC POLYMER THIN-FILM TRANSISTORS. Michael C. Hamilton, Sanderine Martin, and Jerry Kanicki, University of Michigan, Department of Electrical Engineering and Computer Science, Ann Arbor, MI.

We have investigated the response of our organic polymer thin-film transistors (OP-TFTs) to illumination. The structure of the device is an inverted, gate-illuminated, coplanar thin-film transistor. Indium tin oxide (ITO) was used for the source and drain contacts and the polyimide silicon nitride was used for the gate insulator. The organic semiconductor F8BT [poly(9,9-dioctylfluorene-co-bithiophene)] was deposited by spin-coating. These devices exhibit p-type field-effect transistor behavior. Typical values of the linear regime field-effect mobility, threshold voltage, and subthreshold slope parameter for these devices in the dark are 2×10⁻² cm²/Vs, -15 V, and 2.5 V/decade respectively. The devices were illuminated from the back with white light, and measured under dark. The characteristics of our devices in the dark and under various levels of illumination at room temperature. The device OFF-current is increased significantly under illumination, while the ON-current is not significantly affected. The ratio of drain current under illumination to drain current in the dark can be defined as R/IO = IT on/IT off and is a function of the OP-TFT gate voltage (VGS) and the illumination (I). In the strong accumulation regime, R/IO decreases because of the gate voltage dependence of the concentration of accumulated carriers. In the OFF-state, R/IO can reach two to three orders of magnitude depending on the level of illumination, and is not strongly dependent on VGS. R/IO exhibits a power law dependence on the illumination level, increased with the channel width of the device and decreases with the channel length. The timescale for the device to respond to the illumination is approximately 10s at room temperature, while the timescale for the device to return to the original state, after the illumination is removed, is approximately one hour at room temperature in the dark.

L10.18 ELECTRO-OPTICAL PROPERTIES AND INTERFACIAL CHARGES IN POLYMER-DISPERSED LIQUID CRYSTAL DEVICES. R.A. Ramsay, S.C. Sharma, R.M. Henry, and J.B. Attno, Department of Physics, University of Texas at Arlington, Arlington, TX.

Polymer-dispersed liquid crystal (PDLC) is a composite material that consists of sub-micron-size droplets of liquid crystal (LC) material dispersed in a polymer matrix. A device is usually assembled by sandwiching PDLC between ITO-coated glass plates. The electro-optical properties of such a device can be controlled by the application of electric fields, the device acts as a modulator for the transmission of light. The transmission of light through the device can be controlled between almost zero and 100% by applying electric fields. The dielectric properties of the LC and polymer, shape and size distribution of the LC droplets in the PDLC, amplitude and frequency of the applied electric field are among the important parameters for optimizing the performance of such a device. We have investigated the optical properties of PDLC devices fabricated by using several different phase-separation techniques and different LC/polymer materials. We present results for the switching characteristics of these devices as functions of applied electric fields and the size distribution of the LC droplets. We also present results that reinforce the influence of the interfacial charges on the optical properties of the PDLC devices. Research supported in part by the Texas Advanced Technology Program under Grant No. 003656-0123-2001.

L10.19 IMPROVING INTERFACES AND SEMICONDUCTOR MATERIALS FOR OFETs: AN INVESTIGATION OF NOVEL PHENYL CYANECENE MOLECULES AND SURFACE MODIFICATION. Carrie L. Duncan, Rebecca A.P. Zangemeister, Wei Xin, Anthony S. Dinger, Britt Mink, David P. O'Brien, Neal R. Armstrong, University of Arizona, Department of Chemistry, Tucson, AZ.

New organic field effect transistor (OFET) and photovoltaic (PV) technologies will require easily processed materials which demonstrate high charge mobilities and mobilities in those materials (OFET applications), properties which have been achieved only from high order molecular and inorganic materials. We have studied a series of octasubstituted phthalocyanines (Pcs) with a benzyl termination of the side chains linked to the Pcs, with either an oxygen or sulfur atom. The benzyl termination imparts unique stability and coherence to films of these molecules on a Lingmaid Bledgett smooth film. Films of these materials are transferred to substrates by a horizontal transfer technique, and it has been shown that surface modifications are critical in obtaining well ordered films. We have measured charge mobilities in these thin films on two length scales using interdigitated microelectrodes and a tunnelling AFM (TUNA) system. Currents measured by the TUNA system were taken on a 100 nm scale, and the charge mobilities greater than 0.1 cm²/Vs at 10⁻³, and mobilities in mobility of up to 10⁶ for benzothieneylalkylbenzophenene. The tilted version of this material has also been characterized, and it seems to show different properties in thin films than the tilted PV. This material has been incorporated into some PV cells, and the characteristics of these devices will be reported briefly here and in complete detail in an.
accompanying paper for this symposium. We have also investigated a polymerizable PC which contains a styryl functionality in the side chains of the epoxides. A photopolymerization unit and a polymerizable ester allow us to lock the molecules into place, and renders this molecule insuble allowing for photopatterning of thin films of this material. Molecules for this polymerized material on interdigitated microelectrodes were higher than for the benthoylenolate parent molecule.

L10.20 FORMING ORIENTED ORGANIC CRYSTAL NEEDLES BY SOLVENT VAPOR ANNEALING OF AMORPHOUS THIN FILMS ON NANO-PATTERNED SUBSTRATES. Debra J. Mascare, Jeremiy Z. Zermain, Henry J. Smith, Vladimir Bulovic, Laboratory of Organic Optics and Electronics, Electrical Engineering Department, Massachusetts Institute of Technology, Cambridge, MA.

We use solvent vapor annealing to facilitate molecular reorganization in thin films of organic small molecules. In the case of tria-(8-hydroxyquinoline) aluminum (Alq), this reorganization is dramatic, yielding needle-like crystals in the plane of the substrate from initially amorphous thin films. Furthermore, we demonstrate that nano-patterned substrates can control the orientation of the needle crystals, which can reach millimeters in length. The formation of such large area crystals directly on a substrate facilitates electrical characterization and device fabrication. Using optical interference lithography we generate periodic patterns over square centimeters with feature sizes ranging from 100 to 500 nm. The patterns are transferred to silicon substrates using etching, resulting in surface relief gratings with periods of 100 to 150 nm, Alq is vacuum deposited onto the nano-gratings, and the films are subsequently annealed in chloroform vapor. The resulting Alq needles lie in the plane of the substrate and are aligned along the grating direction. Larger needles span several grating periods, but needles confined to a single grating trough are also observed. Needle thicknesses exceed the initial Alq amorphous film thickness by as much as 200 times and the grating depth by as much as 30 times. Typical width thickness ratios are 1:2:1 and a common needle thickness is 500 nm. Needle thicknesses and segment to split and branch, but can be as long as several millimeters. Characterization by AFM and STM reveals terraces and facets at needle surfaces and tips. We have obtained fluorescence spectra of the Alq crystals and observed waveguiding down the length of the needles indicating optically smooth crystal facets in agreement with AFM data. We will report the influence of initial amorphous film thickness, annealing time, nano-grating dimensions and chemical surface modifications on needle formation, and discuss the utility of the needle crystals in active device structures.

L10.21 INVESTIGATION OF SPUTTERING DAMAGE EFFECTS IN ALQ-BASED TOLEDS BY XPS. Ayse Turak, Sijin Han, Daniel Grez, Zongsheng Lu, University of Toronto, Department of Materials Science and Engineering, Toronto, ON, CANADA.

Cathode deposition is a crucial issue for top-emitting OLEDs, due to the induced damage to the underlying organic layers caused by sputtering techniques. The critical effect on device performance and reliability of the sputter damage to the organic layer is well known. Efficient and stable TOLEDS have been produced by the insertion of buffering layers beneath the sputter deposited cathode. The efficacy of the buffering layers has been shown using x-ray photoelectron spectroscopy (XPS) characterization of the cathode/organic interface was undertaken on working OLED devices with varying buffer thickness. Using a previously developed in-situ photoemission technique, the XPS study allowed a direct comparison between observed electrical performance degradation and molecular breakdown at the interfacial limits to the XPS technique. Sputtering damage was determined though correlation of the observed Ns splitting, indicating molecular breakdown, with the reduction in device electrical performance.

L10.22 PURE INFRARED ELECTROLUMINESCENCE FROM CONJUGATED POLYMER HOST/GUEST BLENDS. Matthew R. Balas and Guillermo C. Hauss, Alan J. Heeger, Jack C. Oxtowski, UC Santa Barbara, Department of Materials, Chemistry, Physics, Michael J. Thoren, Kimihito Saito, University of Pennsylvania, Dept of Chemistry, Philadelphia, PA.

Pure near-infrared electroluminescence (no residual visible emission) from a number of conjugated polymer host/guest blends has been realized. The color of the polymer host includes blue, green, and red emitters. The guest molecules include novel infrared-emitting lanthanide complexes and conjugated oligophosphonato zinc molecules. The first system makes use of a novel erbium complex doped into a stable green emitting conjugated polymer host. The ligand incorporates a pentafluorophenyl unit and a metal to the metal center via a beta diketone functionality - necessary for efficient energy transfer to the [infrared] atomic transition. The phosphonatoevident ligands - also designed to the ligand and phosphonatoevident - are not observed. OLED devices made entirely of this complex [without the guest] will also be discussed. A second system of conjugated oligophosphonato zinc molecules doped in both PKVPBD and MEH-PPV (separate experiments) in order to demonstrate the versatility of these dopant materials afforded by their broad absorption spanning the visible region. Emission entirely in the near-IR is observed which is tunable by increasing the conjugation length by adding additional monomers. Although the photoluminescence quantum yield of these materials is less than 0.08, electroluminescence efficiencies up to 0.81% are realized.

L10.23 ALIGNMENT OF END-GRAFTED ALPHA-HELICAL POLYPEPTIDES. Yuli Wang, Ying-Chi Cheng, Department of Chemical Engineering and Materials Science, University of California, Irvine, CA.

Surface tethered aliphatic poly(ethylene glycol) [OPEG] films demonstrate excellent liquid crystalline, electrooptical, and electronic properties due to the non-conceivable dipole moment attributed to individual helical rods. The results here have indicated that such systems consist of randomly distributed molecular rods with average tilt angle of 33-65 deg from the normal surface. It is believed that a unidirectional molecular arrangement would be more desirable to produce not only the highest net dipole but also the organized functional groups at a nanoscale. Here we report a simple quenching method to align PBLG helical rods along the normal direction. In this method, a highly oriented tethered PBLG film was prepared by first immersing a good solvent such as N,N-dimethylformamide, followed by a poor solvent such as water. In a good solvent, the tethered chains are fully stretched to maximize the molecular-solvent interactions; subsequently, a poor solvent was quickly introduced to preserve the fully stretched surface morphology. The resulting FTIR studies indicate that the proposed method successfully erect the helical rods with the resulting average tilt angle of 33 deg from the normal. The change of tilt angle coincide with the increase of overall film thickness from 25 nm to 100 nm (127 deg) detected by ellipsometry. Atomic force microscopic images of the films further confirmed the thickness measurements. In addition, revealing that the surface morphology changes from a relatively smooth and amorphous topography to a periodic pyramidal structures after quenching. The quenched surface contains lower surface energy as evidenced by the increase of water contact angle from 105 deg to 110 deg. The molecular orientation of the tethered films was found to be very stable for months. In summary, this quenching method might offer a simple methodology applicable to creating other highly oriented polymer surfaces.

L10.24 Abstract Withdrawn.

L10.25 SHORT CHANNEL AND CONTACT EFFECTS IN HIGH MOBILITY REGIOREGULAR POLY(THIOPHENE). Michael I. Chabinyc, Alberto Salleo, Robert A. Street, Polo Alto Research Center, Electronic Materials Lab, Polo Alto, CA, Beng Or, Yiying Wu, Xerox Research Center of Canada, Mississauga, ON, CANADA.

Simple measurements of linear or saturation mobility in polymer transistors can often be misleading because of non-Ideal TTF characteristics. The complete current-voltage characteristics of polymeric thin film transistors (TFTs) must be evaluated to understand the physical mechanisms of electronic transport and to obtain the mobility. We have investigated the effects of device geometry on the performance of TTFs fabricated with a regioregular poly(thiophene), [PT]. For example, the apparent field-effect mobility of a PT film can vary from 0.1 to 10 cm2/Vs depending on the device size and contact geometry. We have tested the contact effects by fabricating TFTs with both staggered and coplanar contact geometries in a single device, allowing contact resistance differences to be measured by reversing the device polarity. We also observed the dependence of the extracted saturation mobility on source-drain voltage. The apparent saturation mobility of these PT films can be as high as 0.7 cm2/Vs with high drain voltages in short channel devices. Measurements of output characteristics at channel lengths from 5 to 50 μm confirm the short channel effect. We discuss
the evidence for an actual drain-field dependent mobility based on a model for the short channel effects. The implications of these results for characterization of the intrinsic properties of polymeric semiconductors will be discussed.

L10.20
POLARIZED ELECTROLUMINESCENCE FROM LIGHT EMITTING DIODES CREATED BY SELF ASSEMBLY AND ELECTROPOLARITY. Leiming Li, Keisuke Tujun, John C. Stendahl, Eugene Z. Zubarev, and Samuel I. Stupp, Department of Materials Science and Engineering, Feinberg School of Medicine, Northwestern University, Evanston, IL. Our laboratory developed self-assembling trilobal molecules known as dendron rods or dendrons that contain long amphiphilic-like segments. In certain solvents such as chloroform or 2ethoxyethyl methacrylate these molecules self assemble in long nanorods. These nanorods can have widths of about 10 nanometers, a thickness in the range of 2 nanometers and lengths on the order of microns. Their formation leads to the three dimensional network and therefore gelation of dilute solutions of these molecules. We have found that electrophoresis occurs in DRC gels subject to a DC electric field, creating solid films consisting of DRC nanorods oriented preferentially along the poling direction. We have also dissolved small molecules containing conjugated phenylene vinylene segments in DRC gels and exposed these systems to DC electric fields. This process leads to thin films of unidirectionally oriented DRC nanorods and luminescent phenylene vinylene molecules. Light emitting diodes (LEDs) were fabricated by sandwiching the films between ITO and aluminum electrodes. Interestingly, we found that electroluminescence from these LEDs is anisotropic, with a parallel EL component (parallel to the poling direction) stronger than that perpendicular to the electric field. EL was found to be isotropic from LEDs containing spincoated films using the same molecular components.

L10.27
STRUCTURAL CHARACTERIZATION OF ROD-LIKE AGGREGATE LIQUID-CRYSTALLINE PHthalOYCNINE FILMS BY X-RAY REFLECTIVITY AND DIFFRACTION Xi Wu, Michael D. Carducci, Carrie L. Donley, and Neal R. Armstrong, University of Arizona, Department of Chemistry, Tucson, AZ. Certain phthalocyanines (Pc) modified with benzylterminated ethyleneoxide side chains, and their thio-oxo-counterparts self-organize into rod-like columnar aggregates with a high degree of optical and electrical anisotropy. This paper focuses on the characterization of horizontally transferred LB films of these PCs, using AFM and specular X-ray reflectivity, starting with a single bilayer of Pc columns (ca. 5.6 nm thickness) on Si(100) substrates. For multilayer films, which have been unannealed, the width and position of the Bragg peak in the X-ray reflectivity data are consistent with a dense, regular, hexagonal close packed adjacent rods. For 1- and 2-bilayer films, however, there are shifts in the Bragg peaks, and associated changes in the density and layer density variations, as a function of the stacking structure for those molecules closest to the Si(100) oxide surface. Chemical modification of these interfaces helps to control the initial ordering in these films. Understanding of this interfacial structure is critical in determining whether the electronic properties of these initially deposited materials (e.g. in organic field-effect transistors).

L10.28
CHARACTERIZATION OF HIGH-PERFORMANCE \(F_2O_4CuPc\)-BASED ORGANIC THIN-FILM TRANSISTORS WITH ALKALI FLUORIDE-MODIFIED ELECTRODES. J. Reynen, Y.D. Jin, G. Borghs, R. Mertens, P. Hermans, IMEC, Leuven, BELGIUM. Phthalocyanines have been extensively studied among organic semiconductors for their photovoltaic properties [1]. Copper(I)perfluorothalocyanine(\(F_2O_4CuPc\)) is an airstable material with high mobility [2]. We optimized the deposition properties of copper(I)perfluorothalocyanine(\(F_2O_4CuPc\)-based) n-channel organic thin-film transistors (OTFTs). We achieve high mobilities of the order of 10^{-2} cm^2/Vs when using intensified purified material and optimized growth conditions of the organic films. We fabricated transistor structures on a conventional silicon substrate with different source/substrate electrodes: bare aluminum, gold, LiF/Al and LiF/Au. We deduce the electron injection properties of these different materials into \(F_2O_4CuPc\) from the electrical performance of these transistors. In contradiction to [3], we report well-behaved field-effect and high mobilities (\(10^{-2} cm^2/Vs\)) for n-channel \(F_2O_4CuPc\)-OTFTs with bare Al and Au electrodes. Furthermore, we correlate these results to the shape of electron absorption measurements on the PEDOT:PF6 structure, which allow to measure the electron injection barrier at the organic/metal interface [4]. [1] D. Währle, K. Kreinerop, D. Schlettwein, Phthalocyanines 219, VCH Publishers (1986). [2] Z. Xue, A. J. Leivo, J. Brown, J. Am. Chem. Soc. 120, 207 (1998). [3] S. Hosono, S. Katayama, M. Chikamatsu, M. Mani, Y. Yoshida, N. Watanabe, K. Yase, Jpn. J. Appl. Phys. 31, L114-117 (1992). [4] P.A. Lime, J. Roat aliki, C. Giebel, S. Martin, D.C.C. Bradley, D. Meissner, Sol. Energy Materials & Solar Cells 63, 8 (2000).

L10.29

The performance of organic light emitting devices (OLEDs) and organic solar cells (OSC) can be improved by inserting an ultrathin interfacial layer of LiF between the polymer and the air stable cathode [1,2]. Electro-absorption measures the built-in potential (\(V_B\)) across the photo-active organic film within OLEDs and OSCs. In OLEDs based on PMMA, we found that \(V_B\) increases from 0.15 eV when LiF is inserted between the polymer and the Al cathode. The change in built-in potential is attributed to LiF being liberated from LiF in the presence of Al and diffusing into the polymer. Li serves as a dopant for the polymer at the interface and hence facilitates the formation of an Ohmic contact at the cathode/polymer interface [3]. The solar cells consist of a blend of c60-derivative (PCBM) and MDMO-PPV polymer. \(V_B\) increases by 0.6 eV upon insertion of a LiF interfacial layer between the blend and the Al cathode. Because of the presence of PCBM, Fermi-level pinning is occurring [4]. This is confirmed by electro-absorption characterization of pristine PCBM devices.


L10.30

Optical properties of organic dye molecules incorporated in inorganic matrix materials by high vacuum co-evaporation are reported. The aim of this work is to create a system which is applicable in luminescence conversion devices as a thin layer. The dry vacuum technology offers a fundamental progress in the practical handling and technical expenditure. Furthermore, organic dyes principally allow a big freedom of choice both in the molar concentration and in the emission band parameters for the breakthrough of solid state organic systems are the quantum efficiency and the photostability. Our results show that such systems can meet the requirements of practical applications. We present results about (i) different dye molecules, (ii) different dye materials (SiO2, TiO2) and (iii) the influence of different preparation techniques on the optical properties. Compared to earlier investigations, relatively high dye concentrations can be reached without loss of quantum efficiency by varying the preparation technique. This behavior results in highly absorbent layers even at low thickness.

L10.31
PHOTO- AND ELECTROLUMINESCENT PROPERTIES OF RANDOM AND STRUCTURALLY DEFINED COPOLYMERS BASED ON POLY(FLUORENE-CO-BENZOTHIADIAZOLE). Polly Hegarty, Xiaoxiong Jiang, Michelle S. Lee, Alex T. J. Jen, University of Washington, Department of Materials Science and Engineering, Seattle, WA.

Copolymers based on fluorene and benzothiadiazole exhibit high brightness and quantum efficiencies when incorporated into polymer light-emitting diodes (PLEDs). The emission wavelength is strongly determined by the benzothiadiazole-conjugating portion of the polymer. In order to understand the underlying mechanisms of charge transfer and energy transfer, a series of polymers with different fluorene/benzothiadiazole ratios were made. Even a fraction of as low as 10% of benzothiadiazole shifts the emission of the polymer from blue to yellowish green. The low quantum efficiency of benzothiadiazole required for wavelength tuning leaves room to tune other properties necessary for device development. The charge transport properties can be altered by incorporating a third component structure. Polymers incorporating fluorene, benzothiadiazole and a third component - e.g.
diakoxyphenyl) were synthesized. In a random copolymerization the order of monomers in the structure cannot be predicted. In order to investigate the chemical reaction of monomer segment and copolymer device properties, we have synthesized a series of copolymers with structures of known sequence. A third monomer was chosen from a variety of electron-rich molecules. The properties of the structurally defined copolymer were compared to the properties of the random copolymerized ones with the same monomer ratios. In order to evaluate the device performance of these copolymers, double-layer devices with the general structure of ITO/HTL/Polymer/ITO/Ag were fabricated. The results show that the monomer sequence in the polymer chain does not affect the electro- and photo-luminescent properties of the copolymers, but the device performance is strongly dependent on the sequence.

L 1.0.32
ORGANIC POLYMER DEVICES BASED ON SUPER-YELLOW POLYMERS J Komak, M. Pashour and A. Heeger, Center for Polymer and Organic Solids University of California, Santa Barbara, Santa Barbara, CA; S. Martin and Y. Hong, University of Michigan, Department of Electrical Engineering and Computer Science, Solid-State Electronics Laboratory, Ann Arbor, MI.

We have investigated electrical properties of the organic polymer thin-film transistors (OP-FTTs) based on phenyl-substituted PPVs (known as super-yellow polymer). This organic polymer is also being widely used for organic polymer light-emitting devices (PLEDs). The structure of the OP-FTT is an inverted co-planar thin-film transistor with indium tin oxide (ITO) as gate, amorphous silicon nitride for the gate insulation layer, an organic semiconductor (super-yellow polymer) deposited by spin-coating over the source drain contacts and device was fabricated having a channel length, width from 96 to 960μm and 56 to 116μm, respectively. Electrical performance of these devices were extracted using the MOSFET equations. We typically obtained for our devices the field-effect mobility, threshold voltage, sub-threshold slope and ON/OFF current ratio of about 2x10−5 cm2/Vs, 45 V, and 6 V/dec, respectively. Similar results have been obtained for Dow Chemical red and green light-emitting organic polymers that have been previously described. We also found that the field-effect mobility and threshold voltage were channel length independent. To investigate the possibility of fully integrated opto-electronic organic circuits made from the super-yellow polymer and at the same time, we have fabricated the organic polymer light-emitting devices (PLEDs) from the same material. The PLED has high brightness of ~1,500 cd/m2 at 8V, a high emission efficiency ~5 cd/A at 900 cd/m2 and a good power efficiency ~2 lm/W at 900 cd/m2. Based on our results we can argue that the best PLED materials will not necessarily produce the best OP-FTTs. The implications of these findings for opto-electronic organic circuits will be discussed.

L 1.0.33
CREATION OF A GRADIENT POLYMER-FULLERENE INTERFACE IN PHOTOVOLTAIC DEVICES BY THE MOLDING OF A SOLUTION IN A DETERGENT M. Dres, W. Graupner, K. Premnaran, J.R. Hehn, Dep of Physics, Virginia Tech, Blacksburg, VA; D. Topman, M. Miller, Luna Innovations, Blacksburg, VA; R.M. Dweis, Dep of Chemical Engineering, Virginia Tech, Blacksburg, VA.

Efficient polymer-fullerene photovoltaic devices require close proximity of the two components to ensure photocreated electron transfer from the semiconducting polymer to the fullerene acceptor. We describe studies in which a bilayer system consisting of spin-cast 3-hexylthiophene (HT)/sublimed C60 is heated above the HT/C60 glass transition temperature in an inert environment, inducing an interdiffusion of the polymer and the fullerene layers. With this process, a controlled, bulk junction heterojunction is created bringing the fullerene molecules within the exciton diffusion radius of the HT/C60 throughout the film to achieve highly efficient charge separation. The interdiffused devices show a dramatic decrease in photoluminescence and concomitant order-of-magnitude increase in short circuit currents, demonstrating the improved interface. We also observe the spectral photocurrent of the HT/C60 bilayer system, matched to the short optical penetration depth at the peak of the PPV absorbance, is eliminated following the interdiffusion process. Detailed studies of the effects of the interdiffusion on device performance have become attractive for low-cost light-emitting applications, have become attractive for low-cost light-emitting applications, and also have implications for the use of these materials in photovoltaic devices.
Europium complexes may be used as a source of red emission in light emitting diodes (OLED), and several novel europium cored complexes have been synthesized and incorporated into organic OLED's. These complexes are of interest due to their narrow (FWHM =5 nm) emission at 615 nm, which is ideal for red OLED devices. The europium complexes consist of one equivalent of europium chelated to three equivalents of a non-linear tridentate diketonato ligand. The ligands are created by the Chassignon condensation of a polyyclic aromatic amine and a fluorinated alky ester of a carboxylic acid. The use of a sensitizer such as phenanthrene results in a ligand that has an emission band that directly overlaps with the absorption band of europium. The use of fluorinated chains improves the overall processability as well as the charge transfer capability of the resulting metal cored complexes. The europium core is further encapsulated by the inclusion of an additional polyyclic aromatic compound such as 4,7-diphenyl-1,10-phenanthroline. Emission of 615 nm light is accomplished through excitation of the ligand cage and efficient Förster energy transfer from the ligands to the europium complex.

**L10.37**
HIGH EFFICIENCY POLYMER LIGHT EMITTING DIODES.
Milena Kreger, Sue Carter, Physics Dept., University of California, Santa Cruz, CA, Louis Barzana, Campbell Scott, IBM Almaden Research Center, San Jose, CA.

We report the results of our research on polymer light-emitting diodes (PLEDs) with electroluminescence or poly-p-phenylenevinylene emissive layers. PLEDs have been fabricated with a device architecture using indium-tin-oxide (ITO) as anode, PEDOT-PPS as hole transport layer and Ca as cathode. We have examined how variations in the thickness and annealing conditions of the electroluminescent layer affect device performance. Significant spectral shifts and variations in efficiency are observed as the thickness of the EL layer changes. In addition, device efficiency depends critically on the annealing temperature and whether annealing is carried out in a nitrogen atmosphere. For optimized yellow LEDs, efficiencies of 30 Cd/A and >8% have been observed. The electrical and optical properties have been verified on two different measurement systems. We investigate whether the enhanced device performance is attributable to microcavity effects or significant changes in polymer layer morphology under variable annealing conditions. We will also report preliminary lifetime results and discuss stability of encapsulated devices.

**L10.38**
SYNTHESSES OF PHENANTHROLINE DERIVATIVES AND THEIR APPLICATION TO ORGANIC EL DEVICES. Junji Kido, Scudori Watanabe, Toshiyuki To, Yamagata Univ., Graduate School of Science and Engineering, Yonezawa, Yamagata, JAPAN.

We synthesized phenanthroline derivatives containing aminic groups as new electron-transporting materials. Bilayer EL devices, using phenanthroline derivatives as an electron-transporting layer and NPD as a hole-transporting and emitting layer, were fabricated. Devices with a structure of ITO/PDPP/phenanthroline derivative/Al exhibited blue emission with a luminance of 3000 cd/m² and showed better device characteristics compared with a device using barboraphenine as an electron-transporting layer, which demonstrates that materials of this type can be used as good electron-transporting materials.

**L10.39**
INFLUENCE OF MOLECULAR WEIGHT ON THE CHAIN PACKING AND MOBILITY OF REGIOREGULAR POLYTHIOPHENE.
Joe Kline and Michael McGhee, Stanford University, Department of Materials Science and Engineering, Stanford, CA; Ekaterina N. Kondkova, Jingcong Liu, and Jene F.昕cher, University of California, Berkeley, CA.

Regioregular poly(3-hexylthiophene) (P3HT) is one of the leading candidates to replace amorphous silicon in the active layer of low-cost thin-film transistors. We have studied the effect of molecular weight on charge carrier mobility in thin film polymer transistors made from P3HT. We have observed a substantial increase in mobility with increasing molecular weight. The mobility increases 4 orders of magnitude from a sample of $M_w = 2100$ to a sample of $M_w = 36500$. This trend has been observed in samples synthesized by the McPhillighe route at a range of molecular weights and from samples obtained by film available P3HT synthesized by the Rieke route. We have analyzed films produced by both spin-casting and drop-casting. We have additionally studied the effects of annealing and melt/recrystallization on the charge carrier mobility and device performance. We have characterized the optical and electrochemical properties of P3HT and have used X-ray diffraction to obtain information on the morphology and band structure of the film. The results will be used to discuss the relationship between polymer morphology, chain length, and charge transport.

**L10.40**
PHOSPHORESCENT LIGHT-EMITTING ELECTROCHEMICAL CELLS. Feng-Chang Chen, Yang Yang, Univ. of California, Los Angeles, Dept. of Materials Science and Engineering, Los Angeles, CA; Qing Pei, SR International, Menlo Park, CA.

Due to the harvest of singlet and triplet excitons, highly efficient phosphorescent polymer light-emitting diodes have been demonstrated. However, the driving voltage of those devices remains high because of the carrier trapping at the dopant sites. To achieve high external efficiency, a phosphorescent light-emitting electrochemical cell, which consists of bis[2-(2-benzothienyl)-pyridinato-N,C']iridium(III)acetylide (Ir(ppy)) as the dopant, poly[9,9-di(3,6-dioxynaphthalene)-fluorene-2,7-diyli] (BDHoL-DPI) as the host polymer and lithium trifluoromethane sulfonate (LiCF3SO3) has been demonstrated in this letter. The turn-on voltage for light emission was as low as the bandgap of the host material (2.8 eV). Comparing with the light-emitting diode with the similar device structure, six-fold enhancement in power efficiency has been achieved.

**L10.41**
SYNTHESIS OF NOVEL POLY(9,9-DIOTHYLFLUORENE) DERIVATIVE CONTAINING HEXAPHENYLENENE AND ITS APPLICATION TO ORGANIC EL DEVICES. Junji Kido, Scudori Watanabe, Toshiyuki To, Yamagata University, Graduate School of Science and Engineering, Yonezawa, Yamagata, JAPAN.

A novel poly[9,9-diethylfluorene] containing hexaphenylene was synthesized by the Suzuki coupling method and used as an emitter layer in Organic EL devices. The polymer exhibited blue phosphorescence peaking at 480 nm. Organic EL devices having a structure of ITO/polythiophene derivative/blue polymer/Ca/AI were fabricated. The device showed a blue EL spectrum originated from the emission from the excimer sites.

**L10.42**

White organic light-emitting devices (OLEDs) are currently considered the low cost alternatives for applications such as backlights in liquid-crystal displays or other illumination purposes. There has been some efforts to obtain white light emission from multi-layer OLED structures in which two or more emissive layers emit different lights, and from polymer composites of several different color-emitting polymers or dyes. We have fabricated white OLEDs with an RGB stacked multilayer structure. In RGB stacked OLEDs, 1,4-Dib[2,2-di(3,6-dioxynaphthalene)]phenyl (DPVBi), tetra[3,6-bis(4,4-dialkoxyphenyl)quinoline][Alq3] and [2,6-di(3,5-di(thiophen-2-yl)phenyl)]dicyano-methylene-4-(3-methoxy-4-(2-phenylquinolin-2-yl)phenyl)benzil (DPP-MeQ) were used as a blue, green and red emitting materials, respectively. Through the device optimization, the pure and stable white emission with the CRI indices of (0.33, 0.31) at 100 nit was obtained by balancing the blue, green and red emissions of DPVBi, Alq3 and DPP-MeQ, respectively. Its maximum luminance was 13,200 nit at 12 V, and the luminance efficiency was 1.12 lm/W at 100 nit. The color rendering index of 84 and the color temperature of 5,000 K, were obtained in CIE (1931) (0.33, 0.31). In this presentation, the thickness and the doping concentration effects of emissive layers on the chromaticity and stability of white light emission will be discussed. For the illumination application of white lighting OLEDs, the quality of white light from our OLED will be also discussed.

**L10.43**
NOVEL POLY(MINOARYLENE) DERIVATIVES BASED ON FLUORENE FOR ORGANIC EL DEVICES. Shi-Jin Su, Junji Kido, Yamagata University, Graduate School of Science and Engineering, Yonezawa, Yamagata, JAPAN.

Two novel poly(minoarylene) derivatives based on fluorene were synthesized by Suzuki coupling reaction. They emit pure blue light in both optical and electrochemical properties, and the charge transporting at amino sites and hence excimer formation demonstrated for the previously reported triphenylamine-based polymers were
effectively limited due to the efficient energy transfer to the adjacent fluorene (and anthracene) trimer segments. It offers an effective route to reduce the strong excimer emission of poly (iminocyclopes) and enables them as novel potential candidates for blue-emitting polymers.

**L10.44**

**NANOSTRUCTURED OXIDE – COMPOSITE POLYMER COMPOSITES FOR PHOTOVOLTAIC DEVICES.**  
Sean E. Shakes, Philip A. Parilla, Alexander Miedema, Brian A. Gregg and David S. Ginley, National Renewable Energy Laboratory, Golden, CO; Kathryn E. Brown, Dept. of Physics, Colorado School of Mines, Golden, CO.

One of the intrinsic limitations of polymer based photovoltaic devices is that their light emission efficiencies are typically lower than those of commercialized silicon cells. The solar energy device efficiency is determined by absorption of incident light, followed by charge carrier generation, collection, and transport. The devices can be fabricated using various materials with varying efficiencies. In this manner, a wide range of solar cell materials has been utilized, including organic, inorganic, and organic-inorganic composites. In recent years, research has focused on the development of efficient low-cost photovoltaic devices with high efficiency, power conversion, and stability.

**L10.48**

**FOCUSED MICROWAVE-ASSISTED SYNTHESIS OF 2,5-DIHYDROFURAN DERIVATIVES AS HIGHLY EFFICIENT ELECTRON ACCEPTORS FOR NONLINEAR OPTICAL CHROMOPHORES.**  
Sei Tanaka, Satoru Yuasa, Taisuke Murata, Tadakazu Naito, and Atsushi K. Ito, Department of Materials Science and Engineering, University of Washington, Seattle, WA.

A diversified family of 2,5-dihydrofuran derivatives was synthesized under focused single-mode microwave irradiation. The tunable electron-withdrawing ability in the resultant ‘‘2,5-dihydrofuran acceptor system’’ would potentially balance molecular hyperpolarizability, absorption at near-IR region, and thermal, chemical and photochemical stabilities of the resulting new NLO chromophores. Very large χ(3) value (128 pm/V/nm) (3.1 mm) demonstrated in a polystyrene system with one of the 2,5-dihydrofuran-based chromophores in polymethylmethacrylate (PMMA) at 28% wt % loading level. Excellent χ(3) was recorded in an optimized system with a 1.0% wt load of a single chromophore where a terbium-hexacyanoferrate(III) salt substituted modified variant was doped in pyromellitophenone (PO-100) with high glass transition temperature. Furthermore, hydrolysis containing 2,5-dihydrofuran derivatives have been utilized in this system for the development of nonlinear optical plasmonic nanostructures. These multifunctionalized nonlinear optical chromophores can be tailored at molecular scale to afford the desired topologies such as, dendronized NLO chromophore, NLO dendrimer, and dendritic side-chain polymer systems.

**L10.49**

**STRUCTURE-CARRIER MOBILITY RELATIONSHIPS IN CONJUGATED POLYMERS.**  
Amit B. Bhal, S. Arjani, J. Acevedo, Department of Chemical Engineering, University of Washington, Seattle, WA.

Considerable progress has recently been made in the field of polyelectrolyte-based film transistors for low-cost, large-area electronic applications. In such active-matrix displays, smart cards, identification tags, and sensors. However, the structural factors governing high mobility and charge transport in polymer and semiconductor are not yet fully understood. Because polymer blends represent a facile means of controlling the morphology of polymers, we have investigated blends of conjugated polymers as an approach to probing the effects of morphology and disorder on charge transport and the field-effect mobility of charge carriers. We will present results on the composition-dependent field-effect mobility of holes in 5 different binary blend systems, each containing regioregular poly(3-hexylthiophene), with poly(3-octylthiophene), poly(3-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene), poly(3-ethylvinylene chloride), poly[3-(diocetyltrifluorodiyl)thiophene], and poly[3-(3-hexylthiophene)]. Finally, we have used high-speed scanning probe microscopy in conjunction with field-effect mobility to map out high-mobility regions of the blends. This approach can also be extended to the characterization of other high-performance electronic materials for potential applications in electronic devices.
Poly(paraphenylene vinylene) (PPV) is a common electroluminescent conjugated polymer, and optical nanodevices fabricated with PPV nanowires may be employed in light-emitting diodes and other photonic applications such as optical switches. Aligned PPV nanowires, with diameters of approximately 30 nm, were synthesized by electropolymerization of a, a, a, a'-tetra-cyano-polyacetylene in a 0.1 M tetrabutylammonium tetrafluoroborate DMF solution within the pores of a nanoporous anodic aluminum oxide (AAO) template membrane. The diameter and length of the nanowires can be controlled by changing the aspect ratio of the AAO template. The nanowires were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), micro-Raman, UV-vis absorption, and photoluminescence (PL) spectroscopy.

L10.51
SELF-ORGANIZATION, PROPERTIES AND DEVICE APPLICATIONS OF REGIERGULAR HEAD-TO-TAIL POLY(4-ALKYLQUINOLINE); Yu Sun, Nakadul M. Alam, Samson A. Jeneke, Departments of Chemical Engineering and Chemistry, Univ. of Washington, Seattle, WA.

Two 100 percent head-to-tail regiorregular poly(4-alkylquinoline-2,6-diyiyl) were synthesized and investigated. The 100% regiorregularity of the polymer was achieved by the AB-type nature of the acid-catalyzed Friedel-Crafts condensation polymerization. X-ray diffraction studies showed that solution-cast films of regiorregular poly(4-benzylquinoline) and poly(4-octylquinoline) have self-organized lamellar structures with interlayer spacings of 15.7 Å and 15.9 Å, respectively. They have the same stacking distance around 4 Å. The two polymers emit blue light at 432-435 nm in dilute organic solvent solution and yellow light at 547 nm in the solid state. Light-emitting diodes (LEDs) were fabricated using the two polymers as both the emissive layer and as an electron transport layer. Yellow electroluminescence was observed for both poly(4-alkylquinoline). A large improvement in the performance of mEP-PPV-based LEDs (a luminance up to 700 cd/m² and an external quantum efficiency up to 3.0%) was observed by using the poly(4-alkylquinolines) as the electron transport material, suggesting that they are good electron transport materials for polymer LEDs.

L10.52
SPECTRALLY STABLE BLUE POLYMER LIGHT-EMITTING DIODES BASED ON BLENDS OF POLY(9,9-DIOTOCYL FLUORENE); Abbaskhe P. Kulkarni, Samson A. Jeneke.

Polyfluorophores have emerged as a highly attractive class of electroluminescent conjugated polymers for display applications owing to their high fluorescence quantum yield and good charge transport properties. However, one major drawback of the blue-emitting polyfluorene-based devices is poor spectral stability due to the thermal or photooxidative degradation during operation, giving rise to an unwanted green emission band at 530 nm that has been attributed to the polymer degradation. Various approaches have been attempted to minimize this unwanted wavelength emission band including addition of hole-trapping molecules and addition of bulky side chain molecules. We report spectrally stable blue electroluminescence (EL) from single-layer light-emitting diodes comprising binary blends of poly(9,9-dioctylfluorene) (POF) with an electron-transporting hole-blocking layer of poly(vinyl diglycinebenzyl) (PVO) or with poly(3,4-ethylenedioxythiophene:poly(styrene sulfonate) (PEDOT:PSS). The brightness and efficiency of the PFO/PVO blend LEDs were enhanced by 5-10 times the values for the pure PFO diodes. The observed enhancement in the blue EL was due to energy transfer from PVO to PFO coupled with improved spatial confinement induced exciton stability. The improved stability in the blends is thought to be a result of higher Tg (185°C) of PVO compared to 75°C for PFO, leading to improved thermal stability. The variation in device performance with blend composition was dependent on the phase-separated morphology of the blends. In conclusion, blending PFO with thermally stable charge transport polymers or hole-blocking polymers to achieve balanced charge carrier transport in a simple strategy to achieve stable blue EL with improved performance and spectral characteristics.

L10.53
THERMALLY STABLE POLYFLUORENE DERIVATIVES WITH VARIOUS SPIRO-STRUCTURES; Sejin Shin, Dong Jin Park, Chang-Yong Lee, Ja-Joo Kim, Dong-Yu Kim, Dept. of Materials Science and Engineering, Korea-Ju Institute of Science and Technology, Gwajingu, KOREA.

Recently, spin-structured molecules have received much attention in the field of blinding materials of polymer light-emitting devices (PLEDs). 9,9-diaryl substituted polyfluorenes suffer from aggregate formation which produces an excimer emission band around 550 nm region with low quantum efficiency. Introduction of spiro-structure into polyfluorene is known to suppress the aggregate formation due to their three-dimensional structures. 9,9-diaryl substituted polyfluorenes contain two biphenyl units connected by tetraphenyl dendrimer carbon atom at the center of the two biphenyl units, each of which is perpendicular to each other. This 3-dimensional structure in the polymer could prevent the approach of neighboring polymer chains, thus minimizing the close packing of the polymer. However, 9,9-diaryl substituted polyfluorenes do not have any functionality such as solubilizing alkyl chains. We introduced various atoms such as carbon, oxygen and nitrogen between upper connected spirobifluorene by substitution of alkyl chain. The atoms except oxygen can provide possibility to introduce alkyl chains. Moreover, bulky and for long alkyl chains were introduced at the para position of a new phenyl rings via a new synthetic route. The two-structured polymers with flexible alkyl chains showed improved processability as well as stable amorphous structures. PLEDs based on these polymers were fabricated and characterized.
The power conversion efficiency of a polymer photovoltaic device is determined not only by the short-circuit quantum efficiency, but also by the open-circuit voltage and the shape of the current-voltage curve. We have therefore developed a numerical model to explain and predict the current-voltage curves of bilayer conjugated polymer photovoltaic devices. The model accounts for charge generation, injection, drift, diffusion and recombination, and includes the effect of space charge on the electric field within the device. Charge separation at the polymer/polymer interface leads to the formation of bound polaron pairs without the need for mobile excitons ever being formed into free charges. We find that the short-circuit quantum efficiency is determined by the competition between polaron pair dissociation and recombination. The ground state is a combination of the open-circuit voltage on the incident intensity, as seen experimentally. This additional intensity-dependent voltage rises from the field required to produce a drift current which balances the current due to diffusion of carriers away from the interface.

9:15 AM L11.4

ROLES OF INTERNAL ELECTRODES IN MULTI-HETEROJUNCTION ORGANIC SOLAR CELLS. Tetsu Tsuzuki, Kuenji Iyama, Takeshi Yanush, and Katsuhiko Fujita, Department of Materials Science and Engineering, Faculty of Engineering Science and Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Fukuoka, Fukuoka, JAPAN.

The power conversion efficiency (PCE) of single-heterojunction (HJ) organic photovoltaic cells consisting of Ca:Pc as a p-type semiconductor and hexa(dimethylamino)bithiophene (PTCDI) as a n-type semiconductor has been reported to be around 0.1-0.18% and an open circuit voltage (Voc) was 0.45-0.5 V. We pointed out two essential factors that give low PCE in thin-film HJ solar cells. One is a long recombination length within an active region of the cells and the other is low Voc in comparison with the average photon energy of sun light. One of the possible directions of solving these problems is stacking of HJ cells maintaining penetration of irradiated light with bottom HJ region. An early trial of introducing a metal interlayer brought about drastic increase of Voc, but PCE remained almost unchanged. Recently, large increases of both Voc and PCE have been reported using an Ag nanocohder interlayer (4).

This report focuses on understanding the effect of the insertion of internal electrodes in multiple HJ solar cells. Several types of single-HJ and multiple-HJ solar cells were fabricated. For single HJ cells, ITO/PTCDI/Ca:Pc/ITO electrode structure was fabricated as the standard cells, and multiple heterojunction cells, such as ITO/PTCDI/Ca:Pc/Ag/ITO/PTCDI/Au were stacked using Au electrode, the best values for Voc and PCE (AM1.5) were 1.35 V and 0.16% respectively. Several different external and internal electrodes were investigated.


9:30 AM •L11.5

EXTRINSIC LIGHT GENERATION OF CHARGE CARRIERS IN ORGANIC DONOR-ACCEPTOR SYSTEMS. W. Tim, C. Im, and H. Hasebe, Institute of Physical, Nuclear, and Macromolecular Chemistry, Philips-University Marburg, Marburg, GERMANY; V.I. Alikhanyan, INMC, Heerlee-Leuven, BELGIUM; E.V. Emelchenko, Semiconductor Physics Laboratory, University of Leuven, Heerlee-Leuven, BELGIUM.

In the course of our endeavour to understand how an optical excitation can dissociate into charge carriers in p-i-conjugated polymers we studied cw-photoconductivity in films of a PPV-based p-conjugated polymers and hexaBenzenzoacene doped by tris(pentafluorophenyl)amine within a broad range of concentrations of the acceptor. At moderate acceptor concentration the yield of the photogeneration is almost independent of the system and of concentration because practically every primary excitation dissociates at a donor-acceptor sites and the subsequent escape from the Coulombic potential is virtually system-independent. At acceptor concentrations > 10% the yield of that escape process increases by two to three orders of magnitude because of both shielding of the pair potential and the increased probability of electron motion across the acceptor network. The experimental results are analysed in terms of a recent theoretical approach.

10:30 AM •L11.6

DESIGN AND PERFORMANCE OF NEW FULLERENE MATERIALS FOR BULK-HETEROJUNCTION SOLAR CELLS.


Until now, the most successful fullerene acceptor material in bulk-heterojunction solar cells has been phenyl-C61-butyric acid methyl ester PCBM. One way to improve the energy conversion efficiency of these devices is through the modification of PCBM in such a way that the open circuit voltage of the device is increased. For this purpose, a series of PCBM based on an alkoxy moiety has been prepared and fully characterized. Next, thin films made of blend of MDMO-PPV and the modified PCBM materials were investigated using various techniques. Finally, PV devices, made with the new materials are fabricated and characterized.

11:00 AM L11.7

CHARGE TRANSPORT IN PLASTIC BULK-HETEROJUNCTION SOLAR CELLS. V.D. Mihailas, P.W.M. Blom, J.C. Hummelen, and M.T. Rispens, Materials Science Centre, University of Groningen, Groningen, THE NETHERLANDS.

The charge transport properties of the electron acceptor methanofullerene [6,6]phenyl C61-butyric acid methyl ester (PCBM) and the donor-type conjugated polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) have been investigated. At room temperature the electron mobility of \( \mu_e = 0.1 \cdot 10^{-2} \text{ m}^2/\text{Vs} \) in the PCBM is more than three orders of magnitude larger than the hole mobility of the donor-type C61-butyric acid methyl ester (PCBM). Also the charge transport properties of electron and hole devices in a 1:1 weight ratio of P3HT:PCBM blend have been addressed. The maximum attainable open-circuit voltage of a plastic solar cell has been determined and consistently explained.

11:15 AM L11.8

EXCITONIC SOLAR CELLS. Brian A. Gregg, National Renewable Energy Laboratory, Golden, CO.

Existing types of solar cells may be divided into two distinct classes: conventional solar cells such as silicon p-n junctions and exciton solar cells, XSCs. Most organic-based solar cells, including dye-sensitized solar cells, DSSCs, fall into the category of XSCs. In these cells, excitons are generated upon light absorption and, if not converted directly at the heterointerface, diffuse to the junction in order to generate charge carriers. The distinguishing characteristic of XSCs is that charge carriers are generated and simultaneously separated across a heterointerface. In contrast, generation of free charge-carrier pairs occurs throughout the bulk semiconductor in conventional cells, and separation is a subsequent process. This apparent minor mechanism distinction between exciton and conventional solar cells results in fundamental differences in photovoltaic behavior. The open circuit photovoltage, Voc, in conventional cells is limited to less than the magnitude of the band bending in the XSCs, however, Voc in XSCs is commonly greater than \( \Phi_a \). We describe some early work on solid state exciton solar cells, the use of carrier-selective electrodes to enhance Voc, and excitonic processes in general. Then studies of DSSCs, which provide a particularly simple example of XSCs, are described. A general theoretical description applicable to all solar cells is employed to quantify the differences between conventional and excitonic cells. The key difference between them is due to the predominance in XSCs of the photoinjected chemical potential gradient created by the exciton interface exciton dissociation process. Numerical simulations are employed to demonstrate the difference in photon conversion mechanism caused solely by changing the spatial distribution of the photo-generated carriers. Finally, the similarities and differences are explored between the three major types of XSCs: organic semiconductor cells with planar interfaces, bulk heterojunction cells and DSSCs.

11:45 AM L11.10
"Optical Sciences Center, University of Arizona, Tucson, AZ
"Department of Chemistry, University of Arizona, Tucson, AZ.

We report on the photovoltaic properties of cells containing a new liquid crystalline material based on copper phthalocyanine. In addition to being soluble, these materials also form highly ordered structures. Liquid crystalline mesophases are desired since they can lead to charge mobilities that are higher compared to those of amorphous materials. In addition, the solubility of liquid crystalline materials has been reported recently. However, their photovoltaic performance under standard solar illumination conditions was limited by their small absorption in the red part of the spectrum and by a saturation of the photocurrent at light intensities higher than 1 mW/cm². The new molecules (DL-CuPc) we investigated here are derivatives of CuPc, a well-known molecule with hole-transport properties that has been widely used in photovoltaic devices. It has a relatively high absorption coefficient in the visible spectrum. In contrast to CuPc molecules, the new derivatives are soluble in common solvents and can therefore be processed into devices from solution. For low cost organic electronic applications, wet processing is often desired and is compatible with low cost printing techniques. We fabricated high quality thin films by spin-coating of DL-CuPc. Thermal annealing of these films allows for the molecules to self-organize into a columnar nematic liquid crystalline phase. This phase has been characterized by optical spectroscopy, AFM and small angle X-ray diffraction. Bi-layer solar cells using C60 as an electron transport layer were fabricated. The annealing of the phthalocyanine layer resulted in a 3.5 times increase of the short-circuit current density and a reduction of the series resistance. The performance and limitations of photovoltaic cells fabricated from soluble liquid crystalline phthalocyanines will be discussed.

SESSION L12/H11.1: JOINT SESSION

1:30 PM *L12.1/H11.1
PRINTING APPROACHES TO ORGANIC OPTOELECTRONICS ON PLASTIC, TEXTILE AND PAPER SUBSTRATES. Y. Yoshida and G.E. Jabbour, Optical Sciences Center, The University of Arizona, Tucson, AZ.

The latest developments in the use of inkjet printing as a tool to pattern a given electrode promises a massless non-contact approach to generate functional circuits on various substrates. Many factors including surface tension of the printed solution, substrate surface properties, and moisture have direct effect on the final quality and performance of the organic-based devices. Issues related to device fabrication on plastic, textile and paper substrates will be discussed and results of tested devices will be presented.

2:00 PM *L12.2/H11.1
FULLY PRINTABLE LIGHT EMITTING DISPLAYS. Sue A. Carter, M. Kreger, J. Leventis, Y. Nakazawa, J.J. Breden, M. Wilkinson, University of California, Dept. of Physics, Santa Cruz, CA and Add-vision, Incorporated, Scotts Valley, CA.

One of the main promises of semiconducting polymers is the ability to manufacture inexpensive optoelectronic components that will lead to the wide-scale use of new technologies, such as large area light-emitting displays and photovoltaics. This vision relies on being able to manufacture semiconducting polymers using very inexpensive manufacturing processes where labor and processing costs can be sufficiently low. In this talk we will give an overview of the technical and cost considerations for making polymer displays, and detectors where all layers are deposited under atmospheric conditions using a liquid-based manufacturing technique, such as inkjet, screen-printing, or roll-to-roll processes. I will also discuss our work on low-cost light-emitting polymer displays with focus on the technical challenges in printing the light emitting polymer layer, in particular they are printing the top electrode (cathode), and obtaining sufficient lifetimes and power efficiency on plastic substrates under such manufacturing conditions. I will conclude by showing our most recent results and prototypes of fully printed light emitting polymer displays.

2:30 PM L12.3/H11.3
IN-SITU ELECTRICAL AND SPECTROSCOPIC STUDY OF DEGRADATION MECHANISMS AND LIFE TIME PREDICTION OF ORGANIC BASED ELECTRONIC MATERIALS. Jean Vittorio Mincu, Elke Kesten, Laurotne Lutesen, Lugdish Garsa, Dirk Vanderzande, Jan D'Haen, Marc D'Olesterke, Luc De Scheppe, Limburgs Universiteit Centrum, Institute for Materials Research, Diepenbeek, Belgium
IMEC, IMOMEC, Diepenbeek, BELGIUM, Omero sinon, University of Cagliari, Cagliari, ITALY.

In order to tailor the synthesis of new robust organic materials for electronic applications it is of key importance to understand the underlying degradation mechanisms. The strategy we use to study these mechanisms is to monitor the behavior of the materials submitted to a given stress condition with so-called in-situ electrical and spectroscopical techniques. This talk will present analytical techniques to determine the failure mode, degree of degradation and nature of morphological changes. This approach will be illustrated for several new polymer conductors and semiconductors in films and in light emitting devices. The degradation of organic electronic materials and devices was developed by our institute for a high resolution study of the electrical characteristics and ageing behavior of a given material during thermal annealing, as a function of temperature, time, etc. With this technique, a test structure is submitted to a desired temperature profile and atmospheric conditions, and the electrical property of interest is measured continuously during the treatment, i.e. in-situ. For the in-situ spectroscopical studies (in-situ IR and UV-Vis), a new equipment has been developed in order to be able to be analyzed against temperature and under various atmospheres as free standing films by means of an appropriate measurement cell. Films are heated following the temperature profile of choice and data are collected with a high rate. It will be shown that with these techniques activation energies can be determined for the elimination/polymerization mechanism and the degradation mechanisms can be monitored during in-line heating experiments and during isothermal treatments. With the presented in-situ techniques, the degradation kinetics can be studied under a matrix of stress parameters, allowing the construction of a kinetic degradation model. Such a model is required in order to make a correct prediction of the degradation under operational conditions and to evaluate degradation data obtained under accelerated ageing conditions.

2:45 PM L12.4/H11.4
FABRICATION OF ORGANIC LIGHT-EMITTING DEVICES BY LOW PRESSURE COLD WELDING. Changsoon Kim and Stephen R. Forrest, Dept of Electrical Engineering, Princeton Univ, Princeton, NJ.

We demonstrate a method for high resolution patterning of metal cathode contacts for organic electronic devices using low pressure cold welding. The contacts are formed by transferring a metal film on a patterned, soft elastomer stamp onto an untreated organic and metal layer that is predeposited on a substrate. Use of an elastomeric film allows for a thousand-fold decrease in the pressure needed for a high yield metal transfer compared to that required with rigid stamping techniques. In our demonstration, we fabricate an array of efficient organic light emitting devices (OLEDs) based on the green phosphors for tris[8-phenylpyridine] iridium [Ir(ppy)3] doped into a 4,4'-N,N'-dihexadecylbiphenyl (C16DB) host. Here, the cathodes consist of ultrathin (<1nm) layers of LiF and Al capped by a 15nm-thick layer of Au deposited across the entire organic layer surface. A 100nm-thick layer of Au is transferred onto the Au layer by pressing a stamp onto the substrate under conventional vacuum-seal flip-chip bonding. The cathode patterning is finished by removing the Au layer between the transferred pattern by gentle sputter etching. The 250nm diameter cathode were formed were uniformly obtained over an entire substrate area with a yield exceeding 97%, and the pattern edge resolution was approximately 1 μm. The stamping and Au layer removal processes do not adversely affect the performance of OLEDs fabricated by conventional shadow mask patterning. For example, the voltage corresponding to a current density of 20mA/cm² was
Progress in the growth of pentacene thin films and devices: Basil Tramp, IBM T.J. Watson Research Center, Yorktown Heights, NY

Recently, the growth of pentacene thin films on a variety of substrates has become of interest to the surface and interface science community. For instance, careful preparation of the substrate allows the pentacene thin film grain size to be increased very significantly. In this talk I review recent results on the growth of pentacene films on semiconductor, insulator, and metal surfaces.

Self-aligned vertical channel polymer field-effect transistors: Natalie Stutzmann, Richard H. Friend, Henny S. S Irrgang, Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

Manufacturing of high-performance conjugated polymer transistor circuits on flexible plastic substrates requires patterning techniques capable of defining critical features with submicrometer resolution. We demonstrate here the use of solid-state embossing to produce polymer field-effect transistors with submicron critical features in plane and vertical configurations. Embossing is used for the controlled microcutting of vertical sidewall into polymer multilayer structures without smearing. High-mobility vertical-channel polymer field-effect transistors on flexible plastic substrates have been fabricated in which the critical channel length is defined by the thickness of a spin-coated insulator layer. We demonstrate that gate electrodes can be self-aligned to minimize overlap capacitance by inkjet printing using the embossed grooves to define a surface-energy pattern.

Inkjetted organic transistors using a novel pentacene precursor: Steven K. Voinov, Steven Molen, Brian Martin, Paul C. Chang, and Vivek Subramanian, University of California, Berkeley, Department of Electrical Engineering and Computer Sciences, Berkeley, CA.

Pentacene is one of the most promising organic materials for organic transistor fabrication, since it offers higher mobility, better on/off ratios, improved environmental stability, and better reliability than most other common organic semiconductors. However, its severe insolvability renders it useless for the solution-based fabrication of electronic devices. Solution-based processing of these devices eliminates the need for lithography, subtractive processing, and vacuum-based film deposition. Because it allows the use of entirely additive printing techniques, it is expected to result in the development of low-cost reel-to-reel fabrication methodologies. Promoted by a recent paper from Afnan et al. describing the synthesis of a novel pentacene precursor, we demonstrate the first inkjet-printed pentacene transistor fabricated to date. This is achieved using a substrate-gated transistor structure in conjunction with an inkjet-printed pentacene precursor active layer. A subsequent thermal cycle is used to convert the precursor into a high-quality pentacene film. Unoptimized conditions yield transistors with an on/off ratio of >10,000 and a field-effect mobility of 0.01 cm²/Vs. Further improvement is expected with optimization, to approach the mobility of >0.5 cm²/Vs reported by Afnan. We study the effect of annealing conditions on the pentacene precursor characteristics, and establish qualitative models describing the various effects. The precursor is converted to pentacene via heating, through the decomposition of the Diels-Alder product. As the anneal temperature increases above 120°C, performance increases dramatically. The process is therefore compatible with numerous low-temperature processes. As the anneal time is increased to several minutes, performance likewise increases through increased precursor decomposition. However, exposure to excess temperatures or times tends to degrade performance. This is caused by morphological and chemical changes in the pentacene film.


Recent interest in the science and emerging applications of electro-active organic and bio-organic materials motivates research into non-invasive methods for forming high resolution electrical contacts on these classes of "soft," molecular materials. Many of the lithographic techniques that were developed for traditional microelectronic systems require processing protocols that are too severe for these organic systems. We have developed a soft-contact lamination approach to printing metal-coated elastomeric stamps that provides a convenient and non-invasive way of probing organic materials. This method exploits the surface relief of elastomeric stamps to define, with nanometer resolution, the geometry and separation of electrodes that are formed by directional deposition of thin metal films onto the stamps. Soft contact of these metal-coated stamps with the organic non-invasively establishes multiple independent electrical connections. As proof of concept we demonstrate successful fabrication of top-contact thin film transistors with channel lengths between 250 microns and 150 nanometers on pentacene and PCPDC. Advantages of this approach include a reversible contact that can be established at room temperature without the application of pressure or adhesives that are generally used with traditional lamination or vapor deposition methods. This procedure provides a powerful tool for studying the physics of charge transport in chemically fragile or ultrathin soft materials. We use this method to investigate fundamental interface and contact properties between metal electrodes and organic semiconductors. By comparing the lamination contacts to conventional ones formed by thermal evaporation, it is possible isolate the electrical effects of deposition hot metal onto organic semiconductors.