SYMPOSIUM C
Electronic, Optical, and Optoelectronic Polymers and Oligomers
April 17 - 20, 2001

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Proceedings to be published in both book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as Volume 665
of the Materials Research Society
Symposium Proceedings Series.
POLYVINYL VINYLENE DERIVATIVES IN THE INFRARED RANGE. Yuri Dubskyi, Antonio Zoppe, Piero Cesi, Sipari S.P.A., Milano, Italy; Andrea Zagottini, Giulia Facchin, Silvia Pietrangeli, Mario Martinelli, CoreCom, Milano, Italy.

The non-linear optical properties of poly[1,4-phenylene-1,4-phenyl vinylene], poly[1,4-phenylene-1,4-(di)ethylenoxy)] and poly[1,4-phenylene vinylene] MEHP-PV with different molecular weights were studied by the Third Harmonic Generation (THG) technique. The dispersion of the chi(3) coefficients was measured in the IR and near IR range from 1.2 up to 2.5 μm. It was shown that the highest chi(3) values, observed for the high molecular weight MEHP-PV (Mw 230,000), reaches the maximum of 8 x 10^-11 esu at 1.77 μm. At the same time, the medium molecular weight MEHP-PV (Mw 95,000) was found not significant different chi(3) values of 6 x 10^-11 esu. The dispersion of the chi(3) coefficient was compared to the absorption of the third harmonic beam and strong chi(3) enhancement relative to the excitonic absorption was observed. However, a surprising shift of about 100 nm towards the longer wavelengths between the two peaks was always observed for all studied PV derivatives. The results of THG chi(3) were compared to those obtained by conventional Z-scan technique in the same range. It was shown that the THG chi(3) values in infrared range were until one order of magnitude lower than those of direct Z-scan measurements.

10:45 AM C1.5
OPTICAL GAIN AND AMPLIFIED SPONTANEOUS EMISSION FROM SOLUBLE THIOPHENE-BASED OLIGOMERS. M. Amari, G. Ghe, R. Cingolani, Istituto Nazionale Fisica della Materia (INFN), Dip. Ingegneria dell’Istruzione Università, Milano, Milan, Italy; C. Gedermaier, D. Materia, E. Fichera, Università di Sannio, Sannio, Italy; G. Barbarella, L. Fioretti, Consiglio Nazionale delle Ricerche (CNR), ICOCEA, Area della Ricerca di Bologna, Bologna, Italy.

The interest in optical amplification in organic materials has continuously grown in the last decade. One of the most appealing properties of these materials stands in cheap device technology, which exploits spin coating or direct printing on flexible plastic substrates over large areas, provided the materials are soluble. In this context, the derivatives distinguish themselves for their high chemical stability and easy functionalization which allows to finely tune their optical properties. A lot of studies have been so far reported to investigate these properties but, to date, optical amplification has been reported only for single crystals of insoluble molecules, which are not suitable for technological applications. In this work we present the first evidence of optical gain and light amplification in spin coated films of soluble S,S-dioxide oligothiophenes with different functionalization pattern. The functionalization with alkyl and aryl groups allows us to obtain photoluminescence efficiency up to 70%, good chemical stability and tunable luminescence along the visible range. We demonstrate through pump-probe measurements that the materials show optical gain with a maximum gain cross section up to 8.4 x 10^-18 cm^2. The gain relaxation dynamics shows a lifetime shortening of about one order of magnitude as the pump density varies in the range from 450 μJ cm^-2 to 6 μJ cm^-2. Furthermore the absorption spectrum shows an exponential narrowing when the density is increased which is attributed to Amplified Spontaneous Emission (ASE) assisted by wave-guiding in the film slab. From these measurements we conclude that these soluble oligothiophene-S,S-dioxides are valuable candidates for spin coated thin film organic light amplifier and lasers.

11:00 AM C1.6
OPTICAL PROBING OF POLARON AND TRIPLET EXCITONS IN CONJUGATED POLYMER DEVICES. Anony C. Dicost, Neil C. Greenham, Cavendish Laboratory, University of Cambridge, United Kingdom.

Polaron and triplet excitons in conjugated polymers exhibit subpicosecond absorption which allows them to be identified spectroscopically. We have used this time domain domain time domain absorption techniques on working polymer LEDs to study charge carriers and triplet excitons in devices. By measuring the concentration and lifetime of triplet excitons at low temperatures we are able to estimate the triplet generation rate and to compare it with the single generation rate. We have also used absorption features due to polarons which scale linearly with voltage, consistent with a space-charge limited device current and a polaron cross-section of approximately 10^-18 cm^2. By analysis of the dependence of the triplet generation on the device current we conclude that interaction with polarons is an important triplet decay mechanism in polymer LEDs and we obtain a rate constant for this process.
11:30 AM *C1.7
NOVEL BIOSENSORS BASED ON FUNCTIONALIZED CONJUGATED POLYMERS. Mario Leduc. Laval University, Dept. of Chemistry, Quebec City, CANADA.

Functionalized conjugated polymers have received great attention from both academic and industrial laboratories due to their unique combination of interesting electrical, electrochemical, optical, and mechanical properties. For instance, the optical and electrochemical properties of some processable conjugated polymers can be strongly modified by varying the temperature, the pressure, the solvent, the electrolyte, etc. In other words, these smart polymeric materials can detect, transduce, and, sometimes, amplify chemical or physical information into an optical or electrical signal. In this regard, we report here a study of novel thermochromic and solvatochromic functionalized polythiophenes, polyfluorenes, polyphenylenevinylene, and poly(2,7-carbazole). These results show a good correlation between the conformational flexibility of the conjugated backbone and the presence of chromic phenomena. On the basis of these observations, different responsive supramolecular polymeric assemblies have been rationally designed and have led to the development of interesting ophtalmic and electrochemical biosensors. In particular, ultrathin films of electrochemically-modified biotinylated polythiophenes have shown interesting optical and electrochemical properties which allow the easy detection of as low as femtomoles of the protein avidin in aqueous solutions. This simple methodology has been successfully applied to other important biochemical systems and will be presented in this communication.

SESSION C2: MATERIALS
Chair: Yang Yang
Tuesday, April 17, 2001
Nobl Hill A/B (Merriott)

1:30 PM *C2.1
IMPROVING THE CONJUGATION AND REDOX PROPERTIES OF POLYTHIOPHENES USING FUSED HETERO CYCLIC SUBSTITUENTS. Peter J. Silbiger, Christian Poo-Gonzalez, Department of Chemistry, University of Manchester, United Kingdom.

We have been investigating the synthesis and characterization of new polythiophenes bearing 3,4-dialkylated heterocycles. These units, which are grafted to the polymer backbone, provide additional electronic contributions to the polymer, which can be exploited in a number of ways. For example: the incorporation of tetraphthiafulvalene (a strong electron donor) and trinitrofluorenone (a strong electron acceptor) units improve the doping ability of the polymer; donor-acceptor units provide a mechanism for photoinitiated charge-transfer; nitrogen-containing heterocycles allow the selective and reversible electrochemical detection of transition metal cations; 1,4-diketone substituents assist in the planarization of the polymer chain through intramolecular non-covalent S···S interactions. X-ray crystallography and molecular modeling reveal interesting supramolecular properties in some monomer species, suggesting that intramolecular interactions could significantly affect the electronic properties of the polymeric materials.

2:00 PM *C2.2
NOVEL PHOTOLUMINESCENT POLYMERIC MATERIALS. Richard V. Gregory, Clemson University, NSF Center for Advanced Fibers and Films, Clemson Optical Sciences and Engineering Technology Center, Clemson, SC; Z.V. Vardeny, University of Utah, Department of Physics, Salt Lake City, UT.

Active optical materials are of great academic and industrial interest in a variety of applications, including optical amplification, imaging and display technology. Several novel approaches are being examined in order to take advantage of the unique properties of polymeric materials. Organic-only systems can be handled at low cost for use in non-critical applications. Novel photoluminescent polymers are of considerable interest due to its low band gap (1.6 eV), moderate conductivity (100 S/cm) and remarkable stability. Recently, electron-rich derivatives of 3,4-ethylenedioxythiophene (EDOT) monomers have exhibited strong luminescence, but poor solubility in certain cases. In order to take advantage of the luminescent behavior of these new materials and other luminescent oligomers, these oligomers are being appended to polymers with acceptable solubility behavior to obtain bulk materials. Novel polyvinilenevinylene (PPV) derivatives are being synthesized. Instead of using alkylsubstituents to alter solubility and luminescent properties, conjugation length within the polymer is being determined by the introduction of meta-linkages in controlled positions. This will allow the effect and possible desirable of chain defects to be analyzed. This evolving technology may form the basis for "tunable" emissive polymeric materials. Finally, blends of polymer-hetero-acylate (PMMA) and 2,5-diethoxy-tetraphenylvinylenyne (D0-DPP) is being processed to generate a fiber with the blend containing the core and a clay-polymer composites. The clay-polymer composites will allow the formation of an active fiber. These materials led to greater understanding of the influence of polymer properties on the luminescent behavior.

2:15 PM *C2.3
EFFECTS OF SIDE BRANCHING, END CAPPING AND HOLE TRANSPORT LAYER ON POLYFLUORENE LIGHT EMITTING DIODES. Yuko Nakamura, Kei Ota, Tatsuo Takahashi, Cartesia Santa Cruz, Dept. of Physics, Santa Cruz, CA; Heinz-Georg Nothero, Ulrich Scherf, Max Planck Institute for Polymer Research, Mainz, GERMANY; Victor Y. Lee, J. Campbell Scott, Robert D. Miller, IBM Almaden Research Center, San Jose, CA.

Derivatives of polyfluorene (Poly[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl]) blue light emitting diodes (PLEDs) were studied with different side branch structures. Single and double layer structures were prepared with or without the hole transporting layer (HTL), crosslinkable triphenylamine (x-HTPA), and using PEDOT:PSi covered ITO and Ca as electrodes. IV characteristics, luminescence, quantum efficiency, and changes in the electroluminescence (EL) spectrum with aging were measured. For single layer devices without the HTL, all samples had the highest peak in the EL spectrum at 470nm, followed by another vibrational peak at 440nm. N-[4'-Bromo-biphenyl-4-yl]-N-naphth-2-yl-N-phenylenemer or (4-methylphenyl)phenylenemer (TPA) end cappers seemed to suppress the broad aggregation peak between 510 and 550nm that occurs in samples without end-capping. In addition, phenylenemer capping significantly reduced the operating voltage. 3,5,5-trimethylhexyl side branching introduced two more vibrational peaks at 471nm and 524nm. Slight spiral branching led to a single narrow peak at 472nm, however, it reduced the broad aggregation peak. For single-layer devices, the PF with 5% TPA end-capper and 2-ethylhexyl branching had the best performance, with a device quantum efficiency of 0.22% and a luminance of 3800 cd/m² at 12V. For double layer devices with the HTFA HTL, differences attributed to side branching and end-capping are suppressed. Samples with the HTL had up to 12 times higher quantum efficiency and a reduced aggregation peak. As before, polymers with 5% TPA end-capper and 2-ethylhexyl branching had the highest quantum efficiency of 0.22% at 12V and a luminance of 10,000 cd/m² at 14.5V. A luminance of 10,000 cd/m² was also obtained for samples with 3,5-trimethylhexyl and spiral branching. We observed significant improvements in spectral purity for the polyfluorene materials with spiral branching. The HTL also suppressed the growth of the aggregation peak that occurs with aging. Finally, we discuss how polymer structure and the HTL affect electrical transport through the PLIED device.
and organic backbone may yield novel properties in such hybrid materials. One synthetic approach to this class of materials is to construct electrocopperable monomers containing the transition metal in the desired coordination environment. Examples of polymers and oligomers containing transition metals such as Fe, Pd and Ru which we have prepared using this method will be described, along with some of their significant spectroscopic and electrochemical properties.

4:00 P.M. *C2.6 TERTIARY AND POLYTERIHYLNYL LIGANDS AS REDOX SWITCHABLE HEME-LIKE LIGANDS FOR OXIDATION-STATE-DEPENDENT MOLECULAR UPTAKE AND RELEASE. Chul A. Myeong, Dana A. Weinberger, Thomas B. Higgins, Northwestern University, Chemistry Department, Northwestern University, Evanston, IL.

Tertiary-based redox switchable heme-like ligands, 3\'-[di-2-pyridylphosphinoethyl]-5,5\'-dimethyl-2,2\'-[5\',2\',5\',2\'-terthiophene and 3\'-[2-di-2-pyridylphosphinoethyl]-5\'-terthiophene]-terthiophene have been synthesized and fully characterized. Mononuclear, dinuclear, and polymetallic Ru(II) complexes of these ligands demonstrate that this class of ligand provides control over both electronic properties and coordination environments of bound transition metals. We determined that 3\'-[3\',5\',7\'-Cyclopenta[2,3-b:3',4-b]dipyridylphosphinoethyl]-5\'-dimethyl-2,2\'-5\',2\',5\',2'-terthiophene (CPIE) (1a) has a three orders of magnitude increase in binding affinity for acetoacetate upon terthiophene-based oxidation. Spectroelectrochemical (FT-IR) experiments for 1a indicate that terthiophene-based oxidation removes electron density from the metal center equivalent to approximately 11-17\% of the electronic change that occurs upon direct oxidation of Ru(II) to Ru(III) in analogous complexes. The spectroelectrochemical responses of 1a were compared to those of dimeric and polynuclear analogues of 1a. The dimer has changes consistent with an additional stable ligand oxidation state compared to 1a. In contrast, the polymer exhibits spectroelectrochemical behavior similar to that of 1a. The polymer spectroelectrochemistry shows changes in the metal center electronic properties between two different states, reflective of two discrete oxidation states of the polymeric ligand backbone. We propose that the polymer backbone does not allow one to vary the electronic properties of the metal center through a continuous range of fractional oxidation states due to charge localization within the metalized film. In an effort to explore the molecular uptake and release properties of 1a and its polymer analogue as a function of ligand oxidation state, the oxidation state dependent coordination chemistry of 1a and 1b with a variety of substrates were examined.

4:30 P.M. *C2.7 AZACENES AND POLYACENES BEYOND PENTACENE. Hieu Dang, Yang Cheng, Kyle Starkey, Benjamin J. Schwartz, Ignacio Martini, Fred Wolf, University of California, Department of Chemistry and Biochemistry and Exotic Materials Institute, Los Angeles, CA.

The azacenes consisting of anthracene, tetracene and pentacene have been in the news lately in connection superconductivity and injection lasers discovered at Bell laboratories, Lucent Technologies. We will describe blue and red devices which have a smaller $E_g$ than pentacene and an azaphenylene with an $E_g$ close to that of pentacene. The azaphenylene exhibits very unusual photophysics with two luminescent bands, one in the blue and one in the red region of the visible spectrum.

SESSION C3: ELECTRONIC AND OPTICAL PROPERTIES II

Chair: Neil C. Greenham, Wednesday, May 3, 2001, Nabi Hall A/B (Merrifield)

8:30 AM *C3.1 CHARGE INJECTION IN ORGANIC SEMICONDUCTORS. Yuheng Shen, Daniel Gwinn, David Dunlap and Geoffrey M. Malliaris, Department of Materials Science and Engineering, Cornell University, Ithaca, NY.

Knowing how the current at the contacts depends on material parameters is of fundamental importance for the understanding and optimization of organic optoelectronic devices such as light emitting diodes and transistors. We have measured the electrical characteristics of various contacts between commonly used metal electrodes (such as ITO and Au) and hole transport layers including N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,4-bipheny-4,4'-diamine (TPD) and poly2-methoxy,5-[3-(ethylhexyloxy)]-1,4-phenylene vinylene (MEH-PPV). By carrying out independent measurements of the hole mobility in the organic layers we are able to isolate the injection and the transport processes and study the electrical characteristics of the contact alone. We find that most of the commonly used contacts in organic light emitting diodes are not ohmic-current limiting. The injected current is found to have a similar electric field dependence as the space charge limited current. Surprisingly, the injected current scales with the hole mobility in the organic, which was varied in the range of 100 and 113 cm2/Vsec by diluting TPD into polycarbonate. We show that this unexpected result is due to the hopping nature of transport in the organic material. We demonstrate ways to improve injection by modifying the contact by thinning the metallic layers and implement these modified contacts in organic light emitting diodes. A mechanism for this improvement is proposed.

9:00 AM *C3.2 SUPERQUENCHING OF FLUORESCENT POLYMERS AND APPLICATIONS FOR BIOLOGICAL SENSING. Duncan McBranch, Terry Bergstedt, C. Thomas Buscher, Robert M. Jones, Framke Rinnelsdon, and David Whitten, QTL Biosystems, LLC, Santa Fe, NM.

Polypyrrole polymers including conjugated polymers having positive or negative charges on each repeat unit have been found to exhibit very sensitive quenching upon exposure to very low concentrations of counterions functionized to quench the polymer repeat unit chromophore by electron transfer or energy transfer. In several cases it has been found that efficient quenching can occur at levels of one quencher per polymer chain. The basis for the highly amplified quenching, compared to small molecule quenching, results from a combination of selective binding of the quencher to the polymer based complex with rapid chemical (treated with subsequent following photoexcitation. This highly sensitive quenching can be harnessed for chemical and biosensing applications. For the latter it has been found that synthetic molecular conjugates containing a high molecular weight (QTL polymers) were can be used in conjunction with the fluorescent polymer to provide fluorescent “turn-on” and “turn-off” sensors. Several applications of this approach will be discussed ranging from sensing of biomolecules to drug discovery.


Admittance spectroscopy allows to differentiate between the various physical processes in polymer light-emitting diodes (PLEDs). At low bias inductive contributions show that the transport in PLEDs is governed by space-charge effects. At high bias the capacitive response indicates the presence of an electron-hole plasma in the PLEDs, implying that the recombination is relatively weak. This change from space-charge limited to recombination limited transport demonstrates that the Langmuir recombination in a PLED is not enhanced by the applied electric field.

9:45 AM C3.4 LOW-TEMPERATURE RECOMBINATION KINETICS OF LONG-LIVED, PERSISTENT CHARGE CARRIERS IN FULLERENE DOPED CONJUGATED POLYMERS. N. Schultz, M.C. Scharber, C.J. Brabec, N.S. Saricift, Lins Institute of Organic Solar Cells (LlOS), Physical Chemistry, Johannes Kepler University Linz, AUSTRIA.

The kinetics of photoinduced carriers in fullerenes doped MDMO-PPV has been examined by light induced electron spin resonance (LERS) at low temperatures (T < 100 K). For the photoexcited carriers, it is well known that the decay times at low temperatures extend from very short times (ms, prompt component) up to several hours (slow component). These characteristic kinetics of the LERS carriers agree with a model [1], which considers the universal behavior of the low-temperature manifestation of excited electron-hole pairs in disordered systems. It was already successfully applied to inorganic, amorphous semiconductors. We have applied this model to the kinetics of photoexcited charge carriers in fullerenes doped MDMO-PPV and find that the decay of the LERS carriers is in good agreement with the predicted recombination kinetics of the model. The carrier recombination kinetics over at least the first 2 hours after photoexcitation can be explained by nonmaxemate recombination of randomly distributed carriers assuming charge neutrality. In this model the recombination rate only depends on the interpair distance of the excited carriers and is independent of the specific energy level distribution of their electronic states. Additionally, the theoretically predicted independent of the longtime recombination of LERS on the initial photoexcited carrier concentration is observed. These agreements are particularly surprising, because the model contains only two fundamental parameters, i.e., an effective

10:30 AM *C3.5
TRANSIENT AND STEADY-STATE CHARGE PROCESSES IN MULTI-LAYER ORGANIC LIGHT-EMITTING DIODES. J.C. Scott, IBM, Almaden Research Center, San Jose, CA, R. Balasubramanian, S. Barth, H. Riel, W. Riess, IBM Research Lab, Zurich, SWITZERLAND, S.A. Carter, Physics Dept., Univ of California, Santa Cruz, CA.

In organic light-emitting diodes (OLEDs) high space charge densities are desirable in order to maximize electron-hole recombination rates and achieve correspondingly high efficiencies. The spatially varying electric field which results from these space-charges is comparable to, and may actually exceed, the applied voltages due to the injection of charges at the electrodes. Thus, a complete and quantitative description of the operating characteristics of OLEDs requires a self-consistent analysis of the field dependence of interfacial charge injection, charge transport, trap-state charging and recombination. In this paper, we present an approach to understanding the mechanisms underlying each of these processes, and to determining the relevant parameters.

The nature of the problem dictates a numerical approach. Algorithms have been developed to treat charge injection at the metal-organic [electrode] interfaces and at each organic-organic interface in a multilayered structure. Results are obtained for the dynamic, as well as steady-state solutions, and by comparison with experimental data in both single- and multilayer devices, some of the relevant parameters are obtained for materials and devices of technological interest.

11:00 AM *C3.6
MORPHOLOGICAL CONTROL OF EMISSION FROM EXCITON, EXCIMER, AND EXCIPLEX STATES. A.J. Epstein, T.L. Gustafson, E.M. Kyllo, P.C. Deharia, Jr., T.L. Frost, N. Piskun, and D.K. Wang, Ohio State University, Dept of Physics and Dept of Chemistry, Columbus, OH.

We show that exciton, excimer, and exciplex emission are each strongly dependent on the morphology of the organic material. Completely conjugated polymer and segmented block copolymer (SBC) forms of the three ring metal-organic PPV derive chromophore demonstrate the role of excitation chain-inchain and interchain confinement. Fluorescence lifetimes show that the excitation decay predominates in the SBC. Exciters (a 2.2 ns) are formed in oligomers and polymeric thin films at low temperatures. Exciters in the SBC disrupt thin film morphology, effectively preventing interchain and exciplex interactions. Near unity quantum efficiency of the SBC sample further refines exciton confinement. Early time fs spectroscopy of the SBC shows clear evidence of stimulated emission and ground state depletion, followed by formation of a transient absorption band at 280 nm. In contrast, emissions from poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), an electron transport polymer with Rs/C50 of Cs (11) and C50 of Cs (11) [with [3,1,5)] and PVK (polyvinylcarbazole), a hole transport polymer, have been shown to form an exciplex. We collected time resolved fluorescence decays from the PVK (excimer) emission, and the exciplex emission. We show that the exciplex emission in solution varies from exciplex (dilute) to excimer (concentrated). The PVK film emission is primarily due to exciters with room temperature lifetimes in excess of 10 ns. The long-lived excimer lifetime is ~300 ms. In contrast to the bulk polymers, the interexciplex decay time is very short, no emission energy dependence or temperature dependence.

These results suggest that the exciplex is a highly efficient, highly localized exciton which exhibits highly localized lifetimes and is closely related to the exciplex localized state than an interchain excited state. We find that blends of model oligomers for these materials do not form exciplexes, likely due to closer proximity and a stronger overlap of the electronic ground states. [supported in part by ONR]

11:30 AM *C3.7
METAL-TOSCANDIUM CHARGE TRANSFER STATES IN σ-CONJUGATED SYSTEMS. Kirk S. Schame, Keith A. Walters, Yiting Li and Kevin D. Ley, Department of Chemistry, University of Florida, Gainesville, FL.

There has been a surge of interest concerning the properties of σ-conjugated polymers and oligomers that contain transition metal units that interact with the σ-conjugated backbone. This interest stems from the possible application of such materials in luminescence based sensing, photonics and electronic and electronic device fabrication. Although a number of groups have examined the application and performance of metal-containing σ-conjugated materials, few studies have carefully examined fundamental photophysical properties of transition-metal containing σ-conjugated systems.

We are exploring the photophysical and photochemical properties of σ-conjugated polymers and mono-disperse oligomers that contain d-d transition metal complexes that interact with the σ-conjugated backbone. Recent work has focused on the series of oligomers I 1 and their corresponding [L]Re(CO)3Cl, [L]Re[bpyp]2+ and [L]Os[bpyp]2+ complexes. The focus of these studies has been to examine: (1) How does the metal-complex unit modify the properties of the σ, π, σ, π states of the σ-conjugated system? (2) How does the delocalized σ-conjugated system influence the properties of metal-to-ligand charge transfer (MLCT) excited states? Highlighting recent work on the absorption, luminescence and fs time-resolved spectroscopy of the oligomers and structurally similar polymers will be discussed.

1:30 PM *C4.1
AMORPHOUS SILICON THIN FILM TRANSISTOR PIXEL ELECTRODE CIRCUITS FOR A ACTIVE-MATRIX ORGANIC LIGHT-EMITTING DISPLAYS. Jerry Kaniicki, Solid-State Electronics Laboratory, Department of Electrical Engineering & Computer Science, The University of Michigan, Ann Arbor, MI.

Amorphous Si (a-Si:H) thin film transistor (TFT) pixel electrode circuits for the active-matrix organic light-emitting displays (AM-OLEDs) have been designed, fabricated, and characterized in our laboratory. Experimental results indicate that continuous pixel electrode emission can be achieved with these circuits, and a pixel output current level higher than 5 μA can be observed. For an 11-inch VGA full-color AM-OLED with a pixel electrode size of ~10μm × 200μm2, this output current level is equivalent to a pixel current density of 20 mA/cm2. Assuming the organic light-emitting devices (OLEDs) with an external quantum efficiency of 15%, the display brightness of ~110, ~1200, and ~200 cd/m2 for white (5μm), green (5μm), and blue (480μm) light emission, respectively, can be achieved with this type of pixel circuits. Furthermore, the pixel circuit electrode uses a current driver to automatically adjust their current level for threshold voltage shifts of both the OLEDs and the drive a-Si TFT. Consequently, these circuits have an excellent electrical reliability even when a large threshold voltage shift is present. In addition, the output current level, a high output-input current linearity has been demonstrated with these circuits. This should allow fabricating a good quality gray level AM-OLEDs.

2:00 PM *C4.2
POLARIZED ELECTROLUMINESCEENCE FROM A DOUBLE LAYER OF PERPENDICULARLY ORIENTED POLY(PHENYLENE) AND POLY(3-ALKYLTHIOPHENE). Alberto Bolognesi, Chiara Botti, Daniele Faccinetti, Istituto di Chimica delle Macromolecole CNR, Milano, ITALY; Markus Jandke, Klaus Kneer, Peter Strohriegl, MC-IBMP, Bayreuth University, Bayreuth, GERMANY.

We have prepared and characterized a LED with the active film formed by two polymers emitting in the green/yellow and red region: poly(p-phenylenevinylene), (PPV), and poly(3-alkylthiophene), PAT, respectively. PAT layer was spin coated on a PPV layer previously oriented. PAT layer was also oriented by means of the rubbing technique in the direction perpendicular to the PPV orientation. The polarized electroluminescence obtained from this device shows emission from PPV, yellow/green, or from PAT, red, depending on the orientation of the polarizer.

2:15 PM *C4.3
APPROACHES TO ADVANCED ORGANIC LIGHT-EMITTING DIODES: MATERIALS AND DEVICES. Yasunori Taka, Minamiichi Kna, Toyota Central Research and Development Labs., Aichi, JAPAN.

We present our recent results on the development of organic light emitting diodes (OLEDs). Highly efficient phosphorescent emission over 1% was obtained by using tri(2-phenylpyridine) iridium (Ir[ppy]3) and perfluorinated phenylene dendrimer as hole-blocking electron transporting layer. Thermal stability was also evaluated with
the device structure of emission dopant of phosphorescent [Ir(ppy)3]
in a host material of dicarbocyanine dye (CBD) and dimethyl
dibenzyl (BCP) as a hole-blocking layer. It was found that
external quantum efficiency becomes to decrease rapidly over 60°C
due to morphological changes arising from thermal instability of BCP.
Future challenges of OLED devices based on electrophosphorescent materials will be discussed.

3:15 PM *C4.4
HIGH PERFORMANCE ORGANIC MEMORY, Yang Yang, Liping
Ma, Jie Liu, Department of Materials Science and Engineering,
University of California, Los Angeles, CA

The advantages of large-area substrate processing capability and low fabrication cost of organic semiconductors importation of
electronic and photonic materials for several diverse applications such as displays, field-effect transistors, and photovoltaic cells. Recently, we observed that organic semiconductors also exhibit strong bistable signals for in-plastically different electrical conditions. This
discovery paves the way for newer applications such as low-cost,
large-area, high-density data storage devices. The transition from an
electrically insulating state to a conducting state is accompanied by
an enhancement by six orders of magnitude in the injection currents.
In this presentation, we will discuss the details of this novel organic
semiconductor device.

3:45 PM C4.5
STATISTICAL METHOD TO OPTIMIZE THE EFFICIENCY OF
MULTI-LAYER POLYMER LEDS, Michele Cecchi, Cal Poly State
University, Materials Engineering Dept, San Luis Obispo, CA,
Heather Smith, Cal Poly State University, Statistics Dept, San Luis
Obispo, CA; David Braun, Cal Poly State University, Electrical
Engineering Dept, San Luis Obispo, CA

Research and development of displays and image sensors based on
semiconducting polymers require design of new polymer materials and
evaluation of film properties. Optimizing device performance using a
cosine fit for a distribution (DFI) requires screening the effect of several
parameters, running numerous samples, and may consume
more scarce new material than desired. This paper investigates the
effects of dikyno-poly[phenylene vinylene] and poly(3,4-ethylen
dioxythiophene) layer preparation on device brightness and power
efficiency by performing and analyzing a two-called RSM (response
surface modeling) experiment with 5 repeated center points. Analysis of
variance methodology determines the effect of spin coating factors and
and their two-way interactions.

4:00 PM *C4.6
ELECTROPHOSPHORESCENT LIGHT EMITTING DIodes,
Mark E. Thompson, Sergey Lomskov, Peter Dvorovich, Jason
Brooks, Department of Chemistry, University of Southern California;
Stephen R. Forrest, Marc Baldi, Chihyang Adachi, Department of
Electrical Engineering, Princeton University; Raymond Kwong, Julie
J. Broom, Universal Display Corporation

We have fabricated saturated red, orange, yellow and green OLEDs,
utilizing phosphorescent dopants. Using phosphorescence based
dopants we have eliminated the inherent 25% upper limit on emission
observed for traditional fluorescence based systems. The quantum
efficiencies of these devices are quite good, with measured external
efficiencies as high as 15%. The phosphorescent dopants in these
devices are heavy metal containing molecules i.e. Pt and Ir. We have
prepared as both metalloporphyrins and organometallic complexes.
The high level of spin orbit coupling in these metal complexes gives
efficient emission from triplet states. In addition to emission from the
heavy metal dopant, it is possible to transfer the excitation energy to a
fluorescent dye, by Förster energy transfer. The heavy metal dopant
in this case acts as a sensitizer, utilizing both singlet and triplet
excitons to efficiently pump a fluorescent dye. We will discuss the
importance of paired transition layers for designing electrophosphorescent OLEDs
as well as their strengths and limitations. We will also discuss our recent
progress toward blue electrophosphorescent devices. Accelerated aging
studies, on packaged devices, have shown that phosphorescence based
OLEDs can have very long device lifetimes. These studies will also be
discussed.

4:30 PM *C4.7
DESIGN AND FABRICATION OF WHITE ORGANIC EL
DEVICES, Junji Kido, Junichi Tanaka, Yoshinori Kishigami,
Yamagata University, Graduate School of Engineering, Yamagata, JAPAN

Two type of white organic EL devices, using polymer or small
molecules, were fabricated. For polymer-based devices,
poly(N-vinylnaphthalene) (PVK) was used as an emitter layer, which was
doped with three kinds (RGB) of organic fluorescent dyes to generate
white emission. From the single layer devices, ITO/PEDOT/PVK/
Cathode, luminous efficiency of over 2 lm/W was obtained. For small
molecule-based devices, two kinds (Yellow and blue) of emitter layer
were stuck to obtain white light. By the use of metal-doped
electro-luminescent (ECL) layer, luminous efficiency exceeding 15 lm/W
was achieved. Design rules and device fabrication will be described.

SESSION C5 POSTER SESSION
Chair Rudy Sclafani
Wednesday, April 18, 2001
8:00 PM
Salon 1-7 (Merriott)

C5.1 THE EFFECTS OF POLYMER SOLUBILITY ON THE
MORPHOLOGY AND ELECTRONIC PROPERTIES OF
SEMICONDUCTING POLYMER FILMS, Benjamin J. Schwartz
and Thao Nguyen, University of California, Los Angeles,
Department of Chemistry and Biochemistry

It is becoming increasingly clear that the electronic properties of
conjugated polymers are controlled by the way the films are cast:
changing the solvent, spin speed or concentration changes the film
morphology and thus the performance of devices based on these
materials. In this talk, we show that the way in which a conjugated
polymer is dissolved into solution also affects the interchain
interactions and electronic behavior in the resulting film. First, we
demonstrate using light scattering and other techniques that
conjugated polymers do not necessarily completely dissolve even in
good solvents. This leads to solutions that behave like a suspension
of pieces of polymer film: the solutions exhibit exciton-exciton annihilation at high
excitation intensities and other properties normally associated
with polymer films. The films cast from such solutions have a rough,
alloyed morphology and perform poorly in LEDs. We show that
in order to completely solubilize the polymer, the solutions must be
stored for several days if heated, or stirred for several weeks if kept
at room temperature. Films cast from the heated solutions show a higher
degree of interchain contact than films cast from solutions stored
at room temperature, leading to higher currents and lower
electroluminescence efficiencies in LEDs. Second, we show that
an amino-substituted PPV, lowering the pH of the solution protonates the
amino groups, turning the normally neutral polymer into a
polyelectrolyte without significantly affecting the electronic properties
of the conjugated backbone. By adding multivalent anions or polyelectrolyte
co-solvents, the conformation of the charged polymer in solution can be
varied dramatically, resulting in a new degree of control over the
electrochemical interactions in the films cast from these solutions.

C5.2 NOVEL HIGHLY SELECTIVE MERCURY AND MONO
METHYLLUMINUM MERCURY SENSORS, Johnathan Scaggs, Dale Russell,
Michael Hill, Boise State Univ, Dept of Chemistry, Boise, ID; Christopher Penicuik,
Sidharta Duttagupta, Boise State Univ, Dept of Electrical
Engineering, Boise, ID

A novel mercury ion selective electrode has been constructed to have a
strongly coordinating macrocyclic ligand binding site covalently
attached to polythiophene film using 1,1,1,4,4,4-bistrimethylsilyl-
cyclopentanetetramine-thiophenemethane (TDCD(thiophenemethane)),
as a specific detector. In an asymmetric mode, the current is
proportional to mercury (II) concentrations down to 2 PPB.
Reversible cyclic voltammetric waves show that both mercury (I)
and mercury (II) are stabilized by the ligand. Elements such as oxygen
and bromide show no significant interference even when cadmium is
8 times or greater as concentrated in solution. The polymer surface
shows robust performance for up to two years. Fabrication strategies
will be based on the optimal configuration of various factors that
contribute to minimal performance. Maximal performance will be
achieved by determination of optimizing factors such as, the ratio of
derivatized thiophene (TDCD-thiophenemethane) to thiophene in the
surface polymer, the ratio of thiophene with two chelating rings to
thiophene with only one, the optimal layers of polymer, the optimal
composition of polymer layers, optimal thickness of polymer, and
optimal thickness of the polymer surface.

C5.3 MICROCAVITY EFFECTS IN THIOPHENE-BASED OLIGOMERS,
G. Gighi, M. Ang, R. Cingolani, Istituto Nazionale di Fisica della
Materia (INFN), Dip. di Ingegneria dell'Innovazione, Università di Lecce, ITALY; S. Patane, Istituto
Nazionale di Fisica della Materia (INFM), Dip. di Fisica della Materia e Tecnologie Avanzate,
Università di Messina, ITALY, G. Barbieri, L. Facchetti, Consiglio Nazionale delle Ricerche (CNR), Istituto IOCCEA, Bologna, ITALY

The control of exciton-photon interactions in semiconductors is of
fundamental and technical interest. The modification of the optical
transition of the material due to the confined electromagnetic field
can in fact lead to new device concepts improving the characteristics of light emitting diodes, lasers and photodetectors. Organic materials, both polymer molecules, have, been largely utilized for microcavity based devices due to the low cost, the high flexibility and the possibility to realize large areas. To date no extensive investigation has been however carried out on thiophene derivatives. In the context of organic materials these compounds distinguish themselves for their full color tunability, high chemical stability and carrier mobility. However their typical low photoluminescence efficiency in solid state has discouraged their full exploitation in optoelectronic devices such as light emitting diodes. We report multicolor microcavities with low cost dielectric mirrors, having as active media pure thiophene derivatives characterized by very high solid state PL efficiency up to 70%. Time resolved photoluminescence, single resolved PL and reflectivity spectra have been measured showing strong spectral narrowing and PL intensity enhancement.

C5.4 OPTOELECTRONIC CORRELATION OF CHARGE CARRIER DELOCALISATION WITH INCREASED MICROCRYSTALLINE ORDER IN REGIO-REGULAR POLY (3-AKLYLTIPHIOINE).
Peter J. Brown, Maxim Skumra, Henning Serringhans and Richard H. Friend, University of Cambridge, Department of Physics, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

The high field effect mobilities of up to 0.1 cm²/Vs exhibited by poly(3-hexylthiophene) field-effect transistors have been attributed to the increased intra and interchain order in the polymer films. Important consequences of this is the resulting delocalization of the polaronic charge carriers such that they become two-dimensional in character. Delocalization breaks the symmetry of the isolated-chain, one-dimensional charge carriers and results in the appearance of characteristic new charge-induced, sub-gap optical transitions that can be detected by spectroscopic techniques, such as Charge Modulation Spectroscopy (CMS) [1]. Further to this, we have been able to control the degree of microcrystalline order in the films by varying the length of the side chains in poly (3-alkylthiophene) (PAT) and by changing the solvent used in the film forming process. We present detailed CMS studies of such films and this yields a detailed optical characterisation of charge carriers in PAT. The spectra demonstrate that as the order in the microcrystalline order in the films is increased, as witnessed by X-ray analysis, the degree of electronic and structural relaxation attributed to the formation of polaronic charge carriers in PAT is reduced and the charge carriers exhibit increased two-dimensional characteristics. The detailed optical spectra presented here in turn allow detailed models of the electronic structure of charge carriers in PAT to be developed. [1] H. Serringhans et al. Nature 401, 685-698 (1999).

C5.5 A METHOD FOR THE MEASUREMENT OF CARRIER DENSITY AND DIFFUSION PROPERTIES IN POLYMER LIGHT-EMITTING DEVICES. Lijing Ma, Jie Liu and Yong Yang, Department of Materials Engineering, School of Engineering and Applied Science, University of California at Los Angeles, Los Angeles, CA.

A method for the measurement of the charge carrier density, diffusion velocity and diffusion current in polymer light emitting diodes (PLEDs) by using the transient electroluminescence (EL) technique is reported. When a rectangular forward bias pulse is applied, electrons and holes are injected into the diode. Subsequently, EL is emitted from the junction being probed. At the onset of injection, the minority carrier density is obtained from the EL intensity and the velocity. Formulas about obtaining the carrier density, diffusion velocity and diffusion current density are given. EL experiments for PLED devices have been performed, the transient charge carrier density, diffusion velocity and diffusion current density at the recombination zone of the devices are experimentally obtained for the first time.

C5.6 Abstract Withdrawn.

C5.7 MAGNETIC RESONANCE STUDIES ON A POLYTHIOPHENE WITH DIFFERENT SOLID STATE MORPHOLOGIES. M.C. Scharbeck, N.A. Schultz, C.J. Brucke, N.S. Sarcifichi, Linn Institute for Organic Solids, Johannes Kepler University Linz, AUSTRIA. M.R. Anderson, Department of Polymer Technology and Organic Chemistry, Chalmers University of Technology, Gothenburg, SWEDEN.

We investigated the influence of the film crystallinity on the yield of polaron pair formation in a regioregular soluble polythiophene with an alloyed sidechain on a phenyl ring (POEPT). By spin-coating this material from chloroform solution and additional annealing two different ordered phases denoted as orange and blue phase can be obtained. The optical absorption and photoluminescence of the blue phase is shifted about 100 nm to the red with respect to the orange phase. We performed photoluminescence detected magnetic resonance (PDMR) studies on thin films of the two different phases. We also prepared small polycrystallides (ITO-PEDOT-PEO-AT) and investigated the changes of the short circuit photocurrents under electron spin resonance conditions (PCDMR). The experiments show, that the yield of photogenerated intermediate states is significantly smaller in the more crystalline, blue phase.

C5.8 STRUCTURAL PROPERTIES OF CONJUGATED MOLECULAR MATERIALS UNDER HIGH PRESSURE. G. Heilm, E. Junger, R. Resel, Graz University of Technology, Inst. for Solid State Physics, Graz, AUSTRIA; and K. Weimesser, P. Paschinger, C. Ambrosch-Draxl, University of Graz, Inst. for Theoretical Physics, Graz, AUSTRIA.

Over the last decades a lot of attention has been paid on electronic organic materials. Conjugated molecules, showing promising optical features in the UV/Vis region combined with high electron mobility and fluorescence quantum yield, are of high interest for both, scientific and commercial use, e.g. polarized light emitting diodes on a thin film basis of hexaphenyl [1], an organic solid state injection laser of a high quality tetracene single crystal [2] or efficient organic photovoltaic diodes based on doped pentacene [3] have been proposed. Since the electro-optical properties of these materials are critically influenced by their the crystal and molecular structure, the goal of the project we are involved is to study the influence of the intermolecular interactions by applying hydrostatic pressure. X-Ray powder diffraction experiments were conducted to determine the lattice parameters. These experimental findings then served as an input for an optimization of the atomic positions and molecular orientation. The calculations were performed using the ab-initio bandstructure code WIEN97 [4], a full-potential linearized augmented plane wave (FP-LAPW) method within density functional theory (DFT). Exchange and correlation effects are treated with the local density approximation (LDA).

In the present work we focus on anthracene and para-terphenyl, which crystallize in the monoclinic space group P21/a (two molecular puck cell). A Merz-Basset type Mo infinite wedge cell was used to apply hydrostatic pressure. The lattice parameters up to 60 kbar were extracted from energy dispersive powder patterns recorded with white light synchrotron radiation. Our first-principles methods were then applied to optimize all internal degrees of freedom including bond lengths, bond angles and intermolecular distances. The detailed knowledge of the structural properties is a prerequisite for understanding the electrooptical properties of these systems. The results of analogous investigations performed on biphenyl and the poly(para-phenylene) oligomers have been published recently [5-8].

References

C5.9 ALTERNATING CURRENT PROPERTIES OF PPV DERIVATIVES/PEO LITHIUM SALT BLENDS. Lucas Fugita Santos, Luiz M. Carvalho, Roberto M. Faria, Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, SP, BRAZIL.

The electrical properties of light emitting electrochemical cells (LEC's) and polymeric light emitting diodes (LED's) based on soluble PPV derivatives [poly(5-methoxy-2'-ethylhexyloxy-1,4-phenylene vinylene)] , MEH-PPV, and poly[5-methoxy-2'-ethylhexyloxy-1,4-phenylene vinylene] , MEH-PPV, were measured by means of impedance spectroscopy technique. LEC's were prepared blending PPV derivatives with poly(ethylene oxide) (PEO) and lithium salts in different compositions. The salt concentration in the blends is a parameter that seems to highly affect device performance.
Current voltage (dV) measurements were also performed in order to complete the electrical device characterization. Alternating current measurements were carried out measuring the real and the imaginary parts of the impedance as a function of the frequency of a sinusoidal wave oscillating around a dc level. It was observed that the ac response of the devices depends on both dc bias level and ac waveform amplitude. Experiments realized lowering the TEG, OH, alternative conditions show strong temperature dependence on the observed relaxation times and on the operating voltages of the devices, with a more accentuated effect in LEOs.

C5.10
FABRICATION AND CHARACTERIZATION OF A NOVEL POLY METHYL METHACRYLATE OPTICAL FIBER. Bei Shen*, S.J. Hargreaves?, P.E. Patmore?, Z.V. Vardeny?, H.V. Gregory**

School of Textiles, Fiber and Polymer Science, Clemson University, Clemson, SC, Department of Physics, University of Utah, Salt Lake City, UT.

Optical fiber lasers and amplifiers are the subjects of much current research. Polymer optical fibers potentially offer significant advantages over silica-based optical fibers. A polymethylmethacrylate (PMMA) fiber with PMMA/poly(diisocyanate-polyphenyl vinylene) (DOO-PPV) blend core is fabricated by a preform-drawing technique. The PMMA/DOO-PPV blend is drawn to a high denier fiber called a core preform. This preform is clad with PMMA to form a core/sheath structure. The resultant cylinder is then drawn into a fiber. The PMMA/DOO-PPV blends are characterized by electron microscopy as well as standard thermal techniques. The optical properties of the fibers are presented as well.

C5.11
THE STUDY OF ELECTROCHEMICAL POLYMERIZATION OF POLY(3,4-ETHYNYLENODIOXYPYRIDINE) FROM AQUEOUS SOLUTION OF CYCLODEXTRIN AND 3,4-ETHYNYLENODIOXYTHIOPHENE COMPLEX. Jin Yang, Richard V. Gregory School of Textiles, Fiber and Polymer Science, Clemson Univ., Clemson, SC.

Much effort has been put into the synthesis of poly(3,4-ethylenedioxythiophene) (PEDT). Due to the low solubility of 3,4-ethylenedioxythiophene in water, there are few publications which involve the synthesis of PEDT in aqueous solution. Cyclodextrins (CD) are cyclic oligosaccharides that exhibit a torus-shaped structure with a hydrophobic cavity and a hydrophilic exterior, which can form inclusion complexes with 3,4-ethylenedioxythiophene and increase the solubility of 3,4-ethylenedioxythiophene in water. This allows synthesis in aqueous solution, a much more environmentally friendly and industrially feasible system. Poly(3,4-ethylenedioxythiophene) (PEDT) was electrochemically synthesized from cyclodextrin (CD) and 3,4-ethylenedioxythiophene complex aqueous solution. n-CD, o-CD and hydroxypropy1-CD were used to prepare the host-guest complex with 3,4-ethylenedioxythiophene in aqueous solution. Cyclic voltammograms of these aqueous solutions were studied. Good PEDT films were obtained on FTO, UV-Va and XPS were applied to study these PEDT films. Conductivity and other electronic properties of these films were investigated.

C5.12
ENERGY LEVEL ALIGNMENT AND EXCITON BINDING ENERGIES USING MODEL INTERFACES BETWEEN METALS AND EVAPORABLE ORGANIC ELECTROLUMINESCENT MATERIALS. S.F. Alvarado and W. Riss, IBM Research, Zurich Research Laboratory, Rüschlikon, SWITZERLAND.

We report on measurements of the height of the energy barriers for electron and hole injection of model organic/metal interfaces. The technique used is based on scanning tunneling microscopy, which allows one to probe the alignment of molecular orbitals directly at the organic-metal interface. The samples used were thin films of tri(5-hydroquinonat)aluminum (Alq3) and N,N,N′,N′′,N′-di(naphthalen-1-yl)-N,N′-di(phenylbenzimidazolyl) (NPB) deposited on Ni(111) and Au(111) substrates. For the Alq/Au(111) interface we find, for electron injection, a barrier height of 1.15 ± 0.15 eV, while for hole injection the barrier height is 1.81 ± 0.25 eV. This result compares well with photoemission spectroscopy measurements reported by other research laboratories. We find that the energy band gap for injection of charge carriers into the organic materials is larger than their optical band gaps. The excess energy is due to the binding energy of the exciton, E_b. We obtain E_b = 210 ± 30 meV for Alq3 and E_b = 300 ± 100 meV for NPB. The effect of electron modification will also be discussed. For instance, intercalation of a LiF thin film between Alq3/ and Au(111) increases the reduction of the electron injection barrier by as much as 0.6 eV for a nominal LiF thickness of 0.2 nm.

C5.13
DEPOSITION OF POLY-3-METHYTHIOPHENE ON GOLD-COATED ELECTRODES. Deborah Gonzalez, Inst. de Fisica de San Carlos, Univ de San Carlos, San Carlos, SP, BRAZIL, Eugene A. Irene, Chem Dept., Univ of North Carolina at Chapel Hill, Chapel Hill, NC.

Gold and platinum electrodes are by far the most used metals for electrodeposition of conducting polymers. The importance of evaporated gold as substrate has also been noted in studies of adsorption of self-assembled monolayers containing sulfur, and for field-effect transistors using conducting polymers. In this work, we investigated the viability of using gold deposited on chromium/glass plates as electrodes for electropolymerization of 3-methylthiophene. The polymer films were cycled by cyclic voltammetry in acetonitrile by varying the electrolyte salt, potential range and etching treatment of the gold electrode. After applying final potential values as high as 4.5 V vs Ag, an effect of gold dissolution could be perceived, particularly when tetraethylammonium tetrafluoroborate was used as the electrolyte support salt. The electrode surface treatment also affected the volumetric response of gold, since dissolution occurred particularly after using dilute aq. regin as the etching solution. Complementary techniques such as spectroscopic ellipsometry and X-ray photoelectron spectroscopy were used to determine whether the chromium underlayer is exposed by gold dissolution.

C5.14
SYNTHESIS AND CHARACTERIZATION OF POLY[(N-ALKYL-2,3 CARBAZOLE)-8-BLUE LIGHT-EMITTING MATERIALS. Jean-François Morin, Marie Ledere, Lawal University, Dept of Chemistry, Quebec City, Canada; Isabelle Létangue, Marie Diorio, Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, Canada.

Recently, we have developed a new important class of well-defined conjugated polymers: processable poly(N-alkyl-2,7-carbazole) and related copolymers. Preliminary studies revealed that these novel materials are very promising for many technological applications, in particular for the development of efficient blue light-emitting diodes. Two different pathways for efficient and relatively low cost synthesis of these disubstituted carbazole units and corresponding polymers will be reported in details. Also, some preliminary physical properties of the new polymers including optical, electrical and morphological features will be reported. First results on single-layer light-emitting diode will be reported. The homopolymer is particularly interesting because it show a very pure blue-light emission with no excimer formation. In order to balance charge injection, block copolymers in which hole transport is assumed by carbazole units have been synthesized. These materials have been tested as active layers in light-emitting diodes and the results will be reported.

C5.15
ASYM-BRIDGED BENZimidazoLES AS MODELS FOR N-DOPED POLYMERS. Mark D. McClain, Cedarville University, Department of Science and Mathematics, Cedarville, OH; Douglas S. Dudin, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH; Albert V. Pratn, University of Dayton, Department of Chemistry, Dayton, OH.

The electrical conductivity of poly(p-phenylenebenzimidazole) (PBTZ) was recently shown to increase substantially upon protonation by strong acid and partial chemical reduction (n-doping). In an effort to enhance environmental stability and processability of n-dopable conducting polymers, we have synthesized and alkylated benzimidazole compounds bridged by benzene, pyridine, thiophene, and pyrazine rings. The properties and computationally modeled structures (AM1) and electronic transition energies (ZINDO/S) of these novel materials will be discussed. The π-electron structures of two of the model compounds will also be reported.

C5.16
POLYFLUORENE DERIVATIVES WITH MULTIFUNCTIONAL SIDE CHAINS FOR FIXED JUNCTION OF LIGHT-EMITTING ELECTROCHEMICAL CELLS. Do-Jin Park, Yong-Young, Nho, Jong Ju Kim, Dong-Woo Kim, Kwangjin Institute of Science and Technology, Dept of Materials Science and Engineering, Oryang-dong, Puk-gu, Kwangju, REPUBLIC OF KOREA.

Although light-emitting electrochemical cells (LECs) have various advantages that low operating voltage and insensitivity to film thickness and to the work function of the electrode materials, LECs have a final problem of low response time. This problem can be solved by removing the ion mobility after the p-i-n junction has been formed. We have synthesized polyfluorene derivatives with multifunctional side chains for LECs with fixed p-i-n junction. Both
ethylene oxide and epoxy group were introduced to the side chains of polyfluororenes to make the polymer ion conductor. The epoxy group acts not only as a non-conducting group, but also as a crosslinking group. We have fabricated LEC devices and investigated the effects of crosslinking of side chains on the formation of fixed p-n junction. Crosslinking was carried out under various conditions. We compared the ion conducting property of the polymer before and after crosslinking. In addition, we also compared that with well known ion conducting polymers. The polymer also could be used for solvent resistant thermoelectric organic light-emitting devices with multilayer structures.

**C5.17**

**STABILIZATION OF OPTICAL MOLECULES USING DENDRITIC BOXES AGAINST SINGLET OXYGEN IN PHOTOBLEACHING**

Sonoko Otomo, Akira Otomo, Shinro Miyake, Kansai Advanced Research Center, Communications Research Laboratory, Kobe, JAPAN.

Stabilization effect of dendritic boxes against singlet oxygen has been studied. Towards applications of organic optical molecules for a wide range of photonic devices, the problem of photoinduced degradation [photobleaching] has to be solved. In general, photobleaching mainly consists of two processes, which are photoinduced oxidation and photo thermal decomposition. In this experiment, we focused on photoinduced oxidation, and studied effects of dendritic boxes to protect encapsulated dyes from reactive singlet oxygen. Rubrene, which is commonly used as a singlet oxygen probe, is captured in a dendritic box, and then the box is closed at the surface by other stable molecules to prevent oxygen penetration. We evaluated the efficiency of the Rubrene encapsulated in the dendritic box, and visualized by a laser beam to generate singlet oxygen. It is observed that breaches of the encapsulated Rubrene in the dendritic box is remarkably slower than that of Rubrene. Moreover, we examine the dependence of surface molecules of the dendritic box with several kinds of molecules which are different in quenching efficiency of singlet oxygen. We also study the stabilisation effect with other molecules, such as laser dyes and nonlinear optical chromophores.

**C5.18**

**LANGMUIR FILMS OF GRAPHIC NANOFLAKES OF AMPHIPHILIC HEXABENZOCORONENINE MEAN PHASE TRANSITIONS AND SWITCHABLE ELECTRONIC PROPERTIES**

Niels Reitzel, The Hasselkam, Konstantin Balbashov, Thomas Bjenholm, Laboratory for Materials Science, Department of Chemistry, University of Copenhagen, Copenhagen, DENMARK; Torben R. Jensen, Paul B. Hovas, Kristian Kjaers, Condensed Matter Physics and Chemistry Department, Risø National Laboratory, Roskilde, DENMARK; Andreas Fiehler, Natalia Tchepanovsk, Shahj Ho, Klaus Müllen, Max-Planck Institut für Polymerforschung, Mainz, GERMANY.

The structural and electronic properties of an amphiphilic derivative of hexaalkylhexabenzocorronene (HBC) having one alkyl substituent terminated with a carbonylic acid group is presented. The molecules form well defined Langmuir films when spread from solution at the air-water interface. Grating incidence X-ray diffraction (GIXD) and X-ray reflectivity at low temperature in the Langmuir monolayer reveal two crystallographic phases depending on the pressure surface applied to the film. Very coherent scattering (ca. 300 Å) from extremely well ordered n-stack lamellae of HBC molecules tilted ca. 40° relative to the surface normal is observed from the low-pressure phase. In this phase the HBC molecules pack in a rectangular 2-D unit cell with a = 22.95 Å, b = 4.94 Å. In the high-pressure phase, coherence from the n-stack is lost due to stress induced by crystallization of the substituted alkyl chains in a hexagonal lattice, which is characterized in one direction: a = 15.59 Å, b = 5.20 Å and = 120°. Monolayer thin films can be transferred to solid supports using the Langmuir-Blodgett (LB) technique. Atomic Force Microscopy (AFM) with atomic resolution reveals the crystalline packing of alkyl chains in the high-pressure phase. Kelvin Force Microscopy (KFM) shows a clear potential difference between the high and low pressure phases. This is discussed in terms of orbital delocalization (band formation) in the highly coherent low-pressure phase contrary to the localized molecular orbitals present in the high-pressure phase. This highly coherent n-stack is expected to sustain very high charge carrier mobility.

**C5.19**

**ADSORPTION KINETICS OF AMMONIA GAS ON POLYANILINE IN A N-TYPE GATE-TRANSFET BRIDGE GAS SENSOR**

Hailin Hu, M. Elena Nicolo, National University of Mexico (UNAM), Centro de Investigacion in Ensenada, Temixco, Morelos, MEXICO; Martin Trejo, Augusto Garcia-Velasquez, Jose M. Sivieger, UNAM, Centro de Instrumentos, Mexico D.F., MEXICO.

Polyaniline (PANI) shows electric as well as optical property changes when it is in contact with oxidant/reductor gas. In this work the optical transmission changes in PANI coatings as a function of the semi-oxidized ammonia gas concentrations are detected by a nulling optical transmittance bridge. The adsorption and desorption curves are detailedly analysed using kinetic theory of desorption. The results lead to a description of a physical adsorption of ammonia (adsorption at the rates of 0.12 and 0.20 V/m at different sites in PANI, which should reduce with the assumed unequally distributed positive charge on the nitrogen atoms in PANI chains.

**C5.20**

**GROWTH OF ORGANIC THIN FILMS AND NANOSTRUCTURES BASED ON STRONG HYDROGEN BONDING AND METAL-LIGAND BONDING**

Aurelie Mageau, Xiaolin Deng, Zhongang Xiao, Chengshu Cai, Dept of Chemistry, Houston, TX.

Organic thin-films and nanostuctures have attracted increasing interest for their potential applications in fields such as Microelectronics and Optics. Their performance is strongly dependent on the orientation of the functional molecules in the films. It has been demonstrated by the recent work on thin-films of 4-(pyridin-4-yl) vinyl) tetrameric (PVBA) thin and strong directional intermolecular interactions can be used to generate ordered thin-films [Ch. Cai et al., Adv. Mater. 1999, 11, 745]. The carbocyclic and pyridine end groups allow PVBA to selfassemble in a head-to-tail fashion via hydrogen bonding leading to well-defined polymeric chains of several micrometers long and separated by tens of nanometers [J.V. Barth et al., Angew. Chem. Int. Ed. 2000, 39, 1230]. Based on this concept, we designed oligomers end-capped with a carbocyclic and a pyridine group or two carbocyclic groups. We also expanded the idea to metal-linked oligomers based on metal complexes that can interconnect the molecules via strong coordination with Ru4+ ions. Oligophenylene containing from 3 to 13 phenyl rings with hexyl side chains are used as the backbone. Their rigidity and elongated structure make them interesting building blocks for well-defined molecular architectures and the twisted configuration of consecutive phenyl rings in the chain lowers the strength of bonding to the transition metal substrates and thus facilitates self-assembly. We also expect that larger molecules in the films will facilitate their detection using Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM). The thin-films and submonolayers will be grown by Organic Molecular Beam Deposition (OMBD), Spin Coating and Solution Cast. The studies of the monolayers and submonolayers of these functional molecules will be presented.

**C5.21**

**THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND SPECTROSCOPIC PROPERTIES OF A SERIES OF TRANSITION METAL CONTAINING PHENYLACETHYLENE OLIGOMERS AND POLYMERS**


To develop novel nonlinear dyes for photonic applications, we synthesized a series of transition metal-containing phenylacetylene oligomers and polymers. The optical properties of these compounds were measured by UV/Vis, fluorescence, long-pathlength UV/Vis and flash photolysis. We also prepared thin films of these compounds placed on aminosilane and characterized their surface properties with AFM. The AFM images showed the influence of the rod-like shape of these compounds. The triple state absorption spectrum red shift increased oligomer length. There is a further red shift with polymerization. Steady state UV illumination of degassed room temperature solutions of these compounds caused phosphorescence to appear. Through the use of long path length UV/Vis spectroscopy, we observed forbidden transitions from the ground state to the triplet state. The spectroscopic behavior reflected competition between the spin-orbit coupling induced by the transition metal and the intrinsic fluorescence of the rod-like phenylacetylene oligomers.

**C5.22**

**PYROELECTRIC BEHAVIOUR OF PURE AND LITHIUM DOPED POLYSULFONE POLYMER FILMS**

A.K. Sharma, Y.R. Yadu, D. Kumar and V.V.R.N. Rao, S.V. Univ, Dept of Physics, Tirupati, INDIA.

Polymer films are being used as a substitute for crystalline or ceramic materials in many device applications such as pyroelectric detectors, electrocalibrated radio meters and thermal imaging devices. In the present study the pyroelectric behaviour of pure (undoped) and lithium doped polysulfone (PSF) films is studied to understand the effect of doping on the pyroelectric activity in these films. Pure and lithium doped films of PSF were prepared by thermal immersion technique in a sandwich configuration. The pyroelectric behaviour was studied in a function of dopant concentration under different polarizing fields (5×105 to 1×106 V/m) and polarizing temperatures (303 K to 420 K) using dopant concentrations of
C.5.23
OPTICAL INTERFERENCE STACKS MADE BY PECVD POLYMER FILMS. Hao-Jiang, Aamir Co., Dayton, OH; Walter Johnson, John Grant, University of Dayton Research Institute, Dayton, OH; Kurt Eynik, Dave Tomlin, and Timothy J. Bunting, Materials and Manufacturing Directorate, AFFL/MLP, Wright Patterson AFB, OH.

Controlled multilayer optical interference stacks have been fabricated using plasma enhanced chemical vapor deposition (PECVD) of varying refractive index organic precursors. The low refractive index precursor material was octafluorocyclobutane (OFCB) while the high refractive index material was benzene. Molecules of each precursor interact in the gas phase argon plasma resulting in the deposition of highly crosslinked, smooth, and pin-hole free films. The refractive index of the films formed from OFCB was 1.35 whereas the benzene-based films exhibited nD = 1.65. By temporally varying which precursor is deposited or the balance of each material's deposition rate, one can deposit thin films with spatially varying refractive index profiles (i.e. one-dimensional photonic band gaps). Modulation of the PECVD processing conditions allows varying optical thickness of the films. We report here the fabrication of simple ABAB stacks of these precursors and the correlation of optical spectra and ellipsometry, atomic force microscopy, and scanning electron microscopy to explore structure/property relationships among the deposition variables and the resulting thin film structure.

C.5.24
SELF-ASSEMBLED GROWTH OF HIGHLY ORIENTED PARA-SIPEPHENYL THIN FILMS CONTROLLED BY ELASTIC STRAIN. Andrej Yu. Andreev, C.J. Brabec, N.S. Starcheff, Johannes Kepler Univ. of Linz, Linz Inst for Organic Solar Cells (LIOS), Physical Chemistry, AUSTRIA; H. Sitter, G. Springholz, Johannes Kepler Univ. of Linz, Inst for Condensed Matter Science, Physics, AUSTRIA; P. Hinterdorfer, Johannes Kepler Univ. of Linz, Inst for Biophysics, AUSTRIA.

The ability to control the molecular order in organic thin films consisting of long microporous oligomers like oligo-thiophenes or oligo-phenylene is essential to study the relation between their structure, surface morphology and their optical and electrical properties. Recently reported the para-si-phenyl (PS) molecules occurs during Hot Wall Epitaxy (HWE) on mica resulting in well ordered crystalline needle-like structures with a length to width ratio up to 500. In this work we used small-angle X-ray microscopy to investigate the early growth stage of these structures in detail, in order to find the process controlling parameters. PS films were grown by HWE on freshly cleaved (001)-oriented mica substrates. The vacuum during growth was about 6x10^-6 Torr and the PS source temperature was fixed at 240°C. Substrate temperature was varied from 70 to 170°C, growth time was in a range from 14 sec to 60 min. The results of our investigation are summarized as follows: a) PS grows on mica epitaxially in the Struktur-Kristall growth mode; b) a shape transition from randomly oriented small PS islands with compact shapes to an elongated islands occurs during the growth; c) with further increase of the growth time the islands become elongated, quickly reaching their asymptotic length, and the island sizes remain much smaller than their length and width; d) the critical island size at which the shape transition occurs strongly depends on growth temperature; e) if the surface coverage is large enough the island height increases linearly with perimeter increase over the growth temperature. It is shown that most of these extraordinary features can be qualitatively explained in terms of strain-induced epitaxial island growth well known for inorganic heterostructures.

C.5.25
SYNTHESIS OF 3,4-DISUBSTITUTED POLY(THIOPHENE) VIA SUBSTITUTION OF POLY(3-ALKYLTHIOPHENE). Young Li, George Vanderbilt, Steven Holzknecht, Simon Fraser University, Dept. of Chemistry, Burnaby, BC, CANADA.

The electrochemical substitution of regioregular poly(3-octylthiophene) (P3OT) at 4chlorophenol was investigated for the first time to produce structure well defined 3,4-disubstituted poly(thiophene). When P3OT was treated with N-bromosuccinimide (NBS) in chloroform at 25 to 50°C, the hydrogen atom at 4-position in P3OT was completely substituted by bromine, 1H NMR, 13C NMR and elemental analysis results. Similarly the chlorinated product was obtained by using N-chlorosuccinimide (NCS) at room temperature. However, only 85% of the 4-hydrogen was replaced by chlorine and about 15% of the aliphatic hydrogen was also replaced by chlorine that prevents the further substitution of the 4-hydrogen at the ring. P3OT readily reacted with fuming nitric acid in chloroform at 0°C to generate a nitro product with almost 100% substitution at the 4-position. These new 3,4-disubstituted poly(thiophene) reveals reactive bromine, chlorine, and nitro groups, which potentially allow some further substitution or transformation of these groups to other functional groups. Our preliminary study on the functionalization of these polymers was conducted on the brominated product. Our results showed that the bromine atom in this polymer can be easily further substituted with other groups.

C.5.26
NOVEL GUEST-HOST NLO POLYMIDE BASED ON TWO-DIMENSIONAL CARBAZOLE CHROMOPHORES. Wenchang Song, Ming-Huei Huang, Dept. of Chemical Engineering, National Tsing Hua University, Hsinchu, TAIWAN, ROC; Rong Jeng, Dept. of Chemical Engineering, National Chung Hsing University, Taichung, TAIWAN, ROC.

Second-order nonlinear optical (NLO) materials with one-dimensional charge transfer (CT) molecules have been extensively studied. Doping these CT molecules into amorphous polymer matrices (guest-host systems) or covalently incorporating NLO moieties into polymer backbones exhibit large NLO coefficients. Recently, two-dimensional CT molecules and their polymer systems were developed by Mynta et al. They focused on phase-matching capability. In this work, the structure effect of the two-dimensional CT molecules on the temporal stability was investigated in guest-host polyetherimide. Taking advantage of the multifunctional characteristics of carbazole along with rational molecular design, a series of two-dimensional carbazole-chromophores were synthesized by a facile synthetic route. The carbazole-containing chromophores with various conjugated lengths and receptor group were achieved via Knoevenagel condensation. Doping the chromophores into polyetherimide, a series of NLO-active guest-host polymers were obtained. High doping levels up to 38 wt% were obtained without observing aggregation of NLO chromophores. The compatibility between chromophores and polyetherimide was investigated by SEM and AFM. After incorporating these NLO polyetherimides with large second-order nonlinearities were achieved. Correlations between structure and nonlinear optical characteristics and the chromophore size effect on the thermal and temporal stability have been probed. The effect of two-dimensional structures on the NLO temporal stability was investigated by tracing the second harmonic coefficient as a function of time and temperature, respectively. Moreover, the relaxation behavior of the NLO systems was further examined by dynamic light scattering. Large relaxation volumes make the two-dimensional chromophores possessing excellent orientational stability when the temperature approaches the glass transition temperatures measured by DSC.

C.5.27
INVESTIGATION OF MORPHOLOGY AND INTERFACE IN POLYMER COMPOSITE THIN FILMS. C.K. Chung, R. Peeperl, L.P. Sung and J. Ohrn, NIST, Gaithersburg, MD.

We have investigated morphology and interfaces in composite thin-films of ceramic fillers distributed in polymer matrices. The films were prepared by photopolymerization, solvent casting or hot-pressing methods. The morphology of the films was investigated using optical microscopy and scanning electron microscopy. The photoinduced contrast in the case of composite structures, which was in turn allowed us to examine the distribution of particles and the polymer interface between them. It was found that the polymerization method usually produced uniform particle distribution, while the films from solvents cast and hot-pressing methods may contain air pockets. This observation was also supported by density measurement as a function of the filler content. The data are correlated to the dielectric constant of the composite thin-films.

C.5.28
NEW PATTERNING METHOD IN THE ORGANIC ELECTRO-LUMINESCENT DEVICE. Geoyong Um, Sunhee Yoo, Changhong Yi, Corporate R&D Center SAMSUNG SHC Co., LTD, KOREA.

We report a new patterning method in the polymer based organic electroluminescent device (OLED). This device has a size of meters of micrometers and the manufacturing method is as following. After insulating layer deposition on the ITO glass substrate, active area is
defined by patterning. On the top of that, polymer layer is deposited using spin coating, and cathode metal is deposited using vacuum deposition technique. After general lithography step, metal is etched, and polymer layer is etched using a patterned metal mask. It was confirmed that the electric properties of this type of device are same as those of device with generally manufactured method. The metal patterning using shadow mask and dry etched polymer mask it was found out that there was no degradation due to the difference of process. Currently the comparison test of luminescent efficiency is in progress. This new polymer OLED patterning method can remarkably lower manufacturing cost of high resolution of full-color polymer OLED.

C.5.32
SYNTHESIS AND CHARACTERISATION OF NOVEL POLYPYRIDINE DERIVATIVES. Lockhart E. Horsburgh, Andrew P. Monkman, Organic Electroactive Materials Group, Department of Physics, University of Durham, UNITED KINGDOM.

The highly luminescent, semiconducting polymer, poly[2,5-pyrindenediyll] (PPY), has attracted considerable interest in recent years. In addition to exhibiting unusual and complex photophysical behaviour, it has been used as both an emissive and an electron-transport material in organic light-emitting devices (OLEDs). We will report on the synthesis, characterisation and photophysical properties of several pyridine-based polymers and oligomers. In particular, we will discuss strategies for synthesis of regioregular "head-to-tail" polypyrrolines. Such materials are potentially useful in the production of improved OLEDs, and are also expected to aid our understanding of the photophysical properties of PPY derivatives in general.

C.5.33
TEMPERATURE ACTIVATED DE-TRAPPING PROCESSES IN VACUUM-DEPOSITED QUATERNIOPHENOL THIN FILMS. Francesco Menardini, Michele Cerminara, Silvia Tavazzi, Adele Sassella, Alessandro Bergesio and Riccardo Tubino, Università di Mecleone, Dipartimento di Materiali, Milano, ITALIA.

The origin of optical emission in oligothiophene single crystals and films is still an open question. We have investigated the photoluminescence (PL) from quaterthiophene (4T) thin films grown by organic molecular beam deposition on different substrates. These films have the same crystal structure of one of the two 4T polymorphs but different morphologies, depending on the growth conditions (substrate, substrate temperature, rate of deposition, vacuum conditions…). The PL spectra of all the analyzed films are dominated by the same two vibronic progressions, whose relative intensity changes from a film to another. The higher-energy emission can be considered as arising from deexcited states, while the lower-lying one to trap states. A detailed study of the PL intensity vs. temperature evidences the presence of a thermally activated process quenching the luminescence of the energy progression, which is no more detectable above 100 K. The calculated activation energy of this process of about 50 meV fits well with the energy separation between the origin of the two vibronic progressions. These data can be interpreted on the basis of a two-phonon process in the lower-lying state is thermally depopulated. Quite similar results are already reported for seckyphene thin films suggesting that this phenomenon is a general behavior of oligothiophene films. It is interesting to observe that this interpretative picture strongly resembles the energy level configuration of an inorganic semiconductor where shallow traps are present.

C.5.34
SYNTHESIS AND PROPERTIES OF CONDUCTIVE POLY[ANILINE-COOANTHRANILIC ACID]: EFFECT OF DOPING AGENTS. Chen Shih Ping, POSCO Technology Center, Pohang, SOUTH KOREA.

Polyaniline has an intrinsically high conductivity, so that it may be a potential material to substitute environmentally friendly metals such as chromium and lead in the field of metal coatings. But this polymer has a low resistance in the application because of the lack of solubility in common solvents. On the other hand, poly[aniline-carboxylic acid] has a good processability because of the inherent high solubility in water and other solvents. But, the polymer is unfortunately non-conductive. In this study, poly[milkino-co-anthranilic acid] were synthesized in various compositions and characterized their structure and properties including conductivity. In addition, they were doped with various doping agents and characterized. The results will be discussed in terms of the application because of the lack of solubility in common solvents.

C.5.35
DESIGN, SYNTHESIS AND CHARACTERIZATION OF POLYMERS DERIVED FROM FILORENE FOR APPLICATION IN RGB LIGHT-EMITTING-DIODES. Serge Bénard, Marie Leclerc, Université Laval, CERSIM, Québec, CANADA, Isabelle Lévesque, Marie Dorio, National Research Council Canada, IMS, Ottawa, CANADA.

In order to obtain efficient blue, green or red polycrylic light-emitting-diode (PLED), we report herein the design, the synthesis, and the characterization of new polymers and copolymers derived from fluoranes. We will focus on a versatile synthetic approach that allows the easy design of a whole class of new and tunable electroactive and photoreactive aromatic polymers. The poly[(1-hexyl-9 H-carbazole)-7,7'-diethylenyl] and poly[(1-hexyl-2,7-bis(3,5-diethylenyl)fluorene-2,7'-diethylenyl)] (PPTHC60) and poly[(1-hexyl-2,7-bis[3,5-diethylenyl]fluorene-2,7'-diethylenyl)] (PPPBPPE) exhibit strong emission in the blue range, both in solution and in the solid state. Moreover, PPTTHC60 presents some advantages over other polyfluorene derivatives. For example, its solid-state fluorescence spectrum does not show any excimer formation and does not show any temperature effect. We will also present copolymers derived from fluorene which emit green light and a new approach to obtain red-light-emitting polymers. Optical properties such as absorption, emission, fluorescence quantum yield as well as electrical properties, such as cyclic voltammetry and in-situ conductivity, have been characterized. These CHI films have been coated in LED devices and show promising results for the development of multi-coloured displays based on polyfluorene derivatives.

C.5.36
EFFICIENT WHITE POLYMER EL DEVICES BASED ON POLY[(N-VINYL CARBAZOLE)]. Junji Kido, Junichiro Tanaka, Yamagata Univ., Graduate School of Engineering, Yamagata, JAPAN.

White-light-emitting polymer EL devices were fabricated by the use of poly[(N-vinylcarbazole) (PVK)] as an emitter layer. PVK was doped, or molecularly dispersed, with three kinds (RGB) of organic fluorescent dyes to generate white emission. Single layer devices having the structure of ITO/PEDOT/PVK/electron-injection layer/Al were fabricated. PEDOT was doped with poly(styrene sulfonic acid) and the electron-injection layer was a co-deposited layer of hexaphenylbenzene and Ca metal. By optimizing the layer thickness and cathode structure, luminance of 5500 cd/m2 at 11 V
and external quantum efficiency of 2.2% were achieved. Luminous efficiency was 2 lm/W. White EL devices using blue and yellow dopants were also fabricated and results will be presented.

C5.36 SYNTHESSES OF BLUE-EMITTING ARYLAMINES AND THEIR APPLICATION TO ORGANIC EL DEVICE Tatsuya Ito, Junji Kimoto, Yamanaka Univ., Graduate School of Engineering, Yamanaka, JAPAN.

Holtransporting blue-emitting triiseleno-oxine (TSA) and tetratriphenylenebenzene (TSB) were synthesized. Several multilayer organic EL devices, using TSA and TSB as an emitter layer, were fabricated. Devices with a structure of ITO/NPD (400Å)/TSO/TSA or TSIB (200Å)/BCP (100Å)/TSA/Alq3 (200Å)/LIF (3Å)/Al exhibited blue emission with a luminance of 3400 cd/m2 and 1300 cd/m2, respectively. And a device with a structure of ITO/NPD (400Å)/TSB doped with 10wt% TSA (200Å)/BCP (100Å)/Alq3 (200Å)/LIF (3Å)/Al exhibited blue emission, which indicates that materials of this type are useful as blue-emitters in organic EL devices.

C5.37 HETEROJUNCTION CONTROL IN LIGHT-HARVESTING POLYMERIC SEMICONDUCTORS: AN ULTRAFAST STUDY OF ENERGY AND CHARGE TRANSFER IN COVALENTLY COUPLED DONOR-ACCEPTOR STATISTICAL COPOLYMERS.


We present femtosecond transient absorption spectroscopy of a derivative of poly[9,9-diocybocoumarine] (F8) with red-emitting perylene derivatives covalently linked to the polymer backbone (FP8). This is a model system to study energy and charge transfer in polymerics semiconductors. Efficient energy transfer is observed from the F8 backbone to the perylene side groups on a picosecond time scale. In such covalently banded heterogenation systems the interaction surface area is controllable by blending F8 and FP8. By blending an additional conjugated polymer that exhibits photoinduced charge transfer with the perylene derivative, photovoltaic devices were constructed with external quantum efficiencies of 4% when excited at the peak of the null* transition in F8. This is a result of Förster energy transfer from the F8 backbone to the perylene, followed by charge transfer to the guest polymer. This is a novel approach for the construction of light-harvesting structures in which the distributed surface area of donor-acceptor interfaces is controlled to convert photon energy to photocurrents efficiently. The femtosecond-resolved photophysics are discussed.

C5.38 DEPOSITION AND CHARACTERIZATION OF METAL/ POLYAMINE BL-LAYERS. Lan Yu, Paul Yu, Matt O’Keefe, University of Rolla, Dept of Materials and Materials Research Center, Rolla, MO; Ayse Beyza, Chris Singleton, Tom Schuman, University of Missouri-Rolla, Dept of Chemistry and Materials Research Center, Rolla, MO.

Interest in electrically conducting polymers, such as polyamine, has increased dramatically in recent years. Applications including organic light-emitting diodes, transistors, and corrosion inhibiting coatings have utilized the properties of polyamine to provide improved unique performance over alternative materials. In many instances polyamine is in direct contact with bulk and thin film metal surfaces and the influence of polyamine’s oxidation state on interactions with the metal determines the usefulness of the metal/polymer system. In this study, bilayers of metal/polyamine films were prepared by depositing the polyamine films on substrates via solution chemistry and then depositing metallic films by sputter deposition. The oxidation state of the polyamine before deposition varied from fully oxidized permaminate to fully reduced leucammonium. The metallic films that were deposited on the polyamine included aluminum, copper, iron, and titanium. Electrical, electrochemical and chemical characterization of the metal/polyamine bilayers indicated that the type of metal and oxidation state of the polyamine influenced the optical, electrical and physical properties of the composite.

C5.39 FUNDAMENTAL STUDIES ON N-TYPE POLYMERS AND THEIR INCORPORATION INTO PHOTOVOLTAIC DEVICES.

Michael F. Durstock, Mary A. Alexander, Jeff W. Baer, Thuy D. Dang, Fred E. Arnold, Air Force Research Laboratory, Polymer Branch, Wright-Patterson Air Force Base, OH; Barney E. Taylor, University of Dayton Research Institute, Dayton, OH.

In the field of conducting polymers, many p-type materials are readily available while stable n-type materials are relatively rare. We have been investigating a series of polymers based on poly[bisnaphthoxazine (PBT) and poly[bisphenylylene (PPV)] (PBT) which are capable of n-doping either by chemical or electrochemical means. When these materials are immersed in acidic solutions, they become protonated which lowers their reduction potentials and allows them to be reduced either chemically or electrochemically. The stability of these n-doped systems depends on their electrochemical reduction potential as well as the ability of the polymer to remain protonated. In this vein, we have been examining substituted versions of these materials whereas the sulfur content of the functional group provides the requisite protonation of the polymer.

We have been exploring studies on these materials to examine the effects of various doping conditions on the stability of the doped material. We have furthermore been examining the utilization of these materials in organic photovoltaic devices which are typically made by fabricating a film with both an electron donor and an acceptor. The photoinduced electron transfer reaction that occurs at the donor/acceptor interface is incidentally the reason which then gives rise to a photovoltaic response. We are examining these materials as potential electron acceptors and investigating their photovoltaic response when incorporated into a device.

C5.40 ELECTROCHEMICAL CHARACTERIZATION OF POLY(ORNITRILE VINYLIDENE) PHOTOVOLTAIC. M.A. Kreger, C. Graetz, J.Z. Zhang, Univ of California Santa Cruz, Dept of Chemistry, Santa Cruz, CA; A.J. Bryce, National Renewable Energy Labs, Golden, CO; S. Chasteen, S.A. Carter, Univ of California Santa Cruz, Dept of Physics, Santa Cruz, CA; H. Tillmann, H.-H. Horsch, Univ of Jena, Institute of Organic Chemistry and Macromolecular Chemistry, Jena, GERMANY.

We have investigated the photovoltaic layer in Titanium Dioxide/Conjugated Organic Dye/fuel solar cells. Correlation between optical properties and observed electrochemical behavior offer insight into the design of more efficient polymer based photovoltaics. The existing design is a layered structure consisting of TiO2[50-100 nm]/PPV derivative[50-100 nm]/Au. Devices containing poly[2-methoxy-5-sulfonato1,4-phenylene] and poly[2-methoxy-5-sulfonato1,4-phenylene] and it’s alternating copolymer poly[2-methoxy-5-sulfonato1,4-phenylene] with poly[2-methoxy-5-sulfonato1,4-phenylene] and poly[2-methoxy-5-sulfonato1,4-phenylene] are the photovoltaic layers. Undoped MEH-PPV devices have short circuit current densities of 0.92 mA/cm2, open circuit voltages of 0.7V and power conversion efficiencies of 0.3%. Improvements to charge carrier mobility through the polymer and charge transfer to TiO2 are necessary for optimal device performance. We investigate improving power efficiency and charge transport through the polymer by electrochemical doping. To understand charge transfer from polymer to TiO2 we examine the relative energy level between the HOMO, LUMO and TiO2 conduction band. We report HOMO-LUMO energy levels for several PPV derivatives obtained from a combination of cyclic voltammetry and UV-visible absorption experiments. The polymer layer functions both as primary light absorber and electrolyte in these devices. As an electrolyte, the polymer is required to undergo successive oxidation and reduction cycles. We examine the stability of the conjugated organic layer as a function of potential and make a correlation between stability, lifetime and efficiency.

C5.41 SELF-INFRARED PHOTOVOLTAIC RESPONSE FROM SELF-ASSEMBLED FILMS OF SELF-DOPED CONDUCTING POLYMERS. Jeffery W. Baer, Michael F. Durstock, Barney Taylor, Robert Sprey, Air Force Research Laboratory, Polymer Branch, Wright-Patterson Air Force Base, OH; Philip Chang, Arthur J. Epstein, Ohio State Univ, Dept of Physics and Dept of Chemistry, Columbus, OH.

Large area, flexible photovoltaic devices are of interest to the Air Force for energy generation in both space and terrestrial based applications. Recently, research has been undertaken on fabricating photovoltaic devices from thin films of conjugated polymers and other organic systems. Though many challenges remain, these films offer advantages for the creation of lightweight, flexible, and inexpensive power generation from the visible and near infrared (NIR) portions of the solar spectrum. In this study, we examined electroabsorption self-assembled (ESA) films of self-doped poly[N,N'-bis[4-aminostyryl]octadecylamine] (NSPAN) within organic photovoltaic devices. Specifically, we investigate the near infrared photovoltaic/photocurrent response of these devices and their possible underlying mechanisms. It is demonstrated that a significant enhancement in the absorption and near infrared photocurrent response can be obtained with doped conducting polymers over similar devices based on self-assembled films of poly(phenylenvinylene) (PPV) and functionalized fullerene. Additional devices based on thin films of poly(phenylenevinylene) doped with polyaniline and sulfonated polyethylene (SPE) and bis-arcne-based n-doped poly(phenylenevinylene).
polymers were also investigated. P. Chung and A.J. Epstein supported in part by Dayton Area Graduate Studies Institute Contract No. MF-OSU 08-18.

C5.42 PHASE SEPARATION IN POLYFLUORENE BLENDS: A COMBINED PHOTOVOLTAIC AND MICROSCOPIC INVESTIGATION. Anna C. Arias, J. Devin MacKenzie, Richard H. Friend, Cavendish Laboratory, Cambridge, UNITED KINGDOM; W.T.S. Huck, Melville Laboratory, Cambridge, UNITED KINGDOM.

The concentration dependence of the optical, morphological and photovoltaic properties of PSbT-PPb has been analyzed in order to understand the interrelationships between transformation times, effective mobilities, blend interactions, and the stability of different thin film morphologies. The nature of phase separation is of central importance in the area of conjugated polymer blend optoelectronic devices. It influences critical factors such as charge transport, exciton generation or energy transfer in both LEDs and photodiodes. To address this, our study of blend morphology control has also focused on surface energy effects to control compositional segregation normal to the plane of the film. Controlled phase-separated structures were obtained on treated organic and inorganic substrates. Substrate surface treatments included self-assembled monolayer modification as well as other techniques. Atomic force and fluorescence microscopy was used to reveal film morphology with photovoltaic and photoluminescence efficiencies as a function of surface treatment, concentration, and preparation conditions.

C5.43 IMPROVING POWER EFFICIENCIES IN POLYMER-POLYMER BLENDS PHOTOVOLTAICS. A. J. Breeze, National Renewable Energy Laboratory, Center for Basic Sciences, Golden, CO; S.A. Carter, Z. Schönherr, University of California, Santa Cruz, CA; H.H. Höhfeld, H. Tillmann, Friedrich Schiller-University, Institute of Organic and Macromolecular Chemistry, Jena, GERMANY.

Our previous work on organic-inorganic composite photovoltaics examined the properties of multi-layer devices composed of planar, transparent titanium dioxide (TiO2) solgel and the polymer MEH-PPV with Au electrodes. We demonstrated that the energy conversion efficiency in these devices was limited by low hole mobilities in the polymer; a short exciton diffusion length (limiting the amount of useful absorbed light), and by recombination losses across the polymer layer. Several groups have shown that the short exciton diffusion length problem can be at least partially circumvented by using polymer - polymer blend of hole and electron transporting polymers which create exciton dissociation pathways throughout the polymer layer. Our devices consisting of a 1:1 blend of the hole transporter MEH-PPV and the electron transporter CN-ether-PPV in the polymer ITO/TiO2 solgel/polymer blend/Au device structure have yielded short circuit current densities up to 3.3 mA/cm2, open circuit voltages of 0.65V, and an overall power conversion efficiency of 0.6%. We address the question of whether these blended devices still face the same limitations as the plain devices or are now in the realm of being limited by low absorption in the thin polymer layer, minimizing the efficiency as a function of polymer layer thickness. Preliminary results indicate that although charge collection is improved due to exciton dissociation occurring throughout most of the polymer layer, these devices are still limited by charge transport rather than light absorption.

C5.44 PHOTOCONDUCTIVITY OF SMALL MOLECULE ORGANIC TRANSISTORS. D. Knipp, Xerox Palo Alto Research Center, Palo Alto, CA; K.D. Moust, Xerox Research Center of Canada, Mississauga, Ontario, CANADA; R. Apte, Xerox Palo Alto Research Center, Palo Alto, CA; L. Jiang, Xerox Research Center of Canada, Mississauga, Ontario, CANADA; J.P. Lu, Xerox Palo Alto Research Center, Palo Alto, CA; B.S. Ong, Xerox Research Center of Canada, Mississauga, Ontario CANADA; R.A. Street, Xerox Palo Alto Research Center, Palo Alto, CA.

Recent improvements in electronic materials and the progress in advanced processing technologies such as printing, have made organic thin film transistors (TFT) an interesting element for large area sensor applications and low cost application specific integrated circuits (ASICs). In order to study the electronic transport mechanisms and the optoelectronic behavior of the small molecule materials, we have measured steady state and transient photocurrent on transistor structures. Measurements were made on organic TFTs based on pentacene (PEN) and various phthalocyanine (Pc) compounds (C12H10Pc, VOPc etc.) which were synthesized and thermally evaporated on inverted transistor structures, bonded on a glass substrate with an indium-tin oxide gate insulator or a crystalline silicon substrate with a thermal oxide.

Measurements include the dependence of photocurrent on gate voltage, source-drain voltage, light intensity and wavelength, and a control with non-grated structures. We observe a strong increase of the photocurrent with gate voltage, correlated with the dark transfer characteristics of the transistor. The effect is attributed to electron-hole separation by the gate field. Furthermore, the gate bias modifies the TPT spectral response, enhancing the photocurrent for shorter wavelength (600-750nm), while reducing the extraction of photogenerated carriers for higher wavelength (750-900nm). This effect can be attributed to a stronger band bending at the interface between the organic material and the dielectric for higher gate voltages in combination with the strong wavelength dependent absorption of the materials.

C5.45 POLYMER/DYE BLEND PHOTOVOLTAIC CELLS WITH BROAD PHOTOCURRENT SPECTRUM. Janke J. Dittrich, Olivier Malbouisson, Elisabeth A. Meseguer, Bernd Thiemann, Ludwig-Maximilians-Universität, Cambrige, UNITED KINGDOM; Muhammad S. Kham, Dep. of Chemistry, Sultan Qaboos Univ., Sultanate of Oman; Stefan Becker, Klaus Müller, Max Planck Institut for Polymer Research, Mainz, GERMANY.

The photovoltaic properties of novel blends of soluble organic dyes and soluble conjugated polymers with broad photocurrent spectra are reported: either the electronic donating polymer or the electron-accepting dye was chosen to absorb in the red. Strong quenching of the photoluminescence on blending provides evidence for photo-induced charge transfer at the interface between the two material systems. The photovoltaic response of these blends was found to be a function of blend ratio in sandwich cells between indium tin oxide and aluminum electrodes, and in all cases the external quantum efficiency (EQE) was considerably enhanced with respect to devices made from conjugated single materials. Interesting features of the photovoltaics of polymer/dye blends are: 1) The highest EQEs of about 6% are achieved for devices containing 90% by weight of the dye, 2) the dye forms an electronic conducting crystal network, and 3) we observe EQE enhancement upon thermal annealing.

C5.46 DESIGNING ACTUATOR RESPONSES IN ANISOTROPIC LIQUID CRYSTALLINE ELASTOMERS. Donald L. Thomas III, Patrick Kelle, Devandar Shenoy, Javald Naciri, and Bishal R. Ratna.

"Center for Biomolecular Science and Engineering, Naval Research Laboratory, Washington, DC; Laboratoire Physico-Chimie Curie, CRN'SUR 118, Institut CURS-Section de Recherche, Paris, FRANCE.

Anisotropic liquid crystalline elastomers (LCEs) with laterally affixed liquid crystalline mesogens have been prepared with stress, strain, and temperature properties of a muscle. Several molecular parameters have been changed in the LCEs in order to better understand the relationship between the molecular structure and the mechanical properties in these systems. This work is increased when the sidechain spacer connecting the mesogenic group to the polymer backbone is shorter. These materials with different spacer lengths exhibit a number of different spring constants through the nematoc to isotropic phase transitions. These constants, in spring constants with respect to temperature under constant strain, through the nematic to isotropic phase transition are more than an order of magnitude higher than of typical vulcanized rubbers. These results have been characterized by thermomechanical and dynamic mechanical measurements, along with change parameter measurements of the liquid-crystalline mesogens through the nematoc to isotropic phase transitions by polarized PIF. The understanding of the relation between the chemical structure of the materials and the observed spring constants provides opportunities in increasing the performance of these actuators materials which exhibit elasticity.

C5.47 A COMPARATIVE STUDY OF THE PHOTOPHYSICS IN POLYFLUORENES AND POLYFLUORENES WITH POLYPHENYLENE DENDRONS SIDECHAINS. E.J.W. Lin.

Institute for Solid State Physics, Technical University Graz, Graz, AUSTRIA; C.H. Kim, J. Shinhr, Amos Laboratory-USDOE and Department of Physics and Astronomy, Iowa State University, Ames, IA; M.A. Lii, G. Bongiovanni, A. Musa Dipartimento di Fisica and INFN, Universita di Cagliari, Monserrato, ITALY; S. Segeti, A.C. Grimsdale, T. Weil, V. Enckmann, U. Scherf, K. Miihl Max-Planck-Institut for Polymer Research, Mainz, GERMANY; G. Lexing ATOS Research & Technology, Lechen, AUSTRIA; Institute of Microstructured Materials and Photonics, Johannes Research Inc, Weiz, AUSTRIA.

The development of blue light-emitting polymers has been the subject of intense academic and industrial research directed towards the fabrication of full colour polymer displays. A polfluorene (PFO) has
been prepared in which bulky polyphenylene dendrimer substituents (D-PFO) suppress aggregate formation, thus yielding a polymer with pure blue emission in photoluminescence (PL) as well as electroluminescence. We present experimental data on cw absorption, steady state PL, photoinduced absorption (PIA), PL detected magnetic resonance (PDMR), and transient PL (Ti-PL) spectroscopy in the time domain of 100-femtoseconds in order to study the dynamics as well as the interaction of both emitting and absorbing species in this novel D-PFO. Furthermore, we applied the same set of spectroscopic techniques to characterise a PFO with alkyl sidechains. We observe that the dendrimer sidechains, which fully suppress aggregate formation, also strongly alter the dynamics of excited entities. In particular, the Ti-PL and temperature dependence of the PL from 1.5 to 300 K demonstrate different singlet exciton (SE) dynamics in films of the two polymers, while in the case of the fullerene based material in solution it is essentially the same. Similar results are found for the dynamics and lifetimes of polaron and triplet excitons from PIA and for the interaction between SEs and polaron as studied by PDMR.

C5.48 TRIPLET STATES OF LUMINESCENT POLYMERS. Andy Mitchell, OREM Research Group, Dept of Physics, University of Durham, Durham, UNITED KINGDOM; Hugh Burrows, Dept of Chemistry, University of Coimbra, PORTUGAL.

We have measured the lowest lying triplet energy states in an range of luminescent polymers including a family of substituted polythiophenes and found a linear relationship between the first singlet and triplet energies, irrespective of chain structure. We shall discuss the implications this has on the electron-electron correlation energy in conjugated polymers. One interesting observation from this work is that a polymer with singlet energy gap below ca. 1.5 eV should have a triplet ground state. Further we are embarking on a study of the phosphorescence behaviour in the solid state from these polymers using a new enhanced gated CCD detection system. Detailed studies of solid state effects on the triplet states of the polymers will be presented along with first results from triplet capture cross section measurements.

C5.49 Abstract Withdrawn.

C5.50 Abstract Withdrawn.

C5.51 EFFECTS OF INSERTING SMALL AMOUNTS OF DIELECTRIC MATERIAL BETWEEN THE ACTIVE LAYER AND THE CATHODE OF POLYMERS BASED PHOTOVOLTAIC DEVICES. S.E. Shakur*, C.J. Benboe, F. Palskger, N.S. Sarchilli, G.E. Rubbecke,3 Optical Sciences Center, University of Arizona, Tucson, AZ, 4Linz Institute for Organic Solar Cells (LIOS), University of Linz, Linz, AUSTRIA.

We report on the effects of inserting small amounts of various dielectric materials between the photovoltaic layer and the aluminium cathode in organic photovoltaic devices. Bulk-heterojunction devices based on the conjugated polymer PBDB-T:PC71BMblend with a methanol/fullerene show improvements in the device open-circuit voltage, fill-factor, and power conversion efficiency when this technique is used. These data indicate that the presence of a small amount of dielectric material produces a more cromatic contact at the organic / aluminium interface. This is seen explicitly as a decrease in the series resistance of the devices.

C5.52 DEVELOPMENT OF HYBRID ORGANIC-INORGANIC SOL- GEL MATERIALS AND THEIR APPLICATIONS TO OPTICS AND OPTOELECTRONICS. Aki H.O. Kiiskinen*, Joon T. Rustu, Nasser Al-Hajrah, Michael Desmans, and Ghassan E. Jabbour, VTT Electronics, Oulu, FINLAND, 5University of Arizona, Optical Sciences Center, Tucson, AZ.

We present the fabrication of microoptical and optoelectronic components using photopatternable hybrid organic-inorganic materials. Polyethylene-oxide-acrylate modified hybrid glass materials are used to fabricate active, passive elements and structures. These can be then integrated to optoelectronic devices, such as organic light emitting devices, by using various processing techniques. The synthetic aspects of the hybrid materials are also outlined.

8:30 AM C6.1 ELECTRONIC POLYMERS: NEW HORIZONS IN NANO- ELECTRONIC AND CHEAP DISPOSABLE CIRCUITS. Alain Meier-Hermann, University of Pennsylvania, Philadelphia, PA.

(ABSTRACT NOT AVAILABLE)

9:00 AM C6.2 MODULAR MOLECULAR DESIGN LEADS TO NEW EUROPOLAR MICROPHOTOMIC AND OPTOELECTRONIC PROPERTIES OF NOVEL EUROPOLAR(III) β-
- DIKETONATES. Matthew R. Robinson, Guillermo C. Brown, UC Santa Barbara, Department of Materials, Department of Chemistry, Institute for Polymers and Organic Solids, Santa Barbara, CA; Marie B. Oregan, UNILAN Corporation, Santa Barbara, CA.

Light emitting diodes were fabricated from a blend of tris[N- (dicyanomethylene)3,3',5,5'-tetracyan phenyl methane] (trisDP) and a phthalocyanine (P3P). The composite incorporates a phthalocyanine ligand for electron transport and a carbazole fragment in the diketonate ligand for hole transport. The photoluminescence from films of I is nearly monochromatic, characteristic of the europium ion and proceeds with an efficiency of 50(3)%.

The external quantum efficiency of simple LEDs with the architecture ITO/PVK/C9:PP/PVK/ITO/Ca is 1% with a turn-on voltage of 2V. Furthermore, the six hexoxy groups prevent crystalisation and allow for the formation of transparent clear films directly from solution. Accordingly, LEDs were fabricated from the next complex. Devices were fabricated using the simplest possible device architecture comprising ITO / 1 / Ca. A second type of structure where a PVK layer was introduced on top of the ITO, was also investigated. The external quantum efficiencies are 0.1% (0.3%) with turn-on voltages of 5V (8V) for the devices without [with ] PVK. Over 2 hours of continuous operation is easily accomplished. The corresponding devices using a common europium(III) complex, tris(dinaphthylmethine)mononaphthalene europium(III) [also spin cast from solution, exhibit turn-on voltages over 20V, efficiencies less than 0.05%, and operation lifetimes less than 1 second - devices inferior to complex 1]. These are not optimised products but stand to show the benefit of the modular molecular design approach. The design and synthesis of new europium(III) and erbium(III) complexes are underway. Through the modular approach, it is feasible to add desired properties (high glass transition temperature and better electron transport) to the superior hole transport, stability, and high quantum efficiency of I. LEDs fabricated from these complexes both next and in blends with conjugated polymers are discussed here.

9:15 AM C6.3 SILOLE DERIVATIVES WITH A HIGH AND NON-DISPERSIVE ELECTRON MOBILITY, AND A 100% PHOTOLUMINESCENCE QUANTUM EFFICIENCY. H. Muraoka, G. Malliaras, M. Uchida, Y. Shn, Z.H. Kafafi; “US Naval Research Laboratory, Optical Sciences Division, Washington, DC, 2Cornell University, Department of Material Science and Engineering, Ithaca, NY, 3Chino Corporation, Yokohama, Kanagawa, JAPAN.

Non-dispersive and fast electron transport was realized for an amorphous, vapor deposited film of 2,5-bis[4-((2’ -(4-hydroxyphenyl) )-1,1-dimethyl-3,4-diethylphenylcyclopentadienyl] ethene, exhibiting highly fluorescent blue-green light with an absolute quantum yield close to 100% in the solid state. MOLEDs composed of stacked neat films of these silole derivatives and a hole transporting layer demonstrated a low operation voltage and an external quantum efficiency of 48.8%, close to the theoretical limit.

9:30 AM C6.4 SYNTHESSES AND CHARACTERIZATION OF NOVEL LIGHT- EMITTING POLYMERS. Alex K-Y. Chen, Hong Ma, Xuefeng Jiang, Petra Herghat, Binquan Chen, Department of Materials Science and Engineering, University of Washington, Seattle, WA.

A series of novel conjugated polymers based on the fluorene/bithiophyl and fluorene/benzothiadiazole units were synthesized via the palladium-catalyzed Suzuki coupling reactions. The introduction of a twisted, non-planar bithiophyl structure provided an effective mechanism for tailoring the spectral characteristics of the polymers and improving their solubility and thermal stability. Different conjugated moieties with good hole or electron transporting property were copolymerized with fluorene to fine-tune the HOMO and LUMO levels of the polymers. In addition, aromatic diamine containing perfluorocyclobutanes have been
developed to form robust hole-transporting polymers for the multilayer integration of polymer light-emitting diodes (PLEDs). Highly efficient devices have been developed that possess low turn-on voltage (2.2 V), high external quantum efficiencies (as high as 6%), and high brightness (~38,000 cd/m²). Characterization and detailed device properties of these polymers will be discussed in this paper.

10:30 AM *C0.5

High efficiencies and long lifetimes have been the main fundamental issues to be solved in order to make polymer light-emitting diodes (PLED) a commercially attractive alternative to conventional display technologies. Although good results have been reported for both polymeric and molecular LEDs, blue devices have not matched this, potentially limiting the use of this new technology in full colour display applications. Also, as in monochromatic or backlighting applications, there are always benefits from further improvement in device efficiency, brightness and lifetime. In this paper we report our latest results on both issues. A major mechanism responsible for degradation in blue PLED has been identified, and changes in the device structure have been made to allow us to achieve a predicted lifetime (defined as the time to reach half of the initial brightness when driven at 100 cd/m²) in excess of 50,000 h. This is to our knowledge the longest lifetime ever reported for blue polymer LEDs. We will discuss such degradation mechanisms, our solutions, and propose possible changes to further improve the lifetime. We have also recently developed a green-yellow structure with high efficiency and very high brightness as well as blue, ideal for automotive and backlighting applications. This is based on a blend of two polymers, one is an electron transporter and emitter, the other is a hole transporter. A threshold voltage of 3.5 V, brightness of 100,000 cd/m² at ~5 V and peak efficiency of 20 cd/A/W has been achieved in devices with predicted lifetime in excess of 20,000 h. We present possible mechanisms responsible for such high brightness, based on optical, electrical, and morphological data.

11:00 AM *C0.6
POLYFLUORENE-METAL SURFACE AND INTERFACES. S.T. Lee, Center of Super-Diamond and Advanced Films (COSDAP) & Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, CHINA

Polyfluorene has recently attracted much attention in the research of organic light-emitting diodes (OLEDs) because polyfluorene-based OLEDs have many superior device characteristics. As the interface or contact is extremely influential in the OLED performance, we have undertaken a systematic surface science study of the polyfluorene surface and its interface with metals. Poly (9,9-dioctylfluorene) (PFO), the prototypical polyfluorene, is taken as a case study. Firstly, the surface electronic structure and stability of the PFO film are studied. Secondly, the interfaces of Ca, alkali metals and Ag with PFO are investigated. Bipolar states are induced upon alkali metal deposition on the PFO film, and these states are detrimental to the irradiation recombination of carriers. However, Ag deposition has less influence on the electronic structure of the PFO film. The effect of oxygen on the metal-PFO interface is also investigated. Bipolar states can be eliminated upon oxygen exposure. Fourth, the PFO surface is modified by mild Ar-irradiation to form a barrier against Cu-diffusion, resulting in the formation of a sharper Ca/PFO contact. The implications of the above findings on the PLED device performance are discussed.

11:30 AM *C0.7
POLYTHIOPHENE PHOTODIODES: MOLECULAR ENGINEERING, NANOSTRUCTURE MODIFICATION AND NANO-PATTERNING. Ole Inganæs, Fengling Zhang, Tobias Nyberg, Biomolecular and organic electronics, IPMI Linköping University, Linköping, SWEDEN; Martin Svensson, Mats Andersson, Polymer Technology, Chalmers University of Technology, Göteborg, SWEDEN; Michel Magini, Department of Organic Chemistry, University of Padova, Padova, ITALY

Efficient photoinduced charge transfer is observed in conjugated polymer (donor) and fullerenene (acceptor) complexes. Formation of supramolecular structures in solid films of organic conjugated polymers and fullerenene can help in making use of the very rapid photoinduced charge transfer. Polythiophenes in various forms are our main candidate for these materials, and allow absorption to be moved towards the higher wavelengths, important for the exploitation of the solar spectrum, and towards true molecular engineering by chemical synthesis of the donor and acceptor moieties in copolymers are highlighted. Supramolecular engineering is necessary to enhance performance in many blends, and we report the use of vertically aligned multilayers assembled from polymer and molecule solutions. On a yet larger scale, electrode nanostripping may be used to build new types of devices, with possibilities for enhanced optical absorption in the thin organic layers.

SESSION C7: PHOTONICS AND TRANSISTORS
Chair: Bert W. Meijer
Thursday, April 19, 2010
Nobil Hall A/B (Marriott)

1:30 PM *C7.1
ELECTRONIC PROPERTIES OF POLYMER-FULLERENE SOLAR CELLS. S.V. Dyakonov, J. Riedel, J. Parisi, Univ of Oldenburg, Oldenburg, GERMANY; C.J. Brabec, N.S. Sariciftci, Limi Institute for Organic Solar Cells, Physical Chemistry, Johannes Kepler Univ Linz, Linz, AUSTRIA; J.C. Hummelen, Stratingh Institute and MSc, Univ of Groningen, Groningen, THE NETHERLANDS.

The utilization of conjugated polymers in the solar cell's active layer is based on the phenomenon of photoinduced electron transfer. Most of the activities in the field are devoted to the wide-gap polymers, mainly poly-(phenylene-vinylene), with the semiconducting gap of about 2.4 eV, and fullerene C60, or its derivatives, as an acceptor materials. Following the progress of the charge generation, recombination and transport in this class of materials is decisive for their applicability in photovoltaics. To study the electronic transport properties of the solar cells, temperature and illumination intensity dependent IV analysis has been performed. The behaviour of the cell parameters is found to be more complex as compared to that known for inorganic pn-solar cell. The charge transport in the solar cells studied was found to be bulk space-charge limited. Further studies by admittance spectroscopy reveal frequency dependent contributions to the device capacitance which originate from shallow traps levels located in the bulk of the semiconductor material. An efficient generation of charge carriers and their free in these systems have been studied by electron spin resonance. We can clearly follow the formation of photogenerated electron hole pairs under illumination of the device absorber. Investigation for the cell performance is that photoinduced a-pairs remain in the composites even after the photocurrent is off, implying the presence of defect induced trap states.

2:00 PM *C7.2
TRAPPING OF CHARGES IN PERCOLATION NETWORKS. Janke J. Dittrich, Wendy Hayn, Paul Alivisatos, Dept. of Chemistry, University of California, Berkeley, CA; Elizabeth A. Marzella and Richard H. Friend, Cambridge Lab., Univ. of Cambridge, UNITED KINGDOM

We report a detailed study of optical, photovoltaic and morphological properties of networks of conjugated polymers or smaller organic or inorganic macromolecules, which constitute a very promising class of materials for use in solar cells and photodetectors. We find that in such networks trapping of charges on the non polymeric component is an important factor in determining device performance. These results are discussed in the context of percolation theory.

2:15 PM *C7.3

In the last decade composite films consisting of conjugated polymers and fullerene derivatives have been considered to achieve solid-state polymer photovoltaic cells. Here, we investigate the charge (phenylene vinylene) fullerene dyads (OPVn-C60 n = 1-4, the number of phenyl rings) as model compounds for polymer/fullerene blends in solvents of different polarity. We demonstrate that upon photoexcitation of the OPVn moiety of the dyads a single-photon transfer occurs towards the fullerene moiety in solution. In contrast, photocaeciation of the dyads in a polar solvent results in electron transfer for OPV1-C60, OPV2-C60, and to some extent for OPV3-C60, but not for OPV1-C60. These results are compared to the results obtained for mixtures of OPVn and Ψ-C60 in the same solvents. The solvent-dependent change in free energy for charge separation of the donor/acceptor systems is calculated from the Weller equation and fully explains the observed behavior. Near-infrared state photoinduced absorption spectroscopy and time-resolved fluorescence measurements suggest that the electron transfer in these dyads in polar solvents likely occurs
by a two-step process, i.e., a very fast singlet energy transfer prior to charge separation. Ultrafast femtosecond pump-probe spectroscopy on OPV-3:C60V:1.5 confirms this mechanism. Subsequent to a sub-picosecond singlet-energy transfer, electron transfer occurs on a 30 ps timescale, resulting in a charge separated state with a lifetime of 100 ps. In thin solid films of OPV-3:C60 and OPV-3:C60V, a long-lived (milliseconds) charge-separated state is formed after photoexcitation. The long lifetime in the film is attributed to the migration of charges to different molecules.

3:15 PM C7.4
ANALYSIS AND TWO-DIMENSIONAL MODELLING OF POLYMORPHISM. Nir Taaleri, Technion, Dept of Electrical Engineering, Haifa, ISRAEL.

Analysis of polymer field effect transistors will be reported. To do so, two-dimensional numerical simulation that solves the transport and Poisson equations self-consistently was devised. The simulator structure is the same as that for organic transistors (gate and source/drain on either side of the active layer) with the active layer being intrinsic (un-doped). The 2D charge and potential distributions in a device as a function of space and time will be presented. It is found that the device architecture influence the L/V characteristics and the apparent threshold voltage as well as the dynamic response. Based on the numerical results we derive simple relations that enable better insight and possible optimisation of the operation of such devices in both CW and time domain. Where possible, comparison to experimental data is made.

3:30 PM C7.5
HIGH-PERFORMANCE ORGANIC FIELD EFFECT TRANSISTORS AND INTEGRATED INVERTERS. J. Ficker, A. Ullmann, W. Fieß, H. Rost, W. Clemen, SIEMENS AG, Erlangen, GERMANY.

Integrated plastic circuits (IPC) will be one of the basic parts of future electronics as they are a precondition for the manufacturing of low-cost, all-polymer integrated circuits. We will present our recent results on fabrication of Organic Field-effect-Transistors (OFETs) and integrated inverters for low-cost applications. Top-gate transistors on plastic substrates with organic semiconductor and organic insulator were built. Source-drain structures were made by standard lithography of ITO on PET foil. On top of these electrodes, poly(3-alkylthiophene) (P3AT) as semiconductor and poly(4-hydroxy styrene) (PHS) as insulator were homogeneously deposited by spin-coating. The gate electrodes consist of titanium contacts. With this simple setup, the transistors exhibit excellent electric performance with high source-drain current at source-drain and gate voltages below 1 V. The characteristics show a very good saturation behavior for low bias and they are comparable to results published for precursor pentacene [1]. Furthermore we will discuss organic integrated inverters exhibiting logic capability. All devices show shelf-lives of several hours without any encapsulation.


3:45 PM C7.6

The early demonstrations of field-effect transistors based on organic semiconductors with high dynamic range utilized single devices incorporating p-channel materials such as thiophene oligomers and pentacene. Through end-group substitution and use of electron-deficient cores, we have built a library of semiconductors with a variety of attributes, including p-channel function and chemical sensitivity. The activity of these semiconductors is based on physical and solid state organic chemistry principles that will be outlined in this talk. The assembly and integration of devices incorporating these novel materials will form complementary circuits, pixel drivers, and meso-electro-optic switches will also be discussed.

4:15 PM C7.7
IMAGE SENSORS ARRAY WITH AN ORGANIC PHOTO-CONDUCTOR. R.A. Street, Xerox PARC, Palo Alto, CA; J. Graham, Z. Popovic, J. He, Xerox Research Center of Canada, CANADA; M. Malo, R. Lim, and J. Ho, Xerox PARC, Palo Alto, CA.

A 3-dimensional image sensor array incorporating an organic light sensor is reported, with potential application to digital cameras and x-ray imaging. The 512x512 element array has pixel size of 100 microns, and operates with active matrix addressing using amorphous silicon thin film transistors. The array design allows the use of a continuous layer of the organic sensor material without the need for pixel-level patterning. The sensor comprises a bilayer of BCP (benzimidazole perylene) and TPd (tetracyanobutadiene in a polycarbonate binder) with a thickness of about 10 microns. The layers are deposited by vacuum evaporation and spin coating, covering metal contact pads at each pixel, and a semi-transparent common electrode is deposited on top to apply the bias. Good imaging properties are demonstrated with circuitry that provides a linear output. The dark leakage current is below 5 pA/mm², which is low enough to prevent significant charge build up even for long integration times. High charge collection and good uniformity is obtained at reasonably low bias voltages (~20V). The spectral response covers the range from 400-800 nm matching the known absorption spectrum so that good color imaging is achieved. Careful measurements of the line-spread function and modulation transfer function show that the lateral conduction between pixels is low and independent of bias voltage. We also find that charge created in the gap between pixels is collected. Visible light images confirm the high spatial resolution and we also demonstrate x-ray imaging with a phosphor converter. The talk will discuss the potential benefits of organic sensors in regards signal noise and spatial resolution.
CS.2
POLYMERIZATION AND CHARACTERIZATION OF 1-FLUOROVINYL ARYL ETHER CONTAINING HIGHLY FLUORINATED AROMATICS. Dong Sung Lee, Dong Kee Yi, Dong Yu Kim, Department of MSE, Kwangju Institute of Science and Technology, Kwangju, KOREA [SOUTH].

The use of amorphous, fluorinated polymers in the electronic and photonic industry is expected to increase dramatically due to several unique electrical and optical properties of fluorinated polymeric systems. Poly(ether ketone) (PEK) has already become an active research area, because PEKs have several advantages in comparison to glass optical fibers. The objective of this research is synthesis of amorphous, highly fluorinated polymers with a high glass transition temperature for these applications. We synthesized new monomers containing trifluorovinyl ether which undergo thermal (290°C) cyclopolymerization. So it is synthesized perfluorinated polymer for POFs. Polymerization was carried out under various conditions, such as bath temperature and solvent. The effects of copolymerization with vinyl monomers was studied. The structures of monomers and polymers were characterized by 19F NMR and 13C NMR, and the average molecular weight was determined by gel permeation chromatography and thermal properties were measured by TGA and DSC. Optical properties of prepared polymers will be discussed.

CS.3
THE SEARCH OF HIGH PERFORMANCE POLYMER LIGHT-EMITTING DIODES. Chun-Chi Chang, Feng-Chung Chen, Jie Liu, Yang Yang, University of California at Los Angeles, Dept of MSE, Los Angeles, CA; Geng Lan, University of Southern California, Dept of Chemistry, Los Angeles, CA; Junji Kido, Graduate School of Engineering, Yamagata University, Yamagata, JAPAN.

Recently, it was shown that the singlet and triplet states of phosphorescent dopants significantly improve organic LED efficiency. However, this achievement has not been quite reproducible in polymer LEDs. In this presentation, we report a systematic investigation into this problem. We demonstrate that the use of phosphorescent dyes can be successfully applied to polymer systems to generate high quantum efficiency polymer LEDs. In this research, two host polymers, poly(vinylcarbazole) and poly(9,9-bis(3-(N-carbazolyl))fluorene) were blended with three different phosphorescent iodine complexes were used as the emitting media. Based on the different combinations of polymeric hosts and phosphorescent dopants, device efficiencies ranging from 1.0 to 2.5% have been achieved. The effect of the structure and energy level of different polymeric hosts on device performance will be discussed.

CS.4

The electroluminescence of polyfluorene homopolymers and various styrene copolymers is in the deep blue, with peak emission wavelengths down to 420 nm. These materials are therefore of great interest for use in full-color OLED displays both as the emitter for blue subpixel and as the host for green and red emitting dopants or comonomers. In this work, we compare the properties of single- and multilayer diode structures based on dilauryl and di(2-ethylhexyl) substituted polyfluorenes. A cross-linked polymeric nylanimine hole transport polymer and a polyquinoline electron transport layer are introduced to better balance the charge injection from the electrodes and optimize the recombination in the fluorescent emitter layer. External quantum efficiencies increase from about 0.1% in single layer devices to well over 1% in dual layer devices. The electrical and optical response is determined by steady state and transient measurements. The effects on efficiency, emission spectrum and electrical response resulting from the introduction of dopant dyes into the emitter layer are also determined.

CS.5
CONJUGATED OLIGOMERIC COORDINATED SILVER PHENYLACETYLENE DERIVATIVES WITH ULTRAFAST OPTICAL KERR EFFECT. Yifan Xu, Boon K. Tso, IUC, Dept of Chemistry, Chicago, IL; Y.K. He, H.Y. Chen, Peking Univ, Institute of Polymer Science, Beijing, CHINA; W. Qian, Y.H. Zou, Peking Univ, Dept of Physics, Beijing, CHINA.

Investigations of functionalized transition metal coordinated with organic ligand systems have been greatly intensify in recent years due to the potential for obtaining novel optoelectronic devices. Recently, we have reported a novel organic aromatic macrocyclic ligand system, which are expected to enhance the optical nonlinearity. Silver phenylacetylene (APA) was prepared by one-step process in our lab and was characterized by a linear conjugated polymeric compound through matrix-assisted laser desorption/ionization time-of-flight mass spectrometric analysis. Its prominent third-order nonlinear optical susceptibility of 2 x 10^-12 esu, and second-order hyperpolarizability of 5.1 x 10^-10 esu were obtained via newly developed heterodyne ultrafast optical Kerr effect measurement, while the corresponding Hechtian polyacetylene phenylacetylene only gave very weak signals. Silver phenylacetylene derivatives, such as APA-silver terephthalate, APA-silver 2,4,6-trithiophene-2,5-dicarboxylate, APA-silver triphenyl phosphate and tetrameric APA-tritylphenylphosphate complexes were also prepared, characterized, and their optical nonlinearity properties were compared with those of the silver phenylacetylene under the same conditions. The third-order optical nonlinearity values depended mainly by the configuration geometry, the extent of cationic conjugation, and the solvent used, etc. The relative magnitude of the third-order nonlinear optical susceptibility values decreased with the reduced conjugation state. The aim of this work is to contribute to the response mechanism, seemed to be solvent dependent.

CS.6
A COMPARATIVE STUDY OF PHOTOINDUCED CHARGE TRANSFER IN CONJUGATED POLYMER-ELECTRON ACCEPTOR COMPOSITES AND DONOR-ACCEPTOR "DOUBLE CABLES". Gerald Zerza, Markus C. Schubert, Antonio Cravino, Serdar N. Sireroglu, LIS (Linz Institute for Organic Solar Cells), Physical Chemistry, Johannes Kepler University, Linz, AUSTRIA; Rafael Gómez, José L. Segura, Narciso Martín, Departamento de Química Orgánica, Universidad Complutense, MADRID, SPAIN; Martin Svensson, Martin R. Andersson, Polymer Technology, Chalmers University for Technology Göteborg, Göteborg, SWEDEN.

The photo-induced electron transfer from conjugated polymers to electron accepting molecules is known to proceed on the sub-100 fs timescale and leads to the formation of polaron on the polymer chain and radical anions on the electron acceptor. The recombination happens on the ns timescale and is believed to be dominated by non-radiative. We investigated different composites of thiophene and phenylenevinylene based polymers with fullerene and tetracyanoquinodimethane (TCNQ) derivatives as electron acceptors for charge transfer and recombination. The results for these materials are compared with studies on donor-acceptor "double cables", which are conjugated polymer chains with covalently linked electron acceptor moieties. Low temperature luminescence, photoinduced absorption and Optical Detected Magnetic Resonance (ODMR) studies are presented.

CS.7
OPTICALLY INDUCED BIREFRINGENCE IN POLYSTYRENE DOPED WITH DISPERSE RED 1. A MODEL TO EXPLAIN RESULTS FROM 10 TO 370 K. Fernando F. Dall Agnol, Josmarly R. Silva, S.C. Zlio and José A. Giacometti, Universidade de Sao Paulo, Instituto de Fisica de Sao Carlos, Sao Carlos, SP, BRAZIL.

Polymers withazo groups exhibit reversible trans-cis-trans photoisomerization characteristics that have been used for optical storage, optical switching and photonic surface relief grating. The photoisomerization produced by linearly polarized light leads to the molecular orientation perpendicular to the light polarization (angular hole burning). This process induces a birefringence on the sample and thus the optical storage. In the present work we report on the production of films of polystyrene (PS) doped with disperse red 1 (DR1), performed at various temperatures. The birefringence amplitude arises from 1.0 to 270 K, goes through a maximum and then decays to zero near the PS glass transition temperature, which is ca. 370 K. These results agree with data by Yoshii et al for azobenzene molecules dispersed in a crosslinked silicone resin. The birefringence amplitude, at a given temperature, is proportional to the DR1 content and depends on the rate of the sample cooling process. Results are explained using a model that accounts for the change in free volume with temperature, thus representing an improvement to well known models. We assume that the DR1 molecules are trapped inside a local free volume. The Graviss distribution function is used to describe the local free volume distribution in the sample while the Graviss distribution function gives the thermal free-volume fluctuation. Isomerization of the azobenzene group only occurs if the local free volume is larger than a critical value. Comparison with the experimental data shows that the model explains the temperature dependence of the birefringence, in addition to explaining how birefringence is affected by the thermal cooling process, as the simple free volume depends on such a process.

CS.8
INVESTIGATIONS ON POLYANILINE-POLYVINYLCHLORIDE BLENDS. Mireon Chipara, Department of Physics and
The nature of the metallic phase in conducting polymers is presently the subject of intensive study [1,2]. The high electric conductivity and the outstanding thermal and thermoelectric properties of polyaniline are balanced by poor mechanical properties and a low processability. Blends of polyaniline with different plasticizers are expected to improve the processability and the mechanical features [3]. Electron spin resonance investigations on different polyaniline-polyvinylchloride blends, containing 8, 5%, 10%, 15%, 20%, 40% and 50% polyaniline are reported. The electron spin resonance spectra show JES-NMR X-band spectrometer operating in X band. The temperature dependence of the resonance spectra, in the range 150 K to 450 K was investigated. In the whole range of temperatures and compositions, no resonances were observed. Accordingly, in these blends there are no high spin biphenolns. Supplementary mechanical (elongation is break and tensile strength) and dc conductivity data have been obtained. The presence of high spin biphenolns is covered by the experimental data as the resonance line intensity, the double integral of the resonance spectra, and the dc conductivity increase as the content in polyaniline is increased. The temperature dependence of the resonance line parameters is studied in detail. The connection between electron spin resonance data and transport phenomena is reflected in the temperature dependence of the resonance line width. A description is tentatively proposed. Additional data on the thermoelectric properties obtained by electron spin resonance and dc conductivity measurements, are discussed. REFERENCES: 1. J.J. Joc, S.M. Yong, J.P. Pouget, E.J. Oh, A.G. Mac Diarmid and A.J. Epstein, Phys. Rev. B, 57, 16, 5677 (1998). 2. B. Furchtli, P. Vignolo and G. Grego, J. Phys. Chem. B, 60, 20, 15705 (1996). 3. R. D. Hofstein, A. Zibib, D.B. Trainer, G.G. Jum, T. Ishiguro, Y. G. Min, A. G. Mac Diarmid, and A.J. Epstein, Phys. Rev. Lett., 78, 20, 3915 (1997).

**CS.9 TRIPLET EXCITED STATES IN ORGANIC AND Pb-CONTAINING PHENYLENE ETHYNYLENES**

Ananna Kaiser, Jomme Wilkon, Richard Friend, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM, Mohan Khan, Sultan Qaboos University, College of Science, SULTANATE OF OMAN.

The singlet excited state in conjugated polymers is well understood and the excited state is spin-forbidden in most organic polymers and can therefore only be detected with difficulty. In order to obtain a better understanding of the T1 triplet excited state in organic conjugated polymers, we have investigated a model system consisting of P3-containing polymers and monomers of the general structure [Pt(PBu)]C＝C＝C＝C]n. The analogous organic compounds are of the structure [C＝C＝C＝C]n and the phenyl-based spacer is varied to cover different optical gaps ranging from 1.75 eV to 3.1 eV. It is possible to directly observe the triplet state luminescence (phosphorescence) of the P3-containing polymers since the heavy Pt atom induces a strong spin-orbit coupling. This allows us to access the triplet energy levels of the steady state phosphorescence spectroscopy. For the P3-containing polymers, we find a constant energy gap between the S1 singlet excited state and T1 triplet excited state of about 0.7 eV. We also find the non-radiative decay rate from the T1 triplet excited state to increase exponentially with decreasing energy of the T1 state, in accordance with the energy gap law. For the corresponding series of organic polymers and monomers, we access the non-radiative decay rate of the T1 triplet excited state by measurement of the photoinduced absorption from the state. We discuss to which extent the trends observed in the P3-compounds also apply to the organic polymers and monomers.

**CS.10 CONJUGATED POLYMER FIBERS FOR LIGHT AMPLIFICATION AND LASING**

Takeyuki Kobayashi, Werner J. Blau, Department of Physics, Trinity College Dublin, Dublin, IRELAND, Harwig Tillmann, Hans-Henrich Rösch, Friedrich-Schiller University, Institute for Organic Chemistry and Macromolecular Chemistry, Jena, GERMANY.

We fabricated step index conjugated polymer fibers for light amplification and lasing applications for the first time. The fibers were 0.3 mm in core diameter and a few centimeters in length. Construction of such waveguiding structures provides the reduction of the background absorptions to very low levels for recording of high-density digital information in polymer devices. A conjugated polymer fiber made with CF-P3-PPV was transversely pumped at 355 nm with a frequency-tripled Nd: YAG laser (5 ns duration, 10 Hz repetition rate). The excited length of the fiber was increased in order to observe lasing, which decreased dramatically as the pump energy increased. The full-width at halfmaximum decreased to 17 nm at 548 nm for the pump fluence of 37 mJ per square centimeter. This behavior is indicative of the occurrence of amplified spontaneous emission, also termed as microcavity lasing. Furthermore, we made step index polymer fibers with fluorescent compound-doped polystyrene core. The active dopants incorporated into the fibers were a variety of stilbene compounds with more than 80% quantum yields, designed for blue-green region. The fiber doped with 2.5 wt% of 1-bis-[4-diphenyl amine]vinylene exhibited narrow linewidth emission at 445 nm with a full-width at halfmaximum of 3 nm when it was excited with pump power up to 355 nm with excimer laser specifically for optical feedback. For example, the formation of photobleached gratings will enable the demonstration of compact DFB or DBR fiber lasers.

**CS.11 DYNAMICS OF THE ENERGY TRANSFER IN CONJUGATED POLYMER/LANTHANIDE BLENDS**

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Energy transfer in photo-excited polymer/lanthanide blends proceeds in three distinct steps: (i) polymerized (Föster), (ii) ligand singlet-triplet ISC, and (iii) ligand-lanthanide resonant energy transfer. Here we focus on Eu[M1]3 CNPPP blends, exhibiting relatively high PL and EL efficiencies for nearly monochromatic white light emission. Transmission of Eu[M1]3 [M1=1-[(N-ethylcarboxylato)-1-[(3,9,9'5,9'5-tetraydroxy benzol] methol], that was also synthesized with Gd3 ion, can be spin-coated either alone or with the CNPPP polymer. Such a flexibility permits the distinct energy-transfer steps to be studied separately. We present temperature and power-dependent optical studies of Eu[M1]3, Gd[M3]3 and Eu[M1]3/CNPPP thin films, as well as time-resolved ESA and SE spectra of these compounds. We show that k1/k2 and k3/k4 represent the energy-transfer step. We also find a threshold in power-dependent PL spectra, characterized by the appearance of the ligand S1 ·− S0 emission, coupled with decreasing PL efficiency for Eu3+ 0.12 nm emission. This indicates a saturation condition governed by the long radiative lifetime of the europium S0 state, which for Eu[M1]3 amounts to 294 ± 2 ps.

**CS.12 A UNIFIED MODEL FOR THE SPACE CHARGE LIMITED CURRENTS (SCLC) IN ORGANIC MATERIALS COMBINING TRAPPING AND FIELD DEPENDENT MOBILITY**

Suresh C. Jain, Arupam Malhar, Win Geens, Tom Aernouts, Jef Poortmans, Robert Mertens, IMEC, Leuven, BELGIUM, Vikram Kumar, Solid State Physics Laboratory, Delhi, INDIA; Magnus Willander, Chalmers University of Technology, Department of Physics, Göteborg, SWEDEN.

The space charge limited L− characteristics of conducting organic materials are modified considerably by trapping and/or by field dependent mobility [1]. If the material is distributed with characteristic temperature Tc, the current varies as L− 1.5−2, where Tc = T / T [2]. If field (F) dependent mobility, L− = constant exp(β/F), is used and trapping is neglected, numerical integration of drift-diffusion equations show that L− 1−2 with a large value (≈ 3 to 7) of m [1]. As originally developed, Poole-Frenkel mechanism lowers the energy of ionization of traps and does not have an explicit effect on the mobility [2]. We have used the trapping model including the Poole-Frenkel effect on the ionization energy of the traps in a non-uniform field. We show that this approach is equivalent to combining the trapping and the field dependent mobility in one unified model. We have calculated carrier and field distributions, and L− characteristics for exponentially distributed traps with several trap depths using the same model. We have also made extensive L− measurements of AI/OC18:1/C60 and Al/OC/C60 Schottky diodes in the voltage range 0 to 15 V. The mobility data can be explained satisfactorily with our theory. [1] J. Campbell et al., J. Appl. Phys. 82, 626 (1998); ibid, 84, 6735-46, (1998); B.K. Crane et al., J. Appl. Phys. 86, 5767 (1999); J. Campbell Scott et al., Synthetic Metals, Vol 112, 289 (2000) [2] K. Uchida and W. Hwang, Electrical Transport in Solids, Pergamon Press, 1981.

**CS.13 THE TRIPLET STATE ELECTROLUMINESCENCE OF A Pb-CONTAINING ETHYNYLENIC POLYMER AND MONOMER.**

Jomme Wilkon, Anoop Dhoot, Alexander Seeley, Anna Kaiser, Richard Friend, Univ. of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM, Mohan Khan, Sultan Qaboos Univ, Dept of Chemistry, SULTANATE OF OMAN.
We have observed direct electroluminescence from the triplet $T_1$ excited state in a simple conjugated polymer light emitting diode (LED) structure, which is responsible for the light emission. It is possible to detect the triplet state luminescence (phosphorescence) associated with the conjugated system of this polymer since the heavy Pt atom in the polymer backbone induces a strong spin-orbit coupling. In this way, a slightly higher population of the triplet state in PL. We consider the triplet state luminescence in EL may arise from both, inter-system crossing from singlet state as in PL, and, in addition, direct recombination of excited electrons and holes. The measurements of EL and PL lifetimes and efficiencies of LEDs made with both the polymer and its corresponding monomer allow us to consider the processes associated with the generation and decay of triplet excitons in these materials.

CS.14 MATH-ZEHNDER INTERFERENCE TYPE ELECTRO-OPTIC POLYMER MODULATOR USING A MODIFIED CROSS LINKABLE POLYURETHANE A. M. Ying, Y. Du, X. H. Yang, Z.W. Shi and R.H. Wu, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, PR CHINA; Y. Li, J. Y. Zhou, Y. X. Zhuo, Y Q. Shen, Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing, PR CHINA.

Electro-optic (EO) modulator has been widely applied in optical information processing and communication. Although inorganic crystal such as LiNbO$_3$ based modulator are commercially available, in high speed fields the application of such modulators are restricted due to the large phase velocity mismatching between phase velocity matching the ground optical wave and the modulating micro-wave signal. In comparison to the expensive crystals and their complicated fabrication process, EO polymers have many intrinsic advantages, such as: higher EO coefficients, less phase velocity mismatch, and the flexibility of device fabrication. In the recent years, prominent progress in the EO polymer modulator has been made. Electro-optic polymer modulator operated at 113 GHz was reported. The great advances in EO polymer modulator is the synthesis of new molecules with large optical nonlinearity. However, the poly-methylmethacrylate (PMMA) host used at present shows a relatively low $T_g$ and poor thermal stability for practical devices. In this paper, a novel EO polymer IP-AN-20N with large EO coefficient $d_{33}$ as high as 320 pm/V, good thermal stability ($T_g \approx 160^\circ$), and good compatibility with semiconductor processing technology was synthesized from polyurethane cross-linking with a chromophore. AFM measurement exhibits that the film quality is high. Based on this modified cross-linkable polyurethane, the Math-Zehnder interferometer type waveguide modulator was fabricated and the modulating performance of devices was also measured. Here, the glass transition of the glass-cladding layer at high poling temperature, enhancement of the poled electric field in the EO core layer.

CS.15 Abstract Withdrawn.

CS.16 INORGANIC ORGANIC HYBRID MATERIALS (OR "MOLECULAR") FOR MULTI-LAYER TECHNOLOGY: CORROSION RESISTANCE AND DIELECTRIC BEHAVIOR R. Houtzert, L. Fröhlich, J. Schulz and M. Popall, Fraunhofer Institut für Silicatforschung, Würzburg, GERMANY.

Sol-gel synthesis allows one to produce inorganic-organic hybrid materials with a high degree of reproducibility and fairly low costs. The materials can be functionalized such that their physical and chemical properties can be reproducibly tailored towards the desired application, i.e., electronic/electro-optical or passivating technology. Besides, the material which shows negative resist behavior, can be patterned by UV exposure with good resolution. The material is very well suited for thin and thick film technology using conventional coating technology, particularly for multi-layer technology. Cracking or delamination of the material for thick film application (up to 100 µm) can be overcome by adding specific components. We here present the influence of the sol-gel material for environmental influences, which additionally shows very good dielectric properties. The water vapor permeation is less than 3 g mm⁻² d⁻¹ for layer thicknesses of about 100 µm. The water uptake is less than 0.5 wt.%, which is by far lower than conventional low cost polyimides. Corrosion protection is based on chemical bonds between oxide parts of the network and the oxide parts of various substrates. The combination of these three particular material properties suppresses water uptake at the substrate/glass interface and thus leads to a very high corrosion protection. Besides this, the material shows good dielectric properties such as a relative permittivity $\varepsilon_r$ of approx. 3.2 at 1 kHz and 3 at 1 MHz. The dielectric loss $\tan \delta$ which can be determined from the performance of electrical devices, is 0.004 at 1 MHz. The dielectric strength on a Cu surface is 400 V µm⁻¹. The material properties are discussed with respect to their influence on the polymerization process for different UV resists as well as to their combinational with metal and semiconductor measurements. Initial investigations of the curing behavior on the substrate stress will be demonstrated and discussed with respect to multi-layer technology.

CS.17 VISIBLE AND UV OPTICAL CHARGE CARRIER GENERATION AND TRANSPORT IN MEH-PPV DEVICES. Corn Sch, Douglas Halliday, Andy Munkeme, Department of Physics, University of Durham, Durham, ENGLAND.

MEH-PPV is a promising polymer light emitting diode material. The polymer film thickness and polymer dependence of the steady state photocconductivity for MEH-PPV/ITO devices up to photon energies of 5 eV to elucidate the charge transport mechanism. Features in the photocurrent spectrum above 3 eV may be accounted for by extrinsic dissociation of excitons formed by pi to pi* transitions in MEH-PPV. Features above 3 eV may be accounted for by photocurrent from the excitons. IV characteristics were recorded for samples of poly-phenylvinylether, Alq$_3$, Au, and ITO. The ITO layer is sandwiched between aluminum and calcium electrodes. However, the time required for the decay to steady-state was orders of magnitude higher as compared to the transit time obtained from the current maximum. This can be seen as an indication for dispersive charge carrier transport. The field and temperature dependence of the electron mobility calculated from transient dark injection currents is in good agreement with results from time resolved electro-luminescence on metal-insulator-semiconductor devices with indium tin oxide and calcium electrodes. However, the zero field mobility from the latter method is higher by approximately one order of magnitude. This can be attributed to the dispersive nature of the electron transport in Alq$_3$. While the delay time in transient electro-luminescence is determined by the fastest carriers, in dark current transients the average transit time of all electrons is observed. We obtained a full set of parameters for a modified Poole-Frenkel equation describing the temperature and field dependence of the electron drift mobility. Using these parameters, we were able to numerically simulate the current-voltage characteristics of the same samples over a wide range of temperatures and electric fields.

CS.18 TIME-RESOLVED CURRENT AND ELECTROLUMINESCENCE MEASUREMENTS ON ORGANIC LIGHT EMITTING DIODES Anton G. Meck, Stefan Berke, Wolfgang Brütting, Experimental Physics II, University of Bayreuth, GERMANY.

The dependence of the drift mobility in triphenyl substituted polyfluorene based light emitting diodes was investigated at various temperatures using transient dark injection current and electroluminescence measurements. We were able to achieve transient space charge limited currents in electron-only single layer devices with 10nm to 350nm thick Alq$_3$ layers sandwiched between aluminum and calcium electrodes. However, the time required for the current to decay to steady-state was orders of magnitude higher as compared to the transit time obtained from the current maximum. This can be seen as an indication for dispersive charge carrier transport. The field and temperature dependence of the electron drift mobility calculated from transient dark injection currents is in good agreement with results from time resolved electro-luminescence on metal-insulator-semiconductor devices with indium tin oxide and calcium electrodes. However, the zero field mobility from the latter method is higher by approximately one order of magnitude. This can be attributed to the dispersive nature of the electron transport in Alq$_3$. While the delay time in transient electroluminescence is determined by the fastest carriers, in dark current transients the average transit time of all electrons is observed. We obtained a full set of parameters for a modified Poole-Frenkel equation describing the temperature and field dependence of the electron drift mobility. Using these parameters, we were able to numerically simulate the current-voltage characteristics of the same samples over a wide range of temperatures and electric fields.

CS.19 ELECTRONIC STRUCTURE OF THE CHARGED INDUCED GAP STATES IN SOME ELECTROLUMINESCENT SPIRO-TYPE MATERIALS. M. MEULMANN, C. Crasin, M. Fischbacher, University of Karlsruhe, Dept. of Physics, Linköping, SWEDEN; D.A. dos Santos, Univ de Mora-Haime, Mora, BELGIUM; N. Johansson, Thin Film Electronics AB, Linköping, SWEDEN. J. Bauer, Covion Organic Semiconductors GmbH, Freiburg, GERMANY; P. Weisskroft, J. Salbe, Univ of Kassel, Kassel, GERMANY; J.L. Bréda, Department of Chemistry, Univ of Arizona, Tucson, AZ, U.S. Salbe, Linköping Univ, Dept of Physics, Linköping, SWEDEN.

The electronic structure of propeller shaped spiro-type molecules, 2,7,7'-traphenyl-9,9'-spirofluorene, spiro-terphenyl, and 2,7,7'-trisdi(phenyl-9,9'-spirofluorene), spiro-terphenyl, spiro-fluorene, spiro-terphenyl, spiro-terphenyl, and spiro-terphenyl, respectively, doped with Li atoms or Na atoms has been studied by means of photoelectron spectroscopy and optical absorption. In addition, quantum chemical calculations, including DFT, were performed in order to interpret the experimental data. With lithium atoms as dopant, two charges are stored, on the same molecule, in the form of...
bipolarons, for both spiro-4P and spiro-6P. In contrast, for doping with sodium atoms, the site of the counter ion makes it less energetically favorable to store two charges in one branch, and the charged species are polarons (one charge per molecule) independent of the level of doping. A Coulomb gap opens up between the Fermi level and the upper (lower energy) doping induced state. The role of steric hindrance, therefore, is deciding on Coulomb corrections for the correct description of the electronic states will be discussed.

C8.20
HIGH PRESSURE STUDIES OF POLYAROMATIC MOLECULAR CRYSTALS: OPTICAL AND ELECTRONIC PROPERTIES FROM FIRST PRINCIPLES. K. Wichmann, P. Ruschig, C. Ambrosch-Draxl, University of Graz, Inst. for Theoretical Physics, Graz, Austria; and G. Heimel, E. Zejler, R. Resel, Graz University of Technology, Inst. for Solid State Physics, Graz, Austria.

In the last decades a lot of attention has been paid on electroactive organic materials, which consist of conjugated molecules and show optical features in the UV/Vis region combined with high anisotropic electron mobility. These properties make semiconducting polymers interesting for both, scientific and commercial use. E.g., polarized light emitting diodes on a thin film basis of hexaphenyl [1], an organic solid state injection laser of a high quality tetracene single crystal [2] or efficient organic photovoltaic diodes based on doped pentacene [3] have been proposed. Since the intermolecular interactions critically influence the crystal structure and further the electro-optical properties, our goal is to study those interactions by applying hydrostatic pressure. Based on X-ray powder diffraction experiments under pressure [4] we calculate the electron structure within density functional theory (DFT) applying the self-consistent linearized augmented plane wave (FP-LAPW) method utilizing the WIEN97 code [5]. Exchange and correlation terms are treated by the local density approximation (LDA). Optical properties, calculated within the independent quasiparticle approximation, are subsequently compared with experiment. The results of such investigations performed on biphenyl and the poly(paraphenylene) oligomers have been published recently [6-8]. The theoretical study of para-phenylene type molecules under pressure revealed a red shift of the lowest absorption transition in agreement with experiment [10]. In the present work we focus on anthracene and para-terphenyl, which crystallize in the monoclinic space group P2(1)/c (two molecules per unit cell). We discuss the effect of pressure on their band structure and optical properties.

References.

C8.21
ELLIPSOMETRIC MEASUREMENTS OF CHROMOPHORE REORIENTATION IN A VISCOUS POLYMER MATRIX. Kim, G. Park, M. Jo, and Joensens Optics and Fluid Dynamics Dept. RISO National Laboratory, Denmark; Thomas G. Pedersen, Inst. of Physics, Aalborg University, Denmark.

Experimental investigations of reorientation dynamics in azo-dye containing polymers are presented. We use a modified Teng Mesh ellipsometer setup to measure the electro-optic response of the chromophore distribution to static and alternating electrical fields. The measurements are carried out on a DRI-PIMA co-polymer sandwiched between ITO and gold electrodes. The temperature dependence of the electro-optic order parameter is extracted from turn-on experiments as well as experiments with alternating fields both with and without a doco-Set. The results are successfully modeled by extending the orientated gas model with a local molecular field representing the interaction between the polymer matrix and the chromophore. It is demonstrated that the so-called electro-optic and birefringence contributions to the refractive index modulation can be determined separately from the frequency dependence of the response to combined ac- and dc-fields.

C8.22
ULTRASTFAST CARRIER PHOTOCOUPLING IN CONAGUATED POLYMERS. Pablo B. Miránda, Daniel Moses and Alan J. Heeger, Institute for Polymers and Organic Solids, University of California, Santa Barbara, CA.

We have investigated the mechanism of carrier photogeneration in poly(paraphenylene vinylene) (PPV) and its derivatives using ultrashort pump-probe spectroscopy. Samples were pumped with 100 fs pulses tuned across their absorption spectrum and probed by pulses tuned to the Infrared-Active Vibrational (IRAV) modes. They are a well-known probe of charge excitations in conjugated polymers, and are therefore a unique signature for carrier photogeneration. We observe a significant quantum efficiency for direct carrier generation (δ ~ 1%) within our temporal resolution, and without applied electric field. Together with the weak pump-wavelength dependence of δ and its strong dependence on the quality of the material, the results imply that polaron are primary photoexcitations. Furthermore, we have also investigated the effects of disorder and interchain interactions by comparing experiments with ordered stretch-aligned and disordered spin-cast films, and also films and solutions of PPV derivatives. We will discuss implications of our results to the carrier generation dynamics and mechanisms in derivatives of PPV.

C8.23
PHOTOPHYSICAL PROPERTIES OF NOVEL ISOQUINOLINONE DERIVATIVES FOR ORGANIC OPTOELECTRONICS APPLICATIONS. Ian M. Craig, Hieu Duong, Kyle P. Starkey, Fred Wool, Benjamin J. Schwartz, University of California, Los Angeles, Department of Chemistry and Biochemistry, Los Angeles, CA.

Small bandgap organic molecules such as aluminum triquinolate (Alq3) and polycyanes such as tetracene or pentacene have generated a lot of interest lately for their promise to replace inorganic materials in semiconductor devices such as transistors, light emitting diodes, and lasers. The polycyanes in particular show especially good promise, but also suffer from the disadvantages that only very pure single crystals may be used and that the molecules are subject to photo-oxidative degradation. In this talk, we present data on a new class of molecules, based on isoquinolone, which show promise as a new set of low bandgap organic materials. These materials are two- or three-ring aromatic heterocycles and are more photo stable and more easily processable than the larger polycyanes. Their unusually red absorption arises from a charge separation in the excited state that is stabilized by aromatic conjugation of the amide moiety. Photophysical measurements on N-methyl-1,4-diphenylbenz[ghi]isoquinolone reveals a fluorescent state lying underneath the lowest energy optical absorption band in addition to the more standard Stokes-shifted red fluorescence. Evidence suggests that this absorption band consists of two different transitions, and that the two states are weakly coupled by a band-to-band excitation of the form 2,7-bithiophene produces both the luminescence and the red fluorescence. We believe that the red emission is a T2 2π 2π transition based on steady state fluorescence and absorption measurements, femtosecond pump-probe transient absorption and stimulated emission measurements as well as comparison to quantum chemistry calculations. Altogether, the bright fluorescence, small bandgap, and novel photophysical properties of this and related molecules make them promising candidates for use in organic semiconductor devices.

C8.24
PREPARATION OF DIARYLETHENE SUBSTITUTED POLYMER FILMS FOR OPTICAL RECORDING. Seng Yoon Choe, Byoung Kim, Advanced Materials Division, Korea Research Institute of Chemical Technology, Taejeon, SOUTH KOREA.

UV/Vis recordable polymer films were prepared from photopolymerization of a radical curveable dimer of diaryl ethene metacycloxene and fluoro-alkyldimethacrylate containing a photo initiator. Diaryl ethene metacycloxene was synthesized from 2,3,4,5-tetrahydro-1H-indene and 2-(2-methyl-6-(3-methyl-2-oxopropyl)indene-1-vinyl)tetrahydrofurocoumpolycene (BIT5) in three steps. Fluoro-alkyldimethacrylates were synthesized from the corresponding dialkyl and acryloxy chloride in the presence of a base. The photocurable mixture was coated on a substrate and subjected to actinic irradiation, afforded homogenous transparent recording film. A masked image was fixed on the film by a light of 365 nm and read by a visible light (λ = 780 nm) without destruction of the image. To erase the recorded image, a white light or visible light of λ = 780 nm was irradiated. The photoerasable properties were improved by adjusting the composition and structure of the component in the photocurable mixture. Quantum yield and photophysical properties accompanied by the photochromic conversion of the diarylethene polymer film was determined to optimize recording properties.
CS.25
THE INFLUENCE OF NANOSTRUCTURE FORMATION OF
PROPERTIES FOR Cr-IMPLANTED PET. Wu Yuguang, Zhang
Tonghe, Zhang Huixing, Zhang Xiaoyi, Deng Zhiwei, Key Laboratory
in University for Radiation Beam Technology & Material Modification,
Institute of Low Energy Nuclear Physics, Beijing Normal University,
Beijing Radiation Center, Beijing, CHINA; Zhou Gu, Technical
Analysis Center, Beijing Normal University, Beijing, CHINA.
Polyethylene terephthalate (PET) has been modified by Cr ion
implantation over a range from 1 to 3 x 10^{17} ions/cm^2. The PET
movies were observed by atomic force microscopy (AFM). The Cr atom
precipitation was found. The changes of the structure and composition have been observed by transmission electron microscopy (TEM).
The nanosize of Cr-implanted PET was observed. It is believed that the change would cause the improvement of the conductivity properties and wear resistance. The electrical properties of PET have been changed after metal ion implantation. The resistivity of implanted PET decreased obviously with an increase of ion dose. When metal ion dose of 2 x 10^{17} ions/cm^2 was selected, the resistivity of PET could be less than 10 Ohm, but when Si ions are implanted, the resistivity of PET was up to several hundred Ohm. The result show that the conductive behavior of Cr ion implanted sample is obviously lower than that of Si and Cr-implanted one. After Cr implantation, the surface hardness and modulus increase. The property of the implanted PET has modified greatly. The hardness of Cr implanted PET with dose of 2 x 10^{17} ions/cm^2 is 9.5 and 3.1 times greater than that of pristine PET. The Cr ion beam modification mechanism of PET will be discussed. This work has supported by Chinese High Science Technology [863.75.023.02-01] and The National Natural Science Foundation of China [59671051].

CS.26
FIELD EFFECT TRANSISTORS BASED ON DICSOCIC LIQUID
CRYSTALLINE HEXABENZOCORONENES. Anick M.
van de Craats, Henning Serringer, Richard H. Friend, Univ of.
Cambridge, Dept of Physics, Cambridge, UNITED KINGDOM;
Andre Fechtenkötter, Natalia Tchekotcheva, Klaus Müller, Max Plank-Institut für Polymerforschung (MPI), Mainz, GERMANY.
Field-effect transistors (FETs) constituted of spin-coated films of
discotic liquid crystalline hexabenzocoronene (HBC) derivatives in the
active layer have been investigated. These organic materials are
known to self-assemble into well-ordered columnar stacks which can
serve as efficient pathways for one-dimensional charge transport.
In order to apply this promising conducting system in organic
domain microelectronics, full control over the orientation of the
columnar stacks with respect to a surface is required. The influence
of surface modification and annealing above the solid-to-liquid
crystalline phase transition on the microstructure is investigated by
differential interference contrast (DIC) polarised microscopy. Additionally,
the influence of the FET performance is studied. Different silating
agents, such as hexamethyldisilazide (HMDS), octyltetrachlorosilane (OTS-8),
octadecyltetrachlorosilane (OTS-18), and trimethoxymethylsilane
(TEMOS) have been used to chemically modify the surface. Field-effect
mobilities on the order of 10^{-4} cm^2/Vs are derived from the device characteristics and compared to intrinsic siloxane-scale mobilities of approximately 0.1 cm^2/Vs determined previously with the time-resolved capacitance (TRC) technique. The comparison shows that long-range charge transport in the FET device is hindered by structural defects such as domain or grain boundaries.

CS.27
PHOTOCURRENT MULTIPLICATION IN POLYMERIC
PHOTODETECTORS. Janke J. Dittmer, Elisabeth A. Marseggia,
Richard H. Friend, Cawndish Lab., University of Cambridge,
UNITED KINGDOM; Stefan Becker, Klaus Müller, Max Plank
Institute for Polymer Research, Mainz, GERMANY.
We report the novel effect of photocurrent multiplication in polymer
photodetectors, which we use a blend of a dye (butahelicene) and a perylene polymer. The photoactive response of these blends
was measured as a function of blend ratio in sandwich cells between
indium tin oxide and aluminium electrodes. Under photodetector operation at only 1 V forward bias, we observed an external quantum efficiency of several hundred percent for a large part of the visible light spectrum. These results were interpreted in terms of trapping of charges at the interfaces. This phenomenon has a great potential in future fabrication of photodetectors or new types of optoelectronic devices.

CS.28
POlyMIDE SURFACE MADE ELECTRICALLY CONDUCTING
BY CHEMICALLY DEPOSITED CuC THIN FILM. J. Cardoso,
UAM/ CFI, Depto de Física, México DF, MEXICO; G. Gomez Dura,
M.T.S. Nair, P.K. Nair, Universidad Nacional Autónoma de México,
Centro de Investigación en Energía, Temixco, Morelos, MEXICO.
Copper sulphide thin films of 75 nm and 100 nm thickness were coated on DuPont Kapton HN polyimide films of 25 nm thickness by floating thin films on a chemical bath containing copper sulphate and
thiourea. The coated films were annealed in nitrogen at different temperatures ranging from 150°C to 400°C. After the annealing, the coatings show a sheet resistance of 12-20 ohm/square and, thus, an electrical conductivity in the range of 5-10 x 10^{-4} ohm^{-1} square^{-1}. The treatments in acids (0.1 1 M HCl) for 15 to 120 min retain the sheet resistance within 10^{-4} to 10^{-3} ohm/square, implying its application as a conductive substrate for electrochemical deposition. The coated polyimide has an optical transmission minimum of 25-35% around 550-600 nm, with the transmittance dropping to near zero below 450 nm and below 10% in the near infrared spectral region. The infrared reflectance predicted for the coatings is 67-75% at a wavelength 2.5 micrometers, which is close to these predicted ones have been observed in specular reflectance measurement. The thermal stability of the films and coated films was examined in the temperature range up to 600°C by TGA. The decomposition temperature of the polymer has been placed at above 475°C. XRD measurements indicated that the annealing leads to transformation of the copper sulphide films to a mixture of different CuS compositions. Overall, the electrically conductive coatings of copper sulphide on polyimide polymer may be considered as stable at temperatures up to 400°C for many applications: as a thermally stable substrate for electrollyte and electronic metal coatings to serve as reflectors for concentrating collectors, heat mirrors, of semiconductor coatings, and as photodetection elements or as conducting films which can be applied with noncopper sulphide coatings.

CS.29
SYNTHESIS AND CHARACTERIZATION OF HIGH
PERFORMANCE AND LOW COST OF SUBSTRAITUCTION OF ARYI-SUBSTITUTED ELECTROLUMINESCENT POLY(N-PHENYLENEVINYLENE) [NPV]. Zhun Chen, Nancy Hoi
Sim Lee, Wei Huang, Institute of Materials Research and Engineering (IMRE), SINGAPORE.
Electroluminescent conjugated polymers based on poly(n-phenylene vinylene) [PPV] have been a subject of interest due to their potential applications in polymer light-emitting devices (PLEDs). Among
others, soluble phenyl-substituted PPVs (Ph-PPVs) have shown the most promising features, such as high luminescence efficiencies and power efficiencies, and relatively low driving voltages for PLED applications. However, Ph-PPVs, prepared through the Gilch route, have demonstrated large amount of structural defects in the polymer main chains, which was believed to be one of the key factors limiting the device lifetime. Here, we report the synthesis and characterization of a novel series of aryl substituted Ph-PPVs, which have shown excellent processability, good thermal stability, high photoluminescence quantum efficiency, and low cost of structural defects. The substituents of the polymers were designed with different degree of hindrance effect on the main chain. IR and NMR analysis indicate that the defect structure in the polymer main chain can be effectively depressed by introducing bulk and hindrance substituents. Meanwhile, the solvent used during the Gilch polymerization also plays an important role on the polymer’s structural integrity and identity. The mechanism of the side chain hindrance effect on the structural defects of the polymer backbone will be discussed and the performance of the polymers with different content of structural defects used in the active layers of PLEDs will be presented.
are studied by AFM and fluorescence microscopy as a function of heat treatment. The photoluminescence spectra and quantum yields from this film are solvent dependent. The detection of intermolecular relationships within the amorphous phase. The film forming qualities are useful for the fabrication of light emitting diodes with low turn-on voltages. Device performance is also thermal history dependent. The relationship between bulk morphology, film topology, PL properties, and LED performance is discussed. A comparison of these compounds with the parent oligophenylenevinylene "arms", with respect to morphology, topology, and PL properties is also presented.

**CS.31** SYNTHESIS AND OPTICAL PROPERTIES OF A NOVEL DERIVATIVE OF OLGOPHYRIDINE. Y.-L. Fu, T.K.S. Wang, H.X. Zhang, Division of Materials Science and Engineering, Nanyang Technological University, SINGAPORE; G.M. Wang, X. Hu, Division of Materials Technology, School of Materials Engineering, Nanyang Technological University, SINGAPORE; T.K.S. Fu, M.K. Lu, State Key Laboratory of Crystal Materials, Shandong University.

As the pyridine based counterparts of poly(paraphenylene) (PPP), which is a typical electroluminescent polymer with a blue color, both 2,5-linked poly(paraphyridine) (PPy), and 5,5-linked poly(2,5-bipyridine) have been extensively investigated. 2,5-Linked oligopyridine oligomers are excellent chelating ligands of metals and have been a focus for more than ten years in the field of supramolecular chemistry, but their optical properties have not been well studied. In a previous paper we reported the optical properties of a novel derivative of 2,5-linked oligopyridine and it is suggested that this kind of materials be promising to be used in the field of organic electroluminescence. In this paper, 5,5'-bis[4-methyl]-2,2' bipyridin-4-yl]ethyl-2,2'-bipyridine (BBDVBPYBP) is a novel derivative we synthesized. The spectrum shows strong photoluminescence both in powder and solution state. It is a non-fluorinated oligomeric in structure. In pure powder state, an emission peak at 418 cm can be observed under the excitation of 367 nm. When mixed with KBr, two emissions at 480nm and 430nm are observed. Its solution in chloroform emits at 414nm under the excitation wavelength of 364nm. Films fabricated by vacuum evaporation emit at 409nm and 428nm. Thermal analysis studies indicate that the material is stable enough that it has no weight loss before the temperature is higher than 350°C. Also carried out are preliminary electroluminescent studies. Single layer device, ITO/BBDVBPYBP/AI, emits weakly with a broad peak around 455nm. Double layer device, ITO/ITO/BBDVBPYBP/AI, using TTO as the hole transporting layer, shows an emission at 408nm at low voltage, but shows a much stronger broad emission in the range 408-550nm at higher voltage.

**CS.32** THE CORRELATION BETWEEN FABRICATION PROCESS AND DEVICE PERFORMANCE. Jie Liu, Yang Yang, Univ of California-Los Angeles, Dept of MSE, Los Angeles, CA.

Recently, it has been demonstrated that performance of MEH-PPV based polymer light-emitting diodes (PLEDs) is strongly related to polymer processing conditions. In this presentation, research results about the effect of casting polymer (PF) based PLEDs on the performance of PF copolymer based PLEDs with respect to MEH-PPV based PLEDs. Probably because backbones of the PF copolymer contain both aromatic and non-aromatic groups, the photoluminescence and morphology of the copolymer have been found insensitive to the polymer processing conditions. As a result, turn-on voltages of PF based PLEDs are independent on the fabrication conditions. However, spectra of photoluminescence and electroluminescence of PF based PLEDs show a strong correlation to the processing parameters, such as solvents and spin speed.


**CS.33** MOLECULAR ORGANIC LIGHT EMITTING DEVICES WITH INVERTED DEVICE STRUCTURES AND ENGINEERED ELECTRON INJECTION LAYERS. Gregory P. Kushko and Zokha H. Kafafi, U.S. Naval Research Laboratory, Optical Sciences Division, Washington, DC.

The operational lifetimes of organic light emitting devices (OLEDs) are severely limited by degradation of the low work function metal cathodes commonly used to produce high device efficiency. This problem can be overcome by forming a metal film on the polymer active material layer or by making the metal layer more compact via thermal anneal to circumvent the use of easily oxidized cathode materials such as magnesium, lithium and calcium. In order to investigate possible solutions to this problem, we have constructed bilayer devices with inverted structures wherein the cathode layer is composed of a high work function material (e.g., ITO) used as the cathode and the anode is a high work function metal (e.g., Al). In these devices, an electron injection layer that consists of a metal-free alkylated octadecylamine (H) or (Al) complex (M=Al, magnesium, aluminium, etc.) or a ternary mixture of AlLi salt:Alq has been inserted between the metal oxide and the electron transport layer to aid in electron injection at the cathode/ETL interface. The results show that the inclusion of these composite layers leads to performance improvements, polymer/metal contacts have been found and the use of atmospherically stable, high work function metal films. These results will present the discussion of this study as well as possible mechanisms that lead to an increase in device efficiency.

**CS.34** RECENT DEVELOPMENTS IN BLUE POLYMERIC MATERIALS FOR OLE APPLICATIONS. Kenneth R. Carter, Dirk Mironsky, NSF CTPMA, San Jose, CA.

Poly-2,7-fluorene has shown to be a valuable material for organic light emitting diodes (OLED) applications. Its good blue luminescence, high thermal stability, ease of processing and synthesis has made it one of the more interesting OLED polymers studied. Long lifetime, efficient blue OLED materials have eluded researchers and much work is being performed to identify improved materials. Our work has centered on making structural changes to the poly-2,7-fluorene backbone to provide adequate solubility and help prevent aggregation and excimer formation. We have developed two separate approaches, one in which we synthesis poly-2,7-fluorene with large, bulky dendrimer sidegroups at the 8-position, and secondly by the incorporation of a tetrafunctional spiro-compound. 2,7,7,7-tetramethoxy-9,9-dipropylfluorene. We have synthesized the polymerization of the macromonomer using the nickel(0) mediated Yamamoto reaction exhibits a strong concentration dependence and yields materials with well characterized photophysical properties (2,7,7-PPF) when reactions are conducted under high concentration. We then showed statistical and alternating copolymers of these dendrimer monomers with 2,7-dimethoxy-9,9-dihexyfluorene. The absorption and fluorescence measurements were found to be strongly dependent on molecular weight. We have also developed a novel strategy for the synthesis of aromatic poly-2,7-fluorene by copolymerisation of 2,7-dimethoxy-9,9-dihexyfluorene with a tetrafunctional spiro-compound, 2,2',7,7'-tetramethyl-9,9'-spirofluorene, and 4-bromostyrene as sluggish monomer. The spiro-fluorene leads to a 90° branch of the growing 2,7-PPF chain after a via the feed ratio determined number of repeat units while the formation of the growing network with 4-vinylphenyl endgroups keeps the material soluble and processable. The results show that an increasing amount of the tetrafunctional spiro-compound leads to an increase of the T0 values. The materials exhibit high glass transition temperatures, good photoluminescence properties and potential for incorporation into multi-layer light-emitting diodes (LEDs).

**CS.35** MATERIALS CHARACTERIZATION AND SYNTHESIZE OF CONDUCTIVE AROMATIC BIS(BENZOTHIAZOLES). Max D. Alexander Jr., Douglass S. Duda, B. Robert McKellar, and Balaraman Santhanak, Air Force Research Laboratory, Polymer Core Technology Area, Wright-Patterson AFB, OH.

Functionalized aromatic bis(benzothiazoles) have been synthesized by our group and have shown promise as conductive n-doped polymers and oligomers. When reduced (n-doped) these materials typically exhibit conductivities on the order of tens of 5/cm. There are currently very few n-doped organic materials available and even fewer that exhibit long-term environmental stability. This can be attributed to the molecular composition of the materials and their conjugation reduction potentials. An n-doped material is in a reduced form, which is often susceptible to red-oxidation by oxygen and/or water when exposed to the environment. Full red-oxidation is required to ensure the conductivity level of the reduced material. To exhibit stability toward red-oxidation by water, n-doped polymers and organic compounds must have an electron oxidation potential greater than -0.65V vs. SCE. To be stable in the presence of both oxygen and water the electron oxidation potential must be greater than 0.571V vs. SCE. Most traditional n-doped polymers and organic compounds exhibit reduction potentials less than -1.0V vs. SCE and therefore are not stable in an open environment. In, contrast the materials we have developed have been shown to retain their conducting state for several months, without the need for encapsulation. Here we examine the materials properties of this family of derived, conductive aromatic bis(benzothiazoles). A variety of synthetic approaches have been explored for these polymers and oligomers, and will be discussed. Materials characterization has been accomplished by spectro-electrochemistry.
SYNTHESIS OF NOVEL THIOLEND-CAPPED OLIGO(P-PHENYLENE VINYLENES). Nicola Stahl-Hansen, Jorn B. Christensen, Thomas Bjørnholm, Univ of Copenhagen, Dept of Chemistry, Copenhagen, DENMARK.

The first members of the family of molecules, oligo(p-phenylene vinylenes) (OPVs) with protected thiol termini, has been prepared by MacMillan and Witting type of reactions. New sulfonylurea chemistry allows synthetic experiments to be performed under extremely basic conditions including alkoxide reactions and lithiations. The new method utilizes the tet-butyll moiety as thiol protecting group which is practically inert towards thiols. reactions. A mixture of acetylene and boron trimide in dichloromethane quantitatively exchanged the thiobutyl group on sulfin with the thiol sulfoxyl group. The developed synthetic methods of OPVs may be utilized as templates for synthesis of similar systems via thienylene vinylenes and naphtylene vinylenes analogues. The thiol end-groups may be deprotected in situ prior to formation of e.g. self-assembled monolayers (SAMs) opening for a wide variety of applications of these electroactive and highly fluorescent molecules.

TOWARDS NEW NANOSTRUCTURED MATERIALS BASED ON POLYPYRROLE HELICES WITH PENDANT LUMINESCENT GROUPS. Ruth Müller, Pierre-Louis Brunner, Natalie Zisman, Michael O. Wolf, University of British Columbia, Department of Chemistry, Vancouver, BC, CANADA.

Luminescent materials such as poly(p-phenylene vinylene) have been intensively studied for the last decade due to their interesting applications in various fields. Methods to immobilize molecules in the solid-state in order to control charge transport in thin-films of these materials are needed. In our approach, a polythiophene fiber is used as the support for luminescent side groups, which can subsequently be attached to a surface via the method of Whitesell and Chang (Science 1993, 261, 73). The synthesis of N-cyanoalkyl amino acids with luminescent side groups and the polymerization of these monomers to polypyrroles will be described. In both materials, the helical structure of the polypyrrole backbone is expected to orient the side chain selectively to each other. Efforts towards surface immobilization of these nanostructures will be discussed.

SELECTIVE PHOTON-BREAKING OF C-S BONDS IN POLYPYRROLE TO FORM QUASI-ONE-DIMENSIONAL CARBON CHAINS IN CUBIC NANOCRYSTALS. ZM Ren, YF Lu, HW Chey, TC Chong, Laser Microprocessing Laboratory, Data Storage Institute and Department of Electrical Engineering, National University of Singapore, SIMARGE, S. C. Ng, M. Mo, Department of Chemistry, National University of Singapore, SINGAPORE.

A solid polypyrrole target was ablated by a KrF excimer laser beam to deposit thin films on silicon substrates. The laser-ablated polypyrrole thin films were then used as a chemical emitter to identify the photon-breaking of C-S bonds in the ablated heterocycles. The selective photon-induced bond breaking was also supported by Raman and X-ray photoelectronic spectroscopy measurements of the deposited thin films. After getting rid of sulfur in the molecular structure, the thin films appeared to be composed of cubic nanocrystals with a uniform size of 240 nm. X-ray diffraction measurement determined the cubic crystal structure with a lattice constant of a = 3.38 Å and suggested a quasi-one-dimensional carbon chain structure along the body diagonal of the cube. This can lead to new organic nanostructure and devices.

NANO- AND MICROSCALE CONDUCTIVITY OF CONJUGATED POLYMER FILMS. M. Hansen, D. R. Greve, Niek Reitzen, Thomas Bjørnholm, Dept of Chemistry, University of Copenhagen, DENMARK; Peter Bøggild, Francois Grey, M. C. Technical University of Denmark, DENMARK.

Measurements of conductivity in doped Langmuir-Blodgett monolayers of amorphous regioregular polythiophene which on nanometer scale possess a higher degree of order, have been performed by micro- and nanogrobe techniques[1,2,3,4]. These measurements show that the conformance of the dependence of the conductivity on the scale of the measurement and the value of the conductivity, which increases by several orders of magnitude when the scale is decreased from mm to micrometer scale. The highest reported value of an in-plane conductivity of a monolayer has been measured (σ ~ 150 S/cm on µm scale). Spin cast films of the conjugated polymer has also been investigated by these techniques, and yield very high conductivities.

We have shown directly, by use of Electrostatic Force Microscopy (EFM), that the monolayer has a fine structure on the nanometer scale and is conductivity. Our measurements show directly that the overall conductivity of the monolayer is reduced due to poor electronic transport across domain boundaries. A potential profile has been extracted from EFM data depicting the potential drop across a monolayer bridging two electrodes. A potential profile where ~ 3.0 nm step-like features can be seen. The potential profile thus shows that there is an electronic domain formation in the monolayer giving rise to electronic discontinuities across domain boundaries, and a high density of electronic defects inside the domains.

ENERGY TRANSFERS IN NANOSTRUCTURED OLIGO-PHENYLOXANES. Chiara Borri, Silvia Destri, ICM, CNR, Milan, Italy; Gianni Binggeli and Andrea Ferrera, INFN and Dip. di Fisica, Università di Cagliari, Monserrato (Ca), Italy; Giuseppe Di Silvestro, Dip. di Chimica Organica e Industriale, Università di Milano, Milan, Italy; Riccardo Tubino, INFN and Dipartimento di Scienze dei Materiali, Università di Milano Bicocca, Milan, Italy.

The photophysical properties of oligophenylene co-inclusion compounds in perfluorocyclohexane are reported. Two oligophenylene molecules (quinquephenylene and terphenylene) are incorporated in the parallel monocompartment formed by the host. Excitonic effects are suppressed due to the large intermolecular distances (14 Å) imposed by the host crystal. While long range energy transfers take place under controlled geometrical conditions (intermolecular distances and mutual orientations). The parallel relative orientation of the molecules within the channel of the host is a critical distance that is involved. We observe very efficient long range energy transfers from the shorter to the long oligomer. The time decay of the A and the rise time of the A excited state populations are interpreted in terms of energy transfer processes both within the channel (J aggregates) and between the channels of the host.

NEW PHOTOCALLIGIBLE ORIENTATION LAYER POLYMERS FOR LIQUID-CRYSTAL DISPLAYS. Seong Woo Lee, Ji-Hyung Kim, Woo Young Choi, Moonho Ree, Dept of Chemistry, Center for Integrated Molecular Systems, and BK-21 Functional Polymer Thin Film Group, POSTECH, Pohang, SOUTH KOREA.

A series of new cinnamol moieties with various flexible chain lengths were synthesized, and incorporated into a high performance polymer DIS side chains. Their photoreactivity to UV light was investigated by UV exposure and UV-visible spectroscopy. A photofreezing of polymer chains was achieved with a relatively low exposure dose of 0.25-0.5 J/cm². The preferential alignment of polymer chains was confirmed by optical retardation measurement. With the polymer films, liquid-crystal cells were also examined. A pretilt angle of 90° was achieved, depending on the exposure technique and exposure dose as well as the side chain length of polymer. In addition, structures and basic properties of the polymers were characterized in detail.

[This study was supported in part by the Ministry of Industry & Energy and the Ministry of Science & Technology (G7 Project Program) and by the KOSEF via the Center for Integrated Molecular Systems.]

DESIGNING SURFACE-RELIEF GRATINGS ON AZOBENZENE POLYMERS. Thomas G. Pedersen, Inst. of Physics, Aalborg University, DENMARK; Per M. Johansen and Kim Jespersen, Optics and Fluid Dynamics Dept., Risø Natl Lab, DENMARK.

The photoinduced formation of gratings on surfaces of azobenzene polymers has attracted considerable interest lately. This technique makes it possible to write stable gratings of remarkable quality simply by interfering two or more beams in the material without any need for post-processing such as etching. Recently, a micro-filb theory of surface relief formation on liquid-crystalline azobenzene polymers has been presented [T.G. Pedersen et al., Phys. Rev. Lett. 80, 89 (1998)]. This theory successfully explains a range of features including period, shape and depth of experimentally observed gratings. In the present paper, the micro-filb theory is applied as a tool for methodical design of gratings with desired specifications. From a numerical inversion procedure, the interference pattern required to produce the desired gratings is obtained. Theoretical results for a range of grating profiles are presented and the limitations of the technique are discussed.
CS.43 MOLECULAR ASSEMBLIES, PATTERNING, AND ELECTRODEPOSITION ISSUES OF CONJUGATED POLYMERS; THE IMPORTANCE OF FILM FORMING PROPERTIES FOR APPLICATIONS  
Rigoberto Advincula, Kyoung Park and Chunjuan Xia, Chemistry, University of Akron at  
Birmingham, Birmingham, AL.

In this paper we present a combined protocol and report on issues involving the preparation, formation, and conjugation of polymer film. While much work has been done in investigating the chemistry, synthesis, and properties of these materials, there has not been much focus on the ultra-thin film formation and ordering issues associated with the natural applications. Applications in PLEDs, thin film FETs, sensors, etc., all require well-defined electronically and optically active films. This talk will focus on the issues that are involved with ultra-thin film formation of these materials using wet process technologies and the effect that the structure of the film has on their performance. This includes: a) LB film deposition, b) layer-by-layer deposition techniques, c) electrolytization of precursor polymers, and d) potential patterning strategies. While most conjugated polymers are inherently insoluble, their limited solubility can be used to an advantage in their ability to form multiple multilayers and supramolecular structures.

CS.44 CHARGE TRANSPORT IN HIGHLY ORGANIZED MOLECULAR AND POLYMER THIN FILMS: A QUANTUM CHEMICAL INSIGHT  
Jean-Claude Courtès, David Beljonne, Jean-Philippe Cabaret, and Marcel Frisch  
Service de Chimie des Matériaux Nouvoirs, Université de Mons-Hainaut, BELGIUM;  
Department of Chemistry, The University of Arizona.

The field of organic semiconductors has been truly revolutionized by the recent report of unprecedented electron and hole mobilities in high quality molecular crystals [1]. Moreover, large field-effect mobilities have also been recently observed in highly organized layers of polymer chains [2]. These remarkable developments trigger a renewed interest in understanding the transport properties of oligomer and polymer chains since the stage is now set for a direct comparison between the results of calculations on perfect crystals and experimental data. In the field of structural engineering, one of the most important problems is that of finding the relationship between the macroscopic properties of the film and the microscopic structure. The aim of this work is to shed light on the microscopic behavior of the film and to propose a model for the charge transport in highly organized molecular and polymer thin films.

CS.45 ELECTRIC FIELD INDUCED IONIZATION OF THE EXCITON IN POLY(PHENYLENE VINYLENE)  
Daniel Moses, Joon Wang, Alan J. Heeger, Institute for Polymers and Organic Solids, University of California, Santa Barbara, CA; Natasha Kirova, Sergei Branzovski, IPTMS, Université Paris-Sud, Orsay-Cedex, FRANCE.

The exciton binding energy (E_b) and the band gap energy (E_g) of poly(p-phenylene vinylene), PPV, have been determined by photoconductivity excitation profile spectroscopy as a function of light polarization, electric field, and temperature. The spectral signature of the exciton is a narrow peak [100 meV full width at half maximum] that emerges just below the band edge upon increasing the external field or the defect density. The exciton peak is observed only for light polarized parallel to the chain axes. The exciton binding energy is obtained from the energy of the exciton peak with respect to the band edge, and independently from analysis of the field dependence of the excitation dissociation, and find E_b ~ 60 meV. The rate of dissociation of the excitons into charge carriers exponentially as the temperature is lowered when the exciton is pumped resonantly, and the deduced activation energy, E_a, is consistent with the exciton binding energy as inferred above. The implications of our observations to the proper operation of devices containing excitons in this prototype luminescent polymer will be discussed.

CS.46 ELECTRIC FIELD INDUCED SELF-ASSEMBLY AND TEMPLATE PATTERNING OF POLYMER MICROSTRUCTURES  
Cengiz S. Ozkan, Huanjun Gao, Stanford University, Mechanical Engineering Department, Stanford, CA.

We have developed a method for fabricating polymer microstructures based on electric field induced self assembly and pattern formation. A dielectric fluid placed in between two conductive plates experiences a force in an applied electric field gradient across the plates, which can induce self-assembly of conjugated polymers to form a microfluidic fluid surface. This process is exploited for fabricating self-assembled polymer structures as well as replicated patterns through the use of pre-patterned plates or electrodes. We have used silicon wafers and transparent ITO (Indium-Tin-Oxide) coated glass substrates to fabricate the capacitor structures. The bottom silicon plate is spin coated with a 100 200 nm thick PMMA (polymethylmethacrylate) film. The ITO substrate was placed over the polymer surface at a distance to leave a thin thin film surrounding the dielectric insulators. For dielectric transfer, patterned ITO substrates were used. The capacitor setup was then exposed to a high temperature gradient from the glass transition temperature of the polymer and a voltage was applied across the plates (25-100 volts), which induces electric fields on the order of 10^7-10^8 volts/cm. The capacitor setup was then exposed to the temperature gradient for 30 minutes before being immersed in the polymer. By adjusting the temperature gradient and voltage applied, we are able to control the size and shape of the microstructures, allowing for the fabrication of microfluidic devices with high accuracy and precision. The fabricated microstructures are then used for further applications in microfluidics, lab-on-a-chip devices, and other nanotechnology applications.

CS.47 NANO-AND MICRO-SCALE STRUCTURE OF SELF-ASSEMBLED THIN FILMS OF CONJUGATED AND NATURAL AMPHILYTIRES  
Thomas Bjørholm, Univ of Copenhagen, Dept of Chemistry, Copenhagen, DENMARK.


CS.48 FUNCTIONAL 1D NONLINEAR PHOTONIC CRYSTAL MATERIALS  
JASPER S. Shirk, Richard G.S. Pong, Steven R. Flom, U.S. Naval Research Laboratory, Optical Sciences Div., Washington, DC; Anna Hilmer and Eric Baer, Case Western Reserve University, Dept of Macromolecular Science and Engineering, Cleveland, OH.

We fabricated a series of nano-layered polymer materials by an extrusion technique. These materials can comprise thousands of layers with a thickness down to about 10 nm. We demonstrated the nanoscale layer formation by Atomic Force Microscopy measurements and by fabricating a nanolayered sample with a small index difference between the layers. The latter sample had the linear transmission and reflection properties compared with a conventional multilayer dielectric reflector with the distribution of layer thickness found in the AFM measurements. The analogous nonlinear 1D photonic crystal materials were fabricated by dispersing nonlinear dyes in alternate layers. This gives materials with a modulation in the nonlinear refractive index in the direction normal to the surface of the layers. Like the usual
photonic crystals, they are of particular interest when the period of the modulation is on the order of the wavelength of light. In this case, they act as a new class of dielectric mirrors. The transmission properties of such structures can be altered by the intensity of the incident light. We have demonstrated nonlinear refraction upon laser irradiation in the visible in the nonlinear samples. Such non-destructive materials can be used in several applications and in optoelectronics. For example, when a nonlinear absorbing dye is included in alternate layers, the optical response of such structures can be particularly useful for optical limiting.

### C8.40

**CHROMATIC BEHAVIOR OF SELF-ASSEMBLED POLYDIACETYLENE/SILICA NANOCOMPOSITE FILMS.** Yi Yang, Yanqiu Li, Jinjun He, Gabriel Leger. Unit of New Mexico, Center for Micro-Engineered Materials and Dept. of Chemical and Nuclear Engineering, Albuquerque, N.M. Derry Y. Sawicki, Alan Burns, and C. Jeffrey Brinker, Sandia National Laboratories, Albuquerque, NM.

Polydiacetylenes (PDAs) have important potential applications in electronics and optics due to properties such as thermo-, solvato-, and mechano-chromium, large third order optical susceptibility, and high electron mobility comparable to that of inorganic semiconductors. In the present work, PDA was uniformly incorporated in an ordered mesostructured silica matrix forming an organic/inorganic nanocomposite. The hybrid nanocomposites were synthesized through self-assembly of a series of polymerizable diacetylene glycol functionalized diacetylene (DA) surfaces plus silica precursors prepared in THF/water solvent with surfactant concentration much less than the critical micelle concentration. Thin films were prepared through evaporative dipping-coating, spin-coating or casting procedures on silicon (100) or fused silica substrates. UV irradiation was used to polymerize the colorless DA/silica mesophases into blue PDA/silica nanocomposites with tightly ordered (laminar, hexagonal or cubic), self-assembled architectures. The blue PDA/silica nanocomposites exhibit thermo-, solvato- and tribo-chromatic properties. A rapid reversible thermo-chromatic transition was observed.

### C8.50

**FABRICATION OF HIGHLY-ORDERED POROUS TiO₂ MEMBRANES AND ITS APPLICATIONS IN DYE SOLAR CELLS.** Qingsong Qiu, Zhenggu Fu, S. Hayami, A. Fujishima*, O. Sato. Special Research Laboratory for Optical Science, Kagouga Academy of Science and Technology, Kawasaki, JAPAN. Department of Applied Chemistry, School of Engineering, The University of Tokyo, Tokyo, JAPAN.

In this work, we report a very simple method for fabrication three dimensional highly-ordered porous structure. That is, utilizing capillary forces, ultrathin semiconductor particles are directly used to assemble themselves in the voids of template while the template is being assembled. The highly-ordered porous structures with larger area and uniform orientation can be produced after removing the template. By using this simple method, SiO₂/TiO₂ porous membranes have been successfully fabricated. SEM pictures and transmissivity spectrum of these films have confirmed the success of this simple method. In the meantime, the three dimensional highly ordered TiO₂ porous structures fabricated with this method has been used to fabricated dye sensitized solar cell. The largest open-circuit photovoltage (Voc) is about 0.82V have been achieved by using the ordered TiO₂ porous membrane. This work demonstrates that optimizing the TiO₂ porous structures is one way to get the largest open-circuit photovoltage as well as higher energy conversion efficiency of dye solar-cell.

### C8.51


The transport properties of conjugated polymer thin films are directly related to the packing and orientation of the molecules in the film. Unfortunately, it is very difficult to control these parameters in spin-coated films. Conjugated polymer monolayers provide a unique system to study the 3D transport properties in these materials and the effect of the substrate/polymer interface on the structure and orientation of the film. In the past, monolayers of poly(3-hexylthiophene), P3HT, have been prepared with Langmuir-Blodgett techniques by adding bridging components or using amphiphilic derivatives of polythiophene. In this work, monolayers and ultrathin films of P3HT have been prepared using a modified dipping technique with no added components. Atomic Force Microscopy and X-ray scattering are used to determine the morphology and the thickness of the film. Molecular orientation and the degree of crystallinity are studied by Grazing-incidence X-ray. Field-effect transistor structures are used to probe the transport properties of the ultrathin films. We find that the polymer monolayer is about 2 nm thick and the plane of the aromatic rings is oriented normal to the substrate. The mobility of the P3HT monolayer device is on the order of 10⁻² cm²/V·s. This value is several orders of magnitude lower than in the bulk crystalline chain in spin coated FET's, but directly probes the mobility at the interface and the accumulation layer. We further study the evolution of the mobility from monolayer to bulk.

### SESSION C8: SELF-ASSEMBLY, NANOPRINTING AND PRINT-DBS

**Friday Morning, April 20, 2001**

**Chairs:** Timothy M. Swager

**Nob Hill A/B** (Marriott)

#### 8:30 AM **C8.1**

**IONIC SELF-ASSEMBLY AND LOW CONVERSION TEMPERATURE OF POLY[p-PHENYLENE VINYLENE].** A. Marletta, F.A. Castro, R.M. Parin and F.E.G. Guimarães. Universidade de São Paulo, Instituto de Física de São Carlos, São Paulo, BRAZIL.

The discovery of the extremely rapid (3 min) thermal conversion process of poly[p-phenylene vinylene] (PPV) at low temperatures (< 150°C) has opened up a number of new possibilities to molecularly engineered superstructures with improved properties. It has been accomplished by substituting the chloride counterions of a water soluble PPV precursor, the poly[2-vinylpyridinethiophene] (PPYTH), by a long chain dodecylbenzenesulfonate (DBS) ion. In the present work, we have used the DBS to produce self-assembled multilayers with special features. Rather than alternating layers provided by a polyelectrolyte and a polyelectrolyte, we adopted the alternative approach consisting of substituting the chloride counterion of the water-soluble polyelectrolyte PPYTH by long chain sulfonic acid DBS, which acts as an anion. The internal layer structure of these PPYTH-DBS films is therefore likely to be different from conventional polyelectrolyte-layers films, since DBS is expected to be incorporated into the PPYTH chain. Such a property, together with the rapid conversion process, provides a good control over the conjugation length of PPV segments by the addition of different amounts of DBS, allowing the variation band gap between LUMO and HOMO states along in the PPV film. The resulting PPV films possess less defects and highly resolved vibronic structures in the luminescence and absorption spectra compared to films converted at high temperatures, owing to the narrow distribution of conjugation lengths and absence of carbonyl-related defects, thus leading to higher quantum yields in the luminescence processes. A. A. Marletta, D. Gonsalves, O.N. Oliveira Jr. R.M. Parin and F.E.G. Guimarães, Adv. Mater. 12, p. 64-74 (2000).

#### 9:00 AM **C8.2**

**NEW CONJUGATED OLIGOMERS FOR NANO-ELECTRONICS AND NANO-OPTOELECTRONICS.** Saeed A. Janczeck, Departments of Chemical Engineering and Chemistry, University of Washington, Seattle, WA.

Conjugated oligomers are structurally well-defined organic semiconductors with potential applications in thin film electronic and photonic devices such as thin film transistors, light-emitting diodes, lasers, and solar cells. They have also been explored as molecular wires and components of nanoelectronics. The structural perfection of single crystal of conjugated oligomers recently led to demonstration of electrically pumped diode lasers and very high charge mobilities. We have synthesized and obtained single-crystal X-ray crystal structures of a series of over a dozen conjugated oligoquinolines which are examples of n-type organic semiconductors. The crystal structures of these oligomers revealed various intermolecular packing characteristics which influence their solid state electronic and photophysical properties. Some of these new oligomers have been successfully used to fabricate light-emitting devices. New robust, air stable pentacone derivatives, tetrapienones, have also been synthesized and investigated including crystal structures, charge transport, and light-emitting properties.

#### 9:30 AM **C8.3**

**INKJET PRINTING OF POLYMERS BY REACTION AND BY IONIC SELF-ASSEMBLY.** Paul Calvert and Mouna Ghareem, Arizona Materials Labs., Tucson, AZ.

Previous work on extrusion freeform fabrication has shown that polymer gels can be built up by a layerwise deposition process. In a search for higher resolution we have been depositing gels by inkjet printing with a view to treating the gel layers with mineralizing
solutions. The ideal "inks" for such a process would be pairs of water-soluble polymers or monomers that gel rapidly when printed in successive thin layers that are subsequently crosslinked. A similar approach has been used to print films of sub-micron alumina particles by making a dispersion of alumina with the water-soluble polymer and then overprinting with the other polymer. This approach has also been used to make films of epoxy/novolac resin and a water-soluble deoxidizer. IR studies of films deposited on silicon show that in this case the gelation reaction occurs during deposition. This method can be generalized to allow multiple layers to be overprinted without each subsequent deposition obliterating the previous layers. The approach will be compared with other "direct writing" methods.

**10:30 AM C9.4**

**INTERFACE-LIMITED INJECTION IN AMORPHOUS ORGANIC SEMICONDUCTORS.** S.R. Forrest, M.A. Baldo, Department of Electrical Engineering, Princeton University, Princeton, NJ.

The current-voltage (J-V) characteristics of organic light emitting devices can broadly be categorized as being due to bulk limited or injection limited transport. Both models have limitations, in that they generally fail to quantitatively predict the correct layer thickness or temperature dependence of the J-V characteristics. Nor do many of these models adequately describe the dependence of the transport properties on cathode material. We have examined electron transport in the various organic layers and found that charge hopping from interfacial states in the organic material in the first few monolayers near the cathode can accurately account for all of the observed dependencies noted above. Specifically, the bulk distribution of conduction states is broadened and shifts to lower energies due to charge transfer from the first few monolayers, and to local disorder. Hopping from these states then accounts for the temperature and thickness dependence of transport through the thin amorphous films. Several different techniques such as direct determination of the polaron distribution using phosphor doped layers, J-V characteristics as well as Monte Carlo simulations of the bulk transport properties have all been employed to fully describe the charge transport in the general class of amorphous organic materials typified by Aq

**11:00 AM C9.5**

**SOLVENT VAPOR ENHANCED DYE DIFFUSION FOR FULL COLOR OLEF OLED FABRICATION.** E. Pashenitzka, L. Stirling, and J.C. Sturm, Princeton University, Dept. of Electrical Engineering, Center for Photonics and Optoelectronic Materials (POEM), Princeton, NJ.

To fabricate three color organic displays requires some kind of patterning of the organic layer. For polymer based devices, the conventional spin-coating process forms a uniform polymer layer which is capable of emitting only one color. In previous work we introduced a dye diffusion technology, which locally doped the polymer film after the initial spin coating process and thus changed the emission color. It is crucial to control the amount of dye as well as the dye concentration profile within the polymer layer because the efficiency of the OLEDs is strongly dependent on the dye concentration. However, the diffusion of dye in the polymer film is very limited at temperatures below the glass transition temperature Tg. On the other hand, processing at temperatures above Tg negatively influences the performance of the OLED. In this work we demonstrate a method which temporarily lowers the glass transition temperature of the polymer film and thus enhances the dye diffusion. To this end, after the dye was locally deposited on the polymer film surface, the films were annealed in the presence of a solvent vapor. Due to the absorption of a small amount of solvent, the Tg of the polymer film is substantially lowered and the dye can diffuse more easily within the polymer film. After processing, the solvent evaporates and the film regains its original characteristics. The dye profile was characterized using SIMS and depth-sensitive photoluminescence. Using PVK/PBD matrix with C60 or C70 added as a dye, a dye concentration profile which previously required a diffusion process of 1 hr at 84°C could be accomplished in 10 min at room temperature. The resulting device efficiency was raised by an order of magnitude compared to a control device, and it was found that it was possible to uniformly dope the polymer during the spin coating step. Mechanisms of diffusion in the presence of solvents will also be discussed.

**11:15 AM C9.6**

**SCREEN PRINTING OF ELECTRONIC AND OPTOELECTRONIC MATERIALS AND DEVICES ON RIGID AND FLEXIBLE SUBSTRATES.** G.E. Ingalls, Optical Sciences Center, The University of Arizona, Tucson, AZ.

We will present the use of screen printing in the fabrication of organic, electronic, photonic, and optoelectronic devices. The potential for this technique to print ultrathin films in the range of several tens of nanometers will be discussed. Examples relating to organic light-emitting devices will be shown. This technique will be useful in the fabrication of low cost organic based devices to be used in lighting, signage, low information content displays, and solar cells.

**11:30 AM C9.7**

**SINGLE MOLECULE ELECTROMECHANICAL ACTUATORS BASED ON POLY[(B)ANILINENE].** Michael M. Wetsel, University of California at Riverside, Department of Chemistry, Riverside, CA.

Conducting polymer electromechanical actuators (CP-EMAs) have attracted considerable interest because their ability to function as "molecular muscles." It is well established that bulk CP-EMAs exhibit dimensional changes that occur in the polymer as a result of doping (oxidation-reduction processes). Typical CP-EMAs include traditional redoxactive polymers such as polyaniline, polypyrrole, and polypyrrole. In the aforementioned systems, dimensional changes result from either the incorporation or expulsion of counterions and solvating species into the polymer matrix during electrochemical doping. This mechanism defines electromechanical actuation in conducting polymers as a bulk phenomenon of the conducting composite, not an intrinsic property of the individual polymer chains. In other words, oxidation and reduction of a single, isolated conducting polymer chain would not be expected to elicit a significant muscle-like expansion or contraction. Given the continued interest in single molecule-based devices, we found it an intriguing challenge to pursue the development of conducting polymers specifically designed to function as single molecule CP-EMAs. One such class of traditional CPs lacks the intrinsic ability to function as a CP-EMA at the single molecule level, alternate CP architectures need to be explored. Herein we report the design, synthesis, and properties of a novel electromechanical actuator, poly(cyclooctetetracene) (POTTc). This system integrates both a conducting polymer and a [6]annulene repeat unit. The ability of [6]annulenes to undergo a conformational change as a function of redox state is well known, and allows POTTc to function in principle, expand and contract via redox-induced changes in the length of the repeating unit. Thus, electromechanical actuation in this system is an intrinsic property of the individual chains, not a bulk property of the material. Results to date will be presented.
recently [1] the macroscopic charge carrier mobilities were shown to depend strongly on the orientation of the self-organized domains. However, in the Field Effect Transistor (FET) device, this is not the case, as the carriers are generated in a layer only a few nm deep near the gate-insulator/semiconductor interface, which in general is inaccessible to conventional techniques for structural characterization. Hence for further understanding of the relation between structure and mobility, new ways to characterize this layer must be developed. A typical layered FET device consists of a semiconducting film on an insulating substrate. Using well-calibrated X-ray synchrotron radiation it is possible to create a resonant coupling of the incoming and reflected X-rays, giving rise to X-ray standing waves of variable period, depending on the grazing incidence angle of the primary beam. The amplitude of the enhanced X-ray standing wave field in the film can exceed more than an order of magnitude larger than for the non-resonant case. Measuring the diffraction signal from self-organized domains for various distributions of the electric wave field intensities thus offers an attractive, non-destructive method for gauging their orientation and mobility perpendicular to the interface. [1] H. Srinivasan, P.J. Brown, R.H. Friend, M.M. Nielsen, K. Bedgami, B.M.W. Langeveld-Voss, A.H.J. Spieling, R.A. Janssen, E.W. Meijer, P. Herwig, D.M. de Leeuw, Nature 401, 685 (1999).

2:15 PM C10.3
TETRACENE THIN FILMS GROWN BY HOT WALL EPITAXY.
lsu-Dierk Buchholz, Theo Stegini, Hendrik Schön, Ernst Bauer, Christian Kloc, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Recently measured very high electron and hole mobilities in tetra-cene single crystals inspired us to study a thin film preparation method that uses conditions resembling those of single crystal growth. Thin films formed under similar conditions to single crystal growth are expected to show mobilities similar to single crystals. We have chosen hot wall epitaxy for thin film growth because this method allows a wide range of process temperatures and transport gas pressures to be used. Polycrystalline films have been grown on amorphous substrates like polyimide or glass and on polycrystalline substrates like aluminum and on two dimensional inorganic single crystals like tungsten diselenide (WSe2). Single crystalline films have been obtained only on single crystals in a homoeopitaxial process. The quality of the films has been assessed by x-ray methods and carrier mobility measurements. The effect of different substrate materials, source and substrate temperatures, pressures and gas flows on film properties will be discussed and compared to those of single crystals.

2:30 PM C10.4
HOT-WALL-EPITAXY - THE METHOD OF CHOICE FOR THE GROWTH OF HIGHLY ORDERED ORGANIC EPILAYERS.
Hans-Jürgen Jahn, Helmut Spitzer, Univ. Linz, Inst. of Semiconductors and Solid State Physics, Linz, AUSTRIA.

The most spectacular effects observed in organic semiconductors where shown so far in monocrystals. The high crystallinity of the materials is a prerequisite for the observation of fractional Hall effect or electric field induced superconductivity. The next challenge is to obtain this high crystalline quality for epitaxial layers. Due to the small band gaps organic molecules usually possess charge transport like flash evaporation or molecular beam epitaxy failed to reach this goal. However, by using Hot Wall Epitaxy we obtained monocrystalline layers of C60 and highly ordered para-sexiphenyl structures. In contrast to other growth processes, Hot Wall Epitaxy works close to thermodynamic equilibrium and is therefore most applicable for materials with Van der Waals binding character. The Hot Wall Epitaxy system can be described as a semiclosed growth reactor, consisting of a vertically mounted quartz cylinder, which is heated by three separately controllable ovens, and is closed on top by the substrate. The first oven heats the source material and controls the growth rate. The second heats the hot wall between source and substrate, which is in all cases the clearest of all the three, and helps to avoid loss of volatile material. The third oven controls the substrate temperature and allows to influence the growth process on the substrate surface. We achieved crystalline perfection for C60 layers on silica substrates and fabricated Ba doped n-type layers with mobilities of 2000 cm2/Vs at room temperature. In addition we were able to demonstrate self assembled growth of quantum wires of para-sexiphenyl and highly pronounced anisotropies in photoluminescence. The optical characterization of the para-sexiphenyl layers allowed us to determine the arrangement of the molecules in the quantum wires. We found that the molecules are packed with their long axis parallel to the substrate and perpendicular to the quantum wires.

3:15 PM C10.5
ORGACOM, THE POLYMER ALTERNATIVE TO ITO.
Frank Lowetz, Emiel Verdonck, Tom Ciechomski, Luc Leenders R&D, Agfa-Gevaert NV, Mortsel, BELGIUM.

Transparent conducting electrodes are an important component in electronic devices such as electroluminescent lamps (organic or polymer-based), touch-screen displays, electronic paper. The standard in the market today is indium tin oxide (ITO). (1) on glass or on flexible substrates. The most important characteristics are low surface resistance combined with high transparency in the visible region of the spectrum. About 10 years ago AGFA developed the conducting polymer blend poly(a,4-bisethylidenohydroxophene/poly(styrenesulfonic acid), PEDOT/PSS (2). Although initially applied as an antistatic coating for photographic papers, we further developed a plastic film. The latter has resulted in our ORGACOM™ foil (PEDOT/PSS on PET) that can be applied as an organic alternative to ITO. It combines high transparency, good surface resistance and high stability with easy processing and low cost fabrication. Mechanical stability is important for bending the flexible device. During our contribution we will discuss both synthetic aspects (e.g. polymerization parameters that influence the PEDOT/PSS synthesis) and the new applications that have been and are being currently developed. (1) Lewis, B. J. Paine, D.C.: MRS Bulletin, August 2000, 22-27 (2) Grenemonde, L.; Jonas, F.; Freitag, D.; Piefuck, H.; Reynolds, J. R. Adv Mater. 2000, 12, 481-484 (3) Van Thillo, E., Miyai, B., Samui, R. (Agfa Gevaert NV) - EP 555111 A1, 19950820.

3:30 PM C10.6
THE EFFECT OF SURFACE PREPARATION ON THE STRUCTURE AND ELECTRICAL TRANSPORT PROPERTIES OF AN ORGANIC SEMICONDUCTOR. Laura Kaspar, Christos Dimitrakopoulos, IBM T.J. Watson Research Center, Yorktown Heights, NY, Debra Mastro, MIT, Cambridge, MA.

Organic semiconductors offer promise for the future of low cost, flexible thin film transistors (TFTs). They can be deposited by low temperature techniques that are compatible with inexpensive flexible substrates such as plastics - thus expanding the possibilities for the manufacture of amarerics, RF identification tags, and light weight, flexible flat panel displays. While organic semiconductors have made impressive progress in the past decade, there is still need for improvement of both the performance and reproducibility of electrical transport properties in organic films. Long range order in the films and a crystal structure that results to substantial molecular orbital overlap along the transport direction is critical to the mobility of the film. This is particularly important in the first few monolayers. The interactions of the substrate surface with the depositing films, especially its impact on the morphology of the film, is crucial to achieving adequate device performance. We will review our work to date in modifying surfaces and understanding the effects of such modifications on the ordering and performance of the organic semiconductor pentacene.

3:45 PM C10.7
Determination of the Electronic Structure of OLED Electrode Interfaces. R. Schulz, Dept. of Electrical Engineering, University of South Florida, Tampa, FL.

The determination of the electronic structure of electrode interfaces in organic light emitting diodes (OLED) using photoemission spectroscopy (PES) poses a number of challenges. The goal of such experiments is to obtain precise values for carrier injection barriers, interface dipoles and occurring band bending. Problems typically encountered due to the fairly fragile and weakly conductive nature of most organic materials and the need for an overlap band bending, possibly occurring at an interface screening, chemical interface reactions and x-ray or ultraviolet (UV) light induced surface photochemistry. We conducted a number of model experiments exploring these phenomena. The results of our experiments allowed us to define a methodology helping overcoming these problems, thus allowing a more precise and reliable determination of the electronic structure of organic interfaces. Our results demonstrate the cases of use of above mentioned spectroscopy (XPS) measurements enables a more accurate interpretation of the primarily conducted UV photoemission spectroscopy (UPS) measurements. The high resolution of core level binding energy shift measurements and the magnitudes weaker photo flux of XPS (compared to UPS) allows a detailed investigation of band bending, chemical reactions, and charging artifacts. This will be demonstrated by model investigations on inert and reactive (8H-dicyanvinylindene) gallium (Ga2) facial interfaces and indium tin oxide (ITO) electrode surfaces. The results of these experiments show that careful evaluation of ultrathin overlap XPSpectra in combination with work function measurements using both, XPS and UPS, allows discriminating between different layers enabling more reliable measurement of injection barriers, interface dipole and ITO electrode work functions.

4:15 PM C10.8
CHARGE INJECTION SPECTROSCOPY OF THE MoLPPP/Au CONTACT.

77
Charge carrier injection into ladder-type poly(paraphenylene) (McLPPP) thin films deposited on a Au(111) substrate has been studied by STM spectroscopy performed in tip contact mode. With this newly developed technique the barrier height for electrons and holes at the organic/metal interface can be probed directly. It is found that the injection barrier as well as the energy gap of the polymer show significant variations at different locations of the sample surface. Some regions exhibit an energy gap for charge carrier injection, $E_{gap}$, which is larger than the optical band gap, the energy difference being commonly attributed to the exciton binding energy. Actually, this is what one would consider to be the normal behavior of the polymer. However, on other regions $E_{gap}$ appears to be significantly smaller than the optical band gap indicating the presence of aggregates within the polymer film. Our results show that such inhomogeneities have a strong influence on the charge carrier injection and transport properties of this polymer and is probably a common feature of materials with a tendency to form aggregates. In addition the measurements allow us to determine an exciton binding energy in the range of 0.5 to 0.8 eV. This result will be compared to the photocurrent onset spectrum.

4:50 P.M. C10.0
A JOINT THEORETICAL AND EXPERIMENTAL STUDY OF INTERFACES BETWEEN METALS AND CONJUGATED MATERIALS. X. Crispin, M. Fahlman, A. Crispin, J. Birgersson, A.W. Denier van der Gon, W.R. Salaneck, Department of Physics (IPM), Linköping, Sweden; R. Luzzati, V. Gerskin, Laboratory for Chemistry of Novel Materials, Center for Research in Molecular Electronics and Photonics, Mons, Belgium; J.L. Brédas, Department of Chemistry, Tucson, AZ.

X-ray and UV photoelectron spectroscopies combined with theoretical modeling based on Density Functional Theory (DFT) are used to investigate metal/conjugated material interfaces. In order to understand the behavior of systems (e.g., charge transfer and/or formation of chemical bonds) that occur at these interfaces, simple model systems are required both theoretically and experimentally; conjugated monomers and oligomers interacting with transition metal surfaces provide such model systems. This approach has been followed to investigate three interfaces: (i) The interface between acrylonitrile and transition metals (Cu, Ni, and Fe), for which the changes in workfunction upon adsorption, as well as the partial electron transfer between the metal to the molecule are rationalized. (ii) The interface between gold and ethylenedioxythiophene (EDOT). (iii) Several conjugated molecules [benzoquinodimine, p-phenylenediamine, aniline, and a few trimers] are used to model the interaction between the emeraldine base (EB) form of polyaniline and iron. In cases (i) and (ii), the interpretation of the phenomena occurring at these interfaces can be applied to the metal/organic semiconductor interfaces in organic-based electronic devices, which play a key role in hole and electron injection. In case (iii), the results of the theoretical calculations point out the importance of the electronic chemical potentials, as defined in DFT, in describing charge transfer between iron and the molecules. The XPS measurements suggest a negative charge transfer from iron to the chemisorbed trimer of EB. This charge transfer at the very interface could maintain the metal positively charged, which would explain the protection provided by EB against the corrosion of steel.

4:45 P.M. C10.10
EFFECT OF INTERFACE AND CRYSTALLIVITY ON THE FERROELECTRIC PROPERTIES OF POLY(VINYLIDENE FLUORIDE-TRIFLUOROETHYLENE) COPOLYMER THIN FILMS. Feng Xin, H.S. Xu, Babak Rustai, Q.M. Zhang, Materials Research Laboratory and Electrical Engineering Department, The Pennsylvania State University, University Park, PA.

Ferroelectric polymer thin films are attractive for a wide range of applications such as MEMS, IR sensors, and memory devices. In the talk, we present the results of a recent investigation on the thickness dependence of the ferroelectric properties of poly(vinylidene fluoride-trifluoroethylene) copolymer spin cast films on electrode Si substrate. We will show that as the film thickness is reduced, there exists two thickness regions. For films at thickness above 100 nm, the thickness dependence of the ferroelectric properties can be attributed to the interface effect. However, for thinner films, there is a large change in the ferroelectric properties such as the polarization level, the coercive field, and polarization switching speed, which is related to the large drop of the crystallinity in the ultrathin film region (below 100 nm). The results from X-ray, dielectric measurement, and...