SYMPOSIUM L

Organic and Polymeric Materials and Devices

April 22 – 25, 2003

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Paul W.M. Blom
Materials Science Centre
Univ of Groningen
5118.0005
Groningen, 9747 AG NETHERLANDS
31-50-3634376

Christos D. Dimitrakopoulos
IBM T.J. Watson Res Ctr
Rm 37-206
Yorktown Heights, NY 10598
914-945-2051

Neil C. Greenham
Cavendish Laboratory
Univ of Cambridge
Cambridge, CB3 0HE UNITED KINGDOM
44-1223-766301

C. Daniel Frisbie
Univ of Minnesota
Amundson Hall
Minneapolis, MN 55454
612-624-0779

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*Invited paper
8:30 AM • 11
POLYMER LEDS: RECENT PROGRESS
Alan J. Heeger

I will summarize the results of a series of recent experiments directed toward improved performance in polymer LEDs. These include the following: Stabilization of the blue emission from polyfluorene using anode-capping techniques; Stability of the blue emission from polyfluorene using a novel electron-injection layer; Enhanced performance from polymer LEDs through the use of a novel hole-injection layer; Electrophosphorescence: semiconducting polymers doped with lithium compounds.

9:00 AM • 11.2
THE EFFICIENCY OF POLYMER LEDS OVER A WIDE VOLTAGE RANGE

Polymer LEDs show a strong dependence of the external efficiency on the applied voltage, or on the driving conditions. Generally, the efficiency decreases rapidly above the built-in potential, followed by a slow decrease at higher voltage. The latter is particularly relevant for passive matrix (PM) operation of polymer LED displays, where high peak luminance and constant high driving voltages around 10 V are commonly used. It is well recognized that four factors can contribute to the observed voltage dependence: excitation formation probability, singlet-triplet exciton branching ratio, single photon quantum efficiency $\eta_{total}$, and photon escape probability or out-coupling efficiency $\eta_{out}$. Here, the role of $\eta_{total}$ and $\eta_{out}$ is quantitatively determined by measurement of the photoluminescence yield under forward and reverse bias. The angular dependence of the light emission is measured to locate the emitted zone by means of an optical model including two different layers and taking into account the orientation of the dipoles emitters. With the location known, $\eta_{out}$ can be evaluated. The methods described can also be used to optimize external efficiencies of devices with different layout, e.g. with a different hole-injecting or electron-injecting layer.

9:15 AM • 11.3
ENHANCED LIGHT EMISSION THROUGH TRIPLET-TRIPLET ANHILINATION IN ORGANIC ELECTROLUMINESCENT DEVICES
M. Pujihar and C. Ginzburg, Department of Biomedical Engineering, Tokyo Institute of Technology, Yokohama, JAPAN

We demonstrate here that luminescence increased more than linearly with an increase in current density of tris(8-hydroxyquinoline) aluminon [Alq3]-based electroluminescent (EL) devices and the EL efficiency reached a maximum at 120 mA cm$^{-2}$ when electron-hole injection was well balanced. The well balanced charge injection became possible by enhanced electron injection from an Al cathode with an electron injection layer of alkylmetal carboxylates [1] and hole injection by surface modification of ITO [2]. The luminescence current curves were well fitted with a combination of a linear and a quadratic function of the current. The quadrupole component of electric field at Alq3 from a combination of 1-2 Alq3 layers through triplet-triplet T-T annihilation of triplet excited states (2Alq3) produced significantly with 2 Alq3. The requirement of the well-balanced charge injection implies that the long-lived $^{1}A_{T}$ with quenched efficiently by energy transfer to excess and colored $^{3}A_{T}$ with monochromatic radicals in the emission zone when the charge injection was unbalanced. The short-lived $^{1}A_{T}$ was not quenched efficiently. This is the most important characteristic of Alq3-based EL devices. [1] C. Ginzburg and M. Pujihar, Jpn. J. Appl. Phys., 38, L3348 (1999) [2] C. Ginzburg, K.-J. Kwok, K. Yagi, and M. Pujihar, Appl. Phys. Lett., 79, 272 (2001).

9:30 AM • 11.4
HIGH EFFICIENCY ORGANIC EL DEVICES HAVING CHARGE GENERATION LAYER
Junji Kido, Yamagata Univ, Graduate School of Science and Engineering, Yonezawa, Yamagata, JAPAN; Takeshi Nakada, Jun Endo, Norifumi Kawai, Ichiro Mori, Akira Yokoi, and Tohiko Shimazato, IMES Co., Ltd., Fujisawa, Kawasaki, JAPAN

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

10:00 AM • 11.5
CHARGE INJECTION IN ORGANIC SEMICONDUCTORS
George G. Malliaras, Cornell Univ, Dept of Materials Science and Engineering, Ithaca, NY

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

11:00 AM • 11.6
EXCITON SINGLET-TRIPLET RATIOS IN MOLECULAR AND POLYMERIC ORGANIC SEMICONDUCTORS
M. Bello and M. Segal, MIT, Dept. of Electrical Engineering and Computer Science, Cambridge, MA.

The ratio of singlet to triplet excitons is critical to the efficiency of fluorescent organic electroluminescent (EL) devices. Recent measurements have suggested that the formation statistics of excitons in polymeric semiconductors may favor luminescent singlets over non-emissive triplet excitons. Also, fluorescent polymers may possess intrinsically higher EL efficiencies than low molecular weight fluorescent materials. We present a general technique for measuring the ratio of luminescent to non-luminescent excitons within EL devices. This allows us to determine the singlet fractions under EL conditions in archetypal materials such as tris(8-hydroxyquinoline) aluminon [Alq3] and poly[2,6-di(thienyl)phenylenevinylene]-[2,6-di(2-thienyl)phenylenevinylene] (MEH-PPV).

11:30 AM • 11.7
ELECTROCHEMICAL CHARACTERIZATION OF BLUE EMITTING POLYFLUORENE LED

In an operating LED, electrons are injected into the polymer's LUMO level from the cathode and holes from the anode into the polymer's HOMO level. The value of the electron affinity (EA) is usually inferred (often incorrectly) from the experimental HOMO level energy and the energy value of the optical band gap. Using a combination of experimental and theoretical conditions we can now directly access the EA position. Reduction events have been observed on poly[(9,9-dioclyfluorene) (FS) and blue emitting polymers based on 9,9-dioclyfluorene. This evidence is consistent and reversible. As predicted by theory, the LUMO level is entirely delocalized over FS blocks. An EA of approx. ≈2.3 eV, equal to that of FS, is therefore a common feature of blue polymers containing sequences of 9,9-dioclyfluorene. Blue emitting 9,9-dioclyfluorene-triarylamine (TAA) polymers containing either 4-acetyl phenylidiphenylamine (TFB) or 4,4′-bis(4-butylylphenyl), 4,4′-diphenyl phenylenediamine (PPB) are characterized by an electron affinity of ≈2.1 eV. This result shows that the LUMO wave function in these systems is localized on the FS-1,2 FS units. In the case of FSB donor polymer the LUMO level is again localized, this time on the bipyridyl unit at the junction of each 2 repeating units. The EA for this material is therefore lower than in the other cases ≈1.8 eV, as a result of the increased localization of the LUMO wave function. Electrochemical characterization provides a direct probe for the dynamic of the charge injection in a polymer system, as the HOMO and LUMO are the states into which the holes and electrons are injected. Electrochemical measurement together with theoretical modelling gives a more complete understanding of molecular properties and behaviour. However, electrochemical measurements are not necessarily relevant to the optical energy gap, as the optical excitation does not necessarily involve molecular orbitals probed by electrochemical methods.

11:45 AM • 11.8
ON-CHAIN ELECTROCHEMICAL DEFECTS IN PI-CONJUGATED POLYMERS: FROM EXCITON TRAPPING TO INTRINSIC ELECTROPHOSPHORESCENCE
John M. Lipton, Max Planck Institute for Polymer Research, Mainz, GERMANY, and University of Massachusetts, GERMANY; A. Poole, S. Pick, E.W. List, Institute of Solid State Physics, Graz University of Technology, Graz and
Christian Doppler Laboratory of Advanced Functional Materials, Graz, AUSTRIA; S. Paul and U. Scherf, Institut fuer Chemie, Universitas Potdam, Golm, GERMANY.

On-chain chemical defects in conjugated polymers have previously been associated with luminescence quenching. Recently, however, it was demonstrated that additive defects in polymer backbone emit fluorescence as exciton traps and give rise to a broad emission redshifted from the polymer backbone emission and characteristic of a fluorescent moiety. Using gated fluorescence spectroscopy this emission was clearly identified on isolated chains of pristine polyfluorene polymers and oligomers, suggesting that the previous assignment to an intermolecular excited state is inappropriate (Lupton et al., APL 80, 4489 (2002)). Gated electrochemiluminescence (EL) was also used to study the dynamics of charge trapping and delayed recombination on these defects (Lupton et al., PRB 65, 153092 (2002)). A further highly significant class of defects we have identified in conjugated polymers relate to metal impurities.

We find that contamination of the polymer backbone with 80 ppm of copperbound palladium is sufficient to enable efficient room temperature electrophosphorescence (Lupton et al., PRL 89, 167401 (2002)). The diffusion of triplets to these sites also gives rise to extremely fast phosphorescence observable below 100 nm excitation, without modifying the electronic structure or intersystem crossing of the material. Time resolved EL spectroscopy provides a tool to distinguish between delayed emission resulting from long lived excited states and that resulting from complex structures, such as the internal field of the LED. We believe that the discovery of efficient triplet emission is of interest for LEDs but also for polymer lasers and single molecule devices, where triplets can easily be deactivated.

SESSION I/2/K2.1

ORGANIC MOLECULES ON METAL SURFACES BY HIGH- RESOLUTION STM
Frederic Rouxet*, Y. Naich, M. Schunck, E. Legagnic, J. Steingraber, and F. Beneslavich, Physics Department and LNano, University of Aarhus, DENMARK; P. Jing, A. Gourdon, and C. Joachim, CEMES CNRS, Toulouse, FRANCE.

"Present address: INRS-EMT, Université du Québec, Varennes (QC), CANADA.

The adsorption of large organic molecules on surfaces plays a vital role in the emerging field of nanotechnology. Here we show how the unique resolving power of Scanning Tunnelling Microscopy yields new information on molecular diffusion and assembly at the surface.

First, we investigated the issue of surface diffusion. Adsorbate motion across surfaces can be followed directly by time-resolved STM movies. In the simplest picture of surface diffusion, the adsorbate jumps between nearest neighbor sites. Recent results suggest this is not necessarily true for complex molecules. By studying the diffusion of two related aromatic molecules, DC (C6H8) and HDBDC (C6H6), on Cu(110), we find that their diffusion is dominated by long jumps, spanning multiple lattice spacings. The HDBDC molecule has a more identical to DC, and six additional spacer legs, which increase its diffusion coefficient by four orders of magnitude with respect to DC. This ultimately demonstrates how molecules can be designed to engineer their diffusion properties. Second, we describe the adsorption of the Lander molecule [2] (C6H8) on Cu(110) by STM in the temperature range 100-300 K. The Lander has a central polyaromatic wire (conducting backbone), and four ‘spacer legs’ (5,5-dihexyl-1,4,2-dithiophene) for isolation from the substrate. Lander molecules are imaged as four separate lobes by STM, which may be arranged in three different conformations. Manipulation experiments with the STM at low temperatures on isolated Lander molecules adsorbed on step edges reveal a restructuring of Cu steps [2], when removed from a step, a nanostructure appears, two atomic rows in width (corresponding to the distance between the spacer legs within the molecule). Lander molecules, as nanometer scale templates, reshaping the protrusion of step edges into characteristic nanostructures.

1:45 P.M. I/2.2/K2.2

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

Down-scaling of organic field effect transistors (OFETs) often faster switching speeds as well as higher current capabilities at a given device area. We report on the systematic reduction of the organic channel length down to 70 nm for OFETs using quarter-thin (4T) active material. Thionenes are used because of their possible high carrier mobility values. We use electron beam lithography to manufacture finger source-drain contacts on SiO2/n+-Substrates to fabricate OFETs within the common back gate configuration. Deviations of the standard FET characteristics (short channel effects) are expected for channel length L comparable to junction width of the electrodes and/or to the gate insulator thickness. After deposition of the organic film by UV/evaporation long channel (L > 7 μm) devices exhibit standard characteristics at room temperature also used to nitrogen atmosphere. However, for SiO2 gate insulator of 200 nm thickness we found degradation of the saturation regime for L < 1 μm, while on/off ratios are quite deteriorate for channel lengths of 400 nm or below. The effects will be discussed in comparison with short channel effects on inorganic devices. Further, we will discuss an important result: drain current was found to increase by more than an order of magnitude for channel length L < 400 nm, which coincides with the average grain size in our organic layers. This indicates an important contribution of grain boundary scattering for the transport in the organic channel.

SESSION I/3

STRUCTURAL AND OPTOELECTRONIC PROPERTIES OF THE BLUE LUMINESCENT 6PHASE OF ALO3.
M. Cölfle, J. Greiner, S. Forero, A. Güldl, W. Brütting*, Experimental Physics II, University of Bayreuth, Bayreuth, GERMANY; [Present address: University of Saarland, Electronics and Semiconductor, Saarbrücken, GERMANY.

Tris(8-hydroxyquinolinato)aluminum (III) (Alq3) stands as one of the most successful materials used in organic light emitting devices (OLED) for display applications. Although the partly nanocrystalline character of evaporated films used in these applications is known, so far comparatively few investigations have been devoted to the crystalline state of this molecule. Another unresolved issue concerns the phase of the Alq3 molecule. It is well-known that depending on the mutual orientation of the hydroxyquinoline ligands, Alq3 can occur in two different stereoisomers: meridional and facial [1], however, until recently all existing phases (α, β and γ) have been found to consist of the meridional isomer [2]. In a previous work we have reported on a new crystalline phase of Alq3 (ΔAlq3) exhibiting strongly blue-shifted fluorescence [3]. Its significantly different optical properties have been tentatively ascribed to the presence of the Alq3 molecule. Here we will present an in-depth characterization of the different phases of Alq3 by combined thermal, structural and vibrational analysis. These data provide unambiguous evidence for the existence of the facial isomer in the blue luminescent 6phase of Alq3. Furthermore, an efficient way to fabricate blue luminescent Alq3 in large amounts has been found. These results will be correlated with the optoelectronic properties of Alq3 and Alq3-based thin film electroluminescent devices.

3:30 PM I/3.3

ON THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND ELECTRICAL PERFORMANCE OF OLIGOTHIOPHENE ORGANIC THIN FILM TRANSISTORS.
Research, Munich, GERMANY.

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

We have investigated a series of oligothiophenes with different chain lengths ranging from four to six units (dithienylquaterthiophene, dithienylquinquethiophene, and dithienylethithiophene), and with alkyl side chains ranging from to zero units (dithienylethithiophene, dithienylethynethiophene, and sef-thiophene). We have fabricated top contact organic TFTs with solution-processed polymer gate dielectrics and thermally evaporated active layers and found that the TFT performance depends critically on the length of the side chains and the contact configuration (with mobilities ranging from 0.07 to 1.1 cm² V⁻¹ s⁻¹) or is relatively insensitive to the channel length. We have also fabricated ring oscillators with dithienylethithiophene and measured a signal propagation delay of 30 μs per stage. In addition, we have fabricated substituted thiophene TFTs with ultra thin self assembled monolayer (SAM) gate dielectrics, with the intent to evaluate if long alkyl side chains contribute usefully to the effective thickness of a SAM gate dielectric. We have measured carrier mobilities as large as 0.65 cm² V⁻¹ s⁻¹ and subthreshold swing as low as 200 mV / decade. To our knowledge, this is the first time that the influence of the side chain length and the impact of the contact configuration on the performance of oligothiophene TFTs have been systematically investigated.

3:45 PM L3.3

ENERGIES OF METAL SPECTROISOMERS IN METAL TE 8,8′-HYDROXYQUINOLINE (HQ) CHELATES: IMPLICATIONS FOR CHARGE CONDUCTION IN ORGANIC LIGHT EMITTING DEVICES. Paul E. Burrows, Kim F. Ferris, and Linda S. Sapochak, Pacific Northwest National Laboratory, Richland, WA.

The development of small molecule organic electroluminescence (EL) materials in organic light-emitting devices (OLEDs) has proceeded rapidly since the report of efficient low voltage EL from aluminaria tris(8-hydroxyquinoline) (Alq3). However, further reducing the operating voltage for small-molecule OLEDs in a systematic manner is hindered by an incomplete understanding of the injection and transport of charge carriers across the interfacial and through bulk organic thin films. Full understanding requires that the structures of the molecular semiconductor both in the bulk and at the interfaces be known. In the case of the tris(2-ethyl) EL material, Alq3, the problem is complicated by the presence of two geometric isomers, and facing the problem are the different symmetries and correspondingly different molecular electronic states. We present new electronic structure calculations on Alq3 and the methyl-substituted series, n-MeAlq3 (n = 3, 7) for the mer and fac-isomers providing an improved understanding of their relative abundances. All-in computations performed at the SCF level noted a significantly higher stability (6.7-5.6 kcal/mol) of the mer-isomer over the facial form, which was maintained with treatment of electron correlation. Substitution of methyl on the aluminarian core, Ga3 or In-43 resulted in similar energetic preference of the meridional form, which was supported experimentally by NMR spectroscopy and single crystal X-ray diffraction studies. Our results suggest that the presence of the fac-isomer as a component in Alq3 thin films, therefore, an electron trap, is unlikely, and only the mer-isomer need be considered for modeling conduction mechanisms in OLEDs utilizing Alq3 materials. The implications of these structural results on different charge transport models will be discussed with respect to device performance measurements.

4:00 PM L3.4


The nano-scale electro-optical properties of conjugated polymer films depend strongly on the local morphology. Therefore, the detectability of conventional scanning probes to achieve sufficient resolution on bulk samples is a serious problem. We have developed a method to achieve molecular resolution on films of arbitrary thickness using a commercial atomic force microscope. The detection of the image does not show any molecular resolution, as in the case of such samples, the simultaneously measured phase image clearly does show individual polymer chains. The observed phase contrast is explained to result from a strong van der Waals interaction between the metal-coated tip and the p-electrons in the conjugated backbone of the polymer. A simple but quantitative model is presented. We have used our imaging technique to study the relationship between molecular structure and morphology of PPV derivatives. We found that the chains in the topmost layer of spin-coated films of the asymmetrically substituted polymer O-C6H4OC14H29-PPV (or MDH0-PPV) are highly curved, with a typical radius of curvature of 5-7 nm. In contrast, the surface morphology of these films is entirely different. The O-C6H4OC14H29-PPV shows straight individual chains, showing the causal relation between substitutional [asymmetry and surface morphology. By deliberately blunting the p-electron density at the side of the material under the tip, instead of the response of the nearest individual chain, it was found that the direct visualization of aggregates, using the same phase imaging scheme with a blunt tip. In line with the sharp-tip results, the O-C6H4OC14H29-PPV shows aggregation in 50-200 nm mesoscopic domains, whereas no aggregation is observed on MDH0-PPV. On PSHT the domain size is found to be of the order of 10-50 nm. Annealing the PSHT films increases the domain density, but not the domain size. Both observations are in good agreement with recent literature.

4:15 PM L3.5

ENERGY LEVEL ALIGNMENT AT FULLERENE-PHthalocyanine INTERFACE STUDIED BY ELECTRON SPECTROSCOPIES. Hiroyuki Tohoku University, Institute of Electrical Communication, Sendai, JAPAN; Atsushi Seko, Akiya Kaseki, Yasuo Ouchi, Nagoya University and Graduate School of Science, Nagoya, JAPAN; Kazumori Umemiya, Kazuhiro Seki, Research Center for Materials Science, Nagoya, JAPAN.

Interfacial band offset and band bending of organic semiconductor are critical to understanding and improving organic photovoltaic cells. In this study, the energy level alignment of fullerene(C60) / phthalocyanine(Pc) interfaces which is one of the model interfaces of organic photovoltaic cells has been investigated using UV and X-ray photoelectron spectroscopy and metastable atom electron spectroscopies (MAES). For the interface which was formed by depositing metal-free phthalocyanine on C60 thin film (15nm thick), 0.35 eV core level shift of Cl 2p state was observed by XPS at the deposition of Pc thin film of 0.2mm thickness in average. This result seems to indicate the band bending of the interface. This energy shift is quite steep in contrast to the band bending observed for C60/metal interfaces [N.Higashi et al. J. Appl. Phys. vol.92, 7384(2002)], where thickness of 50nm was required to achieve 0.3eV band bending to get Fermi level alignment between metal electrode and C60. For the reversed interface, C60 on Pc film, similar energy shift of 0.8eV at C60 layer was observed in consistent with the case of Pc on C60 film. However, the observed vacuum level shift due to interfacial dipole is different in polarity between the two interfaces. MAES is extremely sensitive method and can probe outermost surface selectively. MAES spectra revealed that no significant interface dipole formation happened at the interfaces. This means that possible doping of Pc to C60 is not main origin of the observed energy shift. Alternative explanation of the energy shift will be discussed.

4:30 PM L3.6

METAL VS POLYMER ELECTRODES IN ORGANIC DEVICES: ENERGY LEVEL ALIGNMENT, HOLE INJECTION, AND CHARGE INJECTION STRUCTURE. Northern Arizona University, Flagstaff, and University of Virginia, Dept. of Electrical Engineering, Princeton, NJ; Bert Nickel, Jeffrey Schwartz, Princeton University, Dept. of Chemistry, Princeton, NJ; Jacques Ghijen and Jean-Jacques Pierret, FUNDP, LISIE, Namur, BELGIUM; Andreas Eichler, H.C. Starck GmbH, Krefeld, GERMANY.

We have investigated the electronic, structural, and charge injection properties of electrode interfaces formed between three electroactive conjugated organic materials, i.e., N,N-bis[1-ethylhexyl]-N,N'-di-p-pheny1-1,4-bis(4-aminophenyl) (PcP), pentacene, p-xyleneophenol, and two high work function electrode materials, i.e., gold and the conducting polymer poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS). Ultraviolet photoelectron spectroscopy shows that the hole injection barrier between the three organic materials, i.e., a decrease of the Au surface dipole due to adsorption. Accordingly, the device structures built from a-PDTP and pentacene on the two different electrode materials show much higher current densities (up to 100 times of magnitude) for hole injection from PEDOT/PSS to Au. Hole injection from Au for a-PDTP devices is independent of deposition sequence (i.e., a-PDTP-on-Au vs. Au-on-a-PDTP) and
substrate (i.e., Au or PEDOT/PSS). Pentacene devices exhibit significant asymmetries in that respect, due to a strong dependence of the mobility on molecular orientation of the crystalline material on the substrate, as shown by atomic force microscopy and X-ray diffraction. Consequently, great care must be taken when modeling current-voltage characteristics of devices comprised of crystalline organic solids, especially when the influence of film thickness or different substrate materials is to be studied.

4:45 PM L3.7 PROBING CONDUCTING ORGANIC FILMS BY ELECTROCHEMICAL DISSIPATION AND ELECTRIC FORCE MICROSCOPY. John A. Marsin, William R. Sieh, Jenna Horng, Brian To, and Neil E. Jenkins, Dept. of Chemistry and Chemical Biology, Cornell University, Ithaca, NY; Erik M. Miller, Dept. of Physics, Cornell University, Ithaca, NY.

I will describe novel and highly sensitive variable-temperature electric force microscope measurements on conducting-organic films. The goal of these studies is to correlate work function, conductivity, and trap location with surface morphology in both thin films and in working organic field effect transistors. We are studying a number of systems including molecularly doped polymers (polyaniline:PDDA), small-molecule semiconductors (pentacene), and semiconducting polymers (polythiophene). We have custom fabricated silicon cantilevers that are doped in a manner more sensitive to forces than commercially available atomic force microscope cantilevers and have constructed an electric force microscope capable of operating at temperatures from 4 - 350 K. We have used these force-field cantilevers to probe both the electric field-dependent cantilever frequency shifts and lateral conductivity (via voltage-induced changes in cantilever Q factor) at room and cryogenic temperatures.

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

L4.1 FELLOGENATION OF ORMOFIL: A PROMISING ROUTE FOR TAILORING OPTICAL ABSORPTION. Wei Liang, Yudong Zhang, Amir Faridz, NP Photonics Inc., Tucson, AZ.

Although inorganic glasses remain unsurpassed as optical transmission media, they are not universally suitable for fabrication of all ranges of integrated optical devices due to certain inherent limitations such as low flexibility, high brittleness and poor patterning ability. Polymer-based optical materials also have several disadvantages such as low heat resistance, poor mechanical resistance and relatively poor adhesivity. A solution for these contrasting problems may be provided by organic-inorganic approach through the sol-gel process. An attractive feature of the sol-gel process is that it enables the preparation of a variety of inorganic or organic-inorganic materials, which are either impossible or difficult being synthesized via other techniques. Inorganic solgel materials for integrated optical applications are mainly limited to the multi-step coating, conventional resist coating and photolithography. Employing the organic-inorganic materials can alleviate these limitations. This family of materials has received an increasing attention owing to their interesting chemical, mechanical, optical and physical properties that can be adjusted between organic and inorganic behavior. However high concentration of CH groups, thus strong vibrational absorption in 1600-1800 nm range exacerbates the tail of absorption within 1550 nm window. This entails minimizing the number of CH in addition to the introduction of large silsesquioxane silvers to realize low-loss optical devices. A possible way to achieve this goal is to promote the condensation and replace the CH-bonds by CF-bonds. In this paper, we report on a new class of silsesquioxanes, hybrid organic-inorganic materials with wide index and adhesion tuneable properties for integrated optics. Material compositions and process parameters are optimized to achieve absorption <0.2dB/cm at 1550 nm. 1x1.6 mm splitters are designed and fabricated which exhibit <1dB power uniformity and <3 dB coupling loss per interface.

L4.2 ACTA-CATALYZED CATIONIC POLYMERIZATION OF 2,5-DIHALO-3,4-ETHYLENEDIACYLOPHENE CONDUCTING POLY(3,4-ETHYLENEDIACYLOPHENE). Wonphil Bok, Joe Han Park, Youngnam Kim, Sung Kook Jeong, Myongji University, Dept. of Chemistry, Yongin City, Kyungki Do, KOREA.

Among the several conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising material for practical applications because of the good thermal stability, high conductivity, and high transparency in the p-doped state. In addition, it is easy to prepare conducting polymer solutions in aqueous media. Due to the excellent applications, chemical and electrochemical polymerization methods for PEDOT have been developed. Up to now, p-doped PEDOTs were synthesized by chemical and electrochemical polymerization of 3,4-ethylenedioxythiophene both in organic and aqueous solutions, and has been produced commercially by Bayer AG. Herein we are reporting that PEDOTs with bandgaps of 1.5-1.8 eV were first synthesized by acid-promoted chemical polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene. The cationic polycondensation was occurred via thiophenyl cation because of the high stability by strong electron-donning groups. The resulting conducting PEDOTs affected conductivity of 10-4 S/cm. p-Doped of PEDOTs prepared by dibromo-EDOT with acid were treated with hydrazine in water to depoly the sample. After treatment of hydrazine for 24 h, the resulting powders were soluble in NMP essentially the UV-spectrum were obtained. To the best our knowledge, PEDOT prepared by acid catalyzed cationic polycondensation is only one that is soluble in organic solvent to measure the molecular weight and UV-absorbance.


We present a combined experimental and numerical study of current-voltage (LV) and tip-height-voltage (x-V) spectroscopy by STM on conjugated polymer films with a thickness of several tens of nm. It is found that the sharpness of the STM tip crucially affects the potential distribution that determines both LV and xV curves. An LV - xV spectrum is measured by ramping the tip-sample bias through zero with the STM feedback system disabled (active). In the former case the varying current is measured, in the latter case the change in the STM current is measured. The calculations prove that the single particle band gap of the polymer material can directly be extracted from x-V curves taken with a sharp (apex radius of the tip) and blunt tip. For a blunt tip with bulk limited transport geometry the straight line is extrapolated through zero to the x axis as the band gap. In all other cases the tunneling current is shown to be independent of the tip radius. The model presented here is crucial for solving the Poisson transport equations in three dimensions. Both the electron and hole hopping injection at the contacts and their bulk transport are accounted for.


Poly(3,4-ethylenedioxythiophene) poly(styrene sulphonate) (PEDOT-PSS) is one of the most successfull electronically conducting polymers available commercially. PEDOT-PSS can be used as a hole-injecting layer on ITO for polymeric electrochromic devices. Such devices are shown to achieve good stability, lifetime and performance. However, depolining of PEDOT-PSS largely degrades the polymer as a hole transporting material. In our study, we used X-ray photoemission spectroscopy to investigate the chemical nature of PEDOT-PSS/ITO surface and interface, and studied the effects of dopning and depdoping conditions and mechanisms. We found that depolining of PEDOT-PSS occurred in the presence of both water and dissolved indium. The existence of water in PEDOT-PSS is due to its hydroscopic nature while the existence of indium in PEDOT-PSS is due to the etching effect of ITO by the acidic PEDOT-PSS.
L4.6 Abstract Withdrawn.

L4.7 STRUCTURE-OPTICAL PROPERTY RELATIONSHIP STUDIES OF STYRL PYRAZINE DERIVATIVE FLUOROPHORES. Jeremy C. Cotsay, Aaron W. Harper, Donald P. and Katherine B. Loker Hydrocarbon Research Institute, University of Southern California, Department of Chemistry and the Loker Hydrocarbon Research Institute, Los Angeles, CA.

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

L4.8 SYNTHESIS OF POLY(PHENYLENE VINYLENE) VIA RUTHENIUM-BASED ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION. Aaron W. Harper and Cory G. Miller, University of Southern California, Dept of Chemistry, Loker Hydrocarbon Research Inst, Los Angeles, CA.

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

L4.9 AN INVESTIGATION OF THE OPTICAL AND ELECTRONIC PROPERTIES OF SOLUTION PROCESSED POLYCYCLOPENTADIENITHIOPHENES THIN FILMS. Paolo Coppo and Michael L. Turner, Department of Chemistry, University of Sheffield, Sheffield, U.K.

Solution processable conjugated polymers are being extensively investigated as charge transport materials for use in electronic devices such as field effect transistors [1]. The mobility of changes in these materials is limited by the efficiency of hopping between localized sites [2] and therefore close packing of adjacent chains in the solid state is essential for high charge mobilities. Recent studies using regioregular poly-3-alkylthiophenes have shown that the monomer structure and the polymer regiochemistry are critical parameters in achieving the correct thin film morphology [3]. We have recently reported the preparation and optical characterization of solution processable polycyclopentadienithiophenes [4]. These polymers are fused ring derivatives of the extensively studied poly-3-alkylthiophenes and are structural analogues of the polycyclics. This contribution describes an investigation of the structure/property relationship that is governed by solid state self-assembly of fused thiophene ring systems and examines the influence of polymer morphology in these systems on electronic properties such as field effect mobility. [1] Strynadka, H.; Tessler, N.; Friend, R. H., Science, 1999, 580, 1741. [2] Cormil, J.; Beljonne, D.; Calleb, J.-P.; Bedwa, A.; Adv. Mater. 2001, 13, 1053. [3] McMillan, R. D.; Adv. Mater. 1998, 10, 921. [4] Coppo, P.; Cupertino, D.; Cence, S. G.; Turner, M. L.; J. Mater. Chem. 2002, 12, 2597.

L4.10 PHOTOPHYSICS OF EUROPINII] β-DIKETONE COMPLEXES THAT CAN BE EXCITED AT LOWER ENERGIES. Patrick J. Casey, Aaron W. Harper, Donald P. and Katherine B. Loker Hydrocarbon Research Institute, Dept of Chemistry, University of Southern California, Los Angeles, CA.

In preliminary work performed in our lab, it was noticed that the dichloro(dimethylethynyl)iron(III) had an excitation maximum around 410 nm while its absorption maximum was around 375 nm. This sparked interest in seeing if lower energy polymers could be used to synthesize lanthanide complexes. Because of promising results, an effort was made to create more trivalent europium complexes that could be excited around 410 nm. We established a series of novel β-diketone ligands consisting of a naphthyl or phenanthrene unit on the C1 carbon and a thienyl group on the C2 carbon have been synthesized. The photophysics of the ternary and quaternary compounds containing 1,1'-binaphthyl, as well as the effect on changing the heteroatom of the heterocyclic condensed ring from oxygen to sulfur will be presented. Also, effective triple harvesting from a conjugated polymer will be shown.


Energy transfer from polyphenylene-type polymers to a series of organic dyes was studied. Two of the three polymers were synthesized via Suzuki coupling of 1,4-phenyleneboronic acid with 1,4-benzenedione or 1,4-benzocoumarone, to obtain a polyphenylene with only para-linkages, as well as one with alternating para and meta linkages. The third polymer was a polybenzophenone generated by a nido-ane coupling of 2,5-dihalo-4-methylbenzophenone. The resulting polymers, having significant energy differences, were used as the energy donors. A variety of Coumarins were used as singlet acceptors, and several porphyrins were used in triplet acceptors. Photophysical data and energy transfer parameters will be presented.

L4.12 OPTICAL PROCESSES OF A Zwitterion-POLYTHIOPHENE DERIVATIVE CONTROLLED BY SELF-ASSEMBLY OF BIOMOLECULES. Peter Nilsson, Olle Inganäs, Linköping Univ, Dept of Physics, Linköping, SWEDEN.

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

L4.13 ELECTROSYNTHESIS AND PROPERTIES OF POLYTHIOPHENE DERIVATIVE USING CO-SURFACTANT IN AQUEOUS MEDIA. Keith R. Bevansman and Phil M. Lessner, KEMET Electronics Corporation, Greenville, SC; Tourin Y. L., Mount and Richard V. Gregory, School of Material Science and Engineering, Clemson Univ, Clemson, SC.

Using anionic surfactant in aqueous solution allows the increased EDOT solubility in water and produces an important change in the oxidation polymerization mechanism relative to nonaqueous medium. We are currently concerned with the electrochemistry of poly(3,4-ethylenedioxythiophene) PEDOT doped with mixing anions from the electrolyte lithium tetrathionate and co-surfactants sodium dodecyl sulfonate acid and sodium poly styrene sulfonate acid. Strong electrostatic interaction occurring between EDOT+ radical cation and co-surfactant anions DSS and PSS lead to the formation of high quality polymer with high conductivity, and good environmental stability. The films are synthesized by cyclic voltammetry and graintrometric methods, and characterized by UV-visible, and SEM spectroscopy.

L4.14 VIBRATIONAL ANALYSIS OF COPPER PHTHALOCYANINE THIN FILMS ON VARIOUS SUBSTRATES. Suixiong Wang, Xiang
Dong, Chun-Sing Lee and Shuit-Tong Lee, Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, CHINA.

Because of the importance of the structural properties of organic thin films for device performance, study of packing and orientation of the organic molecules on substrates is necessary. High-resolution electron energy loss spectroscopy (HREELS) measurements of copper phthalocyanine (CuPc) thin films on various substrates were performed on a VG1000 spectrometer in ultrahigh vacuum at room temperature, and the vibrational excitations of monolayer, bilayer, and multilayer CuPc films have been studied step by step. The HREELS spectra of the CuPc films on HOPG and on hydrogen-terminated Si [111] surface suggest that CuPc molecules prefer to orient with their molecular planes parallel to the surface. Scanning electron microscopy show that CuPc molecules form isolated crystals on HOPG surface even with high thickness and X-ray diffraction results indicate the molecules are stacked straight along the surface normal. In contrast, continuous films of CuPc are grown on H-terminated Si [111] surface. On some common polycrystalline or amorphous substrates (polished molybdenum plate, ITO coated glass and non-H-terminated Si wafer), HREELS spectra indicate that CuPc films arrange with random orientation due to the disordered nature of the substrate surfaces. The comparison between the HREELS spectra of monolayer and multilayer CuPc films will also be described.

L4.15 ORGANIC LIGHT-EMITTING DIODES BASED ON ALUMINUM DOPED KIFON. Xiaolong Wang, Xin Jing, A. Man Kong Pang, Chun-Sing Lee,
Shuit-Tong Lee. *Center of Super-Diamond and Advanced Films (COSDAF) & Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, CHINA, *Forschung Institute for Thin Film and Surface Engineering (FIBET), Braunschweig, GERMANY.

Transparent conductive oxide (TCO) films, aluminum doped zinc oxide, were deposited on glass substrates by middle frequency magnetron sputtering. Aluminum-doped zinc was used as the sputtering target. By varying the sputtering conditions such as oxygen flow, sputtering power, target, substrate distance, deposition pressure, and the annealing temperature, ZnO:Al films with optimized film properties were obtained. Average optical transmission of 90% and sheet resistivity of 6 ohm/square were achieved. Organic light-emitting diodes (OLEDs) were fabricated on the ZnO:Al films. To achieve 200mA/cm² and 4000cd/m², less than 1V and 2V were required respectively. At 200mA/cm², a brightness of higher than 6000cd/m², corresponding to a power efficiency of higher than 1.5lm/W, was achieved. For comparison, only 0.9lm/W was achieved by the reference OLEDs fabricated on indium tin oxide (ITO) substrates.

L4.16 POLYMER OPTICAL AMPLIFIERS. Justin R. Lawrence, G. A. Sammut, Organic Electronics Department, Ultraplast Electronics Collaboration, School of Physics & Astronomy, University of St. Andrews, St. Andrews, UNITED KINGDOM.

In recent years, semiconducting conjugated polymers have received considerable interest as novel laser gain media. They exhibit optical gain over broad spectral ranges through the visible and are well suited to use in tunable lasers and have the potential to be used as broadband amplifiers. Such materials would be readily compatible with polymer optical fibres and integrated circuits. Polymer optical fibres are a favoured technology to deliver the telecommunication bottleneck in local area networks, and low-cost, integrable optical amplifiers may increase the range and applicability of such systems. We demonstrate a compact, broadband optical amplifier using the conjugated polymer poly(3-methoxy-5-alkyl-2-7-dimethylthiocarbonyl-4-phthalimide vinylene) (OC-C8), in DCM solution. Amplification was measured using a modified dye laser system. Gains of 30-40 dB in a wavelength range of 575 to 640 nm, corresponding to a 50 THz bandwidth, are observed due to the broad luminescence spectrum and large cross-section for stimulated emission of the polymer. The variation in gain as the function of solution concentration is examined with 2 g/l being the optimum. The effect of different probe beam intensities on the gain is also examined. We observe a drop in gain at higher probe powers due to saturation effects and an increase in gain as the probe intensity decreases. Such behaviour is characteristic of optical amplifiers and can be modelled readily. For a 1 cm path length we measured a small signal gain of 44 dB, and deduce, a stimulated emission cross-section for OC-C8 of 5x10^-20 cm². These results for solid-state polymer optical amplifiers will be discussed.

L4.17 Transferred to L4.3

L4.18 Abstract Withdrawn.

L4.19 INFLUENCE OF ORGANIC FILM THICKNESS ON ORGANIC LIGHT-EMITTING DIODE PERFORMANCE. Chen Liu, Chunyang Xu, Sheng Yin, Zhiyao Zheng, Chang-wen Wang, Department of Electronic Science and Technology, Huazhong University of Science and Technology, Wuhan, CHINA.

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


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

L4.21 INITIA- AND INTER-CHAIN ENERGY TRANSFER IN AN END-CAPPED CONJUGATED POLYMER. Emanuella Hennberg, David Wellem, Jean-Luc Bredas, Chemistry of Novel Materials, Mons, BELGIUM, and Department of Chemistry, Tucson, AZ; Greg Scholes, Lash-Miller Chemical Laboratories, Toronto, CANADA.

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

L4.23

The design of an efficient, electrophoresophorescent organic light emitting device (OLED) requires the selection of a host-guest materials combination that allows for exothermic energy transfer between the triplet energy levels of a conductive host and phosphorescent guest molecules. Exothermic refers to transfer from the host to a lower energy guest triplet state, liberating energy in the process. The exothermic energy transfer in blue electrophoresophorescence lies in the lack of suitable high-energy hosts. Here, we demonstrate efficient blue electrophoresophoresence using exothermic energy transfer from a host consisting of N,N′-dioctyl-3,5-dimethylphenyl (mCP) 1 to the phosphorescent iridium complex iridium(III)[(1,1,3-difluoro-2-phenyl)-pyridine-2,3-NCl2]picolinate (Flirpic) 2. By examining the temperature dependence of the radiative lifetime and the photoluminescence of a film of mCP doped with Flirpic, we confirm the presence of exothermic energy transfer. The maximum external electroluminescent quantum efficiency of devices employing mCP:Flirpic is (7.5±0.8)% [with a luminous power efficiency (>8.9±0.5)mW] representing a significant increase in performance versus, endothermic blue electrophoresophoresence host–guest systems. 3


L4.24

We have synthesized a series of functional chromophores based on spirobifluorene (S center), attaching donor and/or acceptor moieties typically (diphenylmino-p-benzyl) and [S ≡ (α, β-diketone)]-benzyl at the ends: D–S–D (301), D–A–A (302) and A–S–A (303). We have investigated the light-emitting properties of these oligomer emitters in single and double layer devices consisting of ITO/PEDOT/PSS/AQ6/Mg:Ag. We were particularly interested in looking into the functional susceptibility of the redox-active moieties of chains toward incoming elecrons and holes, and their influences on the LE properties. EL spectra of 301, 302 and 303 show the emission maxima at 540, 545 and 555 nm, respectively. The common feature throughout these devices is that their turn-on voltages are all less than 4 volts. The D/D and D/A pair chromophores, 301 and 302 show a remarkable increase of EL (ca. 1000 and 400 cd/m², respectively) in the presence of AQ6 layer [as a double layer], compared to those (100 and 20 cd/m², respectively) of respective single layers. A drastic change occurs with A/A pair chromophore, 303 by the presence of AQ6 [double layer]; the EL is decreased by 4 cd/m² from 1000 cd/m² of the single layer. Such a decrease is the consequence of a large excess electrons transferred to the emitting layer, serving as an excitation quencher. Blending of 303 with PVK at 1:1 and 1:5 [303:PVK] to compensate the electron charge transfer, the EL shows blue-shift (65 nm) of emission band from that (555 nm) of pristine 303. However, the blend of 5:1 displays an entirely different EL spectrum that coveres a broad wavelength [330 to 800 nm], emitting a white light.

L4.25
STRUCTURE AND MORPHOLOGY OF SOLUTION PROCESSED PENTACENE FILMS. Sumen Same and Sigurd Wagner.

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

conjugated small molecule materials such as pentacene due to their spinorbit coupling. We studied techniques for the deposition of pentacene from solution without use of precursor routes or derivative molecules. A variety of thermal and surface conditions were studied as they impacted the structure and morphology of the resulting films. A full range of film morphologies was observed, including 50-nm-thick hexagonal platelet films and 400-nm-thick polycrystalline films, by employing various solvents and extraction methodologies. Substrate temperature strongly affected nucleation of the molecule on the surface of our structures. The preparation of solution in inert nitrogen ambient, both the appearance of the solution and the structure of the resulting film was compared to films prepared in air. Other parameters, such as surface energy modification through chemically patterned surfaces and monolayer formation had less pronounced effects on resulting films. Saturated pentacene solutions obtained by sonication extraction yielded planar crystals hundreds of microns in size.

Keywords: Pentacene; Semiconducting organic compounds; Solubility; Solution Processing; Thin Films.

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

Organic light-emitting diodes (OLEDs) in visible spectrum are nearly commercialized, but it is still a challenge to extend the existing OLED technology to the area of optical communications aiming at 1.3 or 1.5 micron emission. We fabricated and characterized Erbium (Er) based OLEDs, and 1.54 micron electroluminescence was observed at room temperature. The physical mechanism behind them is discussed. An approach to further improve on the quantum efficiency of 1.54 micron emission is also proposed.

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

New polyfluorene derivatives, poly[9,9-bis(4′-octyloxyphenyl)]fluorene [POPO-8] and poly[9,9-bis(4′,4′′-2′, 2′′-dimethyl-octyloxy phenyl)]fluorene [POPO-10] were synthesized through the Ni(II) mediated polymerization. The copolymers were characterized using FT-IR, spectroscopy, UV-vis spectroscopy, TGA, photoluminescence (PL) & electroluminescence (EL) spectroscopy, elemental analysis, and molecular weight studies. Interestingly, we have observed significant spectral change and formation of excimer emission were observed even after annealing the polymer film at 101°C for 2h.

Light-emitting devices were fabricated in an ITO (indium-tin oxide) /PEDOT/polymer/Ca/Al configuration. Synthesis and EL properties of new polyfluorene derivatives will be presented.

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

White light-emitting devices were fabricated using the blends of blue, green, red emissive polymers of poly[9,9-bis(3′-hexylphenyl)fluorene] [P3DF], poly[9,9-bis(3′-octylfluorene-2,7-diyl)poly(fluorene)] [P3DFV], poly[2-(3′,7′-dimethyl-9,9-di(2,2′-bis(3′-hexyl-5′-carbazole-1′-yl)pyridine)] [2D-CFV], and poly[2-(2′-ethylhexyl-5′-carbazole-1′-yl)-5′-phenyl-1′-octylbenzene] [GPOV] in 4:3:3 weight ratio. The emission was observed in PL spectra of the blend films, providing a good advantage to get a white light emission due to better blend ratio controllability. The EL devices were fabricated with ITO/PEDOT/blend/Ca/Al configuration and good white light-emission was obtained for a certain blend ratio. The light-emitting properties of polymer blends will be presented.

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

The effect of particulate sol and nanopowder on conjugated polymer was investigated in terms of optical properties and chemical structure in PPV and PPV/TiO2 nanocomposites. TiO2 particulate sol did not
interact with PPV but made the stable nanocomposite. The enhancement of zero-phonon vibronic transition and the increase of vibronic transitions were induced by an increase in polymer content were induced by the reduction of torsional order. The PPV/ThO₃ nanocomposite prepared by using a particulate sol had much better dispersion of nanoparticles than the composite prepared by a conventional method. In case of thermal conversion at 120°C, the conjugation length of PPV/ThO₃ nanocomposite prepared by using a particulate sol was the longest while that of PPV was the shortest. The nanocomposites had slightly shorter conjugation length, compared with PPV when they were converted at 200°C. The PPV/ThO₃ nanocomposite prepared by using nanopowder showed the high vibronic splitting energy.

\[ \text{L4.30} \]
CARRIER DYNAMICS OF CONJUGATED OLGOMERS.
Jean-Claude Viau and Olivier Stéphan, J. Barrier Univ. CNRS, Lab Spectrométrie Physique, Grenoble, FRANCE; C. Andreu, Ecole Normale Supérieures-CNRS, Lyon, FRANCE, Lab Stéphyochim & Intérêt Mol.

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

\[ \text{L4.31} \]
GREEN OLEDs: ELECTROLUMINESCENCE AND THE ELECTRICAL CARRIER TRANSPORT.
L. Perrier, R. Pietsch, P. Lepes, Departamento de Física, Universidad de A Coruña, A Coruña, PORTUGAL.

Organic Light Emitting Diodes (OLED) based on metal chelate complexes as emissive layer (Alq3) and a double hole transport layer of m-MTDATA / NPB has been fabricated. A complete characterization has been made in order to understand their optical and electrical properties. The electroluminescence (EL) shows a broad spectrum peaked near 540 nm (red) and two small bands at 425 nm (blue) and near 565 nm (orange). The result is a “white” EL. The origin of the orange and main green band is clearly the recombination inside the Alq3 layer while the blue band appears to be due to a recombination in a narrow layer in NPB/Alq3 interface. The electrical DC measurements have been performed in order to establish the nature of carrier transport and effectiveness. At low applied voltages, an injection of carriers through a small barrier (\( \approx 0.2 V \)) control the current flow. After the transition to the bulk limited conduction, the results suggest that when the electroluminescence (EL) takes place a trap charged limited conduction (TCL) with characteristic trap energy near 0.13 eV controls the process. A big influence of metal-semiconductor interface and the bulk conduction are also discussed. The investigation of the efficiency dependence on the minority carriers reveals that the triple layer device with two hole transport layer can improve the EL (reduction of the driving voltage and therefore increase the stability), but also contributes to the widening of the EL band. The relationship between the electrical measurements and the luminescence spectrum is analysed. Finally, a general model is proposed based on the experimental results and energy band diagrams.
direction, leading to a richer exciton structure and an increase of radiative efficiency. This has implications for theoretical activity and optoelectronic properties of polymer films. Our results indicate that polymers have an advantage over small molecules in OLED applications.

L4.36
Abstract Withdrawn.

L4.37
BALANCED CHARGE INJECTION AND SINGLE-EXCITON QUENCHING IN ORGANIC ELECTROLUMINESCENT DEVICES. Chined Ganzorig, Masamichi Fujihira, Tokyo Inst. of Tech., Dept. of Biomolecular Eng., Yokohama, JAPAN.

We have recently reported that EL efficiency increased more than linearly with increase of current for triphenylcarbazide (TPC) doped EL devices [1]. In particular, work function control of the cathode seems to play a crucial role on the phosphorescence efficiency of the devices. In this work, we described well balanced electron and hole injection into organic layers of our improved devices [2,3] in order to maximize the EL efficiency. To clarify the balancing between electrons and holes, we also studied carefully using only single layer EL devices with different thicknesses. Moreover, our recent results have shown that the luminance decreased less than linearly with an increase in current of Alq3-based devices with an Al cathode when electron injection was not improved significantly. We have not observed the improvement of the EL efficiency in these devices even for hole injection was enhanced [2,3]. The decrease in the EL efficiency was attributed to quenching of singlet excited state (\(\text{Alq}^*\)) by large excess cation Alq+ radicals with increase in current due to partial overlap between fluorescence spectrum of \(\text{Alq}^*\) and absorption spectrum of Alq+ radical cations, but not the corresponding anion Alq- radicals. [1] C. Ganzorig and M. Fujihira, Appl. Phys. Lett. 81, 337-339 (2002). [2] M. Fujihira and C. Ganzorig, in Conjugated Polymer and Molecular Interfaces, A. Kahn, J.J. Pireaux, W.R. Slivon, and K. Soki editors, (Marcel Dekker, Inc., 2002), p. 817. [3] C. Ganzorig and M. Fujihira, Appl. Phys. Lett. 77, 421 (2000).

L4.38
PROCESS IN EFFICIENCY OF BLUE ORGANIC ELECTROLUMINESCENT DEVICES. Yoo-soo Enum, Chined Ganzorig, Masamichi Fujihira, Tokyo Inst. of Tech., Dept. of Biomolecular Eng., Yokohama, JAPAN.

Compared with green organic electroluminescent (EL) devices, the EL characteristics of blue and red EL devices need to be improved particularly in terms of efficiency and color purity. The loss process in EL efficiency is related to the photoluminescence efficiency of organic materials, as well as other losses due to exciton quenching mechanisms. We report here the EL characteristics of blue organic EL devices with hole transport layer as an emitter i.e., ITO/NPD/PM6/3%-TAPC/Alq3/ILO. Here, ITO, NPD, PM6, and Alq3, and ILO are abbreviations for an indium tin oxide electrode, a 4,4′-bis[N-(1-naphthyl)-N-phenylamino]biphenyl, a bathocuproine, and a triphenylamine-carbazole-aluminum. Different types of amide and carbazole interface materials are used in this study [1]. In these devices modified by charge injection layers of the interface material, we have never observed that the emission from NPD increased more than linearly with increase of current when hole and electron injection was well balanced [2]. Only we found that the EL efficiency decreased in curves with increase in current of all the devices studied. Our experimental results indicated that single excited states (\(\text{NPD}^*\)) was quenched efficiently by large excess cation NPD+ radicals [3] accumulated near and in the emission zone due to large overlap between the fluorescence spectrum of \(\text{NPD}^*\) and absorption spectrum of NPD+. In addition, \(\text{NPD}^-\) is also possible quenched by union NPD− radicals when large excess electron injection. The detailed investigation will be discussed at the symposium. [1] C. Ganzorig, K. J. Kwak, X. Vagi, and M. Fujihira, Appl. Phys. Lett. 79, 272 (2001). [2] C. Ganzorig and M. Fujihira, Appl. Phys. Lett. 81, 3137 (2002). [3] C. Ganzorig, K. Sug, and M. Fujihira, Chem. Lett. 1193 (2000).

L4.39
PRESSURE- AND TEMPERATURE-INDUCED STRUCTURAL ORDERING IN ORGANIC POLYCRYSTALLINE MATERIALS. Sergey Bolkher, V.N. Griner, Iryna Khromovskaya, L. Liessitsk, Tetyana Tetyzhetskya, STC Institute for Single Crystals, NAS of Ukraine, Kyiv, UKRAINE.

Pressure-compacted organic molecular polycrystals (e.g., stilbene, anthracene, p-terphenyl) are known to be a promising class of scintillator material for radiation detectors. The use of such materials allows manufacturing of large-area scintillators of required shapes. However, their scintillation characteristics remain substantially inferior to those of standard single-crystalline scintillators made of the same material. Recently, it has been shown that under certain conditions the combined action of pressure and pre-melting temperatures, structural transitions in the polycrystals could be substantially changed [1,2], and a theoretical model describing ordering processes in such systems has been proposed [3]. In this paper, we report our studies of the pressure/temperature effects on structural and scintillation properties of polycrystalline pellets made of crystalline powders of stilbene and p-terphenyl. Microscopic observations clearly show spontaneous formation of crystal alline regions, with subsequent solid-state reaction of crystal growth. Substantial improvement of scintillation properties is observed. This, for stilbene and p-terphenyl polycrystals, light outputs of up to 85-95% with respect to the corresponding single crystals was obtained. Possible mechanisms are proposed for the observed structural ordering and ways for optimization of the pressure/temperature parameters are discussed. In parallel experiments, we observed similar behavior with more complex substances (including those of biological origin), with marked effects due to special features of supramolecular ordering. It is supposed that the obtained results and the proposed procedures can be very promising for application, specifically, in radiation detectors, especially for detection of short-range ionizing particles, as well as fast neutrons. B.V. Griner, S.V. Badzakovy, L. Liessitsk, V.D. Pankowska, Functional Materials V.1, No.1, p.156-160 (1994). 2 B.V. Griner, S.V. Badzakovy, L. Liessitsk, V.D. Pankowska and E.E. Lukin, Kristallografiya V.42, No.3, p.506-509 (1997). 3 S.V. Badzakovy, L.N. Liessitsk and P.P. Shafaryuk, In Abstracts of European Conference on Liquid Crystals, (Zakopane, Poland, 1997), p.122.

L4.40
Abstract Withdrawn.

L4.41
Abstract Withdrawn.

L4.42
NANOPATTERNED SURFACES FOR CONTROLLED SELF-ASSEMBLY OF 1D MOLECULAR NANOSTRUCTURES. Federico Rosci, Y. Naito, M. Schmuck, E. Leuegued, I. Stangard, and F. Esenciher, Physics Department and L-NANO, University of Aarhus, DENMARK, M. Jiang, A. Gourdon, and C. Joachim, CEMES/CNRS, Toulouse, FRANCE. "Present Address: INRS-EMT, Univ. du Quebec, Varennes (QC) CANADA.

Ordering molecular building blocks into a suitable architecture at the nanoscale is appealing for the development of future integrated nanoelectronics [1]. We used a large organic molecule called Lander [2] (C9H19C8H, and investigated its electronic states at room temperature (RT) by scanning tunneling spectroscopy (STS) and its Self-Assembly on Cu[110] by Scanning Tunneling Microscopy (STM). In recent work, the Lander was observed to act as a nanoscale mold, reshaping portions of step edges into characteristic nanostructures [2]. The Lander has a central polyaromatic molecular wire, and four spacer legs [3]-di-tert-butylyphenyl for isolation from the substrate. The four legs are imaged as four lobes with three different conformations by STM: two rhomboidal (chiral) shapes that are mirror symmetric to each other, and one rectangular shape. In order to create a suitable template for controlled molecular adsorption, the clean Cu[110] surface was exposed to oxygen to form the oxygen-induced 2x1 reconstruction. By dosing a proper amount of Oxygen at 350°C we can make Cu row domains along the [01] direction with 2 Å width between 2x1 domains. When Lander molecules are deposited on this template, they preferentially attach to bare Cu regions. By tuning molecular coverage in a controlled manner we obtain 1D molecular nanostructures. This type of directed self-assembly opens new possibilities for ordering organic molecules on surfaces. In a second set of experiments, spectra from isolated Lander molecules on Cu[110] terrace reveal two broad peaks observed at ~0.5 V and ~4.0 V. These can be tentatively associated with the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) states of the molecule at RT. References. [1] C. Joachim, J.K. Ganzorig, and A. Aviram, Nature 410, 541, (1999). [2] F. Rosci et al., Organic molecules acting as templates on Metal surfaces, Science 296, 338 (2002).

L4.43
Abstract Withdrawn.

L4.44
TRIHYLAMINES CONNECTED VIA PHENYLENENEPHYLENE SEQUENTIALS. Heinz Daten, and Oleg Sadowski, Johannes Gutenberg-Universitas Mainz, Inst. of Organic Chemistry, Mainz, GERMANY.

The well-known hole transport properties of triarylarnines can be combined with the strong luminescence of stilbene chromophores. We present the synthesis of well soluble oligophenylenevinylene)s with conjugation lengths of 2 to 6 styryl units, terminated by different
arylamines. The syntheses were performed via PO-activated olefinations and via PO-catalysed allyl-N-coupling reactions. The fluorescence properties are primarily depending on the central stilbene segment. Cyclodextrin uumetry reveals that the oxidation potential is nearly independent from the conjugated system, whereas the reduction is controlled by the stilbene segment.

L4.45
THE SYNTHESIS, CONDENSATION, AND LUMINESCENCE OF OLOGOPHENYLVINYLENE) WITH ALKYL-3-HEXYLPHENYLNANOFLATERS. Jeffrey A. Merk and C. Daniel Friesle, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

Due to their strong fluorescence, stilbene oligomers are one of the preferred classes of luminescent organic materials for electrooptical applications. The good solubility of alkyl-substituted OPVs is advantageous for the processing, but limits the fabrication of self-assembled thin films. Additionally, the stability of amorphous films is only poor. Here we present the synthesis of novel OPVs with terminal alkylalkane moieties, to allow cross-linking via hydrolysis and formation of alkane networks. The alkylalkanes are rigidly connected to the chromophores via Heck reaction or cross-metathesis. Hydrolysis and condensation yield oligoalkanes with pendant OPVs, thus greatly improving the film forming capability of these well-defined chromophores. The connection to cyclotanols or siloxane networks has a distinct influence on the electronic spectra of the OPVs in the solid film. Additionally, conjugated systems with high electron affinity like 2,5-dihydro-1,3,4-oxadiazoles are functionalised with alkylalkanes. These compounds are interesting for the preparation of organic-inorganic hybrid materials with luminescent units.

L4.46
IN THE DEVELOPMENT AND STUDY OF CONDUCTIVE POLYMER ELECTRODE FILMS ON PVDF SUBSTRATES FOR ELECTRO-ACOUSTIC APPLICATION IN COCHLEAR IMPLANT. A. Kratzik and R. Rosenh, Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH.

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

L4.47
THE CREATION OF A HYBRID PROTEIN/CONDUCTIVE POLYMER THERMOSENSOR. Laurence L. Brot, Rajesh R. Nair, Moshe O. Stone, Materials and Manufacturing Directorate, US Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

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

L4.50
FIELD EFFECT CONDUCTANCE OF REGIOREULAR POLY(3-HEXYLPHENYLNANOFLATERS. Jeffrey A. Merk and C. Daniel Friesle, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

We are examining the electrical conductance of nonfullerene regioregular poly(3-alkylphosphinephene) (RRPSPHT) as a part of a program to elucidate the role of microstructure on electrical transport in conducting polymer films. Nanofibers of RRPSPHT can be prepared by casting dilute solutions of xylene or cyclohexane. Analysis of the nanofibers by atomic force microscopy (AFM) reveals fiber lengths of 2-3 μm, diameters of 20-40 nm, and a complex crystallinity and ordering within the nanofibers are determined by transmission electron microscopy (TEM) experiments. The electrical characterization setup consists of four electrodes and a capacitively coupled gate electrode. The four-electrode setup is used to eliminate the effect of contacts on the measurements. Conductance measurements have yielded hole mobilities as high as 0.06 cm²/Vs and on/off ratios >10⁶. Temperature studies reveal activation energies ranging from 86 kJ/mol depending on the substrate. Threshold voltage is found to increase in magnitude with decreasing temperature. The surface chemistry of the substrate affects the electrical properties of the nanofibers similar to thin films of RRPSPHT. Nanofibers were characterized on silicon dioxide hexamethyldisilazane (HMDS) treated silicon dioxide, alumina, and phosphoric acid treated alumina substrates. Probing transport in doped conductostructures with microscopy and microscopy ex situ to address the role of microstructure in thin films. In particular, conductance measurements on RRPSPHT nanofibers allow separation of the effects on transport of the polymer-dielectric interface versus the nanocrystalline character of thin films. R. J. Bai, J. Moult, and P. Smith, Journal of Polymer Science Part B: Polymer Physics 31, 735 (1993).

L4.50
NANOCRYSTALLINE SEMICONDUCTOR ELECTRODES WITH SIMPLE STRUCTURE AND HIGH EFFICIENCY. Dietrich Bäuerle, Volker Weller, Philips Research Laboratories, Archen, GERMANY, Dimitr Tashin, Horst Weller, University of Hamburg, Hamburg, GERMANY.

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

SESSION 5.5: SPECTROSCOPY AND DEVICES
Chair: George Mallins
Wednesday Morning, April 23, 2013
Session 1-3 (Marrriott)

8:30 AM * L5.1

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


9:00 AM Lecture 5.2
VOLTAGE-INDUCED INFRARED SPECTRA FROM FIELD-EFFECT TRANSISTORS FABRICATED WITH REGIOREGULAR POLY(3,4-ALKYLTHIOPHENE): S. Yukihiro, Hiroki Takano, Jun Yamamoto, Waseda Univ., Dept of Chemistry, Tokyo, JAPAN.

We will demonstrate the usefulness of a combined technique of infrared reflection-absorption spectroscopy and the FT-IR difference-spectrum method to study charge carriers in the polymer nanoparticles in polymer field-effect transistors (FETs). We have fabricated FETs with regiorregular poly(3,4-alkylthiophene) (alkyl: hexyl, octyl and dodecyl). Finger-shaped source and drain electrodes have been made. Each device has been made using a flexible silicon wafer. Drain currents are ca. 80 nm. A single reflection ATR accessory (Specac Golden Gate) has been used for infrared measurements. The upper plate of the accessory has been replaced by a home-made sample stage of a FET. Infrared light from an FT-IR spectrophotometer (Digilab FT3700i) is incident on the side of the finger-shaped source and drain electrodes with an incident angle of 45 degree. A half of the incident light can pass through the polymer layer. Voltage-induced infrared spectra have been measured by the above method. We have observed a voltage-induced infrared spectrum from an FET based on regiorregular poly(3,4-ethylthiophene) between the -10 V and the 45 V voltages applied to the gate electrode with respect to the source and drain electrodes. Positively observed bands are due to the species generated by the application of the bias of -10 V. The measured capacitance-voltage relation of the FET indicates that positive carriers are induced in the polymer layer when a minus bias is applied to the gate electrode. The observed infrared spectrum is quite similar to that of a poly(3-ethylthiophene) film doped with ferric chloride. Thus, the observed infrared bands can be attributed to positive carriers (polaron) injected into the polymer layer by field effect in the polymer FET. We will discuss the voltage-dependent characteristics of field-effect-induced infrared intensity and the effect of alkyl side chains on field-effect-induced infrared absorption.

9:15 AM Lecture 5.3
PHOTO-LUMINESCENCE QUENCHING IN DOPED AQ5 ORGANIC LIGHT EMITTING DIODES: Terri Haskins, Arabinda Choudhury, Ralph Young, and Lee Rothberg, Department of Chemistry, University of Rochester, Rochester, NY, Jerome Lehn, Eastman Kodak Company, Rochester, NY.

Electroluminescent organic materials have recently made their way into display technology. There is considerable research underway to improve these materials to extend their utility. AQ5 [tris(8quinolinolato)aluminum] is widely used in organic light emitting diodes (OLEDs) due to its excellent properties as a host for luminescent dopants. Typically, the light output from an organic device is proportional to the injection current. However, in some important cases [1], the luminescence efficiency decreases with increasing current density. The resulting efficiency would make engineering a full pixel organic display difficult. We report spectroscopic studies of the mechanism responsible for the decrease efficiency. We use in-situ Charge Modulation Spectroscopy (CMS) in both unipolar model devices of the structure ITO/AQ5-doped AQ5 -insulator-carbide and bipolar transporting devices such as the laser dye DCB (4,4'-dicinnamoylthiophene)-2,4,6-trimethylylidylyloxy-2-ethylhexyl-3,5-bis(2,4,6-trimethylylidylyloxy-2-ethylhexyl)polyimides are injected into the photo luminescence quenching. In our studies we have observed the spectral signature of DCB cations (DCB+) excited state in the devices and correlated its temporal behavior with luminescence quenching. From that the cation acts as a quencher in Förster energy transfer, from excited-state DCB to DCB+.

9:30 AM Lecture 5.4
CHARGE TRANSPORT AND ENERGY TRANSFER PROCESSES IN SEMICONDUCTING p-JUNCTIONS: Jean Luc Bredas, University of Arizona, Department of Chemistry, Tucson, AZ.


10:30 AM Lecture 5.5
EXCITON CONFINEMENT AT POLYMER-POLYMER HETERJUNCTIONS IN LEDS: Arne C. Mortensen, Annoq S. Djoft, Judebee Kim, Carlos Silva-Guzman and Richard J. Frens, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

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

11:00 AM Lecture 5.6
CHARGE CARRIER GENERATION IN A CONJUGATED POLYMER STUDIED VIA SUB-20 FS PUMP-PUMP-PROBE EXPERIMENTS: Christoph Gadermaier, Emil J. W. Lai, Christian Doppler Laboratory for Advanced Functional Materials, Graz, AUSTRIA; Gaglielmo Lunardi, Giulio Cerullo, Cristian Mazzoni, Dipartimento di Fisica, Politecnico di Milano, ITALY; Ulrich Scherf, Miiokreolekulelle Chemie, Bergische Universitat Wuppertal, GERMANY.

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

11:15 AM Lecture 5.7
THE EFFECT OF DOPING ON THE ENERGY DISTRIBUTION OF LOCALIZED STATES AND CARRIER TRANSPORT IN DOPED POLYMER ORGANIC SOLID STATE DEVICES: Vladimir Archipov and Paul Herrmann, IMEC, Leuven, BELGIUM; Eugenia Emelinskaya and Guy Adriaensen, Semiconductor Physics Lab., Univ. of Leuven,
BELGIUM, Heinz Bläser, Inst. of Physical, Nuclear, and Macromolecular Chem., Philips Univ. of Marburg, GERMANY.

Charge carrier hopping within a positionally random and energetically disordered system of localized states was shown to be an inadequate model for the description of both equilibrium and non-equilibrium conductivity in amorphous nonlinear organic semiconductors [1]. In a positionally random system, the energy disorder is to a large extent caused by Van der Waals and dipole-dipole interactions within a positionally and orientationally random system of molecules [2]. Doping, i.e., the addition of dopant ions that will Coulombically interact with carriers localized in intrinsic hopping sites, this interaction further increases the energy disorder. This effect is especially important in view of a small value of the dielectric constant and, consequently, low magnitude of the Coulomb interaction typical for molecular semiconductors. Increasing energy disorder with increasing dopant concentration will lead to broadening of the apparent density-of-states (DOS) distribution. Therefore, doping of a disordered organic semiconductor, on the one hand, increases the concentration of charge carriers and lifts up the Fermi level but, on the other hand, broadens the DOS distribution. While the former effect facilitates conductivity, the latter strongly suppresses the carrier hopping rate. The latter effect can dominate at some dopant concentrations such that doping appears to be even counterproductive as far as the carrier mobility is concerned. In the present work, an analytic model describing the DOS distribution and the carrier hopping mobility in doped organic materials is formulated. It is shown that doping shifts some intrinsic hopping sites to the deeper tail of the DOS distribution and, thus, creates additional deep traps for charge carriers. This leads to a reduction in hopping mobility and dopant concentrations. At higher doping levels the filling of deep states takes over leading to steeply increasing mobility at high dopant concentrations.


1300 AM L5.8

SURFACE-EMITTING DISTRIBUTED FEEDBACK LASERS BASED ON SEMICONDUCTING POLYFLUORENES

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

In recent years, semiconducting polymers have attracted considerable interest as novel gain media for devices such as lasers and optical amplifiers. In particular, an important target is the fabrication of chemically pumped solid-state polymer laser diode.

Polyfluorenes are semiconducting polymers with a particularly attractive class of semiconducting polymers for such applications because they show charge carrier transport properties, have low stimulated emission thresholds and are the only family of conjugated polymers that emit in the visible spectrum. Hence, they offer great potential for the fabrication of low cost, compact, highly tunable solid-state lasers. Here, we report on the fabrication of optically pumped (532 nm pulse from a Q-switched Nd:YVO4 microchip laser) polymer distributed feedback (DFB) lasers utilising two blue-emitting polyfluorenes as the gain media. The lasers were made by deposition of thin layers of polymer on top of gratings that were etched into fused silica substrates. Distributed feedback was realised through Bragg scattering induced by the substrate corrugations. We demonstrate laser action in devices based on both polymers. The lasers operate in the blue, one at 455nm and the other at 460nm, and exhibit low threshold energy (5nJ per pulse). The wavelength, threshold energy, output power and efficiency of the lasers are investigated. The shape and divergence of the output beams are measured and correlated with the internal lasing modes and the feedback mechanism present in the structures. Additional experiments were performed to investigate the effect of the grating structures on the polymer light emission. We show that the presence of the grating greatly modifies the emission characteristics of the polymer. This may be due to a photonic stop band around the Bragg wavelength. Lasing occurs at the band edge, as expected for an index-coupled DFB laser.

1145 AM L5.9

THE EFFECTS OF STRUCTURAL DISORDER ON THE THRESHOLD FIELD FOR EXCITON QUENCHING AND THE CARRIER RECOMBINATION DYNAMICS IN POLY(PHENYLENE VINYLENE). Daniel Moser, Centre Soci, Roland Schmechel, Alan Heeger, Institute for Polymers and Organic Solids, University of California, Santa Barbara, CA.

We have determined the exciton binding energy Eb in stretched oriented films of poly(phenylene vinylene) to be about 60 meV, which is significantly smaller than that predicted by other researchers on the basis of measurements on disordered polymer films. It has been claimed that this magnitude of Eb is in contradiction with the operating fields in polymer-based light-emitting diodes (OLEDs), which typically exceeds 1.05 V/µm. The claim has been that if indeed Eb were so small, this operating field would have dissociated the excitons due to the expansion of the external field line and thereby reduced the OLED emission. In recent experiments we have clarified this issue and found that in contrast to oriented PPV disordered polymer films generally exhibit higher threshold field for exciton quenching. We will present variety of data generated by photoluminescence spectra as well as time-resolved experiments under the assumption of the reasons for the higher Eb in disordered polymer films. The second topic of recent interest is related to the carrier recombination dynamics in conjugated polymers. Using transient photoluminescence experiments, we have recently found a molecular carrier recombination mechanisms operating in measurements that utilize very low light intensities. This is the time a mechanism has been found in a t ime range of 1.1 ns in my polymer we have investigated. We will present the experimental, data, analysis, and a discussion on the implications of these findings.

SESSION L6 TRANSISTORS

Chair: C. Daniel Frabike, Wednesday Afternoon, April 23, 2003, Salon 1-3 (Marriott)

1:30 PM L6.1


Polyfluorenes are a class of polyaromatic macromolecules that are characterized by an alternating backbone structure that consists of a 9,9-diarylfluorene unit in combination with another aromatic group. The nature of the aromatic unit plays a key role in the electronic properties of the polymers. For example, polyfluorenes which combine chroomophoric and charge transporting aromatic units have received a great deal of attention over the last several years as the emissive layer in polymer light emitting diodes [LUMATION® Light-Emitting Polymers (LEPs)]. More recently, polyfluorenes have also been designed to perform as the organic semiconductor layer in polymeric field effect transistors (PFETs). This effect has led to a class of polymeric semiconductor with an excellent combination of charge mobility, environment stability and high electrical performance. One such polyfluorene is the polyfluorene-based (dihydro-phenylene) more resistant to doping by atmosphere oxygen than other polymeric semiconductors such as poly (phenylenevinylene). Inks based on solutions of polyfluorene-bithiophene in xylene, mesitylene, and other solvents have also been prepared. The paper will focus on the recent advances in the synthesis, fabrication, and electrical characterization of polyfluorene-bithiophene. *Trademark of The Dow Chemical Company

1:45 PM L6.2

SOURCE/Drain CONTACTS IN ORGANIC POLYMER THIN FILM TRANSISTORS. S Multin Martin, Michael Hamilton, and Jennifer Kacinski, University of Michigan, Dept of Electrical Engineering and Computer Science, Ann Arbor, MI.

Although the electrical performances of most organic polymer thin-film transistors (OP-TFTs) are often limited by the polymer low conductivity, the source and drain contacts play a dominant role in the device operation. The devices used for our study of the role of the S/D contacts are gate-planarized thin-film transistors with a coplanar structure, i.e. source and drain contacts deposited before the organic polymer film. The devices use benzocyclobutene as gate planarization material, amorphous silicon nitride as gate insulator and ITO source and drain electrodes. The organic semiconductor is a solution-based F8T2-poly(9,9-diocylfluorene-co-bithiophene).

Typical performances of our devices are field-effect mobilities about 6x10^-5 cm2/Vs, threshold voltage about 720V, subthreshold swing about 1.5 W/fsec and ON/OFF current ratio about 106.
2:00 PM L6.3
NEW n-CHANNEL ORGANIC SEMICONDUCTORS FOR THIN FILM TRANSISTORS. Reid J. Chesterfield and C. Daniel Franke, Univ. of Minnesota, Dept. of Chemical Engineering and Materials Science, Minneapolis, MN; Todd M. Pappenfuß, Kent R. Mann, and Larry L. Miller, Univ. of Minnesota, Dept. of Chemistry, Minneapolis, MN.

Organic semiconductors that function as p- or n-channel conductors in thin film transistors (TFTs) are an important new class of materials for making inexpensive and flexible, large-area TFT arrays. There are many examples of p-channel TFTs, but reports of n-channel conductors have been rare. We have developed two materials of metals based on quinoidal thieno- and pyrrole dimides for application as n-channel organic semiconductors in TFTs. The redox properties, crystal packing, and thin film microstructure of these materials can be tuned by varying the side chains. These compounds illustrate the elegance of using organic chemistry techniques to design semiconductors. Compounds in both the thieno- and didehydromethane half of the microscale products offer a possible design principle for TFTs.

2:15 PM L6.4
Abstract Withdrawn.

2:30 PM L6.5
HIGH PERFORMANCE ORGANIC THIN FILM TRANSISTORS. Tommie W. Kelley, Dawn V. Moore, Paul F. Brade, Terry P. Smith, Todd M. Pappenfuß, and C. Daniel Franke, Univ. of Minnesota, Chemical Engineering and Materials Science, Minneapolis, MN.

We report new methods of surface modification and device construction which consistently result in large-scale pentacene-based TFTs and integrated circuits with mobilities as high as 0.2 cm²/Vs in a 300 mm vacuum evaporation. Key device parameters such as On/Off ratio, threshold voltage, and sub-threshold slope were also reported. Trapping and activated transport have been investigated as a function of temperature and ambient environment. TFT performance has been measured in a function of pentacene surface chemistry, surface chemistry of the dielectric, and contact metallurgy. There is a nice correlation between the single TFT behavior of these compounds and their solution redox properties, which offers a possible design criterion for TFTs.

3:30 PM L6.6
POLYCRYSTALLINE PENTACENE THIN FILM TRANSISTORS: MORPHOLOGY, STRUCTURAL PROPERTIES, AND ELECTRONIC TRANSPORT. Dietmar Kapp, Palo Alto Research Center, Electronic Materials Laboratory, CA.

The structural and transport properties of pentacene thin film transistors (cTFTs) are reported, showing the influence of the deposition conditions with different organic dielectrics. Dielectrics compatible with large area fabrication were explored to facilitate low cost electronics on glass or flexible plastic substrates. X-ray diffraction and atomic force microscopy show a clear correlation between the morphology and the structure of the highly poly-crystalline films, for all deposition conditions investigated. The roughness of the dielectric has a distinct influence on the morphology and the structural properties, whereas the films on smooth thermal oxide are in general highly ordered independent of the deposition conditions. The ordered films exhibit thin film and bulk phase transition with the bulk phase volume fraction increases with the deposition temperature and the film thickness. Careful control of the deposition conditions give virtually identical thin film on PECDV silicon nitride dielectric. The electronic structure of irradiated TFTs shows that the TFT mobility is correlated with the morphology and structure of the films. The TFTs exhibit similar mobilities of 

4:00 PM L6.7
SYNTHESIS AND APPLICATION OF A PHOTOREACTIVE ORGANIC SEMICONDUCTOR IN THIN FILM TRANSISTORS. A. Afzali, C.D. Dimitrakopoulos, T.O. Graham, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY.

Organic semiconductors have received increasing attention during the past two decades due to potential low cost applications in electronic devices like OTFTs and OLEDs. Both applications require that the organic semiconductor materials be patterned but standard, wet-process lithographic techniques cannot be used for organic semiconductors due to contamination of these materials by hydrocarbons and/or for device performance. The patterning techniques that so far have been used to define the channel width for organic thin film transistors (e.g., microcontact printning, screen printing) do not have high resolution capabilities. In this talk the synthesis of a soluble photosensitive organic semiconductor, patterned by exposure to UV radiation and fabrication of thin film transistors using this novel compound will be discussed.

4:15 PM L6.8
PENTACENE TFTS WITH SUBMICRON CHANNEL LENGTHS. A.G. Schroot and C.R. Kagan, IBM Research Center, T.J. Watson Research Center, Yorktown Heights, NY.

We have investigated the transistor characteristics of pentacene thin film effect devices with sub-micron channel lengths. The devices were fabricated under UHV conditions that minimize the effect of ambient atmosphere on substrate and electrode cleanliness. Pentacene was evaporated to form the semiconducting channel of TFTs deposited onto thermally oxidized, highly doped Si wafers, which serve as the gate dielectric and electrodes. The substrate was patterned with a/c-wafer and passivated using a doped oxide, defining channel lengths ranging from 100 nm to 700 nm. We report the results of measurements of the transistor characteristics of these devices. The channels were defined by a combination of photolithographic patterning and etching techniques. The mobility and on/off ratios were compared with those of the longer channel devices.

4:30 PM L6.9
INTL.GRAIN TOP CONTACT ORGANIC THIN FILM TRANSISTORS. Stijn Verlaan, Stijn Nopp, Dimitri Jensen, Barnabé Datta, Paul F. Brade, Inse, Polymer and Molecular Electronics, Leuven, BELGIUM.

Transistors with channel lengths comparable to the dimension of a grain are a useful tool to study the direct transport properties of organic poly-crystalline thin films, i.e. the intrinsic charge-transport inside one single-crystalline grain and the grain boundary. Moreover, these transistors are capable to probe single-channel device physics, which can be of importance for future applications. Submicron channel lengths normally require photolithographically defined source and drain contacts, defined before growth of the small molecule channel, resulting in so-called bottom-contact devices. Unfortunately, such bottom contacts influence the growth of the thin-film, have limited compatibility with surface cleaning and treatments prior to growth, and possess a lower favorable charge-injection geometry. Therefore, we have micromachined a shallow mask which enables the deposition of contacts on top of the organic thin film, with channel lengths down to 1 micrometer. This
L7.3 MOLECULAR DESIGN, SYNTHESIS AND CHARACTERIZATION OF EBURANI-CORED SUPRAMOLECULAR COMPLEXES BASED ON NEW ARYL ETHER DENDRITIC PORPHYRINS FOR OPTICAL AMPLIFICATION. Nguyen Xuan Linh Phu, Joe Bum Oh, Jie Won Ko, Soo Gyun Roh, Mi-Kook Na and Hwann Kyu Kim, Center for Smart Light-Harvesting Materials and Department of Polymer Science & Engineering, Hannam University, Daejeon, KOREA.

To achieve the superhigh speed telecommunication systems, the development of integrated planar waveguide amplifiers is extremely essential. At present, erbium-doped silica amplifiers are widely used. The Er^{3+} ion shows an intra 4f-shell transition from its first excited state (\(^{4}I_{15/2}\)) to the ground state (\(^{4}I_{11/2}\)), which takes place at a wavelength of 1.54 \(\mu\)m, one of the standard telecommunication wavelengths. However, lanthanide cation (Ln^{3+}) has the poor solubility in conventional inorganic/organic media. So, if higher doping concentration was introduced to get the higher optical gain, clustered Ln^{3+} species can be formed. These lanthanide ion aggregations cause the reduction of luminescent property through the cooperative energy transfer process. To circumvent the solubility and enhancement of the luminescent properties, we have designed and studied the erbium-cored supramolecular complexes based on porphyrins. We synthesized 5,10,15,20-tetraphenyl-26-(4-methoxy carbonylphenyl)porphyrin by the acid-catalyzed condensation of diphenylmethane and aldehyde. And then, we introduced the organic acid in binding site with lanthanide metal by hydrolysis. And, we also prepared the Zn-inserted porphyrin as previously reported method. The structure of porphyrin ligands was identified by FT-IR, 1H-NMR, UV-Vis absorption and PL spectroscopies. And then, we attempted several different synthetic methods to prepare Er-cored supramolecular complexes based on porphyrins and develop new synthetic route using model reactions. The synthesized complexes were characterized by the FT-IR, 1CP, EA, TGA, visible and near IR emission spectroscopies. Also, we have synthesized the Er-chelated complexes based on new aryl ether dendritic porphyrins to enhance the luminescent property by energy transfer process. In this presentation, we will discuss the synthesis and luminescent properties of the erbium-cored supramolecular complexes based on new aryl ether porphyrins.

L7.4 SPECTROSCOPIC PHOTOVOLTAIC CHARACTERIZATION OF PPV THIN FILMS SUITABLE FOR PLED APPLICATIONS.

Grijn Srinok Samar, A.K. Bawas, Y.N. Mohapatra, Materials Science Programme and Samuel Center for Display Technologies, Indian Institute of Technology, Kharagpur, INDIA.

Optoelectronic characterization of active polymer materials to monitor photoinduced charge and radiative processes has been intensively investigated in view of applications in light emitting and photovoltaic devices. In this paper we compare absorption, emission and photovoltaic spectra in order to correlate creation, radiative recombination and separation of charge carriers in PPV. PPV layers were spin coated on ITO biased glass substrates. Photovoltaic experiments were carried out using both conventional single layer LED structure (ITO/PPV/AI), and capacitive structure consisting of ITO/Mg:PPV/ITO in which a thin sheet of magnesium is pressed against the sample using an ITO glass substrate. The capacitive structure is appropriate for modulated surface photovoltaic measurements. The absorption spectra and photoluminescence spectra obtained are as standard for PPV prepared by spin coating. The temperature photovoltaic spectra show features, which both supplement and complement the absorption and emission spectra. The photovoltaic spectra for both types of devices have sharp features and an absorption attribute indicating that the features observed are primarily to PPV material itself. The photovoltaic spectrum shows peaks and valleys corresponding to both absorption and emission features. In addition, we observe two sharp peaks with a separation of 0.8 eV in the energy range of 2.5 - 2.7 eV (i.e. in the range of 500-600 nm) in the photovoltaic spectrum. This line shape of the peaks strongly suggests that the peaks are most probably associated with photoinitiation of either excited state exciton or a defect-polymer complexes giving rise to non-radiative centers. A study of temperature dependence of photovoltaic output in the range of 50K-300K shows that the photovoltaic decreases nonlinearly with increase in temperature and saturates at low temperature. The results are discussed in terms of temperature dependence of mobility and absorption co-efficients, and possible models for photoinitiation of quantum defects.
L7.5 SYNTHESIS OF A ZERO-BIREFOREGENCE OPTICAL POLYMER BY THE BIREFRINGENT CRYSTAL DOPANT METHOD
Hiromi Okita,1,2,3 Masaaki Mukoh,1 Akihiko Tagaya1 and Yusuhito Kikko2,3,4
1Keio Univ, Yokohama, JAPAN, 2JST ERATO, Kawasaki, JAPAN.

Birefringence induced by the orientation of polymer main chains during an injection-molding or extrusion process restricts the application of optical polymers to optical devices that require preserving the anisotropy of the shape of the continuum optics. We propose two methods, the “random copolymerization method” and the “anisotropic molecule dopant method” to prepare transparent zero-birefringence optical polymers. However, neat resist polymers generally exhibit extremely high birefringence, which has not been eliminated yet by the two methods.

In this report, we propose a novel method, the “birefringent crystal dopant method” to compensate the positive birefringence of optical polymers by doping with a birefringent needle-like crystal particles which have negative birefringence. In this method, the crystal particles need to have opposite orientation birefringence to that of polymers. Strontium carbonate SrCO₃ crystal particles were selected for this method and prepared by a reaction of Sr(OH)₂ with carbon dioxide, with a particle length of 100-300nm and an aspect ratio of 2.5. Poly MMA-co-HMMA films with a composition MMA/HMMA = 58/42 (wt/wt) was synthesized with a thickness of approximately 40µm. The SrCO₃ particles were homogeneously doped into the copolymer films and the particle doped films were uniaxially drawn at 130°C and 4mm/min. The positive birefringence of the drawn copolymer films at a wavelength of 658nm was compensated at the SrCO₃ particles concentration of 0.1wt. %. Transmittance of the SrCO₃ particles doped copolymer films was 91.8% at a wavelength of 400nm and the glass transition temperature of the films was 118.7°C. These results confirmed that the synthesized zero birefringent polymer films have the same transparency and heat resistance as the blank copolymer films. Therefore, we conclude that the birefringent crystal dopant method was one of the promising candidates for obtaining heat resistant zero-birefringence optical polymers.

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

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

1.7 TOWARDS SOLID STATE POLYMOLAR LASERS AROSS THE VISIBLE SPECTRUM
George Heliotis, Ruidong Xia, Donal D.C. Bradley, Ufatran Photonics Collaboration, Experimental Solid State Group and Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College, London, UNITED KINGDOM.

Semiconducting (conjugated) polymers are now attracting considerable interest as a new material class for use in electronics and optoelectronics. Currently there is increasing interest in developing these materials for use in novel gain media in devices as lasers and optical amplifiers. Fluorocarbon-based polymers [polyfluorocarbons] are a very attractive class of conjugated polymers for such applications, due to their high photoluminescence and high electroluminescence efficiencies, low stimulated emission thresholds, high stability in air and good properties as host materials for other emitters. Here, we report a systematic investigation of the properties of such polymers by using steady-state and time-resolved fluorescence to establish suitability as gain media for laser applications. We demonstrate light amplification in the blue, green and red parts of the spectrum via amplified spontaneous emission (ASE) measurements on planar nanometric waveguides. The gain characteristics of the nanowaveguides (linewidth, intensity, threshold energy and peak wavelength) are measured as a function of excitation wavelength and intensity, film thickness and film morphology. Low thresholds (≤0.01W/cm²) are demonstrated. Optical gain measurements on the nanowaveguides revealed that the waveguides can exhibit large net gain and have low loss coefficients, making these materials attractive for tunable solid-state lasers with wavelengths that span the entire visible spectrum.

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

Semiconducting (conjugated) polymers are attractive candidates as the gain media for solid-state lasers due to, among other things, their high photoluminescence efficiency and their high optical gain at normal incidence. Two-dimensional, cross-sections. Furthermore, compared with conventional inorganic semiconductors, organic semiconductors offer potential advantages with respect to use of processing, low cost and flexibility. Recent reports of lasing action in conjugated polymers have stimulated great interest in the development of lasers that may eventually compete with inorganic semiconductor structures. Here, we report the fabrication of a two-dimensional distributed feedback laser utilising a novel fluorescent copolymer as the gain medium. The laser was made by depositing a thin polymer layer on top of a suitably patterned substrate. The substrate comprised two crossed gratings etched at right angles into a fused silica plate. This structure provides a better optimised photonic mode density confinement compared with a single grating structure, which leads to reductions in the lasing threshold and increase in the output efficiency. Laser action was demonstrated by pumping the device with a compact diode-pumped, frequency doubled Nd:YVO₄ laser operating at 532 nm. Lasing occurs at 800 nm and is located on the edge of the photonic stop band induced by the two-dimensional microstructure. The laser had a threshold of 4mJ per pulse and the output characteristics of the laser are described in detail and the shape and divergence of the output beam are correlated with the two-dimensional feedback mechanism.

L7.9 SPONTANEOUS ORIENTATION OF Aλ₃G MOLECULE IN EVAPORATED FILM AND ITS VANISHMENT BY LIGHT IRRADIATION
Koji Sugi, Hsiao Iishi, Yasuo Kimura, Michio Ito, Titeko University, Institute of Electronics, Computer and Communication Research, Sendai, JAPAN; Naoki Hayashi, Yukio Oschi, Nagoya Univ, Graduate School of Science, Nagoya, JAPAN; Eisuke Ito, RIKEN, Frontier Research System, Naka, JAPAN; Kazunori Seki, Nagoya Univ, Research Center for Materials Science, Nagoya, JAPAN.

Recently we found that high and persistent spontaneous buildup of the surface potential (SP) upon vacuum deposition of tris(8-hydroxyquinoline)aluminum (Alq). An a substrate under dark conditions (38V for 50nm thick Alq film). Such giant potential is removed by visible-light irradiation. Alq₃ molecule has a permanent dipole and its spontaneous orientation is suggested as an origin of such giant SP [1]. Such properties suggest that Alq₃ molecule has an ferroelectricity, and can open the possible application to various organic devices such as ferroelectric gate for memory FET. In this study, we focus on the mechanism of the removal of giant SP by visible-light and its possible ferroelectricity. The result shows that the decrease of SP was proportional to the logarithm of light irradiation time [1]. Numerical simulation for the decrease of SP was performed on the basis of a simple model where an oriented molecule becomes disoriened upon the absorption of an incident photon. This model well reproduced the observed logarithmic relation, suggesting that not photovoltaic effect but a rotation of the molecule by photocoreaction is plausible as the origin of the removal of the SP. As to the ferroelectricity, the measurements of DE hysteresis well reported. The examination of the retention time of such giant SP by Kelvin

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In many theoretical studies, the electronic and optical properties of conjugated polymers are treated in a single-chain picture. Here, we study the effects of 3D-dielectric screening of the Coulomb interaction and 3D quantum mechanical coherence on the electronic and excitonic excitations in conjugated polymers. We perform a fully ab-initio calculation of the bandstructure and the excitonic spectrum of crystalline polyethylene and polyethyleneoxide, using the GW approximation method. The calculations reproduce the electronic self-energy and including excitonic effects by solving the electron-hole Bethe-Salpeter equation. This calculation includes all effects of 3D screening and quantum mechanical coherence. We compare our results with calculations on a single polyethylene chain (no 3D screening and no 3D coherence), and polymer chains embedded in a dielectric medium (3D screening, but no 3D coherence). The calculated excitonic spectrum for polymer chains embedded in a dielectric medium generally agrees well with available experimental data. The calculation for a single chain leads to an unacceptably large (>1 eV) exciton binding energy, whereas the crystalline calculations lead to too small exciton binding energies and optical gaps. Our conclusion is that in most experimental samples, 3D dielectric screening plays an important role, but quantum mechanical coherence between neighboring chains is absent. The absence of coherence is probably caused by the disordered nature of many polymers. However, our calculations do also show exciton coherence in situations where coherence between chains does occur, such as in a hederotype polypropylene glycol. Due to its stiffness, this polymer is rather prone to aggregate formation. Ordered regions seem to exist in this polymer, where the exciton binding energy is smaller than in the disordered regions. This observation is in line with our crystalline calculations.

L7.11 THE CRYSTAL STRUCTURE OF ANTIRACENE UP TO 22GPa: A X-RAY DIFFRACTION STUDY. Martin Oezkol, Georg Hebel, Roland Rees, Graz University of Technology, Graz, AUSTRIA; Kerstin Hummer, Peter Puschmann, Claudin Ambroise-Drexel, University of Graz, Graz, AUSTRIA; and Atsuko Nakayama, Advanced Carbon Center, AIST, Tsukuba, JAPAN.

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

L7.12 Abstract Withdrawn.

L7.13 FIELD EFFECT OF FULLERENE THIN FILM STUDIED BY DISPLACEMENT CURRENT MEASUREMENTS AND INFRA-RED ABSORPTION SPECTROSCOPY IN THE MULTIPLE REFLECTION TECHNIQUE. Satoru Ogasawara, Yasuo Kimura, Hisao Ishii, and Michio Ninomi, Tohoku Univ., Research Institute of Electrical Communication, Sendai, JAPAN.

Recently, organic field effect transistors (OFETs) have attracted much attention. In spite of extensive studies, the mechanism of OFET is not yet well understood. Especially field effect doping is now under discussion after the observation of the Dr. Schön in Bell Laboratories. Here, we report two questions: one is whether field effect doping actually happens for organic semiconductors or not. Second, where the accumulated carrier comes from. In this study, we prepared a metal/insulator/semiconductor (MIS) structure as a prototype of FET structure. We used fullerene C60 as an organic semiconductor. By changing the displacement current method we investigated the charge accumulation at C60/insulator interface due to applying electrical field. In-situ infra absorption spectroscopy in the multiple internal reflection geometry was also performed for the MIS structure to examine the field effect doping. This technique enables us to investigate the degree of charge transfer of C60 layer under electrical field. As a result, we observed electron injection from Au electrode to C60 followed by the decrease in an IR absorption peak due to FULLERENE. This result suggests that carrier injection into the channel of OFET. The decrease in IR peak of C60 indicates the increase of the amount of neutral C60 molecules, suggesting some doping effect induced by accumulated carriers. The detailed analysis of the observed spectral change due to electric field will be presented.

L7.14 ANALYSIS OF CHARACTERISTIC SHG FOR SBC AT THE AIR-WATER INTERFACE UNDER P-INS-P-OUT LASER CONFIGURATION. Chen-Xu Wu, Xinmen Univ, Dept of Physics, Xinmen, P.R. CHINA; Hang-Qing Wang, Inst. of Chemistry (CAS), The State Key Laboratory of Molecular Reaction Dynamics, Beijing, P.R. CHINA.

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


L7.15 EXCITON DISSOCIATION IN DOPED CONJUGATED POLYMERS. Vladimir Arkhipov and Paul Hermans, IMEC, Leuven, BELGIUM; Eugenia Emelina, Semicon, Physics Lab, Univ. of Leuven, BELGIUM; Heng Biesalski, Inst. of Physical, Nuclear, and Macromolecular Chem., Philips Univ. of Marburg, GERMANY.

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

L7.16 SOL-GEL NANOHYBRID MATERIALS INCORPORATING
FUNCTIONAL THIACALIXARENES FOR NONLINEAR OPTICAL APPLICATIONS. Cedric Desreux, Stéphanie Parodi, David E. Clarke, Géraldine Labourde-Dhé, and Assimenios Vlachopoulos. Interfaces, UMR 5615 CNRS, Université Villeurbanne, FRANCE. Optical Power Limiting (OPL) materials have been developed for the protection of optical amplifiers and lasers. Previous investigations evidenced that the optical limiting behaviour of a given molecule can be related to the de-localization of electrons and may be improved by the formation of heavy metal complexes. We have been investigating thiinalixares on the basis that they display de-localized electrons and can be selectively functionalised either on the upper rings or the lower rings. Moreover, the presence of electron donating sulfur bridges can play an important role regarding nonlinear optical properties and functionalized systems can be functioned with ability to increase the electron de-localisation over the molecule and to form metal complexes. Thiocalixarenes bearing phenylthio, amino, imino or ethylenic groups on the lower rings were prepared and fully characterized. The formation of metal complexes was also investigated. They showed interesting optical properties. Optical limiting materials need to be incorporated into an inorganic matrix in order to be useful for optical limiting devices. It is well known that the sol-gel route allows easy inclusion of organic dyes into an oxide network because of the low temperature of the process. Two major classes of the so-called organic-inorganic hybrids can be considered. In class I hybrids the organic molecules have weak chemical interactions with the inorganic network. In class II hybrids the organic molecules are strongly bonded to the inorganic network (convention). Class I materials were found to be inhomogeneous and only low concentrations of thiocalixarenes could be reached in the final materials. Class II hybrids were thus considered to permit the elaboration of highly concentrated and stable hybrids. A second functionalisation (upper rings) with metal alkoxide groups had to be investigated in order to prepare the class II sol-gel hybrid materials incorporating the optically active molecule.

L7.17 \textsc{Cis/} \textsc{P}EDOT \textsc{P}hotovoltaic \textsc{S}tructure, Sergei Bereznev, Julia Koir, Ivan Melikov, Andrej Opač, Tallinn Technical University, Dept of Material Science, Tallinn, ESTONIA; Igor Kononov, Universität Leipzig, Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry, Leipzig, GERMANY. Photoconductive structures based on combination of electrically conductive polymers with inorganic semiconductors are currently intensively investigated with the aim to prepare photovoltaic devices. Conductive polymers attract interest due to the potential for producing low-cost, large-area and flexible photodiodes and solar cells. In this study, multilayer structures were fabricated. Cis [3,4,4'-ethylenedioxythiophene] (PDOT) doped with polyaniline was used as the active layer and investigated for photovoltaic applications. The photoresponse of CdS/PEDOT structures was investigated as an alternative for the traditional buffer layer and window layer on the CIS absorber layer in the cell structure. As absorber layer, CdS/CdTe/CdMnTe thin films were synthesized and deposited on a tin oxide coated substrate. The absorption spectrum was found to be consistent with the expected results generated from the model thin film structure. The PCE was found to be around 0.1%. The effect of the ratio of the absorber to the buffer layer on the efficiency was studied.

L7.18 \textsc{Ab-initio} \textsc{C}alculation of \textsc{H}omo and \textsc{L}umo \textsc{E}nergies in \textsc{P}oly\textsc{Y}lidy\textsc{E}ne \textsc{S}ystems, W. F. Petase, P. A. Bolbort, M. A. J. M. Hsueh, C. M. Y. W. Lo, and N. Gao. Department of Electronics Engineering, National Chiao Tung University, Hsinchu, TAIWAN. Molecular electrophotovoltaic devices or field-effect transistors (FETs) are based on the use of conjugated polymers or small molecules as the active layer. Both the polymer and the small molecule materials have been extensively studied. However, significant efforts have been made to understand the fundamental physical mechanisms involved in the device performance. In this talk, we will discuss the use of \textsc{Ab-initio} methods to calculate the HOMO and LUMO energies. These methods can provide accurate results and are useful for predicting the electronic properties of the materials.

L7.19 A Novel Patternning Concept for \textsc{P}PV,\textsc{T}ype \textsc{M}aterials Using the \textsc{T}hio\textsc{E}ne \textsc{P}hotoreaction, J. Keplinger, G. Langer, T. Seidl, D. Sandhofer, TU Graz, Institute for Chemistry and Technology of Organic Materials, Graz, AUSTRIA; A. Schmid and E. Zojer, TU Graz, Institute for Chemistry and Technology of Organic Materials, Graz, AUSTRIA; R. S. W. Kern, TU Graz, Institute for Chemistry and Technology of Organic Materials, Graz, AUSTRIA. The variation of the emissive properties of conjugated polymers is of importance for the MM seckup of organic light emitting devices (LEDs). A novel strategy for a patterned modification of PPV films is presented. We employed the photoinitiated addition of thiols (R—SH) to the C=C double bonds in PPV in order to modify the emissive properties. This photoreaction, which is known under the name “Thio-Ene Reaction”, was found to be highly efficient and selective to introduce the thioalkyl units in PPV. The reduction of the conjugation length leads to a dramatic change in the emissive properties and finally to a bleaching of the emission. This technique can be employed for the generation of patterns in PPV films (bleaching). On the one hand, the reaction was carried out by UV illumination of PPV films in the presence of gaseous thiols (e.g. propionethiol). On the other hand, PPV films containing dodecanethiol were coated on substrates and subjected to UV illumination. In both cases the photoinitiated Thio-Ene addition was followed by real-time infrared spectroscopy (RITR). An almost complete conversion of the C=C double bonds was achieved upon prolonged UV irradiation. We investigated the accelerating effect of free radical photoinitiators (e.g. benzyl dimethyl ketone) on the addition reaction. An atmospheric pressure ion beam technique was employed to deposit controlled amounts of the photoinitiator on PPV films. Subsequent UV illumination in the presence of gaseous thiols lead to a photodetection of the rapid change in the emission of the photoinitiator. The relationship between the deposited amount of photoinitiator, the UV illumination time and the resulting emissive properties of the PPV films was investigated. Applying this novel concept in combination with photomasks, lateral resolved photoprocessing of PPV was demonstrated.

L7.20 Abstract Withdrawn.

L7.21 The Characterization of a Silole-Magnesium Thin Film Interface by Photoelectron Spectroscopy, A. J. Mikkelsen, Optical Sciences Division, Naval Research Laboratory, Washington, DC; M. Uchida, Chisso Corporation, Yokohama, JAPAN; Z.H. Kafi, Optical Sciences Division, Naval Research Laboratory, Washington, DC. Photoelectron emission spectroscopy of an interface between Mg and a silole derivative, 2,5-bis(2,2'-bipyridyl)-1,1-dimethyl-3,4-diphenyl silacyclopentadiene (PyPy,SpPy), shows the formation of two gap states both when metal is deposited onto an organic layer and when the organic is deposited onto the metal. The appearance of these states is a result of electron transfer from the metal to the organic layer. Fermi level pinning occurs at the lowest unoccupied molecular orbital of PyPy,SpPy implying barrierless electron injection at the Mg/PyPy,SpPy interface. This result is significant when employing a Mg electrode contact with PyPy,SpPy in electronic, electrooptic, and optoelectronic devices.
L7.22 HIGH-PRESSURE STUDIES ON THE PACKING FORCES AND INTERMOLECULAR INTERACTION IN POLYPHENYLS.
Georg Heimel, Martin Oehrel, Roland Resel, Inst. of Solid State Physics, Graz University of Technology, Graz, AUSTRIA; Peter Paschinger, Kerstin Hummer, Claudia Ambrosh-Driel, Inst. for Theoretical Chemistry, University of Giessen, Koppelhuber-Hitzli, Inst. of Physical and Theoretical Chemistry, Graz University of Technology, Graz, AUSTRIA; Felix Porsch, Inst. of Mineralogy and Petrology, University of Bonn, Bonn, GERMANY.

In this work, we report on pressure induced structural changes in crystalline oligo(paraphenylene)s containing two to six phenyl rings. The results are discussed with particular emphasis put on the implications these changes in intermolecular distances and molecular arrangement have on important bulk properties of this class of materials such as optical response and charge transport. We performed energy dispersive X-ray diffraction in a systematic study on polycrystalline films of high-0, p-quaterphenyl, p-quaterphenyl(p-quinquephenyl) and p-sexiphenyl under hydrostatic pressure up to 60 kbar. Revisiting the crystal structures at ambient conditions reveals details in the packing principle. A linear relationship between the density at ambient conditions and the number of phenyl rings is found. High pressure investigations not only yield pressure dependent lattice parameters and hints towards pressure induced changes in the molecular arrangement but also allow for an analysis of the equations of state of these substances as a function of oligomer length. We report the previously unknown bulk modulus of p-quaterphenyl, p-quaterphenyl(p-quinquephenyl) and p-sexiphenyl (B₀ = 83 kbar, 83 kbar, and 100 kbar respectively) and its pressure derivative (B₀' = 6.4, 7.5, and 5.6). A linear dependence of the bulk modulus on the inverse number of phenyl rings in the molecules and with that on their ambient conditions density is found.

L7.23 INDEX AND RELIEF GRATINGS IN POLYMER FILMS FOR ORGANIC DISTRIBUTED FEEDBACK LASERS.

Gratings in polymer films are important for optoelectronics and for the setup of organic lasers based upon the principle of distributed feedback (DFB). Our investigations were focussed on photosensitive polymer [poly(styreneco-4-vinylethoxycarbonyl)] (PST-co-VBT) which form refractive index (by ionomerisation) and relief gratings (by laser ablation) upon deep-UV irradiation. By gas phase modification withamines additional index changes as well as additional surface relief gratings were obtained with these polymers. Using interference illumination with the fourth harmonic of a Nd:YAG laser, 1D and 2D surface relief gratings were produced. DFB lasing was observed with conjugated polymers and dyes (DCM) and conjugated polymers were embedded into the photosensitive matrix. Also thin films of conjugated polymers cast onto the surface relief structures of PST-co-VBT showed lasing action. The performance of these organic surface emitting lasers devices and their spectral laser mode output were characterized. Strategies towards truly tunable DFB laser devices were investigated. A promising way is the functionalization of electronically dissimilar repeat groups, e.g. CH2=CHN. This approach aims at elastic index and relief gratings with variable DFB emission wavelengths.

L7.24 Abstract Withdrawn.

L7.25 NEW HOLE CONDUCTORS FOR SOLID STATE DYE SENSITISED SOLAR CELLS.
S. Jumla, H. A. Nasr, T. Meeks, S. E. P. Hoekstra, V. V. D. Derijck, Centre for Solar Energy Conversion, University of Oxford, OXFORD, UNITED KINGDOM.

In the quest for photovoltaic devices that are low cost, light weight and ready to produce, new hole conductors for the solid state dye sensitised solar cells (DSSCs) are good contenders. Overall solar light to electrical energy conversion efficiencies of 10% have been reported for devices based upon liquid electrolytes, (typically 12% in the laboratory). However there are a number of drawbacks associated with employing such liquid based electrolytes. For example problems with encapsulation of the liquid electrolyte and leakage of the solvent may seriously hinder the long-term stability of such devices. As a result, recently there has been heightened interest in the development of solid state versions of DSSCs, where the liquid based hole conductor is replaced by a solid state hole-conductor. In this paper we present work on two hole-conductor systems: polymer electrolytes and p-type organic polymers, paying particular attention to the following points: 1) Development of small molecules (Example 1) and polymer based organic hole-conductors with ion solvation tetraethylammonium tetrafluoroborate salts and their application in dye sensitised nanocrystalline solar cells. 2) The charge transfer processes that occur at the semiconductor / dye / hole conductor interface play an important role in controlling the overall efficiency of the device. Here we employ laser based transient absorption spectroscopy to study the charge transfer processes at the semiconductor / dye / hole conductor interface. In particular we highlight the importance of thermodynamic rather than kinetic control of the interfacial charge separation and the influence of energetic inhomogeneities upon the yield of excited states. We also employ insulating metal oxide barrier layers to retard the interfacial recombination and thereby enhance device performance. 3) The development of solid state dye sensitised on flexible plastic substrates. We report flexible DSSCs with overall efficiencies of ~3% (11mWcm^-2 solar light illumination) based upon polymer electrolytes.

L7.26 CONDUCTION MECHANISMS IN PEDOT / PSS THIN FILMS.

Conducting polymers are widely used as electrode or active material in solar cells, Light Emitting Diodes, Field Effect Transistors and other plastic electronic devices. Our interest mainly goes to a specific material: poly(3,4-ethylenedioxythiophene) (PEDOT). This polymer has already been used in solar cells, photographic films and glucose biosensors. The electric conduction mechanism in PEDOT is however not yet completely understood. The goal of our research is to characterize the charge transport mechanism in PEDOT and related polymer thin films and to link this with the morphology. Morphology transport We measured the conductivity of thin films (thickness 200nm) of PEDOT with poly(styrene sulfonate) counterions in a temperature range between 4 and 300K. The Hall resistance in a field of 1.2T has also been studied. The results from both experiments show that there is a hole-type conduction mechanism which obeys the scaling law \( (\sigma \propto T^{1/2}) \). This can be interpreted in terms of two different models: either Variable Range Hopping (VRH) in 3 dimensions with a Coulomb gap in the density of states, or quasi-1 dimensional VRH. We also fitted the temperature dependence of the Hall resistance and found the empirical relationship \( R_{\text{H}} \propto T^{-a} \). From this follows that \( R_{\text{H}} \propto T^{a} \). Morphology The morphology of the PEDOT samples was studied with Transmission Electron Microscopy. This gives information about the density and ordering of PEDOT and PSS molecules inside the film. The data from our measurement is not yet completely interpreted, but no evidence was found for crystalline regions. The PEDOT/PSS thin film therefore has an amorphous arrangement of the polymer chains. Conclusions We gratefully acknowledge support from the IWT in the context of the DOTCON project.

4. L7.27 RELAXATION PHENOMENA OF LAYERED TYPE CONJUGATED POLYMERS PROBED BY SINGLE CHAIN FLUORESCENCE SPECTROSCOPY.

The performance of optoelectronic devices made of conjugated polymers such as light-emitting diodes, photodetectors and lasers is determined by the properties of the excited state of the organic molecules. In particular the extent of electronic delocalisation, the electron-electron interaction and the inter- and intrachain coupling are presently investigated extensively. Typically, spectroscopic data on conjugated polymers are strongly affected by the inherently broadening of the spectral features. The spectroscopy of single molecules avoids ensemble averaging and gives direct access to the optical properties of the individual molecule. Using single molecule spectroscopy we measure the light induced photoluminescence from a single conjugated polymer chain between 5 K and room temperature. We choose a ladder-type
poly(p-phenylene) as a model polymer system as this material exhibits a particularly low degree of inhomogeneous broadening together with a high degree of chemical stability of the conjugated region. In room temperature the spectrum of a single conjugated molecule nearly matches the bulk spectrum. At low temperature however, the single molecule spectrum shows a much smaller line width as compared to the bulk. The extent of the line width becomes as small as 0.6 cm⁻¹ corresponding to a dephasing time of T₂ > 260 fs. In addition, the small line width allows the identification of various vibrational modes coupling to the electronic exciton. Employing a pulsed excitation source and a high-speed timer as detection measure the single molecule photoluminescence spectrum with a time-resolution of 200 ps. The majority of the molecules investigated show a red-shift of the spectrum on a sub-msec time scale. This is a very direct observation of energy transfer between different conjugated segments located on the same polymer chain.

L7.28 Abstract Withdrawn.


Thin films of porphyrins and related compounds have attracted increasing attention in recent years being these molecules an extremely versatile family of compounds for a wide variety of applications. Indeed, their potential employment in many fields of technological interest as photoconductors, optical switches and as well as chemical-sensors has been extensively studied [1]. Bis-zethane-bridged porphyrin dimer [1] has shown unique temperature and solvent dependent syn-anti conformational switching properties in solution [2,3] making these compounds promising candidates for optical switches and sensors applications. In this work, we report on a structural and spectroscopic study of thin films. Monolegers of I have been first prepared at the air/water interface. The related surface pressure-area isotherm showed that in dependence of the film pressure different condensed phases may occur in the monolayer. The inspection of the monolayer by Brewster Angle Microscopy (BAM) and UV-visible spectroscopy lead to the observation of peculiar networks whose structural features and optical properties seemsly change upon film compression. Thin films [1-3 layers] of I have been then transferred on solid surfaces, by the Langmuir Schäfer (LS) horizontal method. Either quartz slides or silicon oxide, previously hydrophilised with 1,1,3,5,3-hexamethyldisiloxane, have been used as substrate. Scanning Force Microscopy (SFM) images performed on these systems at different length scales, showed fractal networks constituted by nanoscopic supramolecular aggregates, whose shape and size depend again on the LS deposition surface pressure. UV-visible spectroscopy measurements showed that the absorption is almost linearly related to the film thickness and directly connected to the surface pressure, i.e. to the film morphology investigated by SFM[1]. F. Kamte, T. Kamte, N. R. E. H. W. Borkovsk, V. Inoue, J. Am. Chem. Soc., 2000, 122, 4403-4404.

L7.30 Abstract Withdrawn.


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

L7.32 PERIODICAL SELF ASSEMBLED PHOTONIC STRUCTURE IN POLYMER BLEND LIGHT EMITTING DIODES. G. Fickel, W. T. S. Huck, M. Melville Laboratory, Department of Chemistry, University of Cambridge, Cambridge, U.K; G. Fudenberg, J. H. A. M. ackenzie, R. H. Friend, Cavendish Laboratory, Department of Physics, University of Cambridge, Cambridge, UNITED KINGDOM.

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


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

L7.34 HYDROSTATIC PRESSURE DEPENDENCE OF THE RAMAN FREQUENCIES IN POLYFLUORENE, C54M, C60M, WORKSHOP ON PHYSICS, University of Tokushima, MO; G. G. A. G. H. H. Fondner, P. Scandicci de Liveis, U. Scherf, Institut für Chemie und Polymere, Universität Potsdam, GERMANY.

We present studies of the Raman scattering from poly[2,7-[9H-bis(2-ethylhexyl)fluorene] (PF2/6) under hydrostatic pressures of 4-100 kbar at room temperature. We observe a Raman peak at the intra-ring mode C60 cm⁻¹ and other peaks at 1582 cm⁻¹, 1500 cm⁻¹, and 1417 cm⁻¹ which are studied as a function of pressure. All Raman peaks shift to higher energies with increasing pressure. Above 40 kbar they exhibit asymmetric and anharmonicity lineshapes. This is indicative of a strong electron-phonon interaction between the Raman phonons and the electronic continuum. The photoluminescence from bulk PF2/6 shows significant changes in the aggregate and defect reduced emissions increase significantly above 40 kbar. Although the Raman spectra are excited with the 1.92 eV laser line, it appears that direct excitation of the aggregate or defect reduced emission occurs, causing real transitions that interact with phonons to produce symmetric line-shapes. The lineshape of the 1500 cm⁻¹ Raman scattering strikingly characteristic of a Breit-Wigner Fano (BWF) resonance. A detailed BWF lineshape analysis for this peak as a
function of pressure shows that the asymmetry (1/3|q|) is relatively small up to about 35 kbar, with 1/3|q| values between 0.005 and 0.1. Beyond this, the asymmetry increases (1/3|q|) increases from 0.3 to 0.6. The linewidth increases as the square of pressure, while the frequency positions almost linearly with pressure.

L.T.35

CHARGE TRANSPORT IN THIN POLYCRYSTALLINE FILMS OF ORGANIC SEMICONDUCTORS

Sujeet Verma, Vladimir Arkhipov, Paul Hesse, Jom, Imec, Polymer and Molecular Electronics, Leuven, BELGIUM.

Thin films of thermally evaporated small-molecule materials, used in organic thin-film transistors (OTFTs), are generally polycrystalline with localized states concentrated within the amorphous phase separating crystalline grains. Therefore, one can expect that the grain boundaries will control charge transport in these materials. A recent model offers an adequate approach to the conductivity in polycrystalline films. Charges, trapped in defects at the grain boundaries, create potential barriers and carrier jumps across these barriers are the rate-limiting step in the carrier transport. We assume a quasi-continuous energy distribution of localized states within grain boundaries rather than a constant interfacially trapped charge. Under such circumstances, the potential barrier height is not determined by the quantum well states. In terms of this model, one can discuss the effects on the carrier mobility of dopant concentration, the lateral and vertical fields, i.e. drain voltage/channel length and gate voltage, as well as the limitations of this model and the differences with other models.

L.T.36

ON THE ORIGIN OF GREEN EMISSION IN POLY-PHENYLENE BASED CONDUCTING POLYMERS

Ernst W. Lutz and Lorenz Romming, Chair and Laboratory Leader at Laboratory for Nanosegregated Materials, Institute of Nanostructured Materials and Photonics, Johannesen Research, Weiz, and Institute of Solid State Physics, Graz University of Technology, Graz, AUSTRIA; Alexander Pugmirsch, Institute of Solid State Physics, Graz University of Technology, Graz; Roland Guentert, Patrik Scanducci de Freitas, and Ulrich Scheer, Bergische Universität Wuppertal, Mikromolekulare Chemie, Fachbereich Chemie, Wuppertal, GERMANY.

For future display applications of conjugated polymers the currently most challenging topic is the realisation of colour stable blue light emission. All available poly(paraphenylene) type materials (PPP), which are the most promising family of blue light emitters, are prone to degradation resulting in an unwanted change in colour due to the emerging of a lower energetic greenish emission peak. This band has been mostly been attributed to aggregate and/or excimer formation in the material. However, as we show, both excimer and aggregate formation are very unlikely to be the origins of the low energy emission band of PPP-type polymers. Instead all experimental observations suggest that this emission comes from a different photophysical process. It will be demonstrated that keto defects can be generated in the material directly during polymer synthesis, photo- or electrooxidative degradation processes and thermal treatment in ambient atmosphere. In addition, the obtained spectroscopic results are compared to results obtained for defined co-polymers of 9,9'-difluorenyl-fluorene with fluorene. Studying such controlled fluorene-fluorene co-polymers model compounds a clear quantitative correlation between the 9-fluorenyl content and the low-energy emission band intensity has been established.

L.T.37

COLOR TUNING OF EMISSION OF IRIUM PHOSPHORS BY USING ANCILLARY LIGAND AND DEEP BLUE IRIDIUM PHOSPHORS FOR OLEDs

Jian Li, Bert D. Alleyn, Vadim I. Advincula, Peter I. Byrnes, Mark E. Thompson, Department of Chemistry, University of Southern California, Los Angeles, CA; Russell Holmes, Stephen R. Forrest, Department of Electrical Engineering, Princeton University, Princeton, NJ.

High efficiency organic light emitting devices (OLEDs) require the phosphorescent emitters. Due to the strong spin-orbit coupling of Ir atom, many cyclometalated Ir complexes are phosphorescent at room temperature, which are used as phosphorescent emitters for dopant emitters in OLED applications. One method of modifying the emission energy, and hence the color, of Ir phosphors is to change the nature of cyclometalating ligand. For example, phenylpyridine-based Ir phosphors have green emission while Ir phosphors with phenylpyridine will emit orange or red. (Ref. S. Linnmayer, et al., Inorg. Chem., 2001, 40, 1704-1711). This presentation will describe a new method of color tuning by employing high triplet energy ancillary ligands for Ir phosphors. Using a series of different ancillary ligands, i.e., a family of pyrazolylborate and phenylpyridine (ppy), it is possible to vary the emission color of Ir phosphors over a wide range. For example, the emission color of mer-Ir(ppy)_3 is orange (λ_{max} = 550 nm) while the emission color of mer-Ir(ppy)(bpy)(ppy)(ppy)(ppy) is green (λ_{max} = 455 nm). Electrochemical analysis of Ir(ppy)_{2}Ir(LX) complexes shows that different ancillary ligands modify the emission energy by affecting the energy of the filled state (HOMO) while leaving the vacant states (LUMO) complexly unchanged.

Tetrakis-pyrazolylborate, pzPb_{2} and fluorinated phenylpyridine ligands, e.g., iridium(III) bis(4H,6H-difluorophenylpyridinol-N, C’2) tetrakis-[1-pyrazolyl]borate, flr6, are highly efficient blue phosphorescent emissive blue phosphors in OLEDs has been also demonstrated. Unoptimized devices using the blue phosphor, flr6, have CIE coordinates of device (0.15, 0.20) (λ_{max} = 455 nm) and maximum external quantum efficiencies near 3.3%.

L.T.38

RUTHENIUM(II) ORGANOMETALLIC COMPLEXES AS NEW HOLE-TRANSPORTING MATERIALS FOR OLEDs

Jian Li, Vadim I. Advincula, Xiaofe Ren, Peter I. Djurovic, Mark E. Thompson, Department of Chemistry, University of Southern California, Los Angeles, CA.

Since the invention of the organic light emitting diodes (OLEDs) in 1987, the investigations into new hole-transporting materials have typically focused on derivatives of triisilylamine, such as 4,4-bis[N-1-naphthyl- N-phenylamino]phenylamine (NP), as NPD. Recently, our group has started to investigate organometallic compounds with reversible redox properties as hole-transporters for OLEDs. The present work describes a novel approach for hole transporting material design as well as introduces a new type of hole transporting materials. Based on the Marcus electron transfer theory, a low energy barrier of electron exchange between bis(4H,6H-difluorophenylpyridinol-N, C’2) tetrakis-[1-pyrazolyl]borate, pzIr[Flr6] and its cationic counterpart, pzIr[Flr6]^+ makes pzIr[Flr6]^+ a potentially good hole transporting material. The report demonstrates that by using one derivative of pzIr[Flr6]^+, bis(9-fluoren-9-yl)perphenylpyridinol-N, C’2) tetrakis-[1-pyrazolyl]borate, flr6, as hole transporting material, the device efficiency and lifetime are enhanced, the device efficiency and lifetime are enhanced compared to the device efficiency and lifetime of the device flr6.

L.T.39

LARGE OPTICAL AND NEAR INFRARED BIREFERENCE IN PHOTODIAPHRAGMABLE POLYMER THIN FILMS

Beth L. Lodha, , Michiel J.A. de Dood, Albert Polman, Harry A. Atwater, , California Institute of Technology, Watson Laboratory of Applied Physics, Pasadena, CA, "FOI Institute for Atomic and Molecular Physics, Amsterdam, NETHERLANDS.

Development of highly birefringent polymer materials is necessary for improving the capacity of data storage and is potentially useful as a waveguide and active device material in integrated photonic devices. Photodiaphragmable polymers (PAPs) show considerable potential for these applications, with an unusually large birefringence of up to 0.2 at 632 nm. We have characterized for the first time, via spectroscopic ellipsometry, the birefringence of such PAP films from 630 - 1700 nm. Birefringence values measured indicate that the PAP is absorbing above 630 nm and maintains a very high birefringence (>0.2) at wavelengths up to 1700 nm. We have also performed morphological characterization using optical and atomic force microscopy indicating that both amorphous and crystalline films are optically smooth but with topographic features on the order of 30 nm high. Absorption spectra of the PAP films indicates that it is strongly absorbing in the visible (400-680 nm), so a 488nm Ar+ laser beam was used for writing while birefringence and photo-bleaching was monitored with a 635nm laser beam. Writing was performed by heating the polymer film above the glass transition temperature, leading to a strong in-plane birefringence due to the induced monolayer photoanisomerization cycle from the trans to cis configuration. This preferentially aligns the polymer side-chains parallel to th photoisomerisation direction. The effect of PAP birefringence on the plasma absorption of arrays of nanometer-scale metallic particles will also be presented.

L.T.40

A NEW CLASS OF ORGANIC/INORGANIC HYBRID COMPLEXES AS PHOTOSENSITIZERS FOR NANOCRYSTALLINE TiO2 BASED DYE SENSITIZED PHOTOVOLTAICS

R. Majaru, T. Tynys, J. Päivänen, B. Riihu, Center for Advanced Materials, University of Massachusetts, Lowell, MA; Lynne A. Stuempcs, Natki Solcier, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

Currently, the investigation of efficient molecular photosensitizers for photovoltaics is of great interest, as it is a crucial step in the construction of cheaper, more efficient solar cells. Several photonic hybrid materials have been used for the construction of dye sensitized solar cells (DSSCs). The most common ones are the metal oxides such as nanocrystalline TiO2, Nafion, TiO2:Fe and Cu2O. The mechanism of charge transfer between the metal oxide and the dye molecule is usually the recombination of an electron and a hole both generated upon light absorption in the dye molecule. The hole is trapped at the dye molecule and the electron is transferred to the metal oxide. This process results in the oxidation of the dye and the production of a charge separated state that is maintained for a short period of time after the light is switched off. The regeneration of the dye molecule at the anode occurs through the electrolyte redox couple. However, manyMANUSCRIPT

Currents are produced by a new class of organic/inorganic hybrid complexes that absorb light and transfer the excitation energy to the metal oxide. This photoinduced energy transfer allows the efficient regeneration of the dye at the anode and can be used to improve the performance of DSSCs. This new approach could lead to more efficient and cheaper solar cells. The use of these hybrid materials is expected to result in the development of more efficient and economical solar cells.
the development of low cost dye sensitized photovoltaic (DSPV) cells has been an area of tremendous interest. Transition metal complexes are used as dyes in photovoltaic devices built on nanocrystalline titanium dioxide [1-2]. Presently the most efficient and stable sensitizers are carbonylated polyphenylidylenes. Among them, [Ru(dcbpy)2(NCS)]2+ known as N3, shows overall photovoltaic efficiency of 8.10% when a liquid electrolyte containing iodine/iodide solution is used [3]. Though, present photo-sensitizers are mostly inorganic complexes, the investigation to find pure organic dye sensitizers is of potential interest to fabricate organic solar cells. We have carried out theoretical modeling of a class of organic dyes using semi-empirical quantum chemical methods to identify photo-sensitzers with well-matched HOMO-LUMO energies and good absorption characteristics. The experimental photophysical and photovoltaic properties were then determined. From our study, Xanthene dyes were found to be efficient photo-sensitizers compared to other dyes and we therefore synthesized a ruthenium based organic/inorganic hybrid complex using efficient Xanthene dye. The absorption dye of a new type of hybrid complex was extended to the near IR region and showed improved overall photoconversion efficiency over the pure organic dye. These organic dye- incorporated hybrid complexes with panchromatic absorption are potential candidates for fabricating efficient dye-sensitized photovoltaic cells. Synthesis, theoretical modelling along with experimental photovoltaic and photophysical properties are presented. References: 1) A. Hoffeldt, M. Gratzel, Acc. Chem. Res., 2000, 33, 269, 2) R. Moskur, Jin-An He, J. Kumar, Lin Li, J. Walker, and L.A. Samuelson, Proc. Mater. Res. Soc. Symp., 2002, 718, 367. 3) B. Offenberg and M. Gratzel, Nature, 1991, 353, 737.

L7.41 CHARGE TRANSPORT DEPENDENCE ON CHARGE CONCENTRATION: EXPERIMENTAL AND THEORETICAL INVESTIGATION OF POLYMER FIELD EFFECT TRANSISTORS
Yohai Reiderman and Nir Tesker, Dept of Electrical Engineering-Technion -Israel Institute of Technology, Haifa, ISRAEL; Shai Tal and Yoram Eisen, Dept of Chemistry Technion, Israel Institute of Technology, Haifa, ISRAEL; Oren Tal and Yossi Rosennik, Dept. of Physical Electronics, Faculty of Engineering, Tel Aviv University, ISRAEL.

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

L7.42 SOLID STATE NMR INVESTIGATION OF THE STRUCTURE AND DYNAMICS OF ALUMINUM TRIS (8-QUNOLINOLATE),
Maghsud Neshagi, Mathew Mathai, Fotios Papapolykaropooulos, Mater Res Inst, University of Materials Science, University of Connecticut, Storrs, CT.

Aluminum tris (8-qunolinolate) (Alq3) is the most widely used electron transport material for organic light emitting diodes. Whereas the structural features of several crystalline polymeric analogues have recently been characterized, much less is currently known about the molecular packing and dynamics in the device-relevant amorphous phase. We have applied advanced solid-state NMR methods, using both the spin-1/2 Carbon-13 and the spin-1/2 Aluminum-27 nuclei, in order to obtain structural and dynamical information from amorphous Alq3 deposits. Comparison of the 27AL spectra from amorphous Alq3 to those obtained from crystal polymorphs with known structure provide a clear experimental estimate of the ratio of facial to meridional isomer in the amorphous material. The molecular dynamics of Alq3 molecules in both crystalline and amorphous forms was quantified using relaxation time measurements as well as 13C exchange spectroscopy.

L7.43 FORMATION OF ONE-DIMENSIONAL CRYSTALLITE CHAINS IN PARA-SXEPHENYL GROWTH ON MCA
C. Teichert, G. Hlavacek, Dept. of Physics, University of Leoben, Leoben, AUSTRIA;
A. Andreussi, H. Sitter, Institute for Semiconductor and Solid State Physics, University Linz, Linz, AUSTRIA; G. Matt and N.S. Saxena, Leibniz Institute for Solid State Research, Stuttgart, Germany, and A. Jäger, University Linz, Linz, AUSTRIA.

High-resolution atomic force microscopy was used to study the initial stages of the well known para-sexiphenyl growth on mica [881]. This stage is characterized by the presence of nanometer scale crystallites and selforganized crystallite chains with micrometer extension in one dimension [1]. These chains are well oriented and exhibit a very narrow frequency distribution. UV/visible spectroscopic analysis in combination with high resolution scanning probe microscopy and photoluminescence imaging data suggest that, as a critical density of crystallites on the surface is present, the existence of densely packed chains and their interior structure indicate that this self-organization process requires the rearrangement of the crystallites as entities. [1] A. Andreussi, et al., Thin Solid Films, 403-404 (2002) 444.

L7.44 ORGANIC LIGHT-EMITTING DIODES BASED ON MULTILAYER PHOTO-CROSSLINKABLE HOLE TRANSPORT COPOLYMERS
Benito Domercq*, Richard D. Hreha, Chet Carter, Jose-Luis Maldonado*, Joshua N. Hardlock*, Christopher Schultz*, Ys-Dong Zhang*, Seth R. Asher* and B. Kippelen*, *Optical Sciences Center, University of Arizona, Tucson, AZ; *Department of Chemistry, University of Arizona, Tucson, AZ.

A series of soluble arylamine-based hole transporting polymers with various ionization potentials have been synthesized. The synthetic methodology allows for substitution of naphthyl groups on the amine with electron withdrawing and electron donating moieties which permits tuning of the redox potential of the polymer. The arylamine-based monomers have been copolymerized with cinnamated-based moieties to obtain photo-crosslinkable polymers. These materials can be crosslinked and patterned using a standard mask aligner designed for photolithographic applications. Using the crosslinked photolabile units we optimized to obtain an insulating hole-transport layer in stable electroluminescent properties. Using a photolithographic mask, these materials have been patterned into 10-50 μm-size features. These polymers have been used as hole transporting layers (HTLs) in multi-layer light-emitting diodes ITO/HTL/Alq3/MgAg [ITO = indium tin oxide, Alq3 = tris(8-hydroxyquinoline)aluminum]. The electroluminescent properties have been evaluated and compared between devices made from polymers with different ionization potentials. Electroluminescent devices were fabricated using a multisclerded structure of spin-coated hole-transport materials to enhance the overall electroluminescent properties. Fully spin-coated devices have also been fabricated by spinning a blend of polystyrene and Alq3 on top of a crosslinked hole-transport layer.

L7.45 SMEATIC GELS FROM SELF-ASSEMBLING BLOCK COPOLYMERS: Neal Scruggs, Rafael Verduzco, Michael Kempe, Julia Kernfeld, California Institute of Technology, Department of Chemical Engineering, Pasadena, CA.

Block copolymers with long side-group liquid-crystalline midblocks (>8000 g/mol) and LC-phobic end-blocks form a physical network that wets readily in an analogous small molecule LC solvent form nematic gels. Using side-group liquid crystalline (LCLCP) for the midblock to enable gelation at relatively low concentration. In contrast to nematic gels made by a photo-initiated polymerization, the present gels have exceptionally uniform optical properties. Under an applied strain, an initially unaligned, polystyrene gel aligns, creating a monodomain that is oriented well enough to generate clear conoscopic figures. In addition, these gels are amenable to various processing strategies for printing large area displays, since the physical crosslinks are reversible by addition of solvent or by increasing temperature. The transition temperature can be tuned by the choice of the end-blocks. The miktoarm polylketal model systems in which the molecular weight between crosslinks is well defined and determined by the length of the polymer midblock. Using polymer-analogous synthesis we prepare SCLCPs with M up to 1,000,000 g/mol and Mφ/Mφ < 1.3. The synthesis and interactions of these SCLCPs with a nLC host are described first for homopolymers, examining the dramatic effects of molecular weight. At these higher molecular weights, we have measured a tumbling parameter less than negative one. We further describe the phase behavior and electrooptic response of nematic gels formed using ABA block-copolymers.

Large area photovoltaic and photovoltaic devices are extremely desirable as a flexible means of energy production and storage. In particular, the effort to develop high performance thin films that can be applied to a broad range of surfaces. Further, the ability to pattern high refractive index inorganic compounds on such systems is of particular interest for the use of photonic and optoelectronic device applications. A bilayer polymeric multilayer assembly process is ideal for the construction of unique nano-structured thin films. We have engineered these systems to contain a high degree of order and control to obtain photovoltaic devices with high performance. The technique involves the use of a process known as self-assembly, where the patterned materials are photopolymerized onto the top of a polymeric layer surface, followed by templated synthesis of TiO2 and polymeric layer. We have investigated the effect of the template process on the patterned TiO2 films, as well as the photoelectronic behavior of organic dye materials on the patterned TiO2 film. Composite films of TiO2 and polyolefins exhibit selective reflectance of visible light wavelengths and good photoelectronic performance.

LT47
CHARGE CARRIER LIFETIMES IN A SAMPLY LIQUID CRYSTALLINE PHOTOCATHODE OF A 3-PHENYL-3-NAPHTHALENE DERIVATIVE. Hiroaki Uno, Junchi Hama, Imaging Science and Engineering Lab., Tokyo Institute of Technology, Yokohama, JAPAN.

Recently, liquid crystals have been recognized to be a quality organic semiconductor, whose mobility exceeds $10^{-6}$ cm$^2$/Vs, since the electronic energy levels are discovered in doped and simple liquid crystals. We have investigated the charge carrier lifetimes for electrons and holes in mesogenic naphthalene of a 3-phenyl-3-naphthalene derivative, 4-(4-octyloxyphenyl) 3-dodecyl-9-naphthalene (8-PNP-012) by time-of-flight (TOF) measurement and found that the carrier transport for holes and electrons is quite different. For positive carriers, the well-defined non-diffusive transient photocurrents were observed in the thin cells containing 500 μm and at the lower applied voltage than 2000 V/cm. On the other hand, we observed two transients for negative carriers in the cells of 5 μm to 100 μm, i.e., fast and slow transients that correspond to the mobility on the order of $10^{-6}$ cm$^2$/V·s and $10^{-7}$ cm$^2$/V·s in the SmA phase and $10^{-7}$ cm$^2$/V·s and $10^{-8}$ cm$^2$/V·s in the SmA phase, respectively. We observed that the origin of the slow transient is due to the ionization of isolated charge carriers by the electrostatic force of the applied field. Thus, we could reveal the charge carrier lifetime of SmA phase and found that the carrier lifetime for holes is much shorter than that for electrons.

LT48
PULSED LASER DEPOSITION OF ALUMINUM TITANATE (STO-2) HYDROXYLINE TFPFMS. Kenji Eibohara, Naoyuki Shim, Takahiro Oshikawa, Tomomitsu Bessho, Kumanoto University, Department of Electrical and Computer Engineering, and Graduate School of Science and Technology, Kumamoto, JAPAN; Toshihiko Nagatachi, Kumanoto Technology and Industry Foundation, Kumanoto, JAPAN.

Organic light emitting devices (OLED) have gained great interest due to their potential application as future flat panel display capable of low voltage operation. The Alq3 (aluminum triisopropylacetylene) has attracted a great deal of attention as a material for OLED. This compound is one of the most reliable organic emitters and is suitable for the fabrication of molecular or organic thin films. Pulled laser deposition (PLD) is suitable for fabricating new material structures such as organic and inorganic. The PLD has advanced techniques in low process temperature, fine controllability of film, high reproducibility and highly perfect structure with high purity level. We deposited the Alq3 films using a pulsed laser (Nd:YAG laser (532 nm) and KrF excimer laser (248 nm) to study the effect of laser wavelength on the deposited organic film quality. The Alq3 targets which were formed by metal Alq3 powder (Daiyoda, GB) were ablated at a laser fluence of 6J/cm$^2$ and 30 J/cm$^2$ for the Nd:YAG laser and for the KrF excimer laser (248 nm) to study the effect of laser wavelength on the deposited organic film quality. The Alq3 devices were fabricated using a shadow mask with a diameter of 25 mm on the target and kept at room temperature. Most of the Alq3 samples deposited at the deposited rate of 1.8 μm/s showed amorphous surface morphology while the Alq3 target had polycrystalline strata by XRD measurement. The films were light yellow color and showed very rough AFM images. The weak UV/visible absorption spectra range of 350, 415 and 535 nm were observed and their intensity increased with increasing laser fluence. On the other hand, when KrF excimer laser with the fluence around 300mJ/cm$^2$ irradiated, the deposited films appeared dark yellow, indicating a decomposition of the Alq3 target.

LT40
QSPR STUDY OF GLASS TRANSITION TEMPERATURES OF TRISOXYLAMINE DERIVATIVES USING GENETIC ALGORITHM AND ARTIFICIAL NEURAL NETWORKS. Dae-Yup Shin, Donghyun Jung, Su-Jin Park, Corporate R&D Ctr., Samsung SDI Co. Ltd., Suwon, KOREA.

Host-guest systems have been widely adapted to achieve sufficiently high luminous efficiency for organic light emitting devices (OLEDs). One of the triarylamine derivatives, CBP has been used as a host for phosphorescent OLED which has attracted a lot of attention due to the high efficiency. But one of the disadvantages of CBP is that they might be easily crystallized by a number of thermal stresses on the OLEDs. For the long lifetime of devices, amorphous states of host materials should be sufficiently stable during OLED operation. Thus, it is required that the host materials of high Tg. We investigated the relationship between molecular structures and glass transition temperatures for 52 triarylamine derivatives (B. E. Koene et al. Chem. Mater. 1998, 10, 2235) which can be used as hosts and hole transporting materials using genetic function algorithm and artificial neural networks. High quality models have been developed for the glass temperature of triarylamine derivatives predicting glass temperature within 10 degree. Genetic function algorithm was used as an alternative to standard regression analysis for constructing QSPR equations. And best subset regression and artificial neural networks were used to construct a prediction equation of QSPR. The constructed and described equation will be used to predict the glass transition temperatures. Field effect mobility of the latter films was about 0.17 cm$^2$/V·s at room temperature and decreased with temperature, indicating that the hopping transport at grain boundaries is dominant. On the other hand, mobility of the film coated by the solid-like but will decrease significantly in the whole range. The charge carrier transport mechanism in relation to crystal morphology will be discussed.

LT50
STUDY ON FIELD EFFECT CARRIER MOBILITY OF ORGANIC THIN FILM TRANSISTORS AT ULTRALOW TEMPERATURE. Hirokazu Tanaka, Hiroyuki Takahashi, Ryo Yamada, Yoshihiro Yamashita.

Much attention has recently been paid to carrier transport in organic thin film-effect transistors (FET). Electrical properties especially at low temperature are of importance to understand the mechanism. We have studied FET characteristics of various organic materials including phthalocyanine and bis-[1,2,5-thiazolo]-p-quinoidim (1,3-di(thiol)) (BTQBT) in the range from 5 to 370 K. It was reported that BTQBT showed very crystal morphology depending on film growth conditions. The films grown on SiO2 at 80°C consisted of needles with a length more than 10μm, while round shaped grains with a diameter of 0.3μm exist on the substrate at room temperature. Field effect mobility of the latter films was about 0.17 cm$^2$/V·s at room temperature and decreased with temperature, indicating that the hopping transport at grain boundaries is dominant. On the other hand, mobility of the film coated by the solid-like but will decrease significantly in the whole range. The charge carrier transport mechanism in relation to crystal morphology will be discussed.

LT51
BLUE LIGHT EMITTING DIODES USING ALKOXY SUBSTITUTED POLY(VINYLFLUORESCENE). S. Jeong, B. Lee, Hye Yong Chae, Hyo Young Lee, Ji Young Oh, Lee Mi Do, Tae Young Zung, Basic Research Lab., ETRI, Daejeon, KOREA; Jejin Lee, Hong Ki Shin, Dept. of Chemistry, KAIST, Daejeon, KOREA.

Polyfluorene has attracted much research interest because of their possible applications to high light emitting material in polymer light emitting devices (PLED). However, troublesome excimer formation upon passage of current was a major drawback for commercial applications. There have been several approaches to overcome excimer formation such as copolymerization and end-capping, but they were not enough to suppress excimer completely. Introducing a sterically hindered spirofluorene into polymer backbone should be one possible method and here, we have synthesized spirofluorene monomer which has alkoy side chains to improve solubility as well as two nyl bromides for polymerization. Poly(3-(6-dioxyk-9,9′-spirofluorene-2,7-diyl) and its copolymer were prepared through Ni(0) mediated polymerization. Photoluminescence (PL) of the homopolymer and copolymer have been measured with thermal annealing time at 150°C under an argon atmosphere and the development of excimer emission has not been observed. The photoluminescence (PL) spectra also exhibited pure blue emission.
somewhat low and then we have prepared the copolymer of 4-butylnylethylsulfonic acid and the above spiropolynitrophenol. The light efficiency has been greatly improved, and the device showed about 10 times higher efficiency than the homopolymer while the CIE coordinate of the emission was almost same to that of the homopolymer. In this presentation, we will explain the detailed preparation method of polymer materials and the device characteristics will be discussed.

SESSION L8: MATERIALS
Chair: Christos D. Dimitrakopoulos
Thursday Morning, April 24, 2003
Salon 1-3J (Marriott)

8:30 AM *L8.1
THE ACENES ROAD TO ORGANIC DEVICES. Hue Duong, Q. Zhang, Hong Meng, Irena Perepichka, Yang Yang and Fred Willi.
Department of Chemistry and Biochemistry and Organic and Macromolecular Materials Institute, UCLA, Los Angeles, CA; Zhenn Bao, Theo Siegrav, Christian Klein and Cheng-Haun Chen, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

We will present our latest results of organic semiconductor devices with newly designed and synthesized molecules. These are members of the acene family, including heteroacenes, containing nitrogen heteroatoms that act as dopable electron-transport layers. We have synthesized substituted acenes (substituts: methyl, methoxy, chloro) as well as usual heteroacenes.

9:00 AM L8.2
OLIGOMERIC AND POLYMERIC TRIPLET EMITTERS FOR LEDS. Albertus J. Sandoe, Nicholas R. Evans, Kay L. Robinson, Andrew B. Holmes, University of Cambridge, Mullvile Laboratory, Cambridge, United Kingdom; Anna Koecher, Richard H. Friend, University of Cambridge, Cavendish Laboratory, Cambridge, United Kingdom.

In recent years the use of inorganic triplet emitters has raised the possibility of harnessing the full electroluminescence energy in organic light emitting diodes. This paper describes the synthesis and photophysical study of a series of solution-processable polymeric triplet emitters. These polymers are hybrid copolymers based on a nitrile-functionalized iridium-pyridylcyclohexadiene complex [Ir(ppy)2]2 trimetallated iridium-fluorene. The objective of the study has been to develop efficient phosphorescent materials that are easily solution-processable. This was accomplished by the attachment of successive fluorenyl segments to the triphenylamino (1,4-phenylamino) at the 4-position of the ligand of a nitrile-functionalized iridium phosphor. It was shown that the stage-wise addition of more fluorenyl repeat units to the phosphor gave rise to a gradual improvement in its yellow-green emission in an OLED device structure. The polymerization to the phosphor was further extended towards the development of a polyfluorenyl phosphor system.

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

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

9:30 AM L8.4
PORPHYRINS AS A NEW CLASS OF SOLUTION-PROCESSIBLE ORGANIC SEMICONDUCTORS. Shuji Aramaki, Mitsui Chemical Corp., Yokohama, JAPAN; Noboru Oto, Ehime University, Dep. of Chemistry, Matsuyama, JAPAN.

Porphyryins have been widely studied because they have unique chemistry and they exist in biological system for special functions, related to its p-electron system. Here, we report tetraceneophoryrin which can be used as n-channel organic transistor properties in the field. Furthermore, the semiconductor film can be formed with solution process. Soluble precursor compound with bicyclic structure forms a thin film by coating. The obtained film is amorphous and shows good film morphology. Then it is converted into an insulating semiconductor film quantitatively at elevated temperature of 150-210°C. Field effect transistors were fabricated by this method. FE-TFT operation appeared only after conversion of the precursor.

10:00 AM L8.5
CONJUGATED WATER SOLUBLE CHROMOPHORES FOR BIOSENSING TECHNOLOGIES: A PRACTICAL METHOD OF AMPLIFIED DNA DETECTION. Brent S. Gaylord, Alan J. Heeger, and Guillermo C. Barman, University of California at Santa Barbara; University of California at San Diego, CA; Bin Liu, Shu Wang, and Chunhui Fan, University of California at Santa Barbara, Chemistry Department, Santa Barbara, CA.

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

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

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

11:00 AM L8.7
POLYMER BRUSHES IN OPTOELECTRONIC DEVICES. Greg L. Whites, William T. S. Hock, Cambridge Univ, Mullvile Laboratory, Dept of Chemistry, Cambridge, United Kingdom; Henry J. Smith, Richard H. Friend, Cambridge Univ, Cavendish Laboratory, Cambridge, United Kingdom.

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

11:15 AM L8.8
A NOVEL STRATEGY FOR THE SOLID PHASE SYNTHESIS OF
ULTRA PURE ORGANIC SEMICONDUCTORS. David Turner and A. Spivey, Sheffield University, Department of Chemistry, UNITED KINGDOM. Domain specific organic functionality is exemplified by the anode, the cathode, and the polyaniline, which forms a conductive surface. The use of single crystal devices is critical for high purity, which is achieved by careful purification of the starting materials. The process has some time-consuming steps, but the ultimate purity of the cleaned devices is critical for success. The method employs a germanium-based linker and explains the advantages of using a double-coupling scheme, as well as the benefits of using a single-coupling scheme.

2:00 PM L9.3 TRIPLET EXCIMER FORMATION IN A MORPHOUS THIN FILMS. Brian W. D’Andrade and Stephen R. Forrest, Princeton University, Dept of Electrical Engineering, Princeton, NJ. Jason Brooks, Alex Alexander, Mark Thompson, Dept of Chemistry, Univ of Southern California, Los Angeles, CA.

Phosphorescent excimers have recently attracted attention for their use in white organic light emitting devices, because they can emit over a wide range of wavelengths, which can be used as a more efficient device. Devices made using this technique have been shown to have a maximum power efficiency of 12.4% at 20kV. The exciton in this system is the phthalocyanine [1], which can be doped with a 3,5-dimethyl-4-phenyl-2,1,3-benzene (mCP) to improve the photoluminescence of the device.

11:30 AM L8.9 HIGH PERFORMANCE p- AND n-CHANNEL POLYMER THIN FILM TRANSISTORS. Simon A. Jendele, Amit Bhow, University of Washington, Department of Electronic Engineering and of Chemistry, Seattle, WA.

Availability of both p- and n-type polymer semiconductors having high carrier mobility will be an important aspect of the future of polymer electronics. The work on polymer thin-film transistors has to date focused on p-type semiconductors due to the scarcity of n-type conjugated polymers with high electron mobility, which is an important issue for the development of polymer electronics. It is important to note that the development of n-type semiconductors with high electron mobility will require a more thorough understanding of the transport properties of these materials.

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

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

1:30 PM L9.1 NANOSTRUCTURED MATERIALS IN ACTIVE ORGANIC DEVICES. Vladimir Balzic, Electrical Engineering and Computer Science Department, Massachusetts Institute of Technology, Cambridge, MA.

Nanostructured integration of organic and inorganic materials into hybrid optoelectronic structures can enable development of active devices that combine the diversity of organic materials with the high performance of inorganic materials and optical properties of inorganic nanocrystals. Optimization of such nanostructured electronic and optoelectronic devices ultimately depends upon the precise positioning of the constituent, functionally distinct nanoscale elements. This talk will describe our recent results of nanoscale device integration, emphasizing the need for developing new nanostructured processes. Application of these methods to development of organic-inorganic heterojunctions and large-scale-planar organic crystals will be described. Repeatability and precision of our recent device work suggests a wide applicability of these new fabrication techniques.

2:30 PM L9.4 ENHANCING PERFORMANCE OF POLYMER LLEDs THROUGH NANOSCALE SELF-ASSEMBLY. James F. Haidasz and Samuel I. Stupp, "Department of Materials Science and Engineering, 3Department of Chemistry, 4Scripps School of Medicine, Northwestern University, Evanston, IL.

The performance of organic electronic devices could be enhanced significantly through the use of self-assembly to control the nanoscale structure of conducting polymer films. We report here on a previous strategy utilizing nanoscale dielectric channels in liquid crystals to control molecular orientation within conducting polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT). This strategy involves confining monomer precursors within the cylindrical
hydrophobic cores of a hexagonal liquid crystal formed in water by the amphiphilic oligo(ethylene oxide) copolymer. By allowing the monomer liquid crystal to self-assemble on an electrode substrate, we can electropolymerize PEDOT within these nanoscale hydrophobic cores to form conducting polymer films that precisely mimic the morphology and optical anisotropy of the liquid crystal template. Films of PEDOT prepared in this way exhibit enhanced optical properties over domains hundreds of microns in size. The thickness and orientation of these domains is controlled by the orientation of the liquid crystal template relative to the applied electric field during polymerization.

Conductivity and charge injection is improved due to alignment of the PEDOT chains. Organic light emitting diodes (OLEDs) prepared using these templated PEDOT films as hole injection layers display increased luminescence and higher injection efficiency. This approach bridges the gap between conventional lithography and molecular self-assembly by orienting polymers within a nanoscale liquid crystal template and self-assembling films of PEDOT, these templated films exhibit high birefringence and exhibit linear dichroism in their optical absorption.

This approach provides a new route for the preparation of high-performance electronic devices. By using electropolymerized PEDOT as an electrode material, we can achieve high conductivity, air stability (without encapsulation), and high current density.

3:30 PM *10.6*
THE USE OF PT AND PT COMPLEXES TO ACHIEVE HIGH EFFICIENCIES IN MULTICOLOR AND WHITE ORGANIC LIGHT EMITTING DIODES. Mark Thompson, Vadim Adamovich, Jack Brown, Bert Alleyne, and Peter Djurovich, University of Southern California, Department of Chemistry, Los Angeles, CA; Stephen Forrest, Brian D’Andrade, and Russel Holmes, Princeton University, Department of Electrical Engineering, Princeton, NJ.

We have fabricated monochromatic organic light emitting diodes (OLEDs). These OLEDs can be fabricated in any color, ranging from blue to red. The key advance in our work is to efficiently utilize all of the excitations created in the electroluminescent process, giving OLEDs with efficiencies close to the theoretical limit of 100%. High efficiencies have been achieved by using phosphorescence-based emitters, which eliminates inherent 25% upper limit on emission observed for traditional fluorescence-based systems. The phosphorescence-based OLEDs have device efficiencies, up to 10%, of organic molecules (i.e., Pt, and Ir). The high level of spin orbit coupling in these metal complexes gives efficient intersystem crossing, leading to strong emissive triplet excited states. We have recently demonstrated white light emitting OLEDs. These devices emit simultaneously from monomer and dimer/eximer states of Ir and Pt dopants. The emission spectrum covers the entire visible spectrum, giving true white illumination. These white light emitting devices give excellent color rendering indices (i.e. 78-80) and high efficiencies (> 6%, 12 lum/W). I will discuss our most recent advances in both monochromatic and white OLEDs.

4:00 PM *10.7*
OPTIMISATION OF CONJUGATED POLYMERS AND PERFORMANCE IN ORGANIC DEVICES. Herman F.M. Schoo, Korrell T. Hockert, Jolanda J.M. Bastiaansen, Albert J.J. M. van Bressem, Ben M.W. Lengeveld-Voits, John A.E.H. van Haren, Peter Herwig, Mieke Koeste, Nicole Kijnen, TNO Institute of Industrial Technology and Dutch Polymer Institute, Eindhoven, THE NETHERLANDS.

The performance of organic semiconductor devices like LEDs, FETs and photovoltaic cells is largely dependent on properties of the organic materials. Factors like crystallinity and, for performance, charge mobility and lifetime are closely linked to material properties. For polymers, the synthetic route and reaction conditions may lead to differences in purity, chemical composition and defect structures. This can cause differences in performance, morphology of polymer films and, ultimately, different device performance. I will give some examples of these relationships.
generally used in Alq3 based organic light-emitting diodes (OLEDs). The surface morphology evolution of the NPb film has been visualized by using variable temperature atomic force microscopy (VT-AFM). It is found that the morphological evolution starts at 60°C, and proceeds until 55°C, and then the evolution remains stagnant until 125°C. This process is very similar to the characteristics of a glass transition. However, as the temperature gradually melts and degrades, leaving completely the exposed underlying layer. The observation on the initial apparent surface glass transition provides a reasonable explanation of the growth findings that the lifetime and luminance reduction is more than one order of magnitude shorter for OLEDs operated at 60°C to room temperature. This is probably due to the fact that a small variation of morphology could be extremely crucial for the change of injection carrier density. The injection carrier number on the orbital overdrive distance of the molecules. The subsequent crystallization may facilitate a complete breakdown of OLEDs. It is suggested that the apparent surface glass transition temperature \( T_g \) be more technically helpful and significant than \( T_g \) to gauge the temperature-dependent luminance and lifetime of OLEDs.


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


Organic field effect transistors (OFETs) show interesting possibilities like cheap production or application as flexible devices (plastic electronics). As active layer oligo(thiophenes e. g. tetrahydrothiophene (4T) and multichain thiophene oligomers in case of organic (O) and mixed (m) electron systems. We present organic field-effect transistors with 4Hlertetrahydrothiophene (DH4T) as active material, a derivative of the Oligothiophene -4T with two hexyl-chains m endgroup. This endgroup substitution makes this molecule suitable not only for vacuum sublimation but also for solution processing which enables cheaper production. First principle calculations of electronic properties yield no significant modification by the alkyl endgroups but structural properties are strongly improved due to higher ordering. Drain and source gold electrodes on top of 200nm SiO2 gate on an highly doped Si wafer produced for channel lengths in the range of 50 μm to 1 μm compare very well with our vacuum-deposited and solution processed 4Hlertetrahydrothiophene (DH4T). The former ones showed typical I-V characteristics and high currents. Temperature dependent measurements of drain-source current show significant variation of charge mobility which are very similar to the behaviour of 3-GT (sexithiophene). While negative gate voltage leads to a band-bias stress of the device due to filling of traps in the accumulation layer, positive gate voltage improves the device behaviour. Therefore the threshold voltage changes, indicating the bias stress shows a shift to higher negative voltages due to trapping of charges.

L10.4 PREPARATION OF NOVEL MACROSTRUCTURES BY ELECTROPOLYMERISATION. P.A. Dyda and D.M. Taylor, Institute of Bioelectronics & Molecular Microsystems, University of Wales, Bangor, Gwynedd, UNITED KINGDOM, D. Lacey, Department of Chemistry, University of Hull, Hull, UNITED KINGDOM, Kogston Department of Chemistry, University of Hull, Hull, UNITED KINGDOM

Electropolymerisation is a potentially powerful technique for electrochemically grafting robust, highly stable nanocrystalline films onto metal surfaces for a wide range of applications including sensors, displays and barrier layers. It is widely accepted [1] that successful electrografting must be preceded by chemisorption of the monomer onto the metal hence electroplexation of the gold film is necessary. Ohno et al. [2], [3], [4], [5] have shown that the gold film is electrografted into the monomer, forming a Au-covalent cross-linked monomer, which is then polymerised to form a gel-like film. This film possesses many desirable properties including excellent chemical, mechanical and electrical properties. Moreover, this film can be electrochemically controlled by applying different potentials. For these reasons, we have carried out a detailed study of the galvanostatic behaviour of the Au film during the electrografting of acrylonitrile to gold and silver and have developed a new technique for the production of such films. This study has provided new insights into the mechanism of electrografting and has led to the development of a new method for the preparation of robust, flexible, highly stable and chemically modified nanocrystalline films, which can be used in a wide range of applications.


Conjugated polymers form an interesting class of materials for photovoltaic devices because of their photo-physical and charge transport properties. Polymer containing bulk heterojunction devices can be divided into three classes: Organic/inorganic hybrid cells, such as polymer/TiO2 and polymer/CdSe composites, form one class. Another class may be defined based on the architecture of the composite polymers with small molecules, as for example blends of conjugated polymers with C60 or perylene-diimide derivatives. This class consists of two conjugated polymers, each with a different light absorption spectrum, which can be defined for a wide range of applications. In the second class, the so-called "passivation peak" in a blend of MDMO-PPV with a cymene-PPV derivative, the EQE increases from nearly 10% to 17% upon a thermal anneal step. This thermal treatment is effective at temperatures higher than the highest glass transition temperature \( T_g \) of either polymer in the blend. This indicates that the morphology of the photovoltaic active layer is one of the key factors with respect to the efficiency of photovoltaic devices. Since for many substituted PVKs, the \( T_g \) is close to the maximum operating temperature of the device, these findings are also important for the development of stable photovoltaic devices that can be used in practical situations.

L10.6 VTSLCE AND 1.55μM QUANTUM DOT ORGANIC LIGHT EMITTING DEVICES. Seth Cee and Vladimir Bulovic, Massachusetts Institute of Technology, Department of Electrical Engineering and Computer Science, and Stavros C. Steckel and Mounir Awadni, Massachusetts Institute of Technology, Department of Chemistry, Cambridge, MA.

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

L10.7 Abstract Withdrawn.

L10.8 HIGHLY RESPONSIVE OPTICAL SENSORS USING PYRENE SURFACE MODIFIED ELECTROSUN MEMBRANES.

Xinyan Wang, Sunhao Yang, Christopher Drew, and Jayant Kumar, Center for Advanced Materials, Departments of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA; Lyndelle A. Samuelson, Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

To date, we have demonstrated that sensors fabricated by electrospraying a fluorophor containing polymer can have 2-3 orders of magnitude higher sensitivities than those from continuous thin films of the same sensing material. The sensitivity of these electrospray sensors was then increased to tens of parts-per-billion detection limits by adsorbing fluorescent conjugated polymers onto the surface of the electrosprayed nanofilms using electrostatic layer-by-layer self-assembly. Here, we report yet further improvement of the sensitivity, reversibility and ease of fabrication of these sensors, by surface modification of electrosprayed nanofilms with a pyrene fluorophor. To fabricate the sensors, the fluorescent indicator, pyreneboronic acid, was covalently attached onto the surface of poly (3-hydroxymethyl methacrylate) electrosprayed nanofilms membranes. This localization of the fluorescent tag to the surface of an already high surface area nanofilms membrane minimized the amount of inactive (embedded) fluorescent indicator, and resulted in significantly improved sensitivities and reversibility compared to similar systems in which the fluorescent polymer was dispersed throughout the electrosprayed nanofilms and allows for more direct control over the concentration of fluorophore used. The fluorescence of these films can be quenched by extremely low concentrations of cationic electron acceptors in aqueous solutions. The high sensitivity is due to the large surface area to volume ratio of the films and improved contact between the quenchers and the fluorescent indicator. The quenching behaviors of these sensors to methyl viologen (MV2+), and metal ions (Fe(3+) and Hg(2+) ) follow Stern-Volmer bioluminescence quenching kinetics, with the sensitivities in the range of a few parts per billion. The fabrication, characterization, and fluorescence quenching properties of the sensors will be presented.

L10.9 METAL OXIDE POLYMER NANOSTRUCTURES.

Christopher Drew, Xin Nian Wang, and Jayant Kumar, Center for Advanced Materials, Departments of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA; Ferdinando F. Bruno and Lyndelle A. Samuelson, Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

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

L10.10 SELF-ASSEMBLY OPTICAL COMPONENTS. Pavel Luznev, Michael Paskhato, Elena Sidorenko, Oprim, Inc., South San Francisco, CA.

Oprim has developed a unique Thin Crystal Film (TCF) technology enabling breakthrough optical components for a wide range of applications. TCF technology is based on innovative self-assembling disulphide bonded micelles which can be printed and then dry in a highly ordered crystalline film. TCF are produced by deposition of water based hydrophobic liquid crystal formed by rod-like supramolecules of heterocyclic sulfuric acids. The supramolecules having thioamine structures form a structure ratio of 1:1 form by Van der Waals interactions between disk-shaped molecules. In the course of deposition shear force is applied and the supramolecules are aligned along the shear force direction in a wet layer about 10 microns thick. While drying, the layer crystallizes to a sub-micron thick semi-crystalline thin film functional layer with dichroic dye molecules aligned over the entire coated surface. The coatings exhibit properties of birefringent film polarizer. The planar anisotropy of reflection and absorption indices induce the TCF to attract the most attention in LCD and OLED related applications. This presentation will provide an overview of TCF technology and will describe material structure, optical properties and characterization, material processing and associated coating equipment.

L10.11 CONNECTING POLYMERS BASED SUPRAMOLECULAR FILMS FOR GAS SENSORS. Munej Kumar Ram, Osten Yevuz, Matt Aldkins, Fractal Systems Inc, Safety Harbor, FL.

Gas sensors based on metal oxide sensing layers, and in particular SnO2 and WO3, are known to be widely used for the measurement of CO, CO2, aromatic hydrocarbon, NO2 but sensors do not primarily exhibit selectivity towards any of these species in general, and operates at a high temperature. Though a certain degree of selectivity is obtained by forming arrays of sensors but still lack selectivity at ambient humidity. To overcome stability, selectivity, portability and cost problems, we have initiated to develop gas sensors based on ordered ultrathin conducting polymers and nanocomposite films that we have previously proven to perform efficiently and selectively within seconds of exposure to gases. The present work focuses on the use of highly organized conducting polymer films with high conductivity, and for/without films of conducting polymer/SnO2 nanocomposites, which will selectively recognize NO2 and CO gases with ph sensitivity. The supramolecular approach will be utilized to fabricate films of conducting materials via the layer-by-layer self-assembly technique to emphasize sensitivity and selectivity issues that are otherwise unattainable with other fabrication methods or microstructures. We have prepared and characterized several polymers, fabricated thin self-assembled films with different layer thicknesses in each polymer-coating process and tested the effect of the number of layers on film properties relative to gas sensing. We have used several characterization techniques to prove feasibility of our approach, including conductivity, impedance, UV-Visible, FTIR, AFM and elemental analysis. With the expected high selectivity and low detection limit and versatility of the measurement procedure, our work will result into a miniaturized device.

L10.12 INFLUENCE OF LOCAL ORDER AND MOLECULAR POLARITY STRENGTHEN THE DISPERSION OF EXCITONIC ENERGIES IN ORGANIC THIN FILMS. Cesar Medina, Vladimir Bulovic, Massachusetts Institute of Technology, Department of Electrical Engineering and Computer Science, Cambridge, MA.

It has been proposed that disorder in organic thin films should lead to dispersion of the molecular energy levels. We recently reported the direct measurement of this dispersion in excitonic energies for [3-ethyl-6-[2-[2,3,6,7-tetrayano-3H,3H-benzene-1,1-diylidene-propyl]-6H-prymyl-4,4dibene] (DCMTW), deposited in films of varying thickness levels in organic thin film materials exists in the literature. In this presentation we apply our technique to a range of technologically important photoluminescent organic materials (including iridium [bis(tri-4-phenylpyridine)1-18]). We study the influence of molecular properties and molecular packing on solid state exciton dispersion using spectroscopic techniques. We find that the two most important material parameters are the local ordering of molecules and the strength of the molecular electric dipole (i.e. the molecule’s polarity). Our data show that increasing local order increases w_e, while increasing polarity increases w_P. Since highly molecular dipoles tend to aggregate (and thereby locally order), some highly molecular materials can also yield films with small w_e. However, for non-polar molecules, a small w_P can be predicted that w_e is negligible regardless of the degree of local order.
L10.13  CHARGE INJECTION IN DOPED ORGANIC SEMICONDUCTORS. Yuk Song Shen, Man Hoi Wong and George G. Malliaras, Department of Materials Science & Engineering, Cornell University, Ithaca, NY; Bing Hsieh, Xerox Corporation; David Dunlop, Department of Physics and Astronomy, University of New Mexico.

A study is done to understand the dependence of injection on the degree of doping of an organic semiconductor. A model organic semiconductor, N,N,N',N'-tetraphenyl-1,1'-biphenyl-4,4'-diamine (PTPD) was used for these experiments. By substituting TPD molecules with a TPD(4)-S-S-4-TPTPD, the degree of doping in the organic semiconductor was systematically varied. Changes in the electrical characteristics of various devices with varying doping levels were analyzed to yield the dependence of injection on the degree of doping. Along with the doping concentration, the temperature and distance between electrodes was also varied. This provided a better understanding of how doping, temperature and electrode spacing affect device performance.

L10.14  PHOTOEMISSION SPECTROSCOPIC AND THEORETICAL STUDIES OF THE FRONTIER MOLECULAR ORBITALS OF QUINQUETHIOPHENE DERIVATIVES. Gary P. Kuselko, Ian G. Hill and Zakyn H. Khalfi, U.S. Naval Research Laboratory, Washington, DC, Ulrich Mitschle and Peter Blunier, University of Ulm, Ulm, GERMANY.

Thiophene oligomers represent a class of materials whose electronic properties can be tuned through control of the n-conjugation length, side or main chain derivatization. The effect of substitution of the central thiophene ring by a furan, an oxazole or a p-methyl thiophene at position 2 was investigated using ultraviolet (UPS) and x-ray (XPS) photoemission spectroscopies. ab initio and semiempirical calculations have been carried out to aid in the characterization of the electronic properties of these materials. These thiophene oligomers are highly luminescent when dispersed in organic hosts. When incorporated as the active emissive layers in molecular organic light emitting devices (MOLEDs) they exhibit interesting carrier trapping effects as well. The results of the photoemission spectroscopic and ab initio studies conducted on these thiophene derivatives will be reported, and their relevance to the operational characteristics of MOLEDs based on them will be discussed.

L10.15  ELECTRONIC PROPERTIES AND DEVICE APPLICATIONS OF CRYSTAL ENGINEERED ACENES. John Anthony, Chad Landis, Marcia Payne, Susan Odum, University of Kentucky, Department of Chemistry, Lexington, KY.

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

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

We have investigated the response of our organic polymer thin-film transistors (OP-TFTs) to illumination. The structure of the device is an inverted, gate-planarized, coplanar thin-film transistor. Indium tin oxide was used for the source and drain contacts and tin-doped silicon nitride was used for the gate insulator. The organic semiconductor F8T2 (poly(9,9-dioctylfluorene-co-bithiophene) was deposited by spin-coating. These devices exhibit p-type field-effect transistor behavior. Typical values for the linear regime are field-effect mobility, threshold voltage, and subthreshold swing. The characteristics of our devices in the dark and under various levels of illumination at room temperature. The device OFF-current is increased significantly under illumination, while the ON-current is not significantly affected. The ratio of drain current under illumination to drain current in the dark can be defined as \( R_{on, ill} = \frac{I_{D, ill}}{I_{D, dark}} \) and is a function of the OP-TFT gate voltage \( V_G \) and the illumination (IL). In the strong accumulation regime, \( R_{on, ill} \) decreases because the gate voltage is on but the concentration of accumulated carriers. In the OFF-state, \( R_{on, ill} \) can reach two to three orders of magnitude depending on the level of illumination, and is not strongly dependent on \( V_{G, ill} \).

L10.18  ELECTRO-OPTICAL PROPERTIES AND INTERFACIAL CHARGES IN POLYMER-DISPERSED LIQUID CRYSTALS. J.A. Barnsley, S.C. Sharratt, R.M. Henry, and J.B. Attnoe, Department of Physics, University of Texas at Arlington, Arlington, TX.

Polymer-dispersed liquid crystal (PDLC) is a composite material that consists of sub-micron-size droplets of liquid crystal (LC) material dispersed in a polymer matrix. A device is usually assembled by sandwiching PDLC between ITO-coated glass plates. The electro-optical properties of such a device can be controlled by the application of electric fields, and these fields act as a means for the transmission of light. The transmission of light through the device can be controlled by applying an electric field to the LC droplets. The dielectric properties of the LC and polymer, shape and size distribution of the LC droplets in the PDLC, and orientation of the electric field are among the important parameters for optimizing the performance of such a device. We have investigated the optical properties of PDLC devices fabricated by using several different phase-separation techniques and different LC/polymer materials. We present results for the switching characteristics of these devices as a function of electric field and size distribution of the LC droplets. We also present results that reinforce the influence of the interfacial charges on the optical properties of the PDLC devices. Research supported, in part, by the Texas Advanced Technology Program under Grant No. 00365651-012-2001.

L10.19  IMPROVING INTERFACES AND SEMICONDUCTOR MATERIALS FOR OFETs: AN INVESTIGATION OF NOVEL PHENYL CYANENE AND SURFACES MODIFICATION. Carol L. Donley, Rebecca A.P. Zangmeister, Wei Xin, Anthony S. Dinges, Brett Minle, David F. O'Brien, Neal R. Armstrong, University of Arizona, Department of Chemistry, Tucson, AZ.

New organic field effect transistor (OFET) and photovoltaic (PV) technologies will require easily processed materials which demonstrate high charge mobilities and microtubules in those materials (OFET applications), properties which are often found in high order, semiconducting materials, known as Pcs. We have studied a series of organic substituted phthalocyanines (Pcs) with a benzyl termination of the side chains linked to the Pcs. The benzyl termination imparted unique stability and coherence to films of this molecule made on a Severn Blight test film. Films of these materials are transferred to substrates by a horizontal transfer technique, and it has been shown that surface modifications are critical in obtaining well ordered films. We have measured charge mobilities in these thin films on two length scales using interdigitated microelectrodes and a tunneling AMF (TUNA) system. Currents measured by the TUNA system are taken on a nA resolution scale, and the film's charge mobilities are greater than 0.1 cm²/V·sec⁻¹, and microtubules in mobility of up to 1000 for a benzylhexyloxy CuPc. The thiol version of this material also has been characterized, and it seems to show different type of aggregation in thin film than the alkylated Pcs. The thiol has been incorporated into some PV cells, and the characteristics of these devices will be reported briefly here and in complete detail in a
accompanying paper for this symposium. We have also investigated a new azobenzene group that contains a nitroxy radical in the side chains of an azo-thiophene polymer. This feature allows us to lock the molecules into place, and renders this molecule insoluble, allowing for photopatterning of thin films of this material. Molecular recognition for this polymer material on interdigitated microelectrodes was higher than that for the benzylmethoxy parent molecule.

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

We use solvent vapor annealing to facilitate molecular recognition in thin films of organic small molecules. In the case of tria-8-hydroxyquinoline aluminum (AlQ3), this recognition is dramatic, yielding needle-like crystals in the plane of the substrate from initially amorphous thin films. Furthermore, we demonstrate that nano-patterned substrates can control the orientation of the needle crystals, which can reach millimeters in length. The formation of such large area crystals directly on substrate surfaces and electronic devices enables the design of devices using organic electronics. Using optical interference lithography we generate periodic patterns over square centimeters with feature sizes ranging from 100 to 500 nm. The patterns are transferred to silicon substrates via etching, resulting in surface relief gratings with periodicities from 150 to 10 nm. AlQ3 is vacuum evaporated onto the nano-gratings, and the films are subsequently annealed in chloroform vapor. The resulting AlQ3 needle-like crystals are oriented along the grating direction. Larger needles span several grating periods, but needles confined to a single grating trough are also observed. Needle thicknesses exceed the initial AlQ3 amorphous film thickness by as much as 200 times and the grating depth by as much as 30 times. Typical thickness with length ratios are 1:2000, and a common needle thickness is 500 nm. Larger needles are segmented and tend to split and branch, but can be as long as several millimeters. Characterization by AFM and SEM reveals terraces and facets at needle surfaces and tips. We have obtained fluorescent excitation spectra of the AlQ3 crystals and observed waveguiding down the length of the needle in agreement with AFM data. We will report the influence of initial amorphous film thickness, annealing time, nano-grating dimensions and chemical surface modifications on needle formation, and discuss the utility of the needle crystals in active device structures.

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

Cathode deposition is a crucial issue for top-emitting OLEDs, due to the induced damage to the underlying organic layers caused by sputtering techniques. The critical effect on device performance and reliability of the sputter damage to the organic layer is well known. Efficient and stable TOLEDs have been produced by the insertion of buffer layers beneath the sputtered deposited cathode. The efficacy of the buffer layer has shown mixed results with different materials, indicating that the relation between damage and device performance is not clear. To examine the effectiveness of these layers, X-ray photoelectron spectroscopy (XPS) characterization of the cathode/organic interface was undertaken on working OLED devices with varying buffer thickness. Using a previously developed in-situ peckoff method, the XPS study allowed a direct comparison between observed electrical performance degradation and molecular breakdown at the interface. The limits to the XPS technique, sputtering damage was determined though correlation of the observed N1s splitting, indicating molecular breakdown, with the reduction in device electrical performance.


Pure near-infrared electroluminescence (no residual visible emission) from a number of conjugated polymer host/guest blends has been realized. The polymer hosts include blue, green, and red emitters. The guest molecules include novel infrared-emitting lanthanide complexes and conjugated oligo[(phenyl)azine] molecules.

The first system makes use of a novel eribium complex doped into a stable green emitting conjugated polymer host. The ligand incorporation of a pentaerythritol, and a dipyridine unit, allows us to lock the molecules into place, and renders this molecule insoluble, allowing for photopatterning of thin films of this material. Mobilities for this polymer material on interdigitated microelectrodes were higher than that for the benzylmethoxy parent molecule.

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

Surface tethered alpha-helical poly(γ-methylbenzyl-L-glutamate) (PBLG) films demonstrate excellent liquid crystalline, electrooptical, and electron-mechanical properties due to the non-conformable dipole moment contributed by individual helical rods. The polar molecules have been indicated that such films consist of randomly distributed molecular rods with average tilt angle of 33°-65° from the surface normal. It is believed that a unidirectional molecular arrangement on such films would be more desirable to produce novel optoelectronic features not only the highest net dipole but also the organized functional groups at a nanoscale. Here we report a simple quenching method to allow PBLG helical rods along the molecular direction. In this method, a highly oriented tethered PBLG film was prepared by first immersing in a good solvent such as N,N-dimethylformamide, followed by a poor solvent such as water. In a good solvent, the tethered chains are fully stretched to the maximum molecular-solvent interactions; subsequently, a poor solvent was quickly introduced to preserve the fully stretched surface morphology. The grazing incident FTIR studies indicate that the proposed method successfully erect the helical rods with the resulting average tilt angle of 33°-65° from surface normal. The change of tilt angles coincide with the increase of overall film thickness from 55 nm [NF = 1.56] to 165 nm [NF = 1.27] detected by ellipsometry. Atomic force microscopic images of the films further confirmed the thickness measurements, in addition, revealing that the surface morphology changes from a relatively smooth and amorphous topography to a periodic, complex surfaces after quenching. The quenched surface contains lower surface energy as evidenced by the increase of water contact angle from 30° to 110°. The molecular orientation of the quenched films was found to be very stable for months. In summary, this quenching method might offer a simple methodology applicable to creating other highly oriented polymer surfaces.

L10.24 Abstract Withdrawn.

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

Simple measurements of linear or saturation mobility in polymer transistors can often be misleading because of non-ideal TFT characteristics. The complete current-voltage characteristics of polymeric thin film transistors (TFTs) must be evaluated to understand the physical mechanisms of electronic transport and to obtain the mobility. We have investigated the effects of device geometry on the performance of TFTs fabricated with a regioregular poly(thiophene), (PT). For example, the apparent field-effect mobility of a PT film can vary from 10 to 100 cm2/V·s depending on the device size and contact geometry. We have tested the contact effects by fabricating TFTs with both staggered and coplanar contact geometries in a single device, allowing contact resistance differences to be measured by reversing the device polarity. We also observe the dependence of the extracted saturation mobility on source-drain voltage. The apparent saturation mobility of these PT films can be as high as 0.7 cm2/V·s with high drain voltages in short channel devices. Measurements of output characteristics at channel lengths from 5 to 50 μm confirm the short channel effect. We discuss
the evidence for an actual drain-field dependent mobility based on a model for the short channel effects. The implications of these results for characterization of the intrinsic properties of polymeric semiconductors will be discussed.

L10.26 POLARIZED ELECTROLUMINESCENCE FROM LIGHT EMITTING DIODES CREATED BY SELF-ASSEMBLY AND ELECTROPHORESIS. Leiming Li, Keisuke Tajimin, John C. Stendahl, Eugenie Z. Zaluzew, and Samuel I. Stupp, Department of Materials Science and Engineering, Feinberg School of Medicine, Northwestern University, Evanston, IL.

Our laboratory developed self-assembling triloblock molecules known as dendrimer rod-coil dendrimers that can form lamellar-like segments. In certain solvents such as chloroform or 2ethylohexyl methacrylate these molecules self assemble into long nanoribbons. These nanoribbons can have lengths of about 10 micrometers, a thickness in the range of 5 nanometers and lengths on the order of microns. Their formation leads to the three dimensional network and therefore gelation of dilute solutions of these molecules. We have found that electrophoresis occurs in DRC gels subject to a DC electric field, creating solid films consisting of DRC nanoribbons oriented preferentially along the poling direction. We have also dissolved small molecules containing conjugated phenylene vinylene segments in DRC gels and exposed these systems to DC electric fields. This process leads to thin films of unidirectionally oriented DRC nanoribbons and luminescent phenylene vinylene molecules. Light emitting diodes (LEDs) were fabricated by sandwiching the films between ITO and aluminum electrodes. Interestingly, we found that electroluminescence (EL) from these LEDs is nematicol, with a parallel EL component (parallel to the poling direction) stronger than that perpendicular to the electric field. EL was found to be isotropic from LEDs containing spin-coated films using the same molecular components.

L10.27 STRUCTURAL CHARACTERIZATION OF ROD-LIKE AGGREGATE LIQUID-CRYSTALLINE PHTHALOCYANINE FILMS BY X-RAY REFLECTIVITY AND DIFFRACTION. Wei Xin, Michael D. Carducci, Carrie L. Donley, and Neal R. Armstrong, University of Arizona, Department of Chemistry, Tucson, AZ.

Cerium phthalocyanines (Pc) modified with benzylterminated ethyleneoxide side chains, and their thio-ether counterparts self-organize into rod-like columnar aggregates with a high degree of optical and electrical anisotropy. This paper focuses on the characterization of horizontally transferred LB films of these PCs, using AFM and specular X-ray reflectivity, starting with a single bilayer of Pc columns (ca. 5.6 nm thickness) on Si(100) substrates. For multilayer films, which have been amened, the width, position and of the Bragg peak in the X-ray reflectivity data is consistent with a dense, regular, hexagonal close packed adjacent rods. For 1- and 2-bilayer films, however, these are shifts in the Bragg peaks, and associated changes in the reflectivity data with molecular packing structure for those molecules closest to the Si(100)-oxide interface - Chemical modification of these interfaces helps to control the initial ordering in these films. Understanding of this interfacial structure is critical in determining which controls the electronic properties of these initially deposited materials (e.g. in organic field-effect transistors).

L10.28 CHARACTERIZATION OF HIGH-PERFORMANCE F4T4CuPc-BASED ORGANIC THIN-FILM TRANSISTORS WITH ALKALI FLUORIDE-MODIFIED ELECTRODES. J. Reynaert, Y.D. Jin, G. Borghs, R. Metens, P. Hermans, IMEC, Leuven, BELGIUM.

Phthalocyanines have been extensively studied among organic semiconductors for their photovoltaic properties [1]. Copper(I)trifluoroethyphthalocyanine (F4T4CuPc) is an airstable material with high mobility at low doping [2]. We report the dielectric and conductivity properties of copper(I)trifluoroethyphthalocyanine (F4T4CuPc)-based n-channel organic thin-film transistors (TFTs). We achieve high mobilities of the order of 10^{-2} cm^2 V^{-1} s^{-1} when using intensively purified material and optimized growth conditions of the organic films. We fabricated freestanding structures grown on glass and different substrates with different source/drain electrodes: bare aluminum, gold, LiF/Al and LiF/Au. We deduce the electron injection properties of these different materials into F4T4CuPc from the electrical performance of these transistors. In contradiction to [3], we report well-behaved field-effect and high mobilities (~10^{-2} cm^2 V^{-1} s^{-1}) for n-channel F4T4CuPc-TFTs with bare Al and Au electrodes. Furthermore, we correlate these results to the change of electron injection measurements on PEDOT:F4T4CuPc structures, which allow to measure the electron injection barrier at the organic/metal interface [4].


L10.29 CHARACTERIZATION OF THE BUILT-IN POTENTIAL OF POLYMER SOLAR CELLS AND LIGHT EMITTING DIODES BY ELECTROABSORPTION SPECTROSCOPY. J. Reynaert, V.D. Juillet, A. Amsterdam, W. Genoe, G. Borghs, R. Metens, P. Hermans, IMEC, Leuven, BELGIUM.

The performance of organic light emitting devices (OLEDs) and organic solar cells (OSCs) is governed by injection of charge across an ultrathin interfacial layer of LiF between the polymer and the air-stable cathode [1,2]. Electro-absorption measures the built-in potential (Vb) across the photo-active organic film within OLEDs and OSCs. In OLEDs based on PDMPS, we found that Vb is between 1.5 and 1.6 eV when LiF is inserted between the polymer and the Al cathode. The change in built-in potential is attributed to LiF being liberated from LiF in the presence of Al and diffusing into the polymer. LiF serves as n-dopant for the polymer at the interface and hence facilitates the formation of an Ohmic contact at the cathode/polymer interface [3]. The solar cells consist of a blend of C60-derivative (PCBM) and MDMO-PPV polymer. The Vb increases by 0.6 eV upon insertion of a LiF interfacial layer between the blend and the Al cathode. Because of the presence of PCBM, Fermi-level pinning is occurring [4]. This is confirmed by electro-absorption characterization of pristine PCBM devices.


Optical properties of organic dye molecules incorporated in inorganic matrix materials by high vacuum co-evaporation are reported. The aim of this work is to create a system which is applicable in luminescence conversion devices as a thin layer. The dry vacuum technology offers a fundamental progress in the practical handling and technical expenditure. Furthermore, organic dyes principally allow a big variety of both the n and p electron density with a different packing structure for the breakthrough of solid state organic systems are the quantum efficiency and the photo stability. Our results show that such systems can meet the requirements of practical applications. We present results about (i) different organic dyes (such as phthalocyanines, AQ3, ...), (ii) different matrix materials (SiO2, TiO2) and (iii) the influence of different preparation techniques on the optical properties. Compared to earlier investigations, relatively high dye concentrations can be reached without loss of quantum efficiency by varying the preparation technique. This behavior results in highly absorbing layers even at low thickness.

L10.31 PHOTOSYNTHETIC AND ELECTROLUMINESCENT PROPERTIES OF RANDOM AND STRUCTURALLY DEFINED COPOLYMERS BASED ON POLY(FLUORENE-CO-BENZOTHIAZOLE). Polychlorothiophene, Xiaoxiang Jiang, Michelle S. Lee, Arizona-Y. Jen, University of Washington, Department of Materials Science and Engineering, Seattle, WA.

Copolymers based on fluoresce and benzo[1]thiophine exhibit high brightness and quantum efficiencies when incorporated into polymer light-emitting diodes (PLEDs). The emission wavelength is strongly determined by the benzo[1]thiophene content ratio of the polymer. In order to understand the underlying mechanisms of charge transport and energy transfer, a series of polymers with different fluorene/benzo[1]thiophene ratio were made. Even a fraction of as low as 1% of benzo[1]thiophene shift the emission of the polymer from blue to yellow to green. The low to high benzo[1]thiophene required for wavelength tuning ranges from 10 to 30% for other properties necessary for device improvement. The charge transport properties can be altered by incorporating a third component structure. Polymers incorporating fluoresce, benzo[1]thiophene and a third monomer - e.g.
diakoxypheynyl were synthesized. In a random copolymerization the order of monomers in the structure cannot be predicted. In order to investigate the effect of monomer sequence on the luminescence and device properties, we have synthesized a series of copolymers with structures of known sequence. A third commoner was chosen from a variety of electron-rich molecules. The properties of the structurally defined copolymers were compared to the properties of the randomly copolymerized ones with the same monomer ratios. In order to evaluate the device performance of these copolymers, double-layer devices with the general structure of ITO/HTL/Polymer/Cl/Ag were fabricated. The results show that the monomer sequence in the polymer chain does not affect the electo- and photo-luminescent properties of the copolymers, but the device performance is strongly dependent on the sequence.

L10.32
ORGANIC POLYMER DEVICES BASED ON SUPER-YELLOW POLYMERS. J. Kowalczyk, M. Puchard and A. Hoeger, Center for Polymers and Organic Solids University of California, Santa Barbara, Santa Barbara, CA; S. Martin and Y. Hong, University of Michigan, Department of Electrical Engineering and Computer Science, Solid-State Electronics Laboratory, Ann Arbor, MI.

We have investigated electrical properties of the organic polymer thin-film transistors (OP-TFTs) based on phenyl-substituted PPVs (known as super-yellow polymer). This organic polymer is also widely used for organic polymer light-emitting devices (PLEDs). The structure of the OP-TFT is an inverted co-planar thin-film transistor with defined planarized Cr gate using benzocyclobutene (BCB). Indium tin oxide (ITO) was used as the source and drain contacts and amorphous silicon nitride was used as the gate insulator material. The organic semiconductor (super-yellow polymer) was deposited by spin-coating over the source drain contacts and device was annealed at 100°C in nitrogen. The resulting TFT channel length and width range from 0.66 to 696 and 56 to 116 mm, respectively. Electrical performances of our devices were extracted using the MOSFET equations. We typically obtained for our devices the field-effect mobility, sub-threshold slope, on/off current ratio of about 2 ± 10 cm²/Vs, -50 V, and - 5 V/dec, respectively. Similar results have been obtained for Dow Chemical red and green light-emitting organic polymers that have been previously described. We also found that the field-effect mobility and on/off ratio were channel length independent. To investigate the possibility of fully integrated optoelectronic organic circuits made from the same organic material and at the same time, we have fabricated the organic polymer light-emitting devices (PLEDs) from the same material. The PLED had a high brightness (>1,500 cd/m² at 8V), a high emission efficiency (>5 cd/A at 900 cd/m²) and a good power efficiency (>5 lm/W at 900 cd/m²). Based on our results we can argue that the best PLED materials will not necessarily produce the best OP-TFTs. The implication of these findings for optoelectronic organic circuits will be discussed.

L10.33
CREATION OF A GRADIENT POLYMER-FULLERENE INTERFACE IN PHOTOVOLTAIC DEVICES BY THERMAL MIXING. A. Deppe, M. Hoogenboom, M. Drees, W. Graugger, K. Preiber, M. H. Helfen, Dept. of Physics, Virginia Tech, Blacksburg, VA; D. Toppan, M. Miller, Luna Innovations, Blacksburg, VA; R. M. Davis, Dept. of Chemical Engineering, Virginia Tech, Blacksburg, VA.

Efficient polymer-fullerene photovoltaic devices require close proximity of the two components to ensure photoexcited electron transfer from the semiconducting polymer to the fullerene acceptor. We describe studies in which a bilayer system consisting of spin-cast 2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene copolymer (MEH-PPV) and sublimed C₆₀ is heated above the MEH-PPV glass transition temperature in an inert environment, inducing an interdiffusion of the polymer and the fullerene layers. With this process, a controlled, bulk heterojunction is created bringing the fullerene molecules within the exciton diffusion radius of the MEH-PPV throughout the film to achieve high efficiency charge separation. The interdiffused devices show a dramatic decrease in photoluminescence and coincident order-of-magnitude increase in short circuit current, demonstrating the improved interface. We also observe that the spectral photocurrent of the MEH-PPV/C₆₀ bilayer system, measured to the short optical penetration depth at the peak of the PPV absorbance, is eliminated following the interdiffusion process. Detailed studies of the effects of the interdiffusion on MEH-PPV thicknesses and the time-temperature profile of the heat treatment on device efficiency will be presented, along with transmission electron microscopy and Auger spectroscopy investigations of the nanoscale film composition.

L10.34
DESIGN AND SYNTHESIS OF DIVALENT OSMIUM COMPLEXES

FOR USE IN ORGANIC LIGHT EMITTING DIODES. Brendan Carlson, Chemistry Department, University of Washington, Seattle, WA; Larry Dukson, Chemistry Department, University of Washington, Seattle, WA; Joo Hyun Kim, Department of Materials Science and Engineering, University of Washington, Seattle, WA; Alex K-Y. Jen, Department of Materials Science and Engineering, University of Washington, Seattle, WA.

There is considerable interest in the use of organic electroluminescent (EL) devices due to their potential application in low-cost, light-weight, easily transportable flat-panel displays. In this purpose new complexes of divalent osmium have been synthesized for use in luminescent organic light emitting devices (OLEDs). 4,4-di(2-methyl-1,4-phenylenevinylene) derivatives were synthesized from o-nitrobenzaldehyde and 3-chloro-1,4-phenylenevinylene, and two equivalents of the ligand ([NN]) were reacted with potassium hexachloroantimonate to give an intermediate of Os([NN])₂Cl₂. One equivalent of a bidentate strong p-nitro ligand ([L]), cis-2,3,9,10-tetrahydrophenanthrene, or cis-1,2,6-tris(diphenylphosphine)ethylene, or 1,2,3-tris(diphenylphosphine)ethylene, was reacted with Os([NN])₂Cl₂ to give a general formula of [Os(II)] [([NN])₂(L)]²⁺ for the luminescent compounds. These molecules of divalent osmium feature strong spin allowed and spin forbidden MLCT absorption bands in the visible region and strong red phosphorescent emission ranging from 612 nm to 651 nm. Relative photo-luminescent quantum yields have been measured as high as 45% and phosphorescent emission lifetimes as fast as 400 ns. Red light emitting diodes (LEDs) were successfully fabricated by doping the divalent osmium complexes into poly(N-vinylcarbazole) (PVK) and (2-tert-butylphenyldiphenylene-1,3,4-oxadiazole) (PKV PB) or poly(2,5-naphthylbenzene) (PNNPB) host materials. Brightness over 1,400 cd/m² for double layer has been reached, with a turn-on voltage of 4.5 V. The maximum external quantum efficiency was measured to be 2.2%. Commission Internationale de l’Eclairage (CIE) chromaticity coordinates (x, y) of the red electroluminescence from the complexes are (0.65, 0.34), which indicates pure red emission.

L10.35
EFFECT OF THERMAL CYCLING ON PERFORMANCE OF POLY(3-HEXYLTHIOPHENE) TRANSISTORS. Brian Martin, Paul Chung, Vaneckubman, UC Berkeley, Dept. of Electrical Engineering, Berkeley, CA.

Semiconducting polythiophene films, with their room-temperature solution-based deposition methods, have become attractive for low-cost electroluminescent applications, while they may potentially be printed on plastic to enable ultralow-cost read-to-reel circuit fabrication. While there have been numerous demonstrations of polythiophene-based TFTs to date, there have been few systematic studies on the thermal stability. This is a particularly important topic, since numerous associated low-cost process modules, including annealing of nanocrystal interconnects and immobilization of polythiophene derivatives will result in the exposure of polythiophene to elevated temperatures. Secondly, studies of thermal cycling provide crucial insights into the operational life and stability of these devices. Furthermore, there are few studies on the effect of thermal cycling as a means of improving polythiophene characteristics. We report upon the effects of thermal annealing upon regioregular Poly(3-hexylthiophene). We observe substantial mobility improvements in devices annealed at low temperatures (-80°C), as well as increases in on/off ratios by as much as two orders of magnitude at moderate annealing temperatures (-120°C). Furthermore, we also study the impact of extended temperature excursions on device performance, extracting maximum process and storage temperature limits. The studies document changes in conductivity, mobility, on current, and on/off ratios with anneal conditions varying in both temperature and thermal budget. In conjunction with material analysis studies, we develop qualitative models for the probable physical mechanisms involved in the annealing / degradation processes. The dedoping of the semiconducting film, as well as its irreversible deterioration as anneal temperatures approach the melting point is described. Hence, this study provided a comprehensive analysis of the performance of polythiophene TFTs to maximize various device performance metrics, and also identifies thermal limits and failure mechanisms for the same.

L10.36
ORGANIC ELECTROLUMINESCENT DEVICE BASED ON FLUORINATED EUROPINIUM COMPLEX. Gregory D. Phelps, Chemistry Department, University of Washington, Seattle, WA; Brenda Carlson, Chemistry Department, University of Washington, Seattle, WA; Larry Dukson, Chemistry Department, University of Washington, Seattle, WA; Joo Hyun Kim, Department of Materials Science and Engineering, University of Washington, Seattle, WA; Alex K-Y. Jen, Department of Materials Science and Engineering, University of Washington, Seattle, WA.

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Europium complexes may be used as a source of red emission in light emitting diodes (OLED), and several novel europium doped complexes have been synthesized and incorporated into organic OLEDs. These complexes are of interest due to their narrow (FWHM ≈5 nm) emission at 615 nm, which is ideal for red OLED devices. The europium complexes consist of one equivalent of europium doped to three equivalents of a nonemissive trivalent diketonate ligand. The ligands are created by the Chaisan condensation of a polyyclic aromatic amine and a fluorinated alkyl ester of a carbocyclic acid. The use of a sensitizer such as phenanthrene results in a ligand that has an emission band that closely matches the emission band of europium. The use of fluorinated chains improves the overall processivity as well as the charge transfer capability of the resulting diketonate complexes. The europium core is further encapsulated by the inclusion of an additional polyyclic aromatic compound such as 4,7-diphenyl-1,10-phenanthroline. Emission of 615 nm light is accomplished through excitation of the ligand cage and efficient Forster energy transfer from the ligands to the europium complex. Red light emitting diodes (LEDs) were fabricated by doping the europium complexes at 5 weight percent into poly(N-vinylcarbazole) and 2-tetra-2-butylyphenyl-5,6-bis(3,5-dioxy-1,4-dihydro-1H-pyran-2-yl) phenanthrene (PVK-PBD) or poly(3-vinyl naphthalene) (PVN-PBD) host materials. Brightness of 215 cd/m² with a turn-on voltage of 5.6 V and efficiency of 0.60% has been reached for double layer devices.

L10.37
HIGH EFFICIENCY POLYMER LIGHT EMITTING DIODES
Michael Kreger, Sue Carter, Physics Dept. University of California, Berkeley, CA, Lusine Barzana, Campbell Scott, IBM Almaden Research Center, San Jose, CA.

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

L10.38
SYNTHESSES OF PHENANTHERINE DERIVATIVES AND THEIR APPLICATION TO ORGANIC EL DEVICES
Yasuaki Ita, Junji Kido, Yamanashi Univ., Graduate School of Science and Engineering, Yonezawa, Yamanashi, JAPAN.

We synthesized phenanthroline derivatives containing aromatic groups as new electron-transporting materials. Bilayer EL devices, using phenanthrolines as an electron-transporting layer and NPD as a hole-transporting and emitting layer, have been fabricated. Devices with a structure of ITO/PEDOT-PSS/PDAP/phenanthroline/Pt/AI exhibited blue emission with a luminance of 3000 cd/m² and showed better device characteristics compared with a device using bluecoporphyrin as an electron-transporting layer, which demonstrates that materials of this type can be used as good electron-transporting materials.

L10.39
EFFECT OF MOLECULAR WEIGHT ON THE CHAIN PACKING AND MOBILITY OF REGioregULAR POLYTHIOPHENE
Joe Kline and Michael McGeehan, Stanford University, Department of Materials Science and Engineering, Stanford, CA, Ekaterina N. Kadin, Jason Liu, and Gene Frechet, University of California, Berkeley, CA.

Regioregular poly(3-hexylthiophene) (P3HT) is one of the leading candidates to replace the precious silicon in the active layer of low-cost thin-film transistors. We have studied the effect of molecular weight on charge carrier mobility in thin film polymer transistors made from P3HT. We have observed a substantial increase in mobility with increasing molecular weight. The mobility increases 4 orders of magnitude from a sample of 3.5×10⁴ to a sample of 3.65×10⁶. This trend has been observed both in samples synthesized by the McCullough route at a range of molecular weights and from samples obtained by film-coated P3HT synthesized by the Rickie route. We have analyzed films produced by both spin-coating and drop-coating. We have additionally studied the effect of annealing and melt/recrystallization on the charge carrier mobility and device performance. We found modulated laser ablation and nanocrystalline photoluminescence, and X-ray diffraction to obtain information on the morphology and band structure of the film. The results will be used to discuss the relationship between polymer morphology, chain length, and charge transport.

L10.40
PHOTOREACTIVE LIGHT-EMITTING ELECTROCHEMICAL CELLS
Ying-Chung Chen, Yang Yang, Univ. of California, Los Angeles, Dept of Materials Science and Engineering, Los Angeles, CA, Qiheng Pei, SRI International, Menlo Park, CA.

Due to the harvest of anglet and triplet excitons, highly-efficient phosphorescent polymer light-emitting diodes have been demonstrated. However, the driving voltage of those devices remains high because of the carrier trapping at the dopant sites. To achieve high light efficiency, a phosphorescent light-emitting electrochemical cell, which consists of bis[(2′-benzo-2-thienyl)]-pyridinato-N,C3′]iridium(III)acetylacetonate (Ir6), the dopant, poly[9,9-bis(3,6-dioxyhexyl)-fluorene-2,7-diyl] (BDOL-PF) as the host polymer and lithium trifluoro-3,5-sulfonate (LiCF3SO3), has been demonstrated in this Letter. The turn-on voltage for light emission was as low as the bandgap of the host material (2.8 eV). Comparing with the light-emitting diode with the same device structure, five-fold enhancement in power efficiency has been achieved.

L10.41
SYNTHESIS OF NOVEL POLY(9,9-DIOTYLFLUORENE) DERIVATIVE CONTAINING HEXAPHENYLENETHIENE AND ITS APPLICATION TO ORGANIC EL DEVICES
Junji Kido, Seiichi Watanabe, Takayuki Itsu, Yamagata Univ., Graduate School of Science and Engineering, Yonezawa, Yamagata, JAPAN.

A novel poly[9,9-dietylfluorene] containing hexaphenylene derivative was synthesized by the Suzuki coupling method and used as an emitter layer in Organic EL devices. The polymer exhibited blue phosphorescence peaking at 470 nm. Organic EL devices having a structure of ITO/polyfluorene derivative/biaxially oriented polyethylene terephthalate (PET) were fabricated. The device showed broad EL spectrum originating from the emission from the excimer sites.

L10.42
WHITE LIGHT EMITTING DEVICES WITH HIGH COLOR RENDERING INDEX

White organic light-emitting devices (OLEDs) are currently considered the low cost alternatives for applications such as backlights in liquid-crystal displays or other illumination purposes. There have been some efforts to obtain white light emission from multi-layer OLED structures in which two or three emissive layers emit different colors, and from polymer composites of several different color-emitting polymers or dyes. We have fabricated white OLEDs with an RGB stacked multilayer structure. In RGB stacked OLEDs, 1,4-bis[2,2-dihexylvinyl]benzene (DPVBi), tri(8-hydroxyquinoline)aluminum (Alq3) and 2,6-bis[(3,5-ditert-butylphenyl)vinyl]pyridine (TDDB) were used as a blue, a green and a red emitting materials, respectively. Through the device optimization, the pure and stable white emission with the CIE coordinates of (0.33, 0.31) at 100 nit was obtained by balancing the blue, the green and the red emissions of DPVBi, Alq3 and TDDB, respectively. Its maximum luminance was 13,200 nit at 12 V, and the luminance efficiency was 1.12 lm/W at 1000 nit. The color rendering index of 84 and the color temperature of 5,000 K were obtained with CIE coordinates of (0.33, 0.31). In this presentation, the thickness and the doping concentration effects of emissive layers on the chromaticity and stability of white light emission will be described. For the illumination application of white lighting OLEDs, the quality of white light from our OLED will be also discussed.

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

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

**L10.44**

NANOSTRUCTURED OXIDE-CONJUGATED POLYMER COMPOSITES FOR PHOTOVOLTAIC DEVICES. Seen E. Shahaen, Philip A. Parilla, Alexander Miedema, Brian A. Gregg, David S. Ginley, National Renewable Energy Laboratory, Golden, CO; Kathryn E. Brown, Dept. of Physics, Colorado School of Mines, Golden, CO.

One of the intrinsic limitations of polymer-based photovoltaic devices is the low charge carrier mobilities that are typical of disordered molecular semiconductors. This ultimately limits the thickness of the active layer, and therefore the amount of light absorbed by the photovoltaic device, since charges that recombine to the ground state before traversing the distance to the electrode do not contribute to the photocurrent. We are investigating a non-planar device geometry to overcome this obstacle by adopting a non-planar device geometry based on inorganic/organic composites. By fabricating a nanostructured, porous oxide electrode, and then filling the pores with a conjugated polymer, a composite material can be made that possesses a long optical path length while retaining a short carrier-to-electrode distance. Here we demonstrate the fabrication of thin oxide films consisting of nanoparticles with a diameter of approximately 10 nm that are sintered together to form a porous structure with pore diameters in the region of 50-100 nm. Prior to filling the pores with a conjugated polymer, a molecular species (i.e., a carboxylic acid derivatized fullerene) is adsorbed onto the oxide surface to facilitate charge separation and electron injection at this interface. The nature of the electric dipole formed at this interface is an important parameter in the operation of the photovoltaic device. We discuss the effect of this dipole by Kelvin probe measurements of the contact potential of the oxide. We then discuss techniques for filling the vacant space in the porous structure with conjugated polymers, and we present preliminary results from photovoltaic devices based on such composite structures.

**L10.45**

LIQUID CRYSTAL AND ORGANIC EL DUAL MODE DEVICES. Junji Kido, Ruyu Ishii, Masahiro Kitakami, Koichiro Yamakawa, Yamanashi Univ., Graduate School of Science and Engineering, Yamanashi, Yamanashi, JAPAN.

Dual mode display devices that function as both a liquid crystal display (LCD) and organic EL device (OLED) have been developed. The typical device structure is glass/indium-tin oxide/polyphenylene derivative (PEDOT)/light-emitting liquid crystal layer/PEDOT/ITO/glass. Conducting PEDOT layers were rubbed to work as alignment layers. The light-emitting liquid crystal layer consists of the blend of 4-cyano-4'-n-pentylbiphenyl (5CB), 4-cyano-4'-n-dodecylbiphenyl (12CBK), and 5,5'-di(3-octyloxyl)indandione (11CB). This device works as LCD at low drive voltages such as 5V and works as an OLED, emitting light, at higher voltages.

**L10.46**

MAIN-CHAIN-TYPE FLUORENE POLYMER-RIDUUM COMPLEXES FOR ORGANIC EL DEVICES. Shinji Suzuki, Junji Kido, Yamanashi Univ., Graduate School of Science and Engineering, Yamanashi, Yamanashi, JAPAN.

Main-chain type fluorene polymer complexes containing iridium metal ion were synthesized by Suzuki coupling reaction. The polymers exhibited orange phosphorescence from the iridium complex units. These polymers were used for organic EL devices and results were presented.

**L10.47**

N-TYPE CONJUGATED POLYANTHRANOLINES AND ANTHRACENE-BASED SMALL MOLECULES: HIGH ELECTRON AFFINITY ELECTRON TRANSPORT MATERIALS FOR DEVICE APPLICATIONS. Christopher J. Tomlins, Masakazu M. Aman, and Simon A. Jenekhe, Deps of Chemistry and Chemical Engineering, University of Washington, Seattle, WA.

Polyanthranolines are thermally robust conjugated polymers with tunable bandgap and good optical properties. We have synthesized a series of conjugated anthracene copolymers and investigated their electronic transport properties. Cyclic voltammetry of all the new anthracene molecules and copolymers showed reversible two-electron reductions. Electron affinities approaching 3.5 eV were observed. Bandgaps approaching 1.5-eV were achieved in the polyanthranolines by using electron-rich arylenes linkages such as ethynediophenylene (EDP). Incorporation of alkylvinylene and hexylene moieties into the backbone allowed for polyanthranoline films to be cast from organic solvents. Films of these polymers were non-emissive indicating possible application as electron transport materials in both light-emitting diodes (LED) and photovoltaic cells. In addition, a series of anthraquinone-based small molecules were synthesized and studied. Single-crystal structures allowed for structure-property relationships to be established with parent polyantrenolines. These small molecules showed solid state fluorescence efficiencies of up to 32%. Efficient polymer LEDs were fabricated using the anthranolines as the electron transport materials.

**L10.48**

FOCUSED MICROWAVE-ASSISTED SYNTHESIS OF 2,5-DIHYDROFURAN DERIVATIVES AS HIGHLY EFFICIENT ELECTRON ACCEPTORS FOR NONLINEAR OPTICAL CHROMOPHORES. Sen Lu, Marie L. Haller, Jingdong Luo, Se-Hum Jung, Hong Mc, Larry Dalton, and Alex K.-Y. Jen, Department of Materials Science and Engineering, University of Washington, Seattle, WA.

A diversified family of 2,5-dihydrofuran derivatives was synthesized under focused single-mode microwave irradiation. The tunable electron-withdrawing ability in the resulting "modified" 2,5-dihydrofuran acceptor system would potentially balance molecular hyperpolarizability, absorption at near-IR region, and thermal, chemical and photochemical stabilities of the resulting NLO chromophores. Very large r33 value (128 pm/V at 1.3 micron) demonstrated in a polar polymer system with one of the 2,5-dihydrofuran based chromophores incorporated in polymethylmethacrylate (PMMA) at 22 wt% loading level. Excellent r33 performance in an optimized polymer film (45% in PMMA) with a large, tunable r33 value (44 pm/V at 1.3 micron) demonstrated in a polar polymer system with one of the 2,5-dihydrofuran based chromophores incorporated in polymethylmethacrylate (PMMA) at 22 wt% loading level. Excellent r33 performance in an optimized polymer film (45% in PMMA) with a large, tunable r33 value (44 pm/V at 1.3 micron) demonstrated in a polar polymer system with one of the 2,5-dihydrofuran based chromophores incorporated in polymethylmethacrylate (PMMA) at 22 wt% loading level.

**L10.49**

STRUCTURE-CARRIER MOBILITY RELATIONSHIPS IN CONJUGATED POLYMERS. Amit Babel, Samson A. Jenekhe, Department of Chemical Engineering, University of Washington, Seattle, WA.

Considerable progress has recently been made in the field of polymeric-based thin film transistors for low-cost, large-area electronic applications in areas such as active-matrix displays, smart cards, identification tags, and sensors. However, the structural factors governing high mobility in polymer transistors in polymer semiconductors are not yet fully understood. Because polymer blends represent a facile means of controlling the morphology of polymers, we have investigated blends of conjugated polymers as an approach to probing the effects of morphology and disorder on charge transport and the field-effect mobility of charge carriers. We will present results on the composition-dependent field-effect mobility of holes in 5 different binary blend systems, each containing regioregular poly[3-hexylthiophene] with poly[3,4-ethylenedioxythiophene], poly[3-methoxy-5-(3-thienyl)phenylenevinylene], poly[4-(3,8-dioctyloctyloxy)-cyclopentadione], poly[3,4-thiophene], and polythiophene. Similarly, nanochannel thin film transistors and field-effect mobility of electrons in binary blends of poly(benzoxazine) with poly[4,4'-biphenyldimethoxy] were also investigated. A "steep step" carrier mobility dependence on blend composition is observed, with the carriers having relatively high and constant hole mobilities (10^-7-10^-8 cm^2/Vs) over a broad blend composition range was observed. Atomic force microscopy investigations of the morphology as a function of composition of all the blends showed that the carrier mobility can be correlated with blend morphology. Structure-carrier mobility relationships in the region of the poly[bis(triarylamine)] was also studied by systematic investigation of thin film transistors based on these poly[(3-alkylthiophene)] with 5 alkyl chain lengths from C3 (n-butylyl) to C12 (n-dodecyl).

**L10.50**

SYNTHESIS OF POLY(PARAPHENYLENE VINYLENE) NANORODS USING AN ANODIC ALUMINUM TEMPLATE. Wei Wang, Richard Czarnecki, Scott Webster, David L. Carroll, School of Materials Science and Engineering, University of Washington, Seattle, WA; Jung Hee Park, Yong-Woo Park, Dept. of Physics and Cond. Matter Research Inst., Seoul National Univ., Seoul, KOREA.
Poly(paraphenylene vinylene) (PPV) is a common electroluminescent conjugated polymer, and optical nanodevices fabricated with PPV nanorods may be employed as light-emitting diodes and other optoelectronic applications such as optical switches. Aligned PPV nanorods, with diameters of approximately 30 nm, were synthesized by electropolymerization of d-a, d-a', d-a-terthiophene-polypyrrole in a 0.1 M tetrafluoroborate electrolyte solution within the pores of a nanoporous anodic aluminum oxide (AAO) template membrane. The diameter and length of the nanorods can be controlled by varying the aspect ratio of the AAO template through electrochemical methods. The aligned nanorods were deposited by electron microscopy (SEM), transmission electron microscopy (TEM), micro-Raman, UV-visible absorption, and photoluminescence (PL) spectroscopy.

L10.51
SELF-ORGANIZATION PROPERTIES AND DEVICE APPLICATION OF REGIOISOMERIC HEAD-TO-TAIL POLY(4-ALKYLQUINOLINE)8 Yan Zhu, Maksudul M. Alam, Samuel A. Jeneke, Departments of Chemical Engineering and Chemistry, Univ. of Washington, Seattle, WA

Two 100 percent head-to-tail regioregular poly(4-alkylquinoline-2,6-diyl) were synthesized and investigated. The 100% regioregularity of the polymer was achieved by the all-type nature of the acid-catalyzed Friedel-Crafts condensation polymerization. X-ray diffraction studies showed that solution-cast films of regioregular poly(4-alkylquinoline) and poly(4-oclylquinoline) have self-organized lamellar structures with interlayer spacings of 15.7 Å and 17.2 Å, respectively, and a lamellar stacking distance of 4 Å. The two polymers emit blue light at 432-435 nm in dilute organic solvent solutions and yellow light at 547 nm in the solid state. Light-emitting diodes (LEDs) were fabricated using the two polymers as both the emissive layer and as an electron transport layer. Yellow electroluminescence was observed for both poly(4-alkylquinoline) and poly(4-oclylquinoline). A large improvement in the performance of the-photon LEDS (α luminescence up to 700 cd/m^2 and an external quantum efficiency up to 3.0%) was observed by using the poly(4-alkylquinoline) as the electron transport materials, suggesting that they are good electron transport materials for polymer LEDs.

L10.52
SPECTRALLY STABLE BLUE POLYMER LIGHT-EMITTING DIODES BASED ON BLENDS OF POLY(9,9-DIOTCYLFLUORENE), Sahibeddin P. Kalkan, Samual A. Jeneke

Polyfluorenes have emerged as a highly attractive class of electroluminescent conjugated polymers for display applications owing to their high fluorescence quantum yield and good charge transport properties. However, one major drawback of the blue-emitting polyfluorene-based devices is poor spectral stability due to the thermal or electro-oxidative degradation during operation, giving rise to an unwanted green emission band at 530 nm that has been attributed to the polymer degradation. Various approaches have been attempted to minimize this unwanted long-wavelength emission band including addition of hole-trapping molecules and addition of bulky side groups. We report spectrally stable blue electroluminescence (EL) from single-layer light-emitting diodes comprising binary blends of poly(9,9-diocytfluorene) (PFO) with an electron-transport/hole-blocking poly(3-dihexylquinoxaline) (PQV) or with polystyrene. Good reproducible EL spectra were obtained even after annealing at 150°C for a period of two hours. The brightness and efficiency of the PFO/PQV blend LEDs were enhanced by 5 - 10 times the values for the pure PFO diodes. The observed enhancement in the blue light may be due to energy transfer from PQV to PFO coupled with improved spatial confinement. This emission is efficient and stable. The emission is efficient and stable. The efficiency and spectral characteristics of the blends are shown to be a function of the blend composition. The increase in brightness and efficiency is a consequence of the better spatial confinement.
The power conversion efficiency of a polymer photovoltaic device is determined not only by the short-circuit quantum efficiency, but also by the open-circuit voltage and the shape of the current-voltage curve. We have therefore developed a numerical model to explain and predict the current-voltage curves of bilayer conjugated polymer photovoltaic devices. The model accounts for charge photogeneration, diffusion, recombination, and includes the effect of space charge on the electric field within the device. Charge separation at the polymer/polymer interface leads to the formation of bound polaron pairs with different mobilities, which combine and/or recombine into free charges. We find that the short-circuit quantum efficiency is determined by the competition between polaron pair dissociation and recombination. The model describes a dramatic increase of the open-circuit voltage on the incident intensity, as seen experimentally. This additional intensity-dependent voltage rise from the field required to produce a drift current which balances the current due to diffusion of carriers away from the interface.

9:15 AM LI1.4
ROLES OF INTERNAL ELECTRODES IN MULTI-HETEROJUNCTION ORGANIC SOLAR CELLS. Tetsu Tsutsumi, Kawan Trayan, Takeshi Yamada, and Katsuhiko Fujita, Department of Materials Science and Engineering, Kyushu University, Fukuoka, Fukuoka, JAPAN.

The power conversion efficiency (PCE) of single-heterojunction (HJ) organic photovoltaic cells consisting of CuPc as a p-type semiconductor, and pentacene, triphenylamine benzimidazole (PTCBI) as a n-type semiconductor, has been reported to be around 1.6-1.8% and open circuit voltage (Voc) of 0.45-0.5 V [1,2].

We pointed out two essential factors that give low PCE in thin film HJ cells. One is the rapid loss of light within an active layer of the cells and the other is low Voc in comparison with the average photon energy of sunlight. [2] One of the possible directions of solving these problems is stacking of HJ cells maintaining penetration of irradiated light into bottom HJ region. An early trial of introducing a metal interlayer brought about drastic increase of Voc, but PCE remained almost unchanged. [3] Recently large increases of both Voc and PCE have been reported using Ag anode electrodes (4).

This report focuses on understanding the effect of the insertion of internal electrodes to multiple HJ solar cells. Several types of single-HJ and multiple-HJ solar cells were fabricated. For single HJ cells, ITO/PTCBI/CuPc/Au and ITO/PTCBI/CuPc/Ag/CuPc structures were fabricated as the standard cells, and multiple heterojunction cells, such as ITO/PTCBI/CuPc/Au/PTCBI/CuPc/Ag/CuPc/Au and ITO/CuPc/PTCBI/Ag/Cp/CuPc structures, were used.

The Voc and PCE (AM 1.5) for the ITO/PTCBI/CuPc/Au cell were 0.50 V and 1.11% respectively. When three ITOs were stacked using Au internal electrodes, the best values for Voc and PCE (AM 1.5) were 1.35 V and 0.41% respectively. Several different external and internal electrodes were investigated.


9:30 AM *LI1.5
EXTRINSIC PHOTOCURRENT GENERATION OF CHARGE CARRIERS IN ORGANIC DONOR-ACCEPTOR SYSTEMS. W. Tim, C. Im, and H. Bae, Seoul Institute of Physical, Nuclear, and Macromolecular Chemistry, Philips University Marburg, Marburg, GERMANY. V. I. Akridge, IBM, Heverlee-Leuven, BELGIUM. E. V. Emelchenova, Semiconductor Physics Laboratory, University of Leuven, Heverlee-Leuven, BELGIUM.

In the course of our endeavors to understand how optical excitation can dissociate into charge carriers in p-conjugated polymers we studied c.w.-photocurrent in films of a PPV-based p-conjugated polymers and hexahexylbenzene doped by trifluorotrichloroethylene, within a broad range of concentrations of the acceptor. At moderate acceptor concentration the yield of the photogeneration is almost independent of the system and of concentration because practically every primary excitation dissociates at a donor-acceptor sites and the subsequent escape from the Coulomb potential is virtually system-independent. At acceptor concentrations > 10% the yield of that escape process increases by two orders of magnitude because of shielding of the pair potential and the resulting high electron mobility across the acceptor network. The experimental results are analyzed in terms of a recent theoretical approach.

10:30 AM *LI1.6
DESIGN AND PERFORMANCE OF NEW FULLERENE MATERIALS FOR BULK-HETEROJUNCTION SOLAR CELLS.


Until now, the most successful fullerene acceptor material in bulk-heterojunction solar cells has been phenyl-C61-butyric acid methyl ester PCBM. One way to improve the energy conversion efficiency of these devices is through the modification of PCBM in such a way that the open circuit voltage of the device is increased. For this purpose, a series of 3-phenyl-substituted phenyl-C61-butyric acid methyl esters has been prepared and fully characterized. Next, thin films made of blends of MD-MO-PPV and the modified PCBM materials were investigated using various techniques. Finally, PV devices, made with the new materials were fabricated and characterized.

11:00 AM LI1.7
CHARGE TRANSPORT IN PLASTIC BULK-HETEROJUNCTION SOLAR CELLS. V.D. Mihalek, P.W.M. Blom, J.C. Hummelen, and M.T. Rispens, Materials Science Centre, University of Groningen, Groningen, THE NETHERLANDS.

The charge transport properties of the electron acceptor methylfullerene [6,6]phenyl C61-butyric acid methyl ester (PCBM) and the donor-type conjugated polymer poly(phenylene-vinylene), P(PhV) have been investigated. At room temperature the electron mobility of μ = 2 x 10-7 m²/V.s in the PCBM is more than three orders of magnitude larger than the hole mobility of the donor-type C61-butyric acid methyl ester (PCBM). Also the charge transport properties of electron donor and holes in 1:1 weight ratio of P(PhV)/MD-MO-PPV blends have been addressed. The maximum attainable open-circuit voltage of a plastic solar cell has been determined and consistently explained.

11:15 AM LI1.8
EXCITONIC SOLAR CELLS. Brian A. Gregg, National Renewable Energy Laboratory, Golden, CO.

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

11:30 AM LI1.9
CHARGE TRANSPORT PROPERTIES IN DISCOTIC LIQUID CRYSTALS: A MOLECULAR SCALE DESCRIPTION. Jerome Comil, Vincent Lemaré, Jean-Philippe Calbert, and Jessica Bredas, University of Marse-Marseille, Laboratoire pour la Chimie de Novels Materials, Marse, BELGIUM. "The University of Arizona, Department of Chemistry, Tucson, AZ.

Due to their high degree of ordering and self-healing capacity, discotic liquid crystals emerge as very attractive organic semiconductor materials for applications requiring efficient charge transport properties, such as field-effect transistors and solar cells. In such nanophases, the charge transport takes place via a phonon-assisted hopping mechanism as a result of large geometric fluctuations and absence of crystalline order. In this contribution, we illustrate that quantum-chemical calculations can be exploited to evaluate the two main parameters governing at the molecular scale the charge transport, and hence the mobility values, namely [1,2]: (i) the transfer integrals for holes and electrons.

11:45 AM L11.10 ORGANIC PHOTOVOLTAIC CELLS CONTAINING LIQUID CRYSTALLINE PHthalocyanines. Seunghyup Yoo1, Benoit Domenov, Carrie L. Donley2, Cht Carter5, Wei Xin3, Brit A. Minch5, David F. O'Brien5, Neil R. Armstrong3, and Bernard Kippelen2. 1Optical Sciences Center, University of Arizona, Tucson, AZ; 2Department of Chemistry, University of Arizona, Tucson, AZ.

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

SESSION L12/H11. JOINT SESSION DEVICES Chair: Jerome Cornil Friday Afternoon, April 25, 2003 Salon L-3 (Merritt)

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

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

260 PM *L12.2/H11.2 FULLY PRINTABLE LIGHT EMITTING DISPLAYS. Sue A. Carter, M. Kreger, J. L. Breden, N. Nakayama, J.J. Breden, M. Wilkinson, University of California, Dept. of Physics, Santa Cruz, CA and Addvision, Incorporated, Scotts Valley, CA.

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

2:30 PM L12.3/H11.3 IN-SITU ELECTRICAL AND SPECTROSCOPIC STUDY OF DEGRADATION MECHANISMS AND LIFE TIME PREDICTION OF ORGANIC BASED ELECTRONIC MATERIALS. Jean Vittorio Mancini, Elke Kesters, Laurence Lutsen, Ludwig Gori, Dirk Vanderzande, Jan D'Hae, Marc D'Olesterge, Lie De Schepere, Limburg Universitair Centrum, Institute for Materials Research, Diepenbeek, Belgium; IMEC, IMOGEC, Diepenbeek, BELGIUM. Omella Santa, University of Catulli, Catulli, ITALY.

In order to tailor the synthesis of new robust organic materials for electronic applications it is of key importance to understand the underlying degradation mechanisms. The strategy used by our group to study these mechanisms is to monitor the behavior of the materials submitted to a given stress conditions with so-called in-situ electrical and spectroscopic techniques. We will illustrate the correlation between the electrical transport properties and the optical spectrum obtained during each degradation process. A model is proposed in order to make a connection between the electrical properties and the optical spectrum obtained during each degradation process.


We demonstrate a method for high resolution patterning of metal cathode contacts for organic electronic devices using low pressure cold welding. The contacts are formed by transferring a metal film from a patterned, soft elastomeric stamp onto an unpatterned organic and metal layer predeposited on a substrate. Use of an elastomer stamp allows for a thousand-fold decrease in the pressure needed for a high-yield pattern transfer as compared to that required with rigid stamping techniques. In our demonstration, we fabricate an array of efficient organic light emitting devices (OLEDs) based on the green phosphor 4,4',4''-tris((2-phenylpyridin-4-yl)phenyl))-triphenylamine (TPI) doped into a 4,4'-N,N'-didecyloxy-dibiphenyl (CDB) host. Here, the cathodes consist of ultrathin (<1 nm) layers of LiF and Au capped by a 15-nm-thick layer of Au deposited across the entire organic layer surface. A 100-nm-thick layer of Au is transferred onto the Au layer by pressing a stamp onto the substrate under conventional non-contact flip-chip bonder. The cathode patterning is finished by removing the thin Au layer between the transferred pattern with gentle sputter etching. The 250 µm diameter cathodes were uniformly obtained over the 1 cm² substrate area with a yield exceeding 97%, and the pattern edge resolution was approximately 1 µm. The stamping and Au layer removal processes do not adversely affect the performance of OLEDs fabricated by conventional shadow mask patterning. For example, the voltage corresponding to a current density of 10 mA/cm² was...
3:30 PM *L12.5/H11.5 PROGRESS IN THE GROWTH OF PENTACENE THIN FILMS AND DEVICES. Basu Trivedi, IBM T.J. Watson Research Center, Yorktown Heights, NY.

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

4:00 PM L12.6/H11.6 SELF-ALIGNED VERTICAL CHANNEL POLYMER FIELD-EFFECT TRANSISTORS. Natalie Sutmann, Richard H. Friend, Henning Sirringhaus, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM.

Manufacturing of high-performance conjugated polymer transistor circuits on flexible plastic substrates requires patterning techniques capable of defining critical features with submicrometer resolution. We demonstrate here the use of solid-state embossing to produce polymer field-effect transistors with submicrometer critical features in planar and vertical configurations. Embossing is used for the controlled microcutting of vertical sidewalls into polymer multilayer structures without smearing. High-mobility vertical-channel polymer field-effect transistors on flexible poly(ethylene terephthalate) substrates have been fabricated, in which the critical channel length of 0.75±0.9 mm is defined by the thickness of a spin-coated insulator layer. We demonstrate that gate electrodes can be self-aligned to minimize overlap capacitance by inkjet printing using the embossed grooves to define a surface-energy pattern.

4:15 PM L12.7/H11.7 INJECTED ORGANIC TRANSISTORS USING A NOVEL PENTACENE PRECURSOR. Steven K. Voller, Steven Molen, Brian Martin, Paul C. Chang, and Vivek Subramanian, University of California, Berkeley, Department of Electrical Engineering and Computer Sciences, Berkeley, CA.

Pentacene is one of the most promising organic materials for organic transistor fabrication, since it offers higher mobility, better on/off ratios, improved environmental stability, and better reliability than most other common organic semiconductors. However, its severe insolvability renders it useless for the solution-based fabrication of electronic devices. Solution-based processing of these devices is the key to enabling ultra-low-cost circuit fabrication, since it eliminates the need for lithography, subtractive processing, and vacuum-based film deposition. Because it allows the use of entirely additive printing techniques, it is expected to result in the development of low-cost resists-based fabrication methodologies. Prompted by a recent paper from Afzali et al. in describing the synthesis of a novel pentacene precursor, we demonstrate the first inkjet-printed pentacene transistor fabricated to date. This is achieved using a substrate-integrated transistor structure in conjunction with an inkjet-printed pentacene precursor active layer. A subsequent thermal cycle is used to convert the precursor into a high-quality pentacene film. Unoptimized conditions yield transistors with an on/off ratio of >1,000 and a field-effect mobility of 0.001 cm²/Vs. Further improvement is expected with optimization, to approach the mobility of >0.5 cm²/Vs reported by Afzali. We study the effect of annealing conditions on the pentacene precursor characteristics, and establish qualitative models describing the various effects. The precursor is converted to pentacene via heating, through the decomposition of the Dink-Akler product. As the annealing temperature increases above 120°C, performance increases dramatically. The process is therefore compatible with a variety of polymeric substrates. As the anneal time is increased to several minutes, performance likewise increases through improved precursor decomposition. However, exposure to excess temperatures or times tends to degrade performance. This is caused by morphological and chemical changes in the pentacene film.

4:30 PM L12.8/H11.8 N- AND P-TYPE BUILDING BLOCKS FOR ORGANIC ELECTRONICS BASED ON OLIGOTHIOPHENE CORES. Antonio Ricciotti, Mishan Mashraki, Howard E. Katz, and Tobin J. Marks.

Organic semiconductors exhibiting complementary-type carrier mobility are the key components for the development of the field of “plastic electronics”. We present here a novel series of α,α′- and isomerically pure β,β'-difluoroalkyl-substituted thiophene oligomers [DFEnTs] and isoDFEnTs, respectively; C6F5-n(chiophene)-C6F5-n (n = 2 - 6) and study the impact of fluoralkyl substitution and conjugation length via both the corresponding fluorine-free analogues [DFEnTs] and isoDFEnTs; C6H13-n[theta] (chiophene) - C6H13-n (n = 2 - 6). Trends between the fluorinated and fluorine-free families in molecular packing, optical absorption, HOMOLUMO gap, and p-p interactions are found to be strikingly similar. However, fluoralkyl substitution substantially enhances thermal stability, volatility, and electron affinity. Thin film transistor (TFT) devices were fabricated employing both vacuum and, for shorter and β,β'-substituted oligomers, solution-deposited semiconducting layer. Field-effect transistor measurements indicate that all the longer members of both DFEnTs and isoDFEnTs series are n-type semiconductors with unoptimized mobilities and 1/cm² V⁻¹ radii approaching 0.05 cm² V⁻¹ at 1 V, respectively. These families represent the first example of α homologous series of variable core α-conjugation length n-type OTFF components.