

SYMPOSIUM L

Organic and Polymeric Materials and Devices

April 22 – 25, 2003

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* Invited paper

SESSION L1: LIGHT-EMITTING DIODES

Chair: Paul W.M. Blom

Tuesday Morning, April 22, 2003

Salon 1-3 (Marriott)

8:30 AM *L1.1

POLYMER LEDs: RECENT PROGRESS. Alan J. Heeger.

I will summarize the results of a series of recent experiments directed toward improved performance in polymer LEDs. These include the following: Stabilization of the blue emission from polyfluorene using end-capping with silesquioxane; Stabilization 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 Iridium complexes.

9:00 AM L1.2

THE EFFICIENCY OF POLYMER LEDs OVER A WIDE VOLTAGE RANGE. Eric A. Meulenkamp, Arjen Rickson, Adeline Perro, Simone I.E. Vulto, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

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

9:15 AM L1.3

ENHANCED LIGHT EMISSION THROUGH TRIPLET-TRIPLET ANNIHILATION IN ORGANIC ELECTROLUMINESCENT DEVICES. M. Fujihira and C. Ganzorig, Department of Biomolecular Engineering, Tokyo Institute of Technology, Yokohama, JAPAN.

We demonstrate here that luminance increased more than linearly with an increase in current density of tris(8-hydroxyquinoline) aluminum (Alq)-based electroluminescent (EL) devices and the EL efficiency reached ca. 5 cd/A at 250 mA/cm² when electron and 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 alkalimetal carboxylates [1] and hole injection by surface modification of ITO [2]. The luminance-current curves were well fitted with a combination of a linear and a quadratic function of the current. The quadratic component can be attributed to additional singlet excited state (¹Alq*) formation through triplet-triplet (T-T) annihilation of triplet excited states (³Alq*) produced simultaneously with ¹Alq*. The requirement of the well-balanced charge injection implies that the long-lived ³Alq* was quenched efficiently by energy transfer to excess and colored Alq⁻ anion or Alq⁺ cation radicals in the emission zone when the charge injection was unbalanced. The short-lived ¹Alq* was not quenched appreciably. This is the most important characteristic of Alq-based EL devices. [1] C. Ganzorig and M. Fujihira, Jpn. J. Appl. Phys., 38, L1348 (1999). [2] C. Ganzorig, K.-J. Kwak, K. Yagi, and M. Fujihira, Appl. Phys. Lett., 79, 272 (2001).

9:30 AM *L1.4

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 Kawamura, Koichi Mori, Akira Yokoi, and Toshio Matsumoto, IMES Co., Ltd., Fujisawa, Kanagawa, 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 the carriers with opposite polarity. Thus, quantum efficiency was substantially improved. An external quantum efficiency of 10% was observed from a device, using fluorescent materials, having one CGL.

10:30 AM *L1.5

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 (doping level) and thickness, and the energy barrier at the interface. We describe a theory that explains the experimental results and discuss similarities and differences with 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 for forming Ohmic contacts will be presented.

11:00 AM *L1.6

EXCITONIC SINGLET-TRIPLET RATIOS IN MOLECULAR AND POLYMERIC ORGANIC SEMICONDUCTORS. MA Baldo 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. If so, fluorescent polymers may possess intrinsically higher EL efficiencies than low molecular weight fluorescent materials. We present a general technique for measuring the maximum fluorescent efficiency of organic materials within EL devices. This allows us to determine the singlet fractions under EL conditions in archetype materials such as tris(8-hydroxyquinoline) aluminum (Alq3) and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV).

11:30 AM L1.7

ELECTROCHEMICAL CHARACTERISATION OF BLUE EMITTING POLYFLUORENE LEP. Ilaria Grizzi, Clare Foden, Simon Goddard, Carl Towns Cambridge Display Technology, Greenwich House, Maddingly Rise, Cambridge, UNITED KINGDOM.

In an operating LED, electrons are injected into the polymer's LUMO level from the cathode and holes from the anode into the polymers HOMO level. The value of the electron affinity (EA) is usually inferred (often incorrectly) from the experimental HOMO level energy and the value of the optical band gap. Using carefully controlled experimental conditions we can now directly access the EA position. Reduction events have been observed on poly(9,9-dioctylfluorene) (F8) and blue emitting polymers based on 9,9-dioctylfluorene. This event is consistent and reversible. As predicted by theory, the LUMO level is entirely delocalised over F8 blocks. An EA of approx. -2.3eV, equal to that of F8, is therefore a common feature of blue polymers containing sequences of 9,9-dioctylfluorene. Blue emitting 9,9-dioctylfluorene-triarylamine AB copolymers containing either 4-sec-butylphenyl diphenyl amine (TFB) or N,N'-bis(4-butylphenyl)-N,N'-diphenyl phenylenediamine (PFB) are characterized by an electron affinity of -2.1eV. This result shows that the LUMO wave function in these systems is localized on the Ph-F8-Ph units. In the case of PFB homopolymer the LUMO level is again localized, this time on the biphenyl unit at the junction of each 2 repeating units. The EA for this material is therefore lower than in the previous cases: -1.84eV, as a result of the increased localization of the LUMO wave function. Electrochemical characterisation 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 L1.8

ON-CHAIN EMISSIVE DEFECTS IN PI-CONJUGATED POLYMERS: FROM EXCITON TRAPPING TO INTRINSIC ELECTROPHOSPHORESCENCE. John M. Lupton, Max Planck Institute for Polymer Research, Mainz, GERMANY, and University of Munich, GERMANY; A. Pogantsch, T. Piok, E.J.W. List, Institute of Solid State Physics, Graz University of Technology, Graz and

Christian Doppler Laboratory of Advanced Functional Materials, Graz, AUSTRIA; S. Patil and U. Scherf, Institut fuer Chemie, Universitaet Potsdam, Golm, GERMANY.

On-chain chemical defects in conjugated polymers have previously been associated with luminescence quenching. Recently, however, it was demonstrated that oxidative defects in polyfluorene act as exciton traps and give rise to a broad emission red-shifted from the polymer backbone emission and characteristic of a fluorenone moiety. Using gated fluorescence spectroscopy this emission was clearly identified on isolated chains of pristine fluorene polymers and oligomers, suggesting that the previous assignment to an intermolecular excited state is inappropriate (Lupton et al., APL 80, 4489 (2002)). Gated electroluminescence (EL) was also used to study the dynamics of charge trapping and delayed recombination on these defects (Lupton et al., PRB 65, 193202 (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 covalently bound palladium atoms 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 under optical 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 neutral excitations and delayed pair recombination by varying the internal field of the LED. We believe that the discovery of efficient triplet emission is of interest for LEDs but also for polymer lasers and single molecule devices, where triplets can easily be deactivated.

SESSION L2/K2: JOINT SESSION
MOLECULAR ELECTRONICS
Chairs: Massimiliano Di Ventra and Junji Kido
Tuesday Afternoon, April 22, 2003
Salon 1-3 (Marriott)

1:30 PM L2.1/K2.1

ORGANIC MOLECULES ON METAL SURFACES BY HIGH RESOLUTION STM. Federico Rosei^a, Y. Naitoh, M. Schunack, E. Lægsgaard, I. Stensgaard, and F. Besenbacher, Physics Department and I-NANO, University of Aarhus, DENMARK; P. Jiang, A. Gourdon, and C. Joachim, CEMES CNRS, Toulouse, FRANCE.
^aPresent 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 Tunneling Microscopy yields new information on molecular diffusion and assembly. First, we address 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 (C₃₆H₁₈) and HtBDC (C₆₀H₆₆), on Cu(110), we find that their diffusion is dominated by long jumps, spanning multiple lattice spacings [1]. The HtBDC molecule has a core identical to DC, and six additional spacer legs, which increase its diffusion coefficient by four orders of magnitude with respect to DC. This ultimately demonstrates how molecules can be redesigned to engineer their diffusion properties. Second, we describe the adsorption of the Lander molecule [2] (C₉₀H₉₈) 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" (3,5-di-tert-butylphenyl) 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 act as nanoscale templates, reshaping portions of step edges into characteristic nanostructures. [1] M. Schunack, T.R. Linderoth, F. Rosei et al., Phys. Rev. Lett. 88, 156102 (2002). [2] F. Rosei et al., Science 296, 328 (2002).

1:45 PM L2.2/K2.2

NANO-SCALE ORGANIC FIELD EFFECT TRANSISTORS AND SHORT CHANNEL EFFECTS. V. Wagner, Universität Würzburg, Physikalisches Institut, EP III, Würzburg, GERMANY (present address: International University Bremen, School of Eng. and Sci., Bremen, GERMANY); T. Muck, M. Leufgen, A. Lebib, M. Tormen, T. Borzenko, G. Schmidt, L. Molenkamp, J. Geurts, Universität Würzburg, Physikalisches Institut, EP III, Würzburg, GERMANY.

Down-scaling of organic field effect transistors (OFETs) offers 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 thiophene (4T) as active material. Thiophenes are used because of their possible high carrier mobility values. We use electron beam lithography to manufacture gold source and drain finger contacts on SiO₂/n⁺-Si-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 UHV evaporation long channel (L > 2 μm) devices exhibit standard characteristics at room temperature in air or nitrogen atmosphere. However, for a SiO₂ gate insulator of 200 nm thickness we found degradation of the saturation regime for L < 1 μm, while on/off ratios strongly deteriorate for channel lengths of 400 nm or below. The effects will be discussed in comparison with short channel effects observed for inorganic devices. Furthermore, as an important result, drain current was found to increase by more than an order of magnitude for channel lengths L < 400 nm, which coincides with the average grain size in our organic layers. This indicates an important contribution of grain boundary scattering for the transport in the organic channel.

2:00 PM *L2.3/K2.3

ELECTRICAL CONDUCTANCE OF SMALL ORGANIC MOLECULES. Norton D. Lang and Phaedon Avouris, IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY.

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

SESSION L3: STRUCTURE, INTERFACES AND GROWTH

Chair: Junji Kido
Tuesday Afternoon, April 22, 2003
Salon 1-3 (Marriott)

3:00 PM *L3.1

STRUCTURAL AND OPTOELECTRONIC PROPERTIES OF THE BLUE LUMINESCENT δ-PHASE OF Alq₃. M. Cölle, J. Gmeiner, S. Forero, A.G. Mückl, W. Brütting^a, Experimental Physics II, University of Bayreuth, Bayreuth, GERMANY. ^apresent address: University of Saarland, Electronics and Semiconductor Devices, Saarbrücken, GERMANY.

Tris(8-hydroxyquinolino)aluminium(III) (Alq₃) stands as one of the most successful materials used in organic light emitting devices 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 material. Another unresolved issue concerns the isomery 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 (δ-Alq₃) exhibiting strongly blue-shifted fluorescence [3]. Its significantly different optical properties have been tentatively ascribed to the isomery of the Alq₃ molecule. Here we will present an in-depth characterization of the different phases of Alq₃ by combining thermal, structural and vibrational analysis. These data provide unambiguous evidence for the existence of the facial isomer in the blue luminescent δ-phase of Alq₃. Furthermore, an efficient way to fabricate blue luminescent Alq₃ in large amounts has been found. These results will be correlated with the optoelectronic properties of Alq₃ and Alq₃-based thin film electroluminescent devices. [1] A. Curioni et al. Chem. Phys. Lett. 294, 263 (1998); [2] M. Brinkmann et al. JACS 122, 5147 (2000); [3] M. Braun et al. J. Chem. Phys. 114, 9625 (2001).

3:30 PM L3.2

ON THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND ELECTRICAL PERFORMANCE OF OLIGOTHIOPHENE ORGANIC THIN FILM TRANSISTORS. Marcus Halik, Hagen Klauk, Ute Zschieschang, Guenter Schmid, Infineon Technologies AG, Polymer Materials and Technology, Erlangen, GERMANY; Sergei Ponomarenko, Stephan Kirchmeyer, H.C. Starck, Leverkusen, GERMANY; Werner Weber, Infineon Technologies AG, Corporate

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, due to their relatively straightforward synthesis and the wide range of possible modifications in their chemical structure. We have investigated a series of α, α' -oligothiophenes with chromophore length ranging from four to six units (didecylquaterthiophene, didecylquinquethiophene, and didecylsexithiophene), and with alkyl side chains ranging from 10 to zero units (didecylsexithiophene, dihexylsexithiophene, diethylsexithiophene, and sexithiophene). We have fabricated top contact and bottom 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 on the contact configuration (with mobilities ranging from 0.07 to 1.1 $\text{cm}^2 / \text{V s}$), but is relatively insensitive to the chromophore length. We have also fabricated ring oscillators with didecylsexithiophene and measured a signal propagation delay of 30 μs per stage. In addition, we have fabricated substituted oligothiophene TFTs with ultra thin self assembled monolayer (SAM) gate dielectrics, with the intent to evaluate if long alkyl side chains contribute usefully to the effective thickness of a SAM gate dielectric. We have measured carrier mobilities as large as 0.05 $\text{cm}^2 / \text{V s}$ 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

ENERGETICS OF MER/FAC ISOMERS IN METAL TRIS(8-HYDROXYQUINOLINE) CHELATES: IMPLICATIONS ON 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 aluminum tris(8-hydroxyquinoline) (Alq3). However, further reducing the operating voltage for small-molecule OLEDs in a systematic manner is hindered by a yet incomplete understanding of the injection and transport of charge carriers across the interfacial and through bulk organic thin film layers. Full understanding requires that the structure of the molecular semiconductor both in the bulk and at the interfaces be known. In the case of the archetypal EL material, Alq3, the problem is complicated by the potential presence of two geometric isomers (meridional and facial), which have different symmetries and correspondingly different molecular electronic states. We present new electronic structure calculations on Alq3 and the methyl-substituted series, $n\text{Meq}3\text{Al}$ ($n = 3-7$) for the mer and fac-isomers providing an improved estimate of their relative abundances. Ab initio computations performed at the SCF level noted a significantly higher stability (6-7.5 kcal/mol) of the mer-isomer over the facial form, which was maintained with treatment of electron correlation. Substitution of the Al+3 metal ion with the larger ions Ga+3 or In+3 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 Mq3 thin films, and therefore as an electron trap, is unlikely, and only the mer-isomer need be considered for modeling conduction mechanisms in OLEDs utilizing Mq3 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

IMAGING INDIVIDUAL CHAINS AND AGGREGATES ON CONJUGATED POLYMER FILMS. M. Kemerink^a, J.K.J. van Duren^b, P. Jonkheijm^b, P.M. Koenraad^a, R.A.J. Janssen^b, H.W.M. Salemink^a, J.H. Wolter^a. ^aDept. of Applied Physics; ^bDept. of Chemistry, Eindhoven University of Technology, Eindhoven, THE NETHERLANDS.

The nano-scale electro-optical properties of conjugated polymer films depend strongly on the local morphology. Therefore, the disability 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 AFM with phase detection. Although the height image does not show any molecular resolution, as is usually the case on 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 relation between molecular structure and morphology of PPV derivatives. We found that the chains in the topmost layer of spin-cast films of the asymmetrically substituted polymer OC₁₀OC₁₀-PPV (or MDMO-PPV) are highly curved, with a typical radius of curvature of 5-7 nm. In contrast, the surface morphology of the symmetrically substituted polymer bisOC₁₀-PPV shows straight individual chains, showing the causal relation between substitutional (a)symmetry and surface morphology. By deliberately blunting the AFM tip the collective response of the material under the tip is probed, instead of the response of the nearest individual chain. It is found that this enables the direct visualization of aggregates, using the same phase imaging scheme with a blunt tip. In line with the sharp-tip results, bisOC₁₀-PPV shows aggregation in 50-200 nm sized domains, whereas aggregation is not observed on MDMO-PPV. On P3HT the domain size is found to be of the order of 10-50 nm. Annealing the P3HT 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. Hisao Ishii, Tohoku Univ, Institute of Electrical Communication, Sendai, JAPAN; Atsushi Seko, Akira Kawakami, Yukio Ouchi, Nagoya Univ, Graduate School of Science, Nagoya, JAPAN; Kazunori Umishita, Kazuhiko Seki, Research Center for Materials Science, Nagoya, JAPAN.

Interfacial band offset and band bending of organic semiconductor are critical to understand and improve organic photovoltaic cells. In this study, the energy level alignment of fullerene(C60) / phthalocyanine(Pc) interfaces which is one of the model interfaces of organic photovoltaic cells has been investigated using UV and X-ray photoemission 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 C1s state was observed in XPS by the deposition of Pc thin film of 0.2nm 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.Hayashi et al, J. Appl. Phys., vol.92, 3784(2002)], where thickness of 500nm 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 0.3eV in 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 an extremely surface sensitive method and can probe outermost surface selectively. MAES spectra revealed that no significant interface diffusion happened at the interfaces. That 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 STRUCTURE. Norbert Koch and Antoine Kahn, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ; Bert Nickel, Jeffrey Schwartz, Princeton Univ, Dept of Chemistry, Princeton, NJ; Jacques Ghijssels and Jean-Jacques Pireaux, FUNDP, LISE, Namur, BELGIUM; Andreas Elschner, H.C. Starck GmbH, Krefeld, GERMANY.

We have investigated the electronic, structural, and charge injection properties of interfaces formed between three electroactive conjugated organic materials, i.e., N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1-biphenyl-4,4'-diamine (α -NPD), pentacene, p-sexiphenyl, 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 and PEDOT/PSS is lower by 0.6-1.0 eV as compared to Au, despite a similar work function of the pristine electrode material surfaces (ca. 5 eV). This very large difference is due to an effective change of the metal work function due to the deposition of organic molecules, i.e., a decrease of the Au surface dipole due to adsorption. Accordingly, model device structures built from α -NPD and pentacene on the two different electrode materials show much higher current densities (up to 4 orders of magnitude) for hole injection from PEDOT/PSS than from Au. Hole injection from Au for α -NPD devices is independent of deposition sequence (i.e., α -NPD-on-Au vs. Au-on- α -NPD) and

substrate (i.e., Au or PEDOT/PSS). Pentacene devices exhibit significant asymmetries in that respect, due to a strong dependence of the morphology and preferred 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 ELECTROMECHANICAL DISSIPATION AND ELECTRIC FORCE MICROSCOPIES. John A. Marohn, William R. Silveira, Jenna Harang, Brian To, and Neil E. Jenkins, Dept. of Chemistry and Chemical Biology, Cornell University, Ithaca, NY; Erik M. Muller, Dept. of Physics, Cornell University, Ithaca, NY.

I will describe novel and highly sensitive variable-temperature electric force microscope measurements on conducting organic thin films. The goal of these studies is to correlate work function, conductivity, and trap location with surface morphology in both thin films and in working organic field effect transistors. We are studying a number of systems including molecularly doped polymers (polycarbonate:TPD), small-molecule semiconductors (pentacene), and semiconducting polymers (polythiophene). We having custom fabricated silicon cantilevers that are orders-of-magnitude 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 our ultrafloppy cantilevers to probe both charge (via voltage-dependent cantilever frequency shifts) and lateral conductivity (via voltage-induced changes in cantilever quality factor) at room and cryogenic temperatures.

SESSION L4: POSTER SESSION

Chair: Neil C. Greenham
Tuesday Evening, April 22, 2003
8:00 PM
Salon 1-7 (Marriott)

L4.1

HALOGENATION OF ORMOSIL: A PROMISING ROUT FOR TAILORING OPTICAL ABSORPTIONS. Wei Liang, Yadong Zhang, Amir Fardad, 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 patternability. 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 sol-gel materials for integrated optic applications are mainly limited to the multi-step coating, conventional resist coating and photolithography. Employing hybrid organic-inorganic materials can alleviate such limitations. This family of materials has received an increasing attention owing to interesting chemical, mechanical, optical and physical properties that can be adjusted between organic and inorganic behaviors. However high concentration of CH groups, thus strong vibrational absorption in 1600-1800 nm ranges exacerbates the tail of absorption within 1550-nm window. This entails minimizing the number of C-H in addition to OH bonds per cubic centimeter for realization of low-loss optical devices. A possible way to achieve this goal is to promote the condensation and replace the C-H bonds by C-F bonds. In this paper, we report on a new class of fluoro substituted hybrid organic-inorganic materials with wide index and adhesion tunable properties for integrated optics. Material compositions and process parameters are optimized to achieve absorption <0.2dB/cm and propagation losses <1 dB/cm at 1550 nm. 1x16 Beam splitters are designed and fabricated which exhibit <1dB power uniformity and <2 dB coupling loss per interface.

L4.2

ACID-CATALYZED CATIONIC POLYMERIZATION OF 2,5-DIHALO-3,4-ETHYLENEDIOXYTHIOPHENE: CONDUCTING POLY(3,4-ETHYLENEDIOXYTHIOPHENE). Woonphil Baik, Jae Han Park, Yongsam Kim, Sang Kook Jeong, Myongji University, Dept of Chemistry, Yongin City, Kyongki Do, KOREA.

Among the several conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of most promising

material for practical applications because of the good thermal stability, high conductivity, and high transparency in the p-doped state. In addition, a special attention is its solubility as a colloidal solution 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 chemically oxidative 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 acids-promoted cationic polymerization of 2,5-dihalo-3,4-ethylenedioxythiophene. The cationic polycondensation was occurred via thiophenyl cation because of the high stability by strong electron-donating groups. The resulting conducting PEDOTs afforded conductivities of 3 ~20 Scm⁻¹ (pressed powder pellet). p-Doped PEDOTs prepared by dihalo-EDOT with acid were treated with hydrazine in water to dedop 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.

L4.3

SCANNING-TUNNELING SPECTROSCOPY ON CONJUGATED POLYMER FILMS. M. Kemerink^a, S.F. Alvarado^b, P.M. Koenraad^a, H.W.M. Salemink^a, J.H. Wolter^a. ^aEindhoven Univ of Techn, Dept. of Appl Phys, Eindhoven, THE NETHERLANDS; ^bIBM Research, Rüschlikon, SWITZERLAND.

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

L4.4

DE-DOPING OF POLY (3,4-ETHYLENE DIOXYTHIOPHENE): (POLY STYRENE SULPHONATE) VIA CHARGE TRANSFER IN THE PRESENCE OF DISSOLUTED INDIUM-TIN-OXIDE AND WATER. H L. Yip, K.W. Wong, K.Y. Wong, W.M. Lau, Dept of Physics and Materials Science and Technology Research Centre, The Chinese Univ of Hong Kong, Shatin, Hong Kong, P.R. CHINA; K H. Low, H.F. Chow, Dept of Chemistry, The Chinese Univ of Hong Kong, Shatin, Hong Kong, P.R. CHINA; Z.Q. Gao, W.L. Yeung, C.C. Chang, Varitronix Limited, TKO Industrial Estate, Hong Kong, P.R. CHINA.

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

L4.5

Abstract Withdrawn.

L4.6

Abstract Withdrawn.

L4.7

STRUCTURE-OPTICAL PROPERTY RELATIONSHIP STUDIES OF STYRYL PYRAZINE DERIVATIVE FLUOROPHORES.

Jeremy C. Collette and Aaron W. Harper, Univ of Southern California, Department of Chemistry and the Loker Hydrocarbon Research Institute, Los Angeles, CA.

A set of six alkyamino-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 analyte concentrations and temperatures are shown to 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 based on well known electron donor-acceptor pair chromophores and are expected to exhibit exceptional two-photon characteristics. Calculated second hyperpolarizabilities relating to the nonlinear index of refraction indicate comparable or greater two-photon activities than known two-photon molecules.

L4.8

SYNTHESIS OF POLY(P-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 alkoxy-substituted divinylbenzene monomer into PPV. The ligand substitution on the ruthenium atom is crucial for enhancing the overall activity of the catalyst to produce high molecular weight polymers. A nitrogen carbene ligand is required in the axial position to facilitate generation of the active ruthenium intermediate as well as stabilization of this intermediate. Variations in catalyst loading relative to monomer, as well as the activity of the catalyst itself, produces materials with different molecular weights and therefore different conjugation lengths. When molecular weights are large enough, this increase in conjugation decreases the singlet energy of the excited state and contracts the band gap.

L4.9

AN INVESTIGATION OF THE OPTICAL AND ELECTRONIC PROPERTIES OF SOLUTION PROCESSED POLY-CYCLOPENTADITHIOPHENES THIN FILMS. Paolo Coppo and Michael L. Turner, Department of Chemistry, University of Sheffield, Sheffield, UNITED KINGDOM; Stephen G. Yeates, Domenico C. Cupertino, Avecia Research Centre, Blackley, Manchester, UNITED KINGDOM.

Solution processable conjugated polymers are being extensively investigated as charge transport materials for use in electronic devices such as field effect transistors.[1] The mobility of charges in these materials is limited by the efficiency of hopping between localized states [2] and therefore close p-stacking 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 polycyclopentadithiophenes.[4] These polymers are fused ring derivatives of the extensively studied poly-3-alkylthiophenes and are structural analogues of the polyfluorenes. This contribution describes an investigation of the structure/property relationships that govern solid state self-assembly of fused thiophene ring systems and examines the influence of polymer morphology in these systems on electronic properties such as field effect mobility. 1) Siringhaus, H.; Tessler, N.; Friend, R. H., Science, 1999, 280, 1741. 2) Cornil, J.; Beljonne, D.; Calbert, J.-P.; Bredas, J.-L., Adv. Mater., 2001, 13, 1053. 3) McCullough, R. D., Adv. Mater., 1998, 10, 93. 4) Coppo, P.; Cupertino, D. C.; Yeates, S. G.; Turner, M. L., J. Mater. Chem., 2002, 12, 2597.

L4.10

PHOTOPHYSICS OF EUROPIUM(III) β -DIKETONE

COMPLEXES THAT CAN BE EXCITED AT LOWER ENERGIES.

Patrick J. Case, Aaron W. Harper, Donald P. and Katherine B. Loker Hydrocarbon Research Inst, Dept of Chemistry, University of Southern California, Los Angeles, CA.

In preliminary work performed in our lab, it was noticed that tris(dithienylmethane)europium(III) had an excitation maximum around 410nm while its absorbance maximum was around 375nm. This sparked interest in seeing if lower energy polymers could be used to sensitize lanthanide complexes. Because of promising results, an effort to create more trivalent europium complexes that could be excited around 400nm was established. A series of novel β -diketone type ligands consisting of a naphthyl or phenanthrene unit on the C₁ carbon and a thienyl or furanyl group on the C₃ carbon have been synthesized. The photophysics of the ternary and quaternary compounds containing 1,10-phenanthroline, as well as the effect on changing the heteroatom of the heterocyclopentadiene ring from oxygen to sulfur will be presented. Also, effective triplet harvesting from a conjugated polymer will be shown.

L4.11

ENERGY TRANSFER STUDIES OF POLYPHENYLENE-TYPE POLYMERS TO A SERIES OF DYES. Sean O. Clancy, Asanga B. Padmaperuma, Aaron W. Harper, Univ of Southern California; Donald P. and Katherine B. Loker Hydrocarbon Research Inst, Dept of Chemistry, Los Angeles, CA.

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-phenyldiboronic acid with 1,4-dibromobenzene or 1,3-dibromobenzene, 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 nickel-mediated coupling of 2,5-dichloro-4'-methylbenzophenone. The resultant 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 as triplet acceptors. Photophysical data and energy transfer parameters will be presented.

L4.12

OPTICAL PROCESSES OF A ZWITTER-IONIC POLYTHIOPHENE DERIVATIVE CONTROLLED BY SELF-ASSEMBLY OF BIOMOLECULES. Peter Nilsson, Olle Inganas, Linkoping Univ, Dept of Physics, Linkoping, SWEDEN.

A chiral, 3-substituted polythiophene with an amino acid function shows pH-dependent visible, emission and circular dichroism spectra in buffered aqueous solution. At pH equal to pI of the amino acid, the backbone adopts a non-planar right-handed helical conformation and the polymer chains are separated from each other. Increasing pH leads to a more planar conformation of the backbone and an aggregation of the polymer chains occurs. A lower pH will also lead to a more planar conformation of the backbone, but aggregation of the polymer chains appears to be absent. The aggregates are disrupted by increasing ionic strength in alkaline buffer systems, indicating that hydrogen bonding is important for aggregation. On the other hand, ions containing an amino group and one or more hydroxyl groups induce a more planar conformation of the polymer backbone. The optical transitions of this polythiophene derivative can also 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. Breneman and Phil. M Lessner, KEMET Electronics Corporation, Greenville, SC; Touriya E.L. Moustafid 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 acetonitrile medium. We are currently concerned with the electrosynthesis of poly (3, 4-ethylenedioxythiophene) PEDOT doped with mixing anions from the electrolyte lithium tosylate and co-surfactants sodium dodecyl sulfonate acid and sodium polystyrene sulfonate acid. Strong electrostatic interaction occurring between EDOT⁺, radical cation and cosurfactant anions DS⁻ 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 galvanostatic methods, and characterized by UV-visible, and SEM spectroscopy.

L4.14

VIBRATIONAL ANALYSIS OF COPPER PHTHALOCYANINE THIN FILMS ON VARIOUS SUBSTRATES. Suidong 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. All the CuPc films were deposited in ultra-high vacuum at room temperature, and the vibrational excitations of submonolayer, monolayer, and multilayer CuPc films have been studied step by step. The HREELS spectra of CuPc films both 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 ZINC OXIDE. Fu Lung Wong^a, Xin Jiang^b, Man Keung Fung^a, Chun-Sing Lee^a, Shuit-Tong Lee^a. ^a Center of Super Diamond and Advanced Thin Films (COSDAF) & Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, CHINA; ^b Fraunhofer Institute for Thin Film and Surface Engineering (FHG-IST), 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 resistance 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 8V and 7V 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, Graham A. Turnbull, Ifor D.W. Samuel, Organic Semiconductor Centre & Ultrafast Photonics Collaboration, School of Physics & Astronomy, University of St. Andrews, St. Andrews, UNITED KINGDOM.

In recent years, semiconducting conjugated polymers have received considerable interest as novel laser gain media. They exhibit optical gain over broad spectral ranges through the visible and so are well suited to use in tuneable lasers and have the potential to be used as broadband optical amplifiers. Such devices would be readily compatible with polymer optical fibres and integrated circuits. Polymer optical fibres are a favoured technology to relieve the telecommunications bottleneck in local area networks, and low-cost integrable optical amplifiers may increase the range and applicability of such systems. We demonstrate a compact, broadband optical amplifier using the conjugated polymer poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-paraphenylenevinylene (OC₁C₁₀-PPV) in dilute 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 a function of solution concentration is examined with 2 g/l being the optimum. The effect of different probe beam intensities on the gain is also examined. We observe a drop in gain at higher probe powers due to saturation effects and an increase in gain as the probe intensity decreases. Such behaviour is characteristic of optical amplifiers and can be modelled readily. For a 1 cm path length we measured a small signal gain of 44 dB, and deduce a stimulated emission cross-section for OC₁C₁₀-PPV of 5.3×10^{-17} cm². The implications of these results for solid-state polymer optical amplifiers will be discussed.

L4.17

Transferred to L8.3

L4.18

Abstract Withdrawn.

L4.19

Abstract Withdrawn.

L4.20

INFLUENCE OF ORGANIC FILM THICKNESS ON ORGANIC LIGHT-EMITTING DIODE PERFORMANCE. Chen Liu, Chongyang Xu, Sheng Yin, Zhiyou Zhong, Chang-an 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 study of the influence of film thickness on those possibilities, we qualitatively analyzed the dependence of external quantum efficiency on organic thin film thickness. At the same time, combining current injection theory and recombination theory, we quantitatively simulated above dependence, which show how did the film thickness of different organic layer affect the external quantum efficiency. In addition, we qualitatively studied the dependence of threshold voltage, and operating lifetime on the film thickness. This work is helpful to optimize the design of OLED, and make it easy to model the performance of OLED by its process parameters.

L4.21

SYNTHESIS AND CHARACTERIZATION OF NOVEL PLATINUM ACETYLIDE OLIGOMERS. Thomas M. Cooper, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH; Daniel G. McLean, Science Applications International Corporation, Dayton, OH; Joy E. Rogers, Technical Management Concepts, Inc, Dayton, OH; Benjamin C. Hall, Systran, Inc, Dayton, OH; Kenneth Turnbull, Dept. of Chemistry, Wright State University, Dayton, OH; Andrew Weis, Dept. of Chemistry, Wright State University, Dayton, OH.

To develop novel chromophores for photonic applications, we synthesized a series of transition metal-containing phenyl acetylidyde oligomers. These compounds have novel structural features, including attachment of a sydnone 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 acetylidydes we recently described in the literature (Rogers, J.E., et al. J. Phys. Chem. A 106: 10108-10115(2002)).

L4.22

INTRA- AND INTER-CHAIN ENERGY TRANSFER IN AN END-CAPPED CONJUGATED POLYMER. Emmanuelle Hennebicq, David Beljonne, 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 polyindenofluorene conjugated chains end-capped with a red-emitting perylene derivative. The polymer chains can be regarded as formed by a statistical distribution of segments with different conjugation lengths and therefore different excitation energies. Upon photoexcitation, unidirectional long-range energy transfer processes thus occur towards lower energy sites, prior to final trapping of the excitations on the perylene derivatives. Both intra- and inter-molecular hopping processes involving different conjugated segments of the polymer chains and the perylene end-group are described in the framework of an improved Förster model based on the use of a monopole expansion of the transition moments. These calculations suggest that in solution, where molecular contacts are rare, exciton transport takes place through hopping along the conjugated chains, which is an intrinsically slow process. In contrast, interchain transport, dominating the energy transfer dynamics in the solid state, is found to be about one order of magnitude more efficient, as a result of larger electronic matrix elements between neighboring molecules. To account for the static disorder inherent to polymer materials (here associated with the presence of different conformers), random chains of increasing size (built from a distribution of conjugated segments with various lengths) were generated and average values of the energy transfer times estimated by means of 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 in aggregates, wherein acceptor states are built as an ad-hoc combination of wavefunctions localized on single conjugated segments.

The results of these simulations will be discussed thoroughly.

L4.23

BLUE ORGANIC ELECTROPHOSPHORESCENCE USING EXOTHERMIC HOST-GUEST ENERGY TRANSFER. R.J. Holmes, Y.-J. Tung^a, R.C. Kwong^a, J.J. Brown^a, S. Garon^b, M.E. Thompson^b and S.R. Forrest, Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, NJ. ^aUniversal Display Corporation, Ewing, NJ; ^bDepartment of Chemistry, University of Southern California, Los Angeles, CA.

The design of an efficient, electrophosphorescent 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 challenge to achieving exothermic energy transfer for blue electrophosphorescence lies in the lack of suitable high-energy hosts. Here, we demonstrate efficient blue electrophosphorescence using exothermic energy transfer from a host consisting of N,N'-dicarbazolyl-3,5-benzene (mCP)¹ to the phosphorescent iridium complex iridium(III)[(4,6-difluorophenyl)-pyridinato-N,C^{2'}]picolinate (FIrpic).² By examining the temperature dependence of the radiative lifetime and the photoluminescence of a film of mCP doped with FIrpic, we confirm the presence of exothermic energy transfer. The maximum external electroluminescent quantum efficiency of devices employing mCP:FIrpic is (7.5±0.8)%, with a luminous power efficiency of (8.9±0.9)lm/W, representing a significant increase in performance over previous, endothermic blue electrophosphorescent guest-host systems.³

[1] V. Adamovich, J. Brooks, A. Tamayo, A.M. Alexander, P. Djurovich, B.W. D'Andrade, C. Adachi, S.R. Forrest, and M.E. Thompson, *New J. Chem.* 25, 1171 (2002).

[2] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R.C. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, and M.E. Thompson, *Inorg. Chem.* 40, 1704 (2001).

[3] C. Adachi, R.C. Kwong, P. Djurovich, V. Adamovich, M.A. Baldo, M.E. Thompson, and S.R. Forrest, *Appl. Phys. Lett.* 79, 2082 (2001).

L4.24

LIGHT-EMITTING PROPERTIES OF REDOX-ACTIVE CHROMOPHORES BASED ON SPIROBIFLUORENE. O.-K. Kim^a, W.H. Kim^{b,c}, Z. Huang^{a,d}, J. Je^{a,d}, and Z. Kafafi^b, Naval Research Laboratory, ^aChemistry Div and ^bOptical Science Div, Washington, DC; ^cSFA Inc., Largo, MD; ^dInstitute of Materials Science, University of Connecticut, Storrs, CT.

We have synthesized multifunctional chromophores based on spirobifluorene (π -center), attaching donor and/or acceptor moiety, typically (diphenylamino-p-benzyl and [2-(*p*-*ter*-butyl-3,4-oxadiazolyl)]benzyl at the ends: D- π -D (**301**), D- π -A (**302**) and A- π -A (**303**).

We have investigated LE properties of these oligomeric emitters in single and double layer devices consisting of ITO/PEDOT//EM//AlQ₃//Mg:Ag. We were particularly interested in looking into the functional susceptibility of the redox-active moieties of the emitters toward incoming electrons 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 diode systems 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 AlQ₃ 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 AlQ₃ (double layer); the EL is decreased to 4 cd/m² from 100 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 exciton quencher.

Blending of **303** with PVK at 1:1 and 1:5 (**303**:PVK) to compensate the electron affinity does not change the EL but a large blue-shift (65 nm) of emission band from that (555 nm) of the pristine **303**. However, the blend of 5:1 displays an entirely different EL spectrum that covers a broad wavelength (430 to 800 nm), emitting a white light.

L4.25

STRUCTURE AND MORPHOLOGY OF SOLUTION PROCESSED PENTACENE FILMS. Samir Succar and Sigurd Wagner.

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

conjugated small molecule materials such as pentacene due to their sparing solubility. 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-micrometer hexagonal platelet films and 400-micrometer 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 affected both the appearance of the solution and the structure of the resulting film as 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 soxhlet 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.D. Feng and Z.H. Lu, Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, CANADA.

Organic light-emitting diodes (OLEDs) in visible spectrum are 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 8-hydroxyquinoline Erbium (Erq) based OLEDs, and 1.54 micron electroluminescence was observed at room temperature. The emission intensity can be tuned by device structures. The physical mechanism behind them is discussed. An approach to further improvement on the quantum efficiency of 1.54 micron emission is also proposed.

L4.27

SYNTHESIS AND LIGHT-EMITTING PROPERTIES OF NEW POLYFLUORENE DERIVATIVES. Do-Hoon Hwang, Kumoh 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'-*n*-octyloxyphenyl)]fluorene (POPF-8) and poly[9,9-bis(4'-2',7'-dimethylcyloxyphenyl)]fluorene (POPF-10) were synthesized through the Ni(0) mediated polymerization. The copolymers were characterized using FT-IR spectroscopy, UV-vis spectroscopy, TGA, photoluminescence (PL) & electroluminescence (EL) spectroscopy, elemental analysis, and molecular weight studies. Interestingly no significant spectral change and formation of excimer emission were observed even after annealing the polymer film at 100°C for 2h. Light-emitting devices were fabricated in an ITO (indium-tin oxide) /PEDOT/polymer/Ca/Al configuration. Synthesis and EL properties of new polyfluorene derivatives will be presented.

L4.28

WHITE LIGHT-EMITTING DEVICES USING POLYMER BLENDS. Do-Hoon Hwang, Dept of Applied Chemistry, Kumoh Natl Inst of Tech, Kumi, KOREA; Ji-Hoon Lee, E-Polymer Lab, Samsung Advanced Inst of Tech, Suwon, KOREA; Jeong-Ik Lee, Basic Research Lab, ETRI, Taejon, KOREA; Chang-Hee Lee, Dept of Physics, Inha Univ, Incheon, KOREA; Yong-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-(2-ethylhexyl)fluorene] (PEHF), poly(9,9-dioctylfluorene-2,7-vinylene) (POFV), poly(2-(3',7'-dimethylcyloxy)-5-methoxy-1,4-phenylene-1-cyanovinylene) (CN-PPV) and poly(2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene) (MEH-PPV). Inefficient energy transfers between the blue polymer and the green or the red polymer, which was observed in PL spectra of the blend films, provides a good advantage to get a white light emission due to better blend ratio controllability. The EL devices were fabricated with ITO/PEDOT/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 NANOCOMPOSITE PREPARED BY USING A PARTICULATE SOL. Byung Duk Yang and Ki Hyun 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 spacing energy with an increase of TiO₂ content were induced by the reduction of torsional order. The PPV/TiO₂ 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/TiO₂ 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/TiO₂ nanocomposite prepared by using nanopowder showed the high vibronic splitting energy.

L4.30

CARRIER DYNAMICS OF CONJUGATED OLIGOMERS.

Jean-Claude Vial and Olivier Stéphan, J. Fourier Univ -CNRS, Lab Spectrométrie Physique, Grenoble, FRANCE; C. Andraud, Ecole Normale Supérieure-CNRS, Lyon, FRANCE, Lab Stéréochim & Interact 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 electronics carriers inside these materials. Indeed they can complement macroscopic information such as carrier mobility and they are more simple to perform because they avoid doping and electrical contacts. We want to demonstrate that on two particular cases. We have synthesized a whole set (from N=2 to 8) of alkyl-fluorene 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 classic red shift when N increase we also measured the quantum efficiency and the photoluminescence decay time in the picosecond range. These measurements are added 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 oligo-alkyl-thiophene 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 measure a quantum efficiency smaller for small N going along with non radiative rates increasing as N decrease. We explain that by a localization of exciton (or carrier) on trap related to Chloride.

L4.31

GREEN OLEDs: ELECTROLUMINESCENCE AND THE

ELECTRICAL CARRIER TRANSPORT. L. Pereira, R. Pontes, P. Lopes, Departamento de Física, Universidade de Aveiro, Aveiro, 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 understanding their optical and electrical properties. The electroluminescence (EL) shows a broad band centred near 510 nm (green) and two other small bands at near 425 nm (blue) and near 565 nm (orange). The result is a "white green" EL. The origin of the orange and main green band is clearly the recombination inside the Alq₃ layer while the blue band appears to be due to a recombination in a narrow layer in NPB/Alq₃ interface. The electrical DC measurements have been performed in order to establish the nature of carrier transport and effectiveness. At low applied voltages, an injection of carriers through a small barrier (~0.2 V) control the current flow. After the transition to the bulk limited conduction, the results suggests that when the electroluminescence (EL) takes place a trap charge-limited conduction (TCL) with characteristic trap energy near 0.13 eV controls the process, but some influence of metal - semiconductor interface and the bulk conduction are also discussed. The investigation of the efficiency dependence on the minority carriers reveals that the triple layer device with two hole transport layer can improve the EL (reduction of the driving voltage and therefore increase the stability), but also contributes to the widening of the EL band. The relationship between the electrical measurements and the luminescence spectrum is analysed. Finally, a general model is proposed based on the experimental results and energy band diagram.

L4.32

SYNTHESIS, PHOTO- AND ELECTRO-LUMINESCENT PROPERTIES OF NOVEL THIOPHENE BASED POLYMERS.

George Vamvounis, Yuning Li, Steven Holdcroft, Simon Fraser Univ, Dept of Chemistry, Burnaby, BC, CANADA; Hany Aziz, Zoran D. Popovic, Xerox Research Center of Canada, Mississauga, Ontario, CANADA.

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

L4.33

STABILIZED BLUE EMISSION FROM POLYFLUORENE-BASED LIGHT EMITTING DIODES: ELIMINATION OF FLUORENONE DEFECTS. Xiong Gong, Parameswar K. Iyer, Daniel Moses, Guillermo C. Bazan, Alan J. Heeger, and Steven S. Xiao^a, Institute for Polymers and Organic Solids, University of California-Santa Barbara, Santa Barbara, CA. ^aAmerican Dye Source, Baie D'Orfe, Quebec, CANADA.

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

L4.34

SYNTHESIS OF MONODISPERSE CHIRAL OLIGO(FLUORENE)S AND THEIR OPTICAL PROPERTIES IN NEAT FILMS.

Yanhou Geng, Anita Trajkovska, Sean W. Culligan, Dimitris Katsis, and Shaw H. Chen, Univ. of Rochester, Dept of Chemical Engineering and Laboratory for Laser Energetics, Center for Optoelectronics and Imaging, Rochester, NY.

Although various chiral π -conjugated systems have been reported, the structural origins of the observed chiroptical properties have not successfully elucidated. Polyfluorenes have been considered to be a prime candidate for optoelectronics due to their superior stability, high fluorescent quantum yield, and their potential for a spontaneous alignment mediated by liquid crystal mesomorphism. To facilitate the fabrication of defect-free glassy liquid-crystal films and hence structural elucidation at the supramolecular level, we have synthesized and characterized the first series of monodisperse chiral oligo(fluorene)s with a number of repeat units (n) up to 16. We have also investigated the effects of chain length and pendant structure on thermotropic and optical properties in neat films. It was found that oligo(fluorene)s with $n \geq 5$ are capable of cholesteric mesomorphism. Pristine spin-cast films, approximately 90 nm in thickness, were found to be amorphous while exhibiting pronounced circular dichroism and highly efficient circularly polarized fluorescence. Nonamers capable of forming glassy cholesteric films were prepared through optimization of the pendant structure. Variable angle spectroscopic ellipsometry was employed to determine the helical sense and pitch length of the cholesteric stack in thin films. It was also instrumental in the interpretation of the resultant chiroptical properties. Furthermore, strongly circularly polarized and highly efficient light-emitting diodes have been demonstrated with monodomain glassy cholesteric films.

L4.35

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

Photoluminescence (PL) of poly[phenylene vinylene] (PPV) and tris-(8-hydroxyquinoline)aluminum complex (Alq₃) under hydrostatic pressure up to 6Gpa is investigated. The exciton energies pressure coefficient is 56.9meV/Gpa-1 for PPV samples, while no obvious energy shift for Alq₃ samples (pressure coefficient is -4.21meV/Gpa-1). We find that the details of crystalline arrangement crucially affect the optical properties. With increase of interchain distance in the Vstack

direction, leading to a richer exciton structure and an increase of radiative efficiency. This has implications for theoretical activity and optoelectronic applications of polymer film. Our results indicate that polymers have an advantage over small molecules in OLED applications.

L4.36

Abstract Withdrawn.

L4.37

BALANCED CHARGE INJECTION AND SINGLET EXCITON QUENCHING IN ORGANIC ELECTROLUMINESCENT DEVICES. Chimed 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 tris(8-hydroxyquinoline) aluminum (Alq)-based EL devices [1]. In particular, work function control of the electrodes plays a crucial role in balancing the rates at which holes and electrons are injected into a two-layer organic thin film with a heterojunction. In this work, we described well balanced electron and hole injections into organic layers of our improved devices [1,2] in order to maximize the EL efficiency. To clarify the balancing between electrons and holes, we also studied carefully using only single layer EL devices with different thicknesses. Moreover, our recent results have shown that the luminance decreased less than linearly with an increase in current of Alq-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 ($^1\text{Alq}^*$) by large excess cation Alq^+ radicals with increase in current due to partial overlap between fluorescence spectrum of $^1\text{Alq}^*$ and absorption spectrum of Alq^+ cation radicals, but not the corresponding anion Alq^- radicals. [1] C. Ganzorig and M. Fujihira, Appl. Phys. Lett. 81, 3137 (2002). [2] M. Fujihira and C. Ganzorig, in Conjugated Polymer and Molecular Interfaces, A. Kahn, J.J. Pireaux, W.R. Salaneck, and K. Seki editors, (Marcel Dekker, Inc., 2002). p. 817. [3] C. Ganzorig and M. Fujihira, Appl. Phys. Lett. 77, 4211 (2000).

L4.38

LOSS PROCESS IN EFFICIENCY OF BLUE ORGANIC ELECTROLUMINESCENT DEVICES. Yasuo Enatsu, Chimed 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 additional losses due to exciton quenching mechanisms. We report here the EL characteristics of blue organic EL devices with hole transport layer as an emitter i.e.

ITO/NPD/BCP/Alq/Al. Here, ITO, NPD, BCP, and Alq are abbreviations for an indium tin oxide anode, a 4,4'-bis[N-(1-naphthyl)-N-phenyl-aminobiphenyl, a bathocuproine, and a tris(8-hydroxyquinoline)aluminum. Different types of anode and cathode interface materials are used in this study [1]. In these devices modified by charge injection layer of the interface materials, we have never observed that the EL 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 singlet excited states ($^1\text{NPD}^*$) 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 $^1\text{NPD}^*$ and absorption spectrum of NPD^+ . In addition, $^1\text{NPD}^*$ is also possible quenched by anion NPD^- radicals when large excess electron injection. The detailed investigation will be discussed at the symposium. [1] C. Ganzorig, K. J. Kwak, K. Yagi, 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. Suga, and M. Fujihira, Chem. Lett. 1032 (2000).

L4.39

PRESSURE- AND TEMPERATURE-INDUCED STRUCTURAL ORDERING IN ORGANIC POLYCRYSTALLINE MATERIALS. Sergey Budakovskiy, Boris Grinev, Iryna Khomiakova, Langin Lisetski, Tetyana Teplytska, STC Institute for Single Crystals, NAS of Ukraine, Kharkov, UKRAINE.

Pressure-compacted organic molecular polycrystals (e.g., stilbene, anthracene, p-terphenyl) are known to be a promising class of scintillator materials for radiation detectors. The use of such materials allows manufacturing of large-area scintillators of required shapes. However, their scintillation characteristics remain substantially inferior to those of standard single crystalline scintillators made of the

same materials. Recently, it has been shown that under certain conditions of the combined action of pressure and pre-melting temperatures, structural properties of the polycrystalline pellets 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 crystalline regions, with subsequent solid-state reaction of crystal growth. Substantial improvement of scintillation properties is observed. Thus, for stilbene and p-terphenyl polycrystals, light outputs of up to 85-95% with respect to the corresponding single crystals was obtained. Possible mechanisms are proposed for the observed structural ordering, and ways for optimization of the pressure/temperature parameters are discussed. In parallel experiments, we observed similar behavior with more complex substances (including those of biological origin), with marked effects due to specific features of supramolecular ordering. It is argued that molecular materials obtained by 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. 1. B.V. Grinev, S.V. Budakovskiy, L.N. Lisetski and V.D. Panikarskaya, Functional Materials.V.1, No.1, p.156 (1994). 2. B.V. Grinev, S.V. Budakovskiy, L.N. Lisetski, V.D. Panikarskaya and E.E. Lakin, Kristallografiya V.42, No.3, p.506 (1997). 3. S.V. Budakovskiy, L.N. Lisetski and P.P. Shtifanyuk, 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 1 D MOLECULAR NANOSTRUCTURES. Federico Rosei^a, Y. Naitoh, M. Schunack, E. Laegsgaard, I. Stensgaard, and F. Besenbacher, Physics Department and I-NANO, University of Aarhus, DENMARK; P. Jiang, A. Gourdon, and C. Joachim, CEMES-CNRS, Toulouse, FRANCE. ^aPresent 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] (C₉₀H₉₈), 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 (3,5-di-tert-butylphenyl) 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 [001] direction with 2 nm 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 1 D 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 +0.8 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. Gimzewski and A. Aviram, Nature 408, 541 (2000). [2] F. Rosei et al., Organic molecules acting as templates on Metal Surfaces, Science 296, 328 (2002).

L4.43

Abstract Withdrawn.

L4.44

TRIARYLAMINES CONNECTED VIA PHENYLENEVINYLENE SEGMENTS. Heiner Detert and Oleg Sadovski, Johannes Gutenberg Universitaet Mainz, Inst. of Organic Chemistry, Mainz, GERMANY.

The well-known hole transport properties of triarylamines can be combined with the strong luminescence of stilbenoid chromophores. We present the synthesis of well soluble oligo(phenylenevinylene)s with conjugation lengths of 2 to 6 styryl units, terminated by different

arylamines. The syntheses were performed via PO-activated olefinations and via Pd-catalysed aryl-N-coupling reactions. The fluorescence properties are primarily depending on the central stilbenoid segment. Cyclic voltammetry reveals that the oxidation potential is nearly independent from the conjugated system, whereas the reduction is controlled by the stilbenoid segment.

L4.45

THE SYNTHESIS, CONDENSATION, AND LUMINESCENCE OF OLIGO(PHENYLENEVINYLENE)S WITH ALKOXYSILANE END GROUPS. Heiner Detert and Erli Sugiono, Johannes Gutenberg Univ, Inst of Organic Chemistry, Mainz, GERMANY.

Due to their strong fluorescence, stilbenoid oligomers are one of the preferred classes of luminescent organic materials for electrooptical applications. The good solubility of alkoxy-substituted OPVs is advantageous for the processing, but limits the fabrication of multilayer devices. Additionally, the stability of amorphous films is only poor. This paper presents the synthesis of monodisperse OPVs with terminal alkoxy silane moieties, to allow cross-linking via hydrolysis and formation of siloxane networks. The alkoxy silanes are rigidly connected to the chromophores via Heck reaction or cross-metathesis. Hydrolysis and condensation yields oligosiloxanes with pendent OPVs, thus greatly improving the film forming capability of these well-defined chromophores. The connection to cyclosiloxanes 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-diaryl-1,3,4-oxadiazoles are functionalised with alkoxy silanes. These compounds are interesting for the preparation of organic-inorganic hybrid materials with luminescent units.

L4.46

IN SITU DEVELOPMENT AND STUDY OF CONDUCTIVE POLYMER ELECTRODE FILMS ON PVDF SUBSTRATES FOR ELECTRO-ACOUSTIC APPLICATION IN COCHLEAR IMPLANT. Arpit Dwivedi and Rodney Roseman, Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH.

Sensorineural hearing loss (profound deafness) is a result of the inability of the transducing structures in the cochlea (organ of Corti) to convert the mechanical displacement of the basilar membrane to neural signals. A class of devices known as Cochlear Implants can significantly enhance the hearing ability in these patients. Fundamentally different from existing cochlear implant technology are the piezoelectric based devices we are developing which are totally implantable. The unit is completely self-contained, designed to work without any signal amplifiers or transmission elements, greatly simplifying the stimulation process, and enhancing the cosmetic appearance of the patient. These devices utilize the bending piezoelectric effect, which has been designed and consists of several elements of piezoelectric polymer film with conductive polymer electrode, embedded in a flexible and dielectric coated substrate. The incoming mechanical energy (Pressure waves) into the cochlea generates electrical charge by virtue of the piezoelectric effect of the film. The generated charge is fed to electrical connections evaporated on the substrate and is used to stimulate surviving nerve fibers in the cochlea. In certain environments where acoustic impedance 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 an important issue, since the conventionally 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. Lawrence L. Brott, Rajesh R. Naik, Morley 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 reducing the complexity of their fabrication. Our research takes a biomimetic approach through the incorporation of thermosensitive proteins to enhance the properties of the infrared sensing device. By integrating these proteins into a matrix of poly(vinyl alcohol) doped with conducting carbon black and plasticizer, 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 through the application of a thin and transparent overcoat, uniform sensors can be fabricated with enhanced sensitivity and increased stability.

L4.48

FIELD EFFECT CONDUCTANCE OF REGIOREGULAR POLY(3-HEXYLTHIOPHENE) NANOFIBERS. Jeffrey A. Merlo and C. Daniel Frisbie, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

We are examining the electrical conductance of nanofibers of regioregular poly(3-hexylthiophene) (RRP3HT) as part of a program to elucidate the role of microstructure on electrical transport in conducting polymer films. Nanofibers of RRP3HT can be prepared by casting from dilute solutions of xylene or cyclohexanone.¹ Analysis of the nanofibers by atomic force microscopy (AFM) reveals fiber lengths of 0.2-5 μm , heights of 3-7 nm, and widths of $\sim 15\text{nm}$. 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 $0.06\text{ cm}^2/\text{Vs}$ and on/off ratios $> 10^4$. Temperature studies reveal activation energies ranging from 60-115 meV depending on the substrate. Threshold voltage is found to increase in magnitude with decreasing temperature. The surface chemistry of the substrate affects the electrical properties of the nanofibers similar to thin films of RRP3HT. Nanofibers were characterized on silicon dioxide, hexamethyldisilazane (HMDS) treated silicon dioxide, alumina, and phosphonic acid treated alumina substrates. Probing transport in discrete conducting polymer microstructures provides a way to address the role of microstructure in thin films. In particular, conductance measurements on RRP3HT nanofibers allow separation of the effects on transport of the polymer-dielectric interface versus the semicrystalline character of thin films.¹ K.J. Ihn, J. Moulton, and P. Smith, Journal of Polymer Science: Part B: Polymer Physics 31, 735 (1993).

L4.49

NANOCRYSTALLINE SEMICONDUCTOR LEDS WITH SIMPLE STRUCTURE AND HIGH EFFICIENCY. Dietrich Bertram, Volker Weiler, Philips Research Laboratories, Aachen, GERMANY; Dimitri Talapin, Horst Weller, University of Hamburg, Hamburg, GERMANY.

Nanocrystalline semiconductor particles exhibit a size dependent bandgap emission, due to size quantisation 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 far, 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 efficiencies, well defined color 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 paves the road to cheap, high quality displays based on inorganic semiconductor nanoparticles.

SESSION L5: SPECTROSCOPY AND DEVICES

Chair: George Malliaras

Wednesday Morning, April 23, 2003

Salon 1-3 (Marriott)

8:30 AM *L5.1

CHARGE RECOMBINATION AND TRANSPORT STUDIES OF POLYMER/FULLERENE BLENDS AND PHOTOVOLTAIC DEVICES. A.F. Nogueira, I. Montanari, R. Pacios, S.A. Choulis, S. Cook, Y. Kim, J. Nelson, D.D.C. Bradley, J.R. Durrant, Departments of Chemistry and Physics, Imperial College, London, UNITED KINGDOM; C. Winder, N.S. Sariciftci, Physical Chemistry, Johannes Kepler University, Linz, AUSTRIA; C. Brabec, Siemens AG, Erlangen, GERMANY.

Organic bulk heterojunctions are currently attracting attention for low cost plastic photovoltaic cells [1]. Devices fabricated from conjugated polymer / methanofullerenes 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 downside of this blending is that photogenerated electrons 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 composite films. These dynamics are studied by nanosecond to millisecond transient absorption spectroscopy and by time of flight studies of charge transport. Results will be presented for a range of polymer / fullerene systems as a function of excitation density, temperature and operating conditions (white light illumination, bias voltage etc.) [3-5]. Our studies will address in particular the role of intra-band gap trap states in controlling the charge carrier dynamics, and therefore the current generation efficiency of photovoltaic devices. [1] N. S. Sariciftci et al, Science 258, 1474 (1992), [2] B. Kraabel, et al, J. Chem. Phys. 104, 4267 (1996), [3] I. Montanari et al, Appl. Phys Lett. (2002), 81, 3001-3003 [4] A. F. Nogueira et al, Journal of Phys. Chem. B, submitted, [5] J. Nelson, Phys. Rev. B, submitted (2002).

9:00 AM L5.2

VOLTAGE-INDUCED INFRARED SPECTRA FROM FIELD-EFFECT TRANSISTORS FABRICATED WITH REGIOREGULAR POLY(3-ALKYLTHIOPHENE)S. Yukio Furukawa, Hiroki Takao, Jun Yamamoto, Waseda Univ, Dept of Chemistry, Tokyo, JAPAN.

We will demonstrate the usefulness of a combination of infrared reflection-absorption spectroscopy and the FT-IR difference-spectrum method for the studies of carriers injected into the polymer layer in polymer field-effect transistors (FETs). We have fabricated FETs with regioregular poly(3-alkylthiophene)s (alkyl: hexyl, octyl, and dodecyl). Finger-shaped source and drain electrodes have been made. Each distance between fingers and the width of a finger is both 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 polymer FET. Infrared light from an FT-IR spectrophotometer (Digilab FTS7000) is incident on the side of the finger-shaped source and drain electrodes with an incident angle of 45 degree. A half of the incident light can pass through the polymer layer. Voltage-induced infrared spectra have been measured by the difference-spectrum method. We have observed a voltage-induced infrared spectrum from an FET based on regioregular poly(3-hexylthiophene) between the -10 V and the +3 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-hexylthiophene) film doped with ferric chloride. Thus, the observed infrared bands can be attributed to positive carriers (polarons) injected into the polymer layer by field effect in the polymer FET. We will discuss the voltage-dependence of field-effect-induced infrared intensity and the effect of alkyl side chains on field-effect-induced infrared absorption.

9:15 AM L5.3

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

Electroluminescent organic materials have recently made their way into display technology. There is considerable research underway to improve these materials to expand their utility. Alq₃ [tris(8-quinolinolato)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 inefficiency would make engineering a full panel organic display difficult. We report spectroscopic studies of the mechanism responsible for the decreasing efficiency. We use in-situ Charge Modulation Spectroscopy (CMS) in both unipolar model devices of the structure anode—Alq₃—doped Alq₃—insulator—cathode and bipolar transporting devices which have no insulator layer. The dopant is the laser dye DCJT_B [4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran]. When holes are injected both devices show photoluminescence quenching. In our studies we have observed the spectral signature of DCJT_B⁺ cations (DCJT_B⁺), evaluated the density of DCJT_B⁺ formed in the devices, and correlated its temporal behavior with that of photoluminescence quenching. We show that the cation acts as a quencher via Förster energy transfer, from excited-state DCJT_B to DCJT_B⁺. The Förster energy transfer

calculated from the measured cation spectra concentrations are consistent with the observed reductions in fluorescence. Our results suggest that the current-dependent efficiency loss can be avoided by judicious choice of emissive dopants. [1] Young et al, APPL PHYS LETT 80 (5): 874-876 FEB 4 2002

9:30 AM *L5.4

CHARGE TRANSPORT AND ENERGY TRANSFER PROCESSES IN SEMICONDUCTING π -CONJUGATED OLIGOMERS AND POLYMERS. Jean-Luc Bredas, University of Arizona, Department of Chemistry, Tucson, AZ.

The chemistry and physics of semiconducting polymers, oligomers, and discotic liquid crystals have attracted much interest following their successful incorporation as active elements in a number of (opto)electronic devices such as light-emitting diodes, solar cells, or field-effect transistors. Energy transfer and electron transfer (that is, transport) processes play a key role in the working mechanisms of these devices. Two of the main issues in the area will be discussed: (i) the impact of chemical structure, molecular packing, and reorganization energy on the hole and electron mobilities [1-3]; and (ii) the relative efficiencies of interchain versus intrachain energy transfer processes [4]. References: [1] J. Cornil et al., Advanced Materials, 13, 1053 (2001). [2] J.L. Bredas et al., Proceedings of the National Academy of Sciences USA, 99, 5804 (2002). [3] N.E. Gruhn et al., Journal of the American Chemical Society, 124, 7918 (2002); V. Coropceanu et al., Physical Review Letters, in press. [4] D. Beljonne et al., Proceedings of the National Academy of Sciences USA, 99, 10982 (2002).

10:30 AM *L5.5

EXCITON CONFINEMENT AT POLYMER-POLYMER HETEROJUNCTIONS IN LEDs. Arne C. Morteani, Anoop S. Dhoot, Ji-Seon Kim, Carlos Silva, Neil C. Greenham and Richard H. Friend, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

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

11:00 AM L5.6

CHARGE CARRIER GENERATION IN A CONJUGATED POLYMER STUDIED VIA SUB-20 FS PUMP-PUSH-PROBE EXPERIMENTS. Christoph Gadermaier, Emil J.W. List, Christian Doppler Laboratory for Advanced Functional Materials, Graz, AUSTRIA; Guglielmo Lanzani, Giulio Cerullo, Cristian Manzoni, Dipartimento di Fisica, Politecnico di Milano, ITALY; Ullrich Scherf, Makromolekulare Chemie, Bergische Universitaet 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 revealed the dynamics of singlet and triplet excitons as well as charge carriers. Charge carriers are essential in the electronic and optoelectronic properties one wants to exploit in the numerous upcoming applications of these materials. However, there is yet no comprehensive picture of the mechanisms that lead to their generation. Information about the charge carrier generation mechanisms can be obtained by modulating their efficiency. We achieve such modulation via a modification of the pump-probe technique, which we call pump-push-probe. The first excited state S₁ is reexcited via a second pulse (push) towards a higher lying state S_n. The broad-band probe reveals the dynamics of the relaxation of this state S_n as well as the kinetics of the states created from S_n. We find a reduction of stimulated emission (SE) and photoinduced absorption (PA) from the S₁ state as well as an increase of PA from the charge carriers. Hence the push pulse leads to an enhanced charge generation from a higher lying excited state S_n, which diminishes the S₁ population. The efficiency of this additional charge generation decreases rapidly with increasing pump-push 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 push and probe durations allow the time-resolution of the ultrafast relaxation of the S_n state and enables us to untangle the contributions of the two mechanisms.

11:15 AM L5.7

THE EFFECT OF DOPING ON THE ENERGY DISTRIBUTION OF LOCALIZED STATES AND CARRIER TRANSPORT IN DISORDERED ORGANIC SEMICONDUCTORS. Vladimir Arkhipov and Paul Heremans, IMEC, Leuven, BELGIUM; Evgenia Emelianova and Guy Adriaenssens, Semicond. Physics Lab., Univ. of Leuven,

Charge carrier hopping within a positionally random and energetically disordered system of localized states was shown to be an adequate model for the description of both equilibrium and non-equilibrium conductivity in non-crystalline 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 such a system will, in addition, create a random distribution of dopant ions that will Coulombically interact with carriers localized in intrinsic hopping sites. This interaction further increases the energy disorder. This effect is especially important in view of a small value of the dielectric constant and, concomitantly, long range of the Coulomb interaction typical for molecular semiconductors. Increasing energy disorder with increasing dopant concentration will lead to broadening of the apparent density-of-states (DOS) distribution. Therefore, doping of a disordered organic semiconductor, on the 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 decreasing mobility at low dopant concentrations. At higher doping levels the filling of deep states takes over leading to steeply increasing mobility at high dopant concentrations.

[1] H. Bässler, Phys. Stat. Sol. (b), 175, 15 (1993).

[2] D.H. Dunlap, P.E. Parris, and V.M. Kenkre, Phys. Rev. Lett. 77, 542 (1996).

11:30 AM L5.8

SURFACE-EMITTING DISTRIBUTED FEEDBACK LASERS BASED ON SEMICONDUCTING POLYFLUORENES.

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

In recent years, semiconducting polymers have attracted considerable interest as novel gain media for devices such as lasers and optical amplifiers. In particular, an important target is the future realisation of an electrically pumped solid-state polymer laser diode. Fluorene-based polymers (polyfluorenes) are a particularly attractive class of semiconducting polymers for such applications because they show excellent charge transport properties, have low stimulated emission thresholds and are the only family of conjugated polymers that emit colours that span the entire visible spectrum. Hence, they offer great potential for the fabrication of low cost, compact, highly tuneable solid-state lasers. Here, we report on the fabrication of optically pumped (355 nm pulses from a Q-switched Nd:YVO₄ microchip laser) polymer distributed feedback (DFB) lasers 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 second-order Bragg scattering induced by the substrate corrugations. We demonstrate laser action in devices based on both polymers. The lasers operate in the blue, one at 455nm and the other at 465nm, and exhibit low threshold energies (3nJ 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 polymers and induces a photonic stop band around the Bragg wavelength. Lasing occurs at the band edge, as expected for an index-coupled DFB laser.

11:45 AM L5.9

THE EFFECTS OF STRUCTURAL DISORDER ON THE THRESHOLD FIELD FOR EXCITON QUENCHING AND THE

CARRIER RECOMBINATION DYNAMICS IN POLY(PHENYLENE VINYLENE). Daniel Moses, Cesare Soci, Roland Schmechel, Alan Heeger, Institute for Polymers and Organic Solids, University of California, Santa Barbara, CA.

We have determined the exciton binding energy E_b in stretched oriented films of poly(phenylene vinylene) to be about 60 meV, which is significantly smaller than deduced by other researchers on the basis of measurements on disordered polymer films. It has been claimed that this magnitude of E_b is in contradiction with the operating fields in polymer-based light emitting diodes (OLEDs), which typically exceeds 105 V/cm. The claim has been that if indeed E_b were so small, this operating field would have dissociated the excitons due to the action of the external field and thereby diminished 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 photoconductivity action spectra as well as field-induced exciton quenching experiments and a discussion of the reasons for the higher E_b in disordered polymer films. The second topic of recent interest is related to the carrier recombination dynamics in conjugated polymers. Using transient photoconductivity experiments, we have recently found a bi-molecular carrier recombination mechanisms operating in measurements that utilize very low light intensities. This is the first time such a mechanism has been found in at a time range of $t_0.1$ ns in any polymer we have investigated. We will present the experimental, data, analysis, and a discussion on the implications of these findings.

SESSION L6: TRANSISTORS

Chair: C. Daniel Frisbie

Wednesday Afternoon, April 23, 2003

Salon 1-3 (Marriott)

1:30 PM L6.1

POLYFLUORENES AS ORGANIC SEMICONDUCTORS FOR POLYMERIC FIELD EFFECT TRANSISTORS. David J. Brennan, Paul H. Townsend, Dean M. Welsh, Mitchell G. Dibbs, Jeff M. Shaw, Jessica L. Miklovich, and Robyn B. Boeke, The Dow Chemical Company, Advanced Electronic Materials, Midland, MI.

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

1:45 PM L6.2

SOURCE/DRAIN CONTACTS IN ORGANIC POLYMER THIN FILM TRANSISTORS. Sandrine Martin, Michael Hamilton, and Jerzy Kanicki, 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 predominant role in the device operation. The devices used for our study of the role of the S/D contacts are gate-planarized thin-film transistors with a coplanar structure, i.e. source and drain contacts deposited before the organic polymer film. The devices use benzocyclobutene as gate planarization material, amorphous silicon nitride as gate insulator and ITO source and drain electrodes. The organic polymer semiconductor is a solution-based F8T2 (poly-9,9-dioctylfluorene-co-bithiophene). Typical performances of our devices are field-effect mobility about 6x10⁻³cm²/Vs, threshold voltage about ?20V, subthreshold swing about 1.5V/dec and ON/OFF current ratio about 10⁵, for

$W/L=116\mu\text{m}/56\mu\text{m}$ and gate insulator capacitance of $7.5 \times 10^{-9} \text{F}/\text{cm}^2$. We observed, as expected, a significant channel length dependence of the TFT field-effect mobility, resulting from a non-negligible effect of the source and drain contacts. The role of the S/D contacts was initially investigated using a method developed for amorphous semiconductor thin-film transistors: the transverse line method. This method assumes ohmic behavior of the S/D contact and access regions and models them by gate voltage dependent series resistances. High values of S/D series resistances, typically in the $10^9 \Omega$ range for a (negative) gate voltage about 10V above threshold, have allowed us to describe accurately the channel length dependence of our OP-TFT field-effect mobility. The OP-TFT intrinsic field-effect mobility and threshold voltage were also extracted. We have also analyzed the OP-TFT ID-VDS characteristics in the ON-state and with floating gate. The obtained results were examined with regards to the S/D contact current-voltage characteristics and we will present the conditions under which ohmic and non-ohmic behaviors were observed. Results will be compared to typical data obtained on a-Si:H TFTs.

2:00 PM L6.3

NEW n-CHANNEL ORGANIC SEMICONDUCTORS FOR THIN FILM TRANSISTORS. Reid J. Chesterfield and C. Daniel Frisbie, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN; Ted M. Pappenfus, 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 because of the prospect for realizing inexpensive and flexible, large-area TFT arrays. There are many examples of p-channel TFT conductors, however, reports of n-channel conductors have been rare. We are examining two families of materials based on quinoidal terthiophenes and perylene diimides for application as n-channel organic semiconductors in TFTs. The redox properties, crystal packing, and thin film microstructure of these materials can be tuned by varying the side chains. These compounds illustrate the elegance of using organic chemistry techniques to design semiconductors. Compounds in both the terthiophene and diimide family have shown n-channel room temperature mobility as high as $0.2 \text{ cm}^2/\text{Vs}$ in vacuum evaporated TFTs. Key device parameters such as On/Off ratio, threshold voltage, and sub-threshold slope will also be reported. Trapping and activated transport have been investigated as a function of temperature and ambient environment. TFT performance has been measured as a function of semiconductor grain-size, surface chemistry of the dielectric, and contact metallurgy. There is a nice correlation between the solid state TFT behavior of these compounds and their solution redox properties, which offers a possible design criterion for TFTs.

2:15 PM L6.4

Abstract Withdrawn.

2:30 PM *L6.5

HIGH PERFORMANCE ORGANIC THIN FILM TRANSISTORS. Tommie W. Kelley, Dawn V. Muires, Paul F. Baude, Terry P. Smith, Todd D. Jones, 3M Company, Science Research Center, St. Paul, MN; C. Daniel Frisbie and Paul Pesavento, University of Minnesota, Chemical Engineering and Materials Science, Minneapolis, MN.

We report here methods of surface modification and device construction which consistently result in lab-scale pentacene-based TFTs and integrated circuits with mobilities at or above $5 \text{ cm}^2/\text{Vs}$. Surface modifications include self-assembled monolayers (SAMs) and polymeric ultrathin films presenting a passivated interface on which the semiconductor can grow. High performance TFTs have been fabricated on a variety of dielectric materials, both organic and inorganic, and are currently being implemented in manufacturable constructions. Our surface modifications have also proven useful for substituted pentacene materials and for a variety of other organic semiconductors. Further experiments and statistical analyses are underway to explain the elevated mobility in our samples, and efforts have been made to confirm these results through collaboration with the University of Minnesota.

3:30 PM *L6.6

POLYCRYSTALLINE PENTACENE THIN FILM TRANSISTORS: MORPHOLOGY, STRUCTURAL PROPERTIES AND ELECTRONIC TRANSPORT. Dietmar Knipp, Palo Alto Research Center, Electronic Materials Laboratory, CA.

The structural and transport properties of evaporated pentacene organic thin film transistors (oTFT) are reported, showing the influence of the deposition conditions with different inorganic dielectrics. Dielectrics compatible with large area fabrication were explored to facilitate low cost electronics on glass or flexible plastic

substrates. X-ray diffraction and atomic force microscopy show a clear correlation between the morphology and the structure of the highly polycrystalline films, for all dielectrics investigated. The roughness of the dielectric has a distinct influence on the morphology and the structural properties, whereas the films on smooth thermal oxide are in general highly ordered independent of the deposition conditions. The ordered films exhibit a thin film and a bulk phase, and the bulk phase volume fraction increases with the deposition temperature and the film thickness. Careful control of the deposition conditions give virtually identical films on thermal oxide and PECVD silicon nitride dielectrics. The electronic properties of inverted staggered transistors show that the TFT mobility is correlated with the morphology and structure of the films. The TFTs exhibit very similar mobilities of $\sim 0.4 \text{ cm}^2/\text{Vs}$ and on/off ratios $> 10^8$ on thermal oxide and PECVD silicon nitride. The impact of the dielectric on the device parameters of mobility, threshold voltage and sub threshold voltage slope are discussed. Temperature dependent measurements of the mobility were performed to study the influence of traps on the electronic transport and to gain understanding of the transport mechanisms of thermally evaporated pentacene TFTs.

4:00 PM L6.7

SYNTHESIS AND APPLICATION OF A PHOTSENSITIVE ORGANIC SEMICONDUCTOR IN THIN FILM TRANSISTORS. A. Afzali, C.D. Dimitakopoulos, 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 semiconducting materials are patterned but standard, wet-process lithographic techniques cannot be used for organic semiconductors due to contamination of these materials by photoresists and/or developers. The patterning techniques that so far have been used to define the channel areas for organic thin film transistors (e.g., microcontact printing, screen printing) do not have high resolution capabilities. In this talk the synthesis of a soluble, photosensitive organic semiconductor, patterning 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. Schrott and C.R. Kagan, IBM Research, T.J. Watson Research Center, Yorktown Heights, NY.

We have investigated the transistor characteristics of pentacene field effect devices with sub-micron channel lengths. The devices were fabricated under UHV conditions that minimize the effect of ambient atmospheres on substrate and electrode cleanliness and on pentacene evaporation. The pentacene was evaporated to form the semiconducting channel of TFTs deposited onto thermally oxidized, highly doped Si wafers, which serve as the gate dielectric and electrode. The substrate was patterned with source and drain electrode, defining channel lengths ranging from $< 100 \text{ nm}$ to 750 nm , to prepare bottom electrode geometry TFTs. Substrates cleaned by in-situ annealing at 200°C produced polycrystalline pentacene thin films with grain sizes of $\sim 2 \text{ nm}$, larger than the electrode separations. The mobility and on-off ratios decreased with decreasing channel length. TFTs with channel lengths of 450 nm have saturation mobilities as high as $0.9 \text{ cm}^2/\text{V-sec}$, a threshold voltage near 0V , and current modulation of $\sim 10^4$. The influence of electrode material and surface derivatization with self-assembled monolayers and the dependence of channel length on transistor characteristics will be discussed.

4:30 PM L6.9

INTRA-GRAIN TOP-CONTACT ORGANIC THIN-FILM TRANSISTORS. Stijn Verlaak, Stijn Noppe, Dimitri Janssen, Barundeb Dutta, Paul Heremans, Imec, Polymer and Molecular Electronics, Leuven, BELGIUM.

Transistors with channel lengths comparable to the dimension of a grain are a useful tool to study the charge-transport properties of organic polycrystalline thin-films, i.e the intrinsic charge-transport inside one single-crystalline grain and the influence of grain boundaries. Moreover, those transistors enable to probe short-channel device physics, which can be of importance for future applications. Submicron channel lengths normally require photolithographically defined source and drain contacts, defined before growth of the small molecule channel, resulting in so-called bottom-contact devices. Unfortunately, such bottom-contacts influence the growth of the thin-film, have limited compatibility with surface cleaning and treatments prior to growth, and possess a less favorable charge-injection geometry. Therefore we have micromachined a shadow mask which enables the deposition of contacts on top of the organic thin-film, with channel lengths down to < 1 micrometer. This

mask is successfully applied to make organic small-molecule thin-film transistors with small molecules such as pentacene. Both fabrication of the shadow mask and the interpretation of the first transistor characteristics will be discussed.

4:45 PM L6.10

TRANSPORT MECHANISMS IN POLY(3-HEXYLTHIOPHENE) TRANSISTORS. D. Natelson and B. Hamadani, Rice University, Dept. of Physics and Astronomy, Houston, TX.

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

SESSION L7: POSTER SESSION

Chair: C. Daniel Frisbie

Wednesday Evening, April 23, 2003

8:00 PM

Salon 1-7 (Marriott)

L7.1

CHEMICAL AND BIOLOGICAL SENSORS BASED ON ORGANIC THIN FILM TRANSISTORS. Jeff Mason, Zhengtao Zhu, Sanjay Aggarwal, George Malliaras, Cornell Univ, Dept of Materials Science & Engineering, Ithaca, NY; Antje Baeumner, Cornell Univ, Dept of Biological & Environmental Engineering, Ithaca, NY.

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

L7.2

MOLECULAR DESIGN, SYNTHESIS AND LUMINESCENT PROPERTIES OF NOVEL ERBIUM(III)-ENCAPSULATED DENDRITIC SUPRAMOLECULES BASED ON PORPHYRINS. Jae-Won Ka, Kyung Lim Paik, Duck-Lae Joo, Min-Kook Na and Hwan Kyu Kim, Center for Smart Light-Harvesting Materials and Department of Polymer Science & Engineering, Hannam University, Daejeon, KOREA.

Recently, erbium-doped fiber amplifiers (EDFA) are widely used in the field of superhigh speed optical telecommunication system. However, the amplification gain of current EDFA is not enough for amplifying the optical signals in small-sized photonic devices, while the amplification gain is not a problem for long distance of several to tens of meters. It is due to the poor solubility of erbium(III) ions in conventional inorganic media, limiting to 100 - 1000 ppm for Er^{3+} -doped concentration on silica optic fiber. If higher than the limiting concentration is to be employed, Er^{3+} -ion interaction between themselves would cause non-radiative process (namely, cooperative processes) to occur, hence reducing the amplification gain. To solve this solubility problem and improve the luminescent properties, erbium(III) ions could be encapsulated by organic ligands. The ligands have to be designed such that it provides enough coordination sites to form a stable complex. Also, it should be considered as a photon antenna for energy transfer process from ligands to erbium(III) ions for getting a higher the amplification gain. To maximize the optical amplification efficiency, we have investigated the design and synthesis of the erbium(III)-encapsulated dendritic supramolecules based on porphyrins. Present dendritic supramolecules consisted of an erbium(III)-chelated azacryptand [222] complex, porphyrins and new aryl ether-typed dendron. Functionalized azacryptand [222] were easily prepared by condensation of orcinol monohydrate and tris-(2-chloroethyl)amine hydrochloride in the presence of base. The reaction was carried out by high dilute reaction concentration at reflux temperature, giving a moderate to good yield. Also, we synthesized the porphyrins bearing phenolic and

bromophenyl substituents at the meso-position from the corresponding aldehyde and pyrrole for the coupling with azacryptand. And, the desired supramolecules based on porphyrins have been synthesized by coupling of a functionalized azacryptand [222] with functionalized porphyrins containing new aryl ether-typed dendron. In this presentation, the synthetic routes and their luminescent properties of novel erbium(III)-encapsulated dendritic supramolecules will be discussed.

L7.3

MOLECULAR DESIGN, SYNTHESIS AND CHARACTERIZATION OF ERBIUM-CORED SUPRAMOLECULAR COMPLEXES BASED ON NEW ARYL ETHER DENDRITIC PORPHYRINS FOR OPTICAL AMPLIFICATIONS. Kyung Lim Paik, Jae Beum Oh, Jae Won Ka, Soo Gyun Roh, Min-Kook Na and Hwan 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 ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$), which takes place at a wavelength of 1.54 μm , 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 enhance the luminescent properties, we have designed and studied the erbium-cored supramolecular complexes based on porphyrins. We synthesized 5,10,15-triphenyl-20-(4-methoxycarbonylphenyl)porphyrin by the acid-catalyzed condensation of dipyrromethanes and aldehyde. And then, we introduced the carboxylic acid as 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, $^1\text{H-NMR}$, UV-Vis absorption and PL spectroscopies. And then, we have attempted several different synthetic methods to prepare Er-cored supramolecular complexes based on porphyrins and develop new synthetic route using model reaction. The synthesized complexes were characterized by the FT-IR, ICP, 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 PHOTOVOLTAGE CHARACTERIZATION OF PPV THIN FILMS SUITABLE FOR PLED APPLICATIONS. Girija Sankar Samal, A.K. Biswas, Y.N. Mohapatra, Materials Science Programme and Samtel Center for Display Technologies, Indian Institute of Technology, Kanpur, INDIA.

Optoelectronic characterization of active polymer materials to monitor photoinduced charge and radiative processes has become important in view of applications in light emitting and photovoltaic devices. In this paper we compare absorption, emission and photovoltage spectra in order to correlate creation, radiative recombination and separation of charge carriers in PPV. PPV layers of approximately 100-200nm were spin coated on ITO coated glass substrates. Photovoltage experiments were carried out using both conventional single layer LED structure (ITO/PPV/AI), and capacitive structure consisting of ITO/Mica/PPV/ITO, in which a thin sheet of mica is pressed against the sample using an ITO glass substrate. The capacitive structure is appropriate for modulated surface photovoltage measurements. The absorption spectra and photoluminescence spectra obtained are as standard for PPV prepared by Xanthate process. The room temperature photovoltage spectra show features, which both supplement and complement the absorption and emission spectra. The photovoltage spectra for both types of devices have sharp features and are identical indicating that the features observed are primarily due to PPV material itself. The photovoltage spectrum shows peaks and valleys corresponding to both absorption and emission features. In addition, we observe two sharp peaks with a separation of 0.1eV in the energy range of 2.5 - 2.7 eV (i.e. above HOMO-LUMO gap). The line shape of the peaks strongly suggests that the peaks are most probably associated with photoionization of either excited state exciton or a defect-polaron complexes giving rise to non-radiative centers. A study of temperature dependence of the maximum photovoltage in the range of 50K-300K shows that the photovoltage decreases non-linearly with decrease in temperature and saturates at low temperature. The results are discussed in terms of temperature dependence of mobility and absorption co-efficient, and possible models for photoionization of quantum defects.

L7.5

SYNTHESIS OF A ZERO-BIREFRINGENCE OPTICAL POLYMER BY THE BIREFRINGENT CRYSTAL DOPANT METHOD.

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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 polarization states of incident light. We have proposed two methods, the "random copolymerization method" and the "anisotropic molecule dopant method" to prepare transparent zero-birefringence optical polymers. However, heat resistant polymers generally exhibit positive orientational 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 homogeneous doping with birefringent needle-like crystal particles which have negative birefringence. In this method, the crystal particles need to have opposite orientational birefringence to that of polymers. Strontium carbonate SrCO₃ crystal particles were selected for this method and prepared by reaction of a suspension of Sr(OH)₂ with carbon dioxide, with a particle length of 100-300nm and an aspect ratio of 2-5. Poly(MMA-co-BzMA) films with the composition MMA/BzMA=78/22(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 633nm were compensated at the SrCO₃ particles concentration of 0.5wt.%. 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 110.7°C. These results confirmed that the synthesized zero-birefringence copolymer films had the almost same transparency and heat resistance as the blank copolymer films. Therefore, we concluded that the birefringent crystal dopant method was one of the promising candidates for obtaining heat resistant zero-birefringence optical polymers.

L7.6

BI-FUNCTIONAL PHOTOVOLTAIC AND ELECTROLUMINESCENT DEVICES USING A STARBURST AMINE AS AN ELECTRON DONOR AND HOLE-TRANSPORTING MATERIAL.

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

L7.7

TOWARDS SOLID-STATE POLYMER LASERS ACROSS THE VISIBLE SPECTRUM. George Heliotis, Ruidong Xia, 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 now attracting considerable attention as a new materials class for use in electronics and optoelectronics. Currently there is increasing interest in developing these materials for use as novel gain media in devices such as lasers and optical amplifiers. Fluorene-based polymers (polyfluorenes) are a very attractive class of conjugated polymers for such applications, due to their high photoluminescence and electroluminescence efficiencies, low stimulated emission thresholds,

high stability in air and good properties as host materials for other emitters. Here, we report a systematic investigation of the properties of a variety of semiconducting polyfluorenes to establish their 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 asymmetric waveguides. The characteristics of the gain narrowing (linewidth, intensity, threshold energy and peak wavelength) are measured as a function of excitation wavelength and intensity, film thickness and film morphology. Low thresholds (~600W/cm²) are demonstrated. Optical gain/loss measurements at the peak ASE wavelengths reveal that the waveguides can exhibit large net gain and have low loss coefficients, making these materials attractive for tuneable solid-state lasers with wavelengths that span the entire visible spectrum.

L7.8

A RED EMITTING TWO-DIMENSIONAL DISTRIBUTED FEEDBACK LASER BASED ON A NOVEL FLUORENE 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, Ifor 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, Thin Film Photonics Group, School of Physics, University of Exeter, Exeter, UNITED KINGDOM; Donal D.C. Bradley, Ultrafast Photonics Collaboration, Experimental Solid State Group and Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College, London, UNITED KINGDOM.

Semiconducting (conjugated) polymers are attractive candidates as the gain media for solid-state lasers due to, among other things, their high photoluminescence efficiencies and large stimulated emission cross-sections. Furthermore, compared with conventional inorganic semiconductors, organic semiconductors offer potential advantages with respect to ease of processing, low cost and flexibility. Recent reports of lasing action in conjugated polymers have stimulated great interest in the development of lasers that may eventually compete with inorganic semiconductor structures. Here, we report the fabrication of a two-dimensional distributed feedback laser utilising a novel fluorene copolymer as the gain medium. The laser was made by depositing a thin polymer layer on top of a suitably nanopatterned substrate. The substrate comprised two crossed gratings etched at right angles into a fused silica plate. This structure provides a better optimised photonic mode density confinement compared with a single grating structure, which leads to reductions in the lasing threshold and increases in the output efficiency. Laser action was demonstrated by pumping the device with a compact diode-pumped, frequency doubled Nd:YVO₄ laser operating at 532 nm. Lasing occurs at 680 nm and is located on the edge of the photonic stop band induced by the two-dimensional microstructure. The laser had a threshold of 4nJ per pulse. 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 Alq₃ MOLECULE IN EVAPORATED FILM AND ITS VANISHMENT BY LIGHT IRRADIATION.

Keiji Sugi, Hisao Ishii, Yasuo Kimura, Michio Niwano, Tohoku Univ, Institute of Electrical Communication, Sendai, JAPAN; Naoki Hayashi, Yukio Ouchi, Nagoya Univ, Graduate School of Science, Nagoya, JAPAN; Eisuke Ito, RIKEN, Frontier Research System, Wako, JAPAN; Kazuhiko 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-hydroxyquinolinato) aluminum(III) (Alq₃) on an Au substrate under dark conditions (28V for 560nm thick Alq₃ film). Such giant potential is removed by visible-light irradiation. Alq₃ molecule has a permanent dipole and its spontaneous orientation is suggested as an origin of such giant SP [1]. Such properties suggest that this molecule has a 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 rate of the decrease of SP was proportional to the logarithm of light irradiation time [1]. Numerical simulation for the decrease of SP was performed on the basis of a simple model where an oriented molecule becomes disordered upon the absorption of an incident photon. This model well reproduced the observed logarithmic relation, suggesting that not photovoltaic effect but a rotation of the molecule by photoabsorption is plausible as the origin of the removal of the SP. As to the ferroelectricity, the measurements of D-E hysteresis will be reported. The examination of the retention time of such giant SP by Kelvin

probe method will be also presented. [1] E. Ito, Y. Washizu, N. Hayashi, H. Ishii, N. Matsuie, K. Tsuboi, Y. Ouchi, Y. Harima, K. Yamashita, and K. Seki, *J. Appl. Phys.* in press.

L7.10

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

In many theoretical studies, the electronic and optical properties of conjugated polymers are treated in a single-chain picture. Here, we study the effects of 3D dielectric screening of the Coulomb interaction and 3D quantum mechanical coherence on the electronic and optical excitations in conjugated polymers. We perform a fully *ab-initio* calculation of the bandstructure and the excitonic spectrum of crystalline polythiophene and polyphenylenevinylene, using the *GW* approximation for 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 polythiophene chain (no 3D screening and no 3D coherence) and polymer chains embedded in a dielectric medium (3D screening, but no 3D coherence). The calculated excitonic spectrum for polymer chains embedded in a dielectric medium generally agrees best with available experimental data. The calculation for a single chain leads to an unacceptably large (>1 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, there is also experimental evidence for situations where coherence between chains does occur, such as in a ladder-type polyparaphenylene polymer. 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 ANTHRACENE UP TO 22GPA: A X-RAY DIFFRACTION STUDY. Martin Oehzelt, Georg Heimel, Roland Resel, Graz University of Technology, Graz, AUSTRIA; Kerstin Hummer, Peter Puschnig, Claudia Ambrosch-Draxl, University of Graz, Graz, AUSTRIA; and Atsuko Nakayama, Advanced Carbon Center, AIST, Tsukuba, JAPAN.

This study concentrates on the crystal structure of anthracene under high pressure. Pressure was applied using the diamond anvil cell technique. In order to guarantee hydrostatic conditions within the sample chamber helium was used as pressure transmitting medium for the highest pressure region. To investigate the structural changes, angle dispersive X-ray diffraction experiments using synchrotron radiation were carried out. The sample was polycrystalline anthracene powder of high purity. The measurements were performed at the Photon Factory beam-line 18C optimised for high pressure X-ray experiments in Debye-Scherrer geometry. These data were analysed by Rietveld refinement methods to obtain the lattice constants under pressure and furthermore orientational parameters of the molecules within the unit cell. Up to 22 GPa the unit cell volume is decreased by 38%. As all changes in the crystal structure are gradual, no phase transition is observed in our X-ray measurements under hydrostatic conditions. The high quality of the measurements 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 GEOMETRY. Satoshi Ogawa, Yasuo Kimura, Hisao Ishii, and Michio Niwano, Tohoku Univ, Reseach 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 objection to the data of Dr. Schön in Bell Laboratory. We focus on two questions; one is whether field effect doping actually happens for organic semiconductors or not. Second is 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 C_{60} as an organic semiconductor. By using displacement current method we investigated the charge accumulation at C_{60} /insulator interface due to applying electrical field. In-situ infrared absorption spectroscopy in the multiple internal reflection geometry was also performed for the MIS structure to examine the field effect doping. This technique enables us to investigate the degree of charge transfer of C_{60} layer under electric field. As a result, we observed electron injection from Au electrode to C_{60} followed by the decrease in an intensity of an IR absorption peak due to fullerene. This result suggests that carrier injection is critical for carrier accumulation in the channel of OFET. The decrease of IR peak of C_{60} indicates the decrease of the amount of neutral C_{60} molecules, suggesting some doping effect induced by accumulated carriers. The detailed analysis of the observed spectral change due to electric field will be presented.

L7.14

ANALYSIS OF CHARACTERISTIC SHG FOR 8CB AT THE AIR-WATER INTERFACE UNDER P-IN-P-OUT LASER CONFIGURATION. Chen-Xu Wu, Xiamen Univ, Dept of Physics, Xiamen, P.R. CHINA; Hongfei 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.¹⁻² Recently many investigations concerning SHG during monolayer compression have been reported.³ SHG signals depend on the configuration of input laser as well as the output laser direction detected. The SHG and surface pressure of 4-cyano-4'-8-alkyl-biphenyl (8CB) monolayers at the air-water interface under different input-output configurations are measured during monolayer compression. Under p-in-p-out laser configuration, a characteristic peak of SHG density rather than a plateau under other laser configurations, is found. A theoretical analysis, which agrees well with experiments, is given for the special SHG characteristics of 8CB monolayers under the p-input-p-output laser configuration.

¹ M. Iwamoto and C.X. Wu, *The Physical Properties of Organic Monolayers* (World Scientific, Singapore, 2001)

² A. Valence and C. Misbah, *Phys. Rev. E* 55, 5564 (1997).

³ A. Tojima, T. Manaka and M. Iwamoto, *J. Chem. Phys.* 115, 9010 (2001).

L7.15

EXCITON DISSOCIATION IN DOPED CONJUGATED POLYMERS. Vladimir Arkhipov and Paul Heremans, IMEC, Leuven, BELGIUM; Evgenia Emelianova, Semicond. Physics Lab., Univ. of Leuven, BELGIUM; Heinz Bässler, Inst. of Physical, Nuclear, and Macromolecular Chem., Philipps 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-chain 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-segmental 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 twin carrier that occupies the polymer segment. In the present work, we suggest a model of exciton dissociation on charge transfer centers, which consists of conjugated segments and adjacent deep electron traps. Since a 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 full carrier separation and, therefore, facilitates exciton dissociation. At high dopant concentrations, exciton dissociation mostly occurs at the interface separating a photosensitive 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 experimentally observed high yield of photogeneration in conjugation-polymer/fullerene blends. [1] V.I. Arkhipov, E.V. Emelianova, and H. Bässler, *Phys. Rev. Lett.*, 82, 1321 (1999).

L7.16

SOL-GEL NANOHYBRID MATERIALS INCORPORATING

FUNCTIONAL THIACALIXARENES FOR NON LINEAR OPTICAL APPLICATIONS. Cedric Desroches, Stephane Parola, David Cornu, Philippe Miele, Laboratoire des Multimateriaux et Interfaces, UMR 5615 CNRS, Universite; Villeurbanne, FRANCE; Patrice Baldeck, Laboratoire de Spectrometrie Physique, Universite; Grenoble I, Saint Martin d'Herès, FRANCE; Cesar Lopes, Swedish Defence Research Agency, Division of Sensor Technology, Linköping, SWEDEN.

Optical Power Limiting (OPL) materials have been developed for the protection of optical sensors and eyes toward intense laser aggressions. Previous investigations evidenced that the optical limiting behaviour of a given molecule can be related to the delocalisation of electrons and may be improved by the formation of heavy metal complexes. We have been investigating thiacalixarenes on the basis that they display delocalised electrons and they can be selectively functionalised either on the upper rims or the lower rims. Moreover, the presence of electron donating sulfur bridges can play an important role regarding nonlinear optical properties and functional groups can be chosen with ability to increase the electron delocalisation over the molecule and to form metal complexes. Thiacalixarenes bearing phenylazo, amino, imino or ethynyl groups on the lower rims were prepared and fully characterized. The formation of metal complexes was also investigated. They showed interesting optical properties. Optical limiting molecules need to be incorporated into an inorganic matrix in order to be useful for optical limiting devices. It is well known that the 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 (Van der Waals, hydrogen bonds). In class II hybrids the organics are strongly bonded to the inorganic network (covalent). Class I materials were found to be inhomogeneous and only low concentrations (<10mM) of thiacalixarenes could be reached in the final material. Class II hybrids were thus considered to permit the elaboration of highly concentrated and stable hybrids. A second functionalisation (upper rims) with metal alkoxide groups had to be investigated in order to prepare the class II sol-gel hybrid materials incorporating the optically active molecule.

L7.17
CuInS₂/PEDOT PHOTOVOLTAIC STRUCTURE. Sergei Bereznev, Julia Kois, Enn Mellikov, Andres Öpik, Tallinn Technical University, Dept of Material Science, Tallinn, ESTONIA; Igor Konovalev, Universität Leipzig, Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry, Leipzig, GERMANY.

Photovoltaic 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 consisting of CuInS₂ (CIS) and poly(3,4-ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonate (PSS) thin films were prepared and investigated for photovoltaic applications. The polymer layer of p-type is considered as an alternative for the traditional buffer layer and window top layer on the CIS absorber layer in the cell structure. As absorber layers, polycrystalline CIS thin films were synthesized on top of a layered structure on Cu tape substrate using a non-vacuum CISCuT technique. Thin PEDOT films doped with PSS were deposited onto KCN etched and vacuum annealed CIS films from an aqueous dispersion of PEDOT/PSS mixed with N-methylpyrrolidone, isopropanol, glycerin and epoxysilane additives using the spin-casting technique. In order to prepare stable PEDOT films of high quality with a good adherence to the surface of inorganic semiconductor CIS, the optimal parameters of spin-coating were selected experimentally. Average film thickness was determined microscopically and was about of 1.5 μm for CIS and 0.5 μm for PEDOT films. Significant photovoltage and photocurrent of the fabricated CIS/PEDOT structures have been observed under standard white light illumination. Our deposition technique gives us an opportunity to prepare photovoltaic structures based on CIS and PEDOT thin films using relatively simple step-by-step method.

L7.18
AB-INITIO CALCULATION OF HOMO AND LUMO ENERGIES IN POLYMER-DYE SYSTEMS. W.F. Pasveer, P.A. Bobbert, M.A.J. Michels, Polymer Physics Group, Dept. of Applied Physics and Dutch Polymer Institute, Eindhoven University of Technology, THE NETHERLANDS; B.M.W. Langeveld, H.F.M. Schoo, TNO Industrial Technology, THE NETHERLANDS.

Recent electroluminescence experiments have shown the possibility of fine-tuning the emission spectrum of dipyrrolomethene dyes by chemical modification of specific sidegroups. This property and the fact that they have a relatively small bandwidth makes these dyes

good candidates for the development of full color polymer displays. We present the results of *ab-initio* (DFT-LDA) calculations in which we examined the influence of the various sidegroups on the electronic structure. Special attention will be paid to the comparison of the trends of the HOMO and LUMO energies. The calculated values for these energies will be compared with those obtained from cyclic voltammetry experiments and the trends agree. We also calculate the HOMO and LUMO energies for some polymers (e.g. PPV and polyfluorene) which are attractive from an industrial point of view to be used as a matrix for the dyes. The knowledge about these energies of the dyes relative to the polymer matrix is necessary to predict and to understand trapping of electrons, holes and excitons. Regarding the charge transport we can draw the following conclusions. We find that for the dyes in the PPV matrix it is favorable for the holes to stay on the polymer and the electrons to be trapped on the dye, although the energy gain is small. There are some experimental indications that indeed the electrons are trapped on the dye molecules. In the case of dyes in a polyfluorene matrix, it is favorable both for holes and electrons to go to the dye molecules. Again the remark should be made that the energy differences can be small (0.05-0.2 eV) and depend on the specific sidegroups of the dyes. Our study shows the feasibility to use *ab-initio* electronic structure calculations as a predictive tool in this research area.

L7.19
A NOVEL PATTERNING CONCEPT FOR PPV-TYPE MATERIALS USING THE THIOL-ENE PHOTOREACTION. J. Keplinger, G. Langer, T. Steindl, D. Sandholzer, TU Graz, Institute for Chemistry and Technology of Organic Materials, Graz, AUSTRIA; A. Pogantsch and E. Zojer, TU Graz, Institute f. Solid State Physics, Graz, AUSTRIA; R. Saf, 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 immediate interest for the setup 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 "Thiol-Ene Reaction", was found to be highly efficient and selective to saturate the vinylene 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. propanethiol). On the other hand, PPV films containing dodecanethiol were cast onto substrates and subjected to UV illumination. In both cases the photoinitiated Thiol-Ene addition was followed by real-time infrared spectroscopy (RTIR). An almost complete conversion of the *C=C* double bonds was achieved upon prolonged UV irradiation. We investigated the accelerating effect of free radical photoinitiators (e.g. benzil dimethyl ketal) 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 photoreaction predominantly in the areas containing the photoinitiator. The relationship between the deposited amount of photoinitiator, the UV illumination time and the resulting emissive properties of the PPV films was investigated. Applying this novel concept in combination with photomasks, laterally 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. Mäkinen, Optical Sciences Division, Naval Research Laboratory, Washington, DC; M. Uchida, Chisso Corporation, Yokohama, JAPAN; Z.H. Kafafi, Optical Sciences Division, Naval Research Laboratory, Washington, DC.

Photoelectron emission spectroscopy of an interface between Mg and a silole derivative, 2,5-bis(6'-(2',2''-bipyridyl))-1,1-dimethyl-3,4-diphenyl silacyclopentadiene (PyPySPyPy), shows the formation of two gap states both when metal is deposited onto an organic layer and when the organic is deposited onto the metal. The appearance of gap states is a result of electron transfer from the metal to the organic. Fermi level pinning occurs at the lowest unoccupied molecular orbital of PyPySPyPy implying barrierless electron injection at the Mg/PyPySPyPy interface. This result is significant when employing a Mg electrode contact with PyPySPyPy in electronic, electro-optic and optoelectronic devices.

L7.22

HIGH PRESSURE STUDIES ON THE PACKING FORCES AND INTERMOLECULAR INTERACTION IN POLYPHENYLS.

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In this work, we report on pressure induced structural changes in crystalline oligo(*para*-phenylenes) 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 powders of biphenyl, *para*-terphenyl, *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*-quinquephenyl and *p*-sexiphenyl ($B_0 = 83$ kbar, 93 kbar, and 100 kbar respectively) and its pressure derivative ($B_0 = 6.4, 7.5, \text{ and } 5.6$). 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. G. Langer, TU Graz, Inst. of Chemistry and Technology of Organic Materials, Graz, AUSTRIA; A. Pogantsch, TU Graz, Inst. f. Solid State Physics, Graz, AUSTRIA; D. Wright and J. Zyss, ENS-Cachan, LPQM, Cachan, FRANCE; K.F. Iskra and T. Neger, TU Graz, Inst. f. Experimentalphysik, Graz, AUSTRIA; W. Kern, TU Graz, Inst. of Chemistry and Technology of Organic Materials, Graz, AUSTRIA.

Gratings in polymer films are important for optoelectronics and for the setup of organic lasers based upon the principle of distributed feedback (DFB). Our investigations were focussed on a photosensitive polymer (poly(styrene-co-4-vinylbenzyl-thiocyanate) / PST-co-VBT), which form refractive index (by isomerization) and relief gratings (by laser ablation) upon deep-UV irradiation. By gas phase modification with amines additional index changes as well as additional surface relief gratings were obtained with these polymers. Using interference illumination with the fourth harmonic of a Nd:YAG laser, 1D and 2D surface relief gratings were produced. DFB lasing was observed when laser 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 laser devices and their spectral laser mode output were characterized. Strategies towards truly tunable DFB laser devices were investigated. A promising way is the functionalization of elastomers with photoresponsive groups, e.g. CH₂-SCN. 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. Saif A. Haque, Taiho Park, Cigang Xu, Ravi Punamurthy, Jenny Nelson, Sara Koops, Niels Schultes, Lucy Otley, Robert J. Potter, Andrew B. Holmes and James R. Durrant, Centre for Electronic Materials and Devices, Department of Chemistry and Physics, Imperial College, London, UNITED KINGDOM.

In the quest for photovoltaic devices that are low cost, light weight and easy to process dye sensitised nanocrystalline semiconductor 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 I₂/I⁻ in acetonitrile). 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 solid-state versions of DSSCs, where the liquid based hole-conductor is replaced by a solid

state hole-conductor. In this paper we present work on two hole-conductor systems: polymer electrolytes and p-type organic polymers, paying particular attention to the following points: 1) Development of small molecule (Example 1) and polymer based organic hole-conductors with ion solvating tetraethylene glycol side chains and their application in dye sensitised nanocrystalline solar cells. 2) The charge transfer processes that occur at the semiconductor / dye / hole conductor interface play an important role in controlling the overall efficiency of the device. Here we employ laser based transient absorption spectroscopy to study the charge transfer processes at the semiconductor / dye / hole conductor interface. In particular we highlight the importance of thermodynamic rather than kinetic control of the interfacial charge separation and the influence of energetic inhomogeneities upon the yield of this reaction. 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% (10mWcm⁻² solar light illumination) based upon on polymer electrolytes.

L7.26

CONDUCTION MECHANISMS IN PEDOT/PSS THIN FILMS. P. Cooreman, L. Goris, P. Wagner, Z. Beelen, J. Manca, and J. D'Haen^a, M. Malfait, I. Gordon, and V. V. Moshchalkov^b, F. Louwet and B. Groenendaal^c. ^aInstituut voor Materiaal Onderzoek, Limburgs Universitair Centrum; ^bLaboratorium voor Vaste-Stoffysica en Magnetisme, Katholieke Universiteit Leuven; ^cAGFA, Mortsel, BELGIUM.

Conducting polymers are widely used as electrode or active material in solar panels, 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 biosensors¹. The electric conduction mechanism in PEDOT however is 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. Charge 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 12T has also been studied. The results from both experiments show that there is a hole-type conduction that obeys the scaling law $\ln(\sigma) \propto T^{1/2}$. 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 states², or quasi-1 dimensional VRH³. We also fitted the temperature dependence of the Hall resistance and found the empirical relationship $\ln(R_H) \propto T^{-1}$. From this follows that $R_H \propto \rho^2$.

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. Acknowledgements We gratefully acknowledge support from the IWT in the context of the DOTCON project.

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L7.27

RELAXATION PHENOMENA OF LADDER-TYPE CONJUGATED POLYMERS PROBED BY SINGLE CHAIN FLUORESCENCE SPECTROSCOPY. J.G. Mueller, U. Lemmer, J.M. Lupton, J. Feldmann, Department of Physics, University of Munich, Munich, GERMANY; M. Anni, Department of Engineering, University of Lecce, Lecce, ITALY; U. Scherf, Department of Chemistry, University of Wuppertal, Wuppertal, GERMANY.

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-lattice interaction and the inter- and intrachain coupling are presently investigated extensively. Typically, spectroscopic data on conjugated polymers are strongly affected by the large inhomogeneous 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 homogeneous line width of the photoluminescence from a single conjugated polymer chain between 5 K and room temperature. We choose a ladder-type

poly(para-phenylene) as a model polymer system as this material exhibits a particularly low degree of inhomogeneous broadening together with a high level of chemical purity. We find that at room temperature the spectrum of a single conjugated molecule nearly matches the bulk spectrum. At low temperature however, the single molecule spectrum shows a much smaller line width as compared to the bulk. The homogeneous line width becomes as small as 5 meV, corresponding to a dephasing time of $T_2 > 260$ fs. In addition, the small line width allows the identification of various vibrational modes coupling to the electronic excitation. Employing a pulsed excitation source and gated fluorescence detection we 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-ns timescale. This is a very direct observation of energy transfer between different conjugated segments located on the same polymer chain.

L7.28

Abstract Withdrawn.

L7.29

STRUCTURAL AND SPECTROSCOPIC STUDY OF LANGMUIR-SCHÄFER FILMS OF BIS ZN-ETHANE-BRIDGED PORPHYRINS DIMER. G. Panzera, S. Conoci, S. Coffa, Si Optoelectronics, Bio-and Nano-Systems, Corporate R&D, ST Microelectronics, Catania, ITALY; B. Pignataro, S. Sortino, G. Marletta, Dipartimento di Scienze Chimiche, Università di Catania, Catania, ITALY; L. Valli, Dipartimento Ingegneria dell'Innovazione, Università di Lecce, Lecce, ITALY; V.V. Borovkov and Y. Inoue, Inoue Photochirogenesis Project, ERATO, JST, Osaka, JAPAN.

Thin films of porphyrins and related compounds have attracted increasing attention in recent years being these molecules an extremely versatile class of compounds for a large variety of applications. Indeed, their potential employment in many fields of technological interest as photoconductors, optical actuators and switches as well as chemical-sensors has been extensively studied [1]. Bis-zinc ethane-bridged porphyrin dimer (1) has showed 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 1 thin films. Monolayers of 1 have been first prepared at the air/water interface. The related surface pressure-area isotherm curve showed that in dependence of the film pressure different condensed phases may occur in the monolayer. The inspection of the monolayer by Brewster Angle Microscopy (BAM) and UV-vis reflection spectroscopy lead to the observation of peculiar networks whose structural features and optical properties seemingly change upon film compression. Thin films (1-24 layers) of 1 have been then transferred on solid surfaces, by the Langmuir-Schäfer (LS) horizontal method. Either quartz slides or silicon oxide, previously hydrophobised with 1,1,1,3,3,3-hexamethyldisilazane, have been used as substrates. Scanning Force Microscopy (SFM) images, performed on these systems at different length scales, showed fractal networks constituted by nanoscopic supramolecular aggregates, whose shape and size depend again on the LS deposition surface pressure. UV-vis spectroscopy measurements showed that the absorption is almost linearly related to the film thickness and directly connected to the surface pressure, i.e. to the film morphology investigated by SFM. [1] F. Kampas et al. Nature, 1980, 284, 40; N.A. Rakow et al. Nature 2000, 406, 710. [2] V.V. Borovkov et al. J. Phys. Chem. B, 1999, 103, 5151-5156. [3] V.V. Borovkov et al, J. Am. Chem. Soc., 2000, 122, 4403-4407.

L7.30

Abstract Withdrawn.

L7.31

EMISSION CHARACTERISTICS OF OLEDs ON PLANAR AND NON-PLANAR SUBSTRATES. M. Scheffel^{a,b}, A. Hunze^{a,b}, R. Pätzold^{a,b}, J. Birnstock^{a,b}, W. Rogler^a, S. Vögele^c, A. Winnacker^b. ^aSiemens AG, Erlangen, GERMANY; ^bInst. für Werkstoffwissenschaften, Universität Erlangen, GERMANY; ^cLehrstuhl für Bildschirmtechnik, Universität Stuttgart, GERMANY.

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 therefore on extraction efficiency. The photon flux emitted from the devices was measured relative to the flux trapped within the substrate by waveguiding effects. The experimental data are compared to our modelling results of the emission of oriented dipoles embedded within a multilayer structure. For the processed devices, we find that a maximum increase of

external quantum efficiency by nearly a factor of two can be expected by additional extraction of waveguided light. As a consequence of this investigations, we modified the architecture of our substrates. 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. Fichet, W.T.S. Huck, Melville Laboratory, Department of Chemistry, University of Cambridge, Cambridge, UNITED KINGDOM; N. Corcoran, J.D. Mackenzie, R.H. Friend, Cavendish Laboratory, Department of Physics, University of Cambridge, Cambridge, UNITED KINGDOM.

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

L7.33

AB-INITIO THEORY OF POLARON BANDWIDTH NARROWING IN OLIGO-ACENE CRYSTALS. K. Hannewald, V.M. Stojanovic, J.M.T. Schellekens, P.A. Bobbert, Eindhoven Univ of Technology, Dept of Applied Physics, Eindhoven, THE NETHERLANDS.

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 a solution of a mixed 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. C.M. Martin, Department of Physics, University of Missouri, Columbia, MO; S. Guha, Department of Physics, Astronomy and Materials Science, Southwest Missouri State University, Springfield, MO; M. Chandrasekhar and H.R. Chandrasekhar, Department of Physics, University of Missouri, Columbia, MO; R. Guentner, P. Scanducci de Freitas, U. Scherf, Institut für Chemie und Polymerchemie, Universität Potsdam, GERMANY.

We present studies of the Raman scattering from poly[2,7-(9,9'-bis(2-ethylhexyl))fluorene] (PF2/6) under hydrostatic pressures of 0-100 kbar at room temperature. We observe a Raman peak due to the intra-ring C-C stretch mode at 1605 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 antiresonance 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 as the aggregate and defect related 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 related emission occurs, causing real transitions that interact with phonons to produce asymmetric lineshapes. The lineshape of the 1605 cm^{-1} Raman peak exhibits a striking asymmetry 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 ($\{1/q\}$) is relatively small up to about 35 kbar, with a $\{1/q\}$ value between -0.005 and 0.1. Beyond 40 kbar however, the asymmetry increases rapidly and $\{1/q\}$ increases from -0.3 to -0.6. The linewidth increases as the square of pressure, while the frequency positions increase almost linearly with pressure.

L7.35

CHARGE TRANSPORT IN THIN POLYCRYSTALLINE FILMS OF ORGANIC SEMICONDUCTORS. Stijn Verlaak, Vladimir Arkhipov, Paul Heremans, Imec, Polymer and Molecular Electronics, Leuven, BELGIUM.

Thin films of thermally evaporated small-molecule materials, used in organic thin-film transistors (OTFT), are generally polycrystalline with localized states concentrated within the amorphous phase separating crystalline grains. Therefore, one may expect that the grain boundaries will control charge transport in these materials and a grain boundary barrier model offers an adequate approach to the conductivity in polycrystalline films. Charges, trapped in defects at the grain boundaries, create potential barriers and carrier jumps across these barriers are the rate-limiting step in the carrier transport. We assume a quasi-continuous energy distribution of localized states within grain boundaries rather than a constant interfacially trapped charge. Under such circumstances, the potential barrier height is self-consistently determined by filling of those states. In terms of this model, we discuss the effects on the carrier mobility of dopant concentration, the lateral and vertical fields, i.e. drain voltage/channel length and gate voltage, as well as the limitations of this model and the differences with other models.

L7.36

ON THE ORIGIN OF GREEN EMISSION IN POLY-PHENYLENE BASED CONJUGATED POLYMERS. Emil J.W. List and Lorenz Romaner, Christian Doppler Laboratory Advanced Functional Materials, Institute of Nanostructured Materials and Photonics, Joanneum Research, Weiz, and Institute of Solid State Physics, Graz University of Technology, Graz, AUSTRIA; Alexander Pogantsch, Institute of Solid State Physics, Graz University of Technology, Graz; Roland Guentner, Patricia Scanducci de Freitas, and Ullrich Scherf, Bergische Universität Wuppertal, Makromolekulare Chemie, Fachbereich Chemie, Wuppertal, GERMANY.

For future display applications of conjugated polymers the currently most challenging topic is the realization of colour stable blue light emission. All available poly(para-phenylene) type materials (PPP), which are the most promising family of blue light emitters, are prone to degradation resulting in an unwanted change in colour due to the emerging of a lower energetic greenish emission peak. This band has been mostly 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 show fluorescence from an on-chain oxidative defect to be the source of this emission band. In this context, using UV-VIS, PL emission and infrared spectroscopy we will present spectroscopic evidence for the formation of keto defect sites in different types of different PPP-type polymers as a consequence of different processes. It will be demonstrated that keto defects can be generated in the material directly during polymer synthesis, photo- or electrooxidative degradation processes and thermal treatment in ambient atmosphere. In addition these obtained spectroscopic results are compared to results obtained for defined co-polymers of 9-9'-difarnesyl-fluorene with 9-fluorenone. Studying such controlled fluorene-fluorenone co-polymers model compounds a clear quantitative correlation between the 9-fluorenone content and the low-energy emission band intensity has been established.

L7.37

COLOR TUNING OF EMISSION OF Iridium PHOSPHORS BY USING ANCILLARY LIGAND AND DEEP BLUE Iridium PHOSPHORS FOR OLEDs. Jian Li, Bert D. Alleyne, Vadim I. Adamovich, Peter I. Djurovich, 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, making these materials leading candidates for dopant emitters in OLED applications. One method of modifying the emission energy, and hence the color, of Ir phosphors is to change the nature of cyclometalating ligand. For example, phenylpyridine-based Ir phosphors have green emission while Ir phosphors with phenylquinoline will emit orange or red. (Ref. S. Lamansky, 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 pyrazolyl ligands and their analogues, and the same cyclometalating ligand, para-tolylpyridine (tpy), it is possible to vary the emission color of Ir phosphors over a wide range. For example, the emission color of mer-Ir(tpy)₃ is orange ($\lambda_{max} = 550$ nm) while (tpy)₂Ir[Ph₂B(CH₂PPh₂)₂] is aqua ($\lambda_{max} = 466$ nm).

Electrochemical analysis of (tpy)₂Ir(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) relatively unchanged. Complexes with tetrakis-pyrazolylborate, pz₂Bpz₂⁻, and fluorinated phenylpyridine ligands, e.g., iridium(III) bis(4,6-difluorophenylpyridinato-N, C^{2'}) tetrakis(1-pyrazolyl)borate, flr6, are highly efficient blue phosphorescent emitters. The use of these deep blue Ir phosphors in OLEDs has also been demonstrated. Unoptimized devices using the blue phosphor, flr6, have CIE coordinates of device (0.15, 0.20) ($\lambda_{max} = 455$ nm) and maximum external quantum efficiencies near 3.3%.

L7.38

RUTHENIUM(II) ORGANOMETALLIC COMPLEXES AS NEW HOLE-TRANSPORTING MATERIALS FOR OLEDs. Jian Li, Vadim I. Adamovich, Xiaofan Ren, Peter I. Djurovich, 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 triarylamine, such as 4,4'-bis[N-(1-naphthyl)-N-phenyl-aminobiphenyl], α -NPD. Recently, our group has started to investigate the use of 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 transporters. Based on the Marcus electron transfer theory, a low energy barrier of electron exchange between bis(hydrotris(1-pyrazolyl)borato) ruthenium(II), Ru(pz₃BH)₂ and its cationic counterpart, Ru(pz₃BH)₂⁺, makes Ru(pz₃BH)₂ a potentially good hole transporting material. The report demonstrates that by using one derivative of Ru(pz₃BH)₂, bis(tetrakis(1-pyrazolyl)borato) ruthenium(II), Ru(pz₃Bpz)₂, as hole transporting material, the device (ITO/Ru(pz₃Bpz)₂(200Å)/NPD(200Å)/Alq₃(500Å)/LiF/Al can achieve a very good performance (max. quantum efficiency 1% at 7.5V, turn-on voltage around 2.5 V).

L7.39

LARGE OPTICAL AND NEAR INFRARED BIREFRINGENCE IN PHOTOADDRESSABLE POLYMER THIN FILMS.

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Development of highly birefringent polymer materials is necessary for improving the capacity of data storage and is also potentially useful as a waveguide and active device material in integrated photonic devices. Photoaddressable polymers (PAPs) show considerable potential for these applications, with an unusually large birefringence of 0.55 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 nonabsorbing above 630 nm and maintains a very high birefringence (> 0.3) at wavelengths up to 1700 nm. We have also performed morphological characterization using optical and atomic force microscopy indicating that both as-spun and written 500 nm thick films are optically smooth but with topographic features of order 30 nm high. Absorption spectra of the PAP films indicate that it is strongly absorbing in the visible (400-630nm), so a 488nm Ar⁺ laser beam was used for writing while birefringence and photo-bleaching was monitored with a 650nm diode laser. Writing was performed by applying a polarized EM field to the polymer, leading to a strong in-plane birefringence due to the induced azobenzene photoisomerization cycle from the trans to cis configuration. This preferentially aligns the polymer side-chains perpendicularly to the polarization direction. The effect of PAP birefringence on the plasmon absorption of arrays of nanometer-scale metallic particles will also be presented.

L7.40

A NEW CLASS OF ORGANIC/INORGANIC HYBRID COMPLEXES AS PHOTSENSITIZERS FOR NANOCRYSTALLINE TiO₂ BASED DYE-SENSITIZED PHOTOVOLTAICS. Ravi Mosurkal, Jayant Kumar, Center for Advanced Materials, University of Massachusetts, Lowell, MA; Lynne A. Samuelson, Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

Currently, the investigation of efficient molecular photosensitizers for

the development of low cost dye-sensitized photovoltaic (DSPV) cells has been an area of tremendous interest. Transition metal complexes are used as photosensitizers in photovoltaic devices based on nanocrystalline titanium dioxide [1-2]. Presently the most efficient and stable sensitizers are carboxylated polypyridyl complexes. Among them, $[\text{Ru}(\text{dcbpy})_2(\text{NCS})_2]$ well known as N3, shows overall photo-to-electric conversion efficiency of 7-10% when a liquid electrolyte containing iodine/iodide solution is used [3]. Though present photosensitizers are mostly inorganic complexes, the investigation to find pure organic dye sensitizers is of potential interest to fabricate all organic solid-state DSPV cells. Thus we have carried out theoretical modeling of a class of organic dyes using semi-empirical quantum chemical methods to identify photosensitizers 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 photosensitizers compared to other dyes and we therefore synthesized a ruthenium based organic/inorganic hybrid complex using an efficient Xanthene dye. The absorption of this 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. Hagfeldt, M. Gratzel, *Acc. Chem. Res.*, 2000, 33, 269. 2. R. Mosurkal, Jin-An He, J. Kumar, Lian Li, J. Walker and L.A. Samuelson, *Proc. Mater. Res. Soc. Symp.*, 2002, 708, 367. 3. B.O'Regan and M. Gratzel, *Nature*, 1991, 353, 737.

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

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Charge transport in conjugated polymers have been widely explored, in particular its dependence on the applied electrical 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/μ 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 characteristics at different temperatures, atomic force microscope scans in both micro Kelvin probe mode and phase mode, time resolved characteristics and noise 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-QUINOLINOLATE). Magesh Nandagopal, Matthew Mathai, Fotios Papadimitrakopoulos, Marcel Utz; Institute of Materials Science, University of Connecticut, Storrs, CT.

Aluminum tris (8-quinolinolate) (Alq_3) is the most widely used electron transport material for organic light emitting diodes. Whereas the structure and properties of several crystalline polymorphs of Alq_3 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-5/2 Aluminum-27 nuclei, in order to obtain structural and dynamic information from amorphous Alq_3 deposits. Comparison of the ^{27}Al spectra from amorphous Alq_3 to those obtained from crystal polymorphs with known structure provide direct experimental estimates of the ratio of facial to meridional isomer in the amorphous material. The molecular dynamics of Alq_3 molecules in both crystalline and amorphous forms was quantified using relaxation time measurements as well as ^{13}C exchange spectroscopy.

L7.43 FORMATION OF ONE-DIMENSIONAL CRYSTALLITE CHAINS IN PARA-SEXIPHENYL GROWTH ON MICA. C. Teichert, G. Hlawacek, Dept of Physics, University of Leoben, Leoben, AUSTRIA;

A. Andreev, H. Sitter, Institute for Semiconductor and Solid State Physics, University Linz, Linz, AUSTRIA; G. Matt and N.S. Sariciftci, Linz Inst. f. Organic Solar Cells, Physical Chemistry, University Linz, Linz, AUSTRIA.

High-resolution atomic force microscopy is used to study the initial stage in hot wall epitaxy of para-sexiphenyl on mica (001). This stage is characterized by a coexistence of nanometer scale crystallites and self-organized crystallite chains with micrometer extension in one dimension [1]. These chains are well oriented and exhibit a very narrow length distribution. They form spontaneously as soon as a critical density of crystallites on the surface is present. The existence of denuded zones around the chains and their interior structure indicate that this self-organization process requires the rearrangement of the crystallites as entities. [1] A. Andreev, et al., *Thin Solid Films*, 403-404 (2002) 444.

L7.44 ORGANIC LIGHT-EMITTING DIODES BASED ON MULTILAYER PHOTO-CROSSLINKABLE HOLE TRANSPORT COPOLYMERS. Benoit Domercq^a, Richard D. Hreh^b, Chet Carter^b, Jose-Luis Maldonado^a, Joshua N. Haddock^a, Christopher Schultz^a, Ya-Dong Zhang^b, Seth R. Marder^{a,b}, and B. Kippelen^a; ^aOptical Sciences Center, University of Arizona, Tucson, AZ; ^bDepartment 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 aryl 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 cinnamate-based moieties to obtain photo-crosslinkable polymers. These materials can be crosslinked and patterned using a standard mask aligner designed for photolithographic applications. UV cross-linking conditions were optimized to obtain an insoluble hole-transport layer with stable electroluminescent properties. Using a photolithographic mask, these materials have been patterned into 10 to 50 μm -size features. These polymers have been used as hole-transport layers (HTLs) in multi-layer light-emitting diodes ITO/HTL/ AlQ_3 /Mg:Ag [ITO = indium tin oxide, AlQ_3 = tris(8-hydroxyquinolato)aluminum]. The electroluminescent properties have been evaluated and compared between devices made from polymers with different ionization potentials. Electroluminescent devices have been fabricated using a multilayered 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 AlQ_3 on top of a crosslinked hole-transport layer.

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

Block copolymers with long side-group liquid-crystalline midblocks (>800 kg/mol) and LC-phobic end-blocks form a physical network that swells readily in an analogous small molecule LC to form nematic gels. Ultralong side-group liquid crystal polymers (SGLCP) are used 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, polydomain 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 materials provide ideal 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 SGLCPs with M up to 1,000,000 g/mol and $M_w/M_n < 1.3$. The synthesis and interactions of these SGLPs with an LC 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 electro-optic response of nematic gels formed using ABA block-copolymers.

L7.46 LAYER-BY-LAYER PHOTOELECTRIC DEVICES: NANO-PATTERNED TiO_2 / ORGANIC DYE / POLYELECTROLYTE MULTILAYER COMPOSITES FOR PHOTOVOLTAIC DEVICES. Hiroaki Tokuhisa, Paula T. Hammond, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

Large area photovoltaic and photoelectric devices are extremely desirable as a flexible means of energy production and storage. In particular, it is desirable to develop inexpensive approaches to 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 photonics and photovoltaic systems. The versatile polyelectrolyte multiplayer assembly process is ideal for the construction of unique nano-structured thin films. We have engineered these systems to contain photocharge generator dyes and solid state electrolyte for photovoltaic applications. We report a novel technique used to pattern TiO₂ on polymer films, and its application to photoelectric devices. The technique involves polymer-on-polymer stamping of polystyrene-*b*-polyvinylpyridine block copolymer (PS-*b*-PVP) on the top of a polyelectrolyte layer surface, followed by templated synthesis of TiO₂. Inhibition of TiO₂ on the PS-*b*-PVP stamped region (hydrophobic region) allows formation of two-dimensional patterned TiO₂ films down to the nanometer length scale. We have investigated the optical properties of the patterned TiO₂ film, as well as the photoelectric behavior of organic dye molecules on the patterned TiO₂ film. Composite films of TiO₂ and polyelectrolytes exhibit selective reflection of visible light wavelengths and good photovoltaic performance.

L7.47

CHARGE CARRIER LIFETIMES IN A SMECTIC LIQUID CRYSTALLINE PHOTOCONDUCTOR OF A

2-PHENYLNAPHTHALENE DERIVATIVE. Hiroaki Iino, Jun-ichi Hanna, Imaging Science and Engineering Lab., Tokyo Institute of Technology, Yokohama, JAPAN.

Recently, liquid crystals has been being recognized to be a quality organic semiconductor, whose mobility exceeds 10⁻² cm²/Vs, since the electronic conduction was discovered in discotic and smectic liquid crystals. We have investigated the charge carrier lifetimes for electrons and holes in smectic mesophases of a 2-phenylnaphthalene derivative, 6-(4'-octylphenyl)-2-dodecyloxynaphthalene (8-PNP-O12) by time-of-flight (TOF) measurement and found that the carrier transport for holes and electrons is quite different. For positive carrier, the well-defined non-dispersive transient photocurrents were observed even in the thick cells over 500 μm and at the low applied electric field of 2 × 10⁴ V/cm. On the other hand, we observed two transits for negative carriers in the cells of 5 μm to 110 μm, i.e., fast and slow transits that correspond to the mobility on the order of 10⁻⁴ cm²/Vs and 10⁻⁵ cm²/Vs in the SmA phase and 10⁻³ cm²/Vs and 10⁻⁵ cm²/Vs in the SmB phase, respectively. We reduced that the origin of the slow transit are due to drift of ionized chemical impurities generated by electron trapping. Thus, we could reveal that the charge carrier lifetime is determined by different regimes for electrons and holes: the hole lifetime is determined by charge carrier recombination and estimated to be 10⁻² sec for SmA phase, while the electron lifetime by trapping at the deep states probably originated from a trace amount of impurity and estimated to be 4~5 × 10⁻⁵ sec for SmA and SmB phases.

L7.48

PULSED LASER DEPOSITION OF ALUMINUM

TRIS-8-HYDROXYQUININE THIN FILMS. Kenji Ebihara, Pail-Kyun Shin, Tamiko Ohshima, Tomoaki Ikegami, Kumamoto University, Department of Electrical and Computer Engineering, and Graduate School of Science and Technology, Kumamoto, JAPAN; Toshihisa Yamaguchi, Takamasa Sakai, Kumamoto Technology and Industry Foundation, Kumamoto, JAPAN.

Organic light emitting devices (OLED) have gained great interest due to their potential application as future flat panel display capable of low voltage operation. The Alq₃ (aluminum tris-8-hydroxyquinine) has attracted a great deal of attention as a material for OLED. This compound is one of the most reliable electron conducting and light emitting organic materials. The Alq₃ has been widely used as light emitting layer in light emitting diode. Several processes including thermal evaporation and ion-assisted deposition have been attempted to optimize the properties of the organic thin films. Pulsed laser deposition (PLD) is suitable for fabricating new material structures such as organic and inorganic. The PLD has alternative advantages of low process temperature, fine controllability of plasma, good reproducibility and highly purified deposition with low impurity level. We deposited the Alq₃ films using a second harmonic 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 press Alq₃ powder (Dojindo Laboratories) were ablated at a base pressure of 5 × 10⁻⁵ Torr. Laser fluence for the Nd:YAG laser were varied from 300 to 500 mJ/cm². The substrate (quartz glass) were placed at a distance of 25 mm from the target and kept at room temperature. Most of the Alq₃ samples deposited at the deposition rate of 1-8 pm/s showed amorphous while the target had polycrystalline structures by XRD measurement. The films were light

yellow color and showed very rough AFM images. The weak UV/visible absorption spectral lines of 345, 415 and 535 nm were observed and their intensities decreased with increasing laser fluence. On the other hand, when KrF excimer laser with the fluence around 300 mJ/cm² irradiated, the deposited films appeared dark yellow, indicating a decomposition of the Alq₃ target.

L7.49

QSPR STUDY OF GLASS TRANSITION TEMPERATURES OF TRIARYLDIAMINE DERIVATIVES USING GENETIC FUNCTION 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 triaryldiamine derivatives, CBP has been used as a host for phosphorescent OLED which has attracted a lot of attention due to their high efficiency. But one of the disadvantages of CBP is that it 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 have high Tg. We investigated the relationship between molecular structures and glass transition temperatures for 52 triaryldiamine 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 triaryldiamine derivatives predicting glass temperature within 10 degree. Genetic function algorithm was used as an alternative to standard regression analysis for constructing QSAR equations. And best subset regression and artificial neural networks were used to construct a prediction equation of QSPR. The configurational descriptors such as the number of rotational bonds and Shadow-xz, and the electronic descriptor, LUMO were selected as dominant descriptors. From this QSPR study, we could obtain good predicting equation.

L7.50

STUDY ON FIELD EFFECT CARRIER MOBILITY OF ORGANIC THIN FILM TRANSISTORS AT ULTRALOW TEMPERATURE.

Hirokazu Tada, Eiichi Fujiwara, Masaki Takada, Ryo Yamada, Yoshiro Yamashita.

Much attention has recently been paid to carrier transport in organic field-effect transistors (FET). Electrical properties especially at low temperature are of important to understand the mechanism. We have studied FET characteristics of various organic materials including phthalocyanine and bis-(1,2,5-thiadiazolo)-p-quinobis (1,3-dithiol) (BTQBT) in the range from 5 to 370 K. It was reported that BTQBT showed various crystal morphology depending on film growth conditions. The films grown on SiO₂ at 80°C consisted of needles with a length more than 10 μm, while round shaped grains with a diameter of about 300 nm exist on the substrate at room temperature. Field effect mobility of the latter films was about 0.1 cm²/Vs at room temperature and decreased with temperature, indicating that the hopping transport at grain boundaries is dominant. On the other hand mobilities of the film consisting of needles showed little temperature dependence in the whole range measured. The carrier transport mechanism in relation to crystal morphology will be discussed.

L7.51

BLUE LIGHT EMITTING DIODES USING ALKOXY

SUBSTITUTED POLY(SPIROBIFLUORENE)S. Jeong-Ik Lee, Hye Yong Chu, Hyoyoung Lee, Jiyoung Oh, Lee-Mi Do, Taehyung Zyung, Basic Research Lab., ETRI, Daejeon, KOREA; Jaemin Lee, Hong-Ku Shim, Dept. of Chemistry, KAIST, Daejeon, KOREA.

Poly(fluorene)s have attracted much research interest because of their possible application to blue 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 spirobifluorene into polymer backbone should be one possible method and here, we have synthesized spirobifluorene monomer which has alkoxy side chains to improve solubility as well as two aryl bromides for polymerization. Poly(3',6'-dialkoxy-9,9'-spirobifluorene-2,7-diyl) and its copolymer were prepared through Ni(0) mediated polymerization. Photoluminescence (PL) spectra of the homopolymer film 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 electroluminescence (EL) spectra also exhibited pure blue emission without excimer formation, which corresponds to the CIE coordinates of (0.16, 0.07). However, the device performance was

somewhat low and then we have prepared the copolymer of 4-n-butylphenyl-bis(4'-bromophenyl)amine and the above spirobifluorene monomer. The light emitting properties have been greatly improved and the device showed about 10 times higher efficiencies than the homopolymer while the CIE coordinate of the emission was almost same to that of the homopolymer. In this presentation, the detailed preparation method of polymer materials and the device characteristics will be discussed.

SESSION L8: MATERIALS

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

8:30 AM *L8.1

THE ACENES ROAD TO ORGANIC DEVICES. Hieu Duong, Q. Zhang, Hong Meng, Inna Perepichka, Yang Yang and Fred Wudl, Department of Chemistry and Biochemistry and Exotic Materials Institute, UCLA, Los Angeles, CA; Zhenan Bao, Theo Siegrist, Christian Kloc and Cheng-Hsuan 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 to produce n-dopable electron transporting layers. We have synthesized tetrasubstituted pentacenes (substituents: methyl, methoxy, chloro) as well as unusual heteroacenes.

9:00 AM L8.2

OLIGOMERIC AND POLYMERIC TRIPLET EMITTERS FOR LEDS. Albertus J. Sandee, Nicholas R. Evans, Kay L. Robinson, Andrew B. Holmes, University of Cambridge, Melville Laboratory, Cambridge, UNITED KINGDOM; Anna Koehler, Richard H. Friend, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

In recent years the use of inorganic triplet emitters has raised the possibility of harnessing the full electroluminescence energy in organic light emitting diodes. This paper describes the synthesis and photophysical study of a series of solution-processible polymeric triplet emitters. The novel phosphors are hybrid copolymers based on a bis-cyclometalated iridium-2-phenylpyridinato complex (Ir(ppy)₂) triplet emitter, and 9,9-dialkylfluorene, which as the homopolymer is an efficient singlet emitting polymer. The objective of the study has been to develop efficient phosphorescent materials that are easily solution-processible. This was accomplished by the attachment of successive fluorenyl segments to the 4-position of the ligand of a bis-cyclometalated iridium phosphor. It was shown that the stepwise addition of more fluorenyl repeat units to the phosphor gave rise to a gradual improvement in its performance as the emissive layer in an OLED device structure. The polyaddition to the phosphor was further extended towards the development of a polyfluorenyl-phosphor hybrid system.

9:15 AM L8.3

NEW CONJUGATED MAIN CHAIN POLYMERIC SEMICONDUCTORS AND THEIR PERFORMANCE IN ORGANIC FIELD EFFECT TRANSISTOR DEVICES. Martin Heeney, Maxim Shkunov, Dave Sparrowe, Mark Giles, Marcus Thompson, Steve Tierney, Iain McCulloch, Merck Chemicals, Chilworth, UNITED KINGDOM.

The performance of the semiconducting component in organic field effect transistors (OFET's), is a key parameter in the advancement of organic electronic devices. New conjugated main chain polymeric semiconductors, have been designed, synthesised, and their performance in transistor devices evaluated. The relationship between polymer molecular structure, its corresponding macrostructure and transistor performance will be discussed. Molecular design methodology 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. Shinji Aramaki, Mitsubishi Chemical Corp., Yokohama, JAPAN; Noboru Ono, Ehime University, Dep. of Chemistry, Matsuyama, JAPAN.

Porphyrins have been widely studied because they have unique

chemistry and they exist in biological system for special functions, related to its pi-electron system. Here, we report tetrabenzoporphyrin that can be used as a semiconductor for transistor applications. Furthermore, the semiconductor film can be formed with solution process. Soluble precursor compound with bicyclo structure forms a thin film by coating. The obtained film is amorphous and shows good film morphology. Then it is converted into an insoluble crystalline semiconductor film quantitatively at elevated temperature of 150-210°C. Field effect transistors were fabricated by this method. FET operation appeared only after conversion of the precursor. Observed mobilities of the devices exceeded 10⁻² cm²/Vs with appropriate process and device structure.

9:45 AM L8.5

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

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

10:30 AM *L8.6

ORGANIC SEMICONDUCTING AND DIELECTRIC MATERIALS FOR PLASTIC ELECTRONICS. Zhenan Bao, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Organic electroactive materials are now being considered as the active materials in displays, electronic circuits, solar cells, chemical and biological sensors, actuators, lasers, memory elements, and fuel cells. The flexibility of their molecular design and synthesis makes it possible to fine-tune the physical properties and material structure of organic solids to meet the requirements of technologically significant applications. In this talk, the performance of several new organic semiconducting 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. Whiting, Wilhelm T.S. Huck, Cambridge Univ, Melville Laboratory, Dept of Chemistry, Cambridge, UNITED KINGDOM; Henry J. Snaith, Richard H. Friend, Cambridge Univ, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

Polymer brushes have been widely used to tailor surface properties such as wettability, biocompatibility, corrosion resistance and friction. The advantage of polymer brushes over other surface modification methods (e.g. self-assembled monolayers) is 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 functionalise surfaces with polymer brushes, should allow full control over the thickness, density and composition of the polymer films, while at the same time be compatible with substrates that are used in polymeric devices. Surface-initiated polymerizations of polymer brushes (or grafting from method) has been very successful in this controlled growth and a variety of polymer brushes has been grown using different "living" polymerization conditions. We have now developed synthetic routes to grow brushes from PEDOT and other polymers. These 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 arylamine-containing brushes in photovoltaic devices show that 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, Domenico Cupertino, Phil Mackie, Remi Anemian, Steve Yeates, Avecia Ltd., Manchester, UNITED KINGDOM.

π -Conjugated heterocyclic oligomers are promising candidates for organic semiconductors but for these, high levels of purity are critical. Traditional approaches towards for example, regioregular oligo-(β -alkylthiophenes) of well-defined length, rely on repetitive transition metal catalyzed cross-coupling of difunctional monomers in solution followed by careful purification of chromatographically similar intermediates after each successive iteration; a process which is time-consuming, and inefficient. Recent publications applying solid phase synthesis (SPS) to the preparation of e.g. oligothiophenes demonstrate that SPS offers an attractive solution to some of the purification issues, however, the ultimate purity of the cleaved oligomer is critically dependent on the yields attained for each individual cross-coupling step. Incomplete cross-coupling results in deletions and leads to a distribution in the final oligomer length. We describe in this work the development of a novel and efficient strategy involving double-coupling, for the iterative solid phase preparation of oligo-(β -alkylthiophenes) and other organic semiconducting materials of well-defined length and high purity. The method employs a germanium-based linker and exploits the orthogonal susceptibility of α -silyl and α -germyl substituted thiophene-derivatives towards nucleophilic ipso-protodemetalation. The germanium-based linker also allows for final cleavage by electrophilic ipso-degermylation. Cleavage with acid will yield α -H terminated oligomers, whereas cleavage with halonium ions will yield α -halo terminated oligomers. Such $\alpha\omega$ -differentiated telechelic oligomers are valuable substrates for block co-oligomer preparation and for oligomer end-capping. The method additionally features a novel "base-free" Suzuki-type cross-coupling protocol.

11:30 AM *L8.9

HIGH PERFORMANCE n- AND p-CHANNEL POLYMER THIN FILM TRANSISTORS. Samson A. Jenekhe, Amit Babel, University of Washington, Departments of Chemical Engineering and of Chemistry, Seattle, WA.

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

SESSION L9: LIGHT-EMITTING DIODES

Chair: Neil C. Greenham
Thursday Afternoon, April 24, 2003
Salon 1-3 (Marriott)

1:30 PM *L9.1

NANOSTRUCTURED MATERIALS IN ACTIVE ORGANIC DEVICES. Vladimir Bulovic, Electrical Engineering and Computer Science Department, Massachusetts Institute of Technology, Cambridge, MA.

Nanoscale 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 electronic 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 nanostructuring

through directed self assembly, emphasizing the need for developing large area nanostructuring processes. Application of these methods to development of efficient hybrid organic-inorganic-nanocrystal LEDs and large-aspect-ratio planar organic crystals will be described. Reproducibility and precision of our recent device work suggests a wide applicability of these new fabrication techniques.

2:00 PM L9.2

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

Phosphorescent excimers have recently attracted attention for their use in white organic light emitting devices, because they can emit over a very broad range, have no absorbance and are efficient. Devices made using this technique have been shown to have a maximum power efficiency of 12 lm/W [1]. A single dopant, platinum(II)(2-(4,6-difluorophenyl)pyridinato-N,C2') (acetyl acetate) (FPt1), can be doped into a 3,5-bis(N-carbazolyl)benzene (mCP) host to efficiently produce white light based on triplet excimer and direct phosphorescent emission. Excimers have a broad spectral lineshape and no optical absorption because they have an unbound ground state [2]. The physics of excimer formation is therefore of much practical and scientific interest. The transient and steady state photoluminescent and electroluminescent properties of FPt1 are used to understand the formation of triplet excimers and dimers in amorphous films grown by thermal evaporation. We find that the excimer and dimer have peak emission intensities at 2.07 eV and 1.83 eV, and have lifetimes of (1.6 \pm 0.3) ms and (800 \pm 80) ns at room temperature, respectively. When films are optically pumped, triplet excitons form on monomers and then diffuse via thermally activated hopping to nearby excimer sites with an activation energy of (37 \pm 4) meV. Further, excitation of triplet aggregate states, or metal-metal dimers via the association of cations and anions of electrically pumped FPt1 is achieved in an organic light-emitting device, which achieves a maximum external quantum efficiency of 2.7 \pm 0.3%. Electrical pumping also reveals dimer states unresolved in photoluminescent studies. The high efficiency of the triplet excimers of FPt1 is significant since dimeric species, especially triplets, are often associated with concentration quenching and low quantum yields. [1] V. Adamovich, J. Brooks, A. Tamayo, A.M. Alexander, P.I. Djurovich, M.E. Thompson, C. Adachi, B.W. D'Andrade and S.R. Forrest, New J. Chem. 26 (2002) 1171. [2] J.B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970.

2:15 PM L9.3

n-TYPE DOPING OF ORGANIC THIN FILMS USING CATIONIC DYES. A. Werner, F. Li, K. Harada, M. Pfeiffer, T. Fritz, and K. Leo, Institut für Angewandte Photophysik, TU Dresden; S. Machill, Institut für Analytische Chemie, TU Dresden, GERMANY.

Highly conductive organic semiconductors are important for many applications, including efficient low-voltage organic light emitting diodes (OLED). Although highly p-conducting materials are available, n-type doping is mostly limited to alkali metal doping which has many problems. We here present a new approach to stable n-type doping of organic matrixes using organic dopants. In order to circumvent stability limitations of strong organic donors, we produce the donor from a stable precursor compound *in situ*. As example, the cationic dye Pyronin B chloride as dopant in 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA) yields conductivities of up to 1.9 \cdot 10⁻⁴ S/cm, two orders of magnitude higher than the conductivity of NTCDA doped with (bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) as investigated previously [A. Nollau et al., J. Appl. Phys. 87, 4340 (2000)] and four orders of magnitude higher than nominally undoped NTCDA films. Field effect measurements are used to prove n-type conduction and to further study the doping effect. Combined FTIR, VIS and mass spectroscopy suggests the reduction of Pyronin B during evaporation. We also show that this doping mechanism can be generalized to other materials.

2:30 PM L9.4

ENHANCING PERFORMANCE OF POLYMER LEDs THROUGH NANOSCALE SELF-ASSEMBLY. James F. Hulvat^a and Samuel I. Stupp^{a,b,c}. ^aDepartment of Materials Science and Engineering; ^bDepartment of Chemistry; ^cFeinberg 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 an aqueous templating strategy utilizing nanoscale dielectric channels in liquid crystals to control molecular orientation within conducting polymers, such as poly(3,4-ethyldioxythiophene) (PEDOT). This strategy involves confining monomeric precursors within the cylindrical

hydrophobic cores of a hexagonal liquid crystal formed in water by the amphiphile oligo(ethylene oxide)₇-oleyl. By allowing the monomer doped 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 a net polymer orientation 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. In contrast to amorphous films of PEDOT, these templated films are birefringent and exhibit linear dichroism in their optical absorption. Conductivity and charge injection is improved due to alignment of the PEDOT chains. Organic light emitting diodes (OLEDs) prepared using these templated PEDOT films as hole injection layers display increased luminescence and higher injection efficiency. This approach bridges the gap between conventional lithography and molecular self-assembly by orienting polymers within a nanoscale liquid crystal template ordered over hundreds of microns. By using this templating process, precursor monomers may be isolated, oriented, polymerized and doped in a single step. The molecular alignment locked-in during polymerization results in enhanced performance and novel anisotropic properties in organic electronic devices.

2:45 PM L9.5
HIGH PERFORMANCE ORGANIC DIODES. Liping Ma; Yang Yang.

High performance organic diodes have been fabricated by vacuum deposition method and post-treatment. The as-fabricated diode shows small rectification behavior, but after post-treatment, the performance of the diodes enhanced tremendously. The rectification ratio of the devices after post-treatment can reach as high as 6 orders in magnitude. Most importantly, the responds speed of the devices to applied AC voltage enhanced tremendously, up to mega-Hz range. The current injection of the devices at 1.4 Volt forward voltage bias can reach 160 A/cm². In an addition, the devices show high stability. To our knowledge, this device is the first organic diode which is high-speed, air stable (without encapsulation), and can handle high current density.

3:30 PM *L9.6
THE USE OF IR AND PT COMPLEXES TO ACHIEVE HIGH EFFICIENCIES IN MULTICOLOUR AND WHITE ORGANIC LIGHT EMITTING DIODES. Mark Thompson, Vadim Adamovich, Jason Brooks, 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 excitons 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 phosphorescent dopants in these devices are heavy metal containing organometallic molecules (i.e. Pt, and Ir). The high level of spin orbit coupling in these metal complexes gives efficient intersystem crossing, leading to strongly emissive triplet excited states. We have recently demonstrated white light emitting OLEDs. These devices emit simultaneously from monomer and dimer/excimer states of Ir and Pt dopants. The result is an emission spectrum that covers the entire visible spectrum, giving true white illumination. These white light emitting devices give excellent color rendering indices (i.e. 75-85) and high efficiencies (> 6%, 12 Lum/W). I will discuss our most recent advances in both monochromatic and white OLEDs.

4:00 PM *L9.7
OPTIMISATION OF CONJUGATED POLYMERS AND PERFORMANCE IN ORGANIC DEVICES. Herman F.M. Schoo, Kornel T. Hoekerd, Jolanda J.A.M. Bastiaansen, Albert J.J.M. van Breemen, Bea M.W. Langeveld-Voss, John A.E.H. van Haare, Peter Herwig, Marc Koetse, Nicole Kiggen, 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 dependant on properties of the organic materials. Parameters like quantum and/or power efficiency, 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 different processing behavior, morphology of polymer films and, ultimately, different device performance. We will present some examples of these relationships.

4:30 PM L9.8
ORIENTED SEMICONDUCTING POLYMER NANORODS. Michael D. Barnes, Adosh Mehta, Pradeep Kumar, Oak Ridge National Laboratory, Division of Chemical Sciences, Jie Zheng, and Robert M. Dickson, Georgia Institute of Technology, Dept. of Chemistry and Biochemistry.

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

4:45 PM L9.9
PHOTOCHEMICAL PATTERNING APPROACHES FOR MULTICOLOR POLYMER LIGHT EMITTING DEVICES. A. Pogantsch, G. Trattng, S. Rentenberger, TU Graz, Institute f. Solid State Physics, Graz, AUSTRIA; H. Tillmann, H.-H. Hoerhold, Univ. Jena, Institut fuer Organische Chemie und Makromolekulare Chemie, Jena, GERMANY; U. Scherf, Univ. Wuppertal, Polymerchemie, Wuppertal, GERMANY; G. Langer, J. Keplinger, W. Kern, TU Graz, Institute for Chemistry and Technology of Organic Materials, Graz, AUSTRIA; E. Zojer, TU Graz, Institute f. Solid State Physics, Graz, AUSTRIA, and Univ. of Arizona, Department of Chemistry, Tucson, AZ.

A convenient photolithographic technique is described that provides for an efficient tuning of the emission color(s) of polymer based light emitting devices. The devices possess a single emissive layer based on a blend of conjugated polymers. In this blend, the lower bandgap material(s) contain(s) vinylene units (e.g. PPV), while the larger bandgap material is a derivative of polyfluorene. Using a photoinduced reaction to reduce the effective conjugation length of the blend's lower bandgap component(s), the energy transfer efficiency from the higher bandgap component to the lower bandgap component(s) is diminished. In this way dual-color and red-green-blue emitting electroluminescence devices are realized from a single spin-cast layer, without deteriorating the device characteristics. To achieve a photoinduced transformation of the vinylene units, we employ either hydrazine (N_2H_4) or propanethiol (C_3H_7-SH) as gaseous reactants or, alternatively, dodecanethiol as an additional component in the polymer blend. While in the presence of N_2H_4 a photoinduced reduction preferentially of the vinylene units takes place, thiols undergo a highly selective photoaddition to $C=C$ double bonds. In this context, the application of the "Thiol-Ene Photoreaction" to conjugated polymers containing vinylene units (e.g. PPV) constitutes a novel approach for the photochemical tuning of the optoelectronic properties of organic materials. Since this process is compatible with regular film casting techniques, such as spin casting or doctor blading, it is a promising alternative to the more complex, traditional patterning approaches.

SESSION L10: POSTER SESSION
Chair: Christos D. Dimitrakopoulos
Thursday Evening, April 24, 2003
8:00 PM
Salon 1-7 (Marriott)

L10.1
IN-SITU NANOSCALE OBSERVATION OF TEMPERATURE-INDUCED SURFACE MORPHOLOGICAL EVOLUTION OF NPB THIN FILM FOR DISPLAY APPLICATION. Mingshen Xu^{a,b}, Jian-Bin Xu^{a,b}, Jin An^{a,b}, Leo W.M. Lau^{b,c}; ^aDept of Electronic Engineering, ^bMaterials Science and Research Center, ^cDept of Physics, The Chinese University of Hong Kong, Shatin, NT, HONG KONG; Harry H.L. Kwok, Dept of Electrical & Computer Engineering, University of Victoria, Victoria, CANADA.

This paper reports on an *in-situ* study of N, N'-di(naphthalene-1-yl)-N, N'-dipthalbenzidine (NPB) film, a hole transport layer having a glass transition temperature T_g at 95 °C and

generally used in Alq₃ based organic light-emitting diodes (OLEDs). The surface morphology evolution of the NPB thin film has been visualized by exploiting variable temperature tapping mode atomic force microscopy (VT-AFM). It is found that the morphological evolution starts at 60°C, and proceeds until 95°C, and then the evolution remains stagnant until 125°C. This process is very similar to the characteristics of a glass transition that generally occurs over a significant temperature range rather than in an abrupt alteration. Crystallization from the glass state swiftly takes place at 135°C, marked unambiguously by the dominant peaks in the micro-Raman spectra. As the temperature rises to above 185°C, the thin film gradually melts and disappears, leaving completely the exposed underlying layer. The observation on the initial apparent surface glass transition at 60°C provides a reasonable explanation of the previous findings that the lifetime and luminance reduction is more than one order of magnitude shorter for OLEDs operated at 60 - 70°C than that operated at room temperature. This is probably due to the fact that a small variation of morphology could be extremely crucial for charge injection since the injection rates exponentially depend on the orbital overlap distance of the molecules. The subsequent crystallization may facilitate a completely 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.

L10.2

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

Polymeric, planar waveguides of pyrromethene dye-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 optically pumped PM567-PMMA planar asymmetric waveguides. We report here studies of gain and loss, time-resolved photoluminescence and tunability of the lasing emission with the thickness of the waveguide.

L10.3

ELECTRICAL CHARACTERISTICS OF VACUUM DEPOSITED AND SOLUTION PROCESSED DH4T THIN FILM TRANSISTORS. T. Muck, M. Leufgen, A. Lebib, T. Borzenko, J. Geurts, G. Schmidt, L. Molenkamp, Univ. Würzburg, EPIII, Würzburg, GERMANY; V. Wagner, International University Bremen, Bremen, GERMANY; H.L. Gomes, Universidade de Algarve, Faro, PORTUGAL.

Organic field effect transistors (OFETs) show interesting possibilities like cheap processing or application as flexible devices (plastic electronics). As active layer oligothiophenes e.g. tetrathiophene (4T) and sexithiophene (6T) are of interest due to their conjugated π -electron systems. We present organic field-effect transistors with Dihexyltetrathiophene (DH4T) as active material, a derivative of the Oligothiophene α -4T with two hexyl-chains as 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 alcy 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 were produced for channel lengths in the range of 50 μ m to 1 μ m by optical lithography. We compare vacuum deposited and solution processed OFETs based on DH4T. The former ones show typical I-V characteristics and higher currents. Temperature dependent measurements of drain-source current show significant variation of charge mobility which is very similar to the behaviour of α -6T (sexithiophene). While negative gate voltage leads to a bias-stress of the device due to filling of traps in the accumulation layer, positive gate voltage improves the device behaviour. Therefore the threshold voltage was studied as function of bias-stress which 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 a Molecular Microsystems, University of

Wales, Bangor, Gwynedd, UNITED KINGDOM; D. Lacey, Department of Chemistry, University of Hull, Hull, UNITED KINGDOM; K.A. Rump, Department of Chemistry, University of Hull, Hull, UNITED KINGDOM.

Electropolymerisation is, potentially, a powerful technique for electrochemically grafting robust, highly stable nanometric 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 explaining the relatively few cases of true electrografting reported in the literature. According to XPS, UPS and SERS measurements, the affinity of acrylonitrile for gold, silver and copper differs widely such that the monomer physisorbs to gold while chemisorbing to silver and copper [2], [3], [4]. Following a detailed study of the growing conditions, however, we have successfully electrografted films of polyacrylonitrile onto all three metals. In particular, we have focused on the kinetics of the grafting process and especially on the use of the so-called 'passivation peak' in the voltammogram as an indicator of film growth. A detailed characterisation of the grafted films has been undertaken using Raman microscopy, FTIR spectroscopy and Atomic Force Microscopy. This confirmed the preparation of smooth polymer films (rms roughness \sim 3 nm) with a molecular structure consistent with that expected for an electrografted layer. We are currently developing an *in situ* technique for monitoring polymer growth in a bid to fully understand the grafting process. In a parallel investigation we are attempting the electrografting of polyacrylonitrile films with (a) hydroxyl and (b) carboxyl moieties which can be used for the specific, chemical functionalisation of the deposited films. [1] Crispin, X. *et al*, *J. Am. Chem. Soc.*, **1999**, 121, 176-187. [2] Parent, Ph.; Laffon, C.; Tourillon, G. *J. Phys. Chem.*, **1995**, 99, 5058-5066. [3] Xue, G.; Dong, J.; Zhang, J.; Sun, Y.; *Polymer*, **1994**, 35, 723. [4] Crispin, X. *et al*, *J. Electron Spectrosc. Relat. Phenom*, **2001**, 121, 57-74.

L10.5

BULK HETEROJUNCTION PHOTOVOLTAIC DEVICES BASED ON CONJUGATED POLYMERS. S.C. Veenstra, W.J.H. Verhees, L.H. Slooff, J.M. Kroon, Energy Research Centre of The Netherlands (ECN), Petten, THE NETHERLANDS, and Dutch Polymer Institute, THE NETHERLANDS(DPI); M.M. Koetse, H.F.M. Schoo, The Netherlands Organization for Applied Scientific Research (TNO), Eindhoven, THE NETHERLANDS and DPI; M.M. Wienk, Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, Eindhoven, THE NETHERLANDS and DPI; J.C. Hummelen, Stratingh Institute and Materials Science Center, University of Groningen, Groningen, THE NETHERLANDS.

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 as devices based on the combination of polymers with small molecules, as for example blends of conjugated polymers with C₆₀ or perylene-diimide derivatives. The third class consists of two conjugated polymers. Here we report on recent progress on the development of these three types of organic photovoltaic devices with focus on polymer-polymer bulk hetero-junction devices. The device characteristics, such as the external quantum efficiency (EQE) and the power conversion efficiency, are strongly related to the processing conditions. For example, in devices containing a blend of MDMO-PPV with a cyano-PPV derivative, the EQE increases from nearly 10% to 17% upon a thermal anneal step. This thermal treatment is only effective at temperatures higher than the highest glass transition temperature (T_g) of either polymer in the blend. This indicates that the morphology of the photoactive layer is one of the key aspects with respect to the processing of efficient polymer photovoltaic devices. Since for many substituted PPV's, the T_g is close to the maximum operating temperature of these devices (\sim 80°C), these findings are also important for the development of stable polymer blends that can be used in practical situations.

L10.6

VISIBLE AND 1.55 μ M QUANTUM DOT ORGANIC LIGHT EMITTING DEVICES. Seth Coe and Vladimir Bulović, Massachusetts Institute of Technology, Department of Electrical Engineering and Computer Science, Cambridge, MA; Jonathan Steckel and Mounji Bawendi, 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 processes from their participation in charge conduction. The fabrication of QD monolayers is enabled by material phase segregation

between the QD aliphatic capping groups and the aromatic organic materials. This fabrication technique is independent of QD size and material, allowing us to change the electronic structure of the 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 CdSe QD-LEDs, as well as PbSe QD-LEDs that emit at $1.55\mu\text{m}$.

L10.7

Abstract Withdrawn.

L10.8

HIGHLY RESPONSIVE OPTICAL SENSORS USING PYRENE SURFACE MODIFIED ELECTROSPUN MEMBRANES.

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

To date, we have demonstrated that sensors fabricated by electrospinning a fluorophor containing polymer can have 2-3 orders of magnitude higher sensitivities than those from continuous thin films of the same sensing material. The sensitivity of these electrospun sensors was then increased to tens of parts-per-billion detection limits by adsorbing fluorescent conjugated polymers onto the surface of the electrospun nanofibrous membranes 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 electrospun nanofibrous membranes with a pyrene fluorophor. To fabricate the sensors, the fluorescent indicator, pyrenebutyric acid, was covalently attached onto the surface of poly(2-hydroxyethyl methacrylate) electrospun nanofibrous membranes. This localization of the fluorescent tag to the surface of an already high surface area nanofibrous membrane minimized the amount of inactive (embedded) fluorescent indicator, and resulted in significantly improved sensitivities and reversibility compared to similar systems in which the fluorescent polymer was dispersed throughout the electrospun nanofibers and allows for more direct control over the concentration of fluorophore used. The fluorescence of these films can be quenched by extremely low concentrations of 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 (Fe³⁺ and Hg²⁺) follow Stern-Volmer bimolecular 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, Xianyan Wang, and Jayant Kumar, Center for Advanced Materials, Departments of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA; Ferdinando F. Bruno and Lynne 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 electrospun from polyacrylonitrile and collected as a fibrous membrane. Metal oxide coatings were subsequently applied by immersing the membranes into an aqueous liquid containing the metal-halogen salt and a halogen scavenger at room temperature for a number of hours. Adding multiple metal salts to the coating solution resulted in mixed metal oxide deposition. Coating solution stoichiometry was compared to metal oxide content in the final coating. Metal oxides studied include titanium dioxide, tin dioxide, and zinc oxide, in coating thicknesses of 10 to 100 nm. Such novel, high surface-area, metal oxide nanostructures 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 Lazarev, Michael Paukshto, Elena Sidorenko, Optiva, Inc., South San Francisco, CA.

Optiva 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 disk-shaped molecules that can be printed on glass or plastic and then dry into a highly ordered crystalline film. TCF are produced by

deposition of water based lyotropic liquid crystal formed by rod-like supramolecules of heterocyclic sulfonic acids. The supramolecules having a columnar structure with an aspect ratio of more than 100 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 strong anisotropy of refraction and absorption indices make TCF very attractive in the 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

CONDUCTING POLYMERS BASED SUPRAMOLECULAR FILMS FOR GAS SENSORS. Manoj Kumar Ram, Ozlem Yavuz, Matt Aldissi, 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 etc. 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 have proved to perform efficiently and selectively within seconds of exposure to gases. The present work focuses on the use of highly organized conducting polymer films with high conductivity, and/or ultrathin films of conducting polymer/SnO₂ nanocomposites, which will selectively recognize CO, CO₂, and NO₂ gases with ppb 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 materials. We have prepared and characterized several polymers, fabricated thin self-assembled films with different layer thickness in each system to study the effect of the number of layers on film properties relative to gas sensing. We have used several characterization techniques to prove feasibility of our approach, including conductivity, impedance, UV-Visible, FTIR, AFM and elemental analysis. With the expected high selectivity and low detection limit and versatility of the measurement procedure, our work will result into a miniaturized device.

L10.12

INFLUENCE OF LOCAL ORDER AND MOLECULAR DIPOLE STRENGTH ON THE DISPERSION OF EXCITONIC ENERGIES IN ORGANIC THIN FILMS. Conor Madigan, Vladimir Bulović, 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 energy levels for [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H, 5H-benzo [i,j] quinolizin-9-yl)-ethenyl]-4H-pyran-4-ylidene] propane-dinitrile (DCM2) doped in films of aluminum tris-(8-hydroxyquinoline) (Alq₃). In the technique, we measure the time resolved photoluminescence following excitation by a 100 fs laser pulse, and observe the spectral shift using a streak camera with better than 5 ps resolution. The time resolved spectral signature is generated by the diffusion of excitons through the film by means of Förster energy transfer between lumophores. A fit of the experimental results to the Monte Carlo simulation of this process obtains a value for w_{DOS} . Aside from our study of DCM2, no quantitative data on w_{DOS} for excitonic 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 fac-tris(2-phenylpyridine) (Ir(ppy)₃), Alq₃, N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1' biphenyl-4,4'' diamine (α -NPD), and N, N'-diphenyl-N, N'-bis(3-methylphenyl)-(1, 1'-biphenyl)-4, 4'-diamine (TPD)) to study the influence of molecular properties and molecular packing on solid state excitonic energy distributions. We find that the two most important material parameters are the local ordering of molecules and the strength of the molecular electric dipole (i.e. the molecular "polarity"). Our data shows that increasing local order decreases w_{DOS} while increasing polarity increases w_{DOS} . Since highly polar molecules have a tendency to aggregate (and thereby locally order), some highly polar molecules can also yield films with small w_{DOS} . However, for non-polar molecules, we find that w_{DOS} is negligible irregardless of the degree of local order.

L10.13

CHARGE INJECTION IN DOPED ORGANIC SEMICONDUCTORS. Yulong Shen, Man Hoi Wong and George G. Malliaras, Department of Materials Science & Engineering, Cornell University, Ithaca, NY; Bing Hsieh, Xerox Corporation; David Dunlap, 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, tetra-methyl triphenyl diamine doped polycarbonate (PC:TMPD) was used for these experiments. By substituting TMPD molecules with a TMPD+SbF₆⁻ salt, the degree of doping in the organic semiconductor was systematically varied. Changes in the electrical characteristics of devices with various electrodes 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. Kushto, Ian G. Hill and Zakya H. Kafafi, U.S. Naval Research Laboratory, Washington, DC; Ullrich Mitschke and Peter Bäuerle, University Ulm, Ulm, GERMANY.

Thiophene oligomers represent a class of materials whose electronic properties can be easily tuned through control of the π -conjugation length, side or main chain derivatization. The effect of substitution of the central thiophene ring by a furan, an oxazole or oxadiazole on the electronic properties of a series of quinquethiophene oligoheterocycles is 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 quinquethiophene derivatives 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

Abstract Withdrawn.

L10.16

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

The solid-state electronic properties of acenes such as pentacene have led to their successful use in numerous electronic devices. The demonstration that crystalline order in thin films was directly linked to improved device performance led us to investigate synthetically-modified acenes, in order to determine the effect of this functionalization on device performance. We have demonstrated that selective functionalization of acenes with simple, alkyne-containing groups leads to improved solubility and increased oxidative stability. By careful selection of substituents, the arrangement of the acenes in the solid state can be controlled to increase both the extent and dimensionality of π -stacking between the aromatic units. Increasing π -stacking leads to a significant increase in conductivity, and decrease in band-gap along the π -stacking axis to well below 1 eV. Using a different set of substituents, π -stacking in the solid can be totally eliminated, leading to the acene units being isolated in a crystalline shell of saturated hydrocarbon. The elimination of π -stacking leads to highly fluorescent solids. The maintenance of crystalline order in evaporated thin films yields electroluminescent devices with greatly increased efficiencies compared with the π -stacking unsubstituted acenes. Fine-tuning of the π -stacking allows us to subtly alter the color of electroluminescence 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 Jerzy Kanicki, University of Michigan, Department of Electrical Engineering and Computer Science, Ann Arbor, MI.

We have investigated the response of our organic polymer thin-film

transistors (OP-TFTs) to illumination. The structure of the device is an inverted, gate-planarized, coplanar thin-film transistor. Indium tin oxide was used for the source and drain contacts and amorphous silicon nitride was used for the gate insulator. The organic semiconductor P8T2 (poly 9,9-dioctylfluorene-co-bithiophene) was deposited by spin-coating. These devices exhibit p-type field-effect transistor behavior. Typical values of the linear regime field-effect mobility, threshold voltage, and subthreshold slope parameter for these devices in the dark are $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$, -15 V, and 2.5 V/decade respectively. The devices were illuminated from the top with broadband white light. We measured the output and transfer 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 $R_{L/D} = I_{\text{Drain}}/I_{\text{Dark}}$ and is a function of the OP-TFT gate voltage (V_{GS}) and the illuminance (IL). In the strong accumulation regime, $R_{L/D}$ decreases because of the dominant effect of the gate voltage on the concentration of accumulated carriers. In the OFF-state, $R_{L/D}$ can reach two to three orders of magnitude depending on the level of illumination, and is not strongly dependent on V_{GS} . $R_{L/D}$ exhibits a power law dependence on the illuminance level, increases with the channel width of the device and decreases with the channel length. The timescale for the device to respond to the illumination is approximately 10s at room temperature, while the timescale for the device to return to the original state, after the illumination is removed, is approximately one hour at room temperature in the dark.

L10.18

ELECTRO-OPTICAL PROPERTIES AND INTERFACIAL CHARGES IN POLYMER-DISPERSED LIQUID CRYSTAL DEVICES. R.A. Ramsey, S.C. Sharma, R.M. Henry, and J.B. Atman, 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 crystalline (lc) material dispersed in a polymer matrix. A device is usually assembled by sandwiching PDLC between ITO-coated glass plates. The electro-optical properties of such a device can be controlled by the application of electric fields; the device acts as a "switch" for the transmission of light. The transmission of light through the device can be controlled between almost zero and 100% by applying ac electric fields. The dielectric properties of the lc and polymer, shape and size distribution of the lc droplets in the PDLC, amplitude and frequency of the applied electric field are among the important parameters for optimizing the performance of such a device. We have investigated the optical properties of PDLC devices fabricated by using several different phase-separation techniques and different lc/polymer materials. We present results for the switching characteristics of these devices as functions of applied electric fields and the size-distribution of the lc droplets. We also present results that reinforce the influence of the interfacial charges on the optical properties of the PDLC devices. Research supported, in part, by the Texas Advanced Technology Program under Grant No. 003656-0123-2001.

L10.19

IMPROVING INTERFACES AND SEMICONDUCTOR MATERIALS FOR OFETS: AN INVESTIGATION OF NOVEL PHTHALOCYANINE MOLECULES AND SURFACE MODIFICATION. Carrie L. Donley, Rebecca A.P. Zangmeister, Wei Xia, Anthony S. Drager, Britt Minch, 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 anisotropies in those mobilities (OFET applications), properties which stem from highly ordered thin film materials. We have studied a series of octasubstituted phthalocyanines (Pcs) with a benzyl termination of the side chains linked to the Pc core with either an oxygen or sulfur atom. The benzyl termination imparts unique stability and coherence to films of this molecule made on a Langmuir Blodgett trough. 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 AFM (TUNA) system. Currents measured by the TUNA system were taken on a ca. 100 nm scale, and they showed mobilities greater than $0.1 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$, and anisotropies in mobility of up to 1000 for a benzyloxyethoxy CuPc. The thiol linked version of this molecule has also been characterized, and it seems to show different types of aggregation in thin films than the oxy-linked Pc. It has been incorporated into some PV cells, and the characteristics of these devices will be reported briefly here and in complete detail in an

accompanying paper for this symposium. We have also investigated a polymerizable Pc which contains a styryl functionality in the side chains of the molecule. Photopolymerization of ordered assemblies 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 polymerized material on interdigitated microelectrodes were higher than for the benzyloxyethoxy parent molecule.

L10.20

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

We use solvent vapor annealing to facilitate molecular reorganization in thin films of organic small molecules. In the case of tris-(8-hydroxyquinoline)aluminum (Alq_3), this reorganization is dramatic, yielding needle-like crystals in the plane of the substrate from initially amorphous thin films. Furthermore, we demonstrate that nano-patterned substrates can control the orientation of the needle crystals, which can reach millimeters in length. The formation of such large area crystals directly on a substrate facilitates electrical characterization and device fabrication. Using optical interference lithography we generate periodic patterns over square centimeters with feature sizes ranging from 100 to 500 nm. The patterns are transferred to silicon substrates via etching, resulting in surface relief gratings with depths up to 150 nm. Alq_3 is vacuum evaporated onto the nano-gratings, and the films are subsequently annealed in chloroform vapor. The resulting Alq_3 needles lie in the plane of the substrate and are aligned along the grating direction. Larger needles span several grating periods, but needles confined to a single grating trough are also observed. Needle thicknesses exceed the initial Alq_3 amorphous film thickness by as much as 200 times and the grating depth by as much as 30 times. Typical thickness:width:length ratios are 1:2:2000, 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 fluorescence spectra of the Alq_3 crystals and observed waveguiding down the length of the needles indicating optically smooth crystal facets in agreement with AFM data. We will report the influence of initial amorphous film thickness, annealing time, nano-grating dimensions and chemical surface modifications on needle formation, and discuss the utility of the needle crystals in active device structures.

L10.21

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

Cathode deposition is a crucial issue for top-emitting OLEDs, due to the induced damage to the underlying organic layers caused by sputtering techniques. The critical effect on device performance and reliability of the sputter damage to the organic layer is well known. Efficient and stable TOLEDs have been produced by the insertion of buffering layers beneath the sputter deposited cathodes. The efficacy of the buffering layer has shown mixed results with different systems, 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 peel-off method, the XPS study allowed a direct comparison between observed electrical performance degradation and molecular breakdown at the interface. The limits of the XPS technique to observing the sputtering damage was determined through correlation of the observed N1s splitting, indicating molecular breakdown, with the reduction in device electrical performance.

L10.22

PURE INFRARED ELECTROLUMINESCENCE FROM CONJUGATED POLYMER HOST/GUEST BLENDS. Matthew R. Robinson, Guillermo C. Bazan, Alan J. Heeger, Jacek C. Ostrowski, UC Santa Barbara, Dept of Materials, Chemistry, Physics; Michael J. Therien, Kimihiro Susumu, University of Pennsylvania, Dept of Chemistry, Philadelphia, PA.

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

The first system makes use of a novel erbium complex doped into a stable green emitting conjugated polymer host. The ligand incorporates a pentaphenylenevinylene unit and is chelated to the metal center via a beta diketonate functionality - necessary for efficient energy transfer to the [infrared] atomic transition. The pentaphenylenevinylene fragment endows the ligand with a suitably red absorption to overlap green-emitting polymers, eliminating the need for inferior blue emitters. Emission is observed almost entirely from the lanthanide, whereas polymer and ligand-centered emission is not observed. OLED devices made entirely of this complex [without the polymer] will also be discussed. A second system makes use of conjugated oligo(porphinato)zinc molecules doped in both PVK:PBD and MEH-PPV (separate experiments) in order to demonstrate the versatility of these dopant materials afforded by their broad absorption spanning the visible region. Emission entirely in the near-IR is observed which is tunable by increasing the conjugation length by adding additional monomers. Although the photoluminescence quantum yield of these materials is less than 0.08, electroluminescence efficiencies up to 0.01 infrared photons per electron are realized.

L10.23

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

Surface tethered alpha-helical poly(γ -benzyl L-glutamate) (PBLG) films demonstrate excellent liquid crystalline, electrooptical, and electromechanical properties due to the non-cancelable dipole moment attributed by individual helical rods. The past studies have indicated that such films consist of randomly distributed molecular rods with average tilt angle of 33 - 65 deg from the surface normal. It is believed that a uni-directional molecular arrangement in films would be more desirable to produce not only the highest net dipole but also the organized functional groups at nanoscale. Here we report a simple quenching method to align PBLG helical rods along the normal direction. In this method, a highly oriented tethered PBLG film was prepared by first immersing 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 maximize the molecule-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 3 deg from surface normal. The change of tilt angles coincide with the increase of overall film thickness from 95 nm ($N_f = 1.56$) to 166 nm ($N_f = 1.27$) 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 pyramid structures after quenching. The quenched surface contains lower surface energy as evidenced by the increase of water contact angle from 70 deg to 110 deg. 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 polymeric surfaces.

L10.24

Abstract Withdrawn.

L10.25

SHORT CHANNEL AND CONTACT EFFECTS IN HIGH MOBILITY REGIOREGULAR POLY(THIOPHENE). Michael L. Chabinyk, Alberto Salles, Robert A. Street, Palo Alto Research Center, Electronic Materials Lab, Palo Alto, CA; Beng Ong, Yiliang 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^{-2} to greater than 10^{-1} cm^2/Vs depending on the device size and contact geometry. We have tested the contact effects by fabricating TFTs with both staggered and coplanar contact geometries in a single device, allowing contact resistance differences to be measured by reversing the device polarity. We also 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 $0.7 \text{ cm}^2/\text{Vs}$ with high drain voltages in short channel devices. Measurements of output characteristics at channel lengths from 5 to 50 μm confirm the short channel effect. We discuss

the evidence for an actual drain-field dependent mobility based on a model for the short channel effects. The implications of these results for characterization of the intrinsic properties of polymeric semiconductors will be discussed.

L10.26

POLARIZED ELECTROLUMINESCENCE FROM LIGHT EMITTING DIODES CREATED BY SELF ASSEMBLY AND ELECTROPHORESIS. Leiming Li, Keisuke Tajima, John C.

Stendahl, Eugene R. Zubarev, and Samuel I. Stupp, Department of Materials Science and Engineering, Department of Chemistry, Feinberg School of Medicine, Northwestern University, Evanston, IL.

Our laboratory developed self-assembling triblock molecules known as dendron rodcoils (DRCs) that contain dendritic, rod-like, and coil-like segments. In certain solvents such as chloroform or 2-ethylhexyl methacrylate these molecules self assemble into long nanoribbons. These nanoribbons can have widths of about 10 nanometers, a thickness in the range of 2 nanometers and lengths on the order of microns. Their formation leads to the three dimensional networks 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 anisotropic, with a parallel EL component (parallel to the poling direction) stronger than that perpendicular to the electric field. EL was found to be isotropic from LEDs containing 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 Xia, Michael D. Carducci, Carrie L. Donley, and Neal R. Armstrong, University of Arizona, Department of Chemistry, Tucson, AZ.

Certain phthalocyanines (Pc) modified with benzyl-terminated ethyleneoxide side chains, and their thio-oxy 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 annealed, the width and position of the Bragg peak in the X-ray reflectivity data are consistent with a dense, regular hexagonal close packed adjacent rods. For 1- and 2-bilayer films, however, there are shifts in the Bragg peaks, and associated changes in the rest of the reflectivity data which suggests a different 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 what controls the electronic properties of these initially deposited materials (e.g. in organic field-effect transistors).

L10.28

CHARACTERIZATION OF HIGH-PERFORMANCE F₁₆CuPc-BASED ORGANIC THIN-FILM TRANSISTORS WITH ALKALI FLUORIDE-MODIFIED ELECTRODES. J. Reynaert, Y.D. Jin, G. Borghs, R. Mertens, P. Heremans, IMEC, Leuven, BELGIUM.

Phthalocyanines have been extensively studied among organic semiconductors for their photovoltaic properties [1]. Copper(II)-perfluorophthalocyanine (F₁₆CuPc) is an air-stable material with high electron mobility [2]. We investigated the device properties of copper(II)perfluorophthalocyanine (F₁₆CuPc)-based *n*-channel organic thin-film transistors (TFTs). We achieve high mobilities of the order of 10⁻² cm²V⁻¹s⁻¹ when using intensively purified material and optimized growth conditions of the organic films. We fabricated transistor structures on thermally grown silicon oxide with different source/drain electrodes: bare aluminum, gold, LiF/Al and LiF/Au. We deduce the electron injection properties of these different materials into F₁₆CuPc from the electrical performance of these transistors. In contradiction to [3], we report well-behaved field-effect and high mobilities (~10⁻² cm²V⁻¹s⁻¹) for *n*-channel F₁₆CuPc-TFTs with bare Al and Au electrodes. Furthermore, we correlate these results to the outcome of electro-absorption measurements on PEDOT/F₁₆CuPc/electrode structures, which allow to measure the electron injection barrier at the organic/metal interface [4]. [1] D. Wöhrle, L. Kreienhoop, D. Schlettwein, Phthalocyanines 219, VCH Publishers (1996). [2] Z. Bao, A.J. Lovinger, J. Brown, J. Am. Chem. Soc. 120, 207

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L10.29

CHARACTERIZATION OF THE BUILT-IN POTENTIAL OF POLYMER SOLAR CELLS AND LIGHT EMITTING DIODES BY ELECTRO-ABSORPTION SPECTROSCOPY. J. Reynaert, Y.D. Jin, T. Aernouts, W. Geens, G. Borghs, R. Mertens, P. Heremans, IMEC, Leuven, BELGIUM.

The performance of organic light emitting devices (OLEDs) and organic solar cells (OSCs) can be improved by inserting an ultra-thin interfacial layer of LiF between the polymer and the air stable cathode [1,2]. Electro-absorption measures the built-in potential (V_{bi}) across the photo-active organic film within OLEDs and OSCs. In OLEDs based on MDMO-PPV, we found that V_{bi} increases by 0.5 eV when LiF is inserted between the polymer and the Al-cathode. The change in built-in potential is attributed to Li being liberated from LiF in the presence of Al and diffusing into the polymer. Li 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 V_{bi} 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.

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L10.30

EVAPORATED ORGANIC-INORGANIC MIXED LAYERS: LUMINESCENCE CONVERSION DEVICES OF HIGH VARIETY IN OPTICAL PROPERTIES. J. Assa, H. Froeb, R. Gelhaar, K. Leo, M. Levichkova, V. Lyssenko, Institut für Angewandte Photophysik, Technische Universität Dresden, Dresden, GERMANY.

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 absorption and emission bands. Key parameters for the breakthrough of solid state organic systems are the quantum efficiency and the photostability. Our results show that such systems can meet the requirements of practical applications. We present results about (i) different organic dyes (such as perylene derivatives, AlQ₃, ...), (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 absorbent layers even at low thickness.

L10.31

PHOTO- AND ELECTRO-LUMINESCENT PROPERTIES OF RANDOM AND STRUCTURALLY DEFINED COPOLYMERS BASED ON POLY(FLUORENE-CO-BENZOTHIADIAZOLE). Petra Herguth, Xuezhong Jiang, Michelle S. Liu, Alex K.-Y. Jen, University of Washington, Department of Materials Science and Engineering, Seattle, WA.

Copolymers based on fluorene and benzothiadiazole exhibit high brightness and quantum efficiencies when incorporated into polymer light-emitting diodes (PLEDs). The emission wavelength is strongly determined by the benzothiadiazole-containing portion of the polymer. In order to understand the underlying mechanisms of charge transfer and energy transfer, a series of polymers with different fluorene/benzothiadiazole ratios were made. Even a fraction of as low as 10% of benzothiadiazole shifts the emission of the polymer from blue (polyfluorene homo polymer) to green. The low fraction of benzothiadiazole required for wavelength tuning leaves room to tune other properties necessary for device improvement. The charge transport properties can be altered by incorporating a third comonomer into the polymer structure. Polymers incorporating fluorene, benzothiadiazole and a third comonomer - e.g.

dialkoxyphenyl - 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 luminescent and device properties, we have synthesized a series of copolymers with structures of known sequence. A third comonomer was chosen from a variety of electron-rich molecules. The properties of the structurally defined copolymers were compared to the properties of the random copolymerized ones with the same monomer ratios. In order to evaluate the device performance of these copolymers, double-layer devices with the general structure of ITO/HTL/Polymer/Ca/Ag were fabricated. The results show that the monomer sequence in the polymer chain does not affect the electro- and photo-luminescent properties of the copolymers, but the device performance is strongly dependent on the sequence.

L10.32

ORGANIC POLYMER DEVICES BASED ON SUPER-YELLOW POLYMER. J. Kanicki, M. Pauchard and A. Heeger, 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 (know as super-yellow polymer). This organic polymer is also being 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 for the source and drain contacts and amorphous silicon nitride was used for the gate insulator material. The organic semiconductor (super-yellow polymer) was deposited by spin-coating over the source drain contacts and device was annealed for 2 hours at 70°C in nitrogen oven. The OP-TFT channel length and width range from 6 to 96 μm and 56 to 116 μm, respectively. Electrical performances of our devices were extracted using the MOSFET equations. We typically obtained for our devices the field-effect mobility, threshold voltage, sub-threshold slope and ON/OFF current ratio of about 2x10⁵ cm²/Vs, -55 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 have also found that field-effect mobility and threshold voltage were channel length independent. To investigate the possibility of fully integrated opto-electronic organic circuits made from the same organic material and at 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 (>2 lm/W at 900cd/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 opto-electronic organic circuits will be discussed.

L10.33

CREATION OF A GRADIENT POLYMER-FULLERENE INTERFACE IN PHOTOVOLTAIC DEVICES BY THERMALLY-CONTROLLED INTERDIFFUSION. M. Drees, W. Graupner, K. Premaratne, J.R. Heflin, Dept of Physics, Virginia Tech, Blacksburg, VA; D. Topasna, 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 gradient heterojunction is created bringing the fullerene molecules within the exciton diffusion radius of the MEH-PPV throughout the film to achieve highly efficient charge separation. The interdiffused devices show a dramatic decrease in photoluminescence and concomitant order-of-magnitude increase in short circuit currents, demonstrating the improved interface. We also observe that a valley in the spectral photoresponsivity of the MEH-PPV/C₆₀ bilayer system, ascribed 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 initial MEH-PPV and C₆₀ 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.

Brenden Carlson, Chemistry Department, University of Washington, Seattle, WA; Larry Dalton, 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, full color flat panel display. For this purpose new complexes of divalent osmium have been synthesized for use as luminophores in organic light emitting devices (OLED). 4,7-bis(aryl)-1,10-phenanthroline derivatives were synthesized from o-nitroaniline and 3-chloro-p-bromopropiophenone in a mixture of phosphoric and arsenic acids, and two equivalents of the ligand (N-N) were reacted with potassium hexachloroosmate to give an intermediate of Os(N-N)₂Cl₂. One equivalent of a bidentate strong p-acid ligand (L-L), cis-1,2-vinylenebis(diphenylarsine), cis-1,2-bis(diphenylphosphino)ethylene, or 1,2-bis(diphenylarseno)ethane, was reacted with Os(N-N)₂Cl₂ to give a general formula of [Os(II) (N-N)₂ L-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) and 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PVK:PBD), or poly(2-vinyl naphthalene) (PVN:PBD) host materials. Brightness over 1,400 cd/m² for double layer has been reached, with a turn-on voltage of 8 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 electrophosphorescence 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 Mattis, Paul Chang, Vivek Subramanian, 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 electronics applications, since they may potentially be printed on plastic to enable ultra-low-cost reel-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 imidization of polyimide dielectrics 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 have been no studies on the use of annealing 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 (<80C), as well as increases in on/off ratios by as much as two orders of magnitude at moderate anneal temperatures (~120C). 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 tailoring 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 EUROPIUM COMPLEX. Gregory D. Phelan, Chemistry Department, University of Washington, Seattle, WA; Brenden Carlson, Chemistry Department, University of Washington, Seattle, WA; Larry Dalton, 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.

Europium complexes may be used as a source of red emission in light emitting diodes (OLED), and several novel europium cored compounds have been synthesized and incorporated into organic OLED's. These complexes are of interest due to their narrow (FWHM = 5 nm) emission at 615 nm, which is ideal for red OLED devices. The europium complexes consist of one equivalent of europium chelated to three equivalents of a nonsymmetrical beta diketone ligand. The ligands are created by the Claisen condensation of a polycyclic aromatic sensitizer and a fluorinated alkyl ester of a carboxylic acid. The use of a sensitizer such as phenanthrene results in a ligand that has an emission band that directly overlaps with the absorption band of europium. The use of fluorinated chains improves the overall processibility as well as the charge transfer capability of the resulting metal cored complex. The europium core is further encapsulated by the inclusion of an additional polycyclic 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 Forrester energy transfer from the ligands to the europium complex. Red light emitting diodes (LEDs) were successfully fabricated by doping the europium compounds at 5 weight percent into poly(N-vinylcarbazole) and 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PVK:PBD), or poly(2-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.

Melissa Kreger, Sue Carter, Physics Dept, University of California, Santa Cruz, CA; Luisa Bozano, 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-para-phenylene vinylene 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
SYNTHESES OF PHENANTHROLINE DERIVATIVES AND THEIR APPLICATION TO ORGANIC EL DEVICES. Takayuki Ito, Junji Kido, Yamagata Univ, Graduate School of Science and Engineering, Yonezawa, Yamagata, JAPAN.

We synthesized phenanthroline derivatives containing aromatic groups as new electron-transporting materials. Bilayer EL devices, using phenanthroline derivatives as an electron-transporting layer and NPD as a hole-transporting and emitting layer, were fabricated. Devices with a structure of ITO/NPD/phenanthroline derivatives/LiF/Al exhibited blue emission with a luminance of 3000 cd/m² and showed better device characteristics compared with a device using bathocuproine 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 McGehee, Stanford University, Department of Materials Science and Engineering, Stanford, CA; Ekaterina N. Kadnikova, Jinsong Liu, and Jean Fréchet, University of California, Berkeley, CA.

Regioregular poly(3-hexylthiophene) (P3HT) is one of the leading candidates to replace amorphous silicon as the active layer of low-cost thin-film transistors. We have studied the effect of molecular weight on charge carrier mobility in thin film polymer transistors made from P3HT. We have observed a substantial increase in mobility with increasing molecular weight. The mobility increases 4 orders of magnitude from a sample of $M_n = 2400$ D to a sample of $M_n = 36500$ D. This trend has been observed both in samples synthesized by the McCullough route at a range of molecular weights and from samples obtained by fractionating commercially available P3HT synthesized by the Rieke route. We have analyzed films produced by both

spin-casting and drop-casting. We have additionally studied the effects of annealing and melt/recrystallization on the charge carrier mobility and device performance. We have used solid-state absorption, photoluminescence, and x-ray diffraction to obtain information on the morphology and band structure of the films. The results will be used to discuss the relationship between polymer morphology, chain length, and charge transport.

L10.40
PHOSPHORESCENT LIGHT-EMITTING ELECTROCHEMICAL CELL. Fang-Chung Chen, Yang Yang, Univ. of California, Los Angeles, Dept of Materials Science and Engineering, Los Angeles, CA; Qibing Pei, SRI International, Menlo Park, CA.

Due to the harvest of singlet and triplet excitons, highly-efficient phosphorescent polymer light-emitting diodes have been demonstrated. However, the driving voltage of those devices remains high because of the carrier trapping at the dopant sites. To achieve high power efficiency, a phosphorescent light-emitting electrochemical cell, which consists of bis(2-(2'-benzothienyl)-pyridinato-N,C3')iridium(acetylacetonate) (BtpIr) as the dopant, poly(9,9-bis(3,6-dioxahexyl)-florene-2,7-diy) (BDOH-PF) as the host polymer and lithium trifluoromethane sulfonate (LiCF₃SO₃), has been demonstrated in this Letter. The turn-on voltage for light emission was as low as the bandgap of the host material (2.8eV). Comparing with the light-emitting diode with the similar device structure, six-fold enhancement in power efficiency has been achieved.

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

A novel poly(9,9-dialkylfluorene) containing hexaphenylbenzene was synthesized by the Suzuki coupling method and used as an emitter layer in Organic EL devices. The polymer exhibited blue photoluminescence peaking at 400nm. Organic EL devices having a structure of ITO/polythiophene derivative/blue polymer/Ca/Al were fabricated. The device showed broad EL spectrum originated from the emission from the excimer sites.

L10.42
WHITE ORGANIC LIGHT-EMITTING DEVICES WITH HIGH COLOR RENDERING INDEX. H.Y. Chu, J.-I. Lee, L.-M. Do, T. Zyung, Basic Research Lab., ETRI, Daejeon, KOREA; B.-J. Jung, H.-K. Shim, Dept. of Chemistry, KAIST, Daejeon, KOREA; J. Jang, Dept. of Information Display, KyungHee Univ., Seoul, KOREA.

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 lights, and from polymer composites of several different color emitting polymers or dyes. We have fabricated white OLEDs with an RGB stacked multilayer structure. In RGB stacked OLEDs, 1,4-bis[2,2-diphenylvinyl]biphenyl (DPVBi), tris-[8-hydroxyquinoline]aluminum (Alq) and [2,6-bis[2-(5-(dibutylamino)phenyl)vinyl]-4H-pyran-4-ylidene]propanedinitrile (DADB) 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, Alq and DADB, respectively. Its maximum luminance was 13,200 nit at 12 V, and the luminance efficiency was 1.12 lm/W at 100 nit. The color rendering index of 84 and the color temperature of 5,940 K were obtained at a CIE chromaticity 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(IMINOARYLENE) DERIVATIVES BASED ON FLUORENE FOR ORGANIC EL DEVICES. Shi-Jian Su, Junji Kido, Yamagata Univ, Graduate School of Science and Engineering, Yonezawa, Yamagata, JAPAN.

Two novel poly(iminoarylene) 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 imino sites and hence excimer formation demonstrated for the previously reported triphenylamine-based polymers were

effectively limited due to the efficient energy transfer to the adjacent fluorene (and anthracene) trimer segments. It offers an effective route to reduce the strong excimer emission of poly(iminoarylene)s and enables them as novel potential candidates for blue-emitting polymers.

L10.44
NANOSTRUCTURED OXIDE – CONJUGATED POLYMER COMPOSITES FOR PHOTOVOLTAIC DEVICES. Sean E. Shaheen, Philip A. Parilla, Alexander Miedaner, 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 promising approach to overcoming 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 tin 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 that 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 nature of this dipole as observed 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, Ryuji Ishii, Masayuki Kurotaki, Koichiro Yonetake, Yamagata Univ, Graduate School of Science and Engineering, Yonezawa, Yamagata, JAPAN.

Dual mode display devices that function as a liquid crystal device (LCD) and organic EL device OLED have been developed. The typical device structure is glass/indium-tin oxide/polythiophene 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(5-CB), 4-carbazole-4'-n-dodecylbiphenyl(12-OKB) and tris(2-octylphenylpyridine)iridium (Ir(8ppy)3). This device works as LCD at low drive voltages such as 2V and works as an OLED, emitting light, at higher voltages.

L10.46
MAIN-CHAIN-TYPE FLUORENE POLYMER-IRIDIUM COMPLEXES FOR ORGANIC EL DEVICES. Shinji Suzuki, Junji Kido, Yamagata Univ, Graduate School of Science and Engineering, Yonezawa, Yamagata, JAPAN.

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

L10.47
N-TYPE CONJUGATED POLYANTHRAZOLINES AND ANTHRAZOLINE-BASED SMALL MOLECULES: HIGH ELECTRON AFFINITY ELECTRON TRANSPORT MATERIALS FOR DEVICE APPLICATIONS. Christopher J. Tonzola, Maksudul M. Alam, and Samson A. Jenkehe, Depts of Chemistry and Chemical Engineering, University of Washington, Seattle, WA.

Polyanthrazolines are thermally robust conjugated polymers with tunable bandgap and good optical properties. We have synthesized a series of conjugated anthrazoline copolymers and investigated their electron transport properties. Cyclic voltammetry of all the anthrazoline 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 polyanthrazolines by using electron-rich arylene linkages such as ethylenedioxythiophene (EDOT). Incorporation of alkyl substituted bithiophene moieties into the backbone allowed for polyanthrazoline 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 (LEDs) and photovoltaic cells. In addition, a series of anthrazoline-based small molecules were synthesized and studied. Single-crystal structures allowed for structure-property relationships to be established with parent polyanthrazolines. These small molecules showed solid state fluorescence efficiencies of up to 32%. Efficient polymer LEDs were fabricated using the anthrazolines 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 Liu, Marnie A. Haller, Jingdong Luo, Sei-Hum Jang, Hong Ma, 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 "mixed" 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 r_{33} value (128 pm/V at 1.3 micron) demonstrated in a poled polymer system with one of the 2,5-dihydrofuran based chromophores incorporated in polymethylmethacrylate (PMMA) at 23 wt % loading level. Excellent r_{33} temporal stability was achieved in an optimized guest/host system where a *tert*-butyldimethylsilyloxy side substituent modified variant was doped in polyquinoline (PQ-100) with high glass transition temperature. Furthermore, hydroxyl containing 2,5-dihydrofuran derivatives had been synthesized through focused microwave irradiation as effective electron acceptors to be incorporated into nonlinear optical chromophore platforms where high molecular nonlinearity and hydroxy functionality can be integrated simultaneously in single molecular structure. Thus these multi-functionalized nonlinear optical chromophores can be tailored at molecular scale to afford the desired topologies such as, dendronized NLO chromophore, NLO dendrimer, and dendritic side-chain polymer systems.

L10.49
STRUCTURE-CARRIER MOBILITY RELATIONSHIPS IN CONJUGATED POLYMERS. Amit Babel, Samson A. Jenkehe, Department of Chemical Engineering, University of Washington, Seattle, WA.

Considerable progress has recently been made in the field of polymer-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 charge transport 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-decylthiophene), poly-[2-methoxy-5-(2-ethylhexoxy)-1,4-phenylene vinylene], poly(4-hexylquinoline), poly(9,9-dioctylfluorene), and polystyrene. Similarly, n-channel thin film transistors and field-effect mobility of electrons in binary blends of poly(benzobisimidazobenzophenanthroline) with poly(p-phenylene benzobisthiazole) were also investigated. A "stair step" carrier mobility dependence on blend composition in most of the blends with relatively high and constant hole mobilities (10^{-5} - 10^{-3} cm²/Vs.) over a broad blend composition ranges 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. Structurecarrier mobility relationship in the regioregular poly(3-alkylthiophene)s was also studied by systematic investigation of thin film transistors based on series of poly(3-alkylthiophene)s with 5 alkyl chain lengths from C₄ (n-butyl) to C₁₂ (n-dodecyl).

L10.50
SYNTHESIS OF POLY(PARAPHENYLENE VINYLENE) NANORODS USING AN ANODIC ALUMINUM TEMPLATE. Wei Wang, Richard Czerw, Scott Webster, David L. Carroll, School of Materials Science and Engineering, Clemson University, Clemson, SC; Jung-Ho Park, Yung-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 able to be employed in organic light emitting diodes and other photonics applications such as optical switches. Aligned PPV nanorods, with diameters of approximately 30 nm, were synthesized by electropolymerization of $\alpha, \alpha', \alpha'', \alpha'''$ -tetrabromo-p-xylene in a 0.1M tetrabutylammonium tetrafluoroborate DMF solution within the pores of a nanoporous anodic aluminum oxide (AAO) template membrane. The diameter and length of the nanorods can be controlled by changing the aspect ratio of the AAO template. The PPV nanorods were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), micro-Raman, UV-vis absorption, and photoluminescence (PL) spectroscopy.

L10.51

SELF-ORGANIZATION, PROPERTIES AND DEVICE APPLICATIONS OF REGIOREGULAR HEAD-TO-TAIL POLY(4-ALKYLQUINOLINE)S. Yan Zhu, Maksudul M. Alam, Samson A. Jenekhe, Departments of Chemical Engineering and Chemistry, Univ of Washington, Seattle, WA.

Two 100 percent head-to-tail regioregular poly(4-alkylquinoline-2,6-diyl)s were synthesized and investigated. The 100% regioregularity of the polymer was achieved by the AB-type nature of the acid-catalyzed Friedländer condensation polymerization. X-ray diffraction studies showed that solution-cast films of regioregular poly(4-hexylquinoline) and poly(4-octylquinoline) have self-organized lamellar structures with interlayer spacings of 15.7 Å and 17.7 Å, respectively, and both showed an interchain π -stacking distance around 4 Å. The two polymers emit blue light at 432- 435 nm in dilute organic solvent solution and yellow light at 547 nm in the solid state. Light-emitting diodes (LEDs) were fabricated using the two polymers as both the emissive layer and as an electron transport layer. Yellow electroluminescence was observed for both poly(4-alkylquinoline)s. A large improvement in the performance of MEH-PPV based LEDs (a luminance up to 700 cd/m² and an external quantum efficiency up to 3.0%) was observed by using the poly(4-alkylquinoline)s 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-DIOCTYLFLUORENE). Abhishek P. Kulkarni, Samson A. Jenekhe.

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 thermo- or electro-oxidative degradation during operation, giving rise to an unwanted green emission band at 530 nm that has been attributed to aggregate and/or excimer formation. Various approaches have been attempted to minimize this unwanted long-wavelength emission band including addition of hole-trapping molecules and addition of bulky side or end-capping groups. We report spectrally stable blue electroluminescence (EL) from single-layer light emitting diodes comprising binary blends of poly(9,9-dioctylfluorene) (PFO) with an electron-transporting/hole-blocking poly(vinyl diphenylquinoline) (PVQ) 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/PVQ blend LEDs were enhanced by 5 - 10 times the values for the pure PFO diodes. The observed enhancement in the blend LEDs is due to energy transfer from PVQ to PFO coupled with improved spatial confinement induced exciton stability. The improved spectral stability in the blends is thought to be a result of the higher T_g (185°C) of PVQ compared to 75°C for PFO, leading to improved thermal stability. The variation in device performance with blend composition was dependent on the phase-separated morphology of the blends. In conclusion, blending of PFO with thermally stable charge transport polymers or hole-blocking polymers to achieve balanced charge transport is a simple strategy to achieve stable blue EL with improved performance and spectral characteristics.

L10.53

THERMALLY STABLE POLYFLUORENES DERIVATIVES WITH VARIOUS SPIRO-STRUCTURES. Sejin Shin, Doo Jin Park, Chang-Lyoul Lee, Jang-Joo Kim, Dong-Yu Kim, Dept of Materials Science and Engineering, Kwang-Ju Institute of Science and Technology, Gwangju, KOREA.

Recently, spiro-structured molecules have received much attention in the field of blue light-emitting materials of polymer light-emitting devices (PLEDs). 9,9-dialkyl substituted polyfluorenes suffer from aggregate formation which produces an excimer emission band around

550 nm region with low quantum efficiency. Introduction of spiro-structure into polyfluorene is known to suppress the aggregate formation due to their 3-dimensional structure. The 9,9'-spirobifluorene contains two biphenylene units connected by tetrahedral bonding carbon atom at the center of the two biphenylene units, each of which is perpendicular to each other. This 3-dimensional structure in the polymer could prevent the approach of other polymer chains, thus minimizing the close packing of the polymer. However, 9,9'-spirobifluorene do not have any functionality such as solubilizing alkyl chains. We introduced various atoms such as carbon, oxygen and nitrogen between upper phenyl groups of spirobifluorene. The atoms except oxygen can provide possibility to introduce alkyl chains. Moreover, bulky and/or long alkyl chains were introduced at the para position of upper phenyl rings via a new synthetic route. The spiro structured polymers with flexible alkyl chains showed improved processability as well as stable amorphous structures. PLEDs based on these polymers were fabricated and characterized.

SESSION L11: PHOTOVOLTAICS

Chair: Ghassan E. Jabbour

Friday Morning, April 25, 2003

Salon 1-3 (Marriott)

8:30 AM L11.1

INFILTRATING SEMICONDUCTING POLYMERS INTO SELF-ASSEMBLED MESOPOROUS TITANIA TO MAKE PHOTOVOLTAIC CELLS. Michael McGehee, Kevin Coakley, Yuxiang Liu, Dept of Materials Science and Engineering, Stanford University; Karen Frindell and Galen Stucky, Dept. of Chemistry, Univ. of California-Santa Barbara.

We have developed a technique for making high-quality thin films of titania with well ordered arrays of pores that have a diameter in the range of 4-10 nm using a titania sol-gel precursor and a structure-directing amphiphilic block copolymer. We have filled the pores with regioregular poly(3-hexyl thiophene) by spin casting the polymer on top of the titania and then heating the polymer at temperatures between 100 and 200°C. We find that 32% of the volume of the film can be filled with polymer in just a few minutes at 200°C. At lower temperatures, the infiltration process takes longer and the amount of polymer that can be incorporated is less. We hypothesize that the polymer coats the walls of the pores and that the coating is thicker when the polymer is incorporated at higher temperatures. Using absorption and photoluminescence spectroscopy we have determined that the polymer chains take on a coiled conformation in the pores and that there is little or no polymer crystallization. The photoluminescence measurements also show that photoinduced charge transfer takes place from the polymer to the titania, but that not all of the excitons are quenched by charge transfer. Since the pores are less than 10 nm in diameter and excitons can diffuse over this distance before emitting a photon in a spin cast polymer film, we think that exciton diffusion is hindered inside the pores. We attribute this to the altered polymer chain morphology. Despite the hindered exciton diffusion, we have been able to make photovoltaic cells with an energy conversion efficiency of 1.3%. Plans for improving the polymer chain morphology and titania films to make better photovoltaic cells will be discussed.

8:45 AM L11.2

HIGH PERFORMANCE SOLAR CELLS OF POLYFLUORENE COPOLYMERS. Mats R. Andersson, Mattias Svensson, Materials and Surface Chemistry, Göteborg, SWEDEN; Fengling Zhang and Olle Inganäs, Biomolecular and Organic Electronics, Linköping, SWEDEN.

The development of conjugated polymer solar cells is still in an early phase, and many issues of materials and device development remain to be resolved. One of our goals is to prepare efficient and stable solar cells and we have presently concentrated our efforts on preparing polyfluorene copolymers with relatively low bandgap. Polyfluorene copolymers generally have high mobility and stability, something that is desired for the use in solar cells. However, they normally also have a relatively large bandgap. To decrease the bandgap we have synthesized polymers based on planar conjugated segments with internal donor-acceptor functions in between the substituted fluorene groups. The prepared alternating polyfluorene copolymers have a relatively low bandgap (red shifted absorption) and show liquid crystalline properties. Sandwich solar cells have been prepared of the polymers blended with a C60 derivative (PCBM). The best devices exhibit power conversion efficiencies higher than 2.5% under simulated solar conditions. The polymer syntheses, polymer properties, device structure, and device characteristics will be presented.

9:00 AM L11.3

MODELING THE CURRENT-VOLTAGE CHARACTERISTICS OF POLYMER PHOTOVOLTAIC DEVICES. James A. Barker, Catherine M. Ramsdale, Neil C. Greenham, Cavendish Lab, Cambridge, UNITED KINGDOM.

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, injection, drift, diffusion and recombination, and includes the effect of space charge on the electric field within the device. Charge separation at the polymer/polymer interface leads to the formation of bound polaron pairs which may either recombine monomolecularly or be dissociated into free charges. We find that the short-circuit quantum efficiency is determined by the competition between polaron pair dissociation and recombination. The model shows a logarithmic dependence of the open-circuit voltage on the incident intensity, as seen experimentally. This additional intensity-dependent voltage arises from the field required to produce a drift current which balances the current due to diffusion of carriers away from the interface.

9:15 AM L11.4

ROLES OF INTERNAL ELECTRODES IN MULTI-HETEROJUNCTION ORGANIC SOLAR CELLS. Tetsuo Tsutsui, Kuwat Triyana, Takeshi Yasuda, and Katsuhiko Fujita, Department of Material Science, Faculty of Engineering Sciences and Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, JAPAN.

The power conversion efficiency (PCE) of single-heterojunction (HJ) organic photovoltaic cells consisting of CuPc as a p-type semiconductor and perylenetetracarboxylic acid benzimidazole (PTCBI) as n-type semiconductor has been reported to be around 1.0-1.8% and an open circuit voltage (V_{oc}) was 0.45-0.5 V.(1,2) We pointed out two essential factors that give low PCE in thin-film HJ solar cells. One is small absorbance of light within an active region of the cells and the other is low V_{oc} in comparison with the average photon energy of sun light.(2) One of the possible directions of solving these problems is stacking of HJ cells maintaining penetration of irradiated light into the bottom HJ region. An early trial of introducing a metal interlayer brought about drastic increase of V_{oc} , but PCE remained almost unchanged.(3) Recently large increases of both V_{oc} and PCE have been reported using Ag nanocluster interlayer.(4)

This report focuses on understanding the effect of the insertion of internal electrodes in multiple HJ solar cells. Several types of single-HJ and multiple-HJ solar cells were fabricated. For single HJ cells, ITO/PTCBI/CuPc/Au and ITO/CuPc/PTCBI/Ag structures were fabricated as the standard cells, and multiple heterojunction cells, such as ITO/PTCBI/CuPc/(Au/PTCBI/CuPc) $_n$ /Au and ITO/CuPc/PTCBI/(Ag/CuPc/PTCBI) $_n$ /Ag ($n=1, 2$) were examined. The V_{oc} and PCE (AM-1.5) for the ITO/PTCBI/CuPc/ Au cell were 0.50 V and 1.11% respectively. When three HJs were stacked using Au internal electrodes, the best values for V_{oc} and PCE (AM-1.5) were 1.35 V and 1.61% respectively. Several different external and internal electrodes were also tested.

1. C.W. Tang, Appl. Phys. Lett., 43, 183 (1986). 2. T. Tsutsui, et al., Synthetic Metals, 71, 2281 (1995). 3. M. Hiramoto, M. Suezaki, M. Yokoyama, Chem. Lett., 1990, 327. 4. A. Yakimov and S.R. Forrest, Appl. Phys. Lett., 80, 1667 (2002).

9:30 AM *L11.5

EXTRINSIC PHOTOGENERATION OF CHARGE CARRIERS IN ORGANIC DONOR-ACCEPTOR SYSTEMS. W. Tian, C. Im, and H. Baessler, Institute of Physical, Nuclear, and Macromolecular Chemistry, Philipps-University Marburg, Marburg, GERMANY; V.I. Arkhipov, IMEC, Heverlee-Leuven, BELGIUM; E.V. Emelianova, Semiconductor Physics Laboratory, University of Leuven, Heverlee-Leuven, BELGIUM.

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

10:30 AM *L11.6

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

J.C. Hummelen, J. Knol, F.B. Kooistra, L.M. Popescu, and H.T. Jonkman, Stratingh Institute and Materials Science Centre, University of Groningen, THE NETHERLANDS; M.M. Wienk, W.J. Verhees, and J.M. Kroon, ECN Solar Energy, Petten, THE NETHERLANDS.

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 alkoxy-substituted PCBM analogues has been prepared and fully characterized. Next, thin films made of blends of MDMO-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 L11.7

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

The charge transport properties of the electron acceptor methanofullerene [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) and the donor-type conjugated polymer poly(2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene) (OC₁C₁₀-PPV) have been investigated. At room temperature the electron mobility of $\mu_e=2.0 \times 10^{-7}$ m²/Vs in the PCBM is more than three orders of magnitude larger than the hole mobility of the donor-type OC₁C₁₀-PPV. Also the charge transport properties of electrons and holes in a 1:4 weight ratio PPV/PCBM blend have been addressed. The maximum attainable open-circuit voltage of a plastic solar cell has been determined and consistently explained.

11:15 AM L11.8

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

Existing types of solar cells may be divided into two distinct classes: conventional solar cells such as silicon p-n junctions and excitonic solar cells, XSCs. Most organic-based solar cells, including dye-sensitized solar cells, DSSCs, fall into the category of XSCs. In these cells, excitons are generated upon light absorption and, if not 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 apparently minor mechanistic distinction between excitonic and conventional solar cells results in fundamental differences in photovoltaic behavior. The open circuit photovoltage, V_{oc} , in conventional cells is limited to less than the magnitude of the band bending, Φ_{bi} ; however, V_{oc} in XSCs is commonly greater than Φ_{bi} . We describe some early work on solid state excitonic solar cells, the use of carrier-selective electrodes to enhance V_{oc} , 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 photo generated carriers. Finally, the similarities and differences are explored between the three major types of XSCs: organic semiconductor cells with planar interfaces, bulk heterojunction cells and DSSCs.

11:30 AM L11.9

CHARGE TRANSPORT PROPERTIES IN DISCOTIC LIQUID CRYSTALS: A MOLECULAR SCALE DESCRIPTION.

Jerome Cornil^{a,b}, Vincent Lemaire^a, Jean-Philippe Calbert^a, Jean-Luc Bredas^{a,b}; ^aUniversity of Mons-Hainaut, Laboratory for Chemistry of Novel Materials, Mons, BELGIUM; ^bThe 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 semiconductors for applications requiring efficient charge transport properties, such as field-effect transistors and solar cells. In such mesophases, 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 transfer rates, and hence the mobility values, namely [1,2]: (i) the transfer integrals for holes and electrons

reflecting the strength of the interaction between the HOMO and LUMO levels of the individual units, respectively; and (ii) the reorganization energy connected to the extent of geometric coupling between the charges and the conjugated backbones. The results reveal that the amplitudes of the transfer integrals are highly sensitive to the relative position of the interacting units and highlight the detrimental impact of geometric fluctuations, in particular ring rotations and translations, on the charge transport along the one-dimensional columns [3]. The present results also demonstrate that, in the search for new discotic materials with enhanced transport properties, quantum-chemical approaches can be very useful to tailor the chemical structures of discs prior to synthesis. [1] J. Cornil, D. Beljonne, J.P. Calbert, and J.L. Bredas, *Adv. Mat.* 13, 1053 (2001). [2] J.L. Bredas, J.P. Calbert, D.A. da Silva Filho, and J. Cornil, *Proc. Natl. Acad. Sci. USA* 99, 5804 (2002). [3] J. Cornil, V. Lemaire, J.P. Calbert, and J.L. Bredas, *Adv. Mater.* 14, 726 (2002).

11:45 AM L11.10

ORGANIC PHOTOVOLTAIC CELLS CONTAINING LIQUID CRYSTALLINE PHTHALOCYANINES. Seunghyup Yoo^a, Benoit

Domercq^a, Carrie L. Donley^b, Chet Carter^b, Wei Xia^b, Britt A. Minch^b, David F. O'Brien^b, Neal R. Armstrong^{a,b} and Bernard Kippelen^a; ^aOptical Sciences Center, University of Arizona, Tucson, AZ; ^bDepartment 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 from being soluble, these materials also form highly ordered structures. Liquid crystalline mesophases are desired since they can lead to charge mobilities that are higher compared to those of amorphous materials. Organic solar cells based on 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-CuPc) we investigated here are derivatives of CuPc, a well-known molecule with hole-transport properties that has been widely used in photovoltaic devices. It has a relatively high absorption coefficient in the visible spectrum. In contrast to CuPc molecules, the new derivatives are soluble in common solvents and can therefore be processed into devices from solution. For low cost organic electronic applications, wet processing is often desired as it is compatible with low cost printing techniques. We fabricated high quality thin films by spin-coating of DL-CuPc. Thermal annealing of these films allows for the molecules to self-organize into a columnar discotic liquid crystalline phase. This phase has been characterized by optical spectroscopy, AFM and small angle X-Ray diffraction. Bi-layer solar cells using C60 as an electron transport layer were fabricated. The annealing of the phthalocyanine layer resulted in a 3.5 times increase of the short-circuit current density and a reduction of the series resistance. The performance and limitations of photovoltaic cells fabricated from soluble liquid crystalline phthalocyanines will be discussed.

SESSION L12/H11: JOINT SESSION DEVICES

Chair: Jerome Cornil
Friday Afternoon, April 25, 2003
Salon 1-3 (Marriott)

1:30 PM *L12.1/H11.1

PRINTING APPROACHES TO ORGANIC OPTOELECTRONICS ON PLASTIC, TEXTILE AND PAPER SUBSTRATES. Y. Yoshioka 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 a specific pattern on given substrate. Many factors including surface tension of the printed solution, substrate surface properties, and moisture have direct effect on the final quality and performance of the organic based devices. Issues related to device fabrication on plastic, textile and paper substrates will be discussed and results of tested devices will be presented.

2:00 PM *L12.2/H11.2

FULLY PRINTABLE LIGHT EMITTING DISPLAYS. Sue A. Carter, M. Kreger, J. Leger, Y. Nakazawa, J.J. Breeden, M. Wilkinson, University of California, Dept. of Physics, Santa Cruz, CA and Add-vision, Incorporated, Scotts Valley, CA.

One of the main promises of semiconducting polymers is the ability to manufacture inexpensive optoelectronic components that will lead to the wide-scale use of new technologies, such as large area light-emissive 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 the materials cost. In this talk, I will give an overview of the technical and cost considerations for making polymer displays and detectors where all layers are deposited under atmospheric conditions using a liquid-based manufacturing technique, such as ink-jet, screen-printing or web-based processes. I will discuss our work on fully screen-printed light emitting polymer displays with 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 fully printed light emitting polymer displays.

2:30 PM L12.3/H11.3

IN-SITU ELECTRICAL AND SPECTROSCOPICAL STUDY OF DEGRADATION MECHANISMS AND LIFE TIME PREDICTION OF ORGANIC BASED ELECTRONIC MATERIAL SYSTEMS. Jean Vittorio Manca, Els Kesters, Laurence Lutsen, Ludwig Goris, Dirk Vanderzande, Jan D'Haen, Marc D'Olielager, Luc De Schepper, Limburg Universitair Centrum, Institute for Materials Research, Diepenbeek, Belgium, IMEC, Division IMOMECE, Diepenbeek, BELGIUM; Ornella Sanna, University of Cagliari, Cagliari, ITALY.

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

2:45 PM L12.4/H11.4

FABRICATION OF ORGANIC LIGHT-EMITTING DEVICES BY LOW PRESSURE COLD WELDING. Changsoo Kim and Stephen R. Forrest, Dept of Electrical Engineering, Princeton Univ, Princeton, NJ.

We demonstrate a method for high resolution patterning of metal cathode contacts for organic electronic devices using low pressure cold welding. The contacts are formed by transferring a metal film from a patterned, soft elastomeric stamp onto unpatterned organic and metal layers predeposited onto a substrate. Use of an elastomeric stamp allows for a thousand-fold decrease in the pressure needed for a high-yield pattern transfer as compared to that required with rigid stamps[1].

In our demonstration, we fabricate an array of efficient organic light emitting devices (OLEDs) based on the green phosphor *fac* tris(2-phenylpyridine) iridium [Ir(ppy)₃] doped into a 4,4'-N,N'-dicarbazole-biphenyl (CBP) host. Here, the cathodes consist of ultrathin (< 1 nm) layers of LiF and Al 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 using a conventional semiconductor flip-chip bonder. The cathode patterning is finished by removing the thin Au layer between the transferred patterns by gentle sputter etching. The 200- μ m-diameter cathodes were uniformly obtained over the whole substrate area with a yield exceeding 97%, and the pattern edge resolution was approximately 1 μ m. 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 J = 10 mA/cm² was

(9.2 ± 0.3) V, and the external quantum efficiency at $J = 1 \text{ mA/cm}^2$ were (6.0 ± 0.3)% for both stamped and control devices. This technique is potentially suitable for roll-to-roll fabrication of a wide range of organic electronic devices including OLEDs, organic thin-film transistors, and photovoltaic cells.

[1] C. Kim, M. Shtein, and S.R. Forrest, Appl. Phys. Lett. 80, 4051 (2002).

3:30 PM *L12.5/H11.5

PROGRESS IN THE GROWTH OF PENTACENE THIN FILMS AND DEVICES. Ruud Tromp, 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 Stutzmann, 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 0.7-0.9 μm 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

INKJETTED ORGANIC TRANSISTORS USING A NOVEL PENTACENE PRECURSOR. Steven K. Volkman, Steven Molesa, Brian Mattis, 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 insolubility 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 reel-to-reel fabrication methodologies. Prompted by a recent paper from Afzali et al describing the synthesis of a novel pentacene precursor, we demonstrate the first inkjet-printed pentacene transistor fabricated to date. This is achieved using a substrate-gated transistor structure in conjunction with an inkjet-printed pentacene precursor active layer. A subsequent thermal cycle is used to convert the precursor into a high-quality pentacene film. Unoptimized conditions yield transistors with an on-off ratio of $>1,000$ and a field-effect mobility of $0.001 \text{ cm}^2/\text{V}\cdot\text{s}$. Further improvement is expected with optimization, to approach the mobility of $>0.5 \text{ cm}^2/\text{V}\cdot\text{s}$ 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 Diels-Alder product. As the anneal temperature increases above 120°C , performance increases dramatically. The process is therefore compatible with numerous low-temperature plastics. As the anneal time is increased to several minutes, performance likewise increases through increased precursor decomposition. However, exposure to excess temperatures or times tends to degrade performance. This is caused by morphological and chemical changes in the pentacene film.

4:30 PM L12.8/H11.8

N- AND P-TYPE BUILDING BLOCKS FOR ORGANIC ELECTRONICS BASED ON OLIGOTHIOPHENE CORES. Antonio Facchetti, Melissa Mushrush, 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,ω - and isomerically pure β,β' -diperfluorohexyl-substituted thiophene oligomers [DFH-nTs and isoDFH-nT, respectively; C_6F_{13} -(thiophene) $_n$ - C_6F_{13} ; $n = 2 - 6$] and study the impact of fluoroalkyl substitution and conjugation length vis-à-vis the corresponding fluorine-free analogues [DH-nTs and isoDH-nT; C_6H_{13} -(thiophene) $_n$ - C_6H_{13} ; $n = 2 - 6$]. Trends between the fluorinated and fluorine-free families in molecular packing, optical absorption, HOMO-LUMO gap, and p-p interactions are found to be strikingly similar. However, fluoroalkyl 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 DFH-nT and isoDFH-nT series are n-type semiconductors with unoptimized mobilities and $I^{\text{on}}/I^{\text{off}}$ ratios approaching $0.05 \text{ cm}^2/(\text{Vs})$ and 10^5 , respectively. These families represent the first example of a homologous series of variable core π -conjugation length n-type OTFT components.

4:45 PM L12.9/H11.9

NON-CONVENTIONAL DEVICES USING HIGH-RESOLUTION RUBBER STAMPS. Jana Zaumseil, John A. Rogers, Vikram C. Sundar, Yueh-Lin Loo, Zhenan Bao, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

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