SYMPOSIUM JJ

Organic Electronic and Photonic Materials and Devices

November 27 – 30, 2000

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* Invited paper

SESSION JJ1: LEDs I
Chair: Olle W. Inganas
Monday Morning, November 27, 2000
Republic B (Sheraton)

8:30 AM *JJ1.1
APPROACHES TO HIGHLY POLARIZED LIGHT EMISSION FROM POLYMER LEDS: LIQUID CRYSTALLINE CONJUGATED POLYMERS AND PHOTON-RECYCLING DEVICES.
Donal Bradley, Martin Grell, Katie Whitehead, Aris Asimakis, University of Sheffield, Dept of Physics & Astronomy, Sheffield, UNITED KINGDOM; Markus Jandke, Peter Strohriegl, Universitaet Bayreuth, Makromolekulare Chemie I, Bayreuth, GERMANY; Masao Oda, Dieter Neher, Universitaet Potsdam, Institut fuer Physik, Potsdam, GERMANY.

We present the results of our recent work[1,2] on developing polarized emission polymer LEDs. Highly linearly polarized emission is obtained from LEDs that contain an aligned monodomain of a liquid crystalline polyfluorene. Rubbed precursor route poly(*p*-phenylenevinylene) is used as the hole transporting alignment layer and polarization ratios of 25:1 are obtained at device brightnesses of 250 cd/m^2. Highly circularly polarized light is obtained using a chiral nematic liquid crystal chiroselective reflector in combination with a standard polymer LED. The LED cathode acts as a photon-recycling mirror and the resulting devices show polarization ratios > 8:1.
We acknowledge the Commission of the European Community (TMR Network EUROLED), The UK Engineering and Physical Sciences Research Council (GR/M08011), The Dow Chemical Company, The Volkswagen Stiftung and Sharp Labs of Europe Ltd for financial support. We also thank M. Bernius of the Dow Chemical Company for provision of polyfluorenes, J. Gmeiner for PPV and D. Richter for assistance.
1. "Highly Polarized Blue Electroluminescence from Homogeneously Aligned Films of Poly(9,9-dioctylfluorene)" K.S.Whitehead, M. Grell, D.D.C. Bradley, M. Jandke and P. Strohriegl, Appl.Phys.Lett. 76 (2000), 2946-2948.
2. "A compact organic device for the efficient, electrically driven generation of highly circularly polarized light" M. Grell, M. Oda, K.S. Whitehead, A. Asimakis, D. Neher and D.D.C. Bradley, submitted.

9:00 AM JJ1.2
HOLE INJECTION IN LIGHT EMITTING DIODES. Yulong Shen, Matthias Klein, Daniel Jacobs, George Malliaras, Cornell University, Materials Science and Engineering, Ithaca, NY.

Knowing how the current at the contacts depends on material parameters is of fundamental importance for the understanding and optimization of organic light emitting diodes. We have measured the electrical characteristics of various contacts between commonly used anode electrodes (such as ITO and Au) and various hole transport layers, including N-N-diphenyl-N-N'-bis(3-methylphenyl)-1-1-biphenyl-4,4'-diamine (TPD) and poly[2- methoxy,5-(2-ethylhexoxy)-1,4-phenylene vinylene] (MEH-PPV). By carrying out independent measurements of the hole mobility in the organic layers we are able to isolate the injection and the transport processes and study the electrical characteristics of the contact alone. We find that most of the commonly used contacts in organic light emitting diodes are in fact not Ohmic, but current-limiting. The injected current is found to have a similar electric field dependence as the space charge limited current. Surprisingly, the injected current scales with the hole mobility in the organic, which was varied in the range of 10-6 and 10-3 cm^2/VΣsec by diluting TPD into polycarbonate. We show that this unexpected result is due to the hopping nature of transport in the organic material. We demonstrate ways to improve injection by modifying the contact and implement these modified contacts in organic light emitting diodes.

9:15 AM JJ1.3
ELECTRO-GENERATED CHEMILUMINESCENCE MECHANISM OF POLYMER SOLUTION LIGHT-EMITTING DEVICES. Shun-Chi Chang, Yongfang Li*, and Yang Yang Department of MS&E, University of California at Los Angeles, Los Angeles, CA. *Institute of Chemistry, Chinese Academy of Sciences, Beijing, PR CHINA.

The traditional polymer light-emitting device is a solid-state device in which the polymer thin film is sandwiched between two electrodes. Recently, we reported a different type of device: the polymer solution light-emitting device (SLED), in which the light-emitting medium is a thin layer of polymer solution sandwiched between two electrodes. In this presentation, we report the results obtained from the study of the light-emission mechanism of the SLEDs by cyclic voltammetry, transient electroluminescence measurement, current-light-voltage (I-L-V) measurement, and the optical microscopy observation on a surface cell SLED. The turn-on speed of the light-emission of the SLED with 1mm gap was found to be ca. 40 ms, which is similar to that of the dye ECL cells. The turn-on voltage for charge injection of the SLED devices agrees with the potential difference between the onset potentials of the oxidation for radical cation formation and the reduction for radical anion formation. However the light emission turns on at a higher voltage, and the turn-on voltage depends on the thickness of the SLED solution layer and the operation temperature. In the surface cell SLEDs, light emission occurs at the cathode side when the solution used is BDOH-PF in DCB, while it is at the anode side when the solution is MEH-PPV in cyclohexanone. For the SLEDs with the addition of dye molecules, the light emits from the luminescent molecules with lower exciton energy (lower energy gap). Based on the experimental results, we conclude that the device mechanism is due to electro-generated chemiluminescence.

9:30 AM JJ1.4
NEAR INFRA-RED ELECTROLUMINESCENCE FROM NEODYMIUM-DOPED POLYMER LIGHT EMITTING DIODES.
L.H. Slooff, A. Polman, FOM-Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS; F. Cacialli, R.H. Friend, Cavendish Laboratory, Cambridge, UNITED KINGOM; G.A. Hebbink, F.C.J.M. van Veggel, Supramolecular Chemistry and Technology, University of Twente, Enschede, THE NETHERLANDS.

Optical amplifiers are an essential part in integrated optics and as a result, rare-earth doped planar inorganic amplifiers are widely studied. Polymer-based planar amplifiers are gaining interest due to their low fabrication costs and easy implementation in existing telecommunication networks. Typically optical amplifiers are optically pumped, but it would be even more interesting if electrically pumped polymer amplifiers could be made. This work will show the first results on 890 nm luminescence from a lissamine sensitized, terphenyl-based neodymium complex, doped into a polymer Light-Emitting Diode, LED. The device structure consists of Indium tin oxide (ITO) as the transparent anode and poly(3,4-ethylene dioxythiophene) (PEDOT), doped with poly(styrene sulfonate) (PSS) as a hole injection layer. The active layer was a blend of poly(dioctylfluorene-alt-benzothiadiazole) and a lissamine sensitized neodymium complex (Ls.Nd). Ca/Al was used as the counter electrode. In addition to the photoluminescence, electroluminescence and I-V characteristics of the sensitized LEDs, we will present measurements on lissamine-free reference devices, showing that the lissamine plays a crucial role in the energy transfer to the neodymium. Relative to the lissamine luminescence, the Nd luminescence intensity is higher under electrical excitation than under optical excitation. This is consistent with a higher population of triplet states in the lissamine under electrical excitation.

9:45 AM JJ1.5
LEDS: INFLUENCE OF THE COMPOSITION OF DIHEXYLFLUORENE-CO-3,4 ETHYLENEDIOXY- THIOPHENE BASED COPOLYMERS. Olivier Stephan Université de Grenoble 1, Franáois Tran-Van, Université de Cergy Pontoise, Jean Claude Vial, Université de Grenoble 1, Claude Chevrot, Université de Cergy Pontoise, FRANCE.

We have synthezised soluble dihexylfluorene-co-3,4-ethylene-dioxythiophene (DHF-co-EDT)copolymers from mixtures in various ratio of the two corresponding dibrominated monomers using zerovalent nickel as a catalyst. As the materials are processable using common organic solvents, thin films of copolymer have been prepared and their electrochemical response has been investigated. IR, UV-visible and macromolecular properties have also been carried out and compared with those of each homopolymer. As shown in the photoluminescence spectra, the ratio of the monomer units have a strong influence on the light emission.As PDHF gives a light emission in the blue part of the visible spectrum centered at 450 nm, for the copolymer, a structured red-shifted emission is observed. It is noteworthy that the shift is directly connected to the incorporation of EDOT-based segments within the copolymer, increasing when increasing the EDOT ratio. Thus, various electroluminescence colors such as blue, green and orange, depending on the composition of the copolymer, have been obtained. In the prelimynary studies we have used the more classical and simple device configurations: ITO/ copolymer/Al. I=f(V) and EL=f(V) curves have shown an important lowering of the threshold voltage which decrease from 14 V for the polyfluorene homopolymer to 7V for the copolymer containing less than 20% of EDT units, strongly indicating that the carrier injection has been improved. For instance, stable luminescence of 200 Cd/m^2 are reached for 10 V applied bias when using the copolymer synthezised with a 4 DHF:EDOT molar ratio. Moreover the use of an additional layer, constituted of PEDOT-PSS has been investigated. Results clearly indicate that the lifetime and the homogenety of the light emission are improved.

10:30 AM *JJ1.6
Robert Jan Visser, Philips Components B.V., Heerlen, THE NETHERLANDS.

ABSTRACT NOT AVAILABLE

11:00 AM JJ1.7
HIGH EFFICIENCY ORGANIC EL DEVICES BASED ON POLY(N-VINYLCARBAZOLE). Junji Kido, Yamagata University, Yonezawa, Yamagata, JAPAN; Akira Ebisawa, TDK Corporation, Ichikawa, Chiba, JAPAN.

We report high efficiency organic EL devices based on poly(N-vinylcarbazole) (PVK). In order to achieve high quantum efficiency, phosphorescent Ir(ppy)3 was used as the emitting center, and, to decrease the drive voltage, highly reactive metal, Cs, was used as the cathode. Typical device structure is ITO / PEDOT / PVK doped with Ir(ppy)3 and oxadiazole derivative / Cs / Al. High luminous efficiency of 12 lm/W at 1000 cd/m^2 and high quantum efficiency of were achieved. Comparing with a device based on coumarin 6-doped PVK, the quantum efficiency is 8 times greater, which is due to the use of triplet excited energy of the Ir complex.

11:15 AM JJ1.8
POLARIZED FLUORESCENCE OF PHOTO-ALIGNED CONJUGATED POLYMER BLEND WITH AZOBENZENE SIDE CHAINED POLYIMIDE. Scott M. Webster, Richard Czerw, David A. Weston, Sung-Goo Lee, Hyung-Suk Woo, David L. Carroll, Clemson Univ, Dept of Physics and Astronomy, Clemson, SC; In-Hang Cho, Eung-Ju Oh, Myungji Univ, Dept of Chemistry, S KOREA.

Photo-alignment in a thin polymer film, a blend of polyimide with an azobenzene side chain (PI-Azo) and carbazole containing phenylene vinylene (PCzPV), was achieved by linearly polarized UV light from a xenon lamp. Thin films with a varied weight percent of 0%, 1%, 10%, 30%, 50%, and 100% of PI-Azo were cast on quartz substrates followed by photo-alignment in order to investigate the polarized absorption and photoluminescence (PL) spectra. We also have fabricated organic light emitting diodes (OLEDs) using this aligned emissive polymer film to obtain polarized electroluminescence (EL). Additionally, surface morphology changes were examined using high resolution scanning electron microscopy and atomic force microscopy. The preliminary results indicate that alignment of the carbazole containing PPV can be induced by the concurrent photo alignment of PI-AZO in the blended films. The optical anisotropy of PL and EL including the polarization dependent current-voltage characteristics and efficiency of the OLEDs will be discussed.

11:30 AM JJ1.9
EXPERIMENTAL AND THEORETICAL STUDIES OF HOLE MOBILITY IN MEH-PPV. A.R. Inigo, C.H. Tan, R. Chang, W.S. Fann and S.H. Lin, Institute of Atomic and Molecular Sciences, Academia Sinica, and Department of Physics, National Taiwan University, Taipei, TAIWAN ROC.

Much effort has been devoted to spectroscopic studies in MEH-PPV (poly(2-methoxy, 5-[2'(ethyl)hexyloxy]-p-phenylene)), a prototypical material for polymer LED. However, a thorough understanding on the properties of charge transport in this material is still lacking. In this work, we report both experimental and theoretical studies of hole mobility in MEH-PPV. The electric field and temperature dependencies of mobility are studied in detail. Relevant work has been reported by Campbell et al [1] recently. Hole mobility measurement is performed by the time-of-flight (TOF) technique, in which the conventional device structure ITO/MEH-PPV/Au is used. The field dependence of mobility roughly follows the Poole-Frenkel form for fields ranging between 25 and 210 kV/cm. Furthermore, the increase of temperature from 200K to 315K leads to great enhancement of mobility by about thirty fold. A microscopic model is constructed to explain the observed phenomena, taking into account the energetic and positional disorders as well as charge-phonon interaction. We find that strong charge-phonon interaction merely leads to slight increase in mobility with temperature. In the presence of strong energetic disorder ($\sim$1500 1/cm), mobility increases by about thirty fold as the temperature varies from 200K to 315K, thus accounting for the experimental results. Meanwhile, the zero-field limit with a non-Arrhenius form is induced as pointed out by Bassler [2], which is also consistent with the experiment. Results in samples prepared from different solvents will also be compared.
References:
[1] I.H. Campbell, et al., Appl. Phys. Lett. 74, 2809 (1999).
[2] H. Bassler, Phys. Stat. Solidi B 175, 15 (1993).

11:45 AM JJ1.10
SOLID-STATE DEMIXING OF POLYMER BLENDS BY CONTACT WITH A NON-SOLVENT. J. Morgado, Instituto Superior Tecnico, Dep. Eng. Quimica, Lisboa, PORTUGAL; R.H. Friend, Cavendish Laboratory, Cambridge, UNITED KINGDOM; E. Moons, CDT Ltd Greenwich House, Cambridge, UNITED KINGDOM; F. Cacialli, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

We report investigations of organic Light-Emitting Diodes with an active layer consisting of poly(9,9-dioctylfluorene), PFO, blended with a green emitting derivative (F8BT). We used Indium Tin Oxide (ITO) anodes with and without a hole transporting layer, consisting of doped poly(3,4-ethylene dioxythiophene), PEDOT. We also studied the incorporation of an oxadiazole based Hole-Blocking/electron transporting Layer, HBL, namely 2-(4-biphenylyl)-5-butylphenyl-1,3,4-oxadiazole, PBD, between the emissive layer and the Ca/Al cathodes. The presence of this layer reduces the range of radiative recombination in a region closer to the HBL interface, and therefore allows investigation of depth-dependent structural non-uniformities of the emissive layer. We find marginal alterations of the electro-luminescence spectra depending on the weight concentration of the F8BT in the range 5-25%. Efficient energy transfer from the host (PFO) to the guest (F8BT) ensures that the emission spectra are dominated by the green component. However, we find that blue emission from the PFO host is much more intense for the structures incorporating the HBL than for those without it. We propose that further de-mixing of the blend, induced by the spin-coating of the PBD-based layer, is responsible for the higher weight of the blue component.

SESSION JJ2: ELECTRONIC PROPERTIES
Chair: Richard H. Friend
Monday Afternoon, November 27, 2000
Republic B (Sheraton)

1:30 PM *JJ2.1
ORGANIC SINGLE CRYSTALS FOR ELECTRONIC AND OPTOELECTRONIC DEVICES. Hendrik Schön, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Organic semiconductors have received considerable attention for potential application as light-emitting diodes, field-effect transistors, solar cells, or lasers. Despite tremendous progress in performance and stability of thin film devices there still remain fundamental question of the intrinsic capabilities or limitations of these materials unanswered. In order to investigate intrinsic electrical and optical properties of small molecule-based organic semiconductors we have grown and studied high-quality single crystals, and have prepared single crystal field-effect transistors. Ambipolar transport, i. e. n- as well as p-channel activity, has been observed in a variety of acenes and oligothiophenes devices. Room temperature mobilities are typically in the range from 1 to 5 cm^2/Vs. Studies of ambipolar inverters and ring-oscillators show that speeds close to 1 MHz can be achieved, still limited by parasitic capacitance. Low temperature measurements revealed band-like charge transport with mobilities up to 10^5 cm^2/Vs in pentacene or tetracene, enabling the observation of Shubnikov-de Haas oscillations and the Fractional Quantum Hall Effect. Moreover, at high electron concentrations gate-induced superconductivity has been observed in anthracene, tetracene, pentacene, and C_{60}. Furthermore, field-effect electrodes can be used for balanced hole and electron injection into organic single crystals leading to efficient exciton generation. As a result, we have achieved electrically driven amplified spontaneous emission and laser action in single crystal based devices.
In collaboration with Ch. Kloc, A. Dodabalapur, S. Frolov, and B. Batlogg.

2:00 PM JJ2.2
NEAR FIELD OPTICAL MICROSCOPY OF CARRIERS IN A CONJUGATED POLYMER. Jason D. McNeill, Donald B. O'Connor, Paul F. Barbara, University of Texas at Austin, Dept of Chemistry, Austin, TX.

A metal-coated pulled optical fiber probe is electrically biased, creating an electric field that either traps or repels majority carriers (polarons) in a thin film of conjugated polymer material (MEH-PPV). Near field photoluminescence is employed to measure carrier concentration and temporal response in a 10^{-16} cm^3 volume with a sensitivity of a few tens of carriers. The temporal response upon application of electrical bias is related to the carrier transport properties. This method may be used to study carrier transport in nanostructured organic semiconductor materials.

2:15 PM JJ2.3
OPTICAL PROBING OF POLARONS AND TRIPLET EXCITONS IN CONJUGATED POLYMER DEVICES. A.S. Dhoot, D.S. Ginger, N.C. Greenham, Cavendish Laboratory, University of Cambridge, UNITED KINGDOM.

Polarons and triplet excitons in conjugated polymers exhibit sub-gap absorptions which allow them to be identified spectroscopically. We have used quasi-steady-state induced absorption techniques on working polymer LEDs to study charge carriers and triplet excitons in devices. We identify absorptions due to charges, and at low

temperatures can also resolve features due to triplet excitons. From the magnitude of the absorption features, we can study the charge and triplet densities as a function of device current. We are thus able to obtain an estimate of the triplet generation rate at low temperatures.

2:30 PM JJ2.4
ORGANIC CIRCULAR–GRATING SURFACE–EMITTING DBR LASER. C. Bauer, H. Giessen, Phillipps-Universität, Fachbereich Physik, Marburg, GERMANY; B. Schnabel, E.B. Kley, Friedrich-Schiller Universität, Institut für Angewandte Physik, Jena, GERMANY; U. Scherf, R.F. Mahrt, Max-Planck-Institut für Polymerforschung, Mainz, GERMANY.

In recent years conjugated polymers have demonstrated their potential as high gain laser media. To obtain proper laser activity, low lasing thresholds and the control of the emission properties are of crucial importance. Therefore an optimal photon confinement is necessary. To fulfill these requirements, the use of complete optical confinement would be ideal. Since this is usually difficult to achieve and modify, we chose for the first time a concept known from inorganic semiconductor lasers: Circular–grating surface–emitting distributed Bragg reflector (DBR) lasers show a good performance with low thresholds and circular beam cross–sections.
In our case a quartz substrate was nano–structured by electron–beam lithography. The resulting concentric circular pattern provides 2D feedback (second–order diffraction) and surface emission (first–order diffraction) of the light. A thin film of a ladder–type poly(*p*–phenylene) acts as emissive layer, where the emitted photons encounter a true 2D confinement caused by the DBR structure of the substrate.
When optically pumped, our samples show a clear threshold behavior combined with directed emission and linewidths below 1 meV. By varying the grating period, tuning of the emission wavelength within the optical gain region is observed.

3:15 PM *JJ2.5
ROOM TEMPERATURE SPIN-POLARIZED CARRIER INJECTION IN ORGANIC MATERIALS. C. Taliani, V. Dediu, Istituto di Spettroscopia Molecolare-Consiglio Nazionale delle Ricerche (CNR), Bologna, ITALY.

Spintronics is a new branch of Electronics based on carriers spin orientation (spin up or down) rather than charge transport which has the potential to become an important technology in the future. Direct injection or excitation of spin-polarized carriers in the active element is the simplest way to submit an input information. The use of organic materials as active elements in Spintronics would open the way to cheap and widely available technologies. For the first time at our knowledge we have demonstrated successfully the polarized spin injection into organic materials (1). The process, which takes place at room temperature, has been shown for different organic thin films ranging from Zn-phtalocynine to sexithienyl. The spin-polarized state of the carriers can be characterized by coherence length of the order of 100-1000 nm. Important results could be achieved by combining Spintronics and Opto-electronics. The efficiency of organic light emitting diodes (OLED) is intrinsically affected by spin statistics of charge carrier recombination. Prompt electroluminescence is due to singlet excitons emission (fluorescence) and singlet excitons are normally one fourth of the injected carriers while triplet are three quarters. Triplets are normally long lived dark excited states which may also cause electrochemical degradation. Controlling the spin polarization at the electrodes allow therefore to improve considerably the efficiency of OLED improving at the same time their stability.
(1) Patent no: MI2000A000603.

3:45 PM JJ2.6
IMPROVING THE PERFORMANCE OF CONJUGATED POLYMER-BASED DEVICES BY CONTROL OF POLYMER FILM MORPHOLOGY. Thuc-Quyen Nguyen, Ignacio B. Martini and Benjamin J. Schwartz, University of California, Los Angeles, Dept of Chemistry and Biochemistry, Los Angeles, CA; Jinlin Yang, Raymond C. Kwong and Mark E. Thompson, University of Southern California, Dept of Chemistry, Los Angeles, CA.

Controlling the polymer film morphology can strongly affect the photophysical and electrical properties of conjugated polymers. The morphology of conjugated polymers can be controlled by 1) changing the solvent from which the films are cast, 2) polymer concentration, 3) annealing, 4) heating the polymer solution, 5) doping the polymer with acid. When the films are cast from these polymer solutions, the aggregates survive the casting process and carry in the films. The evidence of aggregation in the films is shown in UV-VIS, PL, PLE, AFM, and pump-probe experiments. The aggregates affect the device performance as shown by I-V curves, light output, and efficiency. Finally, we show that control over film morphology has a direct effect on the performance of conjugated polymer-based light-emitting diodes.

4:00 PM JJ2.7
ENERGY TRANSFERS IN NANOSTRUCTURED OLIGO-THIOPHENES CRYSTALS. Chiara Botta, ICM, CNR, Milano, ITALY; Gianni Bongiovanni and Andrea Mura, INFM and Dip. di Fisica, Universite di Cagliari, Monserrato (Ca), ITALY; Giuseppe Di Silvestro, Dip. di Chimica Organica e Industriale, Universite di Milano, Milano, ITALY; Riccardo Tubino, INFM and Dipartimento di Scienza dei Materiali, Universite di Milano, Bicocca, Milano, ITALY.

We report on the optical properties of oligothiophene inclusion compounds in perhydrotriphenylene which dictates the specific supramolecular organization of oligothiophene molecules which are incorporated in the parallel nanochannels formed by the host. Excitonic effects are suppressed due to the large intermolecular distances (14) imposed by the host crystal, while long range Foerster type energy transfer can take place under controlled geometrical conditions (intermolecular distances and mutual orientations) Thanks to the parallel relative orientation of the molecules within the channels of the host crystal, quite large critical distances are involved. In a mixture of quinquethiophene (Acceptor A) and terthiophene (Donor D) inclusion compounds we observe very efficient long range energy transfers from the short to the long oligomer. The time decay of the D and the rise time of the A excited state populations are interpreted in terms of energy transfer processes both within the channel (J aggregates) and between the channels of the host.

4:15 PM JJ2.8
Abstract Withdrawn.

4:30 PM JJ2.9
CEO/SEMIEMPIRICAL CALCULATIONS OF EXCITED ELECTRONIC STATES AND NONLINEAR POLARIZABILITIES IN CONJUGATED MOLECULES. S. Tretiak, A. Saxena, R L. Martin and A.R. Bishop, Theoretical Division and Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, NM.

The Collective Electronic Oscillators (CEO) approach based on the time-dependent Hartree-Fock approximation is combined with INDO/S, MNDO, AM1, and PM3 semiempirical Hamiltonians. This technique is applied to compute and analyze electronic structure of donor/acceptor substituted oligomers and several conjugated polymers. Calculated excited states energies and oscillator strengths are in excellent agreement with experimental data and each other. In particular, the results using the Hamiltonians parameterized for ground state calculations such as AM1 and PM3 agree well with the INDO/S results. In particular, the results using the Hamiltonians parameterized for ground state calculations such as AM1 and PM3 agree well with the INDO/S results. To mimic the experimental conditions polarizabilities in substituted molecules are calculated for the isolated complex and in a dielectric medium, whereby the solvent contributions are incorporated using the Self-Consistent Reaction Field approach. Dielectric environment significantly increase second and third orders of off-resonant polarizabilities which calculated values agree well with experimental data. In addition, two-dimensional analysis of corresponding transition density matrices provides an efficient way for tracing the origin of various optical transitions by identifying the underlying changes in charge densities and bond orders. The CEO/semiempirical approach concluded to be an inexpensive and numerically efficient method of computing excited states and nonlinear molecular properties.

4:45 PM JJ2.10
ELECTRIC FIELD INDUCED IONIZATION OF THE EXCITON IN POLY(PHENYLENE VINYLENE). Jian Wang, Dan Moses, Alan J. Heeger, Polymer Institute, University of California at Santa Barbara, Santa Barbara, CA; N. Kirova, S. Brazovskii, LPTMS, Universite Paris-Sud, Orsay-Cedex, FRANCE.

The exciton binding energy (Eb) and the band gap energy (Eg) of poly(phenylene vinylene), PPV, have been determined by photoconductivity excitation profile spectroscopy as a function of applied electric field. The spectral signature of the exciton is a narrow peak (100 meV full width at half maximum) that emerges just below the band edge upon increasing the external field or the defect density. The exciton peak is observed only for light polarized parallel to the chain axis. The exciton binding energy is obtained from the energy of the exciton peak with respect to the band edge and, independently, from analysis of the field dependence of the exciton dissociation: Eb $\sim$ 55 meV.

SESSION JJ3: MATERIALS
Chair: Donal D.C. Bradley
Tuesday Morning, November 28, 2000
Republic B (Sheraton)

8:30 AM *JJ3.1
SYNTHESIS OF NEW BUILDING BLOCKS FOR LIGHT EMITTING POLYMERS. Cedric Fischmeister, Florence Geneste, Andrew Holmes, Yuguang Ma, Rainer Martin, Melville Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM; Franco Cacialli, Richard Friend, Robert Riehn, Cavendish Laboratory, University of Cambridge, Cambridge UNITED KINGDOM.

Conjugated polymers for light emitting diodes are prepared by a variety of polycondensation reactions such as the Gilch dehydrohalogenation or metal-mediated cross coupling reactions. The disadvantage of the preparation of 1,4-bishalomethyl derivatives from the corresponding unsubstituted aromatic precursor is that halomethylation reactions can produce unwanted carcinogeneic side products. Radical halogenation of methyl-substituted precursors can alos be low yielding. In this presentation we demonstrate a new application of directed metallation to prepare novel building blocks with unconventional substitution patterns. These can then be used for the preparation of unsymmetrically substituted poly(1,4-phenylene vinylene)s and poly(fluorene-co-phenylene)s. Improved polymer fluorescence and device efficiencies are realised with such asymmetrically substituted materials.

9:00 AM JJ3.2
FUNCTIONAL POLYMERS AND BLOCK COPOLYMERS FOR ELECTRO-OPTICAL APPLICATIONS. Haridas R. Karickal, Jolita Ostrauskaite, Thomas Breiner, Christoph Schmitz, Mukundan Thelakkat, Macromolecular Chemistry I, University of Bayreuth, Bayreuth, GERMANY.

Efficient hole transport materials (HTM) find application in electro-optical devices like solar cells, light emitting diodes and photorefractive systems. As hole transport materials some novel triphenyldiamine based polymers carrying long alkoxyl groups as sidechains or in the backbone were designed and synthesized using Ullmann reaction. The thermal and electrochemical properties are studied. The soft spacers lower the Tg of the polymers suitably. Additionally, fully functionalized block copolymer carrying photoconductor and NLO dye moieties was synthesized by anionic polymerization and characterized. All the polymers are soluble in usual solvents and form excellent films. The molecular weights as determined from GPC are in the range of 20000g/mol and the glass transition temperature can be tuned between 100 and 230°C. The polymer photoconductors were tested in organic light emitting diodes, ruthenium dye-sensitized TiO_2 solar cell and in photorefractive systems. The penetration behaviour of the low melting polymer in solid state solar cells were studied using scanning electron microscopy. The morphology study of the block copolymer in films was carried out using transmission electron microscopy and atom force microscopy. The first results of both the polymer concepts in OLEDs, solar cells and photorefractive systems are promising.

9:15 AM JJ3.3
CONFORMATIONAL AND SPATIAL INTERACTION EFFECT ON CONJUGATED POLYMER'S OPTICAL PROPERTIES. Jinsang Kim and Timothy M. Swager, Department of Materials Science and Engineering and Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

A conjugated polymer's spectroscopic properties are strongly influenced by both individual polymer's conformations and interpolymer interactions. However, due to their high molecular weight and amorphous character, controlling conformations and interpolymer interactions is challenging. We report, for the first time, precise control of single polymer's conformation and intermolecular interactions by combining unique surfactant design of a family of conjugated polymers (poly(*p*-phenyleneethynylene)s) and spectroscopic studies of their structural monolayers at the air-water interface. Since poly(*p*-phenyleneethynylene)s has a planar-ribbon-like structure, by precise design of hydrophobic and hydrophilic side chains we can make monolayers in three different superstructures. The first is the face-on with co-facial π-plane organization with the air-water interface. The second is the edge-on; the π-plane lies normal to the interface. The third is the zipper with alternating face-on and edge-on. Interestingly, we can mechanically induce conformational changes from face-on to zipper and zipper to edge-on by applying surface pressure. *In situ* UV-Vis and fluorescence spectroscopy of these monolayers reveals the precise inter-relationship of conformation and interpolymer interactions to the intrinsic electronic properties.

9:30 AM JJ3.4
PREPARATION OF ULTRATHIN NANOCOMPOSITE FILM FROM EXFOLIATED ALUMINOSILICATE/COUMARIN DYE COMPLEX AND CATIONIC POLYELECTROLYTE BY LAYER-BY-LAYER DEPOSITION. Dong Wook Kim, Jayant Kumar, Changmo Sung, Sukant K. Tripathy, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA; Alexandre Blumstein, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA.

A nanocomposite film was obtained from exfoliated alumino-silicate/coumarin laser dye complex and a cationic polyelectrolyte through layer-by-layer self-assembly. Coumarin dye molecules were intercalated into the layered aluminosilicate by a cationic exchange reaction. Particles of the hectorite/dye complex were delaminated by extensive shaking and sonication of their water suspension into ~3 nm-thin silicate layers with molecules of the dye adsorbed on their surface. Atomic force microscopy and transmission electron microscopy data are in agreement with such a model. Ultrathin multilayered films were prepared using layer-by-layer self-assembly from exfoliated nanocomposites and a cationic polyelectrolyte polydiallyldimethylammonium chloride (PDAC). UV/visible absorption spectroscopy indicated a linear build-up of the films as a function of the number of deposition cycles. The nanocomposite films displayed fluorescence centered at around 450 nm. Its intensity increased linearly with the number of sequential deposition cycles.

9:45 AM JJ3.5
SYNTHESIS, CHARACTERIZATION AND SELF-ASSEMBLY OF MOLECULAR WIRES: DIAZONIUM SALTS AND FUNCTIONALIZED PYRENES IN MOLECULAR ELECTRONICS. Aaron S. Engel, Dmitry V. Kosynkin, Jiping Yang, James M. Tour, Rice University, Department of Chemistry and Center for Nanoscale Science and Technology, Houston, TX; Philipp Harder, Josh Stapleton, David L. Allara, The Pennsylvania State University, Departments of Chemistry and Materials Science and Engineering, University Park, PA.

Molecular electronics has seen an impressive and rapid evolution over the last decade. The newer subfield of molecular computing is dependent upon the discovery of molecular circuitry capable of complementing current silicon-based technology. We will present the syntheses and self-assembly of several conjugated organic wires including diazonium-terminated oligo(phenylene ethynylene)s and thioacetate-terminated wires containing functionalized pyrene cores. Our preliminary results indicate that the diazonium salts form layers on Au, Pt and Cu surfaces and that the growth rate is dependent on both the metal and solvent employed.

10:30 AM JJ3.6
NANOSCALE ASSEMBLY OF INTERLINKED, MOLECULE-BASED PHOTONIC STRUCTURES. GROWTH, CHARACTERIZATION, PATTERNING, AND DEVICE PERFORMANCE. T.J. Marks, Y. Koide, J. Cui, J.E. Malinsky, Q. Wang, Chem. Dept. and the Materials Research Center, Northwestern U., Evanston IL; A. Richter, P. Dutta, Physics Dept. and the Materials Research Center, Northwestern U., Evanston IL, P.A. Lee, N.R. Armstrong, Optical Sciences Center, U. of Arizona, Tucson, AZ.

Molecular self-assembly approaches using self-limiting, chemisorptive silicon chemistry offer the attractive possibility of constructing robust, conformally adherent, optically-functional arrays composed of designed, photophysically well-characterized building blocks with sub-nm precision. We report here the implementation of such strategies to the fabrication and soft lithography of organic emissive structures. Here layer-by-layer growth techniques are used to assemble charge-blocking, charge-transporting, and emissive building blocks into interlinked 3D multilayers. The resulting structures have been characterized by a battery of nanostructural, electrochemical, spectroscopic, and photonic techniques, and are shown to be structurally regular, essentially pinhole-free, and capable of supporting high luminence efficiencies. In the present study, such structures are used to probe : i)electrode passivation and charge injection balance effects, ii)matrix order vs. disorder effects on charge transport, iii)electrode adhsesion effects on charge injection, iv) pixelation down to 8 micron dimensions, v) the characteristics of unsual electrode materials.

10:45 AM JJ3.7
GENERATION OF CIRCULARLY POLARIZED LIGHT AND OPTICAL ACTIVITY OF HIGHLY ORIENTED POLY(P-PHENYLENE VINYLENE). Alexandre Marletta, Debora Gonçalves, Osvaldo N. Oliveira Jr., Roberto M. Faria and Francisco E.G. Guimarães, Univ de São Paulo, Inst de Física de São Carlos, São Carlos, BRAZIL.

Langmuir-Blodgett (LB) films of poly(p-phenylene vinylene) (PPV) were prepared using an amphiphilic precursor, where the counterion chloride was partially replaced by a long chain dodecylbenzene-sulfonate (DBS) ion. These LB-PPV films are highly ordered along the dipping direction as demonstrated by linear dichroism experiments using linearly polarized optical absorption and emission. The dichroic ratio between the intensity of the emitted light parallel

and perpendicular to the dipping direction was ca. 17, which is much higher than the dichroic ratio of 3.6 found in the polarized absorption experiment. The high dichroic ratio indicates an efficient energy and/or charge transfer between the low conjugated segments (disordered) and the highly conjugated (ordered) ones after excitation. In addition, the LB films display large circular polarization with an asymmetry factor ge which varies from 0.6 to -0.2 when the sample temperature is increased from 30 to 300 K. This chiral nature of the PPV structure can be also demonstrated by strong optical activity (100 mdeg) related to the π-π^* band in circular dichroism (CD) measurements. The origin of the circular dichroism and circular polarization in the LB films will be discussed in terms of molecular order in Z-type LB films, where a non-centrosymmetric arrangement for the molecules was introduced.

11:00 AM JJ3.8
'LINE PATTERNING' OF CONDUCTING POLYMERS: NEW HORIZONS FOR INEXPENSIVE, DISPOSABLE ELECTRONIC DEVICES? Alan G. MacDiarmid, Dirk Hohnholz, Department of Chemistry, University of Pennsylvania, Philadelphia, PA.

We report that electronic polymers can be inexpensively and rapidly patterned to produce flexible liquid crystal display electrodes and simple electronic circuits by a method which does not involve printing of the polymer. The only apparatus needed is a standard office desk-top computer and laser printer neither of which is modified in any way. 'Line Patterning' has general applicability to a variety of different conducting and conventional polymers, different plastic, paper-type or fabric substrates and different types of copying or printing techniques and inks. An electronic circuit is designed on the computer and printed on, e.g. plastic. We exploit the observation that the difference in hydrophobicity / hydrophilicity between the substrate and printing ink can be used so that a solution of a conducting polymer wets the substrate but not the ink. The substrate and printed pattern are treated with the conducting polymer fluid and dried. A conducting pattern separated by insulating lines is produced. This pattern may be used as obtained or the ink may by cleanly removed by ultrasonic treatment to leave only the conductive pattern. We use a water dispersion of poly(3,4-ethylenedioxy-thiohene)-polystyrenesulfonate ('Baytron-P', Bayer AG, Germany) or polypyrrole and polyaniline deposited from aqueous solution. The 2-D circuits obtained may be converted to 3-D circuits by means of, e.g., a desk paper stapler which makes an electrical connection between different conducting layers separated if desired by layer(s) of insulating substrates. We have also exploited the height of a printed insulating line above the substrate (e.g. ca. 4.5 um) so that it acts as a 'spacer' between two adjacent conducting patterns. Selected devices will be demonstrated.
Financial support from:
(a) Subcontract from Kent Displays, Inc., ONR SBIR.
(b) ONR (K.J. Wynne, Contract Officer) is gratefully acknowledged.

11:15 AM JJ3.9
PATTERNED PARTICLE ARRAYS USING POLYELECTROLYTE MULTILAYER TEMPLATES. Xueping Jiang, Kevin M. Chen, Lionel C. Kimerling, Paula T. Hammond, Dept. of Chemical Engineering, MIT, Cambridge, MA and Dept. of Materials Science and Engineering, MIT, Cambridge, MA.

The layer-by-layer assembly process can be used to incorporate a number of functional materials into ultrathin films with great supramolecular control. By utilizing chemically patterned substrates, passive and active polyelectrolyte multilayer films can be patterned onto a surface. We have recently begun to explore the use of such patterned polyelectrolyte multilayer films as a template for the depositon of submicron and micron sized latex colloids. This deposition is driven by the spatially-varied electrostatic and secondary interactions between the colloid and the substrate. In earlier work, we demonstrated control over the density and selectivity of SiO_2 colloidal particle adsorption by adjusting (i) pH of the colloid suspension, which determines the ionization of the uppermost surface of the polyelectrolyte multilayer; and (ii) ionic strength of the suspension, which determines the extent of charge screening about the colloid and polyelectrolyte. We have recently begun to study the deposition of functionalized PS latex spheres with hydrophobic and hydrophilic surfaces have been studied. By adding surfactants to induce charge screening and hydrophobic interactions between the surfactant and polyelectrolyte, both the selectivity and adsorption density, as well as particle ordering can be controlled. Using a patterned polyelectrolyte platform, we also demonstrate directed assembly of single-particle chains of colloidal spheres. The self- and directed organization approaches reported here expand on the possibilities for fabrication of complex micro- to nanoscale structures through the manipulation of submicron particles.

11:30 AM JJ3.10
NANOENGINEERING OF ORGANIC SEMICONDUCTORS. J.M. Lupton and I.D.W. Samuel, School of Physics and Astronomy, University of St Andrews, St Andrews, UNITED KINGDOM; R. Beavington and P.L. Burn, Dyson Perrins Laboratory, Oxford, UNITED KINGDOM.

The degree of order and interaction between molecules is a crucial factor in determining the photophysical and charge-transporting properties of organic materials. For efficient charge transport, strong intermolecular interactions are desirable. However, from a photophysical point of view interactions should be minimised to avoid luminescence quenching by excimers or aggregates. We explore this trade-off using a family of conjugated dendrimers as model systems. The generation number provides an elegant way of controlling the degree of interaction between chromophores. For low generation numbers a red component of the electroluminescence spectrum due to inter-molecular excited states is observed. As the generation number is increased, reducing interaction between the emissive chromophores, this feature disappears, and the spectrum resembles the solution photoluminescence spectrum. The effect of the increase in localisation of excitations is also clearly seen in the transport properties of LEDs based on these materials: the electroluminescence quantum efficiency increases exponentially with generation and the majority carrier current-flow is inhibited. Time-of-flight measurements show highly dispersive transport and a strong increase of transit times and photocurrent decay transients with generation. The increase in hopping distance gives rise to a decrease in mobility by almost 2 orders of magnitude as the generation is increased. This gives rise to a scaling of the mobility with dendrimer radius comparable to the concentration dependence of mobility previously observed in doped polymer host systems. The dendrimer generation hence provides a unique method of studying the effect of intermolecular interactions on charge transport and light-emission.

11:45 AM JJ3.11
POLYMER-BASED AMPLIFIERS VIA SENSITIZED NEAR INFRA-RED LUMINESCENCE OF LANTHANIDE COMPLEXES. Frank C.J.M. van Veggel, Gerald A. Hebbink, Steve I. Klink, Supramolecular Chemistry and Technology, University of Twente, Faculty of Chemical Technology, Enschede, THE NETHERLANDS.

Polymer-based amplifier are attractive as components in the telecommunication. They are potentially low cost and easy to apply in planar devices. Another attractive point is their integration in other polymer-based devices. Both the telecommunication window around 1330 and 1550 nm are of interest and the trivalent lanthanide ions Nd^3 and Er^3 , respectively, have the appropriate optical transition in their 4f shells. The encapsulation of the trivalent lanthanide ion in a polydentate ligand is essential to ensure compatibility with the polymer matrix and to remove efficient quenchers, like OH groups, from the direct vicinity of the lanthanide ion. The excitation of the trivalent lanthanide ions is inherently difficult due to the fact that the intra-f-shell transitions are parity forbidden. To circumvent this disadvantage, sensitizers have been incorporated into the ligand for efficient harvesting of the pump light. After excitation of the dye, energy transfer to the trivalent lanthanide ion occurs, thus leading to the excitation of the lanthanide ion. We have studied in great detail a number of different dyes, some of which allow excitation in the green to red region of the visible spectrum. A Nd^3 complex has been included into a planar waveguide structure and amplification has been demonstrated.

SESSION JJ4: LEDs II
Chair: Junji Kido
Tuesday Afternoon, November 28, 2000
Republic B (Sheraton)

1:30 PM *JJ4.1
ROLE OF STRUCTURE AND DEVICE ARCHITECTURE IN THE OPERATION OF POLYMER SEMICONDUCTOR DEVICES. Richard H. Friend, Univ of Cambridge, Cambridge, UNITED KINGDOM.

Polymer semiconductor diodes now provide good performance as light-emitting diodes and, if appropriately fabricated, as photovoltaic diodes. The operation of these diodes is dependent on the properties of a number of interfaces between different polymer semiconductor materials which may be present and between these semiconductors and electrodes. I will review recent progress in the design and control of these interfaces, and in the resultant properties of these devices.

2:00 PM JJ4.2
OPTICAL MODELING OF ORGANIC LIGHT-EMITTING DIODE MULTILAYER DEVICE STRUCTURES. K.B. Kahen, Eastman Kodak Company, Rochester, NY.

Previous organic light-emitting diode (OLED) optical model

formalisms have been based on the work of Crawford who made use of the Lorentz reciprocity theorem. As a result of this approximation, one can only compute the relative far-field response of the OLED and thus have no knowledge of the field distributions inside of the device (as a result one can only account for ~20% of the emitted light). We have generalized this model by rigorously solving the inhomogenous vector wave equation for all regions of space. The solution is based on a Hertzian vector approach. Having knowledge of the E- and H-fields everywhere enables the computation of the absolute fraction of photons contained in each layer and the absolute far-field response. As a result, we present contour plots showing the distribution of power inside and in the near-field of typical OLED devices. These plots show where the photons get trapped and should help in the engineering of new device structures which make more efficient usage of the available photons. Since the radiative decay rate of excitons is proportional to the total integrated power emitted by the emission layer dipoles, our model can be used to simultaneously optimize a device for CIE coordinates and for radiance. Previously, others have computed an approximation to the radiative decay by integrating over the intensity which exits the device; however, we will show that the total power emitted out of the device is a poor predictor of the total power emitted by the dipoles as a function of layer thickness. Finally, we show that one can accurately predict OLED electroluminescence data based on the layer thicknesses, indices of refraction, and a representative photoluminescence of the emitter layer.

2:15 PM JJ4.3
TRANSIENT CURRENT AND ELECTROLUMINESCENCE RESPONSES: DEVICE PHYSICS OF ORGANIC LIGHT-EMITTING DIODES. Arabinda Chowdhury, Amlan J. Pal, Indian Association for the Cultivation of Science, Department of Solid State Physics, Calcutta, INDIA.

Light-emitting devices have been fabricated based on Langmuir-Blodgett films of different organic semiconductors. Due to the high degree of order and control in film thickness, this technique is very suitable as a model for device characterization. Transient responses have been studied, which offers an opportunity to study the role of space and trapped charges in device operation. We have studied transient current and electroluminescence (EL) by applying two rectangular and saw-tooth voltage pulses, separated by a time delay. The amplitude and width (slope) of the rectangular (saw-tooth) pulse, separation time between the pulses have been varied to gather a wide range of responses. Under rectangular voltage pulses, we have observed an instantaneous EL during the first pulse. The EL subsequently rose and finally decayed exponentially to a steady level. When the delay between the pulses was short, the EL peak was absent during the latter pulses. Intrinsically accumulated charges at the interfaces have been shown to result in the instantaneous EL. The linear rise in EL was due to space charge assisted electron injection. Relaxation of the device occurred during the delay. The application of linearly increasing voltage enabled us to estimate current transients due to extraction of carriers. The transient current under saw-tooth voltage showed a peak in current and light. The time where the peak occurs (t_m), depended on the slope of voltage. The peak current, peak light, and t_m during the second pulse depended on the delay time between the pulses. By applying two saw-tooth voltage pulses, we could separate out the contributions of extracted carriers from other effects. Our results showed that the peak in light under saw-tooth voltage and the instantaneous light under rectangular voltage could originate from the extraction of charge carriers. Role of such carriers in device operation will be discussed.

2:30 PM JJ4.4
DRASTIC IMPROVEMENT IN COUPLING-OUT EFFICIENCY IN ORGANIC LIGHT-EMITTING DEVICES USING THIN SILICA AEROGEL LAYER. Tetsuo Tsutsui, Masayuki Yahiro, Katsuhiko Fujita, Graduate School of Engineering Sciences, Kyushu University and Core Research for Evolutional Science and Technology, Japan Science & Technology Corporation, Fukuoka, JAPAN; Hiroshi Yokogawa, Kenji Kawano and Masaru Yokoyama, Advanced Technology Research Laboratory, Matsushita Electric Works, Co. Ltd., Osaka, JAPAN.

External quantum efficiency in organic light-emitting devices (OLEDs) still remains low although large enhancement of external quantum efficiency, exceeding to 15% has been already attained using triplet emitters. A considerable portion of light originated from emissive centers buried in a thin solid film never escape to air due to internal reflection at air-solid film interface and scattered out as edge emission or dissipated within the solid film. This is one of the major reasons why the external efficiency in OLEDs remains low. Although several trials for overcoming this difficulty have been reported, no comprehensive method solving this problem has been proposed yet. In this report, we show that the insertion of a silica aerogel layer, which has low refractive index less than 1.03, between glass substrate and a transparent anode contribute to the large increase of device coupling-out efficiency. We demonstrate that the insertion of the silica aerogel layer is quite effective for decoupling optical modes within organic layer and transparent anode from those within glass substrate. We fabricated the OLEDs with inserted aerogel layers and succeeded in observing the disappearance of wave-guided component as edge emission on glass substrate. More than 60% increase of device coupling-out efficiency due to the insertion of the silica aerogel layer was confirmed using conventional double-layer devices. with the structure of glass substrate/ITO/HTL/EML/MgAg.

2:45 PM JJ4.5
MODELING OF CHARGE TRANSPORT IN Alq_3 INCORPORATING AN EXPONENTIAL AND GAUSSIAN DISTRIBUTION OF TRAPS. Mathew Mathai, Keith Higginson, Fotios Papadimitrakopoulos,Department of Chemistry, Polymer Program, Nanomaterials Optoelectronics Laboratory, Institute of Material Science, University of Connecticut, Storrs, CT.

The study of charge transport in Alq_3 in the presence of traps has been carried out with the help of a unipolar model. The model is constructed based on an exponential distribution of traps extending from the LUMO into the forbidden gap. The data appears to demonstrate a transition from trap-mediated to space charge-limited transport as predicted by the electron only model. In the devices we prepared, this transition shifts to higher currents based on the number of holes available to Alq_3, possibly due to depletion of a fraction of the trapped electrons by recombination. The model is also used to predict the J-V characteristics of the device based on the generation of trap states in Alq_3 due to degradation reactions. This has been acheived by adding a narrow gaussian band of impurity traps to the existing exponential and re-solving the governing equations. Thus, by means of the model we can predict the current-voltage behavior of these devices and simulate the different processes occurring in the device as evidenced by the J-V data.

3:30 PM *JJ4.6
MATERIAL ASPECTS OF TRIPLET ORGANIC LIGHT EMITTING DEVICES. Yoshiharu Sato, Shouko Ichinosawa, Masayo Fugono and Hideki Sato, Mitsubishi Chemical Corp., Yokohama Research Center, Yokohama, JAPAN.

Organic LED based on electrophosphorescence employs a host-guest system combined with hole-blocking layer, leading to a device structure: ITO/buffer/hole transport layer/emitting layer/hole-blocking layer/electron transport layer/cathode. We investigate the dependence of device characteristics on host materials and dopants of emitting layer, and hole-blocking materials. As a host material of emitting layer, new type of carbazole-containing compounds are examined in terms of energy transfer. Co-doping approach is examined to study the energy transfer between dopants (triplet-singlet and triplet-triplet). Hole-blocking layer is essentially important to confine excited triplet species within the emitting layer, which has been already observed for red- or blue-emitting devices. Energy level of the materials used for triplet OLED will be described in this paper.

4:00 PM JJ4.7
EXTRACTION CURRENT TRANSIENTS: A NEW METHOD TO STUDY CHARGE CARRIER TRANSPORT IN ORGANIC THIN FILMS. G. Juška[1], K. Arlauskas[1], M. Viliunas[1], K. Genevicius[1], R. Österbacka[2] and H. Stubb[2]. [1]Dept. of Solid State Electronics, Vilnius University Lithuania. [2]Dept. of Physics, Åbo Akademi University, FINLAND.

We use a novel method, charge extraction in a linearly increasing voltage (CELIV) [G. Juška et al, PRL 84, 4946 (2000)], to study the charge carrier transport in organic thin films. The advantage of this method is not only the simplicity but also possibility to measure more conductive materials, compared to traditional time-of-flight measurements. By modeling we found that the method enables us to estimate the nature of charge carrier mobility; whether it is caused by mobility dependence on time (stochastic transport), micro-mobility dependence on electric field or whether it is due to the electric field stimulated retrapping of charge carriers. We found that the hole mobility in thin films of poly(p-phenylenevinylene) depends on both micromobility dependence on electric field and stochastic transport, while in regioregular poly(3-hexylthiophene) retrapping stimulated by the electric field is responsible for the observed mobility.

4:15 PM JJ4.8
STRUCTURAL CHANGES IN ORGANIC LIGHT EMITTING DIODES DURING DEVICE DEGRADATION. Dmitry Kolosov, Mark Thompson, Univ of Southern California, Dept of Chemistry, Los Angeles, CA; Douglas English, Paul Barbara, Univ of Texas, Dept of Chemistry, Austin, TX; Vladimir Bulovic, Stephen Forrest, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ.

We present degradation studies on tris-(8-hydroxyquinoline)

aluminum (Alq_3)-based transparent organic light emitting devices (TOLEDs). The device structure was ITO/100Å CuPC/500Å NPD/500Å Alq_3/100Å Mg:Ag/400Å ITO. The devices were not encapsulated and were investigated under room ambient conditions. Spatially correlated topological and optical properties of the TOLEDs are monitored in real time via electroluminescence, photoluminescence, and transmission microscopy in conjunction with atomic force microscopy. The AFM cantilever was observed from below the transparent device, making it straightforward to spatially correlate the optical and AFM images. Degradation processes were examined with and without applied bias. In case when bias was applied, a brightness of 100 cd/m^2 was used. Formation and growth of dark areas are the main reason for TOLED failure under room ambient. AFM images of a region of the device with a growing dark spot show that the cathode surfaces remain uniform and defect free throughout the formation of darks areas. It is shown that formation and growth of electroluminescence dark spots in the devices are field independent and follow at least two different mechanisms, one of which likely involves delamination of device layers. The device areas, which lose their electroluminescence properties, were observed to keep their luminescent Alq_3 layer intact (measured by photoluminescence), unless bias is applied to the device for a long period of time (over 24 hours). Having devices under bias for an extended period destroys both the cathode and Alq_3 layers at centers of the dark electroluminescence spots. As the electroluminescence dark spots grow larger photoluminescence dark spots develop in the centers of the electroluminescence dark spots. The cathode surface above photoluminescence dark spot is heavily damaged.

4:30 PM JJ4.9
STRUCTURE AND MOLECULAR UNDERSTANDING OF THE RAPID GROWTH OF ZINC-BISQUINOLINE SELF-ASSEMBLED OLED'S. J. Mwaura, K. Ray, D.L. Thomsen, T. Phely-Bobin, R. Tipnis, M. Mathai, F. Papadimitrakopoulos, Department of Chemistry, Polymer Program, Nanomaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT.

The layer-by-layer metalorganic assembly of zinc precursors with 8,8'dihydroxy 5,5'-bisquinoline (bisquinoline) have shown considerable potential in producing insoluble and intractable structures, with controllable supramolecular architecture, suitable for semiconducting applications. In this paper we discuss the molecular mechanism that explains the structure and the controllable rapid growth of this layer-by-layer assembly with each layer thickness as high as 4 repeat units. Utilizing carefully engineered substrates, we demonstrated a novel phenomenon associated with the zinc-precursor, and in particular a certain fraction of it, which is labile. The accelerated growth observed is presently explained via a secondary self-assembly process of labile zinc precursors stabilized within cavities formed in the primary structure. We also showed that increasing the order within these assemblies has led to decrease in photoluminescence efficiency. The ability to form ordered as well as disordered assemblies is utilized to produce efficient multilayer light emitting diodes (LEDs) with increased efficiency and stability.

4:45 PM JJ4.10
MONOLAYER DIODES BASED ON INTERFACIAL PROPERTIES OF SELF-ASSEMBLED SYSTEMS. DeQuan Li, Department of Chemistry and Materials Research Center, Washington State University, Pullman, WA; Lin Song Li and Quanxi Jia, Los Alamos National Laboratory (MST-STC), Los Alamos, NM.

We present here a new class of rectifying devices based on self-assembled monolayer of functional organic molecules. Typical device structures are semiconductor/organic monolyaer/metal or metal oxide/organic monolayer/ metal. We found that an organic naonometer thick monolayer can dramatically alter the device properties while incorporated at the interfacial region. The current-voltage relationship (I-V) and turn-on voltage are functions of molecular and electronic structures of the monolayer. In addition, Kelvin probe was used to measure the surface potential change as a function of mono- or multi- layer growth. A single monolayer can change the surface potential as much as 500 mV and hence establishing an intrinsic electrical field functioning as a molecular diode. X-ray reflectometry and surface-FTIR were also used to characterize the surface bound molecular layers.

SESSION JJ5: POSTER SESSION
Chair: Neil C. Greenham
Tuesday Evening, November 28, 2000
8:00 PM
Exhibition Hall D (Hynes)

JJ5.1
THE CURRENT-VOLTAGE DEPENDENCE OF NOMINALLY UNDOPED THIN CONJUGATED POLYMER FILMS. José A. Freire, Marcos G.E. da Luz, Ivo A. Hummelgen, Depto de Física, Univ Fed do Paraná, Curitiba, PR BRAZIL.

The charge transport in conjugated polymer films sandwiched between metalic electrodes, a typical configuration of organic light-emitting devices, is described by means of a one dimensional master equation where the hopping rates are given by thermally activated jumps over barriers separating trapping sites of same energy. An applied electric field along the chain reduces the barrier height leading to a field depedent mobility, $\mu(E) \approx \sinh(E)/E$. We derive exactly the current-voltage characteristics of such a system assuming that the injected carriers generate space charge effects inside the polymer. We find an excellent agreement with the experimental data for different types of conjugated materials and compare our model with others that predict $\exp(\sqrt{E})$ for the field dependence of the mobility, discussing the essencial differences between them.

JJ5.2
RAMAN SCATTERING AND OPTICAL ABSORPTION SPECTROSCOPY OF NANOPOLYACETYLENE. Valerii Kobryanskii, Institute of Chemical Physics RAS, Moscow, RUSSIA.

It was shown, that the polymerization of acetylene on a catalytic system, based on binuclear rhenium complexes, in solution of saturated polymers leads to soluble compositions containing nanoparticles of polyacetylene (PA) with low content of conformational and chemical defects. This material was referred to as nanopolyacetylene (NPA). In contrast to the known PA modifications, compositions of trans NPA are extremely stable, could be prepared as solutions, films and plates, and exhibit a number of unique optical properties. Optical absorption spectra of cis and trans NPA forms show well-defined vibronic structure in the absorption bands and a marked narrowing of the absorption bands, compared to known PA modifications. It was demonstrated that the absorption spectrum of trans NPA is reversibly change when subjected to change in radiation, pressure and temperature. The thermochromic properties of trans NPA in solution are most striking. Firstly, upon temperature decrease, the red shift of absorption band with a thermochromic coefficient equal 0.45 meV/K is observed. Secondly, the temperature change results in change of trans NPA spectrum vibronic structure. At low temperatures four vibronic maximums are clear seen, while in room temperature only three vibronic maximums are observed. It was demonstrated that the Raman spectrum of trans NPA in solution also changed dramatically with temperature. Firstly, upon the temperature decrease, the red shifts of the of the fundamentals of the polyene chain are observed. Secondly, with a decrease in temperature, the lineshape of C=C stretching band changes leading to the appearance of the low-frequency shoulder. It was assumed, that the high mobility of the ground state configuration of polyene chain is responsible for temperature evolution of Raman scattering and optical absorption spectra of trans NPA.

JJ5.3
Abstract Withdrawn.

JJ5.4
FLUORESCENT INTERCHAIN AGGREGATE FORMATION IN POLY (2-ACETOXY-P-PHENYLENE VINYLENE). Marcelo Aguiar and Leni Akcelrud, Departamento de Quimica, Universidade Federal do Parana, Curitiba, BRAZIL; L.O. Peres, Instituto de Quimica de Sao Carlos, Universidade de Sao Paulo, Sao Carlos, BRAZIL; J. Gruber, Instituto de Quimica, Universidade de Sao Paulo, Sao Paulo, BRAZIL; Meire C. Fugihara and Ivo A. Hammelgen, Departamento de Fisica, Universidade Federal do Parana, Curitiba, BRAZIL.

The participation of excimers and/of aggregates as emitting units in PPV and some derivatives has been previously demonstrated. In this contribution the presence of aggregates in the emission of another PPV derivative, poly(2-acetoxy-p-phenylene vinylene), obtained electrochemically has been demonstrated through fluorescence investigations. Substantial changes take place when concentration of the solution is increased . When excited at 320 nm, a peak centered at 450 nm is the main emission for low concentrations. A red-shifted emission is observed at higher concentrations, where the main emission is centered at 550 nm. We associate the dilute spectra to the emission of the singlet excited state of the single chain or isolated chromophore (intrachain exciton) and the red shifted, structureless emission of the higher concentration solution or solid film as originated from associated states like excimers or aggregates (interchain excitons). Various degrees of association can be formed with different characteristic peak maxima. The solid state emission is dominated by aggregate fluorescence and this fact is of fundamental importance in the performance of optoelectronic devices made with this polymer, like light-emitting diodes.

JJ5.5
SPECTROELECTROCHEMICAL RAMAN STUDY OF TWO α, α' -END-CAPPED SEXITHIOPHENES AS SOLID FILMS. THE EFFECT OF THE INTRODUCTION OF A POLARISABLE SULFUR ATOM IN THE SIDE CHAIN. J. Casado, Dept. de Ingeniería Química, Química Física y Química Orgánica, Universidad de Huelva, SPAIN; H.E. Katz, AT&T Bell Laboratories, Murray Hill, NJ; V. Hernández and J.T. López Navarrete, Dpt. Química Física, Universidad de Málaga, SPAIN.

Oligothiohene compounds have been used as active materials in electronic and electro-optical devices (FET's and LED's). Organic transistors with active materials consisting of two sexithiophenes with α, α' positions substituted with *n*-thiohexyl and *n*-hexyl alkyl side chains have been made by Katz et al. The technological properties of these devices depend on the chemical forms involved on the switched on-off states of the molecular substrate. Electrochemistry let us gain knowledge about the oxidized-reduced chemical species, stability or reversibility of the switched on-off processes. On the other hand, Raman spectrocopy is a powerful tool to study the electronic nature of charged defect types present in the active material which determine the polarizability and electronic movility in the FET or the exciton recombination process in the LED. In this scenario, we will study the electrochemical properties of two sexithiophenes as solid films. Simultaneously, we will record the Raman spectra at selected anodic potentials in order to analyse the active species in the oligothiophenes. The most relevant chemical difference among the two oligothiophenes is the presence of a S atom between the π-conjugated system and the alkyl side chains. We will interpret how the introduction of a highly polarisable atom as S affects the electronic structure of the defect. These elemental studies when combined with the engineering ones are crucial to elucidate the microscopic mechanisms responsible for the peculiar properties of thiophene-based materials.

JJ5.6
VIBRATIONAL ANALYSIS AT INTERFACES IN OLEDs. P. He, C.S. Lee, S.T. Lee, City University of Hong Kong, Center of Super-Diamond and Advanced Films (COSDAF) & Department of Physics and Materials Science, Hong Kong, CHINA.

Organic light-emitting devices (OLEDs) have potential application for flat panel displays. Typically, a number of interfaces exists in an OLED. The interaction between the electrode materials and organic films is critical in determining the device performance. Therefore, a comprehensive understanding of the nature of the interface in OLEDs is of great importance. We have recently shown that high-resolution electron-energy-loss spectroscopy (HREELS) can be a very powerful tool for investigating the interactions at the interfaces in OLEDs. Here we report new HREELS measurements of interfaces in OLEDs. We started from the ITO surface, and found that increase in work function of oxygen-plasma treated ITO was correlated with the removal of the CHx group and oxidation of the ITO surface by the oxygen-plasma treatment. HREELS measurements at the NPB/ITO interface showed a strong vibrational coupling between ITO phonon and NPB-derived loss peak at about 71 meV. The HREELS spectra collected at the metal/Alq_3 interface, especially Mg/Alq_3, showed a strong interaction between metal and Alq_3.

JJ5.7
WORK FUNCTION MODIFICATION AND SURFACE CHEMISTRY OF INDIUM TIN OXIDE WITH ORGANOSILANE SELF ASSEMBLED MONOLAYERS. John A. Chaney, Freresheteh Farzad, Naval Research Lab, Geo-Centers, Inc.; Charles S. Dulcey, Ranganathan Shashidar, Center for Biomolecular Science and Engineering; Pehr E. Pehrsson, Gas Phase Surface Dynamics Section, Naval Research Laboratory, Washington, DC.

Attachment of organosilane SAMs with monomers having different dipole magnitude and direction may permit control of the work function (Φ) of indium tin oxide (ITO) substrates used in OLEDs. However, reliable measurement of $\Delta\Phi$ requires reproducible control of the environmental conditions. In this work, ITO substrates were treated with SAMs having different head and attachment groups and then inserted into an ultra high vacuum (UHV) chamber. The relative effects of head vs. tail groups of specific SAM monomers will be discussed with regard to work function modification. The SAM/ITO work function was measured using an in-vacuo Kelvin probe calibrated with a graphite standard. Surface chemistry was probed by high resolution electron energy loss spectroscopy (HREELS), and electronic structure was investigated by energy loss spectroscopy (ELS). The SAM-modified surfaces usually had lower work functions (Φ = 4.8-5.3 eV), than bare, oxygen-plasma treated ITO (Φ = 5.3 eV). The SAM monomers had either one or three Si-OCH_2CH_3 units for attachment to the ITO surface. Trifunctional SAMs gave higher Φ values than monofunctional SAMs. The HREELS of monofunctional SAM/ITO showed structure which may be attributable to bending modes. These modes were more intense than on the trifunctional counterpart, possibly due to tighter binding of the latter with ITO. Most SAM modified surfaces showed significant deviation in Φ with time and temperature (up to 200°C), suggesting that adsorption of ambient gasses, even in UHV, affects the SAM/ITO system. However, the work function of some SAMs with hydrophobic head groups was apparently unaffected by adsorption. Differences in the band edge transitions of clean ITO vs. SAM/ITO indicate electronic interactions between the SAM and substrate.

JJ5.8
POLYMERIC NANOSCALE ALL-SOLID STATE BATTERY. Steven E. Bullock, Peter Kofinas, University of Maryland, Department of Materials and Nuclear Engineering, College Park, MD.

The advent of polymer electrolytes has provided a promising route to an all solid state polymer battery. Such a battery would have greater safety, without potential discharge of liquid or gel electrolyte. Current battery configurations typically involve a metal anode, a solvent-plasticized polyelectrolyte, such as poly (ethylene oxide) (PEO), and a composite cathode. We have synthesized an A/B/C triblock copolymer for use in all-solid state nanoscale polymer lithium batteries. The copolymer was derived using Grubbs' catalyst of narrow polydispersity and is tolerant of functional groups. Self-assembly of block copolymers provides nanodomains whose morphology can be controlled. These domains then act as a template for the formation of nanoclusters containing metals and inorganic moieties. The polymeric battery was synthesized with an anode, electrolyte, and cathode by forming the A/B/C triblock whose phase separation forms lamellar domains. These nanodomains contain lithium metal, a ROMP derivative of PEO and spinel phase $LiMn_2O_4$ as the anode, electrolyte and cathode material, respectively. The first block contains the lithium metal, and provides the source for the electrochemical reaction to begin. The second block is PEO derived from an unsaturated crown ether, and is used for its high ionic conductivity. The third block contains $LiMn_2O_4$, which is currently being investigated as a potential cathode material because of its low toxicity and ease of preparation. Calculations of the battery power indicate the potential for 5.148 mAh per gram of polymer. The nanometer size of the domains in the battery allow for use in unique applications in microelectronics.
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JJ5.9
OPTICAL PROPERTIES OF A NOVEL DERIVATIVE OF 2,6-LINKED QUINQUEPYRIDINE. Y.J. Fu, T.K.S. Wong, B. Srinivasa, H.X. Zhang, Division of Microelectronics, School of Electrical & Electronic Engineering, Nanyang Technological University, SINGAPORE; G.M. Wang, X. Hu, Division of Materials Engineering, School of Applied Science, Nanyang Technological University, SINGAPORE; H. Yuan, Z.S. Gao, State Key Lab of Crystal Materials, Shandong University, Jinan, CHINA.

Molecular organic dyes, chelate metal complexes, and polymers organic materials are the three groups of luminescent materials for organic electroluminescent devices. As the pyridine based counterparts of poly(para-phenylene) (PPP), which is a typical EL polymer with a blue color, both 2,5- linked poly(parapyridine)(PPy), and 5,5'- linked poly(2,2'-bipyridine) have been extensively studied. Although 2,6- linked oligopyridines are excellent chelating ligands for transition and rare earth metals, their optical properties have not been well studied. Until now, only the optical properties of 2,6-substituted pyridine, 2,2'-bipyridine and 2,2':6',2"-terpyridine have been studied together with some of their derivatives and chelate complexes. In this paper, 6,6""-Dimethyl-4, 4"'-diphenyl-2,2':6',2":6", 2"':6"', 2""-quinquepyridine (Dmdpqpy), a derivative of quinquepyridine, originally synthesized to study its supramolecular self-assembly into helical conformation under the direction of metal ions, was found to show strong photoluminescence both in powder and solution state. In pure powder state, its emission peaks change from 510 to 550nm with excitation wavelength change from 355 to 480nm. Powder samples mixed with KBr have two peaks, one at 366nm and the other at 553nm. Its solution in chloroform emits at 358 under the excitation wavelength of 340nm, whereas the solution in acetic acid emits at 400nm with an excitation wavelength of 377nm. Films fabricated by vaccum evaporation emit at 530nm. Films of PMMA using dmdpqpy as dopant emit at 360nm similar to that in chloroform solution. Thermal analysis studies indicate that the material is stable enough that it has no weight loss before the temperature is higher than 300°C. Also carried out are preliminary electroluminescent studies. dmdpqpy is showed to be a promising EL material both as emitter and as carrier transporter. Devices ITO—dmdpqpy—Al do not emit although current was observed prominently. Devices ITO|PVK|dmdpqpy|Al show emissions both from PVK and dmdpqpy.

JJ5.10
POLYMER FILMS WITH PHOTORESPONSIVE IONIC

CONDUCTIVITY. Didier Delabouglise, Isabelle Decker, Laura Cecchetto, Chrystelle Caix-Cécillon, Jean-Pierre Petit, David Djurado†, Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces, St Martin d'Hères, FRANCE. †Laboratoire de Spectrométrie Physique, St Martin d'Hères, FRANCE.

The studied polymer films are made of a mix of polyethyleneoxide of high molecular mass, of lithium perchlorate and of short PEO chains end-grafted by azobenzene groups. Their ionic conductivity - as measured by impedance spectroscopy increases by 30% within 1 mn under UV light illumination. A 50% increase is observed after 2 mn and saturation begins after 5 mn when reaching a 70% increase. The conductivity decreases rapidly following exactly inverse kinetics, after switching off the UV lamp [1]. Diffraction studies show clearly that this conductivity increase is linked to the melting of a crystalline phase due to the trans-cis isomerism of azobenzene groups. So a new amount of previously immobilized ionic species contributes to the overall electrical conductivity. When light is switch off rapid crystallization occurs which fix again a part of the ionic species. Such high optically induced modulation of appreciable ionic conductivity represents a new and promising research field.
[1] Isabelle Decker, Jean-Pierre Petit, Didier Delabouglise, J. Chem. Soc. Chem. Commun. 1997, 833.

JJ5.11
ENERGY LEVEL ALIGNMENT OF ORGANIC THIN FILMS ON THE LAYERED MATERIALS TIN SULFIDE AND HIGHLY ORIENTED PYROLYTIC GRAPHITE. P.G. Schroeder, C.B. France, B.A. Parkinson, Colorado State University, Dept of Chemistry, Fort Collins, CO; R. Schlaf, University of South Florida, Center for Microelectronics Research, Electrical Engineering Dept., Tampa, FL.

Thin films of the organic materials *p*-sexiphenyl (6P), *p*-quaterphenyl (4P), and coronene were grown epitaxially by vapor deposition on the chemically inert layered materials highly oriented pyrolytic graphite (HOPG) and SnS_2. Each growth step was characterized *in situ* using a combination of x-ray and ultraviolet photoemission spectroscopies (XPS,UPS). The shifts of the XPS peaks directly correspond to the magnitude of the band bending in the material since the core level binding energies are sensitive only to the induced charges in the space charge region at the interface. The band bending shifts determined by XPS were incorporated into the frontier orbital alignment measured by UPS, which results in a more correct portrayal of the electronic structure of the heterointerface than UPS alone. The work function of HOPG (Φ = 4.6 eV) is comparable to that of the organic layers while that of SnS_2 (Φ = 5.45 eV) is substantially different. Since band bending occurs at interfaces where the two materials have different work functions, we can use these systems for investigating the extent of band bending. The chemical inertness of the layered substrates provided model systems for studying the phenomena of band bending and interface dipoles without the interference of surface roughness and interfacial chemical reactions.

JJ5.12
CONJUGATED POLYMER THIN FILM TRANSISTORS CONSTRUCTED USING OHMIC AND SCHOTTKY SOURCE/ DRAIN CONTACTS. Giles Lloyd, William Eccleston, Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool, UNITED KINGDOM.

Measurements and theory are presented for accumulation mode P3AT TFTs with Schottky and ohmic contacts. The polymer has been allowed to turn p type through exposure to air. Sample characteristics for gold contact TFTs are presented. Mobility values are 0.2 cm^2/Vs and are comparable to the best reported. Using Schottky contacts as the source and drain can reduce off currents since in the p type polymer depletion layers are much reduced in size. The presence, however, of Schottky depletion region changes the mode of operation. A model is presented to describe the sub-threshold and gradual channel regions. Devices constructed using titanium show good agreement with the model. Transconductance for these devices is reduced when compared to ohmic contact devices with calculated mobilities of 0.01 cm^2/Vs. Much smaller channel lengths are, however, possible in this technology. Off currents are found to be completely independent of gate voltage indicating good control of the off current by the Schottky junctions. Little or no gate modulation has been observed, to date, for aluminium and chromium contact devices.

JJ5.13
LIGHT EMISSION AND POST-ASSEMBLY PROCESSING OF PROGRAMMED ELECTROSTATIC ASSEMBLIES OF CONJUGATED POLYMERS. Myunghwan Kim, Hongyeul Sung, James E. Whitten, Daniel J. Sandman, Univ of Massachusetts Lowell, Dept of Chemistry, Cter for Adv Matls, Lowell, MA.

Conjugated polyelectrolytes which have carboxylic side groups, were processed to programmed electrostatic assemblies with poly (diallyldimethylammonium chloride) - PDADMAC, and a polysaccharide, chitosan as cations. These assemblies were further processed with aqueous or vapor acid and base treatment (Post-Assembly-Processing, PAP). After Post-Assembly-Processing, emission spectra showed enhanced intensity and different maxima compared to those of original assemblies. In addition, achiral conjugated polymers assembled with chitosan showed induced circular dichroism (CD) by means of PAP or different assembly procedures. CD, enhanced emission intensity, and shifts of emission spectra observed via post-assembly-processing are discussed in terms of polyelectrolyte complex effects. Additional characterization of the polyelectrolyte assemblies involves UV and X-ray photoelectron spectroscopy (UPS, XPS) and other techniques. This assembly methodology will be discussed as a novel gateway to light emission devices.

JJ5.14
SYNTHESIS AND OPTOELECTRONIC PROPERTIES OF POLY(PHENYLENEVINYLENE)S CONTAINING TRIPHENYLAMINE UNITS. Minoru Soma, Yong-Jin Pu, Eishun Tsuchida, Hiroyuki Nishide, Department of Polymer Chemistry, Waseda University, Tokyo, JAPAN.

Poly(phenylenevinylene) derivatives involving triphenylamine unit in the main chain as a hole transporting part, poly(4-methyl(or methoxy)triphenylamine-*alt*-*p*(or *m*)-phenylenevinylene)s, were synthesized by Wittig condensation of 4-methyl(or methoxy)-4', 4"-diformyltriphenylamine and *p*(or it m)-xylene-bis(diethyl-phosphonate). The polymers showed a high T_g and thermal stability similar to the previously reported hole-transporting materials, and poly(methyltriphenylamine-*alt*-*p*-phenylenevinylene) fluoresced a strong green color with a quantum efficiency of 50% for its chloroform solution. Cyclic voltammetry showed a relatively low ionization potential (5.18 – 5.44 eV) of the polymers. These results suggest that the polymers satisfy the requisites of polymer materials for a single LED. Poly(phenylenevinylene) derivatives involving triphenylamine unit in the side chain was also prepared.

JJ5.15
POLY(PHENYLENEVINYLENE)S CONTAINING TRIPHENYLAMINE UNITS: THEIR APPLICATION TO ORGANIC LIGHT EMITTING DIODES. Yong-Jin Pu, Minoru Soma, Eishun Tsuchida, Hiroyuki Nishide, Department of Polymer Chemistry, Waseda University, Tokyo, JAPAN; Satoshi Shirai, Junji Kido, Graduate School of Science and Engineering, Yamagata University, Yonezawa, Yamagata, JAPAN.

We synthesized PPV derivatives, poly(4-methyl(or methoxy)triphenylamine-*alt*-*p*(or *m*)-phenylenevinylene)s, involving a triphenylamine unit in the main chain as a hole transporting part. Single layer devices fabricated as ITO/Polymer/Ca/Al, strongly emitted bright blue or green light. The device composed of *p*-PPV involving methyltriphenylamine showed the best electroluminescent property. Its maximum luminance exceeded 880 cd/m^2 at 11 V and its turn on voltage was ca. 3 V. The external quantum efficiency was 0.054%. These results suggest that the polymers could be a practical candidate for single layer LEDs. More balanced charge injection will be necessary to improve the efficiency peformance.

JJ5.16
SYNTHESIS AND CHARACTERIZATION OF NEW LUMINESCENT POLYMERS. Ik-Bum Kim, ZoHong Tsai, Monica A. Rixman, Dorothy Wu and Daniel J. Sandman, University of Massachusetts-Lowell, Department of Chemistry, Center for Advanced Materials, Lowell, MA.

This work presents the synthesis and characterization of a new class of conjugated polymers from dicyanoalkenes and dicyanoarenes, such as 2-benzylidene-4,5-dicyano-1,3-dithiole, via the use of common sugar reagents in solvents that are water miscible. A new luminescent polymer from p-(tricyanovinyl)N,N-dimethylaniline was synthesized via a sugar reagent in methanol. Structures are proposed for the polymer based on 1H and 13C NMR, infrared, fluorescence, and UV-vis spectrum and other techniques. The gel permeation chromatographic analysis showed that the polymers have high molecular weight and narrow polydispersity. We present the optical and electronic properties of new conjugated iminopyrroline polymers. It is found that the polymers have strong photoluminescence. Other properties are under investigation.

JJ5.17
THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF A URETHANE-SUBSTITUTED POLYTHIOPHENE WITH ELECTROLUMINESCENCE APPLICATIONS. Gina J. Herrera, J.E. Whitten, The Dept. of Chemistry and Center for Advanced Materials, The University of Massachusetts Lowell, Lowell, MA.

The fabrication of organic light emitting diodes (OLEDs) made by sandwiching a semiconducting conjugated polymer between a hole-injecting and an electron-injecting material is an intense area of research. Interest in these devices stems from their potential processing advantages for high-area, flexible displays. These devices are approaching commercialization, but their lifetimes often limit performance. In this study, the thermal and photochemical decomposition of spin-cast films of poly[2(3-thienyl)ethanol n-butoxycarbonylmethylurethane], a polythiophene having a hydrogen bond-forming urethane side chain, has been investigated. This polymer has been shown to be electroluminescent and to emit light peaked at approximately 580 nm. Ultraviolet/visible spectroscopy and x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) have been used to study changes that occur in the polymer films. Heating in vacuum and in the presence of oxygen leads to the onset of polymer decomposition between 300 and 400 degrees Celsius, with XPS indicating decomposition of the urethane side chain. Changes in the polymer surface from simultaneous exposure to light in the wavelength range of the electroluminescence and to oxygen have also been investigated by photoelectron spectroscopy and comparison has been made to failed electroluminescent devices.

JJ5.18
PREDICTION OF CHARGE TRANSPORT PROPERTIES OF MOLECULAR MATERIALS BY AB INITIO MOLECULAR ORBITAL CALCULATIONS. Wataru Sotoyama, Tomoaki Hayano, Hiroyuki Sato, Azuma Matsuura, Toshiaki Narusawa, Fujitsu Laboratories Ltd, Atsugi, Kanagawa, JAPAN.

Molecular orbital (MO) calculations to predict the major carrier (hole or electron) of the charge transport process in a molecular material have been investigated. The difference between hole and electron mobilities in a molecular material is considered to arise from the difference between the activation energies of hole and electron hopping in a pair of the molecules. According to small polaron theory, these activation energies are related to the geometry relaxation energies caused by the difference between the equilibrium geometies of the neutral and ionized molecule. The optimized geometries and geometry relaxation energies of each state (neutral, cation, and anion) of molecules are obtained by ab initio MO calculations (RHF/3-21G level of theory for neutral molecules, ROHF/3-21G level of theory for cations and anions). The activation energy of the charge hopping for each carrier (hole or electron) is calculated by using the geometry relaxation energies for neutral and ionized states of a molecule. The major carrier of the charge transport process in the molecular material is predicted as the one with smaller calculated activation energies. The activation energies for eight molecules were calculated. The molecules are classified experimentally as hole transport materials: N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenylyl]-4,4'-diamine (TPD), 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine (MTDATA), and N-methylcarbazole, and electron transport materials: tris(8-hydroxyquinolinato)aluminum (Alq), bis(10-hydroxybenzo[h] quino- linato)beryllium (Bebq), 2-(4-biphenylyl)-5- (4-tert-buthyl-phenyl)-1,3,4-oxadiazole (PBD), 3-(4-biphenylyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (TAZ), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine). The major carriers of the charge transport process predicted by the MO calculations were agreed with the experimentally determined carriers for seven molecules except N-methylcarbazole. These results show the utility of the developed MO calculations.

JJ5.19
NEW TRANSPARENT SUBSTRATE WITH SILICA AEROGEL LAYER FOR SURFACE-EMISSIVE DEVICES. H. Yokogawa, K. Kawano, M. Yokoyama, Matsushita Electric Works, Ltd., Advanced Technology Research Laboratory, Osaka, JAPAN; T. Tsutsui, M. Yahiro, Kyushu Univ, Dept of Applied Science for Electronics and Materials, Fukuoka, JAPAN; Y. Shigesato, Aoyama Gakuin Univ, Dept of Chemistry, Tokyo, JAPAN.

Silica aerogels prepared by sol-gel method with supercritical drying process have transparency and extremely low refractive index equivalent to air. For example, MEW(Matsushita Electric Works, Ltd.)'s hydrophobic silica aerogel modified by trimethylsilyl group has refractive index of 1.030. This extraordinary refractivity is expected to present some new features as optical material. Ordinarily, coupling-out efficiency of surface-emissive light sources has been assumed to be approximately 20%. It is due to the losses organized from internal reflection of emitted light at the air-glass interface and dissipation during wave-guiding propagation within substrates. However, when the material that has low refractive index is inserted between a thin luminescence layer and glass substrate, almost all the light from the luminescence layer can efficiently couples out to air passing through the glass substrate. In this report, we introduce silica aerogel as a low refractive index material to a surface-emissive device, such as the photo-luminescent and electroluminescent device. A silica aerogel layer was fabricated on the glass substrate by spin coating and the photo-luminescence layer was deposited on this aerogel layer. The photo-luminescence intensity through the glass surface by irradiation of ultraviolet rays was measured. The luminance through the silica aerogel layer showed the twice as the glass substrate without the silica aerogel layer. Moreover, we formed a new substrate which contained a transparent electrode on the silica aerogel layer. Using this substrate, we fabricated the organic light-emitting devices (OLEDs) and observed the disappearance of wave-guiding propagation within the glass substrate.

JJ5.20
LIGHT EMITTING ELECTROCHEMICAL CELLS BASED ON POLYFLUORENE. INVESTIGATION OF THE FAILURE MODES. Olivier Stephan, Yann Kervella, Jean-Claude Vial.

A significant new advance in the field of organic light emitting devices has been the discovery of light emitting electrochemical cells. However, although such systems exhibit very interesting properties such as low onset voltages and high quantum efficiency, its short lifetime when compared to the best classical light emitting diodes remains a key problem. We will present preliminary results, based on electrochemical investigations, on the failure modes of electrochemical cells based on polyfluorenes functionnalized by PEO-like segments. As expected, the turn on voltage of the corresponding devices are rather low, close to the electrochemical gap of the polymer. Although turn on speed can be enhanced by increasing the operating voltage, the formation time of the p-n junction is strongly connected to the mobility of the admixed ionic species. On this basis, when using trifluoromethylsulfonyl imide salts, providing large delocalization of the anionic charge in the salt and enhanced ionic conductivity, electroluminescence intensity higher than 10000 Cd/m^2 are reached within few seconds for 5 V applied bias. However for such voltages, lifetimes are very short ranging from 15 minutes to 2 hours. Cyclic voltammetry clearly show that over oxidation or/and over reduction of the polymer occurs leading to destruction of its electronic conductivity. In addition, irreversible reduction of the admixed anions is observed.

JJ5.21
SELF-ORGANIZED SUPRAMOLECULAR STRUCTURES OF POLY(2,5-PYRIDINEDIYL) AND POLY(2,6-PYRIDINEDIYL). Matti Knaapila, Klas Lindfors, Janne Ruokolainen, Pasi Ryytty, Matti Kaivola, Olli Ikkala, Helsinki Univ Tech, Dept of Engineering Physics and Mathematics, Espoo, FINLAND; Mika Torkkeli, Ritva Serimaa, Univ Helsinki, Dept of Physics, Helsinki, FINLAND; Lockhart Horsburgh, Andrew P. Monkman, Univ Durham, Dept of Physics, Durham, UNITED KINGDOM; Wim Bras, Netherlands Organisation for Sci Research (NWO), DUBBLE CRG/ESRF, Grenoble, FRANCE; Gerrit ten Brinke, Univ Groningen, Dept of Polymer Science and Materials Sci Centre, Groningen, THE NETHERLANDS.

Polypyridines are remarkably stable and good charge transport materials having high photoluminescence quantum yield. They allow preparation of efficient light-emitting devices. We have shown that these polymers form self-organized nanoscale structures due to protonation, hydrogen bonding and polar-nonpolar effects combined. Their long period is of order 3 nm (Adv. Mater. 11 (1999) 1206) These procedures are relatively general and result in stable complexes. A selection of such structures is further studied using synchrotron radiation and small angle x-ray scattering method as well as scanning near-field optical microscopy. Their physical properties, phase behaviour and relevant analogies with polyaniline are discussed.

JJ5.22
OPTICAL PROPERTIES OF ORGANIC POLYSILANES IN SiO_2 THIN FILMS PREPARED BY A SOL-GEL METHOD. Shinya Mimura, Hiroyoshi Naito, Osaka Pref Univ., Dept of Physics and Electronics, Osaka, JAPAN; Yoshihiko Kanemitsu, Nara Institute of Science and Technology, Graduate School of Materials Science, Nara, JAPAN; Kimihiro Matsukawa, Hiroshi Inoue, Osaka Municipal Technical Research Institute, Plastics Dept, Osaka, JAPAN.

Organic polysilanes are chainlike polymers with silicon backbone and organic substituent groups, and exhibit a variety of unique and interesting properties, such as strong near ultraviolet optical absorption and photoluminescence (PL) and high hole drift mobility. In this paper, we study the optical properties of organic polysilanes in SiO_2 thin films -polysilane hybrid thin films- to examine new optical properties. The polysilane hybrid materials were prepared from trimethoxysilylpropylmethacrylate-methylphenylsilane block copolymers with a sol-gel method using tetraethoxysilane (TEOS) as a silica matrix. The block copolymers having polysilane segments have been synthesized by photopolymerization of trialkoxysilylpropyl-methacrylate with polymethylphenylsilane (PMPS) as a macro-photoinitiator. We used the polysilane hybrid thin films prepared by spin-coating of the block copolymers (M_n = 10500, M_w =

18200)/TEOS solution. In the optical absorption measurements, the optical absorption spectra of the polysilane hybrid thin films are essentially the same as those of PMPS, indicating that the chemical structures of the polysilane segments embedded in silica matrices are not altered during the synthesis of the block copolymers and the preparation by the sol-gel method. The linear polarization memory of PL is found in the polysilane hybrid thin films. Since such polarization memory has not been observed in PMPS, the interchain energy transfer erasing the polarization memory is considerably suppressed in the hybrid thin films. The degree of the polarization memory is increased with increasing TEOS, suggesting that polysilane chains are homogeneously dispersed in the silica matrix.

JJ5.23
LOW DRIVING VOLTAGE OF ORGANIC LIGHT-EMITTING DIODES USING P-DOPING STARBURST AMINE AS HOLE TRANSPORTER. X. Zhou, A. Nollau, J. Blochwitz, M. Pfeiffer, T. Fritz, and K. Leo Institut für Angewandte Photophysik, Technische Universität Dresden, Dresden, GERMANY.

We investigate the electrical properties and the OLED application of controlledly doped amorphous hole transporters. Thin films of starburst amine, 4,4',4"-tris(N,N-diphenyl-amino) triphenylamine (TDATA), doped by a fully fluorinated form of tetracyano-quinodimethane (F_4-TCNQ), are characterized in situ by temperature dependent conductivity and Seebeck measurements. The conductivity and hole concentration increase with dopant concentration and are many orders of magnitude higher than those of undoped material. Before doping, the conductivity of the thin films is below 10^{-9} S/cm both in vacuum and in air. The room temperature condutivity of the samples increases from $4x10^{-7}$ S/cm to $6x10^{-6}$ S/cm with the molar doping ratio increasing from 1% to 6.8%. OLED devices with the layer sequence ITO/TDATA(200 nm)/Alq_3(67 nm)/LiF(1 nm)/Al were fabricated. At the benchmark luminance of 100 cd/m^2, forward driving voltage and current density are 27.7 V and 14 mA/cm^2, respectively for the undoped device. The driving voltage was strikingly lowered by using a doped TDATA thin film as hole transport layer: for devices with a molar doping ratio of 1.6% in the TDATA, forward driving voltage and current density are 7 V and 27.2 mA/cm^2 , respectively. We conclude that the use of p-doped TDATA thin films with high bulk conductivity and hole concentration reduces the resistance of the devices and leads to a thinner space charge layer which facilitates injection of holes from the ITO anode. For a further improvement of the efficiency, it will be essential to n-dope the electron transport layer to improve the balance of charge injection.

JJ5.24
OPTICALLY INDUCED DYNAMICS OF NON-POLYMERIC ORGANIC FILMS CONTAINING AZOBENZENE CHROMOPHORES. Mi Jeong Kim, Eun-Mi Seo, Yeong-Deuk Shin, Jae-Suk Lee, Dong-Yu Kim, Kwang Ju Institute of Science and Technology, Dept of Materials Science and Engineering, KwangJu, KOREA.

Photofabrication of surface relief gratings on azobenzene-functionalized polymer films has received much attention due to the significance for the potential applications in optical data storage, diffractive optics and nanopatterning. The formation of surface relief gratings has been believed to result from optically induced migration of polymer chains containing azobenzene groups, but the mechanism was not completely understood. Most of surface grating studies were focused on polymeric materials because of the easy film formation using the spin-casting process. In this work, we synthesized low molecular weight tri-isocyanate cyclics containing azobenzenes which form glassy amorphous films upon spin casting. These non-polymeric thin films were capable of forming highly efficient surface grating when exposed to an interference pattern of polarized Ar laser beams at 488 nm. We discuss the grating formation behaviors comparing tri-isocyanate oligomers with polyisocyanate films containing azobenzene groups. The surface grating formation was characterized by monitoring diffraction efficiency using He-Ne laser, optically induced dichroism, and AFM studies.

JJ5.25
PENTACENE FILMS FOR THIN FILM TRANSISTOR APPLICATION. Seong Hyun Kim, Jeong-Ik Lee, Hye Yong Chu, Lee-Mi Do, Taehyoung Zyung, Electronics and Telecommunications Research Institute, Taejon, KOREA.

Organic thin-film transistors were fabricated using organic semiconductor pentacene. Pentacene thin films were thermally evaporated onto the rubbed polyimide insulationg layer. Morphologies and electrical characteristics of the thin films were observed by SEM, XRD, and parameter analyser. The cystal stuctures of the films were also investigated at various heat-treatment temperatures. Finally, the performance of the thin-film transistors were reported.

JJ5.26
CHARGE TRANSPORT IN MEH-PPV. Seong Hyun Kim, Taehyoung Zyung, Hye Yong Chu, Lee-Mi Do, Jeong-Ik Lee, Electronics and Telecommunications Research Institute, Taejon, KOREA.

Polymer light emitting diodes using poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenlenevinylene) (MEH-PPV) were fabricated and impedance spectroscopy was measured. Charge trasoport phenomena in MEH-PPV was discussed using generalized Langevin equation analysis. Voltage dependence of the trasport phenomena was also investigated. The experinatal results were compared with those from other experimetal methods, I-V measurements and equivalent circuit analysis.

JJ5.27
INFLUENCE OF DEVICE CONFIGURATION ON EXTERNAL QUANTUM EFFICIENCY IN ORGANIC LIGHT-EMITTING DEVICES. Masayuki Yahiro and Tetsuo Tsustui Dept of Applied Science for Electronics &Matls, Interdisciplinary Grad School of Engr Sciences, Kyushu Univ, Kasuga, Fukuoka, JAPAN.

One of the most difficult open questions concerning the external quantum efficiency (QE) in organic light-emitting devices (OLEDs) has been on the so-called device coupling-out factor. Based on simple classical optics, a low value of less than 20% has been assumed. On the other hand, some experiments have shown that much higher values should be assumed. In any case, however, a device couple-out factor has been assumed to be independent of detailed device configurations, such as the thickness of organic and ITO layers. In this presentation, we will show the possibility that the device coupling-out factor is largely dependent on detailed device configurations. Our new interpretation well explains the reported experimental facts that QE values can be enhanced by optimizing device configurations. We fabricated conventional double-layer devices, ITO/TPD(50nm)/Alq (L)/MgAg. The thickness of the Alq layer, L, was varied from 25 to 200 nm. Luminance values were determined by using Luminance meter (BM-5A, Topcom). Both relative intensity of emission and emission spectrum were collected by changing viewing angles using a photonic muluti-channel analyzer (PMA-11, Hamamatsu Photonics). True external QE values were calculated using absolute luminance and spatial distribution of emitted light. The external QE values at the same current density were found to depend on the thickness of Alq, the distance between MgAg mirror and emission zone. The origin of large variation of external QEs was attributed to the change of the device coupling-out factor.
This work is supported by the Core Research for Evolutional Science and Technology, Science and Technology Corporation (CREST/JST).

JJ5.28
ENHANCED BLUE LIGHT EMISSION FROM SEXIPHENYL HETEROSTRUCTURE EL DEVICE. Yutaka Ohmori, Takahisa Tsukagawa and Kajii Hirotake, Osaka University, Collaborative Research Center for Advanced Science and Technology, Suita, Osaka, JAPAN.

Enhanced blue electroluminescence (EL) from vapor deposited p-sexiphenyl layer has been investigated utilizing hetero-structure of p-sexiphenyl and carrier transporting layers. EL device consists of an indium-tin oxide (ITO) anode, a hole transporting layer, a p-sexiphenyl emissive layer, an electron transporting layer, and a cathode metal of magnesium containing silver. N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), 8-hydroxyquinoline aluminum (Alq_3) or 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) has been examined for hole transporting or electron transporting layers. Heterostructure device of p-sexiphenyl and TPD hole transporting layer shows the highest performance among these structures, which shows three times stronger emission than that of p-sexiphenyl single layer device. 50 nm-thick p-sexiphenyl and 70 nm-thick TPD device emits blue light centered at 420 nm and the EL intensity reaches as high as 3,500 cd/m^2 at an applied voltage of 10 V, with the efficiency of 2.5 cd/A or 1.2 % of external power efficiency. The highest efficiency in the device reaches as high as 4 cd/A or 2.5 % of at an applied voltage of 6 V. The mechanism of enhanced emission from the p-sexiphenyl heterostructure device has been discussed utilizing energy band diagram of these materials.

JJ5.29
A STUDY OF THE INTERACTION OF ETHYLENEDIOXY-THIOPHENE WITH GOLD AND ITO SURFACES USING PHOTOELECTRON SPECTROSCOPY. J. Birgerson, M. Keil, X. Crispin, M. Lögdlund, W.R. Salaneck, Linkoping University, Dept of Physic and Measurement Technology, Linkoping, SWEDEN.

Poly(3,4-ethylenedioxythiophene), or PEDOT, is commercial polymer, much studied recently in the context of antistatic coatings, rechargeable batteries; polymer based LEDs and much more. In this

work, the interaction of the monomer of PEDOT, ethylenedioxythiophene, or EDOT, with the surfaces of gold and indium tin oxide (IOT) have been studied, using photoelectron spectroscopy and quantum chemical calculations. Films of EDOT have been produced, by vapor deposition onto clean substrates at low temperatures (170K), in UHV. For EDOT deposited onto Au, shifts in the binding energies seen in the C(1s), O(1s) and S(2p) spectra are observed, which depending on the film thickness. The binding energies are different for thick (150) and a thin (monolayer) films on gold substrates. The first monolayer interacts with the surface, while functioning as a surface for adsorption of EDOT overlayers, which remain on the substrate in UHV even at room temperatures. The interaction of EDOT with the gold surface is also seen in the results of quantum chemical calculations carried out in the framework of the density functional theory (DFT). The results of these calculations indicate that the most favorable orientation of the molecules is perpendicular to the surface, with the sulfur atom bonding to the gold surface. For EDOT deposited onto ITO, no interaction was observed. Films deposited at low temperatures evaporated from the substrates while warming up to room temperature.

JJ5.30
ENHANCED ELECTROLUMINESCENCE OF URETHANE CONTAINING PROCESSABLE POLYTHIOPHENE DERIVATIVE BY ADDITION OF DYE MOLECULES. Amarjeet Kaur*, Center for Advanced Materials, University of Massachusetts, Lowell, MA; Mario J. Cazeca, Kethinni G. Chittibabu, Molecular Technologies, Westford, MA; Jayant Kumar, Sukant K. Tripathy, Departments of Physics and Chemistry, Center for Advanced Materials, University of Massachusetts, Lowell, MA. *Permanent Address: Department of Physics, Maitreyi College (Delhi University), Chanakyapuri, New Delhi, INDIA.

Organic electroluminescent (EL) diodes based on fluorescent dyes and conducting polymers have attracted the interest of researchers, mainly because of their emission in the visible region and for application to large area portable flat panel display devices, driven at low voltages. Therefore, for the development of higher efficiency polymer EL diodes the optimal combination of the merits of organic fluorescent dye molecules with that of conjugated polymer is an important approach. We report electroluminescence studies of polymer light emitting diodes (p-LEDs) fabricated with poly[2-(3-thienyl)ethanol n-butoxy carbonylmethyl urethane] (PURET) and its composite with 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H pyran (DCM) dye. These materials have been chosen in view of the fact that PURET exhibits a small overlap between emission and absorption spectra where as DCM has a good efficiency of trapping both electrons as well as holes. Polyaniline has been utilized as hole injecting layer whereas tris-8-hydroxyquinoline-aluminum as electron injecting layer. Enhanced electroluminescence with bright yellow color has been observed in p-LEDs by the addition of dye.

JJ5.31
Abstract Withdrawn.

JJ5.32
SYNTHESIS AND OPTICAL PROPERTIES OF NEW DENDRIMERS BASED ON 6-NITROQUINAZOLINE AND 3,5-DIMERCAPTOBENZYL BLOCK. Hideki Miki, Shiyoshi Yokoyama, Shinro Mashiko, Kansai Advanced Research Center, Nano Technology Section, Kobe, JAPAN.

In the last years, the optical and electrical interests of functional dendrimers is growing up due to their characteristic chemical and physical properties. Novel properties of dendrimers are attributed to both their chemical structure and the three dimensional structure including molecular size, shape and regularity. This work reports on the synthesis and optical properties of a core-shell structured dendrimer,which contains 6-nitroquinazoline as the functional unit and 3,5-dimercaptobenzyl and 3,5-dihydroxybenzyl group as a dendritic unit. In order to protect sulfur atom from the oxidation reaction, 3,5-di-tert-butylbenzyl group was designed as the most outer unit in the dendrimer. Synthesized dendrimers containing sulfur atom are novel, and are interested in their characteristic d-orbital electron property. The chromophore unit used in this study has an electron-transporting property due to its electron-deficient structure. Since large molecular weight dendritic blocks are attached to a chromophore unit, a core-shell structure could be achieved in the synthesized dendrimers. We measured optical property of the core-shell strucured dendrimer, where electronic interaction of cored chromophores was restricted, while chromophore was sensitive to the d-orbital electrons of the dendrimer unit. For the purpose of comparison, the dendrimers modified by 3,5-dihydroxy and 3,5-di-tert-butylbenzyl unit were also synthesized. Details of the synthesis and optical properties of two types of dendrimers will be presented.

JJ5.33
REVERSIBLE THERMOCHROMIC TRANSITION BETWEEN DIFFERENT J-AGGREGATE STATES OF AMPHIPHILIC MEROCYANINE DYE CRSTALLITES. Noritaka Kato, Kentaro Saito, Toshinori Serata, Yoshiaki Uesu, Department of Physics, Waseda University, Tokyo, JAPAN.

Amphiphilic merocyanine dye (MD) forms 2D J-aggregate crystallites on the subphase containing the counter-ion for MD molecules. We found that the MD monolayer exhibit 1st order phase transition accompanying thermochromism when the subphase contains two kinds of ions with different ionic radius. The transition behavior was precisely observed by the multipurpose nonlinear optical microscope, and the drastic morphological change was revealed. For further applications, the airtight cell, where the MD monolayer were bound between the substrate and the binary counter-ion subphase, was developed. The cell exhibited same transition but with long relaxation time.

JJ5.34
A NEW DEVICE OF SOLID STATE LIGHT EMITTING INVOLVING A BINUCLEAR RUTHENIUM COMPLEX. THIN FILM BLEND INCORPORATING 18-CROWN-6 $LICF_3SO_3$. Jean-Claude Lepretre, Frederic Lafolet, Univ J. Fourier, LEOPR, Grenoble, FRANCE; Olivier Stephan, Univ J. Fourier, Spectrometrie-Physique, Grenoble, FRANCE.

Among the electrogenerated chemiluminescence (ECL) of inorganic systems, the tris(2,2′-bipyridine) Ruthenium complex ($Ru(bpy)_3{}^{2}$) has received most interest. Meanwhile, time response and stability versus time remain the main features of such systems. In this context, we will present a new device involving a bis ruthenium complex ($[Ru(bpy)_2(Me\text{-}bpy\text{-}hexyl\text{-}Me\text{-}bpy)Ru(bpy)_2{}^{4}]$) in the presence of an ionic conductor system (18-Crown-6 $LICF_3SO_3$). Whereas, the film do not present electroluminescent properties in the absence of the ionic conductor, the presence of 18-Crown-6 $LICF_3SO_3$ in the film, allows to work at low voltages, close to the electrochemical gap of the material (2.2V). Higher luminescent phenomenon than the regular $Ru(bpy)_3{}^{2}$ complex, with an emission maximum at 630 nm, can be observed at 4V bias. The precharging time can be shortened (to reach few seconds) by a preliminary pulse at 6V. However, in these conditions the light intensity (more than 1000 cd/m^{2}) is decreasing to one half its maximum value after 5 hours the potential was first applied. In addition, at lower voltage bias, higher stability can be obtained (more than 10 hours) in connection with a decrease of the emitting phenomenon. Moreover, regarding the time dependence of current during the light emission, this ECL system seems to be limited by the redox stability of the reduced forms of the bisRu^{II} complex.

JJ5.35
XEROGRAPHIC AND OPTICAL PROPERTIES OF PHTHALOCYANINE CO-DEPOSITED COMPOSITE FILM AND ULTRATHIN MULTILAYERED STRUCTURE PREPARED BY ORGANIC MOLECULAR BEAM DEPOSITION. M.S. Xu, J.B. Xu, Department of Electronic Engineering, The Chinese Univ. of Hong Kong, Shatin, NT Hong Kong, CHINA; M. Wang, D.L. Que, State Key Lab for Silicon Materials, Zhejiang Univ., Hongzhou, PR CHINA.

$(ClInPc/ClAlPcCl)_n$ ultrathin multilayered structures, and co-deposited ClInPc-ClAlPcCl, TiOPc-CuPc, TiOPc-ClInPc and CuPc-ClInPc composite films were prepared under different experimental conditions by high vacuum organic beam deposition technique. The photosensitivity of the co-deposited composite films is much better than that of the single component films. The enhancement of photosensitivity of the co-deposited films is attributed to the efficient photo-induced charge transfer and charge separation among the charge generation materials. Moreover, the photosensitivity of the ultrathin multilayered structures is more than 10 times as good as that of the co-deposited composite films. This observation is probably due to the fact that the ultrafast photo-induced charge transfer and charge separation can be generated from the interfacial potential barrier of the $(ClInPc/ClAlPcCl)_n$ structure and the photogenerated holes can be swept out before the significant fraction recombine with the electrons. UV-visible absorption spectra indicate that the maximum absorption peaks in the Q-band of the co-deposited composite films are shifted relative to that of single component films and the spectral responses are changed. The Q-band absorption of $(ClInPc/ClAlPcCl)_n$ ultrathin multilayered structures are shifted with the change in the number of periods and film thickness and different from that of co-deposited ClInPc-ClAlPcCl film. And the splitting energy of Q-band of $(ClInPc/ClAlPcCl)_n$ is increased up to the maximum value and then decreased with the decrease in the number of periods. The change in optical absorption spectra of the films and structures is most likely to be due to the dipole-dipole and charge transfer interaction among the different molecular assemblies.

JJ5.36
DOPED MOLECULAR FILMS AS STUDIED BY UPS/XPS.
Jan Blochwitz, Andreas Nollau, Martin Pfeiffer, Torsten Fritz, Karl Leo, TU Dresden, Institut fuer Angewandte Photophysik, Dresden, GERMANY; Neal R. Armstrong, Paul A. Lee, Dana M. Alloway, University of Arizona, Dept. of Chemistry, Tucson, AZ.

Former investigations have shown that controlled doping of organic dyes like phthalocyanines (Pc) with strong acceptor molecules like tetra-fluoro-tetra-cyano-quinodimethane (F_4-TCNQ) leads to a strongly increased conductivity and decreased distance between the transport level and the Fermi-level [1]. It was demonstrated that the use of such a doped layer as hole injection and transport layer in an organic LED leads to a strong improvement of the electrical parameters compared to undoped LEDs with the same layer sequence [2]. Here, we present results of the very first investigations of such doped layers with a combined UPS/XPS method in order to study the influence of doping on the energy alignment and the formation of space charge regions at the interface. As a model system we use ZnPc doped with F_4-TCNQ on ITO or Au. The findings clearly show that the distance between the valence states (transport level) and the Fermi-level is much smaller for the doped layers as compared to the undoped. Furthermore, we show that the potential drop across the space charge region at the junction is strongly increased by doping - as it is expected from the classical semiconductor theory of doping. The importance of such doped layers for carrier injection into devices is discussed.
[1] M. Pfeiffer, A. Beyer, T. Fritz, and K. Leo, Appl. Phys. Lett. **73**, 3202 (1998).
[2] J. Blochwitz, M. Pfeiffer, T. Fritz, and K. Leo, Appl. Phys. Lett. **73**, 729 (1998).

SESSION JJ6: INTERFACES
Chair: Antoine Kahn
Wednesday Morning, November 29, 2000
Republic B (Sheraton)

8:30 AM *JJ6.1
SURFACE AND INTERFACE PROPERTIES IN ORGANIC LIGHT-EMITTING DIODES.
S.T. Lee, Center Of Super Diamond and Advanced Films (COSDAF) & Department of Physics and Materials Science City University of Hong Kong, Hong Kong, CHINA.

Device surfaces and interfaces in organic light-emitting diodes have been studied by X-ray photoelectron spectroscopy (XPS), ultra-violet photoemission spectroscopy (UPS), and high-resolution energy loss spectroscopy (HREELS). Our recent results for both metal/organic (molecular and polymeric) and inorganic/organic interfaces are presented, with an emphasis on the fundamental issues critical to the device performance, including stability, charge injection and device efficiency.

9:00 AM JJ6.2
WORK FUNCTION CHANGES AND SURFACE CHEMISTRY OF OXYGEN AND HYDROGEN ON INDIUM TiN OXIDE.
John A. Chaney, Pehr E. Pehrsson, Gas Phase Surface Dynamics Section, Naval Research Laboratory, Washington, DC.

Indium tin oxide (ITO) is used as a transparent semiconducting substrate for organic light emitting diodes. The performance of ITO devices can be improved by modifying the interfacial work function with self-assembled monolayers (SAMs) of organic molecules. However, the respective roles of SAM/ITO surface chemistry in determining the work function are not well understood, due partly to inadequate understanding of ITO surface properties, its interaction with gaseous species, and the physical/electronic changes imposed by these interactions. In this work, the surface physics and chemistry of oxygen plasma treated ITO was investigated under ultra high vacuum conditions. The work function (Φ) of ITO was determined by a vibrating Kelvin probe calibrated with a graphite standard. Sample composition, electronic structure and chemistry were examined by Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), and high resolution electron energy loss spectroscopy (HREELS). Commercial ITO films were heated in-vacuo to remove physisorbed species and then exposed in-situ to oxygen or deuterium activated with a hot metal filament. Oxidation increased the work function from 5.2 to 5.6 eV, but Φ then decayed to ¡5.2 eV, possibly due to oxygen diffusion into the bulk along defects and grain boundaries. The AES oxygen level was stable after oxidation, and the ELS spectrum consistently showed a strong feature at 0.7 eV for oxidized samples. Deuteration visibly metallized the film and sharply reduced the surface oxygen level. The ELS feature simultaneously disappeared, and the work function decreased to 4.6 eV. The HREELS of clean ITO revealed substantial C-H contamination, which persisted after heating to 300°C. Even substantial oxygen treatment did not remove the hydrogen signal, suggesting that C-H permeates the ITO film. Studies of the properties of these ITO surfaces after SAM modification are discussed in a separate presentation.

9:15 AM JJ6.3
p-SEXIPHENYL (6P)/METAL INTERFACES STUDIED BY UPS, MAES AND XPS: CHARGING EFFECT INDUCED BY DEPOSITION OF METAL ATOMS ONTO AN ORGANIC THIN FILM.
H. Ishii, E. Ito, H. Oji, T. Imai, Y. Ouchi, Nagoya Univ, Dept of Chemistry, Graduate School of Science, Nagoya, JAPAN; K. Seki, Nagoya Univ, Research Center for Materials Science, Nagoya, JAPAN.

How energy levels of an organic material and a metal electrode align at their interface is a basic issue for understanding organic electronic devices. So far, we have examined for *organiconmetal* systems, where organic molecules are deposited on metal substrate. However, in real devices, the reverse system, *metalonorganic* is also important. In such system, because deposited metal atoms often penetrate and diffuse in organic film, energy levels observed in electron spectroscopy are not easy to interpret to clarify the energy level alignment at such type of interface. In the present study, we have examined *p*-sexiphenyl (6P)/metal (Au, Mg) interfaces using UV photoemission spectroscopy (UPS), metastable atom electron spectroscopy (MAES), and X-ray photoemission spectroscopy (XPS). In the case of 6P film deposited on the metal, the energy position of the occupied levels of 6P and the vacuum level were almost constant irrespective of the film thickness upto 20 nm, except the initial abrupt lowering of the vacuum level during monolayer-formation. This result indicates flat band behavior of 6P film in this thickness region. On the other hand, in the case of Mg-deposited 6P film, the downward shift of energy levels of 6P was observed. This energy shift is in contrast to the flat band feature observed at 6P on Mg system. At Au on 6P system, no energy shift was observed with very small amount of photon flux (the sample current was typically less than 5pA). With increasing the photon flux, the peaks in the UPS spectrum exhibited energy shift to higher binding energy side. This energy shift can be ascribed to charging of possible Au island cluster formed on 6P film. This result demonstrates that we have to be careful for the interpretation of photoemission data for *metalonorganic* system.

9:30 AM JJ6.4
INTERFACIAL EFFECTS ON OPTICAL, ELECTRICAL AND TRANSPORT PROPERTIES OF TRIS-8-HYDROXYQUINOLINE ORGANIC LIGHT EMITTING DEVICES.
Vincent V. Dinh, Univ of California, Davis at Livermore, Dept of Applied Science, Livermore, CA; Gil R. Delgado, Louis J. Terminello, Howard W. Lee, Boyd Taylor, Tony Van Buuren, Art Nelson, Nicolas Franco, Lawrence Livermore National Laboratory, Livermore, CA; Christoph Bostedt, Univ Hamburg, Dept of Physics, Hamburg, GERMANY.

We present current-voltage (I-V), photoluminescence (PL), photoluminescence excitation (PLE), and electroluminescence measurements for the ITO/PVK/Alq_3/metal structure. In this study, we vary the Alq3 film thickness to isolate the interface effects on the device PL. We also measure the chemistry and bonding structure at the interface using element and chemical state specific synchrotron radiation-based spectroscopy. Our results will be discussed within the context of device performance and lifetime.
Vincent V. Dinh acknowledges a fellowship from Lawrence Livermore National Laboratory. The work is supported by the US-DOE, BES Material Science under contract W-7405-ENG-48, LLNL.

9:45 AM JJ6.5
ENERGY BARRIERS IN ORGANIC LIGHT-EMITTING DIODES DETERMINED BY INTERNAL PHOTOEMISSION.
Philippe Sigaud, Jean-Noël Chazalviel, François Ozanam, CNRS-Ecole Polytechnique, Laboratoire de Physique de la Matière Condensée, Palaiseau, FRANCE; Olivier Stéphan, Université Joseph Fourier, Laboratoire de Spectrométrie Physique, Saint Martin D'Hères, FRANCE.

Internal photoemission has been used to determine the energy barriers for electrode/organic-layer interfaces in organic light-emitting diodes. This method provides a very direct determination of injection barrier by measuring the variation of a photocurrent generated by interface absorption of photons of energy below the absorption threshold of the organic material. The diodes were polymer or small-molecule single-layer structures made from poly-(9-vinylcarbazole) (PVK), poly-(9,9-dihexylfluorene) (PDHF) , tris-(8-hydroxyquinolinate) aluminum (AlQ_3) and N,N'-Bis(3-methylphenyl)-N,N'-diphenyl-benzidine (TPD) with indium-tin-oxide (ITO) or metallic electrodes (Al, Au or Cu). We measured the hole injection barriers for PVK, PDHF and TPD diodes, and the electron injection barriers for AlQ_3 diodes. The internal photoemission yield follows the Fowler theory allowing for a determination of the energy barrier. The resulting energy barriers exhibit a small lowering for increasing internal electric field due to image-force potential. There is an offset of 0.4 to 0.5 eV

between the actual energy barriers for hole injection and the expectations from the difference between the energy levels taken from the literature. Chemical modification and bulk traps cannot experimentaly account for this discrepancy. We conclude that its plausible origins are interface dipole effects or intrinsic uncertainties associated with the electrochemical determination of HOMO levels.

10:30 AM *JJ6.6
THIN INTERFACIAL LAYERS IN ORGANIC-BASED ELECTRONICS. Mats Fahlman, Stina Jönsson, Carl Tengstedt, Linköping Univ, Dept of Science and Technology, Norrköping, SWEDEN; Grzegorz Greczynski, William R. Salaneck, Linköping Univ, Dept of Physics, Linköping, SWEDEN.

The use of (insulating) thin layers between the metal contacts and the molecular/polymer layer(s) has been shown to dramatically improve lifetimes and efficiency in organic-based light emitting devices. The insulating material, most commonly LiF, is deposited as a thin (~5-10≈) layer between the cathode and the polymer layer or as a mixture with the cathode metal, typically Al. Insulating layers (Al_2O_3 or insulating polymers) between the anode and the polymer layer(s) have also been shown to improve performance, as has the use of conducting polymers. The exact nature of these interfaces is not known, however, and significant effort is being invested in studying them. We present here a photoelectron spectroscopy study on the chemical and electronic properties of the Al/CsF/Poly(9,9-dioctyl-fluorene) interface and the results are compared to that of Al/LiF/PFO and Al/PFO. Striking dissimilarities were seen for the interfaces, with dissociation of CsF but not of LiF occurring. The effect of deposition environment on the Al/LiF/PFO interface also was studied. The current-voltage characteristics of PFO model devices with and without such interfacial layers were carried out and compared with the photoelectron spectroscopy results.

11:00 AM JJ6.7
PHOTOEMISSION AND INVERSE PHOTOEMISSION INVESTIGATION OF CuPc AND METAL/CuPc INTERFACES. Li Yan, Yongli Gao, University of Rochester; M.G. Mason, C.W. Tang, Kodak Research Laboratory.

Organic light emitting diodes (OLED) have received considerable attention in recent years because of their scientific and commercial significance. Copper phthalocyanine (CuPc) has become a very important material in OLED device structure engineering. Recently, CuPc, traditionally used as hole transport material in OLED, has been found to improve electron injection when inserted as a buffer layer between the metal cathode and tris(8-hydroxyquinoline) aluminum (Alq_3), the most widely used light emitting material in OLED. To address this new discovery, we have used the combination of X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and inverse photoemission spectroscopy (IPES) to determine the electronic structure of CuPc. The ionization potential, workfunction and the highest occupied molecular orbital (HOMO) of CuPc is determined directly by UPS, while the electron affinity and the lowest unoccupied molecular orbital (LUMO) by IPES. Therefore, the electronic band gap of CuPc is determined experimentally. Furthermore, we have utilized these tools to study the interface formation of metal (Au, Al and Na) and CuPc. Possible charge transfer, dipole formation and energy level bending at the interfaces will be discussed. This information will lead to better understanding of the principle and further improvement in OLED devices.

11:15 AM JJ6.8
THE ROLE OF CsF ON ELECTRON INJECTION INTO A CONJUGATED POLYMER. Pongpun Piromreun, HwanSool Oh, Yulong Shen, George Malliaras, Cornell University, Materials Science, Ithaca, NY; J. Campbell Scott, Phil J. Brock, IBM Research Division, Almaden Research Center, San Jose, CA.

We studied electron injection from Al and Au cathodes into the conjugated polymer MEH-PPV. When a thin CsF layer is inserted between MEH-PPV and Al, a substantial enhancement in electron injection is observed. Insertion of the same layer between MEH-PPV and Au does not have a similar effect, indicating that the enhancement mechanism is specific to CsF and Al. Thin Cs layers enhance electron injection regardless of the cathode metal. A mechanism that explains these observations is proposed.

11:30 AM JJ6.9
INJECTING INTER-LAYERS AND THE BUILT-IN POTENTIAL OF BLUE POLYMER LIGHT-EMITTING DIODES. Thomas M. Brown, Richard H. Friend, Franco Cacialli, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM; Ian S. Millard, Jeremy H. Burroughes, Cambridge Display Technology Ltd, Cambridge, UNITED KINGDOM.

The semiconducting-polymer/injecting-electrode heterojunction plays a crucial part in the operation of organic solid state devices. In polymer light-emitting diodes (LEDs), a common fundamental structure employed is Indium-Tin-Oxide/Polymer/Al. However, in order to fabricate efficient devices, alterations to this basic structure have to be carried out. The insertion of thin layers, between the electrodes and the emitting polymer, has been shown to greatly enhance LED performance, although the physical mechanisms underlying this effect remain unclear. Here, we use electro-absorption measurements of the built-in potential to monitor shifts in the barrier height at the electrode/polymer interface. We demonstrate that the main advantage brought about by inter-layers, such as PEDOT:PSS at the anode and Ca, LiF and CsF at the cathode, is a marked reduction of the barrier to carrier injection. The electro-absorption results also correlate with the electroluminescent characteristics of the LEDs.

11:45 AM JJ6.10
ELECTRONIC STRUCTURE AND ELECTRON TRANSFER DYNAMICS INVOLVING UNOCCUPIED STATES AT ORGANIC/METAL INTERFACES. Hanfu Wang, Gregory Dutton, Xiaoyang Zhu, Department of Chemistry, University of Minnesota, Minneapolis, MN.

It is well recognized that charge injection from metallic electrodes into the molecular layer is a critical step in the operation of organic electronic or optoelectronic devices. Charge injection is a dynamic process involving both occupied and unoccupied electronic states. Unfortunately, due to the lack of suitable experimental techniques, information on interfacial electronic structure and electron dynamics involving unoccupied states has been largely inaccessible in the past. In this presentation, we will demonstrate the successful use of laser two-photon photoemission spectroscopy to probe interfacial electronic structure and electron transport dynamics involving unoccupied states. Using several model systems, including naphthalene, perfluorobenzene, and thiol self-assembled monolayers on Cu (111), we can now start to answer the following questions on charge injection involving unoccupied states: How does a molecular unoccupied state couple to a metal substrate? What is the origin of delocalization for unoccupied molecular states on the metal surface? Are there molecular quantum well states at the interface? Answers to these types of questions are beginning to form the mechanistic framework for our understanding of the charge injection problem.

SESSION JJ7: TRANSISTORS AND PRINTING
Chair: Neil C. Greenham
Wednesday Afternoon, November 29, 2000
Republic B (Sheraton)

1:30 PM *JJ7.1
LARGE AREA, RUBBER STAMPED SHEETS OF ORGANIC ELECTRONICS: ACTIVE MATRIX BACKPLANE CIRCUITRY FOR ELECTRONIC PAPER. John A. Rogers, Kirk Baldwin, Zhenan Bao, Brian Crone, Ananth Dodabalapur, Yen-Yi Lin and V.R. Raju, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Electronic systems that use rugged, lightweight plastics potentially offer attractive characteristics (low cost processing, mechanical flexibility, large area coverage, etc.) that are not easily achieved with established silicon technologies. This talk summarizes work that demonstrates many of these characteristics in a realistic system: organic active matrix backplane circuitry (256 transistors) for large (~6'x6'), mechanically flexible sheets of electronic paper, an emerging type of display. The success of this effort relies on new or improved materials and processing techniques for plastic electronics, including methods for (i) rubber stamping high resolution (~1 microns) circuits with low levels of defects and good registration over large areas, (ii) achieving low leakage with thin dielectrics spin cast surfaces with relief, (iii) constructing high performance organic transistors with robust, bottom contact geometries, (iv) encapsulating these transistors, (v) depositing, in a repeatable way, organic semiconductors with uniform electrical characteristics over large areas, and (vi) low temperature (~100 C) annealing to increase the on/off ratios of the transistors and to improve the uniformity of their characteristics. The sophistication and flexibility of the patterning procedures, the high level of integration on plastic substrates, the large area coverage and the good performance of the transistors are all important features of this effort.

2:00 PM JJ7.2
HIGH ELECTRON AND HOLE MOBILITIES IN PERYLENE SINGLE CRYSTALS. Christian Kloc, J. Hendrik Schön, Theo Siegrist, and Bertram Batlogg; Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Single crystals of organic semiconductor, perylene, have been grown by physical vapor transport in a stream of hydrogen. Multiple sublimation was applied for additional purification in order to prepare

low trap density samples. Crystal structure has been determined by a single crystal and powder x-ray diffraction. Perylene field effect transistors have been fabricated. Electrical parameters such as mobility and electrical conductivity have been measured as a function of temperature. The field effect mobilities increase from 5.5 and 0.4 square centimeters per volt per second at room temperature up to 120 and 30 square centimeters per volt per second at lower temperature for electrons and holes, respectively.

2:15 PM JJ7.3
INTERFACE FORMATION IN PENTACENE BASED THIN FILM TRANSISTORS: A MORPHOLOGICAL AND ELECTRONIC STRUCTURE STUDY. N.J. Watkins, Quoc Toan Le, S. Zorba, Li Yan and Yongli Gao, Department of Physics and Astronomy, University of Rochester, Rochester, NY.

In the past few years, the performance of organic thin-film transistors has improved considerably due, in part, to use of pentacene as an active material. Pentacene based devices have exhibited, at room temperature, performance comparable hydrogenated amorphous silicon devices: on/off current ratios at 10 V in the range of 10^9, room temperature mobilities as high as 2.7 cm^2/Vs, and operating voltages as low as 5 volts. At low temperatures, pentacene device mobilities are as good or better than most inorganic semiconductors as high as 10^5 cm^2/Vs. It is generally believed that device performance is heavily influenced by the characteristics of the interfaces between pentacene and the metals and dielectrics used in fabrication of the thin film transistors. For instance, it has been shown that the morphology of pentacene films affects device mobilities. In order to better understand these interfaces we investigated the interface formation of pentacene on conductors and dielectrics using X-ray photoemission spectroscopy, ultraviolet photoemission spectroscopy, inverse photoemission spectroscopy and atomic force microscopy to examine layer by layer pentacene growth onto these materials. The interfaces that we examined included the interfaces of pentacene with two materials used heavily in device manufacture: gold and silicon dioxide. Possible charge transfer, dipole formation and energy level bending at these interfaces will be discussed. The effect of different morphologies of pentacene growth on the occupied and unoccupied electronic structure in bulk and at interfaces will also be discussed.

2:30 PM JJ7.4
LOW ENERGY ELECTRON MICROSCOPY STUDIES OF THE GROWTH OF THIN PENTACENE FILMS. F. Meyer zu Heringdorf, C. Dimitrakopoulos, J. Shaw, R.M. Tromp, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY.

We have used Low Energy Electron Microscopy (LEEM) to study the growth and structural evolution of thin pentacene films on a variety of surfaces and substrates. LEEM allows the growth process to be followed in real time with high spatial resolution (5 nm), and at videorate. Thin film nucleation and subsequent growth can be studied in much detail. For instance, diffusion of pentacene on the starting substrate (for instance clean Si, or SiO_2) is isotropic, giving rise to fractal two-dimensional islands. These islands are nonetheless crystalline. The second layer grows on this crystalline template, with highly anisotropic diffusion. Substrate and substrate preparation give a certain degree of control over the polycrystalline grain size. In addition to the growth morphology, LEEM allows the observation of what appear to be molecular size defects in the film, giving rise to charge trapping. Such traps charge and discharge on timescales of 0.1 to several seconds. The density on such traps depends critically on the growth conditions. It appears that traps can be eliminated by careful control of the evaporation parameters. These studies, the first to observe the growth of organic semiconductors in real space, and in real time, enable a detailed understanding of the basic processes underlying the growth process. Direct parallels can be drawn between organic thin film growth, and the epitaxial growth of very different materials such as Si and Pt. These basic insight allow a careful optimization of the growth conditions, optimizing defect densities, grain size, and growth morphology.

2:45 PM JJ7.5
ELECTROSTATICALLY GENERATED, ORGANIC ELECTRONIC NANOFIBERS: SINGLE FIBER ELECTRONIC CHARACTERIZATION. Wayne E. Jones Jr., State University of New York at Binghamton, Binghamton, NY; Ian D. Norris, Alan G. MacDiarmid, James Hone, Alan T. Johnson, University of Pennsylvania, Philadelphia, PA; Baohua Han, Frank K. Ko, Drexel University, Philadelphia, PA.

The development of nanometer scale molecular devices is a challenging area of research for next generation electronic technologies. While carbon nanotubes and ropes have received considerable attention in this regard, a simple, inexpensive general method for preparing nanometer fibers of a variety of different electronic polymers seems desirable. In an effort to generate such methods for production of nanometer scale molecular wires and devices, we have prepared nanofibers of organic polymers with average diameters from ¡50 nm to 500 nm by an electrostatic, non-mechanical "electrospinning" technique to give a non-woven mat of random (meters long) fibers. We have prepared electronic nanofibers using this method with blends of conducting polymers such as polyaniline or polypyrrole with polyethylene oxide. Nanofibers of insulating polymers such as polyacrylonitrile or polystyrene have also been coated with a thin ca. 25 nm film of polyaniline or polypyrrole by in-situ deposition. They can alternatively be coated with metals such as gold by electroless deposition. The polyacrylonitrile can also be thermally converted to conducting carbon nanofibers under carefully controlled atmospheric conditions. Single fibers of different types of conducting nanofibers have been electrically characterized by deposition of individual nanofibers on insulating substrates followed by application of sputtered gold contacts separated by ca. 60 micrometers using a copper grid. Current/voltage curves of single fibers demonstrate both linear and non-linear behavior depending upon processing conditions. The authors gratefully acknowledge financial support for this work from the Office of Naval Research (K.J. Wynne, Contract Officer).

3:30 PM *JJ7.6
PROSPECTS OF SCREEN PRINTING IN THE FABRICATION OF ORGANIC LIGHT EMITTING DEVICES. Ghassan E. Jabbour, Optical Sciences Center and Department of MS&E, University of Arizona, Tucson, AZ.

We will discuss the use of screen printing technology in the patterning and fabrication of organic light emitting devices. Issues related to processing and uniformity of printed layers, as well as their effect on device fabrication and lifetime will be presented. Examples will be shown.

4:00 PM JJ7.7
ALL-POLYMER THIN FILM TRANSISTOR CIRCUITS FABRICATED BY DIRECT INK-JET PRINTING. Henning Sirringhaus, Takeo Kawase*, Richard Henry Friend, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM. *also at Epson Cambridge Laboratory, Cambridge, UNITED KINGDOM.

One of the main current directions in organic thin film electronic research is to develop processing technologies that allow the low-cost fabrication of organic thin-film transistor (TFT) circuits by solution processing and printing. In principle, direct ink-jet printing (IJP) of electrically functional materials would be one of the most attractive technologies for printed TFT circuits. However, this has not been explored yet, partly because IJP is regarded as a relatively low resolution printing technique not capable of achieving resolutions of a few μm that are required for most practical TFT applications. Here we demonstrate that it is possible to fabricate conjugated polymer TFT devices with precisely defined channel lengths of 5 μm by IJP. The high-resolution is achieved by directing the flow and spreading of a conducting polymer ink (PEDOT/PSS) on the substrate through a lateral pattern of the surface free energy. High-mobility, all-polymer TFT devices with good operational stability have been fabricated by successive solution deposition of ink-jet printed source-drain electrodes, spin-coated semiconducting and dielectric polymer layers, and ink-jet printed gate electrodes. High mobilities of 0.02 cm^2/Vs and ON-OFF current switching ratios exceeding 10^5 have been achieved. We will illustrate the potential of this process for practical applications by presenting first results on ink-jet fabricated logic TFT circuits.

4:15 PM JJ7.8
NANOPATTERNING POLYMERS FOR OPTICAL DEVICES. Tobias Nyberg, Giuseppe Gigli, Lucimara S. Roman, and Olle Ingan'as , Department of Physics and Measurement Technology(IFM), Linköping Universitet, Linköping, SWEDEN.

Soft lithography is a technique that can supplement or replace standard techniques in the processing and patterning of microelectronic polymer devices. Nanopatterning with elastomer stamps is not limited by optical diffraction - with a nanostructured template, elastomeric replicas may be used to pattern active materials, down to 50 nm structures, over large area surfaces (>1cm^2). We have successfully used soft lithography techniques to pattern micrometer and submicrometer sized features of semiconducting polymers, metals, and dielectrics. These techniques allow the fabrication of polymeric (opto)electronic devices, in conventional and new geometries, by patterning semiconducting, dielectric or conductor materials. We demonstrate here a number of devices, including photodiodes, light emitting diodes, and resonant optical structures.

4:30 PM JJ7.9
ELECTRIC FIELD-DEPENDENT IN-PLANE CONDUCTIVITY IN REGIOREGULAR POLY(3-HEXYLTHIOPHENE). Diederik Rep,

Teun M. Klapwijk, Dept of Applied Physics, Sect Nanotechnology, Delft University of Technology, Delft, THE NETHERLANDS; B.H. Huisman, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

The hopping mobility of many disordered organic semiconductors is found to be electric field-dependent. In recent years it has been established that spatial correlations in the hopping paths are needed to explain why electric fields as low as 1 MV/m can enhance the hopping conductivity. To investigate whether impurities are the origin of these correlations, we have studied the in-plane conductivity in thin films of regio-regular poly(3-hexylthiophene) as a function of temperature and level of oxygen doping. The electric field is found to affect both conductivity prefactor and activation energy for all doping levels. At fields exceeding 3 MV/m the conductivity increases exponentially with the square root of the field, in accordance with established empirical laws. We find that the main parameters describing field-enhancement of conduction in this material are not influenced by the removal of oxygen-related doping. This suggests that the process of field-enhancement of conductivity is 'intrinsic' to the polymer film and not related to 'extrinsic' electrically-active impurities. We will discuss this and present a more general discussion on the relation between conductivity prefactor and activation energy in this material. The latter relation has also been studied in thin-film field-effect transistors prepared from regio-regular poly(3-hexyl-thiophene).

4:45 PM JJ7.10
ELECTRIC INSTABILITIES AND 1/F NOISE IN ORGANIC PENTACENE THIN FILM TRANSISTORS. Peter Necliudov, Michael Shur, Rensselaer Polytechnic Institute, Dept. of Electrical, Computer and System Engineering, Troy, NY; David Gundlach, Thomas Jackson, Pennsylvania State University, Dept. of Electrical Engineering, University Park, PA.

The mobility values as high as 2.1 cm^2/V-s, exceeding those of amorphous Si TFTs, have been reported for pentacene Organic Thin Film Transistors (OTFTs) [1]. Relatively simple fabrication procedure, utilizing low deposition temperatures and virtually any substrates, including flexible ones, has made pentacene OTFTs attractive for large-area applications, such as high-resolution displays [2]. At the same time, the OTFTs exhibit a wide range of electrical instability effects that affect a long-time operation of the OTFTs. We report on electric instabilities in pentacene OTFTs of two different designs. We studied an influence of environment gases, incident light and Bias-Temperature Stress (BTS) on the pentacene OTFT electrical characteristics and 1/f noise level. We proposed a model that links the observed instabilities with reversible and/or irreversible changes in both field-effect mobility and threshold voltage values. The degree of the mobility and threshold voltage change induced by the positive or negative BTS is very sensitive to the OTFT design, contact materials utilized and fabrication process. The current-voltage characteristic change with the BTS time resembles that for amorphous-Si TFTs [3] with the characteristic time of the order of 10^4 sec. However, the instability effects are more pronounced in the pentacene OTFTs for a comparable BTS. We also measured 1/f noise in these devices before and after BTS. The noise level increased by four orders of magnitude after the BTS over the unstressed device noise level. REFERENCES:
[1] D.J. Gundlach, C.C. Kuo, S.F. Nelson, T.N. Jackson, 57th Device Research Conference Digest, p. 164-165, (1999).
[2] H. Klauk, D.J. Gundlach, J.A. Nichols, C.D. Sheraw, M. Bonse, and T.N. Jackson, Solid State Technology, vol. 43, n. 3, pp. 63-77, (2000).
[3] C. Chiang, J. Kanicki, K., Takechi, Jpn. J. of Appl. Physics, p. 4704-4710 (1998).

SESSION JJ8: POSTER SESSION
Chair: James B. Hannon
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

JJ8.1
BRIGHT, HIGH EFFICIENCY WHITE ORGANIC ELECTRO-LUMINESCENT DEVICES. Yasuhisa Kishigami, Yukihiro Kondo, Kenji Tsubaki, Matsushita Electric Works, Ltd., Osaka, JAPAN; Junji Kido, Yamagata Univ., Yamagata, JAPAN.

High-efficiency white EL devices based on vacuum deposited organic thin films are reported. In order to achive high luminous efficiency, metal-doped electron injection layer is used [1], which is composed of electron-transporting bathophenantroline (Bphen) doped with Cs metal. White light was generated by using two emitter layers of blue and yellow. For the blue emitter layer, distyrylbiphenyl derivative is doped with a few percent of distyrylarylene derivative with carbazolyl groups. For the yellow emittier layer, rubrene was doped into hole-transporting arylamine derivative (NPD). The typical device structure is ITO/NPD/yellow-emitting layer/blue-emitting/Bphen doped with Cs/Al. By optimizing the thickness of each layer and dopant concentration, the white EL devices exhibited extremely high luminous efficiency of 15 lm/W and external quantum efficiency of 4% which are the highest values reported for white organic EL devices.
[1] J. Kido and T .Matsumoto, Appl. Phys. Lett., 73, 2868(1998).

JJ8.2
CONTROL OF MOLECULAR ORIENTATION IN LAYER BY LAYER FILMS. David M. DeWitt, Paula T. Hammond, MIT, Department of Chemical Engineering, Cambridge, MA.

Self-assembled multilayer films have been constructed using polyelectrolytes containing side chain non-linear optically (NLO) active chromophores or liquid crystalline (LC) mesogens. By using external reflection-absorption and transmission FTIR, the molecular orientation of the optically active groups has been determined. A parametric study of these films and their construction is underway. Both the structural characteristics of the polymers and the processing conditions under which the films are constructed are being varied in order to establish a set of "rules" for constructing optically active ordered polymer multilayers films. Measurements performed on films consisting of two commercially available azo polymers and four polycations show a different tilt angle depending on the polycation and on pH conditions of both the polyanion and polycation. In addition, two other NLO polymers have been synthesized that allow the varying of different structural parameters. By moving the charged group from the side chain chromophore to the polymer main chain the chromophores exhibit less orientation. Furthermore the number of methylene spacer units separating the chromophore from the main change influences the order within the films. Also, studies on side chain liquid crystalline polymers have been performed.

JJ8.3
PHOTOLUMINESCENCE AND ELECTROLUMINESCENCE CHARACTERISTICS OF TERBIUM CHELATED POLYUREAS AND POLY(URETHANE UREAS). J. Mwaura, X. Xie, J. Chen, F. Papadimitrakopoulos, Dept of Chemistry, Polymer Science Program, Nanomaterials Optolectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT; S. Theodoropoulos, Zotic Corp., West Hartford, CT; T. Goodson III, Dept of Chemistry, Wayne State University, Detroit, MI.

The metal chelating abilities of 2,6-diaminopyridine based poly(urethane-ureas) have been previously reported from our laboratory Presently we report a systematic UV-Visible and photoluminescence studies for both fully aromatic and partial aliphatic polyureas and poly(urethane-ureas) in the presence and absence of Tb(III) ions for solution and solid samples. A variety of model compounds were synthesized and their chelation properties were also investigated With the help of 2-D NMR spectroscopy for both solution and solid samples, a clearer picture was determined for the geometry of the chelating center. Single and multi layer electroluminescence (EL) devices of these complexes were also fabricated. Their EL characteristics were dominated by the presence of Tb(III) ions that contributed to the majority of the emission envelope. The use of these materials as electron-injecting layers in organic light emitting diodes were also investigated and will be discussed in light of our current findings.

JJ8.4
Abstract Withdrawn.

JJ8.5
HIGH EFFICIENCY ORGANIC EL DEVICES USING IRIDIUM COMPLEX. Akio Fukase, Junji Kido, Yamagata University, Yonezawa, Yamagata, JAPAN.

We report high efficiency organic EL devices based on Iridium complex, Ir(ppy)3. In order to achieve high quantum efficiency, phosphorescent Ir(ppy)3 was used as the emitting center, and, to decrease the drive voltage, chemically doped anode interface layer was used. Anode buffer layer is composed of poly(arylene ether) containing tetraphenylbenzidine units doped with lewis acid, Sb compound. Typical device structure is ITO / chemically doped polymer layer / hole transport layer (NPD) / CBP doped with Ir(ppy)3 / BCP / Alq / LiF/ Al. Devices having both of the chemically doped anode interface layer and the Ir complex emitter layer exhibit extremely high luminous efficiency of 50 lm/W at 100 cd/m2 and high quantum efficiency of 16%. Devices having Alq-doped CBP emitter layer, instead of Ir(ppy)3 doped layer, exhibit low efficiency of 1%, indicating the use of triplet excited energy of the Ir complex.

JJ8.6
USE OF HEMATIN FOR THE POLYMERIZATION OF WATER-

SOLUBLE CONDUCTIVE POLYANILINE. Ferdinando F. Bruno, Lynne Samuelson, Materials Science Team, Natick Soldier Center, U.S. Army Soldier and Biological, Chemical Command, Natick, MA; Ramaswamy Nagarajan, Jayant Kumar, Sukant Tripathy, Sucharita Roy, Departments of Physics and Chemistry, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA.

Polyaniline has been one of the most investigated conducting polymers over the past few decades. A considerable part of this research has been focused on exploring new methods to augment conductivity, processability and environmental compatibility. Polyelectrolyte assisted Horseradish Peroxidase (HRP) catalyzed polymerization of aniline, has recently provided a one step biocatalytic route to the synthesis of a water-soluble and conducting polyaniline using very mild chemical conditions. The high cost of the enzyme, HRP, however has limited its commercial application. Hematin (hydroxyferriprotoporphyrin) is the stable, oxidized form of the free heme center of the HRP. Therefore in comparison to the enzyme, HRP, hematin is a small molecule that is much lower in cost. It has already been shown as a promising catalyst for the polymerization of phenol compounds. We report here the use of hematin as a cost-effective alternative to HRP for the synthesis of polyaniline. The conductivity, UV-Vis, FTIR and TGA studies of hematin catalyzed polyaniline in the presence of the template polystyrene sulfonate will be presented. Use of this conductive complex for corrosion protection is also proposed.

JJ8.7
SYNTHESIS AND CHARACTERIZATION OF HIGH-EFFICIENCY BLUE ELECTRONLUMINESCENT MATERIALS. Changqing Chen, Mathew Mathai, Fotios Papadimitrakopoulos, Dept of Chemistry, Polymer Program, Nanomaterials Optoelectronics Lab, Inst of Material Sci, Univ of Connecticut, Storrs, CT.

High-efficiency blue electroluminescent materials are essential for the development of full-color displays. Blue organic light emitting diodes (OLEDs) with good color saturation, low operation voltage and improved lifetime are of great importance. Complexes of 8-hydroxyquinoline have been instrumental in the development of the field, with aluminum (III) tris(8-hydroxyquinoline) Alq_3 at the forefront of the commercialization of OLEDs. The recently reported lithium tetra-(2-methyl-8-hydroxy quinolinato) boron complex has sparked interest in developing stable quinoline based blue emitters. We report the synthesis and characterization of a series of new blue-emitting boron complexes based on analogues of 2-methyl-8-hydroxy quinoline. These materials exhibit improved morphological stability, which results in improved brightness and lifetimes.

JJ8.8
ELECTROLUMINESCENCE FROM 1,3,4-OXADIAZOLE AND ITS MAGNETIC ORIENTATION. Junji Kido, Ryuji Ishii, Koichiro Yonetake, Yamagata University, Yonezawa, Yamagata, JAPAN.

We report here electroluminescence from 2-(4-Diemethylamino-phenyl)-5-(4-cyanophenyl)-1,3,4-oxadiazole(OXD) and its orientation under magnetic field. Organic EL devices having a structure of ITO / OXD(50wt%) doped into poly(N-vinylcarbazole) (PVK) / Mg:Ag were fabricated. The EL device exhibited green light originating from OXD. And various orientated films were prepared from the N-methyl-2-pyrrolidone solutions containing OXD(50wt%) and polymers such as PVK, polystyrene (PS), and poly(methyl methacrylate) (PMMA)) under magnetic field. Crystalline OXD was orientated in cases of PVK and PS, but not in PMMA, which is attributed to the strong dipole-dipole interaction between OXD and host PMMA.

JJ8.9
SET OF FLUORESCENCE QUENCHING BASED THIN FILM SENSORS EMPLOYING ELECTROSTATIC LAYER-BY-LAYER ASSEMBLY. Soo-Hyoung Lee, J. Kumar, S.K. Tripathy, Center for Advanced Materials, Department of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA.

In this work, the fabrication and performance of thin film optical chemical sensors based on the fluorescence quenching of indicator molecules by several analytes such as organic nitro compounds or metal ions are described. To fabricate the sensors, a fluorescent molecule, 1-hydroxypyrene-3,6,8-trisulfonate or pyrene methanol, was covalently incorporated into poly(acrylic acid) and subsequently the polymers were assembled with a polycation employing electrostatic layer-by-layer assembly into thin film structures. Fluorescence intensities decreased with increasing concentration of analytes. Quenching behavior follows Stern-Volmer bimolecular quenching kinetics. Linear increase in absorbance, film thickness and emission intensity was observed with increase in number of bilayers deposited in all multilayer films.

JJ8.10
EXCITON VERSUS CHARGE MOBILITY IN OLIGOTHIOPHENES THIN FILMS. Riccardo Tubino, Alessandro Borghesi, Franco Meinardi, Adele Sassella, Silvia Tavazzi, Dipartimento di Scienza dei Materiali, Univ. Milano-Bicocca, Milano, ITALY; Francis Garnier, Laboratoire des Materiaux Moleculaires, CNRS, Thiais, FRANCE.

The photoexcitations of quaterthiophene (T4) and of the end- capped dihexyl quaterthiophene (DHT4)thin films obtained by controlled ultra-high vacuum evaporation have been studied and the results have been used to account for the large increase of the charge mobility in DHT4 previuosly reported. While their absorption spectra are almost indistinguishable, the analysis of the photoluminescence excitation profiles reveals the presence, in the case of T4, of absorbing centers with enhanced emission quantum yield, consistent with the existence of grain boundaries. In the case of DHT4 the samples appear homogeneous with respect to the emission efficiency, thus supporting the hypothesis that the reported large increase in charge mobility, can be related to the lack of grain boundaries in this film. The formation of macroscopic single crystals in DHT4 can be related the copresence of a rigid thiophenic core and of flexible alkylic chains, which appear to be able to absorb the microscopic strains responsible for the grain segregation in the more rigid unsubstituted T4.

JJ8.11
PHOTOINDUCED CHARGE CARRIERS IN A DONOR-ACCEPTOR **DOUBLE-CABLE** - A POLYTHIOPHENE WITH COVALENTLY BOND TETRACYANO-ANTHRAQUINO-DIMETHANE MOIETIES. Gerald Zerza, Antonio Cravino, N. Serdar Sariciftci, Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Linz, AUSTRIA; Rafael Gómez, José L. Segura, Nazario Martín Departamento de Química Orgánica, Universidad Complutense, Madrid, SPAIN; Mats Andersson, Mattias Svensson, Polymer Technology, Chalmers University for Technology, Goteborg, SWEDEN.

Morphology and phase segregation are still limiting the efficiency of electron donor conjugated polymers / electron accepting molecules heterojunction solar cells. In order to overcome such limitations, *double-cable* materials consisting of a hole conducting conjugated chain carrying pendant electron conducting moieties are promising candidates. Starting from a novel bithiophene, we have electro-synthesized a *double-cable* polythiophene with covalently bond tetracyano-anthraquino-dimethane (TCAQ) moieties. Cyclic voltammetry and UV-Vis absorption measurements reveal that in this electrosynthesized material, both the polythiophene chain and the TCAQ moieties maintain their individual electrochemical and electronic properties. Light induced electron spin resonance (LESR) and photoinduced absorption (PIA) studies clearly indicate photoinduced electron transfer from the polythiophene backbone to the TCAQ. These results were further confirmed by doping induced UV/Vis and NIR absorption spectra. Solar cell devices have been fabricated and characterized.

JJ8.12
ELECTRON SPIN RESONANCE INVESTIGATIONS ON DOPING OF ZINC-PHTHALOCYANINE WITH ACCEPTOR MOLECULES. Andreas Nollau, Martin Pfeiffer, Karl Leo, Institut für Angewandte Photophysik, Technische Universität Dresden, GERMANY; Dirk Habermann, Jürgen R. Niklas, Institut für Experimentelle Physik, TU Bergakademie Freiberg, GERMANY.

The dependence of the electron spin resonance (ESR) signal on doping of zinc-phthylocyanine (ZnPc) with tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ) is studied for dopant concentrations between 0.5 and 3%. Thin films were prepared by coevaporation of the matrix and the dopant. ZnPc / F_4-TCNQ is a good model system for the investigation of the doping process of organic materials with organic π-electron acceptors: The doping increases the conductivity by up to eight orders of magnitude and with Fourier transformed infrared spectroscopy we could show that all acceptor molecules are ionized in this system. The ESR spectra show a single peak for all doping ratios. The intensity of the signal increases linearly with the dopant concentration up to about 2% and then decreases again. This linear dependence is different from the behavior of the conductivity and the hole density (as deduced from thermopower measurements) which both increase strongly superlinearly with the doping ratio. The evolution of the linewidth of the ESR signal upon doping is inverse to the intensity: It first decreases and then increases again for concentrations above 2 %. Hence, it is clear that the signal is caused by the doping, and ESR yields an additional insight into the doping process.

JJ8.13
OLIGO(*P*-PHENYLENE VINYLENE) - FULLERENE DYADS INCORPORATED IN CONJUGATED POLYMER/FULLERENE PLASTIC SOLAR CELLS A. Cravino, C.J. Brabec, A. Andreev, N.S.

Sariciftci, Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Linz, AUSTRIA; E. Peeters and R.A.J. Janssen Laboratory for Macromolecular and Organic Chemistry, Eindhoven University of Technology, Eindhoven, THE NETHERLANDS; J. Knol and J.C. Hummelen, Stratingh Institute and MSC, University of Groningen, Groningen, THE NETHERLANDS.

The discovery of ultrafast, photoinduced electron transfer from a conjugated polymer to C_{60} has fuelled research on semiconducting-polymer based photovoltaic devices. The interpenetrating networks formed between the conjugated polymer and the fullerene acceptor form a bulk-heterojunction with a large donor / acceptor interfacial area that facilitates both the photoinduced creation of mobile charge carriers as well as transport of the carriers to the electrodes. The efficiency of such devices comprising poly[2-methoxy,5-(3*l*,7*l*-dimethyl-octyloxy)-*p*-phenylene vinylene] (MDMO-PPV) as donor and [6,6]-Phenyl C_{61}-butyric acid methyl ester (PCBM) as acceptor was recently improved to 2.5% under AM1.5. In this study it was shown, that the nano-scaled morphology of the interpenetrating network is a critical parameter to allow efficient bipolar charge transport. A novel series of oligo(*p*-phenylene vinylene)-fulleropyrrolidines OPVn-C_{60} (with n = 1-4) was tested for their properties as electron acceptors in PSS. Interestingly, two of these acceptors (OPV3-C_{60} and OPV4-C_{60}) show in the solid phase, e.g. thin films, long-lived photoinduced charge separated states, allowing to produce rather efficient photodiodes from the single compounds. Contradictory to that, OPV1-C_{60} does not show intra photoinduced charge transfer similar to PCBM. We have also fabricated a series of plastic solar cells from MDMO-PPV as donor and the four OPVn-C_{60} molecules as acceptors and and compare their performance to the performance of reference devices utilizing PCBM as acceptor.

JJ8.14
MULTILAYERED STRUCTURES AND LOW TEMPERATURE CONVERSION PROCESS FOR POLY(P-PHENYLENE VINYLENE) THIN FILMS. Alexandre Marletta, Fernando A. Castro, Osvaldo N. Oliveira Jr., Roberto M. Faria and Francisco E.G. Guimarães, Universidade de São Paulo, Instituto de Física de São Carlos, São Carlos, BRAZIL.

The recent discovery[1] of the extremely rapid thermal conversion process into poly(p-phenylene vinylene) (PPV) by incorporation of dodecyl benzene sulfonic counterions (DBS) has opened up a number of new possibilities to molecularly engineer superstructures with improved properties. The main advantage of this novel procedure is that thermal conversion may be performed at considerably lower temperatures, 80-100°C, compared to those conventionally used (> 200°C), within a very short time (down to 3 minutes) and under ambient conditions. Incorporation of DBS improves the processibility of the PPV-precursor to fabricate multilayer Langmuir-Blodgett (LB), self-assembled (SA) and spin-cast films. The resulting PPV films possess less defects compared to films converted at high temperatures, owing to the absence of carbonyl-related defects, thus leading to a dramatic improvement in quantum efficiency of PPV when the conversion temperature is decreased from 230 to 80°C. Furthermore, the conjugation length could also be controlled by varying the immersion time in the self-assembly procedure or the DBS concentration for spin-coating, making it possible to alter the band gap between LUMO and HOMO states in the PPV film. In addition to the possibility of band-gap engineering, confinement structures (such as asymmetric ladder type or "V-type" structures) may lead to distinct results such as the transport of excited or injected carriers to the proximity of the substrate or to the film surface, improving the effective quantum efficiency of the active material.
1. Adv. Mater. 2000, 12, 69-74.

JJ8.15
TWO-PHOTON ABSORPTION PROPERTIES OF SOLUBLE FLUORENE-BASED CONJUGATED POLYMERS. Raoul Schroeder, Bowling Green State Univ., Dept of Physics and Astronomy, Bowling Green, OH and Virginia Tech, Dept of Physics, Blacksburg, VA; Bruno Ullrich, Bowling Green State Univ., Dept of Physics and Astronomy, Bowling Green, OH; Willi Graupner, Virginia Tech, Dept of Physics, Blacksburg, VA; Ullrich Scherf, Max Planck Institut fuer Polymerforschung, Mainz, GERMANY.

Soluble fluorene-based conjugated polymers are known for high chemical purity, high photoluminescence quantum yield (PLQY) and small inhomogeneous broadening in the optical spectra. We have used two-photon absorption at room temperature of laser pulses at 804 nm of 200 fs duration with a repetition rate of 249 kHz to characterize two typical representatives of fluorene-based conjugated polymers. (1) poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) (PF), a material known for exceptionally high PLQY and (2) a methyl substituted laddertype poly(para-phenylene) (m-LPPP), known for very defined optical spectra in emission and absorption. In both materials we detected strong blue/blue-green emission due to two-photon absorption, which is particularly remarkable for the PF since the onset of the optical absorption is at 400 nm (m-LPPP starts to absorb at 470 nm). Both materials show a strongly nonlinear behavior of the transmitted light intensity when plotted versus the pulse energy and a clear quadratic intensity dependence of the PL emission on the same parameter. In order to develop a better understanding of the underlying processes in these very important materials we have investigated both films as well as solutions of several different polymer concentrations.

JJ8.16
OPTICAL SPECTROSCOPY OF SOLUBLE FLUORENE-BASED CONJUGATED POLYMERS. A. Erlacher[1,2], S. Guha[3], R. Schroeder[2,4], W. Graupner[2], U. Scherf[5]. [1]Institut für Festkörperphysik, Technische Universität Graz, AUSTRIA. [2]Dept. of Physics and Astronomy, V. Tech., Blacksburg, VA. [3]Physics Dept. Marquette University, Milwaukee WI. [4]Dept. of Physics and Astronomy, Bowling Green State University, Bowling Green, OH. [5]Max Planck Institut für Polymerforschung, Mainz, GERMANY.

Soluble fluorene-based conjugated polymers are known for high chemical purity, high photoluminescence quantum yield (PLQY) and small inhomogeneous broadening in the optical spectra. (1) poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) (PF) is an intense blue emitter with a PLQY, substantially higher than the one found for (2) the blue-green emitting methyl substituted laddertype poly(para-phenylene) (m-LPPP). PF is known to undergo phase transitions if heated and cooled down, with corresponding changes in the optical spectra. We have used optical absorption/reflection as well as Raman spectroscopy in order to characterize the two materials. The key to the understanding of the fundamental difference in behavior between the two materials is the ribbon-type structure in m-LPPP which determines the conformation of the molecules as opposed to the degree of freedom introduced by only one single bond between two fluorene units in PF. The consequences of this difference both for vibronic and electronic excitations is discussed in this contribution

JJ8.17
ORGANIC LIGHT EMITTING DIODES BASED ON 2 DIMENSIONAL RHOMBOHEDRAL FULLERENE POLYMER DISPERSED IN CONJUGATED CO-POLYMER MATRIX. Hyung-Suk Woo, Richard Czerw, David L. Carroll, Dept of Physics and Astronomy, Clemson Univ, Clemson, SC; In-Hang Cho, Eung-Ju Oh, Dept of Chemistry, Myungji Univ, S. Korea; Zheng Tao Zhu, Janice L. Musfeldt, Dept of Chemistry, State Univ of New York at Binghamton, Binghamton, NY; Yoshihiro Iwasa, Japan Advanced Institute of Science and Technology, Japan.

We present the characteristics of organic light emitting diodes (OLEDs) based on a polymer composite of 2 dimensional rhombohedral fullerene (2D C_{60}) polymer dispersed in a novel copolymer matrix, carbazole contaning phenylene vinylene (PCzPV). We observed that the current - voltage (I-V) characteristics of a device fabricated using this polymer composite with a concentration of 0.1 weight % of 2D C_{60} shows the power dependence of I V^2 while the one of pure PCzPV device has I V^6 with an applied voltage up to 5 V. This indicates that, at lower applied voltage, the origins of charge transport are different for these two types of OLEDs. We propose that the charge trap effect due to 2D C_{60} in the copolymer matrix is responsible for this lower power law dependence in I-V characteristics. Both OLEDs, those with and without 2D C_{60}, show light emission in the range of green with a peak wavelength near 505 nm. The device characteristics including the I-V relation and quantum efficiency will be discussed as a function of the 2D C_{60} concentration in the polymer composite.

JJ8.18
INTERFACIAL BEHAVIOR OF ELECTRO-ACTIVE SURFACE LAYERS BASED ON THIOPHENE-CAPPED SAMS. Katherine Harrison, S. Michael Kilbey, Clemson Univ, Dept of Chemical Engineering, Clemson, SC.

Self-assembled monolayers, particularly those possessing unique or functional moieties are of interest due to the potential applications in the fabrication of materials with novel interfacial properties. We have been investigating the surface and electrochemical properties of monolayers of various chain length made from [ω-(3-thienyl)alkyl] trichlorosilanes. These molecules have an electroactive thiophene ring at the w-position, which can serve as an initiation site for growing polythiophene chains from the monolayer. Monolayers formed from these amphiphiles, as well as mixed monolayers that incorporate n-alkyltrichlorosilanes, have been studied. We report on our efforts to characterize the structure and organization of the layer using FTIR, contact angle, and cyclic voltammetry. Electrochemical oxidation of thiophene-bearing chains occurs at a potential similar to that of β-substituted alkylthiophenes, although mixing n-alkyl chains into the monolayer alters the oxidation potential and subsequent reactivity of

the thienyl groups. The electrical activity of the monolayer can be used to reveal the degree of coupling of tethered thiophene rings along the monolayer and the surface density of active molecules. Contact angle results indicate that the monolayers in which the thiophene rings are coupled by electrochemistry are more hydrophilic (with contact angles similar to polythiophene) than the monolayers prior to electrochemical treatment. We also report the results of XPS experiments aimed at probing the surface composition of mixed monolayers.

JJ8.19
THE ROLE OF CARBON NANOTUBES IN ORGANIC LIGHT EMITTING DIODES BASED ON AN ELECTRON TRANSPORT CONJUGATED POLYMER-NANOTUBE COMPOSITE.
Richard Czerw, Hyung-Suk Woo, David L. Carroll, Clemson Univ, Dept of Physics and Astronomy, Clemson, SC; Jong-Wook Park, Dept of Polymer Science, Chung-Ju National Univ, Chung-Ju, S KOREA; Ji-Hoon Lee, Samsung SDI Co, Ltd, Corporate R&D Center, S KOREA.

Organic light emitting diodes (OLEDs) were constructed from a composite of a novel electron transporting and red emitting conjugated polymer, poly(alkoxy thiazole-co-phenylene vinylene) (PATPV), and single walled carbon nanotubes (SWNTs) in order to study the energy transfer between SWNTs and the polymer as well as the changing the electron transport in the composite. Polyethylene dioxythiophene (PEDOT) was used as a hole injecting buffer. Composites of 0.0%, 0.05 %, 0.1% and 0.2% by weight of SWNTs in the PATPV matrix were used in the devices for comparison. These devices also have been compared with the OLEDs with SWNT's in PEDOT where the SWNTs interact with holes only. All of the OLEDs show light emission near red with a peak wavelength at 595 nm. The current-voltage characteristics, quantum efficiency, and luminosity will be discussed as a function of the varying nanotube concentrations in the composite.

JJ8.20
ELECTROCHROMIC BEHAVIOR OF IONICALLY SELF-ASSEMBLED THIN FILMS. J.A. Janik, J.R. Heflin, Dept. of Physics, Virginia Tech, Blacksburg, VA; D. Marciu, M.B. Miller, Luna Innovations, Blacksburg, VA, R.M. Davis, Dept. of Chemical Engineering, Virginia Tech, Blacksburg, VA.

Ionically self-assembled monolayers (ISAMs), fabricated by alternate adsorption of cationic and anionic components, yield exceptionally homogeneous thin films with sub-nanometer control of the thickness and relative spatial location of the component materials. Individual layers can have thicknesses from 0.3 to 5 nm. Using organic electrochromic materials such as polyaniline, we report studies of electrochromic responses in ISAM films. Reversible changes in the absorption spectrum are observed with the application of voltages on the order of 1.0 V. Measurements are made using both liquid electrolytes and in all-solid state devices incorporating solid polyelectrolytes such as poly(2-acylamido 2-methyl propane sulfonic acid) (PAMPS). Studies of the magnitude of the spectral changes, the reversibility over many cycles, and the response time are reported as a function of film thickness, component materials, and the multilayer nanostructure of the composite films.

JJ8.21
SOLVATOCHROMISM IN HEXADECYLQUINOLINIUM TRICYANOQUINODIMETHANIDE A MOLECULAR RECTIFIER. Jeffrey W. Baldwin and Robert M. Metzger, Laboratory for Molecular Electronics, Chemistry Department, The University of Alabama, Tuscaloosa, AL; Francesca Terenziani and Anna Painelli, Diparti-mento di Chimica Generale ed Inorganica, Chimica Analitica e Chimica Fisica, Universita di Parma, Parma, ITALY.

We recently studied the spectroscopic properties [1] of gamma-hexadecylquinolinium tricyanoquinodimethanide $C_{16}H_{33}Q\text{-}_3CNQ$, a unimolecular rectifier [2]. This molecule has a large dipole moment in the ground state (43 ± 8 Debyes) and a small moment in the excited state (estimated between 3 and 9 Debyes by perturbative treatments of solvatochromism) [1]. The ground-to-excited state gap, and shift in ionicity, is evidenced also by shifts in infrared spectra in solution. A new theoretical approach [3], buttressed by further spectroscopic data, differs from the rigid solute-molecule treatments used previously [1], and should provide a fresh look at the ionicity changes that occur upon excitation in this molecule.
[1] J.W. Baldwin et al., J. Phys. Chem. B103: 4269 (1999).
[2] R.M. Metzger, Acc. Chem. Res. 32: 950-957 (1999). [3] A. Painelli and F. Terenziani, Chem. Phys. Lett. 312: 211 (1999).

JJ8.22
CARRIER DYNAMICS INTO POLY(OCTYLTHIOPHENE) GELS. B. Pépin-Donat[1], J-C Vial[2] and A. Viallat[2]. [1]L. de physique des Métaux Synthétiques, UMR 5819 (CNRS-CEA-Univ. J. Fourier). [2]L. de Spectrométrie Physique, UMR C5588 (Univ. J. Fourier-CNRS).

Carrier dynamics properties into poly(octylthiophene) gels are investigated via their radiative and non radiative recombination rate ($W_r$and W_{nr} respectively) as a function of the fraction of solvent content (Q). Our measurements on photoluminescence decay time (picosecond range) and intensity show a strong intensity increase going along with a shortening of decays as Q increases. This can be explained if W_r decreases and W_{nr} increases simultaneously as Q increases; it shows that Q increases is not a simple dilution effect well known for organic dyes for example. It indicates that the interchain linking and the Q evolution may induce a carrier separation and consequently affects W_r. This observation will be discussed together with results obtained on conductivity which also show a strong variation with Q .

JJ8.23
NOVEL CHEMOENZYMATIC SYNTHESIS OF AZOBENZENE FUNCTIONALIZED RIBONUCLEIC ACID. Sucharita Roy, Ramaswamy Nagarajan, Peichuan Wu, Sukant K. Tripathy, Jayant Kumar, Department of Physics & Chemistry, Center for Advanced Materials, University of Massachusetts Lowell, MA; Lynne A. Samuelson, Ferdinando F. Bruno, U.S. Army Soldier & Biological Chemical Command, Natick Soldier Center, Natick, MA.

Ribonucleic acids, often called a biological jack of all trades, contribute intimately to every aspect of gene expression, including the synthesis of other polypeptide biocatalysts. The fundamental importance of recurring structural motifs, the kinetics and energetics of the complex secondary and tertiary structure of RNA has been shown to be intimately linked with its functions in vivo. We have developed a novel enzymatic synthetic approach for covalent attachment of photoresponsive units into the RNA backbone. The synthesis conditions of this approach are extremely mild involving the reverse micellar solubilization of nucleic acid along with lipase in apolar hydrocarbon solvents. Lipase catalyzed acylation of the 2′ hydroxyl group in the ribose sugars of the RNA molecule has been used to incorporate photo-isomerizable azobenzene groups into the RNA strands. This micellar approach was envisaged for the functionalization of the RNA molecule while maintaining the conformational integrity of the macromolecular backbone in neutral buffer solution. The modification of RNA using covalently attached chromophores or fluorophores can be extended to other biomacromolecular matrices leading to the development of versatile photoactive biopolymers. The photo-isomerizable groups incorporated in the RNA molecule can serve as optical "handles" for manipulation of the conformation of RNA and also open new avenues for application in biophotonics. The detailed characterization and discussion of these studies will be presented.

JJ8.24
NOVEL LASER-BASED DEPOSITION OF ORGANIC AND POLYMERIC THIN FILMS. D.M. Bubb, R.A. McGill, J.S. Horwitz, E.J. Houser, B. Ringeisen and D.B. Chrisey, Naval Research Laboratory, Washington, DC.

Dry film growth techniques that are compatible with conventional PVD and CVD techniques are especially useful for the deposition of organic and polymeric thin films for electronic and photonic devices applications. We have successfully applied pulsed laser deposition (PLD) and a new technique called matrix-assisted pulsed laser evaporation (MAPLE) to produce thin polymer films that demonstrate an enhanced device performance over conventional deposition techniques. Pulsed laser vaporization is a dry technique capable of depositing thin films (50 nm 1 nm) that are highly dense and uniform. The technique is amenable to shadow mask depositions down to 10 micron feature size. Polymers such as polyurethane, polyethylene vinyl acetate, polyethylene glycol, fluoropolyol, and polyepichlorhydrin have been deposited with intact functional chemistry. Our main application is chemical sensing, however these techniques may be generalized to include all organic films for a wide variety of applications. Several classes of polymers have been examined (both addition and condensation polymers) under a range of laser processing conditions to determine the influence of the polymer film transfer mechanism on coating properties. To characterize the functional chemistry and molecular weight of the deposited films Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC) are utilized. We will present the influence of laser wavelength (248 and 193 nm), fluence, background gas (composition and pressure) and matrix composition on the properties of PLD and MAPLE deposited polymer thin films.

JJ8.25
THEORETICAL AND EXPERIMENTAL STUDIES OF THIRD-ORDER NONLINEAR OPTICAL SUSCEPTIBILITIES OF NEW P-N,Ni-DIAMETHYLANILINE TETRATHIAFULVALENE

DERIVATIVES. B. Sahraoui, Univ d'Angers, Laboratoire POMA, Angers, FRANCE; K.J. Pluciòski, Military University of Technology, Warsaw, POLAND; M. Makowska-Janusik, I.V. Kityk, Institute of Physics WSP, Czistochowa, POLAND; M. Sallé, A. Gorgues, Univ d'Angers, Lab d'Ingénierie et Matériaoux Organiques, Angers, FRANCE.

We report on investigations of the nonlinear optical properties of new p-N,N'-diamethylaniline tetrathiafulvalene (TFT) derivatives. Theoretical and experimental studies of third-order nonlinear optical susceptibilities, using the degenerate four wave mixing (DFWM) method, were carried out. To understand the physical nature of the optical nonlinearities, we separate their electronic and nuclear contributions. The electron contribution to the third-order nonlinear optical susceptibilities of the molecules studied turned out to be dominant. From DFWM measurements we also calculated the values of the second-order hyperpolarisabilities which are about 105 greater than these values of CS2. We thus showed that the third-order nonlinear optical properties of the molecules under consideration are much more significant than those of the polyazine derivatives, acetylenic analogues TFT and of the ethylenic TTF derivatives. We found that for molecules studied in this research the electron part of third order susceptibility is dominant and its sign is negative. A complex quantum mechanical calculation of the mentioned optical nonlinearities will also be presented. Our investigations suggest that TFT may be a highly promising material for NLO.

JJ8.26
OPTICAL STORAGE STUDIES IN SELF-ASSEMBLED FILMS FROM POLY(METHACRYLIC ACID-CO-4'(METHACRYLOYLOXY-ETHYL,ETHYLAMINE)-4-NITROAZOBENZENE) (MAcoDR13) AND POLY(ALLYLAMINE HYDROCHLORIDE) PAH. Valtencir Zucolotto, Cleber R. Mendona, David S. dos Santos Jr, Débora Terezia Balogh, Sérgio C. Zilio and Osvaldo Novais de Oliveira Jr., Instituto de Física de São Carlos, DFCM - Grupo de Polímeros - USP, São Carlos, SP, BRAZIL.

The reversible photoinduced trans-cis-trans isomerization of azobenzene polymers is exploited here for optical storage in layer-by-layer films from poly(methacrylic acid-co-4'(methacryloyloxy-ethyl,ethylamine)-4-nitroazobenzene) (MAcoDR13) alternated with the commercially available polycation poly(allylamine hydrochloride) PAH. MAcoDR13 was prepared by solution polymerization of the two comonomers. Films were deposited on glass substrates and various experimental parameters were varied, including pH of the polymer solution, number of layers deposited and time of immersion for each layer. The buildup of the multilayer films was monitored by UV/Vis spectroscopy, which shows that the amount of material adsorbed increases linearly with the number of deposited bilayers. Optical storage is achieved by optically-induced birefringence owing to the anisotropy caused by impinging a linearly polarized laser beam on the film. The writing and erasing times observed in the SA films were about 1000 times longer than that observed in Langmuir-Blodgett (LB) films of azobenzene polymers. Such a huge difference could in principle be due to the rigidity of the polymer and/or the lack of free volume due to the order induced in the self-assembly method. However, MAcoDR13 is not expected to be more rigid than similar polymers and copolymers that we investigated recently in the form of LB films, such as HPDR13. Neither should we expect the layer-by-layer films to be more ordered than LB films. Therefore, the long writing and erasing times are probably related to electrostatic interactions between the polycation and polyanion that would restrict the mobility of the polymeric chain required for the trans-cis-trans isomerization.

JJ8.27
DEPENDENCE OF PHOTOVOLTAIC EFFICIENCY ON FILM THICKNESS, ACCEPTOR SPECIES, AND SPATIAL COMPOSITION IN POLY(PARA-PHENYLENE VINYLENE) IONICALLY SELF-ASSEMBLED NANOSTRUCTURES. J.R. Heflin, K. Kuroda, C. Brands, J.A. Janik, R. Schroeder, W. Graupner, Dept. of Physics, Virginia Tech, Blacksburg, VA; D. Marciu, M.B. Miller, Luna Innovations, Blacksburg, VA; H. Wang, H.W. Gibson, Dept. of Chemistry, Virginia Tech, Blacksburg, VA; R.M. Davis, Dept. of Chemical Engineering, Virginia Tech, Blacksburg, VA.

Organic photovoltaics typically rely on photoexcited charge transfer between electron donors and acceptors. This process cannot occur efficiently if the donor and acceptor are separated by a distance greater than 10 nm. In order to allow precise control of the relative locations of donor and acceptors, we have fabricated photovoltaic devices with alternating layers of poly(para-phenylene vinylene) (PPV) and various electron acceptors. Ionically self-assembled monolayers (ISAMs) are grown by the alternate adsorption of cationic and anionic components. The thickness of each individual layer can be varied from 0.3 to ¿5.0 nm via solution parameters such as pH and salt concentration. Using the electron acceptor copper phthalocyanine tetrasulfonic acid (CuPcTs), for example, the fluorescence is nearly completely quenched and the photocurrent is increased by more than an order of magnitude compared to films in which CuPcTs is replaced by poly(methacrylic acid), which is not an effective electron acceptor. The ISAM fabrication method allows detailed studies of the charge generation and photovoltaic efficiencies as a function of such properties as the total film thickness and the relative spatial location of the donor and acceptor species.

JJ8.28
FORMATION OF TWO DIMENSIONAL WEAK LOCALIZATION IN CONDUCTING LANGMUIR-BLODGETT FILMS OF BEDO-TTF AND STEARIC ACID. Yasuo Ishizaki, Mitsuru Izumi, Hitoshi Ohnuki, Tokyo University of Mercantile Marine, Laboratory of Applied Physics, Tokyo, JAPAN; Tstsuro Imakubo, Keiji Kobayashi, The University of Tokyo, Department of Chemistry, Graduate School of Art and Sciences, Tokyo, JAPAN.

The conducting Langmuir-Blodgett (LB) films of BEDO-TTF (BO) and stearic acid showed the maximum dc conductivity 100 Scm^{-1} at room temperature. The present molecular system forms bi-layer structure with upper stearic acid and lower BO layers leading the formation of charge-transfer complex as $(BO)_2(CH_3(CH_2)_{16}COOH\bullet\bullet\bullet OOC(CH_2)_{16}CH_3)^-$. Consequently, it has become unnecessary neither to attach a long alkyl chan to the electroactive molecule nor to put additional stearic acid to increase the stability. Due to the bi-layer structure of BO and stearic acid, BO molecules have a close packed organization leads to optimal molecular orbital overlap and the two-dimensional BO layer provides us a high electrical conduction layer structurally. Then we have investigated the electron state of the LB films at low temperature. The LB films of BO and stearic acid with 1:1 mixing exhibit the logarithmic decrease of the dc conductance with decreasing temperature below 120 K. As a result of the study of transverse magnetoresistance down to 1.7 K we found out the negative magnetoresistance, for which we interpreted the characteristics of the existence of weakly localized two-dimensional (2D) electronic system. A theory developed by Hikami et al. was applied to the quantitative fit to obtain several microscopic parameters govern the present single carrier quantum interference phenomena. We tried to fit a theoretical magnetoresistance and got the quantitative values of Thouless length as a function of temperature which gives an evidence of 2D electronic system with weak localization under the coherent regime. The present LB films are not superconducting but classified as a dirty metal as in graphite GIC compounds and/or semiconductor superlatice. The suppression of the localization is crucial to do a survey of low-temperature electronic ground sate such as superconductivity with zero resistance in a macroscopic scale.

JJ8.29
PATTERNED LED STRUCTURES. Xueping Jiang, Shoshana Gourdin, M.I.T., Dept. of Chemical Engineering, Cambridge, MA; Erik Handy, M.I.T., Dept. of Material Science and Engineering, Cambridge, MA; John Reynolds, Univ. of Florida, Dept. of Chemistry, Gainesville, FL; Michael Rubner, M.I.T., Dept. of Material Science and Engineering, Cambridge, MA; Paula Hammond, M.I.T., Dept. of Chemical Engineering, Cambridge, MA.

Organic-based light emitting devices (LED) have great potential applications in large area, multicolor displays. Our group is working on fabricating multicolor pixel arrays by directing layer-by-layer sequential adsorption onto chemically patterned surfaces. The advantages of this nonlithographic method include the ability to readily construct complex multilayer heterostructures and control electrode interfaces via versatile sequential adsorption techniques. Two luminescent dyes, ruthenium complex red dye and poly (p-phenylene) anion (PPP(-)) blue dye, have been successfully incorporated into patterned pixel array thin films by controlling counter polyion type and solution pH. Fluorescent microscopy was used to image this periodic ordered structure with blue and red elements next to each other. The photoluminescence spectrum of this pixel array shows the emission of PPP(-) blue dye at about 421nm and red ruthenium dye at about 640nm, consistent with the emission wavelength from the single dye component thin films. Electroluminescence studies are ongoing.

JJ8.30
ENHANCED SECOND ORDER NONLINEAR OPTICAL SUSCEPTIBILITIES IN IONICALLY SELF-ASSEMBLED FILMS INCORPORATING DIANIONIC MOLECULES. P.J. Neyman, Dept. of Materials Science and Engineering, Virginia Tech, Blacksburg, VA; M.T. Guzy, S. Shah, K.E. Van Cott, R.M. Davis, Dept. of Chemical Engineering, Virginia Tech, Blacksburg, VA; H. Wang, H.W. Gibson, Dept. of Chemistry, Virginia Tech, Blacksburg, VA; C. Brands, J.R. Heflin, Dept. of Physics, Virginia Tech, Blacksburg, VA.

Ionically self-assembled monolayers (ISAMs) have been shown to form

spontaneously with the noncentrosymmetric order that is required for a second order nonlinear optical response. Thus, no post-processing, such as the application of a large electric field at elevated temperature, is needed. Because the polar ordering is a thermodyamically stable state, the NLO responses of ISAM films are stable for years at room temperature and for more than twenty hours at 150°C. ISAM films are most commonly grown from polyelectrolytes. In this formulation, there is a substantial degree of cancellation of chromophore orientation from opposite interfaces of an individual layer. In order to overcome this cancellation, we have fabricated films containing dianionic nonlinear optical chromophores. Preferential polar orientation is obtained by control of the pH in the two oppositely charged immersion solutions. Second harmonic generation measurements demonstrate that the nonlinear optical susceptibility in these latter films is more than an order of magnitude larger than those containing polyelectrolytes.

JJ8.31
ITO MODIFICATION FOR MORE EFFICIENT HOLE INJECTION IN ORGANIC LIGHT EMITTING DIODES. Daniel Jacobs, Yulong Shen, George Malliaras, Cornell University, Materials Science and Engineering, Ithaca, NY.

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

JJ8.32
IN SITU MEASUREMENTS OF THE GROWTH OF THE SECOND ORDER NONLINEAR OPTICAL SUSCEPTIBILITY IN IONICALLY SELF-ASSEMBLED MONOLAYERS. C. Brands, J.R. Heflin, Dept. of Physics, Virginia Tech, Blacksburg, VA; P.J. Neyman, Dept. of Materials Science and Engineering, Virginia Tech, Blacksburg, VA; M.T. Guzy, S. Shah, R.M. Davis, K.E. Van Cott, Dept. of Chemical Engineering, Virginia Tech, Blacksburg, VA; H. Wang, H.W. Gibson, Dept. of Chemistry, Virginia Tech, Blacksburg, VA.

The polar order that gives rise to a nonzero second order nonlinear optical (NLO) response can occur spontaneously during the deposition of ionically self-assembled monolayers (ISAMs) due to the internal electrostatic interactions. ISAM films are typically fabricated by the alternate adsorption of oppositely-charged polyelectrolytes. The inherent nature of the ordered state provides exceptional temporal and thermal stability of the nonlinear optical response. Measurement of second harmonic generation (SHG) in situ during film growth allows direct observation of the formation of the polar layers. We report measurements of the growth of successive layers of a non-NLO-active polycation and an NLO-active polyanion. Under proper immersion solution conditions, the NLO susceptibility is observed to form completely in a matter of seconds. Adsorption of a polycationic layer on top of an NLO-active polyanionic layer leads to a decrease in the SHG signal associated with a reorientation of chromophores at the film-solution interface. SHG intensity is also compared for wet and dry films. The results of these studies provide further insight into the molecular ordering and morphology of nonlinear optical ISAM films.

JJ8.33
CONDUCTIVE ANISOTROPY IN SELF-ORGANISING MOLECULAR SEMICONDUCTOR. Hiroki Maeda, Central Research Institute, Dai Nippon Printing Co. Ltd., Chiba, JAPAN; Masahiro Funahashi and Jun-ichi Hanna, Tokyo Institute of Technology, Imaging Science & Engineering Laboratory, Yokohama, JAPAN.

Self-organizing molecular semiconductors, which enjoy interesting natures of both of the liquid crystal and the organic semiconductor, exhibit excellent carrier transport properties characterized by a fast ambipolar mobility up to the order of 10^{-2}cm^2/Vs due to the molecular orientation in self-alignment manner. In contrast to the conventional amorphous semiconductor, electronic and/or optical anisotropy is one of unique natures of this type of materials. Based upon this characteristic, polarized OLED, such as dye-doped 2-phenyl naphthalene derivatives aligned with polyimide films between ITO electrodes, was reported by our research group up to now. On the other hand, when we pay attention to the conductive anisotropy of these materials, they bring a new aspect for the organic electronic materials. Aiming to clarify such the aspect, we have studied the anisotropy with planer-structured devices consisting of the finger-type electrodes, in which the organic semiconductor is homogeneously aligned. We prepared different samples where the organic semiconductor was oriented to parallel, perpendicular, or random to the electrodes. In any case, no molecular orientation layer was applied to avoid additional effect of the layer on carrier injection. We measured steady and transient dark/photo currents in different mesophases. As a result, obvious conductive anisotropy was observed. The maximum current ratio under the same field intensity exceeds 10:1 according to the molecular orientation. This anisotropy is easily available due to their fluidity. This fact tells us that there is a potential application of these materials to FET-type switching devices with a high on-off ratio.

JJ8.34
A NOVEL SOLID-STATE ULTRASENSITIVE FIBER OPTIC HYDRAZINE SENSOR BASED ON CONDUCTING STAR POLYMERS. Krishna C. Mandal, Bryce K. Dille, Job Bello, Fei Wang and R. David Rauh.

Portable fiber optics coupled with electrically conductive polymers (CPs) is an emerging new instrumental technique capable of high-resolution analysis of minute quantities of toxic gases in the environment with high efficiency and throughput. The unprecedented sensitivity of this technique has been used for such new applications as remote sensing trace gaseous substances. At EIC, we have synthesized, deposited and thoroughly characterized two novel STAR polymers and used for detecting hydrazine vapors. The laser induced fluorescence (LIF) detection efficiency of the polymeric prototype detector was measured and the minimum hydrazine vapor sample was quantified on the order of few part-per-billion (ppb). An important advantage of this detection scheme is that it can be easily retrofitted into existing sensing apparatus. In detailed results associated with hydrazine sensing mechanism by these star polymers will be presented.

JJ8.35
EMISSION LIGHT PROPERTIES FROM Ag/RHODAMINE-B LB FILMS DUE TO SURFACE PLASMONS EXCITATION KRETCHMANN AND THE REVERSE CONFIGURATIONS. Takayuki Nakano, Hajime Kobayashi, Keizo Kato, Graduate School of Science and Technology, Niigata University, Niigata, JAPAN; Futao Kaneko, Kazunari Shinbo, Takahiro Kawakami, Dept. of Electrical and Electronic Engineering, Niigata University, Niigata, JAPAN; Takashi Wakamatsu, Dept. of Electrical Engineering, Ibaraki National College of Technology, Hitachinaka, JAPAN.

Studies of mutual energy interactions between organic dye molecule and metal thin film are very important for applications of organic ultrathin films, EL devices, photoelectric cells and so on. In this study, the spectra of emission light from Rhodamine-B (RB) LB thin films on Ag thin film due to surface plasmons (SPs) excitation were measured for the prism/Ag/RB LB films in Kretchmann configuration of the attenuated total reflection (ATR) method and the reverse ATR (R-ATR) method. In the ATR method, emission light exhibiting a luminescent peak at about 605nm was observed from the RBLB film by the irradiation of Ar laser beam at 488nm. The emission peak at 605nm corresponded with the conventional PL peak from the RBLB films. In the R-ATR method, red-shifted emission light with a peak at about 650nm was observed at the ATR resonant angle from the prism side by irradiation of the RBLB film surface with Ar laser beam at 488nm. It is tentatively estimated that there was strong energy interaction between the RB thin films and the Ag thin film in the R-ATR configuration.

JJ8.36
ENERGY LEVEL ALIGNMENT AT THE METAL/Alq_3 INTERFACES INVESTIGATED BY PHOTOEMISSION METHODS. Li Yan, Yongli Gao, University of Rochester; M.G. Mason, C.W. Tang, Kodak Research Laboratory.

Tris(8-hydroxyquinoline) aluminum (Alq_3) based organic light emission diodes (OLED) have been a focus of material research in recent years. Intense investigation had bring the device to early edge of commercialization. One of the key issues in searching for better device performance and fabricating conditions is to find suitable electron-injection materials. It is well known now that cathodes made from low work function metals and some combinations of metal/salt have excellent electron injection properties. However, the mechanism is relatively less understood. We have investigated the interface formation and the energy alignment between different metals and Alq_3 using X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) simultaneously. The combination of these two methods gives us great advantages over previous UPS only experiments. The

interface is formed by depositing target cathode material, such as Ca, Al and Al/LiF, onto Alq_3 film using a stepwise fashion in ultrahigh vacuum environment. While the UPS results show the work function and vacuum level changes during interfaces formation, implying the possible surface dipole layer, XPS results shows more detailed and complex behavior. When low work function metal such as Ca is deposited onto Alq_3 surface, a gap state is observed in UPS. At the same time, a new peak can be observed in N1s core level at lower binding energy. These results can be well characterized as charge transfer from the low work function metal to Alq_3. The shifting of core levels are also observed, which may be explained by doping from metal atom or charge diffusion. These interfaces are drastically differ to Al/Alq_3 interface, which has very poor electron injection. At Al/Alq_3 interface there is a destructive chemical reaction and much smaller core level shifts is observed. Based on the detailed analysis, energy level diagram at the interface is proposed.

SESSION JJ9/D7: JOINT SESSION
MOLECULAR DEVICES
Chair: Alamgir Karim
Thursday Morning, November 30, 2000
Constitution B (Sheraton)

8:30 AM JJ9.1/D7.1
FABRICATION AND CHARACTERIZATION OF METAL-MOLECULE-METAL TUNNEL JUNCTIONS BY CONDUCTING PROBE ATOMIC FORCE MICROSCOPY. C. Daniel Frisbie, David J. Wold, Dept of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Molecular level electrical transport studies require innovative approaches for making electrical contacts to oriented molecules. Conducting probe atomic force microscopy (CP-AFM) provides a convenient approach to electrically contacting monolayer films and the formation of metal-molecule-metal junctions. In CP-AFM, a metal-coated AFM tip is placed in direct contact, under controlled load, with the material to be probed. The technique differs from STM in that the probe is positioned using normal force feedback, which decouples probe positioning from electrical measurements. Using this technique, we show that CP-AFM may be used to make mechanically stable electrical contact to self-assembled monolayers (SAMs) on Au. We have probed the current-voltage (I-V) characteristics of the resulting junctions as a function of the number of SAM thickness and the load applied to the tip-SAM contact. The ease of this technique and the fine control of the probe during measurements make CP-AFM a promising approach for studying transport through molecular junctions. Further studies of the dependence of the junction resistance on conjugation, functional group distributions, molecular orientations, and dimensions will also be discussed.

8:45 AM JJ9.2/D7.2
CARBON NANOTUBE BASED NONVOLATILE RANDOM ACCESS MEMORY FOR MOLECULAR COMPUTING. Thomas Rueckes, Kyoungha Kim, Ernesto Joselevich, Charles M. Lieber, Harvard University, Dept of Chemistry and Chemical Biology, Cambridge, MA.

A new concept for molecular electronics exploiting carbon nanotubes as both molecular device elements and molecular wires for reading and writing information has been developed. Each device element is based on a suspended, crossed nanotube geometry that leads to bistable, electrostatically switchable on/off states. The device elements are naturally addressable in large arrays by the carbon nanotube molecular wires making up the devices. These reversible, bistable device elements could be used to construct nonvolatile random access memory and logic function tables at an integration level of 10^{12} elements/cm^2 and an element operation frequency in excess of 100 GHz. The viability of this new concept is demonstrated both by detailed calculations and by the experimental realization of a reversible, bistable nanotube-based molecular electronics bit.

9:00 AM *JJ9.3/D7.3
DESIGN AND MEASUREMENT OF MOLECULAR ELECTRONIC SWITCHES. M.A. Reed, Departments of Electrical Engineering and Applied Physics, Yale University, New Haven, CT.

Electron transport studies in molecular-scale systems have recently become possible with the utilization of advanced microfabrication and self-assembly techniques. We have performed the measurement of the conductance of a single molecule using a break junction technique [1], the demonstration of molecular diodes [2], and the systematic investigation of metal-molecule contacts in a variety of systems [3]. Most recently, we have observed [4] large and useful reversible switching behavior in an electronic device that utilizes molecules as the active component, specifically a nitroamine redox center. The molecular device exhibits negative differential resistance (NDR) and peak-to-valley ratios exceeding 1000:1 and exceeds that observed in typical solid state quantum well resonant tunneling heterostructures. The designs of molecular switches, memories, and their circuit applications will be discussed.
1. M.A. Reed et al., Science 278, 252 (1997).
2. C. Zhou et al., Appl. Phys. Lett. 71, 611 (1997).
3. J. Chen et al., Chem Phys Lett 313, 741 (1999).
4. J. Chen et al., Science 286, 1550 (1999).

9:30 AM *JJ9.4/D7.4
ADVANCES IN MOLECULAR ELECTRONICS: SYNTHESIS AND TESTING OF NANOSCALE MOLECULAR DEVICES. D.W. Price, S.M. Dirk and J.M. Tour, Center for Nanoscale Science and Technology, Rice University, Houston, TX; J. Chen and M.A. Reed, Department of Electrical Engineering, Applied Physics, and Physics, Yale University, New Haven, CT.

With the miniaturization of current silicon-based electronics possibly approaching its hypothesized limit of 0.01 microns, new realms of electronics are being explored. Our team has shown that single organic molecules can carry significant amounts of electronic current, which has led to a great amount of research in this area. Further, we demonstrated devices with negative differential resistance (NDR) having a peak to valley ratio in excess of 1000:1, which is 10 times that of typical solid state devices. These same devices also display retention of electrons enabling the compounds to act as memory components. The NDR and memory effects were first seen in a solid state "nanopore" device utilizing a self-assembled monolayer comprised of ~1000 conjugated organic molecules. The physical and chemical nature of these effects are currently being explored using cyclic voltammetry and theoretical calculations to explain the effects and possibly predict properties of future molecular devices. Advances in compound synthesis and development will be described.

10:30 AM *JJ9.5/D7.5
DRIVEN DYNAMICS OF MOLECULAR DEVICES AND ASSEMBLIES AT THE NANOSCALE. Alison Noble-Luginbuhl, Hye Jin Kwon, Renee Blanchard, Ralph G. Nuzzo, University of Illinois at Urbana-Champaign, Department of Chemistry, Urbana, IL.

The properties of molecular devices–systems with electrooptical or electronic responsiveness, for example–depend very sensitively on the organizational state of their constituents. The dynamics of these systems, especially those underlying driven processes which effect phase changes in the materials, can be extraordinarily complex and vary sensitively with the dimensions of the structures. In this talk I will describe detailed studies of such cooperativities, especially as are seen in examples of molecular devices that are textured at the nanoscale. Of particular interest to us, and a focus of our recent work, are the roles played by surface interactions and near-surface organization in mediating the structural and field-driven dynamical properties of nanometer-scale organic assemblies exhibiting liquid crystalline order. I will describe fabrication methods and chemistries for surface modification that enable the direct study of such phenomena.

11:00 AM *JJ9.6/D7.6
CHEMICALLY ASSEMBLED MOLECULAR ELECTRONICS CIRCUITRY. Jim Heath, Fraser Stoddart, Pat Collier, Yi Luo and Eric Wong, Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA.

Architectures, devices, and small-scale circuitry will be presented for a chemically assembled molecular electronic nanocomputer. Various reconfigurable switches, capable of robust operation under ambient conditions, will be discussed. Various nano-scale wiring networks, using silicon nanowires and single-walled carbon nanotubes, will be presented and the electronic properties of these networks will be discussed. Schemes for coupling molecular switches and nano-scale wiring structures will be discussed.

11:30 AM JJ9.7/D7.7
DEFINING <10 NM GAPS USING STEP-EDGE LITHOGRAPHY AND IN-SITU TUNNELING CURRENT MEASUREMENTS. Mark J. Dalberth, John C. Price, Charles T. Rogers, University of Colorado-Boulder, Dept. of Physics, Boulder, CO.

The measurement of current-voltage characteristics of a single molecule is an important milestone on the road to utilization of molecular electronics. The difficulty in this measurement lies not only in the attachment of a single molecule across a gap, but in the fabrication of the molecule-sized gap itself. We report on a technique for the fabrication of <10 nm gaps. Starting with a step ion milled into a silicon dioxide substrate, we use electron beam lithography to define a channel in bi-layer electron beam resist that runs across the

step at 90 degrees. The gap for molecular attachment is created by evaporating metal over the step, and, as the metal film thickness increases, the gap closes. During metalization, we monitor tunneling current across the gap giving us an in-situ measure of gap width.

11:45 AM JJ9.8/D7.8
CURRENT AMPLIFICATION USING TWO BACK-TO-BACK UNIMOLECULAR RECTIFIERS IN A LANGMUIR-BLODGETT MONOLAYER BETWEEN ALUMINUM ELECTRODES. Tao Xu and Robert M. Metzger, Dept. of Chemistry, University of Alabama, Tuscaloosa, AL.

Some time ago we confirmed that g-hexadecylquinolinium tricyanoquinodimethanide $C_{16}H_{33}Q\text{-}_3CNQ$, is a unimolecular rectifier both by nanoscopic and macroscopic means [1,2]. We are interested in verifying gain in a three-electrode molecular device. We transferred a 2.3 nm thick [1] Langmuir-Blodgett (LB) monolayer of $C_{16}H_{33}Q\text{-}_3CNQ$ on a base electrode B (100 nm thick Al), then evaporated several cylindrical Al electrodes (1.0 to 1.5 m diameter, 100 nm thick, 1 mm apart), atop the cryocooled monolayer. By Ga/In eutectic drops, Au wires were connected to the base electrode B, and to two adjacent Al pads, call them A and C. The two pads were, one forward-biased (voltage VAB), the other back-biased (voltage VBC). Current amplification or transistor action was not expected from this device, because of the formal absence of a "base" or "gate" or "grid" region. We were astonished that a measurable current amplification was found. When VAB=0, the current IBC, as a function of VBC, was very small for VBC<0; IBC=0 at VBC=0, IBC is large and positive for positive VBC, as before [1]. As VAB is increased from 0 to 0.8 Volts, IBC decreases dramatically in the first quadrant, and becomes larger (more negative) in the third quadrant. In the first quadrant current amplification factors of up to to 2.5 were seen. In the third quadrant the amplification factors were less than 1. The LB monolayer is an electrical insulator in the plane of the monolayer, so this is not a field-effect transistor. For amplification to be understood, energy transfer within the monolayer, or some role of the Al electrodes (with their defective oxide coverings) may account for what we have found: current amplification in a device involving two molecules.
We thank DOE-EPSCoR (DE-FC02-91-ER-75678) for financial support.
[1] R.M. Metzger, et al., J. Am. Chem. Soc. 119: 10455 (1997).
[2] R.M. Metzger, Acc. Chem. Res. 32: 950-957 (1999).

SESSION JJ10: TRANSISTORS AND PHOTODIODES
Chair: Ghassan E. Jabbour
Thursday Afternoon, November 30, 2000
Republic B (Sheraton)

1:30 PM *JJ10.1
RECENT DEVELOPMENTS IN PLASTIC SOLAR CELLS USING CONJUGATED POLYMER/FULLERENE COMPOSITES.
N. Serdar Sariciftci, Physical Chemistry, Johannes Kepler University of Linz, Linz, AUSTRIA.

Recent developments in fabrication, optimization as well as characterization of organic, plastic solar cells will be reviewed. These devices based on photoinduced electron transfer from conjugated, semiconducting polymers onto Buckminsterfullerene are promising for low cost large area photovoltaic solutions. Spectroscopic results on solid state composites of donor-acceptor materials as well as double cable materials will be presented.

2:00 PM JJ10.2
APPLICATION OF SCANNING PROBE MICROSCOPIES TO ELECTRICAL CHARACTERIZATION OF ORGANIC SEMICONDUCTOR DEVICES. C. Daniel Frisbie, Kanan Puntamkembar, Tommie Kelley, Jeff Merlo, Dept. of Chemical Engr and Matls Sci, Univ of Minnesota, Minneapolis, MN.

Scanning probe methods offer excellent opportunities for characterizing the electrical properties of organic semiconductor devices with sub-micron spatial resolution. In particular, high resistance bottlenecks to transport can be identified. The first part of this talk will focus on use of scanning surface potential microscopy (SSPM) to determine potential profiles across the channels of operating organic semiconductor field effect transistors. The potential profiles reveal potential drops in the devices due to high resistance bottlenecks, such as contacts and grain boundaries. The second part of the talk will describe use of metal-coated AFM tips to probe the I-V characteristics and resistances of individual grain boundaries. These SPM methods can be diagnostic tools for determining what makes a good vs poor device. They also provide an approach to fundamental transport studies of organic semiconductor thin films over very small length scales.

2:15 PM JJ10.3
CURRENT-VOLTAGE MEASUREMENTS AS A FUNCTION OF APPLIED TIP FORCE ON PENTACENE BY CONDUCTING PROBE MICROSCOPY. Serkan Zorba, Neil J. Watkins, Li Yan, Yongli Gao, University of Rochester, Dept of Physics and Astronomy, Rochester, NY.

Among the most widely used active materials in organic thin-film transistors and molecular electronics in general, pentacene is the most promising one due to its remarkably high mobility. The relation between the morphology of pentacene and its mobility has already been studied extensively and it is well known that the growth mode of pentacene will affect film mobilty considerably. We studied the applied tip force dependence of current-voltage measurements on the organic semiconductor pentacene as a function of film thickness using conducting probe atomic force microscopy. Pentacene films were deposited on Au substrate by vacuum evaporation at room temperature with controlled deposition rate. The films were scanned by atomic force microscope for morphology information. According to the AFM scans pentacene grew in an unorderly fashion where there was no dendritic structure. We started the acquisition of I-V traces with relatively small load and increased the load gradually taking I-V measurements at each load until we punched through the film. We observed conduction only when the bias was about positive 0.028 volts and the tip force was around 1μN. As we kept increasing the tip force we punched through the film. The turn on voltage indicated the pentacene highest occupied molecular orbitals are just slightly below the Fermi level of the Pt tip, a result consistent with our photo-emission spectroscopy studies. With this investigation we were able to have a better understanding of the I-V characterization of pentacene films.

2:30 PM JJ10.4
PHOTOINDUCED CHARGE CARRIERS IN A DONOR-ACCEPTOR DOUBLE-CABLE POLYTHIOPHENE WITH COVALENTLY BOND FULLERENE MOIETIES. Antonio Cravino, Gerald Zerza, Helmut Neugebauer, N.S. Sariciftci, Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler Univ Linz, AUSTRIA; Michele Maggini, Stefania Bucella, Gianfranco Scorrano, Univ of Padova, Organic Chemistry Dept, Padova, ITALY; Mats Andersson, Mattias Svensson, Chalmers Univ of Technology, Polymer Technology, Goteborg, SWEDEN.

The photo-induced electron transfer between conjugated polymer as electron donors and fullerene derivatives as acceptors has opened a way to inexpensive, light weight and flexible photovoltaic devices. By using polymer/fullerene blends solar cells have been already fabricated. However, such devices are still affected by some limitations. Among them, the occurrence of partial phase separation of the fullerene component within the blend is responsible for a loss of electrons, which are trapped in separated clusters and, therefore, do not contribute to the photovoltaic current. Conjugated polymers with chemically attached fullerene moieties (*double-cable* polymers), represent an interesting alternative: they should have a more intimate donor-acceptor contact with no phase separation. The few *double-cable* polymers described so far show promising ground-state properties that almost coincide to those of physically blended polythiophenes/fullerenes. However, the photo-induced electron transfer in such polymers, which is crucial for photovoltaic applications, has not been investigated yet. Starting from a novel bithiophene derivative, we have electrosynthesized a *double-cable* polythiophene with covalently bond fullerene moieties. Electro-deposited films have been investigated by means of several complementary techniques. Photo-induced FTIR and electronic absorption measurements reveal the presence of photoexcited charged states in this polymer. Their origin is due to electron transfer from the polythiophene chains to the attached acceptor moieties, as concluded from the observation of the fullerene radical-anion line in the light-induced ESR spectrum.

3:15 PM *JJ10.5
ELECTRONIC PAPER AND PAPER ELECTRONICS. Thomas Kugler, Tommi Remonen, Petronella Norberg, Ulrika Jemt, Magnus Berggren, ACREO, Norrkoping, SWEDEN.

Paper is the largest surface ever produced and its use as package and information carrier is well known. Here we present some results from the PAELLA project (paper electronics low-cost applications) in which we focus on developing active functions on the paper surface. The goal is to realise smart packages and dynamic information surfaces. The key materials in this approach are the conjugated polymers and organic molecules. Especially we will present multicolour state pigments together with electronic updating technology realised on paper. This "dynamic image" technology is fabricated on the paper surface through printing and reel-to-reel deposition processes which offer low cost and large area production.

3:45 PM JJ10.6
MORPHOLOGICAL AND TRANSISTOR STUDIES OF ORGANIC MOLECULAR SEMICONDUCTORS WITH ANISOTROPIC ELECTRIC CHARACTERISTICS. Zhenan Bao, X. Linda Chen, Andrew J. Lovinger, Joyce Sapjeta, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Oriented thin films of organic semiconducting small molecules were prepared by crystallization on rubbed alignment layers. Polarized absorption spectra showed that the long axis of the conjugated backbones was highly oriented along the rubbing direction and parallel to the substrates. Transmission electron microscopy and diffraction confirmed that the molecules and in many cases the resulting crystals are aligned. Using the above aligned films as semiconducting layers, we fabricated field-effect transistors having anisotropic mobilities with ratios greater than 15. Several common organic semiconductors have been investigated and the results indicate that this growth method is generally successful for achieving macroscopic alignment of these semiconducting molecules (and frequently their crystals, as well).

4:00 PM JJ10.7
PINNING OF THE FERMI ENERGY IN PLASTIC SOLAR CELLS. C.J. Brabec, A. Cravino, N.S. Sariciftci, Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Linz, AUSTRIA; J. Meyer, V. Dyakonov, J. Parisi, University of Oldenburg, Oldenburg, GERMANY; M.T. Rispens and J.C. Hummelen, Stratingh Institute and MSC, University of Groningen, Groningen, THE NETHERLANDS.

The photoinduced electron transfer in solid composite films of fullerenes embedded into conjugated polymers is reversible, ultrafast (within 100 fs) with a quantum efficiency approaching unity, and metastable, thus giving an interesting system to explore photovoltaic devices. The efficiency of such devices comprising poly(2-methoxy-5-(3',7'- dimethyloctyloxy)-1,4-phenylene vinylene), (MDMO-PPV) as donor and (phenyl-[6,6]-C61)-butyric acid methyl ester (PCBM) as acceptor was recently improved to 2.5% under AM1.5. Typically, the photoactive layer of plastic solar cells is in the range of 100 nm, at least one order of magnitude lower than compared to thin film inorganic solar cells. A highly interesting phenomenon in the plastic solar cell is the observation of unusually high open circuit voltages (Voc), which cannot be explained by the workfunction difference in the metal-isolator-metal (MIM) picture. In this study we present results on the Voc of the photovoltaic devices where the work function of the top metal electrode is varied for more than 2 eV. Additionally, the influence of the reduction potential of the fullerene type electron acceptor on the Voc of the devices is investigated. Results from both measurements suggest that the quasi fermi level of the fullerenes pin the fermi level of the evaporated top metal electrode. Together with results from admittance spectroscopy, we interpret these findings as fermi level pinning of the metal electrode due to surface states and/or local dipole moments at the metal / photoactive layer interface.

4:15 PM JJ10.8
PHOTOCURRENT IN A LANGMUIR-BLODGETT RECTIFYING MONOLAYER. Tao Xu and Robert M. Metzger, Laboratory for Molecular Electronics, Chemistry Department, The University of Alabama, Tuscaloosa, AL.

Some time ago we established that g-hexadecylquinolinium tricyanoquinodimethanide $C_{16}H_{33}Q$-$_3$CNQ, first studied by Sambles et al., is indeed a unimolecular rectifier, both by nanoscopic and macroscopic means [1,2]. We have measured the increase in DC electrical conductivity in a monolayer of $C_{16}H_{33}Q$-$_3$CNQ deposited atop a semitransparent Al electrode on glass, with a cylindrical Al electrode (1.0 to 1.5 m diameter, 100 nm thick, 1 mm apart) evaporated atop the cryocooled monolayer. Preliminary results indicate that the photocurrent is enhanced when light corresponding to the intervalence transfer band (peak at 565 nm) is used.
[1] R.M. Metzger, et al., J. Am. Chem. Soc. 119: 10455 (1997).
[2] R.M. Metzger, Acc. Chem. Res. 32: 950-957 (1999).