

# SYMPOSIUM BB

## Electrical, Optical, and Magnetic Properties of Organic Solid State Materials V

November 29 – December 3, 1999

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\* Invited paper

SESSION BB1: MOLECULAR ENGINEERING AND  
SELF-ASSEMBLY

Chair: Timothy M. Swager  
Monday Morning, November 29, 1999  
Salon G (M)

**8:30 AM \*BB1.1**

**SELF-ASSEMBLED ORGANIC LIGHT-EMITTING ARRAYS. GROWTH, MICROSTRUCTURE, PERFORMANCE, AND LITHOGRAPHY.** T.J. Marks, Q. Wang, J. Cui, J.E. Malinsky, J.A. Belot, W. Li, Chem. Dept. and the Materials Research Center, Northwestern U., Evanston IL; G.E. Jabbour, J. Anderson, B. Kippelen, N.R. Armstrong, N. Peyghambarian, Optical Sciences Center, U. of Arizona, Tucson, AZ.

Molecule-based self-assembly using halosilane self-limiting chemisorption/cross-linking offers the possibility of constructing optically-functional organic arrays composed of tailored, photophysically well-characterized building blocks, deposited with conformal, self-sealing/-healing coverage and with high structural precision. We report the application of this approach to the fabrication and patterning of organic light-emitting diode structures. Here siloxane condensation/coupling processes are used to assemble charge-transporting and emissive building blocks into covalently interlinked arrays. This synthetic approach is also particularly well-suited to soft lithographic techniques for pixel fabrication. The assembled structures have been characterized by a battery of microstructural, electrochemical, spectroscopic, and photonic methodologies. The resultant multilayers have high structural regularity, are essentially pinhole-free, exhibit high luminance, low turn-on voltages, and can be readily patterned into pixelated arrays.

**9:00 AM \*BB1.2**

**SELF-ASSEMBLY STRATEGIES FOR MATERIALS WITH ELECTRICAL AND OPTICAL PROPERTIES.** Samuel I. Stupp, Department of Materials Science and Engineering and Department of Chemistry, Northwestern University, Evanston, IL.

The goal in self assembly strategies for materials should be to use primary structure to design functional three dimensional configurations of molecules that can reach into the scale of microns and even macroscopic dimensions. The achievement of this goal is in its very early stages but steady progress is anticipated over the next few decades. Our laboratory is interested in supramolecular and covalent nanostructures composed of chain molecules as the building blocks of larger assemblies. We have identified systems recently in which a piezoelectric and second harmonic response can be measured in films composed of layered domains of these nanostructures. We have also designed systems in which luminescent dendritic structures migrate spontaneously to surfaces to modify the materials, and others in which self assemblers can induce birefringence in organic glasses over macroscopic dimensions.

**9:30 AM BB1.3**

**SELF-ASSEMBLY OF LOW-DIMENSIONAL ARRAYS OF THIOPHENE OLIGOMERS FROM SOLUTION ON SOLID SUBSTRATES.** Diederik B.A. Rep, Ronald Roelfsema, Groningen Univ, Dept of Applied Physics and Materials Science Center, Groningen, THE NETHERLANDS; Jan van Esch, Franck Schoonbeek, Richard Kellogg, Ben Feringa, Groningen Univ, Lab for Organic Chemistry, Stratingh Institute, Groningen, THE NETHERLANDS; Thomas Palstra, Groningen Univ, Dept of Inorganic Solid State Chemistry and Materials Science Center, Groningen, THE NETHERLANDS; Teun Klapwijk, Delft Univ of Technology, Dept of Applied Physics, Delft, THE NETHERLANDS.

We have developed a chemical route to low-dimensional assemblies of organic semiconductors with the aim of studying their electrical properties. Thiophene oligomers are integrated with urea groups, which form intermolecular hydrogen-bondings, providing a one-dimensional framework in which the oligomers are embedded. Pulse-radiolysis time-resolved microwave conductivity experiments show that this results in relatively high charge-carrier mobilities of at least  $0.005 \text{ cm}^2/\text{Vs}$  for bis-urea-bis-thiophene (U2T2) arrays. We have found that the deposition from solution of U2Tn ( $n = 1,2$ ) results in parallel, flat-lying 1D arrays (on graphite), or upright arrays (on  $\text{SiO}_2$ ). On  $\text{SiO}_2$  substrates it is found that simple methods of preparation yield structures ranging from near-mm-sized fibers to monolayer-sized islands, all of which appear to be built up from 1D arrays containing the thiophene oligomers. The flat-lying arrays on graphite substrates are easily imaged by STM or AFM. We will discuss these results in the light of envisioned low-dimensional charge-transport studies.

**9:45 AM BB1.4**

**INFLUENCE OF STRUCTURAL ORGANIZATION ON OPTICAL AND TRANSPORT PROPERTIES IN ORGANIC MATERIALS.**

Jerome Cornil, Jean-Philippe Calbert, David Beljonne, Donizetti A. dos Santos, Jean-Luc Bredas, University of Mons-Hainaut, Mons, BELGIUM.

Organic conjugated materials emerge as promising active elements for use in devices such as light-emitting diodes, photovoltaic cells, and field-effect transistors; the efficiency of solid-state light emission and/or the mobility of charge carriers are parameters of utmost importance to achieve high performance devices. In this context, we demonstrate that correlated quantum-chemical calculations performed on supramolecular structures, i.e., on clusters formed by several oligomer chains in interaction, are relevant to investigate structure-property relationships in well-organized films. When applied to crystalline phases, this approach allows for quantitative estimates of the interchain transfer integrals between adjacent oligomers, and hence for the determination of the directionality of charge transport. The impact of intermolecular interactions on the optical properties can also be assessed with this supramolecular approach; here, use is made of correlated calculations mixing intrachain and charge-transfer one-electron excitations (thus going beyond traditional excitonic theories). We illustrate that variations in chain packing can lead to dramatically different optical (Davydov) splittings and carrier mobilities; optimal chain organizations for various types of device are suggested.

**10:30 AM \*BB1.5**

**ELECTRO-OPTICAL DYNAMICS OF ORGANIC THIN FILMS IN NANOSCALE CONFINEMENT GEOMETRIES.** Ralph G. Nuzzo, Alison Noble Luginbuhl, Department of Chemistry University of Illinois at Urbana-Champaign, Urbana, IL.

Nanoscale systems and materials present interesting behaviors that frequently demonstrate significant differences from the properties found in related bulk materials. One important contributor to this phenomenon is the dominant role played by interactions occurring at surfaces and interfaces in the overall phase dynamics of the system. In this talk, I will describe our recent studies of the dynamics of organic liquid crystalline materials confined in nanometer scale optical cells. I will highlight the development of specific vibrational correlation spectroscopies for the study of the field responsive dynamics of these materials. I will describe a number of new methods of surface modification based on self-assembly that enable a flexible anchoring chemistry for the LC materials and show how these interactions can be directly probed using time resolved spectroscopic methods.

**11:00 AM BB1.6**

**NEW SOLUBLE ORGANIC SEMICONDUCTORS BASED ON THE BENZODITHIOPHENE AND THE THIENOTHIOPHENE FUSED RING STRUCTURES.** Sylvain L. Gilat, Andrew J. Lovinger, Howard E. Katz, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

As the potential that plastic transistors hold for specific applications is being appreciated (e.g. for electronic paper, cargo tags, smart cards and large area displays), the device specifications to make such applications commercially viable have been carefully refined. First, a simple market analysis shows that the technology must be driven by extremely low cost. In consequence, the design of soluble organic semiconductors is critical, since solubility allows for the simple casting, spin-coating or ink-jet/screen printing of the active semiconductor layer. However, the search for soluble organic semiconductors that retain high performance when processed from the liquid phase has almost exclusively focussed on oligo- and polythiophene derivatives. Clearly, the current library of soluble organic semiconductors has to be enriched in order to ascertain the general principles that govern the processes at work during the liquid phase deposition of a semiconductor on a large area. Second, the actual implementation of organic-based devices has brought the research focus beyond the mere realization of high charge carrier mobilities and on/off current ratios: long term stability and reliability have indeed moved to the forefront of the current materials research in the field: adding diversity to the pool of organic semiconductors already available is a way to provide the additional flexibility needed to optimize overall performance. In this line, a number of new alkylated molecules based on the benzodithiophene and thienothiophene moieties have been synthesized and their transistor performance will be described. Thiophene-containing fused ring structures, where the conjugated core is highly planar and rigid, have been shown to be a viable alternative to unsubstituted oligothiophenes, with the additional advantage of high thermal stability. However, no soluble semiconductor based on a fused ring system has been reported so far. The compounds described here display fair to excellent solubility, and good thermal stability. For some of them, their evaporated films show mobilities higher than  $0.01 \text{ cm}^2/\text{Vs}$ . This is associated with a very high crystallinity, the molecules being aligned parallel to the normal of the substrate, as shown by X-ray and electron diffraction studies. The fabrication of thin films based on these novel semiconductors and cast from the

liquid phase will be described as well, together with their thermal, morphological and FETs properties.

**11:15 AM BB1.7**

SELF-ASSEMBLY GROWTH OF ORIENTED ORGANIC THIN FILMS BY MOLECULAR BEAM DEPOSITION. Chengzhi Cai, Martin Boesch, Ye Tao, Bert Mueller, Armin Kuendig, Christian Bosshard, Ilias Liakatas, Ivan Biaggio, Peter Guenter, Swiss Inst. Tech. (ETH), Nonlinear Optics Lab, Inst. of Quantum Electronics, Zurich, SWITZERLAND.

We have designed a series of chromophores that can self-assemble into supramolecular polymers in which the monomeric units are linked in a linear and head-to-tail fashion via strong hydrogen bonding. Thin films of these materials can be easily grown on glass substrates by organic molecular beam deposition (OMBD) with an oblique incidence. As shown by second harmonic generation experiments, the films have a directional order that is parallel to the projection of the molecular beam direction on the substrate surface. Moreover, the directional order is independent of film thickness at least up to 400 nm, and thermally stable up to 190°C. Therefore, we have developed a new technique to align molecules in multi-layer thin films. The following factors may lead to the observed directional order: self-correcting effect, directional requirement for hydrogen bonding, long range interaction between surface molecules and incoming molecules, self-shadowing effect, and close packing. It appears that the self-correcting effect associated with our materials is the key for the long range ordering.

**11:30 AM BB1.8**

FROM LANGMUIR-BLODGETT FILMS TO ELECTROLUMINESCENT DEVICES WITH AN AMPHIPHILIC PHENYL-ETHYNYLENE OLIGOMER. E. Arias-Marin, J.C. Arnault, D. Guillon, T. Maillou, J.Le Moigne, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR, Strasbourg, FRANCE; B. Geffroy, A. Lorin, J.M. Nunzi, A. Rosilio, LETI (CEA-Technologies Avancées), CEA Saclay, Gif-sur-Yvette, FRANCE.

New rigid rods amphiphilic molecules based on phenyl ethynylene oligomers with hydrophilic side chains were synthesized by step by step method. The two most interesting products, the pentamer and the heptamer are enough amphiphilic to give stable Langmuir films that are able to be deposited as LB film on hydrophilic substrates such as hydrophilic glass, ITO or hydrophilic silicon substrates. A good transfer ratio of 1 is observed only by lifting, which suggests a Z type deposited film. A multilayer deposition can be carried out to 36 layers. The well structured films of 3.7 nm thick which are observed by X ray reflectivity suggest a rearrangement in Y-type bilayer. By AFM, the observed irregular surface with steps of 3.7 nm high or multiples is coherent with a self rearrangement of the single deposited layer to a double layer during the drying phase. The heptamer and pentamer show large Stokes-shifts with high photoluminescence emission peaks at 516 and 504 nm respectively. LED properties are demonstrated using the ITO/oligoPY/ Al sandwich yielding photon emission at 516 nm for the heptamer. The electroluminescent device, not optimized as concerns carrier injection at the electrodes and lifetime, yields in the range of  $10^{-3}$  %. The demonstration of electroluminescence in a LB film of molecules aligned parallel to the substrate is very interesting because it opens the possibility to tailor conduction and emission properties of the devices using a layer by layer deposition technique

**11:45 AM BB1.9**

NANO-SCALE CONTROL OF LAYER THICKNESS FOR EL DEVICES BY MASS-CONTROLLED LAYER-BY-LAYER SEQUENTIAL ADSORPTION PROCESS. Seimei S. Shiratori, Masayoshi Yamada and Takahiro Ito, Keio Univ, Dept of Applied Physics & Physico-informatics, Yokohama, JAPAN; Tom C. Wang and Michael F. Rubner, Massachusetts Institute of Technology, Dept of Materials Science & Engineering, Cambridge, MA.

Layer-by-layer self-assembly method is very promising method for the fabrication of organic light emitting devices because it can be applied for the deposition of various kinds of poly-electrolytes. In this study, electro luminescence (EL) devices were fabricated by using newly developed Mass-controlled automatic dipping machine for layer-by-layer sequential adsorption films. In this system, a quartz crystal micro balance (QCM) with an integrated oscillation circuit was attached to the arm of a robot and the frequency shifts during the adsorption or rinsing of the poly-electrolytes were monitored every second. By feeding back the data acquired by the in-situ measurement using QCM to the dipping time, high quality self-assembly film was produced. The layer thickness and the interface roughness of the layer-by-layer self assembly film formed by the conventional Time-controlled Dipping and by the Mass-controlled Dipping was compared using a cross sectional transmission electron microscope (TEM), an atomic force microscope (AFM) and an ellipsometer. As the results, the interface and the surface roughness of the latter were

much smoother than those of the former conventional method. It was also found that the layer thickness of the polymer was controlled with nm order accuracy by the Mass controlled Dipping. By using this newly built up system the light emitting layer of ruthenium complex was deposited on the surface of ITO substrate and the ITO/ruthenium complex/metal type EL devices were fabricated. The strong effect of the Mass-controlled Dipping was demonstrated because it was found that control accuracy of the layer thickness of light emitting layer have a strong effect on the device efficiency and quality.

SESSION BB2: LIGHT-EMITTING DIODES

Chair: Zhenan Bao

Monday Afternoon, November 29, 1999

Salon G (M)

**1:30 PM \*BB2.1**

VERSATILE SYNTHESSES OF VARIOUS HOMO-AND COPOLYMERS OF POLY(1,4-ARYLENE VINYLENE)S. Rainer E. Martin, Florence Geneste, Beng Sim Chuah, Timothy J. Peckham, Andrew B. Holmes, University of Cambridge, Melville Laboratory, Cambridge, UNITED KINGDOM; Franco Caciali, Richard H. Friend, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

In recent years variously substituted derivatives of poly(1,4-phenylene vinylene)s have emerged as efficient candidates for the emissive layer in polymer light emitting diodes. The synthetic routes for these polymers divide between precursor routes and those leading to fully conjugated solvent-processible polymers. The Gilch dehydro-halogenation polycondensation has largely been used for the latter class. Unfortunately most syntheses of 1,4-bis(halo)phenylene derivatives depend on the chloro- or bromomethylation reaction of aromatic precursors or the N-bromosuccinimide substitution of the corresponding xylene derivatives. Both routes have serious disadvantages. In this paper we report an entirely new approach to 1,4-bis(halo)phenylene derivatives which is based on directed metallation reactions, and offers excellent versatility in the synthesis of monomeric building blocks for the Gilch route. Application of these monomers to the synthesis of some highly fluorescent homo- and copolymeric poly(arylene vinylene)s will be described.

**2:00 PM BB2.2**

SYNTHESIS AND PROPERTIES OF NOVEL BINAPHTHYL-BASED LIGHT-EMITTING POLYMERS. Alex K.-Y. Jen, Lixin Zheng, Michelle Liu, R. Craig Urian, Xuezhong Jiang, Jianyao Wu, Department of Chemistry, Northeastern University, Boston, MA; Yunqi Liu, Institute of Chemistry, Chinese Academy of Sciences, Beijing, CHINA; Qiao-sheng Hu, Lin Pu, Department of Chemistry, University of Virginia, Charlottesville, VA.

Novel conjugated light-emitting polymers were synthesized via a Wittig-Horner condensation reaction between a binaphthyl dicarbonyl and a series of electron-rich or electron-deficient aryl diposphonates. The optical, electrical and thermal properties of these polymers were studied by UV-Vis, cyclic voltammetry, photoluminescence, electroluminescence, DSC, and TGA. After comparing these materials with the model compound, naphthyl vinylene-1,4-phenylene vinylene, it was revealed that the introduction of a twisted, non-coplanar binaphthyl structure, provided an effective approach for tailoring the spectral characteristics of the polymers and improving their solubility and thermal stability ( $T_g > 200^\circ\text{C}$ ). Furthermore, the band offsets between the polymers and electrodes could be fine-tuned by changing the electronic properties of the bridging aromatic units to increase the device efficiency and lower the turn-on voltage. Detailed device properties will be discussed in this paper.

**2:15 PM \*BB2.3**

EXCITON CONFINEMENT IN POLYMERS AND AT INTERFACES FOR HIGH- AND ELECTRO-LUMINESCENCE EFFICIENCY. A.J. Epstein, T.L. Gustafson, E.M. Kyllö, F.C. DeLucia, Jr., R.G. Sun, D.K. Wang, Y.Z. Wang, and Q.B. Zheng, The Ohio State University, Columbus, OH.

The photoluminescence (PL) quantum efficiency of poly(*p*-phenylene vinylene) (PPV) varies with preparation and processing. We report the achievement of essentially 100% PL quantum efficiency through design and synthesis of alternating rigid conjugated segments of PV (three phenyl and two vinyl units) and flexible non-conjugated segments along the polymer backbone. We also have enhanced solubility in desired solvents and increased interchain separation through incorporation of methoxy sidegroups, forming poly [1,6-hexanedioxy-2,6-dimethoxy-1,4-phenylene]-1,2-ethynylene-[3,6-dimethoxy-1,4-phenylene]-1,2-ethynylene-[3,5-dimethoxy-1,4-phenylene], or GDBBC. The nearly temperature-independence of the

PL decay at different emission wavelengths of the alternating block co-polymer (ABC) shows that the excitons are highly localized due to the blocking by non-conjugated segments as well as due to increased interchain separation due to the methoxy sidegroups. The fs-ps transient absorption of GDBBC in solution and films, and comparison with selected temperature- and time- dependent results for the corresponding PV oligomer and PPV, demonstrates the role of exciton confinement in achieving high quantum efficiency. The results are compared to the exciton confinement at the interface of light emitting electron and hole transporting polymers, forming an exciplex. Electroluminescent devices using GDBBC as the light-emitting layer and incorporating poly[1-phenyl-2-(p-n-carbazolylphenyl) acetylene], (PDPA-Cz), as hole transporting layer, in the structure ITO/PDPA-Cz/GDBBC/Alq/MgAg have bright green emission from the GDBBC. High efficiencies also are achieved in EL devices based on exciplex emission. New fabrication techniques especially applicable to devices incorporating conducting polymers are introduced. This work is supported in part by DARPA and ONR.

#### 2:45 PM BB2.4

RGB EMISSION BASED ON DIRECT CARRIER RECOMBINATION IN GUEST HOST SYSTEMS. H. Murata, L.A. Crisafulli, Gary Kushto, Z.H. Kafafi, Naval Research Laboratory, Washington, DC.

Electroluminescence (EL) of the three primary colors (RGB) was achieved with multilayered devices where the emitting layers consist of the hole transport layer (HTL) doped with several polyaromatic hydrocarbons as the guests. Efficient EL emission was realized by the direct carrier recombination on the highly fluorescent guest molecules in the doped HTL. Carrier recombination on the guest molecules was maximized by the dual electronic nature of the guests acting as an electron hopping site and a hole trap in the HTL. Since the emission mechanism based on the carrier recombination on the guest does not require large overlap between the emission spectrum of the host and the absorption spectrum of the guest, the EL with RGB colors was achieved without changing the host material.

#### 3:30 PM \*BB2.5

LOW-VOLTAGE-DRIVING ORGANIC ELECTROLUMINESCENT DEVICES HAVING CHEMICALLY DOPED CARRIER INJECTION LAYERS. Junji Kido, Juno Endo, Yamagata University, Yonezawa, Yamagata, JAPAN; Koichi Mori, Toshio Matsumoto, IMES Co., Ltd., Fujisawa, Kanagawa, JAPAN.

In order to lower drive voltages of organic electroluminescent devices, chemically doped cathode interface layer and anode interface layer are introduced. Typical device structure is ITO / chemically doped organic layer / hole transport layer / electron transport layer / chemically doped organic layer / Al. Chemical doping of the organic layer at the cathode interface with highly reactive metals, such as Li, is effective to lower the drive voltage due to the low barrier height for electron injection, which is due to the formation of radical anions at the cathode interface. Similarly, Lewis acid, such as FeCl<sub>3</sub>, -doping to the organic layer at the anode interface is quite effective to lower the drive voltage due to the formation of radical cations at the interfaces. Devices having the both chemically doped cathode interface and anode interface layers exhibit extremely low drive voltages due to low barrier heights for carrier injection from the electrodes and high carrier mobility of the chemically doped layers.

#### 4:00 PM \*BB2.6

RECENT DEVELOPMENTS IN ORGANIC ELECTROLUMINESCENT DEVICES. B. Kippelen, G.E. Jabbour, D. Guzman, S.E. Shaheen, J.F. Wang, Y. Zhang, N. Peyghambarian, S. Thayumanavan, S.R. Marder, D.L. Mathine, H.S. Woo and N.R. Armstrong, Univ. of Arizona, Tucson, AZ.

We will review some recent developments in the fabrication of organic light-emitting devices. First, we will compare the performance of devices fabricated with different bilayer cathodes using Al and several alkali halide materials with increasing dipole moment. The results suggest that the best performance does not correlate with the highest dipole moment. In view of these results, the high injection efficiency of the cathode is attributed to the decomposition of the alkali halide during deposition, leading to a doping of the Al by the alkali metal and a corresponding reduction of the work function. This effect enabled the fabrication of Al-based devices with efficiencies of 20 lm/W. The second part of the talk will focus on the fabrication of blue devices based on oxadiazole metal complex compounds. We will report on the synthesis and characterization of tris(2-(5-phenyl-1,3,4-oxadiazol-yl)phenonate) aluminum. The results show that oxadiazole metal complexes are good emitters and electron transporters for blue organic LEDs. Finally, we will report on the fabrication of top-emitting arrays of OLEDs micropixels heterogeneously integrated with CMOS drive circuitry.

#### 4:30 PM BB2.7

Alq<sub>3</sub> OLED DEGRADATION BASED ON AN ELECTRO-CHEMICALLY-FORMED GROUND STATE CHARGE TRANSFER COMPLEX. D.L. Thomsen III, E. Shin, K.A. Higginson and F. Papadimitrakopoulos, Department of Chemistry and Chemical Engineering, Polymer Science Program, Nanomaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT.

The hydrolytic decomplexation of Aluminum(III)-tris(8-hydroxyquinoline) (Alq<sub>3</sub>) proposed by our group[1] constitutes one of the major chemical degradation mechanisms for Alq<sub>3</sub>-based organic light emitting diodes (OLEDs). This paper for the first time links this mechanism to the electrochemical OLED degradation proposed by Aziz *et al.* [2] The oxidative degradation of Alq<sub>3</sub> has been experimentally witnessed through cyclic voltammetry, UV/VIS absorption shifts, photoluminescence (PL) decay, and FTIR spectral changes. The delocalized radical cation (hole) of Alq<sub>3</sub> is susceptible to oxidation at the 5-position of the 8-oxyquinolate ligand which forms 5,8-dihydroquinoline. Further facile oxidation of 5,8-dihydroquinoline to 5,8-quinolinedione leads to a non-emissive, charge transfer complex responsible for PL and electroluminescence (EL) quenching of Alq<sub>3</sub>-based OLEDs. This complex exhibits a UV-VIS absorption edge extending up to 810 nm. FTIR spectroscopy indicates that intermolecular hydrogen bonds promote additional stabilization of this charge transfer complex.

[1] F. Papadimitrakopoulos, X.-M. Zhang, D. L. Thomsen III, and K. A. Higginson, *Chem. Mater.*, vol. 8, 1363 (1996).

[2] H. Azis, Z. D. Popovic, N.-X. Hu, A.-M. Hor, and G. Xu. *Science*, vol. 283, 1900 (1999).

#### 4:45 PM BB2.8

RAPID GROWTH OF SMALL MOLECULE ORGANIC LIGHT EMITTING DEVICES USING LOW PRESSURE ORGANIC VAPOR PHASE DEPOSITION. Max Shtein<sup>1</sup>, Herman Gossenberger<sup>2</sup>, Paul E. Burrows<sup>3</sup>, Stephen R. Forrest<sup>3</sup>; <sup>1</sup> Department of Chemical Engineering, Princeton University, Princeton, NJ, <sup>2</sup> PDL Corporation, Princeton, NJ, <sup>3</sup> Department of Electrical Engineering, Center for Photonics and Optoelectronic Materials, Princeton University, Princeton, NJ.

The largely amorphous nature of the organic semiconductors used in OLEDs permits their deposition on large area and low cost substrates such as plastic, potentially enabling extremely rugged and low-cost displays. However, the high capital cost of vacuum equipment required to controllably grow thin films of organic semiconductors, and the relatively low accompanying deposition rates (typically <5Å/s) limit the potential for low cost manufacture of such displays. In past work, we have shown that the alternative technique of low pressure organic vapor phase deposition (LP-OVPD) can be used to uniformly deposit amorphous organic thin films on silicon, glass, and polyester substrates [ref. 1]. Unfortunately, early reactors did not produce high deposition rates, lacked in-situ thickness monitoring, as well as a shutter mechanism allowing for precise control of film thickness. This permitted fabrication of somewhat simple, undoped organic heterostructures. In this work, we introduce an improved multi-barrel, hot wall glass tube reactor where several source materials are sequentially or simultaneously evaporated and transported downstream by a hot carrier gas, typically nitrogen. In the downstream section of the reactor, the organic vapors condense on a cooled substrate at controllable rates of 0.5-20Å/sec. The reactor operates at pressures of 0.03-5 Torr and temperatures of 200 - 400°C; it incorporates in-situ thickness monitoring and a shutter mechanism to enable real-time control of film thickness and individual layer definition. We use LP-OVPD to grow organic heterostructures consisting of pure and doped TPD and Alq<sub>3</sub> layers. Atomic force microscopy reveals that the resulting films, typically 500Å thick, exhibit RMS surface roughness of 5Å when grown at 0.5Å/sec, increasing to 50Å for films grown at 20Å/sec. Devices fabricated using LP-OVPD achieve display-level brightness at 6-7 volts, with external quantum efficiencies ~0.4%. Precise linear control over doping ratios is achieved in the mass-flow regime, rather than by varying the source temperature. The possibility of using different carrier gases and growth conditions is useful for studying the physics and chemistry of growth of many organic films and their interfaces. References: [1] Organic Vapor Phase Deposition, M.A. Baldo, M. Deutsch, P.E. Burrows, H. Gossenberger, M. Gerstenberg, V.S. Ban, S.R. Forrest, invited, *Adv. Mater.* (1998).

SESSION BB3: POSTER SESSION  
Chairs: Zhenan Bao and John R. Reynolds  
Monday Evening, November 29, 1999  
8:00 P.M.  
Exhibition Hall D (H)

### **BB3.1**

#### **MAGNETIC ORIENTATION OF POLYMERS: A NOVEL TECHNIQUE OF CONTROLLING BIREFRINGENCE.**

Tsunehisa Kimura, Eiko Ito, Tokyo Metropolitan Univ, Dept of Applied Chemistry, Tokyo, JAPAN.

Magnetic field induced orientation of crystalline polymers recently reported by our group is briefly summarized and the application of this new phenomenon is reported as a novel method of controlling the birefringence of polymer films. Liquid crystalline polymers are easily aligned under magnetic fields, but melts of crystalline polymers were believed to be unable to align in the magnetic field because of their lack in anisotropic structure necessary for the magnetic orientation. However, we have observed that crystalline polymers including poly(ethylene-2,6-naphthalate) (PEN), isotactic polystyrene (iPS), isotactic polypropylene (iPP), and poly(ethylene terephthalate) (PET) undergo magnetic orientation upon application of magnetic field (6 tesla) to the melts of these polymers above melting point or during melt crystallization. Because the alignment occurs before the start of substantial crystal formation, the aligned samples are transparent without strong scattering by crystallites. We believe that some pre-crystalline order similar to liquid crystalline phase is responsible for the orientation. Since the magnetic field can be applied to a desired direction, alignments of polymer chains, for example, inclined to or perpendicular to the film surface become possible. These alignments are not attained by means of commonly used methods of alignment such as mechanical elongation and shear. As a result, unique distribution of birefringence ellipsoid could be attained. Study on iPS and iPP showed that the helical axis aligns perpendicular to the magnetic field, providing a unique orientation never possible by means of other methods. PET also exhibited perpendicular orientation, while PEN exhibited parallel orientation. Retardation obtained for iPS and PET was about several hundred nanometers.

### **BB3.2**

#### **QUICK RESPONSE ALL-SOLID-STATE ELECTROCHROMIC DEVICE BASED ON POLYANILINE AND WO<sub>3</sub>.** V.F. Ivanov, O.L. Gribkova, A.A. Nekrasov, and A.V. Vannikov, Frumkin Institute of Electrochemistry, Moscow, RUSSIA; V.A. Tverskoj, Lomonosov Moscow State Academy of Fine Chemical Technology, Moscow, RUSSIA.

All-solid-state electrochromic device was developed on the base of electrochemically deposited polyaniline as an anodic electrochromic layer and vacuum deposited WO<sub>3</sub> as a cathodic electrochromic layer. The intermediate ion-conducting solid state layer comprised cation exchange aromatic polyamide containing sulfonate groups. The layer has high conductivity for H<sup>+</sup> ions, which, during the transition from transparent to opaque state, are injected to the WO<sub>3</sub> layer by the cathodic reaction and are ejected from polyaniline by the anodic reaction. The response time vary from 0.1 to 1 s depending on the proton conductivity of the ion-conducting layer and the value of transparency change within the ultimate limits of 80% to 5%. The device exhibits high durability - more than 1,300,000 cycles of transparent/opaque transitions. The most promising applications of this device may be optical filters or mirrors with controlled transmittance and reflectance. The study was supported by the International Science and Technology Center (project 872) and the Russian Foundation for Basic Research grants No.99-03-32077 and No.96-15-97320.

### **BB3.3**

#### **ANTICORROSION APPLICATION OF POLYANILINE BY A NEW ELECTROPHORETIC COATING PROCESS.** Yuan Lin, Frank McClarnon, Sze C. Yang, Univ of Rhode Island, Chemistry Department, Kingston, RI; Richard Brown, Univ of Rhode Island, Chemical Engineering Department, Kingston, RI.

In 1986, D.W. DeBerry demonstrated corrosion inhibition of steel by polyaniline. Recently, B. Wessling developed a polyaniline-based primer coating for corrosion inhibition of steel. Although there have been significant recent progresses, the presently available conducting polymers are still not ideal for coatings application. In the present report, we will discuss the development of new interpolymer complexes of polyaniline and a new coating process for anticorrosion applications. We will report the effectiveness of this new coating for corrosion protection of aluminum alloys. The new interpolymer complexes of polyaniline are functionalized polyanilines with their properties designed to meet the needs for coatings applications. The new material provides high stability in the conductive state, the ease in coating process, and the improved performance in corrosion protection. In this talk we will also present a new electrophoretic coating processes. The cathodic electrophoretic process is a standard coating process in the automobile coating industry. We found that a very small amount of the electroactive ingredient in water-borne epoxy can significantly improve corrosion inhibition for aluminum

alloys. Long-term corrosion tests and electrochemical studies of the coatings will be presented.

### **BB3.4**

#### **INFLUENCE OF SPACER IN MODIFIED-PVK ON PHOTOREFRACTIVE BEHAVIOR IN THREE-COMPONENT LOW-T<sub>g</sub> COMPOSITES.** Yi-Wang Chen, Yuan-Kang He, Hui-Ying Chen, Institute of Polymer Science, College of Chemistry, Peking University, Beijing, CHINA; Feng Wang, Zhi-Jian Chen, Qi-Huang Gong, Dept of Physics, Peking University, Beijing, CHINA.

To investigate the influence of the spacer linking carbazolyl to the main-chain on the photorefractive performance except photo-conductivity, poly(2-carbazolyethyl methacrylate) (PCEMA) and poly(3-carbazolylpropyl methacrylate) (PCPMA), were synthesized. Doped with electro-optic chromophore *l*-*n*-butoxy-2,5-dimethyl-4-(*p*-nitrophenyl)azobenzene and the photosensitizer 2,4,7-trinitro-9-fluorenone, the electro optic response and photorefractive effect were studied experimentally. Due to the shorter spacer between the carbazolyl group and the main-chain and thus having a higher glass-transition-temperature T<sub>g</sub>, PCEMA-based composite exhibited an effective electro-optic coefficient as only a quarter as that PCPMA-based composite did. However, a slight higher two-beam coupling coefficient was observed in the former, a reasonable suggestion was a lower trap number density existed in PCEMA-based sample. Also, much faster photorefractive response was found in PCEMA-based sample. We came to such a conclusion that the T<sub>g</sub> of the polymer, the trap number density in the sample and the photorefractive response rate could be changed by changing the length of the spacer linking the carbazolyl to the main-chain. On the other hand, with the quick translating technique, an orientationally enhanced electroabsorption grating was firstly observed and separated from other gratings in a poly(N-vinylcarbazole)-based photorefractive composite doped with the electro-optic chromophore and the photosensitizer mentioned above.

### **BB3.5**

#### **TETRAPHENYLMETHANE-BASED 1,3,4-OXADIAZOLE AS ELECTRON TRANSPORTING MATERIALS IN ORGANIC LIGHT-EMITTING DEVICES.** Chin-Ti Chen, Tzu-Yao J. Lin, Hsiu-Chih Yeh, Easwaramoorthy Balasubramaniam, Yu-Tai Tao, Institute of Chemistry, Academia Sinica, Taipei, TAIWAN.

Electron transporting (ET) material 2-(biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) has been widely used in enhancing performance of organic light-emitting devices (OLEDs). However, due to the low melting point (137°C), an amorphous film of PBD is prone to crystallize and hence adversely affect the lifetime of OLEDs. To improve the thermal properties of PBD, we newly design and synthesize a series of novel tetraphenylmethane-based 1,3,4-oxadiazole. In addition to their thermal properties, the electro-luminescent (EL) studies based on the double or triple layer devices containing tetraphenylmethane-based 1,3,4-oxadiazole as ET material are presented. The results are compared to those obtained from PBD for the evaluation of the new electron transporting materials.

### **BB3.6**

#### **THE SYNTHESIS OF METALLIC POLYANILINE BY OXIDATION WITH TETRABUTYLAMMONIUM PERSULFATE IN ORGANIC SOLUTIONS.** Iakov L. Kogan, Lubov S. Fokeeva, Evgeniya I. Knerel'man, Irina G. Shunina, Larisa T. Kasumova, Yakov I. Estrin Institute for Problems of Chemical Physics, Chernogolovka, Moscow region, RUSSIA.

A new oxidizing agent ditetrabutylammonium persulfate has been used for aniline polymerization in acetonitrile. This reactant was prepared by interaction of tetrabutylammonium hydroxide and ammonium persulfate at 40 C. The reaction product, identified as polyaniline, had specific conductivity 400–500 S · cm<sup>-1</sup> and metal-dielectric transition at ≈ 25K after film precipitation from *m*-cresol in the presence of 10- camphorsulfonic acid. The basic form displayed optical absorption maxima at 320, 448 and 670 nm while salt at 420 nm with continuous absorption in the near IR region. Gel chromatography of the polyaniline solutions in *N*-methylpyrrolidone allowed us to register two peaks in the region of molecular masses 33 000 (polysterene mark) and *M*<sub>w</sub> ≈ 120000. The decrease of polymerization temperature from +20C to -30C led to the shift of the main peak to 38 000 and disappearance of the second peak at *M*<sub>w</sub> 120 000. The reduction of concentration of initiating agent gave similar effect. The samples of polymer were used as the components of conducting composites with percolation threshold 5% in the case of polyaniline-polymethylmethacrylate. To explore the role of water the initial stage of polymerization was investigated. The storage of persulfate salt in acid aqueous solution led to the significant growth of its potential determined with indifferent platinum electrode. The application of this solution to aniline polymerization resulted in the disappearance of induction period registered by optical absorption.

The analysis showed that the persulfate interacted with water producing peroxydisulfuric acid (Caro acid) which was likely to be the active oxidant of aniline. The utilization of organic media instead of aqueous solutions excludes the formation of Caro acid while tetrabutylammonium persulfate in the presence of initiating agents functioned as more gentle oxidizing agent producing polyaniline samples with low level of defects in the chain.

### BB3.7

ULTRASONIC ATTENUATION IN LAYERED CONDUCTORS. Olga Kirichenko, Valentin Peschansky, Andrei Yermenko, Institute for Low Temperature Physics and Engineering, Kharkov, UKRAINE.

We report on theoretical description of orientational effects in ultrasonic attenuation in layered conducting materials. The proposed theory concerns in particular the low-dimensional charge-transfer salts based on the organic donor molecules of the BEDT-TTF [bis(ethylenedithio) tetrathia-fulvalene] type and related ones. The roles of the Fermi surface topology, external magnetic orientation and vortex electromagnetic fields are analysed under condition of magneto-acoustic resonance. This research was partly supported by the NATO (grant CRG.CRGP972846).

### BB3.8

THEORY OF EVEN PARITY STATES AND NONLINEAR ABSORPTION IN THE POLYPHENYLENES AND POLY(PARA-PHENYLENEVINYLENES). S. Mazumdar, A. Shukla, University of Arizona, Dept of Physics, Tucson, AZ; A. Chakrabarti, Center for Advanced Technology, Indore, INDIA.

Understanding the photophysics of conjugated polymers requires a physical understanding of the excited states involved in the photophysics. We have developed a diagrammatic exciton-basis valence bond theory of excited states in polyphenylenes and poly(para-phenylenevinylene)s that gives physical, pictorial descriptions of all excited states. We show that multiple classes of two-photon states occur in these systems, due to the existence of both delocalized and localized benzene molecular orbitals in the unit cells. While the counterparts of the low energy two-photon states occur also in the polyacetylenes and polydiacetylenes, at higher energy there occur new classes of even parity states that are absent in the linear chain polymers. Detailed comparisons of theoretical results and experimental photoinduced absorption, two-photon absorption and electro-absorption are made. High energy photoinduced absorption, previously unexplained, can be explained naturally within our theory when both the delocalized and localized benzene molecular orbitals, and electron correlations are included explicitly in the theoretical description.

### BB3.9

INTERMOLECULAR COUPLING ENHANCEMENT OF THE MOLECULAR HYPERPOLARIZABILITY IN MULTI-CHROMOPHORIC DIPOLAR DENDRONS. Shiyoshi Yokoyama, Akira Otomo, Shinro Mashiko, Communications Research Laboratory, Kobe, JAPAN.

Dendritic molecules, called dendrons, having a branching structure modified with a second-order nonlinear optical chromophore has been synthesized. An electron donor and acceptor azobenzene chromophore, having a large molecular hyperpolarizability of  $670 \times 10^{-30}$  esu, was chosen. Size exclusion chromatography and MALDI TOF mass measurement indicated that synthesized dendrons had a high purity level and exact molecular weights as expected. The electronic structure of synthesized dendrons, which were expected to be dipolar due to their intermolecular attractive interaction, was proven by second-order nonlinear optical property. The molecular hyperpolarizability of dendrons was measured by the hyper-Rayleigh scattering technique. The technique provided not only molecular hyperpolarizability, but also its tensor components. The highest molecular hyperpolarizability was found to be  $14,600 \times 10^{-30}$  esu for a dendron having 15 azobenzene chromophores. This level of molecular hyperpolarizability was significantly enhanced compared with the values estimated when corresponding the simple additivity of monomer unit. The result indicates that the synthesized dendrons have a rod-shaped structure with a noncentrosymmetric chromophore orientation, which is essential for a large nonlinear optical activity.

### BB3.10

PHOTOLUMINESCENCE PROPERTIES OF THE BLENDS OF POLY(3-ALKYLTHIOPHENES) AND POLY(VINYL CARBAZOLE). W. Li, G.M. Wang, X. Hu, School of Applied Science, Nanyang Technological University, Singapore, SINGAPORE; T.K.S. Wong, B. Srinivasa, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, SINGAPORE.

It is known that poly(3-alkyl thiophene) (P3AT) and poly(vinyl carbazole) (PVK) have photoluminescence and electroluminescence

properties due to their conjugated structure. These two polymers have been used in light emitting diode (LED) in which poly(alkyl thiophene) is used as electron transport layer and poly(vinyl carbazole) as hole transport layer.

In this paper, we present the optical and electronic properties of the blends of poly(butyl thiophene) and poly(dodecyl thiophene) with poly(vinyl carbazole). The blended films were cast from the solutions of the mixture of the two polymers. It is found that the blend emits violet-red light under excitation. By using FT-IR, scanning electron microscopy (SEM), UV-Vis absorption and photoluminescence measurements, the energy interactions of these two polymers at the range of relatively low composition ratio of PAT vs PVK or PVK vs PAT were investigated. It is shown that the luminescence properties of the blends are affected by heat treatment and the effect is also dependent on alkyl side chains length of PAT. Results revealed how these polymers interact with each other and how the morphology changes with blend composition and heat treatment condition. The results also revealed the stability in terms of the luminescence properties of these blends.

### BB3.11

SYNTHESIS OF WATER-DISPERSIBLE INTERPOLYMER COMPLEX OF POLYANILINE. Patrick A. McCarthy and Sze C. Yang, Univ of Rhode Island, Dept of Chemistry, Kingston, RI.

For coatings applications, it is desirable to disperse polyaniline in water. The stability of a colloidal dispersion is sensitively dependent on the polymer aggregation and/or the polymer folding. We have identified the reaction conditions for forming the water dispersible complex of polyaniline. In this talk, we describe the synthesis of interpolymer complexes of polyaniline that are dispersible in water. In the synthesis of the polyaniline:poly(acrylic acid) complex, we found that the dispersibility of the product is critically dependent on two parameters. These two parameters are (1) the concentration of the reagents and (2) the hydrogen ion concentration. After constructing a two-dimensional map of these two parameters, we found an island where the reaction products exist as a stable dispersion. It is interesting to note that the reaction conditions are critical. The reaction product is completely dispersible when the concentrations are within the island of stability, while completely precipitated when the concentrations are slightly outside the island.

### BB3.12

ENVIRONMENTAL EFFECTS ON THE ELECTRONIC SPECTRA OF ELECTROSTATICALLY ASSEMBLED LAYERS OF CONJUGATED POLYMERS. Daniel J. Sandman, Myunghwan Kim, University of Massachusetts Lowell, Department of Chemistry, Center for Advanced Materials, Lowell, MA.

Conjugated polymers, poly[2-(3-thienyl)-ethanolhydroxycarbonylmethylurethane], PDA from 5,7-dodecadiyn-1,12-bis-(hydroxycarbonylmethylurethane), and PDA from hydroxycarbonylmethylurethane of 9-(N,N-diphenylamino)-5,7-nonadiyn-1-ol, were processed to electrostatically assembled multilayers respectively in two media with different refractive indices - one is poly(diallyldimethylammonium) chloride, the other quaternized poly(4-vinyl pyridine) with dimethylsulfate. The film structures of multilayers and post-assembly-processed multilayers are under characterization in order to study environmental effects on the electronic spectra of conjugated polymers through infrared, fluorescence, UV-vis, Raman, XPS spectroscopic and other techniques.

### BB3.13

SYNTHESIS AND OPTICAL PROPERTIES OF PHTHALONITRILE OLIGOMERS. Zohong Tsai, Daniel J. Sandman, Univ. of Massachusetts Lowell, Dept. of Chemistry, Lowell, MA.

Stannous chloride has two kinds of properties, reducing reagent and Lewis acid. It could react with sodium alkoxide to form Sn(II) alkoxide which can react with phthalonitriles to yield polyisoindolines. We can control absorption maximum at 425 nm or 726 nm in DMF from different kinds of reaction conditions. The mass spectrum showed five repeated units at least. Phthalonitrile and its derivatives react with Sn(II) reagents to give linear intensely colored oligomers. Structure are proposed for oligomers based on elemental analysis, infrared,  $H^1$  and  $C^{13}$  spectra, and mass spectra. Room temperature solution absorption and emission spectra will be reported. In semi empirical AM1 calculations, the helical conformation of the oligomer is more stable than that of linear conformation.

### BB3.14

LANGMUIR-BLODGETT FILM OF PROCESSABLE POLYDIACETYLENE WITH  $\chi^2$  CHROMOPHORE AND ITS OPTICAL PROPERTIES. Dong-Chan Lee, John Williams, Daniel J. Sandman, Univ. of Massachusetts Lowell, Center for Advanced Materials and Department of Chemistry, Lowell, MA; Lynne Samuelson, Materials Science Team, US Army Soldier Systems Center,

Natick, MA; Lian Li, Molecular Technologies Inc., Westford, MA.

This work presents the synthesis of soluble and processable polydiacetylenes (PDA) with functionalizable N,N-dialkylaniline group as one side group and glutamate ester substituted alkylurethane group as the other side group. This PDA was further functionalized via postpolymerization functionalization that is a new strategy to functionalize conjugated polymers. Postpolymerization functionalization of the PDA with tetracyanoethylene was performed to give  $\chi^{(2)}$  chromophore as a side group and asymmetric Langmuir-Blodgett (L-B) film of the PDA was fabricated. Second order nonlinear optical properties of the L-B film were studied and compared to those of spin-coated film. Surface properties of the L-B film were also characterized by Atomic Force Microscope (AFM).

#### **BB3.15**

Abstract Withdrawn.

#### **BB3.16**

##### **SIDE CHAIN INFLUENCE ON MAIN CHAIN ORIENTATION.**

Ruth Müllner, Franz Stelzer, Institute of Chemistry and Technology of Organic Materials, TU-Graz, AUSTRIA; Egbert Zojer, Günther Leising, Institute of Solid State Physics, TU-Graz, AUSTRIA; Laurence Noirez, Laboratoire Léon Brillouin, Ce-Saclay, Gif-sur-Yvette, FRANCE.

Conjugated polymers previously oriented by means of liquid crystalline side chains can be used for polarized light emitting diodes. The conjugated main chain is oriented via the mesogenic units which themselves are oriented either by introducing a magnetic or electric field, by shear force or by pre-orientation on a rubbed surface (e.g. polyimide or Teflon). Oligo(*p*-phenylene vinylenes) or oligo(*p*-biphenylene vinylenes) serve as conjugated main chain. 4-oxy-biphenylene-4'-nitrile is the mesogenic unit connected to the main chain via  $-(CH_2)_x-$  spacers with  $x = 3,4,9$ . A Pd(0)-catalyzed reaction (Heck-reaction) is used to synthesize the oligomers starting with either 1,4-dibromobenzene or 4,4'-dibromobiphenyl and 4-(alk- $\omega$ -enyoxy)-biphenyl-4'-nitrile. Prolongation of the oligomeric chain is easily carried out with a mono-substituted alkene at the less sterically hindered C-atom. Once this reaction has taken place though, continuation at the di-substituted alkene is less preferable. That is why only oligomers and no polymers are synthesized with these reaction partners. The orientation of the conjugated main chain is investigated using small angle neutron scattering (SANS) technique. Information on the dependence of the orientation with respect to the length of the spacer will be gathered. Data on the photophysics of the oligomers are gained by means of several spectroscopic methods.

#### **BB3.17**

**RECOVERABLE PHOTODEGRADATION OF LIGHT-EMITTING POLYMERS.** X.H. Zhang, S.J. Chua, Institute of Materials Research and Engineering, National University of Singapore, SINGAPORE; H. Wang, Department of Electrical Engineering, National University of Singapore, SINGAPORE.

Considerable attention has recently been paid to the organic light-emitting diodes (OLEDs) based on light-emitting polymers, due to their potential applications in the flat panel display. One main challenge faced by the OLEDs is the stability. A good understanding of degradation in light-emitting polymers is important to the improvement of stability of these materials and related devices. In this paper, we study the photodegradation of light-emitting polymers by measuring the decay of the photoluminescence with the exposure time to He-Cd laser beam at room temperature. It was found that the photoluminescence intensity decreases very fast initially on the order of several minutes, and then tends to saturate. More interestingly, it was found that the degradation induced by laser beam can be self-healed. Stopping the exposure of the sample to the laser beam, the photoluminescence intensity recovers gradually without any treatment. The mechanism causing this phenomenon will be discussed.

#### **BB3.18**

**FILM GROWTH, BY SEEDED SUPERSONIC BEAMS, OF THIOPHENE-BASED OLIGOMERS WITH CONTROLLED OPTICAL, STRUCTURAL AND MORPHOLOGICAL PROPERTIES.** Tullio Toccoli, Giuseppe Ciullo, Salvatore Iannotta, Maurizio Ferrari, Stefania Ronchin, CeFSA, CNR/ITC Research Center on Aggregates Physics, Povo di Trento, ITALY; Alessandro Podesta, Paolo Milani, INFN, Dipartimento di Fisica, Università di Milano, ITALY.

Thiophene based oligomers are of increasing interest as model systems for their optical, electronic, and electro-optical properties and as prototype conjugated systems for technological applications. Designing and synthesising the right molecules is far from being enough for controlling the properties of the desired material. Characteristics and quality of films are strongly affected by degree of order-disorder and

by orientation of the backbone of the oligomers that is by how molecules assemble to form the solid. Standard deposition methods show limitations in controlling morphology and structure as well as in producing reliable active layers suitable for devices. The urge for better quality films is pushing to explore growth methods which would guarantee better control on deposition parameters. Vacuum deposition has already allowed several groups to investigate growth under better characterised conditions improving films properties. There is also a growing awareness of the need to study and control the role of the film-substrate interface. Our approach is based on a novel seeded supersonic molecular beam combined with a UHV deposition chamber (P. Milani, and S. Iannotta, *Synthesis of Nanophase Materials by Cluster Beam Deposition*, Springer-Verlag, Berlin:1999). This method gives an unprecedented control on films properties. Several T4 films under different beams conditions have been prepared and characterised by optical absorption, photoluminescence, TMAFM and SEM. Centerline heavier species segregation in the beam is exploited to efficiently grow T4 films from impurities present in raw T3 powders. Morphology, structure and optical response of the films are controlled by the beam's parameters that in turn allow to vary flux density, energy and orientation of molecules in the beam. Highly ordered films, up to several hundreds of nm thick, show well resolved vibronic structures in low temperatures PL spectra as only the best published data on films a few monolayers thick do.

#### **BB3.19**

**ELECTRON DRIVEN CHIRALITY SWITCH: POTENTIAL APPLICATION TO REDOX-SWITCHED CHOLESTERIC CRYSTALLINE PHASES AND DATA STORAGE MATERIALS.** Steffen Zahn, James W. Canary, New York University, Dept of Chemistry, New York, NY; Gloria Proni, Università di Bologna, Dipartimento di Chimica, Bologna, ITALY.

A recent and exciting prospect in the area of information technology lies in the development of molecular switching devices that operate with efficiency, reversibility and resistance to fatigue. We recently reported a special type of coordination complex in which the two oxidation states of copper are embedded in a chiral tripodal ligand representing the 0 and 1 states of a binary logic system that can be interconverted rapidly by electrochemical means. This presentation will focus on the optical and electronic properties of our system and the physical aspects of the design and synthesis. Potential device applications such as data storage device materials and liquid crystal displays will be discussed.

#### **BB3.20**

**FORMATION OF POLARON PAIRS AND PS TIME-RESOLVED PHOTOGENERATION OF FREE CHARGE CARRIERS IN CONJUGATED POLYMERS.** Eugene Frankevich, Hisao Ishii, Yasushi Hamanaka, Sergey Li, Akihiko Fujii, Katsumi Yoshino, Arai Nakamura, Kazuhiko Seki.

We have performed time-resolved experiments on substituted polyalkylthiophene (PAT) and polyphenylene vinylene (PPV) films by direct probing the formation of charge carriers responsible for cw photoconductivity (PC) within the ps time domain. PC was induced by laser pulses of 400 nm wavelength, 150 fs width, 1 kHz repetition rate. Red 800 nm pulses delayed in respect to blue ones were revealed to affect the average PC. Effect of the second pulses was zero at zero and negative delay times, but it caused a decrease of the PC in PAT and an increase in PPV at delayed times changed from 0 to 1000 ps. Two characteristic lifetimes were revealed in the dependences of the PC change on the delay time: 15 ps and a few hundreds ps corresponding to lifetimes of free polaron precursors. The results are rationalized as an evidence of delayed not immediate formation of charge carriers belonging to polaron pairs in contrast to what could be expected from the band-to-band model of the PC. A mechanism of formation of free polarons from polaron pairs is suggested based on inter-pair recombination of polarons.

#### **BB3.21**

**DESIGN AND OPTIMIZATION OF HETEROCYCLIC LIQUID CRYSTALS FOR ORGANIC LIGHT EMITTING DIODE APPLICATIONS.** L.I. Sukhomlinova, S. Gu, R.J. Twieg, Dept of Chemistry, Kent State Univ, Kent, OH; R. Fan, D. Culjkovic, G.G. Malliaras, Dept of Materials Science and Engineering, Cornell Univ, Ithaca, NY.

Liquid crystalline materials display unique properties that can be exploited in organic light emitting diodes (LED). It is particularly interesting to design molecules that are capable to function simultaneously as liquid crystals, charge transport agents and fluorophores. We have prepared liquid crystals containing one or two five member ring heterocycles (oxadiazoles, thiadiazoles, etc.) and evaluated the relationship between structure and mesogenic properties. LED activity of these materials has been studied in single and multi layer diodes where the liquid crystalline molecules are

vacuum deposited in mesogenic phase and standard triphenylamines are used as hole transport materials. The electrical and emission characteristics of diodes have been investigated as a function of the substituents of the liquid crystalline molecule. The influence of the electron transporting layer on the device performance has been evaluated.

### **BB3.22**

**LIQUID CRYSTAL ANCHORING ON BULK AND SELF ASSEMBLED AZO POLYMER FILMS.** Dong-Yu Kim, Soo-Hyoung Lee, Jaehyun Kim, Jayant Kumar, and Sukant K. Tripathy, Center for Advanced Materials, Departments of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA.

Liquid crystal (LC) molecules were homogeneously aligned on optically oriented bulk spin coated azopolymer films and self assembled azopolymer films. LCs could be homogeneously aligned on optically induced surface gratings on azopolymer films. The oriented azo chromophores seem to have stronger influence on LC anchoring compared to the grating groove structures. Diffraction switching by applying electric field to the LC cell was demonstrated using grating structures in the alignment layers. Diffraction switching was strongly dependent on the polarization of the incident beam. Ultra-thin electrostatically self-assembled layers of PDAC and polyacrylic acid based azo polymers could also homogeneously align LCs upon exposure to a polarized light. Effects of layer formation conditions on LC anchoring were investigated.

### **BB3.23**

**FLUID MECHANICS MODEL AND ANALYSIS FOR THE PHOTOFABRICATION OF SURFACE RELIEF GRATING IN AZO POLYMERS.** Takashi Fukuda, Hiro Matsuda, Dept of Polymer Chemistry, NIMC, Tsukuba, JAPAN; Kimio Sumaru, Tadae Yamanaka, Dept of Polymer Engineering, NIMC, Tsukuba, JAPAN.

The mass transporting dynamics in the surface relief grating (SRG) photofabrication on azo polymer films is discussed precisely using a fluid mechanics model recently proposed, in which the velocity distribution on the film surface and the spatial distribution of the optically induced driving force caused by the light attenuation in the bulk are fully taken into account. Formulation for the SRG dynamics is derived analytically from Navier-Stokes equation as a function of the film thickness, the grating pitch, the absorption coefficient and the viscosity of the material. The validity of this fluid mechanics model was investigated on comparison with the experimental data obtained for two kinds of azo polymers with different dye functionalization. One is a maleimide based polymer with high glass transition temperature ( $T_g$ ) and the other is a low- $T_g$  acrylic polymer. Disperse Red 1 has been attached to both polymers as an azo chromophore side chain. As a result, the dependence of diffraction efficiency on the film thickness was explained very well in the entire range of film thickness using the proposed model. The analysis for the grating pitch and the dye functionalization dependence of the SRG photofabrication will also be discussed in terms of the corresponding experimental data.

### **BB3.24**

**THE INFLUENCE OF ORDERING ON THE PHOTOINDUCED CHARGE TRANSFER IN COMPOSITES OF PHENYL-TYPE SUBSTITUTED POLYTHIOPHENES WITH METHANO-FULLERENES.** Christoph J. Brabec, N. Serdar Sariciftci, Johannes Kepler University, Christian Doppler Laboratory for Plastic Solar Cells, Linz, AUSTRIA; Mats R. Andersson, Chalmers University of Technology, Department of Polymer Technology and Organic Chemistry, Gothenburg, SWEDEN; Olle Inganäs, University of Linköping, Laboratory of Applied Physics, Linköping, SWEDEN; Jan C. Hummelen, University of Groningen, Department of Organic and Molecular Inorganic Chemistry, Groningen, THE NETHERLANDS.

Regioregular polythiophenes with a diethylene glycol sidechain on the substituted phenyl ring (PEOPT) show high photoluminescence efficiencies. Exposing thin films of this polymer to vapors of chloroform or annealing them by heat treatment results in a red shift of the absorption maximum due to solvent or heat induced ordering which gives rise to more planar conformations. The fact, that annealed thin films of PEOPT exhibit absorption edges at relatively low energies and thus have enhanced spectral range makes them suitable for use in photodiodes / solar cells. The photoinduced charge generation efficiency in PEOPT is significantly enhanced by the addition of a strong electron acceptor like fullerene, as observed by quenching of the luminescence and by photoinduced absorption measurements in the infrared and UV-Vis regime. The efficiency of the photoinduced charge transfer from PEOPT to a methanofullerene is found to depend on the ordering of PEOPT in thin films.

### **BB3.25**

**INVESTIGATION OF PHOTOINDUCED CHARGE TRANSFER IN COMPOSITES OF PPV FROM A NOVEL PRECURSOR**

**POLYMER AND FULLERENES.** Christoph J. Brabec, A. Cravino, G. Zerza, N. Serdar Sariciftci, Johannes Kepler University, Christian Doppler Laboratory for Plastic Solar Cells, Linz, AUSTRIA; Rafael Kiebooms, Limburgs Universitair, Instituut voor Materiaal Onderzoek, Materiaalfysica, Diepenbeek, BELGIUM; Dirk J. Vanderzande, Limburg University, Laboratory of Organic and Polymer Chemistry, Diepenbeek, BELGIUM; Jan C. Hummelen, University of Groningen, Department of Organic and Molecular Inorganic Chemistry, Groningen, THE NETHERLANDS.

The rate of photo-generated charge carriers in conjugated polymers can be largely improved by the addition of a strong electron acceptor like fullerene. In composites of substituted PPVs with fullerenes internal quantum efficiencies near unity have been found, which is explained by subpicosecond photoinduced charge transfer from the conjugated polymer to the fullerene. For the formation of an interpenetrating network composite excellent solubility of both components in the same class of solvents has been necessary and therefore, up to now investigations were limited to substituted PPVs. From the conjugated polymers, pristine PPV (poly(para-phenylenevinylene)), produced from a precursor polymer, is an interesting material for optoelectronic devices due to its environmental stability. A novel PPV precursor polymer, soluble in common organic solvents, has been used for the production of PPV / Fullerene composites in this study. The occurrence of charge transfer in such composites is monitored by photoinduced absorption spectroscopy as well as light induced electron spin resonance (LESR). Furthermore, electrical properties of photovoltaic devices produced from single layers of these composites are reported.

### **BB3.26**

**FREQUENCY DEPENDENT DIELECTRIC PERMITTIVITY STUDIES IN EMERALDINE BASE AND WEAKLY DOPED POLYANILINE AND ITS DERIVATIVES.** N.J. Pinto<sup>a</sup>, G.P. Sinha<sup>b</sup>, and F.M. Aliev<sup>b</sup>, <sup>a</sup>Department of Physics and Electronics, University of Puerto Rico, Humacao, PR; <sup>b</sup>Department of Physics and Materials Research Center, University of Puerto Rico, San Juan, PR.

We report on a systematic study of the complex dielectric permittivity in polyaniline, poly-o-toluidine and poly-o-ethylaniline in the undoped and weakly doped state in the frequency range 1 mHz upto 1 MHz. The doping concentration defined as  $y=[Cl^-]/N$  was chosen so that  $0 \leq y \leq 0.07$ . The objective of this work was to investigate the contribution of the mobile charge defects (polarons and bipolarons) on the conductivity and dielectric relaxation at such low doping levels. The three samples were chosen so as to compare the effects of introducing larger interchain disorder while maintaining a similar conduction mechanism. While in all samples studied we observe the presence of a dielectric relaxation mechanism, the relaxation times depend on the doping level and disorder. The presence of a larger number of polarons as the doping level is increased leads to multiple paths for the system to relax leading progressively non Debye like relaxation mechanism. The results are interpreted in terms of creation and annihilation of polarons and bipolarons and their subsequent diffusion. This work supported in part by: NSF-DMR-9872689 and DoD grant N00014-99-1-0558.

### **BB3.27**

**INVESTIGATION OF PHOTOEXCITED TRIPLET STATES IN VARIOUS SUBSTITUTED FULLERENES WITH AND WITHOUT OPTICALLY ACTIVE SIDEGROUPS.** M.C. Scharber, G. Zerza, N.S. Sariciftci, Johannes Kepler Univ, Physical Chemistry, Linz, AUSTRIA; C.J. Brabec, Christian Doppler Laboratory for Plastic Solar Cells, Johannes Kepler Univ, Linz, AUSTRIA; M. Maggini, Centro Meccanismi CNR, Dept of Organic Chemistry, Univ of Padova, ITALY; M. Prato, Dept di Scienze Farmaceutiche, Univ of Trieste, ITALY; J. Segura, N. Martin, Dept de Quimica Organica, Univ Complutense, Madrid, SPAIN; J.C. Hummelen, Dept of Organic and Molecular Inorganic Chemistry, Univ Groningen, THE NETHERLANDS.

In pristine C60 the dominant photoexcitation is found to be a long living triplet, accompanied by weak photoluminescence. The high interest in the photoexcited states of fullerenes originates from their use in photovoltaic devices. In this work we investigate the influence of various sidegroups attached to the fullerene on the photoexcited optical properties. Three different types of substitutions are of interest. Optically and electronically inactive sidegroups enhancing the solubility and the film forming properties, sidegroups with strongly electron accepting properties to tune the photoinduced charge transfer characteristics and optically active sidegroups, extending the absorption profile. The photoexcited optical properties of the various substituted fullerenes are investigated by means of photoinduced absorption, photoluminescence, ESR and LESR as well as time resolved photoinduced ESR measurements.



### BB3.28

PHOTOINDUCED CHARGE TRANSFER BETWEEN TETRACYANO-ANTHRAQUINO-DIMETHANE DERIVATIVES AND CONJUGATED POLYMERS. G. Zerza, M.C. Scharber, N.S. Sariciftci, Johannes Kepler Univ, Physical Chemistry, Linz, AUSTRIA; J.L. Segura, R. Gomez, N. Martin, Dept de Quimica Organica, Univ Complutense, Madrid, SPAIN.

The photo-induced charge transfer between tetracyanoanthraquino-dimethane (TCAQ) derivatives and poly(2-methoxy-5-(3,7-dimethyl-octyloxy)-1,4-phenylene vinylene) MDMO-PPV was studied by means of cw- and time resolved photoinduced absorption (PIA) spectroscopy and light induced electron spin resonance (LESR) spectroscopy. Three different TCAQ derivatives with alkyl-side chains for increased solubility and one TCAQ functionalized C60 molecule have been investigated. Solid state composites using these electron acceptors in combination with the electron donating conjugated polymer (MDMO-PPV) were prepared from toluene solution on glass substrates for PIA studies and on KBr powder for LESR investigations. The photoinduced absorption in the VIS - NIR range shows a broad plateau around 1.8 eV followed by two absorption bands at 1.35 and 1.24eV. A power law dependence of the PIA signal intensity as a function of the excitation power (I) has been observed ( $PIA \propto I^{0.5}$ ) suggesting bi-molecular relaxation kinetics of the excited donor-acceptor couple. In direct time resolved PIA studies it is also observed the excited state absorption relaxes with a power law. LESR studies show photoinduced ESR absorption line with a g-factor 2.0028 and a linewidth  $\Delta H_{pp} \approx 3.5$  Gauss. No evidence for a stable formation of C60 anion was found in the case of the composites of MDMO-PPV polymer with the TCAQ - C60 acceptor dyad.

### BB3.29

QUENCHING OF THE MAGNETIC FIELD EFFECT ON THE PHOTOCURRENT AND PHOTOCURRENT DETECTED MAGNETIC RESONANCE IN CONJUGATED POLYMER - FULLERENE DIODES. M.C. Scharber, N.S. Sariciftci, Johannes Kepler Univ, Physical Chemistry, Linz, AUSTRIA; C.J. Brabec, Christian Doppler Laboratory for Plastic Solar Cells, Johannes Kepler Univ, Linz, AUSTRIA; F. Padinger, Quantum Solar Energy, Linz, AUSTRIA.

We have studied the effect of a magnetic field (MFE) on the photocurrent of MDMO-PPV and MDMO-PPV/fullerene diodes (plastic solar cells) and performed photocurrent detected magnetic resonance (PCDMR) experiments on these devices. Devices consisting of an active layer sandwiched between a low and a high workfunction metal electrodes have been investigated. Results clearly show that the MFE as well as PCDMR signals are quenched in conjugated polymer/fullerene composite devices in contrast to large signals observed in the pristine conjugated polymer devices. Photoinduced electron transfer from conjugated polymers onto fullerene is proposed to be responsible for this quenching.

### BB3.30

SYNTHESIS AND CHARACTERISATION OF SOLUBLE POLYDITHIENOTHIOPHENE COPOLYMERS. Marinella Catellani, Silvia Luzzati, Istituto di Chimica delle Macromolecole-CNR, Milano, ITALY.

We have recently described a series of narrow band gap isomeric polydithienothiophenes that show low energy gaps (typically 1.1-1.7 eV), and are stable in both reduced and oxidized doped states. Furthermore the copolymerisation of two dithienothiophene isomers in well defined ratios leads to materials with tunable energy gap whose electronic properties depend on the chemical composition of the chain. These materials that exhibit tunable optical properties are quite interesting for symmetric electrochemical devices and for photovoltaic applications. Polydithienothiophenes are prepared via electrosynthesis and are completely insoluble and infusible. The solubility and the processability of polymeric materials are of primary importance in the fabrication of photoelectric conversion devices. With the aim to find new materials for organic photovoltaic cells we have prepared a copolymer series, containing both dithienothiophene and alkylthiophene units in the conjugated backbone, that possess solubility and processability. In this work the synthesis of polydithienothiophene copolymers will be presented, along with their electrical and optical characterisation.

### BB3.31

LINEAR AND NONLINEAR OPTICAL PROPERTIES OF NOVEL IONIC CHROMOPHORES. Xuan-Ming Duan, Tatsuo Wada, Hiroyuki Sasabe, Inst. Phys. Chem. Res. (RIKEN), Wako, Saitama, JAPAN; Shuji Okada, Hidetoshi Oikawa, Hachiro Nakanishi, Inst. Chem. React. Sci., Tohoku Univ., Sendai, JAPAN; Hiro Matsuda, National Inst. Mater. Chem. Res., Tsukuba, JAPAN.

Ionic chromophores, i.e. 4-(dimethylamino)-N-methyl-4-stilbazolium

tosylate (DAST), exhibit significant second-order nonlinear optical susceptibilities ( $\chi^{(2)}$ ). The crystals of stilbazolium salts have been expected to use as organic nonlinear optical materials in various applications of nonlinear optical devices. The large  $\chi^{(2)}$  of stilbazolium salts is due to the large molecular first hyperpolarizabilities ( $\beta$ ) of stilbazolium cations. The significant electron withdrawing ability of pyridinium ring plays a major role in the intramolecular electron transfer of the stilbazolium cations. On the other hand, carbazole derivatives have been reported to have photoconductive, nonlinear optical and photorefractive properties. Because the nitrogen atom of carbazole has a strong electron donating ability, the combination of carbazole and pyridinium ring in one  $\pi$ -conjugation system will make a typical donor/acceptor molecule with large  $\beta$  value. Meanwhile, the other optical properties also can be expected. Recently, we synthesized a new series of ionic chromophores by combining pyridinium ring and carbazole through a double bond, and investigated their linear and nonlinear optical properties. These compounds show strong absorption and strong fluorescence in visible region. The investigations on crystal structures of these salts also have been done by changing their counter anions, and several crystals were discovered to be active for second-order nonlinear optics. These novel ionic compounds could be expected to use as EO materials.

### BB3.32

FLUORESCENCE AND PHOSPHORESCENCE PROPERTIES OF TRIS(PHENYLQUINOXALINE). Sylke Blumstengel, Elio Colabella, Adele Sassella, Riccardo Tubino, Dipartimento di Scienza dei Materiali, Univ Milano-Bicocca, Milano, ITALY; Markus Jandke, Peter Strohmriegel, Univ Bayreuth, Makromolekulare Chemie I and Bayreuther Institut für Makromolekulforschung (BIMF), Bayreuth, GERMANY.

We have studied the photophysical properties of tris(phenylquinoxalines) (TPQ), a new class of starshaped molecules, by cw and time-resolved photoluminescence and photoinduced absorption measurements. TPQs emit blue fluorescence with a peak wavelength of 410 nm as well as green phosphorescence at 520 nm. Fluorescence and phosphorescence quantum yields are strongly dependent on the substituents on the quinoxaline core. TPQs with  $CH_3$  substituents show intense fluorescence but weak phosphorescence, whereas heavier substituents like  $CF_3$  lead to a strong enhancement of the phosphorescence quantum yield while the fluorescence is decreased. Besides the interesting photophysical properties, TPQs are also very efficient electron transport materials for use in organic light-emitting diodes (LEDs). This allows us to prepare LEDs utilizing TPQs as emitter and electron transport layer and to study fluorescence and phosphorescence properties under the conditions of electroexcitation. Comparison of the fluorescence and phosphorescence efficiencies after photo- and electroexcitation should yield information about the branching ratio of singlet and triplet excitations formed by charge carrier injection into the emitter layer. The results of these investigations will be presented.

### BB3.33

SYNTHESIS AND CHARACTERIZATION OF MULTIARM STAR OLIGOANILINES. Lee Y. Wang, Chih-Chian Chu, Long Y. Chiang, National Taiwan University, Center for Condensed Matter Sciences, Taipei, TAIWAN.

An efficient synthetic method for the preparation of star-shaped oligoanilines is demonstrated. It involves the use of polyhydroxylated molecule as a central core for anchoring multiple linear hexadecaaniline chains. Structural characterization of the obtained materials was performed by the use of various spectroscopic methods. Zimm plot, gel permeation chromatography, and MALDI techniques were used to investigate their molecular weight characteristics. GPC data showed the polydispersity index of the oligoaniline star was narrower than that of the corresponding linear constituent, indicating a narrow distribution of the number of polymer arms in each star molecule. Most significantly, these novel conjugated macromolecules not only showed good solubility in common organic solvents, such as THF, DMF, m-cresol and NMP, but also exhibited higher electrical conductivity than their parent arms.

### BB3.34

AN ATOMIC FORCE MICROSCOPY STUDY OF ROD-COIL BLOCK COPOLYMER ASSEMBLIES. R. Lazzaroni<sup>1</sup>, Ph. Leclere<sup>1</sup>, J.L. Bredas<sup>1</sup>, D. Marsitkzy<sup>2</sup>, V. Franke<sup>2</sup>, K. Mullen<sup>2</sup>. <sup>1</sup>Universite de Mons-Hainaut, Mons, BELGIUM. <sup>2</sup>Max-Planck Institut für Polymerforschung, Mainz, GERMANY.

The optoelectronic properties of conjugated materials critically depend on the molecular organization in the solid state. This organization is directly related to the details of the molecular architecture and the conditions used for preparing the devices. In this study, Atomic Force Microscopy (AFM) is employed to investigate the microscopic morphology of thin films of a new class of diblock

copolymers containing a conjugated segment. The conjugated block is either a poly(para-phenylene) or a poly(para-phenylene ethynylene) sequence; it is made soluble by the presence of alkyl side groups on the phenylene rings. The conjugated block is connected to nonconjugated segments such as poly(ethylene oxide), poly(dimethylsiloxane), or poly(tetrahydrofuran). The rigid character of the conjugated chain induces specific morphological characteristics, with respect to the situation observed in coil-coil copolymers. In most cases, the AFM images can be interpreted in terms of assemblies of microfibrils with diameters on the order of 30 nm. When the deposits are prepared from very dilute solutions, individual ribbons can be imaged; their typical dimensions are several microns in length, 30 nm in width and 1-2 nm in height. Theoretical modeling based on molecular mechanics calculations is used to understand the molecular organization within these ribbons. Finally, varying the preparation conditions can also lead to other mesoscopic morphologies: regular arrays of bundles of fibrils or highly porous films. These morphologies are thought to form as a result of a dewetting process.

### **BB3.35**

#### **MULTIFUNCTIONAL DENDRIMERS INCORPORATING DIPHENYLAMINOPOLYENYLIC CHROMOPHORES.**

K. Ashworth, B. Reeves, A. Frost, C. Spangler, Montana State Univ, Dept of Chemistry and Biochemistry, Bozeman, MT.

Bis-(diphenylamino)diphenylpolyenes have been shown to form extremely stable, highly absorbing bipolaronic dications in solution and thin films. More recently, (N-hydroxyethyl, N-ethyl)aminophenyl-diphenylaminopolyenes have also been shown to have equivalent behavior and can be easily attached to 3,5-dihydroxybenzyl alcohol to form derivatized dendrons and dendrimers by attachment to various central core molecules. These new photonic materials display strong fluorescence, and have large two-photon cross-sections. In this presentation we will focus on several diverse photonic properties of these new monodisperse macromolecules, such as optical power limiting via both reverse saturable and two-photon absorption, and incorporation as emitters in organic light-emitting diodes.

### **BB3.36**

#### **ENHANCEMENT OF LUMINESCENCE OF NITROGEN CONTAINING CONJUGATED POLYMERS.** W.Y. Huang, Y.K. Han, T.K. Kwei and Y. Okamoto, Polytechnic Univ, Polymer Research Institute, Brooklyn, NY.

We have synthesized nitrogen containing rigid conjugated polymers; poly(2,5-pyridine), poly(2,6-[p-phenylene]-4-phenylquinoline) and poly(2-alkanoylamino-p-phenylene). They are soluble in acidic solvents such as formic acid, dichloroacetic acid and methanesulfonic acid. The fluorescence intensities of the concentrated solutions of these polymers were very weak and showed featureless emission peaks at around 500-550nm. But in dilute solutions the peaks shifted to around 400-470nm and the intensity increased by as much as one thousand fold. The results suggest that these polymers form aggregates/excimers in concentrated solutions but upon dilution, the polymer chains are separated and result in decrease of aggregation quenching. These phenomena were also observed in blended systems of these polymers with non-fluorescent polymers such as polyvinyl alcohol. When the basic nitrogen atoms of the polymers were protonated or partially methylated, the emission peaks were observed around 400-470nm. These results suggest that when the positive charge on the nitrogen atom reach a critical value, the intermolecular electrostatic repulsion prevents aggregate formation and the emission spectra corresponding to the isolated chain appears. We are currently investigating in detail the fluorescent properties of these polymers incorporated in various matrices. Additionally, Two novel poly(2-alkanoylamino-p-phenylene)s have been prepared by nickel-catalyzed coupling of bis(aryl halide)s as the polymer-forming reaction in a step-growth polymerization of 2,5-dibromoacetylaminobenzene and 2,5-dibromohexanoyl-aminobenzene. The solubility of the polymer was enhanced by increasing the length of the alkyl group of the alkanoyl moiety. Both polymers show photoluminescence peaks at 410nm in concentrated solutions and 350nm in dilute solutions.

### **BB3.37**

#### **PHOTOLUMINESCENT AND ELECTROLUMINESCENT STUDIES OF METAL TRISCHELATES OF METHYL-SUBSTITUTED QUINOLATE LIGANDS.** Linda S. Sapochak,

Asanga Padmaperuma, Nancy Washton, and Greg Schmetz, Dept of Chemistry, University of Nevada, Las Vegas, NV; Paul E. Burrows and Stephen R. Forrest, Dept of Electrical Engineering, Princeton University, Princeton, NJ.

Alq<sub>3</sub> and metal quinolate-type materials are very important as emitter materials and electron transport layer/hosts in OLEDs and dye-doped OLEDs. Systematic experimental and theoretical studies of these materials are crucial in order to elucidate the relationship between structure and function in EL materials and ultimately

optimize device performance. It has been demonstrated that the PL emission energies of Alq<sub>3</sub> can be tuned by adding substituents to the quinolate ligand thus changing the energies of the filled and vacant orbitals. The electronic and structural changes associated with such substitutions can dramatically affect the resulting PL and EL efficiencies. We report the first systematic study of the PL and EL properties of a series of methyl- and dimethyl-substituted quinolate tris-chelates of aluminum, gallium, and indium. The effect of methyl substitution on absorption and emission wavelengths is consistent with previous theoretical calculations, however relative PL quantum efficiencies are significantly higher for chelates with substitution on the pyridyl ring vs. the phenolic ring of the 8-hydroxyquinoline ligand. Electroluminescence properties do not follow this same trend. Detailed structural characterization data, including NMR, FTIR, and X-ray spectroscopy studies of crystalline powders and vapor deposited films will be presented for these materials purified by different techniques. We will show that methyl and metal ion substitutions affect the relative stability of these chelates in EL devices. In particular, methylation on the pyridyl ring destabilizes the metal-quinolate bond, inducing partial decomposition during sublimation.

### **BB3.38**

#### **GATE-FIELD DEPENDENT FIELD-EFFECT MOBILITIES IN REGIOREGULAR POLY(3-HEXYLTHIOPHENE).**

Diederik B.A. Rep, Bart van Wees, Groningen Univ, Dept of Applied Physics and Materials Science Center, Groningen, THE NETHERLANDS; Teun M. Klapwijk, Delft Univ of Technology, Dept of Applied Physics, Delft, THE NETHERLANDS.

In an effort to study the relation between ordering and charge-transport in organic thin films, we have investigated the gate-field dependency of the field-effect mobility in thin layers of regioregular poly(3-hexylthiophene) (RR-P3HT). RR-P3HT self-assembles from solution into a semicrystalline thin film, with the level of crystallinity dependent on surface conditions and the details of solvent evaporation. We have found that in RR-P3HT on SiO<sub>2</sub> the mobility depends on the gate-field, approximately by a power-law. The power  $m$  is a function of temperature, increasing from 1 at 300K to 2.5 at 180K. Furthermore  $m(T)$  is highly dependent on the self-assembly of the first monolayers near the substrate surface. In literature, a gate-field dependent mobility in organic thin films has only been recognized very recently. For disordered organic systems, it has been ascribed to a non-constant density of hopping states. For single-crystalline thin films we recently explained it using a model in which charge tunneling between nearest-neighbors is dominated by Coulomb blockade effects. Surface charges at the organic/substrate interface influence the range of Coulombic energy barriers. For the case of RR-P3HT, we find that the qualitative picture of Coulomb blockade effects can be very well applied to the experimental data, while that of the model developed for disordered media also can. We will discuss the influence of the film ordering on  $m(T)$  in the light of both models and comment on the applicability of the Coulomb charging model for disordered organic films.

### **BB3.39**

#### **HIGHLY ORDERED CRYSTALLINE THIN FILM BILAYERS OF PARA-HEXAPHENYL AND C60 GROWN BY HOT WALL EPITAXY.** Helmut Sitter, Inst for Semiconductor- and Solid State Physics, JK Univ of Linz, Linz, AUSTRIA; Gebhard Matt, Inst for Physical Chemistry and Inst for Semiconductor- and Solid State Physics, JK Univ of Linz, Linz, AUSTRIA; Andrei Andreev, Christoph Brabec, Helmut Neugebauer, Serdar Sariciftci, Christian Doppler Laboratory for Plastic Solar Cells and Inst for Physical Chemistry, JK Univ of Linz, Linz, AUSTRIA.

Small molecule donor-acceptor systems like conjugated oligomer/fullerene bi- and multilayers are very interesting for photovoltaic applications. This work focuses on study of single - and bilayers of para - hexaphenyl (PHP) and C60 grown by Hot Wall epitaxy (HWE). This technique allows the epitaxial growth close to thermodynamic equilibrium, which is essential in the case of van der Waals epitaxy of fullerenes and oligophenyls. A detailed study of the growth process was performed on glass, ITO and (001)- oriented cleaved mica substrates. The ordering of the layers was investigated by Laue- and X-ray diffraction, showing clear diffraction peaks for layers grown on mica. The PHP layers grown on mica show high optical anisotropy effects according the polarization dependent absorption and photoluminescence experiments. The highly ordered structure is also reflected in the surface morphology of the layer as observed by Atomic Force Microscopy. The epitaxial growth on mica is mirrored by the main alignment of the surface structure to the orientation of the mica substrate. Bilayers of PHP/C60, sandwiched between ITO and Al electrodes, show a strongly enhanced photovoltaic effect compared to pristine PHP films of similar thickness.

### BB3.40

EFFECTS OF CONFORMATIONAL DIVERSITY AND STRUCTURAL DYNAMICS ON THE OPTICAL PROPERTIES OF DALM. Kim F. Ferris, Pacific Northwest National Laboratories, Richland, WA; Steven M. Risser, Battelle Memorial Institute, Columbus, OH; Katrina B. Wagner-Brown, Conceptual MindWorks, Inc. San Antonio, TX; Jonathon L. Kiel and Richard A. Albanese, Brooks AFB, San Antonio, TX.

Diazoluminmelanin (DALM) is a luminescent polymer belonging to the broader class of polyphenylene materials which has shown significant optical activity in response to perturbing fields. Detailed information about the electronic origins of luminescence in these systems is limited. In this paper we present results from ab initio and semiempirical electronic structure calculations, and molecular dynamics simulations for the molecular structure and absorption characteristics of model phenolic oligomers. From ab initio 6-31G\* calculations we have found that the relative orientations and ionization state of adjacent hydroxyl groups control the overall conjugative effects, yielding unique torsional potential profiles and multiple structural minima. The interring torsion angle is a critical variable as it relates charge localization effects and electronic excitation energies. The energetic barriers for group rotations (ring,OH) within these systems are low, allowing for interconversion between minima. Molecular dynamics simulations of the phenolic oligomers demonstrate the need for a multistate basis for the absorption properties of this system. Results are compared to available absorption and luminescent data. This work was supported in part by the U.S. Department of Energy, Office of Science, Materials Sciences Division under contract DE-AC06-76RLO 1830, and the United States Air Force Office of Scientific Research and the U.S. Army Medical Research and Material Command under contract DAMD17-94-C-4069.

### BB3.41

EFFICIENT ELECTROLUMINESCENCE FROM TYPE I QUANTUM CONFINED STRUCTURE UTILIZING ORGANIC DYE MATERIALS. Yutaka Ohmori, Takumi Sawatani, Kazumichi Ando and Katsumi Yoshino, Osaka University, Department of Electronic Engineering, Suita, Osaka, JAPAN.

Improvement of EL efficiency by using quantum confined structure of 8-hydroxyquinoline aluminum ( $Alq_3$ ) and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), and that of 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) and  $Alq_3$  are discussed. Energy band diagram of  $Alq_3$ /PBD and that of DCM/ $Alq_3$  are confined structure, so called Type I superlattice structure, in which electrons and holes are confined simultaneously in one material with each other. Enhanced EL emission was obtained using quantum well structure which consists of  $Alq_3$  and PBD. Emission wavelength decreases as decreasing the thickness of  $Alq_3$ /PBD superlattice, which we observed the similar energy shift in  $Alq_3$ /TPD superlattice system. High efficient EL was obtained in the device which consists of 20 periods of 2.5-nm-thick  $Alq_3$  and 2.5-nm-thick PBD, and the device shows green emission of 35,000  $cd/m^2$  under the injection current of 550  $mA/cm^2$ , and the efficiency reaches up to 9  $cd/A$ , which is about 3 times higher than the conventional  $Alq_3$  and TPD heterostructure type of EL device. High intensity red emission was obtained utilizing quantum dot structure of DCM and  $Alq_3$  system. It reaches up to 30,000  $cd/m^2$  and the efficiency reaches as high as 2.5  $cd/A$  at the emission wavelength of 600 nm in the diode of 3.6-mol-% DCM dispersed in  $Alq_3$  in which system DCM plays as quantum dots in  $Alq_3$  barrier layer. Although the emission wavelength shifts to longer wavelength side as increasing the molar fraction of DCM, the emission intensity and the efficiency decreases.

### BB3.42

TEMPERATURE DEPENDENCE OF PHOTOLUMINESCENCE, AMPLIFIED SPONTANEOUS EMISSION AND LASING IN CONJUGATED POLYMERS. Rahul Gupta, Joon Young Park, Vojislav Srdanov, Alan J. Heeger, Institute for Polymers & Organic Solids University of California at Santa Barbara, Santa Barbara, CA.

Temperature dependence of optical absorption, photo-luminescence (PL), amplified spontaneous emission (ASE) and lasing in conjugated polymers has been measured from 77K to 400K. The optical absorption, PL spectra and the ASE wavelength of conjugated polymers red shift as much as 20 nm with decreasing temperature. The thresholds for ASE are almost independent of temperature for BuEH-PPV but go up by a factor of 2 for MEH-PPV on increasing the temperature from 77K to 400K. Distributed feedback (DFB) lasing thresholds vary by as much as an order of magnitude with temperature. The threshold is the lowest at the temperature at which the DFB wavelength (which is almost independent of temperature) is at the peak of the photoluminescence emission spectra (PL red shifts with decreasing temperature) and hence the peak of optical gain. DFB lasers have thresholds as low as 100 Watts/cm<sup>2</sup> at room

temperature. Lasing thresholds for lasers made using cavities that have a high reflectivity over a wide range of wavelengths are expected to have a smaller dependence on temperature.

### BB3.43

NOVEL CONJUGATED POLYMERS CONTAINING FERROCENE. Sung In Cho, Jin-Kyu Lee, Seoul National Univ, Dept of Chemistry, Seoul, KOREA.

Incorporation of transition metal complexes or organometallic compounds into organic polymer backbone has been studied in order to use their unique electronic and optical properties combining with processability of organic polymers. We have prepared conjugated polymers containing ferrocene units. Previous attempts to synthesize such conjugated polymers were reported to yield material that suffers from poor solubility and low molecular weight. Horner-Emmons reaction was used to combine ferrocene unit with organic unit because it has several advantages. When alkyl dialkylphosphonate reacts with aldehyde, it generates only trans double bond. And side product, salt of alkylphosphoric acid, can be easily removed by aqueous extraction. Long alkyl chains are also introduced in organic unit to increase the solubility of conjugated polymers. As expected, the resulted ferrocene-containing conjugated polymer is very soluble in organic solvent such as  $CHCl_3$ , THF and Toluene, and thin film of this polymer can be easily prepared by either simple static casting process or spin coating process, which make it more attractive for many applications. In this presentation preparation and characterization of novel conjugated polymer containing ferrocene will be discussed with some preliminary electronic and optical measurements.

### BB3.44

UNDERSTANDING NON-LINEARITY: A SIMPLE MODEL FOR THE COMPLEX SPECTRAL BEHAVIOR OF PUSH-PULL CHROMOPHORES. Anna Painelli, Francesca Terenziani, Parma University, Dept Chimica GIAF, Parma, ITALY.

Much as it occurs for experimental techniques, also theoretical tools to deal with non-linear phenomena have to be refined. Push-pull chromophores, an interesting class of molecules with large first hyperpolarizabilities, offer an impressive demonstration of the need of new understanding. Experimental and numerical evidences are accumulating proving the important role of vibrations and of the environment on NLO responses of these materials: perturbative, SOS approaches apparently fail in describing these phenomena [1]. Large environment effects are observed in absorption and emission spectra. Solvatochromic shifts are usually described in terms of linearized solute-solvent interactions, but these treatments cannot account for the observation of strongly solvent-dependent bandshapes, nor for the narrower and less-structured emission than absorption bandshapes. The time evolution of emission frequencies is often used to investigate the dynamics of solvent relaxation, but the bandshape time evolution is overlooked. Vibrational frequencies, intensities and bandshapes also show impressive dependence on the embedding medium. Unusual dispersion of the resonant-Raman frequencies with the excitation line is observed for molecules in solution, and intriguing effects on vibrational frequencies following the electronic excitation are observed in femtosecond vibrational spectroscopy. All these seemingly unrelated phenomena are naturally understood based on a simple two-state model, self-consistently accounting for the electron-phonon coupling and for the interaction with the surrounding medium [1]. In terms of a few parameters, that are extracted from experiment, we give a simple and accurate description of the complex spectral behavior of push-pull chromophores. The properties of these materials are governed by simple hamiltonians and can be understood based on simple models, provided the intrinsic non-linearity of the interactions is properly accounted for.

[1] A. Painelli, Chem. Phys. 245 (1999) 183.

### BB3.45

STRUCTURIZATION AND LUMINESCENCE FEATURES OF INTERFACES IN MULTILAYER POLYMER FILMS.

Oleksandr V. Tolmachev, Nina I. Voronkina, Konstantin B. Vodolazhskii, Institute for Single Crystals, NAS of Ukraine, Kharkov, UKRAINE.

The self-organization of the layer interface and formation of specific ordered structures having functional properties inherent in them remains still inadequately studied. Interfaces of LB structures containing alternating layers of different materials are of a special interest. We have studied the molecular organization and luminescence properties of layer interfaces in Langmuir-Blodgett structures consisting of 6 alternating poly(methylmethacrylate) (PMMA) films activated by 2-phenyl-5-(p-amylobiphenyl)1,3,4-oxadiazole (PBD) in 1:3 ratio and poly(vinylcarbazole) (PVK) films activated by 3.0 mol.% of tetraphenylbutadiene (TPB). A model has been proposed for the layer interface, the nature of fluorescence centers has been identified and the electron excitation energy transfer (EET) processes between

all components of the system have been considered. The EET between carbazole groups of PVK and oxazole fragments of PBD occurs at distances up to 4.7 Å what is possible only in the case of the contact between both layers with their mutual penetration on the interface. The revealed spectral differences between individual layers and the 6-layer structure, namely, the appearance of two new bands with maxima at 480 and 640 nm are explained by that PBD molecules oriented perpendicularly to the monolayer plane are built between PVK chains and form mixed, closely-packed ordered structures at interfaces between layers of different compositions. The fluorescence in the 480 nm region seems to be related to singlet exciplex centers, since it has been found under photoexcitation both of PVK and PBD having overlapping singlet excited levels. The 640 nm region emission can arise under PVK excitation due to energy migration over triplet levels of carbazole groups along the interface and its trapping in sites of the sandwich arrangement of adjacent oxadiazole PBD fragments under the triplet exciplex formation.

#### **BB3.46**

**CHARGE ACCUMULATION AND TRANSIENT ELECTROLUMINESCENCE: OPERATION MECHANISM OF LIGHT-EMITTING DEVICES BASED ON ALIZARIN VIOLET.** Sharmistha Das, Arabinda Chowdhury, Sudipto Roy and Amlan J. Pal, Indian Association for the Cultivation of Science, Department of Solid State Physics, Jadavpur, Calcutta, INDIA.

Organic light-emitting devices (LEDs) have been fabricated based on a blend of alizarin violet dye and poly(methylmethacrylate) (PMMA) insulating matrix at different molar ratios. The current-voltage and luminance-current characteristics of the LEDs have been studied in both bias directions. Under the forward bias, Fowler-Nordheim tunneling mechanism has been shown to follow at higher fields. Charge carrier injection was described by Richardson-Schottky thermionic emission at lower fields. Under reverse bias, the latter type of mechanism was applicable for the entire range of fields studied. Luminance in the forward bias was independent of molar concentration of the dye. The turn-on current was also independent of the molar ratio in both bias directions. The reverse-bias luminance at any current density decreased with increase in molar fraction of the emitting dye. Transient electroluminescence (EL) characteristics of these devices have also been studied, where two rectangular voltage pulses separated by a delay were applied. This enabled us to separate out the effect of accumulated charges at metal/semiconductor interfaces from that of injected carriers. An instantaneous peak was observed in EL during the first pulse. When the delay between the pulses was short the peak was absent during the latter pulse. Steady state component of EL was present during both pulses. Intrinsically accumulated charge carriers at the interfaces have been shown to result in the instantaneous peak in EL. Molar concentration of alizarin, delay time (between two pulses), and applied voltage have been varied. The results showed that accumulated charges modified the internal field to assist charge injection. The ratio between the instantaneous EL during the second and first pulse varied from zero to unity as a function of delay time. This dependence will be discussed in terms of growth of accumulated charges at the interfaces.

#### **BB3.47**

**THE INTERNAL FIELD DISTRIBUTION IN LIGHT EMITTING ELECTROCHEMICAL CELLS AND LIGHT EMITTING DIODES: A COMPARATIVE STUDY.** Erik Moderegger, Stefan Tasch, Guenther Leising, Institut fuer Festkoerperphysik, Technische Universitaet Graz, AUSTRIA.

We determined the internal electrical field distribution in light emitting electrochemical cells (LECs) and light emitting diodes (LEDs) based on methyl substituted ladder-type poly(paraphenylene) (mLPPP) by performing electroabsorption (EA) measurements as a function of an external bias voltage. Based on these results we outline and discuss the working principles of both types of devices. In the case of the LEC we observed an abrupt increase in the EA signal above a threshold voltage of about 2 V which we attributed to junction formation due to in-situ electrochemical doping. For single layer LEDs we find the behavior expected for metal/insulator/metal structures, i.e. the electric field drops linearly over the bulk polymer and no space charge regions are observed. These findings are important for improving the performance of organic electroluminescent devices.

#### **BB3.48**

**EXCITED STATE ELECTRONIC INTERACTIONS IN OLIGO-THIOPHENE WITH NOVEL SUPRA-MOLECULAR ARCHITECTURES.** A. Borghesi, M. Gurioli, A. Sassella, R. Tubino, INFN and Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, Milano, ITALY; C. Botta, W. Porzio, Istituto di Chimica delle Macromolecole, CNR, Milano, ITALY; F. Della Sala, A. Di Carlo, P. Lugli, Dipartimento di Ingegneria Elettronica, Università di Roma Tor Vergata, Roma, ITALY.

Oligothiophenes exhibit the remarkable property that a strong perturbation of the excited state levels occurs upon aggregation. We have measured and compared the absorption and emission (both cw and time-resolved) spectra of quaterthiophene possessing two novel solid state organizations, namely isolated molecules embedded in the cylindrical nanochannels of a guest organic crystal and strongly interacting molecules in thin films obtained by layer by layer deposition in ultrahigh vacuum. All the spectra reveal features which are strongly dependent on the strength of the excited state coupling. This comparison adds significant information to the existing energy level scheme and photoexcitation scenario of this important class of organic semiconductors. The experimental data are well accounted for within the framework of the Davydov exciton theory: resonance interactions are calculated directly from the excited state INDO/SCI wavefunctions, without using the common dipole-dipole approximation.

#### **BB3.49**

**INORGANIC-ORGANIC LAYERED MAGNETIC COMPOUNDS BASED ON COMPLEXES OF NITROXYDE FREE RADICALS.** Christophe Lescop, Dominique Luneau, Paul Rey, Laboratoire de Chimie de Coordination, SCIB, DRFCM, CEA-Grenoble, FRANCE.

The synthesis of a new family of layered magnetic compounds has been achieved using an inorganic-organic approach based on complexation of transition metal ions with nitronyl nitroxide free radicals [1-3]. These compounds are made of sheets which have a honeycomb structure of alternating metal ions and free radicals. Anions are not coordinated to the metal centers and are in between the sheets [3]. In the case where the metal ion is manganese(II), these compounds exhibit spontaneous magnetization up to relatively high temperature  $T_c=50\text{K}$ . The ordering temperature ( $T_c$ ) shows dependence related either with the chemical groups on the free radicals, or with the nature of the anionic spacers. **Acknowledgments** : Work supported by CNRS, CEA and European Community TMR Program 3MD. **References** : [1] (a) D. Luneau, P. Rey, *Mol. Cryst. Liq. Cryst.*, **1995**, 273, 81-87; (b) K. Fegy, N. Sanz, D. Luneau, E. Belorizky, P. Rey, *Inorg. Chem.*, **1998**, 37, 4518-4523. [2] K. Fegy, D. Luneau, E. Belorizky, M. Novac, J-L Tholence, C. Paulsen, T. Ohm, P. Rey, *Inorg. Chem.*, **1998**, 37, 4524-4532. [3] K. Fegy, D. Luneau, T. Ohm, C. Paulsen, P. Rey, *Angew. Chem. Int. Ed. Engl.*, **1998**, 37, 1270-1273.

#### **BB3.50**

**SYNTHESIS AND CHARACTERIZATION OF NEW POLYARYLENEETHYNYLENES BASED ON 3-HEXYL MULTI-SUBSTITUTED OLIGOTHIOPHENE BLOCKS.** C. Botta, S. Destri, R. Consonni, W. Porzio, Istituto di Chimica delle Macromolecole, C.N.R., Milan ITALY; I. Khotina, Nesmejanov Institute of Organoelement Compounds, Moscow, RUSSIA.

In the last years, the interest as large area LED for polymers built up by regular sequences of oligothiophene block and hetero residues is growing up. The optical properties of these materials depend both on hetero moiety which may be another conjugated unit, and on the length of oligothiophene block. These factors enable to tune colours in LED devices. Few works report on the synthesis of soluble poly(thiopheneethynylenes) where the thienylene segments bring alkylic chains and only one with a regular head to head or head to tail connection. However the regioregularity effect on photoluminescence in poly(3-hexylthiophene) ethynylenes) appeared to be much smaller than in poly(3-alkylthiophene). This work reports on the synthesis and the molecular, structural and optical characterizations of regioregular copolymers constituted by phenylene or anthracene units and hexylsubstituted oligothiophenes with three or six rings connected by triple bonds. The luminescence properties of these polymers, the starting monomers and some models will be discussed. The luminescence quantum yield of the polymers constituted by anthracene units result to be lower than those of model and starting compounds, while when the polymers contain phenylene unit instead of anthracene one, the opposite occurs. This fact can be related to the lower solubility of the polymers based on anthracene moiety that, if on one hand display high luminescence, on the other makes stiffer the polymers in which is inserted.

#### **BB3.51**

**MOBILITY IN CONJUGATED POLYMERS: ROLE OF MOLECULAR GEOMETRY FLUCTUATIONS.** Z.G. Yu, D.L. Smith, A. Saxena, R.L. Martin, A.R. Bishop, Los Alamos National Laboratory, Los Alamos, NM.

Many conjugated polymers exhibit a field dependent mobility of the Poole-Frenkel form. We propose a model to describe transport in dense films of conjugated polymers in which thermal fluctuations in the molecular geometry modify the energy levels of localized electronic excitations in the material. Based on quantum chemistry calculations we argue that the primary restoring force for these

fluctuations in molecular geometry is steric in origin. Because the restoring force is intermolecular there is a spatial correlation in the molecular distortions. This leads to spatially correlated fluctuations in the on-site energy of the electronic excitations. The phenylene ring torsion, in PPV-like conjugated polymers, is an example of this kind of spatially correlated thermal fluctuation. We show that the model can explain the experimentally observed field-dependent mobility for PPV. We develop a numerical approach which enables us to study the electrical transport in three-dimensional systems. We investigate the density dependence of the mobility and find that when the carrier density is large the mobility can be significantly enhanced.

#### **BB3.52**

**CHARACTERIZATION OF MULTILAYER FILMS PREPARED BY LAYER-BY-LAYER SELF-ASSEMBLY USING SECOND HARMONIC GENERATION.** Mingyuan Gao, Michael Breit, Gero von Plessen, Uli Lemmer, Jochen Feldmann, Univ Munich, Dept of Physics and CeNS, Munich, GERMANY; Steven Cundiff, Univ Colorado, Jila, CO.

The layer-by-layer self-assembly technique is a well-developed approach to build up high quality multilayer films consisting of different types of molecules. Normally, the films are characterized by atomic force microscopy and x-ray reflectivity measurements in combination with different linear optical methods. However, all these methods can hardly give any information on interfaces within a given film. In this report, we use second harmonic generation (SHG) to characterize the interfaces in self-assembled multilayer films consisting of different types of polyelectrolytes. Different polyelectrolytes such as, polyethylenimine (A), polymethylacrylic acid (B), polydiallyldimethylammonium chloride (C) and polystyrenesulfonic acid sodium salt (D) are used as the fundamental components in the preparation of multilayer films. The polyelectrolyte films are amorphous without defined orientations of the monomers in the film. Thus second harmonic can only be generated at the interfaces. The experimental results prove that symmetrically structured two-component films such as (A/B)\*n with n = 1, 20 and A(D/C)\*n with n = 1, 20, 40 show no evident SHG increment with increasing n. The second order polarization generated at opposite interfaces obviously cancel each other leading to the conclusion that the morphology of opposite interfaces (A/B and B/A) are indistinguishable in this two-component multilayer system. As expected from symmetry considerations, asymmetrically structured four-component films (ABCDABCD)\*n show a much higher SHG-signal than more symmetrically structured four-component films (ABCDCBAD)\*n films for various values of n. In both cases we find an increase of the SHG-signal with increasing n. The increment for the symmetric structure is less pronounced, however, it is not found for the symmetric two-component systems and is theoretically not expected when assuming that the interface properties just depend on the properties of the two materials forming the interface. We conclude that in the four-component films the dipping history has influence on the structural details of the interfaces between subsequent layers.

#### **BB3.53**

**SYNTHESIS AND CHARACTERIZATION OF POLYQUINOLINES FOR LIGHT-EMITTING DIODES.** Alex K.-Y. Jen, Michelle S. Liu, Yunqi Liu, R. Craig Urian and Hong Ma, Department of Chemistry, Northeastern University, Boston, MA.

Polyquinoline (PQ) has recently attracted considerable attention as a blue color light-emitting material. It is also a good candidate as an electron-transporting material due to the electron-deficient nature of the quinoline moiety that tends to stabilize the negative charge. However, the single layer LED with PQ as an emitter exhibited low levels of light emission and internal quantum efficiency owing to poor hole injection. This contradictory problem can be circumvented by introducing electron-donating unit into the PQ backbone. Two systems of copolymers were synthesized by incorporating tetraphenyldiaminobiphenyl (TPD) moiety or dialkoxyphenylenevinylene moiety into the conjugated main chain respectively. These polymers demonstrated good LED performance. The same turn on voltages for both current and light indicated a balanced charge injection from the cathode and anode compared to that of the PQ alone. Yellow light was seen for TPD-PQ device, while greenish yellow light was observed from the PQ-MEH-PPV device. The electrical and optical properties of the polymers will be discussed in this paper.

#### **BB3.54**

**OPTIMIZING CONJUGATED POLYMER BLENDS FOR IMPROVED FÖRSTER TRANSFER.** Matthew Stevenson, Rahul Gupta, Alan Heeger, UCSB, Institute for Polymers and Organic Solids, Santa Barbara, CA; Hailiang Wang, UNIAX Corporation, Santa Barbara, CA.

Förster transfer is commonly observed in guest-host conjugated polymer blends, where the absorption spectra are characteristic of the

host and the emission spectra are characteristic of the guest. Due to decreased self-absorption, Förster transfer blends have been used to reduce ASE (amplified spontaneous emission) and lasing thresholds for conjugated polymers. In the best cases, the threshold for the blend is about an order of magnitude lower than that observed in the neat host polymer. In less optimal blends, the energy transfer rate is not sufficient to produce ASE from the guest; instead, emission from the host polymer appears along with the guest emission as the pump intensity is increased. Efficient Förster energy transfer requires a minimum guest concentration; below this minimum concentration emission occurs from both the host and guest, while only guest emission occurs for blends with guest concentrations greater than the minimum. Photoluminescence efficiency measurements show that the blends typically have higher efficiency than the corresponding neat polymers.

#### **BB3.55**

**LUMINESCENT RARE-EARTH MULTILAYER CHELATES FROM SEGMENTED POLYURETHANE-UREAS.** Jeremiah Mwaura, D.L. Thomsen, T. Phely-Bobin, M. Tahar, F. Papadimitrakopoulos, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Science Program, Institute of Materials Science, University of Connecticut, Storrs, CT.

Novel photoluminescent multilayer chelates have been prepared via an anhydrous self-assembly process. A metal-chelating polyurethane-urea based on 2,6-diaminopyridine and 1,6-diisocyanato hexane and chain extended with polyethylene oxide was assembled with a terbium salt to produce multilayer films. UV-VIS spectroscopy and spectroscopic ellipsometry indicate a monotonic but complex increase in film thickness relative to the number of dip cycles. The initial globular deposits increase in both the lateral and vertical directions to form diffuse islands that eventually fuse into more coherent structures as shown by atomic force microscopy. These assemblies show a strong green emission, characteristic of luminescent terbium (Tb<sup>3+</sup>) chelates. The combination of self-organization of block copolymers along with the well-defined emission characteristics of rare-earth metals could enable a wide range of applications of such chelates in photonic devices.

#### **BB3.56**

**CONJUGATED COPOLYMERS CONTAINING 9,9-BIS(4'-ALKOXYPHENYL)FLUORENE FOR EFFICIENT LIGHT-EMITTING DIODES.** Alex K.-Y. Jen, Sen Liu, Hong Ma, R. Craig Urian and Xuezhong Jiang, Department of Chemistry, Northeastern University, Boston, MA.

A series of novel fluorene-based cardo-polymers were synthesized via the Suzuki coupling reaction. Several aromatic conjugated moieties that facilitate either hole or electron transporting properties were copolymerized with 9,9-bis(4'-alkoxyphenyl)fluorene to fine-tune their HOMO/LUMO levels and achieve balanced charge injection. Bulky 4-alkoxyphenyl groups at C-9 of the fluorene unit were functionalized to render copolymer with good solubility and prevent copolymer from aggregating in solid films. Photoluminescence of these polymers and electroluminescence performance of their light-emitting devices have demonstrated the advantages of this design approach.

#### **BB3.57**

**PHOTO AND ELECTROLUMINESCENT PROPERTIES OF A PORPHYRIN - POLY(P-PHENYLENE VINYLENE) DERIVATIVE COPOLYMER.** Jorge Morgado, Cavendish Laboratory, Cambridge, UNITED KINGDOM and Dept Eng Quimica, Instituto Superior Tecnico, Lisbon, PORTUGAL; Rifat Iqbal, Melville Laboratory for Polymer Synthesis, University of Cambridge, Cambridge, UNITED KINGDOM; G. Yahioğlu, L.R. Milgrom, Dept of Chemistry, Imperial College, London, UNITED KINGDOM; Stephen C. Moratti, Andrew B. Holmes, Melville Laboratory for Polymer Synthesis, University of Cambridge, Cambridge, UNITED KINGDOM; Richard H. Friend, Franco Cacialli, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

The solid state luminescence properties of new statistical copolymers of 2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV) and a porphyrin-substituted phenylene vinylene were investigated. The aim of this work was to study the energy transfer from the MEH-PPV main chain to the porphyrin side groups, for both optical and electrical excitation. The photoluminescence emission shows an efficient energy transfer to the porphyrin, in spite of the small absorption coefficient of the porphyrin in the wavelength range of the MEH-PPV emission. At a porphyrin content of 0.08% molar the emission is already dominated by the porphyrin. The photoluminescence efficiency of these copolymers was found to be significantly reduced with respect to the value of the pure MEH-PPV, namely: from 13% (MEH-PPV) to 3% (for the copolymer with 3.94% molar of porphyrin). Efficient energy transfer is also observed in the emission spectra of light-emitting diodes. Interestingly, the reduction

of the electroluminescence efficiency with increasing porphyrin content is much more marked than that observed for the photoluminescence efficiency. Luminescence studies of blends of MEH-PPV and the porphyrin were also carried out, and the results will be compared with those of the copolymers.

### **BB3.58**

**GLASSY LIQUID-CRYSTAL FILMS AS BROADBAND POLARIZERS AND REFLECTORS VIA SPATIALLY REGULATED PHOTORACEMIZATION.** Dimitris Katsis, Philip H. Chen, John C. Mastrangelo, Ansgar W. Schmid, Shaw H. Chen, Materials Science Program, Dept of Chemical Engineering, NSF Center for Photoinduced Charge Transfer, and Laboratory for Laser Energetics, Center for Optoelectronics and Imaging, University of Rochester, Rochester, NY.

Glass-forming liquid crystals consisting of a cyclohexane central core with (S)-1-phenylethylamine and (4-cyanophenyl)naphthalene pendants were synthesized for hosting photoracemizable (R)-dinaphtho[2,1-d:1',2'-f][1,3]dioxepin, a chiral dopant. Chiral-nematic films 14, 22, and 35 micron thick were prepared for thermal and photoinduced racemization at temperatures from 95 to 130°C, i.e. in the mesomorphic temperature range, over a period of hours to days. Spatially modulated photoracemization was accomplished with an insignificant contribution from the thermal process at temperatures around 100°C over a period of up to 3 h. With an absorption coefficient of 6.2 reciprocal micron at 334 nm, the photochemical process was essentially confined to the irradiated surface, thereby setting up counter-diffusion of the two enantiomers through the film and hence the pitch gradient as visualized by atomic force microscopy. The significantly widened selective reflection band was interpreted with the Good-Karali theory extended for a gradient-pitch film. Furthermore, the bandwidth was found to increase with decreasing racemization temperature or with increasing film thickness, further validating the presence of a pitch gradient as a result of controlled photoracemization.

### **BB3.59**

**SYNTHESIS, CHARACTERIZATION, AND OPTICAL APPLICATION OF VITRIFIABLE CHIRAL-NEMATIC FILMS.** Dimitris Katsis, Philip H. Chen, John C. Mastrangelo, Shaw H. Chen, Materials Science Program, Department of Chemical Engineering, NSF Center for Photoinduced Charge Transfer, Laboratory for Laser Energetics, Center for Optoelectronics and Imaging, University of Rochester, Rochester, NY; Thomas N. Blanton, Kodak Research Labs, Eastman Kodak Company, Rochester, NY.

Nematic and left-handed chiral-nematic liquid crystals comprising methoxybiphenylbenzoate and (S)-(-)-1-phenylethylamine pendants to a cyclohexane core were synthesized and characterized. Although pristine samples were found to be polycrystalline, thermal quenching following heating to and annealing at elevated temperatures permitted the molecular orders characteristic of liquid crystalline mesomorphism to be frozen in the glassy state. Left at room temperature for six months, the vitrified liquid crystalline films showed no evidence of recrystallization. An orientational order parameter of 0.65 was determined with linear dichroism of a vitrified nematic film doped with Exalite 428 at a mole fraction of 0.0025. Birefringence dispersion of a blank vitrified nematic film was determined using a phase-difference method complemented by Abbè refractometry. A series of vitrified chiral-nematic films were prepared to demonstrate selective reflection and circular polarization with a spectral region tunable from blue to the infrared region by varying the chemical composition. The experimentally measured circular polarization spectra were found to agree with the Good-Karali theory in which all four system parameters were determined a priori: optical birefringence, average refractive index, selective reflection wavelength, and film thickness.

### **BB3.60**

**GLASS-FORMING LIQUID CRYSTALS WITH AN ELEVATED GLASS-TRANSITION TEMPERATURE.** John C. Mastrangelo, Fred Fan, Dimitris Katsis, Shaw H. Chen, Materials Science Program, Department of Chemical Engineering, NSF Center for Photoinduced Charge Transfer, Laboratory for Laser Energetics, Center for Optoelectronics and Imaging, University of Rochester, Rochester, NY; Patrick J. Hood, Cornerstone Research Group, Inc., Dayton, OH.

Most liquid crystals tend to crystallize on cooling, resulting in polycrystalline films undesirable for application because of light scattering. Liquid crystals that can vitrify into macroscopically ordered films hold promise for numerous optical and photonic applications. Intuitively, molecules consisting of dissimilar fragments should suppress spontaneous crystallization in favor of vitrification. Based on this concept, a wide variety of liquid crystalline molecular glasses have been produced with a glass transition temperature well beyond 100°C and a clearing point exceeding 250°C. Novel material systems and the dynamics of molecular orientation in liquid

crystalline melt with an applied field will be presented to furnish insight into structure-property relationships.

### **BB3.61**

**NEW ASPECTS OF ORGANIC ELECTRIC MATERIALS IN CALAMITIC LIQUID CRYSTALLINE PHOTOCONDUCTORS.** Hiroki Maeda, Central Research Institute, Dai Nippon Printing Co, Ltd, Tokyo, JAPAN; Masahiro Funahashi, Jun-ichi Hanna, Image Science & Engineering Laboratory, Tokyo Institute of Technology, Tokyo, JAPAN.

Calamitic liquid crystalline photoconductors such as 2-(4'-octylphenyl)-6-butyloxynaphthalene (8-PNP-O4) and 2-(4'-octylphenyl)-6-dodecyloxynaphthalene (8-PNP-O12) exhibit fast ambipolar carrier transport in all the smectic mesophases up to  $1.0 \times 10^{-2}$  cm<sup>2</sup>/Vs (SmE phase of 8-PNP-O4.) In contrast to conventional amorphous photoconductors, the liquid crystalline photoconductors are fluid, so that they provide us with new aspects in terms of electric property and application. In the present report, we demonstrate that the structural defects of liquid crystals, i.e. domain boundaries and disclinations in domains, are electrically inactive and cause neither shallow nor deep defect states due to their fluid nature and that the carrier transport does not suffer from these structural defects. In fact, we found that the carrier mobility does not deteriorate even in very thick liquid crystalline layers over 100 μm. This indicates that the porydomain structure of liquid crystal cells is permissible to the photoconductive application. Furthermore, we do that the fluid nature allows us multi-gap processing: we measured the transit times at the different thickness in a wedge cell (10 to 30 μm in thickness) filled with 8-PNP-O12 by time-of-flight technique and found that the transit times can be determined as a function of position illuminated by a slender beam of N<sub>2</sub> pulse laser. This result indicates that it is possible to make a position detection sensor by using wedge cells with the photoconductive liquid crystalline materials. We have concluded that with unique features mentioned above these photoconductive liquid crystals relax the present limitation in practical application of organic photoconductors and will open the door to new horizons.

### **BB3.62**

**OPTICALLY ACTIVE LANTHANIDE-CONTAINING POLYURETHANE IONOMERS.** Quan Gu and William M. Risen, Jr., Brown University, Department of Chemistry, Providence, RI.

Optically active highly branched polyurethane acid polymers containing D- or L- tartaric acid residues have been synthesized and transformed into transparent lanthanide ion containing ionomers. The novel synthetic approach used to form these polymers provides a method for tuning the chirality of the polymers. The chirality of the ionomers differs from the chirality of the acid-form polyurethanes due to modifications effected by their reactions with the lanthanide ions to form the ionomers. These materials also contain photocrosslinkable chain segments based on polybutadiene moieties. The spectral properties of these transparent polymers and ionomers in the solid state, both in the crosslinked and uncrosslinked forms, will be presented. The composition-dependent optical activity of these materials, in the form of the optical rotatory dispersion in the visible and ultraviolet regions, as well as the fluorescence and near-infrared and visible spectral properties of the Er, Er/Yb, and Dy ionomers will be presented.

### **BB3.63**

**ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF NANOCOMPOSITE THIN FILMS FORMED BY A ONE-STEP EXCHANGE-PRECIPIATION ROUTE FROM NANOCRYSTALS AND ORGANIC CROSS-LINKERS.** Frank L. Leibowitz, Wenxia Zheng, Mathew M. Maye, Yoon, A. Kim, Chuan-Jian Zhong, State University of New York, Binghamton, NY.

Nanomaterials derived from core-shell nanocrystals in which the core is encapsulated with functionalized organic monolayer shell serve as ideal building blocks towards fine-tunable interfacial architectures for chemical/biological sensing and energy storage. Recent experiments in our laboratory have demonstrated that nanocomposite thin films can be formed via a one-step exchange-precipitation route from thiolate-encapsulated gold nanocrystals and functionalized thiols (Zhong, C.J., Zheng, W.X., Leibowitz, F.L., *Electrochem. Commun.* 1, 72 (1999)). This paper presents results of the electrical and electrochemical characterizations of the thin films prepared using a variety of organic cross-linkers. In comparison with stepwise preparations, the one-step thin film exhibited remarkably compatible electronic conductive properties as reflected by similar activation energy for electron hopping. These results will be discussed along with spectroscopic and microscopic data characterizing the structures and properties of the nanocomposite thin films. Data from measurements of the electrical responses upon exposures to different vapor and solution environments will also be discussed.

### BB3.64

#### SYNTHESIS AND ELECTROOPTIC PROPERTIES OF NLO POLY(ETHER IMIDES) APPENDING HIGHLY EFFICIENT ISOPHORONE BASED CHROMOPHORES.

Jung Yun Do, Hyung-Jong Lee, Myung-Hyun Lee, Joo-Heon Ahn, Wol-Yon Hwang, Seon Gyu Han Telecommunication Basic Research Lab., Taejon, KOREA.

Highly efficient isophorone based NLO chromophores with various electron-accepting groups such as malononitrile, methylsulfonyl-acetonitrile, perfluorosulfonylacetonitrile, isoxazolone, etc were synthesized. To improve the thermal stability of the chromophore molecules, diphenylamine was introduced as an electron-donating group. As a processible polymer backbone with potentially high chromophore loading density, preimidized hydroxy poly(ether imide) was prepared with oxydiphthalic anhydride and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane. Newly synthesized chromophores with terminal hydroxy group were attached by the reaction with a preimidized hydroxy-poly(ether imide) in the presence of diethyl azodicarboxylate and triphenylphosphine. These coupling reactions were carried out quantitatively. The resulting amorphous electrooptic poly(etherimides) exhibits good solubility in common organic solvents, provided optical-quality thin films by spin coating. The glass transition temperatures of the polymers show the range of 180 to 210°C, which are ensuring the large aligned-orientation stability. The electrooptic coefficients ( $r_{33}$ ) measured at 1300 nm show above 20 pm/V by 125 V/ $\mu$ m electrical contact poling and the decay is about 10% over 2 months at 90°C under atmospheric conditions. The poling efficiency and alignment stability were studied by continuous DC applied poling and high power pulse poling. A polymeric Mach-Zehnder waveguide modulator based on new developed polymer has been fabricated for photonics applications.

### BB3.65

#### PHOTOEMISSION STUDY OF METAL-DEPOSITED

p-SEXIPHENYL FILM. Eisuke Ito, Nagoya Univ., Venture Business Laboratory JAPAN; Norbert Koch, TU-Graz, Inst. f. Festkoerperphysik, AUSTRIA; Hiroshi Oji, Nagoya Univ., Research Center for Materials Science, JAPAN; Hisao Ishii, Nagoya Univ., Dept. Chem., Grad. School of Sci., JAPAN; Guenther Leising, TU-Graz, Inst. f. Festkoerperphysik, AUSTRIA; Kazuhiko Seki, Nagoya Univ., Research Center for Materials Science, JAPAN.

Recently, organic electroluminescent (EL) devices have attracted much attention in relation to application to flat panel display. In order to understand the charge injection mechanism in such devices, the energy level alignment at the interfaces between organic films and metal electrodes is of crucial importance. So far, we have been investigating the electronic structure of organic/metal interfaces, using organic films deposited on metal substrates. The reverse system (metal on organic film) is also of importance in real device structure. In such systems, chemical interaction and diffusion of the metals are expected. In this study, we investigated electronic structures of metals deposited on p-sexiphenyl (6P) films by ultraviolet photoelectron spectroscopy (UPS), metastable atom electron spectroscopy (MAES), and X-ray photoelectron spectroscopy (XPS). MAES is an extremely surface sensitive method because the excitation source is metastable atoms which can not penetrate into a sample. In these measurements, the observed phenomena are different from those of 6P films deposited on metal substrates. The used metals were Au, Mg, and several alkali metals (K, Na, Rb, and Cs). In the case of deposition of Au and Mg, no charge transfer was observed in UPS, MAES, and XPS spectra, while a new intragap state was observed by deposition of alkali metals on 6P film in UPS and MAES spectra. For deposition of alkali metals, an additional feature in the MAES spectrum was observed at the lower binding energy side of the doping state observed in the UPS spectrum. When Au was evaporated with a thickness of 50nm, the spectral feature of 6P dominates in the MAES spectra, suggesting that Au does not cover the 6P film completely, while the intensity of the core level peak of Au gradually increased in XPS spectra with deposition of Au. These results indicate the diffusion of Au into 6P film, leading to formation of the intermixing region.

### BB3.66

MOLECULAR DEFORMATION AND DIELECTRIC PROPERTIES IN CHARGE-TRANSFER COMPLEXES OF 5,10-DIHYDRO-5,10-DIMETHYLPHENAZINE ( $M_2P$ ). Sachio Horiuchi, Reiji Kumai, Yoichi Okimoto, Joint Research Center for Atom Technology (JRCAT), Tsukuba, JAPAN; Yoshinori Tokura, Joint Research Center for Atom Technology (JRCAT), Tsukuba, JAPAN, and Univ of Tokyo, Dept of Applied Physics, Tokyo, JAPAN.

Structural, optical, and dielectric properties have been investigated for a charge-transfer complex with 1:1 mixed stacks of 5,10-dihydro-5,10-dimethylphenazine ( $M_2P$ ) and 2,5-dimethyl-7,7,8,8-tetracyano-*p*-quinodimethane ( $Me_2TCNQ$ ). The X-ray crystal structure and thermal behavior of the totally symmetric modes in the infrared

reflection spectra exhibit the dynamical disorder of the donor  $M_2P$  molecules with out-of-plane displacement of methyl groups at high temperatures. At 170 K, the  $M_2P$ - $Me_2TCNQ$  crystal undergoes a phase transition, upon which the methyl groups of  $M_2P$  cooperatively orders toward the out-of-plane positions. The symmetry breaking by this order-disorder phase transition generates ferroelectric stacks, and is responsible for the relaxational dielectric resonance with large  $\epsilon$  ( $\approx 1600$ ) near the critical temperature. On the basis of CT complexes, the use of such flexible  $\pi$ -electron molecules has been found to produce a new class of molecular dielectrics. This work was partly supported by NEDO.

### BB3.67

CURRENT-INDUCED SWITCHING IN RESISTIVE STATE OF ORGANIC MOTT-INSULATORS. Kumai Reiji, Okimoto Yoichi, Horiuchi Sachio, Joint Research Center for Atom Technology (JRCAT), Tsukuba, JAPAN; Tokura Yoshinori, Joint Research Center for Atom Technology (JRCAT), Tsukuba, JAPAN, and The Univ. of Tokyo, Dept of Applied Physics, Tokyo, JAPAN.

In Organic Mott-insulators, such as BEDT-TTF-TCNQ (ET-TCNQ), K-TCNQ, an electron is localized on the molecular (or molecular dimer) site, because of its fairly large on-site Coulomb repulsion ( $U$ ) as compared to the transfer energy ( $t$ ) between the adjacent molecular (dimer) sites along the molecular column (or sheets). The crystals of such molecular Mott-insulator show nonlinear electric conduction upon application of a high electric-field. Temperature dependence of the resistance of the K-TCNQ crystal upon application of constant-voltage pulses was measured. When the voltage is low the resistance of the crystal steeply increased with decreasing temperature in the same manner as in the conventional small-constant-current measurement. Once the voltage higher than 100 V is applied, the resistance is already decreased at room temperature by an order of magnitude, but jumps at 240K abruptly up to the low-voltage value. When the measurement voltage is higher than 200 V, however, the resistance does not diverge with decreasing temperature even down to 2 K. This suggests that the conduction path generated by the current is metallic in nature. In some cases, the conducting path can be visible by a microscope. The current flow causes a stripe-like periodic phase-segregation into the carrier-rich and -poor regions along the current path. This work was partly supported by NEDO.

### BB3.68

LUMINESCENCE DYNAMICS OF ALQ3-BASED MULTILAYER STRUCTURES IN TERMS OF HOMO AND LUMO ENERGY DISCONTINUITY. Shizuo Fujita, Tadahiro Nakazawa, Mitsuru Asano, Shigeo Fujita, Kyoto Univ, Dept of Electronic Science and Engineering, Kyoto, JAPAN.

Multilayer structures of organic materials are promising for excellent optical functions such as highly efficient luminescence or stimulated emission. This paper demonstrates that the criteria of type-I and type-II lineups, similarly to semiconductor multilayers, of HOMO and LUMO energy discontinuities can be a guideline for the analysis of optical functions. Multilayer structures of aluminumquinoline (Alq3) and oxadiazole (PBD) are classified to be of type-I lineup with respect to HOMO and LUMO energy discontinuity, i.e., HOMO and LUMO of Alq3 are higher and lower, respectively, than those of PBD. While multilayers of Alq3 and cyclopentadiene (PPCP) or Alq3 and diamine (TPD) are of type-II where both HOMO and LUMO are lower in Alq3. The remarkable differences in optical properties were observed between type-I and type-II group samples; (1) PL decay time in PBD for Alq3(5nm)/PBD(5-20nm) was as fast as 10ps independent of the PBD thickness, but that in PPCP for Alq3(5nm)/PPCP(5nm) was longer as 82ps and increased with PPCP thickness (120ps for 20nm), (2) in integrated PL the emission from Alq3 was totally dominant for Alq3(5nm)/PBD(5-20nm) but the emission from PPCP became more apparent with the increase of PPCP thickness in Alq3(5nm)/PPCP(5-20nm), (3) under electric field application the PL intensity did not change in Alq3/TPD but tended to decrease in Alq3/PPCP. The Alq3/TPD samples exhibited the characteristics similar to those of Alq3/PPCP. These results allow us to discuss the optical properties assuming the HOMO and LUMO energy levels being equivalent to valence and conduction band edges of semiconductors. For Alq3/PBD multilayers, the fast transfer of excited states or excitons from PBD to Alq3 followed by confinement in Alq3 are evidenced and are attributable to type-I lineup of HOMO and LUMO energies. Enhanced electroluminescence from Alq3 in Alq3/PBD multilayers has been proved and the concept of HOMO and LUMO energy discontinuities will lead to design of organic optical devices.

### BB3.69

PHASE MEASUREMENT OF SHG FROM A MEROCYANINE SELF-ASSEMBLED MONOLAYER IN SOLVENT. Kazuma Tsuboi, Nagoya Univ, Graduate School of Science, Nagoya, JAPAN; Kotaro Kajikawa, Tokyo Institute of Technology, Interdisciplinary Graduate School of Science and Engineering, Yokohama, JAPAN; Katsuhiko

Fujita, Kyusyu Univ, Interdisciplinary Graduate School of Engineering Sciences, Fukuoka, JAPAN; Kazuhiko Seki, Nagoya Univ, Research Center for Materials Science, Nagoya, JAPAN; Masahiko Hara, Hiroyuki Sasabe, Wolfgang Knoll, The Institute of Physical and Chemical Research (RIKEN), Frontier Research Program; Yukio Ouchi, Nagoya Univ, Graduate School of Science, Nagoya, JAPAN.

A technique of self-assembled monolayer (SAM) can easily provide an ordered surface, where the molecules are highly ordered and a densely packed. We have investigated application of these advantages of SAM to materials for optical devices. Among various chromophores which has a potential of optical function, we adopted a merocyanine dye, 1-alkyl-4-(4-hydroxystyryl)pyridinium bromide, which has a large hyperpolarizability due to strong intramolecular charge transfer. This chromophore has also interesting character, solvatochromism. Solvatochromism is a change of an absorption band by isomerization with pH and polarity of solvent. The merocyanine SAM was prepared by immersion of a gold substrate to 0.025mM ethanol solution of alkane disulfide terminated by a merocyanine dye, (S-C<sub>11</sub>H<sub>22</sub>-merocyanine)<sub>2</sub>. We investigated optical properties of the merocyanine SAM by UV-Visible spectroscopy and second harmonics generation (SHG) measurements. UV-Visible spectroscopy clearly demonstrated that the merocyanine is isomerized (from protonated form to zwitterionic form) by exposure to solution with different pH in spite of the densely packed structure. In contrast SHG response for the isomerization was different. Comparable intensities were measured for the merocyanine SAM in a protonated form and that in a zwitterionic form, while the intensity was weakest in neutral solvent where both forms coexist. There are several factors to induce this situation: molecular orientation, resonance condition, and dispersion. We performed phase measurement with use of a high frequency mode-locked fs Ti:Sa laser to avoid the damage of Au surface, and ingenious design in optical geometry. The results clearly showed the phase difference between two structures are almost 180 degree. This fact clearly explains the reason for the weakest SHG response in a neutral solvent in the SAM.

#### **BB3.70**

**SPECTROSCOPIC STUDY ON CONJUGATED POLYMERS.**  
Cherif Dridi, Hamed Ben Ouada, Hassen Muaref, Monastir Faculty of Sciences, Interface & Semiconductor Physics Laboratories, Dept of Physics, Tunisia; André-Pierre Legrand, LPQ, ESPCI, Paris, FRANCE; Jean-Jacques André, Institut Charles Sadron, Strasbourg, FRANCE; Joel Davenas, Univ Claude-Bernard, Lyon, FRANCE.

Polymer light-emitting diodes (LEDs) have recently attracted considerable attention because of their potential application in flat-panel displays. Therefore, we have electrosynthesized and characterized soluble statistic poly (meta/para phenylene) PMPP. We have used EPR spectroscopy for investigating the properties of mobile spins, such as those carried by polarons which carry both spin and charge, the study of their mobility provides an insight into the charge transport properties of the conjugated polymer in a microscopic scale. In this communication, we have reported also the optical properties evolution with conjugation length studied by means of optical absorption and electron energy loss spectroscopy on PMPP thin films.

#### **BB3.71**

**NEW ELECTRON ACCEPTOR FOR THE CONTROL OF CRYSTAL STRUCTURES AND THE GENERATION OF HIGH OPTICAL NONLINEARITIES.** Lyong Sun Pu, Yasunari Nishikata, Corporate Research Labs, Fuji Xerox Co. Ltd., Kanagawa, JAPAN.

On a base of the study for squaraine chemistry, we have particularly noticed cyclobutenedione (CD) as a new electron acceptor for second order nonlinear optical materials to induce strong polarization in molecules. Then, we have evaluated new materials containing CD as an electron acceptor, instead of the conventional nitro(NO<sub>2</sub>) substituent. From this study, cyclobutenedione (CD) was shown to be an excellent electron acceptor for nonlinear optical materials and to generate very high d-values.<sup>1,2)</sup> At this symposium, CD containing chiral 1-amino-2-propanol is shown as a new electron acceptor for the control of crystal structures. x-Ray crystallographic analyses on crystals of a series of 1-(4-N-methyl-N-alkylaminophenyl)-2-(2-hydroxypropylamino)cyclobutene-3, 4-dione, indicate that directions of molecules in each mono-molecular plate of crystals are perfectly aligned in one dimension, regardless of alkyl chains (C<sub>n</sub>H<sub>2n+1</sub>) bonded to N atom and crystals are formed by accumulating vertically mono-molecular plate. From these investigations on these anilino compounds containing CD, interestingly we have discovered for the first time that crystal structures change periodically from space group P1 to P2<sub>1</sub> depending on alkyl chain length of anilino groups and each mono-molecular plates accumulate vertically on either the same or the reversed direction alternatively. In relation to these crystal structures, second order nonlinear optical properties will be discussed. References 1) L.S. Pu, in Materials for Nonlinear Optics: Chemical Perspectives; S. Marder, J. Sohn and G. Stucky ed.; ACS Symposium Series 455;

American Chemical Society: Washington, DC, p331-342 (1991). 2) T. Tomono, et al., J. Phys. D: Appl. Phys. 26 (1993) B217.

#### **BB3.72**

**INFLUENCE OF THE CHEMICAL STRUCTURE ON THE LUMINESCENCE PROPERTIES OF ORGANIC DYE MOLECULES.** Egbert Zojer, Gunther Leising, Institut für Festkörperphysik, Technische Universität Graz, AUSTRIA; Niels Schulte, Arnulf-Dieter Schluter, Institut für Organische Chemie, Freie Universität Berlin, GERMANY; Petra Buchacher, Ruth Mullner, Franz Stelzer, Institut für Chemische Technologie Organischer Stoffe, Technische Universität Graz, AUSTRIA; Fred Wudl, Exotic Materials Institute, University of California, Los Angeles, CA; Jean-Luc Bredas, Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut, BELGIUM.

In this contribution we compare experimental investigations (of photoluminescence, excitation, absorption and modulation spectroscopy) for a number of novel dye molecules to quantum-chemical simulations. The investigated materials contain phenylene-, phenylenevinylene-, thienylene-, naphthalene- and anthracene units linked either by saturated or non saturated bonds. The primary aim of our studies is to determine: (i) on which part of a molecule consisting of several chemically different building blocks the excited species gets localized; and (ii) how does this influence the material properties. This can be accomplished theoretically by investigating the geometry modifications in the excited state relative to the ground state. To do so, we couple the Austin Model 1 (AM1) approach to a multi-electron configuration interaction technique (MECI). The optical spectra are subsequently obtained from the Intermediate Neglect of Differential Overlap (INDO) Hamiltonian combined with a Single Configuration Interaction (SCI) approach. It is found that minor modifications of the chemical structure can turn a brightly emitting dye molecule with a quantum efficiency close to unity into a material, whose emission intensity lies below the detection limit of our setup. This effect can be well explained by electron-electron correlation effects and by the influence of exciton localization. A comparison of the calculated oscillator strengths to luminescence lifetimes determined by photoluminescence modulation spectroscopy also helps to verify the quantitative validity of quantum-mechanical transition moments calculated by the INDO/SCI approach. The considerations presented in this contribution are intended to provide guidelines helpful for the design of novel dye materials.

#### **BB3.73**

**INFRA-RED PHOTOSPECTROELECTROCHEMISTRY OF GERMANIUM/PEDOT/ELECTROLYTE INTERFACES.**  
Helmut Neugebauer, Teketel Yohannes, N. Serdar Sariciftci, Physical Chemistry, Johannes Kepler University of Linz, Linz, AUSTRIA.

Electrochemically controlled semiconductor/conjugated polymer/electrolyte junctions are both interesting from a fundamental scientific point of view, and also for possible applications in optoelectronic devices. We report on investigations of these interfaces both under illumination and in dark conditions using spectroscopic in situ techniques. Properties of the semiconductor/conjugated polymer electrodes under applied electrochemical potential and during illumination are thus studied. We present results of a novel in situ technique for the study of germanium/polyethylenedioxythiophene (PEDOT) electrodes in different electrolytes using ATR-FTIR spectroscopy under illumination and in dark, comparatively. A germanium reflection element covered with the conjugated polymer film has been used as working electrode in a three electrode spectroelectrochemical cell and has been illuminated with laser light using fiber optics. At various electrode potentials, which correspond to different oxidation states of the polymer, difference spectra between light on and light off are recorded in situ. Furthermore, comparative studies using PEDOT/C60 layers will be reported.

#### **BB3.74**

**ELECTROCHEMICALLY AND PHOTO-INDUCED IR ABSORPTION OF LOW BAND-GAP POLYDITHIEN-OTHIOPHENES: A COMPARATIVE STUDY.** Antonio Cravino, Helmut Neugebauer, N. Serdar Sariciftci, Johannes Kepler University, Physical Chemistry, Linz, AUSTRIA; Mariella Catellani, Silvia Luzzati, C.N.R., Institute for Macromolecular Chemistry, Milan, ITALY.

Poly(dithieno[3,4-b:3',4'-d]thiophene), poly(dithieno[3,4-b:3',2']thiophene) and poly(dithieno[3,4-b:2',3'-d]thiophene) are low band gap polymers that undergo both p- (oxidation) and n- (reduction) type electrochemical reversible doping in organic electrolytes. In this work we report on the in-situ IR spectroscopic characterization of both doping types using ATR-FTIR spectroscopy. Thin polymer films were prepared on Ge reflection elements by electrosynthesis. During electrochemical potential cycling experiments in a spectroelectrochemical cell, the activation of active infrared vibrational modes



(IRAV), correlated with the generation of charge within the polymer chain during the electrochemical processes, was studied. In addition to electrochemical doping, the polymers exhibit also charged excitations by photodoping. FTIR spectra recorded by illumination/dark cycles show photoinduced IRAV bands which are similar to those found for the electrochemically p-doped materials. The IR spectroscopic results are compared with FT-Raman spectra of the neutral polymers and the relationship to the structure of the polymers is discussed.

#### **BB3.75**

**IN SITU ATTENUATED TOTAL REFLECTION FTIR SPECTROELECTROCHEMISTRY OF POLYBENZIMIDAZO-BENZOPHENANTHROLINE (BBL).** Teketel Yohannes<sup>a,b</sup>, H. Neugebauer<sup>a</sup>, N.S. Sariciftci<sup>a</sup>, <sup>a</sup>Physical Chemistry, Johannes Kepler University of Linz, Linz, AUSTRIA; <sup>b</sup>Chemistry Department, Addis Ababa University, Addis Ababa, ETHIOPIA; S. Yi<sup>c</sup>, S.A. Jenekhe<sup>c</sup>, <sup>c</sup>Department of Chemical Engineering, University of Rochester, Rochester, NY.

FTIR spectroscopy is a powerful method to determine doping induced structural changes and electronic band structure modifications of conjugated polymer films. We report results on in situ attenuated total reflection (ATR) FTIR spectroelectrochemical studies of reduction reactions (n-doping) of the conjugated ladder polymer polybenzimidazobenzophenanthroline, BBL. The ATR-FTIR spectra are recorded in situ during continuous potential cycling of a BBL coated germanium reflection element in a three electrode spectro-electrochemical cell. The spectra and the structural changes during the reduction (n-doping) of the polymer film at different electrode potentials are studied. In contrast to most of the other conjugated polymers, this polymer shows four reversible redox states during n-doping, corresponding to various forms of BBL with different conductivities.

#### SESSION BB4: NONLINEAR OPTICS

Chair: Susan P. Ermer  
Tuesday Morning, November 30, 1999  
Salon G (M)

#### **8:30 AM \*BB4.1**

**NONLINEAR PHOTONIC ENGINEERING.** Joseph Zyss, Sophie Brasselet, Michel Dumont, Isabelle Ledoux, Rozenn Piron, Eric Toussaere, Laboratoire de Photonique Quantique et Moléculaire, Ecole Normale Supérieure, Cachan, FRANCE.

Molecular nonlinear optics is currently experiencing a revival with possible impact in other fields, based on the conjunction of two mutually reinforcing trends. Firstly, molecular engineering has widened its scope to encompass 2-D and 3-D multipolar molecules beyond the earlier 1-D polar donor-acceptor template. Experiments based on polarized harmonic light scattering and associated quantum modelling have confirmed this avenue which is being currently implemented by chemistry laboratories following a variety of synthetic routes. Secondly, the traditional electric field thermal poling technique is being increasingly challenged by more advanced configurations whereby the electric field is partially or fully replaced by coherent single- or multi-photon excitations. The dual concept of multipolar molecules and multipolar field tensors proposed by our group has become the corner-stone of these schemes which unique potential to reveal and exploit the full tensorial dimension of multipolar light-matter interactions.

#### **9:00 AM \*BB4.2**

**REALIZATION OF POLYMERIC ELECTRO-OPTIC MODULATORS WITH LESS THAN ONE VOLT DRIVE VOLTAGE REQUIREMENT.** Larry Dalton, Univ of Washington, Dept of Chemistry, Seattle, WA.

Intermolecular electrostatic interactions between chromophores characterized by large molecular hyperpolarizability, polarizability, and dipole moment has been shown to inhibit electric field poling of such molecules. Thus, molecular hyperpolarizability cannot be efficiently translated to macroscopic electro-optic activity. Statistical mechanical calculations suggest logical modification of chromophore shape to minimize this problem and such modification has recently lead to electro-optic coefficients for poled polymer films that exceed 100 pm/V. Recently, these materials have been used to fabricate Mach Zehnder interferometers characterized by drive voltage requirements of less than one volt. Polymeric electro-optic modulators have now been shown to exhibit exceptional bandwidth (> greater than 100 gigahertz), low drive voltage requirements (< 1 volt), and ease of integration with VLSI semiconductor electronics. Recent improvements in optical loss (both material and device insertion loss) and improvements in the thermal stability of polymeric modulators makes these devices competitive with inorganic modulators.

#### **9:30 AM BB4.3**

**SECOND ORDER NONLINEAR OPTICAL FILMS BY ALTERNATING POLYELECTROLYTE DEPOSITION ON HYDROPHOBIC AND HYDROPHILIC SUBSTRATES.** M. Joseph Roberts, Naval Air Warfare Center Weapons Division, Materials and Chemistry Branch, China Lake, CA; Warren N. Herman, Naval Air Warfare Center Aircraft Division, Electro-Optic Sensors Branch, Patuxent River, Warminster, PA.

Alternating polyelectrolyte aqueous solution deposition technique (APD) may be used to process nonlinear optical polymers (NLOP) into noncentrosymmetric ordered films near room temperature. In this study, second-order NLOP APD films of a stilbazolium-substituted polyepichlorohydrin and poly(sodium 4-styrenesulfonate) or polyacrylic acid were prepared by alternately dipping a substrate into aqueous solutions of each polymer. Evidence for uniform layer to layer deposition includes a linear increase of UV-Visible absorbance and quadratic increase of second harmonic generated light intensity as a function of film thickness. Films have been uniformly deposited up to 0.1 micrometer thick. An optical interference technique was used to establish the orientation of the chromophores deposited on hydrophobic versus hydrophilic substrates. Thermal stability experiments show that these films can maintain 90 percent of the polar order up to 150 degrees Celsius. Films have been further characterized by AFM. Work is in progress to deposit thicker films of the same quality and to improve NLO figures of merit.

#### **9:45 AM BB4.4**

**HIGH PERFORMANCE SIDE-CHAIN AROMATIC POLYQUINOLINES FOR ELECTRO-OPTIC (E-O) DEVICES.** Alex K.-Y. Jen, Hong Ma, Xiaoming Wu and Jianyao Wu, Dept of Chemistry, Northeastern University, Boston, MA; Larry R. Dalton, Dept of Chemistry, University of Washington, Seattle, WA.

Organic polymeric second-order nonlinear optical (NLO) materials have attracted considerable attention due to their potential applications in telecommunications, optical signal processing, computing and data storage. Recently, a convenient modular method for making second-order NLO side-chain aromatic polyquinolines has been developed. This approach emphasizes the ease of incorporating NLO chromophores onto the pendent phenyl moieties of parent polyquinolines at the final stage via a mild Mitsunobu reaction, which provides the ease of synthesizing NLO polyquinolines with a broad variation of polymer backbones and great flexibility in selecting suitable chromophores. The resulting NLO side-chain polyquinolines possess high glass-transition temperature ( $T_g > 200^\circ\text{C}$ ), good processability and excellent thermal stability. The promising results of E-O activity (up to 35 pm/V at 830 nm and 22 pm/V at 1300 nm, respectively), optical loss (1.5-2.5 dB/cm) and long-term stability of the poling-induced polar order ( $r_{33}$  values retained >90% of their original values at 85°C for more than 1000 h) have demonstrated the advantages of this design approach. The excellent combination of these properties in the resulting polymers have also provided a great promise in the development of E-O devices.

#### **10:30 AM \*BB4.5**

**LOW HALF-WAVE VOLTAGE ELECTROOPTIC POLYMER MODULATOR TECHNOLOGY.** Yongqiang Shi, Weiping Lin, David Olson, James Bechtel, TACAN Corporation, Carlsbad, CA.

Electrooptic (EO) modulators have wide applications in digital and analog data links. The link performance can be evaluated by the halfwave voltage of the EO modulator used in the transmitter. High link gain and low noise figure can be achieved with low halfwave voltage EO modulators. Therefore, low halfwave voltage becomes an important consideration in EO modulator design. A wide bandwidth EO modulator consists of two waveguides: an optical waveguide and a microwave waveguide. It is the interaction of the two guided modes that results in the modulation of the optical beam. Therefore, the key issue in modulator design is to maximize the interaction between the two fields with minimum loss. Polymer materials have demonstrated a very promising potential for low halfwave voltage, wide frequency bandwidth, and low cost EO modulator applications. The recent progresses in new nonlinear optical chromophores, device design, and fabrication technologies made it possible to obtain sub-1V halfwave voltages in EO polymer modulators. To achieve low halfwave voltages, we have designed several optical push-pull modulator structures that can be used in various applications from materials characterization to high speed modulation. These designs make full use of the available active EO polymer waveguide structure and the flexible polymer material processing technology. The halfwave voltage of the push-pull devices is reduced by 50% when compared with single arm modulated devices. In this presentation, our low halfwave voltage EO polymer modulator design, demonstrative device fabrication, and experimental results will be discussed.

**11:00 AM BB4.6****CRYSTAL ENGINEERING OF ACENTRIC SOLIDS FOR SECOND-ORDER NONLINEAR OPTICAL APPLICATIONS.**

Wenbin Lin, Owen R. Evans, Zhiyong Wang, Dept of Chemistry, Brandeis University, Waltham, MA.

Noncentrosymmetric organization of molecular building blocks is an essential requirement for a bulk material to exhibit second-order NLO effects, and the construction of such acentric supramolecular assemblies still presents a great challenge for synthetic chemists. We have recently initiated a research program on the rational synthesis of acentric solids using molecular building block approaches. We will discuss in this presentation the synthesis of NLO-active coordination polymers based on interpenetrated diamond-like and two-dimensional square grid structures. We will focus on the control of acentricity of these solids by adjusting the ligand length and addressing the structure/property relationships of this interesting class of materials.

**11:15 AM BB4.7****SYNTHESIS AND PHOTO-BLEACHING OF EPOXY-BASED NONLINEAR OPTICAL POLYMERS CONTAINING TRIENE CHROMOPHORES.**

Binod B. De, Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA; K.G. Chittibabu, S. Balasubramanian, L. Li, Molecular Technologies Inc., Westford, MA; J. Kumar, S.K. Tripathy, Center for Advanced Materials, Departments of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA.

Bis(diglycidyl)ether of bisphenol-A-aniline (BP-AN) based second-order nonlinear optical (NLO) polymers containing triene chromophores have been developed through post-polymer functionalization reactions. Post one-pot aldol condensation reaction of dicyanomethylidene functionalized verbenone as well as isophorone compounds with aldehyde functionalized BP-AN polymer enabled the introduction of various chromophore moieties with high functionalization. These polymers were studied using various structural (<sup>1</sup>H NMR, FTIR), optical (UV-Vis) and nonlinear optical characterization techniques. A d<sub>33</sub> value of ca. 139 pm/V at 1.064 μm was determined for a representative polymer containing verbenone unit. We have observed fast photo-bleaching in these polymers. Detailed studies on the photophysical properties of this class of materials have been carried out using various analytical techniques and the structure-properties relationship and photo-bleaching mechanisms will be presented.

**11:30 AM BB4.8****DESIGN AND SYNTHESIS OF NEW ACCEPTOR MOLECULES FOR PHOTO-INDUCED ELECTRON TRANSFER REVERSE SATURABLE ABSORPTION.**

Mamoun Bader, Pennsylvania State Univ, Dept of Chemistry, Hazleton, PA; Scott Tarter, Chales Spangler, Montana State Univ, Dept of Chemistry and Biochemistry, Bozeman, MT; Hu Li, Scientific Materials Corp, Bozeman, MT.

The use of bis-(diphenylamino)diphenylpolyenes for optical power limiting applications has prompted further studies of the mechanism of photo-induced charge transfer in these systems in order to make these materials more efficient. C60 has been utilized in many examples of photo-induced charge transfer as an electron acceptor in the presence of donor moieties such as pi-conjugated polymers and oligomers. However, derivatizing C60 for covalent attachment to various polymer or oligomer backbones is nontrivial, and more processible and effective e-acceptors would be highly desirable. In this presentation we will discuss a systematic approach to new acceptor design based on derivatives of dithienyl polyenes and polythiophene oligomers, and preliminary evaluation of the effectiveness of these new materials to induce e-transfer from donors such as the bis-(diphenylamino)diphenylpolyenes.

**11:45 AM BB4.9****CONTROL OF SECOND-ORDER NONLINEAR OPTICAL SUSCEPTIBILITY IN IONICALLY SELF-ASSEMBLED FILMS BY pH AND IONIC STRENGTH.**

C. Figura, P.J. Neyman, C. Brands, M.A. Murray, S. Hair, J.R. Heflin, Dept of Physics, Virginia Tech, Blacksburg, VA; D. Marciu, M. Miller, Luna Innovations, Inc., Blacksburg, VA; R.M. Davis, Dept of Chemical Engineering, Virginia Tech, Blacksburg, VA.

Ionically self-assembled monolayer (ISAM) films have recently been shown to spontaneously form in the noncentro-symmetric structure required for a second order ( $\chi^{(2)}$ ) nonlinear optical response without the need for electric field poling. The ISAM method simply involves the alternate dipping of a charged substrate into an aqueous solution of a cation followed by dipping in an aqueous solution of an anion. Here, we present detailed studies of the structure of noncentro-symmetric ISAM films as a function of the parameters of the aqueous solutions. These studies indicate that while the thickness of the individual layers can be increased by more than a factor of ten in a

controlled manner, the corresponding increase in the amount of NLO chromophore is not associated with a corresponding increase in  $\chi^{(2)}$ . There is clearly a separate degree of orientation obtained at the interfaces between adjoining layers as compared to that within the bulk of an individual layer. The largest  $\chi^{(2)}$  values are observed in the thinnest films, since these contain the largest fraction of oriented chromophore. The  $\chi^{(2)}$  of a film with a bilayer thickness of 0.3 nm is four times larger than that of one with a bilayer thickness of 5.0 nm. It is also found that, while  $\chi^{(2)}$  remains constant for films with more than ten bilayers,  $\chi^{(2)}$  is substantially larger for fewer bilayers as a result of stronger orientation at the polymer-glass and polymer-air interfaces. As a result of the understanding obtained from these studies, we have developed several novel approaches to substantially increase the NLO response of ISAM films by reducing the orientational competition between chromophores that is inherent in the basic ISAM structure.

**SESSION BB5: CONDUCTING POLYMERS**

Chair: John R. Reynolds  
Tuesday Afternoon, November 30, 1999  
Salon G (M)

**1:30 PM \*BB5.1****DESIGN OF FUNCTIONAL TRANSITION METAL CONDUCTING POLYMER HYBRIDS.**

Timothy M. Swager, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA.

Transition metal centers can impart catalytic, sensing, and electronic functions to materials. General design principles will be illustrated for the integration of transition metals in conducting polymers to create novel functional materials with sensory and catalytic activities. The use of metallorotaxanes for the organization of organic monomers to create interpenetrating novel conducting polymer networks will also be presented.

**2:00 PM BB5.2****HIGHLY ELECTRON RICH CONDUCTING AND ELECTROACTIVE POLYMERS BASED ON 3,4-ALKYLENEDIOXY-PYRROLES.**

John R. Reynolds, Carleton L. Gaupp, Roberta K. Hickman, Philippe Schottland, Christopher A. Thomas, Barry C. Thompson, Kyukwan Zong, Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL.

A new class of electron rich conjugated polymers has been prepared based on the 3,4-alkylenedioxyppyrrrole (XDOP) repeat unit. Synthetic flexibility in the system is key and has allowed the preparation of numerous functionalized derivatives with electroactivity compatible with both aqueous and organic environments. These polymers have the lowest redox switching potential of any of the conducting polymers reported to date, which can be attributed to the highly electron rich character of the XDOP unit, and are electrochromic. Neutral poly(3,4-ethylenedioxyppyrrrole) (PEDOP) exhibits an electronic band gap of 2.0 eV; switching between a red-orange neutral state, through a green intermediate state, and finally to a blue oxidized state. Neutral poly(3,4-propylenedioxyppyrrrole) exhibits an electronic band gap of 2.2 eV; switching between an orange neutral state and a blue fully oxidized state. Both polymers exhibit high levels of redox switching stability. In this presentation, we compare and contrast the properties of these new PXDOP's to their thiophene analogues including poly(3,4-ethylenedioxythiophene) (PEDOT) and similar structural derivatives.

**2:15 PM \*BB5.3****SYNTHESIS AND APPLICATION OF CHIRAL CONJUGATED POLYMERS AND DENDRIMERS.**

Lin Pu, Department of Chemistry, University of Virginia, Charlottesville, VA.

A new class of polymers and dendrimers that contain conjugated units and have inherently stable chiral configuration have been synthesized and studied in our laboratory. These materials are prepared by using optically pure 1,1'-binaphthyls as the chiral building blocks. They are soluble in organic solvents and have been characterized by various spectroscopic methods. The potential applications of these materials for nonlinear optics, electroluminescence, enantioselective recognition and asymmetric catalysis have been studied. A few of these polymers have shown excellent enantioselectivity in catalytic asymmetric organic reactions as well as strong NLO and electroluminescence responses.

**2:45 PM BB5.4****SYNTHETIC APPROACH TOWARD PREPARATION OF**

C60-DERIVED STARBURST POLYANILINES.

Long Y. Chiang, Vijayaraj Anantharaj and Lee Y. Wang, Center for Condensed Matter

Recent intensive research on functionalization chemistry of fullerene molecules made syntheses of polyfunctional fullerene derivatives possible. Molecular C60 and its derivatives are electronegative compounds. Direct chemical bonding of an electron-donating conjugated organic molecule on a fullerene cage forms a molecular charge-transfer complex, when activated, with a A-D array. Application of multiple conjugate donors bound on one C60 molecule leads to a starburst complex with an A-(D)<sub>n</sub> coordination. Fullerene molecules are highly reactive toward a great number of chemical reagents under various conditions. However, synthetic methods suitable for the preparation of rigid-rod-like star polymers of fullerenes remain rare. Recently, we reported the synthesis and characterization of hexanitro[60]fullerenes (HNF), C60(NO<sub>2</sub>)<sub>6</sub>, with a well-defined number of addends using the radical addition of nitrogen dioxide as a nitration method. Reactivity of fullerene nitro groups in HNF was found to be high at ambient to elevated temperatures. As the nucleophilicity of reactants increases, a faster reaction kinetics was obtained. Consequently, enhanced reactivity of primary organo-amines toward the replacement of fullerene nitro groups overcomes the rate-retarding effect induced by the increasing structural complexity of the reactant. This improved precursor approach allows attachment of multiple oligoanilines onto a C60 cage in a moderate to fast rate. Contrarily, synthesis of oligoanilinated fullerenes is difficult using the direct reaction of C60 with oligoanilines even though fullerenes were reported to be reactive with some simple amines. As a result, efficient syntheses of starburst C60-based hexanilino, hexa(dianilino), hexa (tetranilino), and hexa-(hexadecaanilino)fullerenes were demonstrated using HNF as a precursor molecule. Related chemistry and intramolecular photo-induced electron-transfer properties of these new starburst conjugated materials will be discussed.

**3:30 PM \*BB5.5**

V. Percec, Case Western Reserve University, Cleveland, OH.

(ABSTRACT NOT AVAILABLE)

**4:00 PM BB5.6**

INTERFACIAL DESIGN OF SILICON/POLYPYRROLE JUNCTIONS. Namyong Y. Kim, Inge E. Vermeir, Paul E. Laibinis, Massachusetts Institute of Technology, Cambridge, MA.

The poor interfacial interaction of conducting polymer and silicon has been a critical problem in fabricating conducting polymer/silicon junctions. We report formation of a direct junction between an electrodeposited conducting polymer film, namely polypyrrole, and hydrogen-terminated silicon by introduction of a molecular film that covalently links the two phases. This linkage was formed by modification of hydrogen-terminated silicon with a pyrrole-containing organolithium reagent. The reaction produces an organic film that exposes pyrrole units and is connected to silicon by Si-C bonds. Notably, the reaction proceeds with little (or no) surface oxidation to silicon. Electrochemical deposition of polypyrrole onto this modified silicon surface produces polymer films that are smoother and more adherent than those deposited on hydrogen-terminated silicon. The presence of the molecular film provides sites for a more regular nucleated growth of the polypyrrole film. The junctions of polypyrrole and the native and modified substrates exhibit diode-like characteristics, with those on the latter substrate exhibiting higher current densities and superior ideality factors. Impedance measurements revealed that the improved electrical properties of junctions on the modified substrates were not due to a change in barrier height but rather a consequence of enhanced interfacial interaction between polypyrrole and modified silicon. The results point a direction to tailor solid/solid interfaces in electronic devices comprising inorganic and organic materials where electronic communication is required between two phases.

**4:15 PM BB5.7**

A GENERAL ROUTE TO THE FABRICATION OF DISSIMILARLY DOPED CONJUGATED POLYMERS. Xin Zhou, Brandi L. Langsdorf, Mark C. Lonergan, Univ of Oregon, Dept of Chemistry and The Materials Science Inst, Eugene, OR.

We report a general route to the fabrication of interfaces between dissimilarly doped conjugated polymers. The approach uses conjugated polymers specifically derivatized to kinetically stabilize interfaces between differentially doped conjugated polymers that would otherwise react to form a uniformly doped material. Such an approach allows for the fabrication of a wide range of interfaces that would otherwise be unstable, such as doped — undoped interfaces and pn homojunctions. The success of this new method opens the door to the fabrication of numerous device architectures never before possible with conjugated polymers. The specific model system reported consists of substituted poly(acetylene)s from the ring-opening metathesis polymerization (ROMP) of substituted cyclooctatetraenes

(R-COTs). This system is used to demonstrate the feasibility of the approach, and its utility in the fabrication of new types of conjugated polymer device architectures. The kinetics for the ROMP of R-COTs and the utility of this route in the fabrication of soluble, extensively conjugated polymers are also discussed.

**4:30 PM BB5.8**

A POLYANILINE COATING MATERIAL FOR INHIBITING CORROSION IN MARINE ENVIRONMENT. Yuan Lin, Sze C. Yang, Robert Clark, Univ of Rhode Island, Chemistry Department, Kingston, RI; Richard Brown, Univ of Rhode Island, Chemical Engineering Department, Kingston, RI.

Polyaniline has been actively studied as an electroactive component in paint systems for inhibiting corrosion of metals. Corrosion inhibition has been reported for steel samples coated with either the conductive emeraldine salt form, or the insulating emeraldine base form of polyaniline. In our recent studies for coatings on aluminum alloys, we found that the conductive form of our polyaniline complexes is much more effective than their insulating form for corrosion inhibition. Our finding has implication for the use of polyaniline in marine environments. The problem comes from the fact that the pH value of seawater is at pH 8.2. Since most polyaniline materials completely dedope in an aqueous environment with pH value higher than 6, the conventional polyaniline-based material would not be an effective corrosion inhibitor in marine environment. We synthesized a polyaniline complex that remains conductive in pH 8 environment. We have tested its effectiveness as a coating for protecting aluminum alloys exposed to the marine environment. Coatings were immersed in seawater and also in salt solutions buffered at pH 10 for 6 months. Corrosion tests show that the new polymeric complex of polyaniline is effective for improving the corrosion inhibition in seawater.

**4:45 PM BB5.9**

OPTICAL SPECTROSCOPIC STUDY OF CONDUCTING PEDOT: A NEW CLASS OF TRANSPARENT POLYMER ELECTRODE MATERIALS. Kwanghee Lee, Yunhee Chang, Pusan National Univ, Dept of Physics, Pusan, KOREA; R. Kiebooms, A. Aleshin, A.J. Heeger, Univ of California at Santa Barbara, Ipos, CA.

Recent development in organic optoelectronic devices requires a polymeric transparent electrode, which is expected to have low band gap below 1.5 eV and with sufficient dc conductivity. One of the candidate is recently fabricated poly(3,4-ethylenedioxythiophene) (PEDOT)doped with PF6. In this work, we present the reflectance spectra of PEDOT-PF6 with dc conductivity of 230 S/cm at room temperature, measured over a wide frequency range from 50 to 50000 cm<sup>-1</sup> (0.006 - 6 eV). The reflectance, R(w), of PEDOT-PF6 is characterized by metal-like signatures in the infrared (IR), including high R(w) in the far-IR and a plasma frequency of approximately 1.2 eV. The optical conductivity is dominated by intraband contributions below 1 eV, characteristic of a disordered metal near the metal-insulator transition. Since the onset of the interband absorption occurs at lower energy (around 1.5 eV) than in other conducting polymers, PEDOT-PF6 shows low absorption in the visible range between 2 and 3 eV. Our spectroscopic results demonstrate that this doped PEDOT system can be utilized as a transparent electrode for optoelectronic devices.

SESSION BB6: EVENING SESSION

Chair: Martin R. Bryce

Tuesday Evening, November 30, 1999

Salon G (M)

**8:00 PM BB6.1**

BIS(TETRATHIAFULVALENE)S: STOICHIOMETRY CONTROL IN THEIR CONDUCTING RADICAL CATION SALTS.

Martin R. Bryce, Derek E. John, Andrei S. Batsanov and Judith A.K. Howard, Department of Chemistry, University of Durham, Durham, UNITED KINGDOM.

The synthesis of new bis (TTF) derivatives will be presented. They are of interest as a new structural modification to TTF which may allow stoichiometry control in their conducting salts. Their redox properties in solution will be discussed with particular emphasis on interactions between the TTF systems. A range of radical cation salts have been obtained, and their structural, electronic and magnetic properties will be discussed. References

1. D.E. John, A.J. Moore, M.R. Bryce, A.S. Batsanov and J.A.K. Howard, *Synthesis*, 1998, 826.
2. A.S. Batsanov, D.E. John, M.R. Bryce and J.A.K. Howard, *Adv.Mater*, 1998, 10, 1360.

**8:15 PM BB6.2**

THE DEVELOPMENT OF EXTENDED ELECTRON DONORS BRIDGED PENDANT TO CONJUGATED POLYAROMATICS. Ronald L. Elsenbaumer, Ronald L. Meline, The University of Texas at Arlington, Department of Chemistry and Biochemistry, Arlington, TX; Alexander A. Tishkov, Russian Academy of Sciences, N.D. Zelinsky Institute of Organic Chemistry, Moscow, RUSSIA.

Furan and Pyrrole are functionalized at the 3,4 position with tetrathiafulvalene tetrathiolate (TTFTT) donors. The unsymmetric extended electron donors bearing a polymerizable heterocycle are synthesized as precursors to novel conjugated polymers. The effect of conformational freedom between the donor and the heterocycle is examined as the heterocycles are both fused and tethered to the TTFTT donors. Synthesis and properties of the materials are discussed.

**8:30 PM BB6.3**

MAGNETIC PROPERTIES OF LANGMUIR-BLODGETT FILMS OF PURELY ORGANIC MOLECULES. J.L. Gallani, J. Le Moigne, P. Wautelet, M. Moroni, Institut de Physique et Chimie des Matériaux de Strasbourg, FRANCE; P. Turek, Institut Charles Sadron, Strasbourg, FRANCE.

Organic magnetism is currently the object of numerous studies because of many potential applications. For example, organic synthesis makes it possible to combine different physical properties on a single molecule, such as chiral *and* magnetic, or photosensitive *and* magnetic. Still, bulk ferromagnetism requires molecular order and stability of the material, which has proven very difficult to control or even predict for such molecules. The Langmuir-Blodgett technique offers an enticing possibility of handling molecules for the building up of supramolecular architectures with a precise functional structure. In particular it seems very interesting to try imitating the layered structures of molecular electronics, e.g. magnetoresistive films or spin devices. We have synthesized several conjugated molecules bearing one nitronyl-nitroxide radical or two imino-nitroxide magnetically coupled radicals, and the Langmuir-Blodgett technique has been used to create mono- or multi-layers of each species. The structure of these films has been studied with Atomic Force Microscopy and grazing X-rays scattering, their magnetic properties being investigated with Electron Spin Resonance and SQUID measurements. The LB films exhibit 2D-magnetic behavior, which will be discussed in relation to the magnetic behavior of the bulk materials. For one of the molecules, the analysis of the temperature dependence of the magnetic susceptibility of a monolayer indicates that LB technique may provide a convenient way of artificially inducing ferromagnetic interactions.

**8:45 PM BB6.4**

DIRECT OBSERVATION OF 40 FEMTOSECOND CHARGE TRANSFER FROM CONJUGATED POLYMERS TO FULLERENES: QUENCHING OF PHOTOEXCITED COHERENT VIBRATIONAL DYNAMICS. Christoph J. Brabec, Gerald Zerza, Markus C. Scharber, N. Serdar Sariciftci, Johannes Kepler University, Christian Doppler Laboratory for Plastic Solar Cells, Linz, AUSTRIA; Giulio Cerullo, Guglielmo Lanzani, Silvio De Silvestri, Politecnico di Milano, Dipartimento di Fisica, Milano, ITALY; Jan C. Hummelen, University of Groningen, Department of Organic and Molecular Inorganic Chemistry, Groningen, THE NETHERLANDS.

The ultrafast photoinduced electron transfer with long-lived charge separation is investigated by femtosecond pump-probe experiments (fs-PIA) on thin films of conjugated polymers with and without fullerenes. We find that the addition of high concentrations of fullerenes modifies the primary excitation of the conjugated polymer within the first 30 femtoseconds. The photoinduced features attributed to the groundstate bleaching and the excited state absorption of the charge transferred state are clearly observed. Both features have a build up time within 40 - 50 femtoseconds and are metastable within the experimentally observed time frame (> 40 ps). Furthermore, the addition of fullerenes quenches the vibronic oscillations in the PIA relaxation due to the coherent vibrational wavepackets observed in the pristine polymer. The frequencies of these vibronic oscillations in the PIA relaxation are found to correlate directly with the non-resonant Raman frequencies of the polymer.

**9:00 PM BB6.5**

POLYMORPHISM AND PHYSICAL PROPERTIES IN OLIGO-THIOPHENES AND ARENES. Christian Kloc, Theo Siegrist, Hendrik Schön, Steffen Berg, Gordon Thomas, Bertram Batlogg, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Choosing organic semiconducting materials for electronic applications requires, at first, selection of compounds having as high a carrier mobility as possible, which requires an understanding of the relation between structural and other properties. The molecular structure describes only the atomic arrangement within individual molecules

while the crystal structure describes the molecular arrangement and involves the intermolecular bonds. In organic semiconductors the physical properties are determined by both, covalent bonds within molecules, and Van der Waals bonds among molecules. To study their contribution, we have studied the polymorphs of a range of compounds. Single crystals of  $\alpha$ -hexathiophene,  $\alpha$ -quaterthiophene, pentacene and 9,10 bis(phenylethynyl)anthracene have been grown by physical vapor transport, and growth conditions have been established that lead to polymorphs either thermodynamically stable and metastable at room temperature. The crystal structure has been resolved using single-crystal x-ray diffraction. Electrical transport properties, including mobilities and optical transmission of the same compounds in different polymorphic modifications have been measured and will be compared.

**9:15 PM BB6.6**

POLARIZED UV ABSORPTION OF HIGHLY ORIENTED PPV'S AND PPP'S: ELECTRONIC STRUCTURE OF LUMINESCENT CONJUGATED POLYMERS. E. Kirk Miller, Alan J. Heeger, University of California, Santa Barbara, Department of Physics, Institute for Polymers and Organic Solids; Cuiying Yang, University of California, Santa Barbara, Materials Research Laboratory, Institute for Polymers and Organic Solids.

Polarized UV absorption spectra of highly oriented conjugated polymers are crucial understanding the electronic structure of these semiconducting macromolecules. Gel-processed blends of conjugated polymers in a polyethylene (PE) matrix have highly aligned chains and strongly polarized luminescence. The polarized UV (2 eV - 6.2 eV) absorption spectra of chain-extended MEH-PPV and of a soluble polyfluorene derivative (HEH-PF) each reveal a series of absorption bands polarized parallel to the molecular axis and a single absorption band polarized perpendicular to the axis. The 3.7 eV peak in MEH-PPV is seen to be polarized parallel to the molecular axis, indicating that it is an intrinsic feature of the PPV electronic structure. In HEH-PF, the perpendicular-polarized band is at 5.3 eV, as predicted by band-structure calculations in the literature. We use these data to clarify the debate over the electronic structure of phenylene-based conjugated polymers and discuss the implications for efficient light-emitting devices based on luminescent polymers.

**9:30 PM BB6.7**

THE IMPORTANCE OF TRIPLET ANNIHILATION ON THE EFFICIENCY OF ORGANIC ELECTROPHOSPHORESCENT DEVICES. Marc Baldo and Stephen Forrest, Center for Photonics and Optoelectronic Materials, Dept of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, NJ.

We demonstrate that the decrease in efficiency typical of electrophosphorescent organic light emitting devices (OLEDs) at high current densities can be explained and accurately predicted by a simple triplet-triplet annihilation model. Using parameters extracted from transient phosphorescent decays, we model the efficiency versus current characteristics of electrophosphorescent devices containing either platinum octaethylporphyrin (PtOEP) or iridium tris-phenylpyridine (Irppy). The understanding gained explains the dramatic improvement in the performance of Irppy relative to PtOEP-based devices. We also derive an expression for a limiting current density ( $J_0$ ) above which triplet-triplet annihilation dominates. As OLEDs used in practical applications (e.g. displays) are likely to be current-controlled, the expression for  $J_0$  allows us to establish the criteria needed to identify useful phosphors, and to assist in the optimized design of electrophosphorescent devices.

**9:45 PM BB6.8**

DENDRITIC PHENYLENE VINYLENE. Martin U. Pralle, Eugene R. Zubarev, Gregory N. Tew, University of Illinois at Urbana-Champaign, Departments of Materials Science and Engineering and Chemistry and Beckman Institute for Advanced Science and Technology, Urbana, IL; Samuel I. Stupp, Northwestern University, Departments of Materials Science and Engineering and Chemistry, Evanston, IL.

We describe here a class of dendritic molecules having two different molecular architectures and containing phenylene vinylene as the primary monomeric constituent. The photo- and electroluminescent properties of these materials were characterized and their solid state structure was investigated by x-ray and electron diffraction. Blends of these molecules with linear polymers resulted in the discovery of interesting phase segregation behavior. The dendritic molecules segregate to the surface of the blend, even at exceedingly low wt.%, effectively modifying the surface properties of the linear polymer through these dendritic additives. This was observed experimentally by measured changes in the surface properties as well as via fluorescence and electron microscopies. This presentation will discuss the possibility of using this phenomenon in the design of devices with self assembling character.

10:00 AM **BB6.9**

Transferred to BB11.64

SESSION BB7/PP3: JOINT SESSION:  
TWO-PHOTON ABSORPTION AND  
APPLICATIONS

Chair: Joseph W. Perry  
Wednesday Morning, December 1, 1999  
Salon G (M)

8:30 AM **\*BB7.1/PP3.1**

MULTIPHOTON EXCITATION (MPE) OF ORGANIC MOLECULES IN BIOLOGICAL MATERIALS. Watt W. Webb, Applied and Engineering Physics, Cornell University, Ithaca, NY.

Molecular excitation by simultaneous absorption of two or more infrared (low energy) photons by an individual molecule provides a powerful tool for excitation of visible or ultraviolet fluorescence for biological and photophysical research at molecular and microscopic scales. Simultaneous at a Heisenberg uncertainty time of  $\sim 10^{-16}$  s in a typical molecular cross section of  $10^{-16}$  cm<sup>2</sup> requires very bright illumination by femtosecond pulses from a mode locked laser. The quantum photophysics of multiphoton excitation and the features that enable convenient application in biological and organic materials will be introduced. Excitation by a strongly focused pulse train provides laser intensity enhancement by  $\sim 10^{14}$  in a submicron focal point which can be scanned in a video raster for 3-dimensionally resolved multiphoton fluorescence microscopy (MPM). Images in living cells and tissues of the autofluorescence of intrinsic biomolecules such as adenine dinucleotide (NADH), elastin, collagens, serotonin, melatonin and indolamine oxidation products, chitin, and numerous still unknown structures characterize biological structures and processes and provide means for diagnosing disease states. Many common drugs and pathologists stains are conveniently two photon excited in living tissues, providing a convenient means of imaging functional responses. The most important advance of recent years in technology for study of dynamics of molecular process in living animals and tissues is Green Fluorescent Protein (GFP) gene constructs, which can be inserted in the genome of living organisms to label particular proteins and to provide an intrinsic pH indicator. GFP in living materials is best imaged with MPM.

In materials applications of MPM and sometimes in biological preparations extrinsic organic fluorescent marker molecules are needed. Organic fluorophores are notoriously photolabile and of course never bright enough. Unfortunately, the non-organic nanoparticle substitutes have been found to be just as pathological. Nevertheless, the complexity of the photophysics of multiphoton excitation offers new opportunities. The spectra for two photon excitation tend to be blue shifted and broadened relative to twice the one photon excitation wavelengths because the dipole excitation quantum parity is even instead of odd. Progress in design of fluorescent molecules specifically for two photon excitation has only recently begun and progress will be reported in the following lectures. Our data showing the success of early progress in creating fluorophores of large two photon cross sections by electric quadrupole moment enhancement will be illustrated.

9:00 AM **\*BB7.2/PP3.2**

APPLICATIONS OF MOLECULES WITH LARGE TWO-PHOTON ABSORPTION CROSS SECTIONS. K. Cammack, S. Kuebler, S. Marder, J. Perry, University of Arizona, Dept. of Chemistry, Tucson, AZ; B. Cumpston, D. Dyer, California Institute of Technology, Beckman Institute, Pasadena, CA; E. Hendrickx, B. Kippelen, M. Lipson, N. Peyghambarian, University of Arizona, Dept. of Optical Science, Tucson, AZ.

Molecules with large two photon cross sections have been recently reported. It has been shown that such molecules can be used to initiate the polymerization of acrylate monomers. In this presentation the applications of these highly sensitive two-photon absorbing molecules to excited state charge transfer mediated processes will be discussed.

9:30 AM **\*BB7.3/PP3.3**

THEORETICAL DESIGN OF ORGANIC MOLECULES WITH LARGE TWO-PHOTON ABSORPTION CROSS SECTIONS. J.L. Bredas, Department of Chemistry, University of Arizona, Tucson, AZ and Center for Research in Molecular Electronics and Photonics, University of Mons-Hainaut, Mons, BELGIUM.

Previous theoretical work on the design of novel compounds with large two-photon absorption cross-sections,  $\Delta$ , focused on quasi-one-dimensional molecules [1-2] such as oligophenylene vinylenes or diphenylpolyenes. Such compounds can act as efficient optical

limiters. Substitutions that promote charge transfer between the ends and the central part of the molecules were found to be very effective in boosting the  $\Delta$  value. This is done e.g. via substitution with amino donor groups at the ends and cyano acceptor groups in the middle of the oligomer. Such substitutions, by inducing a quadrupolar type charge transfer in the relevant excited states, result in an increase by over a factor of 3 in the transition dipole moment, M12, between the lowest one-photon excited state (S1) and the lowest two-photon excited state (S2); for instance, M12 is on the order of 3.1 D in unsubstituted stilbene and reaches nearly 10 D upon donor/acceptor/donor substitution [1]. Since  $\Delta$  depends on M12 squared, this factor alone enhances the two-photon absorptivity by over one order of magnitude[1].

In this contribution, we discuss other types of compounds, that also provide for major charge transfer between the ends or periphery of the molecule and the center upon excitation, thus potentially opening similar in-out polarization mechanisms for high two-photon absorption response. We focus namely on macrocyclic compounds (phthalocyanines, porphyrins) substituted by a metal in their center. [1] M. Albota et al. Science, 281, 1653-1656 (1998). [2] T. Kogej et al. Chem. Phys. Lett., 298, 1-6 (1998).

10:30 AM **\*BB7.4/PP3.4**

TWO PHOTON PROCESSES FOR OPTICAL LIMITING AND 3D MICROFABRICATION. P.N. Prasad, G.S. He, J. Swiatkiewicz, H. Pudarav, Y.H. Min, S.J. Chung, K.S. Kim and T.Z. Lin.

Recent development has produced novel materials with significantly enhanced two-photon absorption cross-sections and highly efficient up-converted emission. This achievement has opened up doors for many new technological applications. This talk will present our rational approach to design molecules and bulk forms with enhanced two-photon properties. Then the various techniques including ultrashort laser pulses being utilized in our laboratory to study the dynamics of two-photon process will be discussed. Although many applications of the photon technology are being pursued in our laboratory, this talk will focus only on two. Optical limiting and 3D microfabrication. A useful approach for optical limit is to use cooperative manifestations of two effects to broaden the coverage against laser sources of varying spectral and temporal conditions. Examples of 3-D microfabrications will involve 3-D complex optical circuitry in a preformed plastic block and 3-D MEMS type structures.

11:00 AM **\*BB7.5/PP3.5**

DESIGN, SYNTHESIS AND CHARACTERIZATION OF NEW BIOMECHANISTIC OPTICAL POWER LIMITERS BASED ON REVERSE SATURABLE AND TWO-PHOTON ABSORPTION. Charles Spangler, El Hadj Elandaloussi, Berrak Ozer, Kimba Ashworth, Luis Madrigal, Benjamin Reeves, Montana State Univ, Dept of Chemistry and Biochemistry, Optical Technology Center, Bozeman, MT.

During the past few years there has been considerable progress in the design, synthesis and characterization of new organic optical power limiting (OPL) materials. The common dominating mechanisms in organic chromophores are reverse saturable absorption (RSA) and more recently, two-photon absorption (TPA). There have been a number of recent reviews of the structure-property relationships inherent in the design of new materials for either RSA and TPA, but it has only been most recently that our group has proposed that careful design of the chromophore will allow both mechanisms to operate efficiently, albeit at different irradiation frequencies. In this presentation we will review the design and synthesis criteria for new bimechanistic chromophores, such as the bis-(diphenylamino) diphenylpolyene series, and illustrate how these new materials can be used as effective optical power limiters. We will particularly focus on the incorporation of these photonic-active moieties into dendrimer structures, and explore the advantages of dendritic architecture in optical power limiting and other nonlinear absorption processes.

11:30 AM **\*BB7.6/PP3.6**

DIRECT FABRICATION OF THREE-DIMENSIONAL STRUCTURES BY TWO-PHOTON LITHOGRAPHY. Benjamin J. Schwartz, Vinh Doan, UCLA, Dept of Chemistry and Biochemistry, Los Angeles, CA; Bruce Dunn, Pu-Wei Wu, UCLA, Dept of Materials Science and Engineering, Los Angeles, CA; Eli Yablonoitch, George Witzgall, Rutger Vrijen, UCLA, Dept of Electrical Engineering, Los Angeles, CA.

Photolithography is a well-known technique for converting patterns of light into physical structures. Absorption of light initiates a photochemical reaction which changes the solubility of the photoresist, allowing selective etching of the exposed material. Because the absorption of light proceeds from the surface down to the substrate, photolithographic techniques are inherently limited to the production of 2-D structures: etching of the resist must be uniform in the

direction normal to the substrate. Modern applications, however, require the ability to produce fully 3-D structures. Multilayer techniques can produce limited 3-D structures by stacking of a few conventional 2-D layers, but at the expense of difficult layer-to-layer alignment. This talk describes a new photolithographic technique which is inherently capable of fabricating 3-D structures: photolithography by two-photon absorption (2PA). The method uses ultrashort light pulses with high peak-powers whose wavelength is too red to expose the resist by conventional one-photon absorption. When focused with a high numerical aperture objective, however, the peak intensity in a small volume near the focal region is sufficient to expose the resist via 2PA, even though the intensity is insufficient to expose the resist at its surface. By scanning the focal volume in all three dimensions, truly 3-D structures can be fabricated in a single step. We can use this technique to produce 3-D structures in commercial photoresists, including a lincoln log lattice where one layer consists of 2 micron thick logs laid horizontally, while in the next layer the logs are laid vertically. We are also working to use 2PA to write 3-D images in silver-doped sol-gel glasses. The hope is that this form of 3-D photography will allow the direct fabrication of 3-D metal wire networks.

#### SESSION BB8: ORGANIC PHOTONICS

Chair: Michael J. Therien

Wednesday Afternoon, December 1, 1999

Salon G (M)

#### 1:30 PM \*BB8.1

HIGHLY CONJUGATED PORPHYRIN-BASED CHROMOPHORE SYSTEMS WITH UNUSUAL ELECTROOPTIC PROPERTIES. H. Tetsuo Uyeda, Kimihiro Susumu, Stephen M. LeCours, and Michael J. Therien, University of Pennsylvania, Department of Chemistry, Philadelphia, PA.

A new class of chromophores has been fabricated that features both electron-releasing and electron-withdrawing groups fused via an intervening ethynyl moiety to the carbon framework of a (porphyrinato) metal complex. These species possess a number of unusual optical properties that include molecular first-order hyperpolarizabilities ( $\beta$ ) of exceptional magnitude. New structures based on the archetypal [5-(4-dimethylaminophenylethynyl)-15-(4-nitrophenylethynyl)-10,20-diphenylporphyrinato]zinc(II) chromophoric motif have been elaborated that feature both more extensive conjugation and alternative electron releasing and electron donating components. Organized multilayer and polymeric films of these chromophores show that bulk-phase NLO responses can be engineered.

#### 2:00 PM BB8.2

VIBRONIC STRUCTURE OF PTCDA STACKS: MONOMER-DIMER EQUILIBRIUM IN SOLUTION. Z.G. Soos, M.H. Hennessy, Princeton Univ, Dept of Chemistry, Princeton, NJ; V. Bulovic, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ.

Perylenetetracarboxylic dianhydride (PTCDA) forms face-to-face stacks in crystals and thin films. Its spectra indicate mixed Frenkel and CT excitations that are coupled to a characteristic intramolecular vibration of conjugated hydrocarbons. PTCDA monomers in DMSO solution are in equilibrium with aggregates, taken as dimers, as shown by the concentration dependence of absorption and emission spectra. The absorption profile of dimers follows closely those of extended PTCDA stacks and multiple quantum wells, where Frenkel-CT mixing and vibronic coupling give large effective mass at  $k = 0$  that approximates dimer absorption. Monomer fluorescence is red shifted some 600 meV in PTCDA stacks and is orders of magnitude less efficient. This follows from selection rules and the Frenkel bandwidth, with  $J \sim 200$  meV obtained either from fitting spectra or the oscillator strength. The vibronics of mixed Frenkel-CT excitons account for solution equilibria as well as the main features of absorption, electroabsorption, fluorescence, and fluorescence action spectra of PTCDA stacks.

#### 2:15 PM \*BB8.3

APPLICATIONS OF ORGANIC AND INORGANIC OPTICAL THIN FILMS IN TELECOMMUNICATIONS. G.F. Lipscomb, T. Ticknor, M. Stiller and P. Schroeter, Lightwave Microsystems Corp., San Jose, CA.

The demands of exponentially growing internet traffic, coupled with the advent of Dense Wavelength Division Multiplexing (DWDM) fiber optic systems to meet those demands, have triggered a revolution in the telecommunications industry. In the three short years of deployment, DWDM performance has accelerated dramatically. Channel counts have grown from 4 to 80, with 170 announced, and channel spacings have shrunk from 400 GHz to 50 GHz. Practical systems that put 1 TeraBit/sec. of information on a fiber are now on

the horizon. This dramatic increase has been built upon, and has driven, improvements in fiber optic component technology, which has in turn driven improvements in photonic materials. The next generation of systems for the 'all optical network' will require higher performance components coupled with dramatically lower costs. One approach to achieve significantly lower costs per function is to employ Planar Lightwave Circuits (PLC) to integrate multiple optical functions on a single substrate leading to a single component. In this way multiple components can be fabricated and interconnected at once, significantly reducing both the manufacturing and the packaging/assembly costs. The manufacture of PLCs, however, places demanding requirements on materials, design and fabrication processes. Parameters such as index of refraction, absorption and birefringence must be tightly controlled. PLCs have been made using inorganic crystals, such as lithium niobate, oxide glasses or polymers on silicon substrates and semi-conductor materials, such as InP. All except InP are commercially available. In this talk we give an overview of the applications of PLCs in DWDM fiber optic transmission systems and discuss how material's requirements flow down from end-use requirements. Specific examples such as the use of polymer based thermo-optic switches for reconfigurable Optical Add/Drop Multiplexer (OADM) applications will be discussed.

#### 2:45 PM BB8.4

POLARIZATION-INSENSITIVE ELECTROOPTIC POLYMER DEVICES. Ariela Donval, Eric Toussaere, Roland Hierle, Joseph Zyss, Ecole Normale Supérieure de Cachan, Laboratoire de Photonique Quantique Moleculaire, FRANCE.

Polarization insensitivity is a crucial pre-requisite towards insertion of electrooptic (EO) waveguiding devices in optical telecommunication systems. We propose a new architecture for poling insensitive modulators whereby the inherent flexibility of polymers allows to monitor different polar axis directions according to the poling geometry. This property is implemented and demonstrated in novel Mach-Zehnder devices based on monolithic integration within one or both arms of a continuous sequence of balanced in- and out- of plane poled electrooptic sub-units. Optimization issues related to the electrode configuration, the nature of the cladding layers and the overlap between both poling and modulating field distributions with the waveguide cross-section have been addressed. A new polarization-insensitive electrooptic polymer amplitude modulator for integrated optics has been demonstrated along these lines. The design procedure including modelling, fabrication steps and performances, of each of the electrode configurations separately as well as for the two integrated sub-units in the polarization-insensitive polymer device will be also reported.

#### 3:30 PM \*BB8.5

REQUIREMENTS ON ORGANIC ELECTRO-OPTIC DEVICES FOR AEROSPACE APPLICATIONS. W.W. Anderson, S.P. Ermer, T.E. Van Eck, D.G. Girtton, R.E. Taylor, Lockheed Martin Advanced Technology Center, Palo Alto, CA.

Terrestrial digital photonic technology development will not satisfy all of the aerospace requirements since RF links are often required. Organic electro-optic devices are readily adaptable to RF functions into the 100 GHz and above frequency range. In addition to lossless links, they can be utilized for RF signal processing functions such as mixing, efficient harmonic generation and filtering. Devices can be densely packed with negligible cross talk. In addition to the well known survivability requirements for space born applications (lifetime, reliability, thermal, shock, vibration and radiation hardness), issues of weight and power become dominant. Organic devices based on thin film technologies have an obvious potential advantage with respect to weight. However, integration with other optical and/or electronic components needs to be considered since connectors often dominated size and weight. Performance (when translated back into the electronic domain) scales as the optical power and device sensitivity squared. Thus, advances in device sensitivity can be nullified by increases in optical loss.

#### 4:00 PM BB8.6

PHOTOEXCITATIONS IN OLIGOTHIOPHENES: THE ROLE OF CONFORMATIONAL MOBILITY AND INTERMOLECULAR INTERACTIONS. C. Botta, S. Destri, W. Porzio, ICM, CNR, Milano, ITALY; G. Bongiovanni, A. Mura, INFN and Dipartimento di Scienze Fisiche, Univ di Cagliari, Cagliari, ITALY; R. Tubino, INFN and Dipartimento di Scienza dei Materiali, Univ di Milano Bicocca, Milano, ITALY.

The optical properties of substituted and unsubstituted oligothiophenes are analysed with respect to their supramolecular organization in the solid state. The strong excited state interactions, which are responsible for collective excitations in the solid state, are reduced by increasing the intermolecular distances both by side chain substitution or by inclusion in a guest organic crystal. The

photophysical properties of weakly interacting oligothiophenes are strongly influenced by their backbone conformation and conformational mobility. Oligomers included in the channels of a guest crystal show fast torsional relaxation processes during the photo-excitation. Thin films and powders of  $\beta$ -substituted oligomers display optical properties and photoluminescence decay dynamics strongly dependent on their molecular packing.

**4:15 PM BB8.7**  
DESIGNING LIGHT EMISSIVE CONJUGATED POLYMERS WITH SMALL OPTICAL GAPS: A STEP TOWARDS ORGANIC POLYMERIC INFRARED LASERS. Alok Shukla and Sumit Mazumdar, University of Arizona, Tucson, AZ.

Polyacetylenes and polydiacetylenes have weak photo-luminescence, because of the existence of the lowest even parity two-photon  $2A_g$  state below the optical  $1B_u$  state in these systems. The optically pumped  $1B_u$  decays in ultrafast times to the  $2A_g$ , and radiative transition between the  $2A_g$  and the ground state is forbidden. In the common light emitting polymers like the poly-paraphenylenes (PPP) and poly(para-phenylenevinylene)s (PPV), the excited state ordering is reversed: the  $2A_g$  in these is above the  $1B_u$  due to an increase in the effective bond alternation. The increased effective bond-alternation raises the energy of the optical  $1B_u$ , and it therefore seems that light emission can occur only from conjugated polymers with optical gaps larger than trans-polyacetylene. Pictorially, PPV and PPP can be thought of as being obtained by "bond-substitution" of trans-polyacetylene, in which alternate or all double bonds are replaced by phenyl groups. We introduce the concept of "site-substitution", whereby the H-atoms of polyacetylene are replaced by conjugated side groups. We show that site-substitution leads to reduced bond alternation in the backbone polyene chain, as well as a reduced effective electron correlation. As a consequence, not only is the optical gap in the substituted polymer smaller than in the corresponding polyene of the same length, excited state ordering is conducive to photoluminescence. The theory is applied to the recently developed poly(phenyl-disubstituted acetylenes), strong photoluminescence in which has been observed, and is unexpected. The current materials have short conjugation lengths, but light emission in the infrared can be expected within the theory from similar site-substituted materials with long conjugation segments.

**4:30 PM BB8.8**  
CONDUCTING POLYMER PHOTONIC CRYSTALS FOR OPTICAL WAVELENGTHS. M. Deutsch, Yu.A. Vlasov and D.J. Norris, NEC Research Institute, Princeton, NJ.

We show how to pattern conducting polymers on optical wavelengths to produce photonic crystals. We have fabricated three dimensionally patterned poly(p-phenylene vinylene) (PPV) by filling the voids inside self-organized silica templates. For templates we use synthetic opals, which are comprised of monodisperse, closely packed, ordered silica spheres, with sphere sizes ranging from 200nm to 600nm. These opals exhibit photonic band gaps that vary accordingly from visible wavelengths to the near infrared. Previous attempts to fully infiltrate such templates with high molecular-weight polymers were unsuccessful, due to the large size of the molecules, which would block the opal pores. In contrast, we have introduced the PPV into the pores as a low molecular-weight, sulphonium salt precursor. Polymerization is induced by an in-situ base-catalyzed reaction, followed by heat treatment. The opal template may then be removed by selective etching, yielding a robust, luminescent polymer that is three dimensionally patterned on an optical length scale. Such active photonic crystals hold promise for exhibiting a variety of novel optical effects, such as lasing and greatly enhanced optical nonlinearities.

**4:45 PM BB8.9**  
PHOTONIC PROPERTIES OF DENDRONS AND DENDRIMERS INCORPORATING BIS-(DIPHENYLPHOSPHINO) DIPHENYLPOLYENES. Luis Madrigal, Charles Spangler, Montana State University, Dept of Chemistry and Biochemistry, Bozeman, MT.

During the past year a series of bis-(diphenylphosphino)-diphenylpolyenes has been synthesized and their absorption characteristics compared to a similar bis-(diphenylamino)-diphenylpolyenes. Dramatic blue shifts (30-40 nm) were observed in the spectra of the diphenylphosphino materials compared to the equivalent conjugation length diphenylamino counterpart. This blue shift is even more dramatic when one considers that replacement of a first row element with a second row element (e.g. S for O) in a nonlinear optical (NLO) chromophore normally results in large red shifts in the absorption spectra. In this presentation we will elaborate on this scenario in terms of the consequences of this spectral shift in applications such as optical power limiting via reverse saturable and/or two-photon absorption and for third-order NLO materials. The diphenylphosphino substituted polyenes have also now been incorporated into dendrons and dendrimers, and the advantages of

utilizing these monodisperse macromolecules for photonic applications will also be discussed.

SESSION BB9: SEMICONDUCTING POLYMERS  
Chair: Zhenan Bao  
Thursday Morning, December 2, 1999  
Salon G (M)

**8:30 AM \*BB9.1**  
ORGANIC PHOTODIODES AND SOLAR CELLS: PROGRESS, PROBLEMS, PERFORMANCE. Olle Inganäs, Lichun Chen, Lucimara Roman, Dimitri Godovsky, Applied Physics, Dept., Physics, Linköping University, Linköping, SWEDEN; Mats Andersson, Mikael Svensson, Dept. of Polymer Technology, Chalmers University of Technology, Göteborg, SWEDEN.

The use of photoinduced charge transfer between conjugated polymers and molecules, as photoexcited donors and acceptors is a route towards photovoltaic energy conversion. The organization of these different molecules in a solid opens a number of options, which must be utilized in combination with the physical limitations due to short exciton diffusion length, low charge mobility, narrow spectral coverage and optically thin devices. Ways of compensating for these problems based on polymer blends extending the spectral range of absorption, selfstratified polymer/molecule structures for vectorial charge transport and extension of the photon path length in the photodiode structures are reported. High external quantum efficiencies of 40%, and much higher internal quantum efficiencies are obtained in devices.

**9:00 AM BB9.2**  
PHOTOVOLTAIC EFFECT IN MULTILAYER ORGANIC SYSTEMS. G. Meinhardt, E. Moderegger, R. Schreder, G. Leising, Institut für Festkörperphysik, TU Graz, AUSTRIA; D. Faiman, Ben-Gurion National Solar Energy Center, Ben-Gurion University, ISRAEL; G. Winter, M. Hanack, Institut für Organische Chemie, Univ. Tübingen, GERMANY; U. Scherf, K. Müllen, Max-Planck-Institut für Polymerforschung, Mainz, GERMANY.

The organic materials presented here, e.g. methyl-substituted ladder-type poly-para-phenylene (mLPPP), different teryleneimides and conventional as well as substituted forms of phthalocyanines exhibit the advantages of low price, low processing costs and the simplicity of tuning their optical properties. Hence they are promising candidates to be used in large area photovoltaic applications. The cells investigated consist of one or more organic layers sandwiched between electrodes of indium tin oxide (ITO) and aluminum. The experimental techniques of electroabsorption-spectroscopy, photocurrent action spectroscopy and current voltage characterization were used to gain further insight into the process of charge generation, charge separation and transport of the charged species to the electrodes. To enhance the quantum efficiencies of the photovoltaic cells, special combinations of organic materials with electron-accepting and electron-donating properties in multilayer devices or by molecularly doping the active layer with electron-acceptor or donor organic materials were investigated. We chose dopands with HOMO- and LUMO-levels in a way to favor a charge transfer process from the active medium to the dopands in order to increase the photocurrent responsivity by an enhanced exciton dissociation. The thickness dependence of the photocurrent responsivity in our multilayer devices can be described within a model based on the internal filter effect. All the above mentioned organic materials are sensitive to redox-reactions with oxygen and photo-oxidation is one of the biggest problems when using them for solar cells. In order to improve the lifetimes of the photovoltaic devices they were encapsulated in epoxy resin and their stability versus AM 1.5 illumination under desert conditions was tested.

**9:15 AM BB9.3**  
PLASTIC SOLAR CELLS USING CONJUGATED POLYMER/FULLERENE COMPOSITE FILMS. Christoph J. Brabec, Thomas Fromherz, Franz Padinger, D. Gebeyehu, N. Serdar Sariciftci, Johannes Kepler University, Christian Doppler Laboratory for Plastic Solar Cells, Linz, AUSTRIA; Jan C. Hummelen, University of Groningen, Department of Organic and Molecular Inorganic Chemistry, THE NETHERLANDS.

Using the ultrafast photoinduced electron transfer with long-living charge separation in the conjugated polymer/fullerene thin films, photovoltaic devices have been fabricated. The photoinduced charge separation happens with internal quantum efficiency near unity. The performance of such bulk heterojunction photovoltaic devices is critically dependent on the transport properties of the interpenetrating network. Devices with monochromatic power efficiencies around 2.5% at their maximum absorption have been realized. It is also shown, that the efficiency of these cells does not decrease with

increased irradiation intensity. The open circuit voltage in devices using Al and ITO electrodes is different compared to the difference in workfunctions of the two electrodes. Strategies to improve the efficiency of conjugated polymer / fullerene photovoltaic devices will be discussed.

#### 9:30 AM **BB9.4**

**CHARGE TRANSPORT IN POLYCRYSTALLINE ORGANIC FIELD-EFFECT TRANSISTORS.** Gilles Horowitz, Riadh Hajlaoui, Lab Materiaux Moleculaires, CNRS, Thiais, FRANCE.

Although it has been studied for nearly fifty years, the charge transport in organic semiconductors is still a subject of large debates. This comes in part from the experimental data are widely dependent on the morphology of the samples. Measurements on single crystals are scarce, and some of them show mobility that tends to increase as the temperature is lowered. By contrast, practically all measurements on polymeric and polycrystalline materials lead to thermally activated mobility. Such a behavior is usually attributed to hopping transport in a disordered medium. An alternative model is multiple trapping and thermally activated release (MTR), where it is assumed that most of the charges are trapped in levels localized in the energy gap. In this communication, we present data on the mobility of sexithiophene (6T) based thin film transistors. The mobility is shown to depend on the gate bias. The temperature dependence can be divided into three domains. For T between 300K and 100K, the mobility is thermally activated with activation energy of around 0.1 eV. For T between 100K and 25K, the activation energy falls down to 5 meV. Finally, for T lower than 25K, the mobility is temperature independent. Although the MTR model accounts satisfactorily for the gate bias dependence, it cannot explain the temperature behavior, particularly at low temperatures. We therefore develop a new model based on a transport limited by barriers that form at grain boundaries. At high temperatures, charges jump over the barriers, so the transport is thermally activated. At low temperatures, tunnel transfer prevails, and the transport becomes temperature independent. The intermediate regime corresponds to thermally activated tunneling. The present limitations of the model will be outlined, and further checking of its validity presented.

#### 9:45 AM **BB9.5**

**HIGH MOBILITIES IN ORGANIC MOLECULAR CRYSTALS.** Jan Hendrik Schoen, Steffen Berg, Christian Kloc, and Bertram Batlogg, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

First applications of optoelectronic devices are now found in the marketplace. However, several basic questions about the charge transport and the intrinsic performance limits of transistor devices are still open. In order to study the intrinsic material properties, we have grown high quality single crystals from the vapor phase. We also quantitatively studied charge carrier localization as well as linear and non-linear transport phenomena, like hot carrier transport, drift velocity saturation. Mobilities above  $10 \text{ cm}^2/\text{Vs}$  were measured at low temperatures for oligothiophenes and polyacenes, including pentacene, tetracene and rubrene. A maximum mobility as high as  $400 \text{ cm}^2/\text{Vs}$  was obtained for high quality pentacene single crystals. Furthermore, all investigated materials exhibit a strong field-dependence of the mobility, which can be ascribed to acoustic phonon scattering. The room temperature mobilities of these materials, which are the key parameter for applications, lie between 1 and  $3 \text{ cm}^2/\text{Vs}$ , increasing with increasing conjugation length of the material. This strong decrease of the mobility with temperature is explained by a strong electron-phonon interaction, causing an increased effective mass due to dressing of the charge carrier by a polarization cloud. Interestingly, the coupling strength decreases with increasing conjugation length for both material classes (polyacenes as well as oligothiophenes). Therefore the search for materials with small coupling will be beneficial for future device optimization.

#### 10:30 AM **\*BB9.6**

**FACILE DEPOSITION PROCESSES FOR SEMICONDUCTING MOLECULAR SOLIDS.** H.E. Katz, W. Li, A.J. Lovinger, V.R. Raju, Y.-Y. Lin, A. Dodabalapur, Z. Bao and J. Rogers, Bell Labs-Lucent Tech, Murray Hill, NJ.

Research on organic semiconductors for field-effect transistors is becoming more focussed on the manufacture of printed logic circuits. We have designed and synthesized novel heterocyclic oligomers and investigated their deposition as thin films from solution, in some cases achieving semiconductor performance equivalent to vacuum evaporated films. The nature of the solvent and substrate, solution temperature and concentration, and oligomer substituents all markedly influence film quality. Both electrical characteristics and device reliability are additionally sensitive to molecular orbital energy levels in the semiconductor. The application of our results to plastic, multidevice circuits will be discussed.

#### 11:00 AM **\*BB9.7**

**PENTACENE-BASED ORGANIC THIN FILM TRANSISTORS.** Thomas N. Jackson, Center for Thin Film Devices, and Electronic Materials and Processing Research Laboratory, Department of Electrical Engineering, Pennsylvania State University, University Park, PA.

Organic thin-film transistors (OTFTs) and electronics are of interest for low-cost high-information content displays, especially on flexible substrates, and for other large-area electronic applications. Although field-effect carrier mobility as low as about  $10^{-2} \text{ cm}^2/\text{V-s}$  is adequate for some low-performance applications, mobility as large as about  $2 \text{ cm}^2/\text{V-s}$  has been reported for OTFTs, and may allow OTFT use in much higher performance applications. Pentacene is of particular interest since carrier mobility near  $2 \text{ cm}^2/\text{V-s}$  has been measured in field-effect transistors [1] and by space charge limited current measurements [2] in this material.

When deposited by vacuum evaporation onto substrates held at room or moderately elevated temperature ( $\sim 20\text{-}120^\circ\text{C}$ ), pentacene has a strong tendency to form molecular crystals, often with micron-size grains, even on amorphous substrates. Thin film growth is strongly influenced by substrate surface energy and often appears to be Stranski-Krastanov-like which may allow coherence in film layers near the substrate interface even when apparent grain boundaries are observed for the overlying film. The nature of grain boundaries in or near the gate-field-induced carrier channel is of interest since grain boundaries may introduce traps that degrade transport. Pentacene is of interest in this context since its HOMO position may limit the types of impurities and defects that can cause deep hole traps, possibly explaining the nearly identical mobility measured for single crystals and OTFTs fabricated using polycrystalline material [2,1]. [1] D.J. Gundlach, C.C. Kuo, S.F. Nelson, and T.N. Jackson, "Organic thin film transistors with field effect mobility  $> 2 \text{ cm}^2/\text{V-s}$ ," *57<sup>th</sup> Device Research Conference Digest*, p. 164 (1999) [2] J.H. Schön, C. Kloc, R.A. Laudise, and B. Batlogg, "Electrical properties of single crystals of rigid rodlike conjugated molecules," *Phys. Rev. B*, vol. 58, p. 12952 (1998)

#### 11:30 AM **BB9.8**

**POLYMER FIELD-EFFECT TRANSISTORS BASED ON POLYFLUORENE HOMO- AND BLOCK COPOLYMERS.** H. Sirringhaus, R.J. Wilson, R.H. Friend, University of Cambridge, Cambridge, UNITED KINGDOM; M. Inbasekaran, M.G. Dibbs, E.P. Woo, Dow Chemical Company, Midland, MI.

Homo- and block-copolymers based on dioctyl-fluorene (F8) have been investigated extensively for applications in polymer light-emitting diodes. They are prepared by the Suzuki coupling method and exhibit excellent chemical purity and a high degree of structural perfection and long conjugation lengths in the solid state. Here we report a study of their charge transport properties as measured in field-effect transistor (FET) devices. Electron and hole field-effect mobilities will be discussed. In a block-copolymer based on F8 high, hole field-effect mobilities of  $5 \cdot 10^{-3} - 1\text{S} 10^{-2} \text{ cm}^2/\text{Vs}$  and clean normally-off, accumulation-type operation with high ON-OFF current ratio  $> 10^6$  have been observed. The performance is comparable to that of poly-3-hexylthiophene FETs. A method will be demonstrated how to exploit the existence of liquid crystalline phases at elevated temperatures in order to improve structural order in the films and further enhance charge carrier mobilities. Mobility anisotropies have been determined in FET devices with uniaxially aligned polymer films.

#### 11:45 AM **BB9.9**

**ORGANIC-INORGANIC HYBRID MATERIALS AS SEMI-CONDUCTING CHANNELS IN THIN-FILM TRANSISTORS.** C.R. Kagan, D.B. Mitzi, C.D. Dimitrakopoulos, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Molecular-scale composites of organic and inorganic materials, known as hybrids, provide the potentially high carrier mobilities characteristic of inorganic materials, but may be deposited by the simple, low-cost techniques common to organic molecules. We report field-modulated conductance in the first thin-film transistors having organic-inorganic hybrid materials as semiconducting channels. We focus on semiconducting, organic-inorganic hybrids based on the perovskite structure which crystallize from solution to form oriented, thin solid films of alternating anionic, inorganic perovskite sheets and cationic, organic layers. The inorganic sheets extend in 2D to electrically connect source and drain electrodes. In one example, spin-coated thin-films of the organic-inorganic perovskite,  $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4$ , form p-channel transistors with field-effect mobilities of  $0.6 \text{ cm}^2/\text{V-sec}$  and current modulation of  $> 10^4$ . Other organic-inorganic hybrids, based on the tin(II) iodide framework and organic cations with different length and chemical functionality, have also been examined. It is expected that engineering the organic and inorganic components of these hybrids may be used to optimize the performance of organic-inorganic field-effect transistors.



## SESSION BB10: LIGHT-EMITTING DIODES

Chair: Alex K.-Y. Jen

Thursday Afternoon, December 2, 1999

Salon G (M)

### 1:30 PM \*BB10.1

ARCHITECTURES FOR POLYMER LIGHT-EMITTING DIODES. Richard H. Friend, Cavendish Laboratory, Cambridge and Cambridge Display Technology, UNITED KINGDOM; Jeremy H. Burroughes, Cambridge Display Technology, Peter K.H. Ho, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

We report a range of studies on the development of novel architectures for polymer light-emitting diodes. These are optimised for easy injection of charge carriers, and provide for operation with low threshold voltages. Luminous efficiencies of above 20 lumen/W are achieved for emission in the green part of the spectrum, with equivalent quantum efficiencies for red and blue.

### 2:00 PM BB10.2

HIGH EFFICIENCY ORGANIC ELECTROPHOSPHORESCENT DEVICES. P.E. Burrows, M.A. Baldo and S.R. Forrest, Center for Photonic and Optoelectronic Materials, Department of Electrical Engineering, Princeton University, Princeton NJ; S. Lamansky P. Djurovich and M.E. Thompson, Department of Chemistry, University of Southern California, Los Angeles, CA.

We demonstrate small molecule electrophosphorescence at an external quantum efficiency of >10% and luminous efficiency of > 30 lm/W at 5.5V using a light emitting layer consisting of carbazole biphenyl doped with ~6% by mole of fac-tris(2-phenylpyridine) iridium (III) (Ir(ppy)<sub>3</sub>). To achieve high efficiency in phosphorescent OLEDs, the relatively long-lived triplet excitons must be confined in an organic double heterostructure. A typical device structure consists in sequence of an indium tin oxide anode, a hole transport layer, a thin (~200 Å) doped phosphorescent layer, an exciton confinement layer such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, an electron injecting layer such as tris(8-hydroxyquinoline) aluminum and a low work function cathode. We examine the optimization of each layer in phosphorescent OLEDs to maximize the external quantum efficiency and minimize the operating voltage. By also optimizing the emission spectrum and optical outcoupling from the OLED, we demonstrate the potential for luminous efficiencies of > 50 lm/W. We report several other octahedral ortho-metalated Ir(III) complexes of a general structure Ir(C-N)<sub>3</sub>, and OLEDs prepared with them. Examples of complexes include fac-tris(2-thienylpyridine) iridium (III) and fac-tris(benzo[h]quinoline) iridium (III). Upon excitation at the maximum of their metal-to-ligand charge transfer absorption bands in solution, the complexes typically exhibit intense emission close to the maximum of the photopic response function (ca. 550 nm). We present electrophosphorescent data from double heterostructures based on these materials and discuss their application to low cost, high efficiency backlight applications.

### 2:15 PM \*BB10.3

HIGHLY EFFICIENT LIGHT-EMITTING DIODES AND PHOTOVOLTAIC CELLS FROM SEMICONDUCTING POLYMER HETEROJUNCTIONS. Samson A. Jenekhe, Xuejun Zhang and Shujian Yi, University of Rochester, Department of Chemical Engineering, Rochester, NY.

Semiconducting or  $\pi$ -conjugated polymer devices are promising for various optoelectronic applications, including light-emitting diodes (LEDs) and photovoltaic cells. We have prepared a series of p-type (hole transport)/n-type (electron transport) semiconducting polymer heterojunctions and discovered that some of them have dramatically enhanced electroluminescence and photovoltaic properties. EL diodes of the type ITO/poly(p-phenylenevinylene)/polyquinoline/Al combine low turn-on voltages with high brightness (300-800 cd/m<sup>2</sup>) and EL efficiencies of up to 3%. These LEDs also exhibit unusual voltage tunable multicolor emission which is suitable for display applications. Some of the p-type/n-type heterojunctions of conjugated polymers were found to exhibit photovoltaic power conversion efficiencies and fill factors of 2% and 70%, respectively. Nanoscale size effects on the performance of both the EL and photovoltaic devices will also be presented. The electron affinities and ionization potentials of the polymers and hence the energetics at the polymer/polymer interface were found to play critical roles in device performance.

### 2:45 PM BB10.4

POLARIZED LUMINESCENCE FROM LIQUID-CRYSTALLINE POLY (P-PHENYLENE VINYLENE) DERIVATIVES. X. Linda Chen, Zhenan Bao, Andrew J. Lovinger, Martin Meier, Brian Crone, Ananth Dodabalapur, Bell Laboratories, Lucent Technologies, Murray Hill; Rachel Jakubiak, Lewis J. Rothberg, Department of Chemistry and NSF Center for Photoinduced Charge Transfer, University of Rochester, Rochester, NY.

A series of poly (p-phenylene vinylene)s with dendritic side chains have been synthesized and their self-assembling and photophysical properties have been investigated. The polymers are both lyotropic and thermotropic liquid crystals. Various methods were used to align the polymers, including shearing, rubbing, and friction transfer techniques. Anisotropic absorption and luminescence were observed. The results suggest that the combination of highly soluble dendritic-substituted PPVs with alignment techniques might be a simple and general method to achieve polarized electroluminescence and photoluminescence.

### 3:30 PM \*BB10.5

LIGHT EMITTING DIODES BASED ON FLUORENE POLYMERS. Mark Bernius, Michael Inbasekaran, Edmund Woo, Weishi Wu, Lisa Wujkowski, Mitch Dibbs. The Dow Chemical Company, Midland, MI.

This paper describes the development of light emitting diode technology based on fluorene-containing polymers, prepared through the coupling of 9,9-disubstituted 2,7-bis-1,3,2-dioxaborolanyl-fluorene with a variety of aromatic dibromides. In these polymers the polyphenylene-like backbone provides the mechanical and chemical robustness and the C-9 of fluorene provides a site for physical property modifications without introducing significant torsional strain which would adversely affect conjugation. Polymer optical and electronic properties are tailored through selective incorporation of different aromatic unit into the AB alternating structure. LED devices emitting in blue, green, red and other colors are thus obtained.

### 4:00 PM \*BB10.6

NOVEL POLYMERS FOR LED APPLICATIONS. Zhonghua Peng, University of Missouri, Dept. of Chemistry, Kansas City, MO; Mary Galvin; Zukhra Niazimbetova; Anoop Menon; and Subramanian Vaidyanathan, Materials Science & Eng., University of Delaware, Newark, DE.

Since the first report of polymer light emitting diodes (LED) in 1990, the search for new polymers with stable and efficient electroluminescence properties has increased. Particular interest has been directed to the synthesis of polymers with improved electron transport and for polymers emitting blue light. We will report on several novel polymers. Some will contain oxadiazoles in the main chain, others combine ladder-type PPP and PPV segments in an orthogonal arrangement. Such an orthogonal structure was expected to decrease the quenching processes of excitons by preventing the aggregation of the PPV units, thus increasing the electroluminescence quantum efficiency and device stability. Since the conjugation length of the PPV segment is defined and limited, we expect this polymer to emit pure blue light.

### 4:30 PM BB10.7

STERIC AND HEAVY-ATOM EFFECTS ON THE LUMINESCENCE OF THIENYL-BASED POLYMERS. Cheng Yang, Steven Holdcroft, Simon Fraser University, Department of Chemistry, Burnaby, B.C., CANADA.

Poly(3-alkylthiophenes) (P3ATs) are attractive for electroluminescence devices due to their ease of preparation, their versatility, and tunable band gap. This is tempered by their solid state luminescent efficiency, which is very much lower than some other conjugated polymer systems. This is believed due to internal conversion of excitation through molecular aggregates and the existence of sulfur in the thienyl moiety which promotes intersystem crossing via spin-orbital coupling, i.e. the heavy atom effect. In order to test this assertion it is necessary to evaluate their solid state photoluminescence (PL) since EL efficiency is complicated by polymer/electrode, and other interfacial, processes. In addition, PL from polymer solutions is generally a poor indicator of the polymer's ability to yield high EL efficiency because conformation and aggregation of polymer chains in solution is very different to that in the solid state. In this presentation we report a systematic investigation of solid state PL properties of regiochemically controlled polymers of 2,5-di(2-(hexylthienyl)benzenes) (DHTBs), 1,4-di(2-(hexylthienyl)furans) (DHTFs), and 2,5-di(2-(3-(hexylthienyl)thiophene) (3,3'-DHTT). The luminescent efficiencies observed for some of these polymers are the highest reported to date for thienyl based materials. The variations in efficiency can be explained on the basis of steric and heavy atom effects.

### 4:45 PM BB10.8

EFFECTS OF PI-STACKING ON THE ABSORPTION AND EMISSION OF LIGHT BY CONJUGATED OLIGOMERS AND POLYMERS. M. David Curtis, Amy B. Koren, Jeff W. Kampf, The University of Michigan, Department of Chemistry, Ann Arbor, MI.

Solid state morphology, especially pi-stacking, plays an important role in transport of charge carriers or excitons in conjugated oligomers or polymers. In spite of the importance of this structural motif, very

little is known of the effects of pi-stacking on the UV-Vis absorption spectra or on the fluorescence excitation or emission. We have synthesized and crystallized a series of alkyl bithiazole oligomers and have determined the solid state structures by 3-D X-ray diffraction. By introducing groups, e.g., -OH, capable of H-bonding into the side chain architecture, we have been able to alter the structures and observe the effects of pi-stack interactions on the UV-Vis absorption and emission. Powder patterns show that the unit cells of partially crystalline polymers are essentially identical to those of oligomers with 6 rings. From these studies, we are able to assign spectral features that are the optical signature of pi-stacking. These features are observed in a wide variety of conjugated polymers, including P3ATs, PPV, etc., making our assignment of the optical signature of pi-stacking applicable to several classes of conjugated polymers.

SESSION BB11: POSTER SESSION  
Thursday Evening, December 2, 1999  
8:00 P.M.  
Exhibition Hall D (H)

#### BB11.1

OPTICAL PROPERTIES AND ELECTROLUMINESCENCE OF DIOXIDE SUBSTITUTED OLIGO THIOPHENES. G. Ghigli, R. Cingolani, Istituto Nazionale di Fisica della Materia, Dipartimento di Scienza dei Materiali, Univ di Lecce, Via Arnesano, Lecce, ITALY; G. Barbarella, L. Favaretto, ICOCEA, Area Ricerca CNR, Via Gobetti, Bologna, ITALY; F. Cacialli, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM.

We report investigations of the photoluminescence (PL) and electroluminescence (EL) of a family of thiophene oligomers for which we have devised a variety of substitutions aimed at enhancing the solid state efficiency and the colour tunability. We find that the absolute PL quantum efficiency in the solid state is up to 37% for both powders or spin-coated thin films of the compound. To the best of our knowledge this is the highest value measured in thiophene compounds. Furthermore, emission can be tuned so as to span from the blue-region of the visible spectrum to the near infrared. The material is also suitable for application in Organic Light-Emitting Diodes (OLEDs). EL efficiencies up to 1.2 cd/A and turn-on voltage down to 1.9 V are reported in the orange-red region.

#### BB11.2

LIGHT EMITTING DOUBLE LAYER VACUUM EVAPORATED DEVICES BASED ON TRIARYL-DIAMINE MATERIALS [HTM] AND 8-HYDROXYQUINOLINE COMPLEXES OF AL(III) AND ZN(II) [ETM]. Gabriele Giro, Massimo Cocchi, Piergiulio Di Marco, Valeria Fattori, CNR-FRAE, Bologna, ITALY; Pasquale Dembech, Gaia Fabbri, CNR-ICOCEA, Bologna, ITALY; Mauro Ghedini, Università della Calabria, Cosenza, ITALY.

We have constructed and characterized, vapor-deposited double-layer organic light emitting diodes (OLEDs) based on the combination of active materials belonging to the triaryl-diamine family as hole transport materials (HTM) with metal complexes of 8-hydroxyquinoline as electron transport and emitting materials (ETM). Two different HTM materials, all synthesized by us, were used: N,N'-naphthalen-1-yl-N,N'-diphenyl-benzidine (NPB) and N,N'-bis(biphenyl-4-yl)-N,N'-diphenyl-benzidine (NBDB). As ETM and emitting material Alq<sub>3</sub> complex and Znq<sub>2</sub> were used. The typical cell configuration was: ITO/HTM(60nm)/ETM(60nm)/Mg, Ag. A comparison of the electrical and light emitting features between devices constructed with NPB and NBDB and the widely used TPD was made with the aim of improving device efficiency and stability. This work has been partially supported by PF MSTAII of CNR-ITALY.

#### BB11.3

EXCIPLEX FORMATION IN LIGHT EMITTING MOLECULARLY DOPED POLYMER DIODES BASED ON POLYCARBONATE: TPD:PBD BLENDS. Gabriele Giro, Massimo Cocchi, Piergiulio Di Marco, Valeria Fattori, Istituto FRAE-CNR, Bologna, ITALY.

Observation of electroluminescence (EL) in single layer molecularly doped polymer (MDP) films is reported. The EL diodes constructed by spin coating techniques contain a triphenyl-diamine (TPD) and an oxadiazole unit (PBD) with the general configuration: ITO/PC(20w%):TPD(40w%):PBD(40w%)/Ca, Ag. The EL emission ranges in the green-yellow part of the spectrum and is red shifted respect to the photoluminescence of the single components of blends: i.e. PC:TPD and PC:PBD films. The EL emission, due to exciplex formation between TPD and PBD molecules, is similar to photoluminescence as studied by stationary and pulsed spectroscopy in function of the PBD concentration. This work has been partly supported by PF MSTAII of C.N.R. (Italy).

#### BB11.4

PHOTO-INDUCED PROPERTIES OF LIQUID CRYSTAL MOLECULES ON ALTERNATE CHARGED AZO DYES AND POLYELECTROLYTES FILMS INVESTIGATED USING ATTENUATED TOTAL REFLECTION METHOD. Akira Baba, Jun Ishikawa and Keizo Kato, Niigata University, Graduate School of Science and Technology, Niigata, JAPAN; Futao Kaneko and Kazunari Shinbo, Niigata University, Dept. of Electrical and Electronic Engineering, Niigata, JAPAN; Satoshi Kobayashi, Niigata University, Dept. of Material Science and Engineering, Niigata, JAPAN; Rigoberto C. Advincula, University of Alabama at Birmingham, Dept. of Chemistry, Birmingham, AL.

Photo-induced in-plane alignments of the nematic liquid crystal (LC) molecule, 5CB, have been investigated in the cell with alternate layer-by-layer films of polyelectrolyte and low-molecular weight dyes on the gold electrodes using the attenuated total reflection (ATR) measurement method. Direct red 80 (DR80), azo dye, was employed as an anion; poly(diallyldimethylammonium chloride) (PDADMAC) was used as a polycation. The surface plasmon polariton (SPP) was observed in the ATR curves of the LC cells. The properties were sensitively changed by re-orientations of the LC molecules by means of the irradiation of the linearly polarized visible light to the LC cell. In-plane alignments of LC molecules adjacent to the aligning layer were evaluated by fitting the theoretical ATR curves to the experimental ones. It was also estimated that the re-orientation of the LC molecules occurred within about 130 nm from the surface of the aligning layer on the prism by the irradiation of the polarized light. Furthermore, the ATR curves utilizing the GWEMs exhibited that in-plane switching properties of the LC molecules in the bulk region of the LC cell were different from the properties near the aligning layer.

#### BB11.5

OPTICAL SPECTROSCOPY OF NEUTRAL-IONIC PHASE TRANSITION IN CHARGE-TRANSFER COMPLEXES: TETRAHALO-*p*-BENZOQUINONES. Yoichi Okimoto, Sachio Horiuchi, Reiji Kumai, Joint Research Center for Atom Technology (JRCAT) Tsukuba, JAPAN; Eiji Saitoh, Department of Applied Physics, University of Tokyo, Tokyo, JAPAN; Yoshinori Tokura, JRCAT, Tsukuba, JAPAN, and Department of Applied Physics, University of Tokyo, Tokyo, JAPAN.

Physical properties of 1:1 mixed stack charge-transfer (CT) crystals have been extensively investigated in recent years. We measured temperature dependencies of infrared reflectivity spectra in typical charge-transfer complexes, tetrathiafulvalene(TTF)-*p*-chloranil (TTF-CA) and the isostructural analog, TTF-2-bromo-3,5,6-trichloro-*p*-benzoquinone (TTF-QBrC<sub>13</sub>). With decreasing temperature, the C=O stretching phonon spectrum in TTF-QBrC<sub>13</sub> which is closely related to the degree of CT shows anomalous broadening just above the neutral-ionic phase transition temperature, while that in TTF-CA is sharply and discontinuously varied from neutral spectrum ( $\approx 1630 \text{ cm}^{-1}$ ) to ionic one ( $\approx 1590 \text{ cm}^{-1}$ ). This result suggests anomalously rapid fluctuation of molecular valence in TTF-QBrC<sub>13</sub> between quasi-neutral and quasi-ionic state due to the quantum motion of neutral-ionic domain wall (NIDW). We also present far-infrared reflectivity spectra in TTF-CA and TTF-QBrC<sub>13</sub> and discuss an energy scale of the motion of NIDW. This work was partly supported by New Energy and Industrial Technology Development Organization (NEDO).

#### BB11.6

ENHANCED STABILITY USING DOUBLE INSULATOR LAYERS IN ORGANIC LIGHT EMITTING DEVICES. Lee-Mi Do, Heuk Park, Hye-Yong Chu, Do-Hoon Hwang, Jeong-Ik Lee, Seong-Hyun Kim, and Taehyung Zyung, Telecommunications Basic Research Laboratory, ETRI, Taejeon, KOREA.

The stability of organic light emitting devices (OLEDs) which had double insulator layers between the emissive layer and the electrodes was studied. We used N, N'-diphenyl-N, N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4, 4'-diamine (TPD), tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>), lithium fluoride (LiF) as a hole transport layer (HTL), an emitter layer (EML), and an insulator layer, respectively. We investigated the enhanced stability of OLEDs having the insulator layers by studying OLEDs with various structures. These included the devices with the structure of ITO/TPD/Alq<sub>3</sub>/LiF/Al, ITO/LiF/TPD/Alq<sub>3</sub>/Al, ITO/LiF/TPD/Alq<sub>3</sub>/LiF/Al, ITO/TPD/Alq<sub>3</sub>/Al. The half decay times from initial luminance and luminance efficiency were varied depending on the device structures. We found that the double insulator layer system was effective for a longer lifetime. It may be expected that the role of insulator layer between anode and HTL is impeding the hole injection into HTL that leads to the increase of balanced electron and hole injection and prevents the excess hole current. Stability and degradation progress of multiple structure devices will be discussed in detail.

### **BB11.7**

THE THERMAL STABILITY STUDIES OF ORGANIC THIN FILMS IN LIGHT-EMITTING DEVICES BY PHOTOELECTRON SPECTROSCOPY. L.S.Liao, L.F.Cheng, C.S.Lee, S.T. Lee, Center Of Super-Diamond and Advanced Films (COSDAF) and Dept of Physics & Materials Science, City University of Hong Kong, Kowloon, Hong Kong, CHINA.

Alq and NPB are very important materials for application in organic light-emitting devices (OLEDs). Their thermal stability were investigated in situ by x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). A 6-nm-thick Alq film and a 4-nm-thick NPB film were separately deposited on different regions of a Si substrate in an ultra high vacuum chamber with a base pressure of  $1.0 \times 10^{-9}$  mbar. The as-prepared sample was then thermally annealed at 60, 90, 120, 150, 220, and 400 °C for 5 min, respectively. Each annealing step was followed by XPS and UPS measurements. The XPS spectra indicated that thicknesses of Alq and NPB films were reduced significantly after annealing at 90 and 120 °C, respectively. This means that the two materials have substantial vapor pressure at relatively low temperatures. Their N1s core levels also shift towards the lower binding energy side, which suggests that chemical reactions have taken place during the thermal treatment. The UPS spectra indicated that the electron structures of Alq and NPB were totally changed after their thermal decomposition. The HOMO of Alq shifts towards  $E_F$  by more than 1 eV and that of NPB by about 0.5 eV. The above results suggest that thermally induced volatile gas can be responsible for the detachment of metal electrode in OLEDs and the upward shifting of HOMO may be responsible for the increase of the unbalance of injected carriers in OLEDs. Moreover, Alq was observed to be less stable comparing to NPB due to its lower thermal decomposition temperature.

### **BB11.8**

INVESTIGATION OF INDIUM TIN OXIDE PREPARED BY RF MAGNETRON SPUTTERING WITH HYDROGEN-ARGON MIXTURE FOR OLED APPLICATIONS. Keran Zhang, C.H.A.Huan, A.T.S.We, Dept of Physics, National Univ of Singapore, SINGAPORE; Furong Zhu, Ewald Guenther, Chua Soo Jin, Institute of Material Research & Engineering, SINGAPORE.

The chemical composition and work function of different indium tin oxide (ITO) films prepared using RF magnetron sputtering method at different hydrogen partial pressures were characterized by ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). The surface morphology and optoelectronic properties of the films were also investigated. The variation of work function and In/Sn ratio between different ITO samples was very small. The use of hydrogen in the film deposition was shown to reduce the surface roughness and the compressive stress of the films. ITO with less compressive stress and smoother surface showed better device performance when it was used as anode for OLED.

### **BB11.9**

HIGHLY EFFICIENT AND STABLE CHROMOPHORES FOR ELECTRO-OPTIC APPLICATIONS. Chengzhi Cai, Ilias Liakatas, Man-Shing Wong, Martin Boesch, Christian Bosshard, Peter Guenter, Swiss Inst of Tech (ETH), Nonlinear Optics Lab, Inst of Quantum Electronics, Zurich, SWITZERLAND.

We have developed a series of phenylbithiophene stilbene chromophores substituted with an amino donor and a tricyanovinyl or 2-phenyl-tetracyanobutadienyl acceptor. A concise synthesis of these chromophores will be presented. Second-order polarizabilities as high as  $14,000 \times 10^{-30}$  esu were determined for the chromophores by electric field induced second harmonic generation measurements at 1907 nm. The values are among the highest of stable chromophores reported so far. In addition, the chromophores have a high thermal stability with decomposition temperatures ranging from 240°C to 340°C. Moreover, in thin films of polymethylmethacrylate host, they showed a higher photo-stability than the standard Disperse Red-1. These results demonstrated that both very high nonlinearities and excellent stability can be achieved at the same molecule by proper molecular design. Synthesis of high Tg polymers incorporating these chromophores in the side-chain for electro-optic applications is under way.

### **BB11.10**

OPTICAL ABSORPTION AND PHOTOLUMINESCENCE OF (ORGANIC POLYSILANE)-(INORGANIC MATRIX) HYBRID THIN FILMS. Shinya Mimura, Hiroyoshi Naito, Osaka Prefecture 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 high photoluminescence quantum efficiency and high hole drift mobility. These properties are associated with  $\sigma$  conjugation along the Si backbone. In this paper, we study the optical properties of the polysilane hybrid thin films—organic polysilanes embedded in an inorganic glass matrix—to introduce new optical properties. We expect that these hybrid materials reduce the interchain interaction of  $\sigma$  conjugation and improve the durability of organic polysilanes as optoelectronic devices. The polysilane hybrid materials were prepared from trimethoxysilylpropylmethacrylate-methylphenylsilane block copolymers with a sol-gel method using tetraethoxysilane (TEOS) as an inorganic matrix. The block copolymers having polysilane segments have been synthesized by photopolymerization of trialkoxysilylpropylmethacrylate with polymethylphenylsilane (PMPS) as a macrophotoinitiator. We used here 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 measurement, it is found that the optical absorption spectra of the polysilane hybrid thin films are essentially the same as those of PMPS except for the decrease in the absorption coefficient of the one-dimensional exciton peak. In addition, the one-dimensional exciton absorption peak in the polysilane hybrid thin films is shifted by  $\sim 100$  meV to the higher photon energy side with respect to those of PMPS. The photoluminescence peak of the polysilane hybrid thin films under 3.756 eV excitation are also blue shifted by  $\sim 100$  meV. We conclude from these results that the peak shifts are due to the increase in the interchain separation.

### **BB11.11**

THE AFFECT OF CARRIER CONCENTRATION OF ITO FILMS ON THE PERFORMANCE OF ORGANIC LIGHT EMITTING DEVICES. Furong Zhu, Ewald Guenther, Chua Soo Jin, Institute of Materials Research & Engineering, SINGAPORE; Keran Zhang, C.H.A.Huan, A.T.S.We, Dept of Physics, National Univ of Singapore, SINGAPORE.

The thin films of ITO for OLED applications were made from an oxidized target with  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$  in a weight proportion of 9:1 using the RF magnetron sputtering method. The introduction of hydrogen in the sputtering gas mixture was shown to increase the number of charged carriers in the films. The OLED performance indicates that ITO film with high carrier concentration has direct implications for improving OLED performance and durability. The maximum luminance of  $4.36 \times 10^4$  cd/m<sup>2</sup> and the efficiency of 4.14 cd/A were achieved for the devices operated at 15 V. From the devices demonstrated in this work, an enhanced hole injection current in ITO/HTL/EL/Ca/Ag diode suggests that a lower energy barrier for hole injection might be existed when an ITO with higher carrier concentration was used as anode. It is reported that the surface band bending of ITO decreases with the increase of the carrier concentration in ITO film. The enhanced hole current in OLED might be due to the less surface band bending when ITO with higher carrier concentration was used for anode in OLED. The less surface band bending lowers the effective energy barrier seen by the holes at ITO/HTL interface. The enhanced hole-injection also helps to achieve better two carrier current balance for the light emission in OLED, therefore a better device performance and durability are achieved.

### **BB11.12**

A NEW ALTERNATIVE FOR THE LOW-WORKFUNCTION ELECTRODE IN ORGANIC DEVICES. Norbert Koch, Günther Leising, TU-Graz, Inst. f. Festkörperphysik, Graz, AUSTRIA; Aparna Rajagopal, Jacques Ghijsen, Jean-Jacques Pireaux, Univ Namur, L.I.S.E., Namur, BELGIUM; Robert L. Johnson, Univ Hamburg, II. Inst. f. Experimentalphysik, Hamburg, GERMANY.

The application of electroactive organic materials in devices (light emitting diodes, photovoltaic cells) often requires electrodes with a low workfunction. Commonly, aluminum or alkaline earth metals are used, which usually exhibit strong interaction with the organic material, such as the formation of new covalent bonds or doping. This results in a strong modification of the electronic structure of the organic/metal interface, and in most cases does not yield the energy level alignment expected for the unreacted interface. As an alternative to the above-mentioned metals we propose the use of samarium, with a workfunction of 2.7 eV, for the following reason: we have studied the interface formation between Sm and p-sexiphenyl (6P, which exhibits intense blue electroluminescence), with ultraviolet photoelectron spectroscopy. Sm was deposited stepwise onto thin films of 6P in ultrahigh vacuum, and the photoelectron spectra were recorded after each step. We did not find any indication for a strong interaction between the two materials. Metallic Sm is formed instantaneously and the valence electronic structure of 6P remains unchanged upon the metal deposition. However, we find a large interfacial dipole, evidenced by a vacuum level shift of 1 eV. The otherwise weak interaction at

this interface allows one to determine the energy level alignment between a metal and an organic material for the first time in a direct manner from the photoelectron spectra, without the need for making any assumptions on the workfunction or ionization potential.

#### **BB11.13**

**EPITAXIAL THIN FILM STRUCTURES OF ELECTROLUMINESCENT MATERIALS.** Norbert Koch, Günther Leising, TU-Graz, Inst. f. Festkörperphysik, Graz, AUSTRIA; Yoshinobu Hosoi, Hisao Ishii, Nagoya Univ, Dept of Chemistry, Nagoya, JAPAN; Kazuhiko Seki, Nagoya Univ, Research Center f. Materials Science, Nagoya, JAPAN.

Despite the fast-paced new developments and improvements of applications incorporating conjugated organic materials, rather little effort is made to obtain well-defined structures and thin films of these in order to exploit the highly anisotropic properties (e.g. conductivity, polarized light emission) of most conjugated organic materials. It has been shown that oligomers, which can easily be evaporated under ultrahigh vacuum conditions, exhibit heteroepitaxial growth on various substrates. Depending on the nature of the interaction of the organic molecules with the substrate different orientations can be obtained, as well as by simply changing the conditions of evaporation. Therefore, by going from amorphous or polycrystalline structures to highly textured or single crystalline ones new insights into the physical properties of the materials can be expected, and also new applications. We studied the formation of well-defined films of the electroluminescent oligomers *p*-sexiphenyl and *p*-octaphenyl on various metal and semiconductor surfaces and determined the orientation of the molecules by means of low energy electron diffraction (LEED), infrared reflection absorption spectroscopy (IR-RAS) and atomic force microscopy (AFM). Depending on the substrate material we found that the molecules are oriented either parallel or perpendicular to the substrate surface. In addition to that, highly oriented 6P films were doped with alkali metals, and the change in the molecular orientation was investigated with LEED and IR-RAS.

#### **BB11.14**

**INFLUENCE OF HEXADECYL GROUPS IN 4H POSITION ON THE STRUCTURE AND TRANSPORT PROPERTIES OF POLY(4H-CYCLOPENTA[2,1-b:3,4-b']DITHIOPHENE).**

Nadia Camaioni, Giuseppe Casalbore-Miceli, Mario Cristani, Alessandro Geri, Giancarlo Beggiato, Istituto CNR-FRAE, Bologna, ITALY.

The effect of hexadecyl groups in 4h position of poly(4h-cyclopenta [2,2-b:3,4-b']dithiophene) was investigated. It was demonstrated that the steric influence of the alkyl-chains controls the structure and therefore the transport properties of the polymers. The cyclic voltammetry, the optical spectrum and the X-ray diffraction pattern, carried out on electrosynthesised polymer films, pointed out the more regular structure of the disubstituted polymer and the higher compactness of the non-substituted one. These findings were found to be in accord with the photoelectric properties of the Schottky junctions between the three different polymers and aluminium. The junctions were tested both in photovoltaic and photoconductive mode. Better performances were achieved in the case of the system based on the non-substituted polymer. A higher inter-chain carrier mobility for the latter material, due to its more compactness, was hypothesised.

#### **BB11.15**

**SIMULATION OF CARRIER AND EXCITON BEHAVIORS AND EMISSION IN ORGANIC LIGHT-EMITTING-DIODE USING DISCONTINUOUS-MEDIUM CONDUCTION MODEL.**

Kaname Imaizumi, Kazue Kaneko, Tatsuo Mori and Teruyoshi Mizutani, Dept of Electrical Engineering, Nagoya University, Nagoya, JAPAN.

We propose a conduction model in a discontinuous medium (i.e., carrier hopping model) in order to discuss the behaviors of carriers and excitons and the spatial emission distribution in the emitting layer of organic light-emitting diode (OLED) such as the bilayer OLED (TPD/Alq3). In most previously reported models, the emission layer was regarded as the continuous medium. The carrier hopping model represents for the actual charge transfer between the adjacent molecules more clearly than the reported models. Therefore, we assumed that each emitting molecule corresponds to a hopping site. For example, the 50 nm-thickness emission layer corresponds to a series of about 50 Alq3 molecules when an Alq3 molecule is approximated to be 1 nm of the diameter of a sphere. In this model, it is also assumed that carriers and excitons move by a bimolecular hopping process, i.e., an emitting molecule can accept only an electron and a hole. Electrons and holes are assumed to be injected from a metal cathode by the Schottky emission and from the hole transport layer by the thermally emission, respectively. An electron and a hole on a molecule can form an exciton. The decay of an exciton is regarded as a photon emission. The emission rate is the

sum of exciton decay in an over-all emission layer. Dissociation of exciton is not taken into account. We calculated the distributions of the carrier and the exciton, spatial emission distribution, and the time characteristics in the current and the emission. The calculated values of the current-voltage-emission intensity characteristics are compared with the experimental values of those for the OLED of ITO/TPD/Alq3/metal.

#### **BB11.16**

**PHOTO-INDUCED SPIN TRANSITION.** Osamu Sato, Shinya Hayami, Zhongze Gu, Knagawa Academy of Science and Technology, Kanagawa, JAPAN; Akira Fujishima, Dept of Applied Chemistry, The University of Tokyo, Tokyo, JAPAN.

One of the main challenges of molecular material science is the design of compounds whose properties can be controlled by light illumination. We have been recently succeeded in developing photo-chemically tunable spin transition compounds, magnetic materials and colloid crystals. Here we describe a novel photo-chemically tunable spin transition compound. The tunable spin-transition material is a complex [FeII(L)CN]2, where L represents a macrocyclic Schiff-base ligand. This compound exhibits thermally-induced spin-transition at around 150 K. The process can be expressed by FeII(t2g4eg2) → FeII(t2g6eg0). When this compound is illuminated at 5 K, with the visible light guided via an optical fiber into the SQUID magnetometer, an increase of the magnetization value could be observed. The change persisted for periods of several days at 5 K. When the temperature of the sample was raised to 150 K, the magnetic properties quickly relaxed to almost the initial state. Mossbauer spectra shows that the low-spin to high-spin transition, FeII(t2g6eg0) → FeII(t2g4eg2), was induced by light. Because this compound has CN ligands, it can be used as a building block for developing a novel molecular photo-magnet.

#### **BB11.17**

**SOLUBLE AND HIGHLY LUMINESCENT OLIGOMERIC QUINOLINE METAL CHELATES.** M.-S. Jang, K.A. Higginson, M. Mathai, F. Papadimitrakopoulos, Department of Chemistry, Polymer Science Program, Nanomaterials Optoelectronics Lab., Institute of Materials Science, University of Connecticut, Storrs, CT.

Since the initial report of efficient organic light-emitting devices (OLEDs) from Tang and Van Slyke, based on aluminum tris(8-hydroxyquinoline) (Alq3) chelates, the interest to produce polymeric metal chelates, soluble to common organic solvents, has been intense. Our group has already reported the self-assembly growth method of polymeric bisquinoline metal-chelates which are formed from a layer-by-layer process. This approach has a strong potential to produce insoluble and intractable structures, with controllable supramolecular architecture, suitable for semiconducting applications. However, the linear poly(Zn-bisquinoline) structure results in high-packing density assemblies with reduced luminescence efficiency. Changing the chelation center to aluminum results in highly luminescent starburst structures that are processable from common organic solvents. Single layer, efficient EL structures illustrate the importance of this development, which will be described for the first time in this paper.

#### **BB11.18**

**NONLINEAR OPTICAL LAYER-BY-LAYER FILMS OF A METHACRYLIC COPOLYMER.** Paulo Antonio Ribeiro, Maria Raposo, Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Departamento de Física, Monte Caparica, PORTUGAL; David S. dos Santos Jr., Débora Tereza Balogh, José Alberto Giacometti, Osvaldo N. Oliveira Jr., Universidade de Sao Paulo, Instituto de Física de Sao Carlos, Sao Carlos, SP, BRAZIL.

Layer-by-layer films were prepared from a methacrylic copolymer and the cationic polyelectrolyte poly(allylamine hydrochloride) adsorbed onto glass substrates with a conducting layer of indium tin oxide. The methacrylic copolymer was synthesized by the reaction between methacrylic acid and a methacrylic monomer functionalized with the azo chromophore 4-[N-ethyl-N-(2-hydroxyethyl)]-amino-2-chloro-4-nitroazobenzene (Disperse Red 13). This copolymer is soluble in sodium bicarbonate aqueous solutions and is anionic under these conditions. The linear buildup of these layer-by-layer films with the number of layers was monitored by both UV-vis, visible and infrared spectroscopy. Orientational order was introduced by corona poling at elevated temperatures and the electrooptical properties were measured in a MacZehnder interferometer. Although the film preparation parameters and the poling process are not yet completely optimized, these films displayed an electrooptical coefficient  $r_{13}$  of 3 pm/V. A systematic study will be presented of the influence of adsorption conditions such as time of immersion and concentration of the copolymer solution on the nonlinear optical properties and their relaxation.

**BB11.19**

CHARACTERIZATION OF ZINC-BISQUINOLINE SELF-ASSEMBLED OLEDs. K. Ray, J. Mwaura, M.-S. Jang, E. Shin, C. Chen, M. Mathai, F. Papadimitrakopoulos, Department of Chemistry, Polymer Science Program, Nanomaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT.

The self-assembly of metallorganic chelates on different substrates is an unique approach to form multilayered assemblies. Self-assembled films of diethyl zinc and 8,8'-dihydroxy -5,5'-bisquinoline (bisquinoline) shows a strong potential to produce insoluble and intractable structures, with controllable supramolecular architecture, suitable for semiconducting applications. In this paper we discuss the use of zinc chloride to replace the pyrophoric diethylzinc, which is extremely moisture sensitive and results in certain incorporation of ZnO impurities in these assemblies. UV-Vis absorption spectroscopy, spectroscopic ellipsometry and photoluminescence microscopy suggest also a uniform increase of poly(zinc-bisquinoline) as a function of dip-cycles, with the use of ZnCl<sub>2</sub>. The growth process in these films has also been monitored by quartz crystal microbalance along with the change in viscoelastic properties, obtained by impedance spectroscopy. A comparison in electroluminescence performance will be also presented.

**BB11.20**

A MULTILAYER CATHODE FOR ORGANIC LIGHT-EMITTING DIODES USING AN ORGANOLANTHANIDE PHOSPHOR. Olivier Renault, Oleg V. Salata, Peter J. Dobson University of Oxford, Dept of Engineering Science, Oxford, UNITED KINGDOM; Mark Etchells, Victor Christou, University of Oxford, Dept of Inorganic Chemistry, Oxford, UNITED KINGDOM.

A multilayer cathode was developed to improve the contrast of organic light-emitting diodes (OLED) using an organolanthanide complex of terbium as phosphor. This was done by inserting a thin underlayer of conductive carbon before depositing the top metal contact. This provides a reduction of about 50% of the reflectivity of the cathode in the visible, suitable for contrast enhancement. The performances of triple-layer OLEDs with this new cathode and a PTT-derivative as a phosphor will be shown and some aspects of charge injection will be assessed.

**BB11.21**

ELECTRON SPIN RESONANCE OF 1,3-BIS(DICYANOMETHYLIDENE)-INDANE BASED INTRAMOLECULAR DONOR-ACCEPTOR CHROMOPHORES. David Jones, Sam Sun, Rakhim Rakhimov, Center for Materials Research, Norfolk State University, Norfolk, VA.

Organic donor-acceptor chromophores have potential applications as nonlinear optical materials. Amino-phenylenethienylidene (APT) donor-bridge systems coupled with strong electron acceptor such as 1,3-bis(dicyanomethylidene)indane (BDMI) have been demonstrated to exhibit large second order optical linearity as well as excellent chemical stability [1]. Intramolecular donor-acceptor interaction may provide either partial or complete electron transfer from the donor (D) to the acceptor (A) part of the molecule. Studies of the charge transfer bands in optical absorption spectra of chromophores in polymer thin films showed centric alignment of chromophores driven by London forces resulted in attenuation of macroscopic optical linearity [2]. The dipole arrangement in the material is an important factor affecting optical nonlinearity. Such an arrangement should strongly depend on whether or not the electron transfer in intramolecular DA system is partial or complete. Complete intramolecular electron transfer will result in the formation of radical ion pairs D(+)-A(-). Therefore electron spin resonance method can be applied to study the system. In this presentation we show that the state with complete electron transfer D(+)-A(-) does exist in this system. Stabilization of the complete electron transfer state is provided by the formation of antiferromagnetic clusters possessing a D(+)-A(-)-D(+)-A(-) structure. Antiferromagnetic resonance absorption in powder samples of APT-BDMI system is characterized by axial symmetry confirming a linear chain structure of the clusters. The current studies on new organic donor-acceptor chromophores are supported by the U.S. Department of Energy, Grant No. DE-FG01-94EW11493. References: [1]. Dalton L. R., et al. Chem. Mater. 7 (1995) 1060; [2]. Sun S., et al. Polymer Prepr. 38 (1997) 928.

**BB11.22**

HEXA-ALKOXYTRIPHENYLENES AS HOLE TRANSPORTING MATERIALS IN STABLE OLEDs USING AlQ<sub>3</sub> AS EMITTING LAYER. M. Emerich, S. Tasch, G. Leising, Technische Universitaet Graz, Inst. fuer Festkoerperphysik, Graz, AUSTRIA; R. Freudenmann, M. Hanack, Universitaet Tuebingen, Inst. fuer Organische Chemie II, Tuebingen, GERMANY; S. Shaheen, G. Jabbour, N. Peyghambarian, University of Arizona, Optical Sciences Center, Tucson, AZ.

With respect to the considerable increase of efficiency of organic electroluminescent (EL) devices by introducing novel hole transport layers (HTLs) between the anode and the emitting material, devices consisting of hexa-alkoxytriphenylene derivatives as hole transport materials and 8-hydroxyquinoline aluminium (AlQ<sub>3</sub>) as emitting layer with ITO as anode and magnesium as cathode are presented. EL-devices with variations of the HTL thickness were fabricated and characterized by I/V-measurements and EL-performance studies. Additionally devices with the same heterostructural setup but using triphenyldiamine (TPD) or a blend of TPD with hexa-alkoxy-triphenylene respectively as HTL were built for comparative purposes. Moreover X-ray diffraction studies of evaporated triphenylene films were performed leading to a better understanding of crystal structure, morphology and the alignment of the triphenylene molecules on the surface of the substrate. As a result stable long term device operation as well as high luminance green emission up to brightness values of more than 1000 cd/m<sup>2</sup> were obtained. One of us (M. Emerich) would like to gratefully acknowledge the financial support provided by the Stipendium fuer kurzfristige wissenschaftliche Arbeiten im Ausland.

**BB11.23**

BLUE ELECTROLUMINESCENCE FROM PHOSPHORESCENT BENZOXAZOLE DOPED OLEDs. Chihaya Adachi, Marc A. Baldo, Stephen R. Forrest, Department of Electrical Engineering, Princeton University, Princeton, NJ; Mark E. Thompson, Department of Chemistry, University of Southern California, Los Angeles, CA.

Recently OLEDs using phosphorescent molecules, green emitting Ir(ppy)<sub>3</sub>(1), and red emitting PtOEP(2), have opened a new prospect for the achievement of high quantum efficiency (QE) displays based on electrophosphorescence. In this study, we focused on the unique photoluminescent (PL) and electroluminescent (EL) properties of bis(2-(2-hydroxyphenyl)-benzoxazolone) metal complexes, M(BOX), as a potentially efficient blue phosphorescent emitter. We observed that the PL of Zn(BOX) derivative doped HTL films (1 ~10mol%) showed both intense fluorescence and phosphorescence in the blue region (~430nm) at room temperature. Time resolved PL spectra were composed of fast (~10ns) and slow (~0.5ms) decay components. Using the doped films as an emitter layer, we fabricated OLED devices; HTL/ Zn(BOX) doped HTL(emitter-layer)/ HBL(BCP)/ ETL(Alq)/ MgAg, which showed 1.7mW/cm<sup>2</sup> (QE~0.6%) at J=100mA/cm<sup>2</sup> and V=10.3V. As in PL, the EL spectrum exhibited a mixture of both fast (fluorescent) and slow (phosphorescent) components. The EL spectrum also coincided with the PL of Zn(BOX) and the CIE chromaticity color coordinates are (X=0.16, Y=0.059). Based on electrical and optical excitation of M(BOX) layers, we will discuss the detail EL and PL mechanism, in particular, the branching ratio of singlet and triplet excitons in the EL process. To our knowledge, this is the first report of blue electrophosphorescence. The prospect for efficient blue emission using various metals and ligand structures will also be discussed. (1) M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson and S.R. Forrest, Appl. Phys. Lett., 75, (5 July, 1999). (2) M.A. Baldo, D.F.O'Brien, Y.You, A. Shoustikov, S. Sibley, M.E. Thompson and S.R. Forrest, Nature, 395, 151 (1998).

**BB11.24**

PRESSURE AND DEFECTS INDUCED METALLIZATION IN ORGANIC MOLECULAR CRYSTALS. Maija M. Kuklja, A. Barry Kunz, Electrical Engineering Department, Michigan Technological University, Houghton, MI.

Energetic materials belong to a wide class of the technologically important organic molecular crystals. Most of them are composed of poly-atomic molecules having a complicated structure. There have been many theoretical and experimental advances in the understanding the macroscopic properties of these solids while microscale processes are still little understood. This is partly due to the complexity of the structure of energetics and partly due to the large velocity of detonation fronts (7km/s). Modern experimental techniques do not have enough time resolution to observe processes in the detonation fronts. Therefore, theoretical simulations are highly desirable. One of the most prominent mechanisms of detonation initiation suggested by J.Gilman is based on the idea of the optical gap closure during the shock propagating throughout the crystal, which undergo an electronic phase transition. As a result, the materials lose their transparency under high compression. In the presert study, the defect- and pressure-induced metallization in a solid C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>O<sub>6</sub> (RDX) were investigated by means of a first-principle, quantum-chemical method. The Hartree-Fock calculation scheme (CRYSTAL95) combined with the many-body perturbation-theory (LOPAS) permits us to simulate the atomic and electronic structure of a series of lattice defects such as a molecular vacancy, a vacancy dimer, an edge dislocation, a nano-crack, and a (210) surface in both equilibrium and highly compressed RDX. As a result, we can predict how the presence of defects in the crystal will affect the critical pressure for insulator-metal electronic phase transition. The obtained results compared with the relevant experimental data and are of great

practical importance in particular, our conclusions provide useful insights for the predictions for sensitivity of explosive crystals to detonation initiation.

#### **BB11.25**

##### **EFFICIENT ORGANIC HETEROJUNCTION PHOTOVOLTAIC CELLS OPERATING UNDER MULTIPLE SUN ILLUMINATION.**

P. Peumans, V. Bulovic and S.R. Forrest, Center for Photonic and Optoelectronic Materials, Department of Electrical Engineering, Princeton University, Princeton, NJ.

We demonstrate that a record power conversion efficiency of 3% can be achieved under intense simulated solar spectral illumination for vacuum deposited heterojunction thin film organic photovoltaic (PV) cells. Typical devices have a fill factor of 0.55 and an open circuit voltage of 0.45 V under 75mW/cm<sup>2</sup>, AM1.5 (corresponding to 1 sun) illumination. The cell structure improves on the Cu-phthalocyanine (CuPc)/3,4,9,10 - perylenetetracarboxylic bisimidazole (PTCBI) cell first reported by Tang [1] by inserting a large-bandgap, exciton-blocking bathocuproine (BCP) layer under the cathode, allowing for the reduction of the organic layer thicknesses to <10 nm. This device structure solves a major problem of organic PV cells by eliminating light absorption in inactive and resistive organic thin film regions. By recycling the non-absorbed photons, high incident-photon-to-current efficiencies are obtained. In addition, the photocurrent spectrum is well matched to the solar spectrum, leading to high power conversion efficiencies. Monochromatic quantum efficiencies are >20% over the wavelength range of 350 to 750 nm, with peak efficiencies exceeding 25%. The small resistance of thin organic layers facilitates charge extraction, such that these cells can be operated at light intensities of more than 10 suns (~8 kW/m<sup>2</sup>) without a significant loss in conversion efficiency, making these the first organic thin film solar cells compatible with solar concentrators. In contrast to previous studies, we observe a steady improvement in the power efficiency with increasing light intensity, similar to conventional inorganic PV cells. UPS measurements [2] corroborate a model of efficient exciton dissociation at the organic/organic interface, where exciton diffusion is followed by fast electron transfer from a donor (CuPc) to an acceptor (PTCBI) molecule. We model the charge generation and extraction processes taking into account microcavity effects, exciton diffusion and carrier transport. [1] C.W. Tang, *Appl. Phys. Lett.* 48, 183 (1986). [2] I. Hill and A. Kahn, to be published.

#### **BB11.26**

**MODIFIED BIS-QUINOLATE METAL CHELATES FOR ELECTROLUMINESCENCE APPLICATIONS.** Floerfida Endrino, Gregory Schmetz, Nancy Washton, Asanga Padmaperuma, Jeff Marshall and Linda S. Sapochak, Dept. of Chemistry, University of Nevada, Las Vegas, NV.

Intensive investigations of aluminum tris-(8-hydroxyquinoline) (Alq<sub>3</sub>) and other metal tris-quinolate chelates have been reported, but fewer detailed systematic studies of bis-quinolate chelates are available. Zn(bis-quinolates) have been studied as emitter materials in OLEDs and exhibit characteristic yellow emission, and in some cases has been reported to exhibit higher luminance outputs compared to Alq<sub>3</sub>. We report the photoluminescence and electroluminescence properties of a series of Zn bis-chelates of substituted-8-hydroxyquinoline ligands and diazo-derivatives of 8-hydroxyquinoline. The resulting optical properties are strongly affected by both electronic and steric factors of the chelate structure.

#### **BB11.27**

**TUNABLE ELECTROLUMINESCENCE USING SELF-ASSEMBLED FILMS CONTAINING CdTe AND CdSe NANOCRYSTALS.** Mingyuan Gao, Bernd Richter, Constanze Lesser, Stefan Kirstein, Helmuth Moehwald, MPI for Colloids and Interfaces, Golm/Potsdam, GERMANY; Andrey L. Rogach, Horst Weller, Univ Hamburg, Inst of Physical Chemistry, Hamburg, GERMANY.

II-VI semiconductor nanocrystal materials exhibit unique properties which fulfill the requirements for the preparation of electroluminescence devices, because the fluorescence wavelength can be easily controlled by varying the nanocrystal size. Moreover, proper surface modification leads to a high fluorescence quantum yields ~ 50%. CdSe and CdTe nanocrystals were prepared in aqueous solution in the presence of different thiol molecules. These molecules stabilize the nanocrystal against uncontrolled growth and provide a negatively charged surface on the nanocrystals. This is necessary for the usage of layer-by-layer self-assembly method in the preparation of nanocrystal films. The CdSe nanocrystals emit a broad and red-shifted fluorescence with a quantum yield, ~1%, whereas, the fluorescence quantum yield of CdTe nanocrystals reaches 20% at room temperature. Using the layer-by-layer self-assembly method, structured nanocrystal films were prepared in combination with different types of polyelectrolytes such as, polydiallyldimethylammonium chloride (PDDA), polystyrenesulfonic acid sodium salt (PSS), polyallylamine hydrochloride (PAH) and precursor of

poly(p-phenylene vinylene) (PPV). Experimental results showed that the quantum yield of electroluminescence of (CdSe/PAH)<sup>n</sup> or (PPV)<sup>n</sup> with n = 20 was one order of magnitude lower than that from (CdTe/PDDA)<sup>n</sup> or (PAH)<sup>n</sup> with n = 20 and 40. This suggests that a high photoluminescence quantum yield results in a high electroluminescence efficiency. Different colors of electroluminescence from (CdTe/PDDA)<sup>n</sup> films were obtained and could be varied from green to red by employing differently sized CdTe nanocrystals. The electroluminescence is nearly identical to the photoluminescence of the corresponding CdTe nanocrystals in solutions. Due to the existence of surface trap states, CdSe nanocrystals presented weak fluorescence, as well as electroluminescence. However, a self-assembled layer of (CdSe/PAH)<sup>n</sup> stabilize the electroluminescence of a (PPV/PSS)<sup>n</sup> layer which was stacked on top of the particle layer. Detail analysis indicates that the stabilizing effect takes place due to the consumption of oxygen in the device by the CdSe nanocrystals.

#### **BB11.28**

##### **ELECTRO-ABSORPTION STUDIES ON THE INFLUENCE OF POLY(3,4-ETHYLENE DIOXYTHIOPHENE) (PEDOT) ON THE BUILT-IN FIELD IN POLYMER LIGHT-EMITTING DIODES.**

T.M. Brown, J.S. Kim, R.H. Friend, F. Cacialli, Cavendish Laboratory, University of Cambridge, UNITED KINGDOM; R. Daik, W.J. Feast, IRC Polymer Science And Technology, Durham University, UNITED KINGDOM.

Electro-absorption spectroscopy is a powerful non-invasive technique for probing electric fields in semiconductor structures. The built-in voltage we measure for the poly(4-4'-diphenylene diphenylvinylene) (PDPV)-based ITO/PDPV/Ca structure corresponds to the difference between the work functions of the electrodes. We find that the inclusion of a high-work-function-film of poly(3,4-ethylene dioxythiophene) (PEDOT), between the ITO and the emissive layer in the ITO/PEDOT/PDPV/Ca structure, brings about a 0.5 V increase in built-in voltage. The consequent reduction of the hole barrier height at the anode interface is responsible for the improvement in the device performance which has been observed in diodes with ITO/PEDOT anodes.

#### **BB11.29**

##### **THICKNESS MEASUREMENTS OF ULTRA-THIN POLYMERIC FILMS USING ATOMIC FORCE MICROSCOPY.**

Maria Raposo, Rui F. M. Lobo, Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Departamento de Física, Monte Caparica, PORTUGAL; Marcelo A. Pereira-da-Silva, Roberto M. Faria, Osvaldo N. Oliveira Jr., Universidade de Sao Paulo, Instituto de Física de Sao Carlos, Sao Carlos, BRAZIL.

A method for measuring the thickness of ultra-thin polymeric films is described, which employs an atomic force microscope (AFM) tip to create a furrow in the film whose topographic profile is subsequently obtained by the AFM in the tapping mode. This method was successfully applied to layer-by-layer films of poly(o-methoxyaniline) (POMA) alternated with the polyelectrolyte poly(ethenesulfonic acid) (PVS) onto several substrates, provided that the substrates were stiffer than the polymeric sample. The thickness measured increased linearly with the number of deposited layers and the experimental points coincided with the straight line extrapolated from the results obtained for much thicker films measured with profilometry, with a thickness per bilayer of approximately 35 Å. In addition, the thickness obtained with the new method is consistent with ellipsometric measurements, where the change in delta angle upon polymer adsorption is taken as proportional to the thickness of the deposited layer.

#### **BB11.30**

**NEW PYRIDINE-CONTAINING POLYMERS FOR COLOR VARIABLE LIGHT-EMITTING DEVICES.** D.K. Wang, Y.Z. Wang, R.G. Sun, Q.B. Zheng, D. Tigelaar, M.S. Platz and A.J. Epstein, Department of Physics and Department of Chemistry, The Ohio State University, Columbus, OH.

Pyridine-based conjugated polymers are excellent candidates for light-emitting devices due to their high electron affinity, resistance to oxidation and better electron transporting properties relative to phenylene-based polymers [1]. They allow the use of relatively stable metals such as Al as efficient electron injecting contacts. Previously we reported the color variable bipolar/ac light emitting devices based on these polymers, which can operate under either polarity of driving voltage with different colors of light being emitted: red under forward and green under reverse bias [2]. It is very desirable to obtain blue, green, and red colors in a single device, for which the polymers with color changing from blue to green are also needed. New polymer structures were designed to control colors of emission through engineering of the twisting angle of the  $\pi$  electron planes and the localization of  $\pi$  electrons in the conjugated polymer backbone. The synthesized polymers have a substantially blue shifted PL maximum

(>60 nm) and show improved PL efficiency as compared to the earlier reported poly(pyridine vinylene phenylene vinylene) (PPyVPV) derivatives. The EL studies demonstrate that the forward and reverse bias emission differ by ~70 nm, both being blue shifted by ~60nm as compared to the corresponding PPyVPV based devices. This work is supported in part by the Office of Naval Research [1] Y.Z. Wang and A.J. Epstein, Accounts of Chemical Research, 32 (3), 217 (1999) [2] Y.Z. Wang, D.D. Gebler, D.K. Fu, T.M. Swager and A.J. Epstein, Appl. Phys. Lett., 70 (24), 3215 (1997)

#### **BB11.31**

PERFORMANCE OF HIGH TG HOLE TRANSPORT MATERIALS IN ORGANIC LIGHT EMITTING DEVICES. J. Lam\*, M. D'Iorio, A. Donat-Bouillud, T.C. Gorjanc\*, C. Py, Y. Tao, Institute for Microstructural Sciences, National Research Council, Ottawa, CANADA; \*also at University of Ottawa, Dept of Physics, Ottawa, CANADA; J. Lu, A.R. Hlil, Y. Sun, A.S. Hay, McGill University, Dept of Chemistry, Montreal, CANADA; J.-P. Dodelet, I. Bedja, INRS-Énergie et Matériaux, Varennes, CANADA.

Operational stability and performance of organic light emitting devices (OLEDs) are often improved by selection of materials with improved thermal stability. This is especially true in the case of conventional hole transport materials where the low glass temperature of triphenyl diamine (TPD) derivatives restricts the operational temperature of devices to below 80°C. Previous work has produced a hole transport material consisting of TPD with naphthyl substituents known as NPB [1]. The addition of the naphthyl moiety produces a rigid structure, hindering the rotational motion of the naphthyl group and leading in turn to a higher glass temperature. In this paper, we describe the performance of a new hole transport material consisting of TPD with naphthyl and methoxy substituents (MNTPD). The addition of the methoxy groups provides electron donors, lowering the oxidation potential and thus favoring hole transport while providing better solubility of the molecule for synthesis into a polymer. OLEDs prepared using MNTPD have a luminance of over 8000 cd/m<sup>2</sup> at 13 V, a marked improvement from similar structures using TPD or NPB hole transport layers. Near identical results were obtained when MNTPD was modified to form a monomer with two OH groups and further reacted to produce a polymer with a glass temperature of 223.8°C. The results of electronic and optical transport measurements as well as operational lifetimes for the vacuum sublimed and spin coated devices will be discussed. [1] S.A. Van Slyke, C.H. Chen, and C.W. Tang, APL 69, 2160-2162 (1996).

#### **BB11.32**

NOVEL FABRICATION OF ELECTROACTIVE SELF-ASSEMBLED FILMS. Jeffery W. Baur, Patrick T. Mather and Michael F. Durstock, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH.

The process of Electrostatic Self-Assembly (ESA) allows for the fabrication of nanostructured organic thin films using aqueous-based processing. This technique is based on the sequential adsorption of oppositely charged species and provides tremendous flexibility for the fabrication of multilayered electroactive thin films for organic based LEDs, photovoltaics, and electro-optic devices. In addition to the layering achieved normal to the adsorption surface, rapid patterning within the plane of the film is desired for the production of complex three-dimensional structures. Previously, micro-patterning via directed adsorption to chemically functionalized surface regions has been demonstrated (S.L. Clark, et al. Macromol. 30, 7237, 1997). Here we discuss a new and novel solution-less approach to patterning ESA films that uses an uncharged hydrogel host/stamp to deliver polyelectrolyte to the selected surface regions. Additionally, efforts to fabricate ESA films for polymer-based photovoltaics will be discussed.

#### **BB11.33**

UNDERSTANDING SPONTANEOUS ORGANIZATION OF SUPRAMOLECULAR MATERIALS INTO POLAR FILMS. Mehmet Sayar, Samuel I. Stupp, Northwestern University, Departments of Materials Science and Engineering and Chemistry, Evanston, IL.

Experimental evidence suggests that the thermodynamic equilibrium state of films of nanoaggregates formed by triblock rodcoil molecules favors a polar order, with an order parameter less than unity. One possible explanation for this behavior is a multidomain structure influenced by the presence of external effects such as substrate and air interfaces. In this study an Ising type model is used to test the validity of these arguments. In addition to the classical nearest neighbor potential, two long range potentials, a dipole-dipole interaction, and a surface-dipole interaction are added to the Hamiltonian of the system. This system with four thermodynamic variables, three force constants, and temperature exhibits a rich phase diagram which interestingly, includes an equilibrium state with partial polarization that agrees with the experimental data.

#### **BB11.34**

IMAGING SUBSTRATE MEDIATED STRUCTURAL ORGANIZATION OF ORGANIC MATERIALS BY SCANNING TUNNELING MICROSCOPY. Richard Czerw, Clemson University, Dept of Physics and Astronomy, Clemson, SC; Brendan McCarthy, Werner Blau, Trinity College, Polymer Research Unit, Dublin, IRELAND; David L. Carroll, Clemson University, Dept of Physics and Astronomy, Clemson, SC.

Substrate mediated structural organization of high molecular weight polymers of PPV has been studied using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Various forms of PPV have been observed to organize into hexagonal close packed structures with nano-scale periodicity when deposited on highly orientated pyrolytic graphite (HOPG). Tunneling spectroscopy shows a subtle variation in band gap associated with the periodicity. Spectroscopic features are strongly correlated with variations in apparent barrier height across these structures. These results will be discussed in terms of substrate-polymer contact interactions.

#### **BB11.35**

MULTILAYER FILMS AS A METHOD TO INDUCE SPECIFIC MOLECULAR ORIENTATION. David M. DeWitt, Paula T. Hammond, MIT, Dept of Chemical Engineering, Cambridge, MA.

Self-assembled multilayer films have been constructed using polyelectrolytes containing side chain non-linear optically active chromophores or liquid crystalline mesogens. By using external reflection-absorption and transmission FTIR in conjunction with polarized UV/Visible spectroscopy, the 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 guidelines for constructing optically active ordered polymer multilayer films. Measurements performed on films consisting of two commercially available azo polymers and different polycations show a different tilt angle depending on the polycation. In addition, two other non-linear optically active polymers have been synthesized that allow the varying of different structural parameters. The results of the study will be applied to patterned multilayer systems and device manufacture.

#### **BB11.36**

THE EFFECT OF MICRO-PATTERNING ON POLAR ORDER IN SELFASSEMBLING FILMS. Leiming Li, Brad A. Acker, University of Illinois at Urbana-Champaign, Departments of Materials Science and Engineering and Chemistry and Beckman Institute for Advanced Science and Technology, Urbana, IL; Samuel I. Stupp, Northwestern University, Departments of Materials Science and Engineering and Chemistry, Evanston, IL.

We have used a focused ion beam system to create patterns finer than 20 microns on hydrophilic substrates, and also micro-contact printing techniques to create larger patterns. Selfassembling molecules consisting of triblock structures and known to form supramolecular films were deposited on these patterns to cover the entire substrate. A Q-switched 1.064-micron infrared Nd:YAG laser was used for transmission second harmonic generation (SHG) measurements of the films over both the patterned and non-patterned parts of the substrate. The films on the patterned areas were found to have notably larger effective nonlinear susceptibilities compared with those on the non-patterned areas. We attribute the observed increase in second harmonic activity to spatial confinement effects imposed on the molecules by the patterns.

#### **BB11.37**

POLYMER WAVEGUIDES DOPED WITH RARE-EARTH DOPED ORGANIC CAGE COMPLEXES AND NANOCOMPOSITS. L.H. Slooff<sup>a</sup>, S.I. Klink<sup>b</sup>, G.A. Hebbink<sup>b</sup>, L. Grave<sup>b</sup>, F.C.J.M. van Veggel<sup>b</sup>, J.W. Hofstra<sup>c</sup>, A. van Blaaderen<sup>a,d</sup> and A. Polman<sup>a</sup>; <sup>a</sup>FOM Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS, <sup>b</sup>University of Twente, Enschede, THE NETHERLANDS, <sup>c</sup>Philips Research, Eindhoven, THE NETHERLANDS, <sup>d</sup>Debye Institute, Utrecht University, THE NETHERLANDS.

Rare-earth doped polymer waveguides can find applications in planar optical amplifiers operating at the telecommunication wavelengths of 1.3 μm (Nd<sup>3+</sup> and 1.5 μm (Er<sup>3+</sup>)). Unfortunately, the rare earths are insoluble in a polymer matrix, and therefore specially designed routes for the incorporation of these ions must be developed. In this paper we will present two alternative methods. First, using molecular engineering techniques, terphenyl-based organic cage complexes were synthesized, in which the rare earth ion is encapsulated. High concentrations of these complexes (10 vol. %) can

be embedded in a fluorinated polymer waveguide. A lissamine sensitizer was attached to some of the complexes, and serves to efficiently absorb the pump light (cross section  $>10^{-17}$  cm<sup>2</sup> around 500 nm), after which the excitation energy is transferred (at a rate  $>10^7$  s<sup>-1</sup>) to the rare earth by intramolecular energy transfer. Optical measurements on these waveguides will be presented. Second, an Er-doped-silica/polymer nanocomposit was explored. 300-nm diameter silica colloids were doped with Er by ion implantation. After annealing, efficient luminescence at 1.5  $\mu$ m, with a long luminescence lifetime (up to 8 ms) was observed. Relatively high Er concentrations (> 1 at.%) can be incorporated in these nanoparticles, without strong concentration quenching effects. These nanoparticles are then embedded in a polymer waveguide and their optical properties are studied.

#### **BB11.38**

**POLYMER CONTACT MODIFICATION LAYERS FOR ORGANIC LIGHT-EMITTING DIODES DOPED WITH OXIDIZED N,N,N',N'-TETRA-P-TOLYL-4,4'-BIPHENYLDIAMINE.** Bing Hsieh, Xerox Corporation, Wilson Ctr for Research & Tech, Webster, NY; Keith A. Higginson and Fotios Papadimitrakopoulos, Nanomaterials and Optoelectronics Laboratory, Nanomaterials and Optoelectronics Laboratory, Dept of Chemistry, Polymer Sci Program, Inst of Materials Sci, University of Connecticut, Storrs, CT.

The indium tin oxide (ITO) anodes for organic light-emitting diodes were modified with a hole transporting polycarbonate (PC-TPB-DEG) doped with the SbF<sub>6</sub> salt of N,N,N',N'-tetra-p-tolyl-4,4'-biphenyldiamine (TMTPD<sup>+</sup>)\* spin cast over the ITO surface. A thin hole transporting layer (NPB) was vacuum deposited on the polymer, followed by aluminum tris(8-hydroxyquinoline) (Alq<sub>3</sub>) as an emitting layer. A thin layer of cesium fluoride was also used to modify the aluminum cathodes. The polymer layer suppressed surface defects, and very reproducible devices were easily obtainable. The overall resistance of devices modified with the doped polymer was greatly improved over those using bare ITO anodes. The effects of thickness and dopant concentration on the relative external quantum efficiency and electrical characteristics were investigated. Devices with polymer films doped to 10% by weight exhibited turn-on voltages of about 2 V. \* Bing Hsieh, US Pat. #5,853,906, 1999.

#### **BB11.39**

**THE NATURE OF CHEMICAL IMPURITIES FORMED DURING DEGRADATION OF ALUMINUM(III) 8-HYDROXYQUINOLINE: IMPLICATIONS FOR ORGANIC LIGHT-EMITTING DIODES.** Keith A. Higginson, D. Laurence Thomsen III and Fotios Papadimitrakopoulos, Nanomaterials and Optoelectronics Laboratory, Dept of Chemistry, Polymer Sci Program, Inst of Materials Sci, University of Connecticut, Storrs, CT.

The chemical degradation of aluminum tris(8-hydroxyquinoline) (Alq<sub>3</sub>) films and powders was studied by a variety of techniques. The thermal decomposition of Alq<sub>3</sub>, observed chiefly through the evolution of the byproduct 8-hydroxyquinoline (Hq), was characterized with gas chromatography and rate data were measured in order to extrapolate its importance at device operating conditions. Electrochemical reduction of Alq<sub>3</sub> was also found to facilitate dissociation of the complex when bases or nucleophiles are present. Quenching products are obtained through the oxidation of the byproduct, Hq, especially through its anionic form, which is susceptible to oxidation at the 5-position. The decomposition products appear to be primarily quinone and hydroquinone forms of Hq, which form charge transfer complexes or polymers capable of quenching the luminescence of Alq<sub>3</sub>.

#### **BB11.40**

**A QUASI INTRINSIC SEMICONDUCTING STATE OF PHTHALOCYANINE FILMS FABRICATED UNDER ULTRAHIGH VACUUM CONDITIONS.** Hirokazu Tada, Masaki Takada, Hiroshi Touda, Kazumi Matsushige, Dept of Electronic Science and Engineering, Kyoto Univ, Kyoto, JAPAN.

The mechanism of carrier transport in organic semiconductors and carrier injection from metal electrodes becomes the most important subject to be elucidated for the construction of high performance organic thin film devices. The electric properties are modified easily by adsorbed gas molecules, which makes it difficult to obtain reliable experimental results. We evaluated the carrier mobility and carrier density of titanyl-phthalocyanine (TiOPc) films under ultrahigh vacuum (UHV) conditions to avoid the influence of gas adsorption. The field effect measurement revealed that TiOPc films exhibited an n-type semiconducting behavior in UHV as was reported previously by Guillaud et al. for LuPc<sub>2</sub> (Chem. Phys. Lett. 167, 503 (1990)). The electron mobility at room temperature was  $9 \times 10^{-6}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> with activation energy of 0.20 eV. The conductivity and carrier density were estimated to be  $9 \times 10^{-8}$  Scm<sup>-1</sup> and  $6 \times 10^{16}$  cm<sup>-3</sup>, respectively. When the film was exposed to oxygen, electron conduction disappeared immediately and the holes became the majority carrier.

The hole mobility was evaluated to be  $1 \times 10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The conduction type of the film was determined by the delicate balance of the residual gas molecules in UHV. At a certain condition, both p and n-type conduction were observed simultaneously. The donors were thought to be compensated by the same number of acceptors. The hole and electron mobility were  $1.8 \times 10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and  $2.2 \times 10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively. The carrier density, which could be regarded as the 'intrinsic' one, was estimated to be  $10^{13}$  cm<sup>-3</sup> using the conductivity of  $10^{-10}$  Scm<sup>-1</sup>. Energy diagram of the organic-metal junction will also be discussed on the basis of capacitance-voltage measurement in various gas atmospheres.

#### **BB11.41**

**ULTRAFAST SPECTROSCOPIC STUDIES OF CHARGE AND ENERGY TRANSFER IN CONJUGATED POLYMER FILMS AND SELF-ASSEMBLED SUPERLATTICES.** Su Xu, Hsing-Lin Wang, Victor Klimov, Brett Kraabel and Duncan McBranch, Los Alamos National Laboratory, Los Alamos, NM.

We present a comprehensive series of ultrafast spectroscopic studies (from 450 nm to 2700 nm over a wide range of pump densities) of the excitations in films of conjugated polymers from the poly (phenylene vinylene) family. We show that the creation of excitons and charge-transfer states in these materials leads to universal signatures in the excited-state absorption spectra and dynamics. Using polarized femtosecond transient absorption spectroscopy, we studied oriented films of poly (fluorene). The photoinduced dichorism allows us to identify both inter- and intra-chain species separately, due to the different orientations of their excited-state dipole moments. In addition, we report the synthesis and optical characterization of a series of multi-layered organic superlattices made by polyelectrolyte self-assembly. We observe a self-quenching of the luminescence as the thickness is increased in the solid polymer film. This self-quenching can be reversed by inserting additional spacer layers of transparent polyelectrolytes between each active conjugated layer, such that the QE(Quantum Efficiency) grows with thickness. A dramatic red shift of the luminescence (up to 75 nm) is also observed as additional PPV layers are added. This effect persists as the self-quenching is eliminated, implying a longer-range effect. We attribute the red shift and increasing QE to a changing conformation of the polymer chains as the superstructure is assembled, together with efficient Förster energy transfer in a preferred direction away from the substrate toward layers with longer effective conjugation length.

#### **BB11.42**

**SYNTHESES OF NOVEL SEXITHIOPHENE MESOGEN-ATTACHED POLYSTYRENE-POLYSILOXANES VIA ANIONIC POLYMERIZATION.** Yongwoo Lee, Paula T. Hammond, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

Side chain liquid crystalline polystyrene-polysiloxane diblock copolymers containing oligothiophenes as mesogen have been synthesized. The design, synthesis and characterization of this new class of materials will be described. The thermal behavior of those polymers was investigated by the use of DSC and optical microscopy. The potential use of these materials for electro-optical applications, by taking advantage of the inherent ordered nature of liquid crystals, will be discussed.

#### **BB11.43**

**PHOTOVOLTAIC PROPERTIES OF P-TYPE/N-TYPE CONJUGATED POLYMER HETEROJUNCTIONS.** Shujian Yi and Samson A. Jenekhe, Department of Chemical Engineering, University of Rochester, Rochester, NY.

Although interest remains high in developing efficient and low cost solar cells from semiconducting polymers, the power conversion efficiencies achieved to date are very low. The nature of the photovoltaic effect in conjugated polymer heterojunctions has been investigated using p-type poly(p-phenylene vinylene) and a series of n-type semiconducting polymers. The different HOMO/LUMO levels of the n-type polymers, such as polyquinoline PTPQ (EA=2.56 eV), polybenzobisthiazole PpyBT (EA=2.76 eV) and polyquinoxaline PTQx (EA=3.4 eV), allowed us to study the effects of electronic structure of the conjugated polymers on charge separation at the polymer/polymer interfaces. The results showed that power conversion efficiency is increased as the electron affinity of the n-type polymer is increased. The high open circuit voltage (>1.0 V) of the heterojunctions, sandwiched between ITO and Al electrodes, indicates that the driving force for charge separation is the energy level difference between the p- and n-type polymers and not the difference in work functions of the electrodes.

#### **BB11.44**

**DRY MICROPATTERNING OF ORGANIC LIGHT EMITTING DEVICES BY LIFT-OFF USING COLD WELDING.**



Changsoon Kim, Paul E. Burrows and Stephen R. Forrest, Dept of Electrical Engineering, Center for Photonics and Optoelectronic Materials(POEM), Princeton University, Princeton, NJ.

Organic light emitting devices (OLEDs) based on small molecule organic semiconductors have demonstrated high luminous efficiencies (>30 lm/W) and low operating voltages (5V). This has led to intense interest in their application to full color flat panel displays. However, post-deposition patterning of OLEDs is difficult due to the tendency of organic materials to degrade in most solvents used in conventional wet photoresist processing. To produce pixellated displays, therefore, attention has focussed on shadow masking techniques. Due to the mechanical limitations of the shadow mask, such processes are limited to relatively low resolution displays, particularly at large areas. Here, we demonstrate a simple, post-deposition patterning technique based on direct lift-off of the OLED layers. First, small molecule OLED layer structures are vacuum-deposited on an ITO-coated substrate. The OLED uses a Mg<sub>2</sub>Ag alloy cathode capped with a 500Å thick layer of Ag. We then fabricate a textured Si stamp using conventional lithography techniques. An adhesion layer consisting of a 100Å thick layer of Cr capped with a 2900Å thick layer of Ag is deposited onto the stamp. Selective lift-off of the OLED cathode is achieved by pressing the stamp onto the unpatterned substrate, inducing selective cold welding of the cathode to the stamp in the areas defined by its raised features. We demonstrate ~100µm-scale patterning of small OLED arrays using the stamping technique, and compare the results to devices fabricated using a conventional shadow mask process. The effects of varying the dimensions of the stamp feature size are discussed. We discuss the effects of pressure, temperature and pressing time on the quality of the patterned devices. From preliminary results, we estimate the resolution limits achievable by direct patterning of OLED-based displays.

**BB11.45**  
DESIGN AND SYNTHESIS OF HIGHLY EFFICIENT NONLINEAR OPTICAL CHROMOPHORES. Alex K.-Y. Jen, Xiaoming Wu, Jianyao Wu, Sen Liu, Ajay Purohit, Niloufar Mozaffari, Baoquan Chen, Department of Chemistry, Northeastern University, Boston, MA.

Recently, a series of efficient second order nonlinear optical (NLO) chromophores which contain phenyl tetracyanobutadienyl (Ph-TCBD) as the strong electron acceptor, have been prepared. These chromophores possess very good molecular nonlinearity, thermal stability, and chemical stability. More significantly, the 3-D spatial structure of the Ph-TCBD acceptor provides a steric spacer to prevent the electrostatic aggregation of chromophores. This will help decrease the optical loss due to light scattering. The guest-host polymer (PQ-100) films of these chromophores showed good optical properties with a loss of 2.5 dB/cm (at 1.3 µm). The E-O coefficient of a contact-poled polymer film was 31 pm/V at 1.3 µm. Based on these results, a series of multi-hydroxyl functionalized Ph-TCBD chromophores were developed. Incorporation of these chromophores into polyurethane through a cross-linking reaction with isocyanates resulted in an improvement in the alignment stability in comparison to that of the guest-host system.

**BB11.46**  
BLUE LIGHT-EMITTING DIODES FROM A META-LINKED 2,3 SUBSTITUTED ALKOXY POLY(P-PHENYLENE VINYLENE). Franco Cacialli, R.H. Friend, Cavendish Laboratory, Cambridge, UNITED KINGDOM; B.S. Chuah, S.C. Moratti, A.B. Holmes Melville Laboratory for Polymer Synthesis, Cambridge, UNITED KINGDOM.

The presence of a meta-link in poly-arylene vinylenes (PAVs), is known to be an effective way of reducing the conjugation length and hence of increasing the energy of the singlet excitons, providing a possible route to blue-emitting materials. The efficacy of this approach, however, may be reduced by the substitution of the 2,5 hydrogens of the phenyls with alkoxy side-chains, which are often used to make the polymers soluble in common organic solvents. The presence of these chains, in fact, induces a red-shift of the energy gap of the material, owing to the π-electrons donating effects of the oxygen atoms. Recently we found, however, that double substitution of the alkoxy chains onto adjacent (2,3) positions of the phenyl ring could prevent this undesired effect for a para-linked poly(p-phenylene vinylene), PPV. We now report the successful fabrication of blue-emitting LEDs with a meta-linked PPV which also carries 2,3 alkoxy substitution. In agreement with our expectation, both absorption and emission are blue shifted with respect to a similar material with 2,5 substitutions. We recorded maximum efficiencies of ~0.032 cd/A in LEDs structures with Ca cathodes and a plasma-treated Indium Tin Oxide anode coated with a poly(3,4-ethylene dioxythiophene) transport layer. The 1931 CIE coordinates of the electroluminescence spectrum are (0.1881, 0.1812).

**BB11.47**  
MOBILITY OFFSET HETEROJUNCTIONS. Franco Cacialli, J.S. Kim, D. Pinner, N. Tessler, R.H. Friend, Cavendish Laboratory, Department of Physics, University of Cambridge, Cambridge, UNITED KINGDOM; B.S. Chuah, A.B. Holmes, S.C. Moratti, Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Cambridge, UNITED KINGDOM; D.A. dos Santos, J.L. Brédas, Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut, BELGIUM.

We propose a new concept for improvement of the efficiency of Organic Light-Emitting Diodes, namely: the stacking of organic semiconductors with the same Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO), but different charge carrier mobilities. With respect to energy-offset organic heterojunctions, where the difference in the frontier levels ensures charge-carrier and exciton confinement, mobility-offset junctions should benefit from smaller threshold and driving fields, as a result of the removal of energy barriers to carrier injection from one layer to the next, while still improving the efficiency via correction of the electron- and hole-currents imbalance. Although finding the right combinations of materials may seem far from trivial we report the fabrication of a junction with polymers which appear to be 'iso-electronic', namely poly(p-phenylene vinylene), PPV and a derivative with alkoxy substitutions (DB-PPV), designed so as to not alter the electronic structure of PPV. Electrochemical measurements (cyclic voltammetry) confirm that the two materials share the same electronic structure. This is not trivial, since alkoxy functionalisation of PPVs usually leads to asymmetric destabilisation of HOMO and LUMO, but that effect can be avoided via control of the steric interactions between the side-groups, substituted at adjacent position on the phenyl moiety of PPV. In spite of the similarities, however, measurement of charge carrier mobilities shows that the hole-mobility is lower in the substituted material, and therefore that it is suitable for hole confinement. The position of the emission region in the mobility-heterojunction diode (anode/PPV/DB-PPV/cathode) is a function of hole and electron mobility in each layer and is from the substituted PPV, in this case. In unoptimised devices the luminance reaches 4500 cd/sqm at an average field of less than 1MV/cm with a maximum efficiency of 0.6 Cd/A. This amounts to a ten-fold efficiency increase with respect to single-layer devices. We propose that this improvement is due to a reduced charge carriers imbalance.

**BB11.48**  
SPECTRAL SHIFTS INDUCED BY NON-EMISSIVE POLAR DOPANTS IN ORGANIC LIGHT-EMITTING DEVICES. R.S. Deshpande, V. Bulovic and S.R. Forrest, Center for Photonics and Optoelectronic Materials (POEM), Departments of Chemistry and Electrical Engineering, Princeton University, Princeton, NJ.

In the past work[1],[2], we showed that the interaction between the dipole moments of a fluorescent dopant and a conductive host in organic light-emitting devices (OLEDs) can lead to rigid red-shifts in the emission spectra over a large wavelength range. This so-called solid state solvation effect (SSSE) is a powerful means of tailoring the emission color of OLEDs [1],[2]. For the first time, we dope a fluorescent dye, DCM2, into an AlQ3 thin film host and use a second non-emissive polar dopant 4-cyano 4'-hydroxy biphenyl (CHB) to provide the local dipole moment. Surprisingly, the introduction of CHB leads to a monotonic and rigid hypsochromic, i.e. blue, shift in the DCM2 emission of up to 20 nm as its concentration is varied from 2% to 10% while keeping the DCM2 doping constant at 2%. These shifts arise due to the aggregation between the polar DCM2 and CHB molecules such that the resultant molecular complex has a lower dipole moment than either of the monomers. The local field at a given DCM2 molecule is hence reduced as the CHB concentration is increased, causing the resulting spectral blue shift. Absorption studies both in the solid and solution phase as well as the effect of growth temperature on the spectral shifts are investigated to explore the aggregation effects between the various dopant molecules. The ability to blue-shift the spectral peaks complements the previously identified red-shifting of the OLED emission [1],[2] leading to an understanding of the SSSE and extending the range of applicability available to this color tuning technique.

[1] V. Bulovic, A. Shoustikov, M.A. Baldo, E. Bose, V.G. Kozlov, M.E. Thompson, and S.R. Forrest, "Bright, Saturated, Red-to-Yellow, Organic Light-Emitting Devices based on Polarization Induced Spectral Shifts", Chem. Phys. Lett. 287, 455 (1998).

[2] V. Bulovic, R.S. Deshpande, and S.R. Forrest, "Tuning the color emission of Thin Film Molecular Organic Light-Emitting Devices by the Solid-State Solvation Effect", to be published in Chem. Phys. Lett.

**BB11.49**  
LOW VOLTAGE OPERATION OF POLYMER LIGHT-EMITTING DEVICES WITH CONDUCTING POLYMER DISTRIBUTED BRAGG REFLECTOR. Takeo Kawase, Peter K.H. Ho, Richard H. Friend, Univ. of Cambridge, Cavendish Laboratory, Cambridge,

UNITED KINGDOM; Tatsuya Shimoda, Epson Cambridge Laboratory, Cambridge, UNITED KINGDOM.

Polymer light-emitting devices with a conducting polymer distributed Bragg reflector (DBR) are reported. Polymer DBRs were formed from alternate spin-coating of PSS-doped PEDOT for low refractive index medium a hole-transporting polyfluorene derivative for high refractive index medium on an ITO coated glass substrate. The polymer DBR of 5 periods showed reflectivity of about 40%. On the polymer DBR, green-light-emitting polyfluorene derivative was spin-coated for the light emitting layer and Ca/Al was deposited for the electrode. These LEDs successfully worked at low voltages and emitted light of a narrower spectrum (FWHM = 47nm) than that of standard structure (FWHM = 102nm). The peaks varied corresponding to the thickness of the light-emitting layer, that is, cavity length as expected from calculations. The luminescence turn-on voltage of the LED with polymer DBR is at 2V, which is the same as the LED without DBR. The current was found to be limited by injection in the low field region and limited by space charges in high field region. The current does not depend on the period number of the DBR in the low field region, and this implies that there are no effective energy barriers in the polymer DBR.

#### BB11.50

THE ROLES OF BULK MULTILAYERS AND INTERFACES IN IONICALLY SELF-ASSEMBLED POLYMER LIGHT-EMITTING DIODES. M.A. Murray, P.J. Neyman, W. Graupner, J.R. Heflin, Virginia Tech, Dept of Physics, Blacksburg, VA; D. Marciu, M. Miller, A.L. Ritter, Luna Innovations, Inc, Blacksburg, VA; H. Wang, H.W. Gibson, Virginia Tech, Dept of Chemistry, Blacksburg, VA; R.M. Davis, Virginia Tech, Dept of Chemical Engineering, Blacksburg, VA.

Ionic self-assembled monolayer (ISAM) films are a recently developed class of materials that allows detailed structural and thickness control at the sub-nanometer level combined with ease of manufacturing and low cost. The ISAM fabrication method simply involves the dipping of a charged substrate alternately into polycationic and polyanionic aqueous solutions at room temperature. Importantly, the ISAM technique yields exceptionally homogeneous, large area films with excellent control of total film thickness. We describe detailed studies of ISAM light-emitting diodes incorporating poly(para-phenylene vinylene) (PPV) and poly(thiophene) derivatives. The individual thickness of each monolayer and the interpenetration of adjacent layers can be precisely controlled through the parameters of the electrolyte solutions. The effects of the pH and ionic strength of the immersion solutions, the total film thickness, and the PPV thermal conversion parameters on the photoluminescence and electroluminescence yields have been systematically studied. We find, for example, that while PPV precursor adsorbed at pH=6.0 yields greater optical absorbance prior to conversion than that at pH=3.5, the thermal conversion of the precursor in the higher pH film to the conjugated polymer is less efficient, resulting also in weaker electroluminescence. The ISAM process also allows the advantage of depositing well-defined thicknesses of separate polymers at the indium tin oxide and aluminum electrode interfaces. The interface layers are found to dramatically affect the electroluminescence efficiency.

#### BB11.51

RATIONAL SYNTHESIS OF 2D GRIDS FOR SECOND-ORDER NLO APPLICATIONS. Owen R. Evans, Zhiyong Wang, Wenbin Lin, Dept of Chemistry, Brandeis University, Waltham, MA.

The construction of acentric supramolecular assemblies presents a great challenge to synthetic chemists. We will present in this poster the development of a rational synthetic approach toward chiral and acentric, NLO-active polymeric coordination networks based on bifunctional ligands, meta-pyridinecarboxylates. The chiral 2D square grid bis(nicotinato)zinc and the acentric rhombohedral grid bis[3-[2-(4-pyridyl)ethenyl]benzoato]cadmium were synthesized under hydro(solvo)thermal conditions. By coordinating to the pyridyl nitrogen atoms and chelating to the carboxylate groups of exo-tridentate meta-pyridinecarboxylates, the metal centers adopt a cis-octahedral environment and possess a maximum of C<sub>2v</sub> symmetry. The lack of a center of symmetry on either the metal center or the bridging ligand ensures the acentricity of these square and rhombohedral networks. Second-order nonlinear optical properties and thermal stabilities of these materials are also presented.

#### BB11.52

STIMULATED EMISSION FROM A CONJUGATED- NON-CONJUGATED PPV ALTERNATING BLOCK COPOLYMER. Xingyuan Liu, Changchun Institute of Applied Chemistry, Changchun, CHINA, Jimeng Feng, Changchun Institute of Optics and Fine Mechanics, Changchun, CHINA, Run G. Sun, Dept of Physics, The Ohio State Univ, Columbus, OH.

Lasing from a conjugated-nonconjugated PPV alternate block

copolymer poly(1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene) solution is observed. The pumping laser was the third harmonic generation of an active mode locked Nd:YAG laser at 355 nm, with a pulse width of 300 ps. The lasing from this copolymer solution is at 450 nm with 15 nm half width, which is much narrower in comparison with its photoluminescence spectrum of 90 nm half width. The threshold energy for the lasing is ~19 micro joule. The energy conversion efficiency is about 3.4%. The maximum peak power of the polymer laser is as high as 20 kW. This work is supported in part by China National Foundation for Natural Science. The authors would like to thank S. Wang, C. Liang, D. Zhao, Z. Hong, J. Zhao, W. Li, L. Wang, L. Wang, and X. Jing for their help in the experiment and providing samples.

#### BB11.53

MULTI-MODE EMISSION FROM ALQ SINGLE LAYER IN AN OPTICAL MICROCAVITY. Jimeng Feng, Changchun Institute of Optics and Fine Mechanics, Changchun, CHINA, Xingyuan Liu, Changchun Institute of Applied Chemistry, Changchun, CHINA.

Photoluminescent (PL) properties of 8-hydroxyquinoline aluminum (Alq) in a microcavity is studied. The microcavity is composed of a quarter-wavelength distributed Bragg reflector (DBR), an Alq emitting layer, and an Al metallic reflector. The PL from Alq in a microcavity exhibits multi-mode emissions at 446, 497, 555, and 615 nm in blue, green, and red range with ~10 nm spectral width. The emission spectrum of Alq in a microcavity coincides with the resonance structure of the DBR. This work is supported in part by China National Foundation for Natural Science. The authors would like to thank C. Liang, D. Zhao, Z. Hong, S. Er, J. Zhao, W. Li, L. Wang for their assistance in the experiment.

#### BB11.54

1/f NOISE BEHAVIOR IN PENTACENE ORGANIC THIN FILM TRANSISTORS. Pyotr V. Necludov<sup>1</sup>, David J. Gundlach<sup>2</sup>, Thomas N. Jackson<sup>2</sup>, Sergey L. Rumyantsev<sup>3</sup>, Michael S. Shur<sup>1\*</sup>, <sup>1</sup>Rensselaer Polytechnic Institute, Dept of Electrical, Computer and System Engineering, Troy, NY, <sup>2</sup>Pennsylvania State University, Dept of Electrical Engineering, University Park, PA, <sup>3</sup>A.F. Ioffe Institute of Russian Academy of Sciences, Solid State Electronics Division, St. Petersburg, RUSSIA.

The demonstration of pentacene Thin Film Transistors (TFTs) with a field effect mobility as high as 1.5 cm<sup>2</sup>/Vs illustrates a high potential of this technology for display applications. In this paper we will present the results of our experimental studies of 1/f noise in these devices. The 1/f noise is an important measure of a TFT quality that is linked to the carrier transport in the device channel. We investigated pentacene TFTs with gate length and width 20 μm and 220 μm, respectively. SiO<sub>2</sub> dielectric thickness was 30 nm. Measured drain-to-source current in the on-state was as high as 10 μA at V<sub>DS</sub>=50V and V<sub>G</sub>=-40V. The device threshold voltage was -5V. We studied the low frequency noise dependence on the source and drain voltages. The frequency dependence of the relative spectral noise density S<sub>I</sub>/I<sup>2</sup> had a form of 1/f noise in the measured frequency range from 1Hz to 10kHz, with the estimated corner frequency 300 kHz for the -140dB noise level. To compare the device noise level with that of other devices and materials, we extracted Hooge parameter α, which is proportional to the total number of carriers in the channel. In order to estimate the Hooge parameter, we developed a model similar to that for amorphous Si TFTs. The model allowed us to extract the carrier mobility and free carrier concentration, which is a fraction of the total carrier concentration induced by the gate bias. We compared the extracted gate voltage dependent mobility with that predicted by a more simple Universal Constant Mobility model. Both extracted mobility values coincided at the high gate biases. The extracted Hooge parameter was approximately 0.01. For a polymer material this is an extremely small value, which is three orders of magnitude smaller than the Hooge parameter values reported for other conducting polymers [1] and only several times higher than that for amorphous Si TFTs [2]. The spectral density of the voltage fluctuations exhibited a gate voltage dependence close to that reported for Si p-MOS transistors. 1. E.G. Guk, M.E. Levinstein, V.A. Marikhin, L.P. Myasnikova and S.L. Rumyantsev, Phys. Solid. State, v.39, No. 4, p.690, 1997; 2. J. Rhayen, M. Valenza, D. Rigaud, N. Szydlo, H. Lebrun, Journal of Applied Physics, v.83, No. 7, p.3660, 1998.

#### BB11.55

OPTICAL AND ELECTRICAL TRANSPORT PROPERTIES OF ALUMINUM TRIS-8-HYDROXYQUINOLINE (ALQ) FOR ORGANIC LIGHT EMITTING DEVICES. Vincent V. Dinh, Univ of California, Dept of Applied Science, Davis at Livermore, CA; Gil R. Delgado, Louis J. Terminello, Howard W. Lee, Tony Van Buuren, Art Nelson, Nicolas Franco, Lawrence Livermore National Laboratory, Chemistry and Material Science Dept, Livermore, CA; Christoph Bostedt, Univ Hamburg, Inst f. Exp-Physik, Hamburg, GERMANY.

Tris-8-Hydroxyquinoline (Alq) has been the subject of much interest due to its use as an electron transport layer and a light emissive layer in organic light emitting devices (OLEDs). Carrier injection and transport properties are of great importance in determining device performance and lifetime. We present current-voltage (I-V) simulations of an OLED lump model. We correlate these results with measured I-V, photoluminescence (PL), photoluminescence excitation (PLE), and electroluminescence characteristics of working OLEDs. We have also measured the chemistry and bonding structure of these OLED films using synchrotron radiation-based spectroscopies. The consequences of these results are discussed in the context of OLED performance and lifetime.

#### **BB11.56**

**SYNTHESIS AND CHARACTERIZATION OF LINEAR AND STAR SHAPED COORDINATION POLYMERS FOR OPTICAL APPLICATIONS.** Mamoun M. Bader and Phuong-Truc T. Pham, Department of Chemistry, Pennsylvania State University, Hazleton, PA.

Our results on the synthesis and characterization of new linear and star shaped metal-containing polymers will be presented. These polymers are prepared by coordination polymerization of divalent or trivalent metals with bis- or tris- bidentate ligands. These ligands are essentially derivatives of phenanthroline and/or 8-hydroxyquinoline. Functionalities in these polymeric structures are such that they allow a large degree of control of the various physical properties of interest.

#### **BB11.57**

**INTERFACIAL PROPERTIES OF INORGANIC/ORGANIC SEMICONDUCTORS.** Taro Nambu and Akira Suzuki, The Femtosecond Technology Research Association (FESTA), Tsukuba, Ibaraki, JAPAN.

The superlattices of inorganic/organic semiconductors are expected to have an ultra-fast and giant nonlinearity, for the dielectric confinement of excitons in the inorganic semiconductor layer. The organic semiconductor layer should be transparent to excitons and have a smooth interface. However organic crystals have large lattice mismatching to inorganic ones, so their films are multicrystalline and have rough surface. In this paper, the amorphous organic materials named TPD and Alq<sub>3</sub> are introduced. For this purpose we have developed an UHV multi-chamber system free from contamination each other: two growth chambers for an inorganic and an organic materials, and an analysis chamber with a spectroscopic ellipsometer. Device structure is such that Mg(150nm) / Alq<sub>3</sub>(50nm) / TPD(50nm) / ITO(150nm) / glass substrate prepared under UHV(1x10<sup>-7</sup>Pa) but it has large leak current and low breakdown voltage. This is because Mg metal atoms diffuse into Alq<sub>3</sub> film. 1nm thick inorganic barrier layer against Mg diffusion was inserted between Mg/Alq<sub>3</sub> films. At first CaF<sub>2</sub> of 1050°C source was inserted, but Mg re-evaporated and couldn't deposit on the sample surface like on the TPD film surface. However Mg deposited on the CaF<sub>2</sub>/glass substrate, so CaF<sub>2</sub> molecules made mixing between Alq<sub>3</sub>/TPD films. Furthermore inorganic materials of lower heat capacity were also inserted such as SiO<sub>2</sub>, ZnS, CdS, but came out the same result. As<sub>2</sub>Se<sub>3</sub> of 350°C source couldn't deposit on Alq<sub>3</sub> film. Using Se of 150°C source we could make a device. The inorganic materials have the upper limit of 400°C for the smooth interface. The candidate materials for inorganic/organic superlattice are, for an example, TPD (or  $\alpha$ -NPD) for a barrier layer, and PbI<sub>2</sub> of 200°C source for a well layer. This work was supported by NEDO within the framework of the Femtosecond Technology Project.

#### **BB11.58**

**THE AGREEMENT OF POLY-5,5'-(4,4'-DINONYL-2,2'-BITHIAZOLE) SPECTRAL SIGNATURES TO THOSE OF CORRESPONDING OLIGOTHIAZOLES.** Wendy Blanda, Anthony H. Francis, M. David Curtis, University of Michigan, Dept of Chemistry, Ann Arbor, MI.

Conjugated oligomers serve as representative species of their corresponding polymers, which often share the same optical and electrical features. One advantage of studying oligomers is that there is a defined conjugation length, which limits overall conformational morphology, and thereby the possibility that spectral features are due to boundless numbers of conjugation lengths. This separation of features aids in assigning the spectroscopic results of the polymer. Here the monomer, dimer, trimer, and pentamer of poly-5,5'-(4,4'-dinonyl-2,2'-bithiazole) are studied both in solution and in the solid state, and compared to the polymer, P4NonTz. For solution data, the plot of molar extinction coefficient vs. the number of double bonds is linear, as is the Kuhn plot. This is consistent with quantum-chemical molecular modeling calculations, and highly resembles data for other conjugated oligomers, such as polythiophenes and polyenes. However, solid state results show an additional red shift in both absorption and

emission. Thermochromism and solvatochromism, as well as lifetime data suggest that, although similar, polymer solid state behavior fundamentally differs from that of the isolated molecule. By comparing oligothiazoles in solution to film results, anomalous polymer behavior is better understood. We have found that there is correspondence of the solvated oligothiazole molecule data to theory, such as the free electron model, and to other heteroatom oligomers. Furthermore, from the trends in change in spectra with change in number of pi-bonds, effective conjugation length and degree of planarity are predicted. The small molecule data can also be used as a basis of analyzing both the crystalline and amorphous polymer. This thereby sets a foundation for discussions on aggregation, excimers, conformers, or vibronic progressions, which are often used interchangeably to describe spectral features for many conducting polymers.

#### **BB11.59**

**PHOTOEMISSION AND MICROSCOPY STUDY OF PENTACENE/Au AND PENTACENE/SILICON DIOXIDE INTERFACES.** Li Yan, Quoc Toan Le, E.W. Forsythe and Yongli Gao, University of Rochester, Department of Physics and Astronomy, Rochester, NY.

Research on organic thin-film transistors (OTFTs) has been intensified in recent years because of its potential application for electronic devices. Their performances have been significantly improved and demonstrated to be comparable to transistors based on amorphous silicon (a-Si:H) in pentacene-based TFTs. In OTFTs, the metal/organic and insulator/organic interfaces play a critical role in determining the characteristics of the devices. We have investigated the interface formation between pentacene, an organic material often used as an active layer in OTFTs, and different substrates such as SiO<sub>2</sub> and Au, using X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS). XPS results indicate that the deposited pentacene layer is more uniform on SiO<sub>2</sub> than on Au. We found no reaction nor significant level bending for pentacene deposited on Au. For pentacene/SiO<sub>2</sub> interface, the core-level shifts may be attributed to level bending due to the deposition of pentacene on SiO<sub>2</sub>. Furthermore, we will present the results of interface formation of pentacene on SiO<sub>2</sub> substrates treated by different methods. The morphology, obtained by using atomic force microscopy, of pentacene deposited on Au and SiO<sub>2</sub> is also presented.

#### **BB11.60**

**STRUCTURAL AND MICROSCOPIC INVESTIGATIONS OF SELF-ASSEMBLED ZINC-BISQUINOLINE FILMS.** D.L. Thomsen III, T. Phely-Bobin, K.A. Higginson and F. Papadimitrakopoulos, Department of Chemistry and Chemical Engineering, Polymer Science Program, Nanomaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT; A.J. Lovinger, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

The electroluminescence behavior of zinc-bisquinoline self-assemblies has been attributed to the film morphology. Electron diffraction (ED) and X-ray diffraction (XRD) show a material with poor crystallinity or very small crystalline domains, seen by the broad XRD peaks at 34 Å, 12 Å, and 4 Å and prominent electron diffraction halos with distinct outer edges at 10.5 Å and 4 Å. The XRD peak at 34 Å suggests the possibility that the material may preferentially order with a trimer repeat. The polycrystalline nature was observed also by the contrast in both STEM and TEM photographs. The homogeneity of the films can be seen with evidence from X-ray photoelectron spectroscopy (XPS) data and related TEM and ED of zinc oxide and bisquinoline for comparison. TEM investigation of zinc-bisquinoline self-assemblies has revealed a two stage film growth. A surface induced morphology has been seen at film thicknesses under 90 Å. Thicker films can be seen to grow by a nucleation and growth type mechanism. Average domain sizes and the dispersities, determined by scanning transmission electron microscopy (STEM) pictures, increased with film thickness during the self-assembly film making process. These ordered domains contribute significantly to the photoluminescence and electroluminescence response inherent with this self-assembly process.

#### **BB11.61**

**TWO-PHOTON UP-CONVERTED FLUORESCENCE INDUCED PHOTOPOLYMERIZATION.** Lisa R. Denny, Jeffery W. Baur, Max D. Alexander Jr., Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH; Ramamurthi Kannan, Systran Corporation, Dayton, OH; Sean M. Kirkpatrick, SAIC, Dayton, OH; Stephen J. Clarson, Materials Science and Engineering Dept., University of Cincinnati, Cincinnati, OH.

In this study two-photon up-converted fluorescence was used to assist in photopolymerization. An 800 nm pulsed femtosecond laser was used to generate up-converted fluorescence from an organic chromophore incorporated in a monomer/photoinitiator resin system. This

internally generated light then activates the photoinitiator and brings about photocure of the resin system. Novel organic chromophores developed in the Air Force Research Laboratory exhibit large effective two-photon cross-section values which provide efficient visible light fluorescence required to accomplish the photocure. The use of this promising technique provides a relatively new processing method for fabrication of structures ranging from precisely patterned nanostructures to thick structures. This study evaluates the cure of a commercially available thiol-ene resin system via two-photon assisted photocure of film and thick structures. Discussions of critical factors influencing the reaction will include: required two-photon cross-sections, efficiency of conversion, wavelength of emission, power/energy threshold as well as a correlation observed between the local molecular environment and the observed Stoke's shift of the fluorescence.

#### **BB11.62**

**STRUCTURAL VARIATION IN SELF-ASSEMBLED MONOLAYERS (SAMS) OF OMEGA-FUNCTIONALIZED 1-THIAOLIGO(ETHYLENE OXIDES) [TOEO] AMPHIPHILES ON GOLD.** David J. Vanderah, Vitalii Silin, Anne L. Plant, and Curtis W. Meuse, Nat'l. Inst. of Stdrds. & Tech., Gaithersburg, MD.

The SAMS of omega-functionalized 1-thiaoligo(ethylene oxide)<sub>x</sub> [TOEO] amphiphiles, i.e., HS(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>R, where R ≥ C<sub>10</sub>, on Au will be discussed. Structure is found to vary markedly but are highly ordered when x = 3-7 but becomes disordered when x = 8. Structures of the SAMS of a second series - where x = 6 and R = CH<sub>2</sub>CO<sub>2</sub>H, and derivatives - will also be presented.

#### **BB11.63**

**EFFECT OF POLYANILINE ON FILIFORM CORROSION OF ALUMINUM ALLOYS.** Yuan Lin, Frank McClarnon, Sze C. Yang, Univ of Rhode Island, Chemistry Department, Kingston, RI; Richard Brown, Univ of Rhode Island, Chemical Engineering Department, Kingston RI.

This paper discusses the use of polyaniline as an inhibitor for the filiform corrosion of aluminum alloys. Filiform corrosion is a special type of corrosion that occurs under polymer coatings on metal substrates. The corrosion starts at a weak point of the coating and develops into a threadlike structure of corrosion products underneath the coating. Filiform corrosion is an important contributor for the failure of organic coatings on metal. In this study we compared the filiform corrosion between an epoxy primer with or without an additive amount of double-strand polyaniline. The test results show that a small amount of polyaniline (1 to 5%) in the epoxy primer is effective in reducing the filiform corrosion. We will discuss the mechanism for polyaniline to inhibit filiform corrosion.

#### **BB11.64**

**NOVEL BLUE-LIGHT-EMITTING POLYMERS.** Shiyong Zheng, Jianmin Shi, Eastman Kodak Company, Rochester, NY.

Novel blue-light-emitting polymers containing rigid spacer groups were designed and synthesized. The polymers showed high T<sub>g</sub> and T<sub>d</sub>. Single layer LEDs of the polymers emitted blue light at 470 nm and showed low turn-on voltage.

### SESSION BB12/PP7: JOINT SESSION:

#### ORGANIC PHOTOREFRACTIVES

Chair: Joseph W. Perry

Friday Morning, December 3, 1999

Salon G (M)

#### **8:30 AM \*BB12.1/PP7.1**

**HIGH SPEED AND INFRARED SENSITIVE PHOTO-REFRACTIVE POLYMERS.** N. Peyghambarian, E. Hendricks, K.B. Ferio, J.A. Herlocker and B. Kippelen, Optical Sciences Center, University of Arizona, Tucson, AZ; Y. Zhang, V. Alain, S. Thayumanavan, S.R. Marder, J.W. Perry, Chemistry Department, University of Arizona, Tucson, AZ.

We report on a photorefractive polymer with better than 2ms response time. We will also report on two-photon induced photoconductivity in PVK-sensitized with nonlinear absorbers. The results of photorefractive response at 800nm will be presented and efforts to extend the response to longer wavelengths will be summarized. Our recent work on compounds that exhibit 100 percent photogeneration efficiency at 633nm will be reviewed.

#### **9:00 AM \*BB12.2/PP7.2**

**PHOTOREFRACTIVITY IN NEMATIC LIQUID CRYSTALS DOPED WITH A CONJUGATED POLYMER: MECHANISMS FOR ENHANCED CHARGE TRANSPORT.** Michael R. Wasielewski,

Dept. of Chemistry, Northwestern Univ, Evanston, IL; Gary P. Wiederrecht, Chemistry Div, Argonne Natl. Lab., Argonne, IL.

A new mechanism for space-charge field formation in photorefractive liquid crystal composites containing poly(2,5-bis(2'-ethylhexyloxy)-1,4-phenylenevinylene) (BEH-PPV) and the electron acceptor N,N'-diocetyl-1,4:5,8-naphthalenediimide, NI, is observed. Using asymmetric energy transfer (beam coupling) measurements that are diagnostic for the photorefractive effect, the direction of beam coupling as a function of grating fringe spacing inverts at a spacing of 5.5 microns. We show that the inversion is due to a change in the dominant mechanism for space-charge field formation. At small fringe spacings, the space-charge field is formed by ion diffusion in which the photogenerated anion is the more mobile species. At larger fringe spacings, the polarity of the space charge field inverts due to dominance of a charge transport mechanism in which photogenerated holes are the most mobile species due to hole migration along the BEH-PPV chains coupled with interchain hole hopping. Control experiments will be presented, which use composites that can access only one of the two charge transport mechanisms. The results show that charge migration over long distances leading to enhanced photorefractive effects can be obtained using conjugated polymers dissolved in liquid crystals.

#### **9:30 AM BB12.3/PP7.3**

**ENHANCEMENT OF PHOTOREFRACTIVITIES IN MONOLITHIC PHOTOREFRACTIVE POLYMERS.**

Tatsuo Wada<sup>1,2</sup>, Takafumi Sassa<sup>2</sup>, Tetsuya Aoyama<sup>2</sup>, Yadong Zhang<sup>1</sup>, Atsushi Gunji<sup>1,2</sup> and Hiroyuki Sasabe<sup>1,2,3</sup>, <sup>1</sup>Core Research for Evolutional Science and Technology (CREST), JST, <sup>2</sup>Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama, JAPAN, <sup>3</sup>Chitose Institute of Science and Technology, Bibi, Chitose, Hokkaido, JAPAN.

We have developed carbazole oligomers and polymers as monolithic photorefractive materials in which single multifunctional chromophore meets all the requirement of photorefractive. Carbazole oligomers show better photorefractive performance than polymeric ones and provide molecular level of tuning. In order to improve the photorefractive properties of carbazole polymers, additional hole-transporting and electro-optic chromophores were introduced into the side chain, 9-position of the 3-6-linkaged main-chain polymer. In these main- and side-chain polymers, photoconductive properties were enhanced by factor of 10. Electro-optic coefficients and second-harmonic coefficients also increased. Asymmetric energy transfer in two beams with 90° phase shift was observed and the great enhancement of photorefractive was obtained in main- and side-chain polymers. The two-beam coupling net gain of 103 cm<sup>-1</sup> was obtained without an external electric field in carbazole main-chain polymer with p-nitrostilbene in the side chain. The enhancement of two-beam coupling gain can be explained by the refractive index change estimated from the diffraction efficiency in four-wave mixing.

#### **9:45 AM \*BB12.4/PP7.4**

**NANOPHOTONICS: MATERIALS, INTERACTIONS AND APPLICATIONS.** P.N. Prasad, J. Swiatkiewicz, D. Jakubczyk, Y. Shen, Y. Jiang, M. Lal, L. Levy, C. Friend and A. Biswas, Photonics Research Laboratory, Department of Chemistry and Physics, State University of New York at Buffalo, Buffalo, NY.

Nanophotonics is a new frontier dealing with nanoscale optical science and technology. Nanoscale optical interactions can be studied in two ways: (i) nanoscale confinement of radiation field and (ii) nanoscale confinement of the medium by nanostructuring. This paper will present our effort in both areas. Results will be presented from theoretical modeling and near field probing of linear and nonlinear optical processes. In nanostructured material design, two new directions taken by our group are development of photonic crystals and multistep organizational assemblies with enhanced photonic activities. Our work involving nanoscale photochemistry for applications will also be presented.

#### **10:45 AM \*BB12.5/PP7.5**

**TRAP DYNAMICS IN PHOTOREFRACTIVE POLYMER COMPOSITES.** W.E. Moerner, D. Wright, A. Goonesekera, Stanford Univ, Dept of Chemistry, Stanford, CA; M.A. Diaz-Garcia, Univ of Calif San Diego, Dept of Chemistry, La Jolla, CA; R.J. Twieg, Kent State Univ, Dept of Chemistry, Kent, OH.

The high gain and index modulation reported for several new photorefractive polymer composites are due to a combination of factors, including high nonlinearity resulting from orientational enhancement, and the large internal electric fields that can be generated (90 V/mm). In all models, the trap density plays a critical role in establishing strong space-charge fields. For composites based on poly(N-vinyl carbazole) containing amino-dicyanostyrene nonlinear optical (NLO) chromophores and sensitized with the fullerene C60, we

have shown that the radical anion of C60 acts as the primary photorefractive hole trap. In addition, the NLO acts as a temporary reservoir for the photogenerated holes (compensator). The long-time dynamics of the trap density depend upon the position of the highest occupied molecular orbital (HOMO) of the NLO, as estimated by cyclic voltammetry. With this enhanced understanding, the overall trap dynamics can be controlled to an extent by changing the energetics of the NLO. Furthermore, we find that the speed of the photorefractive response is inversely correlated with the depth of the hole trap represented by the NLO, suggesting that the speed of the photorefractive effect is influenced by the possibility that mobile holes can become trapped in the NLO sites during transport. Time-of-flight mobility measurements will be utilized to attempt to quantify this effect. The overall picture that emerges provides an important step toward rational design of these materials, in which the actual trap concentrations and their influence on transport are controlled by composition and irradiation history.

**11:15 AM BB12.6/PP7.6**

SYNTHESIS AND PROPERTIES OF NOVEL PHOTO-REFRACTIVE POLYMERS. C.D. Eisenbach, K. Ewert, Inst. Techn. Chemie II, Univ. Stuttgart, Stuttgart, GERMANY; D. Haarer, U. Hofmann, S. Schloter, Exp.-Physik IV, Univ. Bayreuth, Bayreuth, GERMANY.

Polymers carrying both the photoconducting and nonlinear optically (NLO) active moieties along the polyester or polyurethane chain have been obtained by step-growth polymerization employing specially designed photoactive (NLO and photoconducting) building blocks. This strategy not only allowed to systematically vary the bulk and processing properties of the materials but also the photorefractive properties. The electrooptic properties were investigated by several techniques, and the polymers were found to be fast and stable photorefractive materials. The design and the synthesis as well as the advantageous photorefractive properties of the novel polymers will be discussed.

**11:30 AM \*BB12.7/PP7.7**

PROGRESS IN FULLY FUNCTIONALIZED PHOTOREFRACTIVE POLYMERS. Luping Yu, The University of Chicago, Department of Chemistry, Chicago, IL.

In this talk, we will present our recent progress in the area of photorefractive (PR) polymers. Photorefractive polymers are multifunctional materials which combine the photoconductivity and electro-optic response to show a new phenomenon: reversible modulation of the index of refraction by light. Because of their multifunctional features, designs, syntheses of these materials exhibiting high performances are an intellectual challenge. In the past year, our group has focused on the development of fully functionalized polymers, oligomers and small molecular materials. We have had success in identifying new materials and in gaining understanding in design principles of better materials. Several new PR material systems will be discussed, including conjugated PR polymers containing metalloporphyrin as photosensitizer, oligothiophene-NLO chromophore system exhibiting interesting physical properties and small molecular system containing NLO chromophore and carbazole moieties. All of these systems exhibit large net optical gain and minimized phase separation. The correlation between molecular structure and physical properties is the focal point of this presentation.