SYMPOSIUM S

Electrically Active Polymers

April 24 – 27, 2000

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* Invited paper

SESSION S1: SENSORS AND TFTS
Chair: Mary Galvin
Monday Afternoon, April 24, 2000
Metropolitan II (Argent)

1:30 PM *S1.1
CONJUGATED POLYMERS AS SENSORS, WIRES, AND ANTENNAS. Timothy M. Swager, Dept. of Chemistry, Massachusetts Institute of Technology, Cambridge, MA.

The synthesis of conjugated polymers designed to have specific functions will be presented in particular how a material's collective properties can be used to produce self-amplifying sensory responses will be described. In this process, electronic polymers are used to interconnect receptor or binding sites that interact with specific analytes. By wiring receptors in series with a conjugated polymer, the activation of only a small fraction of the receptors by a target analyte results in a substantial reduction in the overall signal. In this way, sensory schemes have been devised with imprecedented sensitivity. Examples will include the detection of TNT at femtogram levels. Polymers containing the controlled association of polymers into organized structures that provide further signal gain will also be presented.

2:00 PM *S1.2
BIOACTIVE ELECTROCONDUCTIVE POLYMERS: COMBINING MOLECULAR RECOGNITION AND ELECTRICAL TRANSDUCTION. Anthony Guiseppi-Elie, Chemical Engineering Dept., Virginia Commonwealth University, Richmond, VA and ABTECH Scientific Inc., Biotechnology Research Park, Richmond, VA.

Various strategies are pursued to confer the highly specific molecular recognition characteristics of bioactive molecules with the transducer action of conductive polymers. These approaches include physical adsorption, electrostatic entrapment during oxidative electropolymerization and covalent immobilization to redoxactive monomer. Bioactive molecules such as enzymes, antibodies and DNA have been successfully associated with polyaniline and polypyrrole and fabricated into bioactive thin films. This report will review methods and approaches and outline the biospecific responses of these bioactive thin films.

2:30 PM *S1.3
NOVEL BIOLOGICAL AND CHEMICAL SENSORS BASED ON FLUORESCENT POLYELECTROLYTES. Duncan McBranch, Los Alamos National Laboratory, Los Alamos, NM.

ABSTRACT NOT AVAILABLE

3:30 PM *S1.4
ORGANIC TRANSISTOR BASED LARGE SCALE INTEGRATED CIRCUITS. Ananth Dodabalapur, B. Crone, Y.Y. Lin, J. Rogers, Z. Bao, R. Filas, S. Martin, R. Sarpeshkar, H.E. Katz and W.J. Lee, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

The performance characteristics of both p-channel and n-channel organic/polymeric thin-film transistors have reached a level that have enabled the design and experimental realization of large scale complementary integrated circuits. Successful design of such circuits requires a detailed understanding of the basic physics of operation of such transistors as well as the development or modification of a range of software tools. We will describe the DC, transient, and noise properties of transistors made with a number of organic and polymer semiconductors and the characteristics of circuits fabricated by a range of methods. We will also describe the advantages of complementary circuits for applications such as RF Tags. Organic transistors have also been integrated with display elements such as organic light emitting diodes. Design considerations and experimental results from such 'smart pixels' will be outlined.

4:00 PM *S1.5
THIN-FILM ORGANIC-INORGANIC FIELD EFFECT TRANSISTORS. C.R. Kagan, D.B. Mitzi, C.D. Dimitrakopoulos, L.L. Kosbar, IBM-T.J. Watson Research Center, Yorktown Heights, NY.

We report thin-film field effect transistors having organic-inorganic hybrid materials as the semiconducting channels. Organic-inorganic hybrids promise the high carrier mobilities of inorganic semiconductors, but may be deposited by low-cost, low-temperature solution processes common to organic materials. Organic-inorganic perovskites, one subset of hybrid materials, self-assemble from solution to form oriented, molecular-scale composites of alternating inorganic perovskite sheets and organic layers. Spin-coated polycrystalline thin-films of $(C_6H_5C_2H_4NH_3)_2SnI_4$, just one example of an organic-inorganic perovskite, forms conducting channels with field-effect mobilities of 0.6 cm^2/V-sec and on-off ratios of $>10^6$. The flexibility in the chemistry and dimensionality of hybrid materials is exploited to prepare organic-inorganic perovskites with alternate organic layers and inorganic frameworks. Tailoring the organic and inorganic components of the perovskites is expected to improve carrier mobility, current modulation, and stability of hybrid materials in thin-film transistors.

4:30 PM S1.6
CRYSTAL ENGINEERING OF NTCDI DERIVATIVES FOR HIGH MOBILITY ELECTRON TRANSPORT IN FETS. H.E. Katz, A.J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTCDA) and its diimide derivatives (NTCDIs) possess moderate n-channel field effect transistor (nFET) mobilities, observable only under an inert atmosphere. However, by appending suitable substituents on NTCDI nitrogens, 2-3 order-of-magnitude mobility increases are observed, to $>$0.1 cm2/Vs. Certain fluorinated substituents confer sufficient stability for nFET operation in air, and one of them affords the unprecedented capability of solution nFET fabrication. Crystal structures reveal exceptionally favorable packing geometries. These compounds show the highest mobilities and on/off ratios yet reported for organic-based nFETs.

4:45 PM S1.7
TRAPPING IN ORGANIC FIELD-EFFECT TRANSISTORS. J.H. Schoen, Ch. Kloc, B. Batlogg, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Organic field-effect transistors have reached a performance similar to a-Si:H devices with mobilities in the order of 1 cm^2/Vs and on/off-ratios of 10^6. However, thin film devices often exhibit instabilities, like hysteresis effects, threshold voltage shifts, or gate voltage dependent mobilities, during operation. It has been questioned whether this behavior is intrinsic to the organic materials or can be ascribed to extrinsic effects, such as traps or grain boundaries. We have prepared single and polycrystalline field-effect transistors based on pentacene and oligothiophenes using different insulators. The mobility in high-quality single crystal devices increases with decreasing temperature following a power law, indicative of band-like charge transport in delocalized states. However, trapping in the bulk semiconductor, at the semiconductor/insulator interface as well as at grain boundaries can significantly influence the characteristics of the devices. Especially, the formation of a potential barrier at grain boundaries due to trapped charge gives rise to thermally activated and gate voltage dependent transport. Furthermore, charged trapping sites can migrate during device operation causing, e.g. threshold voltage shifts. However, these effects were not observed in pure (intrinsic) single crystalline transistors. Stable operation in air for more than a month is demonstrated.

SESSION S2: CONDUCTIVE POLYMERS
Chair: Zhenan Bao
Tuesday Morning, April 25, 2000
Metropolitan II (Argent)

8:30 AM *S2.1
9,10-ANTHRACENEDIYLIDENE DERIVATIVES: SYNTHESIS, REDOX CHEMISTRY, OPTOELECTRONIC AND STRUCTURAL PROPERTIES. Martin R. Bryce, Department of Chemistry, University of Durham, Durham, ENGLAND.

We will present the synthesis of new 9,10-anthracenediylidene systems, especially those bearing 1,3-dithiole substituents, and demonstrate that they are versatile building blocks for redox-active materials. We will discuss: (i) photoinduced charge-transfer studies and structural properties of donor-pi-acceptor derivatives of this system [1]; (ii) synthesis and properties of novel bridged redox-active cyclophanes [2] (iii) structural studies on intermolecular CT complexes of new functionalised derivatives[3], e.g. with TCNQ; (iv) the synthesis and redox behaviour of dendritic polymers incorporating bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene units.

[1] M.R. Bryce, et al, Chem. Eur. J. 1998, 4, 2580-2592.
[2] T. Finn, M.R. Bryce, A.S. Batsanov, J.A.K. Howeard, Chem. Commun. 1999, 1835-1836.
[3] M.R. Bryce, et al, Eur. J. Org. Chem. 1999, in press.

9:00 AM *S2.2
THE ORGANIC METAL: BASIC SCIENTIFIC BACKGROUND AND TECHNOLOGICAL APPLICATIONS. Bernhard Wessling, Ormecon Chemie, Ammersbek, GERMANY.

A special form of polyaniline exhibits metallic properties, so it can be considered as an "Organic Metal" It will be shown in what aspects the premetallic powder form is different from other polyanilines known from literature (dispersability, density of states), and how it is forced to cross the “insulator-to-metal transitio” to the metallic side. The fundamentals of dispersion of Organic Metals will be highlighted, and industrial applications in the manufacturing of printed circuit boards, in corrosion protection, and in other functional surface coatings like electrodes (for LEDs) or sensors (“chemical nos”) will be explained.

9:30 AM S2.3
ELECTROSPUN NANOFIBROUS MEMBRANES OF CONDUCTING AND PHOTOELECTRIC MATERIALS. Kris J. Senecal, Margaret A. Auerbach, Heidi Schreuder-Gibson and Lynne Samuelson, US Army Soldier Biological Chemical Command, Natick Soldier Center, Material Science Team, Natick, MA.

Electrospinning has been used to prepare nanofibrous composite membranes of conducting and photoelectric materials. Electrospinning is a relatively simple technique where electrical forces are used on polymeric solutions to produce nanoscale fibers. Continuous electrospinning results in porous, high surface area membrane structures of controlled thickness depending on the duration of spinning. Through judicious choice of the materials added to the spin dope, one may tailor the membranes towards specific properties such as mechanical toughness, electrical conductivity and photoelectric conversion. In this work, conducting polyaniline, light harvesting dyes and semiconductor nanoparticles have been electrospun into composite membranes with matrix polymers such as polyacrylonitrile, polyurethanes, poly 4 -vinyl pyridine and polyethylene oxide. UV-Vis absorbance measurements on the electrospun membranes have shown reversible doping-dedoping behavior of the polyaniline in the membrane when subjected to differing pH environments. SEM micrographs show fiber sizes ranging from 100 μm to 2 nm in diameter, with an interconnected fiber structure and a high degree of porosity. The thickness of the fibrous membranes can be varied as needed, and densities of these membranes range from 30-50% fiber content. These continuous fibrous membranes can be processed at ambient conditions adhering and forming air permeable membranes to a variety of substrates such as clothing or other surfaces as well as forming stand alone membranes. It is expected that these new types of electrospun composite materials will have potential use in a wide variety of electronic device applications. The detailed preparation, characterization and morphology of these membranes will be presented.

9:45 AM S2.4
ELECTROACTIVE AND ELECTROCHROMIC POLY(3,4-ALKYLENEDIOXYPYRROLE)S. Philippe Schottland, Kyukwan Zong, Barry C. Thompson, Carleton L. Gaupp, Christopher A. Thomas, John R. Reynolds, Dept of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL.

A series of alkylenedioxy substituted pyrroles has been synthesized and polymerized in organic based electrolytes. These poly(3,4-alkylenedioxypyrroles) (PXDOPs) represent a new class of conducting polymers which display among the lowest oxidation potentials (from -0.7 V to -0.4 V vs. Ag/Ag$^+$) ever observed for conducting polymers. The PXDOPs exhibit multi-color electro- chromism, switching from a red or orange neutral state, to a light blue/gray doped state, while passing through a darker intermediate state (brown) in some cases. High electrochromic contrast ratios have been measured at λ_{max} for the π to π^* transition with a maximum of 76% at 534 nm for the poly(dimethyl-3,4-propylenedioxypyrrole) (PProDOP-Me$_2$). These new polymers have demonstrated outstanding redox switching stability as they are able to undergo tens of thousands of switches between their doped and neutral states while retaining more than 90% of their electroactivity. A further stability to oxidation is also demonstrated by their limited degradation of their electroactivity at potentials almost 2 V above their half wave potential, while polypyrrole irreversibly loses its electroactivity under those conditions. This combination of coloration efficiency and stability makes this new class of polymers a very promising candidate for use in electrochromic devices.

10:30 AM *S2.5
SOLID STATE REACTIONS OF FUNCTIONALIZED POLYTHIOPHENE FILMS. Jianfei Yu, Steven Holdcroft, Simon Fraser Univ., Dept. of Chemistry, CANADA.

(3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene) (THPET) was homopolymerized (PTHPET) and copolymerized with 3-hexylthiophene (PTHPET-co-3HT) to obtain functionalized regioregular pi-conjugated polymers. Thermolytic and catalytic removal of the bulky tetrahydropyran (THP) group from thin solid films of these polymers is described. Elimination of THP enables the deposition of dense, partially ordered, insoluble films, which previously could only be obtained on electrically conducting surfaces via electrochemical polymerization of the appropriate monomer. The extent of p-conjugation in the film is controlled by the composition of the copolymers and conditions employed. The effect of composition on chemical amplified photolithography of these materials is discussed.

11:00 AM S2.6
COLORIMETRIC ANALYSIS OF POLYMER-BASED ELECTROCHROMIC FILMS AND DEVICES. John R. Reynolds, Barry C. Thompson, Philippe Schottland, Irina Giurgiu, Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL.

In this paper, we present results on a set of transmission and reflection designed dual-polymer-based electrochromic (EC) devices. A colorimetric method for the in situ study of EC polymers and devices, based on the CIE system of colorimetry, will be reported. A broad family of cathodically and anodically coloring EC polymers, based on 3,4-alkylenedioxythiophene (XDOT) and 3,4-alkylenedioxypyrrole (XDOP), were investigated using this in situ colorimetric analysis. Demonstration of color control for a dual-polymer EC device based on poly[2-(3,4-ethylenedioxythienyl)-4,4'-biphenyl] (PBEDOT-BP) and poly[3,6-bis(3,4-ethylenedioxythienyl)-N-methylcarbazole] (PBEDOT- NMeCz), which yields green/brown colors (L=48, a*=0, b*=20 and L=44, a*=6, b*=26) interesting for earthtone and natural vegetation chameleon materials, will be shown. This technique is a powerful tool for the design and construction of dual polymer EC devices since it allows for fine tuning and reproducibility of color. In addition, high contrast, laterally oriented EC devices will be discussed.

11:15 AM S2.7
A BIOCATALYTIC APPROACH TO ELECTRONIC POLYMERS. Wei Liu, Ramaswamy Nagarajan, Jayant Kumar, Sukant Tripathy, Depts of Chemisty and Physics, Univ of Massachusetts Lowell, Lowell, MA; Ferdinando Bruno, Kris Senecal, Lynne Samuelson, Natick Soldier Center, U.S. Army Soldier, Biological, Chemical Command, Natick, MA.

An alternative, biocatalytic approach to the synthesis of new conducting and optically active polymers is presented. In this approach, enzymatic polymerization of anilinic and phenolic monomers is carried out in the presence of ionic templates to yield water-soluble complexes of the polymer and the template used. Here the template provides a preferential local environment, which serves to emulsify the monomer prior to polymerization and maintain water solubility after polymerization. In the case of polyanilines, the template also provides counterions to electrostatically align the aniline monomer and dope the final polymer to the conducting form. This approach is particularly attractive in that it is simple (one step), uses very mild conditions (pH 4 - 7) and reagents and requires minimal separation and purification. In addition the process is general as numerous ionic polymeric and surfactant templates and derivatized monomers may be interchanged to build in desired functionalization. The mildness of this approach also allows for the utilization of more delicate biological templates such as DNA. A detailed discussion of the characterization, versatility with various monomers and templates, and electronic properties of these polymers will be presented.

11:30 AM S2.8
NEW SYNTHETIC ROUTES TO CONJUGATED POLYMERS WITH SYSTEMATIC VARIATION OF STRUCTURE AND PROPERTIES. Biwang Jiang, T. Don Tilley, Department of Chemistry, University of California, Berkeley, Berkeley, CA.

Our group has been exploring the use of zirconocene-coupling to provide reactive zirconacyclopendiene-containing conjugated polymers. The metal-containing polymers then serve as useful precursors which could lead to a number of other new conjugated polymers by transforming zirconium units into other functionalities. This method provids a flexible and versatile entry into a large number of conjugated polymers with systematic variation of structure and properties. Particularly, we have been able to obtain many novel conjugated polymers displaying interesting electronic properties. Thiophene-1-oxide copolymers represent one of these new types of materials which possess high emission quantum efficiency and excellent electron transporting properties. We will also present some other interesting polymers including highly conductive polyselenophenes, base-dopable cyclopentadiene-containing conjugated polymers, and amphiphilic conjugated polymers.

11:45 AM S2.9
ORDER DEPENDENT MICROSCALE CONDUCTIVITY OF CONJUGATED POLYMER MONO- AND MULTILAYERS. Peter Bӧggild, Torben M. Hansen, Christian L. Petersen, Francois Grey, Mikroelektronik Centret, Technical Univ of Denmark, Lyngby, DENMARK; Tue Hassenkam, Thomas Björnholm, Laboratory for Materials Research, Chemistry Dept, Univ of Copenhagen, DENMARK.

We present conductivity measurements of single oriented domains in conjugated polymer monolayers, using a novel microscale four-point probe. The microprobe is a linear array of four metallized silicon oxide cantilevers, with inter-electrode spacings ranging from 60 μm to 1μm. The probes are made on a wafer basis using photolithographic silicon microfabrication techniques. By passing a current through the outer electrodes while measuring the voltage drop across the inner electroedes, the conductivity can be determined essentially without contact resistance. We have synthesized polythiophene molecules with alternating hydrophilic and hydrophobic side groups. On a water surface these self-assemble into wire shaped crystallites (5 × 40 nm) with semiconductor-like bandstructure, and subsequently millimetre-size, uniaxially ordered domains, that can be transferred to a solid substrate. By stepping the microprobes across such a monolayer, the conductivity of areas containing both ordered and disordered regions is mapped with microscale resolution. The local conductivity is shown to be strongly dependent of the ordering. In both the mono- and multilayers we observe prominent conductivity enhancements at the domain boundaries. In the multilayers the conducting regions are defined artificially by laser etching of the substrate. From numerical simulations the edge enhancement is shown to be essentially a probe convolution effect, arising from disturbances of the current flow. Very high conductivities are measured in monolayer domains (>100 S/cm). This we attribute to the fact that we measure the local conductivity of a single domain, rather than sample the average conductance of a large area, containing both high- and low-conductivity regions

SESSION S3: PHYSICS OF ELECTRICALLY ACTIVE POLYMERS

Chair: Lewis J. Rothberg
Tuesday Afternoon, April 25, 2000
Metropolitan II (Argent)

1:30 PM *S3.1

WAVELENGTH DEPENDENCE OF ULTRAFAST CARRIER PHOTOGENERATION IN CONJUGATED POLYMERS.

Paulo B. Miranda, Daniel Moses and Alan J. Heeger, Institute for Polymers and Organic Solids, University of California, Santa Barbara, CA.

We have used ultrafast pump-probe spectroscopy to investigate the mechanism of carrier photogeneration and dynamics in conjugated polymers. Samples of poly(phenylene-vinylene), PPV, and its derivatives (e.g. MEH-PPV) were pumped with femtosecond pulses tunable across their absorption spectrum and probed by mid-infrared pulses tuned to the InfraRed Active Vibrational (IRAV) modes. The IRAV modes are a well-known probe of charged excitations in conjugated polymers and are, therefore, a unique signature for carrier photogeneration. We observe a significant quantum efficiency for carrier photogeneration within the temporal resolution (~100 fs), implying that charge carriers are primary photoexcitations. The pump-wavelength dependence of the IRAV mode strength is a measure of the quantum efficiency for direct carrier photogeneration as a function of photon energy. Such a study near the absorption band edge provides a direct measurement of the energy gap in these conjugated polymers. The exciton binding energy is obtained by comparing the measured single particle energy gap with the energy for onset of optical absorption (the optical gap). We present our experimental findings and discuss their implications to the carrier generation mechanism and recombination dynamics in the various derivatives of PPV.

This work was supported by the Air Force Office of Scientific Research (F49620-99-1-0031) and the National Science Foundation (DMR9812852).

2:00 PM *S3.2

ROLE OF INTERFACES IN ORGANIC AND POLYMER OPTO-ELECTRONIC DEVICES.

Georges Hadziioannou, Paul F. van Hutten, Victor V. Krasnikov, Univ of Groningen, Dept of Polymer Chemistry, Materials Science Centre, Groningen, THE NETHERLANDS.

The composite nature of opto-electronic devices implies a prominent role of interfaces to device performance. Well-defined electrical behavior requires an equally well-defined interfacial structure, while mechanical coherence should be ascertained as well. Wetting/adhesion, substrate-induced film growth, interdiffusion, and impurity content are some of the many relevant issues. This presentation focuses on several further aspects, notably (i) the optimization of the geometry of the interface (exemplified by the case of photovoltaic devices), (ii) the electronic energy level alignment at organic-metal interfaces, and (iii) confinement effects, manifested as a variation of film structure with thickness, and found to affect the luminescence gain dynamics.

2:30 PM S3.3

ELECTROPHOSPHORESCENCE FROM A DOPED POLYMER LIGHT EMITTING DIODE.

Diarmuid O'Brien, Physics Department, Trinity College, Dublin, IRELAND; Carsten Giebeler, Ashley Cadby, Robert Fletcher, Leonidas Palilis, David Lidzey, Dept of Physics, Univ. of Sheffield, UNITED KINGDOM; Werner Blau, Physics Dept., Trinity College, Dublin, IRELAND; Paul Lane, Donal Bradley, Dept. Physics, Univ. of Sheffield, UNITED KINGDOM.

Previously, by utilising phosphorescent dopants the electroluminescence efficiency of organic light emitting diodes (LED) has been greatly enhanced. In this work the photophysics and device physics of a phosphorescent polymer LED have been investigated. The emissive host, poly(9,9-dioctylfluorene) (PFO), was doped to a variety of concentrations between 0.2% and 8% with a red emissive phosphorescent dye, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum(II) (PtOEP). The energy transfer mechanisms between the host and the dopant were studied using both photoluminescence (PL) and photo-induced absorption techniques. Förster transfer was observed from the host to the dopant but no evidence of Dexter transfer was found. Interestingly, by monitoring the triplet PA peak in PFO an increase in the PFO triplet concentration was observed on doping, indicating increased intersystem crossing in the polymer due to a heavy atom effect from the dopant molecule. Electroluminescent (EL) devices prepared from PFO/PtOEP blends showed a maximum external quantum efficiency (QE) of 3.5% and a peak brightness > 250 cd/m^2 in continuos mode and > 2000 cd/m^2 in pulsed mode. This is the highest phosphorescent efficiency obtained to date using a polymer host. We attribute this high efficiency to the capturing of both singlet and triplet excitons by direct charge trapping on the PtOEP molecules. The lifetime of phosphorescence was found to be 60 μs and within error to be independent of both current and doping concentration. This indicates a different emission quenching mechanism to what has previously been observed in phosphorescent organic devices, namely triplet-triplet annihilation. Finally we report that the EL and PL quantum efficiencies show notably different dopant concentration dependencies. This questions the linkage between the PL and EL quantum efficiencies in doped organic systems and stresses the importance of differentiating between charge trapping and energy transfer in organic LEDs.

2:45 PM S3.4

A RE-VISIT OF THE EFFICIENCY LIMITS FOR POLYMER LIGHT-EMITTING DIODES.

Ji Seon Kim, Peter K.H. Ho and Richard H. Friend, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM.

The external electroluminescence (EL) quantum efficiency of polymer light-emitting diodes (LEDs) is given by the product of $\xi\ \gamma\ \mathrm{r}_{st}\ \eta$. Here, ξ is the surface out-coupling efficiency, γ is the ratio of the number of exciton forming events to the number electrons flowing in the external circuit, r_{st} is the fraction of excitons formed in the singlet state, and η is the luminescence efficiency of these singlet excitons. Previously, ξ is approximated by $1/2n^2$ where n is the refractive index of the emitting polymer, and r_{st} by 0.25 from spin statistics. Recently, however, we have fabricated single-layer polymer LEDs that are substantially more efficient than predicted on the basis of these limits. For example, a green-emitting phenyl-substituted PPV copolymer shows a 6% external quantum yield in the forward direction (20 cd/A), compared to its photoluminescence yield of 33%. In the light of these results, we have re-examined the efficiency-limiting terms: (i) Using a simple half-space model that takes into account the key optical interference effects, we find that ξ can be considerably larger than $1/2\mathrm{n}^2$, depending on the location and orientation of the emitting dipoles. (ii) Numerical simulations of the EL emission patterns of these devices suggest that the injected carriers recombine at a distance away from the cathode and near the optimal location giving maximum surface emission rate. (iii) We deduced the $\gamma\ \mathrm{r}_{st}$ product of these devices to be 0.35-0.45. Since $\gamma < 1$, r_{st} must exceed 0.35-0.45, indicating the achieved excellent carrier injection balance and recombination efficiency. In this contribution, we will also propose a simple photonic structure design rule for these thin-film polymer LEDs.

3:30 PM *S3.5

IMAGING LOCAL PHOTOCURRENTS IN ORGANIC SEMICONDUCTORS.

Denis Fichou[1], Fabrice Charra[2], and Alexandre Gusey[2]. [1]Laboratoire des Materiaux Molecularies, C.N.R.S., Thiais, FRANCE; [2]ORECAM, CEA Saclay, Gif-sur-Yvette, FRANCE.

Conjugated oligomers and polymers are potentially useful for device applications such as light emitting diodes[1,2], field-effect transistors[3,4], or photovoltaic cells[5,6]. But carrier transport in molecular semiconductors is still poorly understood, which greatly limits technological developments. Since microscopic order plays a central role in carrier dynamics, exploring electronic phenomena at a local scale is essential. We report hereon the use of scanning tunneling microscopy (STM) in combination with optical excitation to image simultaneously local photocurrents and surface morphology in molecular semiconductors at the nanometer scale. Our light-assisted STM setup operates on a fast two-step data acquisition mode (10 μs/data). Its high sensitivity allows to visualize the extremely weak tunneling currents (a few pA) typical of low mobility materials such as conjugated polymers. It also provides a direct through space access to the I/V and I/Z characteristics (Z=tip-sample distance) at each point of the scanned area. We reveal in particular the strong photocurrent reduction along the step edges of sexithiophene single crystals and thin films due to localized surface recombination centers while photocurrent is maximum on top of the defect-free terraces.

4:00 PM *S3.6

MOLECULAR ENGINEERING OF LINEAR π-CONJUGATED SYSTEMS WITH TAILORED ELECTRONIC PROPERTIES. Jean Roncali, CNRS, UMR 6501, Ingénierie Moléculaire et Matériaux Organiques, Angers, FRANCE.

The tremendous development of the advances applications of linear π-conjugated systems in micro and nano-electronics, nonlinear optics, light-emitting devices or advanced electrode materials generates an increasing demand for molecular or polymeric conjugated systems with specific electronic, optical and electrochemical properties.
In this context, recent advances in the molecular engineering of linear conjugated system with tailored properties will be presented with a particular emphasis on two main areas namely 1) electrogenerated conjugated polymers derived from new precursors such as 3,4 ethylenedioxythiophene, bithiophenes and precursors with multiples linking sites and 2) synthetic strategies for bandgap control based on the rigidification of the conjugated system either by covalent bridging or through noncovalent interactions.

4:30 PM S3.7

FULL COLOR EMISSION FROM MULTILAYER POLYFLUORENE LIGHT-EMITTING DIODES. J.C. Scott, J.P. Chen, V.Y. Lee, S.A. Swanson, J.R. Salem, W.J. Zhang and R.D. Miller, IBM Research Division, Almaden Research Center, San Jose, CA.

Triple-layer light-emitting diodes, consisting of a crosslinked hole transport polymer, a crosslinked polyfluorene emitter layer and a spin-coated electron transport layer yield efficient, deep blue electroluminescence. By doping the fluorene emitter layer with small molecule dyes such as coumarins, pyrromethenes, pyrans and phenoxazones, at the level of order 1% by weight, emission colors throughout the visible spectrum, including white, are obtained. The performance of such devices is compared with those in which blue OLEDs are coupled with (external) fluorescent color converters.

4:45 PM S3.8

HIGH EFFICIENCY RED POLYMER LIGHT EMITTING DIODES BASED ON ELECTROPHOSPHORENCE. Leonidas C. Palilis, Carsten Giebeler, David G. Lidzey, Ashley J. Caby, Robert B. Fletcher, Paul A. Lane, Donald C. Bradley, Univesity of Sheffield, Department of Physics and Astronomy, Sheffield, UNITED KINGDOM; Diarmuid F. O'Brien, W. Blau, Trinity College, Physics Department, Dublin, IRELAND.

We describe the performance of polymer light emitting diodes employing the red emissive electrophosphorescent material, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum(II) (PtOEP) doped to a variety of concentrations into an emissive poly(9,9-dioctylfluorene) (PFO) host and a blend of PFO with a hole transport material. In this host-guest system, Forster energy transfer of the singlet excitons from the host to the Soret band of the red emitting phosphorescent material is utilised. Light emitting devices prepared from PFO/PtOEP blends showed a maximum external quantum efficiency (QE) of 3.5% and a maximum brightness >100 cd/m^2. We attribute this high quantum efficiency to the capturing of both singlet and triplet excitons by direct charge trapping on the PtOEP molecules which act as both recombination centres and hole traps. In addition, we report that the electroluminescence and the photoluminescence quantum efficiencies show notably different dopant concentration dependencies. Preliminary results obtained by employing another conjugated polymer as a host material will also be reported.

SESSION S4/Q3: JOINT SESSION: ORGANIC LIGHT EMITTER DEVICES

Chair: Paul H. Holloway
Wednesday Morning, April 26, 2000
Metropolitan II (Argent)

8:30 AM *S4.1/Q3.1

FUNDAMENTAL AND PRACTICAL ISSUES IN LARGE-AREA POLYMER PATTERNING FOR POLYMER LED DISPLAYS. J.C. Sturm, F. Pschenitzka, T.R. Hebner, M.H. Lu, B. Diamond and S. Troian.

To achieve a polymer OLED display capable of high efficiency and full color, some patterning of the organic materials is generally required. This talk will discuss both fundamental and practical issues, and how they may be resolved, four different approaches for achieving such patterning over large area: ink jet printing of red, green, and blue-emitting polymers, ink-jet printing of dyes into polymer films, masked thermal diffusion of dyes into polymers, and the patterned dry etching of organic films. The ink-jet printing approaches have the advantage of conceptual simplicity, but their practice is complicated by the fact that one is printing onto an essentially non-absorbing surface (in contrast to paper, e.g.). Thus in both ink-jet printing approaches one must face very fundamental issues associated with the mass transport dynamics within liquid drops during drying due to edge pinning, Marangoni-driven flows, and other related effects. Dry etching has perhaps the highest potential resolution, but one must address issues of pattern formation on top of the organic film for masking and lateral propagation of etching species under masked regions, as well as the sensitivity of devices to ambients once metal contacts have been formed. Patterned thermal diffusion of dyes in practice turns out to be very straightforward and simple in practice, but high quality results are dependent on soft masking technology which still has good dimensional control.

9:00 AM S4.2/Q3.2

ORGANIC LIGHT EMITTING DIODES BASED ON CARBON NANOTUBES DISPERSED IN A CONJUGATED CO-POLYMER MATRIX. R. Czerw, H.S. Woo, S. Webster, A. Date, D.L. Carroll, Clemson Univ, Dept of Physics and Astronomy, Clemson, SC; B. McCarthy, W. Blau, Polymer Research Ctr, Dept of Physics, Trinity College, Dublin, IRELAND.

We present the characteristics of organic light emitting diodes (OLEDs) based on a polymer composite of single wall carbon nanotubes (SWNT) dispersed in a copolymer matrix, poly (m-phenylene vinylene-co-2,5-dioctoxy-p-phenylene) (PmPV). Polyethylene dioxythiophene (PEDOT) was used as a buffer between the anode and the polymer composite. We observed that the turn-on voltage of a device fabricated using this polymer composite with a concentration of 0.1 weight % of SWNT's was significantly lowered with enhanced electroluminescence (EL) as compared to the pure PmPV device, suggesting that the carbon nanotubes act as a minor charge carrier. Our device shows light emission in the range of green with a peak wavelength near 510 nm. However, photoluminescence (PL) of the polymer composite decreased as we increased the SWNT concentration due to increased photon scattering with the SWNT. The device characteristics including the current-voltage relation and efficiency, as well as the PL and EL, will be discussed as a function of the SWNT concentration in the polymer composite.

9:15 AM S4.3/Q3.3

ELECTRON INJECTION IN HOLE DOMINATED POLYMER LIGHT EMITTING DIODES. Luisa D. Bozano, Sue A. Carter, University of California, Santa Cruz, Dept of Physics, Santa Cruz, CA; Phillip J. Brock, Campbell J. Scott, IBM Almaden Research Center, San Jose, CA.

We use MEH-PPV single-layered device sandwiched between polyaniline and aluminum electrodes to obtain Ohmic injection of holes with minimal electron current. The current and light emission are measured as a function of temperature in a range between 200K and 300K. The low electron injection allows treatment of the sample as a hole-only device and hence determination of the relationship between the measured current and applied bias potential in terms of space-charge limited behavior. Because of the Ohmic-hole-injecting contact, the electric field vanishes at the anode while it reaches its maximum value at the cathode. Similarly, the hole density is large near the anode, and therefore, the small number of electrons injected recombine completely. With these approximations, the radiance is proportional to the electron current. We analyze the experimental data to derive the electric field at the cathode for a Pool-Frenkel-like mobility at the different temperatures. The measured radiance then gives the electric field and temperature dependences of the cathode injection current.

10:00 AM *S4.4/Q3.4

ORGANIC LIGHT-EMITTING DIODES USING TRIPHENYLAMINE BASED HOLE TRANSPORTING MATERIALS. Hisayoshi Fujikawa, Masahiko Ishii, Shizuo Tokito, and Yasunori Taga, TOYOTA Central Research & Development Labs., Inc., Nagakute, Aichi, JAPAN.

Light-emitting diodes (LEDs) based on organic materials are attracting much attention as candidates for flat-panel displays and backlights for liquid crystal displays. Recently, a practical multi-color display has been commercialized in small molecular organic materials. However, further research and development are required to improve the lifetime and the color tunability, especially materials developments are significantly important. In this paper, we briefly review the developments of hole transporting materials and the EL properties of the organic LEDs operated at a high temperature[1,2]. The durability of the tris(8-quinolinolato) aluminum based device is related to the thermal stability of the hole transport layer. Several triphenylamine oligomers were synthesized and used for the hole transport layer. The thermal stability was clearly seen to depend on a glass transition temperature (Tg) of the hole transporting material, and a linear relationship between the Tg and the thermal stability was found. A lowering of "turn-on voltage" for light emission and an increase of luminous efficiency with increasing temperature were also observed. Excellent durability of the organic LED with a tetramer of triphenylamine was achieved at a high temperature of 105°C. Our results indicate that the linear linkage of triphenylamine leads to a high Tg and high device performance at high temperatures.

References

[1] S. Tokito, et al., IEEE Trans. Electron Devices, 44, 1239 (1997).
[2] S. Tokito, et al, Thin Solid Films 363, 290 (2000)

10:30 AM S4.5/Q3.5

OPTICAL PROPERTIES OF MICROCAVITY STRUCTURES USING THE ORGANIC LIGHT EMITTING MATERIALS. Boo Young Jung, Nam Young Kim, Chang Hee Lee, Chang Kwon Hwangbo, Inha Univ, Dept of Physics, Inchon, KOREA; Chang Seoul, Inha Univ, Dept of Textile Engineering, Inchon, KOREA.

We investigated the optical properties of Fabry-Perot microcavity with a tris(8-hydroxyquinoline)aluminum Alq$_3$ organic film by measuring the photoluminescence (PL) and transmittance. An Alq$_3$ layer as an active layer was sandwiched between two mirrors, which were metal or (TiO$_2$/SiO$_2$) dielectric multilayer reflectors. A resonant wavelength of [mirror|Alq$_3$|mirror] cavity was designed to be coincided with a peak of PL intensity of [air|Alq$_3$|glass]. We have used two methods to control the resonant wavelength of the cavity; one is to adjust a cavity length and the other is to control the phase change on reflection of mirrors. An Alq$_3$ layer on glass, [air|Alq$_3$|glass], showed a PL peak around 513 nm and its full width half maximum(FWHM) was about 80 nm. Three types of microcavity, such as [air|metal|Alq$_3$|metal|glass], [air|dielectric|Alq$_3$|dielectric|glass], and [air|metal|Alq$_3$|dielectric|glass], were designed and fabricated by a physical vapor deposition method. The result shows that the FWHM of three Fabry-Perot microcavities for *s*- or *p*-polarized waves was reduced to $16\sim27$, $7\sim11$ and $15\sim16$ nm, respectively, and the microcavity structure is expected to improve the efficiency and tunability of emission spectrum in display. Also the reduction on emission spectrum was described in terms of cavity length, incident angle, and phase change on mirror reflection in this paper.

10:45 AM S4.6/Q3.6

NEW EXPERIMENTAL TECHNIQUES PROBING POLYMER LEDs. Dickon Pinner, Richard Friend, Cavendish Laboratory, Cambridge, UNITED KINGDOM; Nir Tessler, EE Department, Technion, Haifa, ISRAEL.

We present a comprehensive and self-consistent analysis of polymer LEDs that combines experimental and theoretical studies. We show that previously illusive properties such as the temporal and spatial evolution of charges and excitons, as well as the internal electric field can be made accessible. Using pulsed excitation we present, for a wide variety of different polymers, results of: i) the mobility of both electrons and holes (from a single device); ii) the temporal evolution of the internal electric field at the recombination zone during the voltage pulse; iii) the temporal and spatial evolution of the recombination zone itself, and; iv) the motion of charges both during and after the application of a pulse. These processes have been investigated on time scales from ns to s. The implications of these results for device applications will be discussed.

11:00 AM S4.7/Q3.7

EXPERIMENT AND MODELING OF CONVERSION OF SUBSTRATE WAVEGUIDED MODES TO SURFACE-EMITTED LIGHT BY SUB- STRATE PATTERNING. Min-Hao M. Lu, Conor F. Madigan, James C. Sturm, Center for Photonics and Optoelectronic Materials, Department of Electrical Engineering, Princeton University, Princeton, NJ.

In a typical OLED, the external quantum efficiency is severely limited by the great mismatch between the indices of refraction of air, glass substrate, ITO and the organic layer $n_{air} = 1$, $n_{glass} = 1.51$, $n_{ITO} = 1.8$, and $n_{org} = 1.67$ for the PVK/PBD/C6 blend used in this work. A large fraction of the light emission is trapped in the glass substrate and ITO/organic layers by total internal reflection. A simple ray optics model, ignoring microcavity effects and diffusive interfacial scattering, predicts $\sim$ 80% of the light is lost to waveguide modes[1], although the actual figure has never been measured experimentally. In this paper we show how backside substrate (non-OLED side) features and high index-of-refraction substrates can be used to raise the external quantum efficiency by a factor of at least 3.0. Furthermore, we measure not only the change in the far-field intensity pattern, but also the change (reduction) in the substrate-waveguided light after the backside features are applied. Thus we can confirm, for the first time, that the ratio of the substrate-waveguided to the surface-emitted fractions in planar devices is well described by ray optics. Finally we will also show experimentally the dependence of the waveguided fraction and potential improvements in efficiency on substrate index of refraction. Although the initial external coupling efficiency is independent of n_{sub}, the limit to which η_{ext} can be raised by substrate patterning is higher for high index substrates. This work is supported by DARPA and NSF.

[1] L.J Rothberg, J. Mat. Res., vol. 11, pp. 3174-3187, 1996.

11:15 AM S4.8/Q3.8

INTERFACIAL EFFECTS ON OPTICAL, ELECTRICAL AND TRANSPORT PROPERTIES OF TRIS-8-HYDROXYQUINOLINE (Alq3)-BASED ORGANIC LIGHT EMITTING DEVICES.

Vincent V. Dinh, Peter Thielen, Univ of California, Davis, Dept of Applied Science, Davis, CA; Gil R. Delgado, Louis J. Terminello, Howard W. Lee, Boyd Taylor, Tony Van Buuren, Art J. Nelson, Nicolas Franco, Lawrence Livermore National Laboratory, Livermore, CA; Christoph Bostedt, Univ Hamburg, Dept of Physics, Hamburg, GERMANY.

We present current-voltage (I-V), photoluminescence (PL), photoluminescence excitation (PLE), and electroluminescence measurements for the ITO/PVK/Alq3/metal structure. In this study, we vary the Alq3 film thickness to isolate the interface effects on the device PL. We also measure the chemistry and bonding structure at the interface using element and chemical state specific synchrotron radiation-based spectroscopies. We present a charge injection and charge transport model for the OLED that is a conclusion of the observation of the measurements. Our results will be discussed within the context of devices performance and lifetime.

11:30 AM S4.9/Q3.9

NEW DENDRITIC MATERIALS AS POTENTIAL OLED TRANSPORT AND EMITTER MOIETIES. Greg Schmett, Asanga Padmaperuma, Linda Sapochak, Department of Chemistry, University of Nevada, Las Vegas, NV; Kimba Ashworth, Luis Madrigal, Benjamin Reeves, Charles W. Spangler, Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT.

Traditionally, organic light-emitting devices (OLEDs) are prepared with discrete layers for hole and electron transport. Different materials must be used for these layers because most materials will preferentially transport one charge carrier more efficiently than the other. In most cases, the emitter material serves a dual purpose as both the emitter and the hole or electron transporter. One of the major failure modes of OLEDs results from thermal instabilities of the insulating organic layers caused by joule heating during device operation. The problem is most pronounced for the hole transporting materials (HTM) which are usually tertiary aromatic amines (i.e., TPD and NPD). This has been attributed to the relatively lower glass transition temperatures (Tg) and resulting inferior thermal stabilities compared to the other materials making up the device. Many researchers have produced HTMs with higher Tgs, but with a corresponding decrease in charge transport properties. Dendritic materials offer the advantages of high thermal stabilities and multi-functionality. Model dendrimers based on bis-(diphenylamino)-E-stilbene subunits as the dendrimer repeat units have been shown to form exceptionally stable bipolaronic dications upon oxidative doping. These charge states can also be photogenerated in the presence of electron acceptors on the picosecond time scale and are currently being evaluated as optical power limiters. Replacement of P for N reduces the capability for bipolaron formation, but substitution of only some of the N atoms in the dendrimer allows the preferential formation of polaronic radical cations. Thus design of the dendrimer can predetermine which charge states dominate the photophysical processes, a key factor in OLED design. Thus we anticipate that dendrimers based on bis-(diphenylamino) and bis-(diphenylphosphino) substituents incorporated into the dendrimer repeat units can possibly function as not only efficient hole transport materials, but also as emitters in various OLED design configurations. We present a systematic study of the luminescence and thermal properties of dendrimers based on the design paradigms discussed above, and will illustrate the efficacy of controlling the P/N substitution patterns in the dendrimer in terms of device performance.

11:45 AM S4.10/Q3.10

RESONANCE PHOTOLUMINESCENCE OF CHELATE-BASED LANTHANIDE COMPLEXES. Xiaowen Li, J. Yuan, K.W. Cheah and W.T. Wong[1], Department of Physics, Hong Kong Baptist University, Kowloon Tong, HONG KONG. [1]Department of Chemistry, Hong Kong University, Hong Kong, PR CHINA.

Recently, there has been a significant interest on organic lanthanide (La) ion complexes due to their potential applications in full color flat displays, diode lasers, sensors, and so on. These complexes have luminescence spectra that are characterized by the absorption of energy by the ligand and the emission originating from the La ion. In the free La-ion, optical intra-4f shell transitions are parity forbidden. Incorporated in a solid host however, the crystal field of the host induces mixing of the states. This makes some of the transitions allowed. These optical transitions are sharp and atomic like, due to the fact that the partially filled 4f shell is shielded by filled 5s and 5p shells. La ions coordinated through an oxygen or nitrogen to organic ligands possess optical properties which closely parallel the properties of the same ions observed in inorganic salts. The photoluminescence excited spectra (PLE), photoluminescence spectra (PL), and time-resolved PL of different Eu^{3+} and Tb^{3+} complexes were studied. When pumped by near ultra-violet light, the complexes emitted sharp and strong emission lines due to the intra 4f transitions of the La ions, accompanied by broad and weak emission originating from the ligand. From the time-resolved PL results, we conclude that the ligand was firstly excited by the excitation photon. Then the La ion was excited via energy transfer from the ligand. Some of the decay times of the luminescence of Tb^{3+} and Eu^{3+} were longer than the lifetimes of those ions implanted in an inorganic host. We explained this as the result of the mutual excitation between the La ion and the ligand because of the close proximity in the emission energy and the corresponding agreement between the decay time of ligand emission and rise time of the lanthanide emission.

SESSION S5: LEDS

Chair: John R. Reynolds
Wednesday Afternoon, April 26, 2000
Metropolitan II (Argent)

1:30 PM *S5.1
ELECTROPHOSPHORESCENCE: A METHOD FOR ENHANCING OLED EFFICIENCY IN BOTH PHOSPHORESCENT AND FLOURESCENT SYSTEMS. Stephen Forrest, Marc Baldo, Department of Electrical Engineering, Princeton University, Princeton, NJ; Mark Thompson, Department of Chemistry, University of Southern California, Los Angeles, CA.

We discuss the use of organic phosphors as means for generating highly efficient, saturated color emission from organic light emitting devices (OLEDs). We have recently discovered that electrophosphorescence[1], coupled with Dexter energy transfer, can lead to red and green light emission in vacuum deposited OLEDs with external efficiencies exceeding 8% and luminance efficiencies of >20 lm/W. While phosphorescence can be extremely efficient at low intensities, due to triplet-triplet annihilation and color center saturation, the efficiency tends to fall off at higher luminance levels. The effects of triplet-triplet annihilation, and how to minimize their effects in large passive matrix displays will be discussed. Furthermore, we show that triplet-triplet annihilation are reduced by using multiply doped phosphor systems. Finally, we show that organic phosphors can be used to enhance the efficiency of flourescent dyes by converting triplet to singlet states prior to energy transfer to the flourescent molecule. M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson and S.R. Forrest, Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices, Nature (London), vol. 395, pp. 151, 1998.

2:00 PM *S5.2
MULTILAYERED POLYMER/INORGANIC COMPOSITES FOR OPTOELECTRONIC APPLICATIONS. Sue A. Carter, Alison Breeze, University of California, Santa Cruz, CA; Alexi C. Arango, E-Ink Corp., Cambridge, MA; David S. Ginley, NREL, Golden, CO; H.H. Horhold, Fredrich Schiller University, GERMANY; U. Scherf, Max Planck Institute, Mainz, GERMANY; P.J. Brock and J.C. Scott, IBM Almaden Research Center, San Jose, CA.

I will discuss how solution processible inorganic charge transporting layers can be used to improve charge injection, transport, and confinement in polymer based optoelectronic devices by taking advantage of the higher mobility, larger dielectric constant, wider range of energy levels, and greater stability of the inorganic layer in comparison to organics.

2:30 PM *S5.3
NANOSTRUCTURED CONJUGATED SYSTEMS FOR OPTOELECTRONICS. Guenther Leising, Technical Univ of Graz, Graz, AUSTRIA.

ABSTRACT NOT AVAILABLE

3:30 PM *S5.4
FAST SYNTHETIC ENTRY TO ROBUST CONJUGATED POLYMERS FOR SEMICONDUCTOR DEVICE APPLICATIONS. Yongsheng Chen, Meng Hong, Fred Wudl, University of California, Dept of Chemistry and Biochemistry, Los Angeles, CA.

We will describe the efficient (very low number of synthetic steps) preparation of novel highly luminescent and non-luminescent conjugated polymers. The luminescent polymers are based on anthracene and the non-luminescent ones on a very robust PITN derivative. We will also describe the preparation of novel, blue luminescent poly(acrylates) and poly(methacrylates).

4:00 PM *S5.5
ELECTROPHOSPHORESCENT ORGANIC LEDS. Mark E. Thompson, Sergey Lamansky, Peter Djurovich, Andrew Murphy, Department of Chemistry, University of Southern California, Los Angeles, CA; Stephen R. Forrest, Marc Baldo, Paul Burrows, Department of Electrical Engineering, Princeton University, Princeton, NJ.

In order to use organic light emitting diodes (OLEDs) in display applications it is important to be able to accurately tune the color of emission. Doping of OLEDs with fluorescent dyes has been known for many years as a useful means to control the color of OLEDs. Unfortunately, the use of a fluorescent dye leads to an upper limit of 25% on the internal quantum efficiency, due to the small fraction of singlet excitons created on hole-electron recombination. The use of phosphorescent dopants, however, allows the efficient utilization of both singlet and triplet excitons, removing the 25% upper limit on the internal efficiency. We have fabricated saturated red, orange, yellow and green OLEDs, utilizing phosphorescent dopants. The quantum efficiencies of these devices are quite good, with measured external efficiencies as high as 10% (internal eff. > 40%). The phosphorescent dopants in these devices are heavy metal containing molecules (i.e. Pt, and Ir), prepared as both metalloporphyrins and organometallic complexes. The high level of spin orbit coupling in these metal complexes gives efficient emission from triplet states. In addition to emission from the heavy metal dopant, it is possible to transfer the exciton energy to a fluorescent dye, by Förster energy transfer. The heavy metal dopant in this case acts as a sensitizer, utilizing both singlet and triplet excitons to efficiently pump a fluorescent dye. I will discuss the important parameters in designing electrophosphorescent OLEDs as well as their strengths and limitations.

4:30 PM S5.6
DESIGN OF POLYMERIC LIGHT EMITTING DIODES. Mary Galvin, Materials Science and Engineering Dept., University of Delaware, Newark, DE.

One of the applications of organic thin films is in polymeric light emitting diodes. In order to make high-efficiency, flexible LEDs, new polymers with improved luminescence and electron-transporting capabilities are required. This talk will describe some of the critical variables for designing polymers for LEDs.

4:45 PM S5.7
RECENT DEVELOPMENT IN NOVEL CONJUGATED POLYMERS FOR SINGLE-LAYER LIGHT-EMITTING DIODES. Zhonghua Peng, Yongchun Pan, Bubin Xu, Jianheng Zhang, University of Missouri-Kansas City, Dept of Chemistry, Kansas City, MO.

Two basic requirements for the emissive material in a single-layer LED device are high solid-state photoluminescence (PL) quantum efficiency and balanced charge injection/transport properties. We have previously found that introducing 2,5-di(2-biphenyl)-1,4-phenylene (DBPP) into the main chain of a conjugated polymer backbone can dramatically improve its solid-state PL quantum efficiency. We have also reported that incorporating oxadiazole units as main-chain substituents can significantly enhance its electron-transporting properties. However, the resulting polymers did not lead to appealing single-layer LED devices. The puzzle derives from the fact that when one property (such as electron injection) is improved, the other essential property (such as PL efficiency) is decreased. In this presentation, we report our recent work in developing conjugated polymers for single-layer LEDs. We show that a conjugated polymer containing both DBPP and oxadiazole units may possess both high PL efficiency and improved electron-injection properties. We also present our studies on a novel new type of conjugated polymers, 1,5-naphthalene-based conjugated polymers.

SESSION S6: POSTER SESSION

Chair: Mary Galvin
Wednesday Evening, April 26, 2000
8:00 PM
Metropolitan Ballroom (Argent)

S6.1

OLIGO(PHENYLENEVINYLENE)S WITH 1,3,4-OXADIAZOLES IN THE MAIN CHAIN: GOOD SOLUBLE PHOSPHORS WITH INCREASED ELECTRON AFFINITY. Heiner Detert, Erli Sugiono, Johannes Gutenberg-University, Institute of Organic Chemistry, Mainz, GERMANY.

1,3,4-Oxadiazoles with aromatic substituents in the 2- and 5-position are compounds with wide technical importance. Their fluorescence is used in szintillators and optical whiteners, their semiconducting properties made them valuable electron conducting layers in Organic Light Emitting Diodes (OLED). The chemistry and photochemistry of stilbenoid compounds is well known, their application profile ranges from anthelmintics to emissive layers in LEDs. We present the synthesis and electronic spectra of a series of good soluble oligo(phenylenevinylene)s with 1,3,4-oxadiazoles in the main chain. The Huisgen reaction of tetrazoles and fumaroyl chloride reveals a simple and mind route to (E)-1,2-bis (5-aryl-1,3,4-oxadiazolyl) ethenes, X-ray and NMR prove a high degree of planarity of the entire conjugated unit. Using starting materials substituted with stilbenes and higher oligomers leads to compounds with extended conjugation and varying positions of the oxadiazoles. The electron deficient heterocycles increase the electron affinity of these highly luminescent PPV type phosphors, reducing the barrier for electron injection from aluminium cathodes in LEDs.

S6.2

STILBENOID PHOSPHORS FOR LEDS WITH INCREASED ELECTRON AFFINITY. Heiner Detert, Erli Sugiono, Johannes Gutenberg-University, Institute of Organic Chemistry, Mainz, GERMANY.

The preparation of LEDs with poly(dialkoxy-p-phenylenevinylene)s as the emitting material is well established. Due to their low electron affinity and small band gap, these materials show high barriers for electron injection from aluminium cathodes and are sensitive to oxidation. Vinylene substitution with cyanide is a simple and efficient way to increase the electron affinity of PPVs, but also to reduce the fluorescence quantum yields greatly. We are studying the relationship between structural variation (chain length, degree and type of substitution) of monodisperse oligomeric phenylenevinylenes (OPVs) and their electron-, PL-, and EL-spectra. In order to improve the EL efficiency, the electron affinity of the model compounds is increased by reduction of the degree of substitution with alkoxy side chains and by introduction of electron withdrawing substituents. Besides vinylene cyanides we focused our work on substitution of the aromatic subunits with electron acceptors like cyanides, sulfones, trifluoromethyl groups, and 1,3,4-oxadiazoles in order to increase the electron affinity of the phosphor. The influences of the different electron withdrawing groups in varying positions are discussed using an OPVs with five aromatic rings as a model compound carrying two alkoxy groups on the central ring to ensure good solubility.

S6.3

RELATION BETWEEN CHEMICAL STRUCTURE AND LUMINESCENT PROPERTIES OF MODIFIED POLY(1,3,4-OXADIAZOLE)S. Yvette Kaminorz, Ludwig Brehmer, University of Potsdam, Physics of Condensed Matter, Potsdam, GERMANY; Burkhard Schulz, University of Potsdam, Interdisciplinary Research Center of Thin Organic and Biochemical Films, Potsdam, GERMANY.

Poly(1,3,4-oxadiazole)s are already known as electron transport material, but they also attract attention as luminescent material in light emitting diodes because of their high thermal and hydrolytic stability and fluorescence in the blue and green spectral range $^{1-4}$. Poly(p-phenylene-1,3,4-oxadiazole) shows photoluminescence at about 490 to 500 nm but it is insoluble and therefore it is difficult to prepare thin, homogeneous and pinhole-free films. We report the optical and electrical properties of modified poly(1,3,4-oxadiazole)s. The systematic modifications were done to improve the solubility in common organic solvents and preserving the photoluminescence properties at the same time. Moreover, these polymers should be optimised as electroluminescence active materials.
Poly(1,3,4- oxadiazole)s have been functionalised by introducing amidic-bound alkyl side chains so that the solubility in amidic solvents could be improved and thin homogeneous films were preparable by spin coating. By introducing silicon-containing units, the film forming properties as well as the electrochemical stability have been further improved. The optical behaviour, i.e. absorption, photo- and electroluminescence of single layer devices has been investigated and a maximum quantum efficiency of 0.04% has been obtained for a blue emitting LED with ITO and aluminium electrodes. The third group of modified poly(1,3,4-oxadiazole)s contains diphenyl-1,3,4-oxadiazole units in the main chain or as side chains. We found that the optical properties of these polymers are mainly determined by the diphenyl-1,3,4 oxadiazole unit.
The experiments have shown, that the modified poly(1,3,4-oxadiazole)s are quite promising candidates as blue emitting material and optimisations in multi-layer devices could lead to a more balanced charge injection and transport and therefore to a further increase in luminescence intensity and quantum efficiency.

1. T. Tsutsui, E. Aminaka, and H. Tokuhisa, Synth. Met. 85, 1201 (1997).
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3. W. Huang, H. Meng, W. -L. Yu, J. Gao and A.J. Heeger, Adv. Mat. 10, 593 (1998).
4. S. Wang, W. Hua, F. Zhang and Y. Wang, Synth. Met. 99, 249 (1999).

S6.4

PROCESSING DEPENDENCE OF EMISSIVE POLYMER EFFICIENCY. Christine Liberatore, Rachel Jakubiak, Yi Li, Lewis Rothberg, Univ of Rochester, Dept of Chemistry and the NSF Center for Photoinduced Charge Transfer, Rochester, NY.

Electroluminescent conjugated polymers are of particular interest to the display industry due to their unique processing capabilities. Morphological changes induced by variations in processing conditions are evident in polymer film photoluminescence spectra and quantum yields. This is due to a high yield of nonemissive interchain photoexcitations that are formed in ordered regions of the film. We illustrate a direct measurement of the prevalence of the interchain excitations that can be used to determine the film quality, and we use this measure to study a variety of processing conditions.

S6.5

DEVICE PERFORMANCE AND POLYMER MORPHOLOGY IN POLYMER LIGHT EMITTING DIODES: THE CONTROL OF THIN FILM MORPHOLOGY AND DEVICE QUANTUM EFFICIENCY. Yijian Shi, Jie Liu, Yang Yang, University of California Los Angeles, Dept of Materials Science and Engineering, Los Angeles, CA.

We present the results of a systematic study on how the process conditions of spin-coating affect the morphology of the polymer thin films, and how the morphology affects the polymer light-emitting diode (LED) performance. Our results have clarified several misunderstandings in this field. First, the emission peak of MEH-PPV (poly(2-methoxy-5-($2'$)-ethyl-hexyloxy)-1,4-phenylene vinylene) films at ∼630 nm is mainly due to an interchain species rather than the vibronic structure. Second, the quantum efficiency of MEH-PPV based light-emitting diodes has a strong correlation with the morphology of the thin film. Third, the formation of interchain species does not always quench the emission but in certain cases it can enhance the quantum efficiency of polymer LEDs. Our findings indicate that proper aggregation of the polymer chains, which is controlled by the proper selection of solvent, polymer concentration, and spin speed, is essential in order to achieve the highest electroluminescence quantum efficiency.

S6.6

DEVICE PERFORMANCE AND POLYMER MORPHOLOGY IN POLYMER LIGHT EMITTING DIODES: THE CONTROL OF THE DEVICE ELECTRICAL PROPERTIES. Jie Liu, Yijian Shi, Yang Yang, University of California-Los Angeles, Department of Material Science and Engineering, Los Angeles, CA.

We have already demonstrated that the morphology of a spin-cast polymer film can be controlled by the proper selection of solvent, concentration, and the rotational. In this paper, we studied the correlations between the morphology and the electrical properties of MEH-PPV based light emitting diodes. The performance of these devices shows a strong correlation with the processing conditions for spin-casting. It is found the aromatic solvents and non-aromatic solvents have opposite effects on the device performance, which suggests that the solvation effects play an important role in controlling the conformation or aggregation states of the polymer chains. In addition, the centrifugal force can markedly change the shape of the emission spectra and the quantum efficiency of the device. Moreover, the electrical properties of the film, such as the charge injection/transportation properties, are also affected by the solvent and spin speed. For polymer films spun with non-aromatic solvents at lower spin speeds, hole injection and/or transportation is poor. As a result, the device quantum efficiency is low since the injections of hole and electron are unbalanced. In addition, we also studied the influences of morphology on the photovoltaic effects of MEH-PPV and C60 composite devices. It was shown that the non-aromatic solvent (such as Tetrahydrofunan) composite devices have lower photoconductivities and larger open-circuit voltages than aromatic solvent devices (such as Dichrolobenzene). The poor photoconductivity comes from the fact that charge carriers are difficult to be transported along the polymer matrix and meanwhile the higher open circuit voltage results from the reduction of the effective interface area available for the electrons photo-generated under illumination transferring from MEH-PPV to C60 in non-aromatic solvent devices.

S6.7

Abstract Withdrawn.

S6.8

PHOTOVOLTAIC EFFECTS OF C_{60} POLYMER/CONDUCTING POLYMER HETEROJUNCTIONS. Matthias Ramm, Masafumi Ata, Sony Corporation, Frontier Science Laboratories, Yokohama, JAPAN.

The ultrafast photoinduced electron transfer from conducting polymer to C_{60} has suggested the design of organic solar cells with relatively high efficiencies[1]. We studied organic donor-acceptor (D-A) and donor excitonic middle layer-acceptor (D-M-A) based solar cells using C_{60} polymer as acceptor layer. C_{60} was polymerized using the plasma deposition technique[2]. Three different D-A cells were prepared: Plasma deposited tetrathiofulvalene (TTF)/C_{60} polymer, polythiophene (PTP)/C_{60} polymer, phthalocyanine (PC)/C_{60} polymer. The investigated D-M-A cell consisted of PTP/PCSC_{60} polymer. The band structures were determined by photoelectron emission investigations and optical absorption measurements using a Tauc-type approximation. The l-V characteristics were investigated under dark conditions and under photoirradiation. We observed a clear increase of the current density under photoirradiation. The efficiency of the devices can be improved by: 1. Control of the thickness of the films deposited under plasma conditions. 2. Increased conductivity of the films.

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S6.9

ELUCIDATION OF STRUCTURAL EFFECTS AT THE METAL CATHODE/TRIS(QUINOLATO)ALUMINUM INTERFACE. Chongfei Shen, Ian G. Hill, Antoine Kahn, Princeton University, Dept of Electrical Engr, Princeton, NJ; Jeffrey Schwartz, Princeton University, Department of Chemistry, Princeton, NJ.

The reaction chemistry between tris(quinolato)aluminum (Alq3) and superdeposited metal atoms can affect the interface between this organometallic photoemitter and the cathode of an OLED. The structure of the Alq3/cathode interface, the formation of metal ions resulting from the cathode deposition process, and the possibility that these cations might diffuse through the emitting layer, could affect the performance of an OLED. Because of the prevalence of Alq3 in such devices, theoretical treatments of its reaction with Li, K, Mg and Ca have been reported, and some experimental observations have been noted. But, although Mg/Ag is the most commonly used contact, no experimental studies have been reported heretofore which correlate spectroscopic observations with the chemistry of reaction of Mg atoms and Alq3. Theoretical and experimental treatments described in the literature focus on consequences of metal atom deposition for the N of the quinolate ligands; these treatments do not describe any changes at either the O of the ligand, or of the Al. Although alkali and alkaline earth metals have varying propensities toward formation of carbon-metal bonds, these studies ignore the possibility that organometallic species might be the primary reaction products of Alq3 with several of these metals. Coordination lability of metallic cations formed concomitantly with Alq3 reduction, which is related to cation mobility, has not been addressed. We have studied the deposition of Mg and of Al onto thin films of Alq3, and we have found, by XPS, that strong changes do in fact occur both at O and at the Al (of the Alq3); these changes vary as a function of the superdeposited metal. Experimental results and theoretical descriptions involving all key atoms will be presented, and the roles of organometallic complex formation with certain of these metals, and their O coordination tendencies will be described.

S6.10

INTRINSIC PERFORMANCE LIMITS OF PENTACENE FIELD-EFFECT TRANSISTORS. J.H. Schoen, Ch. Kloc, B. Batlogg, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

The electrical performance of organic field-effect transistors has now reached levels comparable to amorphous silicon devices. Among the different organic materials studied for electronic applications pentacene has demonstrated high mobilities (above 2 cm^2/Vs) and high on/off ratios (exceeding 10^8). In this study we focus on intrinsic performance limits based on measurements of single crystalline devices. Room temperature mobilities as high as 2.8 cm^2/Vs and on/off ratios in the order of 10^9 are achieved for single crystalline samples. Sub-threshold swings as low as 200 meV/decade are observed. The mobility increases with decreasing temperature up to 1200 cm^2/Vs. In contrast to that, thermally activated transport is seen in polycrystalline devices. However, room temperature mobilities exceeding 2 cm^2/Vs can be observed in these devices, too, if the trap concentration at the grain boundaries is sufficiently low (small barrier). Furthermore, bulk properties of the material are investigated by space charge limited current measurements in order to examine defect concentrations and charge carrier mobilities. In addition, thin film devices on polyimide substrates are prepared. Their performance is compared to single crystal transistors and the differences are analyzed taking into account extrinsic effects like trapping of barrier formation at grain boundaries.

S6.11

EPITAXIAL GROWTH OF HEXABENZOCORONENE ULTRA-THIN FILMS FROM SOLUTION. Paolo Samorí, Humboldt University, Berlin, Department of Physics, Berlin, GERMANY; Matthias Keil, William R. Salaneck, Linkoeping University, Department of Physics, Linkoping, SWEDEN; Klaus Müllen, MPI for Polymer Research, Mainz, GERMANY; Jürgen P. Rabe, Humboldt University, Berlin, Department of Physics, Berlin, GERMANY.

Benzocoronenes are novel synthetic disc like nano-graphene molecules which are of potential use for the development of molecular nanowires. Interestingly their electronic properties as well as their self-assembly into supramolecular architectures can be tuned by varying the size of the aromatic framework and the chemical functionalization in the peripherical positions. In particular, soluble hexa alkylated-peri-hexabenzocoronene (HBC) can form a discotic liquid-crystalline phase with a remarkably high charge carrier mobility (0.13 cm^2/Vs). Our interest converges on the formation of columnar supramolecular aggregates in dry thin films making use of intermolecular interactions, in particular π-π stacking. We have grown highly ordered layer architectures from solutions. Complementary insights into the molecular order in these films have been gained with Tapping Mode - Scanning Force Microscopy and angle-resolved photoemission measurements. It is found that HBC can self-assemble into layers on highly oriented pyrolitic graphite (HOPG) with the molecular discs lying preferentially flat on the basal plane of the substrate. Varying parameters in the film preparation we could control the rate of the molecular self-assembly. At very slow speeds we produced layers aligned preferentially along the crystallographic axes of HOPG. This suggests that the growth of this molecular systems on crystalline conductive substrates is kinetically governed, leading to a hetero-epitaxial type of growth.

S6.12

ORIENTATION INDUCED MOLECULAR RECTIFICATION IN POLYMER PHOTOVOLTAIC DEVICES: IMPROVEMENT OF DEVICES EFFICIENCY. Carole Sentein, Céline Fiorini, André Lorin, Paul Raimond, Jean-Michel Nunzi, LETI (CEA-Technologies Avancées), DEIN-SPE, Groupe Composants Organiques, Centre d'Etudes de Saclay, Gif-sur-Yvette, FRANCE; Igor F. Perepichka, National Academy of Sciences of Ukraine, Institute of Physical Organic and Coal Chemistry, Donetsk, UKRAINE.

In the field of organic semiconductor devices, such as electroluminescent diodes or photovoltaic cells, a rectifying junction is mandatory to improve the efficiency. In order to build single polymer film photovoltaic cells, we realize an equivalent distributed p-n junction in a polymeric monolayer. For this purpose, we propose an inter-disciplinary principle derived from the application of nonlinear optical techniques to the technology of polymer semiconductors. We give experimental evidence that molecular rectification induced in an oriented amorphous polymer bearing polar chromophores improve the efficiency of polymeric semiconductor devices such as photovoltaic solar cells. One of the major advantages of such a principle is that the depletion zone, in which the majority of charge separation processes takes place, extends over the whole polymer film thickness, as opposed to classical p-n junction devices which are limited by a weak extension of the depletion zone (10 to 50nm). In this way, the entire thickness of the film should participate to the photovoltaic effect. Moreover, rectification implies storage of an internal field, thus reducing potential barriers for charge extraction at both electrodes. Reduction of potential barriers may also slow down oxydo-reduction reactions occurring spontaneously at non-ohmic metal-polymer junctions, thus slowing down device degradation. Orientation is performed through DC-field ordering of the polar molecules contained in the polymer. Second harmonic generation is used as a probe of the molecular order. Next step concerns the optimization of the sample orientation parameters, i.e., orientation-field, sample temperature, poling duration and cooling conditions to achieve the largest stable orientation. In this respect, Schottky-type photovoltaic cells were realized with different polymers as an isotropic binder, and different polar molecules were tested with diverse acceptor and donor groups.

S6.13

PERIODICALLY STRUCTURED POLYMERS FOR TUNABLE LASER APPLICATIONS. Vincent Dumarcher, Licinio Rocha, Celine Fiorini, Christine Denis, Jean-Michel Nunzi, LETI-CEA Saclay, Organic Devices Group, Gif-sur-Yvette, FRANCE; Frank Sobel, Bouchta Sahraoui, Denis Gindre, POMA, Angers, FRANCE.

Patterning and micro-structuring of functional polymers are key technologies to fabricate organic devices. More particularly, one challenging issue today is to pattern and micro-structure organic devices in order to control the emission properties of polymer thin films such as the one used for electroluminescent diodes. A control of the radiation modes of electroluminescent diodes has already been demonstrated using planar microcavities. Following the idea first demonstrated by Kogelnik and Shank, we propose to implement a Distributed FeedBack (DFB) scheme where efficient feedback is obtained from a spatial modulation of both gain and index of refraction of the polymer film. We have investigated the luminescence and lasing properties of dye-doped and semi-conducting polymer thin films by making a dynamic grating using the interference fringes from two pump beams inside the polymer film. Narrow-band emission was tuned simply by changing the angle between the pump beams incident onto the polymer film. Transient index and gain modulation is achieved through photo-induced periodical excitation with the interference pattern produced by the two coherent laser beams. Features related to optical confinement and waveguiding in polymer thin-film DFB lasers will be evidenced and discussed. Several luminescent polymers and waveguide configuration can be studied and evaluated easily using this technique. Next step is to draw permanent gratings in polymers to check their lasing properties. In this respect, photoinduced patterning of surface-relief gratings using laser-controlled molecular motion appears to be an interesting route.

S6.14

SOLID ELECTRIC FIELD INDUCED SECOND HARMONIC GENERATION (SEFISHG): AN ORIGINAL TECHNIQUE FOR THE IN-SITU EVALUATION OF THE INTERNAL FIELD EXISTING IN A SEMICONDUCTOR STRUCTURE. Carole Sentein, Céline Fiorini, André Lorin, Paul Raimond, Jean-Michel Nunzi, LETI (CEA-Technologies Avancées), DEIN-SPE, Groupe Composants Organiques, Centre d'Etudes de Saclay, Gif-sur-Yvette, FRANCE.

Improvement of the efficiency of organic semiconductor devices such as photovoltaic cells requires the existence of a rectifying junction. Rectification implies existence of an internal field thus improving charge separation and transport, and reducing potential barriers for charge extraction at both electrodes. Experimental evidence was recently given for molecular rectification in an oriented amorphous polymer incorporating polar diode-like chromophores [1]. Orientation was performed through DC-field ordering of the polar molecules contained in the polymer. Polar organization of molecular diodes is equivalent to the build-up of a distributed p-n homojunction within a single polymer film. Most interesting is that unlike the case of classical devices, the junction extends over the whole polymer thickness. An increase of the photovoltaic efficiency by a factor of 40 was demonstrated following orientation induced molecular rectification [2,3]. Optimization of both the polymer binder and the polar and photosensitive molecules is currently under process. For this purpose, monitoring of the orientation induced internal field is mandatory. Use of Solid Electric Field Induced Second Harmonic Generation (SEFISHG) measurements will be reported. Considering both second and third order optical nonlinear processes, SEFISHG can indeed be shown to provide evaluation of the internal field stored inside the structure after diode-like molecules orientation [4].

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[3] C. Sentein et al., Proceedings of SPIE, Vol. 3623 (1999) 80.
[4] C. Fiorini et al. , in preparation.

S6.15

SOLID STATE THERMOLYTIC AND CATALYTIC REACTIONS REGIOREGULAR POLYTHIOPHENES. Jianfei Yu, Steven Holdcroft, Simon Fraser Univ., Dept. of Chemistry, CANADA.

Thermolytic cleavage of tetrahydropyran from poly(3-(2-(2-tetrahydro- pyrany- loxy)ethyl)thiophene) occurs with a remarkably high yield in the solid state. Deprotection can be achieved catalytically in the presence of acids, at a significantly lower temperature. An increased degree of conjugation persists upon removal of the THP group. Copolymer films containing the 3-(2-(2-tetrahydropyranyloxy)ethyl group participate in similar reactions but exhibit a melting transition and a subsequent decrease in coplanarity at high temperatures. This disorder prevails upon cooling due to either strong inter-chain H-bonding or the absence of crystallizable side chains. When deprotection is carried out at lower temperatures, a high degree of delocalization can be retained. The influence of composition on the reactivity of the polymers is described.

S6.16

PERYLENE/POLYTHIOPHENE BLEND PHOTOVOLTAIC CELLS. Janke J. Dittmer, Elisabeth A. Marseglia, Richard H. Friend, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM.

The photovoltaic properties of blends of a soluble perylene dye and the soluble conjugated polymer poly(3-hexyl thiophene) are reported. Strong quenching of the photoluminescence on blending provides evidence for photo-induced charge transfer at the interface between the two materials. The photovoltaic response of these blends was measured as a function of blend ratio and thickness in sandwich cells between indium tin oxide and aluminium electrodes, and in all cases the external quantum efficiency (EQE) and the fill factor were considerably enhanced with respect to devices made from corresponding single materials. The most relevant features of this new class of dye/polymer blend are: 1) The highest EQE of about 7% is achieved for devices containing 80% by weight of the perylene dye, 2) the perylene dye forms an electron conducting crystal network, and 3) the EQE is further increased upon thermal annealing.

S6.17

SPACE CHARGE LIMITED CURRENTS IN A DOPED AND DEPLETED CONDUCTING ORGANIC MATERIAL. Suresh C. Jain, Wim Geens, Jozef Poortmans, Robert Mertens, IMEC, Leuven, BELGIUM; Magnus Willander, Chalmers Univ of Technology, Dept of Physics, Göteborg, SWEDEN.

In 1940 Mott and Gurney studied the transport of charge carriers in insulating wide-bandgap crystals such as NaCl [1]. When a voltage is applied on the insulating crystal, electrons are injected. The concentration of the electrons is large at the contact near the cathode and decays rapidly with distance creating a space charge. As used in the recent literature, the Space Charge Limited Current (SCLC) density J and the applied voltage V are related as $J = \frac{9}{8}\mu\ \epsilon\ \epsilon_0 \frac{V^2}{L^3}$. We have studied electrical properties of the Schottky diodes using thin organic active layers. The thickness of the active layers is L=0.1 μm and the layer is doped p-type. The layer is so thin that whole of it is depleted of carriers due to the Schottky junction at the cathode. In forward bias electrons are injected from the low work function metal Schottky contact at the cathode and holes are injected from the ITO anode which makes approximately an Ohmic contact. Coupled Poisson and transport equation are solved taking the space charge due to ionized acceptors into account. Computer plots of J-V are obtained. At the low voltages the drop of voltage across the Schottky junction is a very large fraction of the applied voltage which results in a Shockley like current-voltage relation. At high voltages the current varies as V^2. Results of measurements of I-V curves on the Al/oligo-PPV/ITO Schottky diodes, fabricated by us, are in complete agreement with the predictions of the theory.

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S6.18

INVESTIGATION OF AGING INDUCED TRAPS IN ORGANIC SEMICONDUCTORS. Juergen Steiger, Siegfried Karg, Heinz von Seggern, Darmstadt University of Technology, Materials Science Department, Darmstadt, GERMANY.

The performance of organic semiconductor devices such as light emitting diodes (OLEDs) and field effect transistors (OFETs) is strongly influenced by the presence of electronic traps. Such traps can be assigned responsible for the buildup of internal fields and reduced carrier mobilities which negatively influences device parameters such as driving voltages, efficiencies and response times. In this paper the influence of different aging processes on the occurrence of traps, their quantity and energetic depth in electron and hole transporting materials such as Alq_3, α-NPD, and Naphdata is investigated. The aging is forced by storing the OLEDs in various atmospheres or by device operation. The methods employed to investigate the trap structure and the evolution are the thermally stimulated current (TSC) and thermally stimulated luminescence (TSL) techniques. These methods yield the trap energy of discrete levels and give an estimate for the trap concentration. Moreover, continuous trap distributions can be analyzed by the fractional glow technique. It will be demonstrated that specific changes in the trap spectra are related to a shift in the current voltage characteristics of the respective devices. The nature of such electronic traps will be discussed.

S6.19

DEGRADATION STUDIES OF TRANSPARENT ORGANIC LIGHT EMITTING DEVICES. Dmitry Kolosov, Mark E. Thompson, Dept of Chemistry, Univ of Southern California, Los Angeles, CA; Doug English, Paul F. Barbara, Dept of Chemistry and Biochemistry, Univ of Texas at Austin, Austin, TX; Vladimir Bulovic, Stephen R. Forrest, Dept of Electrical Engineering, Princeton University, Princeton, NJ.

We present electroluminescence degradation studies on tris-(8-hydroxyquinoline) aluminum (Alq_3)-based transparent organic light emitting devices (TOLEDs). The devices were not encapsulated and were investigated under room ambient conditions. Spatially correlated topological and electroluminescence properties of the TOLEDs are monitored in real time via electroluminescence microscopy in conjunction with atomic force microscopy. Two different "slow" and "fast" failure modes are examined. The investigation reveals no cathode surface defects causing formation of nonemissive areas. Evolution of the nonemissive dark spots in the devices leads to degradation of cathode surface through formation either "volcanoes" or "elevated bubbles" depending on experimental conditions. Final device failure is accompanied by total change of cathode surface topography with signs of gas evolution and layer delamination.

S6.20

CONCENTRATION DEPENDENCE OF PHOTOLUMINESCENCE QUANTUM EFFICIENCY IN A TWO DYE COLOR CONVERTER. W.J. Zhang, P.P. Pizzo, Dept. of Materials Engineering, San Jose State University, San Jose, CA; J.P. Chen, S.A. Swanson, J.R. Salem and J.C. Scott, IBM Almaden Research Center, San Jose, CA.

Fluorescent color conversion, using dye doped polymer thin films, is one of the proposed methods of achieving full color in organic light-emitting diodes (OLED) displays. In order to optimize simultaneously the optical density and photoluminescent efficiency, a doubly dye doped system is preferable to a single dye. In this study, we examine coumarin 334 (C334) as the host (absorber) dye and pyrromethene 580 (Py580) as the guest (emitter) dye at various concentrations in a PMMA matrix. The PL quantum efficiency was measured using a modified integrating-sphere method. We find that the addition of a small amount of Py580 into the host C334 improves the PL quantum efficiency in the two-dye system. The PL quantum efficiency of this two-dye system is strongly dependent on the concentration of C334, but weakly on that of Py580. Higher concentration of C334 increases the optical density, but still somewhat decreases the PL quantum efficiency. The results are interpreted in terms of Förster energy transfer and the competition between exciton diffusion to a Py580 molecule and to a non-emissive (quenching) site.

S6.21

PREPARATION OF NEW METAL IONIC CONDUCTING POLYMER BASED ON POLY(PROPYLENE CARBONATE METHACRYLATE) AND OXYMETHYLENE LINKED POLY(ETHYLENE OXIDE). Young Mi Kim and Myung D. Cho, Electrochemistry Lab, Samsung Advanced Institute of Technology, Suwon, KOREA.

New plasticized ionic conducting polymer membrane was prepared with poly (propylene carbonate methacrylate) (PCMA) and oxymethyl linked poly(ethylene oxide) (mPEO) by using UV and heat cross linking techniques. Poly(propylene carbonate metharcylate) and oxymethyl linked poly(ethylene oxide) were synthesized and verified structures with NMR and IR spectroscopy. The prepared ionic conducting membrane was analyzed with various electrochemical tools and applied to lithium polymer battery. The PCMA and mPEO based polymer membrane was prepared with addition of 50wt% of 1M $LiPF_6$ in ethylene carbonate(EC)/propylene carbonate(PC) mixture into a PCMA and mPEO polymer matrix. The EC/PC liquid electrolyte is working as a plasticizer which reduce high crystallinity of PCMA polymer matrix. This plasticized PCA membrane shows excellent mechanical and electrochemical stability in wide ranges of electropotential windows at 0∼5.0V. The obtained PCMA membrane shows ionic conductivity as high as 6×10^{-4}S/cm at the ambient temperature. In terms of ionic conductivity on polymer membrane, the effects of plasticizer in crystalline polymer have been proved through many previously published papers. In addition to increasing ion conductivity by plasticizing effects of PCMA, the propylene carbonate group on PCMA polymer which keep high dielectric constant of polymer matrix itself. In this paper, the effects of plasticizer in the PCMA and mPEO matrix will study and will discuss about the applications of lithium polymer battery with this PCMA and mPEO ionic conducting polymer electrolyte.

S6.22

SYNTHESIS AND CHARACTERIZATION OF POLYIMIDE-BASED LUMINESCENT THIN FILMS. Sara Carturan, Gianluigi Maggioni, National Inst of Nuclear Physics, National Lab of Legnaro, Legnaro (Pd), ITALY; Alberto Quaranta, Gianantonio Della Mea, Univ of Trento, Dept of Materials Engineering, Mesiano (Tn), ITALY.

Thin films of dye containing fluorinated polyimide have been obtained by a two step solvent based method. Soluble precursors and dye molecules have been spin coated on silica and silicon substrates, providing thin films of thickness ranging from 0.5 to 10 micron. 6FDA (4,4'-hexafluoroisopropylidene bis phthalic anhydride) and DAB (diaminobenzophenone) have been used as precursor monomers and rhodamine B as dye. Dye concentration ranging from 0.5 to 1.5 mol% has been chosen in order to obtain a dipole-dipole energy transfer mechanism between the matrix and the dye molecule. The films have been characterized by UV-Visible absorption spectroscopy, excitation and emission fluorescence spectroscopy and FT-IR absorption spectroscopy. The film structure and the light emission process have been studied as a function of the production parameters. In particular the dependence of the optical emission features on the curing temperature and dye concentration has been investigated.

S6.23

CONDUCTING POLYPYRROLE DOPED WITH PHTHALOCYANINESULFONATES - NEW MATERIALS FOR CHEMICAL SENSORS. Günter Appel, Ricardo Pablo Mikalo, Dieter Schmeisser, Brandenburgische Technische Universität Cottbus, Department of Applied Physics - Sensoric, Cottbus, GERMANY.

Polypyrrole - a conducting polymer - is used as an active electrode of a quartz micro ballance and considered as a gate electrode in all-polymer field effect transistors used as chemical sensor. We use substituted phthalocyanines as dopants as they offer the possibility to enhance the dopant concentration as well as to include functionalized groups. We studied films of polypyrrole which were doped with tosylate or sulfonated phthalocyanines by photoelectron spectroscopy, NEXAFS, PEEM, and TEM. These investigations revealed that both, the electronic structure, and the morphology are highly dependent on the dopant's structure. We suggest a new charge transport model for 5-ring heterocycle conductive polymers. Whereas in the standard model only the carbon backbone is considered for the charge transport, we found by NEXAFS investigations that - depending on the structure of the polymer and the dopant - the heteroatom has a considerable high participation in the gap states, which are responsible for the charge transport. Our data demonstrate for the first time, that large organic counterions can be used as dopants for polypyrrole. The π-π-interactions force the nitrogen lone pair wave functions to contribute to the conducting polymer π-system. This is a novel approach concerning the application as chemical sensors since the reversible interaction of the analyte modifies the dopant and not the matrix.

S6.24

SELF-ASSEMBLE PROPERTIES OF POLY(PHENYLENE VINYLENE) DERIVATIVES AND POLARIZED LIGHT EMITTING DIODES FABRICATED USING FRICTION TRANSFERRED SURFACES. Zhenan Bao, Linda Chen, Andrew J. Lovinger, Joyce Sapjeta, Bell Laboratories, Lucent Technologies, Murray Hill, NJ; Rachel Jakubiak, Lewis Rothberg, Department of Chemistry, University of Rochester; Ming Yan, Lawrence Livermore National Laboratories.

In this paper, we report the syntheses and characterizations of a number of poly(phenylene vinylene) derivatives substituted with dendritic sidechains and their self-assemble properties. In addition, we report the application of friction transferred poly(tetrafluoroethylene) (PTFE) for aligning active materials to obtain polarized light-emitting devices. A variety of materials, such as vacuum evaporated small molecules and solution processable conjugated polymers, are easily aligned on friction transferred PTFE. Detailed studies of the effects of molecular structure and shape on the induced alignment will be discussed. Polarized LEDs fabricated on such surfaces showed high dichroic ratios. The device performance can be optimized by introducing a conducting poly(3,4-ethylene-dioxythiophene) (PEDOT) layer to help improve the charge injection and wetting properties. Addition of an electron-transporting layer can further increase the external efficiencies of the polarized LED devices.

S6.25

PHOTOLUMINESCENCE DEPENDENCE ON TEMPERATURE IN WATER SOLUBLE POLYMER SYSTEM AND ITS IMPLICATIONS. Jian Wang, Deli Wang, Daniel Moses, Alan Heeger, University of California at Santa Barbara, Institute for Polymers and Organic Solids, Santa Barbara, CA.

Temperature effects on the photoluminescence of water soluable polymer(MBL-PPV) with quencher(MV^{2+}) in pure water and in SSC buffer, is studied. The photoluminescence dependence on the MV^{2+} concentration exhibits the effects of two quenching mechanisms: dynamic queching and static queching. By fitting the data using a modified Stern-Volmer equation, the active distance of MV^{2+} is estimated to be around 50nm. Another estimation ∼50nm is made by the relative PL increase at high temperature. Those results are consistent with the fact that one quencher could quench the whole polymer chain. When SSC buffer ions are presented in the solution, the binding energy between charged polymer chain and quencher is screened by the electrolyte. Debye Length is used to estimate the distance and the binding energy between polymer and quencher. The theoretically derived values agree with the data obtained from experiments. Estimated distance is ∼1nm, consistent with the effective electron charge transfer distance. The binding energy is estimated to be around 150meV.

S6.26

PHOTOEXCITATIONS IN OLIGOTHIOPHENE MOLECULES. C. Botta, S. Destri, W. Porzio, ICM, CNR, Milano, ITALY; G. Bongiovanni, A. Mura, INFM and Dipartimento di Scienze Fisiche, Universita' di Cagliari, Cagliari, ITALY; R. Tubino, INFM and Dipartimento di Scienza dei Materiali, Universita' di Milano Bicocca, Milano, ITALY.

We report a comprehensive study of the photoexcitation of substituted and unsubstituted oligothiophenes. 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 photoexcitation. Energy transfer mechanisms among oligothiophenes with different length are studied for oligomers included in the channels of the guest crystal.

S6.27

NEW FLUORENE BASED TETRAMERS FOR ELECTROLUMUNESCENCE APPLICATIONS. C. Botta, S. Destri, W. Porzio, Istituto di Chimica delle Macromolecole, CNR, Milan, ITALY; M. Pasini, Dipartimento di Fisica, Universita di Parma, ITALY.

Three different tetramers having fluorenic core have been synthesized through organosynthetic routes. The molecular, optical and elettrochemical characterization of all the compounds in solution has been carried out , togheter with the PLQ.Y. determination which makes the molecules promising for elettroluminescence applications. In this view the optical studies (absorption and emission) were extended to solid state samples in pellets (KBr) or in films (cast or evaporated). These latter thin films were obtained in a UHV apparatus. The optical proprties will be related to the different types of aggregation in the solid state. Moreover these molecules will be compared with the homologous based on thiophene moiety.

S6.28

ELECTROCHEMICALLY PREPARED ALKOXY-POLYTHIOPHENE DERIVATIVES AS HOLE TRANSPORT LAYER IN ORGANIC LIGHT EMITTING DIODES. Valeria Fattori, Giuseppe Casalbore-Miceli, Nadia Camaioni, Massimo Cocchi, Piergiulio Di Marco, Alessandro Geri, Gabriele Giro, CNR, Istituto FRAE, Bologna, ITALY.

Alkoxy-polythiophene derivatives electrochemically polymerized on ITO glass have been used as hole transport layer in double layer light emitting devices. As the other layer, for which electron transport and emitting properties are required, a molecularly doped polycarbonate has been employed. Alq3 and perylene derivatives having high photoluminescence efficiencies have been used as the dopants. Current-voltage and electroluminescence characteristics of the devices are reported.

S6.29

Abstract Withdrawn.

S6.30

CONDUCTIVE THIN FILMS BASED ON (BEDT-TTF)$_2$X SYNTHETIC METALS. H. Hau Wang, Kimber L. Stamm, James Parakka, Argonne National Laboratory, Chemistry and Materials Science Divisions, Argonne, IL.

Organic conductors and superconductors based on BEDT-TTF or ET charge transfer salts have been studied extensively and more than 300 ET salts have been reported during the past fifteen years, where BEDT-TTF is bis(ethylenedithio)-tetrathiafulvalene. These complexes exhibit many interesting phenomena, such as solid-state to solid-state phase transformation, charge density wave and spin density wave transitions, antiferromagnetic transitions, and superconductivity. The large numbers of well characterized charge transfer salts and phase transitions may serve as the basis for potential applications including electronic devices and sensors, etc. These materials are prepared with use of electrocrystallization and typically grown as small crystallites. For device application, the form of thin films is more desirable. Previous effort to fabricate conductive charge transfer thin films is based on vapor deposition techniques. The donor molecules can be deposited as films with subsequent exposure to oxidizing halogens. While superconductivity has been demonstrated with this technique, the method is severely restrictive and only works with one system, i.e., ET/I$_2$. In order to broaden the fabrication procedure, we have devised a totally new strategy. While electrocrystallization at low current density (∼1 μA/cm^2) leads to well segregated crystallites, high current density such as 20 μA/cm^2 leads to rapid oxidation and the formation of a passive blue/green insulating (ET)X$_2$ film. The over oxidized (ET)X$_2$ thin films can be reduced back to the desired (ET)$_2$X thin films. This new solution technique is general and works effectively with PF$_6^-$ and ClO$_4^-$ anions. It is expected to be applicable to segregate and electrochemically inert anions. We will report this new procedure and the characterization of each intermediates, (ET)X$_2$, (ET)X, and (ET)$_2$X with use of Raman microscope, infrared, and ESR spectroscopy. To our knowledge, this is the first time that organic thin films based on charge transfer salts have been prepared with a solution electrochemical technique. The new procedure significantly broadens the scope of charge transfer thin film fabrication.

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S6.31

TRANSPORT PROPERTIES IN THIN FILMS OF REGIOREGULAR POLY(3-HEXYLTHIOPHENE). G. Juška, K. Arlauskas, Dept. of Solid State Electronics, Vilnius University, Vilnius, LITHUANIA; R. Osterbacka, H. Stubb, Dept. of Physics, Abo Akademi University, Turku, FINLAND.

Regioregular poly(3-hexylthiophene) (RRPHT) is an interesting material for polymeric electronics. High field-effect mobilities, of the order of 10^{-1} cm^2/Vs, have been reported. The crystalline order in the thin film samples has been proposed as an explanation for the high mobility. We have studied the hole mobility in thin films of RRPHT fabricated with various techniques, viz. the spin- and solution casting as well as the Langmuir-Blodgett (LB) technique, which should result in different degrees of crystallinity and order. For the study of charge carrier transport features in the sub-nanosecond time scale, we used the integral time-of-flight (TOF) method. For the measurements in the micro- and millisecond time scale we have developed a new method based on the extraction of equilibrium charge carriers in a linearly increasing electric field, the linearly increasing field (LIF) method. Here we use two consecutive triangular voltage pulses and study the difference in the corresponding transients. By changing the delay time between the pulses the recovery of the charge carrier equilibrium can be determined. With the sub-nanosecond TOF method, we observed a very fast current transient component corresponding to an initial mobility of photogenerated holes higher than 10^{-2} cm^2/Vs, independent on film fabrication technique. With the LIF technique, we also observed a slow component with a mobility of the order of 3×10^{-7} cm^2/Vs and 3×10^{-5} cm^2/Vs in thin films prepared by the LB technique and in spin- and solution cast films, respectively. The fast component is independent of temperature, whereas the slower component shows an activated transport, with an activation energy of 0.15 eV.

S6.32

INFLUENCE OF SUPPORTING ELECTROLYTES ON ELECTROPOLYMERIZATION OF ANILINE. Ali Eftekhari, Department of Chemistry, K.N. Toosi University of Technology, Tehran, IRAN.

Electropolimerization of conducting polymer films have attracted considrable interest due to their applications to sensors, electrocatalysis, electrochromic device and organic battries. The most widely used method of producting instrinsically conductive polymers is the anodic oxidation of suitable monomer species. In this electrosynthesis method the electrode catalytically triggers chain growth and consequently the process requires little electricity. More recently, the effect of the substrate on the electrochemical polymerization of aniline have been studied[1]. It is also demonestrated that polyaniline coated film can be used as substrate electrode for codeposition of various films[2]. Polyaniline film usually easily is deposited from an aqueous media. In the present research, electropolymerization of aniline on a platinum electrode were investigated in various both organic and inorganic media. The effect of supporting electrolyte on the electropolymerization of aniline on the iron electrode have been studied by Sazou et al.[3]. The purpose of this study is to obtaining adhering films of a conducting polymer such as polyaniline with wide technological applications. The polyaniline films prepared at a constant potential, 0.9 V vs. a saturated calomel electrode (SCE) in various electrolytes. Usually, a charge of 3.4-4.0 mC was consumed during the electropolymerization of aniline on the electrode with 0.125 cm^2 geometric area. It is reported[4] that 80mC/cm^2 is required to deposit a 1.0 μm thick film therefore, the films prepared in this study were approximately 0.4 μm thick. The effect of the thickness of the electroactive film which is controlled by the charge passed during the electropolymerization process, on the stability and electrochemical behavior of the coated electrode was studied.

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S6.33

ELECTROCATALYSIS OF SCORBIC ACID AT THE POLYPYRROLE FILM ELECTRODE. Ali Eftekhari, Department of Chemistry, K.N. Toosi University of Technology, Tehran, IRAN.

Electrocatalysis at modified electrodes is widely used for the determination of many inorganic and organic compounds. Among the electrocatalysts, conducting polymers have been more used. Electrocatalysis of ascorbic acid has been extensively studied[1,2] due to its importance in biochemistry, neouchemistry and clinical diagnostics applications. Polyheterocyclics such as polypyrrole exhibit high electrical conductivity (100 Scm^2) associated with high stability when exposed to ambient conditions. Electropolymerization is a suitable method for synthesis of conducting polymers with electrochemical stoichiometry of 2.07 to 2.7 faraday/mol of reacting monomer. For electropolymerization of pyrrole it was shown[3] that the film forming process needs only 2 faraday/mole and additional charge serves the pratial, reversible oxidation (doping) of the polymer film. A platinum electrode was modified by electropolymerization of pyrrole which potassium hexacyanoferrate(II) was incorporated into the electroactive film during the electropolymerization. Zinger et al.[4] have been reported that in this case, it is possible to prepare polypyrrole containing ferrocyanide/ferricyanide and ferrocyanide will flush out by reducing the film. The electropolymerization of pyrrole on the electrode surface was carried out at a constant potential, 0.7 V vs. a saturated calomel electrode (SCE) from a solution of 50 mM pyrrole containing 10 M $K_4Fe(CN)_6$. Then the electrode was conditioned in 0.1 M NaCl for 30 min and finally was rinsed throughly with water. The electrocatalytic properties of the electrode for electrochemical oxidation of ascorbic acid was described. The analytical applicability of the modified polypyrrole/$K_4Fe(CN)_6$ film electrode as an electrochemical sensor for the determination of ascorbic acid was investigated. For study of the properties of the mentioned electrode, another modified electrode without ferrocyanide was constructed and the electrochemical behavior of the electrode were compared.

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S6.34

THIN FILM POLY(O-METHOXYANILINE) FIELD EFFECT TRANSISTOR. Rodrigo F. Bianchi, Univ. de São Paulo, DFCM, São Carlos, BRAZIL; Roberto K. Onmori, Adnei M. Andrade, Univ. de São Paulo, LME, BRAZIL; Roberto M. Faria, Univ. de São Paulo, DFCM, São Carlos, BRAZIL.

In the last years a great variety of polymers have been used in different electrical and optoelectronic devices. In this context, poly(o-methoxyaniline) (POMA) is a serious candidate to be used as active material of organic electronic device. This is possible because this polymer presents different electrical conductivity values obtained by acid protonation exhibiting semi-conductive properties. In this work we present a detailed study of field effect transistor (FET) of POMA in a Si/SiO_2 structure prepared with conventional lithographic techniques. This device is built on a highly doped p-Si wafer in which a thermally SiO_2 thin layer, 50-80 nm in thickness, was grown. The source and the drain electrodes were finger-shaped and made of a composition of gold and chromium with finger distance of 10-30 mm and length of 1 cm. Thin film (*ca* 100 nm) of undoped POMA in a chloroform solution is deposited on this structure by spin-coated method. The doping is carried out in the final structure, and the conductivity of the POMA film is controlled by electrical characterization performed in air and under vacuum. The characteristic curve were modulated by the gate voltage similar as in JFETS. Such structure is reasonably environmental stable and producible in manufactory (sponsored by Fapesp).

S6.35

PHOTOVOLTAIC DEVICES BASED ON POLYANILINES. Clarissa A. Olivati, Univ. de São Paulo, DFCM, São Carlos, BRAZIL; Roberto K. Onmori, Ely A.T. Dirani, Adnei M. Andrade, Univ. de São Paulo, LME, BRAZIL; Roberto M. Faria, Univ. de São Paulo, DFCM, São Carlos, BRAZIL.

This work presents a study of photovoltaic devices having a thin layer of doped polyaniline (PANI) and its derivative poly(o-methoxyaniline) protonated by HCl as active element. The devices were built in two different structures: a) a simple glass/ITO/polymer/Al structure, and b) a glass/ITO/a-Si-p/polymer/a-Si-n/Al arrangement. Light absorption and photovoltaic conversion are based, respectively, in photophysical effects which takes place in the polymer bulk and at the polymer interfaces. Depending on the devices structures, the photovoltaic effect occurs at the Schottky barrier or at the p-n junction. The experimental diode current density J vs voltage V shows a rectification property, which, under illumination, generates a short-circuit current J_{sc} under open voltage V_{oc}. The short-circuit current increases with the light intensity. Spectral response studies of the devices were also carried out.

S6.36

FAST AND EFFICIENT ORGANIC MULTILAYER PHOTODETECTORS FOR VISIBLE SPECTRAL DETECTION. Peter Peumans, Vladimir Bulović, Stephen R. Forrest, Princeton Univ, Center for Photonic and Optoelectronic Materials, Dept of Electrical Engineering, Princeton, NJ.

External quantum efficiencies in excess of 75% were obtained in multilayered vacuum sublimed organic photodetectors under a reverse bias of 10V. The corresponding internal quantum efficiencies are as high as ~90% over the visible spectrum. The devices consist of an alternating multilayer of donor (Cu-phthalocyanine) and acceptor (3,4,9,10 - perylenetetracarboxylic bisimidazole, PTCBI) molecular layers with thicknesses ranging from 5$\AA$ to 160$\AA$. The total thickness of the multilayer structure was kept constant to 320$\AA$. These multilayers were grown by the ultrahigh vacuum process of organic molecular beam deposition (OMBD) on ITO-coated glass or flexible plastic substrates, and capped with a 200$\AA$ PTCBI-doped bathocuproine layer prior to the deposition of the reflecting Ag cathode. The large number (1 to 63) and close spacing of the donor-acceptor interfaces provides an opportunity for the photogenerated excitons to dissociate by charge transfer into free electrons and holes. Under reverse bias, the free carriers can be extracted with high efficiency, yielding the high total photon-to-carrier efficiencies observed. The asymmetric device configuration yields leakage currents ~10mA/cm^2 at 10V reverse bias. The photoactive spectrum extends from 400nm to 800nm. Under excitation with a picosecond laser tuned to 670nm, the impulse response of a 64-layer device with an area of 0.07mm^2 exhibited a rise time of 3ns and a bi-exponential decay with characteristic times of 15ns and 40ns. This temporal response depends only weakly on the applied bias. The fast rise time indicates that the charge carriers reach velocities in excess of 1000cm/s, despite the large number of interfaces. These devices can be used for visible spectral detection at frequencies in excess of 100MHz.

S6.37

CARRIER TRANSPORT IN OLIGOMER FILMS STUDIED BY STEADY-STATE AND TRANSIENT PHOTOCONDUCTIVITY. J.T. Shepherd, S. Reynolds, C. Main, School of Science and Engineering, University of Abertay Dundee, UNITED KINGDOM; J.M. Marshall, J.M. Maud, Dept. of Materials Engineering, University of Wales Swansea, UNITED KINGDOM.

Oligomer thin films have shown considerable promise as active layers in control and display devices. However, comparatively little work has been done on the transport mechanisms prevailing in these materials, in contrast to the more extensive literature on molecularly-doped polymers. In a recent study [1] the present authors reported that pentacene and several thienylene-vinylene oligomers exhibit functionally similar transient photoconductivity (TPC) decays, whose temperature-dependence is consistent with a trap-limited hopping transport model. Here we report on two further common aspects of their behaviour, the effects of a steady optical generation ('optical bias') on the TPC decay and the 'persistent' photoconductivity (PPC) or long-time photodecay from the steady-state. Under zero optical bias, the oligomer TPC signals are characterised by two power-law sections; a steep decay extending from nanoseconds to tens of microseconds followed by a shallower, temperature-dependent decay to tens of seconds. When optical bias is applied, a third, steep, decay section appears at longer times. This behaviour signifies the onset of bimolecular recombination, since the time at which the transition takes place is bias intensity-dependent. Further, the steady-state photoconductivity shows a power-law intensity-dependence of index 0.5 - 0.6 as expected for bimolecular recombination. In both cases the detailed behaviour is field- and wavelength-dependent. PPC is observed to occur for each oligomer formulation. At 300 K, the conductivity decays typically by less than one order of magnitude between 1 s and 1000 s after switch-off from the steady-state. However, as the temperature is increased a rapid fall is observed on this timescale. The onset time is temperature-dependent with an activation energy of typically 0.7 eV, which suggests that recombination may be inhibited by a potential barrier of this size.

Possible unifying mechanisms will be discussed.
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S6.38
CHARGE DELOCALIZATION IN CONJUGATED POLYMERS AND OLIGOMERS CONTAINING IRON IN THE BACKBONE.

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Most conjugated polymers which contain metals in the backbone are at best semiconductors when doped, in contrast to organic metals such as polyacetylene and polythiophene. To understand the factors which influence conductivity in such materials, a series of conjugated mono- and bis(ferrocenylethynyl)oligothiophene complexes have been prepared, and the electronic delocalization examined in these compounds. Some of the complexes are suitable as building blocks for conjugated ferrocene-thiophene copolymers. Cyclic voltammetry and electronic spectroscopy have been used to characterize the compounds. The energy and intensity of low-energy transitions which are observed spectroscopically correlate linearly to the difference in oxidation potentials between the metal and oligothiophene groups supporting the conclusion that charge transfer is enhanced when the conjugated organic group and the metal are close in oxidation potential.

S6.39
HIGH TRANSPARENCY EFFICIENT NON-METALLIC CATHODES FOR ORGANIC OPTOELECTRONIC DEVICES.

Gautam Parthasarathy, C. Adachi, P.E. Burrows and S.R. Forrest, Center for Photonics and Optoelectronic Materials (POEM), Princeton University, Princeton, NJ.

There is significant interest in the device engineering of transparent cathodes for organic optoelectronic devices. Applications include OLED displays integrated with Si drivers, low optical loss organic waveguide structures to realize electrically pumped organic solid state lasers, and organic photovoltaic devices. A conventional, vacuum deposited OLED consists of small molecule organic layers such as tris-(8-hydroxyquinoline) aluminum (Alq$_3$), sandwiched between indium-tin-oxide (ITO) and a thick, low work function metal to provide hole and electron injection, respectively. The electron injecting contact is thought to be formed due to chemical reactions between the Alq$_3$ and the low work function cathode. We have previously demonstrated transparent cathodes consisting of ITO deposited on top of an organic buffer layer such as copper-phthalocyanine (CuPc)[1] which provides for electron injection through defect states induced in the organic layer during ITO sputtering. However the external quantum efficiency of these "metal-free" devices was only 0.25 of conventional devices using a Mg:Ag cathode. It has been shown that the insertion of a film of Li between the ITO and CuPc improved the efficiency of such devices,[2] but in both cases the absorption of CuPc limits the transparency of the cathode.
We have now used the highly transparent material bathocuproine (BCP) to form Li/BCP/ITO cathodes. By placing an ultrathin (3 *Å*) layer of Li *between* the BCP and Alq$_3$, we are able to obtain a peak external quantum efficiency of 1.2 % and a transparency of 90 % across the visible portion of the spectrum. Li essentially plays the same role as the thick Mg:Ag in causing a chemical reaction with the underlying Alq$_3$ to facilitate efficient electron injection, but is so thin that there is negligible optical absorption. This is the first report of high efficiency transparent OLEDs with no low work function metal in contact with the ITO cathode. We investigate the dependence of the device characteristics on the position and thickness of the BCP and Li and comment on the underlying mechanisms.
1. G. Parthasarathy, P.E. Burrows, V. Khalfin, V.G. Kozlov and S.R. Forrest, Appl. Phys. Lett. 72, 2138 (1998).
2. L.S. Hung and C.W. Tang, Appl. Phys. Lett. 74, 3209 (1999).

S6.40
HIGHLY EFFICIENT TRANSIENT ELECTROLUMINESCENCE (EL) FROM MULTILAYER ORGANIC LIGHT-EMITTING DEVICES (OLEDS).

Vadim Savvateev, Jon Friedl, Lijuan Zou and Joseph Shinar, Ames Laboratory -USDOE and Department of Physics and Astronomy, Iowa State University, Ames, IA; W. Oldham and L. Rothberg, Department of Chemistry, University of Rochester, Rochester, NY.

Highly efficient transient EL from multilayer blue [triphenyl diamine (TPD)]/[1,4-bis(2,2-diphenyl vinyl)benzene (DPVBi)] and green TPD/[8-tris-hydroxyquinoline Al (Alq3)] OLEDs is described and discussed. It is found that when the devices are excited with voltage pulses above some critical value, a transient flash of EL is emitted that exceeds the steady-state EL at that DC bias. The duration of this transient flash varies from ~1 mks to ~2 ms, depending on the pulse amplitude. Since the respective current pulse is essentially rectangular, the transient EL is proportional to the transient efficiency. Following the transient EL peak, the brightness relaxes to a steady-state level equal to that observed at the same dc bias. The critical voltage for the emergence of the EL peak coincides with the dc voltage which yields the maximal efficiency in dc operation. Since the emission is believed to occur at the interface between the hole- and electron-transporting layers, the quenching process is turned on only as the charges accumulate at the interface. It may occur either through reaction of singlet excitons with free holes [1] or by dissociation in the presence of high local electric field [2]. The transient EL peak enables a high duty cycle driving scheme in which the average brightness and efficiency are enhanced when the exciting pulse duration matches the transient emission peak width. An additional ~10 ns wide transient emission peak is observed at the voltage pulse turn-off. While the occurrence of this peak, resulting from the recombination of the charges accumulated at the O/O interface, was reported previously [3] in polymer-based LEDs, the present work demonstrates its prominence in the small-molecular Alq3 and DPVBi devices. A non-display application of the transient peaks will also be described.
[1] Staudigel et al. JAP 86 (1999) 3895
[2] Tasch et al. PRB 55 (1997) 5079
[3] Nikitenko et al. JAP 81 (1997) 7514.

S6.41
EFFICIENT POLYMER PHOTODIODES BASED ON NOVEL MULTILAYER AND COMPOSITE STRUCTURES.

J.J.M. Halls, J.D. MacKenzie, A.C. Arias, Cavendish Laboratory, Cambridge, UNITED KINGDOM; E.P. Woo, M. Inbasekaran, The Dow Chemical Company, Midland; R.H. Friend, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

We have fabricated polymer photodiodes using pairs of polyfluorene based polymers and copolymers in which exciton dissociation occurs at the interface between the two different polymers. Exciton dissociation, which leads to the production of separated charges free to be collected at the contacts, is driven by the offset in the electron affinities and ionisation potentials at the interfaces between the two materials. We have fabricated photodiodes based on blends of polyfluorene-copolymers, and have demonstrated elsewhere how their efficiency depends on the morphology of the polymer composite active layer. We demonstrate here how the efficiency may be improved by using multilayer structures in which the interface between the two polymers is diffuse and interpenetrating. This increases the surface area of the active interface, increasing the probability of exciton dissociation, and allows effective charge transport through to the appropriate charge-collecting electrodes. We achieve this multilayer structure using lamination processing and other novel deposition techniques. Photodiodes fabricated using these techniques have efficiencies greater than those made from a simple blend of the two components.

S6.42
ELUCIDATION OF THE PRIMARY ISOMERIC FORMS OF *TRIS*(8-HYDROXYQUINOLINATO) ALUMINUM (III) AND *TRIS*(4-METHYL-8-HYDROXYQUINOLINATO) ALUMINUM (III) USING MATRIX-ISOLATION INFRARED SPECTROSCOPY.

Gary P. Kushto and Zakya H. Kafafi, United States Naval Research Laboratory, Washington, DC; Yasuhiro Iizumi, Fubata Corporation, Chousei Chiba, JAPAN; Junji Kido, Graduate School of Engineering, Yamagata University, Yamagata, JAPAN.

Tris(8–hydroxyquinolinato)aluminum (III) (Alq$_3$) and more recently, *tris*(4-methyl–8–hydroxyquinolinato) aluminum (III) (Almq$_3$) have been the subject of numerous investigations because of their important roles in molecular organic light emitting devices (MOLEDs). Each Al complex can exist in two isomeric forms which have significantly different molecular properties with respect to photoluminescence, charge injection and charge transport. This presentation will provide information on the relative populations of the two isomeric forms of Alq$_3$ and Almq$_3$ present in a solid argon matrix based on the results of the infrared spectral analyses and hybrid *ab initio*/DFT calculations. In addition, possible implications of the relative populations of these two isomeric forms on MOLED device performance will be discussed. Photoluminescence spectra of these molecules isolated in a solid argon matrix will also be presented and will be used to analyze the vibronic coupling found in the $S_1 \rightarrow S_0$ transition.

S6.43
SPECTROSCOPIC INVESTIGATIONS ON POLYPYRROLE.

M. Chipara, Cheol-Soo Yang, B. Doudin, Bo Xu, University of Nebraska, Dept. of Physics and Astronomy, Lincoln, NE; E. Goovearts, University of Antwerpen, Dept. of Physics, BELGIUM.

Spectroscopic investigations on a conducting polymer (polypyrrole) are reported. Electron spin resonance data have been recorded using a JES-ME-3X spectrometer, operating in X band (9 GHz). The temperature dependence of resonance spectra parameters (resonance line position, line width, line intensity, double integral of the resonance line) in the temperature range 100 K to 450 K is investigated in detail. In the whole temperature range investigated by us, the resonance line is a narrow single and symmetric line located closed to the free electron value. We have not been able to notice any resonance line at g=4.0. Taking into account the intense signal located at g=2.0 as well as the absence of any resonance line located at g=4.0 we concluded that bipolarons (if present) have a low contribution to the resonance line and hence to the electrical conduction. Additional data have been obtained by dc electrical measurements, using the four probe method, in the temperature range 4K to 300 K. The experimental data are consistent with an one dimensional variable range hopping mechanism of electrons or with the model of the granular metal. The resistance of the polymer is increasing as the temperature is decreased, leading to an almost insulating material below 10 K. Such a behavior is consistent with a hopping of electrons. Taking into account that the resonance spectra recorded at high frequencies (W band) are characterized a low assymetry we have concluded that metallic islands are absent. The characteristic I-V curves have been recorded at various temperatures in the temperature range 10 K to 300 K. Additional data concerning the energy bands of polypyrrole, as obtained by photoemission, are reported.

S6.44

EFFICIENT RED ORGANIC LIGHT EMITTING DEVICES USING PENTACENE DERIVATIVES. L.C. Picciolo, H. Murata and Z.H. Kafafi, Naval Research Laboratory, Washington, DC.

Highly efficient red organic electroluminescent devices were developed using pentacene derivatives doped into various hosts as the emitting layers. For instance, doping 6,13-diphenylpentacene (DPP) into tris(8-hydroxyquinolato) aluminum III led to an electroluminescence quantum efficiency as high as 2.5% at 100 A/m^2 for an unoptimized device. To our knowledge, this efficiency is comparable to that of the best-published data to date, which uses a porphine-based phosphor as the dopant in an optimized device structure. These devices showed a rapid decrease of the quantum efficiency with increasing current density (luminance); less than 2% at a current density of 300 A/m^2. The quantum efficiency of pentacene-based devices does not change (increases slightly) as a function of increasing current density (luminance) reaching a maximum quantum efficiency of 2.7% at 300A/m^2 (1000 cd/m^2). A very narrow emission spectrum in the visible red region was observed for DPP, giving rise to good chromaticity ($x = 0.64$ and $y = 0.34$) in accordance with the Commission International de l'Eclairage (CIE). These chromaticity coordinates are comparable to those of a typical red phosphor used for a cathode ray tube (CRT). The paper will discuss device performance as a function of concentration of guest molecule, host material and device structure. The electroluminescence mechanism(s) that led to this high quantum efficiency will also be covered.

S6.45

OPTICAL AND ELECTRICAL PROPERTIES OF LIGHT EMITTING DEVICES BASED ON POLY[2-METHOXY-5-(2í-ETHYL-HEXYLOXY)-1,4-PHENYLENE VINYLENE]. Lucas Fugikawa Santos, Luisa Magno de Carvalho, Rodrigo F Bianchi, Francisco E.G. Guimarães, Débora Gonćalves, Roberto Mendonća Faria, Inst Física São Carlos, Univ São Paulo, São Carlos, BRAZIL.

In this work, light emitting diodes (LEDs) and light emitting electrochemical cells (LECs) based on poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) have been compared by means of different measurements. LEDs were prepared by spin coating a thin single layer (about 200 nm thick) of MEH-PPV onto ITO coated glass substrates and evaporating Al electrodes over the polymer film. LECs based on MEH-PPV:PEO-lithium triflate blends were prepared at different compositions with a typical composition of MEH:PEO-salt 1:1 (wt./wt.). In order to study the relationship between temperature and recombination processes in these different devices, absorption, photoluminescence and electroluminescence spectra, obtained at different temperatures ranging from 30 up to 320 K, are analized. For LEDs, current density vs voltage curves (JxV) exhibited different temperature behavior for forward and reverse bias indicating different carrier transport mechanisms. Comparatively, JxV curves obtained for LECs were very distinct from those for LEDs and showed a more drastic dependence with temperature, probably due to a smaller effect of ionic transport at low temperatures. Also, alternating current and response time measurements of LEDs and LECs were used to characterize electrical and optical behavior of such devices. In spite of the fact that LEDs have shown very fast current and electroluminescence responses (below 10 μs) when a transient voltage was applied, slower response times have been seen for LECs, ranging from several milliseconds up to few seconds, depending on blend composition and morphology. The addition of a surfactant-like compound in the blends was used to obtain better morphological properties (analyzed by atomic force microscopy, AFM) and to improve electrical and luminescent performances of these devices.

S6.46

HOLE BLOCKING PROPERTY OF CARBON NANOTUBE IN A COPOLYMER MATRIX, POLY (m-PHENYLENE VINYLENE-co-2, 5-DIOCTOXY-p-PHENYLENE). H.S. Woo, R. Czerw, D.L. Carroll, Clemson Univ, Dept of Physics and Astronomy, Clemson, SC; B. McCarthy, W. Blau, Polymer Research Ctr, Dept of Physics, Trinity College, Dublin, IRELAND.

In order to investigate the role of a carbon nanotube in a polymer matrix, organic light emitting diodes (OLEDs) were fabricated with a polymer composite, poly (m-phenylene vinylene-co-2,5-dioctoxy-p-phenylene) (PmPV) and dispersed single wall carbon nanotubes (SWNT). Polyethylene dioxythiophene (PEDOT) and tris-(8-hydroxyquinoline) aluminum (Alq3) doped by Nile Red with 0.1 % by weight (0.1 wt. %) were used as a buffer in the hole injection layer and as an emissive or an electron transport material between the polymer composite and cathode, respectively. Our device without SWNT's in the PmPV emits red near 640 nm, which is the characteristic emission of Nile Red in Alq3. However, the device fabricated with the polymer blended with a SWNT concentration of 0.05 wt. % emits green-yellow in the range of 510 - 580 nm, and the emission peak shifts more green and nearer 510 nm as the SWNT concentration increases up to 0.2 wt. %. This indicates that the SWNT's in a polymer matrix act as a hole blocking material resulting in the shifting of the recombination regions from the doped Alq3 layer to the polymer composite layer. As a function of the SWNT concentration, characteristics of the devices including the current-voltage, the turn-on voltage, the efficiency, and the electroluminescence of the polymer composite will be discussed.

S6.47

BLUE EMITTING ORGANIC LIGHT EMITTING DIODES WITH CARBAZOLE AND CYANOTEREPHTHALIDE BASED SMALL MOLECULES. H.S. Woo, R. Czerw, D.L. Carroll, Clemson Univ, Dept of Physics and Astronomy, Clemson, SC; J.W. Park, Dept of Polymer Engineering, Chungju Nat. Univ, KOREA; J.H. Lee, Samsung Advanced Inst of Technology, KOREA.

We have fabricated organic light emitting diodes (OLEDs) with carbazole and cyanoterephthalide based small molecules, Bis(3-N-ethylcarbazolyl) cyanoterephthalidence (BECCP) and 3,6-Bis (a-cyanostyryl)-N-hexylcarbazole(BCSHC). Polyethylene dioxythiophene (PEDOT) and tris-(8-hydroxyquinoline) aluminum (Alq3) were used as a hole injecting buffer and as an electron transport material, respectively. Aluminum-Calcium alloy with a 2:1 weight ratio was used for the cathode. Our devices show a blue emission for both oligomers, with a peak in the electroluminescence (EL) spectra near 480 nm, with a broader spectrum from BECCP. However, the EL intensity of BCSHC is weaker than that of BECCP, probably because of the lesser number of carbazole units in the BCSHC chain thus more unbalanced charge injection in the emitting layer. This leads us to fabricate another type of blue emitting device, the BECCP as an emissive material and, instead of Alq3, the BCSHC as an electron transport material. The performance of those devices will be compared each other in terms of the EL, current-voltage and efficiency.

S6.48

MULTILAYER ORGANIC LEDS: NUMERICAL SIMULATION OF TRANSPORT AND RECOMBINATION. B. Ruhstaller, S.A. Carter, Univ of California Santa Cruz, Dept of Physics, Santa Cruz, CA; J.C. Scott, IBM Almaden Research Center, San Jose, CA.

We present a numerical study of current-voltage characteristics and charge accumulation effects in multilayer organic light emitting diodes. The bipolar charge transport and recombination problem with field dependent mobilities is solved self-consistently and heterointerfaces are treated by assuming transport at discontinuities in the chemical potential to be governed by Boltzmann statistics. We show that the increased efficiency found in multilayer LEDs can be explained within the framework of our model by charge and recombination zone confinement at heterointerfaces and a resulting increase in the current balance factor. As a function of temperature, we find strongly varying current-voltage characteristics that arise solely from the mobility parameters used and not from trap limited transport as suggested previously. We compare our results to experimental data and find good qualitative agreement.

S6.49

IMPROVED PERFORMANCE IN MULTILAYERED POLYMER - TITANIUM DIOXIDE PHOTOVOLTAICS USING INORGANIC HOLE TRANSPORTING NANOPARTICLES. A.J. Breeze, S.A. Carter, Univ of California, Santa Cruz, Physics Dept, Santa Cruz, CA; Alexi C. Arango, E. -Ink, Cambridge, MA; David S. Ginley, NREL, Golden, CO; Phillip J. Brock, IBM Almaden Research Center, San Jose, CA; H.H. Horhold, Friedrich Schiller Univ, GERMANY.

Our previous work with inorganic/organic composite photovoltaics consisting of transparent, mulilayers of planar titanium dioxide (TiO_2) solgel and polymers PA-PPV or MEH-PPV with stable ITO and Au electrodes has shown promising results, including quantum efficiencies of up to 26% at zero bias, open circuit voltages above 0.8 V, and fill factors up to 50%, corresponding to an overall power efficiency near 4% over the energy range for absorption by the photoactive polymer. The primary limiting factor for higher short circuit currents and efficiencies in these devices is the low hole mobility of the active polymer. To overcome this, we have blended high concentrations of hole transporting inorganic nanoparticles such as NiO, LiNiO, CuI, $CuAlO_2$, and CdTe into the active polymer to help increase the hole mobility and overall charge transport. We have also blended electron transporting nanoparticles, such as TiO_2, for comparision. We analyze the effect that charge transporting nanoparticles have on device performance as a function of nanoparticle concentration and percolating morphology. We will conclude by demonstrating the performance under ambiant conditions of our best polymer-based photovoltaics made entirely via low temperature processing ($<$ 125C) on plastic substrates.

S6.50
POLYMERIC THIN FILM - SILICON MICROSENSORS FOR THE DETECTION OF MICRO-ORGANISMS. S.C.K. Misra, R. Bhattacharya, Subhas Chandra, National Physical Laboratory, New Delhi, INDIA; R.P. Sharma, North Maharastra University, Nandurbar, INDIA; R. Angelucci, P. Maccagnani, F. Corticelli, CNR-LAMEL Institute, Bologna, ITALY.

Food and water contaminated with bacteria can cause a number of food-borne and water-borne diseases. The most commonly diseases are diarrhea, dysentery, gastro-enteritis and food poisoning. Determination of the presence of micro-organisms and identification of specific causative micro-organisms is necessary to control the microbial infestation. Quick and simple methods to detect the type of life threatening microbial species are very essential. The fast detection of microbial species can be achieved by utilizing efficient response sensor supported by microprocessor based technology. Recently, by utilizing the semiconducting polymeric thin films prepared on silicon macroporopus substrates a new technology for detection of micro-organisms has developed. The advantages of the polymeric devices are the ease of fabrication, the high sensitivity to microorganisms , the fast response time and the room temperature operation. The electrical conductivity of the polymeric/silicon microsensors is strongly influenced by the presence of microbes. I this work the current voltage characteristics of the specifically doped polymeric thin films deposited on silicon macroporous membranes upon exposure to E. Coli were studied. The sensors were prepared by vacuum depositing doped polyaniline in the form of thin films on the silicon macroporous structures. By providing suitable electrodes to the polymer films the I-V characteristics of the sensor structure were obtained. The particular doping combination in the polymer makes the sensor specific for detection of E. Coli. The sensitivity of the devices was observed as the ratio of current from the sensor obtained upon exposure to E. Coli with respect to the current obtained without exposure to the microorganism. The response time of the sensor was about 5 seconds. The total response time was a few tens of seconds. We hereby describe the fabrication process, behavioral acceptance tests and performance characteristics of the hybrid polymeric/ silicon microsensors in regard to detection of E. Coli.

S6.51
ENHANCEMENT OF EFFICIENCY IN ORGANIC PHOTOVOLTAIC DEVICES BY OPTICAL DESIGN. Lucimara Stolz Roman, Leif A.A. Pettersson, Tomas Granlund, Tobias Nyberg and Olle Inganas, Applied Physics Laboratory, IFM, Linkoping University, Linkoping, SWEDEN.

The mechanism of charge generation upon light absorption in organic materials impose some constraints on device fabrication. One of the limiting aspects in device physics is the short diffusion length of excited states in conjugated polymers. The optical absorption is strong, but even at the maximum of absorption the penetration depth of light into these materials is in the range of 10-100 nm. In order to obtain maximum photoconversion we may increase the optical electric field near to the dissociation region, i.e., increase the light absorption in the active parts of the device. In sandwich devices where the active layer is between two electrodes, ITO/PEDOT (anode) and Aluminum (cathode), two approaches were investigated: (i) Single organic layer photodiode where a neat polymer or polymer:C60 mixture was the active layer. The improvement on absorption was achieved by trapping light with a grating at the rear part of the device. The grating pattern was soft embossed onto the active organic layer before the aluminum evaporation using a soft lithography method. (ii) Bilayer photodiode where a heterojunction (polymer/C60) was the active layer. The improved efficiency was achieved maximizing the light intensity near to the polymer/C60 interface. Devices with different C60 thickness were investigated. The stationary optical wave created in the devices, due to interference of the incoming wave with the reflected wave from Al electrode, strongly depends on the layer thicknesses, and the photocurrent depends on the resulting optical field distribution inside the device. In order to model transport of the photogenerated charges with electric field in these devices it was necessary decoupling the optical and electric part by means of the internal exciton to charge generation efficiency.

S6.52
A NEW CLASS OF COLOUR-TUNEABLE POLYPARAPHENYLENE-BASED POLYMERS FOR ELECTROLUMINESCENT DEVICES AND ENERGY TRANSFER STUDIES. J. Devin MacKenzie, Carlos Silva, Mark Stevens, David Russell and Richard Friend, Cavendish Laboratory, University of Cambridge, UNITED KINGDOM; Dirk Marsitzky, Sepas Setayesh, Stefan Becker and Klaus Mllen, Max Planck Institut für Polymerforschung, Mainz, GERMANY.

A new class of colour-tuneable polymers have been developed which show impressive potential as a process-consistent materials system for achieving LEDs with emission spanning the visible range and for studying solid-state energy transfer processes. Intermediate ladder polyparaphenylene-based structures, including polyfluorene and polyindenofluorene, have been combined with high efficiency dyes in a novel way. These new materials demonstrate highly efficient solid-state polymer-dye energy transfer resulting in emission over a range of wavelengths with absolute PL efficiencies as high as 50%. The polymers have good film-forming and device properties and overcome the strong tendency towards detrimental aggregation seen in simple polymer-dye blends. Device and microscopy results will be shown comparing the new materials with their polymer-dye blend analogues. Ultrafast spectroscopy results, probing the polymer-dye energy transfer process will also be discussed.

SESSION S7: LEDS
Chair: Mary Galvin
Thursday Morning, April 27, 2000
Metropolitan II (Argent)

8:30 AM *S7.1
LIGHT EMISSION FROM SELF-ASSEMBLED MICROSTRUCTURES OF PHENYLENEVINYLENE POLYMERS WITH DENDRITIC SIDEGROUPS. Ming Yan, Thomas Huser, Ana I. Villacampa, Lawrence Livermore National Laboratory, Livermore, CA; X. Linda Chen, Zhenan Bao, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

The fundamental excitations in light emitting polymers are of interest for their underlying photophysics and LEDs applications. The fluorescence from light emitting polymers is strongly influenced by the aggregation of the polymer backbone. Here, we report on the formation and photoluminescence of self-assembled microstructures, such as polymer sheets with sub-micron thickness, from PPV polymers with dendritic sidegroups. The photoluminescence associated with these microstructures is measured by fluorescence spectroscopic microscopy. The fluorescence spectra show strong dependence on its morphology. The photoluminescence from self-assembled polymer sheets shows distinctive emission properties in comparison to the emission of individual polymers. This provides an understanding of how excitonic properties are influenced by the packing of the polymer backbone. Furthermore, photoluminescence from individual polymer chains is studied by fluorescence confocal microscopy and spectroscopy with single molecule sensitivity. The study of individual polymers and its aggregates due to chemical environments provides an insight toward understanding the effect of chain packing on light emitting properties.
*Work at LLNL performed under the auspices of the USDOE under contract No. W-7405-ENG-48.

9:00 AM *S7.2
DEVELOPMENT OF DEVICE ARCHITECTURES FOR EFFICIENT POLYMER LEDS. R.H. Friend, P.K.H. Ho, J.H. Burroughes, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

ABSTRACT NOT AVAILABLE

9:30 AM S7.3
CONTROLLING INTERCHAIN INTERACTIONS IN CONJUGATED POLYMERS. Benjamin J. Schwartz, Thuc-Quyen Nguyen, Ignacio Martini, Univ of California-Los Angeles, Los Angeles, CA.

Conjugated polymers are remarkable materials which combine the electrical properties of semiconductors with the mechanical and processing advantages of plastics. In this talk, evidence is presented that the electrical and photophysical behavior of these materials depends on the degree of interchain interactions, and that the interchain interactions can be controlled by varying the solvent and polymer concentration of the solution from which the films are cast. The photoluminescence of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene), MEH-PPV, changes both its spectral shape and quantum yield when the films are prepared from different solutions or when the morphology is varied by annealing. Fluorescence spectroscopy shows that red excitation preferentially enhances the red emission, suggesting that the interchain species are aggregates with a distinct ground state absorption. Scanning force microscopy shows topographic features that correlate with the degree of interchain interactions, verifying that the morphology of conjugated polymer films changes with the preparation method. Femtosecond pump-probe experiments reveal a long-lived emissive tail, which in combination with excited-state absorption dynamics that do not match those of the emissive species, provide direct evidence for the production of interchain aggregates. Perhaps most importantly, changing the film morphology has a direct effect on the performance of MEH-PPV-based light-emitting diodes. Higher degrees of interchain interaction enhance the mobility of carriers at the expense of lower quantum efficiencies for electroluminescence. Finally, the dynamics of interchain and intrachain energy transfer are quantified by examining the emission dynamics of aligned chains of MEH-PPV embedded in the channels of an oriented mesoporous silica glass. Taken together, the results provide a a prescription for the optimization of conjugated polymer films for particular device applications.

9:45 AM S7.4
SEMICONDUCTING POLYMER-DIELECTRIC NANOPARTICLE COMPOSITES. Peter K.H. Ho, Nir Tessler, Richard H. Friend, Cambridge Univ, Cavendish Lab, Cambridge, UNITED KINGDOM.

We find that a remarkably high number-density of nanosized particles can be dispersed into conjugated polymer matrices without severely degrading the conjugation length which describes the extent of π-electron delocalisation along the polymer chains. This suggests that the guest inclusions are accommodated by gradual conformational distortion of the polymer chains rather than abrupt hair-pin structures. We have examined poly(p-phenylenevinylene) (PPV) dispersed with up to 50 vol% 50-$\AA$-diameter surface-modified silica particles. These nanocomposite thin films obtained via thermal elimination of the precursor-PPV blend display no significant optical Mie scattering. The silica particles are well-dispersed and have no adverse chemical effects on the thermal conversion. Together with the fact that they are electronically inert and spectroscopically silent over several key spectral windows, this makes PPV-SiO_2 an interesting model system to study the steric interaction and the exciton energy migration in the matrix. For example, using known dispersion relations for phonon modes and the absorption-emission gap, we can quantify the change in conjugation lengths. Our results reinforce the possibility of combining in these organic-inorganic hybrid materials the charge transport property and processability of the host with novel properties of the dielectric nanoparticle or of functional groups anchored to its surface. In a first application, we have demonstrated a PPV-SiO_2 system with composition-tuneable refractive indices (n = 1.6-2.5) that provides solution-processable (and therefore printable) photonic building blocks for polymer-based optoelectronic devices, such as all-polymer microcavities and microcavity light-emitting diodes.

10:30 AM *S7.5
HOW TO MAKE GOOD POLYMER LEDS. Yang Yang, Yijian Shi, Jie Liu, Liping Ma, UCLA, Dept. of Materials Science and Engineering, Los Angeles, CA.

In this presentation, we present results from systematic studies of polymer morphology and related polymer LED performance. We discovered that through the proper selections of organic solvents, polymer solution concentrations, and spin-casting speeds, one is able to control the polymer thin film morphology and subsequently control the physical properties of PLEDs. We will present methods of making good PLEDs, with high quantum efficiency and low turn-on voltage, by the proper selection of polymer process conditions.

11:00 AM *S7.6
SYNTHESIS AND CHARACTERIZATION OF NOVEL LIGHT-EMITTING POLYMERS. Alex K-Y. Jen, Xuezhong Jiang, Sen Liu, Lixin Zheng, Michelle Liu, Hong Ma, Washington Univ, Seattle, WA.

A series of novel conjugated polymers based on the fluorene and binaphthyl units were synthesized via the Wittig condensation or the palladium-catalyzed Suzuki coupling reactions. The introduction of a twisted, non-coplanar binaphthyl structure provided an effective mechanism for tailoring the spectral characteristics of the polymers and improving their solubility and thermal stability. Different conjugating moieties with good hole or electron transporting property were copolymerized with these units to fine-tune the HOMO and LUMO levels of the polymers for achieving efficient charge injection with ITO and Al as electrodes. Very high external quantum efficiencies (as high as 2%) and high brightness (~10,000 cd/m2) could be achieved with these polymers. Characterization and detailed device properties of these polymers will be discussed in this paper.

11:30 AM S7.7
EFFECT OF MORPHOLOGY AND MICRO-STRUCTURE ON THE ELECTRONIC AND OPTICAL PROPERTIES OF ELECTRO-ACTIVE CONJUGATED POLYMERIC FILMS. Richard V. Gregory, NSF/ERC Center for Advanced Fibers and Films, and School of Textiles, Fiber and Polymer Science, Clemson University, Clemson, SC; Robert J. Samuels, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA.

Electronic and optical properties of conjugated polymeric films have been shown to be highly dependent on the orientation, microstructure, and morphology of the film-forming polymer. Refractive indices have been measured in all three dimensions and shown to vary depending on orientation developed during film formation. These differences are observed and quantified using optical waveguide coupling techniques, for polyparaphenylene vinylene (PPV), derivatized PPVs including DOO-PPV (di-octlyoxy-polyparaphenylene vinylene), and polyaniline (PANI). Changes in the electronic and photonic properties, due to morphological changes induced by orientation of the polymeric films prepared from these materials, are related in this study to the polymers optical and molecular chain axis and finally to the formed films morphological structure. The effect of differing orientation on the electronic and optical properties of these polymers, and the potential for tuning these properties to specific end uses by selectively changing the polymer morphology, will be discussed. In addition the use of optical waveguide coupling techniques coupled with X-ray and infrared studies to determine film microstructure and intrinsic electrical, electronic, and optical properties will be highlighted as a tool for predicting the effects of orientation induced by spin coating or other formation methodologies.

11:45 AM S7.8
INTERCHAIN INTERACTIONS IN LIGHT-EMITTING ORGANIC CONJUGATED POLYMERS. M.A. Kreger, N.J. Cherepy, J.Z. Zhang, Univ of Calif, Santa Cruz, CA; J.C. Scott, G. Klaerner, R.D. Miller, IBM Almaden Research Center, San Jose, CA; D.W. McBranch, B. Kraabel, S. Xu, Los Alamos National Laboratory, NM.

Exciton dynamics of 9,9-di-n-hexylfluorene/anthracene (DHF/ANT) statistical copolymers have been measured using femtosecond transient absorption spectroscopy. An investigation of the excitation intensity dependence over the range of 0.1-1.0 mJ/pulse-cm^2 for solutions and 1.0-17 μJ/pulse-cm^2 for thin films has been conducted to explore exciton relaxation mechanisms below excitation densities where exciton-exciton interaction is important. Intrachain relaxation of photoexcited singlet excitons is observed in dilute solutions. In contrast, interchain relaxation mechanisms become predominant in thin films. Decay dynamics are independent of excitation intensity for dilute solutions and thin films of DHF/ANT when probed at 790 nm and 750 nm. In addition, time-resolved measurements for a DHF homopolymer and two copolymer thin films have been carried out as a function of probe wavelength. A stimulated emission (SE) feature and a photoinduced absorption (PA) feature are observed in the visible region. The SE and PA dynamics are similar for the copolymers, suggesting the same excited state species, the singlet exciton, is responsible for both the SE and PA. There is a significant difference between the SE and PA dynamics for DHF thin films on the 0-3 ps timescale. The SE dynamics show a pulse-width limited rise and a subsequent decay. In contrast, both the 600 nm and 750 nm PA show a "double" rise that represents contributions from two separate photophysical processes. These results, in combination with the steady-state photoluminescence spectrum, which indicates excimer emission, lead to the suggestion that interchain species, such as excimers, are formed in <1 ps in DHF films following photoexcitation. That the copolymer dynamics show no evidence of excited state species other than singlet, emissive excitons, is consistent with the interpretation that anthracene substituents in the polymer backbone prevent interchain interactions in films.

SESSION S8: POLYMER TFTS AND LEDS

Chair: Lewis J. Rothberg
Thursday Afternoon, April 27, 2000
Metropolitan II (Argent)

1:30 PM *S8.1
ALL-ORGANIC INTEGRATED CIRCUITS BASED ON BOTTOM

GATE THIN FILM FIELD-EFFECT TRANSISTORS. G.H. Gelinck, T.C.T. Geuns and D.M. de Leeuw, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

Functional all-organic integrated circuits based on thin film field-effect transistors with a bottom-gate geometry have been realized using potentially low-cost technology. The bottom-gate approach offers two major advantages: more freedom of choice for the type of semiconductor and an easy route to fabricate vertical interconnects simply by photochemical patterning of the insulator layer. Bottom-gate devices were made using pentacene, polythienylenevinylene and regioregular poly(3-hexylthiophene) as the active semiconductor. Field-effect mobilities as high as to 10-2 cm2/Vs have been observed. The inverters show voltage amplification at moderate biases and simple 7-stage ringoscillators show switching frequencies up to a few kHz. Currently, 15 bit code-generators consisting of >300 transistors operate a bit rate of 100 bits/s but the work is on going with the focus on increasing the operating frequency by downscaling of the lateral dimensions.

2:00 PM S8.2

NEW ORGANIC AND POLYMERIC MATERIALS FOR THIN FILM FIELD-EFFECT TRANSISTORS. Zhenan Bao, Linda Chen, Andrew J. Lovinger, Y.-Y. Lin, H. Schon, B. Batlogg, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Organic thin-film metal-insulator-semiconductor field-effect transistors (MISFETs) are potentially useful in low-cost large area flexible displays and low-end data storage such as smart cards. Much progress has been made recently in discovering new materials and developing low-cost solution-based fabrication processes, such as screen printing and microcontact printing. In this talk new organic and polymeric materials and field-effect transistor properties will be reported. We have discovered solution processable polymers, which exhibit both n- and p-type transistor behavior under ambient conditions. Field-effect mobility great than 0.01 square centimeter per volt per second can be realized for both n- and p-type conduction. In addition, new structures of regioregular polythiophene derivatives have been synthesized and their transistor behavior will be reported.

2:15 PM S8.3

OBSERVATION OF A STEP VOLTAGE CHARACTEISTIC OF SINGLE ELECTRON TUNNELING DEVICE USING DENDRITE MACRO MOLECULES AS COULOMB ISLAND. Tohru Kubota, Shiyoshi Yokoyama, Tatsuo Nakahama, Shinro Mashiko, Kansai Advanced Research Center, Kobe, JAPAN.

Single electron tunneling phenomena have attracted great interests due to their potential application in nano-electronics devices. In the field of semiconductor electronics, various experimental approaches have carried out to fabricate nano-sized tunneling junctions and to observe the single electron tunneling effect at low and room temperature. In the field of molecular electronics, many investigations have been carried out to build up tunnel junctions and molecular rectifying junctions using organic materials with novel and useful electrical and optical properties. In the present study, we made organic junctions of Au/PI/(Rh-G2+ PI)/PI/Au with an artificially layered structure containing rhodamine dendrite macro molecule (Rh-G2), and observed steps in the current-voltage characteristics of these systems with voltage width of e/C. C is the capacitance between the Rh-G2 molecules and Au electrode. Polyimide (PI) LB films as an electron tunneling barrier were deposited onto base Au electrode layer-by-layer with a monolayer thickness of 0.4 nm by the precursor method coupled with the LB technique. Rh-G2 is a dendritic polymer processing rhodamine at the center of the molecule. The interaction between two rhodamine molecules in our junction is assumed to be small due to the presence of the dendritic polymer which surrounds the rhodamine molecule. That is, we examined the electron tunneling process via Rh-G2 molecule, and then discussed the possibility of the fabrication of Coulomb blockade using rhodamine molecules as quantum dot. This represents the first observation of the Coulomb staircase of organic molecular junctions.

2:30 PM S8.4

INTRODUCTION OF ACENES INTO POLYFLUORENE FOR PURE R-G-B EMISSION IN OLEDs. Karl-Heinz Weinfurtner, H. Fujikawa, S. Tokito, Y. Taga, Toyota Central Research & Development Labs Inc., Nagakute, Aichi, JAPAN.

Recent developments in the field of polymer light-emitting diodes have shown that Polyfluorene (PFO) is a promising candidate for highly efficient blue light-emitting diodes due to its high luminescence quantum yield in the solid state[1]. However, due to the liquid crystallinity of PFO, troublesome aggregation occurs in the device on current flow[2]. One attempt to overcome this problem is the introduction of acenes into the PFO mainchain. The sterical demand of the acene moiety can suppress the aggregation effectively[3]. We herein report on the synthesis and characterization of fluorene-acene-copolymers into which not only anthracene as already reported but also the higher homologues, namely 5,12-naphthacene and 6,13-pentacene, are introduced in order to realize a colour tuning to green and red emission. In that sense, we were strongly interested in the effect of the extended aromatic systems on the morphological properties on the one side and on the optoelectronical properties on the other side.
Colour tuning by doping or blending of polymers often suffers from negative side effects like phase separation which consequently leads to concentration quenching and aggregation. However the bound connection with the polymeric host makes the acene units accessible as an emitting chromophore, although the chemical and optical properties of the acene molecules solely are characterised by low solubility and strong aggregation tendency.
In the present copolymers, the acene moieties are fixed at their position in the polymer chain, leading to a statical distribution of the acene units in the host. Due to the torsion between the acene and the fluorene units the emission behaviour is exclusively dominated by the minor content of acenes, indicating an effective electronic decoupling. Hence above- mentioned disadvantages are suppressed and highly pure and efficient blue, green and red emission can be obtained. In addition all acene-fluorene-copolymers exhibit the expected strongly improved morphological properties.

[1] D.D.C. Bradley, M. Inbasekaran, Appl. Phys. Lett. **73, 1998**, 629-631.
[2] D.D.C. Bradley, M. Inbasekaran, SPIE **3145,1998**, 254-259; D.D.C. Bradley, Optical Materials **9, 1998**, 1-11.
[3] M. Kreyenschmidt, G. Klaerner, Macromolecules **31, 1998**, 1099-1103.

2:45 PM S8.5

CONTROL AND CHARACTERIZATION OF PHOTORESPONSIVE POLYFLUORENE BLEND MORPHOLOGY. A.C. Arias, J.J.M. Halls, J.D. MacKenzie, R.H. Friend, Cavendish Laboratory, Cambridge, UNITED KINGDOM; M. Inbasekaran, E.P. Woo, Central and New Businesses R&D, Dow Chemical Company, Midland, MI.

We have investigated the morphology and photoresponsive properties of polyfluorene composite thin films. We have succeeded in manipulating the morphology of the composite films through careful control of the film preparation conditions. The phase separation length-scale has been varied from several microns to the nanometer scale by controlling the evaporation rate of the solvent through various means. These included spin-coating films from different solvents, heating the substrate during spin coating and drop-casting films under a controlled atmosphere. The nature of the phase separation has been investigated using optical and atomic force microscopy. The structure and morphology of the composite films has been related to the optical response of photodiodes fabricated under the same conditions. An order of magnitude variation in photovoltaic efficiency shows that the nature of the phase separation of the polymer blend plays an important part in determining the efficiency of polyfluorene composites photodiodes.

3:30 PM S8.6

UNRAVELING AGGREGATED PHENYLENEVINYLENE POLYMERS ON THE SINGLE MOLECULE LEVEL. Thomas Huser, Ming Yan, Lawrence Livermore National Laboratory, Livermore, CA.

The formation of excitons in conjugated polymers and their migration is essential for their photophysical properties and potential applications in light emitting devices (LED). Fluorescence spectra of poly(phenylenevinylene) (PPV) related polymers are strongly influenced by aggregation in solution and thin films. In ensemble measurements, the fluorescence spectrum of thin films usually shows a large red shift in wavelength with respect to the solution spectrum. We report on single molecule photoluminescence studies of PPV derivatives with varying conjugation lengths and sidegroups that aim at an understanding of the nature of this fluorescence shift. Fluorescence spectra of single polymer molecules were obtained using a confocal scanning optical microscope. Samples spincast from dilute solutions (10^{-9} M) of the PPV derivatives are shown to consist of single molecules and single molecular aggregates composed of only few (<10) molecules. The total number of molecules of which a single aggregate consists is determined from the number of discrete photobleaching steps in their overall fluorescence intensity. Simultaneously to the millisecond dynamics in fluorescence intensity, spectra of single molecular aggregates were obtained with 1 nm spectral resolution and 5-20 s time resolution. The distribution of spectra from single polymers and their aggregates reveals clear indications of exciton migration. Implications for organic LED applications will be discussed. Work at LLNL performed under the auspices of the US Department of Energy under contract N

3:45 PM S8.7

PHOTOLITHOGRAPHICALLY PATTERNED DYE DIFFUSION

INTO ORGANIC THIN-FILMS FOR OLED APPLICATION USING SOFT MASKS. F. Pschenitzka, J.C. Sturm, Princeton University, Dept. of Electrical Engineering, Princeton, NJ.

One approach to achieving full-color in OLED displays using a single spin-cast polymer film requires the patterned introduction of emissive dyes into the polymer film. To this end, we previously developed a doping technique using (a) a large area dopant source, and (b) a shadow mask made of metal or epoxy which facilitates the locally defined diffusion of dye from the source layer into the target layer at elevated temperatures [1]. A three-color matrix has been demonstrated utilizing this technology. However, the mechanical rigidity of the mask, which was in contact with the polymer film, often resulted in damage to the polymer film of the device thereby causing short circuits. Furthermore, the feature size was limited to about 100μm by mechanical constraints of the thick shadow mask. We now demonstrate a method employing a photolithographically defined soft mask to solve these problems. Instead of a separate hard shadow mask, we used a photoresist layer on top of the dopant source, and patterned this layer by conventional photolithographic means. After the dye transfer process, no damage of the target layer resulting from the contact with the soft photoresist layer could be detected. Finally, since the used soft mask is much thinner than the previously used hard mask, the dye transfer is much more effective allowing us to lower the temperature of the dye diffusion process. This technique has been demonstrated using PVK as the matrix forming polymer with PBD as electron transporting material. The dyes transferred were Coumarin 6, Nile red and Bimane, and transferred patterns much less than 50μm, suitable for small pixels, have been achieved.
This work is supported by DARPA and NSF.
[1] F. Pschenitzka, J.C. Sturm, Appl. Phys. Lett. 74, 1913 (1999).

4:00 PM S8.8
ORGANIC LIGHT EMITTING DIODES BASED ON NOVEL HETEROCYCLIC MATERIALS. Ludmila Sukhomlinova, Shihai Gu, Alexander N. Semyonov, Robert J. Twieg, Dept of Chemistry, Kent State Univ, Kent, OH; Rong Fan, George G. Malliaras, Dept of Material Science and Engineering, Cornell Univ, Ithaca, NY.

Organic light emitting diodes (OLED) represent a new and promising area of technology. Design of organic materials with novel structures and improved device configurations provide the opportunity for important improvements in practical application characteristics such as colors, luminescence and driving voltage. We are focused on the synthesis of novel heterocyclic compounds including both amorphous and liquid crystalline materials and their device fabrication. It is particularly interesting to design molecules that are capable to function simultaneously as liquid crystals, charge transport agents and fluorophores. We have prepared different materials containing five member ring heterocycles (oxadiazoles, thiadiazoles, triazoles etc.) including liquid crystalline materials. We have also now prepared liquid crystalline compounds with multiple heterocyclic rings. The chemical properties and relationships between structure and mesogenic properties have been evaluated. Their electrical and optical properties have been investigated as a function of the degree of molecular orientation. Single and multi layer devices have been fabricated, the latter by using standard hole transport materials, and their performance has been measured as a function of temperature.

4:15 PM S8.9
ORGANIC LIGHT EMITTING DEVICES BASED ON PHOSPHORESCENT HOSTS AND DYES. Raymond C. Kwong, Sergey Lamansky, Mark E. Thompson, Univ of Southern California, Dept of Chemistry, Los Angeles, CA.

Organic light emitting devices with phosphorescent electron or hole transporting materials have been fabricated. Devices with iridium(III) tris(8-hydroxyquinolate) (IrQ$_3$) and platinum(II) bis(8-hydroxyquinolate) (PtQ$_2$) as electron transporting materials showed red electrophosphorescence while iridium(III) tris(2-phenylpyridine) [Ir(ppy)$_3$] as a hole transporting material exhibited green electrophosphorescence. When platinum(II) 2,8,12,17-tetraethyl-3,7,13,18-tetramethylporphyrin (PtOX) was doped into IrQ$_3$ or PtQ$_2$, no energy transfer was observed, because of the low triplet energies of IrQ$_3$ and PtQ$_2$. When PtOX was doped into Ir(ppy)$_3$, triplet-triplet energy transfer occurred. The performance and characteristics of the device with this Ir(ppy)$_3$-PtOX system were compared to the previously studied AlQ$_3$-PtOX system. With increasing current density, the quantum efficiencies of the new system did not decrease as rapidly as in the latter system. This is due to the effect of reduced saturation of phosphor at high current densities.

4:30 PM S8.10
TIME EVOLUTION OF FLUORESCENCE IN ORGANIC THIN FILMS AND DEVICES. V. Bulovic, Universal Display Corporation, Ewing, NJ; E. Schreiber, Center for Ultrafast Laser Applications, Princeton University, Princeton, NJ; S.R. Forrest, Center for Photonics and Optoelectronic Materials, Department of Electrical Engineering, Princeton University, Princeton, NJ.

Our investigation of time resolved fluorescence in organic thin films and organic light emitting devices (OLEDs) reveals large spectral shifts (up to 30 nm) during the first few nanoseconds of light emission. Both neat and doped organic films are probed by picosecond optical excitation pulses and fluorescence response is detected by a streak camera with overall system resolution of 60 ps. We used Alq$_3$ and DCM2 as lumophores doped in NPD, TPD, Zrq$_4$, and Alq$_3$ hosts. The observed spectral shifts occur over a time scale of $<$ 5 ns and originate from the response of the medium to the excitation of the luminescent molecules. When the lumophore is promoted from the ground to the excited state, the change in magnitude and orientation of its dipole moment influences the surrounding molecules to minimize the total system energy. The magnitude of the spectral shift is correlated to the strength of dipole-dipole interactions between the luminescent molecule and the surrounding environment and is investigated as a function of temperature, optical and electrical excitation intensity, and dipole moment of the host matrix molecules. It is surprising that molecular dynamics in van der Waals bonded solids occurs on the timescale of nanoseconds due to the steric confinement in the solid, as compared to much faster ($\sim$10 ps) molecular rearrangements in solutions. Indeed, our study demonstrates that local excitations can strongly influence the surrounding environment for polar lumophores in polar hosts.

4:45 PM S8.11
RECENT ADVANCES IN ELECTROOPTIC POLYMERS. Rebecca Taylor, Lockheed Martin Missiles and Space, Palo Alto, CA.

Because electro-optic devices based on non-linear optical organic dye-doped polymer systems offer large potential advantages over inorganic counterparts in terms of bandwidth and design flexibility, much work has been done in recent years to optimize both these materials and the devices based on them, with the result that many very active chromophores have now been synthesized. However, use of these chromophores in devices based on the electro-optic effect requires that they be aligned in a noncentrosymmetric fashion. In the traditional device, an NLO dye is dispersed in an inert polymer matrix and aligned through electric field poling. This paper will discuss recent work in determining the relationship between dye and polymer material properties and the order parameter achievable by this method.