

SYMPOSIUM D

Organic and Nanostructured Composite Photovoltaics and Solid-State Lighting

November 27 - December 2, 2005

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* Invited paper

TUTORIAL

FTD: Organic Photovoltaic Cells Engineering and Polymeric Light-Emitting Diodes
Sunday, November 27, 2005
1:30 PM - 5:00 PM
Room 203 (Hynes)

This tutorial is intended to give attendees a fundamental background and knowledge of current developments in the fields of organic photovoltaic devices (OPVs) and organic light-emitting diodes (OLEDs). Recent reports of efficiencies exceeding 5% have brought OPVs to the attention of many university, government, and industry researchers as a promising pathway to a low-cost, high-volume manufacturing photovoltaic technology. The first half of the tutorial will discuss the fundamental mechanisms of the operation of these devices along with design concepts for single-layer, bilayer, bulk-heterojunction and organic-inorganic hybrid devices. The topics of optimization of light absorption across the solar spectrum, exciton diffusion, electron transfer, and charge transport will be covered. An engineering roadmap for achieving energy conversion efficiencies greater than 10% will be discussed. The second half of the tutorial will cover the fundamental principals of OLED device physics and design. Along with applications in flat-panel displays, these devices show promise for efficient solid-state lighting for general illumination applications. This part of the tutorial will focus on polymer-based devices obtained by solution processing with special attention paid to cross-linkable materials. Pathways and ideas for obtaining higher device efficiencies will be discussed.

Instructors:

Peter Peumans
Stanford University

Klaus Meerholz
University of Cologne, Germany

SESSION D1: OLEDs for Solid State Lighting I
Chair: Anil Duggal
Monday Morning, November 28, 2005
Room 304 (Hynes)

8:30 AM *D1.1

Electrophosphorescence and its Adaptation to Efficient Solid State Lighting. Stephen Forrest¹ and Mark Thompson²; ¹Electrical Engineering, Princeton, Princeton, New Jersey; ²Chemistry, University of Southern California, Los Angeles, California.

Recent results suggest that phosphorescent organic light emitting devices can provide higher efficiencies than any other active display medium, with the exception of those media using ambient light to provide contrast. The high quality of red, green and blue emission currently achieved using a class of Ir-based organometallic compounds has recently also led to the possibilities that electrophosphorescence can also be useful for generating high brightness and efficient white light needed for solid state lighting. In this talk, we will consider methods and recent advances in achieving very high efficiency OLEDs for solid state white light generation. In particular, we will consider the physics and technology of employing phosphors, and phosphors in combination with fluorescent dopants in small molecular weight organic systems for obtaining the highest possible white light generation efficiencies. In particular, recent results have shown that WOLEDs with >25lm/W power efficiency at >1000 cd/m² and CRI=85 brightness are achievable simply using flat glass substrates, where only 20% of the light is emitted. However, low cost schemes for improving outcoupling can result in a near doubling of this efficiency. In this talk, both device architectures and outcoupling schemes with the aim of achieving lighting sources that significantly improve on incandescence will be discussed.

9:00 AM *D1.2

Highly Efficient OLED for Displays and Lighting. Karl Leo, Gufeng He, Qiang Huang, Karsten Fehse, Gregor Schwartz, Martin Pfeiffer and Karsten Walzer; Inst. f Angewandte Photophysik, TU Dresden, Dresden, Germany.

In this talk, I will review some of our recent progress in the field of highly efficient organic LED. In particular, I will present recent results from our work in Dresden on OLED with doped transport layers: Using such layers, the voltages of OLED can be reduced close to the quantum limit, virtually independent of contact materials and device configuration (top or bottom emitting). Additionally, we have developed a novel double emitter structure which allows high quantum efficiencies even at high brightness. These efforts have

helped to obtain green OLED with efficiencies well above 100 Lumen/Watt; i.e. much better than the best green nitride LED available today. With doped transport layers, it is actually possible to achieve top-emitting OLED which are more efficient than bottom emitters. This is important for both lighting and display applications. Finally, I will discuss how OLED could be further improved. Since both operating voltage and quantum efficiency are already close to their theoretical limit, the next challenge is to raise the optical outcoupling efficiency. This should allow to further increase the efficiency of the devices by at least a factor of two.

9:30 AM D1.3

Low Voltage High Efficiency Blue OLEDs using Organic Phosphine Oxide Compounds as Electron Transporting Host. A. Padmaperuma, L. S. Sapochak, P. Vecchi, K. Ferris and Paul E. Burrows; Pacific Northwest National Laboratory, Richland, Washington.

The steadily increasing efficiency of organic light emitting devices (OLEDs) already exceeds that of incandescent light bulbs and may ultimately rival fluorescent tubes. However, many technological challenges must be overcome before OLED-based white lights can be realized. Many of the published techniques for generating white light (multiple dopants, downconversion etc.) are limited by the efficiency of the blue component. High efficiency small molecule OLEDs utilize energy transfer from a host matrix to an electrophosphorescent dopant but blue phosphorescent OLEDs are particularly challenging because the host triplet energy must be > 2.75 eV to achieve efficient (exothermic) energy transfer. This has recently been accomplished by using an ultra-wide bandgap, non-conductive tetraaryl silane host matrix and an iridium compound as dopant. This yields devices with high quantum efficiency but relatively high operating voltage and limited stability, since charge transport depends on hopping conduction via the dopant molecules. In this paper, we report the development of new wide band gap hosts based on organic phosphine oxides. These materials have triplet state energies up to 3.0 eV and are electron transporting in an OLED device. Simple OLEDs containing these materials show low operating voltages and both weak electroluminescence with a spectral peak at 330 nm and room temperature electrophosphorescence at ~ 460 - 500 nm. Devices doped with green and sky blue Ir-based phosphors demonstrate > 8% external quantum efficiency at 6V at display brightness (>5% and 7V at lighting brightness). Strategies for further improving quantum efficiencies and lowering voltages of both UV-emitting and dye-doped electrophosphorescent OLEDs will be discussed.

9:45 AM D1.4

Saturated, deep blue organic electrophosphorescence using a fluorine-free emitter. Russell Holmes^{1,2}, Stephen R. Forrest^{1,2}, Tissa Sajoto³, Arnold Tamayo³, Peter I. Djurovich³, Mark E. Thompson³, Jason Brooks⁴, Yeh-Jiun Tung⁴, Brian W. D'Andrade⁴, Michael S. Weaver⁴, Raymond C. Kwong⁴ and Julie J. Brown⁴; ¹Electrical Engineering, Princeton University, Princeton, New Jersey; ²Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey; ³Chemistry, University of Southern California, Los Angeles, California; ⁴Universal Display Corporation, Ewing, New Jersey.

The study of blue organic electrophosphorescence has focused on the use of electron-withdrawing fluorine atoms to increase the energy of the molecular triplet state. One drawback to this technique is that the deep blue color required for high performance display applications may not be achievable through fluorination. In addition, the large electronegativity of the fluorine atom may tend to destabilize the molecule as a whole, making the molecule more reactive and the resulting devices potentially unstable. We demonstrate saturated, blue organic electrophosphorescence using the fluorine-free emitter mer-tris(phenyl-methylbenzimidazolyl)iridium(III) (m-Ir(pmb)₃) doped into the wide gap host p-bis(triphenylsilyl)benzene (UGH2). Under electrical excitation, the highest energy vibronic transition occurs at 395 nm, and device electroluminescence can be characterized by Commission Internationale de l'Éclairage co-ordinates of (x=0.16, y=0.10). Peak quantum and power efficiencies of (4.4 ± 0.4)% and (1.6 ± 0.2)lm/W were obtained respectively. This work represents a departure from previously explored, fluorinated sky-blue phosphors, and is the first demonstration of a deep blue/near ultraviolet electrophosphorescent device.

10:30 AM *D1.5

Design and Fabrication of High Performance OLEDs for Lighting Applications. Junji Kido, ¹Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan; ²Optoelectronic Industry and Technology Development Association, Bunkyo-ku, Tokyo, Japan; ³Research Institute for Organic Electronics, Yonezawa, Yamagata, Japan.

High quantum efficiency, high power efficiency OLEDs were fabricated

by using newly synthesized wide-energy-gap materials as the carrier transport materials and host materials for phosphorescent emitters. High external quantum efficiencies of over 20 percent were achieved for sky blue and green OLEDs using Ir chelates as the emitters. Power efficiency of 35 lm/W and 90 lm/W were obtained for sky blue and green OLEDs, respectively. Multi photon OLEDs (tandem-type OLEDs) were fabricated using different emissive units to obtain white light and a high CRI of over 95 was achieved. Large-size OLEDs (30 cmx30 cm) for lighting application was fabricated and prototype lighting devices were demonstrated.

11:00 AM *D1.6

Solution Processed Single Layer Electrophosphorescent Devices for Solid State Lighting (Invited Paper). Franky So, Vi-En Choong, Mathew Mathai and Stelios Choulis; OSRAM, San Jose, California.

In this presentation we present results of high efficiency single layer electrophosphorescent OLEDs fabricated using solution processes. The recent single layer devices based on small molecule dyes dispersed in a polymer matrix have power conversion efficiency up to 24 lm/W [1]. The key to obtaining high efficiency from a single layer electrophosphorescence OLED is the control of charge balance and charge injection. We investigate the effect of incorporation of carrier transport moieties within the host polymeric binder and correlate the results with device performance. We will also present results on several alternative structures studied in order to improve carrier injection efficiency. As an example we have incorporated a Poly(9,9-dioctyl-fluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB) interfacial layer between hole conducting layer (PEDOT:PSS) and light emitting layer (LEP) into a single layer electrophosphorescence device based on 2-(4-(4-tolyl)phenyl)pyridine)iridium [Ir(mppy)3] green-emitting organo-metallic compound and a poly(N-vinylcarbazole) (PVK) non-conjugated polymer co-doped with 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and N,N'-diphenyl-N,N'-(bis(3-methylphenyl)-[1,1-biphenyl]-4,4'-diamine (TPD), electron and hole transporting moieties respectively. With enhancement in carrier injection by the TFB interfacial layer, the devices have power efficiency up to 50 lm/watt and luminous efficiency of 50 cd/A. In addition, we have also demonstrated a single layer blue phosphorescent device with peak efficiency of 22 cd/A. To our knowledge this is the highest reported value for a single layer solution processed electrophosphorescent device in the literature. The results indicate that incorporation of interfacial layer can be used to achieve high efficiency flat panel displays and solid state lighting sources and direct injection to phosphorescence organo-metallic emitters is the key to obtain high efficiency devices. In this presentation we will present results on several alternative device architectures and show how they improve the performance of the electro-phosphorescent polymer LEDs. Reference: [1] X.H Yang and D. Neher, Applied Physics Letters, 84 ,2476, (2004)

11:30 AM D1.7

New Host Polymers and Iridium Complexes for Blue to Green Electrophosphorescence. Andrew B. Holmes^{1,2}, Khai Leok Chan^{2,1}, Chris S. K. Mak², Scott E. Watkins^{1,2}, Nicholas R. Evans², Carl R. Towns³ and Mary J. McKiernan³; ¹Bio21 Institute, University of Melbourne, Parkville, Victoria, Australia; ²Melville Laboratory, University of Cambridge, Cambridge, United Kingdom; ³Cambridge Display Technology Limited, Cambridge, United Kingdom.

Significant advances have been made in recent years using phosphorescent guest molecules to capture the triplet excitation energy in organic light emitting devices fabricated with conjugated materials. There is considerable interest in depositing these materials from solution. This paper will describe the preparation and use of some novel polydibenzosilole derivatives as high energy conjugated polymer hosts for triplet guest molecules that can either be blended with or covalently linked to the conjugated polymer host. Guest blue to green electrophosphorescent iridium complexes have been developed that avoid the potential instability associated with incorporating PEDOT:PSS in EL devices.

11:45 AM D1.8

Deep Blue Phosphorescent Iridium Complexes for Organic Light Emitting Diodes. Shih-Chun Lo¹, Christopher P. Shipley¹, Raghu N. Bera², Ruth Harding², Ebinazar B. Namdas², Ifor D. W. Samuel² and Paul L. Burn¹; ¹Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford, United Kingdom; ²Organic Semiconductor Centre, School of Physics and Astronomy, University of St. Andrews, St. Andrews, United Kingdom.

Organic electroluminescent materials have been intensively studied for use in organic light emitting diodes (OLEDs). For full colour displays, saturated blue, green and red emitters are required. Highly efficient deep green and red phosphorescent OLEDs have been successfully demonstrated. However, room temperature saturated blue

phosphorescent materials are a real challenge and still need to be developed. We will present a new family of phosphorescent materials based on fac-tris(phenyltriazolyl)iridium (III) complexes that emit blue to deep blue light at room temperature. The simple and high-yielding synthetic routes to the complexes will be described and we will show that the introduction of triazole moiety attached to the phenyl ring of the ligands significantly increases the LUMO energy level and hence tunes the triplet energy bandgap of the iridium complexes into the blue and deep blue regime. The solution photoluminescence spectra of the blue materials have λ_{max} ranging from 450 to 430 nm with CIE co-ordinations of (x=0.15, y= 0.19) to (x=0.15, y=0.08). The materials are all luminescent in solution with solution quantum yields in the range of 2%-66%. We will discuss the relationship between the emission colour and photoluminescence quantum yields in terms of the orbital distribution and energies. Finally, the OLED performance of some of the materials will be shown.

SESSION D2: OLEDs for Solid State Lighting II

Chair: Junji Kido
Monday Afternoon, November 28, 2005
Room 304 (Hynes)

1:30 PM D2.1

Crosslinkable Semiconductors for Efficient Polymer-OLED. Klaus Meerholz, Physical Chemistry, University of Cologne, Cologne, Germany.

The synthesis and use of crosslinkable low- and high-molecular-weight semiconductors is reviewed. These material can be applied similar to a standard negative photoresists, whereby soluble precursors with oxetane sidegroups are crosslinked photochemically to yield insoluble polymer networks. This allows for multiple-layer deposition as well as lithographic patterning. The application of this highly promising material class in highly-efficient RGB light-emitting diodes is presented, yielding triplett-based green emission with efficiency of 67 Cd/A. We demonstrate the use relatively thick redoxchemically doped hole-transport layers without loss in device performance. Consecutive deposition of RGB electroluminescent polymers yielded devices with efficiencies and lifetimes comparable to state-of-the-art performances (> 10.000 hours).

1:45 PM D2.2

The improvement of device performances by an electron blocking layer in multilayered polymeric light-emitting diodes. Soo-Hyoung Lee¹, Byung Doo Chin¹, Jai Kyeong Kim¹ and Yiyeol Lyu²; ¹Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea; ²Samsung Advanced Institute of Technology, Suwon, South Korea.

We report high performance blue light-emitting diodes obtained by inserting an electron blocking layer (EBL) into the multilayered polymeric device structure. New materials which have UV or thermally cross-linkable moieties were synthesized and used for electron blocking materials. The devices, with configuration of indium tin oxide (ITO)/ poly(3,4-ethylene dioxothiophene)-poly(styrene sulfonic acid) (PEDOT-PSS) (65 nm)/EBL (10-20 nm)/ poly(octylfluorene) derivative (70 nm)/ BaF₂(2 nm)/Ca(50 nm)/Al(300 nm), were fabricated by spin coating and thermal evaporation. In the devices, the EBL requires a hole transporting property and a relatively higher band gap, especially a lower LUMO level, than the emitting polymer in order to block electrons from cathode effectively and accumulate them in the emitting polymer. Specially, thermally cross-linkable electron blocking molecules show stable film qualities such as small root mean square (RMS) roughness and small thickness variation by an additional emitting layer fabrication. The devices with EBL exhibit a higher luminance efficiency and brightness than those in devices without EBL. The synthesis, characterization, device fabrication, and electroluminescence properties will be presented.

2:00 PM D2.3

White Polymers in OLEDs for Lighting Applications. Margreet de Kok¹, Mark Vorsthove¹, Eric Meulenkaamp¹, Michael Buechel¹, Karsten Heuser² and Ralph Paetzold²; ¹Philips Research, Eindhoven, Netherlands; ²Siemens A.G., Erlangen, Germany.

Organic Light-Emitting Diodes (OLED) are light sources which are well suited for general illumination and signage because of the possibility to extend the emissive area easily to large surfaces. Moreover, these sources are very thin and can be made transparent or reflective and operate at low power. High efficiencies and longer lifetime come into reach and colours can be customised by specially dedicated material systems. The application technology in case polymers are used as organic material (Polymer OLED) can be a

printing technique as the active materials can be processed from solution. Within the framework of the European OLLA project a white emitting polymer from Covion is evaluated. We will show current, voltage, luminance results of double carrier Polymer OLEDs as well as single carrier devices. We have studied the dependence of the colour characteristics on luminance and temperature. At higher current densities the relative contribution of the red dye to the emission of the polymer decreases. Photoluminescence measurements at reverse bias do not indicate a stronger electric field induced dissociation of excitons on the red dye. When increasing the temperature, the relative contribution of the red dye increases again. Faster detrapping of charge carriers, higher mobilities and shorter lifetimes of excitons are probably involved in these observations. When a device is driven at a constant current density, differential ageing of the different dyes is observed, resulting in a change of spectral distribution of the electroluminescence. In conclusion, by temperature, luminance and stress the electroluminescence spectrum and electrical properties are changed. This allows application-dedicated design of materials and driving. We will discuss the possible hypotheses for explanation of these observations.

2:15 PM D2.4

Polymers Containing Terpyridine in the Side Chain: White light emission and beyond. Greg Tew, University of Mass-Amherst, Amherst, Massachusetts.

Polymeric materials have been used as essential components in the synthesis of supramolecular materials rarely, despite their many advantages. Success in this area will deliver multifunctional properties for the next generation of materials. Most importantly, they increase organizational length scales compared to small molecules, opening a range extending from the atomic (0.1 nm) to the mesoscopic (2,000 nm). We focus on metal-ligand interactions since these are discrete, well defined, geometrically constrained, and competitive under a variety of environmental conditions. In addition, the interaction strength is widely tunable based on the choice of metal ion and organic ligand. We were the first laboratory to demonstrate successfully the impact these groups have on solution viscosity. In addition, we recently reported the synthesis of block copolymers in which metal ligands are confined to one or more segments. To prepared block copolymers and narrow polydispersity materials we use 'living' or controlled radical polymerization techniques including atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT). These novel architectures have allowed the discovery of new materials that emit yellow light based on an alloy of terbium and europium or perfectly white light by combining a blue emitter (dysprosium). When iron (III) ions are incorporated novel nanostructures of roughly 700 nm are formed. These have been characterized by TEM, AFM, and SEM. Preliminary studies suggest they are magnetic. This talk will highlight some recent findings from our laboratory, with emphasis on emission properties, from these unique and exciting molecules

3:30 PM D2.5

Efficiency limitation due to spin-conserving carrier recombination in conjugated polymers. John Mark Lupton¹, Manfred Walter¹, Martin Reufer¹, Pavlos Lagoudakis¹, Jochen Feldmann¹, Anne Beate Hummel², Johanna Kolb², Hartmut Roskos² and Ulrich Scherf³; ¹Department of Physics, Ludwig-Maximilians-Universitaet, Munich, Germany; ²Physikalisches Institut, University of Frankfurt, Frankfurt, Germany; ³Department of Chemistry, University of Wuppertal, Wuppertal, Germany.

The question of the ultimate quantum efficiency achievable with polymeric light-emitting diodes (PLEDs) is of utmost importance to future material development and device design. According to simple spin statistics the efficiency is limited to 25%, as generally only singlet excitons contribute to the electroluminescence of the device. Numerous theoretical and experimental indications exist, however, pointing to the possibility of surpassing this barrier by spin-dependent recombination leading to a retardation of triplet formation when compared to singlet formation [1]. In order to impact on the efficiency, this process requires efficient spin mixing due to spin orbit coupling or spin lattice relaxation, which has previously not been accessible experimentally as it is hard to visualise singlets and triplets simultaneously. Tackling the question of spin dependent exciton formation we use a novel class of polymeric material containing traces of metallic complexes which makes it possible to observe singlet and triplet excitations simultaneously. The phosphorescent decay channel of generally invisible triplets is activated by highly localised spin orbit coupling and efficient triplet diffusion [2]. In this way we can efficiently differentiate between spin states by spectroscopic means and directly observe changes of the total spin of the exciton precursors, the bound polaron pairs. Starting from optically generated excitons, polaron pairs are formed and stabilized over timescales relevant to the operation of PLEDs by applying an external electric field. Fast spin lattice relaxation between isoenergetic pair states of

different spin multiplicity should be observable. Surprisingly, during the electrostatic storage such effective spin mixing is not observed, even at room temperature, demonstrating that spin lattice relaxation is extremely slow [3]. Furthermore, perturbation of the polaron pair energy levels by an external magnetic field should influence the singlet/triplet ratio if the exchange energy is small. However, even strong magnetic fields of up to 8 T applied during the pair state formation out of injected free charges do not alter this ratio. Both observations suggest an exceptionally and unexpected strong exchange interaction between carriers constituting the polaron pair and highlight that intersystem crossing is much less efficient in the intermolecular pair state than in the intramolecular exciton. We conclude that in the absence of fast spin lattice relaxation differences in the formation rates of singlet and triplet excitons alone cannot lead to preferential singlet formation, thus imposing the spin statistical limit on the PLED efficiency [3]. [1] M. Wohlgenannt et al., Nature 409, 494 (2001) [2] J. M. Lupton et al., Phys. Rev. Lett. 89, 167401 (2002) [3] M. Reufer et al., Nature Mat. 4, 340 (2005)

3:45 PM D2.6

A general method for achieving high efficiency in polymer light-emitting diodes. Jinsong Huang, Gang Li and Yang Yang; Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California.

We report a general method to significantly increase the efficiency of polymer light emitting diodes (PLEDs) by controlling the charges, via material and device engineering, in the light-emitting polymer (LEP) layer. By blending high bandgap and low bandgap polymers in proper ratios, we are able to introduce charge traps in the LEP layer. Similarly, by introducing an electron injection/hole blocking layer, we are able to enhance the minority carrier (electrons) injection and block holes. Efficient and balanced charge injections as well as charge confinement are attained simultaneously, and as a result, very high efficient devices have been achieved. As an example of this approach, we have blended 0.5%-2% of Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) with poly(9,9-dioctylfluorene) (PFO) as active polymer for PLEDs. A Cs₂CO₃ charge injection and hole block layer is used at the cathode interface. The devices emission covers colors from white to yellow, depending on the blend ratios, with the highest peak efficiency of 16 lumen/watt (lm/W). To our knowledge, this is the highest reported efficiency for white emission fluorescence PLED.

4:00 PM D2.7

Electroluminescent Devices from Ionic Transition Metal Complexes for Lighting Applications. Jason Slinker¹, Jonathan Rivnay¹, John DeFranco¹, Samuel Flores-Torres², Michael Lowry³, Karl Oyler³, Daniel Bernards¹, Leonard Soltzberg⁴, Velda Goldberg⁵, Michael Kaplan¹, Stefan Bernhard³, Hector Abruna² and George Malliaras¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Chemistry and Chemical Biology, Cornell University, Ithaca, New York; ³Department of Chemistry, Princeton University, Princeton, New Jersey; ⁴Department of Chemistry, Simmons College, Boston, Massachusetts; ⁵Department of Physics, Simmons College, Boston, Massachusetts.

Ionic transition metal complexes (iTMCs) are receiving increased attention as these compounds have produced high efficiency organic light emitting devices with air-stable cathodes. In order to be considered for lighting applications, these devices must show efficient emission at multiple colors, long lifetimes, and compatibility with practical lighting architectures. With regard to color, we have demonstrated the first instances of yellow and green emission with iTMC devices. These single-layer devices exhibit efficiencies as high as 10 lumens per watt, comparable to an incandescent bulb. With regard to lifetime, we discuss recent efforts to identify quenching species in our devices with techniques such as time-of-flight mass spectrometry, as well as means of suppressing degradation. Concerning lighting architectures, we report on lighting panels based on an iTMC that can be sourced directly from a standard U.S. wall outlet. With the aid of an ionic liquid, these devices achieve sufficiently fast response to switch at frequencies up to 120 Hz. Fabricated from a single spin cast iTMC layer, these devices are prepared in a sandwich-structure cascaded architecture. This architecture sustains high input voltages, provides fault tolerance, and facilitates the fabrication of large area solid-state lighting panels.

4:15 PM D2.8

Molding the Emission of Organic Light-Emitting Diodes using Non-Periodic Dielectric Photonic Structures. Mukul Agrawal and Peter Peumans; Electrical Engineering, Stanford University, Stanford, California.

The coupling of photons into waveguided modes, surface-plasmon-polaritons or modes that are bound by total internal reflection at the substrate-air interface, results in low OLED photon outcoupling

efficiencies (~20%). Improving the outcoupling efficiency without adversely affecting the angular emission pattern and color variation remains one of the major challenges in OLED design. Here, we demonstrate a novel approach for improving the outcoupling efficiency of OLEDs based on redistributing the local density of photon states in the spectral and spatial domain. A quasi-global optimization technique was developed to design OLEDs with simple non-periodic dielectric stacks inserted between the substrate and transparent anode. By simultaneous optimization in the angular and spectral domain, this method provides improved photon outcoupling and increased exciton optical decay rates while maintaining Lambertian emission over a chosen angular range, in contrast to previous work that use cavity resonances. Using optimized dielectric stacks, our method results in outcoupling efficiencies that exceed those of a typical OLED by 45% to 175%, depending upon the angular range within which a perfect Lambertian response is desired. This is a significant improvement over previously demonstrated techniques. Uniquely, this scheme offers the capability to trade-off the range of angular uniformity against higher brightness and results in a minimal dependence of the CIE coordinates on emission angle. Using our method, OLEDs with effective external quantum efficiencies in excess of 60% and an angular emission pattern that is Lambertian for a 10° half-angle about the substrate normal and essentially dark elsewhere, can be realized. Our method is also advantageous in that it does not require a modification of the OLED structure. Moreover, it can be used in conjunction with other outcoupling schemes.

4:30 PM **D2.9**

Luminance Enhancement of Organic Light-Emitting Display by Microlens Array Attachment. Kuan-Yu Chen¹, Ciao-Ci Lin², J. H. Lee¹, Mao-Kuo Wei² and Chia-Fang Wu¹; ¹Graduate Institute of Electro-Optics, National Taiwan University, Taipei, Taiwan; ²Department of Materials Science and Engineering, National Dong Hwa University, Hualien, Taiwan.

We have demonstrated the luminance enhancement of 42.5% in zero degree (normal direction) and 50.7% in 60 degree by attaching a microlens film to an organic light-emitting display (OLED). Such a film was fabricated by thermal-reflow process that exhibits the advantages of cheap, easy-fabrication, and large-panel-possibility. In our design, we change the microlens shape (rectangular, hexagonal and spherical), size and spacing between the microlens. When the spacing is smaller, the ratio of the patterned area to the combination of patterned and the unpatterned area of the microlens array film, which is called the "area ratio", becomes higher. The luminance enhancement factor linearly increases from 5% to 42.5% when the area ratio increases from 20% to 90% in rectangular microlens. When varying the dimension of microlens, the luminance enhancement factor decreases from 35% to 16% when the unit cell size of microlens increases from 0.0013 to 0.0025 mm². On the other hand, it has little dependence when varying the shapes of the microlens. We obtain similar luminance enhancement factor with rectangular, hexagonal and spherical microlens when they have the same size and area ratio. Here, we used the green OLED with the spectrum peak at 515 nm and a FWHM of 86 nm at normal direction. When observing at larger viewing angle, i.e. 80 degree to the normal, the emission has a blue shift to 510 nm due to the waveguiding effect. When the microlens film was attached, we observe the spectrum was shift from 510 to 495 nm when the view angle increases from 0 to 80 degree to the normal. Besides, the FWHM of the OLED device with microlens array increases to 95 nm. That is clear evidence that the microlens structure destroys the waveguiding effect and extracts the light from the substrate mode.

4:45 PM **D2.10**

Color-Tunable Multi Photon Emission Organic LEDs with Improved Emission Characteristics. Nobuhiro Ide², Takuya Komoda² and Junji Kido^{1,2}; ¹Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan; ²Optoelectronic Industry and Technology Development Association, Bunkyo-ku, Japan.

Multi Photon Emission organic LEDs (MPE-OLEDs) with alternately stacked emissive units and charge generation layers show intricate emission characteristics owing to the optical interference originated in the thick device structure. The emission characteristics can be controlled by tuning the device parameters such as layer thickness and the number of the emissive units. Here, we demonstrate the minimization of the viewing angle dependence of the emission spectra by introducing an interference reduction member into the MPE-OLEDs. Additionally, we fabricated the color-tunable MPE device by using the extra emissive unit in combination with the interference reduction film. This structure can be applicable to the white OLED to control the emissive colors.

SESSION D3: Poster Session
Chairs: Paul Burrows and Franky So
Monday Evening, November 28, 2005
8:00 PM
Exhibition Hall D (Hynes)

D3.1

Hole Transport Layers with Adjustable Solubility for Use in Multilayer Polymeric Light-Emitting Diodes. Cristina Tanase, Jurjen Wildeman and Paul W. M. Blom; Materials Science Centre, University of Groningen, Groningen, Netherlands.

The active part of present state-of-the-art PLEDs consists of only a single layer. The use of only a single electro-optic layer has a large fundamental disadvantage: due to the reduced electron transport in conjugated polymers most of the light in a PLED is generated close to the metallic cathode which acts as a quenching site for the generated excitons, thereby strongly reducing the efficiency of the PLEDs. In a multilayer device electrons and holes are efficiently transported via high mobility layers towards a highly luminescent layer. The hole transport layer also serves as a blocking layer for electron transport and vice versa. A major problem for realizing polymer based multilayer PLEDs is the solubility of the materials used. We demonstrate that the charge carrier mobility of PPV-based derivatives can be optimised by chemical modification. Subsequently, copolymers with selective solubility can be achieved without loss of the enhanced charge transport properties. As a first demonstration dual-layer PLEDs are constructed in which the holes are efficiently transported via a high-mobility copolymer towards the luminescent layer. These dual layer PLEDs exhibit an enhanced efficiency at high voltages (>10V) and a strongly improved robustness against electrical breakdown.

D3.2

External efficiency calculation of OLED for multilayer structures of both coherent and incoherent layers, and with a point source in the emissive layer. Pil Soo Ahn^{1,2}, Tom D. Milster³, Chang Hee Lee², Young-Gu Jin¹, Byoung Ho Cheong¹, Sung Hun Lee⁴, Sang Yeol Kim⁴, Chang Kwon Hwangbo⁵ and Jai Kwang Shin¹; ¹CSE Center, Samsung Advanced Institute of Technology, Yongin, Gyeonggi, South Korea; ²School of Electrical Engineering and Computer Science, Seoul National University, Seoul, South Korea; ³College of Optical Sciences, University of Arizona, Tucson, Arizona; ⁴I-1 Team, Samsung Advanced Institute of Technology, Yongin, Gyeonggi, South Korea; ⁵Department of Physics, Inha University, Incheon, South Korea.

The optical reflectance and transmittance of a multilayer structure for a plane wave source are readily represented by a transfer matrix¹ in the case of the coherent light which is useful to optically isotropic and homogeneous layers. In this case we have supposed the substrates as being one-sided slabs of materials having a semi-infinite thickness. But in almost all practical cases the substrates have finite thickness with much greater than wavelength². OLED can be considered as a structure with an infinitely many incoherent point sources in the emissive layer. In this work, the transfer matrix has been modified to calculate the external efficiency (transmittance of energy) of OLED of both coherent (its thickness is comparable to the wavelength) and incoherent (its thickness is much greater than the wavelength) layers, as well as with a point source in the emissive layer. OLED structures used here are similar to the practical devices. And the simulations are compared with the measurement results of the light intensity and the electroluminescence spectra for the bottom emission type OLED. The position of the emissive point and the internal quantum efficiency are obtained from the device simulation³ and used as input data of optics simulation to get the external efficiency. The transfer matrix used here is applicable to the case of the oblique incidence and the lossy materials. 1. H.A. Macleod, Thin Film Optical Filters, Inst of Physics Pub Inc, 3rd ed.(2001) 2. C.C. Katsidis, D.I. Siapkas, "General transfer-matrix method for optical multilayer system with coherent, partially coherent, and incoherent interference", Applied Optics, V41, No 19, 3978~3987 (2002) 3. H. Houili, E. Tutis, H. Lutjens, M.N. Bussac, L.Zuppiroli, "MOLED: Simulation of multilayer organic light emitting diodes", Computer Physics Communications, 156, 108~122 (2003)

D3.3

Design, Synthesis and Photophysics of Alq₃ Derivatives with tunable properties for application in Organic Light Emitting Diodes. Victor Armando Montes¹, Radek Pohl¹, Gang Li², Joseph Shinar² and Pavel Anzenbacher¹; ¹Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio; ²Physics, Iowa State University, Ames, Iowa.

The unique electron-transport and emissive properties of Alq₃ have made this material extensively used in OLED technology utilizing the so-called small-molecule approach. In order to cover the visible

spectrum with materials that display similar stability, processability, charge-transport and optoelectronic properties to this benchmark compound; it has been long attempted to develop derivatives with tunable energy levels which could act either as energy hosts for guest dyes or as Red-Green-Blue (RGB) emitters. Nevertheless, efforts to prepare stable and easy-to-process Alq₃ derivatives have met only with a limited success, and the literature provides spotty evidence for a rational design of materials with tunable properties mediated simply by variation of substituents attached to the quinoline ligand. In this presentation, we describe how substitution at the 5-position of the quinoline ligand through appropriate aryl modulator groups of different electronic nature allows for an effective tuning of the highest occupied molecular orbital energy of the metalloquinolinolate as well as for its emission fine-tuning. Remarkably, a systematic tuning of the HOMO energy level ($E^{HOMO} = 5.16\text{-}6.13$ eV), as well as of the photoluminescence and electroluminescence ($\lambda_{max} = 479\text{-}616\text{nm}$) was obtained with the novel Alq₃ based materials. In accordance with theoretical studies the energy levels for the frontier orbitals estimated from electrochemical studies showed that while the energy of the HOMO was effectively manipulated, the lowest unoccupied molecular orbital energy was found to be largely unaffected by substitution on the 5-position of the ligand. In general, the introduction of electron-withdrawing substituents induced a higher magnitude for the HOMO energy level and a blue-shifted emission compared to the parent unsubstituted compound, while electron-donating substituents caused a lower energy for the HOMO and a red-shifting in the emission. Correlation of the photophysical properties of the complexes with the Hammett constant of the substituents offered a new and powerful tool for the design of new complexes with predictable emissive properties. More importantly, the OLED devices fabricated using the novel complexes displayed strong electroluminescence, while their spectra essentially reproduced the emission-tuning pattern observed in solution; suggesting that this approach generates potentially useful electron-transporting and emissive OLED materials. In summary, we report the synthetic preparation of novel Alq₃ derivatives, a detailed study of their photophysical properties and electrochemistry, and their electroluminescent behavior in organic light emitting diodes. This work provides insights into design criteria for the development of potentially useful RGB electroluminescent phosphores for OLEDs.

D3.4

High-Efficiency Stacked Organic Electrophosphorescent Devices. Hiroshi Kanno and Stephen R. Forrest; Princeton Institute for the Science and Technology of Materials (PRISM), Department of Electrical Engineering, Princeton University, Princeton, New Jersey.

We demonstrate stacked organic light emitting devices (SOLEDs) using phosphorescent emitters for the high intensity generation of white light. We compare several different thermally evaporated transition metal oxides such as vanadium pentoxide (V₂O₅) for use in a SOLED lacking contacts to the interlayers between separately stacked elements. The SOLEDs studied consisted of two stacked OLED units separated by an interlayer of 10-nm-thick metal oxide, where a red emitter, tris(1-phenylisoquinolinato-C²,N)iridium(III) (Ir(piq)₃) and a green emitter, tris(2-phenylpyridine)iridium(III) (Ir(ppy)₃) were doped in a host, 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP) in each unit. The peak external quantum and power efficiencies for the SOLEDs are 15.8 % and 10.2 lm/W. The quantum efficiencies from each green-emitting and red-emitting OLED unit in the SOLED are 8.4 % and 8.5 %, respectively. It is found that the efficiency of a SOLED with a metal oxide interlayer is nearly doubled over a single element device. We also fabricated white-emitting SOLEDs, which will be discussed in detail in our presentation.

D3.5

Red Phosphorescent Organic Light-Emitting Devices with High Efficiency and Low Driving Voltage. Hsin-Hung Tsai^{1,2}, J. H. Lee¹ and Chin-Ti Chen²; ¹Electro-Optical, National Taiwan University, Taipei, Taiwan; ²Institute of Chemistry, Academia Sinica, Taipei, Taiwan.

In this paper, we demonstrate a high-efficiency and low-driving-voltage red phosphorescent organic light emitting device (PHOLED). Here, we used a new material with red emission based on Iridium complex which can be doped in a typical hole or electron transporting material (HTL, ETL) as the emitting layer (EML) without a hole-blocking layer (HBL). Such device structures can effectively reduce the driving voltage by 6 V at the current density of 100 mA/cm² compared with traditional PHOLED. The maximum efficiency of the device is 12.6 cd/A with the luminance of 1070 cd/m². Triplet-triplet annihilation behavior is not obvious in this device so that an efficiency of 9 cd/A at 10000 cd/m² was obtained. The CIE coordinates of the devices are (0.617, 0.367) and (0.645, 0.35) with HTL and ETL as the host of the EML which shows a deep-red emission, respectively. Typically, the bandgap of the host of the EML in a phosphorescent device is usually larger than that in a fluorescent device for better energy transfer from singlet to triplet state. For

example, 4,4'-N,N-dicarbazole-biphenyl (CBP) is a commonly used host for a PHOLED. However, the highest occupied molecular orbital (HOMO) value of CBP, 6.3 eV, is quite high that obstructs the injection of holes and increases the driving voltage. Besides, such a host material is a bipolar material. That means, hole and electron can both transport in CBP so that a HBL material with higher HOMO value is needed between EML and ETL to impede the holes inject into ETL. The introduction of HBL generally increases the driving voltage and increases the complexity of manufacture. In our experiments, we used 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl(NPB) and bis(10-hydroxybenzo[h]quinolinato)beryllium (Bebq2) as host and Iridium phosphorescent material as red dopant (RD). The device structures is NPB (50 nm) / host: 10% RD (x nm) / Balq2 (40-x nm) / Bebq2 (30 nm) / LiF (1.2 nm) / Al (150 nm). The x value is 30 nm and the host materials are CBP, NPB and Bebq2 in device A, B and C, respectively. In device D and E, the x value is 40 and the host materials are Bebq2 and NPB, respectively. Compared with device A, the driving voltage is reduced from 15 V to 12.5 and 13 V under the driving current density of 100 mA/cm² due to better energy alignment in device B and C, respectively. The current efficiency of device A, B and C are 4.4, 7, and 7.5 cd/A under the same driving current density. When there is no HBL, the driving voltage is further reduced to 10 and 9 V in device D and E while the current efficiency is still kept at 9 and 7 cd/A. We believe such a red dopant material can effectively trap charges when doped in CBP, NPB and Bebq2 which leads to the non-selectivity of the host material. Besides, the mobility of the red dopant material might be not good. So that the recombination zone is near the interface and the hole blocking layer can be removed. However, those assumptions will be proved by a series of experiments.

D3.6

Influence of the electronic properties of hole blocking materials on the device performance of organic light-emitting diodes. Volker van Elsbergen¹, Stefan P. Grabowski¹ and Edward Young²; ¹Philips Research Laboratories, Aachen, Germany; ²Philips Research Laboratories, Eindhoven, Netherlands.

Different hole blocking materials have been tested in organic light-emitting diodes. In addition to standard blocking materials like Alq₃ (Tris-(8-hydroxyquinolate)-aluminum), TPBI (1,3,5-tris-(1-phenyl-1H-benzimidazol-2-yl)benzene), and BAQ (Bis-(2-methyl-8-quinolinato)-4-(phenyl-phenolato)-aluminum) different derivatives of Alq₃ have been used. Methyl-, Chloro-, and Dichloro-Alq₃ are formed by substitution of hydrogen atoms by a methyl group, or one and two chlorine atoms at each ligand, respectively. The organic layer stack of the test devices consisted of an α -NPD (N,N-Di(naphthalen-1-yl)-N,N-diphenyl-benzidine) hole transporting layer, a Rubrene (5,6,11,12-tetraphenyl-naphthacene) doped α -NPD emitting layer, the hole blocking layer, and finally an Alq₃ layer as electron transporter. LiF/Al and ITO have been used as cathode and anode material, respectively. The hole blocking materials have been selected such that they have similar conductivity but varying HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels. HOMO levels vary from 5.5 to 6.5 eV and LUMO levels range from 2.6 to 3.6 eV with respect to the vacuum level. HOMO levels have been determined using ultraviolet photoelectron spectroscopy while the LUMO levels have been estimated using the optical gap. Devices with different hole blocking layers and otherwise unchanged organic layer stack have been characterized measuring electroluminescence, I-V-L curves, and lifetime. Current efficiencies of up to 8.5 cd/A at 10 mA/cm² and power efficiencies of up to 10 lm/W have been achieved for the well-chosen hole blocking architectures. Devices with non-optimal hole blockers perform far worse. For optimum device performance the barrier for holes, i.e. the offset in HOMOs of emitting layer and hole blocking layer, should be at least 0.3 eV. More important, a misalignment in LUMOs of hole blocking layer and electron transport layer reduces device performance considerably. Thus, in case of sufficient hole blocking, device performance depends completely on the LUMO offset. In addition to standard blocking layers, mixed blocking layers have been studied. They have been formed by co-evaporation of two different hole blocking materials. The performance of devices with a mixed blocking layer is in between that of the respective devices with standard blocking layers. In the case of TPBI, known for its poor lifetime, mixing with Alq₃ substantially increased the device lifetime compared to devices with only TPBI as blocking layer.

D3.7

Highly Luminescent Excimers in Chiral Conjugated Polymer Spin-Cast Films. Andrew Satrijo and Timothy M. Swager; Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

It is well known that the luminescence efficiency of conjugated polymers is detrimentally affected by the aggregation of polymer chains. However, the nature of these interchain interactions is still unclear. To investigate this polymer aggregation behavior in solution

and in the solid state, we employed circular dichroism spectroscopy, a widely used technique for the conformational analysis of chiral molecules and materials. We have recently demonstrated that the packing organization in a chiral π -conjugated polymer spin-cast film can be controlled by varying the spin-casting solvent and film annealing conditions. Furthermore, we investigated the aggregation behavior in chiral conjugated polymers that exhibit highly luminescent excimers. Excimers, which are intermolecular excited state complexes, offer fundamental insight into the interchain interactions that are present in organized conjugated polymer films.

D3.8

Current-Voltage Characteristics of Tetrathianaphthacene-Doped Tris(8-hydroxyquinoline) Aluminum (Alq3) Thin Film. Suidong Wang, Kaname Kanai, Eiji Kawabe, Yukio Ouchi and Kazuhiko Seki; Nagoya University, Nagoya, Japan.

Carrier injection and carrier transport are key issues in organic-based electronic and optoelectronic devices, and studies on them are important both in the fundamental understanding and in improving the device performance. We report our study on the current-voltage characteristics of single layer devices employing pure and heavily tetrathianaphthacene (TTN)-doped tris(8-hydroxy-quinoline) aluminum (Alq3) films as active layers. Sandwich structures with magnesium (Mg) top and bottom electrodes were employed in the devices. In the undoped device, the current increases exponentially with the applied voltage and is concluded to be limited by the carrier injection at the Mg/Alq3 interfaces with a small injection barrier. With the same device structure, the device with doped Alq3 shows a bulk-limited current flow much larger than the undoped device, behaving as trap-free space-charge-limited current with a field-independent mobility. The improvement of the current is ascribed to the large enhancement of carrier injection by the doping. An increase of the magnitude of the interfacial dipole has been proposed as the possible cause for the enhancement of carrier injection.

D3.9

Stabilization of Hole-Transport Layer and Film-Substrate Interface by Combining Vapor Deposition Polymerization and SAM. Hiroaki Usui¹, Kiyoi Katsuki¹, Akira Kawakami², Kuniaki Tanaka¹ and Rigoberto C. Advincula³; ¹Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan; ²Technology Research Association for Advanced Display Materilas, Koganei, Tokyo, Japan; ³Department of Chemistry, University of Houston, Houston, Texas.

Thermal stability of thin films is one of the key issues for developing practical organic electronic devices. Moreover, film-substrate interface plays an important role for determining device characteristics such as carrier injection. The conventional device fabrication processes, including the physical vapor deposition and solvent-based coating methods, have not paid much attention to the chemical bond at the interface. The authors propose a new method that combines vapor deposition polymerization and SAM technique to improve thermal stability and interface characteristics of organic thin films. Effectiveness of this method was exemplified in connection with OLED fabrication. SAM layers having azo endgroups were prepared on gold and ITO surfaces, on which either 3-(N-carbazolyl) propyl acrylate (CPA) or N-(4-vinylphenyl)-N,N'-triphenyl-benzidine (vTPD) monomers were evaporated by electron-assisted deposition method. It was found that electron irradiation to the evaporated monomers initiates polymerization of CPA and vTPD to form smooth and uniform thin films of vinyl polymers having hole-transporting pendant groups. On the other hand, the conventional evaporation yielded monomeric thin films that have poor surface smoothness due to partial crystallization of the deposited monomers. The polymerization reaction proceeded both on bare and SAM-coated surfaces. However, thermal stability was much superior when the films were deposited by the electron-assisted method on SAM-treated surfaces, due to the formation of covalent bonds at the film-substrate interface through the azo group of SAM layer. This method was applied to prepare organic LEDs by depositing CPA or vTPD monomers on ITO substrates bearing the SAM. It was found that the combination of SAM and the electron-assisted deposition polymerization substantially improves the device characteristics, reducing the luminescence threshold voltage by 10 V.

D3.10

Identification of Isomorphism and Polymorphism in Alq3. Manju Rajeswaran, Thomas N. Blanton, Ching W. Tang, Denis Y. Kondakov, William C. Lenhart, Steven C. Switalski, Thomas D. Pawlik, David J. Giesen, Nicholas Zumbulyadis and Brian J. Antalek; Kodak, Rochester, New York.

Interest in organic light-emitting diodes (OLEDs) began with the report of efficient green electroluminescence from Alq3,

tris(8-hydroxyquinoline) aluminum. After almost two decades of intense research and development in OLEDs, Alq3 remains to be one of the most widely used materials in OLED display devices and products. Primarily, it is used as the material for the electron-transport layer and also as the host for the emitter layer. Many studies have been published describing the chemical and physical properties of this metal chelate complex. Alq3 is an octahedrally coordinated chelate complex of the type MN3O3, where M is a trivalent metal, and N and O are the nitrogen and oxygen atoms in the quinoline ligand. Such complexes can occur in two different stereoisomers: meridional and facial. In this presentation, we will discuss a combined structural, thermal, and spectroscopic (Raman, fluorescence, EPR and NMR) analysis of the five crystalline phases (α , β , γ , δ , and ϵ) of Alq3 and their relationship to the meridional and facial isomers.

D3.11

Hole injection enhancement by using conjugated polymer interlayers at the interface between PEDOT:PSS and light-emitting polymers. Matthew James Harding^{1,2}, Dmitry Poplavskyy¹, Alasdair Campbell² and Franky So¹; ¹Osram Opto Semiconductors Inc., San Jose, California; ²Blackett Laboratory, Imperial College London, London, United Kingdom.

In organic light emitting diodes various methods are employed to increase carrier injection at the electrodes. In this work we aim to improve device performance by using an interlayer spun between the PEDOT and the light emitting layer. The interlayer may consist of either the same polymer as the subsequent emissive layer, or one of a variety of appropriate hole transporting polymers. The effects of different interlayers on hole injection are studied in single carrier hole-only devices through current-voltage measurements, dark injection space-charge-limited studies, and electro-absorption experiments. The effect of interlayers on OLED device performance is also discussed.

D3.12

Synthesis and Characterization of New Rod-Coil Block Copolymers Incorporating Terfluorene Segments and Hole/Electron Transporting Moieties for Stable Blue Light Emission. Christos Chochos¹, Nikos Tzanetos^{2,1}, Solon Economopoulos¹, Vasilis Gregoriou¹ and Joannis Kallitsis^{1,2}; ¹FORTH-ICEHT, Patras, Greece; ²Chemistry Dept., University of Patras, Patras, Greece.

New rod-coil diblock copolymers incorporating a terfluorene segment in the main chain and hole/electron transporting units such as vinyl-carbazole, quinoline and oxadiazole were synthesized by atom transfer radical polymerization (ATRP) and characterized with respect to their thermal, electrochemical, spectroscopic and optical properties. Electrochemical studies indicate that the electron affinity of the terfluorene segment is increased after the incorporation of the terfluorene segment into the polymeric matrixes, thereby facilitating the electron injection. All the copolymers emit blue light both in solution and in solid state. Furthermore, annealing of the block copolymers at 200 °C for 30 min in air resulted in green light emission due to the appearance of an emission band at 520 nm in the case of the quinoline copolymer while when poly(oxadiazole) and poly(doubleoxadiazole) were used as the coil parts blue light is emitted even after this treatment. In addition, in the case of the oxadiazole copolymer, despite the formation of the keto defects on the polymer backbone the copolymer does not exhibit the low energy emission band at 520 nm after photo-oxidation under diffuse UV radiation at ambient atmosphere. This work is an extension of our recent studies (Ref. 1,2) on a series of rod-coil block copolymers with terfluorene as the rigid segment that demonstrated that the main cause of color instability in fluorene oligomers and polymers is aggregate and/or excimer formation and not the presence alone of keto defects (fluorenone formation) along the molecular chain. Keto defects when are present contribute to the appearance of the undesirable green emission band but are not the leading cause of color instability. Thus, the synthesis of materials where aggregation and/or inter-chain, inter-segment interactions are inhibited is the key approach for the production of stable polymeric light-emitting devices (PLEDs). The potential of this method was verified by the synthesis of photo-oxidative stable fluorene/styrene diblock copolymer blue emitters. 1. C.L. Chochos, J.K. Kallitsis and V.G. Gregoriou J. Phys. Chem. B. 109, 8755 (2005). 2. C. L. Chochos, P. Tsolakis, V. G. Gregoriou and J.K. Kallitsis Macromolecules 37, 2502 (2004).

D3.13

Photoluminescence Characteristics and Energy Decay Processes of Alq3 in Various Host Layers. Noriyoshi Takahashi¹, Kenichi Goushi^{1,3}, Jason Brooks², Julie J. Brown², Hiroyuki Sasabe^{1,3} and Chihaya Adachi^{1,3}; ¹Department of Photonics Material Science, Chitose Institute of Science and Technology, Chitose, Japan; ²Universal Display Corporation (UDC), Ewing, New Jersey; ³CREST

Program, Japan Science and Technology Corporation (JST), Tokyo, Japan.

Tris(8-hydroxyquinolate)aluminum [Alq₃] has been widely used in OLEDs as a light-emitting and an electron transport layers due to the excellent carrier transport and luminescence properties. Therefore, in addition to a research on the electrical characteristics of Alq₃, understanding of the optical properties of Alq₃ is an important subject. In this study, we doped Alq₃ into various host layers and discuss the energy decay processes from singlet excited state (S₁) or triplet excited state (T₁) to the ground state (S₀). As hosts, we used 4,4'-N,N-dicarbazole-biphenyl [CBP] as a wide energy gap host for Alq₃ singlet exciton, and Ir complexes as a promoter for enhancing intersystem crossing from S₁ to T₁ and T₁ to S₀ transitions due to the heavy metal effect^{1,2}). As Ir complex hosts, tris(2-phenylpyridine)iridium [Ir(ppy)₃], fac-tris(4,6-difluorophenyl-pyridyl)-N,C²)iridium(III) [Ir(Fppy)₃], bis(2-phenylquinolyl)(acetylacetonato)iridium(III) [PQ₂Ir(acac)] and bis(2-(2'-benzo(4,5-a)thienyl)pyridinato-N,C³(acetylacetonato)iridium(III) [Btp₂Ir(acac)], which have various triplet energy levels are used. In 2wt%-Alq₃:CBP, the PL quantum yield (Φ_{PL}) was 44% which is significantly higher than that of the Alq₃ neat film (Φ_{PL} =20%), suggesting that the non-radiative decay process that originates from the concentration quenching is dissolved in the molecularly dispersed Alq₃. In the case of Ir complex hosts, we observed an Alq₃ phosphorescence (λ_{max} =664nm) in an Ir(ppy)₃ host even at T=300K, suggesting occurrence of efficient energy transfer from T₁ in Ir(ppy)₃ to T₁ in Alq₃²). Further, in an Ir(Fppy)₃ host, the Alq₃ phosphorescence was only observed at T=8K, even though no Alq₃ phosphorescence was observed at T=300K. Comparing Ir(ppy)₃ and Ir(Fppy)₃ hosts, the heavy metal effect of Ir(Fppy)₃ is smaller compared with that of Ir(ppy)₃. Also, we observed the Alq₃ phosphorescence at T=8K in a PQ₂Ir(acac) host, while emission from PQ₂Ir(acac) with no Alq₃ phosphorescence was observed at T=300K. This can be explained by back energy transfer from T₁ in Alq₃ to T₁ in PQ₂Ir(acac) is well suppressed at low temperature. Furthermore, no Alq₃ phosphorescence was observed in a Btp₂Ir(acac) host due to the lower triplet energy level of Btp₂Ir(acac) than that of Alq₃. 1) K. Goushi, R. Kwong, J. J. Brown, H. Sasabe and C. Adachi, J. Appl. Phys., **95**, 7798, (2004) 2) I. Tanaka, Y. Tabata and S. Tokito, Phys. Rev. B, **71**, 205207, (2005)

D3.14
Strong Electroluminescence from Photoluminescence Quenched Polymer Films. Yufeng Hu, Yanguang Zhang and Jun Gao; Queen's University, Kingston, Ontario, Canada.

We demonstrate that strong electroluminescence (EL) can be obtained from a polymer film whose photoluminescence (PL) is strongly quenched by the addition of a molecular salt. The devices studied are planar polymer light-emitting electrochemical cells (LECs) with extremely large interelectrode spacing of 1 mm. By adding a copper (II) triflate salt to a regular LEC film consisting of luminescent polymer, ion-transport polymer, and lithium triflate salt, the PL of resulting film is close to be completely quenched. However, the device exhibits strong EL with efficiency close to the lithium-only device. Direct imaging of the PL-quenched planar device reveals that the PL of the polymer film is partially recovered near the cathode region upon the formation of a light-emitting junction. Possible mechanisms of PL quenching by copper salt and strong EL from a PL-quenched polymer film are discussed.

D3.15
Imaging Novel Emission Modes in Polymer Light-Emitting Electrochemical Cells. Jun Gao, Queen's University, Kingston, Ontario, Canada.

Light-emitting electrochemical cells (LECs) are solid-state polymer photonic devices. The operation of an LEC involves the formation of a p-n junction by in situ electrochemical doping of the luminescent polymer, which acts to significantly reduce the device resistance. As a result, LECs can be constructed in a planar configuration with large interelectrode spacing. Recently we have demonstrated extremely large planar LECs with millimeter interelectrode spacing. The massive planar device structure allows for the imaging of doping propagation, photoluminescence (PL) and electroluminescence (EL) with unparalleled spatial and temporal resolution. In this symposium we report the observation of several novel EL modes based on the direct imaging of planar LECs with an interelectrode spacing ranging from 0.6 to 11 mm. The novel emission modes include transient EL in a dynamic-junction device, EL from planar polymer/polymer heterojunction devices, and anomalous reverse-bias EL from a frozen-junction device. Transient EL occurs when the polarity of the applied bias is reversed, which causes the initiation and uneven propagation of fresh p-doping within previously n-doped regions, and vice versa. This leads to the formation of transient, discrete light-emitting p-n junctions near the electrodes before a continuous

light emission zone is formed by the complete reversal of the doping profile. In addition, planar cells consisting a side-by-side polymer/polymer heterojunction have been demonstrated and imaged. The heterojunction in all working devices is found to be electronically conductive, but exhibit different ion transport properties. Three types of doping and EL profiles have been imaged in these heterojunction devices. Finally, an anomalous reverse-bias EL has been observed in a planar frozen-junction device. The device was turned on at elevated temperature and then frozen by lowering the temperature to 200K. Stress under a constant reverse bias leads to the activation of an anomalous EL that originates from the same region as forward bias EL. Possible mechanisms are discussed.

D3.16
Spectroscopic Ellipsometry of Organic Composite Thin Films for Electroluminescence Devices. Naohiko Kato¹, Tomoyoshi Motohiro¹, Shyuji Kajiya¹ and Isao Yokota²; ¹Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan; ²Toyota Industries Corporation, Oubu, Aichi, Japan.

For the optical management of the organic electroluminescence (EL) devices, the optical constants of the constituent organic composite thin films are absolutely indispensable. However, they are not always available even in the case of the typical major component materials. Especially those of the organic composite thin films made up of a host fluorescent material and dopant materials have not been available. Using spectroscopic ellipsometry (SE), we inspected the change of spectral optical constants of tris(8-hydroxy-quinoline) aluminum (Alq₃) thin films as a function of concentration of 5,12-dihydroquino[2,3-b]acridine-7,14-dione (Quinacridone) as the green dopant, or 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) as the red dopant. The composite films were fabricated by the co-evaporation of Alq₃ and each dopant. The dispersion of optical constants of the each component material was described using a series of Gaussian oscillators which reflect molecular bond absorption bands, combined with a Sellmeier dispersion model. The optical constants and the compositions of the composite film can be estimated by the effective medium approximation based on Bruggemann theory. With increase in the dopant concentration, the extinction coefficient at 525nm, 560nm (assigned to the Quinacridone absorption bands), and at 471nm (assigned to DCM bands) increased, respectively. The dopant concentrations obtained from SE were consistent with the values obtained from the liquid chromatography in which the film had to be dissolved in the solvent. SE is effective method as the non-destructive inspection means of the dopant concentration of the organic composite thin films.

D3.17
Low Driving-Voltage and High Current-Efficiency Organic Light-Emitting Devices by Using (1,4-bis(2-Hydroxy-Phenylenevinylene)Benzene) Based Polymer Hole-Transport Materials. Kang-Chun Peng¹, J. H. Lee¹, Chai-Huo Kuo², Kuo-Huang Hsieh² and Man-Kit Leung³; ¹Electro-Optical Engineering, National Taiwan University, Taipei, Taiwan; ²Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan; ³Chemistry, National Taiwan University, Taipei, Taiwan.

We demonstrate a low driving-voltage and high current-efficiency organic light-emitting device by using a 1,4-bis(2-Hydroxy-phenylenevinylene)benzene (OPV) based polymer material as the hole-transport layer (HTL). The small molecule OPV is polymerized by the linkage of the polar molecules isophorone diisocyanate (IPDI) and is terminated with 4-tert-butyl phenol. The resulting polymer material is called OPVIPDI and shows a superior performance as the HTL material. As compared with the device using the conventional HTL material, 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl (NPB), device using OPVIPDI has a 2 V voltage reduction under the current density of 100 mA/cm². Current efficiency has 2.37 times improvement as compared with the control device. Such a value can be further improved by fine tuning the electron-hole balance. During synthesis, OPV is blended by the n-type small molecule oxadiazole (OXD), which is called OPV-OXD, for polymerization with the ratio of 3:1 and 1:1 to retard the hole-transport. The maximum current efficiency in the case of 3:1 is increased from 3.84 to 4.12 cd/A while the voltage is nearly the same at 5.5 V as compared with pure-OPVIPDI case. In our experiments, we use poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSSA) as the hole injection layer (HIL), OPVIPDI and OPV-OXD as the hole-transport layer (HTL), 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl (NPB) as the electron blocker layer (EBL), and bis(10-hydroxybenzo[h]quinolinato)beryllium (bebq2) as the emitting layer, respectively. The device structures are ITO / PEDOT:PSSA(20nm) / HTL(30nm) / NPB(10nm) / bebq2 (20nm) / Ca(10nm) / Ag(100nm). The HTL material is NPB, OPVIPDI, OPV-OXD (3:1) and OPV-OXD (1:1)

which is labeled as device A, B, C and D, respectively. The driving voltage is 7.5, 5.5, 5.5, and 7 V at the current density of 100 mA/cm² for device A, B, C and D, respectively. Device B and C exhibits nearly the same driving voltage which is 2V lower than the control device A. It shows a superior hole-transport capability of the OPVPDI. However, when the ratio is 1:1, the hole-transport capability is much suppressed and the driving voltage increases. The maximum current efficiency of device A, B, C and D are 1.62, 3.84, 4.12 and 1.63cd/A under the different operating voltage of 7, 5.5, 7.5 and 6.5V, respectively. The maximum luminance is also improved from 5780 cd/m² in device A to 14900 cd/m² and 13600 cd/m² due to better hole-transport ability in device B and C.

D3.18

Tuning optoelectronic properties in ambipolar organic light-emitting transistors by bulk hetero-junction approach. Maria Antonietta Loi¹, Constance Rost², Mauro Murgia¹, Siegfried Karg², Walter Riess² and Michele Muccini¹; ¹Institut for Nanostructured Materials, CNR, Bologna, Italy; ²IBM Research GmbH, Rueschlikon, Switzerland.

The advancement in organic optoelectronics is witnessed by the performances of organic LEDs and FET which are now close to the market requirements. The possibility to combine in a single device the electrical switching and light emission properties increases the number of applications of organic semiconductors and can be considered as a step towards realizing the idea of completely integrated organic optoelectronics. Recently, such a multifunctional device, namely ambipolar light-emitting field-effect transistors (LET), was reported [1]. Ambipolar charge transport is crucial in light-emitting transistors as it enables to maximize exciton formation and recombination through electron-hole balance. Bulk hetero-junction is demonstrated as a novel approach to produce ambipolar organic light-emitting field-effect transistors with tunable electrical and optoelectronic characteristics. The electron and hole mobilities of a bimolecular mixture consisting of quinque thiophene (T5) and N,N'-ditridecylperylene-3,4,9,10-tetracarboxylic-diimide (P13) are varied over two orders of magnitude in the range 10⁻²-10⁻⁴ cm²/Vs by changing the relative fraction of the hole and electron transport material. The highest EL efficiency is obtained in the samples with equal concentrations of T5 and P13, which also exhibit the most balanced electron and hole mobilities. A higher concentration of T5 results in non-emitting but still ambipolar FETs. Time-resolved PL spectroscopy reveals that light emission is quenched in devices with an excess of T5 owing to the dissociation of P13 excitons upon interaction with T5 molecules. On the other hand, a lower concentration of T5 results in unipolar n-channel FETs, which are still light-emitting. This is a result of T5 cluster formation that is revealed by laser scanning confocal microscopy. By this technique the relative concentration and phase segregation of the structure components are imaged and correlated with the ambipolar transport and electroluminescence emission of the bulk hetero-junction LET device. The electroluminescence emission appears to be a trade off between the microscopic structure of the bulk hetero-junction and the electronic levels of the component materials. The results presented show that the bulk hetero-junction approach can be successfully employed to select and tailor the functionality of field-effect devices, including ambipolar charge transport and light emission. [1] C. Rost, S. Karg, W. Riess, M. A. Loi, M. Murgia, M. Muccini, Appl. Phys. Lett., 85, 1613 (2004).; M. A. Loi, C. Rost, M. Murgia, S. Karg, W. Riess, M. Muccini (submitted).

D3.19

Photophysical properties of Ir carbene complexes having blue phosphorescence. Ayataka Endo^{1,4}, Jason Brooks², Mark E. Thompson³, Julie J. Brown², Hiroyuki Sasabe^{1,4} and Chihaya Adachi^{1,4}; ¹Department of Photonics Material Science, Chitose Institute of Science and Technology, Chitose, Hokkaido, Japan; ²Universal Display Co. (UDC), 375 Phillips Boulevard, Ewing, New Jersey; ³Department of Chemistry, University of Southern California, Los Angeles, California; ⁴CREST Program, Japan Science and Technology Corporation (JST), Higashi, Shibuya, Tokyo, Japan.

Blue phosphorescence materials having high color purity have been demanded for obtaining full-color RGB electrophosphorescence, since the chromaticity coordinates in Iridium bis(4,6-di-fluorophenyl)-pyridinato(N,C2)picolinate [FIrpic] and Iridium bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate [FIr6] were X=0.18, Y=0.36 and X=0.16, Y=0.26, respectively. In this paper, we report on photophysical properties of novel Ir carbene derivatives which are useful for blue electrophosphorescence. We prepared co-deposited films under high vacuum (1×10⁻³Pa) by thermal evaporation using m-CP and PCzCF₃ as a host and mer-Iridium tris(N-dibenzofuranyl-N'-methylbenzimidazole) [m-Ir(dbfmb)] as a guest material, and measured transient PL characteristics and absolute PL quantum efficiency. Further, we prepared m-Ir(dbfmb):PMMA films by a spin-coating method. In a

6wt%-m-Ir(dbfmb):m-CP film, the PL quantum efficiency was limited to $\eta_{PL}=13\pm1\%$ and delay component in addition to the prompt component was observed in a time resolved PL spectrum. Further, PL quantum efficiency was slightly increased in a 6wt%-m-Ir(dbfmb):PCzCF₃ film ($\eta_{PL}=26\pm1\%$) and higher PL quantum efficiency of $\eta_{PL}=32\pm1\%$ was obtained at m-Ir(dbfmb) concentration of 20wt%. This phenomenon indicates presence of back energy transfer from a triplet level of m-Ir(dbfmb) to that of PCzCF₃, similar to the PL characteristics in CBP:FIrpic¹¹. Thus, a wide triplet energy gap host is required to obtain high PL efficiency. With a use of PMMA as a host, very high PL efficiency of $\eta_{PL}=78\pm5\%$ was obtained and $\eta_{PL}=100\%$ at the temperatures less than T=250K was observed. 1) Y. Kawamura, K. Goushi, J. Brooks, J. J. Brown, H. Sasabe and C. Adachi, Appl. Phys. Lett. 86, 071104 (2005).

D3.20

High Efficiency Green Organic LEDs Using Wide-Energy-Gap Boron Compounds as Electron Transport Layer. Daisaku Tanaka², Yuya Agata², Hitoshi Shimizu², Takashi Takeda² and Junji Kido^{1,2}; ¹Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan; ²Optoelectronic Industry and Technology Development Association, Bunkyo-ku, Tokyo, Japan.

Wide-energy-gap charge transport materials are required to build high efficiency OLEDs using phosphorescent materials as the emitting center. In this work, we synthesized electron transport materials containing a trimesityl borane structure with high triplet energy level of over 2.7 eV. Green OLEDs having a structure of ITO / p-doped polymer buffer layer / wide-energy gap arylamine (TAPC) / Ir(ppy)₃ doped carbazole biphenyl (CBP) / trimesityl borane compound / LiF / Al were fabricated. An extremely high luminous efficiency of over 90 lm/W and the external quantum efficiency of over 20 percent were observed at 100 cd/m². These values are the highest so far reported for green OLEDs. Syntheses and characterization of the new boron compounds are also reported.

D3.21

Pyridine-Containing Triphenylbenzene Derivatives as Wide-Energy-Gap Electron Transport Materials for High Efficiency Blue Organic LEDs. Shi-Jian Su², Daisaku Tanaka², Yuya Agata², Hitoshi Shimizu², Takashi Takeda² and Junji Kido^{1,2}; ¹Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan; ²Optoelectronic Industry and Technology Development Association, Bunkyo-ku, Tokyo, Japan.

A series of pyridine-containing triphenylbenzene derivatives were synthesized and used as electron-transport materials (ETMs) in organic LEDs. By using a wide-energy gap arylamine derivative as a hole-transport material (HTM) and a wide-gap carbazole derivative as a host material for triplet blue emitter of FIrpic, the excited energy at FIrpic is confined in the emitting layer due to high triplet energy levels of both HTM and ETM. In addition, efficient charge carrier injection from the anode through p-doped buffer layer and from the cathode via LiF/Al lead to a well-balanced carrier injection ratio, resulting in a record-breaking power efficiency of over 35 lm/W and an external quantum efficiency of over 20 percent.

D3.22

The Chemical Reaction between LiF and Polyfluorene Affect the Performance of Top Emission PLED Devices During Sputtering ITO Cathode. C. W. Teng¹, K. C. Liu¹, W. T. Liu², C. C. Chen² and L. C. Chen²; ¹Electro-Optical Engineering, Chang Gung University, Tao-Yuan, Taiwan; ²Delta Optoelectronics, Hsin-Chu, Taiwan.

Application of transparent cathodes for the organic light emitting device integrated with active-matrix driving circuit for the next generation flat panel display. The critical technique of top emission structure is how to fabricate an efficient transparent cathode which can be employed by thin metal and transparent conductive oxide (TCO) such as ITO. Although the lower work function of metal can be matched to help the electron injection, the thickness of metal will be limited to avoid the low transparency. TCO materials have high transparency and low resistance, especially ITO. However, the ITO thin film has to be deposited at high substrate temperature to achieve the optimum performance. The high work function of ITO cathode will lower the efficiency of device. To overcome the low efficiency problem, the thin insulator layer is employed such as LiF. This material can reduce the electron injection barrier height efficiently by lowering the highly occupied molecular orbital (HOMO) level and enhancing electron tunneling probability. The LiF layer between ITO cathode and organic layer will be affected during the heating substrate of ITO deposition. The heating effect of LiF will cause the diffusion of lithium (Li) and fluorine (F) into the organic layer that degrades the performance of emitting device. From the XPS analysis, the phenomenon can be observed that the Li and F concentration increased as the substrate temperature rose during the ITO cathode

deposition. Due to the Li in organic layer will form non-radiative centers that quench emissive light and the results can be observed from the electroluminescence and current efficiency. With the same operating voltage, the heating substrate device showed the worse luminance and efficiency than the non-heating device. Meanwhile, the SCLC mechanism was also taken to analyze the trap concentration which caused by the Li and F diffusion. The SCLC analysis exhibits the agreement with the previous results; the trap concentration increased by LiF diffusion as the substrate temperature rose. In this work, we present some information about the LiF with heating process will degrade the performance of device through the XPS analysis, optical characteristic, and electrical performance. The phenomenon indicated the LiF material has to be used carefully, especially in the top emission structure that the ITO cathode was employed. We also demonstrate the room temperature deposition ITO cathode of device which shows the best performance than the other substrate heating device; and the room temperature process of ITO cathode is suitable applied in the flexible substrate to conform the requirement of any other display field.

D3.23

High Efficiency Green OLEDs having Chemically Doped Charge Transport Layers. Soichi Watanabe¹, Nobuhiro Ide² and Junji Kido^{1,2}; ¹Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan; ²Optoelectronic Industry and Technology Development Association, Bunkyo-ku, Tokyo, Japan.

In this work, we demonstrate green organic LEDs, using Ir(ppy)₃ as the emitting material, with a high power efficiency of 90 lm/W. The power efficiency of organic LEDs was improved by increasing internal quantum efficiency, reducing drive voltage, and fine-tuning of optical out-coupling efficiency. The high quantum efficiency was achieved by using wide-energy-gap materials as the host materials and the carrier transporting materials. And the reduction of drive voltages was achieved by chemical doping of carrier transport layers. Furthermore, we optimized the carrier balance in the emitting layer and the optical interference effect by varying the thickness of the electron transport layer and the n-doped electron injection layer. The optimized device exhibited green emission peaking at 510 nm, and the external quantum efficiency of 24.5 percent (88 Cd/A). A high power efficiency of 90 lm/W was observed at 100 cd/m² at 3.05 V.

D3.24

Novel Blue Light-Emitting Material for OLED. Kyu-Sik Kim, Nano Fabrication Center, Samsung Advanced Institute of Technology (SAIT), Yongin-shi, Kyungki-do, South Korea.

Although a number of conjugated polymers have been synthesized in an attempt to realize efficient blue electroluminescence (EL), only a few polymers appear promising for use in blue polymer LEDs. The Polyfluorene derivatives are among the most promising candidates because of their thermal and chemical stability, high quantum yields, and facile processability. Especially the spiro-functionalized polyfluorene derivatives exhibits more stable and pure blue emission compared with conventional polyfluorene derivatives. In this study, we report the fabrication and performance of a novel blue light-emitting material for OLED; Uniform and pinhole-free films can be prepared by common organic solvent such as chlorobenzene. Thin films were demonstrated to be amorphous with high T_g and good optical properties. The long wavelength tails, which are results from the aggregates or the excimers, were not observed. OLED devices were prepared with the general structure.

D3.25

High-Efficiency Greenish-Blue and Blue Organo-Iridium Phosphorescent OLED Materials. Heh-Lung Huang, Kou-Hui Shen, Miao-Cai Jhu and Mei-Rung Tseng; Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan.

Red, green, and blue emitters are necessary for full color OLED display or solid state indoor lighting. There is also a great demand for emitters, such as yellow, orange or greenish-blue color, for multicolor display or WOLED usage. We investigated and synthesized different orientation and substituted group of the organo-iridium complexes (PB-series). These materials exhibited greenish-blue and blue light. The photo-luminescent spectra of PB-series are between 460nm and 490nm. We demonstrated high-efficiency and saturated greenish-blue and blue Ir-complex phosphorescent materials for OLED and solid state indoor lighting.

D3.26

Synthesis and Characterization of 5,5'-Bis(3,4-Ethylenedioxythien-2-yl)-4,4'-dinonyl-2,2'-Bithiazole, and 5,5'-Bis(Thiophen-2-yl)-4,4'-dinonyl-2,2'-Bithiazole Co-monomers for Electronic Applications.

Fevzi Cakmak Cebeci, Esmâ Sezer and Sezai A. Sarac; Kimya

Bolumu, Istanbul Teknik Universitesi, Istanbul, Turkey.

Poly(alkylbithiazole)s show high degrees of crystallinity in the solid state, including π -stacking, usually associated with decreased electroluminescence efficiency.[1-3] The synthesis and characterization of poly(alkylbithiazoles) and several co-oligomers of the alkylbithiazole monomers (R; ethyl, butyl, and hexyl group) and their derivatives were recently published.[4] In this study, the donor-acceptor-donor type co-monomers, 5,5'-bis(3,4-ethylenedioxythien-2-yl)-4,4'-dinonyl-2,2'-bithiazole (ENBTE), and 5,5'-bis(thiophen-2-yl)-4,4'-dinonyl-2,2'-bithiazole (TNBTT), were produced by palladium-catalyzed Stille coupling methods.[5] The synthesis and a comparative electrochemical characterization of synthesized co-monomers are described. The cyclic voltammogram of a poly(ENBTE) film indicated that these co-monomers can be either p-doped or n-doped, and the spectroelectrochemical measurements show that polymer films of these co-monomers are stable upon cycling the oxidation state. Materials capable of being reversibly n-doped/undoped undergo reversible reduction/oxidation, makes these materials favorable for useful in several electronic device applications e.g. supercapacitors and solid-state batteries, in light-emitting electrochemical diodes, and in electrochromic displays. Electrochemical characterizations and electrooptical properties of the obtained polymer films were investigated in detail. Introductory studies showed that electrodeposited polymers of these co-monomers show low oxidation potential low band gap, and good stability of the oxidized state. [1] Uchida, M.; Ohmori, Y.; Morishima, C.; Yoshino, K. Synth. Met. 1993, 55-57, 4168 1993. [2] Doi, S.; Kuwabara, M.; Noguchi, T.; Ohnishi, T. Synth. Met. 1993, 55-57, 4174. [3] Xu, B.; Holdcroft, S. SPIE, 1993, 1910, 65. Xu, B.; Holdcroft, S. Macromolecules 1993, 26, 4457. [4] J.I. Nanos, J.W. Kampf, M.D. Curtis, Chem. Mater. 7 (1995) 2232; J. Cao, J.W. Kampf, M.D. Curtis, Chem. Mater. 15 (2003) 404. [5] Stille, J. K. Angew. Chem. Int. Ed. Engl. 1986, 25, 508.

SESSION D4: Organic Photovoltaics I

Chair: Sean Shaheen

Tuesday Morning, November 29, 2005

Room 304 (Hynes)

8:30 AM *D4.1

Organic Optoelectronic Devices: From Solar Cells to photOFETs and Electronic Logic Circuits.

Niyazi Serdar Sariciftci, Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University, Linz, Austria.

Recent developments on plastic optoelectronic elements using fullerenes, semiconducting conjugated polymers as well as nanocrystalline inorganic semiconductors are reviewed. For light emitting diodes (OLEDs) in the infrared energy transfer reactions between conjugated polymers with different band gaps are utilized. The photophysics of photovoltaic devices is based on the photoinduced charge transfer from donor type semiconducting conjugated polymers onto acceptor type conjugated polymers or acceptor molecules such as Buckminsterfullerene, C₆₀ or nanoparticles. Examples of photovoltaic architectures are discussed with their potential in terrestrial solar energy conversion. Furthermore, organic semiconductor based tunnel diodes, as well as organic field effect transistors (OFETs) will be reported with mobilities above 1cm²/Vs. Functionalized fullerene transistors such as photoactive, ambipolar photOFETs are used for the realization of simple circuits and high detectivity (>5 A/W) photosensor arrays and memory elements.

9:00 AM D4.2

4.0% Efficiency Solution Processable Polymer Photovoltaic Cells by Self-organization of Polymer Blends.

Gang Li, Vishal Shrotriya, Jinsong Huang and Yang Yang; MSE, UCLA, Los Angeles, California.

Plastic solar cells have recently evolved as the promising cost effective alternatives to the silicon based solar cells. However, low efficiencies of these plastic solar cells limit their feasibility for commercial use. The efficiencies of polymer photovoltaic cells got a major boost with the introduction of bulk heterojunction (BHJ) concept. BHJ structures consist of an interpenetrating network of electron donor and acceptor materials, and provide efficient charge separation because of large interface area. This concept recently has also been successfully demonstrated in small-molecular organic photovoltaics. It is argued that due to the space charge effects inherent in the BHJ structure, the fill factor is usually low and the disordered structure will be ultimately limited by high series resistance. To achieve highly efficient photovoltaic device, solar radiation needs to be efficiently absorbed, for which the device thickness needs to be increased. However, this will further increase the series resistance. Here, we demonstrate that the series resistance of the polymer BHJ PV cells can be significantly

reduced, while hole mobility significantly enhanced by polymer self-organization. The PV cell is based on poly-(3-hexylthiophen) (P3HT) and methanofullerene (PCBM) blend. The application of this technique allows us to achieve very high fill-factor of >65%, high short circuit current density of >10 mA/cm², low series resistance of 1.5 Ohm.cm². As a result, we have achieved device power conversion efficiency of 4.0% under standard AM1.5G 1-Sun test condition. This efficiency is after spectral mismatch correction and has been verified by National Renewable Energy Laboratory (NREL).

9:15 AM **D4.3**

Polymer heterojunction solar cells with over 4% power efficiency. Klaus Meerholz, Adam - Moule and Joerg Bernd Bonekamp; Physical Chemistry, University of Cologne, Cologne, Germany.

We have performed a detailed study of solar cells based on P3HT and PCBM heterojunctions. The relatively heterogenous character of the devices on a length scale of several 100 microns has been studied by spatially resolved photocurrents and correlated AFM measurements. The local photophysical characteristics give excellent insight into the microstructure of the devices. By improving the composition, adding third components, and the devices' active layer thickness the materials morphology could be improved considerably, yielding solar cells that have a power efficiency above 4% under AM1.5 illumination.

9:30 AM ***D4.4**

A Look into Charge Transport in Organic Bulk Heterojunction Solar Cells: Film Morphology Dependence and Correlation with Device Performances. Mauro Morana^{1,2}, Christoph Waldauf¹, Markus Koppe¹, David Muehlbacher¹, Patrick Denk¹, Markus Scharber¹ and Christoph Brabec¹; ¹Konarka Technologies, Linz, Austria; ²DIEE, Facolta di Ingegneria, Universtia di Cagliari, Cagliari, Italy.

Organic bulk heterojunction solar cells represent a cheap and easy possibility to produce flexible low weight energy sources, fulfilling the requirements of a growing mobility. The understanding of the bulk heterojunction concept, i. e. the correlation between material parameters and device performance has been improved to a level where effective tuning of individual material parameters is demonstrated to improve the efficiency. This contribution points out the correlation between parameters like energy level alignment or morphology and device performance in terms of open circuit voltage, fill factor and short circuit current. In particular, the bipolar charge carrier transport within the donor-acceptor blend and its correlation with the film morphology is object of analysis, due to the key impact of the latter on the extracted photocurrent. A simple and powerful method for characterizing both holes and electron vertical drift mobility in the bulk heterojunctions, through ac measurement, is presented together with experimental results concerning some promising organic photovoltaic materials. The experimental findings concerning transport and the related device performances are described in the frame of a coherent device model. The understanding of the different impacts and the access to the relevant morphology-connected properties of the bulk heterojunction further enables the choice of materials in respect of cell's performance and lifetime, guiding also the optimization of material's processing. These factors are essential for the development of this new generation of photovoltaic products.

10:30 AM **D4.5**

The Effect of Annealing on Charge Transport and Performance of Poly(3-hexylthiophene):Methanofullerene Bulk-Heterojunction Solar Cells. Valentin Mihailetschi, Jan Anton Koster, Bert de Boer and Paul W. M. Blom; Materials Science Centre, University of Groningen, Groningen, Netherlands.

Photovoltaic elements based on thin films of poly(3-hexylthiophene):methanofullerene (P3HT:PCBM) blends have proved to be one of the most efficient material combinations for bulk-heterojunction organic solar cells until now. In this study we have investigated the effect of controlled thermal annealing on charge transport and photogeneration in P3HT:PCBM cells. With respect to the charge transport, we demonstrate that the electron mobility dominates the transport of the cell, varying from 10-8 m²/Vs in as-cast devices to 3*10⁻⁷ m²/Vs after thermal annealing. The hole mobility in the P3HT phase of the blend on the other hand increases more than three orders of magnitude, to reach a value up to 2*10⁻⁸ m²/Vs after the annealing process, as a result of an improved crystallinity of the film. Moreover, upon annealing the absorption spectrum of P3HT:PCBM blends undergo a strong red-shift, improving the overlap with the solar emission, which results in an increase of more than 60% in the generation rate of charge carriers. Subsequently, the experimental electron and hole mobilities were used to study the photocurrent generation in P3HT:PCBM devices as a function of thermal annealing temperature. The results demonstrate

that the most important contribution to the enhanced performance after annealing stems from the enhancement of the hole mobility in the P3HT phase of the blend. Furthermore, numerical simulation indicates that at short-circuit the dissociation efficiency of bound electron-hole pairs at donor/acceptor interface is close to 90%, which explains the large quantum efficiencies measured in P3HT:PCBM blends.

10:45 AM **D4.6**

Reduced Recombination in Conjugated Polymer / Fullerene Bulk Heterojunction Solar Cells. Ronald Osterbacka¹, Almantas Pivrikas¹, Gytis Juska², Kestutis Arlauskas², Gytis Sliuzausys², Attila J. Mozer³, N. Serdar Sariciftci³ and Markus Scharber⁴; ¹Dept. of Physics, Abo Akademi University, Turku, Finland; ²Dept. of Solid State Electronics, Vilnius University, Vilnius, Lithuania; ³LIOS, Johannes Kepler University, Linz, Austria; ⁴Konarka Technologies, Linz, Austria.

In low mobility materials diffusion controlled bimolecular (Langevin) recombination is usually dominating. Since the hopping distance in low mobility materials is much smaller than the Coulomb radius, the carriers will have a lower probability to escape recombination. The magnitude of Langevin bimolecular recombination coefficient can then be calculated using the well known Langevin relation $\beta_L = e\mu_f / \epsilon\epsilon_0$, where, μ_f is the mobility of the faster carrier. In order to reach high solar to electrical power conversion efficiencies for low mobility materials a high current density is usually required. This leads to a reduced carrier lifetime due to bimolecular charge carrier recombination with possible loss of current density. High carrier concentration causes a small lifetime of the charge carriers ($\tau(t) = [\beta n_{ph}(t)]^{-1}$) where β is the bimolecular recombination coefficient and, consequently, short diffusion and drift distances. The necessary condition for a high energy conversion coefficient of a solar cell is that the lifetime of charge carriers must be higher than their transit time in the intrinsic electric field i.e. $n_{ph} < \mu U_{bi}\beta d^2$, where U_{bi} is the built-in electric field. It is therefore clear that the bimolecular recombination coefficient is an important testing and characterization parameter to evaluate the suitability of materials to use in efficient solar cells. In this work we show how bimolecular recombination influences the charge carrier transport, how it limits the efficiency of solar cells and how to estimate the bimolecular recombination coefficient. We have used time-of-flight (TOF) and double injection (DoI) current techniques to study bimolecular recombination in bulk heterojunction solar cells. Using TOF under high light intensity generation, we measured a greatly reduced bimolecular recombination coefficient ($\beta/\beta_L = 10^{-4}$) with low activation energy. Using DoI transients we found double injection with bimolecular recombination limiting the injection current. We have measured the temperature and electric field dependence of the reduced bimolecular recombination coefficient. We found that the activation energy for bimolecular recombination is smaller than for the Langevin recombination by 0.12 eV. Thus, we think, that the bimolecular recombination is partly caused by tunneling through the polymer-PCBM interface.

11:00 AM **D4.7**

Origin of the Light Intensity Dependence of the Short-Circuit Current Density of Polymer/Fullerene Solar Cells.

L. J. A. Koster, V. D. Mihailetschi, H. Xie and P. W. M. Blom; Molecular Electronics, Materials Science Centre Plus/University of Groningen, Groningen, Netherlands.

A typical feature of polymer/fullerene based solar cells is that the current density under short-circuit conditions (J_{sc}) does not exactly scale linearly with light intensity (I). Instead, a power law relationship is found given by $J_{sc} = \text{constant } I^a$, where a ranges from 0.9 to 1. In a number of reports this deviation from unity is attributed to the occurrence of bimolecular recombination. We demonstrate that the dependence of the photocurrent in bulk heterojunction solar cells is governed by the build-up of space charge in the device. The occurrence of space-charge stems from the difference in charge carrier mobility of electrons and holes. In P3HT/PCBM this mobility difference can be tuned in between one and three orders of magnitude, depending on the annealing conditions. This allows us to experimentally verify the relation between space-charge build-up and intensity dependence of J_{sc} . Model calculations confirm that bimolecular recombination leads only to a typical loss of 1 % of all free charge carriers at J_{sc} for these devices. Therefore, bimolecular recombination plays only a minor role as compared to the effect of space-charge in the intensity dependence of J_{sc} .

11:15 AM **D4.8**

Charge transport in conjugated polymers and polymer/fullerene blends: Influence of chemical structure, morphology and blend composition. Sachetan M. Tuladhar¹, Marc Sims¹, Stelios Choulis², Donal D. C. Bradley¹ and Jenny Nelson¹; ¹Physics, Imperial College London, London, United Kingdom; ²OSRAM Opto Semiconductors, Inc., San Jose, California.

The relationship between the chemical and physical structure of organic semiconductors and their charge transport properties needs to be better understood in order to develop more efficient photovoltaic devices. We have studied charge mobilities in a range of molecular materials using time-of-flight mobility measurements, dark injection and steady state current-voltage measurements. We focus on materials of different chemical structure and on donor-acceptor blends of different composition, in order to understand how structure and composition affect mobility. We report on the following: (1) Studies of the influence of side chain length and annealing on the hole mobility of a series dialkoxy poly(phenylenevinylene) (PPV) polymers. In the case of dimethoxy-PPV, changes in hole mobility upon annealing can be correlated to changes in the morphology of the polymer film. (2) Studies of the influence of blend composition on electron and hole mobility in conjugated polymer - fullerene blend and inter polymer fullerene blends. We show that a methanofullerene exhibits ambipolar charge transport and moreover that the fullerene appears to dominate the hole transport characteristics of a polymer-fullerene blend. We use measurements of the temperature and electric field dependence of mobility and Monte Carlo simulations to evaluate alternative models of charge transport, and so to analyse the behaviour in terms of the microscopic physical and chemical structure of the materials. We will comment on the requirements for suitable charge transport materials in organic photovoltaic devices. 1. Tuladhar, S.M. et al. *Advanced Functional Materials*, in press (2005).

11:30 AM *D4.9

Design and Evaluation of New Acceptor Materials for Bulk Heterojunction Devices. J. C. (Kees) Hummelen¹, Lacramioara

Popescu¹, Patrick van 't Hof¹, Alexander B. Sieval², Floris B. Kooistra¹, Valentin D. Mihailescu¹, David Kronholm², Harry T. Jonkman¹ and Paul W. M. Blom¹; ¹Molecular Electronics, Materials Science Centre, University of Groningen, Groningen, Netherlands; ²Solenne BV, Groningen, Netherlands.

We report on the design, preparation, and evaluation of new methanofullerenes as acceptor components in blends with conjugated polymers to form highly functional bulk heterojunction active layers in molecular electronics applications like photovoltaic cells. An analogue of [60]PCBM was designed for improved miscibility with polythiophenes, specifically regioregular P3HT. In this compound, the phenyl group is replaced by a thienyl group. Subtle as this modification may seem, we have observed in the past that even slight modifications of the [60]PCBM structure may lead to significant changes in the most relevant parameters, like solubility, morphology of the blend, charge carrier transport (in both components!), etc., usually necessitating an optimization procedure involving screening of various solvents for the spin coat procedure. Since it has been established that especially in the [60]PCBM:P3HT blends, one can control (improve) the blend morphology by annealing procedures, and because these blends are the most efficient ones in state-of-the-art plastic photovoltaics, it is of great interest to gain more insight in parameters determining the functionality. We investigated the new compound ThBCM as pristine material, in blends with MDMO-PPV, as well as in blends with regioregular P3HT. The results of this evaluation will be presented. Second, we have prepared and evaluated the C₈₄ analogue of [60]PCBM, i.e. [84]PCBM. Since this fullerene has a much smaller bandgap than C₆₀, it is *a priori* of great interest as an alternative acceptor material in bulk heterojunction photovoltaic devices. We will describe the new material and present our results on the performance of MDMO:PPV:[84]PCBM active layers in plastic PV devices.

SESSION D5: Organic Photovoltaics II
Chairs: Paul Blom and Steffen Zahn
Tuesday Afternoon, November 29, 2005
Room 304 (Hynes)

1:30 PM *D5.1

Low Band Gap Polymer Solar Cells. Rene A. J. Janssen^{1,2}, Martijn M. Wienk^{1,2}, Martin P. Struijk^{1,2}, Mathieu G. R. Turbiez^{1,2} and Johann A. G. Nicolas^{1,2}; ¹Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands; ²Dutch Polymer Institute, Eindhoven, Netherlands.

One of the most important parameters that limit the performance of polymer solar cells is the mismatch between the absorption spectrum of the photoactive layer and the solar emission. Nowadays, the best polymer solar cells absorb light with wavelengths below 650 nm, while the solar photon flux maximizes around 700 nm. Low band gap polymers with an optical absorption toward the near infrared may improve on the existing state of the art. We report the synthesis and application of a series of low band gap conjugated polymers that have an improved spectral overlap with solar light. The new materials have high molecular weights and are well soluble in common organic

solvents, allowing easy and reproducible processing. For different polymer films, optical gaps ranging from 1.8 eV down to 1.2 eV (>1000 nm) were determined. Solar cells of these low band gap polymers as donor in combination with a soluble fullerene derivative (PCBM) as an acceptor, display spectral responses that correspond well to the absorption spectra. Hence, spectral sensitivity well into the near-IR region has been established. The overall power conversion efficiency of the devices with the lowest band gaps (1.2 eV) is estimated at ca. 1% under solar illumination and is mainly limited by a low photocurrent, rather than by the fill factor (up to 0.6) or open circuit voltage (up to 0.6 V).

2:00 PM *D5.2

Variable Band Gap Conjugated Polymers for Photovoltaics.

John R. Reynolds, Young-Gi Kim, Emilie Galand, Timothy Steckler and Barry C. Thompson; Chemistry, Univ. of Florida, Gainesville, Florida.

By controlling the energy levels of the HOMO and LUMO states in conjugated polymers, along with the magnitude of the electronic band gap, optoelectronic properties can be optimized for specific applications. To this end, we have developed a family of soluble conjugated polymers with band gaps ranging from 3.2 eV to 1.5 eV and utilized these polymers in photovoltaic devices. This will be discussed for polymers used in PCBM-based solar cells where the HOMO is set for air stability, the LUMO for excited state donation to the PCBM acceptor, and the band gap for broad absorption of the solar spectrum. Regiosymmetric mid-gap (ca. 2.0 to 2.5 eV) polymers are designed using thienylene and dialkoxyphenylene moieties to provide highly ordered semi-crystalline electron donor and hole carrying materials. Of special interest are the narrow gap (ca. 1.5 to 1.8 eV) conjugated polymers that can absorb solar energy most strongly at the peak of solar photon flux near. Our use of 3,4-alkylenedioxythiophene (XDOT) donors, along with cyanovinylene and pyridopyrazine acceptors has led to the development of a representative class of soluble narrow gap polymers. We will discuss fundamental optical and electrochemical results in order to establish the band structure of the newly synthesized polymers, along with presenting results from photovoltaic devices as platforms for materials property optimization. Conjugated polymer blends using polymers of varied band gap have been used in these devices in order to obtain spectral broadening of the absorption characteristics. The importance of device interfaces and current collection is noted via the utilization of conducting inter-facial layers.

3:30 PM D5.3

Tuning the Bandgap of Polyfluorene Copolymers for Solar Cells.

Mats R. Andersson¹, Wendimagegen Mammo¹, Erik Perzon¹, Xiangjun Wang², Fengling Zhang² and Olle Inganäs²; ¹Materials and Surface Chemistry, Chalmers University of Technology, Goteborg, Sweden; ²Biomolecular and Organic Electronics, Linköping University, Linköping, Sweden.

In the search for high efficiency polymer solar cells we have concentrated our efforts on preparing and testing new low-bandgap materials. The polymers in question have been specifically designed to be used in solar cells, something which require materials with high mobility of charges. In order to fulfil this prerequisite, we have chosen to work with polyfluorenes. However, the most common polyfluorenes have a relatively large bandgap and we have therefore synthesized a number of different polyfluorenes with extended absorption to cover the important parts of the solar emission. To decrease the bandgap, our strategy has been to prepare polymers based on planar conjugated segments with internal electron donor-acceptor-donor functions in between the fluorene groups. One of the earlier prepared alternating polyfluorene copolymers has an onset of absorption at 980 nm (1.27 eV) and the obtained power conversion efficiency for this polymer together with a fullerene derivative is 0.69% under simulated solar conditions. Several new polymers with increased molecular weight and tuned HOMO and LUMO position have been synthesized and evaluated. Preliminary results show a power conversion efficiency of 1.4% and an onset of photocurrent generation at 800 nm (1.55 eV) for the best device prepared so far. The polymer synthesis, polymer properties, device structure, and device characteristics will be presented.

3:45 PM D5.4

Characteristics of Conjugated Polymer - Silole Blends for Applications in Organic Photovoltaics. Jessica Joan Benson and Jenny Nelson; Centre for Electronic Materials and Devices, Department of Physics, Imperial College London, London, United Kingdom.

Blends of electron-transporting and hole-transporting molecular materials can lead to efficient photo-induced charge separation, and are therefore of interest as the active layer in organic solar cells. Although a wide range of hole-transporting organic materials have

been studied in such blend systems, relatively few suitable electron-transporting materials have been found, and most studies have been limited to fullerenes or soluble fullerene derivatives. To date, there is insufficient information on alternative electron transporters to determine the necessary conditions for effective charge separation in a blend. Therefore, the specific influences of blend morphology and electronic energy level configuration on charge separation are not yet fully understood. In this work, we report on the use of a soluble silole derivative, 2,5 bis (6' - (2',2' bipyridyl)) - 1,1 - dimethyl-3,4 - diphenyl silole as the electron-transporting component in organic blend films using a conjugated polymer as the electron donor. Silole derivatives are attractive on account of their non-dispersive electron transport properties and high electron mobility, as well as their relative stability in air. Although siloles have been studied as vacuum deposited films for organic light-emitting diode (OLED) applications, they have not previously been investigated as a component in solution deposited blend films for organic solar cells. In this research, we study charge separation, charge recombination, and photocurrent generation in blends of silole with several conjugated polymers using various spectroscopic techniques. Additionally, the morphology of the blend films is studied using atomic force microscopy. In order to gain insight into the factors controlling charge separation in blend systems, we study optical properties of the blend, morphology of the blend and photovoltaic device behaviour as a function of the ionisation potential and electron affinity of the conjugated polymer used, the composition of the blend film, and the processing conditions. We find that energetics, blend compositions and blend morphology (controlled via processing conditions) all influence the charge separation efficiency. In particular, we find that an offset of more than 0.3 eV in the LUMO levels of donor and acceptor is necessary for efficient charge separation. Furthermore, we find that charge separation efficiency is strongly influenced by the choice of solvent, through its effect on the blend morphology. In the first photovoltaic devices, external quantum efficiencies of a few percent are available. These values are comparable with external quantum efficiencies found in polymer-polymer blend solar cells. Finally we investigate the influence of polymer-silole chemical interaction on charge separation by studying blends which do and do not show evidence for exciplex formation. In view of our results we address the material properties needed to enhance solar cell performance.

4:00 PM D5.5
Photoinduced Charge Generation in Conjugated Polymers Studied with Scanning Probe Microscopy. David C. Coffey, Joseph P. Wei and David S. Ginger; Chemistry, University of Washington, Seattle, Washington.

Despite widespread appreciation that nanoscale film morphology is critical to the performance of organic photovoltaics, there are still few direct means to probe carrier generation and recombination dynamics on sub-100 nm length-scales in conjugated polymer films. We combine photoexcitation with high-resolution electrostatic force microscopy to resolve carrier generation and recombination on time and length scales relevant to photovoltaic device operation in model conjugated polymer blends. We validate our local scanning-probe measurements with conventional spatially-averaged optical spectroscopy and use the scanning-probe methods to correlate carrier generation and recombination with local film structure.

4:15 PM D5.6
Solution Processable, High Efficiency Molecular Photovoltaics. Matthew Thomas Lloyd¹, Alex C. Mayer¹, John E. Anthony² and George G. Malliaras¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Chemistry, University of Kentucky, Lexington, Kentucky.

A recently developed soluble pentacene derivative, TIPS-pentacene (triisopropylsilyl ethynyl-pentacene), is receiving considerable attention. Thin film transistors (TFTs) of solution processed TIPS-pentacene show mobilities that rival the best vapor deposited pentacene TFTs. We report on photovoltaic cells utilizing TIPS-pentacene as the donor layer. Theoretical calculations for simple bi-layer cells show that TIPS-pentacene can more than double the efficiency of a standard pentacene/C60 heterostructure due to its higher built-in potential and a broader light absorption spectrum. Evaporated pentacene/C60 bi-layer cells produce efficiencies within 10% of the theoretical maximum, and evidence suggests TIPS-pentacene will follow suit. This presentation will cover efforts to optimize the deposition technique and morphology of the TIPS-pentacene layer as a route to attain maximum theoretical efficiency.

4:30 PM D5.7
Organic double-heterostructure photovoltaic cells employing thick tris(acetylacetonato) ruthenium(III) exciton blocking layers. Barry P. Rand¹, Jian Li², Jiangeng Xue^{3,1}, Russell J.

Holmes¹, Mark E. Thompson² and Stephen R. Forrest¹; ¹Electrical Engineering, Princeton University, Princeton, New Jersey; ²Chemistry, University of Southern California, Los Angeles, California; ³Global Photonic Energy Corporation, Ewing, New Jersey.

The interest in using organic materials for solar energy conversion has grown rapidly due to the demand for inexpensive, clean, and renewable energy sources. One feature that underlies all high efficiency small-molecule based photovoltaic (PV) devices is the double heterostructure, consisting of an exciton blocking layer (EBL) inserted between an acceptor-type molecular layer and the cathode. To date, however, very little understanding of the properties of the EBL that lead to high PV cell efficiency has been provided. In this work, we introduce and study a new EBL, and find that it operates in a manner unanticipated in earlier work [1]. The EBL serves a number of functions, including preventing damage to the photoactive layer during cathode deposition, thereby eliminating exciton quenching at the acceptor/cathode interface. Furthermore, the EBL should be transparent and must transport charge to ensure a low cell series resistance and high responsivity. In the case of a material that satisfies all of these criteria, the EBL should also be sufficiently thick to place the region of highest incident optical light intensity at the donor/acceptor heterojunction. Also, thick EBLs are practically important for fabricating large-area devices with a low density of electrical shorts. We study double heterostructure copper phthalocyanine/C60 organic PV cells with either the previously studied bathocuproine (BCP), or tris(acetylacetonato) ruthenium(III) (Ru(acac)₃) as the EBL. The Ru(acac)₃-based devices have a power conversion efficiency comparable to the BCP-based PV cells even at thicknesses >100 Å, whereas BCP-based devices experience a rapid falloff of both responsivity and fill factor at these large thicknesses. Ultraviolet photoelectron spectroscopy at the C60/EBL interface confirms that charge transport in BCP is due to damage induced during deposition of the Ag cathode, while the small ionization potential of Ru(acac)₃ allows for hole transport to the C60/Ru(acac)₃ interface where recombination with photogenerated electrons occurs. Since the Ru(acac)₃ EBL function is due to energy level alignment rather than metal deposition induced damage, its thickness can be varied over a large range to position the charge generating layers in the region of highest incident light intensity, thereby maximizing the power conversion efficiency in the characteristically thin layers used in organic solar cells. [1] P. Peumans, V. Bulovic, and S. R. Forrest, Appl. Phys. Lett. 76, 2650 (2000).

4:45 PM D5.8
Effects of copper phthalocyanine purity on organic solar cell performance. Rhonda Frances Salzman¹, Jiangeng Xue², Barry P. Rand¹, Alex Alexander^{4,3}, Mark E. Thompson³ and Stephen R. Forrest¹; ¹Electrical Engineering, Princeton University, Princeton, New Jersey; ²Global Photonic Energy Corporation, Ewing, New Jersey; ³Chemistry, University of Southern California, Los Angeles, California; ⁴Universal Display Corporation, Ewing, New Jersey.

The first small molecular weight organic semiconductor bilayer heterojunction photovoltaic cell consisted of a copper phthalocyanine (CuPc) donor layer adjacent to a 3,4,9,10-perylene-tetracarboxylic bis-benzimidazole (PTCBI) acceptor and has a peak power conversion efficiency of (1.1±0.1)%. In our work, we quantitatively assess the affects of materials purity on device performance by measuring hole mobility, and then coupling those results to materials analysis of the impurity concentration. Two different source batches of CuPc were compared: a commercially obtained "unpurified" batch, and a "purified" batch refined by thermal gradient sublimation. The power conversion efficiency under simulated AM1.5G, 1 sun illumination conditions increases from (0.26±0.01)% to (1.4±0.1)%, an improvement of nearly 30% over the previous best result, as the CuPc layer purity increases. Concomitant with the improvements in power conversion efficiency, the hole mobility of the purified CuPc, as measured by space-charge limited current, is nearly three orders of magnitude higher than for the unpurified source material. Mass spectrometry and Fourier transform infrared spectroscopy are used to identify metal-free phthalocyanine as the primary impurity that degrades device efficiency and hole mobility. This work has wide ranging implications on the dependence of organic electronic device performance on materials purity and our ability to accurately determine this characteristic in small molecular weight source materials.

SESSION D6: Poster Session
 Chairs: Mats Anderson and J. C. Hummelen
 Tuesday Evening, November 29, 2005
 8:00 PM
 Exhibition Hall D (Hynes)

D6.1
Thickness Dependence of the Efficiency of

MDMO-PPV:PCBM Solar Cells. Martijn Lenes^{1,2}, V. D. Mihailetschi¹, L. J. A. Koster^{1,2} and P. W. M. Blom¹; ¹Molecular Electronics, Materials Science Centre Plus / University of Groningen, Groningen, Netherlands; ²Dutch Polymer Institute, Eindhoven, Netherlands.

One of the most studied systems in the field of organic photovoltaic devices are bulk heterojunction solar cells based on poly(2-methoxy-5-(3',7'-dimethyloxy)-p-phenylene vinylene (MDMO-PPV) as electron donor and methanofullerene [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) as electron acceptor. A striking feature of these types of solar cells is that at the optimal device thickness of typically 100 nm only 60% of the incident light is absorbed [1]. It is evident that the absorption can be enhanced by increasing the thickness of the active layer. However, in spite of an increased absorption the overall power conversion efficiency shows a negative trend when increasing the device thickness beyond 100nm. This performance decrease has been attributed to an increasing series resistance, although its physical meaning is not clear for solar cells where charge carriers are generated throughout the device. From a device point of view the reduced performance with increasing thickness mainly originates from a decrease of the fill factor. We demonstrate that this fill factor decrease is a result of the formation of space charges in thick devices. At the optimum thickness of 100 nm the photogenerated current in MDMO-PCBM devices is still slightly below the space-charge limit. With increasing thickness the space-charge limited photocurrent [2], characterized by a square-root dependence on voltage, sets in, leading to a reduction of the fill factor. The way to overcome this problem is to enhance the transport of the slowest charge carriers, in this case the photogenerated holes in MDMO-PPV. [1] C.J.Brabec *et al.*, Adv. Fuct. Mater. **11**,15 (2001) [2] V.D. Mihailetschi *et al.*, Phys. Rev. Lett. **94**, 126602 (2005)

D6.2
Device Model for the Operation of Polymer/Fullerene Bulk Heterojunction Solar Cells. L. J. A. Koster, E. C. P. Smits, V. D. Mihailetschi and P. W. M. Blom; Molecular Electronics, Materials Science Centre Plus/University of Groningen, Groningen, Netherlands.

We have developed a numerical device model, based on an effective medium approach, that consistently describes the current-voltage characteristics of polymer/fullerene bulk heterojunction solar cells. The model includes both drift and diffusion of charge carriers and the effect of space charge on the electric field by self-consistently solving the continuity equations and Poisson's equation. Furthermore, bimolecular recombination of free charges and a temperature- and field dependent generation mechanism of free charges are incorporated. The model successfully describes the voltage dependence of the photocurrent, as well the intensity- and temperature dependence. This agreement allows us to investigate the field- and carrier density distributions occurring in these devices and to identify routes to improve on device efficiencies. As a result, it is demonstrated that at short-circuit conditions only a small fraction of all free charge carriers are lost due to bimolecular recombination. This is in sharp contrast to a much higher loss at the maximum power output of the device, where a significant amount of free charges are lost.

D6.3
Efficient, infrared-absorbing organic solar cells employing a tin phthalocyanine donor layer. Barry P. Rand¹, Jianguo Xue^{2,1} and Stephen R. Forrest¹; ¹Electrical Engineering, Princeton University, Princeton, New Jersey; ²Global Photonic Energy Corporation, Ewing, New Jersey.

The power conversion efficiency of molecular organic photovoltaic cells has steadily improved over the last several years, reaching 5.7% under simulated AM1.5G solar illumination [1]. However, one of the limiting parameters for organic photovoltaic (PV) energy conversion is the mismatch of active layer absorption with the solar spectrum. Indeed, approximately 50% of the total solar photon flux is located in the red and near infrared (NIR) spectrum between 600 - 1000 nm. Recently, a polymer-based device with a photoresponse in the NIR range up to 1000 nm achieved a power conversion efficiency of 0.3% under 1 sun AM1.5 illumination [2]. In this work, we discuss the optical, electrical, and morphological properties of tin(II) phthalocyanine (SnPc), and show that it is a good candidate molecule for harvesting NIR solar radiation to a wavelength of 1000 nm when used in small molecular weight PV cells employing the donor/acceptor combination of SnPc/C₆₀. The low intrinsic hole mobility of SnPc, $\mu_h = (2 \pm 1) \times 10^{-10}$ cm²/Vs, ultimately limits the thickness of this layer in the device as it leads to low fill factors and therefore low power conversion efficiencies. However, owing to its strong absorption coefficient, a 50-Å-thick film of SnPc in a device yields external quantum efficiencies of up to 20% at NIR wavelengths. With the double heterostructure of indium-tin-oxide/100 Å copper phthalocyanine/50 Å SnPc/540 Å C₆₀/75 Å bathocuproine/1000 Å Ag, we obtain a power conversion efficiency of (0.9 ± 0.1)% under 1 sun standard

AM1.5G solar illumination and efficiencies of (1.1 ± 0.1)% under intense (10 suns) standard AM1.5G solar illumination. The SnPc/C₆₀ junction can therefore be used to extend the responsivity into the IR in tandem organic solar cells. [1] J. Xue, S. Uchida, B. P. Rand, and S. R. Forrest, Appl. Phys. Lett. **85**, 5757 (2004). [2] X. Wang, et al., Appl. Phys. Lett. **85**, 5081 (2004).

D6.4
Abstract Withdrawn

D6.5
Effect of active layer thickness on electrical properties and efficiency of polymer solar cells. Vishal Shrotriya, Douglas W. Sievers and Yang Yang; Materials Science and Engineering, University of California Los Angeles, Los Angeles, California.

Polymer based photovoltaic (PV) devices have attracted a lot of attention in the last decade for their potential towards application in flexible, renewable, non-conservative energy sources. There have been several efforts to understand the device operation mechanism of polymer PV devices. The effect of variables such as morphology, temperature, light intensity and optical absorption on the device performance, and primarily on the short circuit current characteristics, has been studied extensively. However there has not been any substantial study on the nature of optical effects on short circuit current and their dependence on the thickness of the active polymer layer in PV devices. In this work, we report the consequence of optical effects on the short circuit current of polymer based bulk-heterojunction PV cells, and the effect of active layer thickness on the device performance. Device characteristics of polymer PV cells incorporating poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and methanofullerene [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) as the active materials are examined as a function of active layer thickness. The dependence of short circuit current on optical effects and its oscillatory variation on the polymer layer thickness is explained with the help of a model. Based on the results from the modeling of exciton generation rate in the polymer layer near polymer/PEDOT and polymer/Ca interface, an estimate of photogenerated carrier concentration in the active layer was obtained, whose variation with layer thickness matched well with the variation in measured short circuit current density. Furthermore, the effect of polymer layer thickness on device operation parameters such as open-circuit voltage, fill-factor, and series resistivity are measured. Considering the variation of above mentioned parameters, an optimized power conversion efficiency as high as 2.9% (for 100 mW/cm² illumination under AM1.5G conditions) was achieved for the device with active layer thickness of 55 nm.

D6.6
Study of Organic Photovoltaic Devices Based on Molecularly Doped Polymers. SanthiSagar Vaddiraju, Mathew K. Mathai and Fotios Papadimitrakopoulos; Nanomaterials Optoelectronics Laboratory, Polymer Program, Department of Chemistry, Institute of Material Science, University of Connecticut, Storrs, Connecticut.

Organic photovoltaics are the focus of intense research efforts due to the low-cost in their processing and their potential applications in flexible electronics. Various materials and device architectures have been proposed to achieve higher quantum efficiencies. Oxidized transport layer(OTL) is typically a three component coating comprising of a charge transport molecule, an oxidized charge transport molecule and a polymer binder. Our group had investigated the use of OTL in organic light emitting devices due to its homogenous and tunable conductivity. We herein report on the possibility of the use of this molecularly doped polymer in organic photovoltaic devices. Single layer organic photovoltaic devices based on a poly carbonate of N, N'-bis(3-hydroxymethyl)-N,N'-bis(phenyl) benzidine and diethylene glycol (PC-TPD) as a photoactive material were fabricated and studied. An organic dopant, SbF₆⁻ salt of N,N,N',N'-tetrakis(4-methylphenyl) benzidine(TMPD⁺ SbF₆⁻) was used to increase the conductivity of the polymer. Two types of devices namely ITO/OTL/Al and Al/OTL/Au were fabricated with various amounts of salt in the polymer. In both the devices, the short circuit current as well as the open circuit voltage increased with increasing amount of the dopant in the polymer which was attributed to the increased number of hopping sites. In contrast to the ITO/OTL/Al devices, the Al/OTL/Au devices, wherein the OTL is 0% doped showed negligible amount of short circuit current and open circuit voltage and this can be attributed to the interface dipole effects near the bottom electrode. The effect of variation in the top and bottom contact materials on the short circuit current and open circuit voltage will be discussed. These findings on single layer devices will be important in studying bulk heterojunctions devices based on this polymer and nanostructured materials.

D6.7
Tandem Organic Solar Cells. Afshin Hadipour, Bert de Boer and

One of the limitations of present organic solar cells is the narrow absorption bands. Semiconducting polymers have a bandgaps higher than 2.0 eV (600nm) limiting the possible absorption of the solar spectrum to about 30%. We demonstrate tandem solar cells by stacking two bulk heterojunction single cells in series in order to cover a broader region of the solar spectrum. In this way absorption of incident light can be improved by using low bandgap (red absorption) polymers in combination with high bandgap (blue absorption) polymers. A high open circuit voltage (VOC) of 1.7 volt is achieved which is the sum of each sub cell. The tandem architecture and proper materials gives us the possibility to cover very broad spectral range of the solar spectrum in order to make highly efficient organic solar cells in the near future.

D6.8

Control of molecular orientation of organic p-i-n structures by using molecular templating effect at hetero-interfaces.

Takeaki Sakurai¹, Ryosuke Fukasawa¹, Kazuhiro Saito² and Katsuhiko Akimoto¹; ¹Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki, Japan; ²National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan.

An introduction of the intrinsic layer (i-layer) in organic p-i-n structures drastically improve their solar energy conversion efficiency due to the formation of high density of p/n interface, at which the exciton decomposition resulting in carrier generation proceed smoothly. However, the i-layer, which consists of the mixture of p- (donor) and n-type (acceptor) organic materials, is electrically high resistive because of the random and disordered structure. Therefore, to control the internal structure of the i-layer is one of the most important issues to obtain high efficient photovoltaic cells. In this work, we studied the effect of the template layer on the molecular orientation of both i-layer and p-i-n structure by using phthalocyanine (H₂Pc) and 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) as p- and n-type materials, respectively. The PTCDA was also used as the template layer material. We have already reported that the PTCDA template layer controls the stacking direction of H₂Pc parallel to the substrate surface, therefore, it is important to clarify the effect of the template layer on the molecular orientation of both i-layer and p-i-n structure. H₂Pc, PTCDA and the i-layer (co-deposition of H₂Pc and PTCDA with the volume ratio of 1:1) were deposited on glass substrates by organic molecular beam deposition. After the growth of the thin template layer of PTCDA, the i-layer was deposited on it at room temperature. The molecular orientation of these layers was analyzed by X-ray diffraction (XRD), grazing incidence X-ray diffraction (GIXD) and infrared reflection absorption spectroscopy (IR-RAS). It was found that the orientation of molecular planes of both molecules of H₂Pc and PTCDA in the i-layer, which was deposited on PTCDA template layer, was parallel to the substrate surface. On the other hand, in case of the H₂Pc template layer, for reference, the orientation of molecular planes of H₂Pc in the i-layer was found to be random. These results indicate that the molecular orientation of H₂Pc and PTCDA in the i-layer is strongly affected by the template layer. Moreover, the H₂Pc layer formed on i-layer/PTCDA/glass structure, which corresponds to p-i-n structure, showed parallel arrangement between its molecular plane and the surface. Therefore, it is concluded that the molecular orientation of H₂Pc layer, i-layer and PTCDA layer in p-i-n structure can be controlled by a modification of the substrate surface. It was also found that optical absorption in p-i-n structures is significantly affected by the molecular orientation. Therefore, control of the organic film/substrate interface is important for device applications.

D6.9

Nanostructured Conjugated Polymers for Solar Cell

Application. Dongjuan Xi and Qibing Pei; Material Science, UCLA, Los Angeles, California.

Conjugated polymers have become increasingly attractive as the p-channel materials for organic solar cells. The n-channel is typical made up of inorganic nanoparticles, nanorods, or various derivatives of fullerene (C₆₀). Because of the low hole mobility and short exciton diffusion length in existing conjugated polymers, polymer composites with nanometer-size domains or nanostructures have been used to reduce the distance excitons have to travel to the charge-separation interfaces. We will present our bottom-up approach to fabrication nanostructured polymer solar cells. We use anodized alumina film as the template to grow high-density nanorod arrays of polythiophenes (PT) and polypyrrole. The height of nanorods controlled by the thickness of the nanoporous alumina film and it can vary in a wide range. After the removal of the alumina template, an n-channel material such as [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) is deposited into the polymer nanorods, forming an interdigitated bilayer. We will report our recent results on performance of such nanostructured solar cells.

D6.10

Consequences of a Different Crystal Orientation of the Semiconductor Matrix in ZnO/Dye Hybrid Thin Films on Their Photoelectrochemical Performance. Kazuteru Nonomura¹, Daisuke Komatsu², Tsukasa Yoshida², Hideki Minoura² and Derck Schlettwein¹; ¹Applied Physics, Justus-Liebig-University Giessen, Giessen, Germany; ²Graduate School of Engineering, Gifu University, Gifu, Japan.

Electrodeposition of ZnO from aqueous solutions can lead to photoelectrochemically active thin films. In the presence of molecules with appropriate chemical anchor groups, crystalline but porous ZnO can be obtained. When ZnO is electrodeposited in the presence of Eosin Y (hereafter EY) in the deposition solution, ZnO / EY thin films with the c-axis of ZnO perpendicular to the substrate are prepared [1]. On the other hand, when Coumarin 343 (hereafter C343) is present, ZnO / C343 thin films with the c-axis of ZnO parallel to the substrate are obtained. These dye molecules can be desorbed from the hybrid thin films to then yield a crystalline porous matrix of ZnO with opposite crystal orientation. Such matrix can serve to adsorb a variety of dye molecules and the efficiency is clearly improved, even if the same dye is re-adsorbed again [2]. Here, we re-adsorb EY or C343 to the ZnO films of different crystal orientation and compare their photoelectrochemical properties. From the results of photocurrent transients and IMPS (Intensity Modulated Photocurrent Spectroscopy), ZnO films prepared in the presence of C343 show faster electron transport. This would be expected from an increased charge carrier mobility in ZnO perpendicular to the c-axis. Since the electron transport is coupled to the cations in solution, the ionic movement in the pores must also be faster in this material. From the measurement of IMVS (Intensity Modulated photoVoltage Spectroscopy) at open circuit it was found that both films have a similar electron lifetime. This finding speaks for a decreased recombination rate in ZnO prepared in the presence of C343 and a higher efficiency would be expected for this material. From the I-V curve under white-light illumination and also from the spectral dependence of the photocurrents, however, it is seen that the overall efficiency was higher in the ZnO films prepared in the presence of EY. Aside from the transport properties of the matrix, the electrode texture will also have an important influence on the performance of the electrodes. First experiments of gas sorption [3] indicate a higher surface area of the films grown in the presence of EY which would explain the results but investigations of the pore structure are presently performed to allow a more detailed discussion. 1. T. Yoshida, T. Oekermann, K. Okabe, D. Schlettwein, K. Funabiki, H. Minoura, *Electrochemistry*, 70, 470-487 (2002). 2. T. Yoshida, M. Iwaya, H. Ando, T. Oekermann, K. Nonomura, D. Schlettwein, D. Woehrl, H. Minoura, *Chem. Commun.*, 2004, 400-401. 3. Measurements performed in cooperation with J. Rathousky, Heyrovsky Institute, Prague.

D6.11

First-Principles Optoelectronic Properties of Potential

Organic Polymer Photovoltaic Materials. John W. Mintmire and Shelly L. Elizondo; Department of Physics, Oklahoma State University, Stillwater, Oklahoma.

One major approach for efficient polymeric photovoltaic cells lies in the use of bulk heterojunctions, which mix two different organic polymeric materials which act as donor and acceptor semiconductors. In these bulk heterojunctions the donor polymer typically acts as the light absorber, creating an electron-hole pair and then donating the excited electron to the acceptor polymer. A deep theoretical understanding of the physical processes at work in these materials will require a knowledge of the electron states near the Fermi level for both the donor and acceptor. Recent reports by Kymakis, et al. suggest that mixtures of single-walled carbon nanotubes and poly-3-octylthiophene (P3OT) represent an alternative class of organic semiconducting materials that can be used to manufacture organic photovoltaic cells with improved performance. We can calculate the electronic structure of infinitely long quasi-one-dimensional nanostructures such as carbon nanotubes or electroactive chain polymers, such as the polythiophenes, using a first-principles, all-electron, self-consistent local-density functional (LDF) method. We present results on electronic structure calculations for both semiconducting and metallic SWNTs, and compare these with electronic structure results for model poly-3-alkyl-thiophenes. This work was supported by the US Office of Naval Research and the DoD HPCMO CHSSI program through the Naval Research Laboratory.

D6.12

2-D and Linear Oligophotosensitizers for Bulk Heterojunction Organic Photovoltaic Devices.

Young-Gi Kim¹, Hermona Christian-Pandya², Emilie Galand¹, Zukhra I. Niazimbetova³, Nisha Ananthakrishnan¹, Barry C. Thompson¹, John Walker⁴, Mary E. Galvin² and John R. Reynolds¹; ¹The George and Josephine Butler Polymer Research Laboratory, Department of

Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida; ²Department of Materials Science and Engineering, University of Delaware, Newark, Delaware; ³Rohm and Haas Electronic Materials LLC, Marlborough, Massachusetts; ⁴U.S. Army R.D. and E. Command, Soldier Systems Center, Natick, Massachusetts.

Two classes of oligophotosensitizers comprised of two-dimensional conjugated poly (*p*-phenylenevinylene) (PPV)-based molecule and linear conjugated wide band gap oligomers have been utilized for harvesting incident photons in organic solar cells. The two-dimensional X-shaped photosensitizer (*p*-OXA-X) has octyloxy-phenylene and oxadiazole moieties for enhancing solubility and electron charge transport. As an initial result, AM 1.5 efficiencies of ~0.5% and IPCE of ~27% at 400 nm were observed for the *p*-OXA-X/PCBM solar cell. The morphology of the *p*-OXA-X/PCBM photoactive layer was observed using AFM and SEM and was found to have a significant effect on the photovoltaic performance. With these early results, significant enhancement in photovoltaic performance is foreseeable under optimization of device fabrication. Photovoltaic devices incorporating linear wide band gap oligophotosensitizer poly [1,4-bis(2-thienyl)-2,5-dihexyloxyphenylene] (PBTB(OC₇H₁₅)₂) and PCBM showed AM 1.5 efficiencies of ~0.6% with short circuit current 2.5 mA/cm², open circuit voltage 0.74 V, and fill factor 0.32. The IPCE of the device was observed to be ~16% at 410 nm. A series of linear conjugated wide band gap oligophotosensitizers including PBTB(OC₇H₁₅)₂ have been utilized for elucidating the relationship between electronic band structure and photovoltaic performance along with a variation in molecular structure of the sensitizers. For these studies, we used computer-aided simulation, spectroelectrochemistry, UV/Vis spectroscopy, and x-ray diffraction.

D6.13

Star-Shaped Discotic Organic Materials for Bulk Heterojunction Photovoltaics. Yashpal Bhandari, Olga Y. Zolotarskaya and Mary E. Galvin; Materials Science and Engineering, University of Delaware, Newark, Delaware.

The promise offered by organic small molecules and polymers for potential application in organic-organic and organic-inorganic bulk heterojunction photovoltaics (OPVs) has triggered tremendous interest in the design, development and commercialization of new organic materials. Organic materials are inherently inexpensive to process, have high absorption coefficients enabling use of very thin films, tunable bandgaps and are solution processible. In OPVs the incident photon excites an electron from the HOMO to LUMO to form a bound electron-hole pair which then must split at the interface formed between organic/organic or organic/metal electrode and migrate freely to the anode and cathode to generate electricity. Additionally, absorption in the red and infrared and efficient carrier mobility are required in order to fabricate an efficient OPV. π - π stacking in semiconducting organic materials, induces a 2-D or 3-D delocalization of charge and increases carrier mobility by decreasing the activation energy for interchain carrier hopping. We have developed several phenylene vinylene, cyano phenylenevinylene and oxadiazole containing phenylenevinylene discotic liquid crystalline materials. These novel materials are solution processible and have the potential for 2-D delocalization of charge within the molecule and π - π stacking between molecules, leading to spontaneous molecular self assembly and high electron-hole transport. Structure-property relations in these materials in addition to their application in organic photovoltaics will be discussed.

D6.14

Effects of thermal annealing on highly efficient thin-film solar cells based on pentacene/C₆₀. Seunghyup Yoo^{1,4}, Benoit

Domercq^{1,4}, Zesheng An^{2,4}, Robert Szooszkiewicz^{3,4}, Joshua Haddock^{1,4}, Elisa Riedo^{3,4}, Seth R. Marder^{2,4} and Bernard Kippelen^{1,4}; ¹School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; ³School of Physics, Georgia Institute of Technology, Atlanta, Georgia; ⁴Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia.

We present the photovoltaic properties of multilayer thin-film solar cells based on pentacene/C₆₀ heterojunctions, which exhibit power conversion efficiencies over 3.6 % under broadband illumination (100 mW/cm², 350-900 nm). Thermal processing was shown to increase the open-circuit voltage from 380 mV to 476 mV without significant change in fill factor and short-circuit current. The electrical characteristics are analyzed using an equivalent circuit model to gain knowledge on the influence of thermal annealing on various photovoltaic parameters. The structure and morphology of pentacene thin films are investigated by full X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements. This study reveal the highly polycrystalline nature of pentacene films prepared on ITO which can

be considered one of the key origins for efficient light harvesting in these cells. Mobility of pentacene and C₆₀ before and after annealing will also be presented.

D6.15

Bulk Heterojunction Organic Photovoltaic Device with Dye Material. Changhee Ko¹, Yashpal Bhandari¹, Subramanian

Vaidyanathan¹, Zukhra Niazimbetova¹, Frederick Beyer² and Mary E. Galvin¹; ¹Materials Science and Engineering, University of Delaware, Newark, Delaware; ²Army Research Laboratory, Aberdeen Proving Ground, Maryland.

Since the first development by C.W. Tang, organic photovoltaics (OPV) have been vigorously studied. Their key advantages include the ability to tunable their opto-electrical properties via changes in their chemical structure and the ability to use low cost processing techniques to fabricate OPVs on flexible substrates. Our research is focused on the development of high efficiency OPVs using novel organic heterojunction material systems. Our organic hetero-junction systems are mainly composed of oxadiazole containing polyphenylenevinylene (OxaPPV) and small molecule organics including some dye materials. The oxadiazole moiety is an electron withdrawing group (n-type) which also has significant oxidative stability, so it can be used in long term stable device applications. The organic molecules have been chosen so that they possess high carrier mobilities and long wavelength absorptions. When the oxadiazole containing PPV is blended with organic materials, charge separation is observed by photoluminescence quenching. The optical and morphological properties of these blends and OPV characteristics will be discussed. Also, the effect of thermal aging on the OPV will be discussed.

D6.16

High performance nano-structured organic photovoltaic cells. Kiyoshi Yase^{1,2}, Tetsuya Taima², Susumu Toyoshima², Kohjiro Hara² and Kazuhiro Saito²; ¹Photonics Research Institute, AIST, Tsukuba, Ibaraki, Japan; ²RCPV, AIST, Tsukuba, Ibaraki, Japan.

Introducing of nano-structured p-n heterojunction is promising technique for obtaining high-performance organic photovoltaic (PV) cell. We fabricated this nano-structured active-layer by co-evaporation of p- and n-type semiconducting molecules. The device structure was phthalocyanine (ZnPc)/1:1 co-evaporation (ZnPc:C60)/C60 structure, which are called as p-i-n structure. We investigated the effects of the nano-structured active-layer (i-layer) thickness on the PV properties. The thickness was changed from 0 nm (= p-n heterojunction) to 50 nm (= all i-layer) with the total thickness of 50 nm. While the short-circuit photocurrent density (J_{sc}) increased with increasing the thickness, the Fill Factor (FF) showed the opposite tendency. Therefore, the power conversion efficiency showed a maximum value at the thickness of 15 nm under 80 mW/cm² irradiation of air mass 1.5 global solar condition at room temperature in air. In order to obtain higher PV properties, not only the device structure, but also the purity is the significant factor for it. We also investigated the effects of gas impurity of measurement environment, such as oxygen and humidity. Here we improved the FF value by control of the measurement environment. Because of preventing the electron trapping by oxygen in organic semiconducting layer, the FF value in vacuum environment was increased 40 % compared with that in air environment. Finally, by using optimized PV cell mentioned above, we obtained the power conversion efficiency of 3.6 % in vacuum environment, where the FF was drastically improved up to 0.61.

D6.17

Transferred to D5.6

D6.18

Small Molecule Organic Solar Cells with Improved Stability. Qunliang Song¹, Xiaoyuan Hou¹ and Hong Yang²; ¹Physics Department, Fudan University, Shanghai, China; ²Laboratory of Advanced Materials, Fudan University, Shanghai, China.

The power conversion efficiency of small-molecule organic solar cells has been improved steadily in the past decade, but the lifetime of this type of solar cells is very short. In this report, we demonstrate a stable small-molecule organic photovoltaic device with structure of ITO, donor, acceptor, buffer, cathode. The buffer of the device is a thin layer (about 60 Angstrom) of tris-8-hydroxy-quinolato aluminum (Alq₃) between acceptor (C₆₀) and aluminum cathode instead of bathocuproine (BCP), resulting in a great increase of lifetime more than 150 times longer without encapsulation. The power conversion efficiency of the novel device is 2.11% under 75mW/cm² AM1.5G simulated illumination, which is higher than that of devices with BCP as the buffer. It is supposed previously that the BCP buffer between C₆₀ and Cathode acts as an exciton blocking layer and can absorb the damage from cathode deposition. Our experiments showed

that intentionally adding trace aluminum atoms at donor acceptor interface, into donor layer and into acceptor layer reduced the power conversion efficiency dramatically. The efficiency decrease also happened when no buffer layer was introduced. And no perceptible efficiency degradation was observed for long term storage of the devices. Thus, the role of this thin Alq3 layer is supposed to prevent cathode atoms from diffusing into and oxygen/water from permeating through the thin acceptor layer, which is quite different from the role of this thin layer supposed by previous work. Further work need to clarify the role of this thin buffer. Our results showed that by carefully controlling the interface between acceptor and cathode, the performance of organic solar cells can be improved a lot. Further carefully capsulation of devices will prolong the lifetime of them.

D6.19

Electron and hole transport in all-polymer solar cells.

M. M. Mandoc¹, J. Sweelssen², M. M. Koetse², B. de Boer¹ and P. W. M. Blom¹; ¹Molecular Electronics, Materials Science Centre plus/University of Groningen, Groningen, Netherlands; ²TNO Industrial Technology, Eindhoven, Netherlands.

Polymer-polymer blends are attractive systems for use in an organic solar cell. With respect to the polymer/fullerene systems, in which the light is absorbed in only one component (the polymer), blends of polymers have the advantage that light can be absorbed in both donor and acceptor polymer. This results in an increased exciton generation rate and as a result is expected to increase the device performance. However, the efficiencies reported experimentally for this type of solar cells are relatively low, as compared to their fullerene derivatives counterparts. The origin of this performance gap is not clear. It has been demonstrated that effective charge transfer occurs in blends of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) as electron donor, and poly[oxa-1,4-phenylene-(1-cyano-1,2-vinylene)-(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene)-1,2-(2-cyanovinylene)-1,4 phenylene] (PCNEPV) as electron acceptor [1]. Furthermore, the typical domain size of the polymers in these blends is not far from the exciton diffusion length in PPV derivatives, indicating that the active area in the blend should be large. We have selectively investigated the hole and electron conduction in this type of cells using suited electrodes. We demonstrate that the poor electron conduction properties of the PCNEPV acceptor in the blend, due to trapping, is a major limiting factor of the performance of this type of solar cell. The reduced electron transport leads to a strongly reduced fill factor of only 25%. Model calculations demonstrate that the performance of all-polymer solar cells can be strongly improved when the electron transport in the polymer blends is enhanced. [1] Veenstra, S.C.; Verhees, W.J.H.; Kroon, J.M.; Koetse, M.M.; Sweelssen, J.; Bastiaansen, J.J.A.M.; Schoo, H.F.M.; Yang, X.; Alexeev, A.; Loos, J.; Schubert, U.S.; and Wienk, M.M., Chem. Mater. 16 (2004), 2503.

SESSION D7: Excitons and Charge Transport I

Chair: Rene Janssen

Wednesday Morning, November 30, 2005

Room 304 (Hynes)

8:30 AM *D7.1

Charge Transport and Charge Separation Processes in pi-Conjugated Materials.

Jean-Luc E. Bredas^{1,2}, Veaceslav Coropceanu¹, Demetrio Filho¹, David Beljonne^{2,1} and Jerome Cornil^{2,1}; ¹School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; ²Laboratory for Chemistry of Novel Materials, University of Mons-Hainaut, Mons, Belgium.

Conjugated organic oligomer and polymer materials are being increasingly considered for incorporation as the active semiconductor elements in devices such as light-emitting diodes, photo-voltaic cells, or field-effects transistors. In the operation of these devices, electron-transfer and energy-transfer processes play a key role, for instance in the form of charge transport, energy transport, charge separation, or charge recombination. Here, we provide a theoretical description of electron-transfer phenomena based on Marcus electron-transfer theory and full quantum-mechanical extensions thereof, which allows us to provide a molecular, chemically-oriented understanding [1]. In this presentation, we will first focus on the parameters that impact the mobility of charge carriers, that is the electronic coupling within chains and between adjacent chains and the reorganization energy of the chains upon ionization. Materials under study include conjugated oligomers such as oligoacenes and oligoarylenes. In a second part, we will address the nature of the molecular parameters that impact photo-induced charge separation at an organic-organic heterojunction. [1] J.L. Bredas, D. Beljonne, V. Coropceanu, and J. Cornil, "Charge-Transfer and Energy-Transfer Processes in pi-Conjugated Oligomers and Polymers", Chemical Reviews 104 (2004) 4971-5004.

9:00 AM D7.2

Exciton Quenching and Charge Photogeneration in a Doped Conjugated Polymer.

Vladimir Arkhipov¹, Paul Heremans¹, Evgenia Emelianova² and Heinz Baessler³; ¹MCP, IMEC, Leuven, Belgium; ²Semiconductor Physics Laboratory, University of Leuven, Leuven, Belgium; ³Physical Chemistry, University of Marburg, Marburg, Germany.

Excitonic approach to photophysics of conjugated polymers suggests the following scenario of free carrier photogeneration. Excitation of a conjugated polymer by light creates Frenkel-type singlet excitons with the binding energy of around 0.5 eV. A vibronically relaxed singlet exciton can be quenched and dissociate into a (geminate) pair of charges at a charge transfer (CT) center. Typical CT center in a conjugated polymer consists of a conjugated segment and an adjacent deep electron trap. Exciton dissociation at a CT center is possible if the electron affinity of the scavenger is large enough in order to at least compensate for the exciton binding energy. However, exciton quenching at a CT center does not yet yield free carriers. Instead, a strongly coulombically bound geminate pair of charges is generated. The respective Coulomb binding energy can be estimated as 0.5 eV for a distance between the conjugated segment and electron scavenger of 1 nm and the dielectric constant of 3. Remarkably, it turns out that the charges in a geminate pair are bound not weaker than in a vibronically relaxed singlet exciton. Experimentally, it has been established that the charge photogeneration yield in organic donor/acceptor blends normally reaches maximum at the acceptor/donor ratio as high as 3:1 which is apparently much larger than the thresholds of both electron percolation and phase separation. Furthermore, it has been shown that most efficient 3:1 polymer/PCBM blends do not reveal full phase separation on the polymer side: such blends consist of pure PCBM phase and approximately 1:1 polymer/PCBM mixture as the "donor" phase. Although it is not yet clear whether or not this mixture is really homogeneous on 2-5 nm scale, a high density of strong electron acceptors should anyway dramatically reduce the exciton lifetime and, concomitantly, the exciton diffusion length. If so, this observation challenges the essential role of the interfacial exciton dissociation in efficient charge photoproduction in polymer/acceptor blends. We formulate a model of the dopant-assisted charge photogeneration in the bulk of a conjugated polymer heavily doped with strong electron acceptors. The model is based on the scenario that includes exciton dissociation into short geminate pairs as an intermediate step in the photogeneration process. It also suggests that the on-chain hole becomes "hot" due to ultra-fast structural relaxation that immediately follows exciton dissociation at a CT center. Subsequent separation of the trapped electron and on-chain hole proceeds as described by the model of hot exciton dissociation.

9:15 AM D7.3

Recombination Dynamics in Polymer and Dye-Sensitized Photovoltaic Cells.

Brian O'Regan¹, Sjoerd Veenstra², James Durrant¹, Jenny Nelson¹ and Wiljan Verhees²; ¹Electronic Materials and Devices, Imperial College London, London, United Kingdom; ²Thin Film PV, Energy Research Centre Netherlands, Petten, Netherlands.

Polymer/C60 cells are one variety of "interpenetrating heterojunction" solar cells. Cells using dye-sensitized (DS) oxide nanoparticles are another major class. It has yet to be determined to what extent the structural similarities of these two cell types give rise to functional similarities. The structural similarities are in contrast to differences in scale, materials, and function of the components. We have measured the charge carrier lifetime for a variety of MDMOPPV/PCBM, P3HT/PCBM, polymer/polymer, and DS cells. Using photovoltage transients at differing bias light levels, we have measured the recombination lifetime as a function of cell Voc. Using transient absorption we have shown that the voltage transients give useful information on the recombination processes in the "bulk". We find all cells show an exponential decrease in charge carrier lifetime with increasing Voc. Except for PPV/PCBM, this trend has the form of $\exp(-aV/kT)$ with a near 0.5. PPV/PCBM cells have a closer to 1. These data imply that P3HT/PCBM cells, seemingly similar to PPV/PCBM cells, may closely resemble DS cells. In addition, capacitance measurements show that P3HT/PCBM cells store a considerable amount of trapped charge at Voc, as do DS cells. These data present a challenge to common assumptions about the recombination in each cell type. It is generally thought that recombination in DS cells is a function of electron concentration only, as the electrolyte, is highly doped. (equivalent to $\sim 10^{20}/\text{cm}^3$). On the other hand, it is assumed that both P3HT and PCBM are intrinsic when the cell is in the dark. How these assumptions might be rationalized to give similar trends in lifetime will be discussed. The data also show that variations in the Voc between cells of all types are more likely to be related to shifts in band edge offsets than changes in charge lifetimes. In the absence of chemical modification of the bulk

material, band edge shifts are the result of changes in interfacial dipoles. The contribution of interfacial dipoles is an established effect for TiO₂/Dye based cells, where the dipole is mainly set by the surface charge of the TiO₂. How surface dipoles can contribute to Voc variation in all organic cells is not yet determined. In order to better understand the charge lifetime, we have modeled the electron hole recombination process using a random walk of one charge type in a trap dominated material. Initial results show that this model gives a variety of trends ($\alpha = 0.3$ to 1) depending on the degree of excess of the other carrier. The model also reproduces one interesting aspect of the DS cells, where we have found the value of α is only weakly related to the curvature of the DOS distribution. In summary, it is likely that a general model for DS and P3HT/PCBM cells can be developed, but that some of the standard assumptions concerning each cell type will have to be modified.

9:30 AM *D7.4

Exciton Diffusion Measurements in Organic Solar Cell and LED Materials. Andy J. Lewis, Arvydas Ruseckas, Ebinazar B. Namdas and Ifor D. W. Samuel; School of Physics and Astronomy, University of St Andrews, St Andrews, United Kingdom.

Understanding the operation of organic optoelectronic devices requires a detailed understanding of the underlying photophysics of the materials. One important quantity is the diffusion length of excitons. It is very important in solar cells as it defines the distance an exciton can travel to a heterojunction, and hence the required morphology of the material and/or possible device structure. It is also important for LEDs as exciton diffusion into other layers can lead to quenching and triplet-triplet annihilation can lead to a decrease in efficiency at very high brightnesses. In the context of lasers, singlet-singlet annihilation competes with gain. I will show that quantitative measurements of exciton diffusion lengths can be made by exciton-exciton annihilation measurements, using the intensity-dependence of time-resolved photoluminescence. I will demonstrate the application of this technique to study exciton diffusion in a range of organic semiconductors including materials relevant to photovoltaics such as MEH-PPV and poly(3-hexylthiophene). The results suggest that the morphology of spin-coated films of these materials depends on their thickness. Singlet exciton diffusion will be compared with triplet diffusion (in phosphorescent materials) and the implications for devices assessed.

10:30 AM D7.5

Role of chemical defects on the electronic properties and energy transfer dynamics in phenylenevinylene-based conjugated polymers. Emmanuelle Hennebicq¹, David Beljonne^{1,2} and Jean-Luc Bredas^{2,1}; ¹Chemistry of Novel Materials, University of Mons-hainaut, Mons, Belgium; ²School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

The wide use of poly(p-phenylenevinylene) (PPV) and its derivatives as active materials in photovoltaic devices and bio(chemical) sensors has motivated numerous studies aiming at understanding the microscopic parameters that govern the dynamics of energy transfer processes in conjugated polymers. In this respect, it is of primary importance to shed light on the particular role played by chemical and conformational defects on the electronic properties and, more specifically, on the electronic communication along the polymer backbone, which is central to the efficiency of the excitation diffusion process. The existence of chemical defects in PPV-based materials, namely sat-defects (associated with sp³-hybridized carbon atoms in the vinylene linkages) and cis-defects (double bond of the vinylene moieties in cis conformation), has already been pinpointed from a large number of theoretical and experimental investigations. These chemical defects, which induce conformational kinks along the polymer backbone, are expected to strongly perturb the electronic communication along the polymer backbone. Depending on the type of defects present in the polymer chain, a net disruption of electronic conjugation may occur at the defect points and lead to the partitioning of the electronic system of whole molecule into separated conformational sub-units (chromophores) with various conjugation length and optical properties. These chromophores, which are only weakly coupled together, are believed to act as individual donors or acceptors for the electronic excitations in their excited- and ground-state configurations, respectively. In such disordered systems, energy transfer process is best described as proceeding incoherently through a sequence of hopping events of the electronic excitations between the chromophores and its dynamics can be accounted for within a Pauli Master Equation formalism. Nevertheless, in order to apply this model, one needs first to identify the conformational subunits that correspond to the hopping sites for the electronic excitations. Here, correlated quantum-chemical techniques have been used to determine whether two chromophores separated by a chemical defect act independently or collectively in energy migration processes. To do so, we focused on model systems consisting in two oligomers with variable size connected via either a saturated or a cis-defect. For

all model compounds, the degree of electronic coupling between the two chromophore sites, in both their donor and acceptor configuration, has been evaluated by comparing the electronic and optical properties as predicted by excitonic and supermolecular approaches on the basis of their excited-state and ground-state geometries, respectively. A detailed analysis of the excited-state wavefunctions in these model bi-chromophoric compounds provides a deeper insight into the nature of donors and acceptors in defect-including polymer chains.

10:45 AM D7.6

Exciton Diffusion in Eu-DM Films. Marcie R. Black and B. K. Crone; Organic Electro-optics Team, Los Alamos National Laboratory, Los Alamos, New Mexico.

Ideally, materials used in organic photovoltaics would have an exciton diffusion length comparable to the optical penetration depth (the inverse of the absorption coefficient). In most organic materials, the exciton diffusion length is significantly smaller than the absorption penetration depth (up to several orders of magnitude smaller) resulting in lower energy conversion efficiencies. In metal-organic materials, the exciton diffusion length has been predicted to be large due to strong spin orbit coupling. Measurements of the exciton diffusion length in one particular metal organic film, Tris (dibenzoylmethane) mono (phenanthroline) europium (III) or Eu-DM, by two different measurement methods will be presented. Low energy optical excitation generated excitons with a long exciton diffusion length, while higher energy excitation generated excitons with a diffusion length comparable to other small molecule systems. The photocurrent and absorption data are also presented. The results of the exciton diffusion length, the photocurrent, and the absorption data all show evidence for an extended state in Eu-DM films responsible for the large exciton diffusion length. Samples prepared by evaporation and spin coating of the Eu-DM films give similar results.

11:00 AM D7.7

Resonance energy transfer in organic photovoltaic devices. Yuxiang Liu¹, Melissa A. Summers², Michael D. McGehee², Carine Edder³ and Jean M. J. Frechet³; ¹Department of Chemistry, Stanford University, Stanford, California; ²Department of Materials Science & Engineering, Stanford University, Stanford, California; ³Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California.

Resonance energy transfer (RET) has the potential to overcome a number of limitations associated with exciton transport in organic photovoltaic devices. Using dye-doped polystyrene blend films, we demonstrate that PCBM ([6,6]-phenyl C₆₁-butyric acid methyl ester) is an efficient resonance energy acceptor, despite the fact that its optical absorption is symmetry-forbidden. The implications of energy transfer in the performance of polymer-fullerene devices will be discussed in the context of photophysical results that show that RET leads to an increase in the apparent rate of exciton diffusion and enables excitons to overcome low-energy/long-lived sites. We also report on the use of RET from P3HT (poly[3-hexylthiophene]) to a low bandgap polymer PTPTB (poly-N-dodecyl-2,5-bis(2'-thienyl)pyrrole-2,1,3-benzothiadiazole), located near the electron-conducting electrode in a planar device. This directional resonance energy transfer efficiently places electrons at the exciton splitting interface, and yields a three-fold improvement in photocurrent. This work serves as a proof of concept for RET-based exciton harvesting, and introduces a new approach for photovoltaic cell design.

11:15 AM D7.8

Chemical vs. Field-Effect Doping of Disordered Organic Semiconductors. Vladimir Arkhipov¹, Evgenia Emelianova², Paul Heremans¹ and Heinz Baessler³; ¹MCP, IMEC, Leuven, Belgium; ²Semiconductor Physics Laboratory, University of Leuven, Leuven, Belgium; ³Physical Chemistry, University of Marburg, Marburg, Germany.

The purpose of doping a semiconductor is usually to produce an increase in the density of free carriers. High carrier density can be achieved by accumulation of carriers in a sufficiently strong gate field of a metal-insulator-semiconductor structure (field-effect (FE) doping) [1] or by (electro)chemical (EC) doping [2]. In conventional inorganic semiconductors, these doping modes are equivalent and neither of them noticeably affects the carrier mobility. However, it turns out that the situation is strikingly different in disordered organic semiconductors. Recently, the authors of Ref. [2] directly compared the mobility in poly(3-hexylthiophene) (P3HT) polymer films as a function of carrier concentration controlled by either FE or EC doping. The mobility of EC doped carriers at the moderate doping levels of 1% was found to be two orders of magnitude smaller than the FE mobility at the same carrier concentration. A sharp rise of the mobility with the doping level was found for the EC doping while the FE mobility had much smaller dependence on the carrier

concentration. The aim of this presentation is to explain the difference between these two ways of creating charge carriers. We suggest a model of carrier hopping in doped disordered organic semiconductors and show that this model is able to reproduce the experimentally observed behavior of the mobility. The model is based on the concept of strong Coulomb interaction between charge carriers and ionized dopants. As a matter of fact, doping of an organic semiconductor simultaneously produces extrinsic charge carriers and deep Coulomb traps for those carriers. The presence of Coulomb traps strongly enhances the disorder, especially at low doping levels. Therefore, low-to-moderate doping of a weakly disordered semiconductor leads to decreasing carrier mobility and a sublinear increase of conductivity due to strong carrier localization in Coulomb traps of dopants. In order to shift the Fermi level to the effective transport level and thereby increase the carrier mobility one needs doping levels in excess of typically 1%. At such high concentrations of dopants, their Coulomb potential wells overlap, which results in decreasing activation energies of Coulomb traps and concomitant smoothening of the random potential landscape. In contrast, the field-effect mobility increases with increasing charge-carrier concentration over the complete range of carrier concentrations, because it is not accompanied by the creation of additional Coulomb traps by counterions. [1] S. M. Sze, *Physics of Semiconductor Devices*, 2nd edn. (Wiley, New York, 1981). [2] H. Shimotani, G. Diguët, and Y. Iwasa, *Appl. Phys. Lett.* 86, 022104 (2005).

11:30 AM *D7.9

Doping Excitonic Semiconductors. Brian A. Gregg, Si-Guang Chen, Paul Stradins, Sophie E. Gledhill and Brian Scott; NREL, Golden, Colorado.

An in-depth study of n-type doping in a crystalline perylene diimide organic semiconductor (PPEEB) reveals that electrostatic attractions between the dopant electron and its conjugate dopant cation cause the free carrier density to be much lower than the doping density. Measurements of the dark currents as a function of field, doping density, electrode spacing and temperature are reported along with preliminary Hall-effect measurements. The activation energy of the current, E_{aJ} , decreases with increasing field and with increasing dopant density, nd . It is the measured change in E_{aJ} with nd that accounts primarily for the variations between PPEEB films; the two adjustable parameters employed to fit the current-voltage data proved to be almost constants, independent of nd and temperature. The free electron density and the electron mobility are non-linearly coupled through their shared dependences on both field and temperature. The data are fit to a modified Poole-Frenkel-like model that is shown to be valid for three important electronic processes in organic (excitonic) semiconductors: excitonic effects, doping and transport. At room temperature, the electron mobility in PPEEB films is estimated to be 0.3 cm^2/Vs ; the fitted value of the mobility for an ideal PPEEB crystal is ca. 3.4 cm^2/Vs . The modified Poole-Frenkel factor that describes the field dependence of the current is ca. $2 \times 10^{-4} \text{ eV} (\text{cm}/\text{V})^{1/2}$. The analytical model is surprisingly accurate for a system that would require a coupled set of nonlinear tensor equations to describe it precisely. Being based on general electrostatic considerations, our model can form the requisite foundation for treatments of more complex systems. Some analogies to adventitiously doped materials such as pi-conjugated polymers are proposed.

SESSION D8: Excitons and Charge Transport II
Chair: Brian Gregg
Wednesday Afternoon, November 30, 2005
Room 304 (Hynes)

1:30 PM *D8.1

Controlling and Modeling Charge Transport in Polymer Electronic Devices. Neil Greenham, Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

Interchain charge transport is important in all polymer electronic devices, including photovoltaics and high-performance LEDs. Charge transport depends critically on local morphology and packing, and these parameters are difficult to control and measure reliably. I will present measurements on polymer devices under hydrostatic pressures up to 7 kbar using a capillary pressure cell. These measurements allow interchain interactions to be reproducibly and reversibly altered whilst simultaneously monitoring both electrical and optical properties. Electron-only devices based on the polyfluorene derivative F8BT show mobilities which can be increased by an order of magnitude by the application of high pressures. Red-shifts of up to 20 nm in the electroluminescence spectrum are observed, together with a broadening of the spectrum. Measurements on polymer blend devices will also be reported. In addition, I will present recent results on Monte Carlo modeling of charge transport in heterogeneous hopping systems which closely resemble the structure of bulk heterojunction

photovoltaic devices. These simulations allow the effects of nanoscale phase separation on charge transport to be directly studied.

2:00 PM D8.2

Combined quantum chemical and Monte Carlo modelling of charge transport in rigid-rod type conjugated polymers. Alison Bridget Walker¹, Peter Watkins¹, Jarvist Frost², James Kirkpatrick² and Jenny Nelson²; ¹Physics, University of Bath, Bath, United Kingdom; ²Physics, Imperial College London, London, United Kingdom.

In conjugated polymers, charges are normally localized as polarons on single conjugated segments and, because of weak intermolecular interactions, move between the conjugated units by a non-adiabatic polaron hopping process. To date, hopping transport has been simulated using simplistic Monte Carlo models where charges are assumed to hop between sites on a cubic lattice where site energies and site-to-site interactions are subject to some (typically Gaussian) disorder. Although such models illustrate the consequences of disorder, they are not capable of probing the influence of chemical structure or molecular packing on transport explicitly. We have developed a more physically valid method of simulating hopping transport in conjugated polymers using a combination of quantum chemical (QC) and Monte Carlo techniques. We focus on the conjugated polymer, poly(9,9-dioctylfluorene) (PFO) as a model system, as the hole mobility in this material is known to depend on physical morphology. We model the polymer as an assembly of linked rod-like segments, each representing a conjugated segment (typically 3 monomers) of a conjugated polymer. Assemblies of oligomers with different degree of disorder are generated to represent more or less well ordered polymer films. The parameters relevant to hole charge transport, i.e., the intermolecular electronic transfer integral and the reorganisation energy, are calculated using semi-empirical and hybrid density functional theory (DFT) methods, respectively. Time-of-flight hole transport is then simulated in the assembly using Monte Carlo techniques. We use the model to illustrate the effects of disorder in molecular packing and orientation, and of variation in the direction of electric field, on the temperature and field dependence of hole mobility. We demonstrate the advantages of our approach over more simplistic, cubic-lattice approaches. The simulations presented here show good agreement with experimental time-of-flight hole mobility data on highly aligned PFO samples, which is encouraging given the lack of adjustable parameters.

2:15 PM D8.3

Charge Transport and Recombination in Conjugated Polymer / Fullerene Bulk Heterojunction Solar Cells. Attila J Mozer¹, Gilles Dennler¹, Niyazi Serdar Sariciftci¹, Markus Westerling², Almantas Pivrikas², Ronald Osterbacka² and Gytis Juska³; ¹Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University, Linz, Austria; ²Department of Physics, Abo Akademi University, Turku, Finland; ³Department of Solid State Electronics, Vilnius University, Vilnius, Lithuania.

Charge transport and recombination is studied in the 1:4 mixture of the conjugated polymer poly[2-methoxy-5-(3,7-dimethyloctyloxy)-phenylene vinylene] (MDMO-PPV) and 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6)-C61 (PCBM) using a charge extraction by linearly increasing voltage technique (CELIV). In this technique, charge carriers are photogenerated by a strongly absorbed laser flash, and extracted after an adjustable delay time (t_{del}). From the time to reach the extraction current maximum, the mobility is calculated, and from the delay time dependence of the number for extracted charge carriers, the recombination is studied simultaneously. The measured mobility is $\sim 2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature, which is nearly 2 orders of magnitude higher than that of the MDMO-PPV polymer without PCBM. Moreover, we found that the mobility decreases with increasing delay time especially shortly after photoexcitation. As the temperature is decreased, the time-dependence of the mobility $\mu(t)$ is more pronounced, and attributed to the energy relaxation of the charge carriers toward the tail states of the density of states distribution. The concentration decay of the extracted charge carriers is fitted using a time-dependent bimolecular recombination law. Direct comparison of the time-dependent mobility $\mu(t)$ and the bimolecular recombination coefficient $\beta(t)$ reveals that the recombination in the studied MDMO-PPV / PCBM mixture is nearly Langevin-type at room temperature, i.e. controlled by diffusion encounters of the charge carriers. Deviation observed between $\mu(t)$ and $\beta(t)$ at lower temperatures are discussed. Finally, the drift distance $l_d = \mu \tau$ E the charge carriers calculated from the CELIV measurement indicates that the photocurrent is not limited by bimolecular recombination in MDMO-PPV/PCBM 1:4 solar cells with active layer thickness up to 200 nm, which result is confirmed by the thickness dependence of the short circuit current of solar cells with various active layer thicknesses.

3:30 PM D9.1

Nanowire Solar Cells. Lori E. Greene^{1,2}, Matt Law^{1,2} and Peidong Yang^{1,2}; ¹Chemistry, University California, Berkeley, Berkeley, California; ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Non-silicon based solar cells - including polymer blend, polymer-inorganic hybrid and dye-sensitized cells (DSCs) - hold great promise as inexpensive, efficient designs for large-scale solar energy conversion. The DSC is presently the most efficient of these cells. Traditionally, the DSC is made with 15-30 nm-diameter nanoparticles that form a three-dimensional network through which electron transport occurs by percolation, a slow mechanism that limits device efficiency. Replacing the nanoparticle film with a dense, oriented array of crystalline ZnO nanowires, provides direct electrical pathways for the rapid collection of photogenerated carriers. A full sun efficiency of 1.5% is demonstrated with a ZnO nanowire photoanode that has one-fifth the surface area of a traditional DSC.¹ Nanowire arrays can also improve the polymer-inorganic hybrid solar cell. Typically, blended polymer-inorganic films are produced by spin coating a solution containing a mixture of a conjugated polymer and either a fullerene derivative, chalcogenide nanorod, or oxide nanocrystal onto a transparent conducting substrate. Films made in this way can be sufficiently thick and intimately mixed to efficiently absorb light and separate charges, but they are poorly structured for efficient charge transport to the electrodes because the donor-acceptor interface is convoluted and discontinuous. In principle, a film designed to optimize charge collection would consist of a perfectly ordered array of continuous and crystalline inorganic nanorods oriented normal to the electrode surface and encased in a layer of the polymer. We have developed a method of growing vertical ZnO nanorod arrays from textured nucleation sites created by ZnO nanocrystals with their c axes normal to the substrate.² The ZnO rod arrays are easily filled with hole-conducting polymers such as poly(3-hexylthiophene) to yield functioning solar cells. We have also extended our studies to core-sheath nanowire arrays to reduce power loss via the recombination processes that occur at the nanowire/dye/electrolyte interface. Precise layering of Al₂O₃ and TiO₂ on the ZnO nanowire arrays has been achieved using atomic layer deposition (ALD). (1) Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R. J.; Yang, P. *Nature Mater.* 2005, 4, 455 - 459. (2) Greene, L. E.; Law, M.; Tan, D. H.; Montano, M.; Goldberger, J.; Somorjai, G.; Yang, P. *Nano Lett.* 2005, published online June 18, 2005.

3:45 PM D9.2

Hybrid Conjugated Polymer / Nanostructured Oxide Photovoltaic Devices. Dana C. Olson^{1,2}, Sean E. Shaheen¹, Matthew S. White^{1,3}, Alexander Miedaner¹, Calvin Curtis¹, Reuben T. Collins² and David S. Ginley¹; ¹National Renewable Energy Laboratory, Golden, Colorado; ²Physics, Colorado School of Mines, Golden, Colorado; ³Physics, University of Colorado, Boulder, Colorado.

Conjugated polymer / nanostructured oxide semiconductor composites are promising systems for use in low cost organic photovoltaic devices. Incorporation of a conjugated polymer into a porous oxide semiconductor can result in a bulk heterojunction device in which photogenerated charges have unimpeded transport pathways to the electrodes. These hybrid solar cells can take advantage of the high electron mobilities found in metal oxide semiconductors such as TiO₂ or ZnO, while largely retaining the solution-based processing available to organic semiconductor devices. In addition, the morphology of the composite material can be determined in a systematic way by varying the growth conditions of the inorganic component. Here, we demonstrate solution and electrochemical growth of ZnO and TiO₂ nanofibers and nanotubes that are vertically aligned with respect to the substrate. Once grown, the porous nanostructures are filled with a light absorbing organic semiconductor such as poly(3-hexylthiophene) (P3HT). Limitations in the spacing of the nanostructures can be overcome to a certain extent by blending the conjugated polymer with a soluble acceptor such as (6,6)-phenyl C₆₁ butyric acid methyl ester (PCBM). Here we discuss fabrication and characterization of preliminary composite devices, with power conversion efficiencies of 0.5% and 2.0% for ZnO nanofiber / P3HT and ZnO nanofiber / P3HT:PCBM blend devices, respectively.

4:00 PM D9.3

Improving Organic-Inorganic Photovoltaic Cells through Molecular Surface Modifications. Chia Tzun Goh, Shawn R. Scully, Melissa A. Summers and Michael D. McGehee; Department of Materials Science & Engineering, Stanford University, Stanford, California.

In organic-inorganic hybrid photovoltaic (PV) cells, photogenerated excitons diffuse to the organic-inorganic interface, where they are split by electron transfer. After exciton splitting, the competition between charge collection by the electrodes and charge recombination at the interface determines the efficiency of the PV cell. The interface is hence the most crucial region, whereupon with suitable modifications, the processes of forward charge transfer and back recombination can be favorably engineered to yield efficient devices. The existence of dangling bonds on the surface of inorganic materials may act as surface states trapping charge carriers, but with proper passivation, the opportunity to attach molecular entities on the inorganic surface allows for tuning the energetics to favor photovoltaic process and for affecting the polymer interactions with the surface. The surface modification step can be incorporated naturally before polymers are infiltrated into a nanostructured inorganic matrix by exposing it to modifier-containing solutions. To elucidate the effect of adjusting the interface energetics with molecular dipoles, we have modified the surface of titania with para-substituted benzoic acids. We found that the photocurrent of a bilayer poly(3-hexylthiophene)/titania device tends to increase with stronger dipoles pointing towards the titania. The photocurrent can be effectively doubled from 0.5 to 1 mA/cm² with suitable modifications. We hypothesize that this photocurrent enhancement is due to either a faster charge transfer rate or the existence of an electrical potential barrier reducing geminate recombination. The open circuit voltage on the other hand decreases and this can be explained by the shift in the local vacuum level introduced by the dipoles. The PV cell characteristics, photoluminescence quenching measurements and back recombination rate measurements with and without surface modifications will be presented.

4:15 PM D9.4

Carrier trapping in nanoporous TiO₂/semiconducting polymer heterojunction solar cell. Akira Watanabe¹ and Atsuo Kasuya²; ¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; ²Center for Interdisciplinary Research, Tohoku University, Sendai, Japan.

Recently, TiO₂/semiconducting polymer solar cells have been studied, where the liquid electrolyte of a dye sensitized solar cell is replaced with *p*-type semiconducting polymer as a hole conducting material. Although these photovoltaic devices are promising candidates due to the synthetic flexibility and manufacturing advantage, the maximum energy conversion efficiency is lower than 1%. In comparison with silicon solar cell, the properties of the space charge layer of the TiO₂/semiconducting polymer is very complicated owing to the nanoporous structure of TiO₂ and the heterojunction between inorganic and organic semiconductors. In this study, we investigated the carrier trapping in a bilayer-type cell consisting of TiO₂/semiconducting polymer heterojunction. The poly(3-hexylthiophene) (P3HT) was adopted as a *p*-type semiconducting polymer. The photovoltaic properties of the nanoporous TiO₂/P3HT heterojunction solar cells in vacuo were compared with those in air and O₂ atmosphere. Photovoltaic properties of the TiO₂/P3HT heterojunction solar cell were studied by photovoltammetry under periodic photoirradiation, which is effective in examining the photo- and dark current-potential profiles simultaneously in the same experiment. The open-circuit voltage (V_{oc}) of the TiO₂/P3HT cell significantly depended on the atmosphere in the measurements. Accompanying the increase of the dark current, the photovoltammogram in vacuo showed the lower V_{oc} than that in air. The stepwise increase of the dark current after pulse irradiation was observed in the transient current-time profile for the TiO₂/P3HT cell in vacuo. The difference spectra of the TiO₂/P3HT cell during photoirradiation in vacuo showed the increase of a broad absorption band attributed to trapped charge carriers in the near-IR region. In the case of the TiO₂/P3HT heterojunction in vacuo, the trapped charge carrier is stable and long-lived after the photoirradiation, which induces the increase of the dark current and lowers the V_{oc} . The carrier trapping mechanism was discussed based on the electronic structure of TiO₂ cluster models by *ab initio* calculation. The partial density of states (PDOS) for ideal and hydroxyl-group capping surface models were calculated using Gaussian 03. The PDOS of ideal surface model clearly showed deep trap levels due to the surface states. The deep levels were reduced by the hydroxyl-group capping of the oxygen-deficient surface. The carrier transfer through the TiO₂ nanosurface and the carrier trapping at a deep level of the oxygen-deficient surface were suggested based on the PDOS and the molecular orbitals for the TiO₂ cluster models.

4:30 PM D9.5

Long-term transient phenomena in operation of solar cells based on MEH-PPV/TiO₂ nanocomposites. Christopher Martin, Victor M. Burlakov, Kiril R. Kirov, Michelle Carey and Hazel E. Assender; Materials, University of Oxford, Oxford, United Kingdom.

We studied time dependence of short circuit current ISC and open circuit voltage VOC of composite solar cells under continuous light illumination. It is found that after switching on white light illumination the device never reaches steady state: there is a quick increase of VOC up to its maximum value followed by steep drop down to few percent level over a period of several minutes. Simultaneously ISC keeps increasing even after VOC has significantly dropped and reaches its maximum at much higher exposure time, after which it starts decreasing slowly. Similar investigations of the transient behavior under illumination with the high frequency spectrum filtered off show much smaller time dependent changes in VOC and ISC. Theoretical analysis and simulations of the composite solar device operation show that the observed transients could be explained in terms of a generation of minority carriers (electrons in MEH-PPV and holes in TiO₂) due to either bulk dissociation of excitons in MEH-PPV or light absorption in TiO₂. Generated minority carriers are in dynamic equilibrium with majority carriers and shift their electrochemical potentials making the difference between MEH-PPV and TiO₂ much smaller. At the same time accumulation of minority carriers significantly increases majority carrier density boosting recombination at the MEH-PPV/TiO₂ interfaces and hence decreasing short circuit current. It is shown that minority carriers are detrimental to solar devices of any kind.

4:45 PM D9.6

Light-emitting diodes from self-organized polymers/silica mesostructures. Ekaterina Dovgolevsky¹, Saar Kirmayer¹, Yi Yang², C. Jeffrey Brinker² and Gitti L. Frey¹; ¹Department of Materials Engineering, Technion - Israel Institute of Technology, Haifa, Israel; ²Department of Materials Engineering, The University of New Mexico and Sandia National Laboratories, Albuquerque, New Mexico.

Polymer nanocomposites have found successful applications in a variety of fields such as battery cathodes, nonlinear optics, sensors, microelectronics, etc. In this research novel mesoscopically ordered conjugated polymer/silica nanocomposites are designed, synthesized, characterized and integrated into polymer light-emitting diodes. In these hybrid materials, conjugated polymer chains are confined into well-defined pores of a silica scaffold to protect them from oxidation, control their morphology and opto-electronic properties. The self-organized nanocomposite thin films are prepared by incorporating pre-polymerized conjugated polymers (PFO, F8BT or MEH-PPV) into the ordered channels of a silica matrix during its formation using the evaporation-induced self-assembly technique (EISA). 3D-cubic, 2D-hexagonal or lamellar mesophases are selectively obtained by varying the type and concentration of the structure-directing surfactant. Optical absorption and photoluminescence measurements of the nanocomposite films show a red shift in both spectra relative to those of a polymer film which could be associated with an increase in conjugation length due to chain planarization in the channels of the silica matrix. Light-emitting diodes with the general structure: ITO/PEDOT:PSS/nanocomposite/Ca/Al have been fabricated and tested. The 3D-cubic nanocomposite mesophase provides a through film thickness connectivity of the conjugated polymer and hence, diode characteristics and light emission. Devices based on the 2D-mesophases, on the other hand, result in weak or no diode characteristics due to poor through thickness film connectivity. The discrepancy in the performance of devices prepared from 2D- and 3D-mesophases indicates that the polymer is indeed incorporated in the ordered inorganic matrix and not in voids randomly arranged between silica grains.

SESSION D10: Poster Session
Chairs: Brian O'Regan and Ifor Samuel
Wednesday Evening, November 30, 2005
8:00 PM
Exhibition Hall D (Hynes)

D10.1

Very High Electron Mobility in Discotic Liquid Crystals.

Junsheng Yu^{1,3}, Zesheng An^{2,3}, Jian-Yang Cho^{2,3}, Takeshi Kondo^{1,2,3}, Stephen Barlow^{2,3}, Benoit Domercq^{1,3}, Seth R. Marder^{1,3} and Bernard Kippelen^{1,3}; ¹School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; ³Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia.

Organic semiconductors with high charge mobility play a critical role in organic light-emitting diodes (OLED), photovoltaic cells, organic field-effect transistors (OFET), xerography, and photorefractive systems. Charge mobility in organic semiconductors can be measured using various techniques, including the time-of-flight (TOF) method, the pulse-radiolysis time-resolved microwave conductivity

(PR-TRMC) technique, the space-charge limited current method (SCLC), and the field-effect transistor method. For most of these applications we are interested in the bulk drift mobility in thin films and therefore, TOF and SCLC are often the methods of choice. For high mobility materials ($\mu > 1 \text{ cm}^2/\text{V}\cdot\text{s}$), TOF experiments become limited by the internal time constant of the circuit which is comparable to the transient time the charges need to travel through the sample and therefore SCLC method becomes a method of choice. Amorphous organic molecular materials and polymers have relatively low electron mobility. Discotic liquid crystals based materials have been studied as electron transport materials. Several different cores have been used and materials based on organometallic, perylene and coronene core have been identified as promising materials. These compounds presented a liquid crystalline phase stable from room temperature up to above 200 °C. Very high electron mobility in air at room temperature above 7 cm²/Vs in 5 μm-thick films have been measured using space-charge limited current method. Temperature dependence of the electron mobility have been characterized and showed that mobility stays constant as a function of temperature within the liquid crystalline phase.

D10.2

Modelling Polaron Formation in Poly(paraphenylenevinylene) using Hybrid Density Functional Methods. James Kirkpatrick and Jenny Nelson; Center for Electronic Materials and Devices, Physics Department, Imperial College, London, United Kingdom.

Low charge mobilities in conjugated solids are one factor limiting the efficiency of organic photovoltaic and light-emitting devices. Although charge mobilities are influenced by both the chemical structure and physical morphology of the molecular solid, the relationship between structure and transport properties is not well understood. In conjugated solids, charge transport is understood to occur by charge hopping between localised charged states or polarons, and can be described by the Marcus-Hush equations. In order to understand the parameters governing these charge-transfer reactions, it is first necessary to study the nature of the participating polaron states. For this purpose, we have studied polaron formation in a model system, an oligomer of para-phenylenevinylene (OPV), by relaxing the geometry of charged oligomers using density functional methods. First we compare two different hybrid density functionals: Becke's three parameter hybrid exchange functional with Lee, Yang and Parr's correlation functional (B3LYP), and the half-and-half hybrid exchange functional with Lee, Yang and Parr's correlation functional (BHandHLYP). We show that only BHandHLYP is more suitable of describing polaron localisation. Calculations as a function of oligomer length show that the polaron localises over a chain length that is consistent with results from electron-nuclear double resonance spectroscopy. This suggests that an appropriate description of the exchange interaction is necessary to accurately model polaron localisation. Finally, we present results of studies that demonstrate how polaron localisation is affected by geometric and chemical defects on the oligomer chain. These results will be used to give a better understanding of the microscopic processes involved in interchain and intrachain charge transfer.

D10.3

Carrier Transport and Contact Effect on the Extraction of Carrier Mobility by Admittance Spectroscopy in Organic Semiconductor. Sai Wing Tsang and Shu Kong So; Physics, Hong Kong Baptist University, Hong Kong, China.

We examine the feasibility of admittance spectroscopy (AS) and susceptance analysis in the determination of charge carrier mobility in organic amorphous materials. Via computer simulation, we found that a plot of the negative differential susceptance vs frequency yields a maximum at a frequency $\tau^{-1}r$. The position of the maximum $\tau^{-1}r$ is related to the average carrier transit time τ_{dc} by $\tau_{dc} = 0.56 \tau r$. Thus knowledge of can be used to determine the carrier mobility in the material. Devices with the structure ITO/4,4',4''-tris{N,-(3-methylphenyl)-N-phenylamino}triphenylamine (m-MTDATA)/Ag have been designed to investigate the validity of the susceptance analysis in the hole mobility determination. The extracted hole mobility data from the susceptance analysis is further analyzed by the Gaussian Disorder Model (GDM). The GDM disorder parameters are in excellent agreement with those extracted from time-of-flight (TOF) technique. Different hole transporting materials, with different energy levels of highest occupied molecular orbital (HOMO), are further used to study the injection barrier effect on the extracted mobility by AS. The nature of the carrier injection contact is very important in the delineation of the mobility data in AS. In the case an Ohmic hole contact (e.g. ITO or Au /m-MTDATA), the mobility data is good agreement with TOF results. However, in the case of non-Ohmic contact, the extracted mobility appears to be smaller. The discrepancy is due to the increase of the contact resistance, leading to a reduction in the electric field inside the bulk of the material.

D10.4

Enhanced Charge Carrier Transport in a Quasi One-Dimensional Hexapentylotriphenylene for Photovoltaic Applications. Volodymyr Duzhko¹, Alexandre N. Semyonov², Robert J. Twieg² and Kenneth D. Singer¹; ¹Physics, Case Western Reserve University, Cleveland, Ohio; ²Chemistry, Kent State University, Kent, Ohio.

The idea of producing high efficiency organic photovoltaic cells from nanostructured networks of electron and hole-conducting materials derives from a large effective interfacial area exhibiting efficient exciton dissociation at the interfaces, suppressed recombination of electrons and holes after their spatial separation, and optimized transport of electrons or holes along different paths toward the electrodes. Transport properties of the percolated network of electron and hole transporting materials is one of the factors limiting enhanced performance. Discotic liquid crystal phases are known to possess quasi one-dimensional order. As a result, enhanced electronic transport and a larger diffusion length of charge carriers are expected in comparison to polymers. In this presentation, we report on our investigation of charge carrier transport in the columnar phase of the discotic liquid crystal, hexapentylotriphenylene, by the time-of-flight technique over a range of temperatures and electric fields for liquid crystal layers with different thicknesses. The hole mobility was found to be temperature and electric field dependent with a maximum value of $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$. Its temperature dependence is a monotonically decreasing function of increasing temperature consistent with a T^{-n} power law, with an electric field dependent n varying from 2.5 to 4.5 corresponding to electric field values from $5 \times 10^4 \text{ V/cm}$ to $5 \times 10^3 \text{ V/cm}$, respectively. For a constant temperature, the drift velocity of charge carriers is a linear function of the electric field for small fields below $5 \times 10^4 \text{ V/cm}$ and tends to saturation at strong fields. These results are interpreted in the framework of correlated polaron motion as described by the non-adiabatic low-temperature limit of Holstein's small polaron theory. The larger values of the hole mobility compared to those typically observed in disordered polymers appear as a result of the quasi-one-dimensional order of discotic molecules in the columnar stacks. Both the potential low-cost fabrication based on self-assembly along with the efficient transport of charge carriers suggest the potential of discotic liquid crystals as the active elements of organic photovoltaic cells.

D10.5

Non-ionic Conduction in Nematic Liquid Crystal.

Masanao Goto, Hiroshi Wada, Takehiko Mori, Hideo Takezoe and Ken Ishikawa; Dept. of Organic and Polymeric Materials, Tokyo Inst. of Technology, Tokyo, Japan.

Semiconducting liquid crystalline films have potential to combine high mobility of poly crystalline films and uniformity of amorphous films. For this reason, semiconducting liquid crystals are promising materials for carrier transport layers of OLEDs and photovoltaic devices. Historically, the studies on electric conduction in liquid crystal mesophase were started from ionic conduction of nematic liquid crystals. After the discovery of electronic conduction in a columnar liquid crystal mesophase, most of studies on conducting liquid crystals have been directed to discotic columnar liquid crystals and smectic liquid crystals. Although, many liquid crystals show the electronic conduction, it is thought that nematic liquid crystals do not show electronic conduction throughout the long study on conduction in nematic liquid crystals. We examined carrier mobility in nematic phase of some oligothiophene derivatives whose one-end was substituted for cyano group in order to exhibit nematic phase. Mobility measurement was performed by usual time-of-flight method using third harmonic generation light (wavelength = 355nm, pulse width = 4ns) of Nd:YAG laser as excitation source. For checking the conduction type, applied electric field dependence and temperature dependence were measured. The mobility anisotropy according to nematic director was also measured by changing alignment layer of liquid crystal cells. In these measurements, we found non-ionic conduction with a quaterthiophene(4T) derivative and ionic conduction with a terthiophene(3T) derivative. The 4T derivative had a non-dispersive transient current. The evaluated mobility showed an apparent electric field dependence which is steeper than Poole-Frenkel type relationship. The mobility anisotropy of the 4T derivative was large and inverse from usual ionic conduction. These observations support the non-ionic conduction of the 4T derivative. In this presentation, we show the details of the experimental result and the conduction mechanism which can explain the electric field dependence and the anisotropy of the mobility.

D10.6

Abstract Withdrawn

D10.7

Exciton Diffusion in Conjugated Materials. Shawn Ryan Scully

and Michael D. McGehee; Materials Science and Engineering, Stanford University, Stanford, California.

The nature of exciton migration in conjugated materials is fundamentally and practically important. In spite of its relevance in improving photovoltaics, OLEDs, and organic biosensors, relatively little is known about exciton transport. We measured exciton diffusion lengths for a variety of common conjugated polymers using steady-state photoluminescence quenching. We also investigated the role processing plays in determining the exciton diffusion length for a given material. Care was taken to account for interference effects which if ignored will lead to false measurements. Using the measured diffusion lengths, we predicted quantum efficiencies for bilayer solar cells and compared them with experiment.

D10.8

In-Situ Solid State Polymerized Polydiacetylene as Hole Transport Material in Solid-State Dye-Sensitized Solar Cells. Yanping Wang¹, Ke Yang¹, Xiaoyu Yang¹, Ramaswamy Nagarajan¹, Jayant Kumar¹ and Lynne A. Samuelson²; ¹Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts; ²Nanomaterials Science Team, U.S. Army Natick Soldier Center, RDECOM, Natick, Massachusetts.

Solid-state dye-sensitized TiO₂ solar cells (DSSCs) were fabricated using in-situ solid state polymerized poly (5, 7-dodecadiynoic acid) (PDA-3118) as the hole transport material (HTM). In-situ preparation of HTMs is an effective solution to the problem of incomplete filling of the TiO₂ pores by the HTM and poor contact between the absorbed sensitizer and the HTM when conjugated polymers are employed as the HTM. Polydiacetylenes prepared via solid state polymerization are crystalline, exhibiting relatively high charge carrier mobilities (approx.3 orders of magnitude larger than those of partially crystalline or amorphous conjugated polymers). In comparison to in-situ chemical and photoelectrochemical polymerizations, photoinduced solid state polymerization is a simple process and incorporates minimal impurities into the solar cell system. Here we report some preliminary results: under AM 1.5 condition (100mWcm⁻²), with Ru-N3 dye as the light sensitizer and a polydiacetylene (PDA-3118) as the HTM, the open-circuit voltage Voc over 550mV, short-circuit current density Jsc up to 1.5 mAcm⁻² and fill factor FF of around 0.28 were obtained, yielding an overall efficiency of 0.25%. Further investigation to understand and improve the performance of these cells is on going.

D10.9

Reverse bias annealing improvement of the performance of polymer: TiO₂ nano-composite solar cells. Ajay K. Pandey¹, H. Wang², A. B. Djurisic², K. K. Y. Man³, W. K. Chan³, M. H. Xie², Y. H. Leung² and J. M. Nunzi¹; ¹Laboratory POMA UMR CNRS 6136, University of Angers, Angers, France; ²Department of Physics, University of Hong Kong, Hong Kong, Hong Kong; ³Department of Chemistry, University of Hong Kong, Hong Kong, Hong Kong.

Dye sensitized solar cells, DSSC or Gratzel cells [1] are one of the emerging and interesting applications in the field of materials science research. Considerable attention has been paid to overcome the degradation of such cells, primarily caused by the leakage of the liquid electrolyte used, by namely all solid state DSSC or polymer-TiO₂ based solar cells. While the power conversion efficiency of the solid state dye sensitized cells can reach close to 4%, the polymer-TiO₂ cells lag well behind with a conversion efficiency <1%. Major issue of concern is to make a uniform filling of the polymer in the matrix of TiO₂ nano-porous layers, failing to which in turn leaves voids to act as charge trapping sites or causes localized dipoles leading to reduced power conversion efficiencies. Another problem encountered is the formation of counter diode due to the poor carrier selectiveness of the electrodes, resulting in a reduced filling factor and hence low extraction of the maximum converted power by the composition. We will report our studies on the improved performance of cells made by polymer (MEH-PPV or P3HT) in combination with TiO₂ nano-composites. It has been observed that post fabrication annealing of the cells under reverse biased condition at an elevated temperature (100o C) helps re-orient the dipoles created by uneven filling of polymer inside the nano-composite matrix. Improvements were clearly observed as the current-voltage characteristics of the device became strongly asymmetric (in dark) with doubled filling factor and one order of magnitude higher short circuit current density resulting in overall improved power conversion efficiency. To further refine the approach we have performed experiments to address the origin of the counter diode formation in such compositions which, in common practice, is attributed to the poor carrier selectiveness of the electrodes. We observed that this may not be the case always as the nature of such an appearance might originate from the ITO and TiO₂ interface. To substantiate our claim, we measured the cell performance under AM 1.5 illumination in combination with an UV-cut filter and observed that the counter-diode disappeared totally

or got reduced significantly. Further work is under way to study the phenomenon in a systematic and precise way. References: 1. B. O. Regan and M. Gratzel, *Nature* 1991 353, 737

D10.10

MEH-PPV/TiO₂ Photovoltaic Devices with Enhanced

Efficiency. Kiril Radkov Kirov¹, Hannah E. Smith¹, Aaron Barkhouse¹, Zhibin Xie¹, Bernard M. Henry¹, Hazel E. Assender¹, Christopher R. M. Grovenor¹, Paul L. Burn² and Graham R. Webster²; ¹Department of Materials, University of Oxford, Oxford, United Kingdom; ²Department of Chemistry, University of Oxford, Oxford, United Kingdom.

The efficiency of conjugated polymer/TiO₂ (CP/TiO₂) solar cells has been limited to ~0.45% for devices either in the bi-layer or in the bulk hetero-junction configuration. The reasons for the poor photovoltaic performance are not well understood. We have worked on a model bi-layer cell with the structure ITO/TiO₂/MEH-PPV/Au in order to establish what the limiting factors are and have identified several routes for improving the device efficiency. These include optimising the polymer film thickness, post-production heat treatment, and modification of the metal/semiconductor and electron donor/acceptor interfaces. The post-production heat treatment and the metal/semiconductor interface modification improved the efficiency of the basic cell from ~0.2% to ~0.5%. By modifying the electron/donor acceptor interface the efficiency of the model cell was brought to 1.05%. Our results indicate that the efficiency of CP/TiO₂ solar cells is predominantly limited by inefficient exciton dissociation at the electron donor/acceptor interface and by poor charge transport.

D10.11

Overview of Quantum Dot (QD), Single Wall Carbon Nanotube (SWNT), and QD-SWNT Complexes for Polymeric Photovoltaics. Brian J. Landi¹, Chris M. Evans¹, Stephanie L. Castro², Sheila G. Bailey³ and Ryne P. Raffaele¹; ¹NanoPower Research Laboratories, Rochester Institute of Technology, Rochester, New York; ²Ohio Aerospace Institute, Cleveland, Ohio; ³NASA Glenn Research Center, Cleveland, Ohio.

Photoactive nanomaterials are being investigated as multifunctional additives in polymeric photovoltaic devices. The capabilities to dissociate the polymeric excitons and facilitate carrier transport are essential properties imbued at nanomaterial junctions. However, devices which rely solely on photon absorption by the conducting polymer are bandgap (E_g)-limited (typically > 2 eV) in regard to the solar spectrum (ideal is ~1.4 eV). Therefore, nanomaterial additives with optical bandgaps below the conducting polymer E_g can allow composite devices to absorb a larger portion of the solar spectrum. Synthesis of novel semiconducting QDs like CuInSe₂, GaSb, and InSb are ideal candidates for this role based on the quantum mechanical tuning of their optical bandgaps by size, composition, and surface chemistry. We will review our work on the synthesis of these materials and investigation of cyclic voltammetry measurements to determine the electron affinity (EA) and ionization potential of the QDs based on size and composition. The incorporation of candidate QD materials with appropriate energy level matching to the polymer matrix will enable charge transfer while also contributing to the photoresponse. In addition, appropriate coupling of tailored QDs to single wall carbon nanotubes (SWNTs) can significantly augment charge transport based on the ballistic SWNT conduction. Comparison of our results using covalent and noncovalent bonding strategies for attaching QDs to SWNTs shows the improvement of SWNT structural and electronic integrity for noncovalent products. The optical absorption spectra and optoelectronic performance for photovoltaic devices incorporating each of the described nanomaterials will demonstrate the utility of these additives in polymer photovoltaics.

D10.12

Metal Oxide Semiconductor Nanoparticles as Electron Acceptors in Polymer Based Bulk-Heterojunction Photovoltaic Devices.

Matthew Schuette White^{2,1}, Dana C. Olson^{3,1}, Alexander Miedaner¹, Sean E. Shaheen¹ and David S. Ginley¹; ¹National Renewable Energy Laboratory, Golden, Colorado; ²Department of Physics, University of Colorado at Boulder, Boulder, Colorado; ³Department of Physics, Colorado School of Mines, Golden, Colorado.

Recent investigations have shown metal oxide semiconductors to be effective electron acceptors in hybrid organic-inorganic photovoltaic devices. The low-temperature solution processing and tunable band structures of the nanoparticles make them attractive materials for photovoltaic applications. Capped ZnO and TiO₂ nanoparticles were synthesized at 60C to 75C from organometallic precursors and suspended in chlorobenzene after precipitation before blending with OC1C10-PPV. Devices with ITO/PEDOT and Aluminum electrodes were constructed with efficiencies of roughly 0.9% with ZnO and 0.2% with TiO₂. Further optimization is required for the TiO₂ devices, but

fill factors of roughly 70% have been measured indicating efficient electron transport within the bulk and low series resistance at the aluminum electrode interface. Investigation of organic ligands and capping groups may also change the wetting properties and electron transfer rates.

D10.13

Morphology-dependent luminescence in blends of a phenylenevinylene-based polymer and polyethylene oxide.

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The morphology and admixing of multi-component films is important in the field of organic electronics, where devices such as photovoltaic cells, light-emitting diodes and light-emitting electrochemical cells (LECs) are often based on films of two or more layered or blended organic phases. We use near-field scanning optical microscopy (NSOM) to study the morphology resulting from blending Superyellow, a PPV-based conjugated co-polymer with a high luminescence quantum yield (Covion), with polyethylene oxide (PEO), a semicrystalline non-luminescent polymer. 1:1 mass ratio blends of these materials have been used successfully in LECs. Here, we use NSOM to explore the concentration-dependent film morphology and luminescence properties of blend films with different Superyellow:PEO ratios. As the Superyellow concentration decreases, its morphology changes from aggregated to evenly dispersed in the annealed blend film below a threshold concentration for phase separation. The fluorescence spectrum of Superyellow undergoes a corresponding large blue shift (~80 nm) below the threshold concentration. We use single molecule spectroscopy to attribute this shift to the restricted molecular conformation of isolated Superyellow chains incorporated in the semicrystalline PEO structure. Above the threshold concentration, NSOM reveals no spectral trace of the restricted conformation in the 1:1 films, indicating that there is little or no admixing of the PPV polymer into the PEO phase in working devices. The sensitivity of the PPV polymer to its surroundings will be discussed in terms of its structure, and the implications of our results on working devices will be addressed.

D10.14

Charge Balanced Structure and Efficient Recombination of Organic Electrophosphorescent Devices with Enhanced Efficiency and Lifetime.

Byung Doo Chin, Soo-Hyeong Lee, Jae-Woong Yu and Jai Kyeong Kim; Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

Controlled doping profiles of light emitting and exciton blocking layers were employed for enhanced efficiency and lifetime of electrophosphorescent organic light-emitting device (OLED). Significant hole trapping effect of red-emitting triplet dopants in 4,4'-N,N'-dicarbazole-biphenyl (CBP) host material could explain the proposed mechanism of exciton diffusion and recombination far from emission layer-hole transport layer interface, whereas green-emitting dopants showed less-effective direct charge carrier trapping in a same host material. Moreover, we have compared the color coordinate and lifetime of red and green electrophosphorescent devices with different exciton (hole) blocking materials. Experimental result on significant dependence of red emitting device's lifetime and emission spectrum on doped hole blocking layer could explain the longer diffusion of red triplet excitons. Analysis on the supporting photophysical experiments as well as determination of appropriate energy levels using photoemission yield spectroscopy was performed. We demonstrated that controlled charge trapping, both at the emission and blocking layers with corresponding energy level alignment, is essential for charge-balanced electrophosphorescent OLED having different exciton diffusion and recombination area. Current design method for effective charge confinement and underlying physical concept will be essential for next generation, high-efficiency OLED as well as novel photovoltaic devices.

D10.15

Estimation of EL emission and carrier recombination sites by local doping method in organic light-emitting FET.

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We have reported on bright electroluminescence (EL) from 1wt%-rubrene doped tetraphenylpyrene (TPPy) as an active layer in an organic light-emitting field-effect transistor (OLEFET), demonstrated that TPPy provides compatibility of both transistor and EL characteristics. We observed a maximum EL quantum efficiency (η_{ext}) of $\sim 0.5\%$ with a Cr/Au source-drain electrode and slightly higher η_{ext} of $\sim 0.8\%$ with the source-drain (S-D) electrodes of low-work-function metal/Au multi-layers aiming for simultaneous hole and electron injections. In these devices, source (V_s), drain (V_d) and gate (V_g) voltages significantly influenced on hole and electron injection and accumulation. In this study, to elucidate detailed EL mechanism of the OLEFET device, we investigated carrier recombination and emission sites by local doping method. We inserted a ultra-thin rubrene doped TPPy layer (10 nm) in a TPPy active layer (80 nm) and measured the luminance (L)-drain current (I_d)- V_d characteristics and EL spectra by changing V_g . We demonstrate that the local doping method is a useful technique for estimating width of the carrier recombination and EL emission site in the OFET device. A highly doped n^+ -Si (100) wafer with a 300 nm-thick SiO_2 layer ($C_i=1.18 \times 10^{-8}$ F) was used as a gate electrode. Bottom-contact-type S-D electrodes composed of Cr(0.5 nm)/Au(40 nm) were formed on a SiO_2/n^+ -Si layer using conventional photolithography and lift-off techniques. The channel length between the S-D electrodes was $L_{SD}=0.8 \mu\text{m}$ with a channel width of 2 mm. A d_1 -nm-thick TPPy layer, a 10-nm-thick 1wt%-rubrene doped TPPy layer and a d_2 -nm-thick TPPy layer with a total thickness of 80 nm were successively deposited on the S-D electrodes in a vacuum of $<1 \times 10^{-3}$ Pa. Here, d_1 thickness ($d_1=70$ - d_2) was changed from 0 nm to 70 nm. With the d_1 thicknesses of 0-40 nm, η_{ext} under $V_g=0$ V showed constant values of $\eta_{ext}=0.1\sim 0.2\%$. Furthermore, in the d_1 thicknesses thicker than 40 nm, η_{ext} under $V_g=0$ V gradually decreased, resulted in $\eta_{ext}=0.02\%$. On the other hand, η_{ext} under $V_g=-100$ V showed almost constant values in any d_1 thicknesses. From these results, under the no gate voltage ($V_g=0$ V), it is suggested that carrier recombination width is limited to less than 40 nm which corresponds to the height of S-D electrodes. This suggests that charge carrier injection from the source and drain electrodes uniformly occurs from these side walls. On the other hand, under an applied voltage of $V_g=-100$ V, it is suggested that carrier accumulation and recombination regions are expanding over $d_1 > 40$ nm. 1) T. Oyamada, S. Okuyama, N. Shimoji, K. Matsushige, H. Sasabe, and C. Adachi, Appl. Phys. Lett., **86**, 093505 (2005). 2) T. Oyamada, H. Uchiuzo, S. Akiyama, Y. Oku, N. Shimoji, K. Matsushige, H. Sasabe and C. Adachi, J. Appl. Phys. (submitted)

D10.16

Effects of Novel Wet-Type Hole Injection Materials on Properties of Organic Light Emitting Diodes.

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Organic light emitting diodes (OLEDs) have been widely investigated for many potential applications such as OLED display, backlight for LCD and indoor lighting. In order to fabricate these attractive OLEDs successfully, it is said to decrease non-emitting dark spot is one of most important issues to be dissolved. We report here on satisfactory performance of our novel wet-type conductive materials "ND-series" for hole injection layer (HIL), which could be alternative to traditional vapor deposition materials such as copper phthalocyanine (CuPC). "ND-series" is electrically conductive varnish, which consists of organic conductive material, acceptor, organic solvent and without water that gives serious damage to OLEDs. They can easily form very smooth and uniform film ($R_a < 0.3\text{nm}$) just by overcoat onto rough substrate surface and minute dusts which cause short circuit. The film turns out to be conductive after annealing and shows ohmic behavior. Ionization potential (I_p) of "ND-series" can be changed from 5.3 to 5.8eV by changing the ratio of host/acceptor or replacing the sort of acceptor to be adjusted to that of neighboring hole transporting layer. The results of OLED properties with "ND-series" [device structure: ITO/ND/ α -NPD/Alq3/LiF/Al] showed more uniform emitting, lower operation voltage, higher luminous efficiency and longer life than those with CuPC or without HIL device. These results was supported by cross section TEM observation in which interfaces among all organic layers and anode of OLED with "ND-series" was much smoother than that with CuPC. "ND-series" also demonstrated satisfactory properties in organic phosphorescent device [ITO/ND/ α -NPD/CBP:Ir(ppy)₃/BCP/Alq3/LiF/Al]. From these results it could be concluded that our novel wet-type HIL materials "ND-series" could not only improve electric and luminous properties but also decrease dark spots and improve life. On the other hand "ND-series" could suit to various coating technologies such as spin coating, inkjet printing, spray coating and it will be illustrated.

D10.17

Long term performance and stability of organic-inorganic

light emitting device with cathode materials. Sook Yoon and Hyung-Ho Park; Department of Ceramic Engineering, Yonsei University, Seoul, South Korea.

Conjugated polymers can serve as the active material in organic light emitting devices (OLEDs). There has been considerable interest in developing them with high brightness, high efficiency, and long lifetime for display applications. Organic-inorganic nanoparticle composites have been increasingly studied because of their enhanced properties for OLEDs, consisting of one or more organic layers sandwiched between electrodes. The performance of OLEDs has been known to be strongly affected by the properties of organic layers and electrodes, and also the interface. Cathodes were revealed to play an important role in the overall performance of OLEDs. In this study, we focus on long term performance of OLED and interfacial stability between metal cathode and active layer. The candidates for the cathode were studied including Mg, Ag, and Mg:Ag alloy. Poly(p-phenylenevinylene)(PPV) / SiO_2 nanocomposite was used as an active layer. We have made organic-inorganic nanocomposites for OLEDs by incorporation of SiO_2 nanoparticles into electroluminescent material, conjugated polymer PPV. The role of metal electrodes and interfaces were investigated by using X-ray photoelectron spectroscopy (XPS) and the surface morphology of the structure was observed by using atomic force microscopy (AFM). The current density and electric turn-on voltage were observed. The effect of interface on the optoelectronic properties of the structure system was discussed on the point of views of interfacial polymer degradation. The combination of I-V, XPS, and AFM measurements could contribute toward a better understanding of the chemical states and long term performance of organics, and a role of cathode materials.

D10.18

Abstract Withdrawn

D10.19

Determination of Recombination Position in Mixed-Layer Organic Light-Emitting Devices. Chih-Hung Hsiao, J. H. Lee and Chin-An Tseng; Graduate Institute of Electro-Optical Engineering, National Taiwan University, Taipei, Taiwan.

In this paper, we demonstrated a method to determine the recombination position in a mixed-host (MH) organic light-emitting device (OLED). The host of the emitting layer (EML) material in this device consists of a hole transport layer (HTL) and an electron transport layer (ETL) fabricated by co-evaporation. Here, we use N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB) as the HTL material and tris-(8-hydroxyquinoline) aluminum (Alq3) as the ETL material. The host of the EML consists of the NPB and Alq3 with the volume ratio 1:1. To determine the recombination position, a red dopant 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTb) with the concentration of 2% and the thickness of 1.2 nm was inserted at different positions of the EML as a probe. If such a thin DCJTb layer is inserted just near the recombination position, a strong red peak is observed in spectrum and the driving voltage has a lowest value. If the DCJTb probe is away from the recombination position, a green emission from the MH was observed and the driving voltage is increased. The device structures are NPB (30 nm) / NPB:Alq3 (x nm) / NPB: Alq3:DCJTb (1.2 nm) / NPB: Alq3 (1:1) (40-x nm) / Alq3 (20 nm) / LiF (1.2 nm) / Al (150 nm) on the indium tin oxide (ITO) glass substrate. Five devices were fabricated with the x value ranges from 0, 10, 20, 30 and 40 nm and labeled as device A, B, C, D and E, respectively. The spectra of such devices exhibit two peaks which come from the emission of NPB:Alq3 (525nm) and DCJTb (600nm). The intensity of 525 to 600 nm is defined as the "peak ratio" which has a value of 0.6, 0.25, 0.4, 0.8 and 0.8, respectively, from devices A to E under the current density of 2.5 mA/cm². Lower peak ratio means larger portion of red emission. We can see the device B has strongest red emission that implies it is nearest to the recombination position among the five samples. In device B, when current density increases from 2.5, 25, 100, 200, to 300mA/cm², the peak ratio increases from 0.25, 0.45, 0.55, 0.6, to 0.65. Similar behavior was also observed in other four devices. It contributes to the emission saturation from the limited DCJTb sites. The driving voltage of device A to E is 10.2, 7.5, 9.5, 9.5, and 9.5 V under the current density of 200 mA/cm². Typically, DCJTb acts as a carrier trap to both electron and hole which increases driving voltage. However, when such a DCJTb thin-layer is inserted near the recombination position, the hole and electron are trapped simultaneously and radiate. The higher recombination rate decreases the driving voltage. Such a methodology will be applied to study the recombination position of MH-OLED with different mixing ratios.

D10.20

Effect of Nanoconfinement on the Glass Transition Temperature (T_g) of Substrate Supported Polyfluorene Thin Films. Marc Sims¹, Mariano Campoy Quiles¹, Kaiyu Zheng¹,

Ruidong Xia¹, Pablo Etchegoin² and Donal D. C. Bradley¹;
¹Department of Physics, Imperial College London, London, United Kingdom; ²The McDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, Wellington, New Zealand.

We report on the use of optical probes to determine the effect of nanoconfinement on the thermal transition temperatures of spin-coated films of poly(9,9-dioctylfluorene) [PFO], and poly(9,9-dioctylfluorene-co-benzothiadiazole) [F8BT]. First we introduce the novel use of temperature dependent photoluminescence (PL) measurements to probe thin film thermal transitions. Then we show that the integrated PL intensity reveals clear signatures of the glass transition temperature (T_g), the onset of crystallization (T_c) and subsequent melting into the nematic liquid crystalline mesophase (T_m). The PL intensity determined transitions are shown to be consistent with an independent optical probe, namely spectroscopic ellipsometry. Furthermore, by applying isotropic fits to our ellipsometry data, a clear relationship emerges between the dielectric function of these materials and d . Next we report that the above techniques reveal non-monotonic profiles of both T_g and T_c on decreasing film thickness, and show that these in turn can be mapped by corresponding profiles for extracted exciton energies and oscillator strengths. As the exciton energies are expected to be directly related to chain conformation, we are able to discuss the effects of nanoconfinement on T_g in terms of a thickness dependent morphology. The role of the substrate-polymer interaction will also be presented by comparing films deposited on different substrates. These include fused quartz, silicon, polymethylmethacrylate (PMMA) and ITO-coated glass.

D10.21

Effects of Donor/Acceptor Gradients on the Solid-State Organic Photovoltaics as Constructed by Self-Assembled Multilayers. Hung-Cheng Chen, Jiun-Yu Chen, Jiun-Nan Lin and Changshu Kuo; Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan.

Solid-state photovoltaic cells with donor/acceptor gradients were constructed by self-assembled multilayer techniques (SAMs). Conjugated polyelectrolytes, such as poly(thiophene acetic acid), PTAA, and pyridine-functionalized fullerenes served as electron donors and acceptors, respectively, allowing control of deposition thickness by variation of solution concentrations, pH values and dipping time. While the nano-scale multilayer structures provide a large amount of interfaces for photoinduced exciton formation, the gradient distribution of donor/acceptor introduces an internal potential that directs the exciton diffusion, even for those that are far away from the two electrodes. Effects of donor/acceptor gradients investigated in this research project include gradient degree, layer thickness, and photovoltaic properties.

D10.22

A Time-Resolved Photoluminescence Study of the Excitation Transfer Mechanisms between Semiconductor Nanocrystals and Grafted Electroactive Ligands. Joel Bleuse¹, Claudia Querner², Alessandro Benedetto² and Peter Reiss²; ¹DRFMC / SP2M, CEA-Grenoble, Grenoble, France; ²DRFMC / SPAM, CEA-Grenoble, Grenoble, France.

The proper knowledge of the charge transfer mechanism at the interface between light-absorbing semiconductor nanocrystals and an embedding matrix of conducting polymer is a key for the making of efficient hybrid photovoltaic cells. In particular, since semiconductor nanocrystals are efficient fluorophores, it is of importance to determine whether the exciton dissociation is fast enough to avoid its radiative recombination. CdSe nanocrystals have been functionalized with novel electroactive ligands - oligoaniline- or oligothiophene-carrying derivatives of dithiobenzoic acid ($R-C_6H_4-C(S)SH$) [1] - and their time-resolved photoluminescence (PL) spectra have been recorded with a 5-ps resolution. Being our reference, as-prepared trioctylphosphine oxide-covered CdSe nanocrystals present both a fast (240 ps) and a slow (> 5 ns) PL decay component of their 30-nm wide emission spectrum, which both do not significantly change in the 10 to 300 K range. For the carbodithioate-capped nanocrystals, we observe a strong suppression of the slow PL component, whereas the fast component is shortened - from 130 ps down to a few ps [2]. We relate this to the dissociation of the exciton and the transfer of the hole from the nanocrystal to the surface ligands, the efficiency of this transfer being controlled by the chemical nature of the group R. In addition, for some of these ligands, the dynamics show little change from 10 K to room temperature, a behaviour which should exclude thermally-activated paths for this transfer. We will present calculations of the energy levels of the crystal-ligand system and of the charge delocalisation, within the framework of the DFT approximation, to give further hints on these transfer mechanisms at the interface and on their extension to the

conducting channels of the polymer matrix. [1] C. Querner, P. Reiss, J. Bleuse, A. Pron, J. Am. Chem. Soc. 126(37), 11574-82 (2004). [2] Simultaneously, a spectrally wide, fast, high-energy PL component appears, which should be related to the PL from the phenyl ring.

D10.23

The Photoconductivity of Nanocrystalline Titania Films and its Impact on Photovoltaic Device Performance. Bernard Henry, Zhibin Xie, Kiril Kirov, Hannah Smith, Hazel Assender and Chris Grovenor; Materials, University of Oxford, Oxford, United Kingdom.

Semiconducting TiO₂ is often used as an electron acceptor in heterojunction solar cells consisting of a conjugated polymer which performs as both a light absorber and a hole transporter. Excitons photogenerated in the polymer dissociate at the organic/TiO₂ interfaces injecting electrons into the nanocrystalline titania film. For collection at the anode the electrons must migrate through the TiO₂ film. As a result, to achieve high quantum efficiencies in these solar cells large organic-inorganic interface area is required as well as rapid charge transport. Electron transport is strongly influenced both by crystalline imperfections in the TiO₂ nanocrystals and by the film morphology. To understand how the photovoltaic (PV) device performance is influenced by the electronics property of nanocrystalline porous TiO₂ we have studied the photoconductivity of a range of TiO₂ layers fabricated by sol-gel spin coating, doctor-blading of a paste and glancing angle deposition using evaporation, and related these measurements to the performance of PV devices.

D10.24

Modelling the Photoconductivity of Nanocrystalline Titania Films. Bernard Henry, Zhibin Xie, Victor Burlakov and Chris Grovenor; Materials, University of Oxford, Oxford, United Kingdom.

Nanocrystalline TiO₂ is commonly used in organic heterojunction photovoltaics (PV) as an electron acceptor and transporter. As a result the electrical properties of titania is important in determining the overall quantum efficiency of these PV devices. An experimental and theoretical study has been undertaken to analyse the photoconductivity of nanocrystalline TiO₂. The analysis performed assumed that the relaxation of photoconductivity is controlled by a hole detrapping process influenced by electronic screening of the Coulomb interaction between trapped holes. This approach allowed for the simultaneous determination of the electron mobility and electron concentration. It was found that the electron mobility values obtained from our analysis are similar to values reported in the literature for nanocrystalline TiO₂.

D10.25

Diffusion-limited versus interface-limited exciton photoluminescence decay in MEH-PPV films on TiO₂. Kentaro Kawata¹, Victor M. Burlakov¹, Hazel E. Assender¹, G. A. D. Briggs¹, Arvidas Ruseckas² and Ifor D. W. Samuel²; ¹Materials, University of Oxford, Oxford, United Kingdom; ²School of Physics and Astronomy, University of St Andrews, St Andrews, KY16 9SS, United Kingdom.

We report on a study of time resolved photoluminescence (PL) of MEH-PPV films spin coated on a flat nanocrystalline TiO₂ substrate as a function of the film thickness. Our results show that the PL decay is determined by exciton decay in the bulk of the film and by their dissociation at the MEH-PPV/TiO₂ interfaces. The latter contribution is affected by exciton diffusion to the interfaces and dissociation rate of excitons at these interfaces. Theoretical analysis of experimental results within recently developed model of exciton transport in disordered media [1] suggests that exciton energy levels at the organic-inorganic interfaces are lower than those in the bulk of the film. This lowering of the exciton energy levels makes the dissociation rate of excitons at the interfaces a PL decay rate-determining process. This result implies that the performance of solar cells based on MEH-PPV/TiO₂ nanocomposites should be significantly affected by the quality of the organic-inorganic interface. Possible ways of improving the interface energetics are discussed. 1. Kawata K., Burlakov V. M., Carey M. J., Assender H. E., Briggs G. A. D., Ruseckas A., Samuel I. D. W., Journal of Solar Energy Materials & Solar Cells, 87, 715 (2005).

D10.26

Bulkheterojunction Photovoltaic Devices based on Nanostructured TiO₂ and a Water-soluble Fluorene-thiophene Copolymer. Jang Jo, Doojin Vak, Seok-Soon Kim and Dong-Yu Kim; Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

Recently, photovoltaic (PV) cells based on conjugated polymers have been actively researched for low-cost alternatives to conventional inorganic PV cells. The bulkheterojunction PV cells based on

conjugated polymer/fullerene blend as electron donor/acceptor have made a power conversion efficiency possible to exceed 3%. Although this system is currently the best conjugate polymer-based PV cell in terms of device performance, hybrid PV cells consisting of semiconducting polymers and nanocrystalline inorganic semiconductors such as TiO₂ have also been considered as a promising approach because polymer/fullerene PV cells suffer from a poor stability and low charge mobility of these materials. However, it is very difficult to incorporate the polymer into nanopores less than 20 nm diameter in which excitons generated in organic materials can typically diffuse for efficient charge separation in TiO₂/polymer interface. In this study, we propose a new water-soluble fluorene-thiophene copolymer, ionic poly [9-9'-dioctyl-fluorene-co-bithiophene] (i-F8T2), easily co-dissolved with TiO₂ precursor liquid in the same solvent (water). The film spin-coated from the solution with the polymer and TiO₂ nanostructure can form a 3-D interpenetrating network with the two materials, bulk heterojunction morphology, which shows nanostructures with exciton diffusion length scale. We also report the device performance of the bulk heterojunction PV cell consisting of these.

D10.27

Mechanism of Photocurrent Generation in Organic Thin Film Solar Cells. Takahiro Osasa, Shuhei Yamamoto and Michio Matsumura; Research Center for Solar Energy Chemistry, Osaka University, Osaka, Japan.

Organic thin film solar cells have attracted much interest as next-generation solar cells because of their fabrication at low cost. However, they have the problem of low energy conversion efficiency. Since the understanding of the mechanism is essential to improve their efficiency, we have studied the mechanisms of the organic heterojunction solar cell with the simplest bi-layer structure, i.e., ITO/Cu-phthalocyanine(CuPc)/perylene derivative (PV) or fullerene (C₆₀)/Ag. A conducting polymer (PEDOT/PSS) is sometimes inserted between ITO and CuPc for the modification of ITO surface. The capacitance-voltage (C-V) characteristics of the device consisting of CuPc and PV showed that carriers are accumulated at the CuPc/PV interface under forward bias, whereas no essentially no carriers are present in the organic layers under reverse bias. Since the energy barrier at the ITO/CuPc interface is lower than that at the PV/Ag interface, the accumulated carriers are attributed to holes (in CuPc), which are injected from ITO. On the other hand, under normal operational conditions of the solar cells, carriers are hardly injected from the electrodes. This means that the carriers existing in the solar cells are all photogenerated under the operational conditions. The photocurrent action spectra were measured for the device with the structure of ITO/PEDOT:PSS/CuPc(30 nm)/PV(60 nm)/Ag at different potentials. Under reverse biases, the action spectra were similar to the summation of the absorption spectra of both layers. This result indicates that both of the excitons formed in the CuPc and PV layers contribute to the photocurrent. Under forward biases, however, the photocurrent action spectra were similar to the absorption spectra of PV; the action spectra were affected to some extent by the filter effect of the CuPc layer. From the results of the action spectra and the C-V characteristics, it is suggested that the photocurrent under the forward biases is caused chiefly by the interaction between the excitation of PV and the hole accumulated in CuPc near the CuPc/PV interface, the interaction leaving a hole in the PV layer.

D10.28

Electron Mobility Tuning by Blending MEH-PPV Conjugate Polymers with Fullerenes. Cheol Eui Lee¹, Sung Pyo Lee¹, H. Choi¹, Kyu Won Lee¹, Kyu Hyun Mo¹, Jae Won Jang¹, Eunmo Lee¹ and S. J. Noh²; ¹Physics, Korea University, Seoul, South Korea; ²Applied Physics, Dankook University, Seoul, South Korea.

we report on the effects of blending MEH-PPV conjugate polymers with single-walled carbon nanotubes (SWNTs). MEH-PPV is a hole transporting material in which the high density of the electron traps such as oxygen impurities and conjugational defects inhibits the electron transport. As it has been demonstrated that the SWNTs are efficient oxygen capturing materials, blending MEH-PPV with SWNTs could possibly decrease the oxygen trap density and thus increase the electron mobility, which initiated the present study. The blending ratio of MEH-PPV/SWNTs composites in this work ranged from 0 wt % to 1 wt % SWNTs. From time-of-flight (TOF) measurements, we observed that the electron mobility gradually increased with the weight percentage of SWNTs, while the hole mobility remained almost unchanged. The Poole-Frenkel model showed that an increase in the weight percentage of SWNTs lowers the zero-field activation energy, suggesting that the SWNTs effectively reduce the oxygen trap density. As the concentration of the SWNTs was increased from 0 to 0.2 wt %, the external quantum efficiency was improved as a result of mobility balancing: At 0.2 wt % SWNTs, the electron and hole

mobilities could be tuned for the highest external quantum efficiency.

D10.29

A Complete Microscopic Model of Photocurrent Generation in Organic Bulk-Heterojunction Photovoltaic Cells. Shanbin Zhao¹ and Peter Peumans²; ¹Materials Science and Engineering, Stanford University, Stanford, California; ²Electrical Engineering, Stanford University, Stanford, California.

We have recently shown that geminate recombination (both carriers originating from the same exciton) is the major loss mechanism in bulk heterojunction organic photovoltaic cells if the devices work outside the space-charge-limited-current regime [1]. This led to the surprising conclusion that to achieve high quantum efficiencies, a high carrier mobility *ratio* is required to drive the carrier separation process. Here, for the first time, we present a complete microscopic model that traces the trajectories of excitons, electrons and holes in real-time using Kinetic Monte Carlo simulations such that the space-charge-limited-current transport regime can also be analyzed. In contrast to continuum models, our model accurately reproduces the physics of organic photovoltaic cells including carrier-carrier and carrier-exciton interactions in bulk heterojunctions because of the discrete particle approach. Therefore, our model can be used to evaluate the effect of the nanoscale bulk heterojunction geometry on the photon-to-current conversion process. We find that fine-grained (~10 nm branch size) bulk heterojunction cells under one sun illumination operate in the space-charge-limited regime when one of the carrier mobilities falls below $\sim 1 \times 10^{-5} \text{ cm}^2/\text{Vs}$. Our model accurately reproduces the sub-linear relationship between the incident optical flux and photocurrent observed for such cells. We will show how such measurements can be used to accurately determine charge-carrier mobilities in bulk heterojunction cells. Surprisingly, we find that geminate recombination continues to dominate over non-geminate recombination (carriers originating from different excitons) even in the space-charge-limited-current regime. Based on this analysis, we show that the cell efficiency can be further optimized by increasing the mobility of the faster carrier. It is shown that only specific combinations of donor and acceptor carrier mobilities lead to efficient solar cells. A complete design guide that predicts the required material properties as a function of the bulk heterojunction geometry will be presented. [1] S. Zhao and P. Peumans, "Geminate Charge Separation in Bulk Heterojunction Photovoltaic Cells", MRS Meeting, Spring 2005.

D10.30

Plastic Solid Grätzel Solar Cells Nanoconstructed by Poly(thiophene). Tingying Zeng, Chemistry, Western Kentucky University, Bowling Green, KY.

Inorganic-organic hybrid Solid Grätzel solar cell (SGSC) is a very promising new generation solar cell to compete with commercialized silicon solar cells that are very expensive, fragile, heavy, and have power conversion efficiency in the range of only 7 to 17%. The SGSCs, currently being extensively studied by a number of research groups, have achieved light-to-electricity conversion efficiency around 1 to 10% in most cases using ruthenium complexes as photosensitizers and spirocompound as hole-transport material (HTM) [1~3]. Typically, 2, 2', 7, 7'-tetrakis(N, N-di-p-methoxyphenylamine)-9,9'-spirofluorene (Spiro-OMeTAD) was reported as an effective HTM. But the disadvantages of this HTM are 1) it has relative much smaller molecular weight compared with conducting polymers; 2) it is very expensive and not water soluble. Layer-by-Layer Molecular Self-Assembly (LBL-MSA) has been demonstrated as an effective nanofabrication method to produce the mechanically flexible SGSCs [4-5]. The LBL-MSA prefers using water as solvent. It is hard to produce plastic SGSCs using the spiro-OMeTAD with the conventional spin coat method. Here, we report our efforts to replace the expensive spiro-OMeTAD with poly(thiophene) to nanofabricate the plastic SGSCs. Our primary results have achieved over 4% power conversion efficiency in quantum dot/dye co-sensitized TiO₂ SGSCs, implying the feasibility of using water-soluble poly(thiophene) to fabricate the plastic SGSCs by the LBL-MSA processes. References: [1]. M. Grätzel, et al., Nature, 395: 583-585(1998); Journal Chem. 24, 651-652 (2000); Acc. Chem. Res. 2000, 33, 269-277. [2]. K. Kilsa, et al., Journal of physical chemistry B, 108 (40): 15640-15651 (2004). [3]. I. Kartini, et al., Journal of Materials Chemistry 14(19): 2917-2921 (2004). [4]. T. Zeng, Elizabeth Gladwin and Richard O. Claus, Self-assembled InP Quantum Dot -TiO₂ Solid Grätzel Solar Cell, Proceeding Paper of Materials Research Society Spring Conference, San Francisco (April 2003). [5]. T. Zeng, Quantum Dot/Dye Co-sensitized Solid Grätzel Solar Cell, International Workshop on Nanomaterials, Lexington of Kentucky (Sept 20-21, 2004).

8:30 AM *D11.1**Electric Power Generation by Mesoscopic Solar Cells.**Michael Graetzel, LPI, EPFL, Lausanne, Switzerland.

The cost of photovoltaic electricity production is still too high to be competitive with nuclear or fossil energy. For the best systems installed at well-chosen sites the price per kWh is presently 0.25-0.65 Euro. In order to be competitive the price would have to come down to below 0.05 Euro/kWh. Clearly, a change in paradigm is required to meet this cost goal and the enormous future energy demands. The recently discovered devices based on mesoscopic inorganic or organic semiconductors commonly referred to as bulk junctions due to their bicontinuous three-dimensional structure offer great advantages in this regard. These are formed for example from nanocrystalline inorganic oxides, ionic liquids and organic hole conductor or conducting polymer devices which offer the prospect of very low cost fabrication without expensive and energy intensive high temperature and high vacuum processes, compatibility with flexible substrates and a variety of presentations and appearances to facilitate market entry, both for domestic devices and in architectural or decorative applications. It is now possible to depart completely from the classical solid-state cells, which are replaced by devices based on interpenetrating network junctions. The presence of a mesoscopic junction having an interface with a huge area endows these systems with intriguing optoelectronic properties. Contrary to expectation, devices based on interpenetrating networks of mesoscopic semiconductors have shown strikingly high conversion efficiencies, which compete with those of conventional devices. The prototype of this family of devices is the dye-sensitized solar cell (DSC), which accomplishes the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of mesoporous or nanocrystalline morphology. Conversion efficiencies of laboratory cells exceed now 11% and impressive stability both under long-term light soaking and high temperature stress has been reached fostering first industrial applications. Research is booming also in this field where multijunction devices and a recent break through multiple carrier generation in quantum dot absorbers offer very promising perspectives. M Graetzel, Photoelectrochemical Cells Nature 414, 338-344 (2001).

9:00 AM *D11.2**Improvement of Photovoltaic Performance of Dye-sensitized Solar Cells.** Hironori Arakawa, Department of Industrial Chemistry, Tokyo University of Science, Tokyo, Japan.

Improvement of efficiency up to 10% - 11% In order to improve solar light energy conversion efficiency of dye-sensitized solar cell over 10%, there are some ways, for example, improvement of light harvest efficiency, design of new dyes having a wide absorption area up to infrared region, suppression of back electron transfer and suppression of direct electron transfer from conduction band of TiO₂ to redox reagent in electrolyte, such as I⁻. We have focused on the improvement of light harvest efficiency of dye coated TiO₂ photoelectrode utilizing light confined effect. Several kinds of TiO₂ pastes, in which TiO₂ particles having different diameters such as 20nm (N), 50nm (M) and 250nm (S) were introduced, were prepared. TiO₂ (N) was used mainly for dye adsorption and TiO₂ (M) (M') and (S) were used for light scattering or light reflection. Various kinds of multi-layered TiO₂ film photoelectrodes composed of different TiO₂ pastes were prepared and tested in order to improve solar cell efficiency up to 10%. Finally, we obtained the solar cell efficiencies from 10.2% to 10.5% by utilizing TiO₂ photoelectrode having structure of NMM'S with N719 dye and Black dye, respectively. Solar cell performance was measured under illumination of simulated AM1.5 solar light (100mW/cm²) using an anti-reflecting film and a mask on the cell surface. Efficiency rose up to 11.2% in case of N719 dye and 11.6% in case of Black dye, respectively, without a mask. The detailed data will be introduced. New efficient dye synthesis New dye synthesis of both Ru dyes and pure organic dyes were conducted to expand the possibility of dye sensitized solar cell application. Among more than one hundred dyes synthesized, new efficient Ru dyes such as Ru-terpyridine-beta-diketonato dye, new coumarine dyes and polyene dyes were found. Dye-sensitized TiO₂ solar cells using these dyes had efficiencies from 6.9% to 8.5%. Performances of these solar cells will be also introduced. References 1)Z-S Wang, H.Kawaguchi, T.Kashima, H.Arakawa, Cord. Chem.Reviews, 248, 1381(2004). 2)Z-S. Wang, T.Yamaguchi, H.Sugihara, H.Arakawa, Langmuir, 21, 4272(2005). 3)K.Hara, K.Sayama, Y.Ohga, A.Shimpo, S.Suga, H.Arakawa, Chem.Comm., 2001,569.

9:30 AM *D11.3**Tailor-made synthesis of bifunctional dyes and****blockcopolymers for self-assembly in photovoltaic devices.**Stefan Lindner¹, Katja Fischer¹, Helga Wietasch¹ and Mukundan Thelakkat¹; ¹University of Bayreuth, Bayreuth, Germany; ²University of Bayreuth, Bayreuth, Germany.

A series of novel heteroleptic Ru(II)tris(bipyridyl) complexes Ru(bpyCOOH₂)₂bpyMe₂PF₆, Ru(bpyCOOH₂)₂bpy(TPA)₂PF₆ and Ru(bpyCOOH₂)₂bpy(TPD)₂PF₆ has been designed, synthesized and characterized for application in dye-sensitized solar cells. The heteroleptic complexes carrying donor groups show appreciably broad absorption ranges and extraordinarily high extinction coefficients. These record extinction coefficients are explained as due to the extended delocalization of p-electrons in ligands in these complexes. Moreover, these complexes have been examined via cyclic voltammetry and HOMO / LUMO energy values were determined. The high extinction coefficients and the fact that the dyes carrying donor antenna groups exhibit retardation of recombination dynamics when absorbed on a TiO₂ surface, indicate that the new concept is a very promising approach for the improvement of dye-sensitized nc-TiO₂ solar cells. The solar cell results using these new dyes will also be presented. For charge separation at an internal interface, self-assembling diblock copolymers with a hole transporting segment and an electron transporting / light absorbing dye segment were synthesized for the first time by nitroxide mediated living radical polymerisation. Poly(4-diphenylamino) styrene P(vTPA) acts as a hole transport segment and Poly(peryleneimide acrylate) P(PIAc) fulfills the role of electron transport and light absorption. The polymers were characterised by SEC, DSC, TGA. The phase separation of block copolymers in the nanometer range via self-assembly was investigated with AFM and TEM. First results of solar cells prepared using these blockcopolymers exhibiting microphase separation will also be presented.

10:30 AM D11.4**Division of Roles of the Titanium Chloride Treatment on TiO₂ Electrode for the Dye-Sensitized Solar Cells (DSCs).**Naohiko Kato¹, Kazuo Higuchi¹, Yasuhiko Takeda¹, Akihiro Takeichi¹, Tomoyoshi Motohiro¹, Jyunji Nakajima² and Tatsuo Toyoda²; ¹Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan; ²Aisin Seiki Co.,Ltd., Kariya-shi, Aichi, Japan.

Surface treatments on nanoporous TiO₂ electrode by the deposition of TiO₂ from titanium tetrachloride (TiCl₄) aqueous solution [1] or by the electrodeposition of TiO₂ from titanium trichloride (TiCl₃) aqueous solution [2] are known to enhance performance of dye-sensitized solar cells. The effects of those treatments have been considered to promote interparticle necking and hence electron transportation whereas there has been no evidence reported. Here, we report more detailed analysis in the effects of TiCl₄ treatment on the TiO₂ electrode. These treatments increased short-circuit photocurrent (J_{sc}). Intensity-modulated photocurrent or photovoltage spectroscopy (IMPS/IMVS) indicated that the life times and the diffusion coefficients of the electrons within nanoporous TiO₂ layer increased after the treatments. In addition, when the ionic salts were used as the electrolyte of the cell, TiCl₄ treatment on the TiO₂ electrodes significantly increased open-circuit photovoltage (V_{oc}). This enhancement of V_{oc} was likely due to the contribution of the treatment on the transparent conductive oxide (TCO) film, since the V_{oc} increased also by the treatment only on the TCO film while the J_{sc} did not increase by this treatment. The reductions of the dark currents from the TCO to the electrolyte by the treatment on the TCO or on the TiO₂ electrode were also observed. This means that the effect of the treatment not only improves the electronic contact between TiO₂ particles, but also reduces the back electron transport at the interface between TCO and electrolyte. Similar results were also obtained in the case of TiCl₃ treatment although the J_{sc} enhancement was weaker than TiCl₄ treatment. Since the TiCl₄ solution cause the corrosion of the metal finger electrode, TiCl₄ treatment has not been applied to modules. Here, we successfully got the improvement of the module property by the TiCl₄ treatment after the formation of TiO₂ layer on the TCO film except on the portion where silver collection electrodes was to be printed. Thus, we formed the Art object of plant with transparent leaves yellow, red, light-green, and dark-green DSC module with "leaf-vein" shaped collector electrode, which has been exhibited in the TOYOTA Group Pavilion in EXPO 2005, Aichi, Japan. [1] C.J.Barbe, F.Arendse, P.Comte, M.Jirousek, F.Lenzmann, V.Shklover and M.Gratzel, J.Am.Ceram.Soc., 80, 3157 (1997). [2] M.K.Nazeeruddin, A.kay, I.Rodicio, R.Humphry-Baker, E.Muller, P.Liska, N.Vlachopoulos, and M.Gratzel, J. Am.Chem.Soc.115, 6382 (1993).

10:45 AM D11.5

Development of highly efficient dye-sensitized solar cells employing oligomer-based electrolytes: Effects of cations on the photovoltaic performances. Moon-Sung Kang, Kwang-Soon Ahn, Wha-Sup Lee, Jae-Kwan Lee and Ji-Won Lee; Samsung SDI, Yongin, South Korea.

Dye-sensitized solar cell (DSC) has attracted great attention over the past decade owing to its high energy conversion efficiency and low production cost [1]. Although a respectable photon-to-electricity conversion efficiency (~11.04 % at 1sun) has been achieved for photovoltaic cell employing organic liquid electrolyte, the leakage of liquid solvent from such cells has been suggested as one of the critical factors limiting the long-term stability of the DSC. As a better alternative to volatile organic solvent, the use of polymer solvent with polar ligands has received considerable attention in recent decades. For successful application of polymer electrolyte in DSC, both high ionic conductivity (e.g. $\geq 10^{-4}$ S/cm) of electrolytes and excellent interfacial contact between dye-attached TiO₂ and electrolytes should be achieved. To improve the interfacial contact between nanocrystalline semi-conductor (typically, TiO₂) and electrolyte medium, the balance between the coil size of polymer and the pore size of semi-conductor film should be considered [2]. In this view, the use of low molecular weight polymers (referred to as oligomer, $M_w \leq 2,000$ g/mol) may be essential to the easy penetration of such electrolytes into the nanopores of semi-conductor film. To achieve the best efficiency of DSC employing oligomer-based electrolytes, the optimal composition of the electrolyte should be determined first. In this work, we prepared oligomer-based electrolytes consisting of low molecular weight poly(ethylene oxide) (oligo-PEO) and three different types of iodide salts (i.e. alkali metal salt (KI), imidazolium salt (1,2-dimethyl-3-hexylimidazolium iodide, DMHImI), and molten imidazolium salt (1-propyl-3-methylimidazolium iodide, PMImI)). The ion transport properties of these electrolytes had been systematically investigated by means of the measurements of ionic conductivity and diffusion coefficient and the spectroscopic analyses such as FT-IR and FT-Raman. It was revealed that ionic conduction in the oligomer-based electrolytes critically depends on the concentration and the mobility of the charge carrier, which are mostly associated with the interaction between cations and polar ligands in the oligomer medium. The results showed that the use of oligomer-based electrolytes promises both the excellent durability and the respectable energy conversion efficiency (~7%) of the DSC by the optimization of the electrolyte system. [1] M. Grätzel, J. Photochem. and Photobiol. A: Chem. 2004, 164, 3. [2] M.-S. Kang, J. H. Kim, Y.-J. Kim, J. Won, N.-G. Park, Y. S. Kang, Chem. Commun. 2005, 889.

11:00 AM D11.6

Ion Coordinating Sensitizer in Solid State Hybrid Solar Cells. Henry James Snaith, Shaik M. Zakeeruddin, Lukas Schmidt-Mende, Cedric Klein and Michael Graetzel; Institut de Chimie Physique, EPFL, Lausanne, Switzerland.

The solid state dye sensitized solar cell (DSC) is one of the most promising organic based device concepts demonstrating solar power conversion efficiencies in excess of 4 %. The basic strategy of this "hybrid" system is such that light is absorbed in a dye molecule forming an exciton. Electron-transfer takes place from the excited dye molecule to an inorganic semiconductor where it is transported to and collected at an electrode. Subsequent hole-transfer from the oxidized dye to a hole transporting organic molecule or polymer takes place, where the hole is transported to and collected at the counter-electrode. The fundamental advantage of this system, over two component systems such as polymer-polymer, polymer-molecule and polymer nanoparticle blends, is that the electron and hole transporting components are spatially separated by the dye molecules, hugely suppressing charge recombination, and allowing efficient charge collection through microns thickness of material. Furthermore, the efficiency of such devices has been found to dramatically improve with the addition of various additives to the hole transporting material, with the most efficient devices incorporating specific quantities of ionic salts and electro-chemical dopants. This "cocktail" of additives has been fine tuned and optimized for the current system. However, the precise function of each component is, as of yet, not fully understood. Here, we report on a new charge transfer sensitizer which is endowed with an ion complexing moiety formed by oxyethylene side groups. Lithium coordination to the backbone of this dye is found to induce a striking improvement on photovoltage and performance, with voltages of nearly 900 mV regularly achieved and efficiencies improved from 3.2 % to 3.8 % (under 100 mWcm^{-2} simulated AM 1.5 solar conditions) for the lithium coordinating sensitizer as compared with a non-coordinating analog. A staggering record efficiency of 4.6 % is achieved under 10 mWcm^{-2} simulated AM 1.5 illumination. Our supramolecular approach to the self-assembly of functional components at the interface opens new avenues to control charge separation and recombination, and give us a more comprehensive understanding of the mechanisms occurring within this class of solar cells.

11:15 AM D11.7

A New Low-Temperature Chemical Sintering Route for High Efficiency Dye-Sensitized Solar Cells. Nam-Gyu Park, Kwang Man Kim, Man Gu Kang, Kwang Sun Ryu, Jungho Son and Soon Ho

Nanoparticle TiO₂ films with good inter-particle connectivity at non-thermal sintering condition have been developed to use in plastic substrate-based dye-sensitized solar cells. Addition of small amount of concentrated aqueous ammonia to a liquid-like TiO₂ colloid solution containing acetic acid leads to a cream-like viscous paste in the absence of binders, where viscosity of the resulting paste is as high as 5.3×10^4 cP. The inter-particle connection of the binder-free TiO₂ paste-derived 150 °C-dried film is found to be similar to that of the thermally sintered film using a polymer binder-contained paste, which indicates that the developed binder-free paste renders low-temperature chemical sintering effect. Photoelectrochemical properties of dye-sensitized solar cells based on 150 °C-chemical sintering route are compared with those of cells prepared by a usual 500 °C-thermal sintering method. Energy conversion efficiency and external quantum efficiency of DSSCs based on low-temperature chemical sintering are found to be comparable to or even higher than those of DSSC cells based on thermal sintering.

11:30 AM D11.8

The Location of Electron Transport-Limiting Traps in Electrolyte-Filled TiO₂ Nanoparticle Films. Nikos Kopidakis, Nathan R. Neale, Kai Zhu, Jao van de Lagemaat and Arthur J. Frank; National Renewable Energy Laboratory, Golden, Colorado.

A critical, unresolved issue in understanding electron transport in nanoparticle films used in dye-sensitized TiO₂ solar cells is the spatial location of the transport-limiting traps. In the absence of experimental evidence, it has been speculated that these traps are located either on the surface of the particles, in the bulk, or at grain boundaries between the particles. To address this issue, we have examined by the photocurrent transient technique the effect of altering the internal surface area of the film on the photoinduced electron density and electron diffusion coefficient. Analyses of the data within the framework of the random walk model reveal the predominant location of both the trap density and the transport-limiting sites. This study will be the topic of this presentation.

11:45 AM D11.9

Efficient Light Harvesting Using Porphyrin-Sensitized Nanocrystalline TiO₂ Films. David Leslie Officer¹, Wayne M. Campbell¹, Sanjeev Gambhir¹, Pawel Wagner¹, Qing Wang², Robin Humphry-Baker², Mohammad K. Nazeeruddin², Michael Graetzel² and Lukas Schmidt-Mende²; ¹Nanomaterials Research Centre, Massey University, Palmerston North, New Zealand; ²Laboratory for Photonics and Interfaces, Swiss Federal Institute of Technology, Lausanne, Switzerland.

During the last 10 years, with the development of nanocrystalline films of very high surface area, the photosensitization of wide-bandgap semiconductors such as TiO₂ by adsorbed dyes has become more realistic for solar cell applications. In a porous film consisting of nanometer-sized TiO₂ particles, the effective surface area for dye adsorption can be greatly enhanced and efficient light absorption is achieved from dye monolayers. To date, ruthenium polypyridyl complexes have proved to be the most efficient TiO₂ sensitizers, with the N3 dye demonstrating incident photon-to-electron conversion efficiencies (IPCEs) of up to 85% from 400-800 nm and an overall photovoltaic cell energy conversion efficiency of 11%. Since the earliest reports of the efficient charge injection into nanocrystalline TiO₂ by covalently-bound zinc tetrakis(4-carboxyphenyl)porphyrin (ZnTCPP), the photosensitization of TiO₂ electrodes by porphyrins has been extensively studied. It has been demonstrated that, despite the differences in oxidation potentials and photophysics between carboxylated porphyrin sensitizers such as ZnTCPP and the ruthenium polypyridyl N3 dye, the efficiency of electron injection into the TiO₂ conduction band, and the kinetics of electron injection and recombination are indistinguishable for both these sensitizers. In addition, the rate of charge recombination between conduction band electrons and oxidized porphyrins is in the range of several milliseconds, a time that is sufficiently slow to permit the regeneration of the ground state of the porphyrin by the iodide in electrolyte. Despite these observations, porphyrins have not proved to be as efficient sensitizers as ruthenium polypyridyl dyes. A series of novel metallotetraarylporphyrins, with variable length cyanoacrylic acid or malonic acid linkers conjugated to the β -pyrrolic position, has been synthesized and characterized using various spectroscopic techniques. The porphyrins were investigated for conversion of sunlight into electricity by constructing liquid junction dye-sensitized TiO₂ solar cells using an I^-/I_3^- electrolyte or solid state heterojunction cells utilising the organic hole conducting material 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD). In both cases, the cells yield over 80% incident photon-to-current efficiencies (IPCE) and overall conversion efficiencies of up to 6.1% (liquid junction cell) and over 3% (solid state cell), making these the most efficient porphyrin-sensitized solar

cells reported to date.

SESSION D12: Nanocrystalline and Novel Photovoltaics
Chair: Neil Greenham
Thursday Afternoon, December 1, 2005
Room 304 (Hynes)

1:30 PM *D12.1

Hybrid-Nanorod Polymer Solar Cells. Paul Alivisatos, Lawrence Berkeley National Laboratory, Berkeley, California.

This talk will describe our recent work related to the fabrication of solar cells, based upon blends of inorganic semiconductor nanorods with conjugated polymers such as P3HT. Such blends offer the possibility of paint-on type cells that combine high electron and hole mobilities, but require the development of methods to reliably control the dispersion of the two materials on the nanometer scale. Several approaches will be described, including the incorporation of so-called tetrapods, branched four-armed inorganic nanocrystals that spontaneously align on a substrate.

2:00 PM *D12.2

Towards Low-Cost CIGS Solar Cells by Printing Techniques. Toby Balthasar Meyer¹, Marc Roland Kaelin² and Ayodhya Nath Tiwari^{3,2}; ¹Solaronix SA, Aubonne, VD, Switzerland; ²Thin-Film Physics Group, ETHZ, Zuerich, ZH, Switzerland; ³CREST, Loughborough University, Leicestershire, United Kingdom.

A simple process for the deposition of Cu(In,Ga)(Se,S)₂ (CIGS) absorber layers is described. First, a low-cost CIGS precursor paste is deposited by the doctor-blade technique on Mo-coated glass, then selenization or sulfurization is carried out in a selenium or sulfur atmosphere at 10 to 1000 mbar for 10 min at 550 C. The CIGS absorber layer thus formed is processed into a solar cell by chemical bath deposition of a CdS buffer layer and sputtered ZnO/ZnO:Al front contacts. A maximum efficiency of 6.7 % was achieved with an approximately 0.5 micron thick CIGS absorber layer. Quantum efficiency measurements reveal photon absorption losses for the longer wavelengths, which are attributed to the thin layers and the reduced gallium content. An alternate version of the low-cost chalcogenide cell is achieved by deposition of the precursor paste onto nanocrystalline titanium oxide, coated onto a transparent conducting oxide (SnO₂:F) glass. Sulfurization at atmospheric pressure (at 450 C for 10 min) forms the CuInS₂ layer, acting as a sort of inorganic sensitizer of the TiO₂ electrode. The precursor paste is prepared with metal chlorides and nitrates dissolved in alcohols. The solution is then mixed with celluloses to adjust the viscosity for optimal deposition. The conversion of the precursor to the CIGS phase was confirmed by X-ray diffraction. Grain size and morphology were characterized with electron microscopy.

2:30 PM *D12.3

Organized Assembly of Donor Acceptor Molecular Clusters for Next Generation Solar Cells. Prashant V. Kamat^{1,3}, Taku Hasobe^{1,2} and Shunichi Fukuzumi²; ¹Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana; ²Department of Material and Life Science, Osaka University, Osaka, Japan; ³Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana.

Donor acceptor based molecular clusters in photochemical solar cells provide new ways to improve the efficiency of charge separation and charge transport in photosensitizer-based electrode systems. Porphyrin and fullerene moieties serve as donor (D)-acceptor (A) couple since they produce long-lived charge-separated state with a high quantum yield. Taking into account of the fact that porphyrin and fullerene tend to make a supramolecular complex in solutions as well as in solid state, fullerene is expected to interact with H₂PCnMPC, which would yield D-A nanoclusters with an interpenetrating network. Thus, a combination of H₂PCnMPC and C₆₀ provides an ideal system for fulfilling an enhanced light-harvesting efficiency of chromophores throughout the solar spectrum. The composite molecular clusters with broad absorption in the UV and IR exhibit an incident photon-to-photocurrent efficiency (IPCE) as high as 54% and broad photocurrent spectral response (up to 900 nm). The cooperative effect between porphyrin and C₆₀ clusters is evident from the efficient electron transfer between singlet excited porphyrin and C₆₀ in the composite system and enhanced photocurrent generation. Photoelectrochemical behavior of various carbon nanostructures will also be presented. References: 1. Hasobe, T., Imahori, H., Kamat, P. V. & Fukuzumi, S. Photovoltaic Cells using composite nanoclusters of porphyrins and fullerenes with gold nanoparticles. *J. Am. Chem. Soc.* 127, 1216-1228 (2005).

3:30 PM D12.4

Efficient organic hetero-junction photovoltaic cells based on

triplet materials. Yan Shao and Yang Yang; Materials Sci. & Eng., University of California, Los Angeles, Los Angeles, California.

The power conversion efficiency of organic photovoltaic cells is determined by several factors, such as absorption of photons, diffusion length of exciton, and the collection of electrons and holes after exciton dissociation. A typical exciton lifetime in organic materials is on the order of nano- or sub-nanoseconds, hence the exciton diffusion length is limited. However, this situation can be improved by using organic materials that generate longer exciton lifetime such as triplet exciton, which generally exhibits a lifetime in the range of micro- to milliseconds. In this manuscript, we report the use of organic materials with a triplet energy level as an approach to enhance the device efficiency. A high performance organic photovoltaic heterojunction based on the triplet material, 2, 3, 7, 8, 12, 13, 17, 18-octaethyl-21H, 23H-porphine platinum (II) (PtOEP), was demonstrated. Based on our observations, we believe that, with further material improvement (such as increased mobility), triplet materials will become an important candidate for organic and polymer solar cells.

3:45 PM D12.5

Metal-Nanoparticle-Enhanced Absorption and Exciton Diffusion in Organic Photovoltaic Cells. Jung-Yong Lee and Peter Peumans; Electrical Engineering, Stanford University, Stanford, California.

Because of the exciton diffusion length is much shorter than the optical absorption length, the optimization of organic photovoltaic cells is usually achieved by trading off charge-transport against exciton diffusion using bulk heterojunctions. Metal nanoparticles embedded in an organic matrix have recently been shown to increase the optical absorption [1]. Here, we show using detailed models of exciton migration in metal-organic composite structures and experiments, that the exciton diffusion length can also be increased ~2-fold by incorporating metal-core/insulator-shell nanoparticles in the organic matrix. In our simulations, excitons are modeled as oscillating dipoles that set up an optical electric field calculated using finite element methods. This field distribution allows us to calculate the transfer rate to molecules in the vicinity of the exciton and kinetic Monte Carlo simulations are used to evaluate the effective exciton diffusion length. The redistribution of the optical electric field in metal/organic nanocomposite structures results in a longer average exciton hopping lengths and longer effective diffusion lengths. Furthermore, the enhancement of the optical electric field near the metal nanoparticles results in directed exciton migration along chains of metal nanoparticles that can be used to guide excitons toward the donor-acceptor junction. Exciton quenching by charge-transfer to the metal nanoparticles is prevented by the insulator shell. In agreement with the above models, we observe enhanced optical absorption by the organic matrix upon incorporating 10nm-diameter Ag-core, SiO₂-shell nanoparticles. Exciton diffusion length measurements in such metal-organic composites will be presented. [1] B. P. Rand, P. Peumans, and S. R. Forrest, *J. Appl. Phys.* 96, 7519 (2004)

4:00 PM D12.6

High internal efficiencies due to surface plasmon polariton excitations in thin film organic photovoltaics. Jonathan K. Mapel, Madhusudan Singh and Marc A. Baldo; Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Weak absorption of optical radiation limits the performance of thin film organic devices. We show that the optical absorption may be significantly enhanced by exciting guided modes such as surface plasmon polaritons (SPPs). Our numerical calculations suggest that SPP-mediated excitation can yield near 100% internal quantum efficiency even in certain extremely thin devices, making the technique suitable for pumping nanostructures such as quantum dots and photosynthetic complexes. Experimentally, we demonstrate that excitation of SPPs with monochromatic radiation in a hybrid Kretschmann-Otto configuration can at least double the external quantum efficiency of C₆₀-copper phthalocyanine photovoltaic cells. This setup exploits attenuated total reflection (ATR) in matching the momenta of incident photons with SPP momenta at a certain angle of incidence. The observed angular resonance in the photocurrent is well-correlated with the decrease in the reflectivity from the devices. By contrast, in conventional organic photovoltaics, the need for high optical absorption dictates the use of thicker layers, which in turn yield inferior electrical characteristics. The change in the geometry of energy transfer pathways made possible by the use of SPPs enables separate optimization of electrical and optical functions. We discuss the implications of this work for sensor and photovoltaic applications.

4:15 PM D12.7

Ultra-Efficient Multiexciton Generation in Semiconductor Quantum Dots: Demonstration of a Practical Approach to Photocurrent-Enhanced Generation III Photovoltaics.

Recently, we discovered that extremely high efficiency carrier multiplication (CM) occurs in semiconductor quantum dots for photon energies that are relevant to the solar spectrum [Phys. Rev. Lett. 92, 186601 (2004)]. CM is a physical process, in which absorption of a single photon of sufficiently high energy (at least twice the energy of the material band gap energy) by a semiconductor results in the production of more than one exciton, i.e. internal quantum efficiency may exceed unity. Using this phenomenon one can significantly increase photovoltaic performance via enhanced photocurrent (by up to ~50%) at a fixed photovoltage, CM was first observed (indirectly) in bulk semiconductor materials in the late 1950s, but despite more than 50 years of research, the efficiency of the process is quite low for solar photon energies and, for a theoretically optimized material, increases device performance by only ~1% [Appl. Phys. Lett. 63, 2405 (1993)] We have developed an experimental technique to directly measure efficiencies of multiexciton generation in quantum-confined semiconductor materials (such as quantum dots) and see that quantum dots of different compositions reach 100% efficiency (all excited quantum dots have multiple excitons generated) at photon energies that are pertinent to solar energy conversion. Moreover, we observe exciton multiplicities in quantum dots can be large (more than two excitons can be generated) and, further, can be controlled by the energy of the incident photon. We calculate that this effect raises the theoretically achievable power conversion efficiencies of quantum dot-based, single-gap photovoltaics significantly above the Shockley-Queisser "apparent" thermodynamic limit [J. Appl. Phys. 32, 510 (1961)]. This high efficiency use of blue solar photons has the potential to make photovoltaics competitive with several non-renewable energy sources because the effect can function in low-cost, single gap photovoltaic device structures. However, CM also presents unique challenges such as the requirement that multiple charge separations (or transfers of excitons) take place very rapidly with high efficiency because Auger recombination of multiexcitons (one exciton recombines by imparting energy into an electron or a hole of another exciton) takes place on a ten- to hundred-picosecond timescale in quantum dots. We will also discuss various approaches for achieving fast separation of charges produced by the CM process.

4:30 PM **D12.8**

Molecular Routes of Exciton Multiplication for Ultra-efficient Solar Cells. Justin Johnson¹, Xudong Chen², Geeta Rana², Josef Michl² and Arthur Nozik¹; ¹Basic Sciences Division, National Renewable Energy Lab, Golden, Colorado; ²Dept. of Chemistry, University of Colorado, Boulder, Colorado.

Exciton multiplication has been demonstrated in semiconductor nanocrystals and is considered as a promising route for improving solar cell efficiencies. Singlet fission in molecular systems is an analogous mechanism for generating multiple charge carriers from a single photon, and there are potential advantages associated with utilizing molecules instead of, or in concert with, quantum dots. Fundamental spectroscopic studies of conventional and novel molecular chromophores have been performed in order to identify the molecular properties and environmental conditions that lead to efficient singlet fission.

4:45 PM **D12.9**

Obtaining single wall carbon nanotubes with defined diameter and metallicity. Fotios Papadimitrakopoulos^{1,2},

Zhengtang Luo¹, Sang Nyon Kim¹ and Sang-Yong Ju¹; ¹Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; ²Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Precise control of single wall carbon nanotubes (SWNTs) over diameter, length and metallicity (metallic vs. semiconducting) are of pivotal importance for their future involvement in hybrid photovoltaic devices and flexible transparent electrodes. During the past two years a number of separation methodologies have been debuted and although large-scale enrichment remain to be a challenge, considerable progress have been achieved in this frontier. Our recent efforts on improving separation efficiency for various type and diameter nanotubes indicate that it is feasible to utilize the inherent differences in SWNT electronic properties to impart large-scale separation. In this paper we discuss a variety of enrichment methodologies to obtain controlled diameter and metallicity fractions along with modeling the underlying mechanism. Moreover, we carefully elucidate and model the effect of bundling and discuss how one can constructively utilize aggregation in small bundles to increase separation yield without imparting efficiency.

D13.1

Organic Solar Cells utilising a Carbon Nanotube-Polymer Composite. Anthony J. Miller, Ross A. Hatton and Ravi Silva; Advanced Technology Institute, University of Surrey, Guildford, United Kingdom.

Organic solar cells have enormous potential as a low cost renewable energy source. We report investigations exploring the possibility of utilising multi-walled carbon nanotube (MWCNT)-conjugated polymer composites in bi-layer organic solar cells, to enhance power conversion efficiency and thermal management at the organic heterojunction. In this context the nanocomposite replaces a purely polymeric donor layer. The effects on cell performance of covalently functionalizing the carbon nanotubes and annealing the heterojunction are also reported. The results of this study demonstrate the potential benefits to incorporating MWCNTs within the active layers of organic solar cells.

D13.2

Carbon Nanotube Electrodes for Organic Semiconductor Devices. Carla M. Aguirre¹, Stephane Auvray², Patrick

Desjardins^{1,3} and Richard Martel^{2,3}; ¹Departement de Genie Physique, Ecole Polytechnique de Montreal, Montreal, Quebec, Canada; ²Departement de Chimie, Universite de Montreal, Montreal, Quebec, Canada; ³Regroupement Quebecois sur les Materiaux de Pointe, Montreal, Quebec, Canada.

While much research in the field of organic semiconductors has concentrated on improving organic light emitting diode (OLED) lifetime, emission wavelength range and processability, several fundamental issues surrounding charge injection and transport in these materials need to be resolved. For instance, it has been demonstrated that charge injection can dominate the behavior of organic semiconductor devices and severely limit the performance of organic field effect transistors. This results in large operating voltages and sluggish response times and therefore high power consumption. In this work we investigate a new transparent electrode based on carbon nanotubes (CNT) for use with organic semiconductors. Conducting and flexible CNT membranes, 20 to 400 nm thick and transparent in the visible and infrared range (~80% transmittance), have been fabricated using a room temperature deposition technique that consists on forming a percolative network of CNTs from solutions of individually suspended CNTs in surfactant dispersions. Unlike conducting polymers, we find that CNT membranes are compatible with a range of solvents enabling deposition of successive organic layers. These membranes show conductivity values in the range of 200 S/cm thus exceeding that of most transparent p-type conducting oxides. We show that the conductivity can be further improved by doping in order to approach that of single carbon nanotube ropes (10000 S/cm). Using optical absorption spectroscopy, Raman spectroscopy and x-ray photoelectron spectroscopy as well as electron microscopy we have investigated strategies for optimizing carbon nanotube membrane conductivity through charge transfer doping from absorption of amine containing molecules and from the intercalation of charge acceptor molecules. Our detailed study of the carbon nanotube - organic interface has led us to the design of a novel electrode scheme for organic field effect transistors based on a single carbon nanotube. Finite element analysis was used to design a CNT electrode geometry that avoids the charge injection bottleneck at the electrode - organic interface. We will present recent experimental results that demonstrate that the performance of organic field effect transistors can be dramatically improved.

D13.3

Enhancement in Photoelectric Conversion Properties of the Dye-Sensitized Nanocrystalline Solar Cells Employing Nanoporous CaO-Coated TiO₂ Particles. Hyun Suk Jung¹,

Jung-Kun Lee¹, Michael Nastasi¹, Sang-Wook Lee², Jin-Young Kim², Kug Sun Hong² and Hyunho Shin²; ¹Los Alamos National Laboratory, Los Alamos, New Mexico; ²School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; ³Department of Ceramics Engineering, Kangnung National University, Kangnung, South Korea.

Sol-gel derived Ca(OH)₂ gel was coated on TiO₂ nanoparticles, followed by thermal topotactic decomposition of the gel to form a highly nanoporous CaO crystalline coating. The specific surface area of the core-shell based nanoparticles was significantly improved as compared to the uncoated TiO₂ particles, which was attributed to the topotactic reaction-based highly nanoporous CaO layer. Such feature promoted the dye adsorption and subsequent cell performance. When

coated by optimum amount of CaO, energy conversion efficiency increased as much as 18 % compared to the case of the uncoated TiO₂ electrode. It was emphasized that increasing the specific surface area by coating nanoporous CaO layer (extrinsic factor) is one of the very effective ways to improve the dye adsorption and conversion efficiency of a TiO₂-based solar cell, in addition to intrinsic factors.

D13.4

Abstract Withdrawn

D13.5

Improvement of the Optimum Thickness of the Nanoporous TiO₂ Films by using Nb₂O₅ Energy Barrier for Highly Efficient Dye-Sensitized Solar Cells. Kwang-Soon Ahn, Moon-Sung Kang, Wha-sup Lee, Jae-Kwan Lee and Ji-Won Lee; Energy Lab. Corporate R&D Center, Samsung SDI, Yongin-si, Gyeonggi-do, South Korea.

The dye-sensitized solar cell (DSC) is one of the most promising candidates for a high-performance solar cell, because of simple manufacturing process at relatively low cost and environmental compatibility. When a DSC is illuminated by sunlight, the adsorbed dye molecules on the surface of the mesoporous TiO₂ absorb the light and become excited. The absorption of light by the dye is followed by the injection of an electron from the excited state of the dye to the conduction band of the TiO₂ and its subsequent transfer to the transparent conducting oxide. Finally, the electron flows through the external circuit. High surface area by using the nanoporous TiO₂ films is necessary for the efficient light-to-energy conversion because of the low absorbance of the dye monolayers. Increasing the thickness of the nanoporous TiO₂ film, as well as decreasing the TiO₂ particle size, is practically useful method to increase the amount of the dye molecules adsorbed on the TiO₂ films for the highly efficient DSCs. However, the use of the high surface area may also cause the enhancement of recombination rate between the photoinjected electrons in the TiO₂ film and the holes in the electrolyte. Therefore, the increase of the TiO₂ film thickness will be limited, indicating the existence of the optimum thickness of the TiO₂ film and the limit of the cell efficiency. Zaban et al. previously reported that the Nb₂O₅ thin layer coated on the TiO₂ film forms an inherent energy barrier at the electrode/electrolyte interface, leading to the reduced recombination rate and better performances for all parameters at the similar thickness, compared with the cell without the Nb₂O₅ thin layer. [1] In addition, we report that the optimum thickness of the nanoporous TiO₂ film can be also affected and improved by the Nb₂O₅ thin layer, because the Nb₂O₅ energy barrier can reduce the recombination rate and the recombination lifetime (τ) was increased as well, leading to the enhanced electron diffusion length ($L = \sqrt{D\tau}$), where D is electron diffusion coefficient) of the nanoporous TiO₂ film. In this presentation, the improved optimum thickness of the nanoporous TiO₂ film with the Nb₂O₅ thin layer will be discussed with respect to the electron diffusion length, which was evaluated by the D and τ values measured by the photocurrent and photovoltage transient measurements. [1] S. G. Chen, S. Chappel, Y. Diamant, and A. Zaban, Chem. Mater. 13(12); 4629 (2001).

D13.6

Dye-sensitized solar cells with a quasi-solid-state and gel electrolyte based on a trimethoxysilane derivatized ionic liquid and its nanocomposite with tetramethoxysilane. Boris Orel¹, Robi Jese¹, Angela Surca Vuk¹, Vasko Jovanovski¹, Lidija Slemenik Perše¹, Elias Stathatos² and Panagiotis Lianos²; ¹Laboratory for Spectroscopy of Materials, National Institute of Chemistry, Ljubljana, Slovenia; ²Engineering Science Department, University of Patras, Patras, Greece.

The electrolyte is an important component of a Dye-sensitized Solar Cell (DSSC) of the Graetzel design. Even though organic solvents, which are capable to dissolve both iodide salts and iodine, assure the light-to-electricity efficiency of cells higher than 10 %, the solvent volatility problems and the necessity of the cell sealing instigated the search of alternative materials in laboratories worldwide. With this in mind, p-type inorganic semiconductors, organic hole-transport materials and polymeric materials incorporating I⁻/I₃⁻ redox couples have been considered as substitutes for liquid DSSC. Ionic liquids based on dialkylimidazolium cations with iodide, have been extensively considered as non-volatile substitutes for liquid electrolytes in DSSC. Solidification of ionic liquids was attempted through the addition of solid particles, by incorporation of ionic liquids in polymers or the addition of small molecular weight gelators. We have exploited the last possibility using chemically different concept of gelling. A new imidazoliumiodide type ionic liquid was synthesized, namely MTMSPIm⁺I⁻, which due to the trimethoxysilane groups, exhibits self-assembling properties. Following the addition of an acidified water catalyst, the viscosity of the hydrolyzed MTMSPIm⁺I⁻ increased and finally solidified to a quasi-solid-state. In order to make a nanocomposite gel, we mixed

MTMSPIm⁺I⁻ with tetramethoxysilane (TMOS), the latter acting as an amorphous phase in which the MTMSPIm⁺I⁻ was embedded. The structure of the MTMSPIm⁺I⁻ in its non-hydrolyzed and a quasi-solid-state, was studied employing time-dependent infrared and ²⁹Si NMR spectroscopic measurements. The structure of the condensed species was correlated with the viscosity, the specific conductivity and apparent diffusion coefficients (D_{app}) measurements [1]. The final product of the condensation of MTMSPIm⁺I⁻ sols was described as a positively-charged ladder-like polysilsesquioxane with T_n end groups exhibiting a single T³ signal in the ²⁹Si NMR spectra and characteristic doublet bands at 1138 and 1049 cm⁻¹ in IR. This structure was retained to a large extent in TMOS/MTMSPIm⁺I⁻ gels, confirming their nanocomposite structure. DSSC cells (unsealed) made with TMOS/MTMSPIm⁺I⁻ gels and MTMSPIm⁺I⁻ sols condensed in a quasi-solid-state in combination with TiO₂ films (Ti(OiPr)₄ + Brij + AcOH) and Pt counter-electrodes, produced the cells with efficiency of 2.7 % and 3.3 %, measured 5 months after the assemblage, providing the V_{OC} of about 0.6 V and J_{SC} in the range 8.0 up to 9.4 mA/cm². [1] B. Orel, A. —*ucarons*—urca Vuk, V. Jovanovski, R. Ješe, L. Slemenik Perše, S. B. —*ucarovs*—urca Vuk, V. B. Ogorevc, A. Jesih, Electrochem. Comm., 7 (2005) 692.

D13.7

Surface-modified Nanocrystalline ZnO Electrode for Dye-Sensitized Solar Cell. Yu-Ju Shin, Ki-Seok Kim, Yoon-Sik Kang and Ji-Hyun Kim; Chemistry, The Catholic Univ. of Korea, Bucheon, Gyeonggi-do, South Korea.

Nanocrystalline semiconducting electrode plays a key role in Dye-Sensitized Solar Cell (DSSC). It harvests the photo-induced electrons from the activated dye molecules and also ensures the diffusion pathway for electrons to the front contact with potential as high as possible. Up to now, TiO₂ electrode has been proved to exhibit the best photovoltaic performance among various semiconducting oxides like Nb₂O₅, SnO₂, WO₃, ZnO, etc... Considering that the electronic structure of ZnO is very similar to TiO₂, and the recent striking achievement with ZnO in nanochemistry, nanocrystalline ZnO electrode seemed us interesting for DSSC application. For this reason, we prepared nanocrystalline ZnO electrodes and also made some modification of ZnO electrode surface, on which nano-coating of various oxides including MgO, NiO, Al₂O₃, SnO₂, TiO₂ and SiO₂ were applied. A striking enhancement of energy conversion efficiency more than 10 times was achieved by this surface modification. In this presentation, we will report the obtained results on the photovoltaic properties of as-prepared surface modified ZnO-electrodes and discuss on the origins of such an impressive increase of energy conversion efficiency.

D13.8

Abstract Withdrawn

D13.9

A Strategy to Increase the Efficiency of the Dye-Sensitized TiO₂ Solar Cells Operated by Photoexcitation of Dye-to-TiO₂ Charge-Transfer Bands. Eunju Lee Tae, Jae Kwan Lee, Seung Hwan Lee, Su San Yoo, Eun Ju Kang and Kyung Byung Yoon; Chemistry, Sogang Univ., Seoul, South Korea.

Dye-sensitized nanoporous TiO₂ solar cells (DSSCs) were classified into two types, namely, Type-I and Type-II. Type-I DSSCs are the DSSCs in which electrons are injected from the adsorbed dyes by photoexcitation of the dye followed by electron injection from the excited dye to TiO₂ (pathway A). Type-II DSSCs are the DSSCs in which electrons are injected not only by pathway A but also by direct one-step electron injection from dye to TiO₂ by photoexcitation of the dye-to-TiO₂ charge-transfer (DTCT) bands (pathway B). The DSSCs employing catechol (Cat) or its derivatives as the sensitizers have been the typical examples of Type-II DSSCs whose solar energy-to-electricity conversion efficiencies (η_s) have never exceeded 0.7% and the external quantum efficiencies (EQE) at the absorption maximums of the DTCT bands not overlapping with the local bands have never exceeded 10%. We found that the attachment of electron-donating heteroaromatic compounds such as pyridine and quinoline, respectively, to Cat through an ethylene unit (designated as Cat-en-P and Cat-en-Q, respectively), leads to 2- and 2.7-fold increases, respectively, in η , driven by large increases in short circuit current (J_{sc}). The EQE increased from 8.5% to 30% at 400 nm upon attaching pyridine to Cat, at which only the DTCT band absorbs. In the case of the Cat-en-Q-sensitized DSSC, even the η obtained by exciting only the DTCT band was higher than 1%. Interestingly, the illumination of only the DTCT band resulted in the increase of fill factor from 62.6% to 72.3%. This paper provides for the first time an insight into the strategy to increase the η_s of Type-II DSSCs.

D13.10

Dye-Sensitized Photoelectrochemical Solar Cells Based on Nanocrystalline TiO₂ with Poly(3,4-ethylene

dioxythiophene)-Poly(styrenesulfonate) as a Plastic Counter Electrode. [Anna Kanczurzewska](#)¹, Ewa Dobruchowska², Elin Carlegrim¹, Amir Baranzahi¹ and Mats Fahlman¹; ¹Dep. of Science and Technology (ITN), Linköping University, Campus Norrköping, Norrköping, Sweden; ²Department of Molecular Physics, Technical University of Lodz, Lodz, Poland.

Dye-sensitized solar cell (DSSCs) using nanocrystalline TiO₂ electrodes have attracted worldwide attention since 1991 [1]. A typical DSSC consist of nanocrystalline TiO₂ electrode covered with a mono-layer of sensitizing dye, a redox electrolyte (e.g. I⁻/I₃⁻) and a counter electrode such as platinized conductive glass. Platinum is one of the most expensive component materials in DSSC. Therefore, the use of non-insulating plastic materials, which belong to the class of so-called conjugated polymers, instead of Pt is expected to reduce production costs, particularly in case of large-scale manufacturing. Among the conjugated polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most attractive materials for device construction, due to its excellent conducting and electro-optical properties. Recently, several attempts have been undertaken to apply PEDOT in dye-sensitized solar cells. Saito et al. [2,3] fabricated solar cells using chemically polymerized poly(3,4-ethylenedioxythiophene) on a conductive glass as a counter electrode. In the present work, we checked the performance of DSSCs with commercially available PEDOT-PSS coated on flexible polyester substrate, since the next generation of solar cells will probably be based on thin organic film technology due to its potential for lower production costs. Moreover, flexible electrodes present some other advantages, relative to electrodes on glass substrate, e.g. lower weight, impact resistance and less form and shape limitation. The behavior of such plastic counter electrode in the presence of I⁻/I₃⁻ redox electrolyte has been investigated with X-ray photoelectron spectroscopy. We have found that some of iodine species are "trapped" within the PEDOT-PSS layer. The presence of I₃⁻, I₂ and PEDOT charge transfer complexes with iodine species may block the surface of the electrode. Furthermore, the PEDOT may be further oxidized (p-doped) during cell operation, which in turn may cause overoxidation and loss of conductivity in the PEDOT-PSS film. Additionally, the interactions between PEDOT and iodine species may be enlarged because of the partial loss of PSS protective counter ion. That has resulted in decrease of PEDOT-PSS catalytic activity for reduction of I₃⁻ to I⁻ in the redox electrolyte and has caused decreased cell performance than in case of DSSC with Pt counter electrode. [1] B. O Regan, M. Gratzel, *Nature* 353 (1991) 737. [2] Y. Saito, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *Chem. Lett.* 31 (2002) 1060. [3] Y. Saito, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *J. Photochem. Photobiol. A: Chem.* 164 (2004) 153.

D13.11
Mesoporous TiO₂ Electrodes Derived from Templated Growth. [Lai Qi](#), Dunbar P. Birnie and Judith D. Sorge; Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Due to the unique physical and chemical properties, TiO₂ has found applications as the photon active material in solar energy conversion and photocatalysis devices. The crucial role of the TiO₂ electrodes is to provide an interface where exciton separation and one-way charge flow can happen. To achieve high efficiency, the TiO₂ electrodes have to be manufactured to accommodate optimized fluxes of photons (low scattering), electrons (low exciton recombination rate) and materials (electrolyte circulation). Therefore, surface area, average pore size and porosity are among the main parameters contributing to high working efficiency. In this work, we present the fabrication of sol-gel derived TiO₂ electrode films, which are grown from templates of polystyrene nanoparticle assembly. The polystyrene nanoparticles are synthesized by a modified microemulsion method with average particle size from 100nm to 500nm. The TiO₂ films can be fabricated with thickness of from 400nm to 10um, and with varied pore size. These mesoporous TiO₂ films are characterized as electrode material under simulated AM 1.5 sunlight, and found to have potential for application in the dye-sensitized solar cells.

D13.12
Efficiency and Fill Factor Improvement of Dye-sensitized Nanocrystalline Solar Cells. [Amir Baranzahi](#)¹, Ewa Dobruchowska² and Mats Fahlman¹; ¹Science and Technology, Linköping University, Norrköping, Sweden; ²Department of Molecular Physics, Technical University of Lodz, Lodz, Poland.

Dye sensitized nanocrystalline solar cells, DSNCS, with silver reflector at the backside of the counter electrode are studied. The cell efficiency is increased by up to 16% upon applying a silver reflector. The overall cell efficiencies of 11.5% are achieved at illumination intensity of 10 mW/cm². By introduction of a dense TiO₂ interfacial layer between the mesoporous TiO₂ and the transparent conducting layer, TCO, open circuit voltage variations are reduced. An electrical model is used to show that the dense interfacial layer increases the shunt

resistance. Fill factors of up to 0.78 are recorded. Fill factor decreases with the increase of photo electrode thickness, indicating increase of series resistance of the cell.

D13.13
Modeling and Synthesis of Acridine Dyes as Potential Sensitizer Dyes for Photovoltaic Applications. Ravi Musurkal², [Landa Hoke](#)¹, Stephen A. Fossey¹, Jayant Kumar², Russell Gaudiana³, David Waller³ and Lynne A. Samuelson¹; ¹U. S. Army Natick Soldier Center, Natick, Massachusetts; ²Center for Advanced Materials, University of Massachusetts, Lowell, Massachusetts; ³Konarka Technologies, Inc., Lowell, Massachusetts.

There has been tremendous interest in the investigation to find pure organic dye sensitizers for dye-sensitized photovoltaic (DSPV) cells. We have investigated novel acridine dyes as potential candidates for the photosensitizer in DSPV cells. We carried out the synthesis of the dyes by the substitution of the triphenylamine moiety at the 9-position on acridine with COOH groups for chelation onto TiO₂. The quaternization of acridine nitrogen led to acridine dyes with extended absorption from 400-700 nm. Modeling consisted of geometry optimizations using DFT followed by prediction of the longest wavelength absorptions associated with these optimized structures using the semi-empirical ZINDO method. Modeling was used to evaluate a variety of structures to achieve insights for correlating these types of molecular structures with predicted absorption spectra. Pertinent dihedral angles as well as bond lengths were evaluated to assess and compare planarity and conjugation for these dyes. Two COOH groups were included on some of the dyes as attachment groups for the dyes to a semiconductor such as TiO₂. The positions of attachment of these groups were investigated to achieve optimal performance as a sensitizer for light harvesting applications. The effect of protonation on the optimized structures and also on the predicted longest wavelength absorption was investigated with modeling. Other predictions include plots of the HOMO and LUMO to qualitatively examine electron distributions and the potential for electron injection, as well as evaluation of the HOMO and LUMO energies. In addition, the effects of a solvent on the absorption wavelength were examined with modeling. The results from modeling along with the experimental data consisting of synthesis, characterization and photophysical properties of the selected dyes will be presented.

D13.14
Magneto-resistance Measurements of Organic Diodes. [Brian Crone](#), Ian Campbell and Darryl Smith; Los Alamos National Laboratory, Los Alamos, New Mexico.

Large room temperature magneto-resistance (>10%) has recently been reported in polymer and small molecular weight organic semiconductor diodes [1]. We have investigated magnetotransport in organic diodes for a variety of organic materials (including poly[(2-methoxy-5-(2'-ethyl-hexyloxy)phenylene vinylene)] (MEH-PPV) and poly(9,9-dioctylfluorene) (PFO)) and contacts (including Au, Indium Tin Oxide, poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT-PSS), Ca and Al). Magneto-resistance measurements were done as a function of fixed device current, device thickness, temperature, applied magnetic field, and frequency of the applied magnetic field. Temperature was varied from 90 K to 350 K. Magnetic field was varied sinusoidally from 0 to ~0.4T at frequencies from 0.05 Hz to 0.2 Hz. Magnetic impurities in the organic materials were characterized with X-ray fluorescence measurements. The observed magneto-resistance under these conditions was always < 0.5%. We will discuss possible sources for magneto-resistance in these structures. [1] T.L. Francis, O. Mermer, G. Veeraraghavan and M. Wohlgenannt, *New J. of Phys.*, 6, 185 (2004); O. Mermer, G. Veeraraghavan, T.L. Francis and M. Wohlgenannt, *Solid State Comm.*, 134, 631 (2005).

D13.15
Polymer Bulk Homo-junction Light Emitting Devices. [Corey Tracy](#) and Jun Gao; Physics, Queen's University, Kingston, Ontario, Canada.

Recently in planar light-emitting electrochemical cells (LECs) with large inter-electrode spacing we have demonstrated novel bulk homo-junction light-emitting devices. This has been achieved by the simultaneous formation of thousands of point-like p-n junctions in the bulk of the polymer film through the simple addition of metallic ITO particles to the electrochemical/electroluminescent LEC solution. In a normal LEC device under bias, in-situ electrochemical n- and p-doping is initiated at the anode and cathode respectively, and these doped regions propagate towards the centre of the device until contact is made forming a light-emitting p-n junction. In devices with electrically floating metallic particles embedded in the polymer film, additional doping is initiated at the sides of the metallic particles, p- and n-doping forming on the sides closest to the anode and cathode

respectively. These doping regions then propagate outwards forming many point-like light-emitting p-n junctions. In such a manner it is possible to create surface emitting devices with large inter-electrode spacing exhibiting near uniform emission to the naked eye. Additionally, these devices have been demonstrated to provide a photovoltaic open circuit voltage (Voc) of up to 25.5V, much higher than the intrinsic band gap of the light-emitting species. Here we present detailed studies of bulk homojunction light-emitting devices as a function of the light emitting species and metallic particle material.

D13.16

Highly Enhanced Polyfluorene Emission Based on Electrochemically Crosslinked Gold Nanoparticles with Carbazole Ligands. Rigoberto Advincula, Prasad Taranekar and Chengyu Huang; Department of Chemistry, University of Houston, Houston, Texas.

Nanocomposites involving metal nanoparticles display many novel properties, such as high catalytic activities, interesting optical properties, and various properties from a fundamental viewpoint. Conducting polymers with gold nanoparticles have been previously reported. When doped with Au nanoparticles, a low-Tg polymer composite, is expected to have an effective enhancement on its photorefractivity, porosity, and should exhibit interesting opto-electrical behavior based on energy transfer mechanisms. Our interest primarily lies in investigating the energy transfer of electrochemically crosslinked carbazole and polyfluorene copolymer derivatives to gold nanoparticles and the resulting enhanced properties for applications. A polyfluorene copolymer, P-Fl-C, and the ligand, 11-(9H-carbazol-9-yl)undecane-1-thiol were successfully synthesized and the later was well capped onto Au nanoparticles to form CBZ-S-Au. Ultrathin films of P-Fl-CVK and P-Fl-CVK-CBZ-S-Au nanocomposite were spin coated and then electrochemically crosslinked. The films were characterized using CV, UV-vis., photoluminescence spectroscopy and AFM microscopy. The photoluminescence and the absorption spectra of the CBZ-S-Au nanoparticles to that of P-Fl-CVK crosslinked polymer in the composite films were well matched, which showed an energy transfer phenomenon. AFM results further confirmed the presence of CBZ-S-Au nanoparticles and the formation of homogeneous thin films. Device performance and applications will be discussed based on the observed high efficiency and ultrathin formation.

D13.17

Triplet Exciton Diffusion and its Application in Organic Light Emitting Devices. Noel C. Giebink¹, Yiru Sun¹, Mark E. Thompson² and Stephen R. Forrest¹; ¹Electrical Engineering, Princeton University, Princeton, New Jersey; ²Chemistry, University of Southern California, Los Angeles, California.

Triplet excitons have been shown to possess long diffusion lengths (~1000 Å) in typical host materials used for organic light emitting devices (OLEDs) [1]. To prevent triplet diffusion away from the emissive layer (EML), the design of high-efficiency phosphorescent OLEDs dictates the use of wide energy gap barrier materials at either side of the EML [2] for confinement. Attempts to make use of the extended diffusion length [3] have recognized that triplet exciton management is an important aspect in the design of phosphorescent OLEDs. In this work, we study triplet diffusion with the combination of both transient and steady-state techniques in the commonly used OLED host material 4,4'-bis(N-carbazolyl)biphenyl (CBP). Previous work has examined triplet diffusion in this host [4], however the results were clouded by the issue of charge-trapping and direct exciton formation on the phosphorescent guests. Here we avoid this ambiguity by co-doping a wide-gap hole transporting material 4,4',4'-tris(3-methylphenylphenylamino) triphenylamine (MTDATA) along with the phosphors to promote hole transport, thereby preventing exciton formation by direct trapping on the phosphors. We find that addition of the MTDATA modifies the diffusion constant by nearly two orders of magnitude in the regions in which it is doped. We further recognize that such modifications in the diffusion constant can be used to tailor the steady-state triplet density profile in the EML, hence providing a means to selectively enhance the operation of certain phosphorescent regions of a multiply doped device. We employ the results of this study to understand and optimize the efficiency of very high performance white OLEDs employing a combination of fluorescent and phosphorescent dopants. [1] M.A. Baldo, D.F. O'Brien and S.R. Forrest. Phys. Rev. B 60, 14422 (1999). [2] C. Adachi, M.E. Thompson and S.R. Forrest. IEEE J. Sel. Top. Quant. 8, 372 (2002) [3] B.W. D'Andrade, M.E. Thompson and S.R. Forrest. Adv. Mat. 14, 147 (2002) [4] M.A. Baldo and S.R. Forrest. Phys. Rev. B 62, 10958 (2000).

D13.18

Abstract Withdrawn

D13.19

Spin-Orbital Coupling Effects on Magnetic Field-Dependent Electroluminescence in Organic Materials. Yue Wu and Bin Hu; Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

Due to the multiplicities of singlet and triplet states, pi-conjugated organic materials can exhibit magnetic field-dependent electroluminescence. In this representation, we report the studies of electroluminescence in magnetic field based on both fluorescent and phosphorescent organic materials: poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV), Aluminum tris [8-hydroxyquinolate] (AlQ3), and iridium complex molecules (Ir(ppy3)). We found that the spin-orbital coupling largely affects such electroluminescence-magnetic field dependence when non spin-polarized charge carriers are injected from non magnetic electrodes. The detailed characterizations of the electroluminescence and photoluminescence indicate that an external magnetic field changes the triplet-triplet annihilation through singlet-triplet intersystem crossing and consequently enhances electroluminescence in organic light-emitting diodes under non spin-polarized charge injection.

D13.20

Photoluminescence of PMMA filled with red, green and blue phosphors. Rosario Gerhardt, Runqing Ou, Richard Gilstrap and Christopher J. Summers; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Many optical applications, such as light sensors, flat panel displays and light emitting diodes use phosphor materials in paste form or thin film form. However, the high atomic number of most of the phosphor constituents precludes their application where lightweight or low cost are desired. Limited work combining transparent polymers with phosphor materials has been carried out. Most previous work uses the deposition of the phosphor films as a coating on the polymer. In this paper, we will report on the fabrication and characterization of nanocomposites obtained by intimate mixing of poly(methyl-methacrylate (PMMA) with various ratios of Eu-doped Y2O2S, (Cu, Al, Au)doped ZnS and Eu-doped CaSrP2O7. The photoluminescence properties of these specimens were measured between 350-650 nm. As expected, the specimens containing yttrium oxysulfide luminesce in the red region of the spectrum while the ZnS-containing specimens have maximum luminescence at 529nm. Blue luminescence is obtained from CaSrP2O7 at a peak wavelength of 436 nm. The red phosphor nanocomposite gave a characteristic narrow spectra at 625 nm and other wavelengths below. The green phosphor had the widest emission spectra, which spanned from the blue to the red region while the blue phosphor specimen emission extended into the ultraviolet. The photoluminescence is seen to depend on the ratio of each of the phosphors used to the amount of polymer present in a non-linear way. At the same compositional phosphor content, the intensity of the light was in the order: red, green and then blue. Experiments designed to combine these materials in order to achieve white light emission are underway.

D13.21

Ligand Effect of Electroluminescence of Semiconductor Nanocrystals. Yongqiang Andrew Wang^{1,3}, Qingjiang Sun², Yongfang Li², David Goorskey⁴ and Xiaogang Peng⁴; ¹Ocean NanoTech, LLC, Fayetteville, Arkansas; ²CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China; ³NN-Labs. LLC, Fayetteville, Arkansas; ⁴University of Arkansas, Fayetteville, Arkansas.

Though Nanocrystal organic light-emitting diodes (NanOLEDs) have generated more and more attention due to their strong color tenability, wide emission range and narrow emission profile, short lifetime and low device efficiency of NanOLEDs are still two main obstacles that hinder their applications. We have made great progress on fabricating high-performance NanOLEDs through the stabilization of semiconductor nanocrystals and the configuration of devices. Several core/shell semiconductor nanocrystals with both improved fluorescent quantum yield and adjusted energy level were prepared; the nanocrystal surface with low dielectric ligand coating for low charge transfer barrier was designed; and the hole and electron transfer component is optimized to match the nanocrystals energy level. Overall the lifetime, stability and brightness of NanOLED devices have been significantly improved and the narrowest electroluminescent spectral profile has been reached to less than 30 nm for CdSe/CdS core/shell nanocrystals.

D13.22

Radical Beam Deposition of Silicon Nitride towards Passivation for Organic Devices. Kohshi Taguchi¹, Masamichi Yamashita², Mitsuo Yamazaki¹, Akiyoshi Chayahara³, Yuji Horino³, Takashi Iwade² and Masahiro Yoshimoto⁴; ¹Sakigake-Semiconductor,

Kyoto, Japan; ²Toray Engineering, Ohtsu, Japan; ³AIST Kansai, Ikeda, Japan; ⁴Kyoto Institute of Technology, Kyoto, Japan.

New deposition technique of silicon nitride (SiN_x) films, termed radical-beam deposition (RBD), has been developed for passivation of organic devices. In this technique, dense SiN_x films are deposited from an organic source at a low substrate temperature around room temperature. Since the substrate is located away from RF plasma, damage by charged particles can be avoided on growing surface. The comparison of initial passivation characteristics between organic light emitting devices (OLEDs) with and without SiN_x films suggested that the deposition process at around room temperature in RBD did not significantly damage the growing surface and underlying OLED. In this paper, film properties of SiN_x films by RBD and their passivation effects on OLED are discussed. SiN_x films are deposited from hexamethyldisilazane (HMDS). HMDS has a structure similar to that of disilazane that is a precursor in the conventional plasma chemical vapor deposition (CVD) using SiH_4 . In RBD technique, HMDS is decomposed in a reaction with atomic nitrogen generated in RF plasma. The carbon concentration of the film was estimated to be of the order of 10^{19} cm^{-3} at most, based on secondary ion mass spectroscopy (SIMS), although the organic matter was used as a source. For the films deposited by RBD at a substrate temperature above 400°C , the mass density was evaluated to be 3.2 g/cm^3 by Rutherford backscattering spectroscopy (RBS). This value is comparable to that of Si_3N_4 formed by sintering method, indicating a dense structure of SiN_x films fabricated by RBD. For the films deposited at room temperature and 100°C , the mass density of was evaluated to be as large as 2.6 and 2.8 g/cm^3 , respectively. An OLED was fabricated on a patterned ITO glass substrate by vacuum evaporation of tris-8-hydroxyquinoline aluminum (Alq_3) as a luminescent layer. The SiN_x film with a thickness of 100 nm was deposited on the luminescent layer at room temperature by RBD, followed by deposition of a 900-nm thick SiC_yN_x film at 80°C by conventional plasma CVD using HMDS and the same reaction chamber for RBD. While dark spots were observed in emission of the OLED covered only with the SiC_yN_x film deposited by the conventional plasma CVD, no dark spot is observed for the OLED passivated with the SiN_x film deposited by RBD. The emission intensity of OLEDs did not show significant degradation by SiN_x deposition, indicating that RBD can deposit the SiN_x film without giving serious damage to the underlying OLEDs. A preliminary characterization showed that the degradation of OLED was markedly suppressed compared to that without the SiN_x coating. The SiN_x film deposited by RBD is very promising to form a passivation layer in direct contact with a luminescent layer of OLED. Since HMDS is neither explosive nor corrosive, the easiness in handling the source material of HMDS is another significant advantage for RBD compared to the conventional plasma CVD using SiH_4 .

D13.23

Low-damage ITO formation using a unique cylindrical sputtering module and high-performance transparent organic light-emitting diode. Hidetoshi Yamamoto^{1,2}, Takahito Oyamada^{1,2}, Chihaya Adachi^{1,2}, Shoichi Aoshima³, William Hale⁴ and Hiroyuki Sasabe^{1,2}; ¹Department of Photonics Materials Science, Chitose Institute of Science and Technology, Hokkaido, Japan; ²CREST Program, JST, Shibuya, Tokyo 150-0011, Japan; ³ALS Technology, Mitaka, Tokyo 181-0013, Japan; ⁴AJA International, Inc., 809 Country Way, North Scituate, Massachusetts.

We demonstrate a low-damage technique of forming indium-tin-oxide (ITO) on an organic layer by using a cylindrical sputtering module and the fabrication of high-performance transparent organic light-emitting diodes (TOLEDs). The ITO target has an off-axis alignment to the substrate, and it confines plasma to the inside of the module, thereby forming ITO with little damage to the underlying organic layers. We found that the composition ratio of In_2O_3 (90%) and SnO_2 (10%) in the deposited film is the same as the target composition, and that the composition ratio distribution was spatially uniform, showing no angular dependence. We fabricated an ITO (110 nm) / $4,4'$ -bis[N(1-naphthyl)-N-phenyl-amino]biphenyl (a-NPD) [50 nm] / tris-(8-hydroxy-quinoline) aluminum (Alq_3) [30 nm] / Cs:2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) [20 nm] / ITO [100 nm] device, using the cylindrical target for the top ITO cathode fabrication. The device had excellent J-V characteristics, with a current density of $J=123 \text{ mA/cm}^2$ at an applied voltage of 10 V and a maximum external quantum efficiency of $\eta_{\text{ext}}=0.77\%$. This unique fabrication technique is applicable for various other organic optoelectronic devices which need transparent electrodes.

D13.24

Comparison of Cathode Deposition on Organic Light-Emitting Devices by using Thermal Evaporation and Electron Beam Evaporation. Jeong-Woo Park and Dong-Yu Kim; Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

Organic light-emitting devices (OLEDs) are of great importance for their potential as a new coming generation of flat panel displays because of their high luminescence, high efficiency, wide color range, easy of fabrication processes, and possibility of flexible displays. In the fabrication processes of OLEDs, cathode layers, such as metal and transparent conducting oxides, are conventionally deposited by evaporation and dc/rf sputtering techniques, which have been commonly used in the semiconductor processes. In particular, thermal evaporation (resistive heating evaporation method) has been commonly used in the cathode deposition of OLEDs. However such a method has some limitation. That is, it is able to evaporate relatively low melting materials (e.g. Al, Cu, Ag, Au) for evaporating cathode materials. Moreover, it has a considerably rough surface characteristic among the physical vapor deposition (PVD) after depositing. Instead of resistive heating evaporation methods, electron beam evaporation is another good way for evaporating. In this method, when electron is accelerated in a magnetic field it impact on source material. During impacting on source material, the kinetic energy of electrons is able to heat the source locally above 3000°C so it can easily evaporate even low vapor pressure cathode materials compared to thermal evaporation. Further more, it unable us to evaporate the transparent conduction oxides such as ITO with no difficulty. In our presentation, cathode layers are deposited on an organic layer by using thermal evaporator and electron beam evaporator and their device characteristics will be compared.

D13.25

Efficiency of OLEDs incorporating quantum dots. Krisztian Kohary, Victor Burlakov and David Pettifor; Materials, Oxford University, Oxford, Oxfordshire, United Kingdom.

Inorganic quantum dots incorporated into organic light emitting diodes (OLEDs) have been suggested as a new form for solid-state lighting [1-3]. This hybrid device exploits the large variety of potential applications of organic materials combined with the high performance electronic and optical properties of inorganic quantum dots. Based on rate equations we performed a theoretical analysis of the efficiency of OLEDs activated by a single layer of quantum dots embedded between n- and p-type organic semiconductors. Assuming diffusion controlled charge transport in the organic media, we studied the formation of excitons and their injection into the quantum dots via the Forster exchange mechanism. We also included exciton formation within the quantum dots via direct charge injection. In addition, electroluminescence quenching due to quantum dot ionization was taken into account. The highest energy transfer efficiency is described by having the best compromise between the model parameters such as exciton formation rate in the organic media, exciton capture rate by quantum dots, and charge injection rate into quantum dots. [1] S. Coe, W-K. Woo, M. Bawendi, V. Bulovic, Nature 420 (2002) 800. [2] N. Tessler, V. Medvedev, M. Kazes, S. Kan, U. Banin, Science 295 (2002) 1506. [3] J. Zhao, J. Zhang, C. Jiang, J. Bohnenberger, T. Basche, A. Mews, J. Appl. Phys. 96 (2004) 3206.

D13.26

Influence of Deposition Rate on Morphology and Optical Properties of Organic Light Emitting Small Molecule Alq3. Vivek Kumar Shukla^{1,2} and Satyendra Kumar^{1,2}; ¹Physics, IIT Kanpur, UP, India, Kanpur, Uttar Pradesh, India; ²Samtel Center for Display technologies, IIT Kanpur, Kanpur, India.

The microstructure and surface morphologies of thin films affect the device behavior of organic light emitting devices (OLEDs), particularly, when films are very thin. This study is important for the throughput, performance and stability of OLED based displays and white lights. Film deposition rates during vacuum evaporation influences the nucleation and growth of thin films affecting the film microstructure and hence the physical and device properties. We are reporting a systematic study on the role of film deposition rate in determining the microstructure of small molecular organic thin films. In this work a large number of organic thin films of popular small molecular material Alq_3 (Tris (8-hydroxyquinoline) aluminium) are deposited at a wide deposition range from ~ 1 to 100 \AA/s . The influence of deposition rates on the surface roughness and optical properties of Alq_3 films has been studied using atomic force microscopy (AFM), photoluminescence, UV- VIS transmission and spectroscopic ellipsometry. We find a correlation between deposition rates, film densities and surface roughness that will be discussed in detail.

D13.27

Semiconductor/ Dye Hybrid Materials to Utilize the Intense Absorption of Visible Light by Aromatic Dye Molecules. Derck Schlettwein, Kazuteru Nonomura, Christian Kelting and Thomas Loewenstein; Applied Physics, Justus-Liebig-University Giessen, Giessen, Germany.

Organic dye molecules are characterized by absorption coefficients in the visible spectrum that are significantly larger than those of inorganic semiconductors. This increased extinction is caused by the extended conjugated electronic p-system of organic dyes. It can be successfully used to absorb a photon in the visible range and inject electrons from the excited molecular state to a semiconductor electronic system. Sensitization of TiO₂ (Graetzel cell [1]) is a well known example using Ru complexes as sensitizers that have a rather broad absorbance spectrum almost covering completely the visible range at, however, rather low absorption coefficients. Aromatic dye molecules have a significantly higher absorbance allowing to use thinner films, providing superior charge transport in the matrix. Further, by use of appropriate chemical substituents, the energy levels of the dye frontier orbitals can be tuned in detail and hence the contact formation with the semiconductor and the injection probability can be well controlled and optimized. Two approaches are presented that utilize organic dye molecules as sensitizers: - Microcrystalline Si is an almost ideal material for thin film photovoltaics when judged from its electrical characteristics, based on an indirect band gap. This in turn leads to weak optical absorption, an ideal starting point for sensitization with an organic dye. Hybrid materials with embedded phthalocyanines could be prepared in a vacuum based CVD reaction [2]. The luminescence of the dye is quenched in the hybrid material and a photoconduction is measured that is sensitized by the absorption in the phthalocyanine. - As an alternative to TiO₂ in electrolyte-based cells, thin films of crystalline ZnO have been deposited from aqueous solutions in an all-low-temperature process, an electrochemical self-assembly reaction of ZnO in the presence of a structure-directing agent (SDA). This SDA forms a well-crystallized yet highly porous matrix of ZnO. Following desorption of the SDA this ZnO matrix is then used to bind dye molecules with appropriate chemical anchoring groups [3]. Efficient electron injection from the chemisorbed dye molecules is obtained, recombination could be successfully suppressed so external quantum efficiencies up to 90 % were reached, thanks to the intense absorption of the dye molecules, efficient injection and good conduction in the highly crystalline ZnO matrix as also proven by time-resolved photocurrent and photovoltage measurements. [1] M. Graetzel, *J. Photochem. Photobiol. A* 164, 3 (2004). [2] Consortium of TU Darmstadt (W. Jaegermann, Th. Mayer), Uni Bremen (D. Woehrle), HMI (M. Kunst) and JLU Giessen (D. Schlettwein), supported by the Volkswagen Foundation. [3] T. Yoshida, M. Iwaya, D. Komatsu, T. Oekermann, K. Nonomura, D. Schlettwein, D. Woehrle, H. Minoura, *Chem. Commun.* (2004), 400.

D13.28

Self organization and hole transport in carbon nanotube/poly(hexylthiophene) composites.

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Drawing on the success of bulk heterojunction concepts, composite of poly(alkylthiophene) and carbon nanotubes have recently been investigated for organic photovoltaics. From the pioneering work of Friend and co-workers[1], it is shown that self-organization of poly(hexylthiophene) P3HT is directly responsible for its optical and transport properties. From our study of P3HT/SWNT composites, we found that doping with nanotubes increases the ordering in the polymer. We present spectroscopic and microscopy evidence of increased ordering in P3HT/SWNT composites. Analysis of the I-V characteristics of hole-only devices in the dark under forward bias reveals a clear field dependence of hole current. At low bias, current density increases by an order of magnitude, but at high bias, it increases by as much as 3 orders of magnitude; Moreover, the transport regime changes from a space charge limited current model (SCLC) to a trap filling model with exponential trap distribution with SWNT doping; this not only shows that the nanotubes have the effect of increasing the hole conductivity but that hole traps are introduced; possibly through the defect sites on the acid purified nanotubes. At present it is not entirely clear whether the increase in hole current is due to more ordered polymer or to the introduction of nanotubes as SWNT have been known to be p-doped by oxygen in air; since the nanotubes are processed in ambient conditions, oxygen doping might have conferred on it p-type characteristics. [1] Brown P. J.; Thomas D. S.; Kohler A.; Wilson, J. S.; Kim, J-S; Ramsdale, C. M.; Sringhaus, H.; Friend, R. H., *Phys. Rev. B* 67 (2003) 064203.

D13.29

Organic Photovoltaic Devices based on Phenyl Cored Thiophene Dendrimer/PCBM Bulk Heterojunctions.

Nikos Kopidakis, William J. Mitchell, Garry Rumbles, David S. Ginley and Sean E. Shaheen; National Renewable Energy Laboratory, Golden, Colorado.

We have synthesized a new family of solution processable conjugated dendrimers, composed of a phenyl core and thiophene dendrons. The number of dendrons around the core, as well as the length and degree of branching of the dendrons was varied systematically. We report the properties of spin cast thin films of the dendrimers and correlate them to their molecular structure. Bulk heterojunction photovoltaic devices with dendrimers as electron donors and [6,6]-phenyl C60 butyric acid methyl ester (PCBM) as the electron acceptor were fabricated and tested under AM1.5 illumination. Considering their high bandgap, the high short circuit currents achieved suggest that this family of conjugated dendrimers is a promising candidate for application in organic photovoltaic devices.

D13.30

Conducting and Transparent Single Wall Carbon Nanotube Anodes for P3HT-PCBM Solar Cells. Aurelien Du Pasquier, H. Emrah Unalan, Steve Mil and Manish Chhowalla; Materials Science and Engineering, Rutgers University, North Brunswick, New Jersey.

Single-wall carbon nanotubes (SWNTs) have already been used in organic photovoltaics as electron acceptors in blends with poly(octyl)thiophene [1]. Here, we describe the use of SWNT thin films as transparent and conducting electrodes [2] for hole collection in P3HT-PCBM (poly (hexyl) thiophene- [6-6] phenyl-C61-butyrac acid methyl ester) organic photovoltaics. The device layer configuration is Glass/SWNT/PEDOT: PSS/P3HT-PCBM/In-Ga. The P3HT-PCBM layers were drop-cast from a chlorobenzene solution. By adjusting the SWNT work-function with a coating of PEDOT: PSS, we show that they can form a large area, transparent and conducting hole conducting electrode. We also introduce the use of Indium-gallium eutectic cathode top-contact as a convenient replacement to evaporated aluminum. We report a power conversion efficiency of 0.95%, a fill factor (FF) of 0.3 and a short-circuit current of 6.5 mA/cm² under 100 mW/cm² polychromatic white light measured in air. These values are comparatively higher than our reference cells of similar thickness (800 nm) made on ITO-PET (Indium-Tin oxide-Polyester) substrates. This is attributed to the three dimensional nature of the interface among the carbon nanotubes and the P3HT-PCBM nanocomposite. The SWNT coating thickness is controllable, and linked to its transparency and conductivity. We correlate these parameters with the performance of the solar cells. Our results indicate that transparent SWNT thin films could be a viable alternative to ITO for photovoltaic devices. References [1] E.Kymakis, I. Alexandrou and G.A.J. Amaratunga, *Journal of Applied Physics* 2003, 93, 1764 [2] Zhuangchun Wu, Zihong Chen, Xu Du, Jonathan M. Logan, Jennifer Sippel, Maria Nikolou, Katalin Kamaras, John R. Reynolds, David B. Tanner, Arthur F. Hebard, Andrew G. Rinzler *Science* 2004, 305, 1273.

D13.31

Single-wall Transparent Carbon Nanotube Coatings on ITO Anodes for P3HT-PCBM Solar Cells. Aurelien Du Pasquier, H Emrah Unalan, Steve Miller and Manish Chhowalla; Materials Science and Engineering, Rutgers University, North Brunswick, New Jersey.

We describe a solution process for coating ITO coated glass with transparent single-wall nanotubes. The coatings are then impregnated with a (poly (hexyl) thiophene- [6-6] phenyl-C61-butyrac acid methyl ester) (P3HT-PCBM) [1] solution, and the characteristics of the resulting photovoltaic devices are measured. We demonstrate an improvement in short-circuit current, fill factor and efficiency over reference cells of same thickness (800 nm). At 100 mW/cm² of white halogen light, the power conversion efficiency measured with carbon nanotubes is 1.8%, while it is only 0.8% without carbon nanotubes. The fill factor increases from 0.33 to 0.47. We argue that this improvement is related to better hole collection at the anode, due to the increased electrical contact area between the ITO and the P3HT-PCBM composite. The improved hole mobility measured using ITO/SWNT/P3HT:PCBM/Au and field effect transistor devices was found to be responsible for the improved performance. The device structure investigated by SEM revealed that the bottom SWNT layer is impregnated and covered with the P3HT-PCBM composite. It is necessary that the P3HT-PCBM layer be thicker than the SWNT layer for the device to function without shorting. The total thickness of ~ 800 nm was identified as the main limitation to the conversion efficiency, and thinner SWNT films were implemented. Latest results showing improved performance with thin spin coated films will be also presented. References [1] F. Padinger, R.S. Rittberger, N.S. Sariciftci, *Advanced Functional Materials* 2003, 13, 85. [2] D. Chirvase; J. Parisi; J.C. Hummelen; V. Dyakonov *Nanotechnology* 2004, 15, 1317. [3] Kanzen Inoue, Ross Ulbricht, Pallavi C. Madakasira, Miaoxin Zhou, Sergey B. Lee, John Ferraris, Anvar A. Zakhidov *Mater. Res. Soc. Symp. Proc.* 2005, 836

D13.32

Extending the Spectral Response of Organic Solar Cells via

Multi-Component Heterojunction Structures.

Paul Christopher Dastoor¹, C. McNeill¹, W. Belcher¹, I. Blake², P. Thordarson², M. Crossley², J. Reimers², N. Hush², W. Campbell³ and D. Officer³; ¹Physics, University of Newcastle, Callaghan, New South Wales, Australia; ²Chemistry, University of Sydney, Sydney, New South Wales, Australia; ³Chemistry, Massey University, Palmerston North, Manawatu, New Zealand.

Although the performance of organic solar cells (OSCs) has improved significantly over recent years, the power conversion efficiencies of even the best polymer devices is only a few percent [1]. Typically these "bulk heterojunction" structures involve a two-component blend consisting of a semiconducting polymer (electron donor and hole conductor) and a methanofullerene derivative (electron acceptor and conductor) [2,3]. By carefully controlling phase segregation, two interpenetrating conduction networks are formed resulting in a high density of interfacial dissociation sites for the strongly bound photogenerated excitons [4]. However, the spectral response of these devices is limited to a range below the wavelength defined by the polymer band-gap energy. Motivated by the observation that natural porphyrins are efficient light harvesters [5], here we report multi-component bulk heterojunction structures containing a range of chemically tailored porphyrins. By blending the porphyrin with the conjugated polymer and methanofullerene in a common solvent from which the active layer is spin-coated, we show that light is harvested from the porphyrin in the composite with an internal quantum efficiency of up to 15 %. No dramatic change in the morphology of the ternary porphyrin/polymer/methanofullerene blend film is observed compared to the binary polymer/methanofullerene blend film, indicating that highly efficient charge generation and conduction networks are maintained for this bulk-heterojunction architecture. Moreover, this phenomenon is observed generically for a variety of porphyrins. By tailoring the porphyrin chemistry, we demonstrate that it is now possible to fabricate organic solar cells that exhibit enhanced current generation across the entire visible solar spectrum. References: 1. Munters, T. et al. *Thin Solid Films* 403-404, 247-251 (2002). 2. Halls, J. J. M. et al., *Nature* 376, 498-500 (1995). 3. Granström, M. et al., *Nature* 395, 257 (1998). 4. Brabec, C. J., Sariciftci, N. S. & Hummelen, J. C., *Adv. Funct. Mater.* 11, 15-26 (2001). 5. Fukuzumi, S. In *The Porphyrin Handbook*, Kadish, K.M., Smith, K. M., Guillard, R., (eds), (Academic Press: San Diego, CA), 8, 115, (2000).

D13.33

Fabrication and Characterization of Ordered Nanorod-Organic Solar Cells. Susan Huang¹, Harry Efstathiadis¹, Pradeep Halder¹, Brian Landi², Ryne P. Raffaele² and Hee-Gyoun Lee³; ¹College of Nanoscale Science and Engineering, SUNY Albany, Albany, New York; ²Nanopower Research Laboratory, Rochester Institute of Technology, Rochester, New York; ³Korean Polytechnic University, Siheung, South Korea.

Organic solar cells have drawn research interest since the development of conducting polymers due to the potentially lower costs and easy processing. One of the main limits of efficiency for organic solar cells is that excitons have short lifetimes and often recombine before they are able to reach a dissociation site. The distance that excitons must travel to a dissociation site can be reduced by creating an ordered array of dissociation sites within the photoactive material. We investigate the effect of incorporating ordered, aligned nanorods within the photoactive polymer on the efficiency of the solar cell. Aligned copper nanorods attached to a silver film substrate were fabricated by electrodeposition of copper into porous anodic aluminum oxide (AAO) membranes. The AAO membrane was then dissolved in NaOH to leave freestanding aligned Cu nanorods, which were characterized by SEM. These rods were incorporated in an organic solar cell by lamination. The structure of the solar cells were ITO/PEDOT:PSS/MDMO-PPV:PCBM: aligned Cu nanorods/Ag. Efficiencies of these nanorod-organic solar cells were then measured under AM1.5 conditions and compared with a baseline solar cell that did not contain Cu nanorods.

D13.34

Alignment of Supramolecular Nano-Fibers by Shear Stress within Conventional Polymers. Kazunori Sugiyasu^{1,2}, Norifumi Fujita², Isamu Akiba³, Kazuo Sakurai³ and Seiji Shinkai²; ¹Department of Chemistry, MIT, Cambridge, Massachusetts; ²Department of Chemistry and Biochemistry, Kyushu University, Fukuoka, Japan; ³Department of Chemistry Processes and Environment, the University of Kitakyushu, Kitakyushu, Japan.

Supramolecular chemistry has provided numerous intriguing architectures and functions, which can be applied to new materials such as organic devices. In materials sciences, one limitation of these supramolecular assemblies is that, although they are well defined at the nm-scale, it is rather difficult to bottom-up them to a larger scale (> mm). Because they can be designed to function with unique photo-

and electrochemical properties arising from individual organic molecules, alignment of these supramolecular assemblies will light up a new foothold in the organic devices. We here report on an easy and versatile approach for alignment of the supramolecular nano-fibers. We used a commercially-available polymer as a matrix which can be easily processed and handled. We first prepared cast-film wherein supramolecular nano-fibers are deposited. Obtained film was sheared above the glass transition temperature of the used polymer. Alignment of the supramolecular nano-fibers was confirmed by SAXS, polarized IR spectra, and electron micrographs: all results indicate that the supramolecular nano-fibers are oriented along shearing direction. Sheared film should lead to novel anisotropic materials endowed with supramolecular functions.

D13.35

Dye Sensitized Photoconduction in Silicon Thin Films: A Possible Starting Point for New Photovoltaic Devices.

Christian Kelting¹, Ulrich Weiler², Thomas Mayer², Wolfram

Jaegermann², Dieter Woehrl³, Ossamah Abdallah⁴, Marinus Kunst⁴ and Derck Schlettwein¹; ¹Institute of Applied Physics, Justus-Liebig-University Giessen, Giessen, Germany; ²Institute of Materials Science, Technical University Darmstadt, Darmstadt, Germany; ³Institute of Organic and Molecular Chemistry, University Bremen, Darmstadt, Germany; ⁴Department of Solar Energy, Hahn-Meitner-Institute, Berlin, Germany.

A promising way to increase the light harvesting efficiency and hence the conversion efficiency of Si thin film photovoltaic cells is the utilization of the intense optical absorption of organic dye molecules (in the long wavelength region of the visible light) in the absorber layer. Based on molecular orbital calculations unsubstituted zinc phthalocyanine (PcZn) was chosen as a promising candidate molecule also because of its thermal and chemical stability needed in the deposition step. Composite materials of PcZn in Si were prepared by simultaneous physical codeposition of PcZn into growing films of amorphous or microcrystalline Si from a plasma-enhanced (hot-wire) chemical deposition reaction (CVD). Thin films of PcZn (10 nm) were prepared as model systems by physical vapour deposition on thin Si films (100 - 500 nm) by the CVD process. Optical absorption spectroscopy was used to analyze the intermolecular coupling of the Pc molecules. Spectrally resolved photoconductivity measurements of pure Si films, phthalocyanine (PcZn) coated Si films and composite Si-Pc-films were used to proof the injection of charge carriers from the dye to silicon. The photoconductivity of thin silicon films in the spectral range of the main absorption (Q-band) of the Pc increased after coating with 10 nm of Pc. The photoconductivity spectra of the composite materials correspond to their absorption spectra, in particular the Pc contribution correlates to the phthalocyanine Q-band. Since the sensitized photoconduction was obtained in the steady state under continuous illumination, the results are taken as evidence for the injection of both types of charge carriers (electrons to the conduction band and holes to the valence band of Si) since otherwise only transient photocurrents would be expected. In parallel, the alignment of the energy levels of PcZn and its fluorinated derivatives has been deduced from Ultraviolet Photoelectron Spectroscopy studies [1]. The frontier orbital positions of the partly fluorinated derivatives should allow a more efficient charge transfer from dye to silicon than the unsubstituted Pc. Such films are presently under investigation. A p-i-n solar cell with a dye sensitized intrinsic absorber layer will be developed for determination of the photovoltaic parameters. Aside from the technical context, such a device will also be helpful to optimize the absorbing dye silicon hybrid material. 1. U. Weiler, T. Mayer, W. Jaegermann, C. Kelting, D. Schlettwein, S. Makarov D. Woehrl Electronic Energy Levels of Organic Dyes on Silicon: A Photoelectron Spectroscopy Study of ZnPc, F16ZnPc and ZnTPP on p-Si(111):H, *J. Phys. Chem. B* 108, 19398 (2004).

D13.36

Organisation of Covalently Linked Donor-Acceptor Dyads.

Paul H. J. Kouwer and Timothy M. Swager; Chemistry, MIT, Cambridge, Massachusetts.

Photovoltaic devices based on organic materials have rapidly developed since their introduction in the mid 1980s. Impressive steps forward were realised by changing the morphology of the device from bilayered devices to heterojunction and dispersed heterojunction devices. The latter shows promising results in terms of commercial applications. In order to have increased control over the morphology of such system, we prepared a covalently linked donor-acceptor dyad; the two chromophores linked by a short flexible spacer. The materials were found to form intramolecular sandwich complexes in solution, even at elevated temperatures, which allowed us to study them with a variety of NMR techniques. Molecular modeling studies supported the conclusions. The results of these studies will increase understanding of the interactions between the donor and acceptor species.

D13.37

Donor-Acceptor Solar Cells Comprised Exclusively of Inorganic Nanocrystals Spin-Cast From Solution. Ilan Gur^{2,3,1} and A. Paul Alivisatos^{1,3,2}; ¹Chemistry, UC Berkeley, Berkeley, California; ²Materials Science and Engineering, UC Berkeley, Berkeley, California; ³Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

We introduce the first solar cells based entirely on colloidal semiconductor nanocrystals. They are ultra-thin, solution-processed, and stable in ambient environments. Comprised of dense nanocrystal films that mirror the basic properties of semiconducting polymers, these cells function as a new class of diffusion assisted donor-acceptor heterojunction. Sintering is found to enhance the performance of these devices, allowing for efficient, air-stable solar power conversion. The nanocrystal solar cells presented here offer a new research direction and serve as a key development toward achieving stable and low-cost solar energy conversion.

D13.38

Abstract Withdrawn

D13.39

Self-Assembly of Tryphenylene-Based Discotic Molecules Into Columnar Stacks Studied by Scanning Probe Microscopy. Volodymyr Duzhko¹, Zhilei Liu², Brian A. Todd², Steven J. Eppell², Alexander N. Semyonov³, Robert J. Twieg³ and Kenneth D. Singer¹; ¹Physics, Case Western Reserve University, Cleveland, Ohio; ²Biomedical Engineering, Case Western Reserve University, Cleveland, Ohio; ³Chemistry, Kent State University, Kent, Ohio.

A promising concept for organic photovoltaics involves the construction of a photovoltaic cell from a blend network of donor and acceptor materials possessing a large internal interfacial area. Interest in organic photovoltaic materials derives from the promise of flexible, light-weight and easily processed materials. Such fabrication processes could be carried out on a large scale with low cost solution-based deposition techniques. The efficiency of these photovoltaic cells greatly depend on the morphology of the blend network, most advantageous when the scale of the interfacial distances are comparable with the typical exciton diffusion length of a few 10s nm. Compared to disordered polymers, discotic liquid crystals possess enhanced charge carrier transport with larger carrier diffusion length deriving from quasi one-dimensional structures organized in the liquid crystal mesophase by self-assembly. We used tryphenylene-based discotic molecules known to form a hexagonal columnar liquid crystal mesophases as the building blocks for the construction of self-standing one-dimensional columnar stacks. Fabrication of the columnar structures from solution precursors by spin-coating on various substrates (glass, mica, ITO coated glass) will be discussed. We implemented scanning probe microscopies to image the columnar stacks of discotic molecules and study the self-organization processes. Blind reconstruction of the tip with Nioprobe calibration sample and morphological erosion modeling were used to eliminate tip-related shape artifacts and in-plane broadening for visualization of columns with high height-to-width ratio, and also to image columns with diameters below 10 nm (the size comparable to the single disc diameter of 2 nm). The orientation of the columns on the substrates, shape and size distribution of the columnar stacks of discotic molecules will be discussed. The study of the self-assembly processes of discotic liquid crystals provides a promising opportunity for nanoscale engineering of a blend network morphology for fabrication of highly efficient organic photovoltaic cells.

D13.40

Electric Force Microscopy of Photoexcited, Conjugated Polymer Films. David C. Coffey² and David S. Ginger¹;

¹Chemistry, University of Washington, Seattle, Washington; ²Physics, University of Washington, Seattle, Washington.

The nanoscale morphology of conjugated polymer films is well-known to impact the performance of polymer photovoltaic and light-emitting devices. To study this issue with high spatial resolution we have coupled photoexcitation with electric force microscopy (EFM). We demonstrate that it is possible to follow photoinduced charge generation, equilibration, and recombination in polymer films with sub-ms time resolution (time-scales comparable to carrier transit times in many thin-film devices). We correlate our EFM data with conventional photoinduced absorption measurements on the same films. Additionally, we show how the probe tip's electric field can be used to measure field-dependent carrier generation and recombination processes with high-spatial resolution.

SESSION D14/I11: Joint Session: Interfaces in Organic and Hybrid Devices

Chairs: Sean Shaheen and Xiaoyang Zhu
Friday Morning, December 2, 2005
Room 302 (Hynes)

8:00 AM D14.1/I11.1

Buried organic/inorganic interfaces in polymer optoelectronic devices: functional nanocomposites.

Gitti L. Frey, Materials Engineering, Technion, Haifa, Israel.

Charge injection and extraction from polymer devices is controlled by the structure and interfacial interactions at the electrode-polymer interface. Charge separation in photovoltaic devices, on the other hand, is dominated by semiconductor/semiconductor interfaces buried in the active layer. Similarly, designed buried interfaces could be used to govern charge recombination and transport in polymer devices. Hybrid materials based on the incorporation of organic molecular species into the galleries of inorganic scaffolds have already been applied in the fields of catalysis, separation, data storage and optics. Organic-in-inorganic hybrids present several advantages as optical materials due to the ability to tailor the optical properties through host/guest material selection and control of organic/inorganic interaction at the molecular level. In polymer/inorganic guest/host composites the polymer is confined into well-defined voids of an inorganic scaffold. Such hybrid materials have been used as active components in polymer devices. For example 3D TiO₂ scaffolds infiltrated with MEH-PPV have been utilized in photovoltaic cells and 2D layered MoS₂ intercalated with polyfluorenes have shown stable blue emission in light-emitting diodes. A variety of 2D and 3D guest/host hybrids have been designed, synthesized, characterized and integrated into devices. The device performances, in these systems, provide insight into the electronic processes across the molecular interfaces.

8:15 AM D14.2/I11.2

Towards Transparent Inorganic and Plastic

Low-Workfunction Electrodes. Linda Lindell², Fredrik Jakobsson¹, Wojciech Osikowicz², Peter Andersson¹, William Salaneck², Magnus Berggren¹, Jerome Cornil³ and Crispin Xavier¹;

¹Department of Science and Technology, Linköping University, Norrköping, Sweden; ²Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden; ³Chimie des Matériaux Nouveaux, University of Mons-Hainaut, Mons, Belgium.

Although many essential elements involved in low-cost production of polymer (opto)electronics are available, reduction in cost is still inhibited by the complex fabrication of the electron injecting electrode. In a p-LED or a solar cell, the low work function (WF) metal electrode is deposited onto a polymer layer under high vacuum conditions. Unfortunately, almost all low WF metals are highly reactive, and quickly oxidized in air. Consequently, they are difficult to handle in processing steps. Therefore, alternative routes for the preparation of cathodes are highly desirable in order to fully exploit the potential of low-cost fabrication of polymer (opto)electronics, such as roll to roll or bar coating combined with lamination. Tuning the workfunction of an electrode surface can be achieved by controlling the orientation of an electric dipole, the interface dipole D_{int} . The metal work function change, DW , upon monolayer adsorption is a measure of this interface dipole. Although there are various possible origins for the dipole potential eD_{int} [1], it generally consists mainly of the following three contributions [2]: (i) the reduction of the metal surface electron density tail upon adsorption, which always decreases the metal surface dipole potential eDD_{met} , (ii) the intrinsic dipole moment D_{mol} of the adsorbed molecule, and (iii) the chemical dipole potential eD_{chem} created by partial electron transfer between the metal and the adsorbate upon chemisorption. Therefore, DW can be written as a function of these contributions: $DW = eD_{int} = f(eDD_{met}, eD_{mol}, eD_{chem})$. In this work, we propose a route to produce transparent low-workfunction indium tin oxide and plastic electrodes (Poly(3,4-ethylenedioxythiophene), or PEDOT). The workfunction of the transparent electrode is decreased upon chemisorption of a monolayer of strong electron-donor molecule, namely tetrakis(dimethylamino)ethylene -TDAE- ($\{Me_2-N\}_2-C=C-\{N-Me_2\}_2$). Upon electron transfer reaction at the interface, the TDAE molecules become positively charged and an chemical dipole potential eD_{chem} is created leading to a significant workfunction decrease (>1.3 eV). High workfunction surfaces such as ITO [3] and PEDT-PSS [4] ($WF=4.9$ eV) have been transformed in stable, transparent low-workfunction electrodes ($WF=3.6$ eV). We demonstrate that electrons can now be injected from those modified electrodes, allowing to form novel all-transparent polymer light-emitting diodes. [1] H. Ishii, K. Sugiyama, E. Ito, and K. Seki, Advanced Materials, 11, 605 (1999). [2] X. Crispin, V. M. Geskin, A. Crispin, J. Cornil, R.Lazzaroni, W.R Salaneck, J.L. Bredas, Journal of the American Chemical Society, 124, 8132-8141 (2002). [3] W. Osikowicz, X. Crispin, C. Tengstedt, L. Lindell, Th. Kugler, W.R.

Salaneck, *Applied Physics Letters*, 85, 1616-1618 (2004). [4] L. Lindell, F. Jackobsson, J. Cornil, P. Andersson, W. R. Salaneck, M. Berggren, X. Crispin, submitted.

8:30 AM *D14.3/I11.3

Ultrafast electron transfer at the molecule-semiconductor nanoparticle junction. Tianquan Lian, Chemistry, Emory University, Atlanta, Georgia.

Interfacial electron transfer (ET) at the molecule-nanoparticle junction plays important roles in many nanoparticle-based devices, such as hybrid molecule/semiconductor photovoltaics and molecular electronics. We are carrying out systematic studies of photoinduced electron injection dynamics from molecular adsorbates to semiconductor nanoparticles. The rate of ET from molecular excited state to metal oxide nanoparticles was directly measured using femtosecond transient absorption spectroscopy. We will discuss the dependence of ET rates on the nature of semiconductors, molecules (anchoring group, spacer and chromospheres), and junction environments (solvent, pH). We will also present recent advances on probing electron transfer dynamics at the single-molecule-nanoparticle junction using single molecule spectroscopy.

9:00 AM *D14.4/I11.4

Interfacial control of electron transfer dynamics in dye sensitised and organic solar cells. James Durrant, Imperial College London, London, United Kingdom.

Electron transfer dynamics across donor / acceptor interfaces are central to the function of excitonic solar cells. Optimisation of device function requires the systematic control of both charge separation and recombination dynamics at this interface. In this paper we will address the parameters controlling electron transfer dynamics in such devices, and evaluate strategies to achieve optimization of these dynamics. We will start off by considering what are optimum electron transfer dynamics which yield highest device efficiency. We will then go on to consider a range of interface engineering based strategies to achieve more optimised dynamics. Examples will be taken from a range of different excitonic solar cells, including dye sensitised nanocrystalline, hybrid polymer / metal oxide and all organic devices. Our paper focus on the correlation between interfacial electron transfer dynamics and materials design / morphology, and their impact upon device function. Particular attention will be paid to supermolecular strategies to achieve electron transfer cascades, leading to long lived charge separation at nanostructured interfaces. References 1. Durrant et al. *Coord. Chem. Rev.* (2004) 1247-1257 2. Haque et al. *J. Am. Chem. Soc.*, 125 (2005) 3456-3462. 3. Handa et al. *Angew Chemie* (2005) in press.

9:30 AM D14.5/I11.5

Tripod Thiolate Self-Assembled Monolayer: A Novel SAM to interface Zeolites to Gold(111). Andrew S. Ichimura and Wanda Lew; Chemistry and Biochemistry, San Francisco State University, San Francisco, California.

A number of applications for thin films or monolayers of zeolites on surfaces have been proposed. For example, they may be used as porous membranes for separations or as low-k dielectric materials. Our interest zeolite monolayers originates in the unique optical properties of alkali metal doped pure silica zeolites, such as, cesium doped MFI (ZSM-5), or, Cs@MFI. Cs@MFI exhibits broad near infrared (NIR) absorptions characteristic of nearly free electrons.[1] A related material, Cs@IFR, has been characterized [2,3] and was predicted to have metallic properties [4]. In order to take advantage of the electronic properties of these novel materials and to facilitate the measurement of their fundamental properties, we set out to interface silica zeolites with a conducting surface. Our strategy employs bifunctional molecules to tether the zeolite to a gold (111) surface. The molecular tether uses the thiolate-gold interaction on one end and a functional group that can react with the surface silanol (Si-OH) groups of the zeolite on the opposite end. In order to prepare mechanically robust self-assembled monolayers to act as linking molecules, we devised a strategy whereby a mercaptoethanol SAM is reacted with silicon tetrachloride to form a tripod thiolate monolayer. In this SAM, three adjacent mercaptoethanol molecules form silyl ether linkages leaving a reactive silicon chlorine bond in a suitable position to react with zeolite silanol functional groups. One advantage of this SAM is that the zeolite may be tethered close to the gold surface, which should minimize the tunneling barrier between the zeolite and gold surface. Upon doping with alkali metals, the zeolite monolayer may find applications as sensors or detectors. In addition, this tripod SAM can be used under hydrothermal synthesis conditions to prepare continuous thin films of crystalline MFI. This report will focus on our spectroscopic and theoretical studies of the tripod thiolate SAM, and preliminary XRD and SEM measurements of the zeolite monolayers and films. 1. Ichimura, A. S.; Lew, W. unpublished results. 2. Ichimura, A. S.; Dye, J. L.; Cambor, M. A.; Villaescusa, L.

A. J. *Am. Chem. Soc.* 2002, 124, 1170-1171. 3. Wernette, D. P.; Ichimura, A. S.; Urbin, S. A.; Dye, J. L. *Chem. Mater.*, 2003, 15(7), 1441-1448. 4. Li, Z.; Yang, J.; Hou, J. G.; Zhu, Q.; J. Am. Chem. Soc., 2003, 125, 1170-1171.

9:45 AM D14.6/I11.6

Organic Light Emitting Device Stability Dependence on the Metal Halide Salt Electron Injection Layer. Brian D'Andrade, Hitoshi Yamamoto, Mark Rothman, Min-Hao Lu and Julie Brown; Universal Display Corporation, Ewing, New Jersey.

Organic light emitting devices (OLEDs) are beginning to play a significant role in commercially available flat panel displays, so improvement in the lifetime of these devices is an important challenge. There are many degradations mechanisms that decrease the operational stability of OLEDs. In particular, the cathode deposited on the organic layers may be a source of instability [1,2]. A common compound cathode consists of a ~1 nm thick metal halide salt deposited on the electron transport layer before the deposition of a thick >10nm aluminum layer, so the effect on stability of the choice of metal halide salt, and the thickness of the salt chosen is examined. For this study, all OLEDs were fabricated by sequentially depositing onto solvent-cleaned and dried indium-tin-oxide coated glass, using vacuum (~6x10⁻⁸ Torr) thermal evaporation, 10 nm of copper phthalocyanine (CuPc), 50 nm of 4,4'-bis[N-(1-naphyl)-N-phenyl-amino]biphenyl (NPD), and 50 nm of tris-(8-hydroxy-quinoline)aluminum. The cathode consisted of various thicknesses (1-10 nm) of either CaF₂, CsCl, CsF, KF, LiCl, LiF, NaBr, NaCl, NaF, or AgCl and 100 nm of Al. The thickness of the salt layer is a crucial factor in device stability and operating voltage, so this layer thickness was optimized for maximum stability. Except for devices with AgCl, the initial current-density versus voltage (J-V) and external quantum efficiency of all optimized devices were similar, within experimental error. For example, the mean and standard deviation of the peak efficiency, of devices without AgCl, was 1.6% (5.2 cd/A) and 0.04%, respectively, and the operating voltage deviated from a mean value by ±0.5 V, at any given current-density. Devices were electrically stressed at 40 mA/cm² for 400 hrs or until they attained 90% of their initial luminance. The mean initial luminance was 2100 cd/m², and the amount of time needed to degrade to 90% initial luminance increased according to the salt used in the following order : AgCl < NaBr (3 hrs) < NaCl (10 hrs) < LiCl (183 hrs) < CaF₂ (210 hrs) < LiF (290 hrs) < CsF (296 hrs) < CsCl (317 hrs) < NaF (348 hrs) < KF (395 hrs). The luminance after 400 hrs also depended on the salt and increased as follows: AgCl (0 cd/m²) < NaBr < NaCl < LiCl < KF < CaF₂ < CsF = CsCl = LiF < NaF (1870 cd/m²). These results are interesting because devices have the same initial performance characteristics regardless of the salt used in the OLED, and there seems to be no correlation between the properties of the salt used, such as density, ion size, or sublimation temperature, and the stability of an OLED. [1] Y. Cao, G. Yu, I. D. Parker, and A. J. Heeger, *J. Appl. Phys.* 88, 3618 (2000). [2] M. Y. Chan, S. L. Lai, M. K. Fung, C. S. Lee, and S. T. Lee, *J. Appl. Phys.* 95, 5397 (2004).

10:30 AM *D14.7/I11.7

Zn-porphyrin/C₇₀ complexes for solar cell devices: Molecular orientations, electronic properties and charge transfer time. Andrea Goldoni¹, Carla Castellarin-Cudia¹, Paolo Vilmercati¹, Luca Petaccia¹, Guillermo Zampieri¹, Silvano Lizzit¹, Cinzia Cepek², Luca Floreano², Alberto Verdini², Alberto Morgante³, Albano Cossaro², Rosanna Larciprete³, Luigi Sangaletti⁴, Stefania Pagliara⁴, Chiara Battocchio⁵ and Giovanni Polzonetti⁶; ¹Sincrotrone Trieste S.C.p.A., Trieste, Italy; ²Lab. Nazionale TASC-INFM, Trieste, Italy; ³CNR-Istituto dei Sistemi Complessi, Rome, Italy; ⁴Dip. Matematica & Fisica, Universita' Cattolica del Sacro Cuore, Brescia, Italy; ⁵INFM-Ogg, ESRF, GILDA CRG, Grenoble, France; ⁶Dip. Fisica, Universita' "Roma Tre", Rome, Italy.

Molecular dyes composed of electron donors capable of photo-induced electron transfer to linked acceptors have been used to mimic the natural photosynthetic reaction centers in photochemical devices. Porphyrins are among the most employed building blocks as electron donors [1]. Intriguing is the system formed by metallo-porphyrins directly bonded and facing fullerenes, actually realized in co-crystallites and solution form only [2], for which the typical fluorescence decay of the excited porphyrins is strongly quenched [3], i.e. non-radiative decay channels are favored. Next step toward an efficient solar cell is the deposition of similar metallo-porphyrin/fullerene systems on substrates, with the ability to control and tailor the orientation of both molecules (geometric structure and arrangement of the molecules are responsible for the physical properties of the system). Here, we demonstrate that the UHV deposition of porphyrins and C₇₀ molecules on clean substrates allows the formation of films having selected intermolecular interactions and electronic properties. Using polarization-dependent x-ray absorption and photoemission spectroscopy we have investigated the growth, molecular orientation and electronic properties of

Zn-Tetraphenyl-porphyrin (ZnTPP)/C₇₀ films deposited on Ag(110), Si(111) and TiO₂(110). The quite strong ZnTPP-fullerene interaction allows the growth of a single ZnTPP layer on top of a C₇₀ monolayer (and vice versa), as well as it allows the self-assembling of the two molecular species in ordered multilayer structures when co-deposited. The interactions with the substrate and with C₇₀ modify the ZnTPP electronic states, indicating formation of bonds and charge redistribution. Resonant photoemission, which probes the delocalization (charge transfer) of an excited electron on the time scale of the core-hole lifetime [4], indicates that the ZnTPP/C₇₀ mixed systems delocalize more efficiently the excited electrons as compared to pure ZnTPP films. The charge transfer time depends on the empty $\langle \pi \rangle^*$ state in which the electron is excited and on the relative molecular orientations, but in general is below 10 fs and in some cases faster than 5 fs. [1] J. Chen et al, Science 286, 1550 (1999); A. Tsuda et al, Science 293, 79 (2001). [2] Y.P. Sun et al, J. Org. Chem. 62, 3642 (1997); P.D.W. Boyd et al, J. Am. Chem. Soc. 121, 10487 (1999); T. Ishii et al, Coordination Chem. Rev. 226, 113 (2002). [3] M.E. Milanese et al, J. Phys. Org. Chem. 15, 844 (2002). [4] W. Wurth & D. Menzel, Chem. Phys. 251, 141 (2000); J. Schnadt et al, Nature 418, 620 (2002).

11:00 AM D14.8/I11.8

Internal Electric Fields and Charge Injection in PFO Based Diode Structures. Ian H. Campbell, Brian K. Crone and Darryl L. Smith; Los Alamos National Lab, Los Alamos, New Mexico.

We present measurements of internal electric fields and charge injection in poly(9,9-dioctylfluorene) (PFO) and PFO/poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) blend based diode structures. In PFO/F8BT blend diodes with poly(2,3-ethylenedioxythiophene)/polystyrene sulfonic acid (PEDOT:PSS) anodes the internal electric field in the device, measured using electromodulation techniques, has been reported to be smaller than expected [1,2]. This electric field screening was attributed to electron trapping near the anode. Here, we present complementary electromodulation measurements of PFO/F8BT blend diodes nominally identical to those previously reported that do not exhibit this electric field screening. We discuss the possible origins of the different results observed in these internal electric field measurements. Similarly, electrons trapped near the anode have been invoked to explain enhanced hole injection from PEDOT:PSS into PFO [3]. Electron injection leads to an increase in diode built in potential that was attributed to a trapped electron layer near the anode. This trapped electron layer increases the effective work function of the PEDOT:PSS contact. Here, we present measurements of charge injection in devices employing platinum and PEDOT:PSS anodes with identical built-in potentials. We find that charge injection from PEDOT:PSS is significantly greater than that from Pt. We discuss the differences in charge injection in these two structures that appear to be independent of contact energy levels. [1] P.A. Lane, J.C. deMello, R.B. Fletcher, and M. Bernius, Appl. Phys. Lett. 83, 3611 (2003). [2] P.A. Lane, J.C. deMello, R. Fletcher, and M. Bernius, Proc. SPIE 5214, 162 (2004). [3] D. Poplavskyy, J. Nelson, D.D.C. Bradley, Proc. SPIE 5214, 197 (2004).

11:15 AM D14.9/I11.9

Tuning of Injection Barrier for Organic Electronics with Self-Assembled Monolayers. Bert de Boer, Magda Mandoc, Vally Mihailetchi, Afshin Hadipour and Paul Blom; Molecular Electronics, Materials Science Centre / University of Groningen, Groningen, Netherlands.

Metallic contacts in organic, opto-electronic devices are determinative for the ultimate device performance. Preparation methods, diffusion of metal atoms, reactivity of metals toward air and organics, can have a detrimental influence on the stability and performance of organic thin-film devices like light-emitting diodes (LEDs), photovoltaic (PV) cells, and (ambipolar) field-effect transistors (FETs). Although these influences have to be addressed before a reliable and reproducible opto-electronics device can be measured, one first has to take into account the intrinsic properties of the metal namely its work function. We demonstrate the tuning of metal work functions by modifying the metal surface through the formation of self-assembled monolayers (SAMs) derived from 1H,1H,2H,2H-perfluoro alkanethiols and hexadecanethiol. The ordering inherent in the SAMs creates an effective, molecular dipole at the metal/SAM interface, which increased the work function of Ag (4.4 eV) to 5.5 eV for 1H,1H,2H,2H-perfluoro alkanethiols. Hexadecanethiol on the other hand shifted FAg to 3.8 eV. On Au, the SAM of 1H,1H,2H,2H-perfluorodecanethiol raised the work function of Au (4.9 eV) with 0.6 eV to 5.5 eV, whereas hexadecanethiol decreased the work function of Au by 0.8 eV. These chemically modified electrodes were applied in the fabrication of polymer LEDs and the hole injection into MEH-PPV was investigated. An Ohmic contact for hole injection between a silver electrode functionalized with the perfluorinated SAMs, and MEH-PPV with a HOMO of 5.3 eV was

established. Conversely, a silver electrode modified with a SAM of hexadecanethiol lowered the Ag work function to 3.8 eV blocked the hole injection into PPV, which enables studying the electron transport in composite devices. The electron-only current was measured in a polymer/polymer blend photovoltaic cell based on MDMO-PPV and PCNEPV. This method demonstrates a simple and attractive approach to modify and improve metal/organic contacts in organic electronic devices like LEDs, photovoltaic cells, and FETs.

11:30 AM D14.10/I11.10

Tailored Doping and Modification of Indium Oxide Thin Films for Organic Photovoltaics with Increased Photoactivity. Michael T. Brumbach¹, Thomas Schulmeyer¹, Neal R. Armstrong¹, Simon Jones^{2,1} and Seth Marder²; ¹Chemistry, University of Arizona, Tucson, Arizona; ²Chemistry, Georgia Institute of Technology, Atlanta, Georgia.

Transparent conducting oxides (TCOs) are a significant component of molecular electronic devices such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs); however, the chemistry at the inorganic/organic interface has not been optimized. Small molecule chemisorption from solution or the gas phase has been developed as a strategy for enhancing the physical and chemical compatibility of the freshly deposited inorganic material with organic thin films, thereby increasing the chemical stability while tuning the effective work function and rates of charge injection. This contribution will discuss the effect of small molecule modified ITO interfaces with near-IR absorbing highly photoactive phthalocyanines (trivalent and tetravalent metal Pcs) in optimized Pc/C60 OPV devices. This scheme produces, on average, photopotentials which are higher by ca. 0.1 volts (as predicted from UV-photoemission studies) and higher photocurrents from near-IR excitation, than conventional phthalocyanine OPVs (e.g. those using CuPc/C60). New device architectures will also be presented which arise because of the development of low work function, highly conductive TCO films.

11:45 AM D14.11/I11.11

Properties of Polymer/Inorganic Semiconductor Interface Barriers Used in WORM Memories. Xin Xu and Stephen R. Forrest; Electrical Engineering, Princeton University, Princeton, New Jersey.

A simple, non-volatile, write-once-read-many-times (WORM) memory device can be formed by an organic-inorganic heterojunction (OI-HJ) diode that serves both as a fuse and a rectifier in a 2D memory array[1]. A layer of polyethylene dioxythiophene: polystyrene sulfonic acid (PEDOT:PSS) spun onto the surface of an inorganic semiconductor have been shown to form a highly asymmetric rectifying junction that can be open circuited on the application of current. For the first time, we analyze the nature of the PEDOT:PSS/SC (where SC=Si, InP, GaAs) heterointerface. A model for charge transport over this barrier is applied, and application to the analysis of the experimental data illustrate that thermionic emission over the PEDOT:PSS/inorganic contact barrier dominates at low current densities under forward bias. For the PEDOT:PSS/n-Si interface, for example, a contact barrier energy of Ebn=0.50+/-0.01 eV is obtained. There is no dependence of the measured barrier on the top contacting metal, indicating that control of charge in the rectifying junction is largely dependent on the organic/inorganic interface. Under reverse bias, the activation energy is (0.56+/-0.02 eV), or half the value of the Si bandgap, indicating that the reverse current is due primarily to generation-recombination in the Si bulk. Complementary results are obtained for a p-Si device. Polymer/III-V semiconductor heterojunctions will also be discussed in this work, which provides fundamental insights into the nature of charge transport across hybrid organic/inorganic interfaces. [1] S Moller, C Perlov, W Jackson, C Taussig, S R Forrest, Nature, 426, 166 (2003)