

N Plastic Electronics



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Symposium N

Plastic Electronics

Chairs

Peter HO, *Department of Physics, National University of Singapore, Singapore*

Hardy CHAN, *Department of Chemistry, National University of Singapore, Singapore*

Richard FRIEND, *Department of Physics, National University of Singapore; and Cavendish Laboratory, JJ Thomson Road, CB3 0HE, United Kingdom*

Correspondence

Peter HO

Department of Physics

National University of Singapore

Singapore

Email: phyhop@nus.edu.sg

Scope of Symposium

This symposium covers recent advances in the physics, chemistry and engineering aspects of solution-processed organic semiconductors for plastic electronics applications, including organic light-emitting diodes (OLEDs), thin-film transistors (OTFTs), photovoltaics (OPVs) and memory devices. We would like to emphasise advances in materials and device physics and chemistry, in device architecture, and in patterning and fabrication of devices and circuits. Materials classes covered include solution-processed pi-conjugated polymers and oligomers, graphenes, small molecules, self-assembled monolayers, dielectric materials, and conductor materials.

Symposium Topics

- Materials and device physics and chemistry
- Device architectures (OLEDs, OTFTs, OPVs, memories, and others)
- Novel solution-processing methods (inkjet and other forms of printing)
- Organic thin-film and interface morphology and structure-property correlations

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Abstracts

A00084-03662

Microwave Plasma Surface Modification of Polyimide for Improving Adhesion to Electroless Copper Metallization

Trieu NGUYEN; In-Seob BAE; Sang-Jin CHO;
Jin-Hyo BOO
*Department of Chemistry, Sungkyunkwan University,
Suwon, South Korea*

Microwave plasma was applied to the surface of polyimide (PI) films as a treatment to enhance the adhesion of electroless copper deposition layers. The influences of oxygen or/and nitrogen microwave plasma treatment of PI films on adhesion of electroless copper coatings as well as on the chemical composition of the film surface morphology were investigated at various operating parameters, namely, time, flow rate and discharge power. The surface morphologies of PI films before and after treatment were characterized with atomic force microscopy. The surface properties of PI films were identified with contact angle measurement. The results showed that the contact angle of untreated PI film was 72.1° reducing dramatically to 8.4° at the optimal conditions, 0.3 Torr of system pressure, 400 W of discharge power and 3 minutes of discharge time. However, the root mean square roughness of treated PI film at the optimal conditions had only a small increase at 1.5 nm in comparison with 1.1 nm of untreated PI films. Electroless copper depositions were carried with the free-formaldehyde method using glyoxylic acid as the reducing reagent. T-peel test was used to estimate relative adhesion strength. The characteristics of the modified PI films and the properties of the peel strength were discussed.

A00102-00345

Adsorption Structure of Organic Molecules Based on Coverage

Dandan GUAN; Fei SONG; Weidong DOU;
Han HUANG; Bin LV; Hanjie ZHANG; Haiyang LI;
Pimo HE; Shining BAO
*Department of Physics, Zhejiang University, Hangzhou,
China*

Organic materials have potential applications as organic light emitting diodes (OLEDs) and organic field transistors (OFETs). Due to the limitations of organic materials, such as the low conductivity or the low mobility of charge carriers, the molecular orientation and packing of the organic layer at the interface will significantly influence the charge transfer and separation. In this work, the adsorption structures of the highly symmetrical molecules (perylene and tetracene) on different substrate of Ru(1010) and Ag(110) have been studied. The results revealed that the

adsorption structure of organic molecules depends on the interaction between organic molecules and the interaction between organic molecule and the substrate. When the interaction between molecule and substrate is strong, the adsorption structure of organic molecules mainly relies on the molecule-substrate interaction. In this case, long range ordered structure was hardly formed. While the interaction between molecules is comparable to those between molecule and substrate and plays a manifested role in the growth process, the adsorption structure of organic molecule mainly depends on molecule-molecule interaction. With increasing the adsorption coverage of organic molecules, different well-ordered organic films will be formed.

A00149-01140

Tandem Polymer Solar Cells Processed from Solution

Ari Handono RAMELAN¹; Harjana HARJANA¹;
Yung Hsu FU²
*1. Research Center for Smart Materials, Department of
Physics, Universitas Sebelas Maret, Surakarta, Indonesia
2. Department of Materials Engineering, Mingchi
University of Technology, Taishan, Taiwan*

The emerging field of stacked layers in organic photovoltaic cells was investigated. Owing to the limited absorption width of organic molecules and polymers, only a small fraction of the solar flux can be harvested by a single-layer bulk heterojunction photovoltaic cell. Furthermore, the low charge-carrier mobilities of most organic materials limit the thickness of the active layer. Consequently, only part of the intensity of the incident light at the absorption maximum is absorbed. A tandem or multi-junction solar cell, consisting of multiple layers each with their specific absorption maximum and width, can overcome these limitations and can cover a larger part of the solar flux. In addition, tandem or multi-junction solar cells offer the distinct advantage that photon energy is used more efficiently, because the voltage at which charges are collected in each sub-cell is closer to the energy of the photons absorbed in that cell.

In this tandem cell a highly transparent titanium oxide (TiO_x) layer was used to separate the two sub cells of the tandem device. This transparent middle electrode demonstrates the possibility to realize fully solution-processed solar cells (tandem or multiple cells) without using vapor-deposited contacts. The advantages of using TiO_x for the middle electrode is the optical transparency of the layer and the compatible solvents used for processing all layers. The cell was processed onto a glass/ITO substrate covered by a 50 nm thick layer of PEDOT:PSS. The transparent TiO_x interlayer was fabricated by spin coating from methanol

solution by means of sol-gel chemistry. For the bottom bulkheterojunction (BHJ) cell a 140 nm thick layer of PCPDTBT:PCBM was used that was processed from chlorobenzene. The top BHJ cell was fabricated from a 180 nm thick P3HT:PC₇₀BM blend, which was processed from chloroform. The two sub cells have complementary absorption spectra, which leads to coverage of the whole visible and part of the infrared of solar spectrum by the tandem device. On top of the TiO_x interlayer layer, the highly conductive hole transport layer poly (3,4-ethylene dioxothiophene): polystyrenesulfonic acid (PEDOT:PSS) was spin coated. The photovoltaic cell was tested and investigated for its illuminated current density/voltage characteristics. Overall results are reported in the paper.

A00171-00841

A Rare Solution-Processable Molecular Host Material for Blue Phosphorescence Dopants in Organic Light-Emitting Diodes

Chin-Ti CHEN¹; Shun-Wei LIU¹; Min-Fei WU¹; Jwo-Huei JOU²; Wei-Ben WANG²; Mao-Feng HSU²
 1. Institute of Chemistry, Academia Sinica, Taipei, Taiwan
 2. Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

We present a novel, molecular host material, bis-[(3,5-di(9H-carbazol-9-yl)phenyl)diphenylsilane (SimCP2). SimCP2 possesses superb thin film amorphous stability, high charge carrier mobility, near balanced ambipolarity, and large triplet-state excitation energy. It has a high glass transition temperature of 144 °C, a high hole mobility of $6.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a nearly equivalent electron mobility of $4.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at an electric field of $1.6 \times 10^5 \text{ V cm}^{-1}$. SimCP2 has a sufficiently high triplet state energy of 2.9 eV, which is larger than most commonly used phosphorescence sky blue dopants, FIrpic (bis(3,5-difluoro-2-(2-pyridyl)-phenyl-(2-carboxypyridyl) iridium (III)), having $\lambda_{\text{max}}^{\text{em}} \sim 470 \text{ nm}$ (2.6 eV). We can simply use SimCP2 as the solution-processed host material in the fabrication of highly efficient phosphorescent organic light-emitting diodes (OLEDs) with external quantum efficiency as high as 17.7 % or power efficiency of 24.2 lm W⁻¹ at brightness of 100 cd m⁻². Moreover, it was found that the performance of all-solution processed OLEDs can be improved, when the device adopted SimCP2 as the doping component in PVK (polyvinylcarbazole) host material containing FIrpic dopant. Particularly, “efficiency roll-off”, a common problem found in most phosphorescence-based OLEDs, was much alleviated. Possible application of such unusual system in plastic electronics (OLED built on a flexible substrate) will be discussed.

A00200-04491

Filed-effect in Organic Thin Film with Wet Gate Dielectrics

Takashima WATARU¹; Andersson MATTIAS³; Kaneto KEIICHI²; Ingnas OLLE³
 1. Advanced Eco-fitting Technology, Kyushu Institute of Technology, Fukuoka, Japan
 2. Graduate School of Life Science and Systems Engineerings, Kyushu Institute of Technology, Fukuoka, Japan
 3. Department of Physics, Linkoping University, Linkoping, Sweden

Electronic double layer (EDL) capacitor is a candidate to from the metal-insulator-semiconductor (MIS) capacitor in organic field-effect transistor (OFET). We successfully demonstrated the OFET characteristics with pure liquid as gate-insulator. The OFET characteristics were identified to the dipole moment of liquid dielectric. Sensing application of volatic organic chemicals (VOC) was also demonstrated by using polymeric gate-insulator with vapor adsorptive functionality, in which the VOC adsorption caused to modulate the EDL capacitance.

A00241-00732

Donor-Acceptor Conjugated Polymers for Photovoltaic Applications

Wenjing TIAN; Yaowen LI; Shanpeng WEN; Jianing PEI; Lili XUE; Hui LI
 State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun, China

Donor-acceptor (D-A) conjugated copolymers have attracted considerable attention because their electronic and optoelectronic properties could be efficiently tuned by the intramolecular charge transfer (ICT) between the donor and acceptor, which is beneficial for the optoelectronic devices applications, such as light-emitting diodes (LED), photovoltaic cells (PVC), and field-effect transistors (FETs). Recently, ICT from an electron-rich (Donor) unit to an electron-deficient (acceptor) moiety has been extensively used to obtain low band gap conjugated polymers for photovoltaic applications. However, only relatively low performances of photovoltaic cells have been obtained due to the mismatch between the absorption of the polymer and the solar spectrum, low air-stability, and low carrier mobility of the polymers. Therefore, design and synthesize pi-conjugated polymers with the suitable absorption, high air stability, and high carrier mobility are the challenge in the research filed of photovoltaic materials. Herein, we reported the synthesis and characterizations of two series of D-A conjugated copolymers: PFPB, PPPB, PTPB, and PFTMT, PPTMT, PDTTMT. UV-vis absorption spectra of the two series copolymers showed that the absorption spectra were broadened and red-shifted with the increase

of donor ability, which indicated that the stronger electron-donating ability of the donor, the higher degree of the electronic delocalization and ICT of the polymer. Electrochemical properties of the polymers showed that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) level can be tuned by the donor and the acceptor moieties, respectively. The photovoltaic properties of the polymers were investigated by fabricating photovoltaic cells with the structure of ITO/PEDOT/polymer:PCBM/LiF/Al. The power conversion efficiency (PCE) of 1.55% was obtained for PPPB.

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A00279-02758

Highly Optical Transparency and Low Dielectric Constant of Fluorinated poly(ether ketone imide)s Derived from a Novel Unsymmetrical Diamine Containing Trifluoromethyl and Methyl Pendant Groups

Chenyi WANG; Guang LI; Jianming JIANG
College of Material Science and Engineering, Donghua University, Shanghai, China

Novel fluorinated poly(ether ketone imide)s (PEKIs) were prepared from an unsymmetrical diamine, 3-methyl-4-(4-amino-2-trifluoromethylphenoxy)-4'-aminobenzophenone, with three aromatic dianhydrides via a one-step high-temperature polycondensation procedure. All the obtained PEKIs could be soluble in some polar solvents. Flexible and tough PEKI films could be prepared by casting from polymer solution. The PEKI films exhibited highly optical transparency with a cutoff wavelength of 349–365 nm and good mechanical properties with tensile strengths of 78–91 MPa and elongations at break of 7.5–16.5%. They showed glass transition temperatures in the range of 238–271 °C and the 10% weight loss temperatures in the range of 517–530 °C in nitrogen atmosphere. Meanwhile, the PEKI films possessed low dielectric constants (1.95–2.20 at 1 MHz) and low moisture absorption (0.33–0.51%). Due to their properties, the fluorinated PEKIs could be considered as photoelectric and microelectronic materials.

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A00304-00565

Non-traditional Aromatic Systems Employed in the Design of New Organic Electronic Materials

John D. TOVAR^{1,2}

1. Chemistry, Johns Hopkins University, Baltimore, MD, United States

2. Institute for NanoBioTechnology, Johns Hopkins University, Baltimore, MD, United States

Although many of the current challenges in realizing the full potential of organic electronics will be met through new processing and engineering paradigms with established pi-conjugated materials, so too will new materials lead to new innovations and properties. To achieve new materials, development of new chemistry and exploration of new or uncommon electronic structures must be pursued. This contribution highlights some of these approaches as practiced in our labs at Johns Hopkins involving the molecular design of unusual pi-conjugated materials with non-traditional aromatic topologies, representative of the many exciting efforts being pursued in parallel in laboratories throughout the world. For example, larger aromatic systems beyond the 6-pi-electron ring should facilitate the electronic reorganization that accompanies charge injection. To illustrate this concept, a case study will be presented with two 10 pi-electron aromatic motifs, that of the aromatic cyclic polyene methano[10]annulene and of the more benzenoid aromatic, naphthalene. Thiophene-based semiconductors derived from the annulene show much greater propensities to delocalize charge as deduced from the structural changes that accompany electrochemical oxidation. The design, synthesis and electrochemical characterization of new organic electronic platforms built from 2 pi-electron aromatics and n-channel boron-based aromatics will also be addressed.

A00309-00636

Synthesis, Characterization and Optical Properties of Light-Emitting Polyfluorene Derivatives

Philaiwan AIAMSEN¹; David L. CARROLL²; Sukon PHANICHPHANT¹

1. Chemistry, Chiang Mai University, Chiang Mai, Thailand

2. Physics, Wake Forest University, North Carolina, United States

New single-polymer electroluminescent system containing three individual emission species of polyfluorenes as a blue host, 2,1,3-benzothiadiazole unit as a green dopant and phenylene derivative unit as a red dopant on the main chain were synthesized and characterized. All of the polymerizations were carried out by palladium(0) catalyzed Suzuki coupling reaction with equivalent molar ratio of the diboronic ester monomer to the dibromo monomers under dry argon protection. The monomers were bis(4,4,5,5-

tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-didecylfluorene, 4,7-dibromo-9,9-didecylfluorene, 4,7-dibromo-2,1,3-benzothiadiazole, and 1,4-dibromo-2,5-bis(8-quinolinyl) benzene. At the end of polymerization, small amount of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-didecylfluorene was added to remove bromine end groups, and bromobenzene was added as a monofunctional end-capping reagent to remove boronic ester end group. The mixture was precipitated in methanol and washed with acetone to remove oligomers and catalyst residues. The synthesized emitting polymers, Poly(fluorene-benzothiadiazole-quinoline) [PF-BT-QL] was found to be thermally stable and readily soluble in common organic solvents. The optical band gaps of polymers were 2.97 eV and 2.51 eV corresponding to Polyfluorene (PF) and PF-BT-QL respectively were calculated from the onset of UV-vis spectra. The fabricated light-emitting devices showed good performance in terms of turn on voltage and electroluminescence. The new PF-BT-QL copolymer was successfully used as emissive polymer layer in polymer light-emitting devices (PLEDs). By changing the molar ratios of these monomer units, the electroluminescence spectra can be adjusted to white-light emission.

A00357-01177

Characterization of Polymer Light-Emitting Diodes Interlayers using AFM and CS-AFM

Quirina FERREIRA¹; Ana CHARAS¹;
Gabriel BERNARDO¹; Luis ALCACER^{1,2};
Jorge MORGADO^{1,2}

1. *Technology and Materials, Instituto de Telecomunicacoes, Lisbon, Portugal*

2. *Dep. Eng. Química e Biológica, Instituto Superior Técnico, Lisbon, Portugal*

The formation of very thin layers of conjugated polymers on poly (ethylenedioxythiophene) doped with polystyrenesulfonic acid, PEDOT-PSS, known as interlayers, has been explored to improve polymer light-emitting diodes, PLEDs, efficiency and lifetime. The thickness of these interlayers can vary from less than 1 nm up to about 10nm, depending on the annealing conditions and on the conjugated polymer molecular weight. The nature of the interaction between PEDOT-PSS and the conjugated polymer that leads to the formation of the insoluble interlayer is still a matter of debate. The role it plays in PLEDs characteristics has been mainly related to hole transport, injection barriers and reduction of exciton quenching by PEDOT-PSS due to its separation from the luminescent layer.

We have recently reported on the use of cross-linkable polymers to form thicker interlayers. The properties of PLEDs with these thicker interlayers could be related to the frontier levels energy of the polymers forming

the interlayers. However, this relation was not found for PLEDs containing very thin (<1nm) interlayers.

To obtain further insight into the conjugated polymer distribution on top of PEDOT-PSS we have carried out AFM and current sensing AFM (CS-AFM) studies of the interlayers formed with a conjugated polymer of two different molecular weights. Scaling laws analysis was performed on the microroughness results obtained from non-contact AFM.

Phase separation is evidenced at the PEDOT:PSS surface, with the valleys showing higher current, which we associate to doped PEDOT. CS-AFM studies on the PFO-based interlayers showed the presence of electrical current domains, with current values and domain sizes depending of the PFO molecular weight. The results suggest a preferential deposition of PFO in the valleys, i.e. it is mainly anchored in the PEDOT rich regions.

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A00386-00919

NIR Direct Thermal Lithography of π -Conjugated Polymers (π CPs)

Terry J. GORDON; Han XU; Steven HOLDCROFT
*Department of Chemistry, Simon Fraser University,
Burnaby, Canada*

Patterning π -conjugated polymers (π CPs) is crucial for their application in organic microelectronic devices. Standard lithographic techniques require dedicated equipment and can involve multiple, elaborate processing steps. Alternative techniques for spatially-controlling the deposition of polymeric semiconductors with micron resolution are being investigated. A method being investigated in our laboratory makes use of the thermal lability of certain functionalized polymers. In this presentation, patterning of π CPs is reported wherein exposure of a NIR absorbing dye, incorporated into a π CP film, to a 830 nm NIR laser beam induces localized heating which initiates a thermal cleavage reaction. The latent image formed in the π CP film is further developed to yield negative tone patterns of the polymer. Direct thermal patterning of π CP films containing NIR dye offers the advantage of single step film preparation, rapid computer-to-plate direct patterning, and < 10 μ m resolution pixels.

A00407-00790

Aggregation-induced Photoluminescence Enhancement of Small Organic Molecule and PolymerYijie XIA; Jianyong OUYANG*Department of Materials Science and Engineering, National University of Singapore, Singapore*

The optical properties of conjugated organic compounds and polymers have attracted strong attention due to the interesting fundamental science and practical application. Here, we report a new observation of aggregation-induced photoluminescence enhancement of pyrene solution, which has interesting photoluminescence in dilute solution. Both the monomer emission and excimer emission increased when small amount of additive was added into the pyrene solution. The enhancement of the excimer emission is more than that of the monomer emission. The photoluminescence intensity enhancement by a factor of 4 was observed. The photoluminescence enhancement is attributed to the increase of the rigidity of the pyrene molecule induced by the additive. Based on this understanding, we also observed aggregation-induced photoluminescence enhancement on conjugated polymer. This finding may be helpful for the understanding and improvement in the photoluminescence of materials. It also has application potential in sensors.

A00427-01382

Dynamic Model for Magnetoresistance Effect in Organic Light Emitting Diode(OLED) based on Singlet-Triplet Exciton Conversion Enhancement in Magnetic FieldChavis SRICHAN; Tanom LOMAS;
Adisorn TUANTRANONT*Nanoelectronic and MEMS Lab, National Electronic and Computer Technology Center, Pathumthani, Thailand*

We propose a dynamic model based on singlet-triplet exciton conversion enhancement due to magnetic field to describe the newly discovered large magnetoresistance (MR) effect in organic light-emitting diodes (OLED). This effect are mostly negative magnetoresistive and reaches up to 10 percent in magnetic field of 10mT at room temperature. This model could be used to calculate dynamic exciton conversion rate. The condition for positive magnetoresistance are found based on this model.

A00443-01796

Selected-area in-situ Generation of Highly Fluorescent Organic Nanowire Embedded in Polymer Film: Solvent-vapor-induced Self Assembly ProcessJong Won CHUNG¹; Byeng-Kwan AN¹;
Fumio HIRATO²; Hiroshi JINNAI²; Soo Young PARK¹*1. Department of Materials Science and Engineering, Seoul National University, Seoul, South Korea**2. Department of Macromolecular Science and Engineering, Kyoto Institute of Technology, Kyoto, Japan*

The preparation of highly fluorescent one-dimensional (1D) nanostructures over the selected area of solid substrates is a challenging requirement for the realization of various future opto-electronic nanodevices. We present a novel method of fabricating fine 1D fluorescent organic nanowires (NWs) embedded in various polymer films through the combined process of photochemical lithography and solvent-vapor annealing (SVA). For that, we designed and synthesized a photoresponsive organic fluorophore bearing a self-assembly modulator, which can be *in situ* self-assembled into ultralong nanowires only in the desired regions of the polymer matrix *via* a simple selected-area SVA(S-SVA) process. This unique fabrication approach, combining photochemical lithography and SVA, eliminates the difficulties of transferring preformed 1D organic nanostructure onto fixed locations on substrates, thereby paving a new way to the practical opto-electronic nanodevice applications of organic nanostructure.

A00460-00957

Polymeric Piezoelectric Cantilever and Tubular ActuatorsSisi NI; Tao LI; Jan MA*School of Material Science and Engineering, Nanyang Technological University, Singapore*

Electroactive Polymers (EAPs), which could exhibit large strain and energy density, have attracted great deal of attention for both fundamental material research and enabling technology. Their unique properties make them highly attractive candidates for a broad range of practical applications, such as sensor, actuators, flexible electronics as well as biomimic applications. Among the EAPs, Poly(vinylidene fluoride) PVDF based polymer have been studied extensively due to their large piezoelectric response and clear molecular and crystalline structure. Physical and chemical modifications have been tempted to attain large strain, high energy density with small loss associated. The notable achievements in improving polymer properties herald promising potential for EAPs to fill niche areas where single crystals and piezoceramics are incapable of performing effectively. Nevertheless, the lack of established constitution relationships for EAPs limits

their usefulness to produce effective actuators. In order to fully realize the excellent electromechanical property of EAPs, efforts should be undertaken to produce an arsenal of effective EAP driven system by studying and modeling various possible configurations, such as unimorph, bimorph, tubular etc. In order to contribute to a better understanding on the uniqueness of this class of materials and facilitate the implementation of EAPs to practice, the present work investigates the feasibility of adapting cantilever and tubular configuration to the polymeric piezoelectric actuator.

Samples with four structures, unimorph, bimorph, simple tube and segmented tube (each had samples with varying geometry parameters and electrode), were fabricated from P(VDF-trifluoroethylene) [P(VDF-TrFE)] thin film. Their polarization and displacement were measured under both dynamic and static driving condition. The polarization loops for all the samples exhibit little hysteresis under weak-field and the P_{Max} changes linearly with V_{Max} for most samples. The frequency dependent polarization behavior is consistent with previous reported work. The displacement for both cantilever and tubular samples agree with the theoretical prediction provided taking into account of the variation of piezoelectric constant with the electric field. Significant displacement has been achieved for several samples even under weak-field (1079 μm displacement has been observed under electric field of 60V/ μm). For samples possessing same configurations yet different geometry parameters, the constitute relationship predict the performance well. In sum, the results and analysis suggest that the relationship between geometric variables (length, thickness and diameters) and the performance derived from ceramic material are also applicable to polymeric materials. Thus the modified constitute relationship can be used as a guideline for designing and optimizing the polymeric tubular actuators. Furthermore, the effect of silver and gold electrode have also been examined and discussed. By distinguish their advantages and disadvantages, improvement can be implemented to further optimizing the actuating system. Concepts obtained in present study can also be applied to EAPs other than P(VDF-TrFE). Therefore, with synergy from the continuous advancement in EAPs material properties, the skillful design of the configurations for polymeric actuators would provide wide range of actuation modes for diverse applications.

A00460-00961

Polymeric Piezoelectric Actuators with Helical Configuration

Sisi NI; Tao LI; Jan MA

School of Material Science and Engineering, Nanyang Technological University, Singapore

Large displacement generated from piezoelectric actuators with small dimensions is highly attractive or essential for

many advanced applications. Although the displacement obtained by actuators with relatively simple shape (blocks, plate and beams) could be enlarged through several various amplification mechanisms, complicated shapes provide a vital approach to further expand the range. In the last decades, several theoretical designs claim to generate large linear and rotational displacements using various structures based on helix, spirals and other curved forms. However, they suffer from the being difficult to manufacturing due to the rigidity of ceramic materials. Despite recent success on unconventional process for producing ceramic actuators with complicated shape, the rigid and brittle properties of ceramic materials have significantly limited the choice of configurations. In contrast, Electroactive Polymers (EAPs) present to be promising candidates to fully utilize the potential of complicated shapes with their flexibility and compliant nature. Compared to ceramics, the dielectric EAPs have low density, low cost, larger strain, higher energy density and is easier to process. Moreover, lead-free EAPs show better biocompatibility compared with widely used PZT, which makes it highly attractive candidates for biomedical components and biomimetic applications. Among the EAPs, Poly(vinylidene fluoride) PVDF based polymer have been studied extensively due to their large piezoelectric response and clear molecular and crystalline structure.

In present work, helical and super-helical samples made from Poly(vinylidene fluoride) film have been fabricated with an innovative yet simple procedure by taking advantage of flexibility of polymeric material. Their polarization and static displacement behavior under various driving voltage and frequencies have been measured and analyzed. The performance of the components was characterized and analyzed. It was found that the polarization varies linearly with the voltage within the range tested, as suggested by theory. For the simple helix samples, the radial displacement follows either linear or quadratic relationship with driving voltage in well defined pattern. This novel configuration can be incorporated into micro-pump for biomedical devices in various ways. One actuating mechanism of the helix can produce a calculated volumetric displacement ranging from 0.86 μL to 2.39 μL per stroke under 300V. For super helix sample, linear relationship is observed between the displacement and the driving voltage. Moreover, it exhibits significant displacement under driving voltage as low as 300 V. The results have shed light to the application of complex configuration with polymeric piezoelectric materials and their electromechanical response can be further enhanced with notable improvement in material properties. Therefore, the polymeric piezoelectric actuators with complicated shapes could play a key role in advanced applications, such as bio-inspired microrobotics, flat-panel speakers, micro-pumps, with the large displacements and versatile actuating modes they provide.

A00468-00866**Organic Memory Devices Based on Thin Films of Pentacene and Polymethylmethacrylate**

Mohammed F. MABROOK^{1,2}; Youngjun YUN¹;
Christopher PEARSON¹; Dagou A. ZEZE¹;
Martin TAYLOR²; Michael C. PETTY¹

1. *Engineering, Durham University, Durham, United Kingdom*

2. *Electronic Engineering, Bangor University, Bangor, United Kingdom*

Memory, in various guises, is a key component in modern computers. This can store extremely large amounts of data compared to five years ago; the USB memory stick is a typical example. However, as the size of microelectronic devices becomes ever smaller, new approaches and designs are needed to address many of the current silicon fabrication issues, e.g. scalability, fabrication on flexible substrates, room temperature processing and processing costs. Devices based on organic materials have the potential to overcome these problems. Until now, research into organic memory systems has focused on using nanoparticles for charge storage, e.g. gold, germanium, and aluminium. Such structures can operate as memories with high speed, high density, low voltage and low cost.

Here, relatively low-voltage operation of all organic memory devices based on metal-insulator-semiconductor (MIS) and organic thin film transistor (OTFT) structures is reported. The devices have been realised using thermally evaporated pentacene (semiconductor) and spin-coated polymethylmethacrylate (PMMA) (insulator). The drain and source electrodes have been fabricated by evaporating 30 nm gold, while the gate electrode was made from 100 nm evaporated aluminium on a clean glass substrate. A 40 nm thickness insulating layer was formed by spin coating PMMA (8 mg ml⁻¹ in chloroform) at 6000 rpm spinning speed. Pentacene was thermally evaporated at a pressure of 7.5×10^{-7} mbar, at a rate of 0.05 – 0.1 nm s⁻¹, to a thickness of around 40 nm. We demonstrate the use of gold nanoparticles, deposited at room temperature by chemical self-assembly technique, as charge storage elements incorporated into the OTFTs. Control devices without nanoparticles were also fabricated. Distinct capacitance-voltage (*C-V*) hysteresis is observed with a memory window that increases linearly with increasing voltage programming range. This is attributed to the presence of the nanoparticles and is almost certainly the result of their charging and discharging with the applied dc voltage. The counter-clockwise direction of this hysteresis indicates that the nanoparticles can become charged from the semiconductor surface. Current-voltage (*I-V*) characteristics at room temperature also show the memory behaviour of the fabricated OTFT memory devices. The detailed programming and erasing operations are discussed. Charging and discharging of the OTFT memory devices take place by applying different voltage pulses to

the gate electrode resulting in a clear shift in the threshold voltage. Charge retention properties reveal that the devices have non-volatile behaviour. The low fabrication temperature of the organic layers and the low cost are the main benefits of the fabricated memory devices. Also, the memory structures reported here offer a useful advance in the development of flexible organic memory devices.

Acknowledgement:

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A00484-00892**High Mobility and Low Hysteresis Pentacene Thin-film Transistors with Surface-modified High-k Oxide Gate Dielectrics**

Aifang YU; Qiong QI; Chao JIANG

National Center for Nanoscience and Nanotechnology, Beijing, China

High mobility and low hysteresis pentacene thin-film transistor (TFTs) were successfully fabricated by modifying the HfO₂ gate dielectrics with spin-coated hydroxyl-free polystyrene (PS) thin film. Initial nucleation and growth of the pentacene film on two kinds of dielectrics were observed by atomic force microscope (AFM). Various initial growth mechanism and morphology of pentacene film on different dielectrics highly associate with the observed mobility enhancement from 0.09 to 0.59 cm²/Vs. In contrast to three-dimensional island-like growth mode on HfO₂ surface, Stranski-Krastanov growth mode on smooth and nonpolar PS/HfO₂ surface was believed to be origination of the excellent carrier mobility of the TFTs. A large, well-connected first few monolayers with fewer boundaries was formed via Stranski-Krastanov growth mode, which facilitates a charge transport parallel to the substrate and promotes higher carrier mobility. Meanwhile, grain boundaries and/or surface scattering which limit the carrier transport were suppressed.

Negligible hysteresis is observed in current-voltage (*I-V*) measurements of the PS-modified pentacene TFTs. In our case, judging by the hysteresis direction, traps in pentacene thin film produced by poor growth and -OH on PS/HfO₂ interface might be responsible for the hysteresis. So, Stranski-Krastanov growth with large and dendritic grains on the OH-free PS/HfO₂ gate dielectric surface was estimated to contribute to the significant decrease in the hysteresis behavior. Moreover, gate leakage current is considerably reduced, which were evidenced from the decent output curves and the much higher output drain current.

A00572-01047

Charge Balance in High Efficiency Blue Phosphorescent Organic Light Emitting Diodes

Neetu CHOPRA; Jaewon LEE; Franky SO
Materials Science and Engineering, University of
Florida, Gainesville/Florida, United States

Organic light emitting devices have demonstrated the potential for solid state lighting as well as full color display applications. The efficiency and lifetime of OLEDs are being continually improved through numerous research efforts. Use of triplet harvesting phosphorescent materials in OLEDs has led to very high efficiency organic light emitting diodes especially in green and red phosphorescent OLEDs. However in case of blue OLEDs the efficiency achieved is still low and hence there is lot of room for improvement.

In order to improve the efficiency of blue OLEDs, it is important to understanding the factors limiting the device performance. One of the key factors affecting the device performance is charge balance. Charge balance is determined by the difference in carrier transport and injection of electrons and holes in the device. In most OLED devices, hole mobility of hole transport layer is orders of magnitude higher than the electron mobility of electron transport layer. We study how this affects the charge balance and hence the device performance in the blue phosphorescent OLEDs with Iridium (III)bis [(4,6-difluorophenyl)-pyridinato-N,C2'] picolinate (FIrpic) emitter. Charge balance is studied in these devices and the devices are found to be hole dominant. This is further verified by probing the location of the recombination zone in these devices. Additionally, the effect of charge balance on device performance is demonstrated with different electron transport layers. Upon tuning the charge balance, a very high efficiency of 60 Cd/A (50 lm/W) is achieved with 3,5'-N,N'-dicarbazole-benzene (mCP) host and the device shows a 3X improvement over previous results published with same host. Hence, charge balance was found to be a key factor limiting the device performance.

A00589-01073

Synthesis and Characterization of Electroactive Starburst Block Copolymers

Che-Jung HSU¹; Leeyih WANG²
1. Institute of Polymer Science and Engineering, National
Taiwan University, Taipei, Taiwan
2. Center for Condensed Matter Sciences, National
Taiwan University, Taipei, Taiwan

Recent studies have demonstrated that polymer composite particles with nonconjugated core and conducting polymeric shell possess a very low conductivity percolation threshold, enabling the mechanical and optical properties

of conjugated moieties to be optimized, such that they can be used practically in coating and optoelectronic industries. These core-shell particles are generally prepared by coating sterically stabilized latex, such as polystyrene, poly(methyl methacrylate), and polyurethane, with a thin overlayer of conducting polymers via in-situ oxidative polymerization. This work elucidates a novel route for synthesizing conductive core-shell-like polymer film by the solid-state oxidation polymerization of thieno[3,4-*b*]pyrazine-terminated starburst poly(methyl acrylate)s. This approach is easy to implement and rapidly produces a large uniform conducting film on almost any substrate.

The synthesis of these new block copolymers includes preparing 12-armed poly(methyl acrylate)s (PMA) by atom transfer radical polymerization method, followed by transferring the α -bromo ends in stars into hydroxyl moieties with ethanolamine and then capping them with 5,7-dithien-2-yl thieno[3,4-*b*]pyrazine to generate conjugated moiety-terminated star polymers. Finally, these peripheral groups were chemically linked by oxidative route to yield unimolecular core-shell nanoparticles. Chemical structure and molecular weight characteristics of the starburst polymer were characterized using IR, ¹H & ¹³C NMR and GPC techniques. The optoelectronic properties of these new electroactive polymers will be also presented.

A00610-01110

Effect of MoO₃ as an Interface Layer in High Performance Organic Photovoltaic Cells

Jegadesan SUBBIAH; Do Young KIM; Franky SO
Department of Material Science and Engineering,
University of Florida, Florida, United States

Organic solar cell has evolved as a potential alternative to conventional silicon based solar cells for sustainable energy sources due to its low production costs. One of the fundamental requirements for efficient operation of polymer solar cell is effective carrier extraction from the active layer to the electrode. However, poor understanding of interfacial phenomena of electrode and active layer limits the efficient charge collection and hence affects the cell performance. Here, we demonstrate that the power conversion efficiency (PCE) of both small molecule organic and polymer solar cells can be enhanced by using molybdenum oxide (MoO₃) as an anode interface layer. In this work, we have studied the effect of MoO₃ interface layer on small molecule organic as well as polymer photovoltaic cells. The devices we studied includes copper phthalocyanine (CuPc):C60, chloroaluminum phthalocyanine (ClAlPc):C60, poly(3-hexylthiophene (P3HT) : {6,6}-phenyl-C61 butyric acid methyl ester (PCBM), poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene (MDMO-PPV):PCBM bulk heterojunction cells. In both types of cells, the MoO₃

interface layer exhibits higher short circuit current (JSC) and higher fill factor (FF) resulting in higher PCE. Specifically, we have observed a 16% enhancement and a 38% enhancement in CuPc and P3HT cells, respectively. The enhanced device performance can be attributed to the reduction in contact resistance between the active layer and the anode due to the change in interface energetics by the MoO₃ interface layer. In addition, we also studied the effect of MoO₃ and poly (9,9'-dioctylfluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB) double interface layer in MDMO-PPV:PCBM cells and the performance of the cell shows that the double interface layer further enhances the power conversion efficiency compared to the single MoO₃ interface layer.

A00649-01165

Molecular Diodes and Functional Molecular Wires

Geoff ASHWELL

Centre for Advanced Functional Materials and Devices, Bangor University, Bangor, United Kingdom

Interest in molecular scale electronics now focuses upon non-invasive electrical contacting to isolated molecules and ultra-thin films as well as self-assembling components that act as molecular wires and molecular diodes, which may be considered as the organic counterpart of the pn junction. In these, a donor and acceptor are linked via a σ -electron bridge or, if sterically hindered, a π -electron bridge whereby the induced non-planarity breaks the conjugation and safeguards the integrity of the electroactive moieties.

The presentation will focus on the design of molecular diodes as well as increases in the rectification ratio from 5 at ± 1 V in 2001 to more than 10^4 at ± 1 V today. An *in-situ* step-by-step method of synthesising rectifying molecular wires on planar electrodes and across nano-sized electrode gaps has been developed. It involves the sequential reaction of chemical building blocks on solid supports and may be used to readily yield complex wire-like structures. Rectification occurs when one end of the wire is electron-donating and the other is electron-accepting and, in each case so far studied, the direction of forward bias electron flow is from the cathode to acceptor on one side and from the donor to anode on the opposite side. Significantly, the electrical asymmetry may be suppressed by ensuring that the molecular sequence is symmetrical and the bias for rectification reversed by sequencing donors and acceptors in the opposite sense. Dependence of the I-V characteristics on the donor-acceptor arrangement confirms that the behaviour is molecule induced.

Methods of contacting isolated molecules and self-assembled monolayers will be discussed. They include (a) magnetically induced contact to ultra-fragile organic

monolayers by using gold wire attached to a ferromagnetic cantilever and the field is controlled by a miniature solenoid; (b) *in-situ* step-by-step growth of molecular wires across predefined nano-sized electrode gaps in which the top and bottom gold contacts are separated by an insulating mushroom-shaped core and a single string "molecular necklace" may be self-assembled around its circumference.

A00649-01174

Growth of Functional Molecular Wires on Solid Supports

Susan BARNES; Aled WILLIAMS; Ben ROBINSON; Geoff ASHWELL

Centre for Advanced Functional Materials and Devices, Bangor University, Bangor, United Kingdom

This presentation will focus on the development of an *in-situ* step-by-step method for synthesising complex molecular wires on solid supports (e.g. gold and silicon electrodes) and it may be used to bridge molecules across nano-sized electrode gaps. The technique involves the self-assembly of suitable molecules to provide reactive groups (e.g. CHO) at the surface of a monolayer which is then followed by sequencing chemical building blocks with complementary ends (first NH₂ and then CHO) to extend the wires via the formation of imino links between component parts. The sequence as well as the length is user-defined and our work focuses upon conjugated wires that range from 2 nm to in excess of 10 nm.

Functionality may be induced by ordering the sequence. For example, rectification occurs when the wire is electron-donating at one end and electron-accepting at the other and, in every case, the direction of electron flow at forward bias is from the cathode to acceptor on one side and from the donor to anode on the opposite side. This dependence of the current-voltage characteristics on the donor-acceptor sequence confirms that the behaviour is induced by the molecule and we note that electrical asymmetry is suppressed by molecules in which the molecular sequence is symmetrical and that the bias for rectification may be reversed by altering this sequence.

In this work, the self-assembly of 4-[(3-mercaptophenylimino)-methyl]-benzaldehyde yielded a surface to react first 2,6-diaminoanthra-9,10-quinone and then terephthalaldehyde which were sequentially introduced to increase the molecular length before terminating with dimethylaminonaphthaldehyde. Formation of the imino link has been verified by X-ray photoelectron spectroscopy and the expected increase in molecular mass upon lengthening has been confirmed from the frequency change following deposition onto the gold electrodes of 10 MHz quartz crystals. Molecular wires with one to five anthraquinone units have been synthesised

and the dependence of the single molecule current and rectification ratio on the length of the electron-accepting anthraquinone bridge will be discussed.

A00691-01246

Time-Resolved Electroluminescence Studies of Ir(PPY)₃-based Organic Light Emitting Devices

Faxin ZANG; Michael KURNIAWAN; Tze Chien SUM; Alfred HUAN

Physics and Applied Physics, Nanyang Technological University, Singapore

Organo-transitional metal compounds with triplet emitters have attracted widespread attention due to its high efficiency. Theoretically, the efficiency due to a process called triplet harvesting can be as high as 100%. It is very likely that within some years, large flat panels and also small-size displays will be available. Other than the high efficiency, organo-transitional metal compounds are more desirable than pure organic compounds because of their short lifetime, which is in microsecond regime compared to the pure organic compounds which have lifetime in millisecond range. This advantage means that displays fabricated with the organo-transitional metal compounds can have a much faster refresh rate.

In this work, we report on the observations of a competing behavior between the 514 nm and 556 nm electroluminescence peaks in the time-resolved electroluminescence (TR-EL) spectra of Ir(ppy)₃-based organic light emitting devices (OLEDs). The Ir(ppy)₃ is doped in the CBP host with the mass ratio of 6:94. With this CBP doped with Ir(ppy)₃ being the Emissive Layer (EML), the OLED device is constructed from 2-TNATA/NPB as the Hole Transport Layer (HTL), TCTA as the electron blocking layer, BCP as the hole blocking layer, BPY-OXD as the Electron Transport Layer (ETL) and LiF/Aluminium as the Cathode. All of the layers are thermal deposited on the ITO substrate. The TR-EL data were collected using a streak camera based system where simultaneous spectra and temporal information is accessible. Temperature dependent time-resolved photoluminescence (TR-PL) and TR-EL measurements were also performed. Through comparing these TR-PL and TR-EL results, the origins of this competing behavior in the Ir(PPY)₃ system were also discussed in light of these new findings.

A00714-01465

Organic Photo-detector for Integrated Surface Plasmon Resonance Biosensors

Mihail BORA¹; Kemal CELEBI¹; Jorge ZUNIGA²; Colin WATSON⁴; Kaveh MILANINIA⁴; Marc BALDO²

1. Department of Physics, Massachusetts Institute of Technology, Massachusetts, United States

2. Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Massachusetts, United States

3. School of Electronic Engineering, Bangor University, Bangor, United Kingdom

4. Department of Materials Science and Engineering, Massachusetts Institute of Technology, Massachusetts, United States

Surface plasmon resonance (SPR) is a highly sensitive and powerful technique allowing real time, label free measurement of biomolecular interactions. Current techniques for SPR biosensing involve the use of carefully aligned optics, often resulting in large, costly systems. This work demonstrates progress toward an integrated, inexpensive, mobile device. Surface plasmons are electromagnetic waves which propagate along a metal/dielectric interface. They occur when plane-polarized light is incident (through a prism) upon the metal surface at the angle of total internal reflection. At this angle the wavevectors of the incident photons and electrons are matched resulting in energy transfer from the photon, inducing electron waves or surface plasmons. This process results in a corresponding dip in reflectivity of the incident light: any changes (caused, for example, by binding of biomolecules) in the refractive index of the adjacent dielectric media will cause a shift in the resonant angle. In this work, the traditional far-field detector has been replaced by a thin-film organic photovoltaic (PV) cell. The SPR condition is detected by coupling the electric field of the plasmon modes with generation of excitons within the PV. These excitons separate into holes and electrons at the donor/acceptor interface of the PV cell producing a photocurrent proportional to the plasmonic excitation. Test results show a strong correlation between the (plasmon generated) photocurrent and simultaneously measured reflectivity, which is dependent upon the incident angle. To perform the specific binding assay for neutravidin-biotin the gold layer was functionalized using a mixture of polyethylene glycol and biotin. With a baseline current established using a saline buffer, pulses of neutravidin were injected; the resultant photocurrent and reflectivity again showed similar sensitivity to binding events at the gold surface, demonstrating that the PV based near-field detector is comparable to the usual far-field device.

A00786-01402**Obtainment and Properties of Hybrid Langmuir-Blodgett Films of Xanthene Dye and Polyampholytic Polymer**

Niyaz IBRAYEV; Aitbek AIMUKHANOV;
Evgenia SELIVERSTOVA; Dmitry AFANASYEV
Institute of Molecular Nanophotonics, Karaganda State University, Karaganda, Kazakhstan

Obtainment method and transfer conditions of thin films of hydrophobically-modified polyampholytic polymer, namely poly(N,N-diallyl-N-octadecyl amine-alt-maleic acid) (PDOAM), and xanthene dye amphiphilic analog onto solid substrate surface are adduced. Mixed monolayers were formed at the water-air interface using Langmuir trough. The trough is equipped with a Wilhelmi pressure pick-up system, a lifting-dipping mechanism, and moving barriers. The compression rate of the polyampholyte monolayer was 0.0012 square nm/s/ repeat unit in the course of measuring π -A isotherm and transferring monolayer on substrate. The surface tension of twice-distilled deionized water was equal to 72.8 mN/m at pH=5.6 and temperature 20 Celsius. Fused nonluminous quartz was used as substrate. Mixed monolayers of the polyampholyte and the fluorophores were spread from ethanol/chloroform. The relative concentrations of dye in two-component monolayers of the polyampholyte and the fluorophore were 10, 25, 50, 75 mol %. Monolayers were transferred onto quartz supports by vertical dipping according to Y type transfer (transfer during downward the upward stroke only). The dipping speed through the monolayer was 0.02 mm/s. The thickness of the films was 20 monolayers. The stability of mixed monolayers of PDAOAM and the dye was studied. In the first case the change of monolayer area was studied at constant surface pressure (π =30 mN/m). During an observation period of 1h, the area changed only insignificantly within the first 10 min, and then became constant. In second case, at initial pressure the change of surface pressure upon stopping the barrier in the course of compression was observed. The surface pressure decreased only by 2 mN/m within 2 h. These results confirm the high stability of the PDOAM and dye monolayer. The π -A isotherms of the mixed monolayers of dye and the polymer differ considerably from those of the individual compounds. The surface pressure begins to rise at much lower surface areas, and the increase of the surface pressure upon compression is much steeper. The collapse area is about 125 square Angström per molecule with a collapse pressure of 30 mN/m for a molar mixing ratio of 50/50, and 105 square Angström per molecule with a collapse pressure of 36 mN/m for a molar mixing ratio of 10/90 (dye/polymer repeat unit). The strongly enhanced packing density of both components, of dye and polymer, in the mixed monolayers is observed. It might be explained by insertion of hydrophobic parts of dye molecules into the defectively packed octadecyl side chains of the polymer, as well as by a conformational

rearrangement of the hydrophilic parts of the polymer due to strong electrostatic interactions between the anionic groups of the PDOAM and cationic groups of dye.

A00795-01408**Organic Rectifying Junctions**

Benjamin ROBINSON;
Barbara URASINSKA-WOJCIK; Geoff ASHWELL
College of Physical and Applied Sciences, Bangor University, Bangor, United Kingdom

Molecular electronics represents the ultimate level of device miniaturisation, and as such highlights a way forward for future architectures of components in integrated circuitry. There has been considerable interest in molecular diodes – the organic counterpart of the semiconductor *pn* junction – but recent systems have consistently demonstrated inefficient current suppression at reverse bias when compared to conventional devices.

This presentation reports the progress from unimolecular diodes to ultra-thin organic rectifying junctions with improvement in their current rectification ratios. Design and deposition of these structures will be discussed. Unimolecular diodes comprise an electron-donating moiety separated, by a σ -bridge or a twisted π -electron bridge, from an electron-accepting moiety. In contrast, rectifying junctions, which consist of adjacent accepting and donating layers, may be formed *via* ionically coupling two electroactive components, for example, cationic acceptor and anionic donor.

This presentation will report recent results that demonstrate a considerable improvement of the rectification. The highest confirmed rectification ratio reported for a unimolecular system is *ca.* 150 at ± 1 V, a value too low to have any practical significance. Organic rectifying junctions that comprise discrete layers of cationic acceptors (4,4'-bipyridinium) and anionic donors (copper phthalocyanine-3,4',4'',4'''-tetrasulfonate) exhibit ratios of *ca.* 50-100 at ± 1 V. However, this is increased to an unprecedented ratio of greater than 10000 at ± 1 V *via* the incorporation of an ultra thin film of poly(*tert*-butyl methacrylate) to isolate the acceptor and donor. Additionally, the coupling of an anionic donor to a previously investigated unimolecular diode has shown an increase in ratio to greater than 1000 at ± 1 V.

These nano-scale organic systems mimic conventional semiconductor diodes, those discussed in this talk demonstrates rectification ratios comparable to, or better than, the electrical asymmetries obtained from metal-insulator-metal structures where oxide-induced Schottky barriers dominate the behaviour.

A00823-01430

Ion Transport Property Studies on Ag⁺ Ion Conducting Hot-pressed PEO-PVP Based Solid Polymer Electrolyte Membranes

Angesh CHANDRA¹; Rakesh AGRAWAL²;
Yugal MAHIPAL²

1. Department of Applied Physics, Shri Shankaracharya
Institute of Professional Management and Technology,
Chhattisgarh, India

2. School of Studies in Physics, Pt. Ravishankar Shukla
University, Chhattisgarh, India

The ion transport property studies on Ag⁺ ion conducting PEO-PVP based solid polymer electrolyte (SPE) membranes: (1-x) [90 PEO: 10 AgNO₃]: x PVP, where x = 0, 2, 3, 5, 7, 10, 15 (wt. %), are reported. SPE films were casted using a novel hot-press technique instead of the traditional solution cast method. The conventional solid polymeric electrolyte (SPE) film: (90 PEO: 10 AgNO₃), also prepared by hot-press method and identified as the highest conducting composition at room temperature on the basis of PEO-AgNO₃ - salt concentration dependent conductivity studies, was used as Ist -phase polymer electrolyte host into which PVP was dispersed as IInd - phase dispersoid. A conductivity enhancement of approximately two times from that of the pure SPE host could be achieved at room temperature for PVP-based SPE film composition: 98 (90 PEO: 10 AgNO₃) : 2 PVP. This has been referred to as Optimum Conducting Composition (OCC). The ion transport mechanism in SPE OCC has been characterized with the help of basic ionic parameters viz. conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}) etc.

A00859-01493

Inkjet Printing of Copper and Nickel Conductors for Flexible Electronics

Paul CALVERT

Materials and Textiles, UMass Dartmouth, MA,
United States

Inkjet printing can be used to deliver dots, lines and areas of material with a lateral resolution of about 100 microns and a thickness resolution of about 100 nm. By printing different materials sequentially it should be possible to build complex electronic or medical devices.

We have printed lines of copper and nickel conductors onto various flexible substrates by sequentially printing metal salt and reducing agent. We use multipass printing of alternating “colors” from a color cartridge filled separately with metal salt and reducing agent. Unlike silver, copper cannot normally be printed from nanoparticles because they oxidize in air. We find that this reactive approach produces heavily oxidized layers initially but highly

conducting unoxidized layers after multiple passes. This reactive method is generalizable to many other electronic materials.

Just as semiconductor manufacturing can draw on a wide range of materials and methods to make every-more complex structures, so we need to develop a palette of materials and methods to allow us to inkjet print new families of devices that incorporate metals, semiconductors, dielectrics and possibly biological molecules and cells. This talk will also summarize our efforts to print for antennas, diodes and sensors.

A00860-01492

Organic and Hybrid Electron-Transporting Solution-Processed Semiconductor Devices

Howard E. KATZ; Qingdong ZHENG; Byung Jun JUNG;
Bhola Nath PAL; Bal Mukund DHAR

Materials Science and Engineering, Johns Hopkins
University, Baltimore, MD, United States

While solution-deposited hole-transporting materials have been readily available for many years, there is a scarcity of electron transporters that can be solution processed and operated in air as parts of semiconductor devices. In this presentation, two new approaches to this goal will be discussed. First, we append long and remotely fluorinated side chains to tetracarboxylic diimide molecular structures to produce a series of molecular solids with electron mobilities on the order of 0.5 cm²/Vs. Among the core dimides used is the simplest one, pyromellitic tetracarboxylic diimide, which has long been thought to be a monomer strictly for use in constructing polyimide insulators. Because of the small conjugated area, such derivatives are suitable for solution-deposited electron-carrying semiconductors. As a complementary alternative, we have made all-solution-deposited devices using alumina-based dielectrics, ZnO-based semiconductors, and conducting polymer inks for source and drain, on ITO-glass. Mobilities in such devices exceed 20 cm²/Vs. Besides transistors, these new electron transporters are being utilized in self-aligned pn junctions, chemical sensors, and photovoltaic devices. In all cases, significant electron transport capability is maintained in the ambient atmosphere. In addition, many of the new semiconductors are transparent to visible light. Fabrication methods and device performance parameters will be discussed.

A00890-03809**Enhanced Switching Characteristics of Ferroelectric P(VDF-TrFE) for Organic Memory Devices**

Damar Yoga KUSUMA; Ahn Chien NGUYEN;
Pooi See LEE
School of Material Science and Engineering, Nanyang Technological University, Singapore

The switching dynamics in ferroelectric P(VDF-TrFE) is contributed by the amorphous phase and the crystalline phase as well as the interface between them. While the polarization reversal within the crystalline phase is almost instantaneous, the interfacial polarization is not. The interfacial polarization switching is limited by the availability and mobility of the compensating charges within the amorphous region. Hence, a slow polarization reversal in typical P(VDF-TrFE) film in the order of 10 ms is observed at 50MV/m and room temperature.

In this work, we report an approach to shorten the switching time of P(VDF-TrFE) film by blending with metallic nanoparticles into the ferroelectric polymer. Enhanced crystallization of the ferroelectric beta phase is observed with the addition of metallic nanoparticles as revealed from the X-Ray Diffraction analysis. Two electrode capacitors are fabricated for the switching time measurement. Ferroelectric response measurements give remanent polarization and coercive field at 10 $\mu\text{C}/\text{cm}^2$ and 50 MV/m respectively. Reduction in dielectric constant from 11.6 down to 7.7 is also observed with increasing nanoparticles content from 0 to 1 $\times 10^{-2}$ wt%. More than 50% decrease in switching time is observed for the blend with nanoparticles amount ranging from 1 $\times 10^{-6}$ to 1 $\times 10^{-2}$ wt%. The reduction in the switching time, however, occurs at the expense of increasing leakage current across the film when certain amount of nanoparticles inclusion is reached.

A00892-01567**Conductive Gels of Nanometer Organic Materials with Ionic Liquids**

Xiaoguang MEI; Jianyong OUYANG
Materials Science and Engineering, National University of Singapore, Singapore

Gels usually are soft and easy to handle. They have many unique applications, such as to replace the liquid electrolyte of dye-sensitized solar cells. It has been discovered that ionic liquids are good liquid for making gels with various materials. They can even form gels with carbon nanotubes. Here, we report a simple way to prepare conductive gels of nanometer organic materials with ionic liquids. The gels can be soft and highly conductive. Their appearance and properties can be readily tuned by adjusting the ratio of the organic material to ionic liquid.

A00897-01569**Electrochemical Cross-linking of Layer-by-Layer Polyelectrolyte Ultrathin Films**

Paralee WAENKAEW¹; Sukon PHANICHPHANT¹;
Advincula RIGOBERTO C.²
1. Department of Chemistry, Chiang Mai University, Chiang Mai, Thailand
2. Department of Chemistry, University of Houston, Texas, United States

Substituted polythiophenes and polycarbazoles are materials of great interest as charge-carrier transport materials and have been utilized in PLED and FET applications. The layer-by-layer (LbL) self assembly has been used to fabricate polymer thin films on any substrates. The multilayer polymer thin films are constructed by alternating adsorption of anionic and cationic polymers. Polyelectrolyte multilayer ultrathin films containing anionic poly[2-(thiophen-3-yl)ethyl methacrylate-co-methacrylic acid]; P(TEM-co-MA) and cationic poly[4-(9H-carbazol-9-yl)-N-butyl-4-vinyl pyridium bromide]; P4VPCBZ, were fabricated. The growth of multilayer ultrathin films was followed by UV-Vis absorption spectrophotometer and surface plasmon spectroscopy (SPR). The deposition of P(TEM-co-MA)/P4VPCBZ as multilayer self-assembled ultrathin films regularly grow which showed linear growth of absorbance and thickness with increasing the number of layer pair. The LbL multilayer films were electrochemically polymerized anodically by cyclic voltammetry (CV) to study the copolymerization behavior. Cross-linking of the layers was verified by UV-Vis and electrochemical surface plasmon resonance (EC-SPR) spectroscopy with good electro-copolymerizability.

A00921-01677**Structural, Optical and Morphological Properties of Poly(*p*-phenylene vinylene) based Polymer/Oligomer Blends for Organic Photovoltaic Applications**

Than Zaw OO¹; Teck Lip TAM¹; Lydia Helena WONG¹;
Nripan MATHEWS¹; Subodh MHAISALKAR¹;
Alan SELLINGER²
1. School of Materials Science and Engineering, Nanyang Technological University, Singapore
2. Department of Materials Science and Engineering, Stanford University, United States

Two oligomers, 2,5-bis(cyanomethyl)-1-methoxy-4-(2-ethylhexyloxy)-benzene-4 bromobenzaldehyde-1 pyreneboronic acid [hereafter called $\alpha\text{CNPhPyOPV}$] and 2,5-bis(aldehyde)-1-methoxy-4-(2-ethylhexyloxy)-benzene-4-bromophenylacetone-1-pyreneboronic acid [hereafter called $\beta\text{CNPhPyOPV}$] were synthesized. The structural difference between two materials lies on the position of cyano groups. The blends of the different weight

proportion of electron donating polymer MEHPPV [poly(2-methoxy-5-(2'-ethyl)-hexyloxy-*p*-phenylenevinylene)] and electron accepting oligomer CNPhPYOPV were prepared by solution blending technique. The blends were characterized in solid film by means of the x-ray diffraction (XRD), the atomic force microscopy (AFM), the ultraviolet-visible absorption and photoluminescence (PL) spectroscopic techniques. The photovoltaic devices with device configuration of indium tin oxide (ITO)/poly(3,4-ethylene dioxothiophene):poly(styrene sulfonate) (PEDOT:PSS) /polymer:oligomer blend/Al were fabricated. The enhanced solubility in 1,2-Dichlorobenzene is achieved with α CNPhPyOPV and it is postulated to improve the morphology and photovoltaic device property of the bulk heterojunction. The correlation among the structural, optical and morphological properties of the films and device performances has been studied.

A00945-01930

Organic Thin Film Transistors with Isotypic Heterojunction

Chengang FENG¹; Ting MEI¹; Pavel NEUZIL²

1. Nanyang Technological University, Singapore

2. Institute of Microelectronics, Singapore

In this report, pentacene and poly(N-vinylcarbazole) (PVK) employed as the isotypic channel layer, both hole transporters, were studied in the typical Organic Thin Film Transistors (OTFTs) structure. Since the highest occupied molecular orbital level of pentacene is closer to vacuum than that of the PVK, it can be expected that the field-induced carriers transfer to the pentacene despite the PVK being adjacent to the gate dielectric. Compared to the performance of pentacene based OTFTs without PVK, this heterostructure device possesses an enhanced field-effect mobility in pentacene ($0.2 \text{ cm}^2/\text{V}\cdot\text{s}$), and a higher on/off current ratio of larger than 10^4 , benefiting from the discontinuities in energy levels at the hetero-interface and improved interface property between SiO_2 the dielectric layer and pentacene. This provides a simple way to enhance the functionality in OTFT structure.

Acknowledgements:

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A00982-03629

Determination of Localized-state Distributions and Charge-carrier Mobility in Organic Light-emitting Diodes by Impedance Spectroscopy

Takayuki OKACHI; Takashi NAGASE;

Takashi KOBAYASHI; Hiroyoshi NAITO

Department of Physics and Electronics, Osaka Prefecture University, Osaka, Japan

Impedance spectroscopy (IS) enables us to obtain physical quantities governing device characteristics of organic light-emitting diodes (OLEDs) such as charge-carrier mobilities and localized-state distributions. In this presentation, we propose a method for the determination of localized-state distributions in OLEDs by IS measurements, and apply the method to the study of localized-state distributions in polyfluorene-based Green K (SumationTM) light-emitting polymer (LEP). We show that IS measurements are simple and accurate, and hence are a powerful tool for the simultaneous determination of localized-state distributions and drift mobility in organic semiconductors.

The analytical expressions relating impedance spectra to a localized-state distribution have been derived on the basis of a theory for single-injection space-charge-limited current in the presence of localized states. The localized-state distributions can be determined from the frequency dependences of conductance and capacitance. IS measurements were carried out using a Solartron 1260 impedance analyzer with a 1296 dielectric interface in the frequency sweep range from 10 mHz to 10 MHz.

We have determined the frequency dependences of conductance and capacitance of electron-only device (EOD: Al/Green K LEP (72 nm)/Ba/Al) and hole-only device (HOD: ITO/PEDOT:PSS/Green K LEP (69 nm)/Au), where ITO and PEDOT:PSS are indium-tin-oxide and poly(3,4-ethylenedioxythiophene)/polystyrenesulphonic acid, respectively. The localized-state distributions below the conduction-band mobility edge E_c and above the valence-band mobility edge E_v were calculated. The localized-state distributions consisting of two exponential tails are mapped out in energy range about 0.4-0.8 eV below E_c and above E_v . The characteristic temperatures of conduction-band tail state are $T_0=190$ and 350 K, and those of valence-band tail state are $T_0=170$ and 480 K. Studies of operation mechanisms and degradation processes in thin organic devices such as OLEDs and organic solar cells will be possible on the basis of information on localized-state distributions and drift mobility determined by IS measurements.

A00990-02202**Effect of Solvents on Film Morphology for Application in PV**

Jun Yan LEK; Lifei XI; Teddy SALIM;
Lydia Helena WONG; Yeng Ming LAM
School of Materials Science and Engineering, Nanyang Technological University, Singapore

Development and research on renewable solar energy become more and more important as one of the remedies for energy crisis. Organic photovoltaics (OPV) devices offer attractive properties such as low-cost, low-weight, large scale and mechanical flexibility. Bulk heterojunction device made of Poly (3-hexylthiophene) (P3HT) and fullerene-derivative is one of the most promising OPV systems. However, PV performance is limited by the low charge carrier mobility in fullerene. Inorganic chalcogenide nanoparticles as well as nanorods, possess better electron mobility by providing percolation pathway for the charges to flow. Performances are enhanced with increasing rod length but long rods suffer from the limited solubility in solvents. Binary solvent mixture of pyridine and chloroform was used to dissolve P3HT CdSe blends. In order to improve the nanorods dispersibility in solvent and film nanostructure, different solvents have been investigated to replace chloroform. The photovoltaic and optical properties were studied too.

A00990-04021**Thermal-Free Approach in Improving Organic Photovoltaic Devices Based on Polythiophene and Fullerene Blends**

Jun Yan LEK; Hong LI; Teddy SALIM;
Lydia Helena WONG; Yeng Ming LAM;
Subodh MHAISALKAR
School of Materials Science and Engineering, Nanyang Technological University, Singapore

Organic thin film solar cells that is made up of polythiophene and fullerene moieties is known to benefit substantially from having good organization in the polythiophene components. Solvent annealing has been recently employed as one of the thermal-free approaches in reorganizing polythiophene chains in such an as-cast film. In this study, we found that device performance is strongly correlated with the annealing time and an optimum annealing condition. We have also coupled this approach with indium-tin-oxide (ITO)-free substrates based on poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). PEDOT:PSS sheet resistance have been improved with the use of additives such as dimethyl sulfoxide (DMSO) and ethylene glycol. By avoiding the use of ITO and thermal annealing, we have provided a solution for the low-cost fabrication of highly efficient organic solar cells on flexible substrate.

A01017-01772**Relative Interdependence of Processing Parameters on the Ordering and Performance of P3HT:PCBM Solar Cells**

Ayse TURAK¹; Jonas HANISCH²; Esther BARRENA¹;
Udo WELZEL¹; Franziska WIDMAIER²;
Erik AHLWEDE²; Helmut DOSCH¹
1. Low Dimensional and Metastable, Max Planck Institute for Metals Research, Stuttgart, Germany
2. Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW) Baden-Württemberg, Stuttgart, Germany

Photovoltaic devices based on organic semiconductors offer a promising avenue for renewable energy sources; however, for tailoring device design, a microscopic understanding of the key structural parameters affecting the device performance is necessary. We report a grazing incidence x-ray study of the bulk polymer microstructure and its effects on the performance of P3HT:PCBM solar cells. While we clearly find enhancement in the open circuit voltage and cell efficiencies upon different processing conditions and upon introduction of a LiF interlayer at the cathode/polymer interface, we could not – in contrast to current wisdom – always correlate this observation with associated modifications in various aspects of the bulk microstructure of the organic layer in all cases. Devices produced far from optimal conditions can be improved by thermal annealing induced changes to the bulk crystal structure; closer to the optimal morphology and crystal structure, post-processing mostly affects the interfaces. Unlike previous studies, which usually examine optimized films grown on Si, without an inorganic electrode layer, we directly examined films in device architectures. The results strongly indicate that engineering of the interfaces is necessary for future device optimization.

A01021-01776**Surface Morphology and Electrical Characteristics of Electrochemically Synthesized H₂SO₄-doped Polypyrrole (PPy)**

Menandro MARQUEZ; Marvin HERRERA
IMSP, University of the Philippines Los Banos, Philippines

Polypyrrole (PPy) film was synthesized using an electrochemical method with sulfuric acid as dopant. The following conditions were imposed in fabricating the film; (1) 13.0 V driving potential, (2) aluminum plates as electrodes (3) sulfuric acid as electrolyte. Fourier Transform Infrared Spectroscopy (FTIR) verified the production of PPy in the aluminum substrate. Scanning Electron Microscopy (SEM) on the other hand was used in characterizing the surface morphology of the film while linear four point probe was used to determine the bulk resistivity of the

film. Final result from these characterizations showed that surface roughness and bulk resistivity increases with the rate of electrochemical synthesis.

A01040-02315

Small-signal Admittance Measurements: A Diagnostic Tool for Organic Electronic Devices

David Martin TAYLOR

School of Electronic Engineering, Bangor University,
Bangor, United Kingdom

Small-signal a.c. measurements have proved particularly useful for investigating the behaviour of inorganic devices. This presentation will show that the technique can be applied to great effect not only for identifying the process occurring in organic devices but also for extracting values of the essential parameters that define device operation. Examples of systems that have been investigated and which will be discussed include those described below. Following the approach first advocated for silicon devices, we show that the energetic density of states for hole trapping states at the semiconductor-insulator interface in organic metal-insulator-semiconductor (MIS) devices is readily determined for the case of a p-type semiconductor such as poly(3-hexylthiophene). Minority carrier effects at the semiconductor-insulator interface can be investigated using photocapacitance measurements. Furthermore, the relatively low bulk mobility of holes in P3HT (and other organic semiconductors) gives rise to a Maxwell-Wagner dispersion in the mid-frequency range, 1-100 kHz, which is sensitive to phase changes in the semiconductor and to the degree of charge injection from the electrode into the semiconductor. This effect is also observed in notionally undoped semiconductors such as pentacene. A thin film transistor (TFT) with appropriate structure, in particular one with self-aligned gate geometry, is amenable to analysis using small-signal measurements and provides an alternative technique for measuring carrier mobility in the accumulation channel. Recently, application of the technique proved useful in identifying pre-switching events in resistive random access memory (RRAM) devices. We are now applying the technique in the study of organic photovoltaics where effects similar to those occurring in organic light emitting diodes (OLEDs) are observed. In the latter case, Bruetting in Germany has shown that the technique can identify charge trapping effects at the interface between the electron and hole transporting layers, an effect that has been related to the loss of efficiency due to ageing in OLEDs. Minority carrier effects, space-charge limited carrier transport and recombination processes all contribute to the small-signal response and can be investigated using the technique.

A01065-01853

The Influence of Hole-Transporting Layer on The Performance of White-Electrophosphorescent Devices

Yu WANG^{1,2,3}; Yulin HUA^{1,2,3}; Xiaoming WU^{1,2,3};
Lijuan ZHANG^{1,2,3}; Qingchuan HOU^{1,2,3}

1. Institute of Materials Physics, Tianjin University of
Technology, Tianjin, China

2. Key Laboratory of Display Materials and Photoelectric
Devices, Ministry of Education, Tianjin, China

3. Tianjin Key Laboratory of Photoelectric Materials and
Device, Tianjin, China

We demonstrate high-efficiency, white organic light-emitting devices based on different hole-transporting layers with two structures of indium tin oxide (ITO)/N, N'-bis(naphthalen-1-yl)-N, N'-bis(phenyl)-benzidine (NPB) / 4, 4'-N, N'-dicarbazole-biphenyl (CBP): bis[1-(phenyl)isoquinoline] iridium (III) acetylacetonate [Ir(piq)₂(acac)] / CBP / CBP: N-(4-((E)-2-(6-((E)-4-(diphenylamino)styryl)naphthalen-2-yl)vinyl)phenyl) -N-phenylbenzenamine (N-BDAVBi)/ 2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline (BCP) / (8-hydroxyquinoline) aluminum (Alq₃) / LiF / Al and ITO / PVK: TPD / CBP: Ir(piq)₂(acac)/CBP: Ir(ppy)₃ / CBP: TBPe / BCP / Alq₃ / LiF / Al. These structures possessed the maximum luminous efficiency of 9.25 cd/A at a current density of 0.17 mA/cm² and 11.9 cd/A at 0.015 mA/cm², respectively. As the brightness varying from 5 to 14 300 cd/m², the Commission Internationale De L'Eclairage coordinates of the former changed only from (0.47, 0.33) to (0.35, 0.32), while the latter varied only from (0.31, 0.30) to (0.38, 0.29).

In addition, we also investigate the influence of the thickness of NPB on the performances of the devices. The enhanced performances of the latter can be attributed to the improvement of charge balance by introducing the PVK: TPD layer to reduce the hole-transporting.

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A01083-01878**Host-Guest Energy Transfer in DCM Doped Zn(mq)₂**Deepa RAJWAR^{1,2}; Ritu SRIVASTAVA²;
M. N. KAMALASANAN²; A. C. GRIMSDALE¹

1. School of Materials Science and Engineering,

Nanyang Technological University, Singapore

2. Centre for Organic Electronics, National Physical
Laboratory, Delhi, India

Zn(mq)₂ has been developed as a new green emitter similar to Alq₃. The emission colour of Zn(mq)₂ can be changed by using suitable dye. This paper reports the energy transfer mechanism from excited Zn(mq)₂ molecules to dopant dye (DCM) molecules. In this system energy transfer from Zn(mq)₂ molecule to DCM dye dopant takes place via exciton diffusion, giving rise to a shift in the emission spectrum from green to red as DCM concentration increases from 0.05 wt% and 3 wt%.

A01191-02409**Aggregation-induced Enhanced Emission and Amplified Spontaneous Emission from Imidazole-containing Excited-state Intramolecular Proton Transfer Molecules**Sanghyuk PARK; Seong-Jun YOON; Jong Won CHUNG;
Ji Eon KWON; Soo Young PARKDepartment of Materials Science and Engineering, Seoul
National University, Seoul, South Korea

For the practical application of fluorescent organic molecules, higher solid-state luminescence efficiency is generally required, because the actual devices such as organic light-emitting diodes (OLEDs) and organic lasers generally demand highly dense solid-state systems. In this respect, the excited-state intramolecular proton-transfer (ESIPT) materials are one of the most promising candidates due to their characteristics of large Stokes' shifted emission without self absorption, which minimize the spectral loss, as a consequence of its 4-level nature. However, the intermolecular interactions in the condensed phase often give rise to the problem of significant concentration quenching in the fluorescence intensity, which is a serious challenge in the ESIPT materials as well. Recently, we have demonstrated that either the site-isolation by dendritic architecture or the specific J-aggregation with favorable intermolecular interaction could effectively suppress the concentration quenching and even enhance the fluorescence emission in the solid state. As a continuing effort in this work, we came to report a novel class of imidazole-containing ESIPT molecules with high solid-state luminescence efficiency ($\Phi_{\text{pl}} \sim 0.52$) in this work. It was found that the unexpectedly high efficiency is attributed to the aggregation-induced enhanced emission (AIEE) phenomenon working on the principle of restricted

molecular motion together with simultaneous frustration of the intramolecular charge transfer. Making use of the characteristic large Stokes' shifted emission and 4-level photocyclic scheme of ESIPT process, it was demonstrated that the synthesized HPI-CF₃ molecule showed low-threshold amplified spontaneous emission (ASE) in a single crystal.

A01209-02103**High-Performance OTFTs from Solution-Processable Dithieno[3,2-b;2',3'-d]thiophene-based Polymer Semiconductors**Jun LI^{1,3}; Chang Ming LI²; Wei ZHANG³; Jingui QIN³;
Zhikuan CHEN¹; Beng S. ONG¹1. Institute of Materials Research and Engineering,
Singapore2. School of Chemical and Biomedical Engineering,
Nanyang Technological University, Singapore3. Chemistry Department, Wuhan University, Wuhan,
China

In this presentation, we report a new class of solution-processable polymer semiconductors, poly(2,6-bis(3-alkylthiophen-2-yl)dithieno[3,2-b;2',3'-d]thiophene)s (PBTDT) through rational molecular design to achieve good solution-processability, efficient self-assembly, and greater ambient stability.

Preparation of nanoparticle dispersion of poly(2,6-bis(3-alkylthiophen-2-yl)dithieno[3,2-b;2',3'-d]thiophene) polymer semiconductor in an environmentally benign solvent is described. This nanoparticle dispersion has enabled fabrication of a high-performance organic thin-film transistor (OTFT) which exhibits excellent thermal stability and resistance to photo-induced oxidative doping as well as high field-effect mobility and current on/off ratio. This is in sharp contrast to most high-mobility polymer semiconductors which require toxic chlorinated aromatic solvents for fabrication to achieve high mobility. The use of non-toxic processing solvent eliminates the safety concerns associated with use of chlorinated aromatic solvents, thus potentially rendering mass manufacturing of OTFT possible.

A01277-03527

Three-dimensional Anisotropic Density of States (DOS) and Carrier Mobilities in Solution Grown Organic Single Crystals Measured by Space-Charge Limited Current (SCLC)

Alessandro FRALEONI-MORGERA¹;
Beatrice FRABONI²; Anna CAVALLINI²

1. Sincrotrone Trieste SCpA, Trieste, Italy
2. Department of Physics, University of Bologna, Bologna, Italy

Organic single crystals (OSCs) are attracting growing interest under the point of view of a useful source of information for clarifying the charge transport mechanisms in organic materials. They represent in fact ideal paradigms of organic materials for electronics: absence of defects related to grain boundaries, well defined geometrical disposition of molecules, high degree of order, reproducible results, good charge transport properties with respect to those of polymeric or multicrystalline organic thin films.

In this view, OSCs are also ideal to probe the anisotropic transport expected for intrinsically asymmetric systems such as the organic ones. Indeed, many reports about two-dimensional anisotropy of the transport properties of OSCs have been issued recently.

Here we present a study on the three-dimensional anisotropic electronic properties of several different samples of OSCs made up from 4-hydroxycyanobenzene, 4HCB) easily and effectively grown from solutions. In particular, using the Space-Charge Limited Current (SCLC) method for studying the charge transport, we determined the charge mobility in all the three dimensions of the crystals, obtaining highly reproducible and markedly anisotropic values for the hole mobilities (i.e. 5×10^{-2} cm²/Vs for the main axis a, 5×10^{-3} for the axis b and 3×10^{-6} cm²/Vs for the axis c, i.e. along the crystal thickness; all the values are averaged over measurements carried out over 30 different crystals.

The SCLC-determined mobilities are in very good agreement with those previously obtained, for other solution-grown crystals of the same material, by FET techniques, pointing to the likely intrinsicity of these values for the considered crystals.

In addition, the SCLC technique allowed us to determine the Density of States (DOS) distribution of deep trap states. This distribution for 4HCB crystals resulted also clearly and reproducibly anisotropic along the three different dimensions of the crystals, being centered at 0.49, 0.50 and 0.45 eV for the axes a, b and c, respectively. The corresponding activation energies and concentrations have been also determined, and resulted to be anisotropic in the three dimensions as well.

A01307-02287

Improvement of Charge Injection in Organic Solar Cells by Introduction of an Ultra-thin Interlayer of Dithiapyranylidene

Stephane BERNY; Ludovic TORTECH; Denis FICHOU
Organic Nanostructures & Semi-Conductors Laboratory,
Universite Pierre et Marie Curie, France

Charge injection at the organic/inorganic interfaces is a key issue for reaching high efficiencies in organic photovoltaic (OPV) devices. Well-known surface treatments of the ITO electrode such as deposition of PEDOT:PSS thin films or alkythiols self-assembled monolayers increase the ITO work function and lowers the interfacial resistance, thus resulting in the improvement the OPV device performances.

In this work we show that evaporation on ITO of an ultra-thin film of dithiapyranylidene (DITPY), a novel family of sulfur-containing organic compounds having a conjugated quinoïd core, increases by more than 20% the current density of OPV devices based on P3HT:PCBM as the active material. It appears that the HOMO and LUMO of DITPY as determined by optical absorption, cyclic voltammetry and UPS, are suitably located to create a weak injection barrier with ITO. Furthermore, thermally evaporated thin films of DITPY are polycrystalline with monodisperse grains due to an efficient intermolecular π -stacking. Finally, current-detection AFM of DITPY thin films reveals large areas of highly conducting pathways and hole mobility values more than 10 times higher than that of P3HT.

In conclusion, DITPY thin films possess the appropriate structural and electronic properties to make them very promising as electroactive interlayers in OPV solar cells.

A01325-02324

Three-Dimensional Molecular Packing of Thin Organic Films of PTCDI-C₈ Determined by Surface X-ray Diffraction

Tobias N. KRAUSS¹; Esther BARRENA^{1,2};
Dimas G. DE OTEYZA¹; Xue N. ZHANG¹;
János MAJOR¹; Volker DEHM³; Frank WÜRTHNER³;
Helmut DOSCH^{1,2}

1. Max-Planck-Institute for Metals Research, Stuttgart, Germany

2. Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Stuttgart, Germany

3. Institut für Organische Chemie, Universität Würzburg, Würzburg, Germany

Small conjugated organic molecules have yielded encouraging performance in organic field effect transistors (OTFTs) because, in contrast to polymers, they can be

grown in highly ordered films whereby the charge carrier mobility can largely be improved as the degree of order in the thin films increases. The determination of the molecular orientation and packing of organic semiconductors in the thin film geometry (which may be significantly different from its bulk structure) is a crucial input for modeling the electronic band structure and the associated intrinsic charge-transport properties.

We report for the first time the 3D molecular packing and thin film structure of the archetype organic *n*-type semiconductor *N,N'*-dioctyl-3,4:9,10-perylene tetracarboxylic diimide (PTCDI-C₈) determined by surface x-ray diffraction. The strongly increasing interest in this organic system has been sparked by the most compelling results obtained for its OFET performance making perylene diimide (PTCDI) derivatives promising and versatile materials to fabricate *n*-channel OFETs.

This compound forms extraordinary well-ordered films on single crystalline Al₂O₃ and on SiO₂. By combining x-ray reflectivity, grazing incidence x-ray Diffraction (GIXD) and atomic force microscopy (AFM) we elucidate the structure, morphology and molecular packing of PTCDI-C₈ films. The thin-film structure is found to consist of a triclinic unit cell which differs significantly from the bulk structure. The plane of the aromatic core is found to be tilted by ~ 67° with respect to the surface plane. The 3D crystallites extend with vertical coherent order across the entire film thickness. In addition, the influence of different substrate temperatures and the effect of a post-annealing will be discussed in detail.

A01329-03342

Effect of TiO₂ Nanoparticles on Organic Solar Cells Based on Fullerene/ Poly (3-octyl-thiophene-2, 5-diyl) Using Inkjet Printing Technique

Ashkan SHAFIEE¹; Muhamad MAT SALLEH¹; Muhammad YAHAYA²

1. *Institute of Microengineering and Nanoelectronics, University Kebangsaan Malaysia, Selangor, Malaysia*
2. *School of Applied Physics, University Kebangsaan Malaysia, Selangor, Malaysia*

Organic solar cells (OSC) have become a focus of attention to provide the new low cost, low weight and flexible energy sources. Nevertheless there are still challenges to improve their low efficiency comparing to silicon counterparts. Novel deposition methods such as inkjet printing technique may help to prepare high quality thin films and more efficient devices consequently. Furthermore nanoparticles such as TiO₂ are employed to enhance the organic solar cells performance. In this paper the effect of TiO₂ nanoparticles on inkjet printed organic solar cells have been studied. The main devices consist of an active layer sandwiched between ITO bottom electrode

and aluminum as top electrode. Two different devices with two different active layers were fabricated and were characterized under dark and illumination. Active layers of device consist of a blend of [6, 6]-Phenyl C61 –butyric Acid 3-ethylthiophene ester (PCBE) as acceptor and Poly (3-octyl-thiophene-2, 5-diyl) (P3OT) as the donor with TiO₂ and without TiO₂ nanoparticles. Based on current density- voltage characterization, it has been shown that the devices show higher efficiency in presence of nanoparticles. Further studies to improve the performance in terms of annealing the device using microwave oven and TiO₂ concentration are described.

A01357-02375

Interplay between Supramolecular-organization and Optical Properties of Blue-emitting PPVs with Fluorinated Vinylene Units

Maria LOSURDO¹; Maria GIANGREGORIO¹; Pio CAPEZZUTO¹; Antonio CARDONE²; Gianluca FARINOLA²; Francesco BABUDRI²; Giovanni BRUNO¹; Francesco NASO²

1. *CNR-IMIP, Italy*
2. *Chemistry, University of Bari, Italy*

There has been growing interest in developing new semiconducting polymers for applications in optoelectronics (OLEDs), photovoltaics, thin film transistors and sensors, due to their exceptional processability and appealing characteristic of manipulating electronic and optical properties by tuning of molecular structure and self-assembling.

For applications based on optical emission, the ability to tune emission colors is essential.

In this frame, there is interest in stable deep-blue emitting polymers.

In this contribution, we present the synthesis and properties of thin films of a new class of poly(p-phenylenedifluorovinylene) (PPDFV), which contain two fluoro atoms in the vinylene units. This class of fluoropolymers is effective in reducing the barrier of electron injection. Specifically, we report on the correlation existing between the structure and optical functionality of thin films of poly-methoxy-ethylexyloxy-phenylenedifluorovinylene (MEH-PPDFV).

In particular, we demonstrate that the above films have the largest HOMO-LUMO transition energy (above 3.75eV) ever reported for organic films and intense room temperature blue photoluminescence at 450nm and electroluminescence at 500nm. Films of the above polymers have been deposited by spin coating and drop-casting on a variety of substrates including Corning glass, quartz, ITO. Since, the performance of organic materials in devices is

strongly dependent on self-assembly of polymer in the solid state, which induces a modulation of morphological and optical properties, we discuss the effects of deposition methodology, substrate and film thickness, concentration of the precursor polymer solution and of the solvent on the aggregation structure in the solid state, structural order and anisotropy, and its subsequent impact on the electronic and optical properties.

With the ultimate technological perspective of understanding and controlling self-aggregation, morphology and associated optical properties of films, which is a key factor for optimization of polymer-based devices, the focus of our investigation is also on the analysis of the substrate/polymeric film interface that primarily determine the aggregation and optical response and on the resulting optical anisotropy which depends on self-aggregation. The anisotropy and optical properties are mainly investigated non destructively by spectroscopic ellipsometry (UVISEL-Jobin Yvon). Atomic force microscopy, photoluminescence and electroluminescence corroborate results.

In order to modify the self-aggregation of the polymer chains, O₂ plasma treatments of the substrates are investigated and proposed to improve wettability by the polymer chains and reduce substrate/film interface roughness, which also affects carrier injection and transport.

It is demonstrated that the F-atoms in the vinylene units yields the maximum of the HOMO-LUMO transition at 3.74 eV (331 nm), intense room temperature photoluminescence at 2.71 eV (458 nm) and homogeneous blue-greenish electroluminescence at 2.46 eV (504 nm). Furthermore stability of the electroluminescence under continuous operation of device has been demonstrated proving stability of the fluorinated polymers against photooxidation.

A comparison and discussion with the optical properties of fluorinated polyfluorenes is also discussed.

A01379-02406

Synthesis and Properties of Poly(thioether imide)s Based on Aromatic Heterocyclic Diimide

Xiaoyan ZHAO; Long CHEN; Meifang ZHU
College of Material Science and Engineering, Donghua University, Shanghai, China

Novel poly(thioether imide)s were prepared from aromatic heterocyclic chlorodiimids and 1,6-hexanediol by a nucleophilic substitution reaction in the presence of alkali catalysts. All the polycondensation proceeded smoothly in DMAc and the polymers were obtained quantitatively. The poly(thioether imide)s could be soluble in some polar solvents and possessed excellent thermal properties. The glass transition temperatures of polymers were beyond 215

°C and 10% weight loss temperatures were in the range of 450-500 °C in nitrogen atmosphere. Meanwhile, the dilute solution of these polymers in chloroform showed strong optical absorption in ultraviolet region, and exhibited green yellow fluorescence with emission maxima at 400-650 nm. Due to their properties, these poly(thioether imide)s could be considered as good potential candidates for high-temperature resistant materials and fluorescent materials.

A01383-03554

High Gain in Vertical Organic Transistors with Pentacene Emitter

Jiachun DENG¹; Kai ZHAO¹; Xiaoming WU¹;
Yulin HUA¹; Jun WEI^{1,2}; Shougen YIN¹
1. Institute of Material Physics, Tianjin University of Technology, Tianjin, China
2. Singapore Institute of Manufacturing Technology, Singapore

The characteristics of vertical organic transistors fabricated by using two pentacene back-to-back Schottky diodes with different metal base thicknesses are reported. All organic materials and metal electrodes were deposited in a thermal evaporation chamber at a base pressure of 10⁻³ pa. The samples structure were consisted of glass/gold(40 nm, as the collector electrode)/pentacene (60 nm)/ Calcium (70 nm, as the base electrode)/pentacene (120 nm)/ gold(40 nm, as the emitter electrode). The organic layers were deposited at the rate of 0.1 nm/s, the metal layers were deposited at the rate of 0.2 nm/s and the device area is 2 mm². The current-voltage (I-V) characteristics of the devices were measured by Keithley 2400 sourcemeter and Keithley 6485 picoammeter in darkness at situ environments. The output current (I_c) flowing between the emitter and collector electrodes increased remarkably after applying the input base voltage (V_b). At V_c=0.5 V, I_c was increased from 0 to 16 μA when the V_b was changed from 0 to 0.5 V. On the other hand, the base current (I_b) remained at a small value, and the changed in I_b for V_b=0.5 V was less than 0.2 μA. As a result, the common-emitter current amplification factor (h_{FE}), defined as the ratio of the change in I_c (ΔI_c) to the changed in I_b (ΔI_b) for the input voltage (V_b) application from 0 V to the given value. The output characteristics (I-V curves between the emitter and collector for various constant values) of the devices exhibited the good performance. Compared with the former reported device structure: (1) Au/CuPc/Al/LiF/NPB/CuPc/Au, h_{FE}=1.9 (APL 90:153509,2007)(2) ITO/Me-PTC/Al/C60/LiF/Al (h_{FE}=24.3), ITO/Me-PTC/Al/C60/Ag (h_{FE}=33), ITO/Me-PTC/Al/C60/Au (h_{FE}=60.5) (APL, 88:153512, 2006), the common-emitter current gain (h_{FE}) of our device reaches 80.

A01410-04089**Synthesis and Characterization of Chitin-Polyaniline Blend**Ramaprasad A. T.; Vijayalakshmi RAO*Department of Materials Science, Mangalore University, Karnataka, India*

In this paper we report the preparation and characterization of conducting chitin – polyaniline blends by solution blending method using N, N- Dimethyl acetamide/LiCl as solvent. Miscibility of chitin-PANI blend has been investigated by solution viscometric method. The characterization of the blends was done by UV-Vis absorption spectrum, FTIR, scanning electron microscope (SEM) and conductivity studies. Conductivity of the self doped blends increases from less than $\approx 10^{-7}$ S/cm to 2.15×10^{-5} S/cm, depending on the percentage of polyaniline in the blend. When these blends are doped with HCl, conductivity increases to $\approx 9.68 \times 10^{-2}$ S/cm. Krigbaum and Wall polymer-polymer interaction parameter (Δb) is calculated from Viscosity measurement and is found to be positive for all compositions of the blend. SEM observations show homogeneous and continuous structure of blend in the case of blends prepared using 5% LiCl. Homogeneous and fibrillar structure is observed in the case of blends prepared with less than 5% LiCl. Fibrous structure improves as the composition of PANI increases. FTIR analysis confirms interaction between chitin and polyaniline. Effect of humidity on the conductivity of the blend has been studied. The blend shows very good response in the temperature range 10 - 60°C as a humidity sensor.

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A01449-03296**Investigation of Charge Carrier Injection and Transport in DCM Doped Alq₃ Films**Gayatri CHAUHAN¹; Ritu SRIVASTAVA¹;P. C. SRIVASTAVA²; M. N. KAMALASANAN¹*1. Polymeric and Soft Material Section, National Physical Laboratory, Delhi, India**2. Department of Physics, Banaras Hindu University, Varanasi, India*

The optical properties of organic semiconductors are usually modified by doping with organic dyes. We have made detailed investigation of the effect of these optical doping on the electrical properties of 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) doped amorphous tris (8-hydroxyquinolinato) aluminum (Alq₃) films. Four electron only devices have been fabricated with the device configuration Al/ DCM (x):Alq₃ (1-x)/Al. The

doping concentration of DCM was $x = 0.0$ wt%, 0.01 wt%, 0.05 wt% and 0.1 wt%. The current density–voltage (J – V) characteristics of the electron only devices were studied from 300 K to 100 K. The J-V characteristics show that for low doping concentration the electron conduction is injection limited. As the dopant concentration is increased to 0.1 wt% there is transition from injection limitation to the bulk limitation.

A01484-02580**The Preparation of Micro-pattern Thin Film with Nanoparticles onto the Flexible Substrate by the Electrophoretic Deposition and Flexible Electrochromic Application**

Yi-wen CHUNG; Huang-Cheng FANG

Laser Application Technology Center, Industrial Technology Research Institute, Tainan, Taiwan

Recently, there have been extensive interests in application and process of the Flexible electronic products. In this work, it is reported that the electrophoretic deposition process (EPD) possessing lower working temperature was used to fabricate microstructure based on CdSe, TiO₂ nanoparticles onto the flexible substrate. Because these nanoparticles possess characteristic charge of zeta-potential, the driving potential with opposite charge will be provided during the EPD process. According to the trend of current curve, the EPD behavior can be monitor with process time. Moreover, the different current curve will appear the different depositing mechanism, including plane, straight-nano-channel and network-nano-channel deposition. These phenomenons will result in thin film, nano-fiber and macroporous structures, respectively. In EPD system, the thickness of thin film can be controlled by manipulating accurately EPD time. Due to the controllable depositing region of EPD, the pattern layer consisting of nanoparticles can be fabricated onto the flexible substrate during 1min. By the colloidal-template-mediated EPD process, the macroporous array consisting of nanoparticles onto flexible substrate can be also obtained. Further, the 3D macroporous structure called the inverse opal structure can be fabricated. Finally, by combining TiO₂ fabricated by EPD process and Prussian blue flexible thin film, the flexible electrochromic device can be formed. Therefore, this result manifested that the fabrication of nanostructure onto the flexible substrate is easy by EPD process. Moreover, it is the potential process for combining EPD and R2R together due to flexible and fast process.

A01564-02724

High Efficient Photoelectrochemical Cells Based on Single Wall Carbon Nanotube Electrode and Organic Dye

Lin KE; Szu Cheng LAI; Bin Dolmanan SURANI
Analysis and Characterization Group, Institute of Materials Research and Engineering, Singapore

Titanium dioxide nanoparticles were dispersed on carbon nanotube enhanced indium tin oxide (ITO) glass substrate. Organic N3 dye was used to further improve the absorption. improve photoinduced charge separation and transport of carriers to the collecting electrode surface. The photoelectrochemical cell can boost the photoconversion efficiency by a factor of 2. The shift of 100 mV in apparent Fermi level of the ITO surface modified by CNT boost the shottkey barrier in the interface as compared to the unsupported TiO₂ system indicates the Fermi level equilibration between the two systems. The interplay between the TiO₂ and SWCNT of attaining charge equilibration is an important factor for improving photoelectrochemical performance of nanostructured semiconductor based solar cells. The feasibility of employing a CNT-TiO₂ composite to drive the water photoelectrolysis reaction has also been explored.

A01592-02772

Effects of Carbon Black on Physical and Electrical Properties of LLDPE/EVA/Carbon Black System

Kim J. P.¹; Kim S. S.²; Jeon I. R.³; Seo K. H.¹
 1. *Department of Polymer Science, Kyungpook National University, Daegu, South Korea*
 2. *Advance Materials Division, Korea Research Institute of Chemical Technology, Daejeon, South Korea*
 3. *School of Fire and Disater Prevention, Kyungil University, Gyeongbuk, South Korea*

In general, polymers are non-conductive material. But it is possible to get conductive polymers by blending them with highly conductive filler such as carbon black, metal, etc.. Among them, carbon black is widely used for imparting conductivity to polymers. Proper selection and content of carbon black for these application is critical in formulating for optimum conductivity, physical properties, processability and cost.

In this research, we chose several kinds of carbon blacks for conductive filler. Blend of LLDPE with EVA was used as base resin. The blend was compounded with each type of carbon black for various content by using twin-screw extruder. Physical properties of the compounds were investigated by Instron. Rheological properties were also measured. ASTM D 991-89 procedure was used for measuring the volume resistivity, which is direct index of electrical property, of the compound.

The major factors which affect properties of those blends are particle size, surface area and volatile content of carbon black, as we know from earlier reports. The results showed that physical and electrical properties of the compounds directly depend upon the kind and content of carbon blacks.

A01607-03064

Effect of Dye Doping on the Electrical and Luminescence Properties of Zn(hpb)₂

Ritu SRIVASTAVA¹; Virendra K RAI²;
 Gayatri CHAUHAN¹; M. N. KAMALASANAN¹
 1. *Polymeric and Soft Material Section, National Physical Laboratory, Delhi, India*
 2. *Department of Materials Science, Saitama University, Saitama city, Japan*

In the present paper we have doped 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) dye in Zn(hpb)₂ matrix and studied its PL and EL properties at various dye concentrations. DCM doped Zn(hpb)₂ emissive layers shows charge trapping as the mechanism controlling the electroluminescence properties. To understand this phenomenon we have made a detailed study on the transport properties of dye doped Zn(hpb)₂ OLED device. Our observation shows severe electron trapping in these films and enhancement in hole mobility. Which shows that the electroluminescence properties are controlled by the hole transport properties in dye doped films.

A01644-02849

Metallic Nanoparticle Network for Photocurrent Generation and Photodetection

X. N. XIE; Y. XIE; X. GAO; C. H. SOW; A. T. S. WEE
National University of Singapore, Singapore

Photocurrent generation and photodetection are usually based on inorganic and organic semiconductors. This work demonstrates, for the first time, the usage of metallic Au nanoparticles (NPs) for photocurrent generation and photodetection. Due to the hindrance of intrinsic carrier conduction by ligand passivation, photoelectrons excited from the NPs form the major component of the current, thus enabling photodetection and a large on/off current ratio. The generation and conduction mechanism of photoexcited electrons in the Au NP electron tunneling network is proposed. Good photocurrent generation is associated with high NP content and the close-packed NP network. The inherent features of metallic NPs for photocurrent generation are also discussed. Our results show the possibility of using ligated metallic NPs as an alternative to semiconductors for photocurrent and photodetection applications.

A01667-03867

Fluoropolymer Interlayer for Polymer Light-emitting DiodesGianluca LATINI^{1,2}; Li Wei TAN²; Franco CACIALLI³; S. Ravi P. SILVA²*1. Department of Materials, Faculty of Engineering, Imperial College London, United Kingdom**2. Nanoelectronics Centre, Advanced Technology Institute, University of Surrey, Guildford, United Kingdom**3. Department of Physics and Astronomy and London Centre for Nanotechnology, University College London, United Kingdom*

Plastic electronics have reached quite impressive performance in many areas as for example for light-emitting diode, however stability and ageing of the devices are still open issues and the relatively short lifetime of devices is limiting their mass commercialization. Their performance strongly depends on the charge injection and confinement in the emitting layer since these control the brightness of the devices and electroluminescence efficiency. Furthermore, electrochemical reactions that shorten the lifetime of the devices, often occur at the interfaces where different materials are in contact.

In this work we show that the insertion of thermally evaporated thin layer of polytetrafluoroethylene, PTFE, at the (poly(ethylene dioxythiophene):poly(styrene sulphonic acid)/poly(9,9-dioctylfluorene), PEDOT:PSS/PFO, interface in organic light emitting devices, LEDs leads to an improved control of the charge balance and device longevity. The PTFE film morphology has been investigated with atomic force microscopy that display the coverage of the PEDOT:PSS substrate. The effective work function of PEDOT:PSS/PTFE results increased of up to ~100 meV when compared to PEDOT:PSS alone as a result of the formation of an interfacial dipole. This allows a better confinement of electrons into the emissive layer and reflects in an increase of the external quantum efficiency of the devices that, when fully on, doubles without affecting the luminance. We analyze the effect of the reduced photoluminescence efficiency quenching as a consequence of the insertion of the insulating layer between PEDOT:PSS and PFO and demonstrate the improved charge balance in the devices. The longevity of the devices shows a remarkable increase when PTFE is incorporated (~4 times for the most efficient devices). Such improvement is likely to be due to the reduced electrochemical interaction between the electroluminescent polymer and PEDOT:PSS as a consequence of the chemical inertness of PTFE.

A01667-03869

Revisiting Molecular-Weight Dependence of Charge-Carrier Mobility in Polymer SemiconductorsMohammed A. BAKLAR^{1,2}; Avinesh KUMAR¹; Christian MULLER³; Nikolai ZHIGADLO³; Theo KREOUZIS²; Paul SMITH^{1,2}; Gianluca LATINI¹; Natalie STINGELIN-STUTZMANN^{1,2,3}*1. Department of Materials Faculty of Engineering, Imperial College London, United Kingdom**2. Centre for Materials Research, Queen Mary, University of London, United Kingdom**3. Department of Materials, ETH Zurich, Switzerland*

Electronic properties of organic semiconductors are critically depending on their ability to order on the molecular level - as is true for many other material properties, such as mechanical characteristics. In crystalline semiconducting polymeric species, structural features that extend the π -conjugation are generally thought to be favorable for good charge transport. Therefore, understanding of the molecular assembly process will be critical to further advance the field of organic electronics, be it molecular or thin-film based. We reestablish that molecular order, and therewith charge transport properties in the model system poly(3-hexylthiophenes) (P3HT) can be widely varied according to the processing pathways employed. More importantly, however, we find that it is of key importance to adjust processing parameters to the molecular weight of the polymer grade utilized. Neglect of the latter may have led to the widespread believe that field-effect mobilities *increase* with molecular weight (1-5), which is at remarkable odds and indeed of *opposite* trend when contrasted with results obtained in time-of-flight (TOF) experiments (6). Here we present a study of the influence of different processing means - ranging from solution- and melt-casting to high-pressure crystallization - on the solid-state structure and properties P3HT of a wide range of molecular weights. We conclude that classical understanding of polymer crystallization provides a simple rationale for the numerous discrepancies that appear to exist regarding the molecular weight dependence of charge carrier mobilities for this [model] semiconducting polymer.

A01708-02979

Density of BandGap States in Copper Phthalocyanine Thin-Films Measured from the Temperature Dependence of Field-Effect Structures

Joaquim PUIGDOLLERS¹; Monica DELLA PIRRIERA¹; Stephanie CHEYLAN²; Cristobal VOZ¹; Ramon ALCUBILLA¹

1. *Enginyeria Electronica, Universitat Politecnica Catalunya, Barcelona, Spain*

2. *Institute Photonic Sciences, Spain*

In this work we have fabricated Copper Phthalocyanine (CuPc) Thin-Film Transistors (TFTs) on c-Si substrates using thermally grown silicon dioxide as a dielectric. CuPc TFTs exhibits hole conductivity with room temperature field-effect mobility up to 0.4 cm²/V·s and on/off ratios up to 10⁵.

We have also measured the current-voltage characteristics of the TFTs over a range of temperature (30 – 90°C) and determined the activation energy (E_a) of the channel conductance as a function of the gate bias. The channel conductance is thermally activated and this behaviour has been used to track the position of the Fermi level inside the band gap.

From the dependence of the activation energy as a function of V_{gs} it is observed that for small positive V_{gs} the activation energy is around ~0.5 eV. This value is around 30% of the optical activation energy, probably due to the asymmetrical distribution of traps which pin the Fermi energy (E_F) level toward the valence band. For large negative V_{gs}, E_a decreases to lower value. This behaviour could be described in terms of a standard semiconductor model. The dependence of E_a on V_{gs} corresponds to a gradual shift of the Fermi energy level toward the valence band as more empty traps become filled due to the injected holes from contacts.

From the dependence of the derivative of the activation energy with respect to the gate bias the density of localized states could be estimated. The density of localized states was around 10¹⁷ cm⁻³eV⁻¹ in the midgap and increases one order of magnitude towards the conduction band. The DOS distribution could be roughly described by the sum of two exponential contributions. The electronic properties of thin-film organic semiconductors are usually interpreted assuming, as in the case of amorphous silicon, the presence of localized states in the band gap. Hence, we can attribute the exponential regions in the DOS distribution to the presence of deep and band tail states. These densities of localized states have a detrimental effect in the electrical behaviour of electronic devices based on organic semiconductors. Therefore, this characterization could be very helpful to optimize the material in order to obtain performance devices with a better performance.

A01716-03343

Nano Polyaniline and Poly-o-Anisidine: Synthesis by Emulsion Polymerization and their Characterization

Rajendra JADHAV; Dilip HUNDIWALE; Pramod MAHULIKAR
School of Chemical Sciences, North Maharashtra University, Maharashtra, India

Conducting polymers are considered as important class of materials because of their potential applications in various electronic devices such as chemical sensors, biosensors, gas sensors electrochromic displays, light emitting diodes in solar cells and in electrochromic devices (ECDs). Among the various conducting polymers, polyaniline has attracted considerable interest because of its electroactivity, low density, good electrical conductivity, unique properties and environmental stability. On the basis of these superiorities, PANI and POA have been applied in the fields of antistatic materials, corrosion inhibitors in paint formulations batteries and sensors.

Nanoparticles of electroconductive polymers are generally prepared in micellar solution as a polymerization medium to overcome the poor processability of electroconductive polymers. In present investigation the nanoparticles of polyaniline (PANI) and poly-o-anisidine (POA) have been synthesized by emulsion polymerization method in micellar solution of SDS (sodium dodecyl sulphate). The synthesized conductive polymers were characterized by FT-IR, UV-Visible spectroscopies; X-rd (X-ray diffraction technique), TGA (Thermal gravimetric analysis), TEM (Transmission electron microscope) and the conductivity were measured by Four-probe method.

A01729-03080

Low Band Gap Polymers Based on Terthiophene and Quaterthiophene for Organic Solar Cell Applications

Kok Haw ONG^{1,2}; Zhikuan CHEN¹
1. *Institute of Materials Research and Engineering, Singapore*
2. *Department of Chemistry, Imperial College London, London, United Kingdom*

Environmental concerns over the carbon emissions from fossil fuels and the finite supply of these fuels have driven increasing interest in renewable and clean energy sources such as solar energy. However, at present, solar energy is too expensive to be cost-competitive with conventional energy sources. Organic bulk heterojunction solar cells have the potential to reduce the cost of solar energy, as they can be manufactured using low cost, large area techniques such as roll-to-roll printing. However before that can be realized, the power conversion efficiencies of these cells must be

improved. One of the key challenges for organic solar cells is that most of the donor polymers are unable to absorb light of wavelengths longer than 700nm, where there is a significant amount of solar flux. Low band gap polymers can help to overcome this problem, as they can harvest light at longer wavelengths and hence increase the proportion of incident photons that are absorbed. We present here our work on the synthesis and characterization of low band gap polymers based on terthiophene or quaterthiophene and benzo[2,1,3]thiadiazole. These donor-acceptor type polymers have been designed to possess both low band gaps and high charge carrier mobilities. The polymers have been synthesized with molecular weights of above 20 kDa using Stille co-polymerization. By adjusting the polymer structures, the polymer band gap can be tuned from around 1.6eV to 2.0eV. Further optimization of the polymer structures by introducing conjugated side chains is expected to improve the absorption properties of the polymers and improve the power conversion efficiencies of the solar cells.

A01793-03194

Plastic Photovoltaic Device Based on P3HT and Carbon Nanomaterials

Kao-Yu KUO¹; Pritesh HIRALAL¹;
Husnu Emrah UNALAN¹; Hang ZHOU¹;
Yasuhiko HAYASHI²; Emmanuel KYMAKIS³;
Gehan AMARATUNGA¹

1. *Engineering Department, University of Cambridge, Cambridge, United Kingdom*
2. *Department of Environmental Technology and Urban Planning, Nagoya Institute of Technology, Nagoya, Japan*
3. *Electrical Engineering Department, Technological Educational Institute of Crete, Crete, Greece*

Conjugated polymer-based PV cells have rapidly developed during the last decade. Tremendous progress has been made in improving the efficiency. Many authors have reported that poly(3-hexylthiophene) (P3HT) based polymer solar cells show very good photovoltaic performance. In our previous work we have shown that inclusion of CNTs within a polymer matrix can enhance solar cell performance through the operation of internally distributed charge separation and transport junctions [1,2,3].

In this work we report results on the use of CNTs, C60, C70 fullerenes and their derivatives for enhanced performance in polymer solar cells. Sandwich-structured polymer solar cells with nanocomposite layers have been investigated. Different types of carbon nanomaterials were blended with P3HT to form the active layers of the devices. The photovoltaic properties of these blends were investigated to compare their performance in the report.

A01814-03868

Study on the Performance of Polymer Solar Cells by Inkjet Printing Process

Seung Hun EOM¹; Hanok PARK¹; Jongsun LIM²;
Sung Cheol YOON²; Changjin LEE²; Soo-Hyoung LEE¹
1. *School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju, South Korea*
2. *Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, South Korea*

In this report, we report efficient methods for fabrication of polymer solar cells by inkjet printing. We prepared polymer solar cell devices with a hole transporting layer of poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) and photo-active layer of poly (3-hexylthiophene) (P3HT): [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) mixture (1:0.7) on the ITO by inkjet printing. In order to find the optimum fabrication conditions for both layers, we have investigated inkjet printing parameters such as drop formation behaviors, solvent mixtures, additives and substrate temperatures of polymer inks. The controlled printing parameters and ink formulations led to obtain pin-hole free surface films achieving power conversion efficiency over the 3.5% for photovoltaic devices with inkjet printed-all-polymer layers under illumination, 100mW/cm² at AM1.5 simulated light.

A01900-03276

Electroluminescence from Poly (9,9-di-n-hexylfluorenyl-2,7-diyl) PHF-ZnCdTe Quantum Dots Hybrid Light Emitting Diode

Nor 'Izzati MOHD. A'ASRI¹;
Mohd. Shahrul Akram MOHD. MOKHTAR¹;
Norhayati ABU BAKAR¹; Akrajas ALI UMAR¹;
Muhamad MAT SALLEH¹; Muhammad YAHAYA²
1. *Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia, Selangor, Malaysia*
2. *School of Applied Physics, Universiti Kebangsaan Malaysia, Selangor, Malaysia*

In this study, we report the results on the investigation of hybrid light emitting diode consist of blended poly(9,9-di-n-hexylfluorenyl-2,7-diyl) (PHF) and ZnCdTe quantum dots (QDs). PHF is a blue light-emitting polymer with wavelength of 414 nm, while ZnCdTe is a red QDs with photoluminescence of 650 nm. Light emitting diode of structure ITO/PEDOT:PSS/PHF:ZnCdTe/Al was fabricated and studied for this purpose. The devices were prepared by using spin coating technique. A microwave annealing technique was used to optimize the device structure. Our electroluminescence study found that the device without QDs emitted high brightness blue light with turn-on voltage of 22.0 V. Meanwhile, performance of the device that contains QDs was improved with high

brightness orange light emission and the turn-on voltage in the range of 8.0 V to 9.0 V.

A01913-03325

Study of Temperature Dependent Carrier Mobility in P3HT/TiO₂ Nanocrystals Hybrid Bulk Heterojunction Photovoltaics

Yun-Heng TSENG; Shao-Sian LI; Chia-Hao CHANG; Wei-Feng SU; Chun-Wei CHEN
Material Science and Engineering, National Taiwan University, Taipei, Taiwan

A concept of phonon-assisted hopping of disorder conjugate polymer matrix is employed to explain the charge transport behavior, the most popular model of charge carrier hopping transport in the disorder system is the Gaussian Distribution Model (GDM) pioneered by H. Bässler. In this work, the charge carrier mobility of the organic/inorganic hybrid bulk heterojunction devices will be addressed based on the P3HT/TiO₂ hybrid materials by employing the charge extraction by linearly increase voltage (CELIV) method. By adding different concentration and sizes of the TiO₂ nanocrystals, an enhancement of the hole mobility can be observed. From temperature dependent CELIV measurement, the correlation of the energetic and positional disorder parameters to the transport properties can be evaluated based on the GDM. The result shows that the values of energetic disorder parameter decreases with increasing TiO₂ hybrid concentration which is corresponding to the decrease of the Gaussian distribution width and hence in favor of charge transport. The correlation between the organic photovoltaic devices morphology and the disorder parameters will be discussed. To further improve the charge transport efficiency, the post-treatment of solvent and thermal anneal effects will also be addressed and the effect of different sizes of the TiO₂ nanocrystals on transport will be also discussed.

A01971-03405

Preparation and Characterization of C₆₀ Doped PANI / PC Blend Thin Film

Shyam Sunder SHARMA^{1,2}; S. SRIVASTAVA¹; M. SINGH¹; D. BHATANAGAR¹; Y.K. VIJAY¹
1. Physics, University of Rajasthan, Jaipur, India
2. Physics, Govt. Women Engineering College, Ajmer, India

In this paper, we report the preparation and characterization of the conducting polymer blends of camphorsulfonic acid (CSA)-doped polyaniline/polycarbonate (PANI/PC). These blends were prepared by solution mixing process. C₆₀ was also incorporated in these blends using ultrasonication. The thin films of these blends were prepared by spin coating. These blends were characterized

by Raman spectroscopy, an X-ray diffraction technique and conductivity measurements. It was found that the electrical conductivity of the blends increased with the increase of PANI-CSA as well as C₆₀ content. The XRD spectrum shows the some crystalline nature of blend after the doping of C₆₀.

A01978-03416

Thiophene-benzothiadiazole Based Donor-Acceptor-Donor (D-A-D) Materials: Synthesis, Characterization and OFET Device Performance

Prashant SONAR¹; Samarendra SINGH¹; Ananth DODABALAPUR^{1,2}; Alan SELLINGER^{1,3}
1. Institute of Materials Research and Engineering, Singapore
2. Microelectronics Research Center, University of Texas, Austin, United States
3. Department of Materials Science and Engineering, Center for Advanced Molecular Photovoltaics (CAMP) Stanford University, Stanford, United States

Conjugated semiconducting materials have been the focus of intense research over the last two decades as they exhibit a variety of interesting optical, electrochemical, morphological and electrical properties. These materials are promising for (OLEDs), organic photovoltaic devices (OPVs) and organic thin film transistors (OTFTs) devices due to charge transporting properties, band-gap energy, and light absorption/emission characteristics. Of these materials, low band-gap conjugated materials are of interest because of their utility in harvesting visible wavelength photons, tunable red-ox and in ambipolar transistors. Additionally, this system enhances the intramolecular charge transfer, which can promote charge carrier mobility. The synthesis and characterization of solution processable donor-acceptor-donor (D-A-D) based conjugated molecules with varying ratios of thiophene as donor (D) and benzothiadiazole as acceptor (A) are reported. Optical, electrochemical, thermal, morphological and organic thin film transistors (OTFT) device properties of these materials were investigated. The thermal and polarized optical microscope analysis indicates that the materials having higher D/A ratios exhibit both liquid crystalline (LC) and OTFT behavior. Vacuum deposited and solution processed OTFTs of 4T1B and 3T1B have shown charge carrier mobilities of 0.17 cm²/Vs and 2 x 10⁻² cm²/Vs on SAM modified and bare Si/SiO₂ substrates. We discuss the inter-relationships between molecular structure, morphology, and charge carrier mobility. We will also report on efforts to achieve ambipolar transport in this material with the use of alternate dielectrics.

A01989-03438

A Meaningful Analogue of Pentacene: Understanding Charge Transport, Polymorphs and Electronic Structures of DihydrodiazapentaceneQin TANG¹; Dieqing ZHANG¹; Ning KE²; Jianbin XU²; Jimmy C. YU¹; Qian MIAO¹*1. Department of Chemistry, The Chinese University of Hong Kong, Hong Kong, China**2. Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, China*

Better understanding structure-property relationship is a key to rational design of organic semiconductors better than pentacene, the leading organic semiconductor for organic thin film transistors (OTFTs). 6,13-dihydro-6,13-diazapentacene (DHDAP), having two nitrogen atoms replacing two carbon atoms of pentacene, is a meaningful analogue of pentacene. This presentation will detail a comprehensive investigation of DHDAP highlighting the relationship between charge transport, polymorphs and electronic structures.

Three crystalline polymorphs are found from the thin films of DHDAP depending on the substrate surface structures. Our surprising finding is that the field effect mobility of DHDAP is extremely sensitive to the polymorphs with the “12.9 Å phase” yielding a mobility of $0.45 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is over 5000 times higher than those of the other two phases. This unusually large effect of the crystalline polymorph on charge transport can be understood in terms of molecular packing using the models developed by de Wijs and Brédas.

The comparable field effect mobilities and highly relevant structures of DHDAP and pentacene imply that the common structural features shared by the two molecules may be key factors that benefit the good electrical performance while the different structural features should not be important. The electronic structure of DHDAP is studied in comparison with that of pentacene using both computational and experimental methods. It is found that DHDAP has a delocalized HOMO with the energy level essentially the same as that of pentacene although the HOMO-LOMO gap of DHDAP is significantly larger. The environmental stability of DHDAP suggests that a relatively high HOMO energy level does not necessarily lead to environmentally unstable organic semiconductors.

A02004-04068

Efficiency and Stability Study of a Family of Fluorene-Phenylenediamine Statistical CopolymersBoon Kar YAP¹; Donal BRADLEY²*1. Department of Electronics and Communication Engineering, University Tenaga Nasional, Selangor, Malaysia**2. Experimental Solid State Physics, Imperial College London, London, United Kingdom*

Recently, PLEDs have attracted interest in the transport sector for application to “display and lighting on the move” which involves stringent safety standards due to the possible rugged conditions and harsh environments. Therefore, good electrical stability is crucial to meet these requirements. We report the impact of inserting a 10 nm thickness interlayer between the poly(3,4-ethylenedioxythiophene):poly(styrenesulphonate) (PEDOT:PSS) and light-emitting layers on degradation, in particular the electrical stability of the injecting electrodes, in encapsulated polymer light emitting diodes (PLEDs). Continuous electrical stress testing is carried out to study the time evolution of dark injection hole transients for devices with and without a poly[2,7-(9,9-di-n-octylfluorene)-alt-(1,4-phenylene-((4-sec-butylphenyl)imino)-1,4-phenylene)] (TFB) interlayer. A Sumitomo Chemical Company dibenzothiophene phenylenediamine copolymer (SC002) was used as light emitting layer and PLED characteristics with and without the interlayer are discussed together with lifetime data. SC002 is chosen due its Highest Occupied Molecular Orbital (HOMO) energy level being well matched to PEDOT:PSS and the TFB interlayer, thus forming an ohmic contact. This ensures that the dark injection transient exhibits a prominent peak, the changes to which can then be clearly followed. Monitoring the time evolution of this current maximum and the corresponding current density, for devices with and without the interlayer, provides a comparative study of the anode interface degradation rate. Recently, PLEDs have attracted interest in the transport sector for application to “display and lighting on the move” which involves stringent safety standards due to the possible rugged conditions and harsh environments. Therefore, good electrical stability is crucial to meet these requirements.

A02033-04595

Type-II Lateral Heterostructure based Bipolar Organic Field Effect Transistors

Samarendra P. SINGH¹; Prashant SONAR¹;
Alan SELLINGER^{1,2}; Ananth DODABALAPUR^{1,3}

1. Institute of Materials Research and Engineering,
Singapore

2. Department of Materials Science and Engineering,
Stanford University, Stanford, United States

3. Department of Electrical and Computer Engineering,
The University of Texas at Austin, Austin, United States

Organic field effect transistors (OFETs) are interesting due to their diverse potential applications in flexible displays, electronic circuits and sensors. The unique properties of organic semiconductors are motivating researchers to explore new device designs and applications of OFETs. Balanced electron and hole injection is always sought as a basic requirement in light emitting devices but is often hard to achieve. In this presentation we describe the unique electrical characteristics of bipolar lateral heterostructure OFETs which operate in the steady state always having balanced electron and hole injection from the source and drain.

The lateral heterostructure based bipolar OFETs are designed having hole and electron transporting materials on either side of the junction which is a type II lateral heterojunction, located approximately midway between the source and drain. We have used dihexyl quarter thiophene (DH- α 4T) and dihexyl-benzothiadiazole-quarter thiophene (DH-BTZ-4T) as hole transport materials in combination with naphthalene-tetracarboxylic-dianhydride (NTCDA) and N-ditridecylperylene tetracarboxylic diimide (PTCDI-C₁₃H₂₇) as electron transport materials. Each of the semiconductor materials on either side of the heterojunction supports the transport of only one carrier type, with the other becoming trapped. This leads to unusual shaped current-voltage characteristics which we have measured and analyzed. The transfer characteristics of lateral heterostructure transistors shows electric field driven charge injection across the heterointerface formed in between the transistor channel. For a constant drain-source voltage, the drain current initially does not increase with gate-source voltage and then starts to increase followed by decrease approaching to zero resulting a Gaussian-like transfer characteristic. The device current follows the changing lateral electric field in the vicinity of the heterojunction. The drain current reaches to maximum at highest lateral electric field when the electron and hole concentrations are equal in the two sides of the heterojunction. In this presentation, we will discuss the electrical characteristics of type-II lateral heterostructure based OFETs for two systems of hole and electron transport materials. The balanced charge injections in such type II lateral heterostructure transistors make it beneficial to realize light emitting transistors. A device model for heterostructure transistors will also be discussed.

A02056-03532

Probing Evolving Interface Energetics and Film Morphology During the Growth of an Organic Photovoltaic Device Structure

Gruffudd WILLIAMS; Owain ROBERTS;
David LANGSTAFF; Andrew EVANS
Institute of Mathematics and Physics, Aberystwyth
University, Aberystwyth, United Kingdom

The quest for improved photovoltaic devices is driven by a need to achieve the optimum combination of performance and cost. There are several competitive technologies in terms of materials and fabrication methods and the usual optimisation approach is to systematically work through the parameter spaces (e.g. new materials, new combination of materials, growth rates/temperatures/pressures, substrate preparation, encapsulation, etc.) by producing and testing a range of devices. The parameter space for organic semiconductor devices is particularly vast.

In most of these competing technologies the device is made up of multilayer structures and often the device performance is limited by interfaces between the materials in each layer. The physical, chemical and electronic properties of these interfaces are interconnected and it is rarely possible to predict these theoretically. Few experimental characterisation methods can provide all the important information and it is not always possible to apply these methods in-situ. In most cases, one piece of information is obtained from a series of experiments on test structures.

One technique that provides a direct probe of electron energy levels and, in parallel, information on chemical bonding and film morphology is photoelectron spectroscopy, but it is not widely applied as it can be expensive, complex and slow. We have addressed these limitations by developing a dedicated organic molecular beam deposition (OMBD) spectrometer that combines an efficient electron analyser/detector with intense radiation sources to enable real-time monitoring of organic device structures based on small conjugated molecules.

The first application to organic photovoltaics has focused on simple test structures made up of OMBD-grown layers of fullerenes and phthalocyanines on transparent conducting substrates with a metallic top electrode. Using UV and x-radiation, multilayer growth has been monitored by real-time photoelectron spectroscopy. Core level emission spectra reveal the chemical state of elements at the interface and the band-bending within the semiconducting layers. The valence band emission spectra probe the evolving density of occupied electronic states and give a direct measurement of the valence band offset at each interface. The onset energy of the overall photoelectron emission spectrum provides the surface work function or ionisation energy.

A02058-03534

Modification and Real-time Characterisation of Hybrid Inorganic-organic Semiconductor Diodes

Owain ROBERTS; Alex VEAREY-ROBERTS;
Gruffudd WILLIAMS; David LANGSTAFF;
Andrew EVANS
*Institute of Mathematics and Physics, Aberystwyth
University, Aberystwyth, United Kingdom*

The integration of organic and inorganic semiconductor technology is attracting interest in many areas such as bio-sensors and photovoltaics and central to the successful application of novel structures is the control of the hybrid interface. The usual approach is to fabricate organic layers on inorganic substrates and this can be achieved using chemical or physical techniques. To address the fabrication challenges, suitable characterisation techniques are needed and these, ideally, should provide parallel information in-situ and in real-time.

The system reported here is an organic modified inorganic semiconductor device consisting of an ultrathin interlayer of phthalocyanine of variable thickness in a III-V semiconductor – metal device structure. I-V characteristics for a range of nanometre-scale interlayers reveal a strong modification of the diode rectification by control of the interlayer thickness. For example, a n-GaAs – Ag diode can be rendered ohmic by the inclusion of a 4nm SnPc interlayer.

The origin of this behaviour has been determined by following the evolution of the organic-inorganic interface in real-time using photoelectron spectroscopy. This reveals a film thickness-dependent band bending in the substrate due to charge transfer at the interface that decreases the depletion width in the GaAs and hence reduces the interfacial potential barrier in the modified diode. Furthermore, the morphology of the organic layer as determined from real-time photoelectron spectroscopy and AFM is found to be dependent on thickness, substrate temperature and time. The latter in particular has important consequences for the wider application of these small conjugated molecules in organic semiconductor devices and similar behaviour has been found for growth on a wide range of semiconductor and metal substrate surfaces. The essential features of the experimental data have been reproduced using monte-carlo modelling.

A02140-03712

Electrochemistry for Dye-sensitized Solar Cells

Qing WANG¹; Michael GRAETZEL²
*1. Materials Science and Engineering, Nanocore,
National University of Singapore, Singapore
2. Laboratoire de photonique et interfaces, Ecole
Polytechnique Fédérale de Lausanne, Switzerland*

After more than one decade of research, dye-sensitized solar cells (DSC) currently present a credible alternative to conventional solar cells. At the heart of the DSC is a nanocrystalline semiconductor oxide (typically TiO₂) film that is covered by a monolayer of sensitizer. During the illumination of the cell, electrons are injected into the conduction band of the oxide by the photoexcited dye molecules adsorbed on the nanoparticle surface. The sensitizer is regenerated by hole injection into a redox electrolyte or solid p-type conductor. As a photoelectrochemical cell, electrochemical and photoelectrochemical processes play the major roles and govern the operation of the device. For example, the interfacial charge transfer process at TiO₂-dye-electrolyte interface dominates the recombination kinetics of the injected electrons in TiO₂. In addition, electron propagation in mesoscopic semiconducting metal oxide film shows a trap-limited ambipolar diffusive behavior when immersed in an electrolyte, and presents one of the key kinetic processes in DSC. Here we will highlight some of our electrochemical studies on the mesoscopic charge transport process in DSC. The important kinetic processes of recombination-limited mesoscopic charge transport, cross surface charge percolation, surface redox reaction/dye regeneration and mesoscopic ionic transport will be addressed by employing various electrochemical techniques, such as cyclic voltammetry, chrono amperometry, impedance spectroscopy, etc. Their influences on the device performance will be discussed in detail. It is expected that the outcome of the measurements will contribute to a deeper understanding of the electronic and ionic processes that govern the operation of DSC, providing important hints for improving the performance of DSC.

A02173-04067

Photophysics and Electro-optical Investigations of the Interface of a Polyfluorene/Cross-linked Hole-injecting Layer

Gustaf WINROTH¹; Sergio BROVELLI¹;
Loke-Yuen WONG²; Lay-Lay CHUA²; Peter K. H. HO²;
Franco CACIALLI¹

1. Department of Physics and Astronomy, University
College London, London, United Kingdom

2. Department of Physics, National University of
Singapore, Singapore

Poly(ethylene dioxythiophene) doped with poly(styrene sulphonic acid), or PEDOT:PSS, is a common water-soluble hole-injection layer that is incorporated between the transparent conducting oxide anode and the organic semiconductor active layer in polymer light-emitting diodes, LEDs, or photovoltaic cells, PVs.

We investigate the effect of photo-cross-linking of a layer of PEDOT:PSS with an added bis(fluorinated phenyl azide), on the photophysical and electrical properties of light-emitting diodes incorporating a polyfluorene derivative as active layer and cross-linked PEDOT:PSS as anode. Current-voltage-luminance characteristics and time-resolved photoluminescence experiments reveal that cross-linking and rinsing of the PEDOT:PSS layer reduce low-voltage leakage current and luminescence quenching at the PEDOT:PSS/polyfluorene interface. The decrease in operating voltage of the light-emitting diodes is observed despite the slight increase in the surface roughness, as measured by atomic force microscopy.

Electroabsorption (EA) measurements indicate a reduction of the trap density close to the ionization potential of the polyfluorene, while sub-band gap traps seem to be unaffected by the cross-linking process. We present an extended model of the EA dependence as a function of modulation frequency as a method to estimate the lifetimes of the traps detectable in our experimental setup.

A02279-03888

Calixarenes and Thiacalixarenes as 3D-Scaffolds for Organic Electronic Materials

Khai Leok CHAN¹; Alan SELLINGER²

1. Institute of Materials Research and Engineering,
Singapore

2. Department of Materials Science and Engineering,
Stanford University, Stanford, United States

Nanocomposite dendrimers based on 3-dimensional scaffolds represent a new class of materials for application in organic electronics. 3D-scaffolds such as cyclic phosphazenes and silsesquioxanes with emissive or charge transporting peripheral dendrons have been prepared

as solution processible materials, with the rigid scaffold forcing the alignment of the dendrons in such a way as to provide materials with interesting electronic, mechanical and morphological properties. Here we explore the use of calixarenes and thiacalixarenes as alternative scaffolds for dendrimers targeted at organic electronic applications. The dendrimers are easily prepared from readily available materials using Buchwald-Hartwig amination, Heck and Suzuki coupling chemistry to decorate the periphery of the scaffold with dendrons having electronic properties. Dendrimers containing a variety of ligands can be prepared with a high degree of purity and monodispersity. The HOMO and LUMO energy levels of the dendrons can be simultaneously tuned by changing the carbon bridges in calixarenes to sulphur bridges in thiacalixarene without appreciable change in the emissive properties of the dendrons. The relative orientations of dendrons within each dendrimer and therefore the inter-dendrimer packing can also be controlled by judicious choice of scaffold configuration (cone vs. 1,3-alternate) and dendrons. These observations and their implications on the photophysical properties of the resulting bulk material will be presented.

A02289-04293

Deep Level Transient Spectroscopy Studies of Organic Semiconductor/ Dielectric Interfaces

Victor WANG BOCHUAN; Nripan MATHEWS;
Huei Shuan TAN; Wei Lin LEONG; Tommy CAHYADI;
Subodh MHAISALKAR

School of Materials Science and Engineering, Nanyang
Technological University, Singapore

The semiconductor-dielectric interface is of critical importance in the operation of organic field effect transistors. The presence or absence of trap states on the semiconductor-dielectric interface has been linked to the mobility of the charge carriers as well as to the unipolar nature of charge transport measured organic transistors. We have employed Deep Level Transient Spectroscopy as a tool to study this critical interface. This quantitative trap analysis technique uses the principle of thermal release of charge carriers from traps to characterize and identify the trap profiles in fabricated devices.

The investigation will focus on the electrical characterization using DLTS and the sample fabrication techniques that will inevitably lead to formation of various traps. Specifically, pentacene devices with a variety of polymeric dielectrics and inorganic dielectrics were compared and contrasted. The polymeric dielectrics studied were PVP-PMMA (polyvinyl phenol-polymethylmethacrylate) and PVP (polyvinyl phenol). Temperature dependent measurements of released charge carriers, which previously filled the traps, were performed to investigate the origin of trapping centers in the forbidden band-gap. Pentacene-SiO₂ interfaces were also studied for comparison and yielded

the presence of traps with an energy level of 0.365eV. All the interfaces studied showed high trap densities in the range of 10^{13} to 10^{17} cm⁻³.

Energetic distributions are investigated to find relations with impurities, surface morphology, structure and different processing techniques. Measurement of spectroscopic trap levels will yield unique quantifiable profile data, such as, energy levels, activation energies, trap concentration densities and trapping capture cross-sections. Such information will be useful in investigating and eliminating these traps that may prove detrimental to device performance.

A02317-03963

Relation between Optical Properties and Film Morphology of Polymer/TiO₂ Nanorods Hybrid Bulkheterojunction Solar Cells

Chia-Hao CHUANG; Tsung-Hung CHU; Wei-Fang SU; Chun-Wei CHEN

Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan

Recently, the use of mixed solvents or processing additives has been demonstrated to improve the performance of solar cells based on conjugate polymer and fullerene derivatives. In this work, we control the morphology of pristine poly(3-hexylthiophene)(P3HT) thin films and blend films comprising of P3HT/TiO₂ nanorods by using single solvent and mixed solvents. The mixed solvents contain pyridine, a good solvent for TiO₂ nanorods but poor solvent for P3HT. Clear vibronic features in absorption spectra are observed in films spin-cast from mixed solvents as a result of ordered structure and stronger interchain interaction in polymer. Photoluminescence (PL) spectra also change significantly in shape and peak position and the PL lifetime decreases due to enhanced ordering. Further, when blended with TiO₂ nanorods, films spin-cast from mixed solvents show higher PL quenching efficiency, indicating more efficient charge separation process. The surface morphology of these films is investigated by atomic force microscopy that the correlation between optical properties and film morphology are discussed. We find that using mixed solvents can not only improve molecular ordering but lead to optimal phase separation morphology of organic/inorganic hybrid materials for bulk heterojunction solar cells.

A02328-04098

Controlling of Surface Energy of Gate Dielectric in Organic Field-effect Transistors by Polymer Blend

Jia GAO^{1,2}; Jian-Bin XU^{1,3}; Jin AN¹; Asadi KAMAL²

1. Electronic Engineering Department, The Chinese University of Hong Kong, Shatin, Hong Kong

2. Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands

3. Materials Science and Technology Research Center, The Chinese University of Hong Kong, Shatin, Hong Kong

In this presentation, we report on the gate dielectric modification by polymer blend in organic transistors. We demonstrate that by blending insulating polymers one can fabricate an insulating layer with controllable surface energy for organic field-effect transistors. As a model system, we used copper phthalocyanine (CuPc) evaporated on layers of polymethylmetacrylate (PMMA) blended with polystyrene (PS) with different blending ratios, and measured the field-effect mobility in transistors. We show that the highest field-effect mobility is achieved for identical surface energies of the dielectric and the semiconductor. This simple technique demonstrates the viability of using the blends of insulating polymers to systematically control the surface energy of the gate dielectric toward achieving better performances.

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A02329-03987

Enhanced Performance of Organic Field Effect Transistor Based on High Quality Copper Phthalocyanine Thin Film

Pramod KUMAR; Subhasis GHOSH

School of Physical Sciences, Jawaharlal Nehru University, New Delhi, India

Among the wide range of p-type organic semiconductors copper phthalocyanine (CuPc) is one of the most promising candidates for the fabrication of organic field effect transistor (OFET). The success of organic electronic devices is strongly dependent on the ability to tailor the properties of thin films and interfaces which in turn depends on how well the crystalline growth has taken place in the layer by layer growth. Highly oriented layer by layer growth of organic molecules will depend on the initial molecule to substrate interaction and then molecule to molecule interaction, so the first few molecular layers will have an impact on the subsequent layers. Hence by the controlled growth of the first few monolayer by engineering the growth parameters, highly oriented crystalline films can be achieved. CuPc is a well known organic semiconductor

for its crystalline growth on SiO₂ and other substrates using simple and easy fabrication technique of vacuum evaporation. However the room temperature films show less crystalline growth and low mobility. In this study we have investigated the effect of substrate temperature and evaporation rate on the crystalline growth i.e. effect of temperature on the initial substrate-molecule interactions and then molecule-molecule interactions. CuPc thin films are grown on different substrate, such as quartz, SiO₂(500nm)/n++-Si and on au(30nm)/glass using vacuum evaporation technique with substrate temperature and evaporation rate varied from 30°C to 150°C and 1Å/sec to 0.1 Å/sec, respectively. The x-ray diffraction(XRD) pattern, absorption spectroscopy, scanning tunneling microscopy(STM), and current-voltage characteristics of OFET based on these films are analyzed.

The XRD pattern of films deposited on quartz substrates from room temperature to 105°C show increasing peak intensity with decreasing FWHM and there is a decrease in intensity at 120°C. After 120°C increase in peak intensity is observed upto 150°C, this increase in peak intensity could be due to the local confinement of the single crystal grains at high temperatures. The absorption spectra of all the CuPc thin films(100nm) at various substrate temperature on quartz substrate have shown strong peak at ~330nm and ~620nm as B-band and Q-band, respectively. The 620nm(second π - π^* transition) peak shows continuous red shift as substrate temperature varied from 30°C to 105°C and then blue shift upto 150°C. STM results show better surface morphology with bigger grains.

OFETs were fabricated with gold contacts with channel length of 20 μ m. In comparison with other substrate temperature, the best output characteristics are observed in OFETs fabricated with substrate temperature of 105°C and evaporation rate of 0.1 Å/sec. Hence the charge carrier mobility of the fabricated OFET devices is found to be strongly dependent on the crystalline growth of the thin films as supported by the X-ray, STM and absorption spectroscopy measurements, which in turn found to be dependent of substrate temperature and evaporation rate. A max mobility of ~0.1cm²/Vs with on off ratio of 10⁴ is observed in OFET fabricated under optimized growth conditions.

A02332-03995

Triplet Exciton in Poly Phenylene Vinylene: Fullerene Based Organic Solar Cells Doped with Iridium Complex

Teddy SALIM; Jun Yan LEK; L.H. WONG;
Yeng Ming LAM; Subodh MHAISALKAR
School of Materials Science and Engineering, Nanyang Technological University, Singapore

Short singlet exciton lifetime in conventional organic solar cells is one of the reasons for its low efficiency compared to silicon and thin films devices. The presence of organometallic complexes such as iridium complexes can enhance the activation of triplet excitons. As compared to singlet excitons, triplet excitons with longer lifetimes resulting in a higher probability for them to reach the donor-acceptor interface in a blend heterojunction organic solar cell. We investigated the effect of incorporation of tris(2-phenylpyridine) iridium [Ir(ppy)₃] in poly [2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene] (MEH-PPV): [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) organic solar cell system. Upon incorporation of iridium complex, the power conversion efficiency (PCE) increases due to the enhancement of short-circuit current. When the MEH-PPV:PCBM ratio was reduced, PCE improvement was observed and the triplet contribution through incorporation of Ir(ppy)₃ was also observed to vary with different MEH-PPV:PCBM ratio. This is assumed to be due to the different interaction strength between PCBM and MEH-PPV when the PCBM amount is varied thus affecting the exciton dissociation, which affects the conversion efficiency of the singlet excitons present in the system.

A02332-04010

Poly (3-hexylthiophene) Nanofibers for Organic Photovoltaic Applications

Teddy SALIM; Shuangyong SUN; Jun Yan LEK;
L.H. WONG; Yeng Ming LAM; Subodh MHAISALKAR
School of Materials Science and Engineering, Nanyang Technological University, Singapore

Self-assembly of polymeric π -conjugated systems, such as in the case of poly (3-hexylthiophene) (P3HT) nanofibers, has been reported to improve charge transport in bulk heterojunction photovoltaic devices. In this study, a mixture of these P3HT nanofibers, prepared by gradually cooling the hot solution of P3HT in *p*-xylene, with [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) resulted in highly efficient organic photovoltaic devices. The high efficiency is attributed to the interconnected fibrillar P3HT structures, as observed by Atomic Force Microscopy, formed even without thermal annealing. Investigation on the effect of cooling rate on the efficiency of the cells and the optimum P3HT:PCBM ratio were also conducted.

In addition, further improvement of the device performance was observed when P3HT nanofibers were coupled with another thermal-free approach using alkanethiol additive. The combination of these two approaches shows great potential in the fabrication of highly performing devices at room temperature, thus enabling fabrication on flexible substrates.

A02338-04014**Solution-based Direct Fabrication of Organic Field-effect Transistors by Surface Selective Deposition**

Takeo MINARI¹; Masataka KANO²;
Tetsuhiko MIYADERA³; Kazuhito TSUKAGOSHI^{3,4,5}

1. *RIKEN, Wako, Japan*
2. *Dai Nippon Printing Co. Ltd., Kashiwa, Japan*
3. *AIST, Tsukuba, Japan*
4. *MANA, NIMS, Tsukuba, Japan*
5. *JST-CREST, Kawaguchi, Japan*

We have developed the surface selective deposition technique as a bottom-up fabrication method for the preparation of organic field-effect transistors (OFETs), which allows large area integration of OFETs from solution. This technique exploits the effect of patterned surface wettability, which leads the selective crystallization of soluble organic semiconductors on a desired area. The self-organized organic films deposited selectively in this manner grow to form the channels of OFETs and circuits. The proposed method satisfies several important requirements of printable electronics, including reduction of energy consumption, minimization of facilities, and the on-demand use of molecular materials. In the present study, the selective organization of OFETs is demonstrated on plastic substrates as a solution-processable fabrication method for flexible plastic electronics.

The proposed fabrication method is based on patterning of the surface of a polymer insulator with phenyl and alkyl functional groups as wettable and unwettable regions, respectively, which involves removal of the surface alkyl groups by irradiation under vacuum ultraviolet light, followed by the formation of phenyl self assembled monolayer in the regions that will form the channel region of the OFETs. The phenyl-modified surface is wettable by the organic semiconductor solution, likely due to π - π interaction between the surface and the solvent. The self-organized OFETs display an average mobility of 0.53 cm²/V s, on/off ratio of 10⁹, and subthreshold slope of 0.18 V/dec, with near-zero and narrowly distributed threshold voltage. An inverter circuit prepared using these devices is demonstrated with high signal gain at low input voltage.

A02376-04065**Preparation of Electrospun TiO₂ Nanofiber Electrode for Solid-State Dye-Sensitized Solar Cells**

Min-Kang SEO; Soo-Jin PARK
Department of Chemistry, Inha University, Incheon, South Korea

Electrospun TiO₂ nanofibers were prepared for an electrode of dye-sensitized solar cells (DSSCs). TiO₂ nanofiber electrode was electrospun directly onto a FTO substrate from a mixture of titanium isopropoxide and poly(vinyl acetate) (PVAc) in dimethyl formamide. The TiO₂ nanofibers were composed of one-dimensionally ordered fibrillar structure with ca. 30-nm thick. The DSSCs with electrospun TiO₂ electrodes with gel electrolyte based on PVDF-HFP revealed the conversion efficiency of 3% which was found to be over 88% of liquid electrolyte. Therefore, we have successfully demonstrated that the electrospun TiO₂ nanofiber electrode could be provide a new alternative to the use in DSSCs of conventional nanostructure electrode, enhanced penetration of the polymer gel electrolyte.

A02388-04446**Organic Insulators for Transparent & Flexible OTFT**

Saumen MANDAL^{1,2}; Monica KATIYAR^{1,2}
1. *Department of Materials & Metallurgical Engineering, Indian Institute of Technology Kanpur, Uttar Pradesh, India*
2. *Samtel Centre for Display Technology, Indian Institute of Technology Kanpur, Uttar Pradesh, India*

Development of organic thin film transistor (OTFT) for flexible and printable electronics will lead to many new applications of displays, radio frequency identification tags (RFID), sensors etc. Therefore, OTFT fabrication using insulating, semiconducting and conducting materials on polyethyleneterephthalate (PET) substrate, which is flexible and transparent, is an emerging field of research. The challenge is to find materials that can be solution processed to allow formation of inks for printing. In this paper, we compare OTFT performance based on three different organic insulator, Poly(4-vinylphenol) (PVPh), Polyvinyl alcohol (PVA) and Poly(methyl methacrylate) (PMMA). First we characterize the structural and dielectric properties of these materials after spin coating them on ITO coated PET. Annealing time and temperature is optimized based on Differential thermal analysis (DTA) and Thermo gravimetric analysis (TGA) data. Optical transmission, capacitance and leakage current of dielectric film are measured. It is also structurally characterized using X-ray diffraction (XRD), Atomic force microscopy (AFM) and Raman spectral analysis.

Finally, pentacene is deposited on vacuum baked dielectric film and then gold on pentacene using shadow mask. Transistor characteristics are measured in ambient atmosphere without any encapsulation. Microstructure analysis of pentacene film is performed by X-ray diffraction (XRD), Atomic force microscopy (AFM) and Raman spectral analysis.

A02483-04247

Light Emitting Organic p-i-n Homo Diodes Based on Chemically Doped Wide Band Gap Materials

Sami HAMWI; Jens MEYER; Stephan SCHMALE; Thomas WINKLER; Hans-Hermann JOHANNES; Thomas RIEDL; Wolfgang KOWALSKY
Institute for High-Frequency Technology, Technical University of Braunschweig, Braunschweig, Germany

A detailed fundamental analysis of the analogy of organic light emitting diodes (OLEDs) and their inorganic counterparts is still lacking. One approach to shed more light on this question is to study an organic p-i-n device consisting only of one organic material in order to reduce the number of hetero-interfaces and keep the overall system as simple as possible. Therefore, we will present the first small molecule homo p-i-n OLED based on 4,4'-Bis(carbazol-9-yl)-biphenyl (CBP). As a wide band gap material CBP emits violet light with a peak wavelength at 427 nm, if an efficient injection of holes and electrons is facilitated by chemically doped p/n regions near the electrodes.

As a prerequisite, we will first demonstrate that CBP can be chemically p-doped with transition metal oxides such as MoO₃. Ultraviolet photoelectron spectroscopy (UPS) reveals the energy levels of MoO₃ with an electron affinity of 6.7 eV which is favourable for p-type doping of CBP with ionisation energy of 6.34 eV. With in-situ Kelvin probe measurements of MoO₃ doped CBP deposited onto indium tin oxide (ITO) we were able to estimate the free carrier density as well as the doping efficiency in the CBP:MoO₃ system. By a similar study we were able to evidence an elevated free electron density and a low work function of 2.4 eV for Cs₂CO₃ doped CBP, seeding the prospect of an efficient injection layer at the cathode side of the diode.

Since no blocking or accumulation layers are inserted into the homo p-i-n diode we studied the location of the exciton generation zone in dependence of the thickness of the intrinsic layer. Luminance *I-V* measurements in connection with angular resolved analysis of the spectral emission characteristics and concomitant device simulation localized the emission zone near the n-type doped layer. The results will be interpreted in the context of the charge transport properties of CBP.

In analogy to inorganic p-i-n diodes, under the irradiation of the solar simulator our organic homo p-i-n structure functions as a photo-diode and shows an open-circuit voltage of 2.9 V corresponding to the built in voltage of the CPB p-i-n diode. The exciton dissociation is induced by the intrinsic electrical field.

Our results represent the first organic homo p-i-n structure that works both as LED and photodiode.

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A02485-04893

Molecular Orientation Dependent Formation of Interfacial Dipole at Organic Donor-Acceptor Heterojunction: C₆₀/6T Interfaces

Chaw Keong YONG¹; Dongchen QI¹; Mi ZHOU¹; Xingyu GAO¹; Wei CHEN^{1,2}; Kian-Hoon Peter HO¹; Thye-Shen Andrew WEE¹
 1. Department of Physics, National University of Singapore, Singapore
 2. Department of Chemistry, National University of Singapore, Singapore

The energy level alignment of organic donor-acceptor heterojunction is focused in this work. We found the interface dipole of organic heterojunction is controlled by the molecular orientation. Organic donor-acceptor heterojunction based on sexithiophene (6T) and fullerene (C₆₀) were fabricated on series of substrate. The interfacial charge transfer and energy level alignment were studied by photoemission spectroscopy (XPS/UPS) and near edge x-ray adsorption fine structure (NEXAFS) measurement while the surface morphology and molecular orientation were studied by surface probing microscopy (SPM). For C₆₀ deposited on standing phase 6T layer, interface dipole of ca. 0.45eV was observed, which resulting in Fermi-level pinning at the interface and regardless of the substrate work function. NEXAFS revealed the partial occupation of C₆₀ lowest-unoccupied molecular orbital (LUMO) state which is responsible for the formation of interfacial dipole with negative pole at C₆₀ side. By probing the heterojunction at different angle, we found the ultrafast electron transfer from 6T to C₆₀. For C60 deposited on lying phase 6T, UPS measurements revealed the vacuum level alignment across the interface and no interfacial charge transfer was observed. Our results suggested the spontaneous interfacial charge transfer at donor-acceptor interface is controlled by the molecular orientation and hence the donor-acceptor molecular configuration, which is also a function of ionization potential.

A02596-04477

UV-Visible Spectroscopy as an Effective Method to Determine Salt Nature of Polyaniline and its Composites with V₂O₅

Uendra MAHATME¹; Vilas TABHANE²;
Subhash KONDAWAR³; Sunil DONGRE⁴;
Prashant DABARASE⁴

1. Department of Physics, K. Z. S. Science College, Maharashtra, India
2. Department of Physics, Institute of Science Mumbai, Maharashtra, India
3. Department of Physics, Shree Shivaji Science College, Maharashtra, India
4. Department of Physics, Bhalerao Science College, Maharashtra, India

PANI salt and its composites with V₂O₅ have been prepared by chemical oxidative polymerization by taking various mass % of V₂O₅ xerogel with monomer in polymerization mixture in presence of sulfuric acid as dopant. Homopolymer and its composites were undertaken for UV-VIS and XRD spectroscopic analysis. Salt nature, different oxidation states (Quinoid / Benzenoid ratios) and required electronic transitions ($n-\pi^*$ and $\pi-\pi^*$) of these composites has been discussed by their UV-VIS analysis. From their XRD analysis all composites are found to be of polycrystalline nature and of orthorhombic crystal type. Calculated average crystallite size of most composites from XRD spectra are found to be in the nano range. The temperature dependent electrical conductivity and activation energy of all samples have been calculated in the range of applicability of Arrhenius type equation. All samples of PANI/V₂O₅ shows the increment in conductivity with rise in temperature [$\sigma = \sigma_0 \exp(-E_a / 2kT)$], which is the characteristic of semiconductor nature, indicates that the tunneling is the most prominent transport mechanism. These composites follow the equation $\sigma(\omega) = A \omega^s$ for their ac conductivity [$\sigma(\omega)$] and in case of each of these composite value of exponent 's' found to be less than one which is independent of temperature. This is well agreement with the acceptance of quantum mechanical tunneling (QMT) of charge carriers in these composites as like PANI. The ac conductivity increases linearly with the frequency and it is the characteristics of the disordered materials like conducting polymers.

A02605-04450

Scanning Probe Microscopy on Active Organic Electronic Devices: Solar Cells

David GINGER

Chemistry, University of Washington, Seattle, WA, United States

We correlate processing and nanoscale film morphology with the performance of active organic electronic devices ranging from solar cells to light-emitting electrochemical cells by developing and applying electrical scanning probe microscopy techniques. In this talk we discuss the use of conductive Atomic Force Microscopy (cAFM), scanning Kelvin probe microscopy (SKPM), photoconductive Atomic Force Microscopy (pcAFM), and time-resolved Electrostatic Force Microscopy (trEFM) to map local transport, photocurrent generation, surface potentials, and recombination/trapping in active polymer solar cells with sub-100 nm resolution. These techniques reveal variations in performance across both the nanoscale and microscale. Our results indicate that better morphological control could still improve performance in many blends, that the polymer/anode contact may negatively affect performance in some devices, and that improving uniformity in transport will be important to the successful implementation of tandem polymer solar cells. We also discuss our recent measurements on several model polymer blend cells such as the effects of annealing on the formation of hole transport, electron transport and photocurrent collection networks in the archetypal polythiophene (P3HT) fullerene (PCBM) system. and we investigate the formation of mesoscopic PCBM crystallites and their impact on the performance of polyfluorene-copolymer/PCBM cells during solvent-vapor annealing.

A02647-04542

Enhanced Thermal Stability of Conducting Polymer Composites PANI/ZrO₂ of Nano Crystallite Size

Sunil DONGRE¹; Vilas TABHANE²;
Uendra MAHATME³; Subhash KONDAWAR⁴;
Deoram NANDANWAR⁵

1. Physics, Bhalerao Science College, Nagpur, India
2. Physics, Institute of Science, Mumbai, India
3. Physics, K Z S Science College, Nagpur, India
4. Physics, Shree Shivaji Science College, Nagpur, India
5. Physics, M. M. Science College, Nagpur, India

Polyaniline salt and its composites with zirconium dioxide were polymerized by chemical oxidation method in presence of ammonium persulphate as oxidant and sulfuric acid as dopant. All samples are of dark green colour found to be of salt nature. Homopolymer and its composites were characterized by FTIR, XRD, TGA and DTA. Structural information of these composites was discussed by their

FTIR spectroscopic analysis. From their XRD spectroscopic analysis all composites are found to be of polycrystalline nature and of orthorhombic crystal type. Calculated average crystallite size of most composites from XRD spectra are found to be in the nano range. Thermo gravimetric curves reveal the increment in thermal stability of composites with rise in mass % of ZrO_2 and it is highest for PANI/40 % ZrO_2 . Lower thermal stability has observed for more conductive PANI / 32 % ZrO_2 composite. The calculated values of T_g / T_m from DTA curves of all samples are 0.582 K to 0.585 K, ensure the symmetrical polymer type of all composites including PANI. Presence of both T_g and T_m on DTA curve shows that PANI and all its composites are partially crystalline. The temperature dependent electrical conductivity and activation energy for polymer and its composites has been estimated and all of them follow the Arrhenius type equation. All samples shows the increment in conductivity with rise in temperature (semiconductor nature) indicates that tunneling is the most prominent charge transport mechanism and also agreed with VRH model. These composites follow the equation $\sigma(\omega) = A\omega^s$ for their ac conductivity and in case of each of these composites value of exponent 's' found to be less than one which is independent of temperature. This is well agreement with the acceptance of quantum mechanical tunneling (QMT) of charge carriers in these composites as like PANI. The ac conductivity increases linearly with the frequency and it is the characteristics of the disordered type materials like conducting polymers.

A02789-04764

Optimization of Bridged Phenylene Materials for Optoelectronics Applications

Andrew GRIMSDALE

School of Materials Science and Engineering, Nanyang Technological University, Singapore

Bridged phenylene oligomers and polymers represent one of the most important classes of materials for organic electronics applications. In this talk I will provide an overview of my work on designing and synthesizing new phenylene-based materials for use in organic electronic devices such as light-emitting diodes and solar cells. Particular emphasis will be on structure-property relationships and on how synthetic design can be used to optimize the device properties, e.g. through the minimization of defects.

A02791-04774

Role of Solvent Water Content in Organic Photovoltaic Devices

Chung-How POH; Bofei XUE; Warwick BELCHER; Paul DASTOOR

Centre for Organic Electronics, University of Newcastle, New South Wales, Australia

It is known that the active layer in organic solar cells is susceptible to performance degradation caused by UV radiation and the presence of oxygen and moisture. This paper examines the degradation in device performance brought about solely by water contamination in the active layer. P3HT:PCBM devices are used as a test-bed in this study. Devices with varying solvent water content were prepared and characterised using spectroscopic and standard photovoltaic testing methods. The relationship between photovoltaic performance degradation and the level of water contamination in the film is discussed. This work highlights the effect of moisture in the blend when its content is relatively low, such as that which is likely to occur during device fabrication or encapsulated devices operating under high humidity conditions for extended periods.

A02801-04792

Electrochemical Deposited Organic Luminescent Films: A New Approach for Fabricating Low-cost, High Performance OLEDs

Ma YUGUANG

State Key Laboratory of Supramolecular Structure and Materials, Changchun, China

Recently all of the researchers in the area of organic electronics were excited by the news from Sony Co. that commercial OLED TV with display size of 11 inch has come into the market. In the meanwhile, we must realize that it is imminently required to depress the cost of OLED to complete with other display technology c.a. LCD screen. Conventional methods to fabricate OLEDs are spin-coating, vacuum deposition and ink-jet printing, but all the three methods have their own benefits and shortcomings. For example, the waste of materials, complex technology and low resolution are main problems in these three methods. Recently, electrochemical deposition (ED) has been developed by our groups as a simple, economical and high-resolution patterning technology to solve these problems.

We reported here the preparation of high quality ED films with high luminescent efficiency and smooth surface morphology, which can be used as emitting layer for OLEDs. The red, green and blue device arrive an efficiency level of 5 cd/A, 20cd/A, and 7cd/A, respectively. In ED technique, "RGB color pixel" can be fabricated by

controlling the potential on the ITO strip with state “on” or “off” and changing the electrolytic cell containing various color ED precursors. It has the advantage of simplicity compared with current techniques such as ink-jet printing for polymer-based LEDs and shade masking for small-molecular LEDs.

Acknowledgment:

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A02806-04799

A New Ruthenium(II) Complex with Peripheral Carbazole Substitution and the Application in Electrochemical Deposition Organic Light-Emitting Diodes

Zhu YINGYING; Ma YUGUANG

State Key Laboratory of Supramolecular Structure and Materials, Changchun, China

Ruthenium(II) complexes as kind of phosphorescent materials have attracted great attention in the field of organic light-emitting diodes (OLEDs) for their high efficiency and the features in electrochemistry and exhibiting several reversible redox processes and are chemically, photochemically and thermally stable. However, the fabrication of these phosphorescent devices is relatively intricate. Thus searching for new OLED materials and especially new film-formation techniques is the key item for the future development of OLEDs industry.

A new kind of peripheral carbazole substituted ruthenium(II) complex $[\text{Ru}(\text{bpy})_2(\text{tkdp-bpy})(\text{AsF}_6)_2]$ (bpy = bipyridine, tkdp-bpy = 4,4'-(3,5-bis(6-(9H-carbazol-9-yl)hexyloxy) phenyl)methoxycarbonyl-2,2'-bipyridine) is synthesized, which can form high quality film using electrochemical deposition (ED) technique, thus be used for OLEDs fabrication. This complex displays intense deep red phosphorescent emission centered at 660 nm both in fluid solution and solid state at room temperature, which comes from the transitions of ³MLCT. The great extension of substituted ligand tkdp-bpy effectively reduces the extent of complex aggregation in solid state. Complex $[\text{Ru}(\text{bpy})_2(\text{tkdp-bpy})(\text{AsF}_6)_2]$ exhibits two reversible oxidation processes with the oxidation potentials of 0.75 and 1.13 V, attributed to the oxidation of carbazole and Ru metal center, respectively. The introduction of electron-withdrawing ester functionality into Ru^{II} complex through 4,4'-positions of ligand bpy leads to the increasing of metal center potential, meanwhile, the oxidation potential of electroactive group carbazole is much lower than that of metal center, thus in positive electropolymerization process under relative low potential (c.a. 0.8 V), the complex can be electropolymerized by coupling the peripheral carbazole groups without affecting the center part of metal complex. A highly luminescent co-polymerized ED film of complex

$[\text{Ru}(\text{bpy})_2(\text{tkdp-bpy})(\text{AsF}_6)_2]$ and a blue-emitted carbazole substituted spirobifluorene compound TCPC-6 is obtained under carefully controlled ED process, in which Ru^{II} complex acts as dopant and TCPC-6 acts as host, and used as emitting layer in OLEDs. The diode with structure of ITO/ED film/BCP (50 nm)/Alq₃ (70 nm)/LiF (0.5 nm)/Al shows good performance with the maximum luminous efficiency of 3.9 cd A⁻¹. It gives out strong red emission with the CIE coordinates of (0.61, 0.32) and the maximum brightness of 293 cd m⁻². It is the first electropolymerized phosphorescent OLEDs as has been reported so far. For comparison, a common spin-coated device based on complex $[\text{Ru}(\text{bpy})_2(\text{tkdp-bpy})(\text{AsF}_6)_2]$ doped in TCPC-6 is also fabricated. It is found that with increasing the driving voltage, ED device exhibits higher efficiency and much lower turn-on voltage as well as relative stability in efficiency reduction than spin-coated device. It indicates that complex $[\text{Ru}(\text{bpy})_2(\text{tkdp-bpy})(\text{AsF}_6)_2]$ is a good candidate for ED device and the new developed ED technique has great potential in the field of OLEDs.

A02806-04801

Highly Efficient Pure Yellow Organic Light-emitting Devices Based on an Iridium(III) Complex with Spirobifluorene in the Ligands

Fei TENG; Ma YUGUANG; Li FENG

State Key Laboratory of Supramolecular Structure and Materials, Changchun, China

Highly efficient yellow emission materials are important in multicolor display, and they are also useful for white organic light-emitting diodes (OLEDs). A great deal of effort has been done to fabricate the white OLEDs comprising just two colors, yellow and blue, with a certain ratio. OLEDs based on fluorescent yellow emission materials, such as [2-methyl-6-[2,3,6,7-tetrahydro-1H,5H-benzof[1j]quinolizin-9-yl]ethenyl]-4H-pyran-4-ylidene] propane-dinitrile (DCM2), 4-(dicyanomethylene)-2-tert-butyl-6-(p-diphenylaminostyryl)-4H-pyran (DCTP), and 5,6,11,12-tetraphenyl-naphthacene (rubrene), show low efficiencies, in which only the singlet excitons contribute to the light emission. Phosphorescent complexes are regarded as the promising materials for highly efficient OLEDs because they can harvest the energy not only from the singlet but also from the triplet excitons. Up to date, many blue, green and red electrophosphorescent devices based on phosphorescent complexes incorporating heavy metals platinum(II), rhenium(I), ruthenium(II), osmium(II), and iridium(III) have been reported. However, there are relatively few works on the yellow or orange electrophosphorescent OLEDs.

Herein, we report the electroluminescent (EL) properties of five organic light-emitting devices (OLEDs) based on a yellow phosphorescent complex, iridium(III) bis(2-(9,9'-spirobifluorene)-7-yl)pyridine-N,C²) acetylacetonate

((SBFP)₂Ir(acac)), N,N'-dicarbazolyl-3,5-benzene (mCP) is used as the host. Highly efficient yellow OLEDs based on the complex (SBFP)₂Ir(acac) have been fabricated. The optimized device shows a maximum luminance of 37219 cd/m², a maximum luminous efficiency of 50.6 cd/A, a maximum power efficiency of 46.8 lm/W and a maximum external quantum efficiency of 15.4%. To our knowledge, the maximum power efficiency of device E is the best ever reported for vacuum evaporated OLEDs in the yellow and orange chromaticity region. After a thin electron-blocking layer of fac-tris(1-phenylpyrazolato-N,C^{2'})iridium(III) Ir(ppz)₃, replacing the hole-transporting layer of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB), highly pure yellow electroluminescence with the Commission Internationale de l'Eclairage coordinates of (0.46, 0.53) is obtained.

A02818-04833

Design and Synthesis of Novel Blue Light Emitting Naphthalimide

Yi WANG; Yan HUANG; Zhiyun LU; Minggui XIE
Department of Chemistry, Sichuan University, Sichuan, China

Six novel blue light-emitting naphthalimide derivatives were designed and synthesized, their molecular structures were confirmed by ¹H NMR and MS, and their photoluminescence properties were studied. All of these compounds have highly photoluminescence efficiencies with their λ_{EMmax} fall in 440~460 nm in solution, suggesting that they are potential candidates as pure blue dopants in the fabrication of OLEDs. Moreover, by incorporation of bulky substituents, *i.e.* *tert*-butyl and biphenyl substituent groups, into the naphthalimide skeleton, the resulting molecules have much improved solid state photoluminescence properties compared with other common naphthalimide derivatives, since the increased molecular size and steric hindrance have prevented the concentration quenching effectively. Their solid fluorescence emission spectra peaks locate in 450~480 nm, indicating they are perspective materials as emitter for the fabrication of non-doped blue OLEDs.

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A02824-04865

Synthesis and Characterization of Novel Broad-Absorption-Banded Conjugated Copolymers Bearing Perylene Bisimide Moieties

Erfu HUO; Yan HUANG; Zhiyun LU; Qing JIANG; Minggui XIE
College of Chemistry, Sichuan University, Chengdu, China

In the fabrication of organic photovoltaic devices, solution-processible fullerenes derivatives, *e.g.*, PCBM, are mostly used in scientific literatures. However, the aggregation of the conjugated polymer and the PCBM may be unfavorable to the good IPN formation, thus the poor performance of the cell. Moreover, PCBM has weak absorption in the visible and near-infrared region. Thus the seeking for polymeric electron acceptor with improved absorption has been an ever hot issue, but met with limited success.

In this paper, an excellent n-type semiconductor segment--perylene diimides (PBIs) is introduced into the p-type polymer skeletons, such as fluorene and carbazole, to improve their electron affinity, and the resulting copolymers, poly {[N,N-bisdodecyl-3,4,9,10-perylene diimide-1,7-diy]alt-[9-(2-ethylhexyl)carbazole-3,6-diy]}, and poly {[N,N-bisdodecyl-3,4,9,10-perylene diimide-1,7-diy]alt-[9,9-dihexyl]fluorene-2,7-diy]}, have relative low band-gaps due to of the prolonged conjugation length. Their UV-visible absorption spectra indicate that they have broad and strong spectral responses in 200~720 nm, suggesting that they are perspective candidates as polymer solar cell materials.

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A02824-04867

Novel Copolymers with Substituted Thiophene and Squaraine Moieties Having Large Coverage with Solar Spectrum

Erfu HUO; Yan HUANG; Zhiyun LU; Qing JIANG; Minggui XIE
College of Chemistry, Sichuan University, Chengdu, China

In the fabrication of polymer solar cells (PSCs), efficient absorption to the solar spectrum and effective charge transportation of the photosensitive layer are of crucial importance, while the relative low energy conversion efficiency of PSCs is mainly suffered from the unmatched absorption with the solar irradiation. In this paper, novel low band-gap conjugated copolymers are designed to extend their optical absorption to longer wavelengths, and synthesized *via* polycondensation reaction. The UV-Vis spectra indicate that these polymers, when dissolved

in CH_2Cl_2 , exhibit broad and strong spectral responses in 200~900 nm, which have good coverage with solar spectrum. Moreover, by the incorporation of electron-trapping squaric acid into the electron-donating 2,5-Bis[(E)-N-alkylpyrrol-2-ylvinyl]-3-alkylthiophene (PVTVP) unit, efficient charge separation may be realized in the D-A interface inner the polymer molecule, thus donor-acceptor bulk heterojunction structures can be formed. All these results indicate that these novel polymers are potential candidates as good organic photovoltaic material.

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A02833-04855

Polymer White-Emitting Materials and Devices

Yong CAO

Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou, China

In recent years, white polymer light-emitting diodes (WPLEDs) have received great attention due to their potential application in full-color flat-panel displays and solid-state lighting. Varieties of approaches have been proposed for the realization of white emission in PLEDs. In this report we summarize our recent efforts on synthesis of novel white-emitting polymers and fabrication of high-efficiency white-emitting polymer devices. It includes:

1. White light-emitting emission from single copolymer with simultaneous blue, green, and red chromophores (singlet or triplet or their mixture) incorporated into conjugated polymer backbone;
2. White-emitting devices based on triplet complex or singlet chromophores doped into polymer host.
3. Multi-layer white-emitting devices with high work-function metal as cathode for all-printable white devices.

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A02878-04921

Synthesis of Phosphorescent Conjugated Polymers Containing Cationic Iridium(III) Complexes and Their Applications in Polymer Memory Device and Chemosensors

Qiang ZHAO; Shujuan LIU; Qidan LING; Wei HUANG
Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing, China

Cationic Ir(III) complexes have many features that make them one of the best candidates for optoelectronic applications. Introducing cationic Ir(III) complexes into conjugated polymers by means of chemical bonds is an effective way for realizing solution-processed cationic Ir(III) complexes and their applications in optoelectronic devices, which can solve the problem of phase separation in the doping systems.

In our previous works, we have reported the synthesis of several series of phosphorescent conjugated polymers containing cationic Ir(III) complexes and their applications in polymer light-emitting diodes (PLEDs). Recently, we have been extending the application of this kind of materials in polymer memory devices and chemosensors.

Firstly, nonvolatile flash memory device based on a phosphorescent conjugated polymer containing cationic Ir(III) complexes was realized, which exhibited excellent memory performances including low reading, writing, and erasing voltages and a high ON/OFF current ratio of more than 10^5 . This work extended the application of phosphorescent polymers in polymer memory devices.

Secondly, we also studied the application of this kind of phosphorescent polymers as chemosensors. Novel phosphorescent polymer chemosensors for fluoride anion, cation and pH were designed, which exhibited excellent detection performances such as high sensitivity and naked-eye detection.

In conclusion, our research works have extended the applications of phosphorescent conjugated polymers containing cationic Ir(III) complexes in other fields, such as polymer memory devices and chemosensors.

A02880-04927

Solution Processed Organic Semiconductors for High Performance OPVs and OLEDsZhi-Kuan CHEN*Institute of Materials Research and Engineering, Singapore*

In this talk, I will first present our recent research progress made in blue light emitting materials for OLEDs. Blue emitter is the bottle-neck for OLED technology due to its relatively lower efficiency and shorter lifetime than other emitters. To address this issue, a series of novel fluorescent deep blue light emitting oligomeric materials with device efficiency of 10% and CIE (0.15, 0.09) has been developed. These materials combine the merits of solution processability of polymers and high purity of small molecules, to offer extremely good efficiency and lower cost for OLED devices.

In the second part, I will talk about the newly developed p-type and n-type organic semiconductors for OPVs. Over the past decade there have been extensive efforts to develop organic photovoltaic cells (OPVs). To achieve high efficient OPV devices, both electron donor (hole transporting) and electron acceptor (electron-transporting) materials with good chemical stability, solution processibility, charge carrier mobility with controllable HOMO-LUMO energy levels are essential. So far, the best performance of OPV devices is demonstrated by P3HT and PCBM system with power conversion efficiency of 5.4%. However, P3HT can only absorb sunlight with wavelength less than 650 nm. While PCBM tends to have low absorption coefficients in the visible range. Thus there is a great demand to develop low bandgap polymers as well as new n-type materials which can have better light absorption efficiency than P3HT/PCBM system. In this talk, I will present the design and synthesis of a series of new low bandgap polymers and n-type materials and their OPV application. Film morphology on the device performance and OPV device degradation mechanism will also be addressed.

A02888-04936

Organic Semiconductors Nanostructures via Scanning Probes PatterningFranco CACIALLI*Department of Physics and Astronomy & London Centre for Nanotechnology, University College London, London, United Kingdom*

We interpret nanotechnology as the ability to produce nanostructures “a la carte”, rapidly and reproducibly over large areas, for a host of different materials, since this is necessary for exploitation of the full potential of nanoscience, i.e. of the physical and chemical processes taking place at the nanoscale.

Within this context we are particularly interested in direct writing of organic semiconductors nanostructures, since they provide a remarkably versatile “materials platform”, with functional properties suitable for electronics and optoelectronics, sensors, and, possibly, biomedical applications.

In addition to our latest results on scanning near-field optical lithography (SNOL) of photosensitive conjugated polymers (or of their precursors), that enabled us to achieve minimum features of 60 nm, I will present an approach to high-resolution lateral patterning of electroluminescent and/or inert polymer systems, based on scanning thermal lithography (SThL) of thin films prepared on a variety of substrates. Minimum features sizes of less than 30 nm are possible, despite the use of micron sized thermal probes, as well as fast writing speeds of up to 100 μ m/s. We investigate the origin of this high resolution by both experiment and finite element modelling of the tip-sample system, and find that these resolutions can be achieved with a tip-sample contact area of 100nm. Nevertheless, we predict a further resolution enhancement once an optimised probe is adopted.

N90001**Excitons at Organic Semiconductor Heterojunctions**Richard H. FRIEND*Department of Physics, National University of Singapore; and Cavendish Laboratory, JJ Thomson Road, CB3 0HE, United Kingdom*

Not available at press time.

N90002**Not available at press time.**Jeremy H. BURROUGHES*Cambridge Display Technology Ltd, Bldg 2020, Cambourne Business Park, Cambridgeshire, CB3 6DW, United Kingdom.*

Not available at press time.

N90003**Thiophene-containing Copolymers for Organic Photovoltaics**Marc A. HILLMYER*University of Minnesota, Minneapolis, MN 55455, USA*

Poly(thiophene)s, poly(thienylene vinylene)s and poly(isothianaphthene)s can all be used as active materials in organic photovoltaics. Syntheses of these polymers generally rely on catalytic polymerizations of appropriately functionalized monomeric precursors.

Controlled polymerization approaches can facilitate the formation of copolymers or hybrid macromolecules that incorporate other functional components to enhance the performance of these materials. Higher efficiency plastic solar cells could be realized by tuning the key properties of these polymers such as their band gaps, compatibility with other materials, and nanoscale self-assembly behavior. In this talk I will discuss our recent approaches to the controlled preparation of new copolymers within this class of materials, emphasizing monomer design, catalytic polymerizations, block polymer self-assembly, and photovoltaic device performance.

N90004**Mesostructures and Metal Oxides in Solid-State Dye-Sensitized Solar Cells**Henry J. SNAITH*University of Oxford, Department of Physics, Clarendon Laboratory, Parks Road, Oxford, OX13PU*

Dye-sensitized solar cells (DSCs) are composed of mesostructured electron transporting electrodes, typically fabricated from metal oxides. These electrodes are sensitized with a light absorbing dye and in filled with a redox active electrolyte or hole-transporter. There has been considerable recent interest in solid-state DSCs which use a molecular hole-transporter in place of the corrosive redox active electrolyte typically employed.

The highest reported efficiencies for solid-state DSC are around 5%, and two major aspects of this device require significant improvement for this to be increased to values greater than the electrolyte based counterpart (c.a. 12%). The first is to simply enhance the light absorption in the active layer. The second is to improve the conversion of absorbed photons to collected charge (i.e. all aspects of the photovoltaic conversion process).

In the first part of the presentation we will specifically highlight the electronic losses in the “state-of-the-art” solid-state DSC. We will then present a device and materials based investigation into a range of metal oxides and mesostructures employed in solid-state DSCs, which exhibit both improved electronic and optical performance, in comparison to the state-of-the-art titania nanoparticle based devices.

N90005**Insight Into The Synthesis, Design and Processing Of Narrow Band Gap Organic Semiconducting Polymers For Solar Cell Fabrication**Guillermo C. BAZAN; Jeff PEET, Robert COFFIN; James ROGERS; Thuc-Quyen NGUYEN; Ed KRAMER; Alan HEEGER*Center for Polymers and Organic Solids, University of California, Santa Barbara, California, 93106, USA*

High charge separation efficiency combined with the reduced fabrication costs associated with solution processing (printing and coating) and the potential for implementation on flexible substrates make “plastic” solar cells a compelling option for tomorrow’s photovoltaics. The control the donor/acceptor morphology in bulk heterojunction materials as required for achieving high power conversion efficiency have is therefore of primary concern. We showed that by incorporating a few volume percent of high boiling point additive, the power conversion efficiency of photovoltaic cells (AM 1.5 conditions) is

increased from 2.8% to 5.5% [1]. Subsequent efforts centered on understanding the mechanism of action of the additives and this will be discussed in some detail [2,3,4]. More recently, the improved synthesis of polymers has been studied, in particular those backbone systems that lead to aggregation in solution and high performance devices. We will present polymerization procedures that lead to high molecular weight product in short reaction times and involve simple purification protocols. Emerging structure/function relationships will be examined, as well as those polymer systems that allow fabrication of devices that have power conversion efficiencies approaching 6 %.

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N90006

Highly Efficient Organic Devices

Karl LEO

Visiting Professor, Institute of Materials Research, Tohoku University, Sendai 981-8003 and Institut für Angewandte Photophysik, Technische Universität Dresden, 01062 Dresden, Germany

Organic semiconductors with conjugated electron system are currently intensively investigated for optoelectronic applications. This interest is spurred by novel devices such as organic light-emitting diodes (OLED), and organic solar cells. For both devices, high efficiency is a key parameter for many applications. In this talk, I will discuss some of the recent progress on highly efficient OLED and solar cells, in particular results using doped transport layers /1/: Surprisingly, doping (for raising the conductivity) has been largely ignored till now in organic devices, in contrast to classical silicon technology where controlled n- and p-type doping has always been a standard technique needed for virtually all devices.

The concept of molecular doping allows realizing green OLED devices with the highest efficiencies reported so far /2/, well exceeding the efficiency of current inorganic GaN LED! The devices were pin-devices where the emitting layer is embedded between a p-doped hole transport layer and an n-doped electron transport layers. It has been shown that these pin-structures can also achieve extremely long lifetimes. White OLED have recently achieved very high efficiencies of 90lm/W /3/, significantly higher than fluorescent tubes, opening the path to a new form of high-efficiency area lighting devices.

The doping concepts can be applied in organic solar cells as well. Here, the use of electrically doped transport layers is helpful for an optimized optical design since it yields large freedom in the choice of window layer thickness, this making it easy to put the absorber layers in the electric field maximum in the cavity. Also, doped layers are a key point in efficient charge recombination junctions for tandem solar cells: It has been shown that a pn-junction is an excellent recombination contact causing very small voltage loss.

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N90007

Doping Of Organic Molecular Films: New Dopants And Direct Visualization Via Stm

Sieu HA, Yabing QI, Michael KRÖGER, Calvin K. CHAN; Antoine KAHN

Department of Electrical Engineering, Princeton University, NJ 08544, USA

The first part of the talk describes our recent progress on n- and p-type doping of molecular semiconductors using organic as well as inorganic molecular dopants.^{1,2,3} The electronic structure, in particular the ionization energy and electron affinity, of high performance (p-dopant) molybdenum compounds and (n-dopant) cobalt compounds will be reported, along with current-voltage measurements on doped hole and electron transport layers. These measurements, and the improvement of characteristics of doping-modified devices such as organic photovoltaic cells,⁴ demonstrate the highly beneficial impact of doping molecular films in organic electronics.

The second part of the talk focuses on the physics of doping, in particular charge release/trapping, in organics as seen from the observation of single dopants in ordered molecular films via STM/S.⁵ The system investigated is pentacene p-doped with tetrafluorotetracyanoquinodimethane (F₄-TCNQ). Pristine pentacene films grown on Si(111)/Bi(001) are doped with F₄-TCNQ. Molecular resolution is obtained on the pentacene film. The topographic effects of the dopants are predominantly localized and are directly dependent on sample bias. Surface F₄-TCNQ molecules presumably diffuse into pentacene vacancies and appear negatively charged, as expected for ionized acceptors, and their bias-dependent behavior is well explained based on DFT calculations of the ionized dopant density of states. Subsurface dopants, however, exhibit the characteristics of positively charged species. This is attributed to the hole donated to the lattice, which remains localized near the dopant at equilibrium, and is spread over several molecular sites. The corresponding positive charge masks

the effects of the underlying dopant in STM images. STS spectra show potential energy lowering near a subsurface dopant, in agreement with the proposed model. These results provide the first molecular-scale visualization of the localization of donated carriers in the doping process in molecular films.

* currently at National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

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N90008

Direct Evidence for the Role of the Madelung Potential in Determining The Work Function of Doped Organic Semiconductors

Perq-Jon CHIA¹; Sankaran SIVARAMAKRISHNAN¹; Mi ZHOU¹; Rui-Qi PNG,¹; Lay-Lay CHUA^{1,2}; Richard H. FRIEND^{1,3}; Peter K. H. HO¹

1. Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 117542, Singapore

2. Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore 117543, Singapore

3. Cavendish Laboratory, University of Cambridge, JJ Thomson Road, Cambridge CB3 0HE, United Kingdom

The work function of a model degenerately doped organic semiconductor p-doped poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonic acid) can be systematically tuned over an eV-wide range by exchanging excess matrix protons with spectator cations, without altering the organic semiconductor doping level or polaron density. Ultraviolet photoelectron spectroscopy reveals this to arise not from an interface dipole, but from a bulk effect due to a shift in the Madelung potential set up by the local counterand spectator-ion structure at the polaron sites. Electrostatic modeling of this potential is in agreement with the observed shift in carrier energetics. The spectator cations also cause a systematic shift in electronphonon coupling and carrier delocalization, as revealed by infrared and Raman phonon modes, and charge-modulated absorption, which can be related to disorder in this potential.

N90009

Engineering Approach to Materials and Devices Development

Nir TESSLER; Ariel BEN-SASSON; Nir YAACOBI, Eran AVNON; Michal SORENI; Yang-Jun YU; Olga SOLOMESHCH

Sara & Moshe Zisapel nanoelectronic center, Electrical Engineering Dept., Technion, Israel Institute of technology, Haifa 32000, Israel

Semiconducting polymers and small molecules form an extremely flexible class of amorphous materials that can be used in a wide range of applications some of which are display, RF-tags, and solar cells. The rapid progress towards functional devices is occurring despite the lack of sufficient understanding of the physical processes and very little experience in device engineering. In this talk we will outline, through examples, our involvement with controlling material properties, better understanding of the physical processes (in the relevant context), and rational design of device structures.

An example of our efforts to control material properties and generate device-applicable building blocks is the use of high band gap cross-linkable conjugated polymers as host in versatile electronic formulations with varying functionalities. As an example of a rational device design we will describe a new structure of a vertical TFT which is applicable to both organic and inorganic fabrication procedures. This new TFT structure was implemented using soft lithography techniques relying on block-copolymer lithography. Typically, the vertical Organic Field Effect Transistor (OFET) we fabricated exhibit ON/OFF ratio of 10^4 - 10^5 , high on current density (10 - 100 mA/cm²), and low gate leakage currents (10^{-5} - 10^{-4} mA/cm²).

N90010

Micron order Direct Patterning Technology, Super Ink Jet (SIJ)

Kazuhiro MURATA

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan

Inkjet printing has several prominent features for printable electronics. It is on-demand, efficient and the smallest amount of energy to position the ink. Each one of these features is attractive when considering possible applications of inkjet technology to manufacturing processes. Conventional inkjet heads can eject droplets of 1 to 2 pL and are widely used as the main component of personal printers. Typical ink of 1 pL volume results in a droplet that is 13 μm in diameter while in flight, but once deposited on engineering substrates, such as glass, silicon, and ceramics, the droplet can spread to up to 100 μm in diameter.

N90012

Negative Differential Resistance of Gold and Polyaniline Nanocomposites

Tao WEN¹; Jiahua SHI¹; Minrui ZHEN²;
Chorng-Haur SO²; Hardy S. O. CHAN¹

1. Department of Chemistry, National University of Singapore

2. Department of Physics, National University of Singapore

Negative Differential Resistance (NDR) is an interesting phenomenon of some electronic materials. It was observed previously in scanning tunneling microscopy (STM) in various molecules such as cobalt phthalocyanines. More recently, NDR appeared in a triple layered organic/metal nanocluster/organic architecture sandwiched between electrodes or a simple polymer/metal nanoparticles single-layer structure.

In recent years, there has been growing interest in conducting polymer micro/nano structures as well as hybrid composite systems because of their unique confinement effect at the nanoscale. Polyaniline (PANI) has been widely studied in conducting polymer hybrid systems because of its thermal stability, unique reversible doping properties, and good compatibility.

We report here the synthesis of Au-PANI micro/nano core-shell structures which show stable and robust NDR along with memory effect (hysteresis). PANI is polymerized by using chloroaurate acid as the oxidizer in distilled water of controlled pH. In a typical reaction, gold nanoparticles are encapsulated inside PANI to form a cable-like core-shell structure at the bottom of the reactor, while pure PANI nano-spheres are found in the upper solution.

The composite structures are formed in-situ by a self-assembly process. The products are studied by SEM, EDS, TEM, XRD, FT-IR and UV-vis. I-V curves of large devices incorporating the Au-PANI nanocomposite as the active layer are measured by a two-terminal electrical probe station. I-V curves for stand-alone single nanostructures such as spheres and wires are measured via a nano-manipulator.

The gold-PANI film would show NDR when subjected to either a positive or negative voltage, but only if a large enough reverse voltage is applied first. Under repeated application of reverse voltages, the NDR current would increase until saturation, which suggests charge injection into the composite. Depending on the amount and dispersion of gold particles in the composite, single gold-PANI cable would exhibit different I-V responses such as semiconducting, ohmic as well as NDR.

We have developed a super-fine inkjet technology which enables fine pattern processing by super fine droplets measuring less than 1 micrometer. By using conductive ink, which is based on super fine metal particles, we have demonstrated direct drawing of metal circuits having a width of just a few microns. Diverse materials, such as conductive polymers, fine ceramics, metal particles etc., can be used as inks. Using a nano metal paste as an ink material, we achieved the direct printing of metallic wires of only a few micrometers in width without any pre-patterning treatment of the substrate.

The drying rate of the liquid is strongly dependent on its specific surface area, so the drying of SIJ droplets is much more rapid compared with that of a conventional ink jet droplet. Because the SIJP droplet surface area to volume ratio is very high, their evaporative speed is extremely high. Even though the organic solvent we commonly use for ink materials made of silver Nanopaste has a high boiling point of about 530 K, nonetheless, when the ink droplets have a diameter on the sub-micron scale, they evaporate in an instant. By using this effect, direct forming of three-dimensional structures anywhere on a substrate has also been demonstrated, and is possible by taking advantage of the rapid drying of the small volume droplets printed. The process is simple and the entire setup can be carried out on a desktop, in an ambient environment, and at room temperature.

N90011

Raman Spectroscopy And Imaging From Organic Conducting Polymers And Photovoltaic Devices

Ken P.J. WILLIAMS

Renishaw plc, Spectroscopy Product Division, Old Town,
Wotton under Edge, Gloucestershire, UK

The new technical developments and methods for capturing high speed Raman spectra from the surface of materials will be discussed. The subsequent transformation of these data sets into two dimensional surface chemical images will be demonstrated. Large areas can be surveyed with micron spatial resolution, whilst better defined areas can be imaged with nanometre resolution both in a very short timescale.

The presentation will be illustrated with data taken from organic conducting polymers. Mention will also be made to the use of Raman spectroscopy in the manufacturing environment for the in line determination of cell efficiency for the more mature polysilicon photovoltaic devices.

N90013**Molecular Weight Effect Of A High-Mobility Crystalline Semiconducting Polymer Poly(Bithiophene-Alt-Thienothiophene)**Jie-Cong TANG¹; Rui-Qi PNG²; Li-Hong ZHAO²; Loke-Yuen WONG²; Hardy CHAN¹; Peter K-H. HO¹ Lay-Lay CHUA^{1,2}

1. *Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, S117543, Singapore*
2. *Department of Physics, National University of Singapore, Lower Kent Ridge Road, S117542, Singapore*

Narrowly-dispersed poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) encapped with phenyl groups has been synthesized by Suzuki coupling to give number-average molar weight (MW) from 6k to 35k (polydispersity index, ≈ 1.4 – 1.8). The film morphologies of these materials are strongly dependent on MW in this range, varying from the well-known terrace to leaf and then needle morphology as MW decreases. The field-effect mobility measured on a passivated SiO₂/Si dielectric-gate shows a corresponding variation levels off for MW greater than 15k. Differential scanning calorimetry together with powder X-ray diffraction reveal the these well-ordered materials show a complex interconversion between several distinct phases. With increasing MW, the liquid crystalline order persists to increasing temperatures, but other transitions primarily related to side chain disorder are MW independent. Variable-temperature solution-state UV-Vis spectroscopy also reveals an unexpected isobestic signature of a distinctive chain folding only at high MW. Infrared and Raman vibrational spectroscopy show only weak MW dependences suggesting that polymer chain-end effects do not significantly perturb the skeletal vibrations of the π -conjugated polymer.

N90014**Sparse Monolayer-Protected Metal Nanoparticles: A General Route To High Water Dispersibility And Low Solid-Sate Coalescence Temperature**Bibin T ANTO¹; Sivaramakrishnan SANKARAN¹; Lay-Lay CHUA^{1,2}; Peter K.H. HO¹

1. *Department of Physics, National University of Singapore, Lower Kent Ridge Road, S117542, Singapore*
2. *Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, S117543, Singapore*

In order to use the metal nanoparticle (NP) films in the plastic electronics applications, it has to be annealed to eliminate the protective monolayer ligand shell or displace the polymeric dispersant to effect coalescence to a nanocrystalline “bulk-like” continuous film. We here demonstrate a new concept of sparse monolayer protection by ω -ionic functionalised alkylthiol ligands that can offer both high water and alcohol solubility; and at the same

time low coalescence temperature ($T_p \approx 145$ °C). This allows, for example, Au NP films to be coalesced to continuous metallic films with conductivity near half the value of bulk gold conductivity after only brief annealing (few min) at this temperature, far shorter than that required for commercial Ag NP systems. This method is, therefore, compatible with commercially available plastic substrates that are sensitive to temperature and organic solvents. Detailed study by Fourier transform infrared spectroscopy reveals that the coalescence of metal nano-cores is not due to thermodynamic size effects on melting as widely speculated in the literature, but dominated by desorption of protective ligands. This, therefore, allows the possibility to control the insulator-to-metal transformation without restriction on NP size.

N90015**Temperature Dependence Of Field-Effect Mobility On Different Defect Density In Graphene Sheets**Roland G-S. GOH²; Wang-Zhi CHUA¹; Zhi-Li CHEN²; Li-Hong ZHAO²; Peter K-H. HO² and Lay-Lay CHUA^{2,3}

1. *Hwa Chong Institution, 673 Bukit Timah Road, S269735, Singapore*
2. *Department of Physics, National University of Singapore, Lower Kent Ridge Road, S117542, Singapore*
3. *Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, S117543, Singapore*

Five commercial sources of natural and synthetic graphites were investigated as potential starting materials for solution-processable graphenes for device applications. These sources differ considerably in defect densities as evaluated by the intensity ratio of the Raman D to G bands, which in turn correlates in a simple way with the ease of Staudemaier chemical oxidation evaluated by Fourier-transform infrared and Raman spectroscopies, and de-oxygenation step height in thermogravimetry. The most defective graphites readily oxidize to give carboxylic acid surface groups, while the least defective ones give primarily epoxy functional groups. This was found to correlate with the ease of thermal de-oxidation, with the least defective and hence the epoxy-derivatized materials most able to re-graphenize to give more perfect graphenites with higher effective field-effect mobilities than the most defective and hence carboxy-derivatized materials.

N90016

Polymer Chain Segment Morphology And Packing Of Organic Semiconductor As Deposited By Ink-Jet Printing Into Well Structures

Loke-Yuen WONG¹; F. B. Shanjeera L. SILVA¹;
Xing-Yu GAO^{1,2}; Andrew T.S. WEE^{1,2}; Peter K.-H. HO¹
1. Department of Physics, National University of
Singapore, Lower Kent Ridge Road
S117543 Singapore, Singapore
2. Singapore Synchrotron Light Source, National
University of Singapore, S117603, Singapore

Inkjet printing of organic semiconductor (OSC) into lithographically defined well is an important manufacturing process for OLED devices. In order to study separately the dielectric spectra of both air and substrate interfaces of such films, a novel fluorine-based, self-assembled monolayer-defined well was developed on glass to confine the printed film. Poly(9,9-dioctylfluorene) (F8) was inkjet printed into the well in a single pass with multiple nozzles. Variable Angle-Spectroscopic ellipsometry (VASE) measurements were done using on the air-film interface from the top and substrate interface by measuring through the microscope. By imposing both Kramers–Kronig and optical self-consistencies on the modeling, we found differences in the conjugation length distribution, packing density and order in the spectra between the two interfaces. By delamination of the polymer film, we are able to reveal the buried substrate interface for Near-edge X-ray Absorption Fine Structure (NEXAFS) studies. Results reveal that the biphenyl-ring orientation and packing at the frontier layers of these interfaces which is different from Poly(3-hexylthiophene) (P3HT) with respect to the orientation of the alkyl side chains and molecular plane of the thiophene.

N90017

Direct Spectroscopic Evidence for a Photo-Doping Mechanism in Polythiophene and Poly(bithiophene-alt-thienothiophene) Organic Polymer Semiconductor Thin Films Involving Sorbed Moisture

Jing-Mei ZHUO^{1,2}; Li-Hong ZHAO¹;
Sankaran SIVARAMAKRISHNAN¹; Rui-Qi PNG¹;
Perq-Jon CHIA¹; Jie-Cong TANG²; Loke-Yuen WONG¹;
Mi ZHOU¹; Eric C.-W. OU³; Soo-Jin CHUA³;
Wee-Sun SIM²; Lay-Lay CHUA^{1,2}; Peter K.-H. HO¹
1. Department of Physics, National University of
Singapore, Lower Kent Ridge Road, Singapore 117542,
Singapore
2. Department of Chemistry, National University of
Singapore, Lower Kent Ridge Road, Singapore 117543,
Singapore
3. Institute of Materials Research and Engineering,
3 Research Link, Singapore 117602, Singapore

Fourier-transform infrared spectroscopy of two prototypical high-mobility polymer organic semiconductors (OSCs), regioregular poly(3-hexylthiophene) (rr-P3HT) and poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno(3,2-b)thiophene] (PBTTT), identifies a photoinduced electron transfer pathway to water molecules dissolved in the polymer matrices that accounts for the doping and shift in electrical characteristics of these materials in the ambient. About $1 \times 10^{19} \text{ cm}^{-3}$ of water molecules are present as clusters, primarily monomers and dimers, in these films when exposed to ambient air at room temperature and humidity (60%). Exposure to light then generates a limiting polaron density of a few 10^{17} cm^{-3} , together with charge-compensating hydroxide ion species. This mechanism contributes to the known degradation of both the saturation and off characteristics of organic field-effect transistors (FETs). The greater stability of PBTTT is found to be largely kinetic in origin and related to exclusion of moisture from the crystallite domains.

N90018**A New Order-to-Disorder Transition Observed in a High-Mobility Semiconducting Polymer Poly(bithiophene-alt-thienothiophene) (PBTTT)**

Li-Hong ZHAO¹; Jie-Cong TANG²; Rui Qi PNG¹;
 Loke Yuen WONG¹; Jing-Mei ZHUO^{1,2}; Perq Jon CHIA¹;
 Lay-Lay CHUA^{1,2}; Peter K.-H. HO¹

1. *Department of Physics, National University of Singapore, Lower Kent Ridge Road*

Singapore 117543, Singapore

2. *Department of Chemistry, National University of Singapore, Lower Kent Ridge Road*

Singapore 117543, Singapore

The tetradecyl substituted poly(bithiophene-alt-thienothiophene) (PBTTT) shows a broad reversible order-to-disorder transformation of its alkyl side-chains between room temperature (295K) and 373K, well below the liquid crystal melting temperature (423K). During this transition, variable temperature XRD indicated the inter-lamellar spacing shows a step-like increase, and variable temperature FTIR indicates the ν CH₂ stretching modes, δ CH₂ bending modes and rocking modes all blue shift simultaneously. Variable temperature Raman and UV-Vis spectroscopies indicate the π -conjugated backbone get progressive disordered over this temperature range. Therefore the order-to-disorder transformation of the alkyl side-chain triggers a torsional disordering of the backbone. Variable temperature FET measurements shows that during this transition, mobility increases strongly at first and the apparent activation energy becomes very large before it decreasing as temperature increases towards the liquid crystal melting temperature. This suggests that charge carrier mobility can be strongly promoted by excitation of phonon modes.

N90019**A General Method for Multi-layered Heterostructure and Columnar Nanostructured Polymer Semiconductor Devices**

Rui-Qi PNG¹; Perq-Jon CHIA¹; Lay-Lay CHUA^{1,3};
 Sankaran SIVARAMAKRISHNAN¹; Jie-Cong TANG³;
 Mi ZHOU¹; Siong-Hee KHONG²; Hardy S.O. CHAN³;
 Jeremy H. BURROUGHES⁴; Richard H. FRIEND^{1,2};
 Peter K.H. HO¹;

1. *Department of Physics, National University of Singapore, Lower Kent Ridge Road, S117542, Singapore.*

2. *Cavendish Laboratory, University of Cambridge, JJ Thomson Road, Cambridge, CB3 0HE, United Kingdom.*

3. *Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, S117543, Singapore.*

4. *Cambridge Display Technology Ltd, Bldg 2020, Cambourne Business Park, Cambridgeshire, CB3 6DW, United Kingdom.*

Heterostructures enable the efficient manipulation and control of charge carriers, excitons and photons crucial for high-performance semiconductor devices. With solution-processed polymer organic semiconductors (OSCs) however, there are only few ways to form the required structures. Previous efforts to crosslink solution-processed layers have focussed on chemical derivation of the OSCs with a high concentration of crosslinking groups that often compromise device performance. Here we have developed a simple steric-substituted bis(fluorinated phenylazide) (FPA) methodology that can efficiently crosslink a wide range of semiconducting polymers, such as p-phenylenevinylenes, fluorene copolymers and thiophene copolymers, at very low concentrations of the crosslinking moiety (< 1 mol%) and without causing significant degradation of their semiconducting properties. The steric substitution is key to suppressing the arene-perfluoroarene interaction to allow the desired nitrene photo-insertion to proceed at the alkyl chain sites, without carrier trapping and exciplex formation. This allows generic photo-patterning of field-effect transistor and light-emitting diode arrays, and the fabrication of high-quality separate-confinement organic light-emitting diodes. By combining the crosslinking with a novel sacrificial nano-template technique, we have generate self-organised columnar nanostructures with ensured continuity of the electron and hole conduction paths to their collector electrodes. This overcomes the "carrier-loss" mechanism to give improvement in the photovoltaic efficiencies by a factor of 4.5 compared to the bulk-distributed heterostructures. These results illustrate just a few of the many new possibilities that can now be realised in polymer OSC devices.

N90020**Direct Spectroscopic Evidence for a Delta-Hole-Doped Interface at Ohmic Contacts to Organic Semiconductors**

Mi ZHOU¹; Lay-Lay CHUA^{1,2}; Rui-Qi PNG¹;
 Chaw-Keong YONG¹; Sankaran SIVARAMAKRISHNAN¹;
 Perq-Jon CHIA¹; Andrew T.S. WEE¹; Richard H. FRIEND³;
 Peter K.H. HO¹

1. *Department of Physics, National University of Singapore, Lower Kent Ridge Road, S117542, Singapore.*

2. *Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, S117543, Singapore.*

3. *Cavendish Laboratory, University of Cambridge, JJ Thomson Road, Cambridge, CB3 0HE, United Kingdom.*

Electromodulated absorption spectroscopy of the hole-injection contact between a model organic semiconductor (OSC) poly(dialkoxy-p-phenylenevinylene) and a set of p-doped poly(3,4-ethylenedioxythiophene) electrodes with different work-functions ϕ_{vac} reveals the formation of a δ -hole-doped polaron OSC interface for the case of ohmic contacts. Modulation of this interface charge density exhibits a remarkably small barrier of a few meV,

N90022

and so carriers are directly injected into the EF, which are then cascaded down to the transport level of the OSC. The 0.6-eV gap between the pinned Fermi level (EF) and the highest-occupied-molecular-orbital (HOMO) transport level that has traditionally been assumed to give the hole-injection barrier is not relevant. This explains the apparent anomaly that carrier-injection efficiency can continue to improve with ϕ_{vac} even while EF is pinned.

N90021

Dendrimers for Photon Harvesting in Dye-sensitised Solar Cells

Paul BURN; Byeong-Kwan AN; Paul MEREDITH
*Centre for Organic Photonics and Electronics (COPE),
The University of Queensland, QLD, Australia 4072*

Dendrimers are branched macromolecules into which multiple functions can be engineered. Highly efficient dendrimer-based solution processed organic light emitting diodes have been demonstrated¹, but to date, there have been fewer reports of their use in organic photovoltaics. Irrespective of the OPV device platform (thin film bulk heterojunction or photoelectrochemical) the challenges for device architecture and materials design remain the same - one must absorb as much of the solar spectrum as possible and efficiently separate and transfer the generated charge. These processes require optimisation and careful design of the absorber (donor) and acceptor electronic properties and control of their nanophase behavior. The overall aim is to achieve this optimisation in materials that can be solution processed to create large area devices. The architectural flexibility of dendritic systems has meant that these issues have been successfully addressed in dendrimer OLEDs.

In this presentation we will discuss recent progress in applying molecular engineering to optimize the properties of dendrimers that can be used in dye-sensitised solar cells (DSSCs). We will present the development of asymmetric heteroleptic dendrimers that have multiple functions incorporated into the one macromolecule; strong visible-light photon absorption, specific site binding, and solubilization. We will discuss the relationship between molecular volume and photon harvesting capacity and show how this is particularly important in DSSC architectures. We will also show how the dendritic architecture affects dye binding, and that the materials can be used in efficient DSSCs.

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Organic Bioelectronics

George G. MALLIARAS
*Materials Science and Engineering, Cornell University
Ithaca, NY 14853-1501, USA*

The coupling of electronics with living tissue holds the key to a variety of important life-enhancing technologies. One example is bioelectronic implants that record neural signals and/or electrically stimulate neurons. These devices offer unique opportunities to understand and treat conditions such as hearing and vision loss, epilepsy, brain degenerative diseases, and spinal cord injury. A second example is sensor arrays that utilize living cells as the biorecognition element. These devices offer tremendous value in new drug development and in “canary in a coal mine” detectors protecting human and animal health and the environment. Key to these technologies is a fundamental understanding of electrical communication at the interface between electronic materials and living cells. Improved understanding of this interface will translate to implants that are more stable and dissipate less power, and sensors that offer better sensitivity and lower detection limit, addressing unmet and pressing needs in the field. Organic electronics – a technology that relies on carbon-based semiconductors to deliver devices with unique properties – seems to be ideally suited for the interface with biology. The “soft” nature of organic materials offers better mechanical compatibility with tissue than traditional electronic materials, while their natural compatibility with mechanically flexible substrates suits the non-planar form factors often required for biomedical implants. More importantly, their ability to conduct ions in addition to electrons and holes opens up a new communication channel with biology. I will review recent progress in the field and subsequently focus on two emerging areas: (a) The development of biosensors using conducting polymer transistors, and in particular their integration with microfluidics to create multi-analyte sensors, and, (b) the development of active substrates for cell growth, in which a potential applied on a conducting polymer substrate controls cell density and morphology.

N90023

Soluble and Stable Near Infrared Dyes

Junhong YAO; Chongjun JIAO; Jinling LI;
Kian-Ping LOH; Jishan WU
*Department of Chemistry, National University of
Singapore, 3 Science Drive 3, Singapore 117543*

A series of stable and soluble bisanthracene carboxyimides M1-M4 were synthesized and their optical and electrochemical properties were studied. All of them showed intensive absorptions in the NIR region (600 -1000 nm), suggesting that they can be used as useful NIR

dyes for many applications. The fully fused bisanthene carboximide M1 showed absorption maximum at 830 nm, with more than 130 nm bathochromic shift in comparison with the partially fused anthracene dimers M2-M4. Molecule M1 represents one successful example of a family of zigzag edged nanographenes, the so-called periacenes, and the methodology developed here provides clues to the synthesis of stable and soluble higher order zigzag edged nanographenes.

N90024

Low Band Gap and Solution Processable Diketopyrrolopyrrole-based Materials for Applications in Bulk Heterojunction Solar Cells

Thuc-Quyen NGUYEN

Center for Polymers and Organic Solids and Department of Chemistry & Biochemistry, University of California, Santa Barbara, CA 93106, USA

Organic solar cells potentially offer a low cost, large area, flexible, light-weight, clean, and quiet alternative energy sources for indoor and outdoor applications. Our research in this area focuses on the design and synthesis of solution processed small molecules having a broad absorption spectrum and high charge carrier mobility. Conjugated small molecules have the advantage of relative ease of synthesis and functionalization, tunability and purification over polymers. Most important, small molecules do not suffer from batch to batch variations, broad molecular weight distributions, end group contamination, and difficult purification methods, as is the situation for their polymeric counterparts. The molecular design incorporates the high mobility and ordered molecular packing of oligothiophenes together with the large optical density of the diketopyrrolopyrrole (DPP) core [1]. The resulting molecules exhibit strong absorption at long wavelengths, up to 800 nm when in the solid state [2]. Functional groups attached to the DPP core can be used to tune the energy level, the bandgap, the solubility, and hence, the film morphology and charge mobility [3,4]. Furthermore, this material in combination with the widely-used acceptor C71-PCBM can be used to form the active layer in organic solar cells with high power conversion efficiencies under simulated AM 1.5 solar irradiation [2,3]. Additionally, we successfully demonstrated the use of low band gap solution processed small molecule chromophores in polymer bulk heterojunction solar cells to increase carrier generation in the near infrared and the overall short circuit current [5]. In parallel with materials synthesis and processing, we have developed characterization techniques to probe film morphology and interfaces in multilayer optoelectronic devices [6,7], to image the donor-acceptor networks laterally and vertically, to assign phase domains to the donor and the acceptor components, and to study nanoscale charge transport and photocurrent in polymer solar cells [8,9].

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N90025

Synthesis, Characterization and Device Properties of Solution-Processable Graphitic Materials

Wallace W. H. WONG

School of Chemistry, Bio21 Institute, University of Melbourne, Vic. 3010, Australia

Hexa-peri-hexabenzocoronene (HBC) is a planar aromatic molecule consisting of 13 fused six membered rings. They are in the family of polycyclic aromatic hydrocarbons consisting of flat disc-like cores enabling assembly into columnar mesophases. The self assembly of materials into ordered structures in a bulk heterojunction could increase the efficiency of the photovoltaic device by facilitating charge separation and transport. Although the synthesis of the HBC moiety is well-established in the literature, highly-soluble easily-functionalized HBC building blocks have only been reported recently. The primary challenge in the synthesis of these systems is the incorporation of the conjugated substituents as well as alkyl groups for solubility. The 9,9-dioctylfluorenyl-hexabenzocoronene (FHBC) moiety fits both criteria of solubility and ease of functionalization. In addition, the incorporation of the 9,9-dioctylfluorenyl groups did not hamper the π - π stacking of the HBC core unit enabling the ordered assembly of these molecules in solution as well as in thin films. In preliminary device studies, solution-processed organic field effect transistors with selected FHBC molecules show hole mobilities of up to $3 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and on-off ratio of 6×10^6 . Bulk heterojunction solar cells with thiophene dendrimers based on the FHBC core as electron donor and fullerene derivatives as electron acceptor showed good performance reaching power conversion efficiencies of 2.5%.

N90026

Quantifying Loss Currents in Organic Bulk Heterojunction Solar CellsZi-En OOI¹; Alan SELLINGER^{1,2}; John C. DEMELLO³*1 Institute of Materials Research and Engineering (IMRE), Singapore**2 Current address: Centre for Advanced Molecular Photovoltaics (CAMP), Stanford University**3 Department of Chemistry, Imperial College London, U.K.*

The photocurrent-voltage (*J*-*V*) curve of a solar cell provides a basic means of quantifying device performance; its shape describes how the photocurrent of the device deteriorates from its practical maximum current *J*_{SC} (at short circuit) to zero as the voltage across the electrodes increases from zero to the open circuit voltage *V*_{OC}. This loss in photocurrent may be attributed to a combination of opposing currents arising from various loss mechanisms. Using remarkably symmetric ‘*S*’-shaped corrected photocurrent (*J*_{ph}) data from an organic bulk heterojunction solar cell, we present here a technique for determining the magnitudes of these loss currents as functions of voltage. With this information, we can therefore quantitatively compare the relative importance of the various loss processes occurring in such a device.

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Not available at press time.Christoph J. BRABEC*Konarka Technologies, U.S.A.*

Not available at press time.

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Charge Transport in Doped Poly(p-phenylene vinylene)Paul W.M. BLOM*TNO Holst Centre, High Tech Campus 31, 5656 KN, Eindhoven, The Netherlands*

Not available at press time.

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Enhanced Efficiency in Triple-Tandem Organic Solar CellsDewei ZHAO^{1,2}; Xiaowei SUN^{1,2}; Changyun JIANG²; S. T. TAN²; A. K. K. KYAW¹; G. Q. LO²; D. L. KWONG²*1. School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore**2. Institute of Microelectronics, A*STAR, Singapore*

We present an enhanced efficient polymer-small molecule triple-tandem organic solar cell, consisting of poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61 (PCBM) bulk heterojunction as the first and second bottom cells, and small molecules copper phthalocyanine (CuPc) and fullerene (C60) as the third top cell. These sub-cells are connected by an intermediate layer of Al(1 nm)/MoO₃(15 nm), which appears to be highly transparent, structurally smooth, and electrically connected. Compared to our previous triple-tandem polymer solar cell, this polymer-small molecule triple-tandem organic solar cell achieves an improved power conversion efficiency (PCE) of 2.18% with short-circuit current density (*J*_{sc}) = 3.02 mA/cm², open-circuit voltage (*V*_{oc}) = 1.51 V, and fill factor (FF) = 47.7% under simulated solar irradiation of 100 mW/cm² (AM1.5). This is attributed to the increased photocurrent generation in the third cell since the third cell has the complementary absorption with the bottom cell despite slightly reduced *V*_{oc}. Therefore, it is demonstrated that organic materials with complementary absorption spectra play a crucial role in the performance of tandem organic solar cells. In addition, our developed intermediate layer shows the most potential application to multiple-tandem organic solar cells and light-emitting diodes.

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