

Final Report

submitted to the

Office of Basic Energy and Sciences

of the

Department of Energy

for the period

May 2008 – April 2011

“Understanding and Design of Polymer Device Interfaces”

Grant # DE-FG02-05ER46165

submitted by

Antoine Kahn

Princeton University

Department of Electrical Engineering

Princeton, NJ 08544

Tel: 609-258-4642

Email: kahn@princeton.edu

The research performed during the three years of the grant (DE-FG02-04ER46165) was a broad investigation of the electronic and chemical structure of organic semiconductor interfaces, and polymer interfaces in particular. The goal of this work was to achieve control of these interfaces in order to optimize injection, extraction and transport of charge carriers into, from and across, respectively, all (opto)electronic devices made of these semiconductors. The team assembled for this work included Prof. Jean-Luc Brédas at the Georgia Institute of Technology, Prof. George Malliaras at Cornell University, Dr. Anil Duggal at General Electric, and Prof. Antoine Kahn (lead PI) at Princeton University. During the last year of the grant, Prof. Bernard Kippelen at the Georgia Institute of Technology replaced Prof. Malliaras, who moved to Europe.

The first two years of the grant were mainly devoted to (i) determining the electronic structure of polymer (F8 and TFB) interfaces and related charge carrier injection/extraction efficiency; (ii) modify electrode surfaces with self-assembled monolayers or ultra-thin layers of poly-styrene morpholine to enhance charge injection in polymer films; (iii) the experimental and theoretical investigations of polymer interfaces with the widely used hole-injection doped polymer PEDOT:PSS; and (iv) the p-doping of polymers (TFB) with molecular dopants to enhance carrier injection. Highlights of this research are summarized in the first two Progress Reports, which were submitted in February 2009 and 2010, respectively, and which are appended at the end of this 3rd year / final report.

Scientific Achievements of Year 3 (March 2010 – February 2011)

The last year of the grant was devoted predominantly to three topics:

- The p-doping of organic semiconductors
- The formation of polymer interfaces via soft-contact lamination
- The determination of the electronic structure of buried interfaces in polymer blends

1. p-doping of organic semiconductors

Following the development of the high electron affinity p-dopant molybdenum tris[1,2-bis(trifluoromethyl) ethane-1,2-dithiolene] ($\text{Mo}(\text{tfd})_3$), reported in year 2009-2010 (see below), we investigated the p-doping of molecular hole transport materials (HTM) like N,N'-di[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl-4,4'-diamine (α -NPD). The reason for this temporary shift away from polymers was to be able to co-evaporate host and dopant and investigate the confinement of the dopants in a specific region of the film. Indeed, interface doping is a well-known technique to create low barrier contacts without changing the nature of the bulk of the active layer of a device. The second topic outlined below emphasizes soft-contact lamination of polymer films on top of each others, which eventually opens the way to *interface doping in polymer systems*.

Work on p-doping of α -NPD included a complete determination of the ionization energy and electron affinity (IE, EA) of both host and dopant materials; verification of the Fermi level shift toward the highest occupied molecular orbital (HOMO) of the host upon p-doping; conductivity measurements as a function of dopant concentrations; determination of the hole-

hopping activation energy as a function of dopant concentration; and finally implementation of interface doping, by restricting the dopant position within 8 nm of the contact, with clear demonstration of enhanced hole injection (Fig. 1). This work was published in two papers [1,2] and resulted from a Bredas-Kahn collaboration supported by this grant.

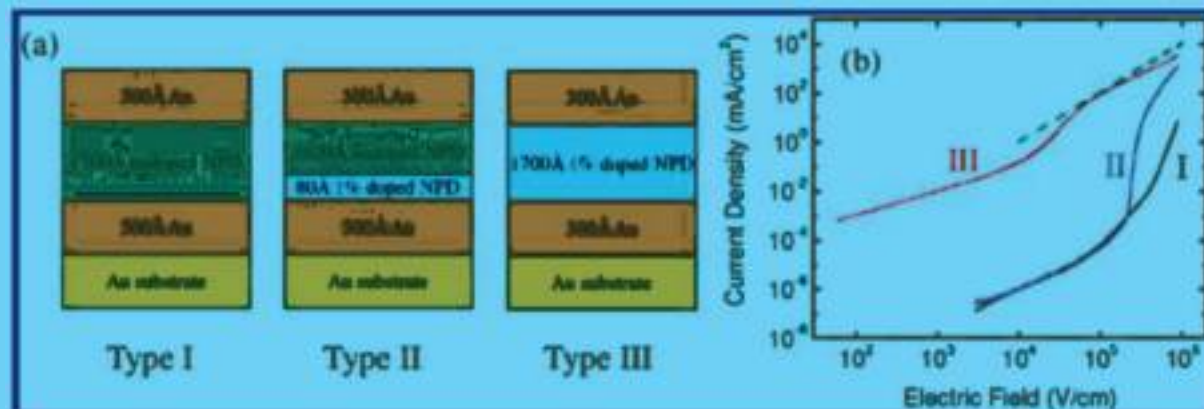


Figure 1: (a) Structure of the three device types. (b) J-F characteristics of the three Au/ α -NPD/Au devices. The bias polarity corresponds to holes injected from the bottom contact. The green dashed curve represents the SCLC limit calculated using a hole mobility of $6.1 \times 10^{-4} \text{ cm}^2/(\text{V s})$

2. Formation of polymer interfaces via soft-contact lamination

We investigated the formation of polymer/polymer homo- and heterojunctions via soft-contact lamination, a technique by which a polymer layer spin-coated separately on a substrate is transferred to a soft PDMS stamp, then brought into physical contact, and is eventually transferred to, the top of another polymer layer (Fig. 2left). One of the key questions pertained to the electronic structure / electrical behavior of such an interface.

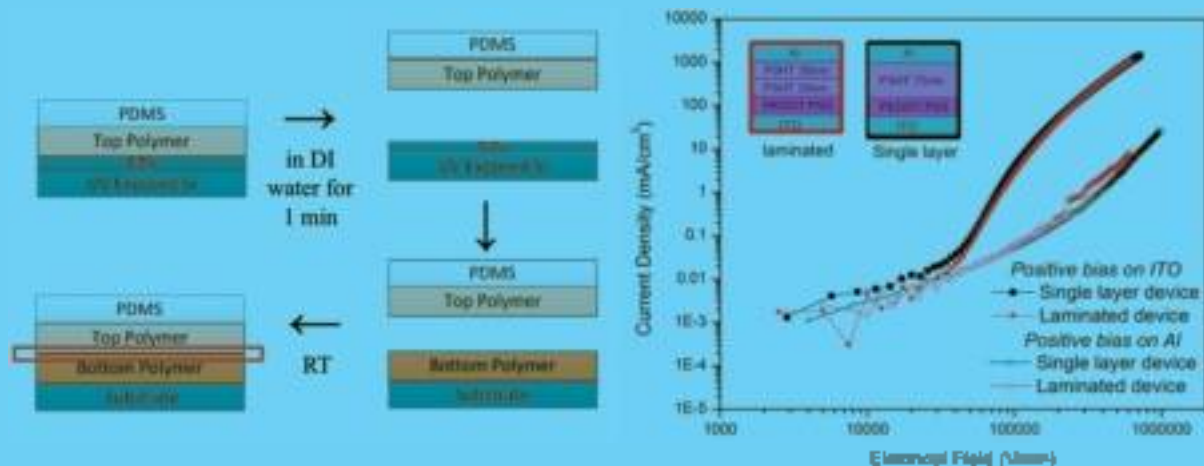


Figure 2: (left) soft-contact lamination scheme, showing the de-lamination from the first substrate and the deposition on the bottom polymer film; (right) I-V characteristics of hole injection in a PJHT device made of a full polymer layer or two laminated layers sandwiched between PEDOT:PSS and Al. The overlap between red and black curve demonstrate that the laminated interface is electrically seamless

Inorganic counterparts would be entirely dominated by dangling-bond-related electronic trap states and recombination centers, leading to very poor (opto)electronic behavior. We used a combination of electron spectroscopy (ultra-violet photoemission), scanning Kelvin probe

force microscopy (KPFM) and current-voltage measurements on single and laminated films, and demonstrated that these interfaces are electrically and electronically “seamless” (Fig. 2right) [3]. This work was extended to two polymers, P3HT and F8BT.

The important result illustrate in Fig. 2 eventually opened the way to more recent investigations (not supported by this DOE grant) of interface doping of polymer devices. The fact that the laminated junctions were electronically and electrically “transparent”, or “seamless” led to the idea of doping one of the two layers prior to lamination, and producing a doped interface/contact with spatially confined dopants good carrier injection/extraction characteristics.

In collaboration with the group of L. Loo at Princeton Univ., the lamination and delamination process was extended to two additional systems. In the first one P3HT and PCBM were laminated in different order and incorporated in planar heterojunction solar cells, in order to test ideas of electron or hole blocking. In the P3HT:PCBM blend device, the usually observed segregation of the polymer to the surface of the film renders the evaluation of these processes more difficult [4]. The ability to laminate organic semiconductors and establish effective and efficient charge transfer interfaces enabled the fabrication of model planar-heterojunction devices in which the processing of the constituent organic semiconductors can be systematically varied. Thermal annealing after lamination was intentionally avoided to eliminate constituent interdiffusion and maintain the pristine charge transfer interface. In that study, the effective decoupling of the contributions of constituent crystallization to devices characteristics was demonstrated.

In the second process, Au contacts were laminated and delaminated from the active blend layer before and after critical annealing sequences [5]. This ability to laminate and delaminate top metal contacts led us to uncover the peculiar dependence of the open-circuit voltage of the cell (V_{oc}) on the annealing sequence. Specifically, thermally annealing inverted polymer solar cells having bulk-heterojunction photoactive layers after top electrode deposition above 100 °C leads to lower V_{oc} compared to analogous devices with unannealed photoactive layers or photoactive layers that have been annealed prior to metal electrode deposition. This reduction in V_{oc} , however, can be reversed when the top electrodes are replaced. These observations strongly link changes in V_{oc} with annealing sequence to changes at the top electrode/active layer interface, and not structural changes in the bulk of the photoactive layer. Electronic characterization conducted on the active layers and metal contacts after dissection of the polymer solar cells via delamination suggests the role of an interfacial chemical reaction between the active layers and the metal electrodes. This chemically generated interfacial layer is removed upon electrode delamination, effectively reverting the V_{oc} to its original value prior to thermal annealing when the top electrodes are replaced.

3. Determination of the electronic structure of buried interfaces in polymer blends

The relationship between the open circuit voltage V_{oc} produced by a polymer bulk heterojunction (BHJ) solar cell and the electronic structure of the donor/acceptor interface has been a difficult one to establish over the past decade [6]. The reason is that the latter, i.e. the photovoltaic gap or real energy gap between the LUMO of the acceptor and the HOMO of the donor, is rarely experimentally determined, and is generally assumed to be simply the

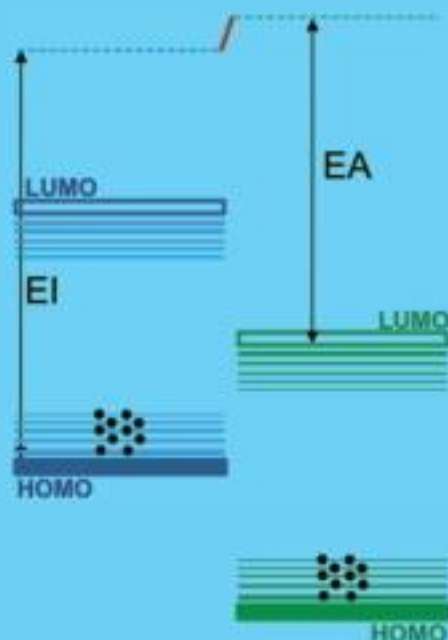


Figure 2. schematic energy diagram of the donor/acceptor interface; the interface dipole (red), which results from a small charge transfer between overlapping gap states, minimizes the overlap.

difference between the ionization of the donor and the electron affinity of the acceptor. The assumed value is generally a few 100 meV off due to the presence of interface dipoles, and has led to much of the uncertainty. In the context of this grant, we devoted a significant fraction of the last year measuring the photovoltaic gap of two standard BHJ systems, P3HT:PCBM and P3HT:ICBA using a combination of direct and inverse photoemission spectroscopy [6,7]. Using the de-lamination/lamination technique described above, we were able to flip the BHJ layer around, thereby avoiding the difficulty posed by the segregation of the polymer at the surface of the film and being able to measure the energy gap of the blend. The key result for these two systems is that a significant interface dipole (~ 0.3 eV) is present at the donor/acceptor interface and increases the true photovoltaic gap by the same amount. The difference

between V_{oc} and the photovoltaic gap is therefore larger than originally believed, which suggests that additional mechanisms limit the slip between the quasi-Fermi levels under operation. We have hypothesized that one of these mechanisms is related

to the tail of electronic gap states that are found in most organic semiconductors.

References:

1. A high electron affinity molybdenum compound for p-doping molecular semiconductors, Yabing Qi, Tissa Sajoto, Stephen Barlow, Eung-Gun Kim, Jean-Luc Brédas, Seth R. Marder and Antoine Kahn, *J. Am. Chem. Soc.* **131**, 12530 (2009)
2. A molybdenum dithiolene complex as a p-dopant for organic semiconductors: a detailed study by UPS, IPES, XPS, RBS, and variable-temperature conductivity measurement, Y. Qi, T. Sajoto, M. Kröger, A. Kandabarov, W. Park, S. Barlow, E.-G. Kim, L. Wielunski, L. C. Feldman, R. A. Bartynski, J.-L. Brédas, S. R. Marder and A. Kahn, *Chem. Mat.* **22**, 524 (2010)
3. Electronic structure and carrier transport at laminated polymer homojunctions, Andrew Shu, An Dai, He Wang, Yueh-Lin Loo, and Antoine Kahn, *Org. Electr.* **14**, 149 (2013)
4. Modular Construction of P3HT/PCBM Planar-Heterojunction Solar Cells by Lamination allows Elucidation of Processing Structure-Function Relationships, Jong Bok Kim, Zelei Guan, Stephanie Lee, Eleni Pavlopoulou, Michael F. Toney, Antoine Kahn and Yueh-Lin Loo, *Org. Electr.* **12**, 1163 (2011)
5. Annealing Sequence Dependent Open-Circuit Voltage of Inverted Polymer Solar Cells Attributable to Interfacial Chemical Reaction between Top Electrodes and Photoactive Layers, Jong Bok Kim, Ze-Lei Guan, Andrew L. Shu, Antoine Kahn, and Yueh-Lin Loo,

Langmuir, **27**, 11265 (2011)

6. Offset energies at organic semiconductor heterojunctions and their influence on the open-circuit voltage of thin-film solar cells, B. P. Rand, D.P. Burke and S.R. Forrest, Phys. Rev. B, **75**, 115327 (2007)
7. Direct determination of the electronic structure of the poly(3-hexylthiophene):phenyl-[6,6]-C₆₁ butyric acid methyl ester blend, Zelei Guan, Jongbok Kim, Yueh-Lin Loo, and Antoine Kahn, Org. Elect. **11**, 1779 (2010)
8. Electronic structure of the poly(3-hexylthiophene):indene-C₆₀ bisadduct bulk heterojunction, Ze-Lei Guan, Jong Bok Kim, Yueh-Lin Loo, and Antoine Kahn, J. Appl. Phys. **110**, 043719 (2011)

Personnel (partially or totally) supported by the DOE Grant (other than summer support for PIs)

Hon Hang Fong: Post-doctoral fellow, Cornell University (2008-10)

Zelei Guan: Post-doctoral fellow, Princeton University (2008-11)

Eung-Gun Kim: Post-doctoral fellow, Georgia Institute of Technology (2008-11)

Alexis Papadimitratos: Graduate student, Cornell University (2008-10)

Andrew Shu: Graduate student, Princeton University (2010-11)

Cumulative list of publications supported by the grant.

1. “Impact of Functionalized Polystyrenes as the Electron Injection Layer on Au and Al surfaces: A Combined Theoretical and Experimental Study”, Theodoros A. Papadopoulos, Hong Li, Eung-Gun Kim, Jie Liu, James A. Cella, Christian M. Heller, Andrew Shu, Antoine Kahn, Anil Duggal, and Jean-Luc Brédas, Israel Journal of Chemistry (Michael Bendikov memorial volume) **54**, 779 (2014)
2. “Annealing Sequence Dependent Open-Circuit Voltage of Inverted Polymer Solar Cells Attributable to Interfacial Chemical Reaction between Top Electrodes and Photoactive Layers”, Jong Bok Kim, Ze-Lei Guan, Andrew L. Shu, Antoine Kahn, and Yueh-Lin Loo, Langmuir, **27**, 11265 (2011)
3. “Modular Construction of P3HT/PCBM Planar-Heterojunction Solar Cells by Lamination allows Elucidation of Processing Structure-Function Relationships”, Jong Bok Kim, Zelei Guan, Stephanie Lee, Eleni Pavlopoulou, Michael F. Toney, Antoine Kahn and Yueh-Lin Loo, Org. Electr. **12**, 1163 (2011)
4. “Electronic structure of the poly(3-hexylthiophene):indene-C₆₀ bisadduct bulk heterojunction”, Ze-Lei Guan, Jong Bok Kim, Yueh-Lin Loo, and Antoine Kahn, J. Appl. Phys. **110**, 043719 (2011)
5. “Device Characteristics of Bulk-Heterojunction Polymer Solar Cells are Independent of Interfacial Segregation of Active Layers”, He Wang, Enrique D. Gomez, Jongbok Kim, Zelei Guan, Cherno Jaye, Daniel A. Fischer, Antoine Kahn, and Yueh-Lin Loo, Chem. Mat. **23**, 2020 (2011)

6. "A Molybdenum Dithiolene Complex as p-Dopant for Hole-Transport Materials: A Multi-technique Experimental and Theoretical Investigation", Y. Qi, T. Sajoto, M. Kröger, A.M. Kandabarow, S. Barlow, E.G. Kim, L. Wielunski, L.C. Feldman, R.A. Bartynski, J.L. Brédas, S.R. Marder, and A. Kahn, *Chemistry of Materials*, **22**, 524-531 (2010).
7. "Direct determination of the electronic structure of the poly(3-hexylthiophene):phenyl-[6,6]-C₆₁ butyric acid methyl ester blend", Zelei Guan, Jongbok Kim, Yueh-Lin Loo, and Antoine Kahn, *Org. Elect.* **11**, 1779 (2010)
8. "Use of a High Electron-Affinity Molybdenum Dithiolene Complex to p-Dope Hole-Transport Layers", Y. Qi, T. Sajoto, S. Barlow, E.G. Kim, J.L. Brédas, S.R. Marder, and A. Kahn, *Journal of the American Chemical Society*, **131**, 12530-12531 (2009).
9. "Energetics of Metal-Organic Interfaces: New Experiments and Assessment of the Field", Jaehyung Hwang, Alan Wan and Antoine Kahn, *Materials Science and Engineering*, **R 64**, 1-31 (2009)
10. "Organic Photovoltaics", B. Kippelen and J.L. Brédas, *Energy & Environmental Science*, **2**, 241-332 (2009).
11. "Hole injection in a model fluorene-triarylamine copolymer", Hon Hang Fong, Alexis Papadimitratos, Jaehyung Hwang, Antoine Kahn and George G. Malliaras, *Adv. Funct. Mater.* **19**, 304 (2009)
12. "Electronic and Vibronic Interactions at Weakly-bound Organic Interfaces: The Case of Pentacene on Graphite", P.B. Paramonov, V. Coropceanu, and J.L. Brédas, *Physical Review B*, **78**, 041403/1-041403/4 (2008).
13. "The Interface Energetics of Self-Assembled Monolayers on Metals", G. Heimel, L. Romaner, E. Zojer, and J.L. Brédas, *Accounts of Chemical Research*, **41**, 721-729 (2008).
14. "Enhancement of electron injection into a light-emitting polymer from an aluminum oxide cathode modified by a self-assembled monolayer", Yana Vaynzof, Joseph T. Dennes, Jeffrey Schwartz and Antoine Kahn, *Appl. Phys. Lett.* **93**, 103305 (2008)
15. "Electronic Evolution of Poly(3,4-ethylenedioxythiophene) (PEDOT): From the Isolated Chain to the Pristine and Heavily Doped Crystals", E.-G. Kim and J.L. Brédas, *Journal of the American Chemical Society*, **130**, 16880-16889 (2008).
16. "Improving charge injection in organic thin-film transistors with thiol-based self-assembled monolayers", P. Marmont, N. Battaglini, Ph. Lang, G. Horowitz, J. Hwang and A. Kahn, *Org. Elect.* **9**, 419 (2008)
17. "Photoelectron Spectroscopic Study of the Electronic Band Structure of Polyfluorene and Fluorene-Arylamine Copolymers at Interfaces", J. Hwang, E.-G. Kim, J. Liu, J.-L. Brédas, A. Duggal and A. Kahn, *J. Phys. Chem. C* **111**, 1378 (2007)

Progress Report

submitted to the

Office of Basic Energy and Sciences

of the

Department of Energy

for the period

March 2008 – February 2009

“Understanding and Design of Polymer Devices Interfaces”

Grant # DE-FG02-05ER46165

PI: Antoine Kahn

Princeton University

Department of Electrical Engineering

Princeton, NJ 08544

Tel: 609-258-4642

Email: kahn@princeton.edu

Scientific achievements

With the start of the second DOE grant in the Spring of 2008, in accord with the goals stated in the proposal submitted in the Fall of 2007, the team of four PIs (Prof. Jean-Luc Bredas at Georgia Tech, Prof. George Malliaras at Cornell Univ., Dr. Anil Duggal at GE and Prof. Antoine Kahn at Princeton Univ.) established several research directions aimed at:

- Understanding the fundamental limits of engineering of polymer/electrode interfaces, in particular with respect to reducing carrier injection barriers
- Devising new methods, including electrode surface modification and chemical doping, to circumvent the limitations on conventional barrier engineering.
- Investigating the technique of physical lamination of polymer films as a new paradigm for building devices with independently optimized injection contacts and heterojunctions.

This progress report focuses specifically on recent work done on (i) understanding the limitation of hole injection into our fluorene-based model polymers – the fluorene homopolymer poly(dioctyl-fluorene) (F8) and the fluorene-arylamine copolymer poly(dioctyl-fluorene-co-N-(4-butylphenyl) diphenylamine) (TFB); and (ii) the electron injection side and the modification of cathodes to minimize electron barriers.

Limitations of hole-injecting electrodes

Recent developments in synthesis and purification have yielded conjugated polymers with high hole mobilities. Essential to harvesting the potential of these materials in organic light emitting diodes (OLEDs) is the identification of suitable ohmic contacts. As already reported in two publications supported by this grant [1,2], the Cornell group demonstrated hole

mobilities in excess of $0.01 \text{ cm}^2/\text{V}\cdot\text{sec}$ and non-dispersive hole transport in our model fluorene copolymer TFB. Using this high performance material, they demonstrated that electrodes commonly used as anodes in OLEDs are very poor hole injectors in TFB. Figure 1 (left)

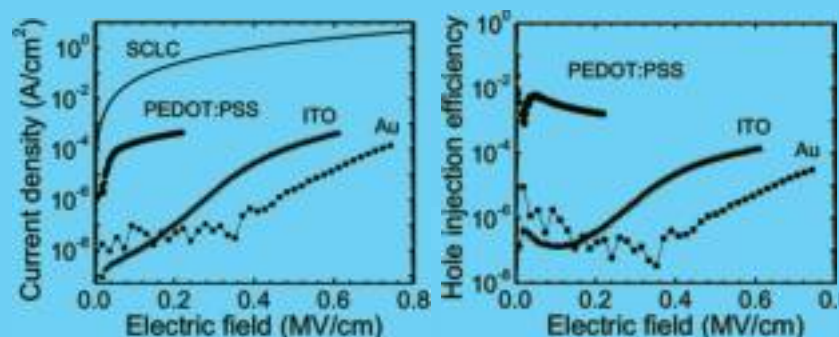


Figure 1. (left) Current density versus electric field of devices with different anodes. The solid line represents the space charge limited current (SCLC). (right) Injection efficiency versus electric field for the different anodes. [2]

(SCLC) calculated using the experimentally determined hole mobility, which constitutes the theoretical maximum current density that can be injected in the materials, and the currents injected from three electrodes. Injection from Au and indium tin oxide (ITO) anodes is limited by energy barriers of 0.75 and 0.65 eV, respectively, and the injected current is found to be temperature independent – a prediction that was not reproduced by the leading injection model for disordered organic semiconductors. The hole injection barrier from poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS), on the other

hand, is 0.35 eV. Figure 1 (right) shows the hole injection efficiency for Au, ITO and PEDOT:PSS. All three are low, even with the latter electrode. Furthermore, injection from PEDOT:PSS is found to become less efficient with increasing electric field [2], a behavior which is currently not understood. In thinner TFB films, which are of relevance to OLEDs, ohmic losses on the PEDOT:PSS layer are found to limit the flow of current. Figure 2 compares the resistance $\times$ area in two TFB films (based on SCLC) and in two different PEDOT:PSS films. These results illustrate the opportunity to further improve the performance of OLEDs as well as the challenge posed by high mobility conjugated polymers for the design of hole injection layers.

Electron injection in fluorene-based model polymers

Following the successful demonstration of aluminum as the bottom contact cathode by the GE group in the previous funding period [3], the Georgia Tech and Princeton groups began to investigate using the oxidized surface of Al, and modified versions of it, as a bottom cathode for electron injection into TFB. Using aluminum as the bottom contact cathode metal and a lamination step to assemble components into a high-performance OLED provides

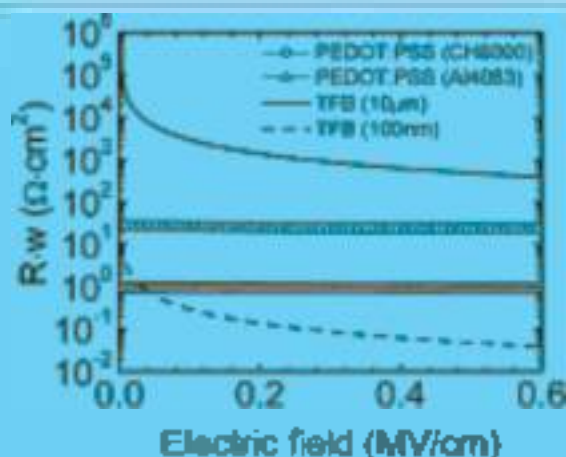


Figure 2: Resistance $\times$ area vs. electric field for a 60 nm thick PEDOT:PSS (C118000) film (open circles), and a 40 nm thick PEDOT:PSS (A14083) film (open triangles). The lines indicate the resistance $\times$ area that correspond to SCLC flow in TFB films that are 10 nm thick (solid) and 100nm thick (dashed). [2]

many advantages over the conventional top contact metal deposition. Well-defined electrode surfaces offer an opportunity not only to better understand organic-metal interfaces but also to modify and improve charge injection and adhesion at the interfaces. The Georgia Tech and Princeton groups investigated the structure and energetics of oxidized aluminum surfaces and interfaces using density functional theory (DFT) methods and electron spectroscopy, respectively. The main objective was to better understand their relationship to the improved electron injection. The study was then extended to the workfunction modification via phosphonic acid self-assembled monolayers (SAMs), and its impact on electron injection.

The work function (WF) of AlOx surfaces was investigated via ultra-violet photoemission spectroscopy (UPS) on films of Al deposited on flat Si and exposed to ambient atmosphere (no specific oxidation procedure). The thickness of the native oxide resulting from this exposure is in the order of 1~1.5 nm. The WF of the sub-oxide AlOx on the as-loaded sample is found to vary between 3.5 and 3.7 eV [4]. This value is already 0.5-0.7 eV smaller than that of clean Al, advantageous in the context of electron injection.

The AlOx surface was then systematically modified with SAMs of alkyl phosphonates ($\text{PO}_2\text{C}_n\text{H}_{2n+1}$; $n=4, 6, 8, 10, 18$). The initial investigation focused on the C_4 molecule [4]. The SAM was found to lower the AlOx WF by ~ 0.4 eV, to 3.1-3.3 eV. The original assumption was that the polar P-O bond at the SAM/AlOx interface introduces a dipole that lowers the

system WF. The SAM was also found to survive the spin-coating of TFB, and to reduce the electron injection barrier from 1.14 eV to 0.72 eV, in accord with the WF lowering.

Most importantly, electron injection was tested in AlOx/SAM/TFB/Hg structures, and found to increase by nearly two orders of magnitude with respect to the current obtained without the SAMs (Figure 3) [4]. A series of SAMs with different length (C_n , $n = 4, 6, 8, 10, 18$) was

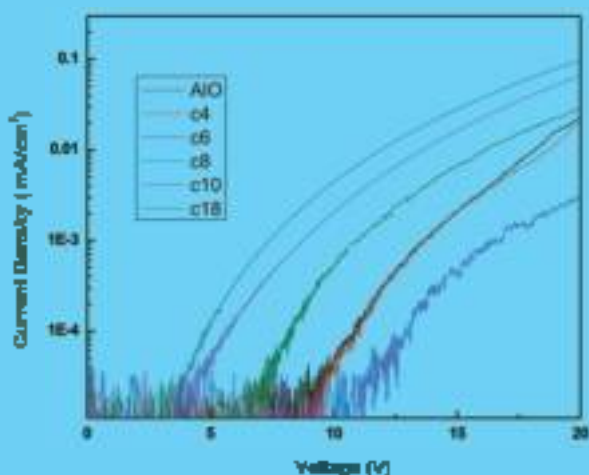


Figure 3: Current density measured with a Hg probe in AlOx/SAM/TFB(90 nm)/Hg

molecules. NEXAFS, AFM and contact angle measurements are being applied to this problem [5].

A key aspect of the analysis of electron injection is the understanding of electron transport and mobility, a topic that has remained largely untouched for these polymers. The Cornell group is currently using the time-of-flight method to obtain electron mobility as a function of electric field and temperature. Unfortunately the transients have been highly dispersive. The electron mobility obtained from the inflection point in a log-log plot appears to be about two orders of magnitude lower than the hole mobility. The Cornell group is conducting thickness dependent measurements to establish whether this dispersive transport is intrinsic or caused by traps. They then plan to evaluate the injection efficiency by measuring ratio between the injection electron current and the space charge limited one calculated by the bulk electron mobility, as was done for hole injection [2].

The Georgia Tech group modeled the oxidized aluminum surfaces by combining slabs of Al(111) (7 atomic layers) and α -Al₂O₃(0001) (12 O layers), each consisting of two surface unit cells. Figure 4 shows the optimized Al₂O₃ with different surface structures. The 'bare' oxide surface contains two Al atoms (or one Al atomic layer) and is the most stable but only in H-free environments [6]. The 'OH+H' surface has one OH group attached to a surface Al atom and one H atom attached to an O atom in the second layer, and corresponds to a saturated hydroxyl coverage after room temperature water exposure [7]. The 'H' surface is obtained after removal of the OH group from the 'OH+H' surface. On the '6OH's' surface, the O layer is the topmost layer and all six O atoms have a H atom, corresponding to a coverage after an acidic treatment [8]. The 'PA' surface has three methylphosphonic acid

also investigated to evaluate the impact of chain length and molecular orientation on electron injection into the polymer film. The preliminary results are given in Figure 3. The C₁₀ and C₁₈ show a decrease in current w.r.t. to C₈, a result that can be attributed to the larger tunneling gap. However, even though C₄ and C₆ are shorter and produce the same WF on AlOx than their longer counterparts, the current density obtained with these molecules is either the same (C₄) or smaller (C₆) than with bare AlOx. This result, which remains under investigation, could be related to a different morphology of the polymer film, e.g. polymer chain alignment, or the short, less oriented

molecules with a corresponding experimental packing density for phosphonic acid SAMs [9].

Figure 5 shows the ionization energies of the aluminum oxide slab with varying hydroxyl coverage. The vacuum level of the bare oxide surface is shown on the left and those of the hydroxyl-covered surfaces are on the right. Surface hydroxyls modify the ionization energy

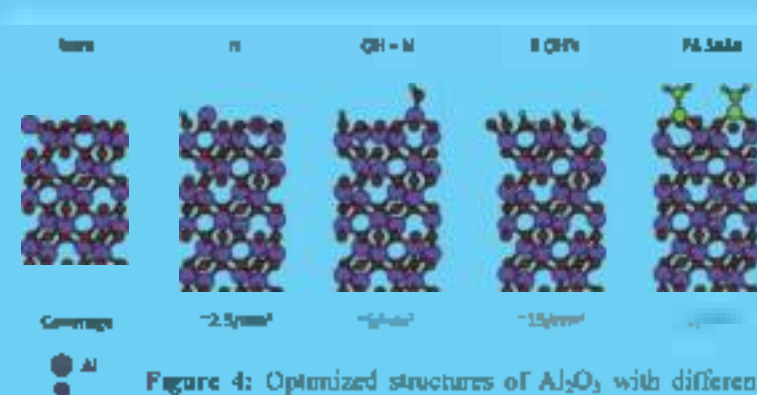


Figure 4: Optimized structures of Al_2O_3 with different surface structures (see text for details)

greatly, and can also elevate the vacuum level. Whereas the Al-topped surface is the most stable, oxide surfaces are not free of hydroxyls unless annealed at >700 K [7]. Our results, therefore, indicate that the experimental work function of the oxidized aluminum can be very sensitive to the history of the sample preparation.

The calculated work functions of the combined Al and Al_2O_3 slabs are shown in Figure 6. The Al/ Al_2O_3 interface adds an offset of 1.1 eV to the spectrum of energy levels obtained for the dielectric oxides in Figure 5. Interestingly, at a hydroxyl coverage between the ‘H’ and ‘OH+H’ surfaces, the modification via the oxide layer of the Al work function can be compensated by the presence of surface hydroxyls, resulting in a work function equivalent to that of the Al metal without any oxide layer [10]. This is consistent with the experimental

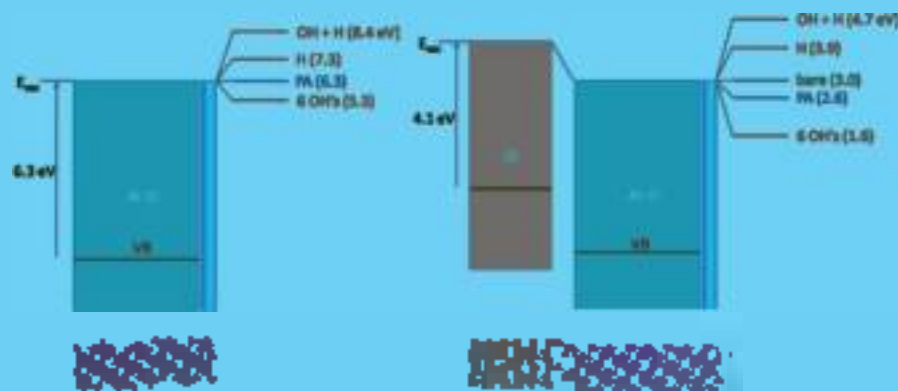


Figure 5: Calculated ionization energies of $\alpha\text{-Al}_2\text{O}_3(0001)$ for different surfaces (see Fig. 4 for labels).

Figure 6: Calculated workfunctions of Al(111)/ $\alpha\text{-Al}_2\text{O}_3(0001)$ for different surfaces (see Fig. 5 for the labels).

observation of no change in work function after growing a thin oxide overlayer. According to our energy level diagrams, the downshift of 0.4 eV reported by the Princeton group [4] suggests that their oxide surface may be covered with a small number of hydroxyl groups.

The Georgia Tech group also investigated the impact of deposition of a SAM made of alkyl phosphonic acids. They first considered just the oxide. In that case, the SAM is calculated to modify the surface structure greatly; however, the combined effects of the molecular dipoles of the SAM molecules and the structural relaxations within the oxide layer, result in no significant change of the ionization energy with respect to the bare oxide (see Figure 5).

When considering the aluminum/aluminum oxide system, the SAM leads to a calculated reduction of the work function by some 1.5 eV (see Figure 6). This decrease is consistent with—although larger than—that observed experimentally by the Princeton group (0.8 eV with respect to Al metal) with PA molecules containing longer alkyl tails [4].

In a parallel effort to understand cathodes and electron injection, the Cornell group developed a photovoltaic measurement technique to extract the built-in potential of a diode made from TFB sandwiched between different electrodes. Al and CsF/Al were chosen as cathodes. The device had a ITO/PEDOT:PSS/TFB (100nm)/cathode structure. The TFB film was spin-coated from p-xylene to achieve a thickness of $\sim 100\text{nm}$. Prior to cathode deposition, the films were baked at 130C for 15min in a nitrogen environment. The cathodes were then thermally deposited under high vacuum.

The photovoltaic measurement was performed using a Xenon lamp with a light intensity of $100\text{mW}/\text{cm}^2$, in a nitrogen environment. The open circuit voltage (V_{oc}) was extracted from the standard current-voltage characteristics. This V_{oc} , when corrected for a short arising from the dark current, represents the built-in potential (V_{bi}) of the device [11].

According to the UPS study shown in [11], ITO which is exposed to chlorinated solvent has a work function of 4.85eV. The CsF buffer layer reduces the effective work function of the Al cathode by $\sim 1\text{eV}$. Hence, the effective work function of Al and CsF/Al cathode is found to be 4.25eV and 3.25eV, respectively. Since the LUMO of TFB is 2.5eV, it is then suggested that the electron injection barrier of Al/CsF/TFB and Al/TFB is 0.75eV and 1.75eV, respectively.

Device	Anode	Cathode	Vbi (V)
1	ITO	CsF/Al	1.66
2	PEDOT:PSS (CH8000)	CsF/Al	1.7
3	ITO	Al	0.6
4	PEDOT:PSS (CH8000)	Al	0.76

Table 1: Summary of built-in-potential (V_{bi}) measured for different anode/polymer/cathode configurations.

PEDOT:PSS has a work function of 5.15eV. The V_{bi} 's of devices 2 and 4 are therefore expected to be 1.9eV and 0.9eV, respectively, if band bending or surface dipole effects do not occur at the anode interface. The 0.2 and 0.14eV discrepancies are tentatively attributed to band bending ($\sim 0.25\text{eV}$) at the PEDOT:PSS/TFB interface, consistent with the UPS observations [12].

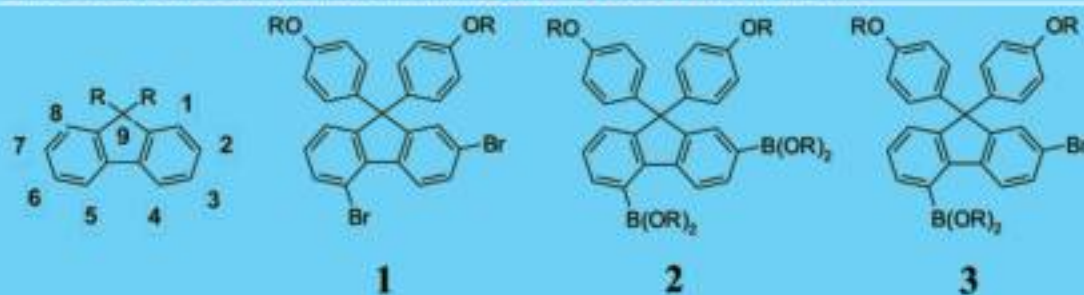
Model Polymers

Our joint efforts have so far utilized two polymers – the homopolymer of polyfluorene and the copolymer TFB that have proven high performance capability in OLEDs at GE and elsewhere in the world. These polyfluorenes are obtained by coupling suitably functionalized fluorene monomers at the 2 and 7 positions. Recently, GE discovered a process that yields substantial quantities of an isomeric fluorene monomer that enables coupling at the 2 and 5-positions (see chemical structures below). These materials are of great interest within the context of this program because in contrast to the typical linearly coupled 2,7 materials, the aryl linkage joined at the hindered 5-position cannot achieve co-planarity with the adjacent

fluorene ring. At the same time, these isomeric monomers can be functionalized at the 9-positions enabling control of physical properties (solubility, charge mobility, morphology) in the same way as standard polyfluorene materials.

This subtle change in structure is likely to lead to noticeable changes in the single polymer electrical properties because it causes the disruption of conjugation at the linkage sites. Hence, this should result in a larger charge transport gap which, in turn, should yield different electrical interface properties. Similarly, the change in steric packing due to the non-coplanarity should yield different electrical transport properties.

The GE team is now exploring the synthesis of these materials with the aim of creating the 2,5 analogues of the two model polymers that have been investigated to date. These materials are of practical interest because their higher band gap makes them compatible with phosphorescent dopants. More importantly from the scientific aspect, they will provide a useful contrast to the model materials since their chemical identity will be identical but their electronic behavior will *likely* be different. Hence they will provide a test of the predictive powers of the models and understanding that we have built up to date.



An interesting feature of incorporating an unsymmetrical monomer into a polyfluorene chain is that the longest conjugation length obtained from homo coupling at the 2 and 5-positions depends on the method of coupling. For example, self-coupling of monomer **1** either directly *via* Yamamoto coupling or with reaction with the bis-borate, **2**, *via* a Suzuki coupling protocol affords a polymer in which some segments will be derived from 2,2' coupling. The expected singlet and triplet energies for these materials should be the same as that of a fluorene dimer. However, homo coupling of a monomer bearing a bromide and borate at each of the non-equivalent positions should afford a polymer having only 2,5-linkages in the chain hence a higher singlet and triplet energy than those just described. We have been able to obtain such a monomer, **3**. Indeed, the polymer derived from homo coupling of **3** exhibits a wider band gap than that derived from coupling **1** with **2**.

To this point, we have not been able to obtain high molecular weight polymers from coupling **1** with **2** or by homo coupling of **3**. This is likely due to retardation in the rate of coupling at the 5-position due to hindrance. This enables side reactions to compete kinetically with chain-growth and limits the ultimate molecular weight obtainable. We are currently optimizing the polymerization conditions in an effort to overcome this problem.

References

1. H.H. Fong, A. Papadimitratos, and G.G. Malliaras, Appl. Phys. Lett. **89**, 172116 (2006).
2. H.H. Fong, A. Papadimitratos, J. Hwang, A. Kahn, G.G. Malliaras, Adv. Funct. Mater. **19**, 304 (2009)
3. J. Liu, L. N. Lewis, T. J. Faircloth, and A. R. Duggal, Appl. Phys. Lett. **88**, 223509 (2006).
4. Y. Vaynzof, T. J. Dennes, J. Schwartz, and A. Kahn, Appl. Phys. Lett. **93**, 103305 (2008).
5. Z. Guan, L. Loo and A. Kahn (in preparation)
6. X.-G. Wang, A. Chaka, and M. Scheffler, Phys. Rev. Lett. **84**, 3650 (2000).
7. J. W. Elam, C. E. Nelson, M. A. Cameron, M. A. Tolbert, and S. M. George, J. Phys. Chem. B **102**, 7008 (1998).
8. P. J. Eng, T. P. Trainor, G. E. Brown, Jr., G. A. Waychunas, M. Newville, S. R. Sutton, and M. L. Rivers, Science **288**, 1029 (2000).
9. M. J. Pellerite, T. D. Dunbar, L. D. Boardman, and E. J. Wood, J. Phys. Chem. B **107**, 11726 (2003).
10. R. A. Chapman, J. Appl. Phys. **35**, 2832 (1964).
11. G.G. Malliaras, J.R. Salem, P.J. Brock, J.C. Scott, J. Appl. Phys. **84**, 1583 (1998).
12. J. Hwang, E.-G. Kim, J. Liu, J.-L. Brédas, A. Duggal, and A. Kahn, J. Phys. Chem. C. **111**, 1378 (2007).

Planned activities for the following year

The remainder of the first period (through 3/31/09) and the second year of the grant will be devoted, in large part, to the investigation of electron injection into, and transport through, our model polymers. The promising work on SAM-modified oxide (AlOx) surfaces outlined above will be continued to:

- investigate the origin of the difference in energy level offsets between the dielectric oxide and the oxide-covered metal of Al.
- establish the optimal SAM structure (length, termination) for minimizing electron barrier and maximizing injection
- determine the interfacial structure of SAMs with longer alkyl groups, and examine the effects of different tail groups on the work function
- examine the excitation energies (singlet and triplet energies) of F8 and TFB as a function of linkage position using time-dependent DFT
- measure electron mobility in our model polymers, and determine the real injection efficiency of SAM-modified oxide electrodes

We will begin the investigation of new polymers synthesized at GE and evaluate performance in terms of carrier mobility and injection.

We will investigate the use of alternate hole-injection layers that present lower ohmic losses than the widely used PEDOT:PSS [2], and we will revisit the (p-)doping of polymer layers with strongly oxidizing agents to circumvent the problem of Fermi level pinning reported in our earlier work on TFB [12].

Finally, with a handle on both electron and hole injection, we will begin to investigate the performance of simple PLED devices built by lamination of two sides for which injection has been optimized.

Interactions between institutions

The four institutions kept a tight level of interaction with frequent consultations during the first year of this grant. In addition to frequent bi-lateral interactions, the four groups met on October 14, 2008 at Princeton University. The four groups will hold a conference-call later in February 2009, and will meet again before the summer. These frequent full-group discussions have proven extremely useful for PIs, post-docs and students, and have allowed a high level of coherence in the research. The groups also meet more informally on regular basis at various meetings around the country, e.g. MRS or APS.

Personnel (partially or totally) supported by the DOE Grant (other than summer support for PIs)

Hon Hang Fong: Post-doctoral fellow, Cornell University

Zelei Guan: Post-doctoral fellow, Princeton University

Eung-Gun Kim: Post-doctoral fellow, Georgia Institute of Technology

Alexis Papadimitratos: Graduate student, Cornell University

Publications supported by the grant

(since May 2008)

1. *Modification of the Electronic Properties of Aluminum Oxide Surfaces by Octylphosphonate Self-Assembled Monolayer Deposition*, Yana Vaynzof, Joseph T. Dennes, Jeffrey Schwartz and Antoine Kahn, Appl. Phys. Lett. **93**, 103305 (2008)
2. *Hole injection in a model fluorene-triarylamine copolymer*, Hon Hang Fong, Alexis Papadimitratos, Jaehyung Hwang, Antoine Kahn and George G. Malliaras Adv. Funct. Mater. **19**, 304 (2009)
3. *Electron injection properties of low work function electrodes: limitation by Fermi level pinning*, Y. Vaynzof, J.T. Dennes, J. Schwartz and A. Kahn (to be submitted)
4. *Electron injection and transport in a fluorene-triarylamine copolymer*, H.H. Fong, A. Kahn, and G.G. Malliaras (in preparation).

Progress Report

submitted to the

Office of Basic Energy and Sciences

of the

Department of Energy

for the period

March 2009 – February 2010

“Understanding and Design of Polymer Device Interfaces”

Grant # DE-FG02-05ER46165

submitted by

Antoine Kahn

Princeton University

Department of Electrical Engineering

Princeton, NJ 08544

Tel: 609-258-4642

Email: kahn@princeton.edu

Scientific achievements

During the second period of the current grant, March 2009 – February 2010, the team of four PIs (Prof. Jean-Luc Brédas at Georgia Tech, Prof. George Malliaras at Cornell Univ., Dr. Anil Duggal at GE and Prof. Antoine Kahn at Princeton Univ.) continued their investigations of polymer interfaces and related issues of chemical and electronic structures, charge carrier injection, transport and chemical doping.

This progress report focuses specifically on recent work done on (i) interfaces between the hole injection layer PEDOT:PSS and the fluorene-triarylamine copolymer poly(dioctylfluorene-co-*N*-(4-butylphenyl)-diphenylamine) (TFB); (ii) the p-type doping of TFB to enhance carrier injection and conductivity; and (iii) the role of PS-morpholine in enhancing electron injection from the Al cathode into TFB.

Acid-base interactions at TFB/PEDOT:PSS interfaces

Among conjugated polymers, polyfluorene and its copolymers exhibit high luminous efficiency and low driving voltage. Recently, the Cornell and Princeton groups reported a systematic study of hole transport in TFB and evaluated hole injection using the conducting polymer PEDOT:PSS as a hole injection electrode.[1] It has been widely suggested that upon thermal post-annealing of the PEDOT:PSS/triphenylamine contact, an interlayer that can lead to enhanced device lifetime is formed.[2] Previous reports show that the enhancement of device lifetime arises from better polymer packing and reduced interface roughness due to the annealing of the light-emitting polymer above its glass transition temperature. However, there is not yet conclusive evidence to explain the improved electrical performance of OLEDs that utilize this contact.

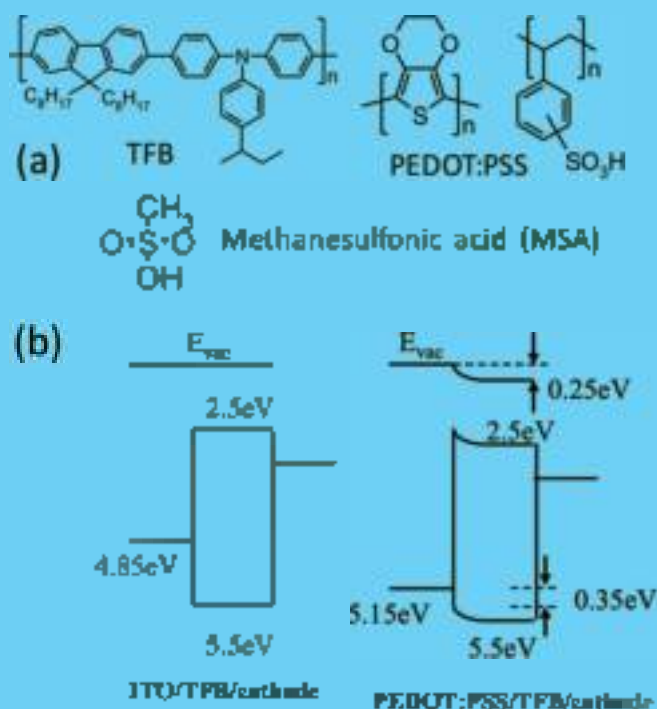


Figure 3: (a) Molecular structure of TFB and PEDOT:PSS, and chemical formula of methanesulfonic acid. (b) Energy diagram of ITO/TFB/cathode and ITO/PEDOT:PSS/TFB/cathode

During this second period, the Cornell group considered a new effect at the PEDOT:PSS/TFB interface. Results show that this widely used contact (PEDOT:PSS and triphenylamine) is subject to the formation of a solid-state organic acid-base junction, where PSSH acts as a strong organic acid while triphenylamine compound such as TFB acts as a weak organic base. The organic salt “interlayer” therefore appears in between PEDOT:PSS and TFB and this interlayer region is able to be adjusted according to the “efficiency” of proton diffusion

Fig. 1(a) shows the molecular structure of TFB and PEDOT:PSS. Our previous study

[1] shows that when PEDOT:PSS is inserted in between the ITO and the TFB layer, a downward surface band bending of 0.25 eV w.r.t. PEDOT:PSS occurs (Fig. 1(b)). Our previous ultra-violet photoemission spectroscopy (UPS) study of PEDOT:PSS shows that a 3.5 nm thick PSSH layer forms on the surface of the PEDOT:PSS film upon thermal annealing.[3] We also observed that thermal baking of PEDOT:PSS is able to liberate protons, which then diffuse to the overlayer polymer film.[4] A direct example is that the cross-linkable light-emitting polyfluorene is responsive to the proton and forms a 30 nm thick insoluble cross-linked film upon thermal baking of the PEDOT:PSS underlayer.

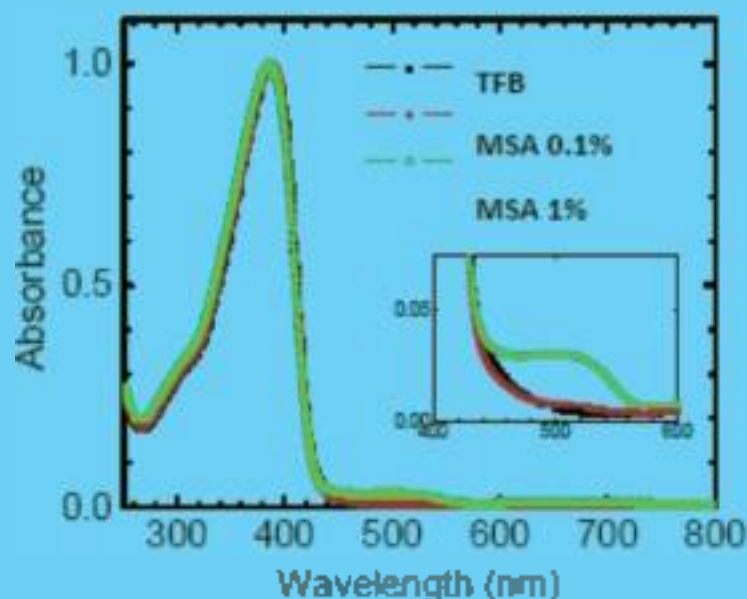
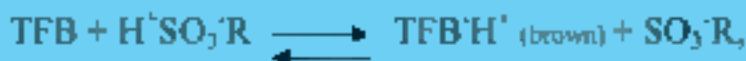


Figure 4: Optical absorption spectra of TFB solution (0.1 mg/mL in p-xylene) (black), TFB solution mixed with 0.1% MSA (red), and TFB solution mixed with 1% MSA.

different concentrations. It is clearly shown that an additional absorption near the band edge appears when the MSA concentration reaches 1%. This new absorption shoulder suggests that the optical band gap of TFB after MSA doping is reduced from 2.8 eV to 2.2 eV. Therefore, the TFB:MSA solution turns to a pale yellow color. Fig. 3 further illustrates the optical image of the pristine TFB solution (Fig. 3(a)) and the TFB solution mixed with an excess amount of MSA (weight ratio of TFB:MSA = 1:24.5) (Fig. 3(b)). An insoluble brownish precipitate is formed upon an excess amount of MSA doped into TFB. This TFB:MSA mixture shows a weak fluorescence under 365 nm excitation, indicating that a small portion of the TFB remains undoped while the large portion of TFB converts to an organic TFB salt due to protonation. The following reaction pathway generalizes the interface interaction between TFB and PSSH⁺:



where R represents an alkyl chain.

To confirm that the protonation occurs at the triphenylamine unit of TFB but not at the fluorene unit, we further study the reaction between MSA and a triphenylamine molecule (TPA). Fig. 3(c) shows the optical images of a pristine TPA solution (dissolved in

Here, we further investigate the influence of the proton diffusion to TFB. In order to further understand the origin of band bending, we first attempt to evaluate the effect of PSSH⁺ to TFB by replacing the PSSH with a simple model organic acid, namely methanesulfonic acid (MSA) (Fig. 1(a)). Note that PSSH⁺ is soluble in water but not miscible with organic solvents while MSA is relatively miscible with non-polar organic solvents such as chloroform, xylene, and toluene up to certain extent.

Fig. 2 shows the optical absorption spectra of the pristine TFB solution and the TFB solution mixed with MSA at

chloroform; 200 mg/mL) and the corresponding TPA solution mixed with MSA (weight ratio of TPA:MSA = 1 : 0.74). This solution of TPA doped with MSA turns to green color at such a low concentration of MSA. This direct evidence indicates that the TSA reacts with the nitrogen atom in the tertiary amine of TFB and reduces the optical band gap of TFB.

Therefore, we experimentally demonstrate that the proton is able to co-ordinate to the tertiary amine in the TFB polymer that leads to formation of an insoluble interlayer along the PEDOT:PSS/TFB interface. This study suggests that the ratio of PEDOT to PSS can cause

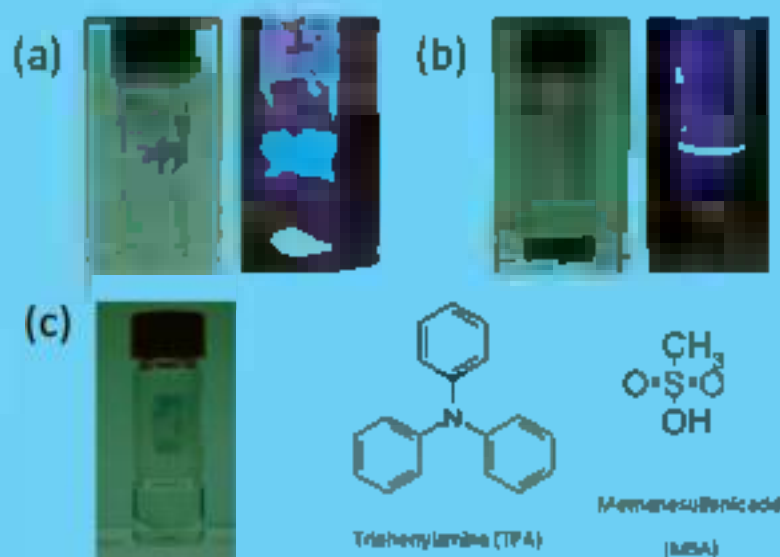


Figure 5. (a) TFB dissolved in p-xylene (15mg/mL) (left) and TFB solution illuminated by 365 nm (right). (b) TFB dissolved in p-xylene (15 mg/mL) mixed with MSA (left) and TFB solution mixed with MSA illuminated by 365 nm (right). (c) TPA dissolved in chloroform (left) and TPA solution mixed with MSA (right). Inset: Molecular structures of triphenylamine molecule (TPA) and methanesulfonic acid (MSA).

different degrees of proton diffusion into the overlayer polymer. Furthermore, the ratio of tertiary amine of the fluorene-triphenylamine copolymer can cause different degrees of protonation. In conclusion, the triphenylamine and sulfonic acid moieties form a specific solid-state organic acid-base junction pair that results in an insoluble organic interlayer in the PEDOT:PSS/TFB interface. This principle can be generally applied to explain the interface behavior between PEDOT:PSS and other triphenylamine copolymers.

The theoretical aspect of the interactions between TFB and protons released from PSSH was investigated by the Georgia Tech group. The theoretical methodology was based on the following. Density functional theory (DFT) calculations were performed on model oligomers of TFB. Oligomers of FTFTFTF (F for fluorene and T for triphenylamine) were used to represent TFB. The alkyl side groups on both fluorene and triphenylamine units, which would not affect the properties of interest significantly, were replaced with a hydrogen atom to reduce the computation time. Three different levels of protonation, $n/3$ (n denotes the number of protonated amine groups and 3 the total number of amine groups in the oligomer), were modeled by adding a proton to the amine nitrogen; the central triphenylamine unit was protonated at 1/3 and the two peripheral triphenylamine units were used at 2/3. No counter ions were considered.

The ground-state molecular geometry was obtained at the B3LYP/6-31G(d,p) level. Time-dependent DFT (TDDFT) was then used on the ground-state geometry to calculate singlet excited states (up to 20 states). Transition energies and oscillator strengths were subsequently convolved with a Gaussian function of FWHM (full width at half maximum) =

0.3 eV to simulate optical absorption spectra. All calculations were performed using the Gaussian 03 package.⁶¹

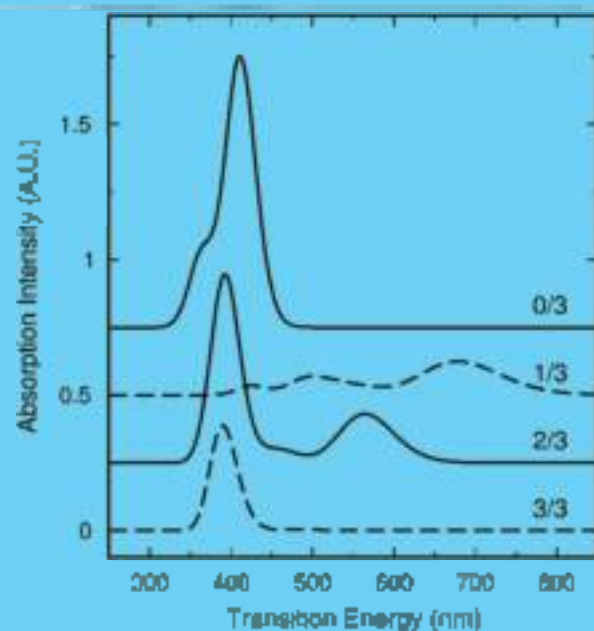


Figure 6: Simulated absorption spectra of TFB at different protonation levels. $n/3$ denotes the number of protonated amine groups, n , out of the total number, 3, of amine groups in the TFB oligomer.

Fig. 4 shows the simulated optical absorption spectra of TFB at different protonation levels obtained from TDDFT-calculated singlet excited states. Our simulation reproduces the experimental spectral features of pristine (0/3) TFB very well. Both the strong-intensity peak (at 412 nm) and the shoulder are slightly red-shifted with respect to experiment. Subsequent protonation red-shifts the lowest energy peak, but the red-shift decreases with further protonation to ultimately become negative at full protonation (the shift with respect to the pristine state is 266, 152, and -22 nm at 1/3, 2/3, and 3/3, respectively). It is now straightforward to reproduce the experimental absorption spectra of protonated TFB featuring the “in-gap” band, by combining the simulated 0/3 and 2/3 spectra (note that the experimental spectra contain contributions from both the

pristine and protonated portions of TFB). Our DFT calculations are consistent with an interfacial Lewis acid–base reaction between the amine of TFB and the proton dissociated from PSSH and furthermore suggest that the level of protonation is rather high with on the order of every other amine group protonated

The dependence of the absorption spectrum on the protonation level can be understood from the molecular orbital picture. In pristine TFB, both the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals are delocalized over both fluorene and triphenylamine units (see Fig. 5, left); at the HOMO level, triphenylamine units are more populated

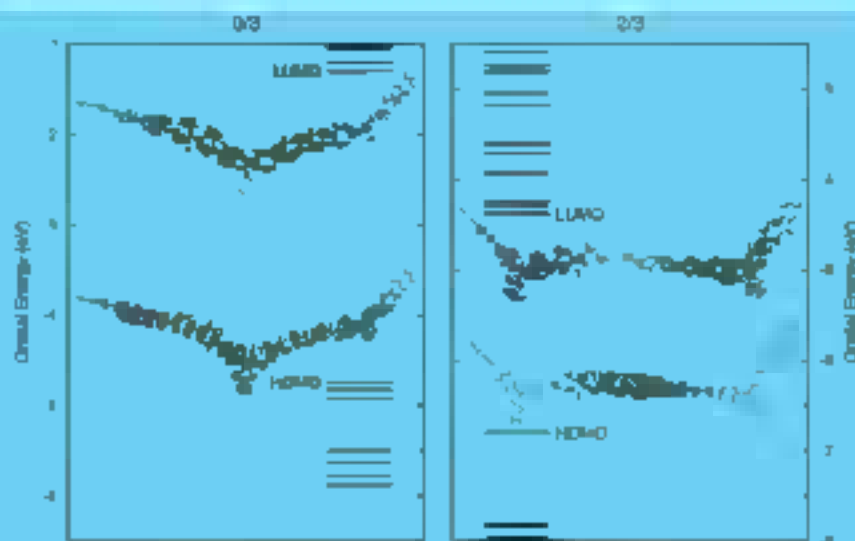


Figure 7: Calculated molecular orbital energy levels of TFB before (0/3) and after (2/3) protonation

than fluorene units whereas it is opposite at the LUMO level (the triphenylamine phenyl that is not directly linked to a fluorene unit is even barely populated). When an amine group is protonated, the positive charge is localized over the hosting triphenylamine unit and about half a fluorene unit on each side; the torsion at the T—F bond changes by only a few degrees from -36° . Sharing the lone pair electrons with a (positively charged) proton stabilizes *locally* both the occupied and unoccupied energy levels. The new LUMO is localized over the protonated triphenylamine unit whereas the HOMO remains delocalized along the chain with an interrupted conjugation only at a protonated site (Fig. 5, right); as a result, the HOMO is less impacted by the protonation than the very local LUMO. With the transition to the first singlet excited state being from the HOMO to the LUMO (in all except for the 3/3 case), the optical bandgap narrows, producing the in-gap band in the absorption spectra.

p-doping of TFB via co-solution

Chemical doping is being implemented in organic thin films for increasing bulk conductivity and enhancing carrier injection via tunneling through narrow depletion regions. The Princeton group initiated an investigation of p-type doping in TFB via co-solution of the polymer with the strongly oxidative molecule molybdenum tris[1,2-bis(trifluoromethyl) ethane-1,2-dithiolene] ($\text{Mo}(\text{tfd})_3$) (inset Fig. 6). This molecule had been previously found to exhibit an electron affinity (EA) of 5.6 eV, which is 0.1 eV larger than the TFB ionization energy (IE) [6,7]. Several groups have studied and reported doping small molecule films by controlled co-evaporation of host and dopant molecules. However, only a few reports are available for the formation of doped polymer films by co-solution.[8]

Doped films were prepared by dissolving TFB in anhydrous p-xylene at 65°C , and adding either 2, 10 or 12 wt% $\text{Mo}(\text{tfd})_3$, and spin-coating under controlled atmosphere on Si or ITO, depending on the specific experiment. Films were then transported (under controlled atmosphere) to the UHV chamber for photoemission experiments, or to a mercury probe

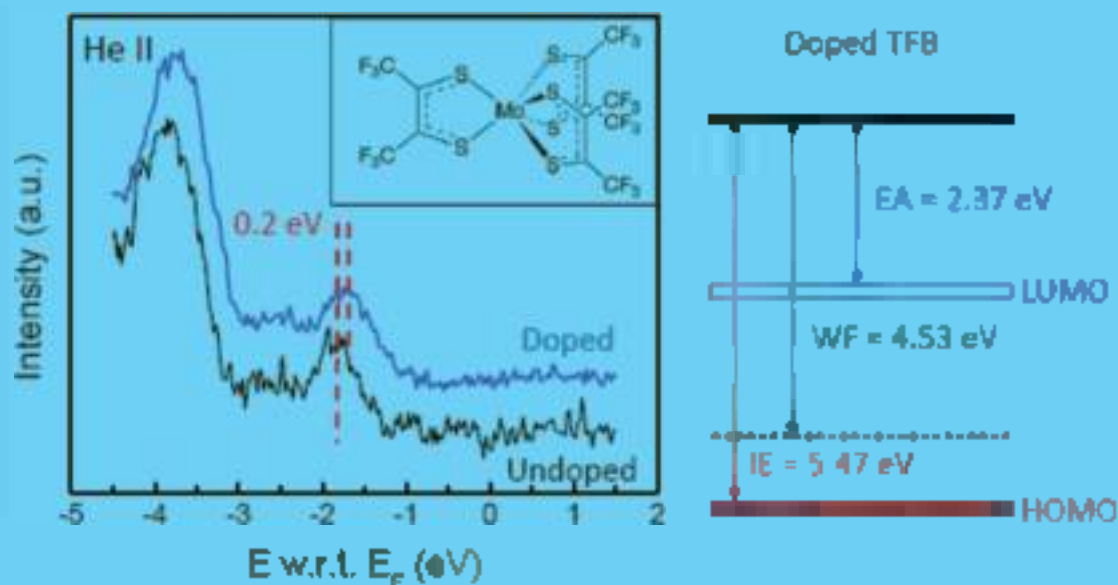


Figure 8: (Left) He II UPS spectra of the frontier valence states of undoped and doped TFB films. The doping concentration is 10 wt%. Inset: chemical structure of the $\text{Mo}(\text{tfd})_3$ molecule. (Right) energy diagram of the doped TFB film showing ionization energy (IE), electron affinity (EA) and work function (WF).

suation for electrical measurements. Fig. 6 (left) shows the TFB valence states closest to the Fermi level (reference at 0 eV) for the undoped and doped (10%) films. The valence states clearly shift toward E_F , indicative of p-doping, yet the shift is smaller than expected based on the electronic levels of the constituents and on previous experience with poly(9,9'-dioctylfluorene) (F8) doped with F₄-TCNQ.[5] The position of E_F in the gap of the doped polymer is shown on the right of Fig. 6.

Electrical characteristics obtained on the ITO/TFB(1000 Å)/Hg probe are shown in Fig. 7. The (hole-only) current corresponds to holes injected from ITO (Hg probe biased negative) or from the Hg contact (Hg probe biased positive). TFB is either undoped, or doped at 2 or 12 wt%. The first significant result is that doping increases the film conductivity. The conductivity of the undoped film is very low, and the low-field current density (ohmic conduction) is in the noise of our experimental set-up. The 2% doped film exhibits several orders of magnitude larger current, in particular in the ohmic regime, which indicates a significant boost of the film conductivity. This boost in doped films is due to: (i) preferential filling of deep traps by carriers released by the dopants, which reduces activation energy for hopping transport; and (ii) availability of more „free“ carriers. The conductivity of the 12% doped film increases by another 1 ½ orders of magnitude. Doping efficiency remains under investigation.

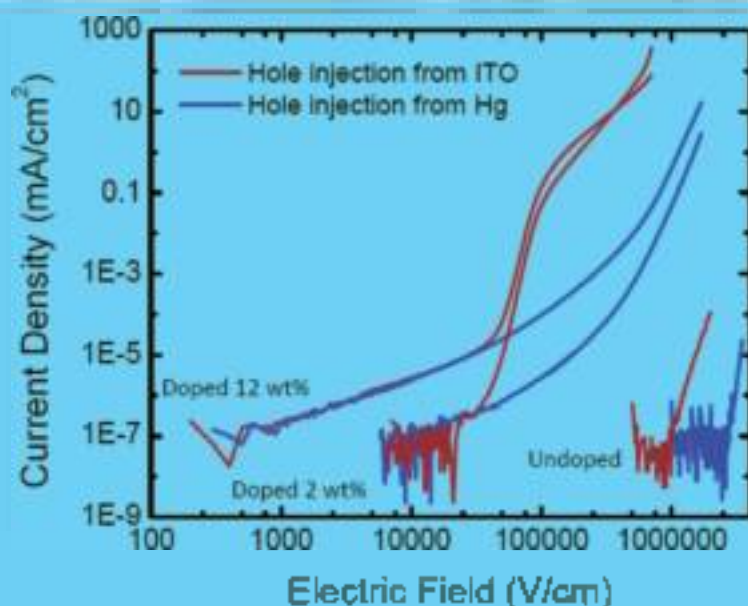


Figure 9: J vs. E characteristics of ITO/TFB(1000Å)/Hg. The polymer film is either undoped or doped with 2 or 12wt% Mo(tfd)₃.

region. A very similar result was obtained on a Si substrate. The above explanation, however, pre-supposes that doping is highly inhomogeneous in the TFB film, with significant segregation at the bottom interface. This point is currently being investigated via Rutherford back-scattering analysis of element (e.g. Mo) depth distribution in the polymer film.

Role of PS-morpholine in enhancing electron injection from Al to TFB

The GE group recently showed that a thin layer of trialkylamine functional polymers, such as poly(*N*-methyl-*N*-ethylaminomethyl)styrene (PS-morpholine) (Fig. 8), inserted between an EL polymer, e.g. TFB, and an electrode (Al, Au) enhances electron injection. The Princeton

The second interesting result is the large increase in bottom injection, which translates into the rapid turn-on just below 10^5 V.cm⁻¹. This onset is believed to be due to higher doping at the TFB/ITO interface, as has been seen specifically in interface-doped systems, i.e. where dopants are spatially restricted to one of the two organic interfaces.[9] Injection at the undoped interface is „normal“, i.e. the barrier between the metal Fermi level and the TFB HOMO controls injection. Injection at the doped interface is enhanced by hole tunneling through the doping-induced depletion

group investigated the electronic structure of PS-morpholine and its interface with TFB and Al.

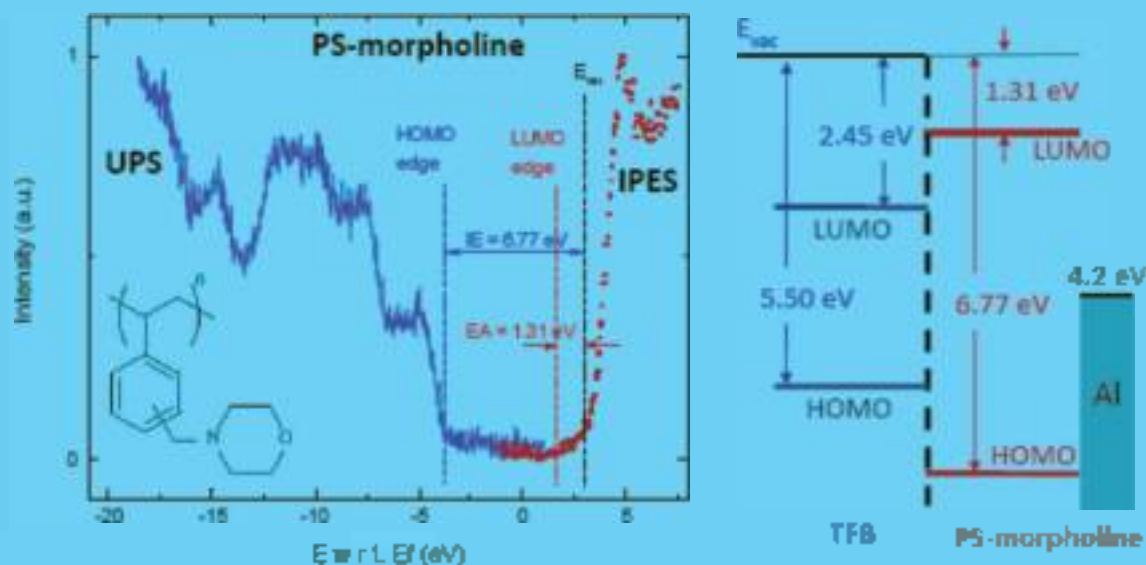


Figure 10: (Left) UPS/IPES from a 3 nm PS-morpholine film on Si. The edges of the filled and empty states, HOMO and LUMO, are indicated, as well as the vacuum level. The chemical structure of PS-morpholine is shown in inset. (Right) Energy diagram showing the frontier orbitals of PS-morpholine aligned with those of TFB. The Fermi level of Al is shown on the right.

A 3 nm of PS-morpholine was spin-coated on n^+ -Si and studied by UPS and inverse photoemission spectroscopy (IPES) to determine filled and empty state energies. Fig. 8 shows the combined UPS and IPES spectra (left) and the relevant electronic levels (HOMO, LUMO) deduced from these measurements. The TFB HOMO and LUMO levels (determined in previous studies under this grant) clearly fit in the large PS-morpholine gap.

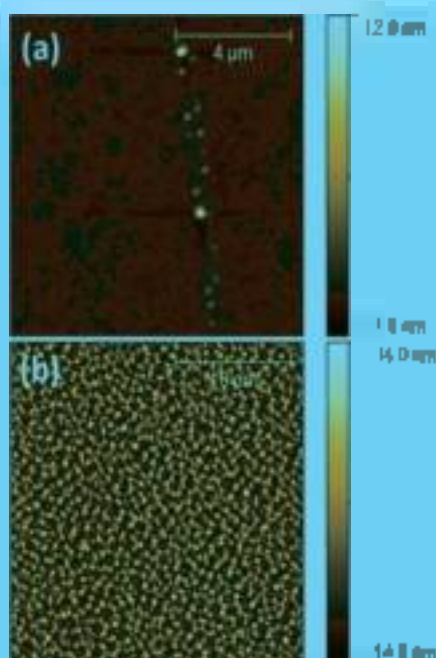


Figure 11: AFM micrographs of (a) 11-B on Si, and (b) PS-morpholine on TFB.

XPS investigations of interfaces between Al and Au and PS-morpholine do not show any evidence of chemistry that could lead to the formation of gap states that, in turn, could explain the enhancement in electron injection. One possibility is therefore that the PS-morpholine layer plays the role of a tunneling barrier, whereby part of the bias drops across it. This process would shift the electrode Fermi level closer to the TFB LUMO, enhancing injection. However, Fig. 8 shows that the Al Fermi level is about 1.8 eV below the TFB LUMO. A significant increase in injection would require that between 0.5 and 1 V be dropped across the PS-morpholine layer. Given that the GE experiment was done with 5 nm thick PS-morpholine film, this would imply an extremely high field in the insulator. Another possibility is hinted by an AFM study of a 5 nm PS-morpholine on TFB. Fig. 9a shows the micrograph of the TFB surface, which exhibits an RMS roughness of about 0.3 nm on a $100 \mu\text{m}^2$ area. A

similar area exhibits a 9 nm RMS roughness for PS-morpholine on TFB (Fig. 9b). This type of morphology could introduce considerable inhomogeneity in the contact structure, leading for example to high field contact areas. These preliminary results will be followed up in the next few months.

References

1. H.H. Fong, A. Papadimitratos, J. Hwang, A. Kahn, and G.G. Malliaras, *Adv. Funct. Mater.* **19**, 304 (2009).
2. A. R. Duggal, C. M. Heller, J. J. Shiang, J. Liu, and L. N. Lewis, *J. Disp. Technol.* **3**, 184 (2007).
3. J. Hwang, F. Amy, and A. Kahn, *Org. Electron.* **7**, 387 (2006).
4. J.-K. Lee, M. Chatzichristidi, A.A. Zakhidov, H.S. Hwang, E.L. Schwartz, J. Sha, P.G. Talyor, H.H. Fong, J.A. DeFranco, E. Murotani, W.W.H. Wong, G.G. Malliaras, and C.K. Ober, *J. Mater. Chem.* **19**, 2986 (2009).
5. Gaussian 03, Gaussian, Inc., Pittsburgh, PA (2003).
6. Y. Qi, T. Sajoto, S. Barlow, E.-G. Kim, J.-L. Brédas, S.R. Marder, and A. Kahn, *J. Am. Chem. Soc.* **131**, 12530 (2009).
7. Y. Qi, T. Sajoto, M. Kröger, A. Kandabarow, W. Park, S. Barlow, E.-G. Kim, L. Wielunski, L. C. Feldman, R. A. Bartynski, J.-L. Brédas, S. R. Marder, and A. Kahn, *Chem. Mater.* **22**, 524 (2010).
8. J. Hwang and A. Kahn, *J. Appl. Phys.* **97**, 103705 (2005).
9. W. Gao and A. Kahn, *J. Appl. Phys.* **94**, 359 (2003).

Planned activities for the following year

The remainder of the second period (through 3/31/10) and the third year of the grant will be devoted to the investigation of key polymer interfaces, polymer doping and charge carrier injection.

- The Cornell and Georgia Tech groups will continue their investigation of the TFB (and other polymer)/PEDOT:PSS interface. Raman and FTIR techniques will be used to further investigate the origin of the chemical bonding in the protonation of triphenylamine units and extend our studies to different fluorene-triphenylamine copolymers. Experimental results will be compared with computational studies using quantum mechanical calculations to understand the influence on the energy levels of TFB upon protonation of tertiary amines and explain the consequence on the band alignment of the PEDOT:PSS/triphenylamine interface.
- The Princeton and Georgia Tech groups will continue to pursue the experimental and theoretical investigation of the role of an interlayer for electron injection including polystyrene-morpholines.
- The Princeton group, in collaboration with the Cornell group, will investigate carrier transport in polymer films doped by co-solution, in particular with respect to the role of the dopants in filling deep traps and enhancing carrier mobility. The impact of doping on carrier injection will be studied as well. Theoretical support on the nature of new p- and

n-dopants will be provided by the Georgia Tech group.

- Finally, the Princeton group will continue a study of the electronic structure of polymer blend bulk heterojunctions with applications to photovoltaic cells. A recent study by this group of the P3HT:PCBM system shows that measurements of the LUMO(acceptor) – HOMO(donor) is possible in the blend. (see # 8 in Publications from this Grant).

Interactions between institutions

During this past year, the four groups have kept in close contact, via bi-lateral interactions and two conference calls of the four PIs. Members of the team have met on various occasions at conferences (Spring and Fall MRS, ESPMI-V in Japan). A conference call of the groups will be organized in February 2010 to plan for the next year.

Personnel (partially or totally) supported by the DOE Grant (other than summer support for PIs)

Hon Hang Fong: Post-doctoral fellow, Cornell University

Zelei Guan: Post-doctoral fellow, Princeton University

Eung-Gun Kim: Research scientist, Georgia Institute of Technology

Alexis Papadimitratos: Graduate student, Cornell University

Publications supported by the grant (since April 2009)

1. *Hole Injection in a Model Fluorene-Triarylamine Copolymer*, H. H. Fong, A. Papadimitratos, J. Hwang, A. Kahn and G. G. Malliaras, *Adv. Funct. Mater.* **19**, 304 (2009).
2. *Use of a High Electron-Affinity Molybdenum Dithiolene Complex to p-Dope Hole-Transport Layers*, Y. Qi, T. Sajoto, S. Barlow, E.-G. Kim, J.-L. Brédas, S.R. Marder, and A. Kahn, *J. Am. Chem. Soc.* **131**, 12530 (2009).
3. *Energetics of Metal-Organic Interfaces: New Experiments and Assessment of the Field*, J. Hwang, A. Wan, and A. Kahn, *Mater. Sci. Eng. R* **64**, 1-31 (2009)
4. *A Molybdenum Dithiolene Complex as p-Dopant for Hole-Transport Materials: A Multitechnique Experimental and Theoretical Investigation*, Y. Qi, T. Sajoto, M. Kröger, A.M. Kandabarow, W. Park, S. Barlow, E.-G. Kim, L. Wielunski, L.C. Feldman, R.A. Bartynski, J.-L. Brédas, S.R. Marder, and A. Kahn, *Chem. Mater.* **22**, 524 (2010).
5. *Degradation of Hole Injection at the Interface between PEDOT:PSS and a Fluorene-Triarylamine Copolymer*, H.H. Fong, A. Batra, and G.G. Malliaras (submitted)
6. *Acid-Base Interactions at TFB/PEDOT:PSS Interfaces*, H.H. Fong, E.-G. Kim, J.-L. Brédas, and G.G. Malliaras (in preparation)
7. *Hole transport in TFB p-Doped by Co-solution with the Strongly Oxidizing Molecule Mo(tfd)₃*, Y. Qi, T. Sajoto, S. R. Marder and A. Kahn (in preparation)
8. *Energy Level Alignment of Organic-Organic Bulk Heterojunction: The Case of the Poly(3-hexylthiophene) Phenyl-[6,6]-C61 Butyric Acid Methyl Ester Blend*, Z. Guan, J. Kim, Y.-L. Loo, and A. Kahn (to be submitted)