Advanced Surface Modification of Indium Tin Oxide for Improved Charge Injection in Organic Devices

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Abstract: A new method is described for surface modification of ITO with an electroactive organic monolayer. This procedure was done to enhance hole injection in an electronic device and involves sequential formation of a monolayer of a π-conjugated organic semiconductor on the indium tin oxide (ITO) surface followed by doping with a strong electron acceptor. The semiconductor monolayer is covalently bound to the ITO, which ensures strong adhesion and interface stability; reduction of the hole injection barrier in these devices is accomplished by formation of a charge-transfer complex by doping within the monolayer. This gives rise to very high current densities in simple single layer devices and double layer light emitting devices compared to those with untreated ITO anodes.

Introduction

As is widely known, significant barriers to charge injection may exist at interfaces between dissimilar materials such as between inorganics and organics. Such junctions are found at the anode (for example, indium tin oxide, ITO) and cathode of organic light emitting diodes (OLEDs), or at electrodes in other novel (opto-)electronic devices comprising conjugated organic materials.[1] It is therefore of interest to develop methods to suitably modify interactions at the interfaces of such dissimilar materials so that desired electronic properties of devices incorporating them can be realized. One way to accomplish this is by attaching a functional organic onto the electrode surface: It is proposed that charge transport across interfaces can be enhanced in this way, so it is not surprising that considerable research has been reported[2−12] on methods for bonding organics onto an anode surface such as ITO.

One way to change the efficiency of hole injection from ITO into an organic hole transport layer (HTL) is by surface dipole manipulation:[13] If the negative end of this dipole were oriented away from the ITO surface, then the work function of ITO (ϕ_{ITO}) would be increased, and the hole injection barrier (ϕ^*_h) would be reduced compared to bare ITO (ϕ_h).[14] Conversely, if the negative end of the dipole were oriented toward the ITO surface, ϕ_{ITO} would decrease, and ϕ^*_h would increase. This surface dipole introduction can be accomplished by depositing discrete, small molecular species onto the ITO surface.[15] Indeed, the hole injection efficiency in simple diode devices has been shown to decrease or increase by ITO surface adsorption of phosphonic acids substituted with electron donating or withdrawing groups, respectively.[7,12,16]

A second means to increase current density through an OLED is to bond films of silane-derivatized HTL molecules onto the ITO surface. It was found[17] that by using such silanized films the light output of the OLEDs increased proportionally with the thickness of the film, but device current density was enhanced by less than an order of magnitude versus unmodified ITO.

Yet another way to modify charge injection properties at the anode-HTL interface is to synthesize doped layers. For example, introducing a small amount of the strong electron acceptor tetrafluorotetracyanoquinodimethane (F_4-TCNQ) at the anode/HTL interface[18,19] resulted in an increase in the hole injection

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density in simple devices by several orders of magnitude versus the untreated anode (Au[18] or ITO[19]). In the case of Au,[18] this effect was attributed to a narrowing of the depletion region via doping of the HTL, thereby reducing the barrier for charge carrier injection.

We now report a new approach to reducing the barrier to hole injection at the ITO/HTL junction that can be realized by bonding a monolayer (ML) of an organic semiconductor onto the ITO surface as an intermediary ITO/ML/HTL interface. Indeed, we show that this ML, when p-type doped, in fact gives rise to very high current densities in simple hole-only or OLED devices. Our approach combines complementary aspects of surface modification chemistry and leads to excellent interfacial properties. The key steps in our process are as follows: (1) form a self-assembled monolayer (SAM) of a phosphonic acid on the ITO surface; (2) convert the SAM to a covalently bonded ML on the ITO to ensure strong adhesion and interface stability; (3) use a SAM of extended π-conjugated moieties (vs aliphatic, insulating ones[4,7,10,20] that yield *increased* barriers for charge carrier transport across the ITO/HTL interface); and (4) reduce the hole injection barrier by formation of charge transfer complexes within the ML (corresponding to p-type doping). Our surface modification technique is not limited to use with ITO, and thus should be applicable for surface modification of virtually any oxide surface (including transparent, conductive oxides).

Experimental Section

General. ITO-coated glass (Colorado Concepts) samples were cut into 20 mm × 20 mm coupons. A 10 × 20 mm strip of ITO was defined by covering the appropriate area with electrical tape and etching the surrounding ITO in 37% HCl; the tape was then removed. These samples were cleaned by hand polishing in a silica (grade 60, 230–400, Aldrich)/distilled water slurry for 30 s, rinsing in 1 M NaOH (to remove remaining SiO₂) and distilled water. These polished samples were sonicated in detergent (2% Tergitol [Aldrich]/distilled water) for 20 min, rinsed with copious amounts of distilled water followed by sonication (10 min) and removal from boiling acetone. These samples were then further rinsed by boiling first in electronic grade isopropyl alcohol, then methylene chloride. Samples were dried under N₂ and used immediately. α-Quarterthiophene-2-phosphonic acid was prepared as previously described.[21] A Zeiss LSM 510 confocal fluorescence microscope was used for fluorescence imaging.

T-BAG Preparation of α-Quarterthiophene-2-phosphonate/ITO. Yellow-green solutions of α-quarterthiophene-2-phosphonic acid (4TPA) were made by dilution of a stock solution of 4TPA in 50 mL THF (0.73 m*M*, 15 mg), and diluted solutions were passed through a 0.2 *μ* PTFE syringe filter before use. The monolayer film of α-quarterthiophene-2-phosphonate/ITO was prepared according to the T-BAG procedure[21] as follows: ITO/glass coupons were held vertically using a small clamp in a solution of 4TPA in a 50 mL beaker. The solvent was allowed to evaporate slowly over 3 h, until the level of the solution fell below the glass coupon. Under these conditions, the concentration of the 4TPA in the remaining solution increased by about 30%. The treated ITO coupon was then removed from its holder and was heated at 140 °C in a simple glass tube under nitrogen for 2 days to bond the SAM to the ITO as a monolayer of α-quarterthiophene-2-phosphonate (4TP). Any multilayer 4TPA was removed by sonication in 5% triethylamine (Aldrich) in ethanol, typically for 30 min, followed by

extensive rinsing with ethanol and then distilled/deionized water. Samples were then dried in a stream of dry N₂. It is important to note that extensive loss of surface phosphonate material occurs if coupons are base-rinsed prior to heating.

Quartz Crystal Microgravimetry Measurements. ITO-electrode equipped quartz crystals (10.000 MHz, AT-cut, 1000Å ITO on 500Å Al) were obtained from International Crystal Manufacturing and were used as received. Quartz crystal microgravimetric (QCM) measurements were made using an ICM 35360 crystal oscillator powered by a Hewlett-Packard 6234A dual output power supply. The crystal frequency was measured using a Hewlett-Packard 53131A universal counter. In each experimental run, the fundamental frequency (f_0) of an untreated QCM crystal was measured. Then a 0.1 μM solution of 4TP in THF was used to deposit SAMs of 4TP on both sides of the crystal by T-BAG; the crystals were then baked at 130 °C under N₂ for 90 min. Rinsing with THF, methanol and triethylamine (Acros) was done successively until the crystal frequency was unchanged. Repeated cycles of T-BAG, baking and rinsing were performed to ensure full coverage of the densely packed monolayer on the ITO electrode. Measuring identical frequency readings for two successive cycles was deemed to represent that point when the entire surface was fully covered. The frequency change from f_0, $\Delta f = 183 \pm 1$ Hz, was used to calculate the surface loading.[21]

X-ray Photoelectron Spectra. XPS data were collected using a Phoibos 150 hemispherical energy analyzer (SPECS) and a monochromatized Al (1486.6 eV) source. A pass energy of 30 eV was used for wide range (survey) scans, while a 10 eV pass energy was used for high-resolution measurements. For quantitative estimations of surface compositions standard atomic photoionization cross-section values from the SPECS database were used. All measurements were carried out at normal and grazing takeoff angles. The sampling depth at normal takeoff angle is considered to be 60–80 Å, while grazing angle measurements (75° from the surface normal) are more surface sensitive (sampling depth of about 20 Å).

Preparation and Testing of Single Layer and Double Layer OLED Devices. Depositions of *N,N′*-bis-(1-naphthyl)-*N,N′*-diphenyl-1,1-biphenyl-4,4′-diamine (99.9%; Aldrich; α-NPD, tris(8-hydroxy-quinoline)aluminum (99.995%, Aldrich; Alq₃) and Al layers were performed using an Edwards 306A thermal evaporation system at a base pressure of <10⁻⁶ mbar. α-NPD was used as received and was deposited at a rate of 2–3 Å/sec to a thickness of 1500 Å. Aluminum (Alfa Aesar) contacts were defined by a shadow mask and deposited at a rate of ca.12 Å/sec to a total thickness of ca. 750 Å. The overlap of the ITO stripe and Al contacts define the active device areas (ca. 4 mm² and 8 mm²). Single layer device testing was accomplished using a Keithley 2400 Sourcemeter controlled by Labview software. All device characterization measurements were made under ambient conditions. Devices were cycled from 0 to 10 V until the current–voltage (J–V) curves were reproducible within <5% (typically, 1 cycle). OLEDs were fabricated using a similar procedure to have 500 Å α-NPD, and 500 Å Alq₃ deposited successively at rates of 2 Å/sec for each organic layer, and 750 Å Al deposited at a deposition rate of 12 Å/sec to serve as the cathode material. In addition, OLEDs equipped with LiF/Al cathodes were prepared (ITO/500 Å α-NPD/500 Å Alq₃/5 Å LiF/500 Å Al). A Hewlett-Packard 4145B semiconductor parameter analyzer with a Newport 1835-C optical power meter and a Newport model 818-UV silicon photodetector was used to measure J–V and luminance-voltage (L–V) characteristics.

Results and Discussion

Monolayers of α-quarterthiophene-2-phosphonate (4TP) were prepared on indium tin oxide (ITO) using the T-BAG method (Figure 1);[21] the reaction between phosphonic acids and ITO is similar to that for SiO₂ [21,22] and TiO₂;[23] these surface oxides are all similar in surface hydroxyl group (OH) content.[24] XPS

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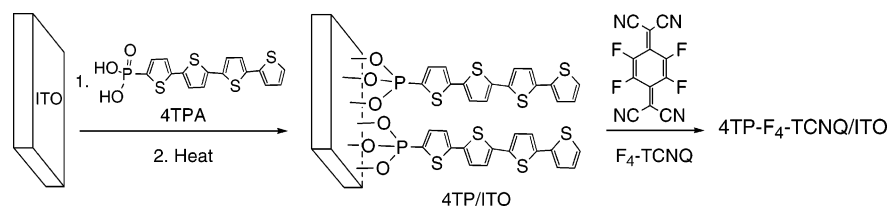
Figure 1. Preparation of 4TP−F$_4$−TCNQ/ITO.

analysis of the O(1s) region for nonchemisorbed 4TPA showed peaks at 534.7 eV (P=O) and 538.0 eV (P−OH).[25] Significantly, neither peak was present in the O(1s) region for surface-bonded 4TP/ITO, and a new peak, tentatively assigned to P−O−Sn/In, was found at 533.1 eV, in accordance with Figure 1.

T-BAG procedures effected on SiO$_2$/Si had been followed by QCM which, after correcting for surface roughness factor 1.21,[26] indicated surface molecular packing of 4TP to be 0.6 nmol/cm^2.[21] Similarly, the loading of 4TP on ITO was measured by QCM and, after correcting for surface roughness factor 1.45,[26] was also found to be 0.6 nmol/cm^2. These values correspond to a molecular footprint area of 25.1 Å^2/molecule, intermediate between those measured crystallographically for films of α-quarterthiophene deposited at high and low substrate temperatures (23.4−25.6 Å^2/molecule[27]), and demonstrate that the 4TP/ITO is molecularly dense.

A nearly 0° tilt angle was determined by AFM for the 4TP ML on the SiO$_2$/Si substrate; the 4T moieties are almost perpendicular to the surface.[21] This AFM determination was corroborated by X-ray reflectivity studies, which showed the 4TP ML to be 1.8 nm thick, with some microscopic disorder within the film;[21] similar packing is likely on ITO because molecular densities of 4TP on the two materials are the same. Density functional theory calculations[28] show that the extent of π−π overlap between neighboring 4T units is dramatically affected by their orientation, and 4T molecules have the highest amount of π−π overlap when the ring systems line up, as is apparently the case for 4TP MLs here. Fluorescence observed from a ML of 4TP/ITO appeared (by fluorescence microscopy) to cover the ITO evenly after rinsing, especially compared to multilayered films of 4TP, which suggests that the 4T units are not chemically altered by the T-BAG and heating steps (e.g., by incorporation of adventitious dopants).[29]

Doping an HTL can increase the hole injection efficiency in bilayer OLEDs;[18,19] doping the 4TP/ITO ML was accomplished simply by soaking in a solution of F$_4$−TCNQ in CH$_2$Cl$_2$ overnight followed by copious rinsing with CH$_2$Cl$_2$ with sonication (Figure 1). The fluorescence of the 4TP ML was completely quenched after its submersion in this solution. Charge-transfer complexes of 4T and TCNQ are known,[30,31]

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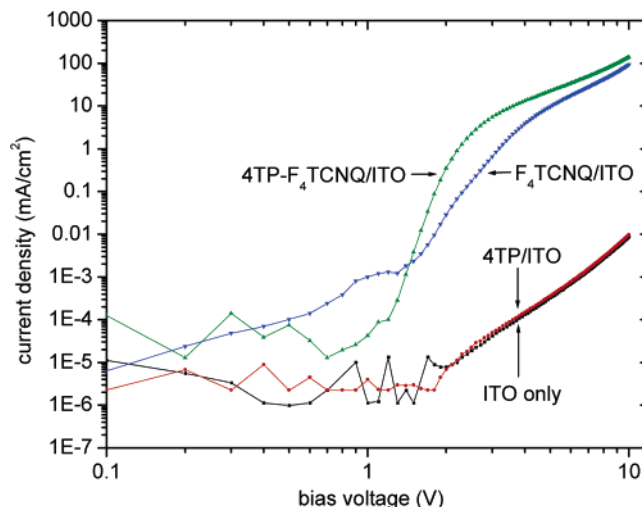(31) Brocks, G. *Phys. Rev. B* **1997**, *55*, 6816.

Figure 2. Effects of different surface treatments on current density. The type of ITO modification is indicated for each curve.

and the reaction between 4TP and F$_4$−TCNQ likely generates an analogous complex, which should not fluoresce. Calculations regarding such charge transfer[31] have been done for bulk systems, and density functional theory calculations done for the gas-phase F$_4$−TCNQ system[32] yield similar conclusions. Therefore, we are confident that charge transfer also occurs for our monolayer system.

Single layer devices were fabricated to test the effects of 4TP and 4TP−F$_4$−TCNQ MLs on hole injection. α-NPD and Al were used as the HTL and cathode, respectively; electron injection from Al into α-NPD is poor. The effects of different surface treatments on the current density are summarized in Figure 2. The change in the work function (Δϕ) for ITO on formation of the 4TP/ITO ML was determined using a Kelvin probe[12] which showed a small decrease (−0.28 ± 0.02 eV); using this anode a small change in current density (10 V, 9.8 μA/cm^2) versus unmodified ITO was measured (10 V, 8.4 μA/cm^2). However, doping the SAM of 4TP/ITO with F$_4$−TCNQ (followed by extensive rinsing and sonication in CH$_2$Cl$_2$ to remove excess F$_4$−TCNQ) resulted in an increase in the work function, Δϕ = 0.35 ± 0.05 eV vs unmodified ITO, and an increase in the current density that was quite dramatic (10 V, 142 mA/cm^2). In fact, this more than 10 000-fold increase in current density was even greater than that obtained (10 V, 95 mA/cm^2) by deposition of 15 monolayers of F$_4$−TCNQ on ITO (as measured by quartz crystal microgravimetry) from solution without subsequent rinsing, even after 10 "burn in" cycles of the F$_4$−TCNQ/ITO device.

The increase in current density measured in a simple diode when F$_4$−TCNQ is deposited onto clean ITO is likely due to a decrease in the hole injection barrier that occurs by doping of

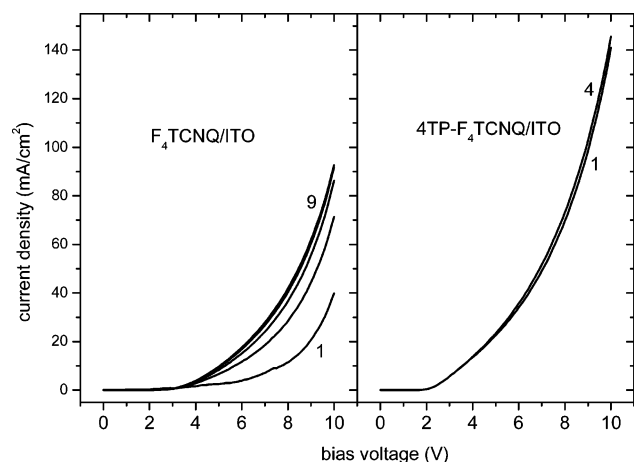(32) Koch, N.; Pascal Jr., R. A., unpublished results.

Figure 3. Diode burn-in characteristics with (a), F_4−TCNQ/ITO (b), 4TP−F_4−TCNQ/ITO anodes.

the subsequently deposited α-NPD by these adsorbed layers of F_4−TCNQ.[18] In contrast, the large increase in current density observed for the doped 4TP/ITO in the diode experiments described above is not likely due solely to doping of the α-NPD layer by any F_4−TCNQ that might desorb from the 4TP/ITO. Were such doping to be the case, then the effect on the current density of depositing several layers of F_4−TCNQ on ITO *without rinsing* would be expected to be greater than that measured from simply immersing the 4TP/ITO in a solution of F_4−TCNQ, but *with* extensive rinsing with sonication; indeed, the opposite effect was recorded. Another interesting observation relates to the different "burn-in" characteristics for devices prepared by the surface treatments described above. Devices made using clean ITO, 4TP/ITO (not shown) and 4TP−F_4−TCNQ/ITO all showed negligible changes in current density with each successive cycle from 0 to 10 V, but the F_4−TCNQ/ITO device showed a 4-fold increase in current density after about 10 cycles (Figure 3), i.e., the F_4−TCNQ/ITO device showed poor performance stability compared with the 4TP−F_4−TCNQ/ITO one.

We suggest that charge transfer between the ITO surface-bound 4TP and F_4−TCNQ leads to a new distribution of occupied and unoccupied molecular states compared with the HOMOs and LUMOs of the pristine partners.[18,31,32] This, in turn, pins the position of the newly occupied states closer to the ITO substrate Fermi level, leading to the observed increased work function. Electronic levels of subsequently deposited organics (the HTL components) are then aligned closer to the ITO Fermi level than they were in the absence of the doped monolayer, giving rise to a substantial reduction in the barrier to hole injection and, consequently, the measured increase in hole injection observed for devices comprising this F_4−TCNQ/ 4TP/ITO system.

Current density−voltage (J−V, Figure 4a) and luminance-voltage (L−V, Figure 4b) characteristics were determined for OLEDs fabricated with and without 4TP−F_4−TCNQ in which Alq$_3$ was the light emitter. Significantly, a 10 000-fold increase was measured for both current density and luminance of the 4TP−F_4−TCNQ/ITO OLED versus the one made with un-treated ITO.

Evidence that the 4TP−F_4−TCNQ-doped 4TP ML acts as a highly efficient anode treatment for increasing hole injection
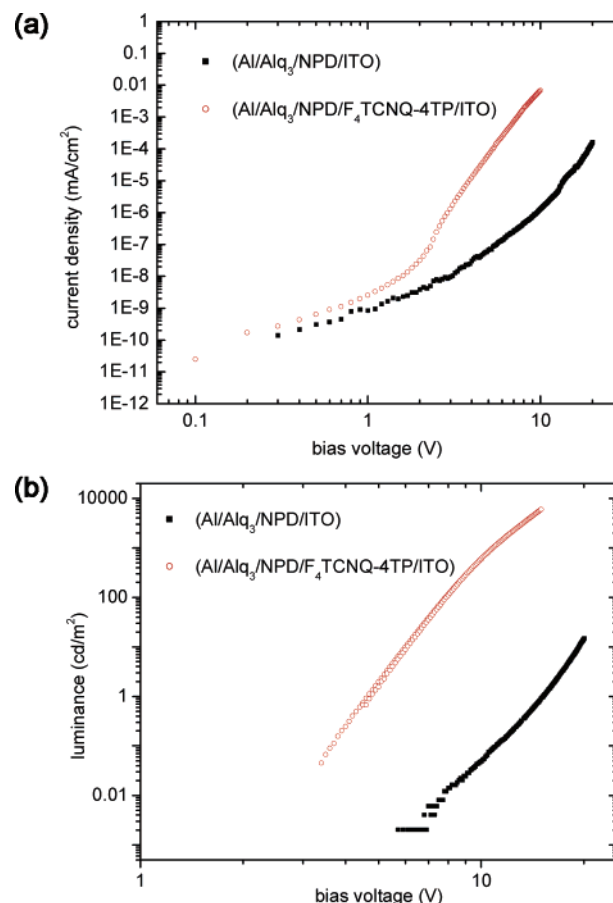

Figure 4. Current-voltage (a) and luminance-voltage (b) characteristics of OLEDs fabricated with blank ITO and F$_4$TCNQ-4TP modified ITO anodes, and Al cathodes.
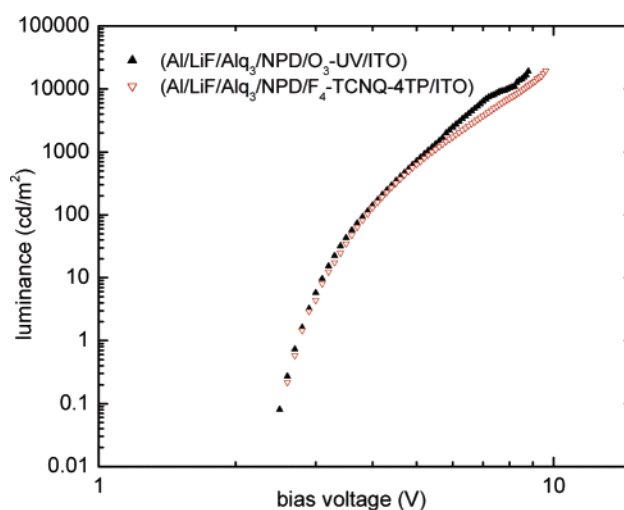

Figure 5. Comparison of luminance-voltage characteristics of OLEDs with UV−O$_3$ treated ITO and one fabricated with F4TCNQ-4TP modified ITO. Both with LiF/Al cathodes.

was further substantiated by its use in an OLED fabricated using state-of-the-art procedures. Here, the 4TP−F_4−TCNQ treatment step was compared with UV/O$_3$-treated ITO in OLEDs, which also used LiF/Al as the cathode material.[33] (Ozone treatment leads to an increase in the ITO work function by ∼ 0.5 eV.[34]) Remarkably, almost no difference between these devices was

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measured in either the J−V or L−V plots (Figure 5). It remains to be determined how the 4TP−F$_4$−TCNQ anode treatment compares with UV-ozone in terms of effects on long-term device stability.

Conclusions

A new methodology based on self-assembly has been developed for bonding organic monolayers to ITO. We have shown that a phosphonate monolayer can be bound to the surface of ITO and subsequently doped with an electron acceptor. This treatment apparently reduces the barrier to hole injection into the HTL, thereby increasing the carrier density transported across the doped ML-modified ITO/HTL interface (here, by 10 000-fold compared to the untreated ITO one) and consequently decreasing the operating voltage of the device. Indeed,

use of these MLs in OLEDs has now been shown to result in performance comparable to that of state-of-the-art devices.

Supporting Information Available: Supporting Information Available. QCM frequency change determination of 4TP surface loading on ITO. This material is available free of charge via the Internet at http://pubs.acs.org.

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