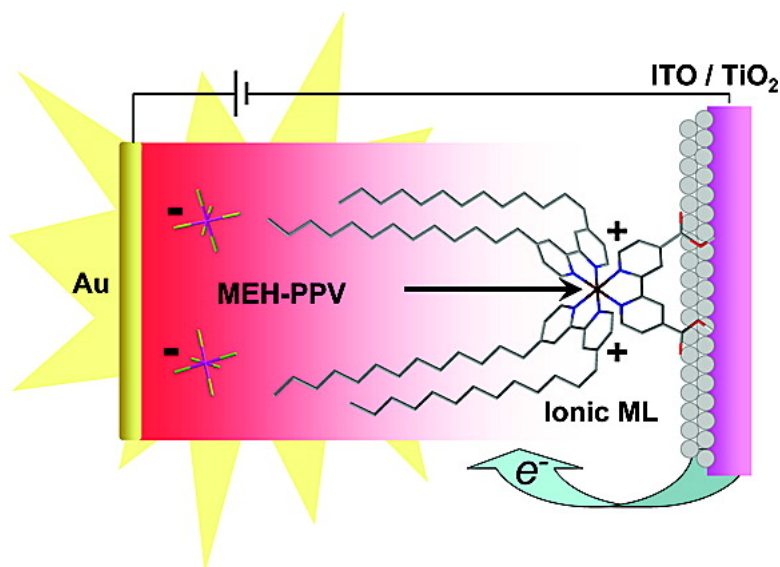# Langmuir

Letter

Molecular Ionic Junction for Enhanced Electronic Charge Transfer

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Molecular Ionic Junction for Enhanced Electronic Charge Transfer

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We present the first evidence of charge injection improvement in an organic electroluminescent device provided by a single ionic molecular layer. A hole-dominated, hybrid organic−inorganic light-emitting device is used as a probe to verify the effectiveness of the ionic compound monolayer on modifying the metal oxide cathode. The rearrangement of ions under an applied bias induces a strong field at the electrode−organic interface resulting in an enhancement of the electron injection into the organic semiconductor. A strong decrease in turn-on voltage for electroluminescence is observed for the device containing the ionic molecular monolayer.

Introduction

Electronic charge transfer between molecular materials to metals and semiconductors plays a large role in the overall efficiencies of a large number of devices, such as organic photovoltaic devices (OPVs) and organic light-emitting diodes (OLEDs).[1] Of particular importance for charge transfer from one material to the other is the difference in energy between the conduction and valence bands and the HOMO and LUMO of the molecular materials, respectively. Additionally, charge injection from conductors to semiconductors is governed by interfacial states that are located in between the conductor and the bulk of the semiconductor.[2] To enhance charge injection from the metal to the semiconductor materials, various strategies exist that mainly consist of decreasing the gap between the energy levels implicated. One approach involves the surface modification of the metal and or semiconductor by self-assembling molecules capable of forming a highly ordered, dense 2D layer with a dipole in the desired direction. Carboxylic acid,[3,4] phosphonic acid,[5] and silane derivatives[6] have been used to functionalize the ITO anode whereas noble metal cathodes have been widely modified with monolayers of thiol derivatives.[7] Charge injection has been shown to be improved by the dipoles at the (semi)conductor−organic interface. Another approach to increasing and controlling charge injection into organic electronic devices such as OLEDs and OPVs makes use of ionic species in the organic semiconductor to modify the work function of the electrodes. This has been demonstrated in light-emitting electrochemical cells (LECs)[8] but
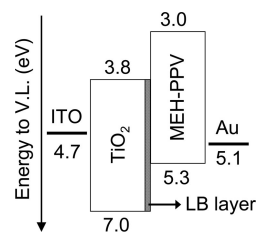

Figure 1. Scheme of the energy levels of the materials employed in the device.

also using conjugated polyelectrolytes.[9] The redistribution of ions under the applied bias creates an ionic space charge at the interface that assists and promotes the charge transfer from the organic to the semiconductor or metal and vice versa in OPVs and OLEDs, respectively. In these cases, multimolecular layers of the ionic compounds were employed. It is therefore of interest to verify if a monolayer of an ionically charged molecule is sufficient to change the electron-transfer properties between an electrode and a molecular semiconductor.

Transition-metal oxides are transparent semiconductors frequently used as electrodes in OLEDs and OPVs. Recently, some reports have appeared on the use of titanium oxide (TiO_2) and zinc oxide (ZnO) as the electron-injecting contact in a polymer light-emitting diode (PLED), demonstrating the possibility to prepare air-stable electroluminescent devices.[10−12] Nevertheless, the reported devices yield only high luminance when the difference between the conduction band of the metal oxide and the lowest unoccupied molecular orbital (LUMO) of the light-emitting polymer (LEP) is small. The conduction band edge for TiO_2 and ZnO lies at about −4 eV. Common LUMO energies for most light-emitting polymers range between −2.5 and −3 eV, resulting in a large energy mismatch with the conduction band of TiO_2 and ZnO. As a consequence, the metal oxide−LEP interface lends itself as an excellent probe to verify the

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effectiveness of the use of an ionic molecular monolayer on improving the charge injection.

To verify if a monolayer of an ionic molecule is able to modify the charge injection, we prepared a special ionic transition-metal complex capable of binding to metal oxide surfaces and containing aliphatic chains to facilitate monolayer deposition using the Langmuir−Blodgett technique (LB). The formation of the monolayer can be achieved by self-assembly; however, LB was used because it offers a level of control over the orientation and placement of the molecules that is not available with other techniques.[13,14] There are many examples of the use of this technique to prepare emissive,[15−18] hole-injecting,[19] and insulating layers[20,21] for OLED applications. However, most of these LB films are formed by neutral species.

The observation of electroluminescence in a hole-dominated hybrid metal oxide−organic light-emitting diode is a good way to prove the effect of a monolayer of a molecular ionic species on charge injection because electroluminescence is limited by electron injection.

In this letter, a hybrid organic−inorganic electroluminescent device based on nanofunctionalized titanium oxide, using the polymeric semiconductor poly[2-methoxy,5-(2′-ethyl-hexyloxy)-phenylene-vinylene] (MEH-PPV) as the light-emitting material, was prepared with and without a monolayer of an ionic transition-metal complex to verify the effect on electron injection. MEH-PPV was chosen because it is a well-studied polymer that has found applications in both light-emitting and photovoltaic devices.[22,23] We show that is possible to significantly improve the injection of electrons into the LUMO of the MEH-PPV by modifying the metal oxide cathode with a monolayer of an ionic transition-metal complex.

Experimental Section

TiO$_2$ layers were prepared by using spray pyrolysis following a method described previously.[24] Briefly, an ethanolic solution of diisopropoxy titanium bis(acetyl acetonate) was sprayed with nitrogen gas on hot ITO substrates that were subsequently annealed at 520 °C for 2 h. Then, a monolayer of the ruthenium charged complex was deposited onto the ITO substrate covered with TiO$_2$ by using the Langmuir−Blodgett technique.

A solution of the chloride salt of the N965 complex in CHCl$_3$ was used as a spreading solution. An appropriate amount of this solution was carefully spread onto a 10^{-3} M KPF$_6$ aqueous subphase, and the spreading solvent was allowed to evaporate for 10 min prior to compression. The monolayer was compressed up to a surface pressure of 27 mN m^{-1} for transfer. The compression isotherm is shown as complementary information. The LB film was assembled on the substrate by the vertical lifting method (i.e., immersion and withdrawal of the substrate through the interface covered with the charged complex monolayer). The dipping speed of the substrates
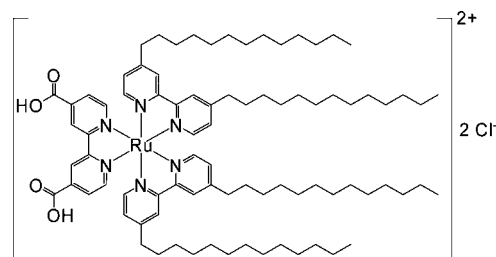
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Figure 2. Chemical structure of bis(4,4′-tridecyl-2,2′-bipyridine)-(4,4′-dicarboxy-2,2′-bipyridine) ruthenium(II)-bis(chloride) (N965).

was 1 cm min^{-1}, and one dipping cycle was performed. Because of the hydrophility of TiO$_2$, transfer took place only for the upstroke of the substrate with a transfer ratio close to unity. Therefore, one monolayer of the Ru complex was deposited. A KSV3000 trough was used to prepare these samples. The PF$_6^-$ anions of the aqueous subphase were adsorbed onto the Ru complex monolayer, replacing the Cl$^-$ anions of the Ru salt used to make the spreading solution. The presence of PF$_6^-$ on the LB film has been confirmed by IR spectra of multilayer films deposited onto a CaF$_2$ substrate (Figure S1).

Devices were prepared by spin coating a thin layer (50−100 nm) of MEH-PPV from a toluene solution on the TiO$_2$/ITO glass-covered substrates. Before spin coating, the solutions were filtered over a 0.20 μm PTFE filter. Afterward, the thin films were dried and transferred to a high-vacuum chamber integrated in an inert atmosphere (<0.1 ppm O$_2$ and H$_2$O) glovebox. Gold was thermally evaporated under a base pressure of 10^{-6} mbar and served as the anode contact and as an optical mirror to enhance the unidirectional illumination of the device. The layer thickness was determined using an Ambios XP1 profilometer. J−V characteristics were collected using either a Keithley 2400 source measurement unit or an AutoLab PGSTAT30 potentiostat. Electroluminescence was detected using a Si photodiode coupled to a Keithley 6485 picoamperometer. The photocurrent was calibrated using a Minolta LS100 luminance meter. Electroluminescent spectra were recorded using an Avantes fiber optics photospectrometer.

Results and Discussion

Bis(4,4′-tridecyl-2,2′-bipyridine)-(4,4′-dicarboxy-2,2′-bipyridine) ruthenium(II)-bis(chloride) (N965) was chosen because of its peculiar characteristics (Figure 2). First, it is a charged complex, and for this reason, it is suitable as a charge-injecting layer from the metal oxide to MEH-PPV. Second, it can form LB films thanks to its amphiphilic character and because the carboxylic groups can covalently bond to the TiO$_2$ surface.[25] Cl$^-$ has been replaced with PF$_6^-$ because larger ions have higher mobility as a result of diminished electrostatic interaction with the counterion.[26]

Proof of the presence of the molecular layer is given by the distinct contact angle of a water droplet on the bare TiO$_2$ and the monolayer-modified substrate (Supporting Information). Although TiO$_2$ is hydrophilic, after the deposition of N965 the surface becomes hydrophobic because of the long aliphatic chains. In contrast to what is usually observed for LB films, the monolayer of the N965 complex is strongly grafted onto the TiO$_2$ surface through its hydrophilic part (the bpy ligand functionalized with two carboxylate groups) whereas the hydrophobic part (the bpy ligand functionalized with long alkyl chains) is directed away from the substrate.

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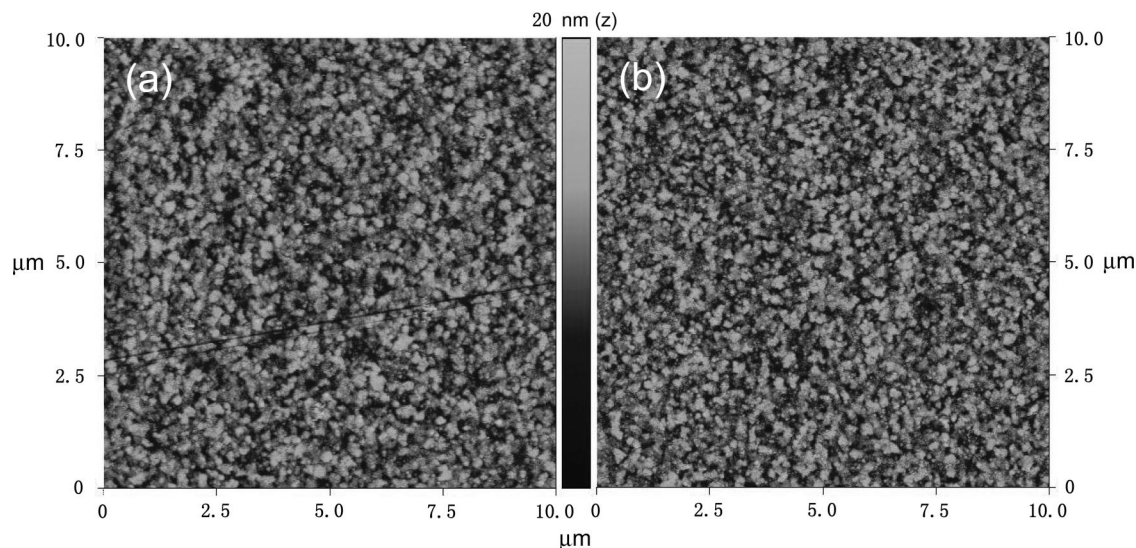(26) Rudmann, H.; Shimada, S.; Rubner, M. F. *J. Am. Chem. Soc.* **2002**, *124*, 4918.

Figure 3. AFM topographies of the TiO$_2$ surface (a) before and (b) after the deposition of 1 monolayer of N965 via the Langmuir−Blodgett technique.

The hydrophobic character of the monolayer-modified TiO$_2$ substrate does not disappear after exposure to large amounts of toluene. This indicates that the adsorption of the Ru complex monolayer onto the TiO$_2$-modified substrate is not due to weak intermolecular interactions (as for other LB films that are easily removed from the substrate after similar treatment) but it implies attachment to the surface via the formation of covalent ester bonds.[27]

Further evidence of the formation of a monomolecular layer of N965 on the TiO$_2$ substrate is obtained by atomic force microscopy (AFM) analysis. As a first indication, the morphology of the functionalized surfaces has been investigated. In Figure 3, AFM images acquired in tapping mode (a) before and (b) after the deposition of the monolayer are shown. The characteristic TiO$_2$/ITO morphology[12] is preserved after the deposition of the molecular monolayer, and both samples exhibit similar roughness (rms roughness = 2.5 nm and 2.8). In the case of inhomogeneous film growth (such as incomplete coverage or aggregate formation), the roughness would increase considerably, whereas for homogeneous coverage and because of the relatively small size (∼2 nm) of the deposited molecules the film roughness is mainly determined by the substrate morphology. Therefore, our results suggest the presence of a homogeneous monolayer of N965 molecules on the metal oxide substrate.

Besides being a powerful tool for acquiring images with molecular resolution, AFM allows the study of the adhesion forces between the tip and the sample.[28] For these measurements, the AFM is operated in contact mode. In Figure 4, cantilever deflection as a function of piezo z displacement is shown (a) in the case of a bare TiO$_2$ substrate and (b) in the case of the monomolecular N965/TiO$_2$ substrate. At a fixed lateral position, the tip is moved toward the sample (dashed line) until it comes into contact with the surface (point A). After reaching a preselected piezo displacement, the tip is retracted from the sample. Because of adhesion forces, contact is maintained until the repulsive elastic force of the cantilever overcomes the attractive van der Waals interaction between the sample and tip (point B) and the tip jumps off to the rest position (point C). The stronger the adhesion,
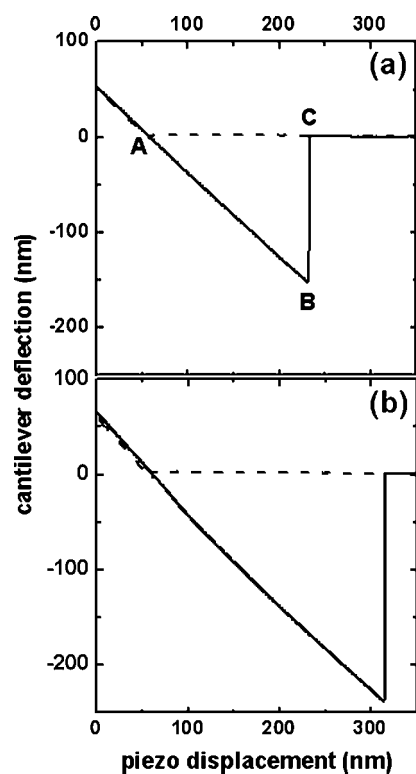

Figure 4. Cantilever deflection as a function of z-piezo displacement measured on (a) TiO$_2$ and (b) LB-N965/TiO$_2$ during the approach (---) and withdrawal (−) of the AFM tip.

the larger the difference in cantilever deflection between points A and B. Actually, for force measurements performed in an air atmosphere, most of the adhesion is due to the capillary force at the meniscus of water between the tip and the surface.[29] Despite this, a reproducible difference in the adhesion force was observed for measurements performed on the bare TiO$_2$ and on the substrate covered with a monolayer of N965. The adhesion is clearly stronger in the presence of the N965 monolayer than without it. This observation corroborates the results obtained with the contact angle of water and the morphological analysis.

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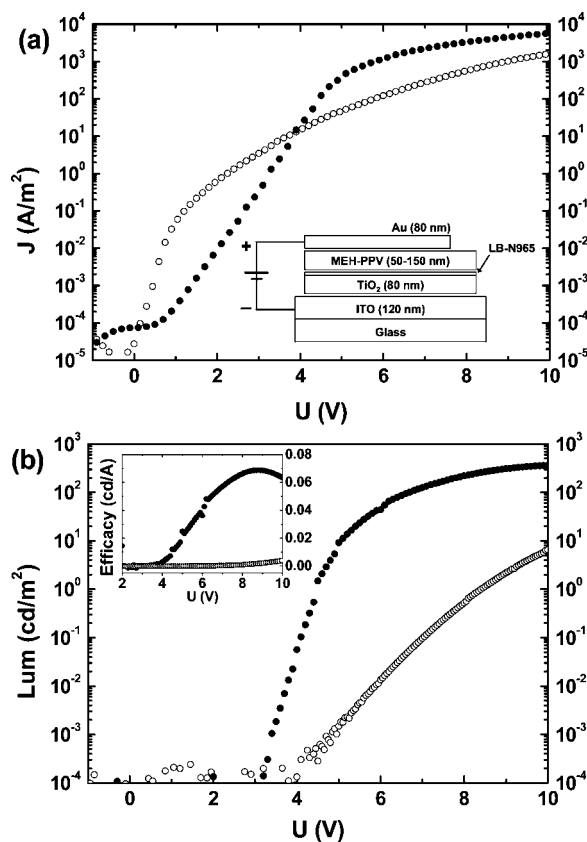(29) Salerno, M.; Bykov, I. *Microsci. Anal.* **2006**, *20*, S5.

Figure 5. (a) Current density and (b) luminance vs applied bias for an ITO/TiO$_2$/MEH-PPV/Au device (open symbols) and for an ITO/TiO$_2$/LB-N965/MEH-PPV/Au device (solid symbols). (a) The inset shows a schematic presentation of the device layout and the employed layer thicknesses. (b) The inset shows the efficacy versus applied bias of the devices without (open symbols) and with (solid symbols) the N965 monolayer-functionalized TiO$_2$.

Now that we have established that indeed it is possible to obtain a monolayer of N965 on a TiO$_2$ substrate, simple electroluminescent devices are prepared to evaluate the effect of the monolayer on electronic charge injection. The current density versus voltage for an ITO/TiO$_2$/MEH-PPV/Au and for an ITO/TiO$_2$/LB-N965/MEH-PPV/Au device is depicted in Figure 5a. The measurements were carried out with a negative bias at the ITO/TiO$_2$ electrode. In the device prepared without the LB monolayer, the current flowing through the device is likely to be mainly a hole current. This is deduced from similar devices based on light-emitting polymer poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) and because the barrier for hole injection is low ($\sim$0.2 eV), allowing for efficient hole injection into the polymer.[12]

In this device, electroluminescence is detected at approximately 4 V (Figure 5b). The current density flowing through this device at 4 V, however, is orders of magnitude larger, resulting in very poor current efficiency. The high current density indicates that TiO$_2$ is not acting as a good blocking layer for holes or that excitons are created close to the metal oxide interface, which induces their quenching. Even at voltages higher than 4 V, the light output of the device is small, reaching a brightness level of only 5 cd m^{-2} at 10 V. These observations are a clear indication of very poor electron injection.

The current density versus voltage characteristics of the device employing the nanofunctionalized metal oxide demonstrate that new processes are taking place. After the threshold voltage of 0.8 V is overcome, the current density increases rapidly to values
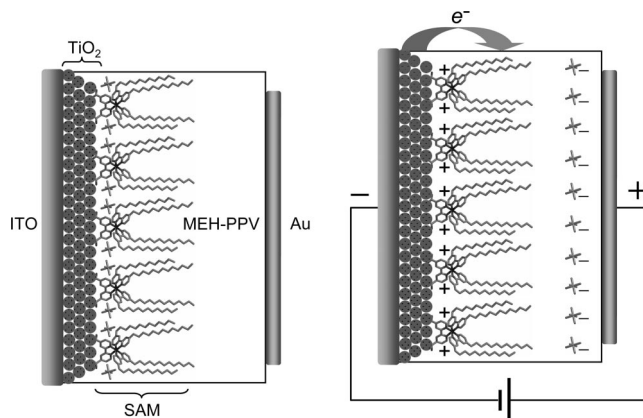

Figure 6. Schematic picture of the device with a monomolecular layer of ionic complex N965 and a representation of the displacements of the ions after the application of an electric field.

significantly higher than those observed for the device without the N965 monolayer. Electroluminescence starts at 3 V and rises rapidly before leveling off around 100 cd m^{-2} and reaches a maximum of 370 cd m^{-2} at 10 V. Electroluminescence is typical of the MEH-PPV with a maximum emission at 590 nm. This very strong increase indicates that the monolayer of N965 is indeed capable of enhancing electron injection over the TiO$_2$-MEH-PPV interface.

A simple model that explains the mechanism of electron injection is illustrated in Figure 6.

The N965 molecules are grafted onto TiO$_2$, and the hexafluorophosphate anions lie close to the metal oxide surface because of the electrostatic interaction with the cationic ruthenium complex. After a voltage is applied, the anions start to separate from the cationic complex and migrate in the direction of the gold anode, forming a charged double layer close to the surface of the TiO$_2$. This charged double layer, localized at the organic/metal oxide interface, creates a strong interfacial field that reduces the energy difference between the work function of TiO$_2$ and the LUMO of MEH-PPV and allows electrons to be injected more easily. The turn-on voltage for light emission is decreased by as much as 1 V, indicating a lowering of the injection barrier by as much as 1 eV.

A counter experiment was performed in which the TiO$_2$ substrate was modified by the small-molecular-weight dipole molecule 4-guanidinobutyric acid. In this case, no appreciable improvements in the current density and the luminance were observed. Hence, this confirms that the presence of the large mobile ions plays a crucial role in decreasing the electron injection barrier whereas a simple superficial dipole is not sufficient to improve the device performance. Additionally, a device in which a monolayer of the N965 complex with chloride anions was prepared did not show any improvement in device performance, in accordance with results published for LECs (Figure S4 in Supporting Information).[26]

Conclusions

We have shown that the barrier for charge injection can be reduced significantly by introducing a single molecular layer of ionically charged transition-metal complexes. The formation of the monolayer was obtained using the LB technique and was verified by differences in the contact angle of water droplets as well as by AFM morphological and indentation analysis. The results show that a molecular salt containing large ions is able to induce a strong interfacial field upon application of an external bias. This has important implications for optoelectronics devices

making use of electronically and ionically conducting molecular materials and opens the door to further improvement in these novel classes of devices.

Supporting Information Available: Experimental details, structural analysis, and supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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