A High Surface Area Organic Solar Cell Prepared by Electrochemical Deposition

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A new design of a high surface area solid state organic solar cell is presented. The solid cell consists of a PPEI/TiOPc junction deposited inside a nanoporous TiO$_2$ electrode, utilizing its high surface area (where PPEI=Perylenebis(phenethylimide) and TiOPc=Titanylphthalocyanine). The deposition of the organic semiconductors was performed by a new electrochemical deposition method, which is based on a simultaneous ionic dissolution and electrochemical re-neutralization of the organic materials. Although the overall conversion efficiency of the solid state cell is low, the analogous wet cell, TiO$_2$/PPEI/TiOPc electrode in contact with redox electrolyte mediator, shows a photoresponse throughout the PPEI spectrum. The efficiencies of the various processes of photocurrent generation were examined and the results suggest that all steps are efficient except the electron transfer from the PPEI to the TiO$_2$. This limitation is attributed to a thin dipole layer formed during the electrodeposition process, which alters the relative energetics at the PPEI/TiO$_2$ interface. [DOI: 10.1115/1.1755243]

Introduction

The use of organic semiconductors (OSC) such as perylenes and phthalocyanines in photovoltaic cells is motivated by the low cost, photochemical stability and high absorption coefficient of the OSCs. These solar cells offer the ability to tune optical parameters such as transparency and color of the cell by synthetic methods [1–3]. From an environmental point of view the organic solar cells have the advantage of low manufacturing energy consumption [4,5]. However, photovoltaic cells that are based on OSCs have shown low efficiency of solar energy conversion [6–12]. It is believed that part of the inefficiency results from the high resistivity of these materials to charge migration [13–16].

The process of photovoltaic energy conversion in organic solar cells can be divided into three steps; creation of a movable exciton in the OSC by light absorption, charge separation and charge collection at the two metal contacts. Usually charge separation occurs at the interface between the OSC and a hole (or electron) selective material that dissociates (quenches) excitons across the interface. To complete the circuit, the charges created at the OSC/quencher interface must be collected selectively at the metal contacts. In many cases an electron (or hole) selective material is placed between the OSC layer and the metal in order to improve the collection selectivity and avoid losses resulting from exciton quenching on the metal electrode [7,10]. Since the charge generated at the OSC/quencher interface has to travel across the OSC layer, the collection efficiency depends on the electrical resistivity of the OSCs. In other words, efficient charge separation requires long exciton diffusion length and high quality of the selective quencher/OSC interface [17–21], while efficient light conversion depends also on the electrical resistivity of the OSC layer.

One of the promising OSC-quencher combinations for solar cells is the PPEI (perylene bis(phenethylimide))–TiOPc (Titanyl phthalocyanine) system [7]. This cell consists of a transparent conducting oxide (TCO) electrode, a thin TiO$_2$ reflecting layer, polycrystalline PPEI, TiOPC quencher and a silver contact. Figure 1 presents a schematic energy diagram of the system including the bandgap energy and the relative potentials. The exciton diffusion length in the PPEI (a in Fig. 1) is larger than 1μm [21,22] and the quality of the hole-selective quencher/OSC interface with respect to the exciton quenching process (c in Fig. 1) is good [18,20]. The delicate match between the TiO$_2$ and the exciton energetics results in a reflection of the exciton towards the PPEI/TiOPc interface (b in Fig. 1). Simultaneously, the TiO$_2$ serves as a selective material to the dissociated electron, which has a more negative potential than the excited electron (e in Fig. 1). However, despite having a good quantum yield, these cells are limited to thin PPEI layers that will enable reasonable collection of the electrons separated at the PPEI/quencher interface (d in Fig. 1). Consequently the overall optical density and thus the conversion efficiency of the solar cell are low.

Recently, we reported on a new electrochemical method that enables the deposition of PPEI on high surface area nanoporous TiO$_2$ electrodes (roughness factor of 100–1000) [23,24]. Thus while maintaining a thin PPEI layer with good electron collection efficiency, the electrode exhibit a high optical density due to the large electrode area. The electrode was tested in a wet cell utilizing I$^-$/I$_3^-$ based electrolyte as a quencher. The photocurrent action spectrum of the cell resembled the absorption spectrum of PPEI, indicating photoresponse of the PPEI. However, the overall conversion efficiency of the cell was low due to the low selectivity of the electrolyte quencher, leading to significant charge recombination at the PPEI electrolyte interface [23].

The electrodeposition method and critical parameters, which affect the properties of the deposited material, are described elsewhere [24]. In brief, the deposition is based on the insolubility of PPEI in most solvents unless it is ionized. Thus, it is possible to electrochemically dissolve and deposit the PPEI by ionization and re-neutralization. In this work, the PPEI ions were produced by electrochemical reduction. Once the material dissolved from a source electrode, an insoluble PPEI layer was deposited on another electrode (the target electrode), by electrochemical re-neutralization. Since electrochemical deposition is not limited to flat electrodes, using this method enabled the fabrication of a molecular layer inside nanoporous TiO$_2$ electrodes.

The current study involves the fabrication of a solid quencher layer *inside* the nanoporous electrode, hence forming a high-surface-area solid-state organic solar cell. Both the PPEI and the organic quencher, TiOPc, were sequentially deposited on the TiO$_2$ by the electrochemical shuttle process described above. Contact to the TiOPc was achieved by evaporation of a thin Ag layer. Action
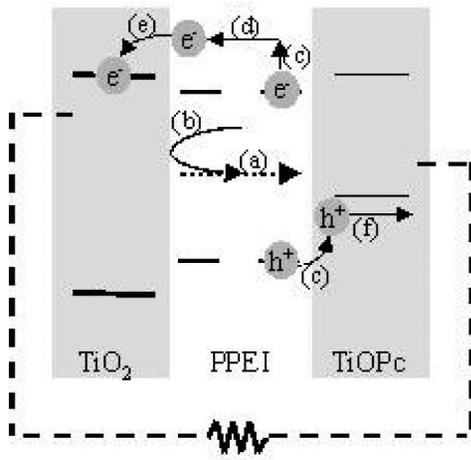
Fig. 1 Energetic diagram of organic solar cell operation. (*a*) exciton diffusion to the charge separating interface (*b*) reflection of the exciton from the TiO_2/PPEI interface (*c*) charge separation at the PPEI/TiOPc interface (*d*) electron collection through the PPEI (*e*) electron transport at the TiO_2/PPEI interface and (*f*) hole collection through the TiOPc.

Fig. 3 A schematic view of the high surface area, solid state organic solar cell. Both the PPEI and the TiOPc were deposited on the TiO_2 by the new electrochemical deposition method.

spectrum of the high surface area TiO_2/PPEI/TiOPc electrode in contact with redox electrolyte mediator (Fig. 2*a*) shows photoresponse throughout the PPEI spectrum (with some contribution of the TiO_2 electrode at the short wavelength region). However, the overall conversion efficiency of the solid state cell is low. In the remaining of this paper we analyze the efficiency-limiting factor of this cell and suggest methods to overcome this limitation.

Experimental

Electrode Preparation. TiO_2 and SnO_2 colloids were synthesized via hydrothermal method using procedures published elsewhere [25]. The conducting glass support (Hartford glass, 8 ohm/square F-doped SnO_2, FTO) was washed with water and soap, soaked for 10 minutes in HF solution (1:40 mixture of HF:H_2O), washed again with deionized water, and finally dried in a nitrogen stream. The colloids suspension was spread on the glass support with a glass rod using adhesive tapes as spacers. The films were sintered at 450°C for 30 minutes in air. The TiO_2 and SnO_2 films had a thickness of 3 μm measured with a profilometer (Mitutoyo, Surftest SV 500) and particles size of 23 and 18 nm, respectively.
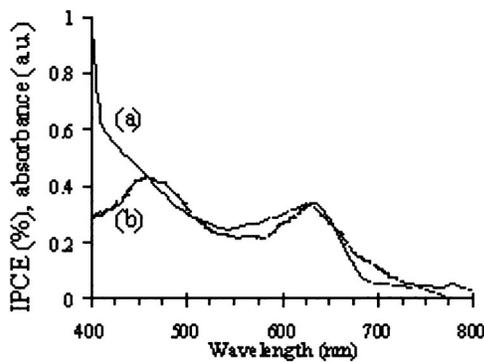

Fig. 2 (*a*) Action spectrum of the high-surface-area TiO_2/PPEI/TiOPc electrode in contact with a redox electrolyte mediator (I^-/I_3^-) and (*b*) the absorption spectrum of the electrochemically deposited PPEI, which indicates the formation of a polycrystalline layer. The light harvesting and energy photogeneration of these cells extends throughout most of the visible spectrum.
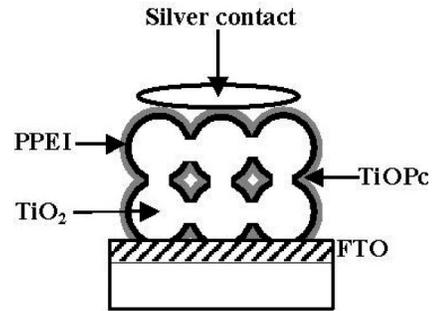
Perylenebis(phenethylimide), PPEI, and titanylphthalocyanine, TiOPc, were purchased from SynTec and used as received. The electrochemical deposition was preformed in a four electrodes cell consisting of: Pt wire as counter electrode, Ag/AgNO$_3$ as a reference electrode and two working electrodes. One working electrode consisted of OSC spread on FTO. The OSC, desorbed by reduction from this electrode, was deposited on the nanoporous working electrode. The deposition was done in a dry nitrogen glove box ($<$1 ppm H_2O and O_2) using a dry electrolyte solution of 0.4 M (TBA)ClO$_4$ (tetra-n-butylammonium perchlorate) in acetonitrile.

Measurements. Fluorescence measurements were conducted using an SLM Aminco Series 2 spectrofluorometer. The excitation wavelength was 460 nm. Emission was not corrected to the wavelength dependant detector response. Absorption spectra were measured by an HP 8453 spectrophotometer.

The measurements of wet solar cells were carried out in a standard two-electrode cell in which Pt coated conducting glass was used as the counter electrode with an electrolyte solution of 0.5 M LiI/0.05 M I_2 in 1:1 acetonitrile-NMO (3-methyl-2-oxazolidinone).

The back contact of the dry cell was fabricated by evaporation of 1 mm^2 silver dots on the phthalocyanine side of the electrode.

Photocurrent-photovoltage dependence was measured under illumination of a 250 W Xe lamp calibrated to 1 sun intensity in the visible region. For the IPCE measurements, a monochromator (ScienceTech) and a 420 nm long pass filter were coupled with the Xe lamp.

An Eco Chemie Autolab 20 potentiostat was used for the electrodeposition and the solar cell measurements.

Results and Discussion. Figure 3 presents a schematic view of the high-surface-area solid-state organic solar cell. The cell consists of a nanoporous TiO_2 electrode coated with two OSC layers: first the PPEI and than the TiOPc. Both organic layers are deposited by the electrochemical method described above except for the specific deposition parameters that relate to the reduction potentials of the two materials.

Figures 4*a* and 4*b* present the current-voltage curves of the two depositions; first the PPEI (a) and on top, the TiOPc (b). The material dissolution from the source electrodes is done by cyclic voltammetry in order to allow fine control of the four-electrode system. The anodic depositions on the target electrodes are done under constant potential. The delay between the deposition and dissolution onsets depends on the distance between the source and target electrodes. During the reverse scan of the source electrode, a significant fraction of the ions that did not reach the target electrode are re-deposited on the source one. This allows for the utilization of each source electrode for several successive depositions.

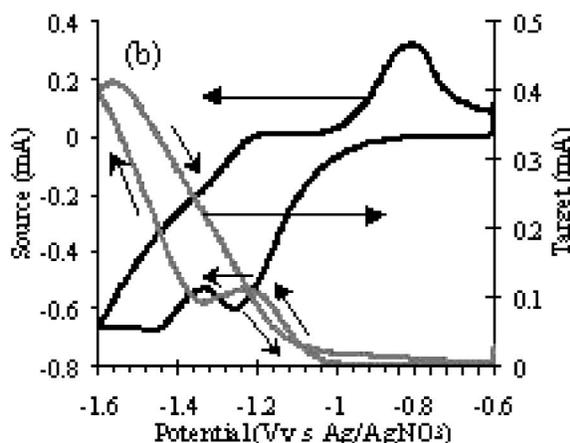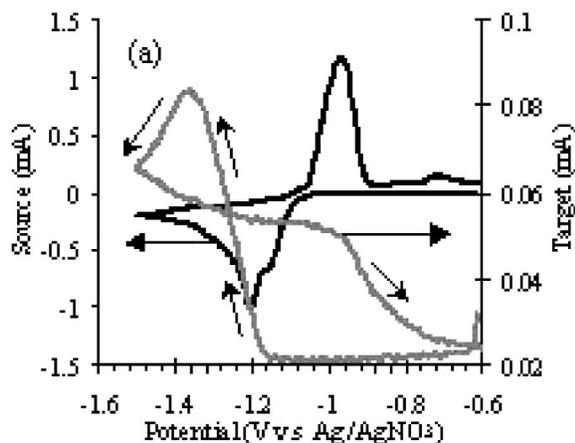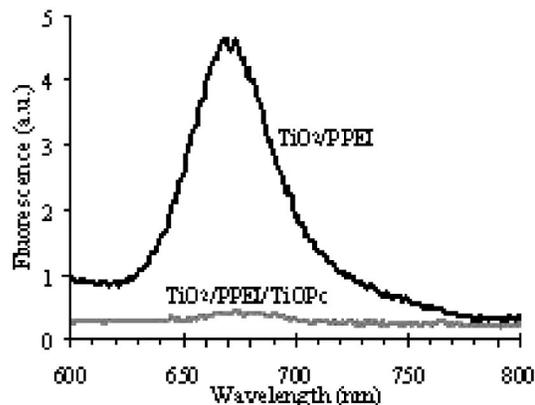The absorption spectrum of the electrochemically deposited

Fig. 5 Fluorescence spectra of the deposited PPEI measured from the glass support side. The PPEI fluorescence is quenched almost to background level in the presence of the TiOPc, indicating efficient exciton dissociation in the solar cell.

cence was measured from the glass support side; i.e., opposite to the electrochemical deposition direction. Figure 5 shows that the PPEI fluorescence is quenched almost to a background level in the presence of TiOPc, indicating efficient dissociation of the excitons. Furthermore, this result indicates deep penetration of the TiOPc throughout the PPEI coated nanoporous TiO_2 film. In other words, the charge separation process at the PPEI/quencher interface is not the limiting process in this solar cell.

In a more general view, we note that the high quality of the PPEI/TiOPc interface in these electrodes should be attributed to the electrochemical deposition method. As shown previously [24], in the electrochemical process the PPEI crystals grow along the more conductive axis of the anisotropic PPEI [22], thus having a specific orientation with respect to the TiO_2 substrate. The TiOPc growth follows the same trend [28], thus, we expect an oriented crystal layer deposition on top of the PPEI layer. Therefore, we assume that the high quality quenching reflects orientation of the two molecular crystals with respect to each other and to the TiO_2 substrate.

The second process examined is the hole transport from the TiOPc to the back contact. This process was studied in the wet analogue of this solar cell, as shown in Fig. 6. This cell consists of the FTO/TiO_2/PPEI/TiOPc electrode with the addition of redox electrolyte mediator (I^-/I_3^- in acetonitrile) and a platinum counter electrode. The redox potential of the I^-/I_3^- couple is more negative than that of the TiOPc [5]. Thus, under operating conditions

Fig. 4 Typical electrodeposition of (a) PPEI and (b) TiOPc on the nanoporous TiO_2 electrode. The cathodic dissolution of the OSC during a potential scan is shown in black and the anodic deposition on the target electrode under constant potential is shown in gray. The two reduction peaks during the dissolution process are assigned to the formation of the radical anion and the dianion of the OSC.

PPEI is presented in Fig. 2b The spectrum indicates the formation of polycrystalline PPEI [18,20,26,27]. In comparison with the amorphous material, crystalline PPEI exhibits longer exciton diffusion length and higher charge carrier mobility [18–20] rendering it the preferred structure for solar cell applications. Furthermore, the PPEI absorbs light efficiently throughout most of the visible range, resulting in efficient harvesting of the solar radiation by this solar cell.

The high-surface-area organic solar cell exhibited photocurrent of 212 nA/cm^2 and low photovoltage of 140 mV. This performance is significantly lower than the performance of the wet cell that utilizes redox electrolyte as a quencher, although the electrolyte quencher acts as a recombination center [23]. The low performance of the solid cell may have resulted from one of the following processes: the charge separation at the PPEI/TiOPc interface (c in Fig. 1), charge collection through the TiOPc quencher (f in Fig. 1), electron transport across the PPEI layer (d in Fig. 1), or transfer of the electron to the TiO_2 support (e in Fig. 1). In the following discussion, we examine each process separately in order to resolve the performance limiting factor of the solid organic solar cell.

Figure 5 presents the fluorescence spectra of two halves of a nanoporous TiO_2 electrode coated with the PPEI layer, one of which was further coated with the TiOPc quencher. The fluores-
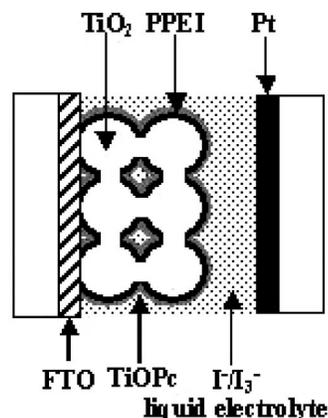

Fig. 6 Schematic representation of the wet solar cell analogous to the solid cell. This cell was employed to examine the hole transport from the TiOPc to the back contact.
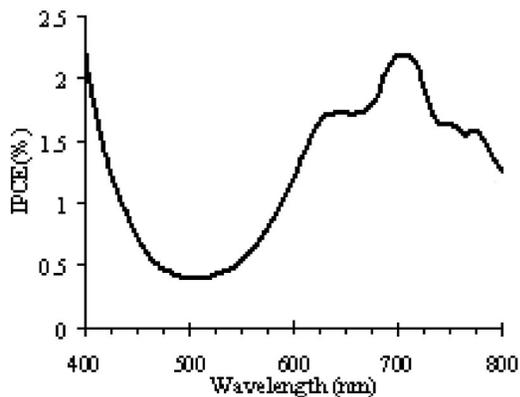
Fig. 7 IPCE spectrum of a wet cell containing a TiOPc coated nanoporous SnO$_2$ electrode in contact with I$^-$/I$_3^-$ redox electrolyte and a Pt counter electrode. The action spectrum resembles the absorbance spectrum of TiOPc, indicating its participation in the energy conversion process.

the electrolyte added to the cell transfer holes in the form of oxidized ions, from the TiOPc to the counter electrode. The efficiency of this mediation process with respect to the TiOPc/I$^-$/I$_3^-$ combination is presented in Figs. 8 and 9, utilizing a Pc sensitized solar cell. This cell consists of a nanoporous SnO$_2$ electrode coated with a TiOPc layer, the I$^-$/I$_3^-$ based redox electrolyte and a counter electrode. Under illumination, the TiOPc layer injects electrons into the SnO$_2$ followed by hole transport to the electrolyte. The electrons are collected via the SnO$_2$ network while the holes in the form of oxidized ions diffuse to the counter electrode. This process is evident in the photocurrent action spectrum presented in Fig. 7, which resembles the TiOPc absorption spectrum. Figure 8 presents the i-V curve of the TiOPc sensitized solar cell, showing generation of 1.23 mA/cm^2 short circuit photocurrent. If the hole transport in the TiOPc layer is the limiting process, one would expects a significant improvement in the performance of the solid-state high-surface-area organic solar cell upon electrolyte addition. However, this is not the case. The addition of the I$^-$/I$_3^-$ based electrolyte increased the photocurrent by less than 24 μA/cm^2, showing that the limiting step in this cell is related to another process.

The third possible limitation relates to the electron transport across the PPEI layer following charge separation. In this case, one expects that the high surface area of the PPEI/TiOPc interface will accelerate the recombination processes. To examine this pos-
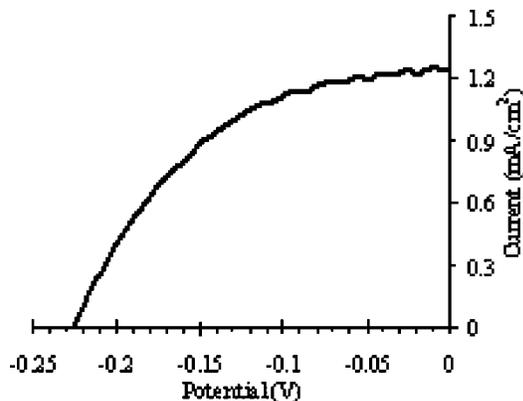
sibility, a flat multilayer analogue of the high-surface-area cell was fabricated. The cell consisted of a thin TiO$_2$ electrode successively coated with thin layers of PPEI, TiOPc and a silver contact. The two organic layers were coated by the electrochemical method, thus filling the TiO$_2$ pores to some extent. However, due to the thickness of the TiO$_2$ layer, the surface area and pore volume of the electrode was more than an order of magnitude lower than in the case of the high-surface-area cell. The semi-flat configuration resembles the bilayer organic solar cell reported by Gregg et al.,[7] where the organic materials were evaporated onto the TiO$_2$ substrate. This solar cell generated short circuit photocurrent of 1.47 mA/cm^2, open circuit photovoltage of 447 mV and a fill factor of 32.7%. In contrast, the efficiency of the semi-flat cell produced by the electrochemical deposition method was more than an order of magnitude lower, mainly due to the low photocurrent value. Thus, the low performance of the cell fabricated by the electrochemical method cannot be attributed to large surface area effects.

The results presented above show that the electrochemically prepared solar cell exhibited efficient light harvesting by the PPEI and efficient exciton dissociation at the PPEI/TiOPc interface. The performance of the solar cell is not limited by the positive charge collection via the TiOPc or by massive recombination along the large surface area system. Thus, by elimination, we attribute the inefficient operation of the cell to the PPEI/TiO$_2$ interface that seems to block the transport of the photo-generated electron.

As mentioned above, a delicate energetic tuning is required at the TiO$_2$/PPEI interface. The TiO$_2$ should reflect the exciton (TiO$_2$ conduction band negative of the excited state energy of the PPEI) while allowing the separated electron to enter the TiO$_2$ (TiO$_2$ conduction band positive of the PPEI/PPEI$^-$ redox potential). Comparing the performance of the electrochemically fabricated cell with previous reports seems to indicate that this energetic mismatch is induced by the electrochemical deposition. In the basic study of the electrochemical deposition [23,24], we showed that the crystal growth follows a passivation of the electrode by a thin PPEI layer that controls the crystal concentration, shape and size [24]. This compact layer does not exist in the electrodes fabricated by evaporation of the OSCs. It is possible that the passivation layer acts as an energy barrier between the crystal and the TiO$_2$. The large over potential applied during the deposition can overcome this barrier. However in the case of operating solar cell such a barrier can block the photogenerated electron transfer to the TiO$_2$. Another possibility relates to the coverage fraction of the electrochemically deposited PPEI. In the electrodes fabricated by the evaporation and annealing method, the contact area between the PPEI and the TiO$_2$ is very small due to the amorphous to crystalline transformation [21]. In contrast, the electrochemically deposited PPEI crystals that grow on top of the passivating layer cover a large fraction of the TiO$_2$ area. Such interfaces can alter the energetics of the contacting materials due to dipole induced effects that scale linearly with the contact area [29–31]. In the discussion above, we mentioned the crystallographic orientation induced by the electrochemical deposition of the polycrystalline PPEI layer. This orientation should also be considered in the context of the surface dipole effect.

While trying to resolve the exact mechanism for the electron transport blocking at the TiO$_2$/PPEI interface, we plan to examine alternative perylene derivatives that may match the TiO$_2$ energetics better. We note however, that improved matching will depend on the perylene energetics as electrochemically deposited crystals. That is, measurements of the perylene crystals provide only an energy window but not the exact values at their contact with the TiO$_2$.

Conclusions

The fabrication and testing of a solid state, high surface area organic solar cell were described. The cell consists of a PPEI/

Fig. 8 i-V curve of the cell presented in Figure 7 (TiOPc coated nanoporous SnO$_2$ electrode in contact with I$^-$/I$_3^-$ redox electrolyte and a Pt counter electrode).

TiOPc junction and TiO$_2$ as the electron selective contact. The cell performance is lower than the flat bilayer analogue of the cell.

Eliminating several possibilities, the low cell performance is attributed to the TiO$_2$/PPEI interface that seems to block the transport of the photogenerated electrons. The blocking is attributed to an energy barrier at the TiO$_2$/PPEI interface, induced by the electrochemical deposition of the PPEI. One of the general advantages of the organic semiconductors is the ability to change their properties moderately by synthetic methods. Thus, several perylene derivatives are currently considered in order to achieve better energetic matching at the TiO$_2$/organic semiconductor interface.

Acknowledgments

References

[1] Tamizhmani, G., Dodelet, J. P., Cote, R., and Gravel, D., 1991, Chem. Mater., **3**, pp. 1046–1053.
[2] Wrobel, D., and Boguta, A., 2002, J. Photochem. Photobiol., A, **150**, pp. 67–76.
[3] Yanagi, H., Tamura, N., Taira, S., Furuta, H., Douko, S., Schnurpfeil, G., and Wohrle, D., 1995, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A, **267**, pp. 435.
[4] Muneer, T., Asif, M., and Kubie, J., 2003, Energy Convers. Manage., **44**, pp. 35.
[5] Wohrle, D., and Meissner, D., 1991, Adv. Mater. (Weinheim, Ger.), **3**, pp. 129–138.
[6] Gregg, B. A., 1995, Appl. Phys. Lett., **67**, pp. 1271.
[7] Gregg, B. A., 1996, Chem. Phys. Lett., **258**, pp. 376.
[8] Breeze, A. J., Salomon, A., Ginley, D. S., Gregg, B. A., Tillmann, H., and Horhold, H. H., 2002, Appl. Phys. Lett., **81**, pp. 3085.
[9] Shaheen, S. E., Brabec, C. J., Sariciftci, N. S., Padinger, F., Fromherz, T., and Hummelen, J. C., 2001, Appl. Phys. Lett., **78**, pp. 841–843.
[10] Thelakkat, M., Schmitz, C., and Schmidt, H. W., 2002, Adv. Mater. (Weinheim, Ger.), **14**, pp. 577.
[11] Rostalski, J., and Meissner, D., 2000, Solar Energ. Mater. Solar Cells, **63**, pp. 37.
[12] Tsuzuki, T., Shirota, Y., Rostalski, J., and Meissner, D., 2000, Solar Energ. Mater. Solar Cells, **61**, pp. 1.
[13] Yuan, Y., Gregg, B. A., and Lawrence, M. F., 2000, J. Mater. Res., **15**, pp. 2494.
[14] van de Craats, A. M., Warman, J. M., Schlichting, P., Rohr, U., Geerts, Y., and Mullen, K., 1999, Synth. Met., **102**, pp. 1550.
[15] Horowitz, G., Kouki, F., Spearman, P., Fichou, D., Nogues, C., Pan, X., and Garnier, F., 1996, Adv. Mater. (Weinheim, Ger.), **8**, pp. 242.
[16] Forrest, S. R., Leu, L. Y., So, F. F., and Yoon, W. Y., 1989, J. Appl. Phys., **66**, pp. 5908.
[17] Forrest, S. R., 1997, Chem. Rev. (Washington, D.C.), **97**, pp. 1793.
[18] Gregg, B. A., 1996, J. Phys. Chem. B, **100**, pp. 852.
[19] Adams, D. M., Kerimo, J., Olson, E. J. C., Zaban, A., Gregg, B. A., and Barbara, P. F., 1997, J. Am. Chem. Soc., **119**, pp. 10608–10619.
[20] Conboy, J. C., Olson, E. J. C., Adams, D. M., Kerimo, J., Zaban, A., Gregg, B. A., and Barbara, P. F., 1998, J. Phys. Chem. B, **102**, pp. 4516–4525.
[21] Gregg, B. A., Sprague, J., and Peterson, M. W., 1997, J. Phys. Chem. B, **101**, pp. 5362–5369.
[22] Landau, A., Diamant, Y., Melamed, O., and Zaban, A., J. Phys. Chem. B, in press.
[23] Zaban, A., and Diamant, Y., 2000, J. Phys. Chem. B, **104**, pp. 10043–10046.
[24] Diamant, Y., and Zaban, A., 2001, J. Electrochem. Soc., **148**, pp. C709–C714.
[25] Zaban, A., Aruna, S. T., Gregg, B. A., and Mastai, Y., 2000, J. Phys. Chem. B, **104**, pp. 4130.
[26] Gregg, B. A., and Cormier, R. A., 1998, J. Phys. Chem. B, **102**, pp. 9952.
[27] Lu, W., Gao, J. P., Wang, Z. Y., Qi, Y., Sacripante, G. G., Duff, J. D., and Sundararajan, P. R., 1999, Macromolecules, **32**, pp. 8880.
[28] Diamant, Y., and Zaban, A., *Unpublished results*.
[29] Zaban, A., Chen, S. G., Sukenik, C. N., and Pizem, H., 2001, "Molecular Modification of the Electronic Properties of Nanoporous TiO2 Electrodes," J. Am. Chem. Soc., Chicago.
[30] Vilan, A., Shanzer, A., and Cahen, D., 2000, Nature (London), **404**, pp. 166.
[31] Kruger, J., Bach, U., and Gratzel, M., 2000, Adv. Mater. (Weinheim, Ger.), **12**, pp. 447.