

# Photo-induced electron transfer from a dithieno thiophene-based polymer to TiO<sub>2</sub>

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## Abstract

A spectroscopical study of composites made with a new conjugated polymer, polydithienothiophene, and nanocrystalline TiO<sub>2</sub> is carried out by optical absorption, photoluminescence and steady state photo-induced absorption spectroscopy. Sintered nanoporous TiO<sub>2</sub> films have been stained by dipping the inorganic semiconductor films into dithienothiophene polymer solutions. The optical absorption spectra indicate that this polymer is well absorbed into nanoporous TiO<sub>2</sub> films, showing a remarkable interaction with the inorganic semiconductor as compared to other alkyl substituted thiophene based conjugated polymers. The photoluminescence quenching and the steady state photo-induced absorption spectra evidence that TiO<sub>2</sub> acts as an efficient electron acceptor toward the polymer in the excited state. These features indicate that this conjugated polymer is a promising material to develop new hybrid organic/inorganic photovoltaic cells. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Polydithienothiophenes; TiO<sub>2</sub>; Photo-induced charge transfer; Hybrid photovoltaic device

## 1. Introduction

Dye-sensitized nanoporous TiO<sub>2</sub> photoelectrochemical solar cells are considered a potential low-cost alternative to conventional inorganic semiconductor photovoltaic devices [1]. The photoelectrochemical cells consist of Ru-bipyridil-based dye molecules, absorbed to the surface of a nanoporous sintered film of TiO<sub>2</sub>, whose function is to absorb visible light and to inject electrons to the TiO<sub>2</sub> conduction band. This is combined with an iodide/triiodide redox couple in a liquid electrolyte to regenerate the photooxidized dye molecule. Photovoltaic energy conversion efficiency as high as 10–11%, at AM 1.5 standard solar spectrum, have been reported [2].

Although the dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells show excellent power conversion performances, their commercial applications are still limited due to stability problems like the evaporation of the electrolyte and the degradation of both the electrolyte and the

dye. For these reasons the research on nanoporous TiO<sub>2</sub> solar cells has been focussed in assembling all-solid devices. Various approaches have been reported in the literature to replace the liquid electrolyte, like a polymer gel electrolyte that conduct ions [3] or an organic hole transport material in which positive charges are transported by hopping process [4].

The advantageous concept of creating a large interface on a nanoscopic scale of donor and acceptor materials, which is the basic idea of dye sensitized nanoporous TiO<sub>2</sub>, has been also utilized in plastic photovoltaic cells based on a blend of a conjugated polymer with a fullerene derivative and a blend of two conjugated polymers with different electronic affinities [5–7]. Many conjugated polymers in their undoped semiconducting state are electron donors upon photoexcitation and they are known as good hole conductors, which can carry current densities of several mA/cm<sup>2</sup> [8]. Therefore, conjugated polymers may replace, in principle, the dye and the electrolyte, bringing together the function of sensitizer and hole transporter in a single material.

The capability of conjugated polymers to act as sensitizer of TiO<sub>2</sub>, for the visible light, have been

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demonstrated for polyphenylvinylenes (PPVs) and polythiophenes (PTs) by spectroscopical [9,10] and time resolved microwave photoconductivity measurements [11,12]. The photo-induced charge transfer from the conjugated polymer into  $\text{TiO}_2$  has been found to be comparable with the ultrafast ( $<100$  fs) charge transfer from conjugated polymers to fullerenes [13]. In a bilayer configuration, the quantum efficiency for the interfacial electron transfer from a soluble PPV to  $\text{TiO}_2$  was estimated to reach 60%, when the thickness of the polymer film is below the exciton diffusion length (approx. 20 nm) [12].

The photovoltaic response has been detected for hybrid devices containing PPV and its soluble derivative MEH-PPV [10,11,14] as well as for polythiophene based materials [15,16]. The idea of combining the excellent sensitization properties of Ru-based dyes with conjugated polymers, as hole transport materials have been also investigated. However, since now, the polymer based hybrid devices reported in the literature exhibit a poor efficiency, staying in any case below 0.2% at AM1.5 [10,14,15].

The major problem, which has to be solved in order to improve the performances of hybrid polymer/ $\text{TiO}_2$  devices, is the poor interaction and absorptive properties of conjugated polymers to nanoporous  $\text{TiO}_2$ .

In this paper we investigate, by means of optical absorption, photoluminescence and steady state photo-induced absorption spectroscopies, the absorptive properties as well as the capability to inject electrons to  $\text{TiO}_2$  upon photoexcitation of a new dithienothiophene copolymer. Some measurements done on different  $\text{TiO}_2$  hybrid materials, prepared, respectively, with other conjugated polymers and with a Ru-based dye molecule, have been added for discussion.

## 2. Experimental

Poly(Bis(3-decyl-2-thienyl)-dithieno[3,2-*b*:2',3'-*d*]thiophene-4,4-dioxide), herein PTOX, has been synthesized by chemical oxidative coupling using  $\text{FeCl}_3$ . The synthesis and characterization will be reported elsewhere [17]. The other conjugated polymer used in this study are: regioregular polyoctylthiophene (P3OT), regiorandom polybutylthiophene (P3BT) and poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene (MDMO-PPV). Cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)bis-tetrabutylammonium dye (Ru-dye) has been supplied by Solaronix.

Nanoporous  $\text{TiO}_2$  films have been prepared on glass substrates by doctor blading a paste from Solaronix (Ti. Nanoxide T, colloidal anatase particle size approx. 13 nm); the layers have been then sintered at  $450^\circ\text{C}$  for 30 min.

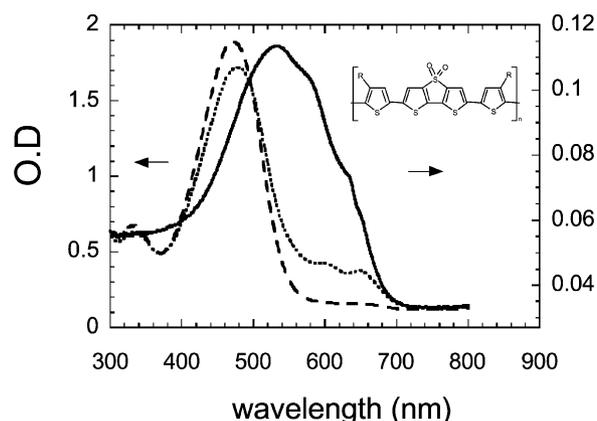


Fig. 1. UV-Vis absorption spectra of PTOX. Spin coated film (—); THF solution (0.2 mg/ml):  $20^\circ\text{C}$  (...),  $50^\circ\text{C}$  (---). The structure of the PTOX polymer is displayed.

The composites have been prepared by dipping the substrates into polymer solutions made with different solvents (0.2 mg/ml) for periods ranging from 5 h to 2 days, rinsing them in the solvent and then drying them under vacuum.

The spectroscopical measurements have been carried on stained  $\text{TiO}_2$  films and on KBr pellets where the films, removed from the glass substrates, have been dispersed. PTOX/ $\text{TiO}_2$  composites have been also prepared with Degussa P25  $\text{TiO}_2$  nanoparticles, by spin coating or drop casting on glass or KBr substrates, from solutions containing a weight fraction of the two components.

The absorption spectra have been measured with a Cary 2400 Varian spectrophotometer. Cw photoluminescence spectra have been obtained, in a back scattering configuration, with a flat field spectrograph equipped with a  $\text{N}_2$  cooled CCD detector and Argon laser lines excitations. The spectra were corrected for the instrumental spectral response and normalized to the absorbed photons.

The photo-induced absorption spectra have been measured with a FTIR spectrometer covering a spectral range from 0.05 to 1.85 eV. The fractional changes in transmission in response to a laser line incident on the sample for 10 s have been measured. The spectra have been corrected for the differences in optical density.

## 3. Results and discussion

The UV/Vis absorption spectra of PTOX are reported in Fig. 1. In solution the more twisted conformation of the polymer backbone leads to a reduction of the mean conjugation length with a subsequent blue shift of the spectrum. The weak features in correspondence to the film absorption suggest the coexistence of dissolved and aggregated chains. By increasing the temperature there

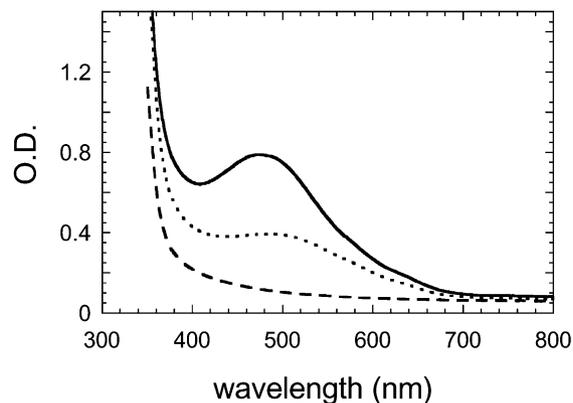


Fig. 2. UV-Vis absorption spectra of nanoporous  $\text{TiO}_2$  films dipped into PTOX THF solutions (0.2 mg/ml) for 12 h at 20°C (...) and for 48 h at 50°C (—). The spectrum of the  $\text{TiO}_2$  film is also displayed (---).

is a better solubilisation with a reduction of the aggregated phase.

Fig. 2 displays the absorption spectra of  $\text{TiO}_2$  nanoporous films dipped into PTOX tetrahydrofuran (THF) solutions. The polymer stained the  $\text{TiO}_2$  films but not the glass surface, indicating a much better interaction with  $\text{TiO}_2$  than with the glass substrate. In fact it can be seen that the staining increases with the dipping time and at higher temperatures, where the chains are well separated and penetrate into the pores more efficiently. For this reason we have tested the solubilisation properties of PTOX in several solvents, finding that anisole at 80–90°C is a better solvent for PTOX than THF at 50°C. Indeed the staining features in anisole solutions, displayed in Fig. 3, demonstrate that the good separation of the chains leads to a better penetration of PTOX into nanoporous  $\text{TiO}_2$ .

In order to get further hints about the potential use of this new conjugated polymer in hybrid devices, we have compared its staining features to other conjugated polymers (see Fig. 3). By dipping  $\text{TiO}_2$  films in P3BT solutions the staining was by far much weaker than with PTOX. For regioregular P3OT, the increased steric hindrance due to longer alkyl substituents and the stiffness of the conjugated chains prevents completely the diffusion of polythiophenes into the nanoporous matrix. One reason for the better absorptive properties of PTOX is that this polymer has a low molecular weight, being around 10 repeating units. This may facilitate the diffusion of the chains into the nanoporous matrix but it is not a sufficient argument to explain the good staining properties of PTOX. In fact we have found that the use of low molecular weight polyalkylthiophenes is not sufficient to induce the diffusion of the polymers into nanoporous  $\text{TiO}_2$ . Therefore, the main reason of the better staining properties of PTOX has to

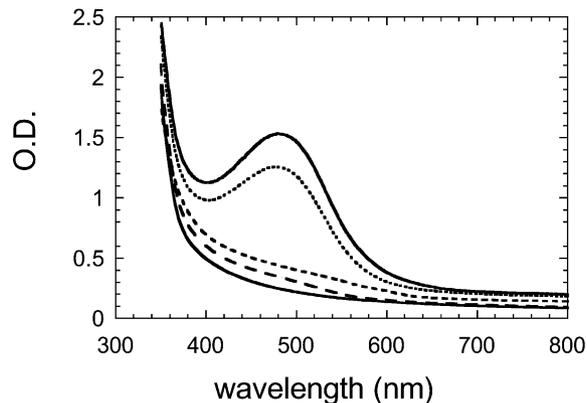


Fig. 3. UV-Vis absorption spectra of nanoporous  $\text{TiO}_2$  films dipped into solutions (0.2 mg/ml) of: (a) PTOX in anisole at 85°C for 5 h (...), for 18 h (—); (b) P3BT in THF, 48 h at 20°C (---); (c) MDMO-PPV in THF solution 48 h at 20°C (—). The spectrum of the  $\text{TiO}_2$  film is also displayed (—).

be ascribed to its chemical structure, which makes the interaction with  $\text{TiO}_2$  particularly favorable. PTOX copolymer contains a dithienothiophene moiety in the repeating unit that has two S–O bonds on the central thiophene ring. The macromolecule is very polar because of the presence of S,S-dioxide groups, and therefore its interaction with  $\text{TiO}_2$  is good. MDMO-PPV has two ethereal oxygens in the substituents which may favor the compatibility to  $\text{TiO}_2$ , however, it can be seen from Fig. 3 that also in this case the staining of the nanoporous matrix is by far less effective than with PTOX.

The visible light harvesting features of PTOX absorbed in nanoporous  $\text{TiO}_2$  are compared in Fig. 4 to a Ru-dye which is an excellent sensitizer in photoelectrochemical cells [2]. It can be seen that the capability for PTOX of absorbing photons in the visible spectrum is weaker but not too dissimilar to the Ru-dye.

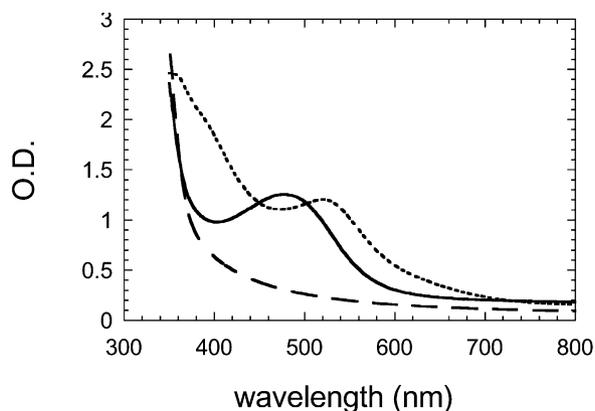


Fig. 4. UV-Vis absorption spectra of nanoporous  $\text{TiO}_2$  films dipped into: PTOX in anisole, 85°C for 5 h (—); Ru-dye in ethanol at 20°C for 5 h. The spectrum of the  $\text{TiO}_2$  film is also displayed (---). The concentration is 0.2 mg/ml.

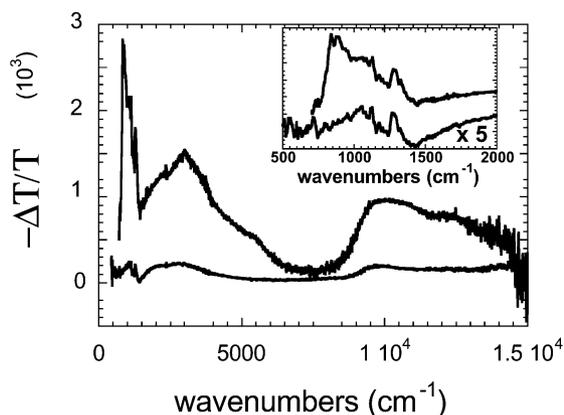


Fig. 5. Photo-induced absorption spectra of pristine PTOX film (lower intensity) and of a composite containing 1:1 weight fractions of PTOX and of P25 TiO<sub>2</sub>. Exc. wavelength: 514 nm, 80 mW/cm<sup>2</sup>; T: 78 K.

After demonstrating the remarkable compatibility of this conjugated polymer and TiO<sub>2</sub> and the possibility to use it to stain nanoporous TiO<sub>2</sub> films with good visible light harvesting, we have investigated, by spectroscopical means, the capability of PTOX to inject electrons, upon photoexcitation, into the TiO<sub>2</sub> conduction band.

The PTOX photoluminescence, (measured with the selective excitation of the conjugated polymer at 488 nm) is quenched by blending with TiO<sub>2</sub> nanocrystalline particles. We find that, giving a value of 1 to the PL of the pristine PTOX, the PL in the composites is reduced to 0.65, 0.60 and 0.5, respectively, at 5, 20 and 50% TiO<sub>2</sub> weight fractions. This is suggesting that electron transfer from PTOX to TiO<sub>2</sub> is occurring and that the charge transfer is fast enough to compete with the radiative recombination of PTOX excitons (typical time constants for the singlet exciton decay in conjugated polymers are in the range of some tenth of ns). Similar values of photoluminescence quenching have been reported for other conjugated polymer/semiconductor nanocrystal composites where photo-induced charge transfers have been demonstrated [18]. The photo-induced absorption (PA) measurements are also a useful tool to detect photo-induced charge transfer.

Fig. 5 shows the photo-induced absorption spectra of a PTOX pristine film and of a 1:1 PTOX/TiO<sub>2</sub> composite film. The pristine polymer exhibits two broad sub-gap transitions that may originate either from charged species or from neutral excitations and some vibrational modes, the IRAV bands, which are the spectroscopical signature of photogenerated charged species. In the composite material a significant enhancement of the PTOX photoactivity is observed, suggesting an increased efficiency of charge photogeneration due to a photo-induced charge transfer from the polymer to the TiO<sub>2</sub>. A broad absorption background in the mid-IR

region, which is monotonously increasing in intensity by decreasing the wavenumbers (the cut-off around 900 cm<sup>-1</sup> arises from the strong IR absorption of the TiO<sub>2</sub>) is also detected. This spectral feature is usually ascribed to free charge carrier transitions in semiconductors [19], and monitors the presence of electrons into the TiO<sub>2</sub> conduction band. In a sample of pure TiO<sub>2</sub>, the PA signal obtained with the same experimental conditions is too weak to be detectable. Therefore, the observed spectral features are ascribed to electrons injected into TiO<sub>2</sub> from the photoexcited polymer.

In conclusion, in this work we have shown by spectroscopical means that PTOX, like other conjugated polymers, injects electrons into the TiO<sub>2</sub> conduction band upon photoexcitation. The remarkable compatibility to TiO<sub>2</sub>, with respect to other conjugated polymers, makes this polymer a promising candidate for testing in hybrid organic/inorganic photovoltaic cells. This feature should allow to overcome the staining limitations (complete filling of the network, adhesion onto TiO<sub>2</sub>) recently pointed out for alkyl-substituted polythiophenes [15].

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