

State selective electron injection in non-aggregated titanium phthalocyanine sensitised nanocrystalline TiO₂ films†

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Received (in Cambridge, UK) 27th May 2004, Accepted 5th July 2004

First published as an Advance Article on the web 3rd August 2004

We describe a novel titanium phthalocyanine that shows no aggregation when anchored to nanocrystalline TiO₂ films through its axial carboxylated ligand without the use of co-adsorbents; state selective electron injection into the TiO₂ is demonstrated, resulting in efficient photocurrent generation in dye sensitised photoelectrochemical solar cells.

The dye sensitisation of wide-band gap nanocrystalline semiconductors is attracting renewed interest due to the development of efficient photoelectrochemical solar cells¹ based on ruthenium bipyridyl dyes. The efficiency of these devices is, however, significantly limited by the low optical absorbance of such dyes in the red/near infrared spectral regions. Hence, extensive research efforts are targeting new sensitizer dyes with stronger absorbance over this spectral region.

Phthalocyanines (Pc) are well known chromophores for their intense absorption in the UV/blue (Soret band) and the red/near IR (Q band) spectral regions, as well as for their electrochemical, photochemical and thermal stability. They are therefore attractive as sensitizer dyes for dye sensitised solar cells (DSSC's),² as well as other photovoltaic devices.³ However, the applications of Pc dyes in DSSC's to date have been limited due to problems associated with aggregation of the dye on the metal oxide surface. Moreover, phthalocyanines suitable for DSSC's typically have a poor solubility in organic solvents, and a strong tendency to aggregate on the film surface, resulting in rapid deactivation of the dye excited state and low sensitising efficiency. Several groups^{2,4} have studied the co-adsorption of small organic acids with the Pc sensitizer to minimise the aggregation process, resulting in a limited improvement in device performance.

Here we report the synthesis of a new titanium phthalocyanine (TiPc) and its application to the sensitisation of nanocrystalline, mesoporous TiO₂ films. The choice of Ti as a central metal allows axial ligation to the metal center, as reported previously,^{5,6} the axial ligand being employed to anchor the dye to the nanocrystalline particles and to prevent the aggregation of the macrocycles. On the other hand, the bulky peripheral *tert*-butyl substituents help to solubilise the dye in common organic solvents and to avoid dye aggregation. Using this axial ligation approach we are, moreover, able to control the distance between the HOMO orbital of the chromophore and the TiO₂ surface and thereby the electron injection and recombination dynamics.

Titanium(IV) tetra(*tert*-butyl)phthalocyanine (TiPc) was synthesised according to a literature procedure⁷ and characterised by ¹H NMR and UV-Vis spectroscopies, MALDI-TOF spectrometry and elemental analysis.

The compound TiPc showed electrochemical stability, with reversible dye oxidation being observed with a mid-point potential of 0.950 V vs. Ag/AgCl. The solution absorption spectrum showed

the expected intense Q-band absorption transition ($\lambda_{\text{max}} = 702 \text{ nm}$, $\epsilon = 135\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). ZINDO/1 semi-empirical calculations indicated that both the HOMO and LUMO orbitals are delocalised over the conjugated macrocycle, with only minimal contributions from either the central metal or axial ligand. Full synthetic details and characterisation of the compound are given in the supplementary information.

The dye showed strong adsorption to nanocrystalline TiO₂ electrodes, as illustrated from the TiPc/TiO₂ film spectrum shown in Fig. 1. From the magnitude of the TiPc/TiO₂ Q-band optical absorbance, we estimate a saturated dye loading of 31 nanomoles per cm² for the 4 mm TiO₂, consistent with monolayer surface coverage assuming a dye area of 290 Å².

The Q-band optical absorbance of the TiPc/TiO₂ film exhibits a small broadening relative to the solution spectrum, typical of most adsorbed sensitizer dyes, but no change in structure or peak position was observed, therefore, indicating minimal dye aggregation. The absence of significant dye aggregation is further supported by transient emission studies of the dye adsorbed to control nanocrystalline ZrO₂ films, as shown in Fig. 2. The high conduction band edge of ZrO₂ precludes electron injection from the dye excited state. The TiPc/ZrO₂ exhibits an intense, near monoexponential fluorescence decay ($\tau \sim 1.6 \text{ ns}$) indicative of negligible dye aggregation.

As illustrated in Fig. 2, strong quenching of the TiPc emission was observed for the TiPc/TiO₂ films assigned to electron injection from the excited state of the phthalocyanine into the conduction band of the TiO₂. The occurrence of efficient electron injection was further confirmed by transient absorption studies as shown in Fig. 3. Following excitation at 450 nm, a long-lived absorption transient is observed, assigned to the photoinduced absorption of the TiPc⁺/TiO₂(e⁻) state. This transient signal exhibits slow decay dynamics, assigned to interfacial charge recombination with a half lifetime of $\sim 0.01 \text{ s}$.

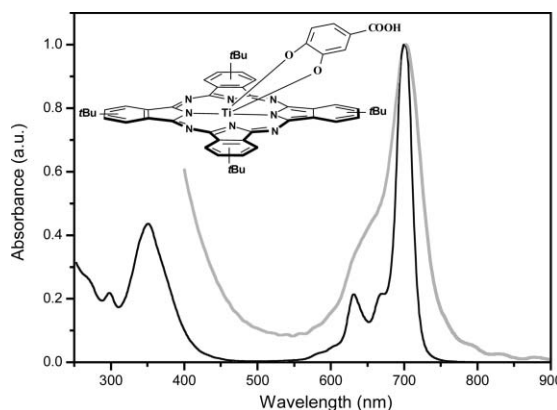


Fig. 1 Normalised absorption spectra of TiPc in dichloromethane (black) and adsorbed to a TiO₂ film (grey). The inset shows the dye structure.

† Electronic supplementary information (ESI) available: calculated LUMO and HOMO orbitals, excitation and emission spectra, cyclic voltammetry and experimental details. See <http://www.rsc.org/suppdata/cc/b4/b407860h/>

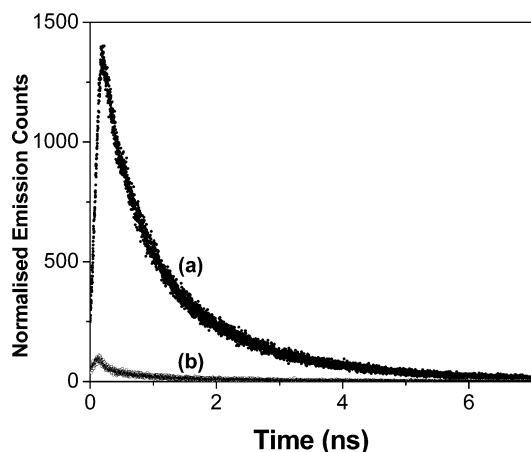


Fig. 2 Single photon counting fluorescence decays for (a) TiPc/ZrO₂ and (b) TiPc/TiO₂ films ($\lambda_{\text{exc}} = 405 \text{ nm}$, $\lambda_{\text{det}} = 750 \text{ nm}$). Data have been normalized to the number of photons absorbed, allowing quantitative comparison of both the signal decay dynamics and magnitudes.

The slow recombination dynamics we report here are consistent with the expected axial attachment of the sensitiser dye to the TiO₂, with the Pc macrocycle orientated parallel to the TiO₂ surface. ZINDO/1 calculations assuming this orientation yield a dye HOMO–TiO₂ separation of 12 Å. In a previous study of a series of ruthenium bipyridyl dyes, we have reported a strong correlation between the recombination dynamics and the spatial separation of the dye HOMO orbital from the TiO₂ surface.^{7,8} The 12 Å separation ($\sim 10 \text{ Å}$ to the carboxylate group), calculated here is in good agreement with the slow (0.01 s) recombination dynamics we observed here.

Remarkably, the magnitude of the TiPc⁺/TiO₂(e⁻) transient absorbance signal was strongly dependent upon excitation wavelength, with negligible signal amplitude for excitation wavelengths of $\geq 600 \text{ nm}$, as shown in Fig. 3. This observation is strongly indicative of state selective electron injection, with efficient charge separation following Soret band excitation but only negligible charge separation following Q-band excitation. Further support for this assignment comes from the incident photon-to-electron conversion efficiency spectra (IPCE) for the TiPc/TiO₂ films in complete ‘sandwich configuration’ DSSC’s, which shows efficient photocurrent generation in the UV/blue spectral region, but only very low red photocurrent generation as illustrated in Fig. 4. The

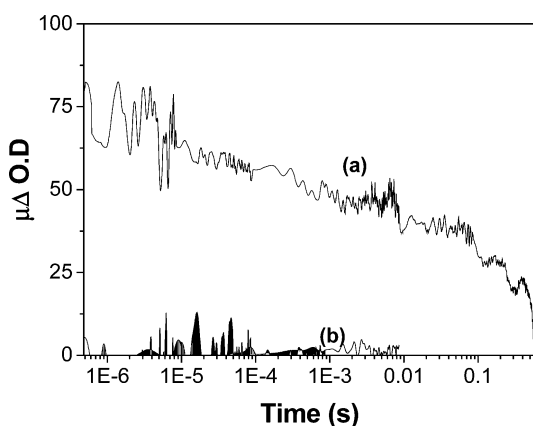


Fig. 3 Transient absorption data for TiPc/TiO₂ films after excitation at 450 nm (a) and 600 nm (b) ($\lambda_{\text{probe}} = 850 \text{ nm}$).

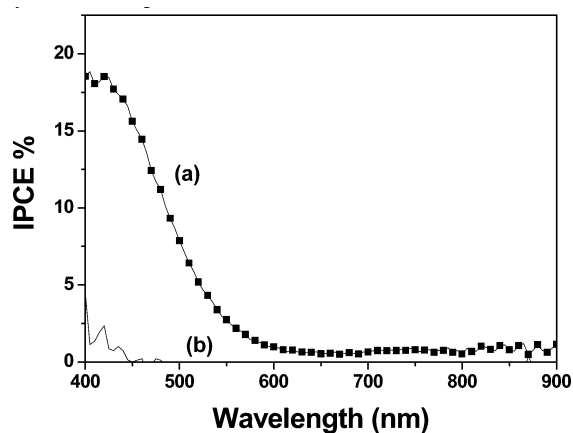


Fig. 4 IPCE spectra for 1 cm² transparent DSSC’s with (a) TiPc/TiO₂ photoelectrode and (b) control unsensitised TiO₂ films. The electrolyte composition was 0.1 LiI and 0.01 I₂ in propylene carbonate. TiO₂ film thicknesses of 4 μm.

overall device energy conversion efficiency under AM1.5 irradiation was 0.2 %.

The observation of state selective electron injection for the TiPc/TiO₂ is indicative of efficient kinetic competition between electron injection from the S₂ excited state of TiPc and internal conversion/vibrational relaxation of this state to the lower lying S₁ state of this dye. The absence of efficient electron injection from the S₁ state is consistent with the low $E(D^*/D^+)$ mid-point potential for this state ($\sim -0.8 \text{ V}$ versus Ag/AgCl—close to the TiO₂ conduction band edge) and the large dye LUMO–electrode surface separation determined from the semi-empirical calculations (see supplementary information†). Clearly, optimisation of the photovoltaic energy conversion of DSSC’s employing such dyes will require efficient electron injection from the S₁ state. Nevertheless we have shown for the first time the potential of TiPc’s for the sensitisation of nanocrystalline TiO₂ films. We have furthermore demonstrated that the combination of catechol axial attachment to the TiO₂ surface and *tert*-butyl peripheral groups allows efficient sensitisation with no dye aggregation and without the use of any co-absorbents. It can be concluded that such TiPc dyes represent an attractive route to the development of efficient, red absorbing sensitiser dyes for dye sensitised photoelectrochemical solar cells.

The authors are grateful to the EPSRC and to the EU (Marie Curie Fellowship Contract No. HPMF-CT-2002-01744 for EP) for their financial support. This work was supported by CICYT (Spain), Comunidad de Madrid (Spain) and the European Union through grants BQU2002-04697, 07N/0030/2002 and HPRN-CT-2000-00020, respectively.

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