



Photoinduced electron transfer from a terrylene dye to TiO₂: Quantification of band edge shift effects

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ARTICLE INFO

Article history:

Received 23 May 2008

Accepted 14 November 2008

Available online 3 December 2008

Keywords:

Dye-sensitized

Mesoporous

Solar cell

ABSTRACT

A terrylene chromophore exhibiting a high extinction coefficient has been developed as a sensitizer for photovoltaic applications. The photophysical and photochemical properties of the dye were analyzed both experimentally and theoretically. Terrylene-sensitized nanocrystalline TiO₂ solar cells yielded good photocurrents providing more than 60% in external quantum efficiency. The photoinduced electron transfer from the dye to TiO₂ was found to be very sensitive to conduction band edge shifts in TiO₂ induced, either by changes in the composition of the redox electrolyte or by UV-illumination. This sensitivity was observed in quantum efficiencies for photocurrent generation of terrylene-sensitized solar cells and in photoinduced absorption experiments. The conduction band shifts were quantified using charge extraction methods. The observed sensitivity of the injection efficiency suggests that photoinduced electron transfer occurs from the relaxed excited state, possibly due to poor electronic coupling between TMIMA excited states and TiO₂ conduction band states.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted a great deal of interest since the seminal papers of Grätzel and coworkers [1,2]. DSSCs have the potential for an efficient generation of electricity from solar energy at low costs [3,4]. The solvent-based electrolyte used in DSSC gives, however, problems with sealing and long-term stability. A lot of attention in recent years has therefore been given to replacement of the solvent-based electrolyte with ionic liquids or solid state hole conductors. These alternatives have in turn specific problems, such as slower mass transport and poor pore filling. These require adjustments to the nanostructured TiO₂ electrode, e.g. a decrease of the film thickness and an increase of the pore size. As this will lead to less internal area in the nanostructured TiO₂ electrode, dyes with higher extinction coefficients are needed to obtain good light harvesting. In this paper, we introduce a new organic chromophore from the photo-stable rylene dye family: a terrylenemonoimidmonoanhydride denoted TMIMA, with a much

stronger absorption compared to the conventional DSSC sensitizer N719 [Ru(4,4'-dicarboxylic acid-2,2'-bipyridine)₂ (NCS)₂].

The TMIMA dye is characterized spectroscopically and electrochemically and the relevant energy levels in the dye are compared to the acceptor levels in the TiO₂ conduction band (CB). TMIMA is further analyzed with quantum chemical calculations using density functional theory (DFT). In Section 2, we describe the experimental and theoretical methods used and in Section 3, the photophysical and photochemical properties of the dyes are determined and put in context regarding the internal and external quantum efficiencies for photocurrent generation in DSSCs. In particular, we quantify the steady state electron transfer with photoinduced absorption (PIA) spectroscopy for conditions with different effective surface charge at the TiO₂/dye interface, giving band edge shifts.

2. Experimental and theoretical methods

2.1. Materials

Nanocrystalline TiO₂ particles were prepared by hydrolysis of titanium tetraisopropoxide [5] and prepared into a screen printing paste with the addition of ethyl cellulose as binder in α -terpineol. TiO₂ (anatase) electrodes were prepared by screen printing the

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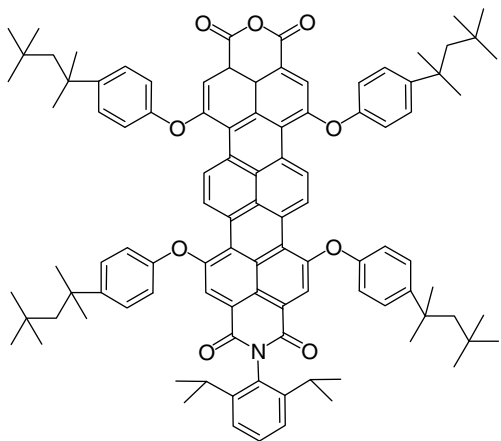


Fig. 1. The molecular structure of TMIMA.

resulting colloidal solution onto a conducting glass (Pilkington TEC15, fluorine-doped SnO_2 glass, sheet resistance: $15\Omega/\text{square}$).

TMIMA (terrylenemonoimidmonoanhydride, Fig. 1) is obtained via the saponification of *N,N'*-(2,6-Diisopropylphenyl)-1,6,9,13-tetra[4-(1,1,3,3-tetramethylbutyl)-phenoxy]terrylene-3,4,11,12-tetra carboxidiimide [6] with KOH in tert-butanol under reflux overnight [7]. The desired monoanhydride can be isolated in 30–40% yield with column chromatography using silica gel and toluene as eluent. Details on the dye synthesis and characterization can be found in the supporting information.

The screenprinted TiO_2 photoelectrodes were sintered at 450°C for 45 min and cooled down to $80\text{--}100^\circ\text{C}$ before immersing into a $200\ \mu\text{M}$ dye solution in dichloromethane (DCM) or *N*-methyl-pyrrolidinone (NMP). The TiO_2 films were sensitized for 24 h at room temperature. After completion of the dye adsorption, the electrode was washed with dry >99.9% NMP and dried under a stream of N_2 . The dye-sensitized TiO_2 electrodes were assembled together with thermally platinized FTO counter electrodes using a $50\ \mu\text{m}$ thick Surlyn frame. Redox electrolyte was injected into pre-drilled holes in the counter electrode and the holes were then sealed to give the final DSSC device.

2.2. Experimental methods

External quantum efficiencies (EQEs) for photocurrent generation were recorded using a computerized setup consisting of a xenon arc lamp (300 W Cermox, ILC Technology), a $1/8\ \text{m}$ monochromator (CVI Digikröm CM 110), a Keithley 2400 source/meter, and a Newport 1830-C power meter with 818-UV detector head. Power conversion efficiencies were measured using $1000\ \text{W}/\text{m}^2$ illumination with AM1.5G spectral distribution (1 Sun) from a Newport Oriol 300 W solar simulator (Model 91160), calibrated with a certified silicon reference cell. Charge extraction measurements at open-circuit condition were performed as specified elsewhere [18].

Cyclic voltammetry was performed with a CH Instruments 660 potentiostat using $0.1\ \text{M}$ tetrabutylammonium hexafluorophosphate (TBAPF_6) in dry DCM (Fluka > 99.9%) as supporting electrolyte. A platinum working electrode, platinum counter electrode, and an Ag pseudo reference electrode were used and internally calibrated with ferrocene/ferrocenium (Fc/Fc^+) for each measurement. UV-vis spectra were recorded on an HR-2000 Ocean Optics fiber optics spectrophotometer.

Photoinduced absorption (PIA) experiments were performed using white probe light provided by a tungsten-halogen lamp and superimposed on/off modulated red light (635 nm) from a

diode laser for excitation. The transmitted probe light was focused onto a monochromator (Acton Research Corp. SP-150) and detected by an UV enhanced silicon photodiode connected to a current amplifier and lock-in amplifier (Stanford Research Systems models SR570 and SR830, respectively). The samples used were dye-sensitized TiO_2 films on a microscope glass with a drop of electrolyte and a cover glass.

2.3. Theoretical methods

Density functional theory calculations were carried out with the Turbomole program package [8]. Calculations were done for the anhydride as well as the disodium-dicarboxylate form of the dye. Neutral and cationic states were optimized at the BP86/def-SV(P) level [9,10]. The ionization potential (IP) was obtained from single point energies at the BP86/def-TZVP level [11], at the BP86/def-SV(P) optimized neutral and cationic geometries, respectively. Vertical electronic excitation energies were obtained from time dependent-DFT [12] at the B3LYP/def-TZVP level [13]. The ionization potential of the excited state (IP^*) was estimated by adding the vertical S_1 excitation energy to the ionization potential, neglecting relaxation in the S_1 state.

3. Results and discussion

3.1. Spectroscopical and electrochemical characterization

The anhydride moiety on TMIMA undergoes a ring opening upon attachment on TiO_2 , giving two carboxylate groups [14]. The most relevant energy levels for the solar cell are therefore that of the ring-opened structure, i.e. for the dye attached on a surface or as a $-\text{COO}^- \text{Na}^+$ salt. The formal potential for oxidation of TMIMA was measured by cyclic voltammetry of the dye attached on a conducting glass (FTO: Fluorine-doped SnO_2). The oxidation potential was determined to 1050 mV vs. NHE, and the electron transfer process was fully reversible (see supporting information).

The absorption spectrum of TMIMA in DCM, Fig. 2a, shows a strong band with maximum absorption at 680 nm and shoulder at 625 nm. The molar extinction coefficient at 680 nm is very high, $\epsilon = 178,000\ \text{M}^{-1}\ \text{cm}^{-1}$. With a molar weight $M_w = 1495\ \text{g}/\text{mol}$ the mass extinction coefficient becomes $119\ \text{g}^{-1}\ \text{cm}^{-1}$. This can be compared to the conventional N719 dye [2] having molar extinction coefficient of $14,000\ \text{M}^{-1}\ \text{cm}^{-1}$ at 530 nm with a mass extinction coefficient of $20\ \text{g}^{-1}\ \text{cm}^{-1}$. The molar extinction coefficient is thus more than a magnitude higher for the TMIMA dye and even when compensating for size, which scales with the molecular weight, TMIMA absorbs up to six times more than the Ru-bipyridine complex. Also compared to smaller organic dyes with high molar absorption coefficient, having mass extinction coefficients of typically in the range $60\text{--}90\ \text{g}^{-1}\ \text{cm}^{-1}$, the mass extinction coefficient of TMIMA is exceptionally high. Comparing the absorption and emission profiles a fairly strong mirror symmetry is observed, indicating the similarity of the electronic structure of excited state and ground state. This is also supported by the relatively small Stoke shift between the absorption and emission maximum, 41 nm, corresponding to 0.10 eV.

The absorption and emission spectra of the ring-opened disodium salt of TMIMA is shown in Fig. 2b. The absorption maximum of the ring-opened form is slightly blue-shifted to 667 nm and the shoulder at higher energy has disappeared or is strongly weakened. The shoulder is thus related to transitions that involve orbitals near the anhydride group. For the TMIMA salt we see less mirror symmetry when comparing the absorption and emission profiles, with a Stoke shift of 116 nm (0.28 eV). This is indicative of a change in geometry from the relaxed ground state to the relaxed excited

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