Synthesis of a Hemicyanine Dye Bearing Two Carboxylic Groups and Its Use as a Photosensitizer in Dye-Sensitized Photoelectrochemical Cells

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Two hemicyanine (aminostilbazium) dyes, one bearing two carboxylic groups while the other being its ester analogue, were synthesized for use as photosensitizers in dye-sensitized photoelectrochemical cells (DSPEC). Only the dye with carboxylic groups is covalently attached on mesoporous TiO_2 films. The ester analogue, however, is physically adsorbed and it is easily washed off by several solvents. DSPECs of the Graetzel type, made of mesoporous TiO_2 films (in our case, synthesized through the reverse-micellar route), of the aminostilbazium bicarboxylate photosensitizer and of a I^-/I_3^-/propylenecarbonate electrolyte were tested and were found to yield more than 45% maximum photon to electron conversion efficiency and 0.72% overall photovoltaic efficiency. The cells yielded a linear response within a wide range of illumination intensities.

Introduction

The discovery that ruthenium bipyridyl derivatives can be successfully employed with mesoporous titanium dioxide films and iodine/iodide electrolytes to efficiently convert light into electricity[1,2] has instigated a vast amount of research worldwide. This new type of photoelectrochemical cells promises to offer an inexpensive alternative for the photovoltaic conversion of solar energy. The cells are usually called dye-sensitized photoelectrochemical cells (DSPEC) or Graetzel-type cells and their main component is a high band gap, metal-oxide mesoporous, n-type semiconductor in combination with an adsorbed photosensitizer absorbing in the visible. Many dyes can photosensitize SnO_2, TiO_2, or ZnO nanoparticles;[3−5] it is, however, well established that only covalently attached dyes can offer a satisfactory cell efficiency.[2,6] Up to date, the best performance has been obtained with ruthenium bipyridyl derivatives. Thus, by employing *cis*-X_2bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) photosensitizers ($X = Cl^-$, Br^-, I^-, SCN^-) and a liquid electrolyte, the reported maximum photovoltaic efficiency[2] has been around 10%. This record has not been broken for several years. However, research on DSPEC goes on at a high pace. Reports are published on modifications of all three main components of the cell, that is, the mesoporous oxide semiconductor, the photosensitizer, and the electrolyte. Even though the record efficiency is not broken, the accumulation of knowledge on these systems is valuable for several applications other than energy conversion, such as sensors and photoreproduction systems.

We have recently found that hemicyanine (aminostilbazium) dyes act as photosensitizers of TiO_2 nanoparticles.[7] In the present work, we present two new derivatives of the previous compound where two carboxylic groups or their ester analogues are attached on the aniline group. With this, we expected that the dye could be covalently attached on TiO_2 and thus obtain efficient photosensitization. The present work presents synthesis of these new compounds and their testing in a DSPEC.

Experimental Section

Materials. Titanium(IV) isopropoxide, polyoxyethylene(10) isooctylphenyl ether (Triton X-100), and propylenecarbonate were purchased from Aldrich and used as received. Bromoethyl acetate (97%) was from Janssen. Aniline and morpholine were distilled over KOH before use. Diethyl ether was distilled over $CaCl_2$ and CH_2Cl_2 was distilled over CaH. Tetrahydrofurane (THF) was distilled over sodium metal. The rest of the reagents were from Merck, while Millipore water was used in all experiments. Optically transparent electrodes (OTE) were cut from an indium tin oxide (ITO) coated glass (<10 Ω/square) purchased from Pilkington-Flabeg, Germany.

Synthesis and NMR Data of the Photosensitizers. The two aminostilbazium dyes, abbreviated PVC1 and PVC2 (cf.

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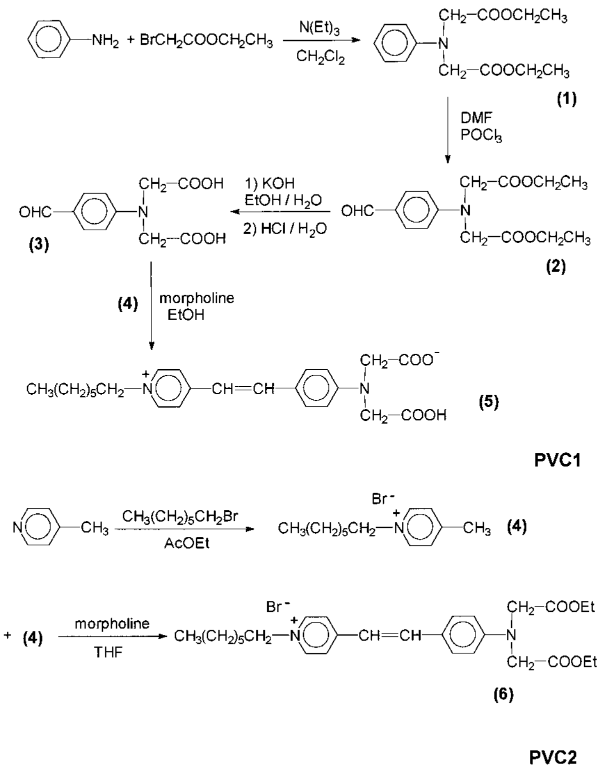

Figure 1. Reaction schemes for the synthesis of aminostilbazium dyes with carboxylic groups (PVC1) or the ester analogue (PVC2).

Figure 1), were synthesized according to the schemes of Figure 1 (see also Results and Discussion). Column flash chromatography was performed on silica gel 60 (Merck, 230−400 mesh). Melting points were determined with a Gallenkamp capillary apparatus and uncorrected NMR spectra were recorded on Varian Gemini 200 and Varian Gemini 300 spectrometers. Chemical shifts are given in ppm and coupling constant values in Hertz. Mass spectrometry was carried out on TSQ 700 Finnigan MAT in the FAB or EI mode.

*Phenyliminodiacetic Acid Diethyl Ester (**1**).* Aniline (0.81 g, 8.8 mmol) and ethylbromoacetate (1.00 g, 5.9 mmol) (97%, Janssen) were stirred for 30 min at 20 °C. Then, another 3.50 g (29.9 mmol) of ethylbromoacetate, 2.72 g (26.9 mmol) of triethylamine, and 15 mL of CH_2Cl_2 were added. The reaction mixture was refluxed for 7 h and cooled to ambient temperature and 15 mL of CH_2Cl_2 was added. The solution was extracted with water (3 × 10 mL), the organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The product was purified by column chromatography (eluent: diethyl ether/pentane 1/3 v/v) to yield 1.28 g (55%) as colorless, viscous oil.

^1H NMR ($CDCl_3$, 200 MHz): 7.24 (m, 2H), 6.79 (m, 1H), 6.63 (m, 2H), 4.22 (q, 4H, $J = 7.1$), 4.15 (s, 4H), 1.29 (t, 6H, $J = 7.1$).

^{13}C NMR ($CDCl_3$, 50 MHz): 171.8 (2C), 148.2, 129.8 (2C), 119.5, 113.1 (2C), 61.6 (2C), 54.1 (2C), 14.7 (2C).

MS (EI) for $C_{14}H_{19}NO_4$ (MM = 265.31) found M^+: 265.1 (18%).

*4-[N,N-Bis(ethoxycarbonylmethyl)amino]benzaldehyde (**2**).* $POCl_3$ (8.66 g, 56.3 mmol) was added dropwise at 5 °C to a stirred mixture of 3.00 g (11.3 mmol) of aniline (**1**) and 4.13 g (56.3 mmol) of *N*,*N*-dimethylformamide. After the mixture was kept for 30 min at 5 °C, it was heated at 60 °C for 3 h and finally stirred at ambient temperature overnight. The mixture was diluted with 40 mL of CH_2Cl_2 and slowly poured into 100 mL of cold 0.1 M aqueous NaOH. The aqueous layer was extracted by 4 × 20 mL of CH_2Cl_2, the organic layers were collected, concentrated to a volume of 30 mL under reduced pressure, extracted by brine (3 × 10 mL), and dried over Na_2SO_4. Removing the solvent under reduced pressure afforded 2.54 g of slightly yellow crystals (77%): mp 60−61 °C (63−64 °C).[8]

^1H NMR ($CDCl_3$, 200 MHz): 9.71 (s, 1H), 7.70 (d, 2H, $J = 8.9$), 6.71 (d, 2H, $J = 8.9$), 4.33 (s, 4H), 4.13 (q, 4H, $J = 7.1$), 1.19 (t, 6H, $J = 7.0$).

^{13}C NMR ($CDCl_3$, 50 MHz): 190.3, 169.7 (2C), 152.7, 131.4 (2C), 126.2, 111.7 (2C), 60.7 (2C), 52.5 (2C), 14.1 (2C).

*4-[N,N-Bis(carboxymethyl)amino]benzaldehyde (**3**).* KOH (1.03 g, 18.3 mmol) in 10 mL of H_2O was added dropwise to 1.80 g (6.1 mmol) of (**2**) in 20 mL of ethanol at ambient temperature, and the mixture was stirred for 12 h. Ethanol was removed under reduced pressure and the aqueous layer was acidified to pH 2 by 2 M HCl. NaCl was added and the aqueous layer was extracted by ethyl acetate (4 × 40 mL). The organic layers were collected and dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield 1.46 g (94%) of white solid: mp 212−213 °C (213−214 °C).[8]

^1H NMR (DMSO, 200 MHz): 9.69 (s, 1H), 7.69 (d, 2H, $J = 8.7$), 6.77 (d, 2H, $J = 8.7$), 4.22 (s, 4H).

^{13}C NMR (DMSO, 50 MHz): 190.1, 171.1 (2C), 152.8, 131.4 (2C), 125.8, 111.3 (2C), 52.7 (2C).

*1-Heptyl-4-methylpyridinium Bromide (**4**).* 1-Bromoheptane (10.0 g, 56.2 mmol) was added dropwise to 3.54 g (38 mmol) of 4-methylpyridine in 10 mL of ethyl acetate, and the mixture was stirred for 12 h at 60 °C. The mixture was concentrated under reduced pressure and washed with 20 mL of pentane. The crude product was crystallized in a mixture of ethyl acetate/diethyl ether (8/2 v/v) to yield 8.51 g (84%) of colorless crystals: mp 62−64 °C.

^1H NMR (DMSO, 200 MHz): 8.83 (d, 2H, $J = 6.9$), 7.93 (d, 2H, $J = 6.9$), 4.57 (m, 2H), 2.67 (s, 3H), 2.00 (m, 2H), 1.36−1.22 (m, 8H), 0.88 (m, 3H).

^{13}C NMR (DMSO, 50 MHz): 160.9 (2C), 114.9, 129.9 (2C), 62.1, 32.6, 32.3, 29.7, 27.0, 23.5, 22.1, 14.4.

*Stilbazium Dye (**5**) (PVC1).* Aldehyde (**3**) (0.30 g, 1.1 mmol), picolinium salt (**4**) (0.37 g, 1.34 mmol), and morpholine (0.66 g, 7.5 mmol) were stirred in 10 mL of dry ethanol over 4-Å molecular sieves. The mixture was refluxed for 72 h and then filtered on Celite. The solvent was removed under reduced pressure and 10 mL of water was added. The mixture was extracted with CH_2Cl_2 (3 × 30 mL) and diethyl ether (20 mL), and the aqueous layer was brought to pH 2 by 2 M HCl. The precipitate was filtered off, redissolved in dilute aqueous NaOH, and reprecipitated by the addition of 2 M HCl to give 0.40 g (betain form, 0.9 mmol, 46%) of a red solid, which was repeatedly recrystallized from water: mp 191−193 °C.

^1H NMR (DMSO, 300 MHz): 8.86 (d, 2H, $J = 6.3$, CH Ar pyr.), 8.10 (d, 2H, $J = 6.3$, CH Ar pyr.), 7.95 (d, 1H, $J = 15.8$, CH vinyl.), 7.59 (d, 2H, $J = 8.5$, CH Ar anil.), 7.22 (d, 1H, $J = 15.8$, CH vinyl.), 6.62 (d, 2H, $J = 8.5$, CH Ar anil.), 4.44 (t, 2H, $J = 6.6$, CH_2N^+), 4.20 (s, 4H, $N{-}CH_2{-}COO$), 1.84 (m, 2H, $CH_2{-}C{-}N^+$), 1.26−1.13 (m, 8H, CH_2), 0.83 (m, 3H, CH_3).

^{13}C NMR (D_2O with NaOH, 75 MHz): 179.3 (2C, COO), 154.9 (2C, CH Ar), 152.2 (CH Ar), 143.8 (CH Ar), 142.6 (CH vinyl), 131.5 (2C, CH Ar), 123.8 (CH Ar), 123.6 (CH vinyl), 118.3 (2C, CH Ar), 112.9 (2C, CH Ar), 61.3 (CH_2N^+), 56.9 (2C, CH_2N), 31.5 (CH_2), 31.2 (CH_2), 29.2 (CH_2), 26.4 (CH_2), 23.2 (CH_2), 14.8 (CH_3).

MS (FAB) positive mode $(M + 1)^+$: 411.1(35%); negative mode $(M - 1)^-$: 409.7 (20%).

Elemental analysis: Calculated for $C_{24}H_{30}N_2O_4$ (MM 410.51): C, 70.2; H, 7.3; N, 6.8. Calculated for $C_{24}H_{30}N_2O_4 + 2H_2O$: C, 64.5; H, 7.6; N, 6.2. Found: C, 64.4; H, 7.5; N, 6.2.

*Ester Analogue (**6**) (PVC2).* Compound (**2**) (0.61 g, 2.3 mmol), picolinium derivative (**4**) (0.64 g, 2.3 mmol), and morpholine (1.18 g, 13.5 mmol) were stirred in 20 mL of dry THF over 4-Å molecular sieves. The mixture was refluxed for 16 h and filtered on Celite. The solvent was removed under reduced pressure and the mixture was washed with 20 mL of diethyl

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ether and then purified by column chromatography (eluent: CH_2Cl_2/EtOH 96/4 v/v) to give 0.2 g (18%) of dye: mp 108−110 °C.

^1H NMR ($CDCl_3$, 300 MHz): 8.81 (d, 2H, $J = 6.7$, CH Ar pyr.), 7.87 (d, 2H, $J = 6.8$, CH Ar pyr.), 7.54 (d, 1H, $J = 15.9$, CH vinyl.), 7.44 (d, 2H, $J = 8.9$, CH Ar anil.), 6.90 (d, 2H, $J = 15.9$, CH vinyl.), 6.49 (d, 2H, $J = 9$, CH Ar anil.), 4.49 (m, 2H, CH_2N^+), 4.15−3.90 (m, 8H, CH_2 anil. and CH_2 ester), 1.81 (m, 2H, CH_2), 1.25−1.10 (m, 14H, CH_2 alkyl and CH_3 ester), 0.72 (m, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): 170.3 (2C, CO), 154.2 (1C, CH Ar.), 150.3 (1C, CH Ar.), 143.9 (2C, CH Ar), 142.3 (1C, CH vinyl), 130.9 (2C, CH Ar), 125.1 (1C, CH vinyl), 123.7 (2C, CH Ar), 118.8 (1C, CH Ar), 112.8 (2C, CH Ar), 61.8 (2C, CH_2 ester), 60.7 (1C, CH_2N^+), 53.7 (2C, CH_2N), 32.0 (1C, CH_2), 31.8 (1C, CH_2), 29 (1C, CH_2), 26.3 (1C, CH_2), 22.8 (1C, CH_2), 14.5 (2C, CH_3 ester), 14.4 (1C, CH_3).

Elemental analysis: Calculated for $C_{28}H_{39}N_2O_4Br$ (MM 547.55): C, 61.4; H, 7.2; N, 5.1, Br, 14.6. Calculated for $C_{28}H_{39}N_2O_4Br + H_2O$: C, 59.4; H, 7.3; N, 4.9, Br, 14.1. Found: C, 58.9; H, 6.6; N, 4.8, Br, 14.7.

Preparation of TiO_2 Mesoporous Films Deposited on OTE-ITO Glasses. Mesoporous TiO_2 films were deposited on transparent-conductive ITO glasses by the following procedure. A reverse micellar solution of 0.2 M Triton X-100 and 0.4 M water was prepared in cyclohexane. To this solution we added 0.2 M titanium isopropoxide under vigorous stirring and at ambient conditions. Other concentrations of the above components have also been tried but optimal results were obtained with the present combination.[9] Hydrolysis and condensation of titanium isopropoxide begins as soon as it is introduced in the reverse micellar solution, but it takes about an hour before the solution becomes a visible gel.[9,10] The thus-prepared composite material can be deposited as thin film on an ITO slide by dip coating. A slide 20 × 30 mm was cut from an ITO glass, sonicated for 20 min in ethanol, and, finally, copiously washed with Millipore water and dried in a stream of N_2. The thus-prepared slide was dipped into the gelling solution at an early stage of gelation and was quickly withdrawn at a speed of 2 cm/s. The composite organic−inorganic film was left to dry in air and the dipping was repeated two more times. The film was deposited on only the ITO side of the glass. The other side was covered with a tape. After the three dippings, the back tape was pealed off and the glass surface was locally washed with acetone. Then, the film was slowly heated in air, up to 450 °C, at a rate of 7 °C/min. The film was finally sintered at 450 °C for about 15 more min. The procedure was repeated two additional times so that 3 × 3 depositions were made. Its thickness was measured by profilometry and was found to be 1.2 μM. The obtained film was transparent. Thicker films could be made by further successive coatings; however, thickness grows at the expense of transparency. AFM and SEM images of the films prepared by the above method and published in previous publications[9−11] reveal a mesoporous structure that consists of TiO_2 nanoparticles of practically monodispersed size with exceptional reproducibility. The size of the nanoparticles can be easily controlled by choosing the water/surfactant ratio in the original reverse micellar solution.[9,11] Larger nanoparticles are made when more water exists in the solution. The advantage of the reverse-micellar route in making TiO_2 particles, as compared with other methods, exactly lies on this capacity to control the mesoporous structure of the obtained films. The diameter of the nanoparticles employed in the present work, as estimated by using AFM images, was around 30 nm.

Procedure for the Adsorption of the Photosensitizer (PVC1 or PVC2) on TiO_2 Films. When the TiO_2 film was taken out of the furnace and while it was still hot, it was dipped into a 2 mM $CHCl_3$ solution of PVC1 or PVC2 and was left there for about 24 h. Then, it was copiously washed with $CHCl_3$ dried in a stream of N_2 and studied by absorption spectrophotometry. Only PVC1 was steadily attached on the TiO_2 film, obviously, by means of its carboxylate groups.[2,6] Figure 2 shows the absorption spectra of the TiO_2 film with and without the adsorbed dye. The absorption of visible light by the film is, obviously, possible only through the dye.

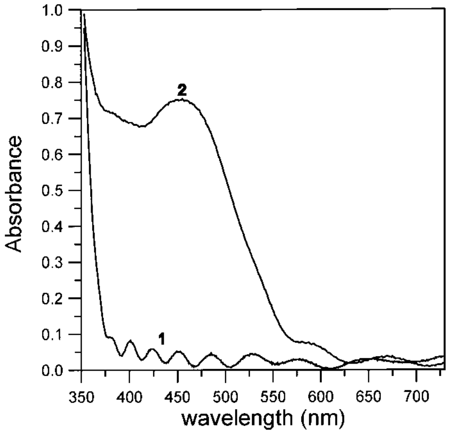

Figure 2. Absorption spectra of a TiO_2 mesoporous film without (**1**) or with the attached photosensitizer PVC1 (**2**).

Fabrication of the Photovoltaic Cell. On the top of the ITO glass bearing the TiO_2 film with the adsorbed dye photosensitizer, we placed the counter electrode separated from the TiO_2 electrode by plastic spacers of a thickness of about 100 μm. The counter electrode consisted of another ITO glass on which a thin Pt layer was deposited by thermal evaporation. The presence of Pt is known to improve the cell performance. The system of the above two electrodes was then sealed with silicone. The electrolyte was introduced with a syringe. It consisted of 0.4 M KI and 0.04 M I_2 dissolved in propylenecarbonate.

Photophysical Measurements. Absorption measurements were made with a Cary 1E spectrophotometer and fluorescence measurements with a spectrofluorometer made of Oriel components. Incident photon to current efficiency (IPCE%) values[2] have been measured by illumination of the samples with a 250-W Phillips tungsten halogen lamp through a filter monochromator (Oriel-7155). The lamp spectrum satisfactorily simulates solar radiation at the surface of the earth. The number of incident photons was calculated by employing a radiant power/energy meter (Oriel-70260).

Results and Discussion

Synthesis of the Aminostilbazium Dyes with Carboxylic or Ester Groups. The aminostilbazium dyes (**5**) (PVC1) and (**6**) (PVC2) of Figure 1 were obtained in a five- and four-step synthesis, respectively, from aniline and 4-methylpyridine, according to the scheme of Figure 1. Note that the yields of phenyliminodiacetic acid diethyl ester (**1**) varied strongly with the quality and the supplier of the ethylbromoacetate used. The intermediate aldehyde (**2**) was prepared by Vilsmeier reaction from tertiary aniline (**1**). An aldol condensation of the aldehydes (**2**) and (**3**), respectively, with 2-methyl *N*-heptylpyridinium bromide (**4**) provided the stilbazium dyes (**5**) and (**6**).[7,12]

Photophysical Characteristics of the Dyes in Solution. The absorption and luminescence spectra of PVC1 and PVC2 have been recorded in dilute solutions in some different solvents. The best solvents are alco-

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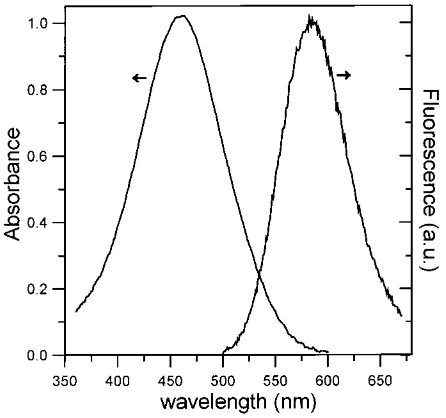

Figure 3. Absorption and fluorescence spectrum of 2×10^{-5} M PVC1 in methanol.

Table 1. Absorption and Fluorescence Data of 2×10^{-5} M PVC1 in Different Solvents

solvent	absorbance max.	fluorescence max.	fluorescence intensity (a.u.)	ϵ (M^{-1} cm^{-1})	dielectric constant
methanol	460	582	183	24782	32.6
ethanol	465	585	195	25304	24.3
pentanol	478	590	308	20391	13.9
decanol	485	593	410	16521	8.1
chloroform	451	595	48	16173	4.8
acetone	471	608	90	26521	20.7
acetonitrile	461	604	108	26434	37.5
DMSO	455	593	326	22173	46.5
formamide	488	620	33	23217	109.5

hols, especially methanol, and DMSO. An example of an adsorption and a luminescence spectrum is given in Figure 3. Table 1 shows the adsorption and luminescence maxima as well as the molar extinction coefficient and the relative luminescence intensity in some solvents for PVC1. Similar data were also obtained with PVC2. Table 1 reveals a symmetric solvatochromic effect on the photophysical behavior of PVC1, that is, the absorption maximum is blue-shifted and the fluorescence maximum is red-shifted in polar solvents. This behavior is normal only in the case of linear alcohols of Table 1 and only for the absorption spectra and it is explained by Born-Marcus- type theory of intramolecular charge migration upon excitation.[13,14] In solvents other than alcohols, the solvatochromic behavior is complicated by the tendency of this molecule to form aggregates, same as its analogue without carboxyl groups previously studied.[7] An important parameter to retain from the data of Table 1 is the relatively high molar extinction coefficient ϵ that PVC1 possesses in polar environments. This is important since we may expect that ϵ shoul also be high when the dye is adsorbed on TiO_2 films, as will be seen below.

Photophysical Characteristics of the TiO_2 Film with Attached Photosensitizer. Dyes bearing carboxylic groups can be covalently attached on oxide semiconductors through the following reaction scheme[6] due to hydroxyl groups at the surface,

$$-M-OH + RCOOH \rightarrow -M-OOCR + H_2O$$

where M is the metal and R the dye. In the present case, both carboxylic groups may participate in similar reactions, providing a stable attachment of PVC1 on TiO_2 films. We have attached carboxylic groups on the amine part of the molecule to have two of them and secure anchoring of the dye on TiO_2 nanoparticles. We have also tried the ester analogue PVC2 but this material was only physically adsorbed on TiO_2 and was easily washed off by several solvents. Figure 2 shows the adsorption spectrum of the TiO_2 film without and with the attached PVC1. The oscillating part of the pure TiO_2 spectrum (curve 1) is due to interference fringes. The high optical density of curve 2 demonstrates the successful attachment of PVC1 on the semiconductor film. Indeed, the absorbance of the film in the spectral region around 450 nm is 0.75, which means that, at this wavelength, about 82% of the incident photons are absorbed. The above semiconductor–dye system has then a very high absorption cross section, higher than those recorded in other cases.[15,16] However, an important part of the visible spectrum is not covered by PVC1 and this is one of its disadvantages. No luminescence emission was recorded from the dye attached on TiO_2 film, indicating efficient quenching, presumably, by excited electron transfer from the dye to the semiconductor.

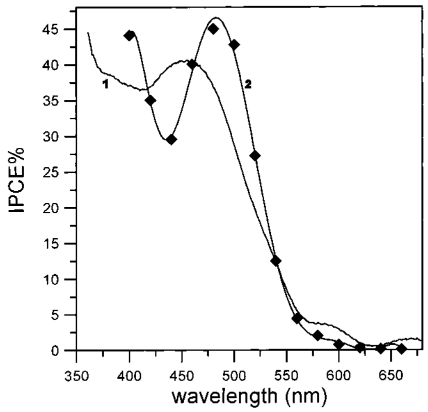

Figure 4. Absorption spectrum of PVC1 on a TiO_2 film (a.u.) (**1**) and IPCE% values of the corresponding DSPEC (**2**).

Performance of the Photoelectrochemical Cell. Whereas dye PVC2 could not be employed as a photosensitizer because it was not covalently attached to TiO_2, a cell was constructed as described in the Experimental Section using PVC1. The cell was illuminated through the ITO glass by controlling both the intensity of the incident light and its wavelength. The efficiency of the photoelectrochemical conversion of the absorbed photons can be judged by measuring the so-called IPCE% value which is given by the following relation,[2]

$$\mathrm{IPCE\%} = \frac{1240 \times I(\mu\mathrm{A/cm^2})}{\lambda(\mathrm{nm}) \times P_{\mathrm{inc}}(\mathrm{W/m^2})}$$

where P_{inc} is the incident light power at the wavelength λ and I the produced photocurrent. IPCE% thus gives the percentage of the number of electrons produced with respect to the number of photons absorbed. Figure 4 reveals that the maximum efficiency recorded with the

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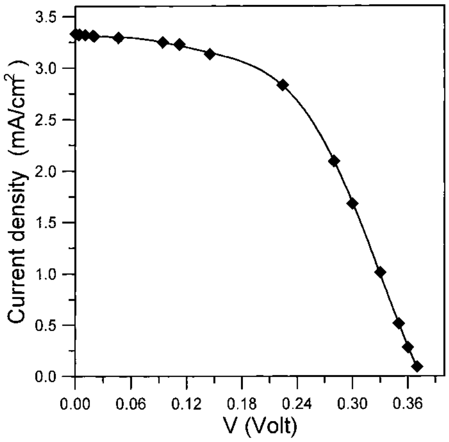

Figure 5. Current–voltage relationship of a DSPEC containing PVC1 under AM1.5 illumination.

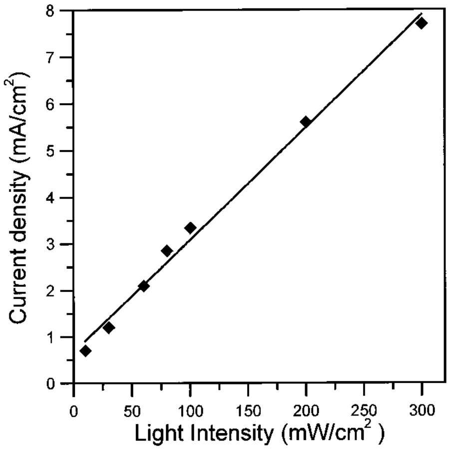

Figure 6. Short-circuit current under various white light illumination intensities.

TiO_2/PVC1 system was 45%. This value is underestimated since it is measured under the assumption that all incident photons are absorbed, which is not true. The IPCE% and the adsorption spectrum do not strictly overlap but they are very close, indicating that the photoelectrochemical conversion is achieved through photosensitization, that is, that photons are adsorbed by the dye and the excited electrons are transferred to the conduction band of the semiconductor.[17] There are some literature values available which offer an estimation of the HOMO and LUMO levels for PVC1 that justify its performance as a photosensitizer of TiO_2. Nanocrystalline TiO_2 valence band edge is located around −7.2 to −7.5 eV with respect to vacuum (i.e., $\approx$2.7−3.0 eV vs NHE).[18,19] In our case, where the TiO_2 absorption onset is at 375 nm (cf. Figure 2), the corresponding energy band gap is 3.3 eV, which brings the conduction band edge at a highest value of about −3.9 eV. Published values of the HOMO level of molecules almost identical to PVC1, save for the two carboxylic groups,[20,21] are around −5.5 eV with respect to vacuum. We believe that the attached carboxylic groups will have only a very weak effect on the HOMO level of PVC1. This brings the corresponding LUMO level to −3.3 eV (i.e., a band gap of 2.2 eV that corresponds to 570 nm, cf. Figure 2). This value is substantially higher than the conduction band edge of TiO_2, which justifies electron transfer from the excited photosensitizer to the conduction band of the semiconductor. Figure 5 shows the current−voltage relationship of the cell. These data are obtained under the following procedure: a variable resistor is connected parellel to the cell and the current and the voltage is measured at different resistance values. Figure 5 shows that the open-circuit voltage, produced by illumination with a source providing AM1.5 ($\cong$100 mW/cm^2), is 0.36 V, while the short-circuit current density is 3.34 mA/cm^2. The overall efficiency of the cell is given by the ratio of the produced power over the incident power, which is usually calculated from the data of the diagram of Figure 5 according to the following relation,[22]

$$n = \frac{I_{sc}V_{oc}ff}{P_{inc}}100$$

where I_{sc} is the short-circuit current (3.34 mA in our case), V_{oc} is the open circuit voltage of the cell (0.36 V in our case), and ff is the so-called fill factor, which was calculated from the above diagram for the maximum product IV divided by the product $I_{sc}V_{oc}$ (0.57 in our case). Thus, n was 0.72%, i.e., a satisfactory value, considering that the maximum DSPEC efficiencies recorded so far are 10%.[2] The above cell also gave satisfactory performance with respect to the level of illumination. Thus, in Figure 6 it is seen that the short-circuit photocurrent was linear up to 300 mW/cm^2.

Conclusions

We have constructed a Graetzel-type DSPEC by employing a hemicyanine photosensitizer bearing two carboxylic groups. The dye was thus covalently attached on TiO_2 nanoparticles, leading to a satisfactory photoconversion efficiency with more than 45% maximum IPCE% and 0.72% overall photoelectrochemical conversion efficiency. We believe that there is ground for improving cell efficiency, but even if this photosensitizer is judged inefficient for energy applications, it can be useful for other applications such as in sensors or in photoreproduction systems.

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