Sensitization of Nanocrystalline TiO_2 Films with Carboxy-Functionalized Bis(indolyl)maleimide

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Keywords: Photochemistry / Electron transfer / Sensitizers / Thin films / Time-resolved spectroscopy

The immobilization on a semiconductor surface of a bis(indolyl)maleimide functionalized with two carboxylic acid groups by alkylation of the indole nitrogen atoms is presented and its synthesis is described. The compound, 3,4-bis[1-(carboxymethyl)-3-indolyl]-1*H*-pyrrole-2,5-dione is strongly colored and emissive and the imide part can coordinate an oxidizable substrate. Its absorption and emission spectra on TiO_2 are substantially changed as compared to the spectra obtained in neat acetonitrile, indicating surface bonding through the carboxy groups. The quenching of the fluorescence of the sensitizer by the TiO_2 surface is almost complete, reflecting the high degree of association between the TiO_2 and the dye, fast charge injection and good electronic coupling between the sensitizer and the semiconductor. Nanosecond transient absorption spectra of the free sensitizer and of TiO_2 surface bound sensitizer are recorded and compared. While the free chromophore in neat acetonitrile shows a transient absorption spectrum that decays on the nanosecond timescale (like the emission), the transient absorption spectra of the sensitized TiO_2 film show a band at 360 nm, and a decay on the microsecond time scale. This is assigned to a slow recombination reaction of the charge-separated state. The properties discussed indicate that our system can be considered as a model compound for the development of photocatalysts immobilized on surfaces.

Introduction

The main reason for the current interest in supramolecular chemistry is its potential application in nanoscale molecular devices that are capable of mimicking, at the molecular level, functions normally performed by natural systems or by artificial macroscopic devices.[1–3] In many of these molecular devices, the input to promote a function is light and much effort has been devoted to the understanding of the energy and/or electron transfer processes taking place between the molecular components within the supramolecular structure.[2–9] In particular, long-range electron transfer processes with the final goal to achieve long-lived charge separation could lead to the realization of such devices. Incorporation of the active components on a solid support is the next step in order to interface the molecular systems to the external world and make it suitable for applications.[6] Furthermore, the molecular components that are immobilized on a solid substrate through adsorption or covalent attachment, can lead to a well-organized arrangement and the interaction between the components and the solid substrate can result for example in an improved charge separation or photocatalytic conversion. Nanocrystalline semiconductors are particularly attractive candidates for these active solid supports. Transparent nanocrystalline semiconductor electrodes have been investigated in detail because of their practical applications in solar cells, photo- and electrochromic windows and lithium intercalation batteries.[1,3,4,8,10] Nanostructured semiconductor films have been applied as antibacterial coatings and for the light-assisted degradation of organic pollutants.[11] Metal oxides such as TiO_2, ZnO, NiO, SnO_2 have been coated with molecular components and the light-driven processes of these assemblies have been studied. TiO_2 has attracted special attention as a semiconductor because of many advantages. It is cheap, nontoxic, biocompatible and widely used in health care products as well as in paints.[9] There are several examples showing the ability of TiO_2 surfaces modified with a range of organic[4,12] and inorganic[2–5] molecular components, to act as efficient photovoltaic cells.

Grätzel and co-workers[4] and several other groups[7,14] have studied nanocrystalline TiO_2 surfaces modified with (polypyridine)ruthenium complexes in the construction of efficient solar energy devices. The first dye-sensitized nanocrystalline solar cell with a conversion yield of 7.1% was announced in 1991,[3] and presently the certified efficiency is over 10%.[9] These dyes contain carboxy, phosphate or

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DOI: 10.1002/ejoc.200500043

ester groups, which serve to attach the compound covalently to the oxide and to establish a good electronic coupling between the adsorbed species and the TiO_2 surface.[15] It has been demonstrated by quantum mechanical calculations and infrared spectroscopy that carboxy compounds are attached to the oxide substrate by carboxylate bridges,[5] to either hydroxy groups or Ti^{IV} ions.

The dyes must fulfil the conditions dictated by the electronic properties of the solid materials described in terms of the bandgap. Their excited states must lie above the conduction band of the semiconductor so that photoexcitation of the sensitizer attached to the surface results in the injection of an electron into the conduction band of the oxide. For many sensitizers the injection process is extremely fast in the femtosecond timescale, depending on the type of linkage and distance used for the anchoring to the surface.

More generally after excitation of the dye, the excited state can either be deactivated by emission (that can also be observed in solution), by non-radiative interaction with its surrounding, or by injection into the semiconductor surface. In the study of Willig and co-workers,[16] the time-scale of the photoinduced electron injection from the molecular component, a ruthenium compound, to the solid substrate was determined by femtosecond transient absorption spectroscopy. Upon injection of electrons, an absorption band with a maximum at 1200 nm was observed. The rise time of this band (< 25 fs)[16] can be taken as an indication for the rate of electron injection from the dye to TiO_2.

The fundamental and practical attraction of the dye-modified TiO_2 surfaces lies in the next step, the back reaction. Charge separation needs to be both fast and long-lived. It is of great interest to develop sensitizer systems for which the rate of the electron injection is high and that of the back reaction is low. Interfacial charge separation at dye-sensitized TiO_2 surfaces has been the subject of many studies.[8,17] In the case of (polypyridine)ruthenium complexes the recombination process is several orders of magnitude slower than the injection rate, thus resulting in long-lived charge separation. This aspect is particularly interesting if the long-lived charge separated species is used for practical applications such as photocatalysis. In fact, the time of diffusion of the oxidized species can be rather slow and must compete with this back reaction.

Indolylmaleimide systems are interesting chromophores that can complex through a coordinative bond with metallocycles such as (cyclen)Zn^{II}.[13] The first step in the direction of their use in photoresponsive self-organized aggregates is their attachment to an, e.g., semiconductor surface. The resulting assembly will show different photophysical properties and the investigation of the electron injection and charge recombination reaction could lead to the design of new photocatalysts.

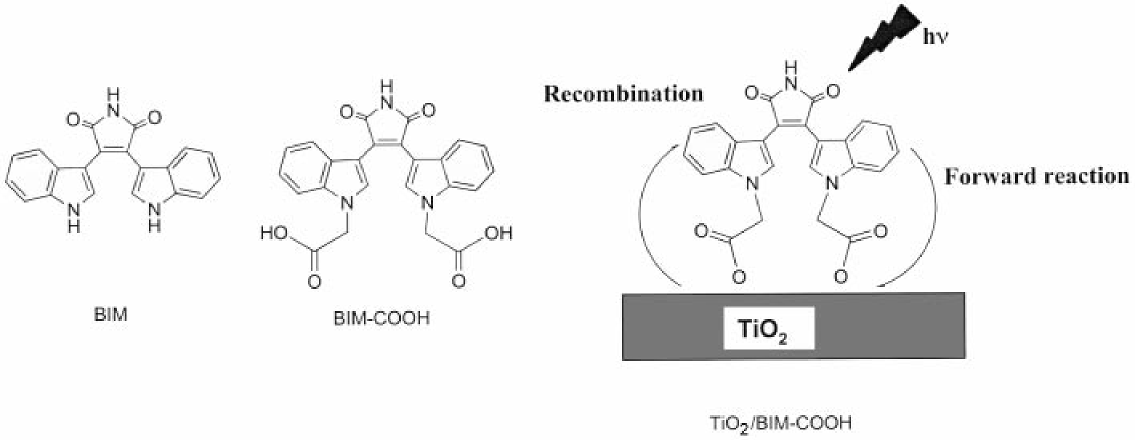
In this paper we report the synthesis and spectroscopic characterization of a bis(carboxy)-functionalised bis(indolyl)maleimide, 3,4-bis[1-(carboxymethyl)-3-indolyl]-1*H*-pyrrole-2,5-dione (**BIM–COOH**). The compound has been designed for its immobilization on a TiO_2 surface through the carboxy functions (**TiO_2/BIM–COOH**) and to investigate its possible use as a sensitizer for TiO_2. UV/Vis absorption, steady-state and time-resolved emission and nanosecond transient absorption spectra both in solution and on a semiconductor surface were recorded to obtain a full photophysical characterization as well as information on the electron injection and charge recombination processes. The compound investigated and its anchoring to the TiO_2 surface as well as the reference compound, **BIM,** are depicted in Scheme 1.

Results and Discussion

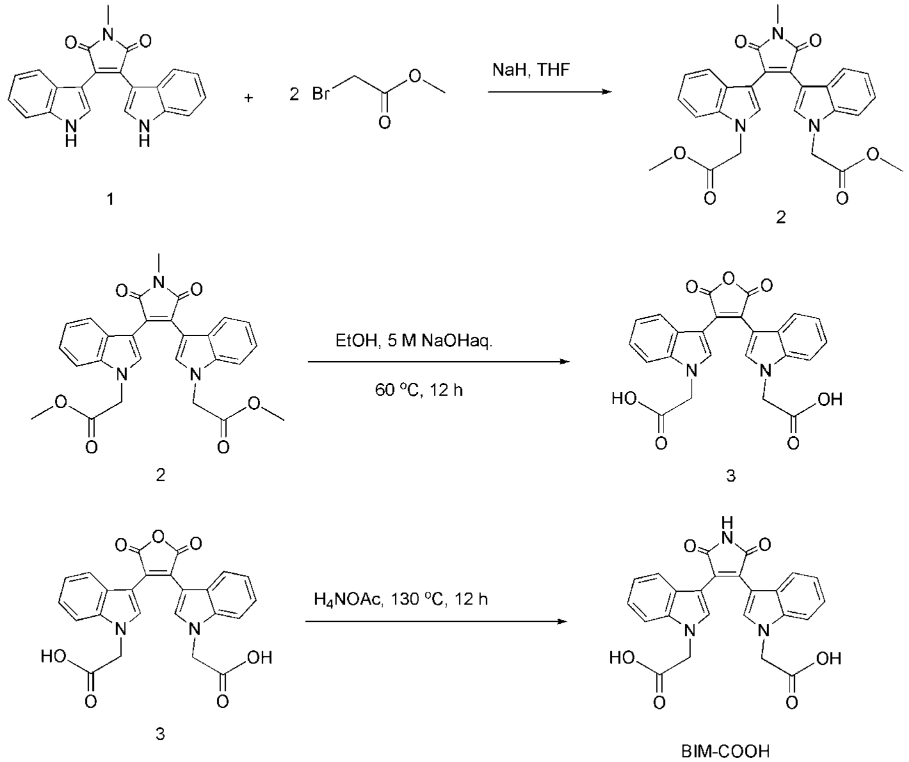
Synthesis of BIM–COOH

In order to functionalize the bis(indolyl)maleimide on the indole nitrogen atoms only, the nitrogen atom of the maleimide unit, that is the most basic one, must be protected. For this purpose, *N*-methylbis(indolyl)maleimide **1** was chosen as the starting compound for the synthesis and prepared according to a procedure published by Steglich et al.[18]

3,4-Bis[1-(carboxymethyl)-3-indolyl]-1*H*-pyrrole-2,5-dione (**BIM–COOH**) was prepared according to an adapted procedure described by Xie et al.[19] (see Scheme 2) Methyl



Scheme 1. The compounds studied: **BIM–COOH** and **TiO_2/BIM–COOH**. The reference compound **BIM** is also shown.



Scheme 2. Schematic procedure for the synthesis of **BIM–COOH**.

bromoacetate was treated with **1** to obtain the ester-functionalized indolylmaleimide **2** (Scheme 2). Compound **2** was treated with 5 N KOH to convert the ester groups into the acid functions. The *N*-methylmaleimide unit was also converted into the anhydride **3** in this step. Heating of compound **3** in an excess amount of ammonium acetate resulted in the desired compound, **BIM–COOH**. The detailed synthetic procedures, including purification and characterization, are given in the Exp. Sect.

Preparation of a BIM–COOH-Coated TiO_2 Surface

A small aliquot of a TiO_2 suspension (Ti nanoxide-HT, 9 nm particle size, Solaronix) was spread onto a glass slide, using a glass rod with adhesive tape as spacer (thickness ca. 42 µm). The layer thus formed was dried in air at room temperature for 10 min. The film was heated at 400–450 °C for 30 min in an oven. As a result of the heating process, a transparent colorless film was obtained. The films were kept in the dark and were dried in an oven at 150 °C for 30 min prior to use. In order to coat the TiO_2 surfaces with the dye, the semiconductor surfaces were immersed in a 1×10^{-4} M solution of **BIM–COOH**, in absolute ethanol overnight. Then the coated layers were rinsed with ethanol and dried in air. After the coating, the transparent red films were ready for spectroscopic studies.

UV/Vis Absorption Spectroscopy

The absorption spectra of **BIM**, **BIM–COOH** in acetonitrile and of the dye-coated TiO_2 film, **TiO_2/BIM–COOH** are depicted in Figure 1. The absorption spectra of **BIM** and **BIM–COOH** are almost identical. They show two major absorption bands around 446 nm, with shoulders at 366 nm and around 277–281 nm, which can be assigned to π–π* transitions from S_0 to the S_1 and S_2 states, respectively. The functionalization of the indole moieties does not change the UV/Vis spectrum.

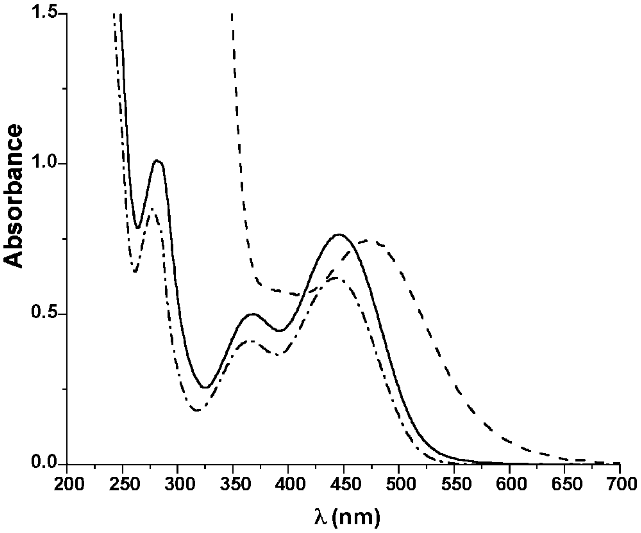


Figure 1. The UV/Vis absorption spectra of **BIM–COOH** (solid), **BIM** (dash-dotted) in acetonitrile [10^{-4} M], and the dye-coated TiO_2 film **TiO_2/BIM–COOH** (dashed).

In the thin film, the main interaction responsible for chemisorption is the coordination of the carboxylate groups to the Ti^{IV} centers on the surface. Indeed, systems lacking such groups, e.g. compound **2** (having ester functions instead of acid groups, see Scheme 2), do not adsorb on these surfaces. In the absorption spectrum of **TiO$_2$/BIM–COOH** the strong absorption of the TiO_2 at $\lambda \leq 400$ nm is clearly visible. Furthermore a bathochromic shift of 30 nm (1413 cm^{-1}) accompanied by some broadening of the long-wavelength absorption band of **BIM–COOH** is observed, as compared to the model compound in solution. These spectral changes indicate a strong electronic coupling of the two carboxylate units with the TiO_2 surface, which are likely to involve deprotonation of the acid.[20] The visible absorption band, centered at 476 nm (see Figure 1) enables selective excitation of the **BIM–COOH** chromophore.

Emission Spectroscopy

Figure 2 shows a comparison between front-face emission spectra of **BIM**, **BIM–COOH** in acetonitrile and as a solid material on a TiO_2 surface (excitation at 460 nm). The emission centered at 584 nm for both **BIM** and **BIM–COOH** in solution is characterized by a high quantum yield ($\Phi \approx 0.1$ to 0.15, respectively) and excited state lifetimes of 8.5 and 11 ns, respectively.

Comparison of the emission intensities clearly shows that the emission of **TiO$_2$/BIM–COOH** is strongly quenched, i.e. almost no emission is observed (see Figure 2). This strong quenching indicates that electron injection from the excited state of **BIM–COOH** into the TiO_2 surface occurs.

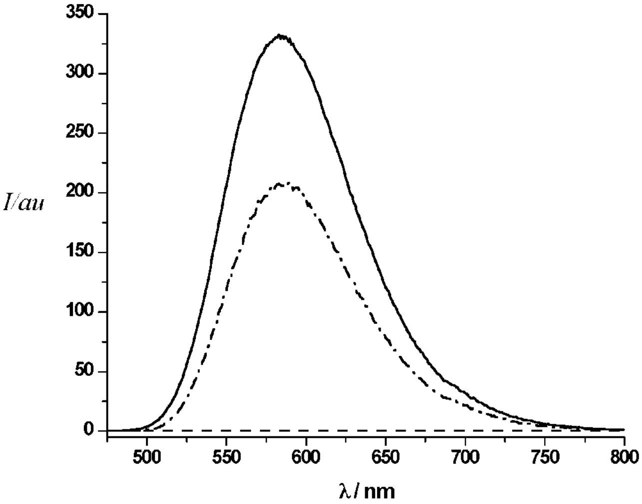


Figure 2. The front-face emission spectra of **BIM–COOH** in acetonitrile (A_{460} = 0.72) (solid), a saturated **BIM** solution (A_{460} = 0.72) (dash-dotted) in acetonitrile, and the dye-coated TiO_2 film **TiO$_2$/BIM–COOH** (A_{460} = 0.73) (dashed); λ_{ex} = 460 nm. The strong quenching of **BIM–COOH** by TiO_2 is clearly visible.

The absorption and emission data are summarized in Table 1.

Nanosecond Transient Absorption Spectroscopy

As expected for a dye covalently linked to TiO_2 through carboxylate groups, possessing suitable excited-state properties, the charge injection is too fast to be detected even with our sub-picosecond equipment. However, the charge recombination reaction is expected to be rather slow because of charge trapping in the semiconductor and nanosecond transient spectroscopy could be a useful tool to monitor such processes.

Nanosecond transient absorption spectra of **BIM–COOH** in acetonitrile and the **BIM–COOH**-modified TiO_2 films were recorded and compared. The transient absorption spectra of **BIM–COOH** and **TiO$_2$/BIM–COOH** are shown in Figures 3 and 4 and 5, respectively.

The transient absorption spectrum of **BIM–COOH** in acetonitrile is quite similar to the transient obtained for bis(indolyl)maleimide (**BIM**). There is a strong ground-state bleaching centered at ca. 450 nm and two broad positive absorption bands around 600 and 750 nm (Figure 3). To record this spectrum, emission correction is used because of the high emission quantum yield of **BIM–COOH**. The decay kinetics of the transient absorption spectra closely matches the lifetime obtained with time-resolved emission spectroscopy (τ = 11 ns).

Two transient absorption traces of **TiO$_2$/BIM–COOH**, recorded at 8 ns and 10 ms after the laser pulse, are depicted in Figure 4 and a combination of traces belonging to the same sample at different time scales are shown in Figure 5. The dye is selectively excited at 450 nm and the absorbance changes are recorded. For the dye adsorbed onto TiO_2, substantially different spectral changes are observed as compared to **BIM–COOH** in solution (Figure 3).

There are three obvious features in the spectrum of the thin film: ground-state bleaching at 487 nm and positive absorption bands at 360 and 650 nm. The intense band at 360 nm, together with the bleaching at 487 nm, decays on a very long time-scale, between 100 µs and 1 ms, with a multiexponential behaviour. The difference in the spectral profiles and the decay kinetics clearly indicate the generation of a long-lived state, which we attribute to a charge-separated state**.** The long-lived 360 nm band has been observed before and is attributed to the injected electron in TiO_2. Wilkinson et al. made similar attributions of a feature at 380 nm, decaying on a microsecond timescale.[21] The broad

Table 1. Photophysical properties of **BIM/BIM–COOH** and **TiO$_2$/BIM–COOH** including emission quantum yields (Φ) and lifetimes (τ).

BIM[a]				BIM–COOH[a]				TiO$_2$/BIM–COOH	
λ_{abs}/nm	λ_{em}[b]/nm	Φ	τ[c]/ns	λ_{abs}/nm	λ_{em}[b]/nm	Φ	τ[c]/ns	λ_{abs}/nm	λ_{em}[b]/nm
366/446	585	0.10	8.5	368/446	584	0.15	11	476	[d]

[a] In acetonitrile. [b] Front-face measurements. [c] λ_{ex} = 450 nm. [d] Too weak signal.

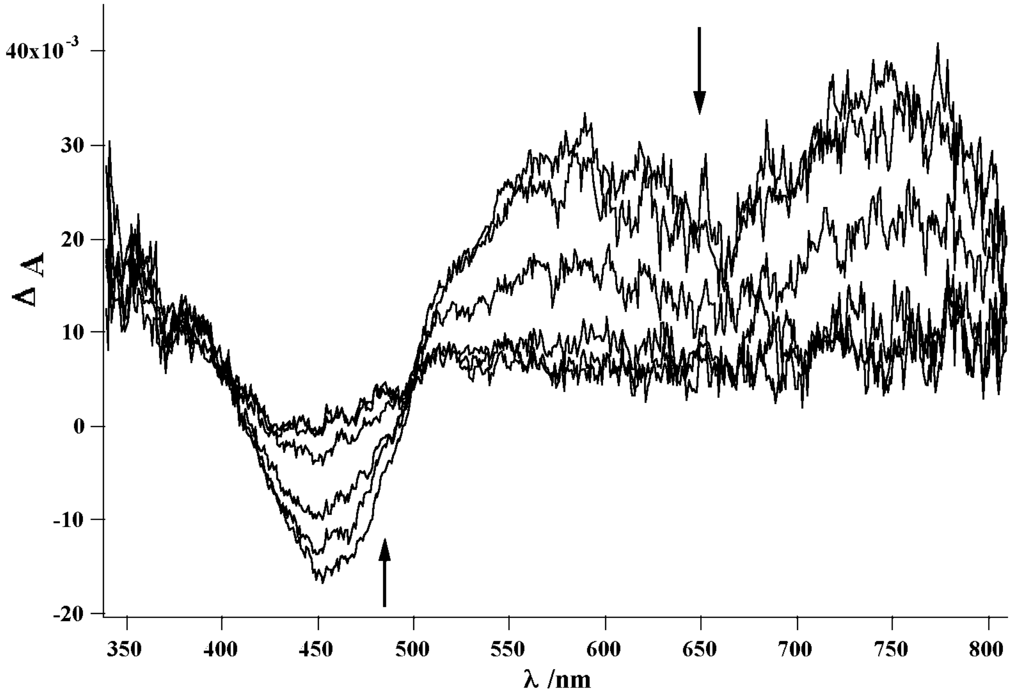


Figure 3. Time-resolved transient absorption spectra of **BIM–COOH** in acetonitrile; incremental time delays: 0, 10, 15, 25, 35 and 45 ns; λ_{ex} = 450 nm/10 Hz.

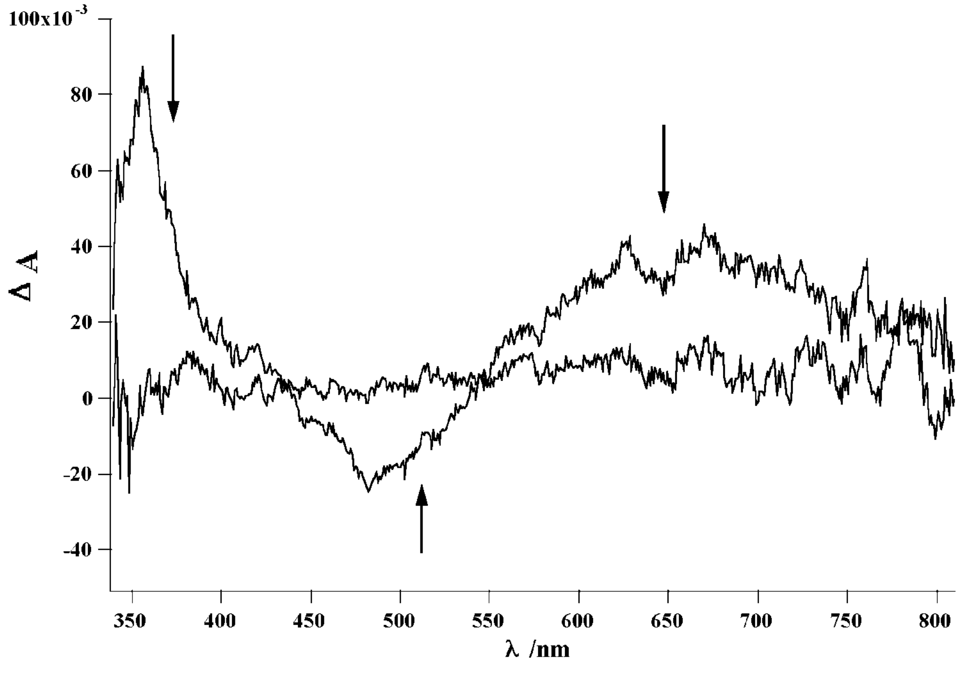


Figure 4. Time-resolved transient absorption spectra of **TiO_2/BIM-COOH**; traces: 8 ns, 10 ms after laser pulse; λ_{ex} = 450 nm; 1 Hz.

transient absorption signal centered at 650 nm, on the other hand, decayed in ca. 150 ns. We believe that this band is due to the radical cation of the dye that is shorter lived then the injected electron. This would imply that another oxidized species, with a low extinction coefficient, is formed as an intermediate state, which than recombines with the electron injected into the conduction band of TiO_2. This could be an oxidized surface or internal state of the TiO_2.

The findings reported in this section together with the strong emission quenching, indicate that electron injection from **BIM–COOH** into the conduction band of TiO_2 occurs on a (sub-)nanosecond timescale and that the interfa-

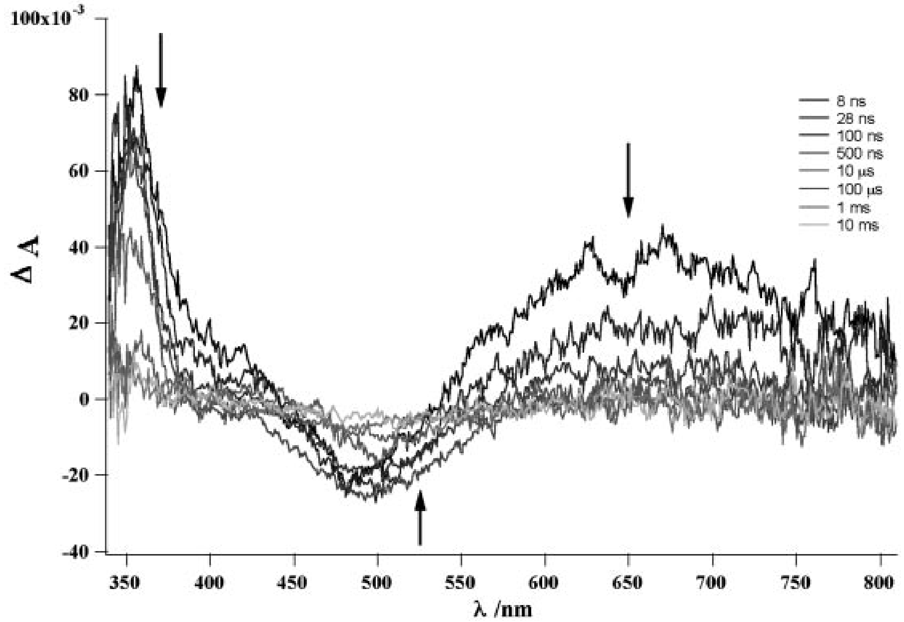


Figure 5. Time-resolved transient absorption spectra of **TiO_2/BIM–COOH**; incremental time delays: 8, 28, 100, 500 ns, 10, 100 µs, 1, 10 ms after laser pulse; λ_{ex} = 450 nm; 1 Hz.

cial charge-separated state has a microsecond lifetime, thus allowing further reaction steps in supramolecular functional systems.

Conclusions

The synthesis of a bis(indolyl)maleimide that is functionalized with two carboxylic acid groups by alkylation of the indole nitrogen atoms is presented and the compound is used as a sensitizer for charge injection into a transparent TiO_2 film.

The absorption and emission spectra of the TiO_2-bound sensitizer **BIM–COOH** are very different from those measured in neat acetonitrile, allowing the direct monitoring of the adsorption of **BIM–COOH** onto TiO_2. The quenching of the sensitizer fluorescence by the TiO_2 surface is almost complete, reflecting the high degree of association between the dye and TiO_2. Comparison of nanosecond transient absorption spectra of **BIM–COOH** in solution and bound to semiconductor surface (**TiO_2/BIM–COOH**) give clear evidence for fast charge injection and a slow recombination reaction, which occurs in the microsecond timescale.

Experimental Section

Materials: All solvents used were spectroscopic grade and purchased from Acros and Merck Uvasol, and used as received unless otherwise indicated. Commercially available deuterated solvents were used as received for the characterization of the compounds. For column chromatography, Merck silica gel 60 was used. TLC was performed on TLC aluminum sheets silica gel 60 F_{254}. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz in $CDCl_3$ and [D$_4$]MeOH. The multiplicity of the ^{13}C signals was determined using the DEPT technique for compound **2** and quoted as (+) for CH_3 or CH, (–) for CH_2, and (C_{quat}) for quaternary carbon atoms. All reagents used were obtained from available commercial sources and used without additional purification unless otherwise indicated. The synthesis of 3,4-bis[1-(carboxymethyl)-3-indolyl]-1*H*-pyrrole-2,5-dione (**BIM–COOH**) was carried out according to the adapted procedure described by Xie et al.[19]

Synthesis

3,4-Bis[1-(ethoxycarbonylmethyl)-3-indolyl]-1*H*-pyrrole-2,5-dione (2): To a stirred solution of **1** (200 mg, 0.59 mmol) in dry THF, sodium hydride (113 mg, 4.71 mmol) was added as a solid. The mixture was stirred for at room temperature 5 min and methyl bromoacetate (0.120 mL, 200 mg, 1.30 mmol) was added. The reaction mixture was stirred at room temperature for 5 h and then filtered through a short silica gel column util the orange fraction of the product was completely eluted by ethyl acetate. The solvent was evaporated in vacuo to give **2**. Yield 160 mg (0.33 mmol, 56%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.19 (s, 3 H), 3.77 (s, 6 H), 4.90 (s, 4 H), 6.71–6.78 (m, 2 H), 6.93–6.99 (m, 2 H), 7.05–7.12 (m, 2 H), 7.14–7.21 (m, 2 H), 7.71 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.22 (+), 47.94 (–), 52.72 (+), 107.12 (C_{quat}), 108.95 (+), 120.48 (+), 122.43 (+), 122.71 (+), 126.36 (C_{quat}), 127.24 (C_{quat}), 132.16 (+), 136.46 (C_{quat}), 168.35 (C_{quat}), 172.32 (C_{quat}) ppm.

3,4-Bis[1-(carboxymethyl)-3-indolyl]-1*H*-furan-2,5-dione (3): A solution of **2** (177 mg, 0.36 mmol) in ethanol (5 mL) was treated with 5 N KOH (3 mL) and stirred at 50–60 °C for 12 h. The reaction mixture was cooled to room temperature, diluted with brine (15 mL) and washed with ethyl acetate (2 × 15 mL). The water layer was acidified with 5 N HCl, and the product was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was evaporated in vacuo to provide the anhydride **3** as a red solid (127 mg, 78%). ^{1}H NMR ([D$_4$]MeOH, 300 MHz): δ = 5.06 (s, 4 H, CH_2), 6.71 (t, 2 H, *J* =

7.5 Hz), 6.91 (d, 2 H, 7.5 Hz), 7.07 (t, 2 H, 7.5 Hz), 7.31 (d, 2 H, 7.5 Hz), 7.89 (s, 2 H) ppm.

3,4-Bis[1-(carboxymethyl)-3-indolyl]-1*H*-pyrrole-2,5-dione (BIM–COOH): The anhydride **3** (137 mg, 0.31 mmol) and ammonium acetate (2 g, 26 mmol) were heated as a melt at 130 °C for 20 h. The reaction mixture was diluted with brine (10 mL) and extracted with ethyl acetate (10 × 10 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (SiO_2; ethyl acetate/acetic acid, 10:1) and yielded imide **BIM–COOH** (62 mg, 0.14 mmol, 45%). ^1H NMR ([D$_4$]MeOH, 300 MHz): δ = 5.02 (s, 4 H), 6.65 (t, 2 H), 6.89 (d, 2 H), 7.01 (t, 2 H), 7.25 (d, 2 H), 7.76 (s, 2 H) ppm.

Instrumental

Steady-State Spectroscopy: Electronic absorption spectra were recorded with a Hewlett Packard UV/Vis diode array 8453 spectrophotometer. Steady-state emission spectra were obtained with a SPEX 1681 Fluorolog spectrofluorimeter equipped with two double monochromators (excitation and emission). To compare the sensitized films with neat solutions, the emitted light from the samples was monitored from the front face compartment of the instrument. Emissions are not corrected. The emission quantum yield measurement for **BIM–COOH** in acetonitrile was performed using the optically dilute technique[22] with quinine bisulfate solution in 1 N H_2SO_4 solution as reference.[23]

Time-Resolved Spectroscopy: In nanosecond pump-probe experiments for excitation a (coherent) Infinity Nd:YAG-XPO laser was used. The laser illuminated a slit of 10 × 2 mm. Perpendicular to this, the probe light provided by an EG&G (FX504) low-pressure xenon lamp, irradiated the sample through a 1 mm pinhole. The overlap of the two beams falls within the first 2 mm of the cell after the slit. The probe light from both the signal and the reference channels is then collected in optical fibers which are connected to an Acton SpectraPro-150 spectrograph which is coupled to a Princeton Instruments ICCD-576-G/RB-EM gated intensified CCD camera. Using a 5 ns gate this camera simultaneously records the spectrally dispersed light from both optical fibers on separate stripes of the CCD. The coated TiO_2 film was placed diagonally in a sample holder and the excitation beam was directed at 45° to the film surface.

Acknowledgments

B. K. thanks the Fonds der Chemische Industrie for support. Financial support from the DPI (Dutch Polymer Institute) for M. Z. and from the UvA (Universiteit van Amsterdam) is gratefully acknowledged. We thank Dr. Claudia Longo for her assistance in the preparation of the TiO_2 films.

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Received: January 17, 2005