Photoinduced Electron and Energy Transfer Processes in Non-convalently Assembled Imide Systems

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Chapter 4

Part B

Towards Immobilized Photocatalysts on Semiconductor Surfaces – Sensitization of Nanocrystalline TiO$_2$ Films with Carboxy-functionalized Bisindolylmaleimide

Abstract

The synthesis and immobilization on a semiconductor surface of an indolylmaleimide that is functionalized with two carboxylic acid groups by alkylation of the indole nitrogens is presented. The compound, 3,4-Bis[1-(carboxymethyl)-3-indolyl]-1H-pyrrole-2,5-dione is a model compound for the development of photocatalysts immobilized on surfaces. Its absorption and emission spectra on TiO$_2$ are substantially changed as compared to the measurements performed in neat acetonitrile. 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 sensitizer in neat acetonitrile shows a transient absorption spectrum that decays on the nanosecond timescale, the transient absorption spectra of the sensitized TiO$_2$ film shows a maximum 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 results open up new pathways for the development of immobilized photocatalytic systems for oxidative conversions.
4.1 Introduction

The main reason for the current interest in supramolecular chemistry is its potential application in nano-scale molecular devices that are capable of mimicking, at the molecular level, functions normally performed by natural systems or by artificial macroscopic devices. In many of these molecular devices, a fundamental role is played by light and the device function relies on energy and/or electron-transfer processes taking place between the molecular components within the supramolecular structure with controlled rates and in an appropriate sequence. To achieve active functionalities in these artificial light-driven devices is not a trivial task since a proper organization of the systems and e.g. a long-lived charge separation is needed. Incorporation of the active components on a solid support is the next goal in order to achieve a “real” device. 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 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. Nanostructured semiconductor films have been applied as antibacterial coatings and for the light-assisted degradation of organic pollutants. 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$_2$ 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. There are several examples showing the ability of TiO$_2$ surfaces modified with a range of organic and inorganic molecular components, to act as efficient photovoltaic cells.

The self-cleaning properties of TiO$_2$ surfaces under UV irradiation already indicate that this material is a good candidate for use as an active support material in photocatalytic oxidative conversions. To introduce reaction selectivity, tempering of oxidative power can be achieved by visible light sensitization of the semiconductor surface, thus reducing the excess energy. By using a supramolecular approach, this
sensitization can be accompanied by introduction of a binding site for a substrate. In this way the sensitizer also acts as a supramolecular mediator of oxidative reactivity.

As discussed in Chapter 3 and 4 part A, indolylmaleimide systems are interesting chromophores that can complex via a coordinative bond with metallo-cycles such as Zn (II)-cyclen. Metal porphyrins are other candidates that can be used in this coordination. Through the complex formation with the metallo-macrocycle a binding site is incorporated into the indolylmaleimide systems, and in this way a versatile photocatalyst can be build up, if the indolylmaleimide systems can be attached to a surface. This idea is depicted in Scheme 1, where the immobilized chromophore, indolylmaleimide, binds a substrate through its metallo-macrocycle and a selective oxidation is performed.

**Scheme 1.** Schematic illustration of the photocatalysis concept of immobilized indolylmaleimide on a TiO$_2$ film and the assembly of metallo-macrocycle substrate.

Thus we envisage the design, synthesis and investigation of self-organized aggregates with novel structural, photophysical and electrochemical properties. The self-assembling process will occur via the coordinative bond between the maleimide and metallo-macrocyclic compound. The large tunability in terms of redox potential, excited state properties and binding strengths employing a variety of metal containing azamacrocyclic complexes and imide derivatives will allow the construction of different assemblies with well-defined properties and addressable photoinduced
functions. In particular, the focus will be on photoinduced processes such as electron transfer reactions in extended ordered structures that are non-covalently bound. The self-assembly process of the building blocks in different solvents (particular attention can be devoted to water), will be conveniently monitored by the changes of the spectroscopic properties of the single components. With the results obtained, we aim to understand the different parameters that control the formation of two and three-dimensional organized assemblies. The use of functionalized imides suitable to bind to surfaces will allow organization of the systems and investigations in the condensed phase. This will provide an important tool to test the potential of these aggregates as light driven photocatalysts.

The first step in this direction is the attachment of an indolylmaleimide derivative to a semiconductor surface, and to study the sensitization of (or electron injection into) the surface. This relates strongly to the research on photovoltaic devices, where TiO₂ is used for the development of dye sensitized solar cells.

Grätzel and co-workers⁵ and several other groups⁸,⁹,¹²,¹¹ have studied nanocrystalline TiO₂ surfaces modified with ruthenium polypyridyl 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 1991,⁴ and presently the certified efficiency is over 10%.¹¹ These dyes contain carboxy, phosphate or ester groups, which serve to attach the compound covalently to the oxide surface to establish a good electronic coupling between the adsorbed species and the TiO₂ surface.²²,²³ Quantum mechanical calculations and infrared spectroscopy provided evidence that carboxy compounds are attached to the oxide surface by carboxylate bridges.⁶ to either hydroxyl groups or Ti (IV) ions.

The electronic properties of solid materials are described in terms of the band gap, which is the energy needed to promote an electron from the valence band to the conduction band. Besides thermal activation, population of the valence band can also be obtained by optical means. Semiconductors absorb radiation only if its energy matches the band gap. The photosensitization of wide band gap semiconductors such as TiO₂ by adsorbed dyes has been studied since the late 1960s. Photoexcitation of the sensitizer molecules attached to the surface results in the injection of an electron into the conduction band of the oxide (Scheme 2).
Scheme 2. Illustration of the photoinduced processes expected to occur for a TiO$_2$-attached dye/sensitizer.

Scheme 2 outlines the fundamental photophysical properties expected for a dye immobilized as a monolayer on a TiO$_2$ surface. After excitation of the dye, the electron can either be deactivated via emission, ($k_1$) that can also be observed in solution), by non-radiative interaction with its surrounding, or by injection into the semiconductor surface with a rate $k_2$. In the study of Willig and coworkers$^{24}$, 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 of 1200 nm was observed. The rise time of this band ($< 25$ fs)$^{24}$ can be taken as an indication for the rate of 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 ($k_3$). Charge separation needs to be both fast and long-lived. It is of great interest to develop sensitizer systems for which the value of the electron injection, $k_3$, is high and that of $k_3$ low. Interfacial charge separation at dye sensitized TiO$_2$ surfaces has been the subject of many studies.$^{10,25}$ In case of ruthenium polypyridyl complexes, it has been known that the injection of electrons into nanocrystalline TiO$_2$ surfaces is in the sub-picosecond range. The recombination process is several orders of magnitude slower, thus resulting in long-lived charge separation.

In this chapter, the synthesis of bis-carboxy-functionalised N-H bisindolylmaleimide, 3,4-Bis[1-(carboxymethyl)-3-indolyl]-1H-pyrrole-2,5-dione
Sensitization of Nanocrystalline TiO$_2$ Films with Carboxy-functionalized Bisindolylmaleimide (BIM-COOH) is presented. The aim is to attach this compound to a TiO$_2$ surface through the carboxy-functions (TiO$_2$/BIM-COOH) and to investigate the ability to use BIM-COOH as a potential sensitizer for TiO$_2$. For this UV-Vis absorption, steady state and time-resolved emission and nanosecond transient absorption spectra were recorded to obtain information on the electron injection and charge recombination. The compounds studied are depicted in Scheme 3.

![Scheme 3](image)

**Scheme 3.** The compounds studied in this Chapter BIM-COOH and TiO$_2$/BIM-COOH. The reference compound BIM (see Chapter 4A) is also shown.

### 4.2 Results and Discussion

#### 4.2.1 Synthesis of BIM-COOH

In order to functionalize the bisindolylmaleimide on the indole nitrogens only, the nitrogen of the maleimide unit, that is the most basic one, must be protected. For this purpose, N-methyl-bisindolylmaleimide ($\text{1}$) was chosen as the starting compound for the synthesis and prepared according to procedure published by Steglich *et al.*

3,4-Bis[1-(carboxymethyl)-3-indolyl]-1H-pyrrole-2,5-dione (BIM-COOH) was prepared according to the adapted procedure described by Xie *et al.* (see Scheme 4) Methyl bromoacetate was reacted with 1 to obtain the ester-functionalized indolylmaleimide (2) (Scheme 4). Compound 2 was treated with 5 N KOH to convert the ester groups into the acid. The N-methyl maleimide unit was also converted into the anhydride in this step (3). Heating compound 3 in an excess amount of ammonium acetate resulted in the desired compound, BIM-COOH. The detailed synthetic
4.2 Results and Discussion

procedures, including purification and characterization, are given in the experimental section.

\[
\text{Scheme 4. Schematic procedure for the synthesis of BIM-COOH.}
\]

4.2.2 Preparation of BIM-COOH coated TiO\textsubscript{2} surface

A small aliquot of TiO\textsubscript{2} suspension (Ti nanoxide-HT, 9 nm particle size, Solaronix) was spread onto a conductive glass slide (Philips), coated with indium-tin oxide (ITO), using a glass rod with adhesive tape as spacer (thickness ~42 \textmu m). The layer thus formed is dried in air at room temperature for 10 min. The film is heated at 400-450 °C for 30 min. in an oven. As a result of the heating process, a transparent colourless film is obtained. The layers are kept in the dark and are dried in an oven at 150 °C for 30 min. prior to use. In order to coat the TiO\textsubscript{2} surfaces with the dye, the layers are immersed in a 1 x 10\textsuperscript{-4} M solution of BIM-COOH, in absolute ethanol overnight. Then the coated layers are rinsed with ethanol and dried in air. After the coating the transparent red films are ready for spectroscopic studies.
4.2.3 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 $\pi-\pi^*$ transitions from $S_0$ to the $S_1$ and $S_2$ states, respectively. As reported in Chapter 4A, functionalization of the indole moieties does not change the UV-Vis spectrum.

![Absorption Spectra of BIM and BIM-COOH](image)

**Figure 1.** The UV-Vis absorption spectra of BIM-COOH (solid), BIM (dash dotted) in acetonitrile, 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, complexes lacking such groups, e.g. compound 2 (having ester functions instead of acid groups, see Scheme 4), do not adsorb on to 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 observations
indicate a strong electronic coupling of the two carboxylate units with the TiO$_2$ surface. The visible absorption band, centered at 476 nm (see Figure 1) enables selective excitation of the BIM-COOH chromophore.

### 4.2.4 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 of BIM and BIM-COOH in solution is characterized by a high quantum yield and a maximum at 584 nm (see also Chapter 4A).

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 is a very good indication for electron injection from the excited state of BIM-COOH into the TiO$_2$ surface.

![Figure 2](image)

**Figure 2.** The front-face emission spectra of BIM-COOH ($A_{460}=0.72$) (solid), BIM ($A_{460}=0.56$) (dash dotted) in acetonitrile, and the dye-coated TiO$_2$ film, TiO$_2$/BIM-COOH ($A_{460}=0.73$) (dashed), $\lambda_{ex}=460$ nm.

Absorption and emission maxima ($\lambda$) for BIM and BIM-COOH, as well as for TiO$_2$/BIM-COOH are summarized in Table 1. For BIM and BIM-COOH the emission quantum yields ($\Phi$) and lifetimes obtained in acetonitrile are also reported.
Table 1. Absorption, Emission and Emission Quantum Yields ($\Phi$) and Lifetimes ($\tau$) of BIM, BIM-COOH and TiO$_2$/BIM-COOH.

<table>
<thead>
<tr>
<th></th>
<th>BIM$^a$</th>
<th>BIM-COOH$^a$</th>
<th>TiO$_2$/BIM-COOH</th>
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<tr>
<td>$\lambda_{obs}$</td>
<td>(nm)</td>
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<tr>
<td>$\lambda_{em}^b$</td>
<td>(nm)</td>
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<tr>
<td>$\Phi$</td>
<td>(ns)</td>
<td>(ns)</td>
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<tr>
<td>$\tau^c$</td>
<td>(ns)</td>
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<td>366.44</td>
<td>585</td>
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<td>476</td>
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<td>55</td>
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<td>11</td>
</tr>
<tr>
<td>0.10</td>
<td>11</td>
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</tbody>
</table>

$^a$in acetonitrile, $^b$front-face measurements, $^c$ $\lambda_{obs} = 450$ nm, $^d$very weak signal.

4.2.5 Nanosecond Transient Absorption Spectroscopy

As expected for a dye covalently linked to TiO$_2$ via carboxylate groups, 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 into the semiconductor and nanosecond transient spectroscopy could be a useful tool to monitor such processes.

Figure 3. Time-resolved transient absorption spectra of BIM-COOH in acetonitrile, incremental time delays: 0, 10, 15, 25, 35 and 45 ns. $\lambda_{obs} = 450$ nm, 10 Hz.
Nanosecond transient absorption spectra of BIM-COOH in acetonitrile and the BIM-COOH-modified TiO₂ films were recorded and compared. The transient absorption spectra of BIM-COOH and TiO₂/BIM-COOH are depicted in Figure 3 and 4, respectively.

The transient absorption spectrum of BIM-COOH in acetonitrile is quite similar to the transient obtained for N-H bisindolylmaleimide (BIM in Chapter 4A). 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).

![Figure 4](image)

**Figure 4.** Time-resolved transient absorption spectra of TiO₂/Bis-COOH, traces: 8 ns, 10 ms after laser pulse, λₘₐₓ = 450 nm, 1 Hz.

Two transient absorption traces of TiO₂/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 TiO₂, substantially different spectral changes are observed as compared to BIM-COOH in solution (Figure 3).
Figure 5. Time-resolved transient absorption spectra of TiO$_2$/BIM-COOH, incremental time delays: 8, 28, 100, 500 ns, 10, 100 µs, 1 and 10 ms after laser pulse, $\lambda_{ex} = 450$ nm, 1 Hz (See Appendix for colour representations).

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 decay on a very long time-scale, between 100 µs and 1 ms, with a multi-exponential behaviour. A kinetic trace of the band decaying at 360 nm, which is obtained from Figure 5, is depicted in Figure 6. 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 microsecond time-scale. The broad 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 TiO₂. This could be an oxidized surface or internal state of the TiO₂.

![Graph](image.png)

**Figure 6.** Kinetic trace of TiO₂/BIM-COOH probed at 360 nm.

The findings reported in this section together with the strong emission quenching, indicate that electron injection from BIM-COOH into the conduction band of TiO₂ occurs on a (sub-)nanosecond timescale and that the interfacial charge-separated state has a microsecond lifetime, thus allowing further reaction steps in supramolecularly expanded systems.

### 4.3 Conclusions

The synthesis of a bisindolylmaleimide that is functionalized with two carboxylic acid groups by alkylation of the indole nitrogens is presented and the compound is used as a sensitizer for charge injection into a transparent TiO₂ film.

The absorption and emission spectra of the TiO₂-bound sensitizer BIM-COOH are very different from those measured in neat acetonitrile, allowing the direct monitoring of the adsorption of BIM-COOH onto TiO₂. The quenching of the sensitizer fluorescence by the TiO₂ surface is almost complete, reflecting the high degree of association between the dye and TiO₂. Comparison of nanosecond transient absorption spectra of BIM-COOH in solution and bound to semiconductor surface (TiO₂/BIM-COOH) give clear evidence for fast charge injection and a slow recombination reaction, which occurs in the microsecond time scale. Work is in progress to understand whether the system can be used as a photocatalyst and if the
imide function can still bind a metallo-macrocycle once the molecule is attached to the surface.

4.4 Experimental Section

4.4.1 Materials

All solvents used are 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 F254. 

$\text{H}$ NMR spectra were recorded at 300 MHz and $\text{C}$ NMR spectra at 75 MHz in CDCl$_3$ and methanol-d$_4$. The multiplicity of the $\text{C}$ signals was determined using the DEPT technique for compound 2 and quoted as (+) for CH$_3$ or CH, (-) for CH$_2$, and ($C_{\text{quat}}$) for quaternary carbons.

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]-1H-pyrrole-2,5-dione (BIM-COOH) was prepared according to the adapted procedure described by Xie et al. and has been synthesized and characterized with the help of Dr. Valery N. Kozhevnikov at the University of Regensburg (Germany).

4.4.2 Synthesis

3,4-Bis[1-(ethoxycarbonylmethyl)-3-indolyl]-1H-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 5 minutes at room temperature and methyl bromoacetate (0.120 ml, 200 mg, 1.30 mmol) was added. The reaction mixture was stirred for 5 hours at room temperature and then filtered through a short silica gel column till the orange fraction of the product was completely eluted by ethyl acetate. The solvent was evaporated in vacuum to give 2. Yield 160 mg, (0.33 mmol, 56%). $\text{H}$ NMR (CDCl$_3$, 300 MHz): $\delta$ 3.19 (s, 3H), 3.77 (s, 6H), 4.90 (s, 4H), 6.71-6.78 (m, 2H), 6.93-6.99 (m, 2H), 7.05-7.12 (m, 2H), 7.14-7.21 (m, 2H), 7.71 (s, 2H). $\text{C}$ NMR (CDCl$_3$, 75 MHz): $\delta$ 24.22, 47.94, 52.72, 107.12, 108.95, 120.48, 122.43, 122.71, 126.36, 127.24, 132.16, 136.46, 168.35, 172.32. $\text{C}$ NMR (CDCl$_3$, 75 MHz, DEPT 135): $\delta$ 24.22, 47.94(-), 52.72, 108.95, 120.48, 122.43, 122.71, 132.16.

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3,4-Bis[1-(carboxymethyl)-3-indolyl]-1H-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 hours. The reaction mixture was cooled to room temperature, diluted with brine (15 ml) and washed with ethyl acetate (2 x 15 ml). The water layer was acidified with 5 N HCl, and the product was extracted by ethyl acetate (3 x 15 ml). The organic layer was dried over Na₂SO₄ and the solvent was evaporated in vacuum to provide the anhydride 3 as a red solid (127 mg, 78%). ¹H NMR (methanol-d₄, 300 MHz): δ 5.06 (s, 4H, CH₂), 6.71 (t, 2H, J=7.5Hz), 6.91 (d, 2H, 7.5Hz), 7.07 (t, 2H, 7.5Hz), 7.31 (d, 2H, 7.5Hz), 7.89 (s, 2H).

3,4-Bis[1-(carboxymethyl)-3-indolyl]-1H-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 hours. The reaction mixture was diluted with brine (10 ml) and extracted with ethyl acetate (10 x 10 ml). The organic layer was dried over Na₂SO₄ and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (SiO₂, ethyl acetate/acetic acid 10:1 as eluent) and yielded imide, BIM-COOH (62 mg, 0.14 mmol, 45%). ¹H NMR (methanol-d₄, 300 MHz): δ 5.02 (s, 4H), 6.65 (t, 2H), 6.89 (d, 2H), 7.01 (t, 2H), 7.25 (d, 2H), 7.76 (s, 2H).

4.5 Instrumentation

4.5.1 Steady State Spectroscopy

Electronic absorption spectra were recorded on a Hewlett Packard UV-VIS, diode array 8453 spectrophotometer.

Steady state emission spectra were obtained from 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 with quinine bisulfate solution in 1 N H₂SO₄ solution as reference.

4.5.2 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 x 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 two millimeter 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.

4.6 References


