

# Controlling Dye (Merocyanine-540) Aggregation on Nanostructured TiO<sub>2</sub> Films. An Organized Assembly Approach for Enhancing the Efficiency of Photosensitization

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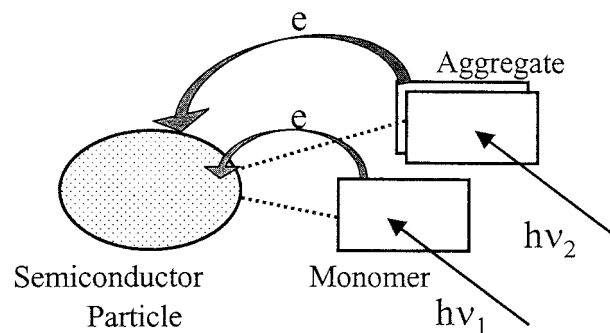
The anionic cyanine dye Merocyanine 540 (MC540) dissolved in Aerosol-OT (AOT) solutions of heptane and toluene possesses a significantly higher fluorescence quantum yield and excited singlet lifetime than the acetonitrile solutions of the dye. The difference in the photophysical properties observed upon incorporation of the dye into the AOT micelles is attributed to the decrease in the photoisomerization efficiency. The presence of AOT also controls the aggregation and photosensitization behavior of MC540 adsorbed onto TiO<sub>2</sub> semiconductor nanoparticles. MC540 adsorbed onto nanostructured TiO<sub>2</sub> films from acetonitrile solutions contains both the aggregated and monomeric forms of the sensitizer, while the dye-modified films obtained from AOT/heptane solutions contain mainly the monomeric form of the sensitizer. Significant enhancement in the photocurrent generation efficiency has been achieved in photoelectrochemical cells using the AOT encapsulated dye films. An electroactive polymer (poly(4-vinylpyridine)) film cast on the dye-modified TiO<sub>2</sub> electrode has been found to be effective in promoting charge mediation and minimizing dye desorption from the electrode surface. The incident photon-to-photocurrent generation efficiency (IPCE) exhibited by the monomeric form (~40%) is nearly five times greater than the corresponding efficiency of the aggregate form (~8%). The beneficial aspects of incorporating dyes in organized assemblies for the purpose of suppressing nonradiative decay of the excited-state sensitizer and minimizing the aggregation effects on semiconductor surfaces are discussed.

## Introduction

Spectral sensitization of wide band-gap semiconductors in photoelectrochemical cells is an attractive approach for conversion of the visible part of solar energy into electricity (see, for example, 1–4). Nanoporous semiconductor (e.g., SnO<sub>2</sub>, TiO<sub>2</sub>) films which are designed to have monolayer coverage of sensitizing dye molecules facilitate appreciable absorption of the incident light.<sup>4–6</sup> Power conversion efficiencies greater than 10% have been achieved with ruthenium(II) polypyridyl complexes as sensitizers. Although several organic dyes possessing the necessary redox and excited-state characteristics have been considered as photosensitizers, the observed photocurrent efficiencies have been generally very low.<sup>7–13</sup> A major factor responsible for the low photoconversion efficiency of an organic dye-sensitized solar cell is the formation of dye aggregate on the semiconductor surface. Such an aggregation effect can bring about significant changes in the absorption and photosensitizing properties of the sensitizing dye molecules.<sup>10,12</sup> Several strategies have been considered for controlling the aggregation behavior of dyes on semiconductor surfaces. Willner et al. investigated the use of  $\beta$ -cyclodextrin-encapsulated dye molecules for the photosensitization of TiO<sub>2</sub>.<sup>14</sup> Other methods have included the structural modification of the dye molecules and the use of inorganic additives.<sup>15,16</sup>

Self-aggregation of amphiphilic molecules can generate microdomains which can systematically bind organic molecules

SCHEME 1. Participation of Excited Monomer and Aggregate Forms of the Dye Molecule in Sensitizing a Semiconductor Particle



by electrostatic or hydrophobic interactions providing an ordered assembly of molecules in liquid media. We have recently shown that the self-aggregation behavior of Aerosol-OT in heptane and toluene can be utilized to control the aggregation and excited-state properties of thionine.<sup>17</sup> The possible use of dye aggregates as light-harvesting antennae by absorbing the light in different spectral regions and the triplet energy transfer to monomeric thionine was demonstrated. Alternatively, these dye aggregates along with monomer can directly participate in the charge injection process (Scheme 1).

While one can consider using different absorption bands of monomer and aggregates to harvest a broader range of visible light, it is necessary to elucidate the photochemical processes that influence the charge injection process of different molecular aggregates on semiconductor surfaces. The question that needs to be addressed is whether the excited-state dye aggregates can efficiently transfer charge into the semiconductor particle. If

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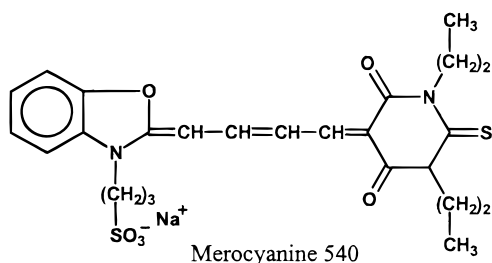
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not, how might one discourage the aggregation of dye molecules on the semiconductor surface? Thus, a direct comparison of the photosensitizing behavior of aggregate and monomer forms of the dye on semiconductor surfaces is important for the utilization of organic dyes in photoelectrochemical solar cells. By employing a surfactant, Aerosol-OT (AOT), we have now succeeded in controlling the aggregation of a sensitizing dye, Merocyanine 540 (MC540), on nanostructured TiO<sub>2</sub> films.

MC540, an anionic cyanine dye, is used extensively in a number of areas such as photographic sensitizers, filters, textiles, chemotherapy, and more recently as a sensitizer in photoelectrochemical cells for solar energy conversion.<sup>18</sup> The photophysical properties of MC540 have been investigated in a variety of homogeneous<sup>19–24</sup> and microheterogeneous media including micelles and vesicles.<sup>25,26</sup> The enhanced photostability and fluorescence yield of the dye in heterogeneous media have been attributed to the increased microviscosity of the medium. A restriction on the excited-state rotation in the heterogeneous environment makes the photoisomerization event less efficient. The fluorescence yield of MC540 is also highly dependent on the polarity of the solvent, and increases with decreasing solvent polarity.<sup>22,23</sup> The experimental results that elucidate photophysical properties of MC540 in AOT/heptane and acetonitrile solutions and photosensitization aspects of the MC540 adsorbed on nanostructured TiO<sub>2</sub> films are presented here.



## Experimental Section

**Materials and Methods.** Aerosol-OT and Merocyanine 540 (MC540) were obtained from Aldrich Chemicals. All other chemicals and solvents were analytical reagents of the highest available purity. The surfactant solution was prepared by dissolving 12.8 g of AOT in 500 mL of heptane or toluene ( $5.8 \times 10^{-2}$  M). A known amount of MC540 (6–8 mg) was added to 100 mL of the AOT solution and stirred using a magnetic stirrer. With continued stirring the color of the solution deepened. Stirring continued for 2 days to ensure complete dissolution of the dye. Please note that the dissolution was carried out in the absence of water. Absorption spectra were recorded using a Shimadzu 3101 spectrophotometer.

**Laser-Flash Photolysis Experiments.** Nanosecond laser flash photolysis experiments were performed with a Quanta Ray Model CDR-1 Nd: YAG system using 532 nm (second harmonic) laser pulse ( $\sim 6$ -ns-laser width) for excitation.<sup>27</sup> The laser output was suitably attenuated to less than 10 mJ/pulse and defocused to minimize multiphotonic processes. The experiments were performed using a rectangular quartz cell of 6-mm path length with a right angle configuration between the direction of laser excitation and analyzing light. The photomultiplier output was digitized using a Tektronix 7912 AD programmable digitizer.

Picosecond laser flash photolysis experiments were performed using 532 nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (output 2–3 mJ/pulse, pulse width  $\sim 18$ ps). The white continuum picosecond

probe pulse was generated by passing the fundamental output through a D<sub>2</sub>O/H<sub>2</sub>O solution. The output was fed to a spectrograph (HR-320, ISDA Instruments, Inc.) with fiber optic cables and was analyzed with a dual diode array detector (Princeton Instruments, Inc.) interfaced with an IBM-AT computer. The details of the experimental setup and its operation are described elsewhere.<sup>28,29</sup> Time zero in these experiments corresponds to the end of the excitation pulse. The lifetimes and rate constants reported in this study have an experimental error of  $\pm 5\%$ .

Pulse radiolysis experiments were performed using 2-ns pulses of 8 MeV electrons from a Model Titan Beta-8/16-1S Electron Linear Accelerator.<sup>30,31</sup> Dosimetry was based on the oxidation of SCN<sup>−</sup> to (SCN)<sub>2</sub><sup>•</sup> (*G* value = 6 in N<sub>2</sub>O-saturated aqueous solutions). The solutions were saturated with nitrogen and flowed continuously through the sample cell during radiolysis.

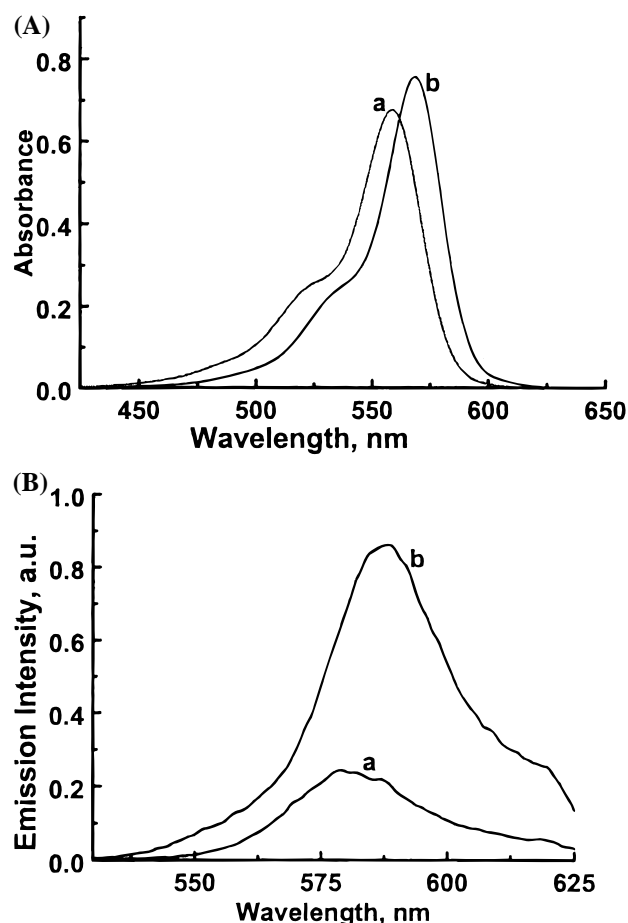
**Preparation of Semiconductor Particulate Films.** The procedure for preparing nanostructured TiO<sub>2</sub> film was similar to the one proposed earlier.<sup>11,32,33</sup> A small aliquot (usually 0.2–0.3 mL) of the colloidal TiO<sub>2</sub> suspension was applied to a conducting surface of  $0.8 \times 5$  cm<sup>2</sup> of optically transparent electrode (OTE) and was dried in air on a warm plate. The electrodes were further annealed at 673 K for 1 h. The typical thickness of the semiconductor particulate film was  $\sim 2$ – $4$   $\mu$ m. These electrodes were further modified with MC540 by dipping them in acetonitrile or AOT/heptane solutions containing the dye.

**Electrochemical and Photoelectrochemical Measurements.** These measurements were carried out with a standard three-compartment cell consisting of a working electrode and Pt wire gauze counter electrode. All photoelectrochemical measurements were carried out in 0.1 M LiI in acetonitrile. Photocurrent measurements were carried out with a Kiethley model 617 programmable electrometer. A collimated light beam from a 150 W xenon lamp with a 400 nm cutoff filter was used for excitation of the dye-modified electrode. A Bausch and Lomb high-intensity grating monochromator was introduced into the path of the excitation beam for selecting wavelengths.

## Results and Discussion

**Photophysical Properties of Merocyanine 540 in Acetonitrile and AOT/Heptane Solutions.** *a. Absorption and Emission Spectra.* The absorption spectra of merocyanine dyes in water have been observed to be dependent on the concentration of the dye, with the absorbance ratio,  $A_{\text{monomer}}/A_{\text{dimer}}$  decreasing with increasing dye concentration.<sup>34</sup> This behavior arises mainly from the fact that the dye readily undergoes aggregation at higher dye concentrations. This effect is significantly enhanced in colloidal TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> suspensions as the adsorption of dyes facilitate aggregation. The low- and high-energy bands in the absorption spectrum have been attributed to the monomeric and dimeric forms of the dye in solution and in films.

The absorption and fluorescence emission spectra of MC540 in acetonitrile and in AOT/heptane solutions are shown in Figure 1. MC540 has a sharp absorption band in the visible with a maximum at 555 and 565 nm in acetonitrile and AOT/heptane, respectively. The shoulder around 525 nm is indicative of the presence of dye aggregates (H-type) in these solutions. The maximum observed in both absorption and emission spectra in AOT/heptane is slightly red-shifted (5–10 nm) compared to that in acetonitrile. This red shift arises from the micellar environment that provides a relatively nonpolar medium. MC540 is a negative solvatochromic dye and therefore exhibits a red-

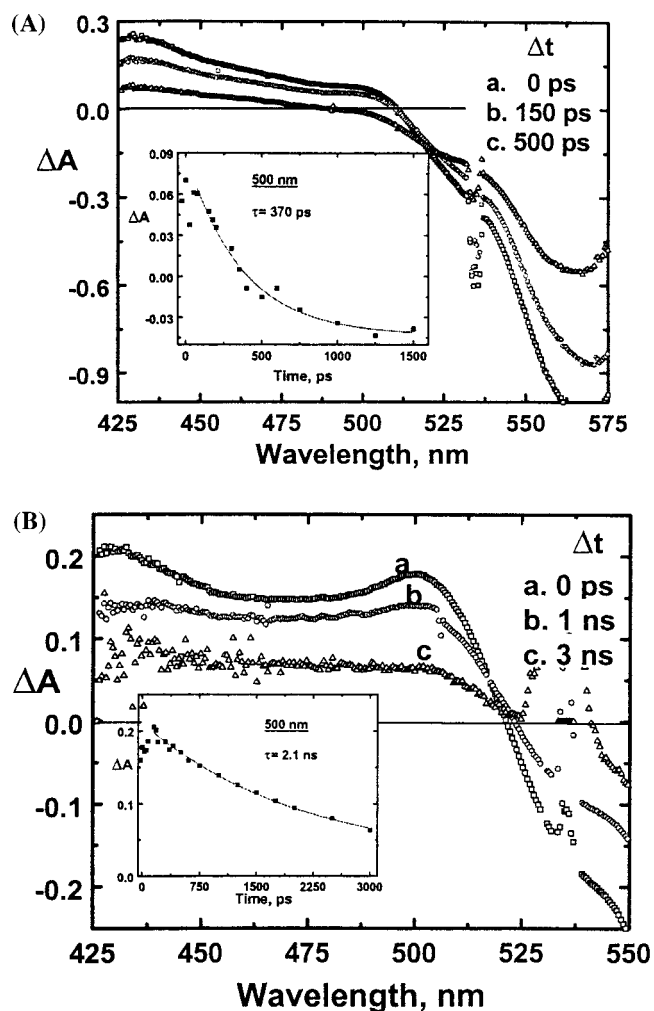


**Figure 1.** (A) Absorption and (B) fluorescence emission spectra of MC540 in acetonitrile (3  $\mu$ M) and in AOT/heptane (6  $\mu$ M) solutions. The absorption at the excitation wavelength (515 nm) was matched for recording emission spectra.

shift.<sup>23</sup> A more detailed analysis of the solvent polarity-dependent absorption and emission maxima has been presented earlier.<sup>22,23</sup>

A more pronounced effect of the micellar medium is seen in the fluorescence yield of MC540 in AOT/heptane solutions. A 4-fold increase in the fluorescence yield is seen as a result of encapsulation in AOT. As shown earlier,<sup>20</sup> photoisomerization is one of the major decay pathways available for the excited singlet in solvents such as alcohol or acetonitrile. In neat ethanol, for example, the contribution of photoisomerization is as high as 66%. In the excited state the dye not only rotates, but also undergoes trans–cis isomerization about the central C=C bond of the polymethine chain and this is accompanied by intramolecular charge transfer.<sup>22</sup> The zwitterionic nature of the excited-state thus favors stronger interaction with the solvent.

The enhanced fluorescence yield observed in AOT solutions is indicative of the fact that the isomerization in the confined micellar core is restricted and the excited singlet decays mainly via a radiative process. Suppression of the trans–cis isomerization has also been noted in other media. For example, a significant increase in the fluorescence quantum yield (from  $\Phi_f = 0.15$  in ethanol to 0.6 in vesicles) has been observed upon incorporating the dye in emulsions, surfactants, or vesicles.<sup>19,25,26</sup> Similarly, an increase in the fluorescence quantum yield observed in a 40% glycerol–ethanol mixed solvent has been attributed to the unfavorable photoisomerization conditions.<sup>20</sup> According to Dixit and Mackay,<sup>26</sup> the enhanced fluorescence emission in micellar solution arises mainly from the decreased

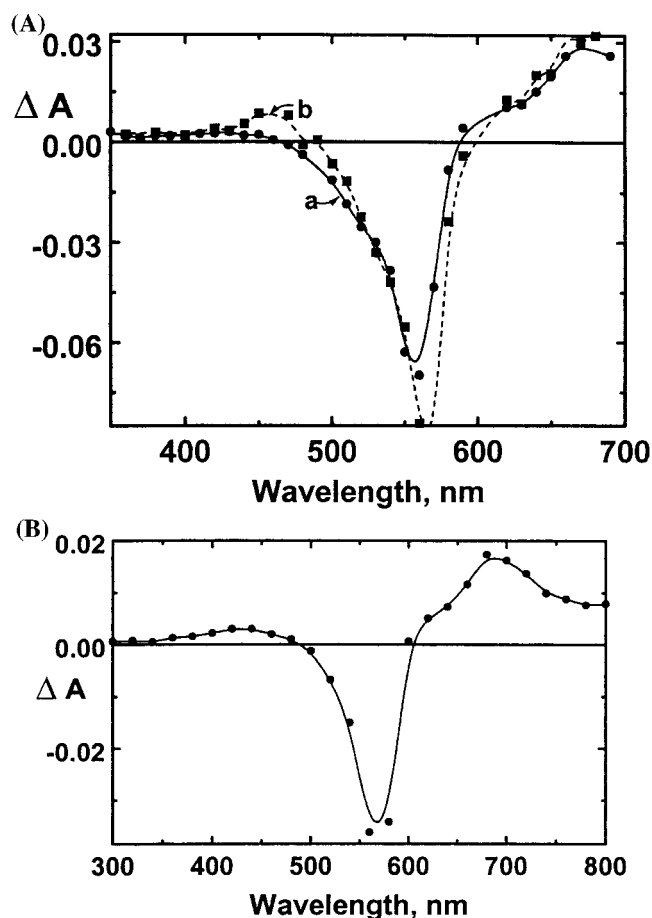


**Figure 2.** The difference absorption spectra of the excited singlet state of MC540. Time-resolved transient absorption spectra were recorded following the 532-nm laser pulse excitation of 6  $\mu$ M MC540 (A) in acetonitrile, and (B) in AOT/heptane solutions.

polarity around the dye molecule. Quitevis and co-workers<sup>22,23</sup> carried out a systematic study in alcohols and nitriles and concluded that both solvent polarity and viscosity can influence the isomerization.

In nonpolar solvents such as heptane and toluene the AOT molecules self-organize into reverse micellar domains with the polar headgroups forming an inner core and the long alkyl chains projecting outward into the solvent. The dye is insoluble in heptane and the polarity in the inner core is expected to be very high due to the polar headgroups of AOT. Hence, the likely location of the dye molecules in the AOT/heptane solutions is the domain provided by the alkyl chains of AOT. The red shift in the absorption and emission spectra as well as the enhanced fluorescence of MC540 in the AOT/heptane solutions indicate that the dye is located in a domain possessing high microviscosity and low polarity.

**b. Singlet Excited State.** The singlet excited state of the dye was characterized in a picosecond laser flash photolysis apparatus using a 532-nm laser pulse as the excitation source. Time-resolved transient spectra recorded following the excitation of MC540 in acetonitrile and AOT/heptane are shown in Figure 2A and B, respectively. The transient absorption spectrum that corresponds to the singlet excited state of the dye in acetonitrile and AOT/heptane solutions exhibits difference absorption maxima around 430 and 505 nm and strong bleaching at wavelengths greater than 530 nm. Because of interference from



**Figure 3.** The difference absorption spectra of excited triplet state of MC540. (A) Transient absorption spectra were recorded following 532 nm laser pulse excitation of 6  $\mu\text{M}$  MC540 (a) in acetonitrile, (b) in AOT/heptane solutions. (B) Transient absorption spectra recorded by triplet-triplet energy transfer method using pulse radiolysis of AOT/toluene solution containing 0.05 M biphenyl and 30  $\mu\text{M}$  MC540.

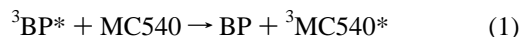
the dye emission, we could not probe the spectra at longer wavelengths. With increasing time, the excited singlet decays via radiative and nonradiative processes. As discussed earlier, trans-cis isomerization contributes significantly to the nonradiative deactivation of the singlet excited state.

The excited singlet state has a lifetime of 370 ps in acetonitrile and 2.1 ns in AOT micellar solution. The long-lived singlet excited state in AOT/heptane further confirms the stabilization of the excited singlet state in the reverse micellar system. Thus, rigid conformation of the excited-state prevents the energy loss via isomerization. A fraction of the excited state also undergoes intersystem crossing to form the triplet excited state. The transient absorption spectrum recorded at longer times ( $\tau = 500$  ps) essentially corresponds to the long-lived triplet excited state.

*c. Triplet Excited State.* The long-lived transient formed during laser excitation was further characterized in a separate experiment using nanosecond laser flash photolysis. The transient absorption spectra recorded 0.1  $\mu\text{s}$  after 532 nm laser pulse excitation of MC540 in acetonitrile (spectrum a) and AOT/heptane (spectrum b) are shown in Figure 3A. The absorption spectra recorded in these two media were similar and we attribute the transient absorption to the long-lived triplet excited state. The difference absorption spectrum shows a maximum around 420 nm and a bleaching at 560 nm. Some contribution from the photoinduced trans-cis isomerization of MC 540 to the difference absorption spectra recorded in Figure 3A is possible. However, both isomers exhibit similar absorption bands

in the visible and any changes in the difference absorption spectrum caused by isomerization would be minimal. As shown earlier,<sup>35</sup> contribution from the cis-isomer formation is expected to result in increased bleaching of the absorbance signal at 560 nm.

The identity of the spectral characteristics of the triplet excited state was further confirmed from a triplet-triplet energy transfer approach. The triplet excited MC540 was indirectly generated by pulse radiolysis. Radiolysis of toluene solutions containing a high concentration of biphenyl yields a relatively long-lived excited biphenyl triplet with an absorption maximum at 360 nm. The resulting biphenyl triplet ( $E_T = 64.8 \text{ kcal mol}^{-1}$ ) is capable of transferring energy to a molecule with lower triplet energy. This method has been conveniently used for probing the triplet excited states of many organic molecules.<sup>36-38</sup> In the present study we have used  $^3\text{BP}^*$  to initiate the primary triplet energy transfer to the dye molecules present in solution.



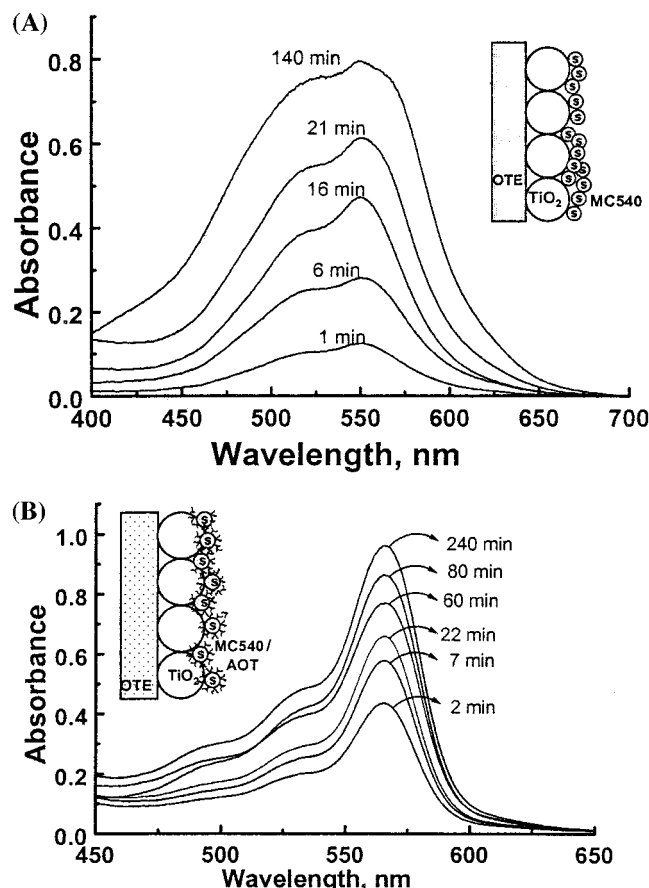
The transient absorption spectra recorded in Figure 3B were obtained upon completion of the decay of the biphenyl triplet. The difference absorption spectrum shows maxima around 420 and 670 nm. Since the triplet excited state was generated without direct excitation of MC540, we can rule out any contribution arising from isomer formation. The transient absorption spectrum has spectral features similar to that observed in the laser flash photolysis experiment (Figure 3A). The triplet excited state has a lifetime greater than 100  $\mu\text{s}$  in AOT/toluene.

**MC540 Modified  $\text{TiO}_2$  Films. a. Photophysical Properties.** Efforts have been made elsewhere<sup>13,39-43</sup> and in our laboratory<sup>12,44-48</sup> to modify semiconductor films with a variety of dyes and to study their electrochemical and photoelectrochemical properties.

Nanostructured  $\text{TiO}_2$  films cast on optically transparent electrodes (OTE/ $\text{TiO}_2$ ) have great affinity to bind with MC540. Upon immersion of a OTE/ $\text{TiO}_2$  electrode in an acetonitrile solution containing MC540 ( $\sim 1 \text{ mM}$ ) we observe strong coloration of the film within a short time. Figure 4A shows the absorption spectra of dye-adsorbed  $\text{TiO}_2$  films recorded at different immersion times. With increasing time of exposure of the  $\text{TiO}_2$  film to MC540 solution we observe an increased absorbance in the 400–600 nm region. The absorbance of the film tends to saturate in about 2 h with maxima at 550 and 500 nm corresponding to the monomer and aggregate forms of the dye. The broad and prominent absorption around 500 nm indicates significant contribution from dimer and possibly higher aggregates. Close packing of dye molecules on the semiconductor particulate surface facilitates intermolecular interaction, thus causing the aggregation effects. Similar dye aggregation of thiazine, oxazine, and rhodamine dyes bound to  $\text{SnO}_2$  nanocrystallites have been observed in our earlier studies.<sup>10,12,46</sup> The appearance of strong absorption in the high-energy region (blue-shifted compared to the monomer absorption band) indicates that the dye aggregates are mainly H-type.

A similar experiment was also performed by dipping the OTE/ $\text{TiO}_2$  electrode in an AOT/hexane solution containing MC540. Within minutes, the film gains a bright pink color, thus, confirming the incorporation of the AOT-encapsulated MC540 into the  $\text{TiO}_2$  film. The absorption spectra recorded at different immersion times are shown in Figure 4B. In contrast to Figure 4A, the absorption band is sharper with a maximum at 565 nm and resembles more closely the spectrum of the monomeric dye in solution. The ratio of  $A_{520}/A_{565}$ , which represents the extent of aggregation, is much smaller in these films. The monomer

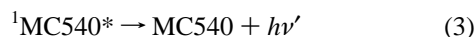




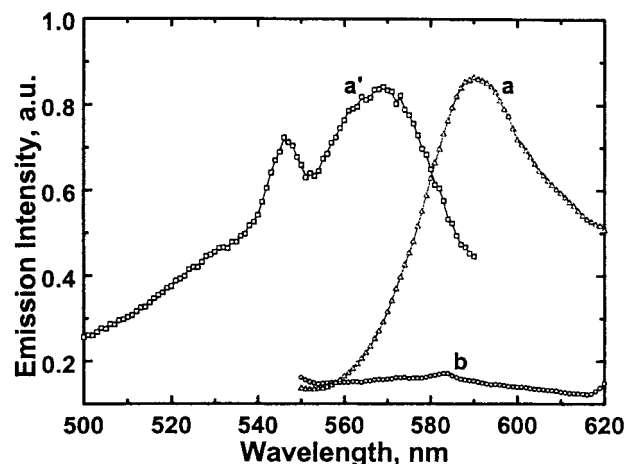
**Figure 4.** Absorption spectra of an OTE/TiO<sub>2</sub> electrode recorded at different time intervals following its dipping in MC540 (~1 mM) solution in (A) acetonitrile, and (B) AOT/heptane.

absorption band continues to dominate even at highest dye concentration levels. The different medium conditions employed in these two sets of experiments clearly resulted into two different types of bound dye molecules on the TiO<sub>2</sub> surface (Scheme 2). The AOT molecules that surround the dye act as spacer molecules, thus preventing the intermolecular interaction that leads to aggregation effects.

Figure 5 shows the emission and excitation spectrum of the dye coated on silica films. The OTE/SiO<sub>2</sub> films were modified with the dye by immersing them in MC540 solution in AOT/heptane. As shown earlier, insulating oxides such as silica provide a reference to probe the excited behavior of the dye on different substrates. Because of the insulator's large band gap and highly negative conduction band, the excited dye is not energetic enough to inject electrons into silica. The fluorescence emission spectrum of MC540 on silica indicates the appearance of only monomer emission band (reactions 2 and 3).

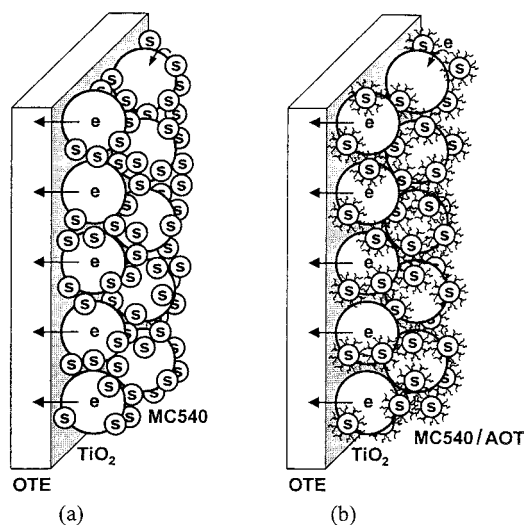


In contrast, MC540 adsorbed on TiO<sub>2</sub> film exhibits negligible emission, thus indicating an additional deactivation pathway for the excited singlet state. The excited singlet of MC540 has an oxidation potential around ~-1.0 V vs NHE and hence it is capable of injecting electrons into the conduction band of TiO<sub>2</sub> ( $E_{CB} = -0.5$  V vs NHE) (reaction 4).



**Figure 5.** Excitation (a') and emission (a) spectra of MC540 adsorbed on nanostructured SiO<sub>2</sub> film. The emission spectrum (b) of TiO<sub>2</sub>/MC540 recorded under similar experimental conditions with matching absorbance at excitation wavelength (500 nm) is compared.

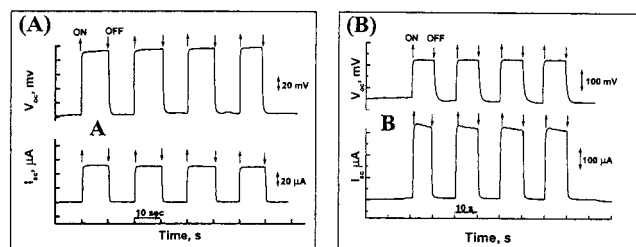
**SCHEME 2.** (a) Direct Binding of Dye Molecules to TiO<sub>2</sub> Nanoparticles and (b) the Possibility of Minimizing the Aggregation Effects by Encapsulating the Dye in a Surfactant (e.g., AOT) System



In a strongly coupled system, the charge injection from excited singlet into TiO<sub>2</sub> can occur as rapidly as 50 fs. However, in nanostructured semiconductor films the time constants for the charge injection can extend up to a few hundred picoseconds. Further details on the quenching of excited dyes on semiconductor nanoparticles can be found elsewhere.<sup>49–54</sup>

**b. Overcoming the Problem of Dye Desorption from the TiO<sub>2</sub> Surface.** Desorption of the dye from the TiO<sub>2</sub> surface was encountered as a major problem during the photoelectrochemical measurements. Because of the high concentrations of redox electrolyte employed in the photoelectrochemical cell, MC540 quickly leached into the solution. To overcome this problem we dip-coated a thin film of poly(4-vinylpyridine) (PVP) onto the dye-modified TiO<sub>2</sub> film. The dye-modified electrode (OTE/TiO<sub>2</sub>/MC540) was dipped in an ethanol solution of the polymer (1%) and air-dried before using it in the photoelectrochemical cell.

As shown earlier,<sup>55–58</sup> PVP films under protonated conditions (pH ~3) readily bind negative ions and carry out the redox processes by transporting the charges across the film efficiently. For example, croconate dye-modified PVP films have been



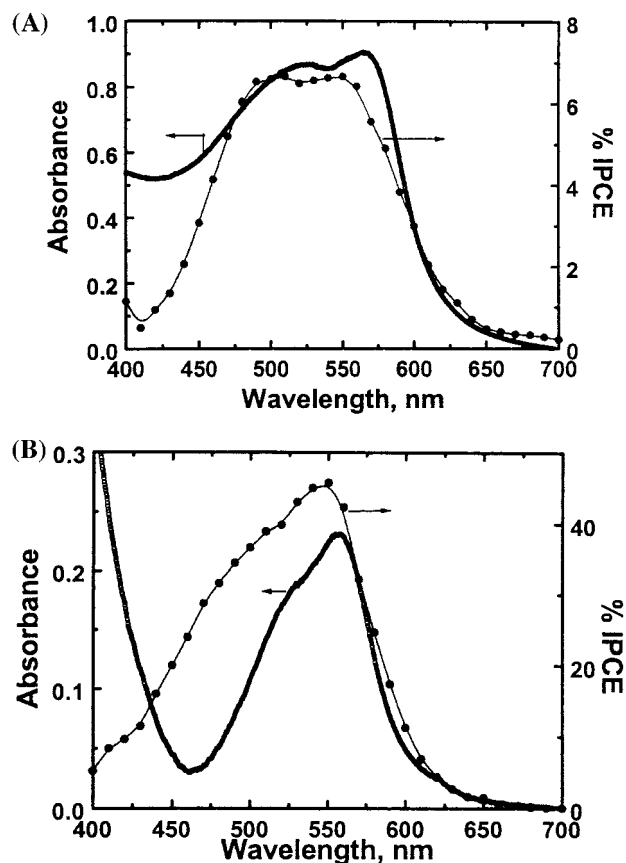
**Figure 6.** Photoreponse of OTE/TiO<sub>2</sub>/MC540/PVP electrode to visible light excitation. Photovoltage and photocurrent responses of the electrode were recorded during on/off cycles of illumination (560 nm). The electrodes were prepared by (A) dipping in acetonitrile and (B) in AOT/heptane solutions of MC540. (Electrolyte: 1 M LiI and 0.2% CF<sub>3</sub>COOH in acetonitrile.)

shown to possess excellent electrocatalytic properties by inducing redox processes at the polymer/electrolyte interface.<sup>59</sup> The polymer layer cast on an electrode surface can be considered as the statistical equivalent of several monolayers where charge propagation occurs through electron hopping between adjacent reduced and oxidized states.<sup>60,61</sup> In the present experiments, we expect negatively charged I<sub>3</sub><sup>-</sup> and I<sup>-</sup> species from solution to bind to the pyridine groups of the PVP film and propagate the charges across the polymer layer. To facilitate this process it is necessary to acidify the electrolyte with small amounts (0.1–0.2%) of trifluoroacetic acid. These experimental modifications were found to give stable photocurrent without noticeable desorption of the dye from the electrode surface.

**Photosensitization Aspects of MC540-Modified Nanostructured TiO<sub>2</sub> Films.** The photoelectrochemical response of the MC540-modified TiO<sub>2</sub> electrode to visible light excitation is shown in Figure 6. Upon illumination of the dye-modified TiO<sub>2</sub> electrode with visible light (560 nm), a rise in the photovoltage and photocurrent is seen. The photoreponse of the electrode to visible light excitation was prompt, thus confirming the photosensitization mechanism to be operative following the excitation of the dye. The open-circuit photovoltage remained steady as long as the irradiation was continued. When the lamp was turned off, the open-circuit voltage quickly dropped back to the original dark value. The photoelectrochemical effect at the OTE/TiO<sub>2</sub>/MC540/PVP was reproducible over several on/off cycles of illumination. The selective excitation of MC540 was accomplished by employing a monochromatic light at 565 nm.

The photocurrent exhibited by the OTE/TiO<sub>2</sub>/MC540/PVP electrode that was obtained from AOT/heptane solution was higher than that of the electrode obtained from the acetonitrile solution. The open-circuit voltage observed in both these examples ( $V_{oc} \leq 250$  mV) was significantly lower than that observed for Ru(II)-modified TiO<sub>2</sub> film electrodes ( $V_{oc} \approx 700$  mV).<sup>62</sup> The acidic electrolyte employed in the present experiments shifts the energy of the conduction band to more positive potentials, thus causing the open-circuit potential to decrease. It should be possible to overcome this problem of low open-circuit voltage by finding an alternate approach of anchoring the dye molecule to the semiconductor film and/or choosing a different charge-transporting polymer film that does not require acidic medium.

The photoaction spectrum of the OTE/TiO<sub>2</sub>/MC540/PVP electrode obtained from two different methods (i.e., from acetonitrile and AOT/heptane solution) are shown in Figure 7, parts A and B. The spectra were recorded by measuring the photocurrent at different incident wavelengths of light and normalizing the values for incident intensity and energy of the light. These values which correspond to the incident photon-



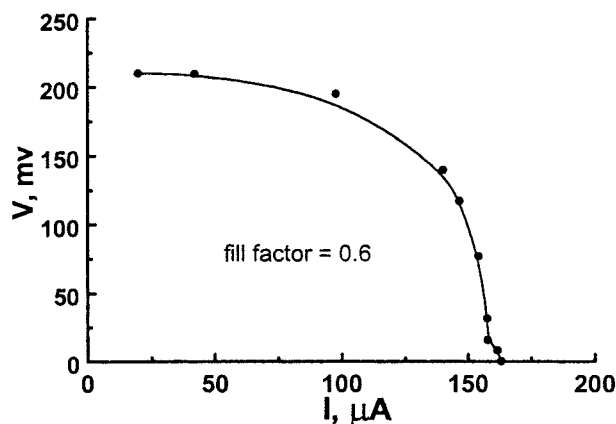
**Figure 7.** Photocurrent action spectra of OTE/TiO<sub>2</sub>/MC540/PVP recorded in terms of IPCE (see text for details). (Electrolyte: 1 M LiI and 0.2% CF<sub>3</sub>COOH in acetonitrile.) Absorption spectrum of the electrode recorded prior to photoelectrochemical measurement is also shown. The TiO<sub>2</sub> film was modified by dipping it in (A) acetonitrile, and (B) AOT/heptane solutions of MC540 for 4–8 h.

to-photocurrent efficiency (IPCE) at various excitation wavelengths were determined from the following expression (eq 5):

$$\text{IPCE}(\%) = \frac{i_{sc}}{I_{inc}} \frac{1240}{\lambda} \times 100 \quad (5)$$

where  $i_{sc}$  is the short-circuit photocurrent (A/cm<sup>2</sup>),  $I_{inc}$  is the incident light intensity (W/cm<sup>2</sup>), and  $\lambda$  is the excitation wavelength. The absorption spectrum of the corresponding electrode recorded prior to the photocurrent measurement is also shown for comparison. The close match in the absorption and action spectra indicates that the photoinjection occurs from the excited states of monomer and aggregate form of the dye resulting in the generation of the anodic photocurrent (reaction 3). The monomeric dye is the major contributor to the photocurrent generation for the electrode containing AOT as spacers. However, both monomeric and aggregate forms contribute to the photocurrent generation for the electrodes modified from the dye solution in acetonitrile.

A maximum IPCE of 45% was observed for the OTE/TiO<sub>2</sub>/MC540/PVP electrode prepared from AOT/heptane solution. This value is about five times greater than the maximum IPCE of the OTE/TiO<sub>2</sub>/MC540/PVP electrode obtained from immersing the OTE/TiO<sub>2</sub> electrode in MC540–acetonitrile solution. This suggests that the monomeric form of the dye is more efficient in generating photocurrent. It is also worth noting that the presence of inert AOT spacers does not adversely affect the photocurrent generation efficiency, instead they favor the desired spatial confinement of MC540 molecules on the TiO<sub>2</sub>



**Figure 8.** Power characteristics of the photoelectrochemical cell using OTE/TiO<sub>2</sub>/MC540/PVP as a photosensitive electrode and a Pt gauze as a counter electrode. (Electrolyte: 1 M LiI and 0.2% CF<sub>3</sub>COOH in acetonitrile.) The electrode was subjected to monochromatic illumination of 550 nm (1.3 mW/cm<sup>2</sup>).

surface. As discussed in the earlier section, the encapsulation of the dye with AOT has an added advantage of increasing the stability of excited singlet state and minimizing the photoisomerization. Significantly higher IPCE observed in the present experiments (45%) indicate the ability of the MC540/TiO<sub>2</sub> system to convert the light energy into electricity quite efficiently. These values are comparable to previously reported IPCE values of 80–90% for Ru(II) polypyridyl complex/TiO<sub>2</sub> systems.

**Power Characteristics.** We also evaluated the power characteristics of a simple prototype photoelectrochemical cell by employing an OTE/TiO<sub>2</sub>/MC540/PVP electrode as a photoanode and a Pt wire gauge as a counter electrode. The power characteristics were evaluated by recording the photocurrent and photovoltage at different load resistance (Figure 8). The maximum photovoltage and photocurrent obtained were 200 mV and 165  $\mu\text{A}/\text{cm}^2$ , respectively. The fill factor obtained from the results in Figure 8 was 0.6 with a maximum power output of 19.6  $\mu\text{W}/\text{cm}^2$  at an incident light (560 nm) intensity of 1.3 mW/cm<sup>2</sup>. These parameters yield a net power conversion efficiency of 1.5%. Please note that the photocurrent values reported here are our conservative estimates and are routinely reproduced during our measurements. In a few instances we have observed photocurrent values as high as 300  $\mu\text{A}/\text{cm}^2$  (or maximum power conversion efficiency of 3%). Although the conservative estimate of 1.5% net power conversion efficiency is lower than the values of Ru(II) polypyridyl complex-based cells, it is comparable to the efficiencies of recently reported photoelectrochemical cells based on organic dye sensitization.<sup>11,13</sup> The mere fact that we were able to achieve significantly higher photocurrents using a surfactant-encapsulated organic dye puts us onto the right track of exploring new ways to control the sensitization properties on the semiconductor surface. It should be possible to achieve improvements in the power output (and also the power conversion efficiency) with further optimization of the cell configuration.

As illustrated in Scheme 1, both the aggregates and monomer form of MC540 are capable of injecting electrons into TiO<sub>2</sub> nanoparticles and initiating the photocurrent generation. However, they do so with different net charge injection efficiency. One of the major factors responsible for lower IPCE in Figure 7A is the fact that the dye exists mainly in the aggregate form. There are two possibilities for the dye aggregates to contribute to the photocurrent generation: (i) Transfer energy to the adjacent monomeric dye which can then inject electrons into

TiO<sub>2</sub> particles, and (ii) Inject electrons from the excited aggregate directly into the semiconductor nanoparticles. The photoaction spectrum in Figure 7A does not rule out either of the two possibilities.

In a recent study we have demonstrated the possibility of using dye aggregates as light-harvesting antennae. The triplet energy transfer from aggregates to monomeric thionine was demonstrated in a transient absorption experiment. If such an energy transfer process was dominant in the present experiment we would have observed relatively similar photocurrent generation efficiencies in the experiments illustrated in Figure 7, parts A and B. The decreasing photocurrent observed with increasing aggregate fraction in the dye-modified film ruled out a possible contribution from energy transfer process. Therefore, we conclude that the excited dye aggregates and monomers independently participate in the charge injection process. As shown earlier, the H-type aggregates are capable of injecting electrons from their singlet and triplet excited states in a few picoseconds to nanoseconds.<sup>63,64</sup> However, such dye aggregate-modified semiconductor electrodes exhibit significantly lower photoconversion efficiency.<sup>10,12,64</sup>

The use of polymer coating (PVP) necessitated its protonation for transporting negative ions for the dye regeneration. The acidic electrolyte used in the present experiments is responsible for the lower photovoltage which, of course, became a limiting factor in achieving higher power conversion efficiency in the present experiments. Electroactive polymers are considered to be important in developing solid-state photoelectrochemical and photocatalytic devices. A few attempts have already been made in this regard with limited success (see, for example,<sup>65–68</sup>). Electrochemically active polymers such as I<sub>3</sub><sup>−</sup>/I<sup>−</sup>-doped PVP can also provide an alternate means of coupling dye-modified semiconductor films with polymers for developing photoelectrochemical cells. Indeed, our first attempt has demonstrated the feasibility of such an approach.

A caution may be added regarding the photostability of the dye. In the absence of a redox couple or in dry films, MC540 adsorbed on TiO<sub>2</sub> film undergoes rapid photodecomposition. In the case of thermal printing applications there have been a series of studies to incorporate additives and counterions, which essentially quench the excited state and make the merocyanine dye more photostable.<sup>69</sup> In our experiments, the redox couple facilitates the quick regeneration of the dye following its oxidation on the semiconductor surface. Stable photocurrents observed in our photoelectrochemical cell indicates that the dye stability is not a major issue during short-term low-intensity irradiation experiments. Little changes in the photocurrent (<5%) were observed during the illumination period of about an hour. Further experiments are necessary to establish the long-term stability of these dyes for photoelectrochemical applications.

## Conclusions

H-aggregates of the merocyanine dye, MC540, are less efficient than its monomer counterpart in sensitizing TiO<sub>2</sub> nanoparticles. One can minimize the aggregation effects on the TiO<sub>2</sub> surface by using molecular spacers such as AOT molecules. Microencapsulation of the sensitizing dye molecules in a surfactant system such as AOT prior to deposition on the semiconductor surface is a useful and convenient procedure to retain the molecules in the monomeric form. The difference between the interconversion rates of excited monomer and aggregate is a major factor limiting the efficiency of electron transfer at the semiconductor interface. Microencapsulation with



AOT rigidizes the excited state and makes the deactivation pathways such as isomerization less competitive. These beneficial aspects of surfactant microencapsulation of the dye render higher efficiency in the photoelectrochemical experiments. Deposition of electroactive polymer (i.e.,  $I_3^-/I^-$ -doped PVP film cast on dye-modified  $TiO_2$  film) can also bring about additional advantages of charge mediation and minimizing the effects of dye desorption.

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