Photosensitization of Colloidal Titania Particles by Electron Injection from an Excited Organic Dye−Antennae Function

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Electron transfer from an excited organic dye−antennae device, the diester formed between fluorescein and anthracene-9-carboxylic acid (FL−AN), to colloidal TiO$_2$ particles has been examined by absorption, photoluminescence, and laser flash spectroscopies and by electron spin resonance techniques under steady-state laser excitation. This diester FL−AN is chemisorbed to the TiO$_2$ particles through the phenolic function of the fluorescein moiety; the anthracene component of FL−AN acts as the energy donor component, which is not in contact with the semiconductor particle surface. The apparent association constant (K_{app}) is ca. 200 mol^{-1} L. Exciting the fluorescein side with visible light (around 470 nm) induces electron injection from its singlet excited state onto the conduction band of TiO$_2$ ($k_{et} = 2.30 \times 10^8$ s^{-1}). Excitation of the anthracene moiety with ultraviolet light ($\lambda \approx 355$ nm) first causes energy transfer from its singlet excited state to the lowest excited singlet state of fluorescein ($\Phi_{enT} = 0.98$, and $k_{enT} = 2.23 \times 10^{10}$ s^{-1}), following which electron injection occurs from the fluorescein singlet to the conduction band of TiO$_2$ at a rate otherwise identical to direct excitation of fluorescein. This greatly improves sensitization efficiency in applications to solar energy conversion. Electron spin resonance and laser flash spectroscopies demonstrated formation of the radical cation FL$^{•+}$−AN on electron injection.

Introduction

During the past decade, much attention has been paid to the modification of wide bandgap semiconductor particles (e.g. TiO$_2$) by organic dyes to extend their photoresponse to visible light. Numerous studies in this area have been carried out in heterogeneous media,[1] aqueous solution,[2] and nonaqueous media.[3−7] Furthermore, M. Graetzel et al.[8] have designed successfully an efficient and stable solar cell by using semiconductor films consisting of nanometer-sized TiO$_2$ particles and charge-transfer dyes. The dye is typically adsorbed on the surface of the semiconductor particles and acts as an electron donor, injecting electrons from its excited state(s) into the conduction band of the semiconductor under visible light irradiation. Chemisorption of these sensitizing dyes on the surface of such wide bandgap semiconductors as titanium dioxide colloids plays an important role in sensitization efficiency. Dyes possessing carboxylate or hydroxyl functions, in particular, interact with the surface of TiO$_2$ particles, thereby providing the path for electron transfer from the excited dye adsorbate to the semiconductor.[4−7,9]

Although such sensitizing organic dyes as eosin-Y and erythrosin-B have high absorption cross sections in the visible spectral region, absorption of ultraviolet radiation between 300 and 400 nm is rather low. By contrast, anthracene-9-carboxylic acid has a high extinction coefficient in the ultraviolet region, but has little absorption at wavelengths longer than 400 nm. Fluorescein is a dye of the xanthene class that is widely used in dye lasers,[10] in solar energy conversion,[11,12] and to photo-

sensitize reactions.[13,14] Photosensitization by electron-transfer sensitizers in the presence of semiconductors and subsequent electron transfer across the semiconductor/solution interfaces play a significant role in light energy conversion processes in such devices as photoelectrochemical cells.

To extend the photoresponse to the whole solar light range (wavelengths longer than 290 nm), we synthesized the diester between anthracene-9-carboxylic acid and fluorescein (FL−AN) linked by a butylene chain. The fluorescein moiety in FL−AN adsorbs on the surface of TiO$_2$ semiconductor particles through the phenolic function, while the anthracene moiety, which acts as an energy donor substrate, is maintained away from the surface of the TiO$_2$ particles. In this manner, photosensitization of wide bandgap semiconductor devices by photoactive dye molecules with high absorption cross sections across the whole sunlight region can augment the photoresponse of these semiconductors and improve the net charge-transfer process efficiencies. F. Scandola et al.[15] have reported another sensitizer−antenna molecule, [Ru(bpy)$_2$(CN)$_2$]$_2$Ru(bpy(COO)$_2$)$_2$$^{2-}$, to improve the light absorption efficiency of a sensitized semiconductor. Both the light directly absorbed by the sensitizer and that absorbed by the antenna can be used to effect charge injection, thus leading to an increase in the overall cross section for light absorption.

The displacement of the band maxima and changes in the extinction coefficient in the absorption spectra in the presence of TiO$_2$ colloids demonstrated the occurrence of surface interactions between the sensitizing dye and the particle surface. Quenching of the fluorescence emission and changes in the fluorescence lifetime of the dye afforded useful information of the process of electron injection. Moreover, time-resolved transient absorption spectra and ESR spectra of the dye radical provided confirming evidence for the occurrence of electron

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injection from the excited state of the dye to the conduction band of the semiconductor.

Experimental Section

1. Syntheses. Anthracene-9-carboxylic acid and fluorescein were reagent grade chemicals obtained from the Sigma Chemical Co.; 1,4-dibromobutane (Beijing Chemical Co.), titanium(IV) isopropoxide (Aldrich Chemical Co.), and other chemicals were also reagent grade and were used without further treatment.

The *n*-bromobutyl ester of anthracene-9-carboxylic acid (intermediate product) was prepared by stirring a mixture of 1.28 g (22 mmol) of anhydrous KF and 2.16 g (10 mmol) of 1,4-dibromobutane in 10.6 mL of dimethylformamide at ambient temperature for 1 min, after which 2.22 g (10 mmol) of anthracene-9-carboxylic acid was added. The resulting mixture was stirred at 60 °C for 1 h. After cooling to ambient temperature, about 150 mL of water was added to the solution, following which a light yellow solid formed that was filtered, washed with water and with diethyl ether repeatedly, and then dried in vacuo. The product was recrystallized from ethanol (yield about 75%).

The diester formed between anthracene-9-carboxylic acid and fluorescein (denoted FL−AN) and the model compounds (i) ethylfluorescein (FLEt), (ii) diethylfluorescein (FLEt$_2$), and (iii) the ethyl ester of anthracene-9-carboxylic acid (ANEt) were synthesized according to procedures described earlier in the literature.[16] Specifically, the dye−antenna device (FL−AN) was prepared by stirring a mixture of 0.38 g (6 mmol) of anhydrous KF and 1.1 g (3 mmol) of the *n*-bromobutyl ester of anthracene-9-carboxylic acid in 20 mL of dimethylformamide at ambient temperature for 1 min. After addition of 1.0 g (3 mmol) of fluorescein, the mixture was stirred for 12 consecutive hours at 70 °C. The dimethylformamide solvent was subsequently partially removed using a rotary evaporator. About 100 mL of water was then added to the resulting orange-red solid mixture. The ensuing solid was filtered, washed with water and diethyl ether several times, dried in vacuo, and subsequently chromatographed on silica gel with a CHCl$_3$/CH$_3$OH (10/1 v/v) mixture; the red component was collected. This procedure was repeated three times. Partial removal of the CHCl$_3$/CH$_3$OH solvent by a rotary evaporator and subsequent addition of *n*-hexane yielded a red solid, which was washed with *n*-hexane several times and dried in vacuo: yield was ca. 10%.

After separation and purification, the four compounds FLEt, FLEt$_2$, ANEt, and FL−AN were characterized by UV−visible and infrared spectroscopy, by either 300 or 400 MHz ^{1}H NMR spectroscopy, and by mass spectral measurements.
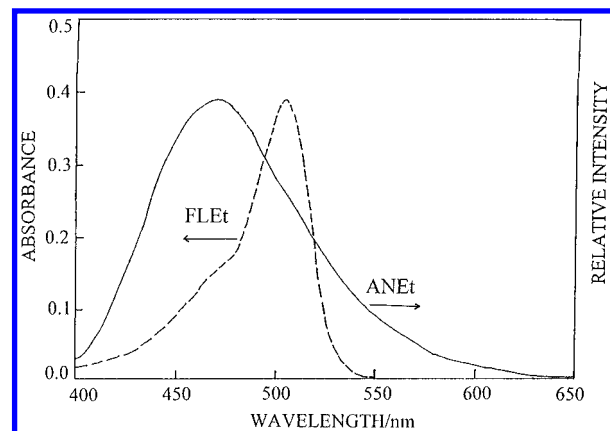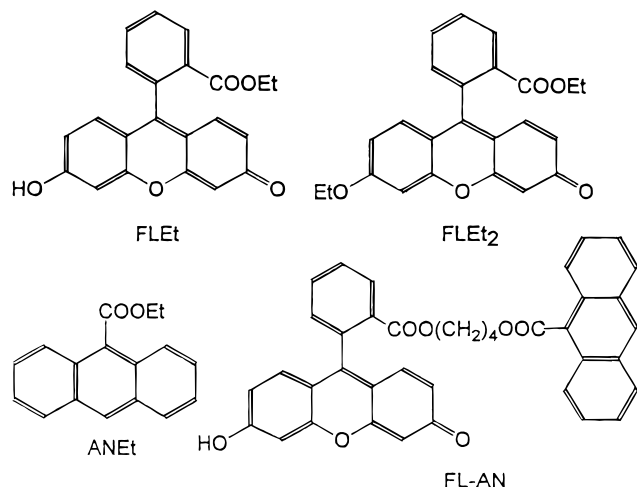

Figure 1. Fluorescence spectrum of ANEt (solid line) and absorption spectrum of FLEt (dashed line) in ethanol.

2. Preparation of Colloidal TiO$_2$. The TiO$_2$ colloidal suspension was prepared under a nitrogen atmosphere and under vigorous stirring by the hydrolysis of a 2-propanol solution of titanium(IV) isopropoxide (10%, 1.63 mL) in 100 mL of ethanol containing about 1% water. The stock solution was 5.0×10^{-3} mol L^{-1} in colloidal TiO$_2$. The freshly prepared colloidal TiO$_2$ solution was diluted with ethanol to obtain the desired concentration of TiO$_2$ in the samples; traces of 2-propanol in the colloid were not removed. Electron spin resonance and transient absorption nanosecond spectra were obtained on a 2.5×10^{-2} M solution. The absorption threshold of the colloidal TiO$_2$ in ethanol is at about 350 nm. Stock ethanol solutions of colloidal TiO$_2$ were very stable, as evidenced by their absorption spectra, which persisted unchanged for several weeks to (even) several months.

3. Photophysical Measurements. Absorption spectra were recorded on a Shimadzu 1600 UV/visible spectrophotometer; fluorescence and fluorescence excitation spectra were recorded on a Perkin-Elmer LS-5 spectrofluorimeter equipped with a computer for data acquisition, storage, and manipulation. Fluorescence lifetimes were determined using a Hiroba WA.ES 1100 single photon counting instrument which permitted automatic fitting of the data. Electron spin resonance spectra were obtained on a Bruker Model ESP 300E ESR spectrometer coupled to a computer for data acquisition and instrument control; the excitation source was a Quanta-Ray Nd:YAG laser system. Transient absorption spectra were determined on a flash photolysis apparatus which consisted of a Quanta-Ray Nd:YAG DCR 2(30)A laser, a pulsed xenon lamp, and a multichannel analyzer interfaced to a computer. All solutions were deaerated with nitrogen for 30 min prior to the measurements.

Results and Discussion

1. Photophysics of the Model Compounds FLEt and ANEt. Intramolecular energy transfer takes place from the singlet excited state of the ester of the anthracene-9-carboxylic acid component to the fluorescein partner in FL−AN, as determined from an analysis of the photophysical properties of the respective model compounds, ANEt and FLEt. The energies of the singlet excited states are 3.21 and 2.43 eV, respectively, assessed from their respective absorption and fluorescence spectral data.[17] The singlet excited state of ANEt is some 0.78 eV at higher energy than the corresponding singlet state of FLEt. Moreover, there is good overlap between the fluorescence spectra of ANEt and the absorption spectra of FLEt (Figure 1). Hence, energy transfer from the singlet excited state of ANEt to the FLEt state is thermodynamically permitted. When the anthracene moiety in FL−AN is excited, its fluorescence is
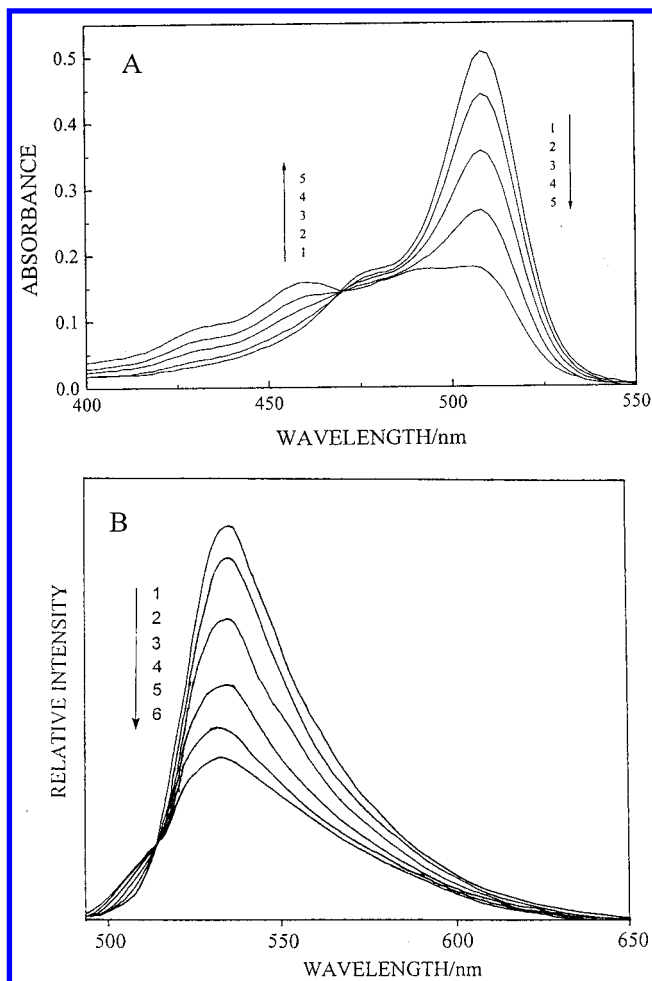
Photosensitization of Colloidal Titania

J. Phys. Chem. B, Vol. 101, No. 44, 1997 **9029**

Figure 2. (A) Absorption spectra of FLEt in ethanolic media (5.0 × 10^{-6} M) with (1) 0, (2) 5.0 × 10^{-4} M, (3) 1.0 × 10^{-3} M, (4) 2.0 × 10^{-3} M, and (5) 4.0 × 10^{-3} M TiO$_2$ colloid. (B) Fluorescence spectra of FLEt in ethanolic media (5.0 × 10^{-6} M) with (1) 0, (2) 5.0 × 10^{-4} M, (3) 1.0 × 10^{-3} M, (4) 2.0 × 10^{-3} M, (5) 3.0 × 10^{-3} M, and (6) 4.0 × 10^{-3} M TiO$_2$ colloid.

totally quenched by the fluorescein component, whose emission is observed at longer wavelengths, indicating indeed that singlet energy transfer does take place between the singlet excited state of the anthracene-9-carboxylate moiety and the fluorescein moiety in FL−AN.

   Addition of titania colloids to a solution of ANEt had no effect on either the absorption or the fluorescence spectra. This contrasts with the behavior of the FLEt absorption and fluorescence spectra, where addition of a TiO$_2$ colloidal sol leads to significant quenching of the emission at 540 nm (Figure 2B) and significantly reduces the absorption intensity at ca. 510 nm with an additional spectral feature growing at about 460 nm (note isosbestic point at ∼470 nm in Figure 2A).

   The efficiency of intramolecular singlet energy transfer (η_{enT}) in FL−AN can be estimated by comparing the relevant absorption spectra with the fluorescence excitation spectra (Figure 3; emission wavelength, 560 nm; at this wavelength, the anthracene moiety does not luminesce). We denote the area under the absorption band for the anthracene moiety between 330 and 400 nm as A_1 and describe A_2 as the area under the absorption feature for the fluorescein component from 450 to 550 nm; we also define the corresponding areas from the fluorescence excitation spectra for both components in the same wavelength range as E_1 and E_2, respectively. If η_{enT} is zero, then the ratio E_1/E_2 is also zero. On the other hand, if η_{enT} is unity, then $E_1/E_2 = A_1/A_2$. In general, this efficiency can be
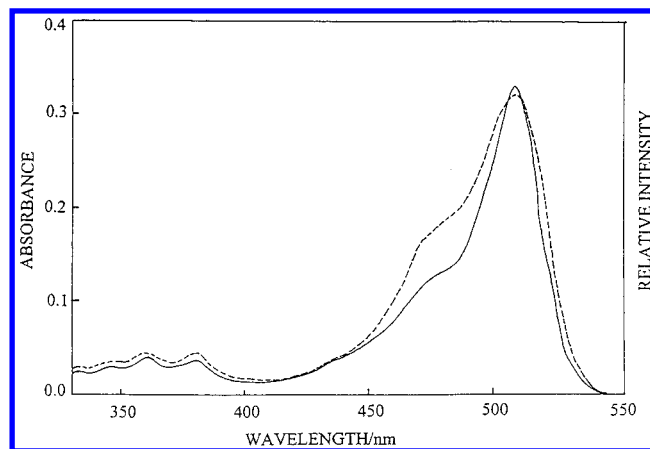

Figure 3. Absorption spectra (solid line) and fluorescence excitation spectra (dashed line) of FL−AN in ethanolic media.
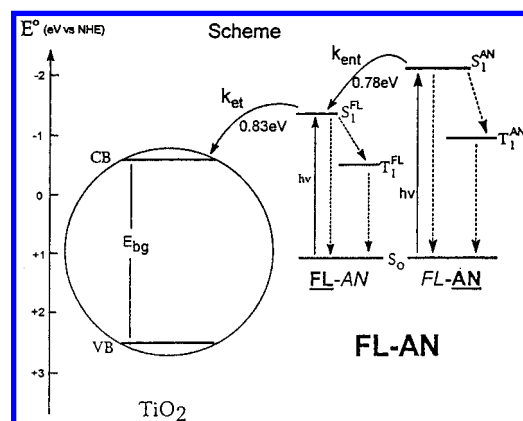

Figure 4. Diagram illustrating the energetics of sensitization of colloidal TiO$_2$ particles in ethanolic media by the dye−antenna device FL−AN.

computed from (eq 1)

$$\eta_{enT} = \frac{E_1/E_2}{A_1/A_2} \tag{1}$$

which yields $\eta_{enT} = 0.98$ as the efficiency of the intramolecular singlet energy-transfer process.

   The rate for the intramolecular energy transfer (k_{enT}) between the singlet states of the fluorescein and the anthracene-9-carboxylate fragments in the FL−AN diester can be assessed by considering the Jablonski-type diagram shown in Figure 4. We note again that the singlet state of the anthracene component S_1^{AN} is situated at 0.78 eV above the corresponding state S_1^{FL} for the fluorescein component. Thus,

$$\eta_{enT} = \frac{k_{enT}^{AN}}{k_{enT}^{AN} + \{k_{nr}^{AN} + k_{isc}^{AN} + k_{ic}^{AN} + k_r^{AN}\}} \tag{2a}$$

and

$$\eta_{enT} = \frac{k_{enT}^{AN}}{k_{enT}^{AN} + \tau_{AN}^{-1}} \tag{2b}$$

where τ_{AN} is the lifetime of the energy donor state S_1^{AN} in the absence of energy transfer and which we take to be equivalent to the emission lifetime for the singlet state of the related compound ANEt (see above) in ethanol media: $\tau_{AN} = 2.20$ ns. From eq 2b and $\eta_{enT} = 0.98$, we obtain $k_{enT}^{AN} = 2.23 \times 10^{10}$ s^{-1}. Clearly, when the anthracene component in FL−AN is

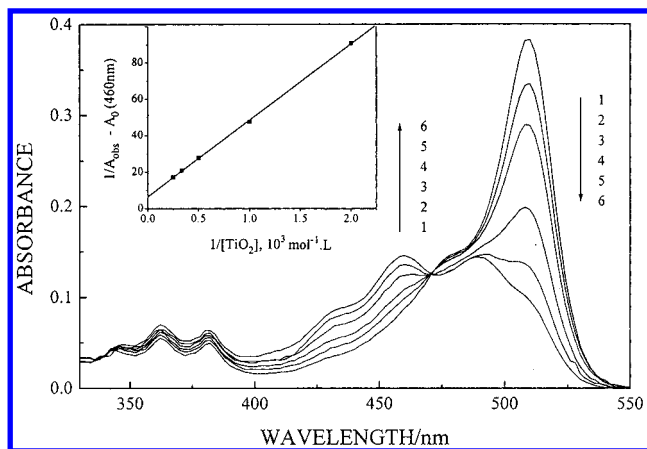9030   *J. Phys. Chem. B, Vol. 101, No. 44, 1997*

He et al.

Figure 5. Absorption spectra of FL−AN in ethanol (5.0×10^{-6} M) with (1) 0, (2) 5.0×10^{-4} M, (3) 1.0×10^{-3} M, (4) 2.0×10^{-3} M, (5) 3.0×10^{-3} M, and (6) 4.0×10^{-3} M TiO$_2$ colloid. Inset shows the plot of $1/(A_{obs} - A_o)$ versus $1/[TiO_2]$.

excited, it transfers nearly all its singlet energy to the fluorescein moiety rapidly and very efficiently.

2. Absorption Characteristics. Absorption spectra of the diester FL−AN in ethanol show two basic features: the spectral features from 330 to 400 nm are those of the anthracene component, whereas the features between 400 and 550 nm correspond to absorption by fluorescein (Figure 5, curve 1). Similar features were displayed by a mixture of the reference model compounds, FLEt and ANEt, at equal molar concentrations.

Changes in the shape or position of the absorption band on addition of colloidal TiO$_2$ determine whether adsorption on the TiO$_2$ particles takes place. Figure 5 shows the absorption spectra of FL−AN in neat ethanol and in ethanol containing colloidal TiO$_2$ at different concentrations. On increasing the colloidal TiO$_2$ concentration, the absorption band at 508 nm decreases and is accompanied by the appearance of a new absorption band at about 460 nm; note the clean isosbestic point at 470 nm. Such extensive changes in the absorption spectra must arise from a relatively strong interaction between the dye and the TiO$_2$ particle surface. We take the appearance of the isosbestic point at 470 nm to be indicative of adsorbed and unadsorbed FL−AN molecules (see reaction 3 below).
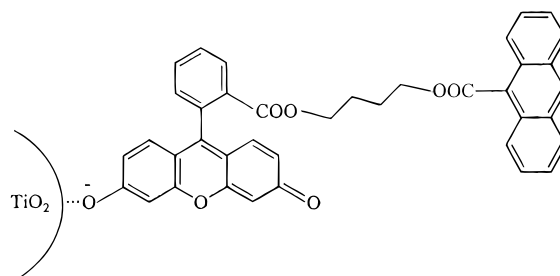
To determine which moiety or group in FL−AN is adsorbed to the surface of the TiO$_2$ particles, we carried out comparative experiments with the model ester compounds, FLEt, FLEt$_2$, and ANEt. The absorption spectra of FLEt exhibit the same effect as the diester FL−AN when colloidal TiO$_2$ is added in different concentrations (Figure 2). The new absorption band appearing at 460 nm is nearly identical to the corresponding band of FLEt$_2$ in which the hydrogen of the phenolic group in FLEt is substituted by an ethyl group. For the FLEt$_2$ and ANEt esters, addition of colloidal TiO$_2$ at varying concentrations to the dye solutions incurred no changes in their absorption spectra, indicating little, if any, interaction between FLEt$_2$ or ANEt and the surface of the TiO$_2$ particles; that is, the FLEt$_2$ and ANEt esters are not adsorbed on the TiO$_2$ particles. The ANEt/ colloidal TiO$_2$ system is apparently different from the anthra-cene-9-carboxylic acid/colloidal TiO$_2$ one in acetonitrile[3,18] in which the anthracene-9-carboxylic acid can associate with the semiconductor. The possible reason is that anthracene-9-carboxylic acid has a free −COOH group and ANEt has not. We deduce therefore that the fluorescein moiety in the FL−AN diester adsorbs on the surface of the TiO$_2$ particles through the phenol group. The anthracene moiety does not contact the surface of the semiconductor. This is confirmed by the

TABLE 1: K_{app} Values Determined from Fluorescence Quenching and Absorption Changes

	K_{app} (mol^{-1} L)			
compound	fluorescence (exc. 475 nm)	fluorescence (exc. 355 nm)	absorption	average
FL−AN	208	262	157	209 ± 51
FLEt	176		265	221 ± 44

fluorescence characteristics of FL−AN and its reference model compounds in neat ethanol and in ethanol containing colloidal TiO$_2$ (see below).

Earlier studies[19] of the relationships between structure and absorption spectra of FLEt in aqueous media and in organic solvents suggested that the ethyl fluorescein ester FLEt exists in its monoanionic form in ethanol. Under similar conditions, we also expect the FL−AN diester also to be present in the monoanionic form in ethanol. However this notwithstanding, the diester FL−AN can be adsorbed on the TiO$_2$ particle surface by dissociative chemisorption through the phenolic −OH group:

Formation of this surface complex (reaction 3) leads to extensive changes in the absorption spectra of FL−AN (Figure 8), and the new absorbance feature at the shorter

$$\text{FL−AN} + \text{TiO}_2 \underset{}{\overset{K_{app}}{\rightleftarrows}} \{\text{TiO}_2 \cdots \text{FL−AN}\} \qquad (3)$$

wavelengths is then due to the absorbate complex. The apparent association constant in the formation of this surface complex, K_{app}, can be estimated from the changes in absorbance intensity of the new band at 460 nm from a Benesi−Hildebrand-type plot:[20]

$$A_{obs} = (1 - \alpha)A_o + \alpha A_c \qquad (4)$$

where A_{obs} is the absorbance of the dye solution containing different concentrations of colloidal TiO$_2$ at 460 nm, and α represents the degree to which FL−AN is associated to TiO$_2$; A_o and A_c are the absorbances of FL−AN and of the complex $\{\text{TiO}_2 \cdots \text{FL−AN}\}$ at 460 nm, respectively. At relatively high TiO$_2$ concentrations, α can be equated to $\{K_{app}[TiO_2]/(1 + K_{app}[TiO_2])\}$. In this case, eq 4 becomes eq 5:

$$\frac{1}{A_{obs} - A_o} = \frac{1}{A_c - A_o} + \frac{1}{K_{app}(A_c - A_o)[TiO_2]} \qquad (5)$$

Therefore, if the enhancement of absorbance at 460 nm is due to the absorption of the surface complex, a plot of $1/(A_{obs} - A_o)$ versus $1/[TiO_2]$ should yield a linear relationship with a slope equal to $1/(K_{app}(A_c - A_o))$ and an intercept equal to $1/(A_c - A_o)$; see inset in Figure 5. From the slope and intercept, we obtain $K_{app} = 157$ mol^{-1} L. A similar plot is obtained for FLEt, from which we estimate K_{app} to be 265 mol^{-1} L (Table 1).

3. Fluorescence Characteristics. The fluorescence spectra of FL−AN in neat ethanol (curves 1) and in ethanol containing colloidal TiO$_2$ in various concentrations are illustrated in Figure 6a,b. The emission spectra of Figure 6a were determined using
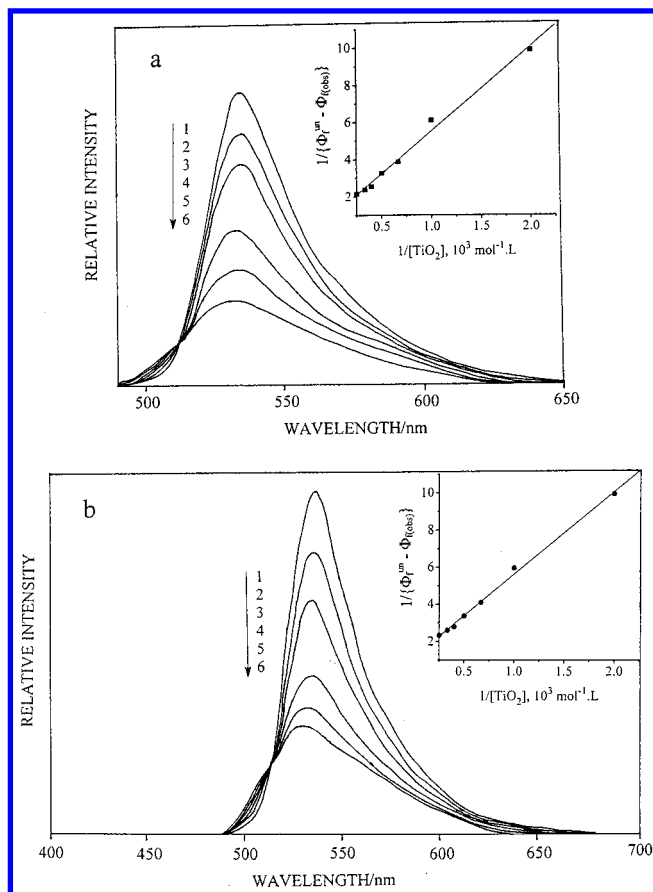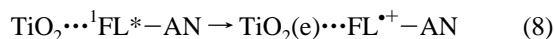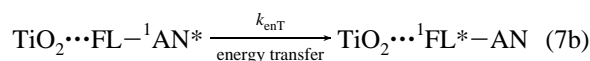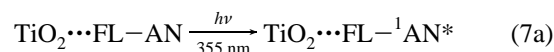
Figure 6. Fluorescence spectra of FL−AN in ethanol (5.0×10^{-6} M) with (1) 0, (2) 5.0×10^{-4} M, (3) 1.0×10^{-3} M, (4) 2.0×10^{-3} M, (5) 3.0×10^{-3} M, and (6) 4.0×10^{-3} M TiO$_2$ colloid. (a) The excitation wavelength was 470 nm. (b) The excitation wavelength was 355 nm. Insets show the dependence of $1/\{\Phi_f^{un} - \Phi_{f(obs)}\}$ on the reciprocal concentration of colloidal TiO$_2$.

the excitation wavelength 470 nm (i.e. at the isosbestic point), at which only the fluorescein moiety in FL−AN is excited. The anthracene component has no absorption features at this wavelength. The resulting fluorescence emission with a maximum at 533 nm is therefore attributed to the fluorescein moiety. Increasing the concentration of colloidal TiO$_2$ leads to a decrease in the fluorescence intensity; nearly 60% of the FL−AN (5.0×10^{-6} mol L^{-1}) emission is quenched by 4.0×10^{-3} mol L^{-1} colloidal TiO$_2$. In Figure 6b, the excitation wavelength was 360 nm, at which only the anthracene component in FL−AN shows any absorption. The fluorescence emission of the anthracene moiety should be similar to that of ANEt with a maximum at ca. 470 nm on excitation at 355 nm. No such emission was observed. Rather, as illustrated in Figure 6b, excitation of the TiO$_2$/Fl−AN system at 355 nm results in an emission whose position (533 nm) and behavior parallel the emission behavior seen in Figure 6a for the fluorescein moiety. We deduce that the emission of the anthracene component in FL−AN is totally quenched and that energy transfer has occurred from S$_1^{AN}$ to S$_1^{FL}$ (see Figure 4).

Clearly, irrespective of the excitation wavelength in the TiO$_2$/FL−AN system, addition of TiO$_2$ colloids results in the quenching of the fluorescence emission, whose decrease may be due either to (i) an interfacial electron-transfer process, (ii) to concentration quenching (singlet−singlet annihilation) of the excited adsorbate molecules,[2,9] or (iii) to an energy-transfer process between the excited diester FL−AN and colloidal TiO$_2$.

Of the three possibilities for the quenching of the FL−AN emission, interfacial electron transfer to TiO$_2$ is most likely on

the basis of the following considerations (also see below for experimental evidence in support of this process). The difference between the conduction band and the valence band of the TiO$_2$ semiconductor particle (bandgap energy, 3.2 eV for the anatase polymorph; absorption threshold ca. 385 nm) is greater than the singlet excited state energy of ca. 2.33 eV (see Figure 6). Thus no energy transfer from the singlet excited state S$_1^{FL}$ to the TiO$_2$ colloids is possible. The continuous decrease in the fluorescence emission with increasing colloidal TiO$_2$ concentration indicates a negligible (if any) contribution from a concentration quenching process for the emission quenching of ^{1}FL*−AN (Figure 6). The redox potential of the singlet excited state of FLEt, a reference model compound for FL−AN, is ca. −1.33 V versus NHE[21] (estimated from the redox potential of FLEt and its singlet state energy), whereas the Fermi level of colloidal TiO$_2$ is ca. −0.5 V (versus NHE).[3] This renders possible the occurrence of interfacial electron transfer. The quenching behavior is therefore ascribed to electron injection from S$_1^{FL}$ of the fluorescein moiety in FL−AN to the conduction band of colloidal TiO$_2$ (see Figure 4 and reactions 6−8).

$$\text{TiO}_2\cdots\text{FL−AN} \xrightarrow[475 \text{ nm}]{h\nu} \text{TiO}_2\cdots{}^1\text{FL*−AN} \qquad (6)$$

$$\text{TiO}_2\cdots\text{FL−AN} \xrightarrow[355 \text{ nm}]{h\nu} \text{TiO}_2\cdots\text{FL−}^1\text{AN*} \qquad (7a)$$

$$\text{TiO}_2\cdots\text{FL−}^1\text{AN*} \xrightarrow[\text{energy transfer}]{k_{enT}} \text{TiO}_2\cdots{}^1\text{FL*−AN} \quad (7b)$$

$$\text{TiO}_2\cdots{}^1\text{FL*−AN} \rightarrow \text{TiO}_2(e)\cdots\text{FL}^{\bullet+}\text{−AN} \qquad (8)$$

In control experiments, the fluorescence spectra of FLEt exhibited the same effect as FL−AN in neat ethanol and in ethanol containing various concentrations of colloidal TiO$_2$. Also, nearly 60% of the fluorescence emission of 5.0×10^{-6} mol L^{-1} FLEt was quenched by 4.0×10^{-3} mol L^{-1} TiO$_2$. By contrast, the fluorescence emissions from FLEt$_2$ and ANEt were not quenched by colloidal TiO$_2$, under otherwise identical conditions. The effect of colloidal TiO$_2$ on the fluorescence spectra of ANEt conflicts with that on the fluorescence spectra of anthracene-9-carboxylic acid.[3,18] The reason is that the latter can adsorb strongly on the TiO$_2$ surface and inject electrons to the conduction band of TiO$_2$ effectively, but the former cannot. This further confirms the adsorption model of FL−AN on the surface of TiO$_2$ particles in which the fluorescein moiety is adsorbed on the semiconductor particle surface through its anionic form (see above) and the anthracene moiety does not directly contact the surface of the semiconductor.

The observed fluorescence quantum yield of the sensitizer FL−AN in a colloidal TiO$_2$ dispersion $\{\Phi_{f(obs)}\}$ is related to the corresponding quantum yields for the unadsorbed sensitizer (Φ_f^{un}) and for the adsorbate $\{\Phi_f^{ads}\}$ by eq 9a:[3]

$$\Phi_{f(obs)} = (1 - \alpha)\Phi_f^{un} + \alpha\Phi_f^{ads} \qquad (9a)$$

where α is again the degree of adsorption of FL−AN onto TiO$_2$; under conditions of high [TiO$_2$], we obtain

$$\frac{1}{\Phi_f^{un} - \Phi_{f(obs)}} = \frac{1}{\Phi_f^{un} - \Phi_f^{ads}} + \frac{1}{K_{app}(\Phi_f^{un} - \Phi_f^{ads})[\text{TiO}_2]} \tag{9b}$$

The fluorescence quantum yields of FL−AN and FLEt were measured in ethanol taking fluorescein as a reference, $\Phi_f = 0.93$ in 0.1 mol L^{-1} NaOH media.[22] The quantum yields are

TABLE 2: Photophysical Data of Model Compounds and FL−AN with and without TiO$_2$ Colloids[a]

sample	excitation (nm)	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	χ^2	k_{et} (s^{-1})
FL−AN	355	4.71	100			1.20	
	475	4.76	100			1.15	
FL−AN + TiO$_2$	355	4.65	33	2.13	67	1.24	2.54×10^8
	475	5.40	23	2.41	77	1.12	2.30×10^8
FLEt	475	4.76	100			1.20	
FLEt + TiO$_2$	475	5.46	13	2.83	87	1.00	1.70×10^8

[a] [FL−AN] = [FLEt] = 1.0×10^{-6} mol L^{-1}; [TiO$_2$] = 4.0×10^{-3} mol L^{-1}. A_1 and A_2 are the percentages of the component with the defined fluorescence lifetime. The emission wavelength is 550 nm; the anthracene moiety displayed no emission at this wavelength because of the singlet energy transfer process (see text).
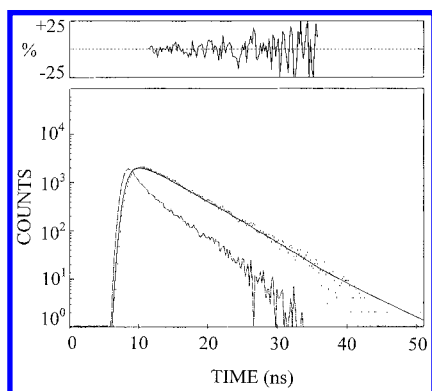

Figure 7. Fluorescence emission decay and normalized instrument response curves for 1.0×10^{-6} M FL−AN in 4.0×10^{-3} M colloidal TiO$_2$/ethanol solution. The excitation wavelength was 475 nm, and the fluorescence emission was recorded at 550 nm.

0.77 and 0.78 for FL−AN and FLEt, respectively. Excellent linear plots are obtained for $1/\{\Phi_f^{un} - \Phi_{f(obs)}\}$ versus $1/[\text{TiO}_2]$ for FL−AN {insets to Figure 6a,b}, and this regardless of which component is excited. An identical plot was obtained for FLEt under similar conditions. K_{app} can be assessed from the slopes and intercepts of the two plots. The results are listed in Table 1 together with those from the corresponding absorption spectral changes. The various values of K_{app} are in fairly good agreement: average, 209 ± 51 mol^{-1} L.

The K_{app} values are of the same order of magnitude as those obtained for SCN$^-$ with colloidal TiO$_2$ particles[23] and diethyldithiocarbamate with colloidal CdS particles;[24] however, they are an order of magnitude smaller than for the anthracene-9-carboxylic acid/colloidal TiO$_2$[3] and chlorophyllin/colloidal TiO$_2$[5] systems in acetonitrile. Adsorption interactions between the phenolic O−H group and the metal-oxide semiconductor surface are probably weaker than those seen when the adsorbing group is a carboxylate.

4. Fluorescence Lifetimes. Molecules adsorbed on a colloidal semiconductor particle surface typically display significantly shorter fluorescence lifetimes than unadsorbed molecules; this decrease in lifetimes can be correlated with the interfacial electron-transfer process.[3−5] When either the fluorescein or the anthracene moiety in FL−AN was excited in neat ethanol, the fluorescence decay could be described by single-exponential kinetics: $\tau = 4.76$ ns if the fluorescein moiety was directly excited and $\tau = 4.71$ ns for exciting the anthracene component. In the presence of colloidal TiO$_2$, the fluorescence emission decay of FL−AN deviates from a single-exponential decay irrespective of whether the fluorescein or anthracene moiety was excited. In the latter case, the emission decay follows two-exponential decay kinetics, with the longer-lived component reflecting the emission lifetime of the unadsorbed
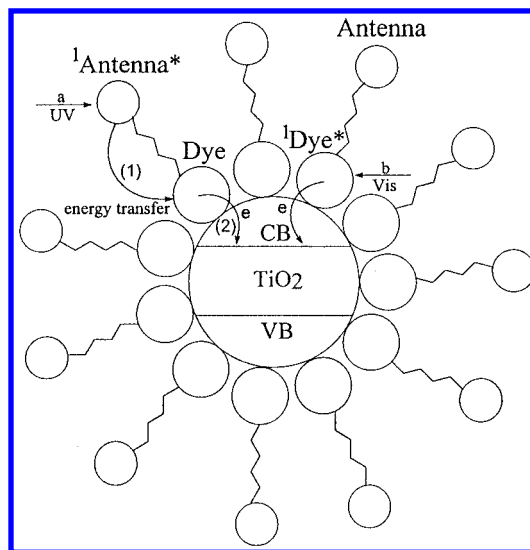

Figure 8. Schematic model of adsorption and interfacial electron transfer from the dye−antenna to the semiconductor particle: (a) excitation with ultraviolet light; (b) excitation with visible light.

FL−AN, whereas the shorter-lived component arises from the FL−AN/TiO$_2$ surface complex (see Table 2). Figure 7 illustrates the observed emission decay for a system defined by 1.0×10^{-6} mol L^{-1} FL−AN in ethanolic media containing 4.0×10^{-3} mol L^{-1} TiO$_2$ and which followed biphasic kinetics when the fluorescein moiety was directly excited at 475 nm. The fluorescence lifetimes for FL−AN and for the model compound FLEt are collected in Table 2.

In keeping with earlier studies,[3,5] we assume that the radiative and nonradiative decay processes of the singlet ^{1}FL*−AN state associated with colloidal TiO$_2$ occur at rates otherwise identical to those of ^{1}FL*−AN in neat ethanol in the absence of TiO$_2$. Under these conditions, the observed lifetimes of Table 2 can be correlated to the rate for interfacial electron transfer (Table 2) by eq 10:

$$\frac{1}{k_{et}} = \frac{1}{\tau_{ads}} - \frac{1}{\tau_{un}} \tag{10}$$

where τ_{ads} and τ_{un} denote the emission lifetimes for the FL−AN/TiO$_2$ surface complex and for the unadsorbed sensitizer, whereas k_{et} is the specific rate constant for the charge injection process (see Figure 4). These rates are in fair agreement with those reported earlier[3] for the anthracene-9-carboxylic acid/TiO$_2$ system in acetonitrile (4.8×10^8 s^{-1}) and for the eosin-Y/TiO$_2$ system in aqueous media (8.5×10^8 s^{-1}).[2] We noted earlier that the energy-transfer rate from the FL−^{1}AN* state to the ^{1}FL*−AN state is 2.23×10^{10} s^{-1}, about 2 orders of magnitude faster than charge injection from ^{1}FL*−AN into the conduction band of TiO$_2$ (see Figure 4). Evidently, charge injection is rate-determining. Also, whether the fluorescein dye is excited directly or the anthracene antenna molecule is excited first seems to have little effect on the charge injection rate.

Most remarkable from the above discussion is that the dye−antenna device, FL−AN, can photosensitize colloidal TiO$_2$ through absorption of ultraviolet and visible light, thereby greatly improving the light-harvesting efficiency and the ultimate application of TiO$_2$ in solar energy conversion devices. This collection and the structural capping of the TiO$_2$ particle by the dye−antenna system is schematically portrayed in Figure 8.

5. ESR Measurements under Steady-State Laser Irradiation. Interfacial electron transfer between FL−AN or FLEt and the semiconductor colloid particles was further elucidated by
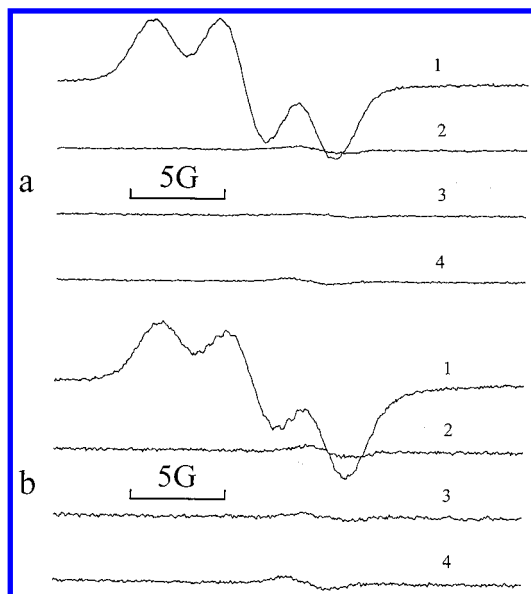
Figure 9. ESR spectra for samples of (1) 2.5×10^{-4} M FL−AN in 2.5×10^{-2} M colloidal TiO$_2$/ethanol solution under steady-state laser irradiation, (2) 2.5×10^{-4} M FL−AN in 2.5×10^{-2} M colloidal TiO$_2$/ ethanol solution without irradiation, (3) 2.5×10^{-4} M FL−AN, and (4) 2.5×10^{-2} M colloidal TiO$_2$ in ethanol under steady-state laser irradiation: (a) 532 nm steady-state laser irradiation; (b) 355 nm steady-state laser irradiation.

electron spin resonance spectroscopy under steady-state laser irradiation, a technique that has proven useful to examine photoinduced electron transfer[25] and reaction mechanisms.[26−28] Figure 9a illustrates that the ESR spectra recorded under 532 nm laser irradiation leads to excitation of the fluorescein component of the FL−AN diester; the relevant concentrations were 2.5×10^{-4} mol L^{-1} in FL−AN and 2.5×10^{-2} mol L^{-1} of colloidal TiO$_2$ in ethanol (curve 1); g was 2.0047. In the absence of laser irradiation, no ESR signal was observed (curve 2). Also, no signals were detected when the irradiated ethanolic solution contained either FL−AN (2.5×10^{-4} mol L^{-1}; curve 3) or colloidal TiO$_2$ (2.5×10^{-2} mol L^{-1}; curve 4).

A similar sequence of ESR spectra was obtained for the FL− AN/colloidal TiO$_2$ system by irradiating the anthracene moiety in FL−AN at 355 nm (Figure 9b, curve 1); the g value is also 2.0047. No ESR signal was detected for the FL−AN/colloidal TiO$_2$ system in the absence of irradiation; 355 nm steady-state laser irradiation of the ethanolic solution containing only FL− AN or colloidal TiO$_2$ also gave no signals (Figure 9b, curves 2−4).

In other control experiments, similar ESR spectral results were obtained for the FLEt system under 532 nm laser irradiation; also, a solution of colloidal TiO$_2$ in ethanol (2.5×10^{-2} mol L^{-1}) gave no observable ESR signals when irradiated at 266 nm.

From the above results, the ESR signals of curve 1 in Figure 9a and curve 1 in Figure 9b are ascribed to the cation radical of the fluorescein moiety in the diester, FL$^{\bullet+}$−AN. This further supports the inference made earlier that adsorption of the FL− AN diester to the TiO$_2$ particle surface implicates the fluorescein moiety. The fact that the same cation radical, FL$^{\bullet+}$−AN, is formed upon exciting either the fluorescein component or the anthracene moiety subsequent to electron injection to the semiconductor particles confirms the optical spectroscopic results noted above.

6. Laser Flash Photolysis. Previous reports[2−5,9] have shown that laser flash photolysis is another convenient and effective technique with which to investigate interfacial electron-transfer
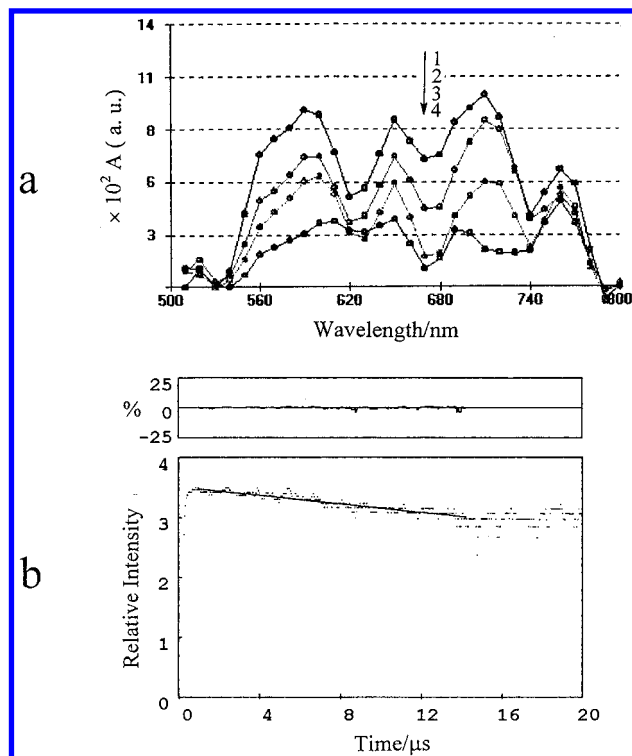

Figure 10. (a) Time-resolved transient absorption spectra of 2.5×10^{-4} M FL−AN in 2.5×10^{-2} M colloidal TiO$_2$/ethanol solution upon 532 nm laser pulse excitation, (1) 1.0 μs; (2) 6.7 μs; (3) 11.7 μs; and (4) 19.4 μs after the laser pulse. (b) Decay profile at 700 nm and normalized instrument response curve.

processes between sensitizers and colloidal semiconductor particles. If quenching of the FL−AN fluorescence in the presence of colloidal TiO$_2$ in ethanol were due to charge injection from the singlet excited state of the fluorescein moiety, ^{1}FL*−AN, to the conduction band of the semiconductor, it should be possible to detect and confirm the cation radical FL$^{\bullet+}$−AN. Laser flash photolysis experiments were carried out by 532 nm laser pulsed excitation of FLEt and of the fluorescein moiety in FL−AN and also by the 355 nm laser pulsed excitation of the anthracene component.

Figure 10a shows the time-resolved transient absorption spectra for an ethanolic solution containing 2.5×10^{-4} mol L^{-1} FL−AN and 2.5×10^{-2} mol L^{-1} colloidal TiO$_2$ obtained by excitation at 532 nm. Similar spectral results were obtained for an ethanolic solution of 2.5×10^{-4} mol L^{-1} FLEt and 2.5×10^{-2} mol L^{-1} colloidal TiO$_2$. By contrast, ethanolic solutions containing either 2.5×10^{-4} mol L^{-1} FL−AN or 2.5×10^{-4} mol L^{-1} FLEt but in the absence of colloidal TiO$_2$ showed negligible transient absorption in this region. We therefore attribute the spectra shown in Figure 10a to absorption by the cation radicals of the fluorescein moieties in FLEt and FL− AN. The decay profile at 700 nm illustrated in Figure 10b infers a lifetime of about 12.2 μs for the cation radical FL$^{\bullet+}$−AN.

A similar sequence of time-resolved transient absorption spectra was obtained for FL−AN in the presence and absence of colloidal TiO$_2$ in ethanol upon 355 nm laser pulsed excitation of the anthracene moiety in FL−AN; they are shown in Figure 11a. The decay profile at 700 nm shown in Figure 11b suggests a lifetime of about 9.7 μs for the FL$^{\bullet+}$−AN radical.

These results further support an interfacial electron transfer taking place between the ^{1}FL*−AN and the TiO$_2$ semiconductor and confirm the earlier suggestion that owing to singlet energy transfer, exciting the anthracene moiety in FL−AN using ultraviolet light has the same effect as exciting the fluorescein
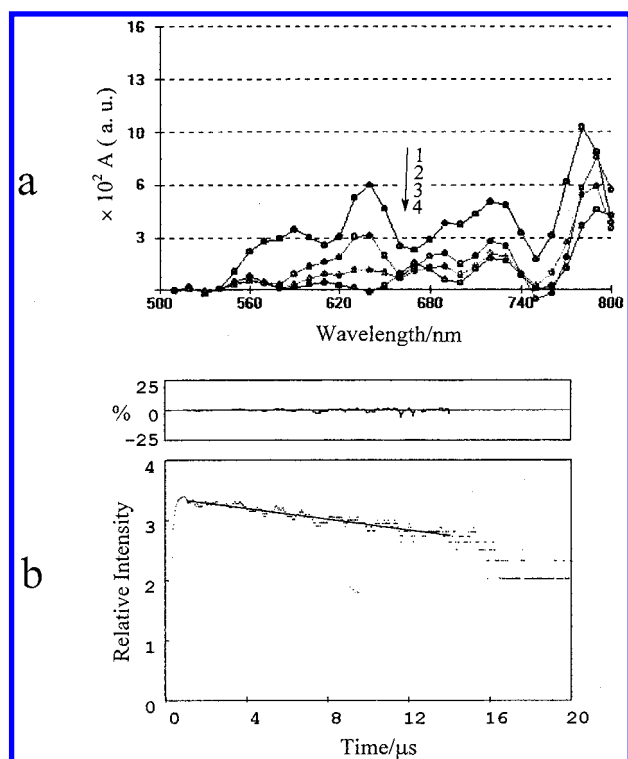
Figure 11. (a) Time-resolved transient absorption spectra of 2.5 × 10^{-4} M FL−AN in 2.5 × 10^{-2} M colloidal TiO_2/ethanol solution upon 355 nm laser pulse excitation, (1) 1.0 μs; (2) 6.7 μs; (3) 11.7 μs; and (4) 19.4 μs after the laser pulse. (b) Decay profile at 700 nm and normalized instrument response curve.

component with visible light in the sensitization of the wide bandgap TiO_2 semiconductor.

Conclusions

The FL−AN diester adsorbs to the surface of colloidal TiO_2 particles through the anionic form of the phenolic group of the fluorescein moiety, with the anthracene moiety acting as an energy donor but not in contact with the surface of the semiconductor. Exciting the fluorescein moiety with visible light induces electron injection from its singlet excited state ^{1}FL*−AN to the conduction band of TiO_2. When the anthracene moiety in FL−AN is excited with ultraviolet light, it first transfers its singlet excited state energy to the fluorescein singlet excited state of FL−AN, subsequently followed by electron injection from ^{1}FL*−AN to TiO_2, thereby greatly improving solar energy harvesting and conversion.

The present report follows an earlier study from one of our laboratories[29] in which we examined the subnanosecond relaxation dynamics of the 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) monoanion, ABTSH(−H$^+$), and the dianion ABTS(−2H$^+$), together with the chlorpromazine cation C1PMZ(+H$^+$) in the presence and absence of TiO_2 colloids to assess the photosensitization of wide bandgap metal oxide semiconductors. Fluorescence emissions from ABTSH(−H$^+$) and ABTS(−2H$^+$) were quenched by TiO_2 by an interfacial

electron-transfer process that implicated the singlet excited states of the dyes and the conduction band and/or surface states of TiO_2 (electron injection). Current work[30] addresses similar subnanosecond relaxation dynamics of FL−AN with and without TiO_2 colloids together with the model compounds ANEt, FLEt, and FLEt$_2$ to obtain a more complete portrait of the events of the photosensitization process(es) taking place in faster time for the attendant dye−antenna system.

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