# Electron Transfer

# Extensive Reduction in Back Electron Transfer in Twisted Intramolecular Charge-Transfer (TICT) Coumarin-Dye-Sensitized TiO<sub>2</sub> Nanoparticles/Film: A Femtosecond Transient Absorption Study

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Abstract: We report the synthesis, characterization, and optical and electrochemical properties of two structurally similar coumarin dyes (C1 and C2). These dyes have been deployed as sensitizers in TiO<sub>2</sub> nanoparticles and thin films, and the effect of molecular structure on interfacial electron-transfer dynamics has been studied. Steady-state optical absorption, emission, and time-resolved emission studies on both C1 and C2, varying the polarity of the solvent and the solution pH, suggest that both photoexcited dyes exist in a locally excited (LE) state in solvents of low polarity. In highly polar solvents, however, C1 exists in an intramolecular chargetransfer (ICT) state, whereas C2 exists in both ICT and twisted intramolecular charge-transfer (TICT) states, their populations depending on the degree of polarity of the solvent and the pH of the solution. We have employed femtosecond transient absorption spectroscopy to monitor the charge-transfer

# Introduction

Dye-sensitized solar cells (DSSCs) based on organic dyes and transition metal complexes have attracted great attention since Grätzel and co-workers reported their seminal work in 1991.<sup>[1]</sup> Globally, scientists have directed enormous research efforts towards improving the power conversion efficiencies of DSSCs to make them economically viable.<sup>[2]</sup> To date, the best efficiencies obtained have been about 11–12% using the classical N3 dye and a porphyrin-based sensitizer system. In addition to testing the efficacies of different sensitizer molecules in DSSCs, significant effort in this area of research has been di-

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dynamics in C1- and C2-sensitized TiO<sub>2</sub> nanoparticles and thin films. Electron injection has been confirmed by direct detection of electrons in the conduction band of TiO<sub>2</sub> nanoparticles and of radical cations of the dyes in the visible and near-IR regions of the transient absorption spectra. Electron injection in both the C1/TiO<sub>2</sub> and C2/TiO<sub>2</sub> systems has been found to be pulse-width limited (< 100 fs); however, backelectron-transfer (BET) dynamics has been found to be slower in the C2/TiO<sub>2</sub> system than in the C1/TiO<sub>2</sub> system. The involvement of TICT states in C2 is solely responsible for the higher electron injection yield as well as the slower BET process compared to those in the C1/TiO<sub>2</sub> system. Further pH-dependent experiments on C1- and C2-sensitized TiO<sub>2</sub> thin films have corroborated the participation of the TICT state in the slower BET process in the C2/TiO<sub>2</sub> system.

rected towards gaining a better understanding of the factors that actually control interfacial electron-transfer dynamics, so that the efficiency of the devices may ultimately be improved.<sup>[3]</sup> The most important processes, that are directly relevant for achieving better efficiency of DSSCs, are electron injection from the photoexcited dye to the conduction band of the semiconductor and slow back electron transfer from the semiconductor to the parent dye cation.<sup>[3]</sup> In this regard, Ru<sup>II</sup>-based complexes, such as N3, N719, and black dyes have been at the forefront, showing photoconversion efficiencies above 11%. Recently, Grätzel and co-workers<sup>[2d]</sup> have reported porphyrinsensitized solar cells with a cobalt(II/III)-based redox electrolyte, the efficiencies of which exceeded 12%. Although Ru<sup>II</sup>-based polypyridyl complexes continue to be investigated, metal-free organic dyes have also been attracting much research effort due to their comparatively low cost, high molar absorptivities, and facile synthetic modification, whereby their spectral range can be extended through judicious selection of attached functional groups.<sup>[4]</sup> The efficiencies of DSSCs based on organic dyes are generally lower than those of cells based on Ru<sup>II</sup> dyes, although the highest photoconversion efficiency of an organic dye-sensitized solar cell hitherto reported is above 9%. Among the organic dye sensitizers tested in DSSCs, coumarin dyes are



strong candidates because of their good photoelectric conversion properties.<sup>[4a-c]</sup> One of the main reasons for the high efficiencies of N3, N719, and black dyes is reduced charge recombination in these thiocyanate-substituted Ru<sup>II</sup> dyes, with the electron density of the HOMO extending over the Ru<sup>II</sup> centre and NCS ligands.<sup>[5]</sup> Holes can thereby be localized away from the TiO<sub>2</sub> surface. Ancillary ligands in Ru<sup>II</sup> complexes and metalfree organic dyes have likewise been used for hole localization away from a TiO<sub>2</sub> surface.<sup>[6]</sup> We have also demonstrated slow charge recombination in TiO<sub>2</sub> nanoparticles sensitized with Ru<sup>II</sup>-polypyridyl complexes by introducing an electron-donating ligand at the Ru<sup>II</sup> centre on which holes can be localized.<sup>[7]</sup>

Some organic dye molecules possessing donor and acceptor groups can exhibit dual emission, the second emission being associated with highly polar excited electronic structure.<sup>[8]</sup> Such polar forms usually originate from the transfer of an electron from a donor group to an acceptor group within the molecular structure. The charge-separation process within the molecule is facilitated by a polar environment, with the formation of a twisted intramolecular charge transfer (TICT) state. Clearly, if the solvent polarity induces a change in the excited electronic state leading to a highly polar form through charge separation within the molecule, an ideal situation for electron injection into the conduction band of the TiO<sub>2</sub> nanoparticle can be created. Previously, we demonstrated more efficient electron injection from 7-diethylamino-coumarin 3-carboxylic acid (D-1421) as compared to coumarin 343 (C-343).<sup>[9]</sup> These dyes are structurally similar, except that D-1421 exists in a twisted intramolecular charge-transfer state (TICT) whereas C-343 exists in an intramolecular charge-transfer (ICT) state after photoexcitation in a polar solvent.<sup>[9a]</sup> Similarly, Sun and co-workers<sup>[10]</sup> found evidence for the involvement of a TICT state in a dye-sensitized solar cell and showed improved efficiency in the case of TICT molecules. In both cases, a conformational change in the excited state during electron injection seems to provide an ideal environment for efficient electron injection and slow charge-recombination kinetics between the injected electron and the oxidized dye. To understand the effect of the TICT state on the conversion efficiency in a DSSC, it is very important to monitor both the electron injection and charge re-

combination dynamics on the ultrafast time scale. However, to the best of our knowledge, no such reports have appeared in the literature except our preliminary report on the D-1421/TiO<sub>2</sub> system.<sup>[9b]</sup>

To understand the effect of molecular structure on electron injection and back electron transfer in dye-sensitized  $TiO_2$  nanoparticles, in the present investigation we have synthesized two new structurally similar coumarin dyes (**C1** and **C2**). These have been characterized and their optical properties have

been studied. Both the ground- and excited-state optical properties suggest that photoexcited C1 and C2 both exist in a locally excited (LE) state in solvents of low polarity. However, in highly polar solvents, C1 exists in an intramolecular chargetransfer (ICT) state, whereas C2 exists in both ICT and twisted intramolecular charge-transfer (TICT) states, depending on the polarity of the solvent and the pH of the medium. To elucidate the effect of the ICT and TICT states on the ET dynamics, we have carried out femtosecond transient absorption spectroscopy on both C1- and C2-sensitized TiO<sub>2</sub> nanoparticles and thin films, and have monitored the transients in the visible and near-IR regions. Electron injection and back-ET dynamics have been monitored by direct detection of electrons in the conduction band of the nanoparticles and the radical cations of the dyes. Electron injection and back-ET dynamics have been compared in the C1/TiO<sub>2</sub> and C2/TiO<sub>2</sub> systems. To verify the participation of the TICT state, pH-dependent experiments have been carried out on C1- and C2-sensitized  $TiO_2$  thin films.

### **Results and Discussion**

#### Solvatochromic behaviour of C1 and C2

The main aim of this investigation has been to ascertain the effect of the structures of the newly synthesized coumarin dyes C1 and C2 on the interfacial electron-transfer dynamics. Hence, it was very important to study their solvatochromic behaviour, that is, the solvent-dependent optical properties of these coumarins, in order to delineate their charge-transfer properties. We measured the steady-state absorption and emission properties of C1 and C2 in solvents of different polarity as shown in the Supporting Information, and the related photophysical data are summarized in Table 1. Interestingly, we observed that both the absorption and emission bands of C1 and C2 were red-shifted with increasing polarity of the solvent. Figure 1 (upper panel) shows the steady-state optical absorption and emission spectra of C1 in cyclohexane (low polarity) and in water (high polarity). C1 shows optical absorption and emission peaks at 430 nm (a) and 450 nm (b) in cyclohexane and at 482 nm (c) and 510 nm (d) in water. The absorption

 Table 1. Absorption ( $\lambda_{abs}$ ) and fluorescence ( $\lambda_{em}$ ) maxima, Stokes shifts ( $\Delta \nu_{st}$ ), and lifetimes ( $\tau_t$ ) of C1 and C2 in different solvents of different polarity.

 Dye
 Solvent
 Dielectric constant
  $\lambda_{abs}$  [nm]
  $\lambda_{em}$  ICT/LE [nm]
  $\Delta v_{st}$  [cm<sup>-1</sup>]
  $\tau$  ICT/LE [ns]

| Dye | Solvent       | Dielectric constant | $\lambda_{abs}$ [nm] | $\lambda_{\rm em}$ ICT/LE [nm] | $\Delta v_{\rm St}  [\rm cm^{-1}]$ | $\tau$ ICT/LE [ns]     |
|-----|---------------|---------------------|----------------------|--------------------------------|------------------------------------|------------------------|
| C1  | water         | 80                  | 482                  | 510                            | 1139                               | 4.19                   |
|     | acetonitrile  | 37.5                | 443                  | 498                            | 2493                               | 3.46                   |
|     | ethanol       | 24.55               | 442                  | 494                            | 2381                               | 3.37                   |
|     | ethyl acetate | 6.02                | 436                  | 483                            | 2232                               | 2.94                   |
|     | cyclohexane   | 2.02                | 430                  | 450                            | 1034                               | 2.5                    |
|     |               |                     |                      | $\lambda_{\rm em}$ ICT/LE,     | $\Delta v_{St}$ 1,                 | $\tau_{\rm av}$ ICT/LE |
|     |               |                     |                      | $\lambda_{em}$ TICT            | $\Delta v_{St}$ 2                  | $\tau_{av}$ TICT       |
|     |               |                     |                      | [nm]                           | [cm <sup>-1</sup> ]                | [ns]                   |
| C2  | water         | 80                  | 442                  | 498, 625                       | 2544, 6624                         | 0.16, 0.09             |
|     | acetonitrile  | 37.5                | 421                  | 485, 523, 633                  | 3134, 4632, 7955                   | 1.08, 0.38             |
|     | ethanol       | 24.55               | 420                  | 485, 555                       | 3191, 5791                         | 2.02                   |
|     | ethyl acetate | 6.02                | 414                  | 474, 500                       | 3058, 4155                         | 1.311                  |
|     | cyclohexane   | 2.02                | 406                  | 443                            | 2057                               | 2.4                    |

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Figure 1. Upper panel: Absorption (a, c) and emission spectra (b, d) of coumarin 1 (C1) in cyclohexane and in water, respectively. Lower panel: Absorption (e, g) and emission spectra (f, h) of coumarin 2 (C2) in cyclohexane and in water, respectively.

spectra generally consist of one broad band in the visible region and a less intense absorption band in the near-UV region, which correspond to the locally excited (LE)  $\pi$ - $\pi$ \* transition in a nonpolar solvent (cyclohexane) and the ICT transition in a highly polar solvent (water). The narrower emission band in cyclohexane can be attributed to LE emission, whereas the broader band in water can be attributed to ICT emission.

We also recorded the optical absorption and emission spectra of C2 in cyclohexane and water (Figure 1, lower panel). The optical absorption spectra of C2 are typical of a coumarin, the absorption peak appearing at 406 nm in cyclohexane (e) and being bathochromically shifted to 442 nm in water (g). We have also monitored the emission behaviour of C2 in different solvents with increasing polarity, and the results are reported in the Supporting Information. Figure 1 f, h show the emission spectra of C2 in cyclohexane and water, respectively. It can clearly be seen that the emission spectra of C2 and C1 in cyclohexane are guite similar, being attributable to the LE state emission. However, the spectrum of C2 in water features an emission peak at 498 nm with a broad red-shifted shoulder at 620 nm. The molecular structures of C1 and C2 differ in that C2 bears a diethylamino group, whereas the nitrogen atom is incorporated into a ring in C1 (Scheme 1). In our previous investigation,<sup>[9a]</sup> we reported that the photophysical properties of coumarin dyes are very sensitive to rotational hindrance of 7-amino substituents. The rotation of the amine functionality results in excited-state conformers, that is to say, near-planar and near-perpendicular twisted conformers.<sup>[3]</sup> Photoexcitation



Scheme 1. Molecular structures of coumarin 1 and coumarin 2.

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to LE states leads to ICT and TICT states, the populations of which depend on the freedom of the 7-amino moiety to rotate in the local environment.<sup>[2]</sup> A separate emission band from a TICT state, red-shifted with respect to that of the ICT state, was first detected by Rettig and co-workers<sup>[14]</sup> for for *p*-(*N*,*N*-dimethylamino)benzonitrile (DMABN) due to charge localization in this donor–acceptor molecule. Thus, in the present investigation, the second red-shifted emission band can be attributed to TICT emission. From the emission spectra of **C1** and **C2** recorded in different media, it is clear that the second emission band appears for **C2** in highly polar solvents, whereas no such emission is observed for **C1**.

To confirm that the second emission band for **C2** was due to TICT emission, we examined the pH dependence of the emission spectra of **C1** and **C2** in water. Figure 2 (upper panel) shows the emission spectra of **C1** recorded at different pH of



**Figure 2.** Upper panel: Emission spectra of ICT state of **C1** at different pH values (decreasing order: 7–1) in water. Inset: Emission spectra of LE state of **C1** in the a) presence and b) absence of acid in cyclohexane. Lower panel: Emission spectra of ICT and TICT states of **C2** at different pH values (decreasing order: 7–1) in water. Inset: Emission spectra of LE state of **C2** in the a) presence and b) absence of acid in cyclohexane.

the solution. It can clearly be seen that the ICT emission band intensity of **C1** gradually decreases with decreasing pH of the solution. Interestingly, in the emission spectra of **C2**, which consist of both ICT and TICT emission bands, the ICT band decreases with decreasing pH whereas the TICT band completely vanishes at lower pH. It is clear from Scheme 1 that these coumarin molecules are donor–acceptor in nature, and upon photoexcitation electrons are localized on the coumarin moiety and holes are localized at the nitrogen atom. In **C2**, holes are localized at the nitrogen atom of the diethylamino group. At lower pH, due to protonation of the nitrogen atom, hole delocalization will not take place, and as a result no TICT emission can be observed. Interestingly, no change in emission intensity due to the LE state (in cyclohexane) was observed for either **C1** or **C2** in acidic solution (inset in Figure 2).



#### Time-resolved fluorescence (TCSPC) measurement

To understand the involvement of different charge-transfer states for the coumarins **C1** and **C2**, we measured their fluorescence lifetimes ( $\tau_f$ ) in solvents of varying polarity, and the results are summarized in Table 1. Figure 3 (upper panel) shows



Figure 3. Panel A: Time-resolved emission decay traces of coumarin 1 (C1) a) in cyclohexane at 460 nm and b) in water at 500 nm after excitation at 405 nm. Panel B: Time-resolved emission decay traces of coumarin 2 (C2) c) in cyclohexane at 460 nm, d) in water at 500 nm, and e) in water at 620 nm after excitation at 405 nm.

the emission decay traces of C1 in cyclohexane at 460 nm (a) and in water at 500 nm (b). Emission quantum yields for C1 were determined to be about 40% in cyclohexane and 20% in water; however, those for C2 drastically reduced from about 50% in cyclohexane to 4.5% in water. The emission decay traces of C1 could be fitted by single exponentials with time constants of 2.5 ns in cyclohexane and 4.19 ns in water (Table 1 and Table S1). The emission decay traces of C2 are depicted in Figure 3 (lower panel), as obtained in cyclohexane at 460 nm (c) and in water at 500 nm (d) and at 620 nm (e) after excitation at 405 nm. It is interesting to note that the emission decay trace in cyclohexane can be fitted by a single exponential with a time constant of  $\tau = 2.4$  ns, whereas that in water at 500 nm can be fitted multi-exponentially with time constants of  $\tau_1\!=\!0.05~\text{ns}$  (80.8%),  $\tau_2\!=\!0.22~\text{ns}$  (16.5%), and  $\tau_3\!=\!3.15~\text{ns}$ (2.7%), with  $\tau_{av} = 0.16$  ns. That at 620 nm can be fitted multiexponentially with time constants of  $\tau_1 = 0.05$  ns (87.6%),  $\tau_2 =$ 0.18 ns (11.4%), and  $\tau_3 = 2.24$  ns (1%), with  $\tau_{av} = 0.09$  ns (Table 1). It is clear that the majority of the luminescence in water decays with pulse-width limited time. Rettig and coworkers have reported that dimethylamino-benzoic acid ethyl ester (DMABEE) decays non-exponentially with a very short lifetime in highly polar solvents. They attributed this to excitation of the molecule to an LE (locally excited) or ICT state, followed by very fast relaxation to the TICT state. Non-radiative decay rates for this molecule were found to be very high. The transition from LE/ICT state to TICT was considered to be barrierless.<sup>[14]</sup> Similarly, in our previous investigation,<sup>[9a]</sup> we also observed fast non-exponential emission decay for coumarin D-

1421, which exists in a TICT state in a highly polar solvent such as water. It is interesting to note that the emission lifetime and quantum yield of C1 changed only marginally with the polarity of the solvent, whereas the average emission lifetime and emission quantum yield of C2 decreased drastically with increasing polarity of the solvent (Table 1). The faster emission decay for C2 in a highly polar solvent can be ascribed to the presence of a fast non-radiative decay channel from the LE/ICT state to the TICT state. However, there is still a minor contribution from a slower time component of 2-3 ns, which can be attributed to the lifetime of the LE/ICT state. From the above experimental observations of steady-state absorption and emission, as well as the time-resolved studies, we can conclude that both C1 and C2 exist in an LE state in solvents of low polarity, but that in a highly polar solvent C1 exists in an ICT state whereas C2 exists in both ICT and TICT states, their populations depending on the degree of polarity. We then proceeded to investigate the effect of molecular structure and the involvement of the ICT and TICT states in interfacial electron-transfer dynamics on the surface of TiO<sub>2</sub> nanoparticles/thin films sensitized with these coumarin dyes.

# Optical absorption and emission studies on TiO<sub>2</sub> nanoparticle surfaces

The main aim of the present investigation has been to design and synthesize new, tailor-made coumarin dyes capable of serving as more efficient solar sensitizers. To delineate the effect of molecular structure, which in turn affects solar conversion efficiency, it was imperative to study interfacial electron transfer (IET) dynamics on the surface of  $TiO_2$  nanoparticles. For this, it was essential to study the optical absorption and emission behaviour of **C1** and **C2** on  $TiO_2$  nanoparticles. Figure 4 depicts the optical absorption and emission behaviour



**Figure 4.** Steady-state absorption spectra of C1 (upper panel) and C2 (lower panel) in the absence and presence of different TiO<sub>2</sub> nanoparticle concentrations a) 0.0, b) 0.039, c) 0.078, d) 0.312, e) 0.625, f) 2.5, and g) 5 g L<sup>-1</sup> in 35  $\mu$ m dye in water. Inset in upper panel: Emission spectra of C1 in the m) absence and n) presence of 5 g L<sup>-1</sup> TiO<sub>2</sub> nanoparticles. Inset in lower panel: Emission spectra of C2 in the p) absence and q) presence of 5 g L<sup>-1</sup> TiO<sub>2</sub> nanoparticles.

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of **C1** and **C2** free in solution and when adsorbed on a TiO<sub>2</sub> nanoparticle surface. The effect of increasing amounts of TiO<sub>2</sub> on the absorption spectra of **C1** and **C2** is shown. On addition of TiO<sub>2</sub> nanoparticles, the optical densities at the absorption peaks of the respective dyes are seen to increase. The peaks are also broadened and slightly red-shifted. These observations strongly suggest that both the dyes interact quite strongly with the surface of the TiO<sub>2</sub> nanoparticles. The equilibrium constants ( $K_{eq}$ ) for adsorption of **C1** and **C2** on TiO<sub>2</sub> nanoparticles were determined as  $0.6 \times 10^6 \,\mathrm{m^{-1}}$  and  $1.5 \times 10^6 \,\mathrm{m^{-1}}$ , respectively, according to the Benesi–Hildebrand (B-H) equation.<sup>[15]</sup>

The charge-transfer interaction between dye and TiO<sub>2</sub> nanoparticles in the excited state was investigated by luminescence spectroscopy. The emission spectra of C1 and C2 in the absence and presence of TiO<sub>2</sub> nanoparticles are shown in the inset in Figure 4. It can clearly be seen that in the presence of TiO<sub>2</sub> nanoparticles the emission intensities of both C1 and C2 are drastically reduced. This reduction of emission intensity can be attributed to electron injection from the photoexcited coumarin dyes to the conduction band of the TiO<sub>2</sub> nanoparticles. It is interesting to note that for C2 free in solution, two emission bands are seen at 496 and 620 nm, assigned to ICT and TICT states, respectively, whereas in the presence of TiO<sub>2</sub> nanoparticles the ICT emission is greatly diminished and that due to the TICT state completely vanishes. This suggests that the TICT state is a better injecting state than the ICT/LE states of coumarin dyes. Recently, Zietz and co-workers<sup>[16]</sup> have reported that photoisomerization due to molecular rotation of the dye D-149 is suppressed on a ZrO<sub>2</sub> surface. One can envisage similar behaviour (suppression of molecular rotation) for dye C2 on both  $ZrO_2$  and  $TiO_2$  surfaces (TiO<sub>2</sub> and  $ZrO_2$  are chemically very similar).<sup>[17]</sup> As a result, the TICT state might not be observed on  $TiO_2$  or  $ZrO_2$  surfaces. In fact, however, we clearly observed the TICT state on a ZrO<sub>2</sub> surface (Supporting Information). On this basis, we expected that the TICT state might also be seen on a TiO<sub>2</sub> surface. However, due to efficient electron injection from the TICT state, no emission band due to a TICT state on the TiO<sub>2</sub> surface was observed. It is very difficult to elucidate the effect of TICT on IET dynamics from steady-state absorption and emission spectra. To comprehend the effect of TICT on IET dynamics, we carried out ultrafast transient absorption measurements on the  $C1/TiO_2$  and C2/TiO<sub>2</sub> systems, exciting the samples with 400 nm laser light, and compared the dynamics (see below).

# Ultrafast transient absorption measurements on the C1/TiO<sub>2</sub> and C2/TiO<sub>2</sub> systems

To study the effects of molecular structure and the TICT states of coumarin dyes on interfacial electron-transfer dynamics, we carried out transient absorption measurements on both **C1**and **C2**-sensitized TiO<sub>2</sub> nanoparticles excited with 400 nm femtosecond laser pulses. Figure 5 shows the time-resolved transient absorption spectra of the **C1**/TiO<sub>2</sub> (upper panel) and **C2**/ TiO<sub>2</sub> (lower panel) systems in water. For both systems, the spectrum at each time delay consists of bleach below 570 nm, a positive absorption band in the region 580–700 nm with



Figure 5. Transient absorption spectra of the  $C1/TiO_2$  (upper panel) and  $C2/TiO_2$  (lower panel) systems in water at different time delays after exciting the samples with 400 nm laser light.

a peak at around 650 nm, and a broad positive feature in the whole spectral region (750-900 nm). The bleach signal can be attributed to the degradation of coumarin molecules adsorbed on the TiO<sub>2</sub> surface due to photoexcitation. The band in the region 580-700 nm can be attributed to the radical cations of the coumarin dyes (both C1 and C2). This band has been assigned on the basis of results obtained from a complementary pulse radiolysis experiment, in which the radical cations of the coumarin dyes were selectively generated by reactions of N<sub>3</sub> radicals with C1 and C2 in N<sub>2</sub>O-saturated aqueous solution (5% acetonitrile + 95% water), as shown in the Supporting Information. The broad absorption band in the region 700-900 nm has been attributed to conduction-band electrons in the nanoparticles.<sup>[3b-f]</sup> It has previously been reported by ourselves and many other research groups that conduction-band electrons can be detected on the basis of characteristic visible<sup>[3b-f]</sup> and mid-IR bands.<sup>[3a]</sup> Injection times in the present investigation were determined by monitoring the appearance times of the signals of the radical cations of 1 and 2 ( $1^{+}$  and 2<sup>.+</sup>) at 650 nm and of the injected electron at 905 nm, and were found to be pulse-width limited (<120 fs) in both the  $C1/TiO_2$  and  $C2/TiO_2$  systems. To determine the back electron transfer (BET) in both systems, we monitored the transient signals at 650 nm (due to the radical cations) and 905 nm (due to injected electrons in TiO<sub>2</sub>), and the results are shown in Figure 6. The kinetic decay trace at 650 nm was fitted multi-exponentially for the C1/TiO<sub>2</sub> system, with time constants of 0.8 ps (71.2%), 5 ps (11%), 30 ps (7.6%), and >400 ps (10.2%) (Table 2). The kinetic decay trace at 650 nm for the  $C2/TiO_2$ system was similarly fitted with time constants of 1 ps (43.8%), 5 ps (12.7%), 30 ps (10%), and >400 ps (33.5%) (Table 2). We also fitted the kinetic decay traces multi-exponentially for the injected electrons at 905 nm for both the C1/TiO<sub>2</sub> and C2/TiO<sub>2</sub> systems, as shown in Table 2. It is interesting to note that the kinetic traces for both radical cations and injected electrons decay faster for the  $C1/TiO_2$  system than for the  $C2/TiO_2$ 

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**Figure 6.** Panel A: Transient absorption decay kinetics at 650 nm for a) C1/ TiO<sub>2</sub> and b) C2/TiO<sub>2</sub>. Panel B: Transient absorption decay kinetics at 905 nm for c) C1/TiO<sub>2</sub> and d) C2/TiO<sub>2</sub> after exciting the samples with 400 nm laser light.

**Table 2.** Parameters for the multiexponential fits of the back-electrontransfer (BET) kinetics for C1/TiO<sub>2</sub> and C2/TiO<sub>2</sub> nanoparticles and thin films, after monitoring the coumarin radical cations at 650 nm and electrons in the conduction band at 905 nm, under different conditions after excitation of the samples with 400 nm laser light.

| System/<br>probe wavelength [nm]            | τ <sub>1</sub> [ps]<br>([%]) | τ <sub>2</sub> [ps]<br>([%]) | τ <sub>3</sub> [ps]<br>([%]) | τ <sub>4</sub> [ps]<br>([%]) |
|---|------------------------------|------------------------------|------------------------------|------------------------------|
| <b>C1</b> /TiO <sub>2</sub> /650            | 0.8 (71.2)                   | 5 (11)                       | 30 (7.6)                     | >400 (10.2)                  |
| <b>C1</b> /TiO <sub>2</sub> /905            | 0.8 (70.7)                   | 5 (5.7)                      | 30 (10)                      | >400 (13.6)                  |
| <b>C2</b> /TiO <sub>2</sub> /650            | 1 (43.8)                     | 5 (12.7)                     | 30 (10)                      | >400 (33.5)                  |
| <b>C2</b> /TiO <sub>2</sub> /905            | 1 (53.5)                     | 5 (5.5)                      | 30 (4.1)                     | >400 (36.9)                  |
| C1/TiO <sub>2</sub> film/650                | 1 (48.8)                     | 5 (18.4)                     | 30 (15.0)                    | >400(17.8)                   |
| <b>C1</b> /TiO <sub>2</sub> film (pH 2)/650 | 1 (55.2)                     | 5 (18)                       | 30 (15.2)                    | >400 (11.6)                  |
| C2/TiO <sub>2</sub> film/650                | 1 (49.4)                     | 5 (6.1)                      | 30 (6.2)                     | >400 (38.3)                  |
| <b>C2</b> /TiO <sub>2</sub> film (pH 2)/650 | 0.5 (77.2)                   | 3 (9.7)                      | 20 (6.95)                    | >400 (6.1)                   |

system. This observation clearly suggests that the molecular structure affects the BET dynamics, with photoexcited **C2** existing in a TICT state and **C1** existing in an ICT state in a highly polar solvent.

To confirm the involvement of TICT states in the interfacial ET dynamics of coumarin dye-sensitized TiO<sub>2</sub> nanoparticles, we carried out experiments on TiO<sub>2</sub> thin films similarly sensitized with dyes **C1** and **C2**. So far, we have discussed the interfacial electron-transfer dynamics of **C1** and **C2** on the surface of nanoparticulate TiO<sub>2</sub>. However, a dye-sensitized solar cell is constructed from a TiO<sub>2</sub> thin film. Hence, it was considered very important to study the IET dynamics on a TiO<sub>2</sub> thin film in order to assess the utility of the sensitizer molecules in real devices. In the previous section, we noted that the existence of TICT states is strongly affected by lowering the pH of the medium. To assess the effect of pH on the IET dynamics in the above systems, we carried out ultrafast transient studies on TiO<sub>2</sub> films sensitized with **C1** and **C2** at pH 7 and pH 2.



**Figure 7.** Panel A: Transient absorption decay kinetics at 650 nm for a) C1/ TiO<sub>2</sub> thin film at pH 7 and b) C1/TiO<sub>2</sub> thin film at pH 2. Panel B: Transient absorption decay kinetics at 650 nm for c) C2/TiO<sub>2</sub> thin film at pH 7 and d) C2/ TiO<sub>2</sub> thin film at pH 2. The samples were excited with 400 nm laser light.

Figure 7 shows the normalized transient absorption kinetics at 650 nm at pH 7 and pH 2 for C1/TiO<sub>2</sub> (Panel A) and C2/TiO<sub>2</sub> films (Panel B). The decay traces were each fitted multi-exponentially, as shown in Table 2. It was observed that the decay dynamics, indicating BET dynamics, was slower in thin films than on the surface of nanoparticles (Table 2). The BET process in dye-nanoparticle systems depends on electronic coupling between the injected electron and the parent cation. In the case of a nanoparticle surface for the same dye-nanoparticle pair, coupling will be much stronger due to the proximity of the electron and the radical cation as compared to that in a film. In the case of a film, the nanoparticles are interconnected, and hence immediately after injection the electrons can diffuse to another particle within the film. As a result, the effective electronic coupling between the injected electron and the parent cation (dye<sup>+</sup>) becomes weak for the BET process on the film surface. Consequently, a slower back-electron-transfer process is observed on the film surface as compared to that on the nanoparticles for both the  $C1/TiO_2$  and  $C2/TiO_2$  systems. It is interesting to note that the effect of pH on the BET dynamics in a  $C1/TiO_2$  film is negligible; however, in a  $C2/TiO_2$ film, we have observed that the signal intensity of the transient absorption decreases, at the same transient signal decay, faster at lower pH (pH 2). The kinetic decay trace at 650 nm for the C2/TiO<sub>2</sub> film at pH 7 could be fitted multi-exponentially with time constants of 1 ps (49.4%), 5 ps (6.1%), 30 ps (6.2%), and >400 ps (38.3%). However, at pH 2, the kinetic decay trace could be fitted with time constants of 0.5 ps (77.2%), 3 ps (9.7%), 20 ps (6.95%), and >400 ps (6.1%). This observation clearly suggests the involvement of TICT states in the interfacial ET dynamics in these dye-semiconductor nanoparticle systems. We have already mentioned that at lower pH the C2 molecule exists only in an ICT state, whereas at pH 7 it exists in a TICT state, which is primarily a charge-separated state. Hence, the recombination (BET) dynamics is expected to be slower in the TICT state as compared to that in the ICT state.



# Charge-transfer dynamics between ICT and TICT states and $TiO_2$ nanoparticles

From the above-mentioned steady-state optical absorption and emission studies, as well as time-resolved emission studies, changing the polarity of the solvents and the pH of the media, we concluded that the photoexcited C1 molecule exists in an ICT state, whereas the C2 molecule exists in both ICT and TICT states in highly polar solvents. Ultrafast transient absorption studies on C1/TiO<sub>2</sub> and C2/TiO<sub>2</sub> indicated that electron injection in both systems is pulse-width limited, and a slower backelectron-transfer rate has been observed in the C2/TiO<sub>2</sub> system as compared to the C1/TiO<sub>2</sub> system. The results clearly indicate that the TICT state of C2 facilitates a higher electron injection yield and a slower back-electron-transfer process. In a dye-sensitized electron-transfer reaction, the excited molecular state of the dye molecule overlaps with high density states of the conduction band of the TiO<sub>2</sub> nanoparticles, which means that all of the vibrational and rotational states of the excited electronic state of the dye molecule overlap with the conduction band. However, it has been reported in the literature<sup>[18]</sup> that for moderate coupling (with carboxylic binding), electron injection and vibrational relaxation are competing processes in photoexcited dye/TiO<sub>2</sub> nanoparticle systems. This model suggests that a portion of the excited dye molecules will relax to the ground vibrational state of the first excited electronic state, from which nonradiative and radiative (emission) processes are possible. In the present investigation, we have also observed that a certain percentage of photoexcited states do not inject an electron (inset in Figure 4), with non-injecting states relaxing through nonradiative and radiative transitions. To illustrate the mechanism of electron transfer from different states (ICT and TICT) of

the coumarin dyes, we have drawn Scheme 2, which shows the energetics of the ground and excited states, that is, the energetic positions of the ICT and TICT states of both C1 and C2, and the conduction band edge of the TiO<sub>2</sub> nanoparticles. The ground state (GS) oxidation potentials for C1 and C2 were measured by cyclic voltammetry against an Ag/AgCl electrode. The redox reactions were seen to be reversible. The excitedstate oxidation potential of the dyes was measured by adding the  $E_{00}$  and GS oxidation potentials. E<sub>00</sub> was measured from the crossing point of the excitation and emission spectra of the dye molecules. The approximate energy level of the TICT state of C2 was determined from the energy shift from the ICT state to the TICT state in Figure 2. It can

clearly be seen in Scheme 2 that the ICT state of **C1** lies above the conduction band edge, hence the majority of the photoexcited state of **C1** can inject electrons  $(k_{inj})$ , with a certain fraction emitted as luminescence. In the case of the **C2**/TiO<sub>2</sub> system, however, upon excitation with laser pulses, the dye molecule attains the ICT state. From the ICT state, it can inject an electron into the conduction band of TiO<sub>2</sub> and relaxes very rapidly to the TICT state ( $k_{BA}$ ). Since the TICT state is a chargeseparated state, in which an electron is localized on the coumarin moiety and a hole is localized on the nitrogen atom of the diethylamino group, the electron injection ( $k_{inj'}$ ) is highly facile. It is for this reason that we observed higher electron injection yield in the **C2**/TiO<sub>2</sub> system.

Finally, we consider the charge recombination reaction (BET) for both systems. Although the coupling between dye and TiO<sub>2</sub> nanoparticle is the same for both C1 and C2, the free energy of the BET process for the C2/TiO2 system is higher  $(-\Delta G^{C2/TiO2} = 1.92 \text{ eV})$  than that for the C1/TiO<sub>2</sub> system (– $\Delta G^{\text{C1/TiO2}}$  = 1.83 eV). As a result, the BET process for the C2/ TiO<sub>2</sub> system is slower as it falls in the Marcus inverted region of electron-transfer reaction. The difference in BET process can also be envisaged in Scheme 3, which shows the orbital schemes for BET for both the ICT state of C1 and the TICT state of C2 with TiO<sub>2</sub> nanoparticles. Prior to electron injection in the C1/TiO<sub>2</sub> system, holes are localized in the orbital of the ICT state and electrons are localized in TiO<sub>2</sub> and eventually BET can take place (Scheme 3). On the other hand, in the C2/TiO<sub>2</sub> system, holes are localized on the nitrogen atom of the diethylamino group of the TICT state, in which the spatial charge separation is much larger than that in the ICT state of C1. As a result, we observed much slower charge recombination in the  $C2/TiO_2$  system than in the  $C1/TiO_2$  system. The participa-



**Scheme 2.** Schematic diagram of electron transfer from electronically excited dye to the conduction band of  $TiO_2$  nanoparticles for the coumarin dyes (**C1** and **C2**).  $S_0$  is the ground electronic level of the coumarin dyes,  $S_1$  (ICT) is the intramolecular charge-transfer state, and  $S_1$  (TICT) is the twisted intramolecular charge-transfer state.  $k_{BA}$  indicates the relaxation rate from the ICT state to the TICT state and  $k_{BET}$  is the back-electron-transfer rate from  $TiO_2$  to the  $S_0$  level of the coumarin dyes.



Scheme 3. Orbital scheme showing back-ET processes in the ICT state of the C1/TiO<sub>2</sub> system and the TICT state of the C2/TiO<sub>2</sub> system.

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hoped that our investigation may expedite the design and synthesis of more efficient organic solar-harvesting dyes that might significantly improve the efficiencies of DSSCs.

### **Experimental Section**

#### Materials

Titanium(IV) tetraisopropoxide (Ti- $[OCH(CH_3)_2]_4$ ; Aldrich, 97%) and isopropyl alcohol (Aldrich) were purified by distillation. Nanopure

tion of the TICT state was further confirmed by pH-dependent experiments on both systems on TiO<sub>2</sub> thin films. It can clearly be seen in Figure 7 (Panel A) that the BET dynamics was unchanged in the **C1**/TiO<sub>2</sub> system at pH 7 and pH 2. On the other hand, in the **C2**/TiO<sub>2</sub> system, the BET dynamics (Figure 7, Panel B) was much faster at pH 2, at which the TICT states are considered to be absent, on the basis of the results presented herein. From the above experimental observations, we can conclude that TICT states facilitate higher electron injection yields and at the same time retard the back-electron-transfer process at the dye–semiconductor nanoparticle surface.

## Conclusion

To determine the effect of molecular structure on interfacial electron dynamics in dye-sensitized TiO<sub>2</sub>, we have synthesized and characterized two structurally similar coumarin dyes (C1 and C2). These have been used to sensitize TiO<sub>2</sub> nanoparticles and thin films. Steady-state optical absorption, emission, and time-resolved emission studies on these dyes, changing the polarity of the solvent, suggest that photoexcited C1 and C2 both exist in a locally excited (LE) state in solvents of low polarity. In highly polar solvents, however, C1 exists in an intramolecular charge-transfer (ICT) state, whereas C2 exists in both ICT and twisted intramolecular charge-transfer (TICT) states, their populations depending on the degree of polarity of the solvent. The existence of the TICT state has been further supported by changing the pH of the medium. Electron-transfer dynamics (both electron injection and back ET) has been determined by directly monitoring the radical cation and injected electrons in the conduction band of TiO<sub>2</sub> nanoparticles/films in the visible and near-IR regions by femtosecond transient absorption spectroscopy. Pulse-width limited (<120 fs) electron injection was observed in both the C1/TiO<sub>2</sub> and C2/TiO<sub>2</sub> systems; however, back ET dynamics was found to be slower in the latter than in the former. Higher free energy of reaction  $(-\Delta G)$  in the C2/TiO<sub>2</sub> system is one of the reasons for a slow BET process. However, our results clearly indicate that involvement of the TICT state in C2 is the main reason for the slower BET process, which leads to higher electron yields. Ultrafast transient absorption measurements performed at different pH of the TiO<sub>2</sub> thin film have clearly demonstrated the participation of the TICT state of C2 in the slower BET process. It is

water was used to prepare aqueous solutions. All solvents and chemicals used for synthesis were procured from SD Fine Chemicals (India) and were used without further purification. Chemical reactions were monitored by TLC on 0.25 mm Merck silica gel 60 F<sub>254</sub> precoated plates; spots were visualized under UV light. <sup>1</sup>H NMR spectra were recorded on a 300 MHz Varian Mercury Plus spectrometer. Chemical shifts are expressed in  $\delta$  (ppm) with reference to TMS as an internal standard. Mass spectral data were obtained on Micromass-Q-TOF (YA105) spectrometer.

#### Preparation of TiO<sub>2</sub> nanoparticles

Nanometer-size TiO<sub>2</sub> was prepared by controlled hydrolysis of titanium(IV) tetraisopropoxide.<sup>[11]</sup> A solution of Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (5 mL) in isopropyl alcohol (95 mL) was added dropwise (1 mL min<sup>-1</sup>) to nanopure water (900 mL) at 2 °C and pH 1.5 (adjusted with HNO<sub>3</sub>). The solution was continuously stirred for 10–12 h until a transparent colloid was formed. The colloidal solution was concentrated at 35–40 °C in a rotary evaporator, and the residue was dried with a nitrogen stream to yield a white powder. In the present work, all colloidal samples were prepared after dispersing dry TiO<sub>2</sub> nanoparticles in water (15 g L<sup>-1</sup>). The coumarin dyes were added to the TiO<sub>2</sub> colloid and sonicated for some time (2–3 min) to prepare the sensitized nanoparticles.

#### Preparation and sensitization of the thin films

TiO<sub>2</sub> nanocrystalline thin films were prepared by a method similar to that used by Zaban and co-workers.<sup>[12]</sup> Briefly, a colloid of TiO<sub>2</sub> nanoparticles was prepared by the controlled hydrolysis of titanium(IV) isopropoxide in a mixture of glacial acetic acid and water at 0°C. It was heated at 80°C for 8 h and then autoclaved at 230°C for 12 h. The resulting colloid was concentrated to 150 g L<sup>-1</sup> and spread onto polished sapphire windows, which were baked at 400°C for 36 min. The TiO<sub>2</sub> films were sensitized by first immersing them in a solution of 200  $\mu$ M coumarin dye and 20 mM chenodeoxycholic acid in ethanol at room temperature, whereby the dye was adsorbed on the porous film surface. All experiments were performed with thin films exposed to air under ambient conditions. Film samples were moved rapidly during measurement to avoid long-term photo-product build-up.

#### Synthesis of coumarin dyes

**Synthesis of coumarin 1 sensitizer**: A 100 mL three-necked round-bottomed flask fitted with a mercury-sealed stirrer was charged with a mixture of 3-chloro-3-(11-oxo-2,3,5,6,7,11-hexahy-dro-1*H*-pyrano[2, 3-*f*]pyrido[3,2,1-*ij*]quinolin-10-yl)acrylaldehyde [8,

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Supporting Information] (1.5 g, 4.5 mmol) and cyanoacetic acid [9, Supporting Information] (0.60 g, 6.8 mmol) in absolute ethanol (15 mL) containing piperidine (0.5 mL). The stirred reaction mixture was heated under reflux for 4 h. The progress of the reaction was monitored by TLC, and after its completion the mixture was poured into cold water and the product was extracted with ethyl acetate. The ethyl acetate layer was washed with water and then concentrated under vacuum in a rotary evaporator to obtain the product, coumarin 1. The crude product was further purified by column chromatography on silica gel, eluting with toluene/ethyl acetate (6:4). Yield: 0.97 g (54%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta =$ 8.30 (s, 1H; aromatic CH), 8.18-8.09 (m, 2H; vinylic CH), 7.20 (s, 1H; aromatic CH), 2.75-2.60 (m, 4H; aliphatic CH<sub>2</sub>), 2.50-2.40 (m, 4H; aliphatic CH<sub>2</sub>), 1.90–1.75 ppm (m, 4H; aliphatic CH<sub>2</sub>); <sup>13</sup>C NMR  $(CDCI_{3}, 75 \text{ MHz}): \delta = 163.2, 158.1, 151.1, 149.2, 148.7, 145.3, 142.5,$ 127.4, 119.9, 115.4, 109.8, 108.2, 104.5, 49.7, 49.2, 26.7, 20.4, 19.4 ppm; MS: m/z: 297, 269, 261 (corresponds to ion peak after characteristic fragmentation).

Synthesis of coumarin 2 sensitizer: A three-necked 100 mL round-bottomed flask was charged with 3-chloro-3-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]acrylaldehyde [12, Supporting Information] (1 g, 3.2 mmol) in absolute ethanol (10 mL). Cyanoacetic acid [9, Supporting Information] (0.55 g, 6.5 mmol) and piperidine (3-4 drops) were then added and the reaction mixture was vigorously stirred at reflux temperature for 4 h. The progress of the reaction was monitored by TLC, and after its completion the mixture was poured into cold water and the product was extracted with ethyl acetate. The ethyl acetate layer was washed with water and then concentrated under vacuum in a rotary evaporator to obtain the product, coumarin 2. The crude product was further purified by column chromatography on silica gel, eluting with toluene/ethyl acetate (6:4). Yield: 1.0 g (89%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 8.44$ (s, 1H; aromatic CH), 8.18-8.15 (m, 1H; aromatic CH), 8.04-8.01 (d, 1H; vinylic CH), 7.64-7.62 (d, 1H; aromatic CH), 6.79-6.76 (d, 1H; vinylic CH), 6.59 (s, 1H; aromatic CH<sub>2</sub>), 3.63-3.44 (m, 4H; aliphatic CH\_2), 1.15–1.11 ppm (t, 6H; aliphatic CH\_3);  $^{13}\text{C}$  NMR (CDCl\_3, 75 MHz):  $\delta = 172.0$ , 163.0, 158.2, 155.9, 152.2, 144.5, 144.4, 137.4, 131.3, 122.3, 117.5, 112.4, 110.1, 108.0, 95.7, 62.7, 44.3, 12.3 ppm; MS: m/z: 373  $[M^+]$ , 337  $[M-CI]^+$ . The synthetic procedures for other intermediates are described in detail in the Supporting Information.

#### Time-resolved emission spectrometer

Time-resolved fluorescence measurements were carried out using a diode-laser-based spectrofluorimeter from IBH (UK). The instrument works on the principle of time-correlated single-photon counting (TCSPC). In the present work, 405 and 445 nm laser pulses were used as excitation light sources, and a TBX4 detection module (IBH) coupled with a Hamamatsu PMT was used for fluorescence detection.

#### Femtosecond visible spectrometer

A combined regenerative/multipass amplifier (1 kHz repetition rate at around 800 nm, 50 fs, 1 mJ/pulse) from Thales (Alpha 1000) was used for 400 nm pump/480–1000 nm probe measurements. The output of a mode-locked Ti:sapphire laser (FEMTOSOURCE Synergy 20) pumped by a CW-Nd:YVO<sub>4</sub> laser (Finesse, Laser Quantum, 532 nm, output power: 3.8 W) was used as a seed pulse train (102 MHz). The 20 fs pulses from the oscillator were stretched using an Offner stretcher (XS-type, supplied by Thales) and preamplified in a Ti:sapphire regenerative cavity pumped by around 35% of the output power of an Nd:YLF laser (Jade–Thales, 532 nm,

18.4 W, 1 KHz). The amplified pulse at the power saturation point of the regenerative cavity was extracted for second stage amplification in a two-pass Ti:sapphire amplifier pumped by around 65% of the output power of the Nd:YLF laser. Finally, after passage through a compressor encompassing a two-grating assembly, the amplified pulses of around 40 fs FWHM, 800 nm at 1 KHz repetition rate were obtained. For the pump-probe set-up, 30% of the output power of this amplifier system was split into two parts to generate pump and probe pulses. Frequency-doubled 400 nm pump pulses were generated using 200 µJ/pulses of 800 nm in a barium  $\beta$  borate BBO crystal. Probe pulses in the region 480-1000 nm were generated by focusing around 3  $\mu$ J of the 800 nm beam onto a 1.5 mm thick sapphire window. The noise of the white light continuum was controlled by adjusting the 800 nm beam intensity through an iris and neutral density (ND) filter placed before the sapphire window. The probe pulses were split into signal and reference beams before the quartz cell (sample), and were detected by two matched photodiodes with variable gain. The pump and probe beams were focused on the same position of the cell at the crossing point around 500 and 300  $\mu$ m. The excitation energy density (400 nm) was adjusted to around 2500  $\mu$ J cm<sup>-2</sup>. The noise level of the white light was about 0.5% with occasional spikes due to oscillator fluctuation. We have noticed that most laser noise is low-frequency noise and can be eliminated by comparing adjacent probe laser pulses (pump blocked vs unblocked using a mechanical chopper). The typical noise in the measured absorbance change was <0.3%. The instrument response function (IRF) for 400 nm excitation was obtained by fitting the rise time of the bleaching of the sodium salt of meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) at 710 nm, and was found to be 100 fs.<sup>[13]</sup> Kinetic decay traces were fitted using the Lab-view program based on differential equations. The kinetic traces were freely fitted, with both amplitudes and time constants being closely coupled. The deviation or error bar in both lifetime and amplitude measurements was no higher than  $\pm 2\%$ .

#### Cyclic voltammetry

Voltammetric experiments were performed with an Autolab PGSTAT 20 (manufactured by Eco-Chemie, The Netherlands) coupled to a Metrohm 663 VA standard electrode system comprising glassy carbon (GC)/Pt/Ag/AgCl. The PG STAT was driven by Autolab software. The temperature of the solution was maintained at 25  $\pm$  0.1 °C. Measurements were made in solutions of tetrabutylammonium hexafluorophosphate (TBAP) in acetonitrile as supporting electrolyte under N<sub>2</sub> atmosphere. The redox potentials of **C1** and **C2** were determined as 1.11 V and 1.19 V, respectively, against the Ag/ AgCl electrode.

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