# Effect of Molecular Structure on Interfacial Electron Transfer Dynamics of 7-*N*,*N*-Dimethyl Coumarin 4-Acetic Acid (DMACA) and 7-Hydroxy Coumarin 4-Acetic Acid (HCA) Sensitized TiO<sub>2</sub> and ZrO<sub>2</sub> Nanoparticles

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Ultrafast transient absorption spectroscopy has been employed to understand the effect of molecular structure on interfacial electron transfer (ET) dynamics of 7-N,N-dimethyl amino coumarin 4-acetic acid (DMACA) and 7-hydroxy coumarin 4-acetic acid (HCA) sensitized TiO<sub>2</sub> and ZrO<sub>2</sub> nanoparticles. Electron injection is confirmed by observing the cation radical of the dye molecules as well as the conduction band electron in the visible and near-IR regions. Electron injection efficiency has been found to be higher for the HCA/TiO<sub>2</sub> system as compared to the DMACA/TiO<sub>2</sub> system. Both dyes are structurally similar except that HCA has a hydroxyl group at the 7-position while DMACA has a dimethyl amino group at the 7-position. Steady-state and time-resolved fluorescence measurements confirmed that, in highly polar solvent, the excited state of DMACA dye exists both in twisted intramolecular charge transfer (TICT) and intramolecular charge transfer (ICT) states, whereas excited HCA exists only in the ICT state. Because the charge in the case of the TICT state of DMACA is localized away from the nanoparticle surface, electron injection from that state is not efficient. However, ICT states of both DMACA and HCA can inject electrons efficiently as the charge is delocalized. Hence, the quantum yield of electron injection is high in the case of HCA compared to DMACA. We have also observed that photoexcited DMACA whose energy level lies above the conduction band of ZrO<sub>2</sub> nanoparticle can inject electrons after exciting with 400 nm laser light. Back electron transfer (BET) rates have been determined by following the decay kinetics of the cation radical and conduction band electron in different systems. The BET rate is found to be slower for HCA/TiO<sub>2</sub> compared to DMACA/TiO<sub>2</sub>, as they fall in the inverted region of Marcus electron transfer theory. The BET is faster in the DMACA/TiO<sub>2</sub> system as compared to that of the DMACA/ZrO<sub>2</sub> system. However, the residual absorption after 460 ps is less in the case of the DMACA/ZrO<sub>2</sub> system.

## 1. Introduction

Incessant efforts are going on throughout the world to understand the interfacial electron transfer from molecular adsorbates to wide band-gap semiconductors. The never-ending thrust in this area is largely owed to their application in various fields such as photochemical solar energy conversion and storage,<sup>1,2</sup> nonlinear optics<sup>4</sup> and heterogeneous photocatalysis.<sup>5-7</sup> Among such studies, dye-sensitization of wide band-gap semiconductor electrodes has gained sufficient attention in recent years, mainly because of demonstration of the dye-sensitized solar cells with conversion efficiency as high as 10%.<sup>1,2</sup> The mechanism of these devices is based upon the injection of an electron from the excited state of the sensitized dye into the conduction band of the semiconductor. Studies on dye-sensitization of TiO<sub>2</sub> nanoparticles have been carried out by  $us^{8-15}$  as well as by many other groups.<sup>16–20</sup> The efficiency of the dyesensitized solar cells depends critically on the rates of the forward (dye to semiconductor) and back (semiconductor to dye) electron-transfer reactions. For efficient solar energy conversion, it is necessary to establish the conditions of both higher electron injection efficiency and slow recombination. For that purpose, many new sensitizer molecules have been synthesized, and the solar cell performance has been evaluated.<sup>21-26</sup> It is a very

important task to understand the relation between the solar cell performance and the molecular and structural properties of the sensitizer molecules. Many molecular properties, such as excited-state properties and their lifetimes, injection efficiency, and redox potential, have significant impact on the overall solar cell performance.

The molecular structure of the sensitizing dye is an important factor, which can affect the solar cell performance. Recently, Arakawa and co-workers have reported the effect of the number of anchoring carboxyl groups<sup>24</sup> and the effect of ligand structure on the efficiency of electron injection into TiO<sub>2</sub> nanoparticles from the excited states of Ru-phenanthroline complexes, which in turn affect the solar cell performance. They have observed that electron injection efficiency of a dye molecule with four anchoring groups is four times as large as that of a dye molecule with one anchoring group. Lian and co-workers<sup>27,17</sup> have reported the effect of molecular structure of Ru-polypyridyl dyes on their ground and excited energy levels, which in turn affect the quantum yield of electron injection. We have also reported earlier<sup>11</sup> the effect of molecular structure on the electron injection efficiency of 7-diethyl amino coumarin 3-carboxylic acid (D-1421) and coumarin 343 (C-343) sensitized TiO<sub>2</sub> nanoparticles. We have shown that, with a little change in molecular structure, excited-state properties of the dye can be influenced drastically, which in turn affect the injection quantum

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SCHEME 1 : Molecular Structure of 7-*N*,*N*-Dimethyl Coumarin 4-Acetic Acid (DMACA) and 7-Hydroxy Coumarin 4-Acetic Acid (HCA)



yield. It is a very important task to optimize the molecular structure of the sensitizer molecules which will have higher injection quantum yield and at the same time will have a low charge recombination rate.

Reports are available on interfacial electron transfer dynamics, mainly based on dye-sensitized TiO<sub>2</sub>, SnO<sub>2</sub>, and ZnO nanoparticles, where energy levels of the photoexcited dyes are higher than the conduction band edge of the semiconductor nanoparticles. However, in most cases, the photoexcited dyes cannot inject electrons into the  $ZrO_2$  nanoparticles because energy level of the photoexcited dyes are lower than the conduction band edge of  $ZrO_2$ . Some reports are available on electron injection into  $ZrO_2$  nanoparticles by Huber et.al.,<sup>28</sup> Hao et al.<sup>29</sup> and us,<sup>14,15</sup> where electron injection takes place in the surface states of  $ZrO_2$ . It will be very interesting to see the electron injection band of  $ZrO_2$  nanoparticles and the corresponding back electron-transfer reaction.

In the present investigation, we have studied electron injection and back electron-transfer dynamics of of 7-N.N-dimethyl amino coumarin 4-acetic acid (DMACA) and 7-hydroxy coumarin 4-acetic acid (HCA) sensitized TiO<sub>2</sub> and ZrO<sub>2</sub> nanoparticles using ultrafast transient absorption spectroscopy. Electron injection has been confirmed by observing the cation radical of the dye molecules as well as the conduction band electron in the visible and near-IR region. To see the effect of molecular structure on electron injection and BET dynamics, these two dyes are chosen. Both the dyes have same anchoring group, which binds to the nanoparticle with similar structure except DMACA has a dimethyl amino at the 7-position and HCA has a hydroxy group at the 7-position (Scheme 1). Steady-state and time-resolved fluorescence measurements confirmed that, in highly polar solvent, the excited state of DMACA dye exists both in the TICT and the ICT state, whereas excited HCA exists

only in the ICT state. Time-resolved absorption studies show that electron injection efficiency is higher ( $\sim 1.6$  times) in the case of HCA sensitized TiO<sub>2</sub> nanoparticles compared to DMACA sensitized nanoparticles under similar conditions. It is seen from Scheme 2 that, in the TICT state of DMACA, an electron gets localized at the 3-position oxygen atom, and from there the possibility of electron injection is remote. However, ICT states of DMACA can inject electrons (Scheme 2). As the population of ICT states is higher in HCA compared to DMACA, injection quantum yield is high in the HCA/TiO<sub>2</sub> system. The other important observation we made is the electron injection into the conduction band of ZrO<sub>2</sub> nanoparticles from photoexcited DMACA. BET rates have been determined by following the decay kinetics of the cation radical in different systems. The BET rate is found to be slower for HCA/TiO<sub>2</sub> compared to DMACA/TiO<sub>2</sub>, where both systems follow the equation of the ET reaction in the Marcus inverted region. BET dynamics is faster in DMACA/TiO<sub>2</sub> as compared to the DMACA/ZrO<sub>2</sub> system. However, the residual absorption is less in the case of  $ZrO_2$  as compared to  $TiO_2$ .

#### 2. Experimental Section

(a) Materials. 7-*N*,*N*-Dimethyl amino coumarin 4-acetic acid (DMACA) and 7-hydroxy coumarin 4-acetic acid (HCA) were obtained from Aldrich and used without further purification. Titanium(IV) tetraisopropoxide {Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>} (Aldrich, 97%) and isopropyl alcohol (Aldrich) were purified by distillation. Zirconium(IV) isopropoxide 2-propanol complex  $Zr[OCH(CH_3)_2]_4$ ·(CH<sub>3</sub>)<sub>2</sub>CHOH (Aldrich, 99.9%) was used without further purification. Nanopure water (Barnsted System) was used for making aqueous solutions.

(b) Sample Preparation. Nanometer-size TiO<sub>2</sub> was prepared by controlled hydrolysis of titanium(IV) tetraisopropoxide.<sup>30-32</sup> A solution of 5 mL of Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (Aldrich, 97%) dissolved in 95 mL of isopropyl alcohol (Aldrich) was added dropwise (1 mL/min) to 900 mL of Nanopure water (2 °C) at 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 with a rotary evaporator and then dried with a nitrogen stream to yield a white powder. ZrO<sub>2</sub> nanoparticles were also prepared by adopting the above procedure. In the present work, all colloidal samples were prepared after dispersing the dry TiO<sub>2</sub> or ZrO<sub>2</sub> nanoparticles in water (15 g/L). A transparent clear colloidal solution was formed. For all measurements, sample solutions were deoxygenated by continuously bubbling high purity nitrogen (99.95 Iolar grade from Indian Oxygen Co. Ltd., India) through the





solutions. The solutions flowed through a 1 mm path quartz cell during all the measurements.

(c) Femtosecond Spectrometer. The femtosecond tunable visible spectrometer has been developed based on a multipass amplified femtosecond Ti:sapphire laser system from CDP-Avesta, Russia (1 kHz repetition rate at 800 nm, 50 fs, 300  $\mu$ J/pulse) and has been described earlier.<sup>12</sup> The 800 nm output pulse from the multipass amplifier is split into two parts to generate pump and probe pulses. One part, with a 200  $\mu$ J/pulse, is frequency doubled in BBO crystals to generate pump pulses at 400 nm. To generate visible probe pulses, about 3  $\mu$ J of the 800 nm beam is focused onto a 1.5 mm thick sapphire window. The intensity of the 800 nm beam is adjusted by iris size and neutral density filters to obtain a stable white light continuum in the 470 nm to over 1000 nm region. The probe pulses are split into the signal and reference beams and are detected by two matched photodiodes with variable gain. We have kept the spot sizes of the pump beam and probe beam at the crossing point around 500 and 300  $\mu$ m, respectively. The excitation energy density (at 400 nm) was adjusted to  $\sim 2500 \,\mu\text{J/cm}^2$ . The noise level of the white light is about  $\sim 0.5\%$  with occasional spikes due to oscillator fluctuation. We have noticed that most laser noise is low-frequency noise and can be eliminated by comparing the adjacent probe laser pulses (pump blocked vs unblocked using a mechanical chopper). The typical noise in the measured absorbance change is about <0.3%. The instrument response function was obtained by fitting the rise time of the bleach of sodium salt of meso-tetrakis(4 sulfonatophenyl) porphyrin (TPPS) at 710 nm, which has an instantaneous response.

(d) Cyclic Voltammetry. Voltammetric experiments were performed with Auto Lab PGSTAT 20 (Manufactured by Eco-Chemie, Netharlands) coupled to a Metrohm 663 VA stand 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 acetonitrile solution with TEAP (triethylammonium perchlorate) as a supporting electrolyte and in N<sub>2</sub> atmosphere. Redox potentials of DMACA and HCA have been determined to be 1.0 and 1.6 V against Ag/AgCl electrode, respectively.

## 3. Results and Discussion

(a) Steady-State Absorption and Emission Spectroscopy. We have carried out steady-state absorption<sup>33</sup> and emission studies of both DMACA and HCA molecules in water and in the presence of TiO<sub>2</sub> and ZrO<sub>2</sub> colloidal solutions. Our measurements have shown that both the dye molecules are adsorbed on both the nanoparticle surfaces. The fluorescence intensity of both DMACA and HCA molecules has drastically reduced in the presence of TiO<sub>2</sub> nanoparticles as compared to that in aqueous solution, which has been attributed to the electron injection into the TiO<sub>2</sub> nanoparticles. It is very interesting to see that the fluorescence from DMACA is also quenched even in the presence of ZrO<sub>2</sub> nanoparticles indicating the electron injection from DMACA into the ZrO2 nanoparticles. On the other hand, fluorescence from the HCA molecule does not change much on the ZrO<sub>2</sub> nanoparticle surface as compared to that in water showing negligible excited-state interaction of the dye with the  $ZrO_2$  nanoparticle surface.

(b) Excited-State Dynamics of Free DMACA and HCA Molecules. We have carried out transient absorption measurements to study the excited-state dynamics of both DMACA and HCA molecules in water upon excitation with 400 nm laser



**Figure 1.** Transient absorption spectra of (a) DMACA and (b) HCA in water at the end of the laser pulse. The transient absorption peak at 690 nm has been attributed to the excited singlet state, and the negative absorption band at 470 nm has been attributed to stimulated emission for both the dyes. [Inset: transient absorption decay at 670 nm for (a) DMACA and (b) HCA.]

light. Figure 1 shows the transient absorption spectra of DMACA (Figure 1a) and HCA (Figure 1b) in water at the end of the laser pulse. The HCA molecule does not absorb at 400 nm at pH 2.5.33 To perform transient absorption studies of HCA, we have increased the pH of the free dye solution to 9. At this pH, HCA exists as an anion, which absorbs at 400 nm. Transient absorption spectra of the excited state of DMACA show an absorption peak at 690 nm and negative absorption band from 470 to 580 nm (Figure 1a). On the other hand, the excited state of HCA shows an absorption peak at 675 nm and a negative absorption band from 470 to 580 nm (Figure 1b). The transient absorption peak at 690 nm for the excited DMACA and the peak at 670 nm for the excited HCA have been attributed to the excited singlet state absorption (ESA), and corresponding negative absorption bands have been attributed to the stimulated emission of the respective molecules. The inset of Figure 1 shows the kinetic decay trace of ESA for both DMACA (Figure 1c) and HCA (Figure 1d) molecules. Excited states of DMACA and HCA show little decay up to 400 ps indicating longer lifetimes. However, it is clear that the excited state of DMACA decays faster than that of HCA. We have also carried out timeresolved emission measurements of both the molecules using time-correlated single photon counting. Emission lifetimes of DMACA and HCA are found to be 1.4 ns and 5.65 ns, respectively.

(c) Transient Absorption Measurements in DMACA/TiO<sub>2</sub> and HCA/TiO2 Systems. To study the effect of molecular structure on interfacial electron-transfer dynamics we have carried out transient absorption measurements for both DMACA and HCA sensitized TiO<sub>2</sub> nanoparticles excited with a 400 nm femtosecond laser pulse. Figure 2 shows the time-resolved transient absorption spectra of the DMACA/TiO<sub>2</sub> system in water. The spectrum at each time delay consists of a positive peak at  $\sim$ 630 nm with a shoulder at 690 nm and a broad positive feature in the whole spectral region (800-1000 nm). In the DMACA/TiO<sub>2</sub> system, we did not observe any ESA and stimulated emission, which can arise due to a free excited DMACA molecule in the solution that does not take part in the interfacial process. The broad spectral absorption in the 800-1000 nm region is attributed to the absorption of conduction band electrons in the nanoparticles  $(e_{CB}^{-})$ . It has already been shown by many workers that the conduction band electrons can be detected both by visible<sup>34,35,8-14</sup> and infrared absorption.<sup>16,17</sup> The positive peak at 630 nm has been attributed to the cation



**Figure 2.** Transient absorption spectra of DMACA sensitized  $TiO_2$  nanoparticle in water at (a) 200 fs, (b) 5 ps, and (c) 10 ps after excitation at 400 nm (fwhm = 50 fs). The spectrum at each time delay consists of an absorption peak at 630 nm and a broad positive absorption feature in the whole spectral region (800–1000 nm). These features are assigned to the cation radical of DMACA dye and the injected electron in nanoparticles, respectively. [Inset (d): kinetic decay trace of DMACA cation radical at 630 nm.]



**Figure 3.** Transient absorption spectra of HCA sensitized  $\text{TiO}_2$  nanoparticle in water at (a) 200 fs, (b) 5 ps, and (c) 10 ps after excitation at 400 nm. The spectrum at each time delay consists of an absorption peak at 610 nm and a broad positive absorption feature in the whole spectral region (800–1000 nm). These features are assigned to the cation radical of HCA molecule and the injected electron in nanoparticles, respectively. [Inset (d): kinetic decay trace of HCA cation radical at 610 nm.]

radical of DMACA molecule. Assignment of this band has been made on the basis of the results obtained in separate pulse radiolysis experiments,33 where DMACA++ was generated selectively by the reaction of a N<sub>3</sub><sup>•</sup> radical with a DMACA molecule in N<sub>2</sub>O saturated aqueous solution. The transient spectrum obtained from the above experiment shows an absorption peak at 630 nm with a shoulder at 690 nm. We have measured electron injection time by monitoring the appearance signal of DMACA<sup>++</sup> at 630 nm as well as  $e_{CB}^{-}$  at 900 nm, and it was found to be  $\sim$  100 fs (Figure 4). However, in the transient spectra (Figure 2) we have observed that the transient signal in the 630 nm region and also that in the near-IR region decay rapidly with time. This decay of the transient signal has been attributed to charge recombination or BET from the electron in the nanoparticle to the parent dye cation radical (Figure 2, inset). The decay kinetics at 630 nm has been fitted with a multiexponential function with the time constants of 1.1 ps (44%), 13 ps (23.8%), and >400 ps (32.2%) (Table 1). We have also observed that the kinetic decay trace of the injected electron at 900 nm can be fitted multiexponentially with similar time constants to that of cation radical at 630 nm.



**Figure 4.** Transient absorption spectra of DMACA sensitized  $ZrO_2$  nanoparticle in water at (a) 500 fs, (b) 1 ps, (c) 5 ps, and and (d) 10 ps after excitation at 400 nm. The spectrum at each time delay consists of an absorption peak at 630 nm and a broad positive absorption feature in the whole spectral region (800–1000 nm). These features are assigned to the cation radical of DMACA dye and the injected electron in nanoparticles, respectively. [Inset: kinetic decay trace of DMACA cation radical at 630 nm.]

 TABLE 1: Electron Injection and Back Electron Transfer

 (BET) Dynamics of Different Dye-Sensitized Nanoparticle

 Systems Monitoring at Different Wavelength

DMACA/TiO <sub>2</sub> , 630 nm	$\begin{split} \tau_{inj} &= 100 \text{ fs} \\ \tau_1 &= 1.1 \text{ ps} (44\%) \\ \tau_2 &= 13 \text{ ps} (23.8\%) \\ \tau_3 &> 400 \text{ ps} (32.2\%) \end{split}$	$\langle \tau_{\rm av} \rangle = 5.05 \text{ ps} (67.8\%)$
DMACA/ZrO <sub>2</sub> , 630 nm	$\begin{aligned} \tau_{inj} &= 100 \text{ fs} \\ \tau_1 &= 2.7 \text{ ps} (38.1\%) \\ \tau_2 &= 38 \text{ ps} (50\%) \\ \tau_3 &> 400 \text{ ps} (11.9\%) \end{aligned}$	$\langle \tau_{\rm av} \rangle = 22.6 \text{ ps} (88.1\%)$
HCA/TiO <sub>2</sub> , 610 nm	$\begin{aligned} \tau_{inj} &= 100 \text{ fs} \\ \tau_1 &= 3.8 \text{ ps} (22.2\%) \\ \tau_2 &= 110 \text{ ps} (35.1\%) \\ \tau_3 &> 400 \text{ ps} (42.7\%) \end{aligned}$	$\langle \tau_{\rm av} \rangle = 68.2 \text{ ps} (57.3\%)$

Similarly, transient absorption experiments have been carried out on the HCA/TiO<sub>2</sub> system in water and are shown in Figure 3. The spectrum at each time delay consists of a positive peak at 610 nm with a shoulder at 710 nm and a broad positive feature in the whole spectral region (750–1000 nm). The peak at 610 nm with the shoulder at 710 nm has been attributed to the HCA cation radical (HCA<sup>•+</sup>) as confirmed by pulse radiolysis experiments,<sup>33</sup> and the band at 750–1000 nm has been attributed to the electron in the conduction band of the nanoparticles. This decay of the signals has been attributed to charge recombination or BET with the nanoparticles (Figure 3, inset). The decay kinetics at 610 nm has been found to follow a multiexponential function with typical time constants of 3.8 ps (22.2%), 110 ps (35.1%), and >400 ps (42.7%) (Table 1).

(d) Transient Absorption Measurements in the DMACA/ ZrO<sub>2</sub> System. As the surface nature of  $ZrO_2$  nanoparticles is very similar to that of TiO<sub>2</sub> nanoparticles,<sup>30</sup> in our previous investigations<sup>8,9</sup> on dye-sensitized TiO<sub>2</sub> nanoparticles reaction to understand the photophysics of the dye molecule on a noninjecting nanoparticle surface, we have used  $ZrO_2$  nanoparticles. As the conduction band edge of  $ZrO_2$  nanoparticles is 1.3 eV higher than that of TiO<sub>2</sub> nanoparticles,<sup>14</sup> electron injection is not possible from the photoexcited dye molecules. So in the earlier studies,<sup>8,9</sup> we have observed that excited-state properties of the dye molecules on  $ZrO_2$  nanoparticles surface are very similar to those of bulk solvents. It is observed from steadystate emission measurements that the fluorescence intensity of DMACA is drastically reduced in the presence of  $ZrO_2$ 

SCHEME 3 : Mechanistic Scheme for Electron Transfer from the Electronically Excited Dye to TiO<sub>2</sub> and ZrO<sub>2</sub> Nanoparticles<sup>*a*</sup>



<sup>*a*</sup> Here, S\*/S<sup>+</sup> is the excited sensitized dye/cation radical couple,  $E_c$  is the conduction band edge,  $E_v$  is the valence band, SS is the surface states, ICT is the intramolecular charge transfer state, and TICT is the twisted intramolecular charge transfer state.  $k_{\text{BET}}$  is the back electron-transfer rate.

nanoparticles, which indicates that ZrO<sub>2</sub> nanoparticle surface is not a noninjecting surface for the photoexcited DMACA molecule. However, the ZrO<sub>2</sub> nanoparticle is an inert surface for an excited HCA molecule. In the present investigation, we have carried out femtosecond transient absorption experiments on DMACA molecules adsorbed on the ZrO<sub>2</sub> nanoparticle excited with 400 nm, to study the excited-state dynamics of the dye on ZrO<sub>2</sub> surface. Figure 4 shows the time-resolved transient absorption spectra of the DMACA/ZrO2 system in water. The spectrum at each time delay consists of a positive peak at  $\sim$ 630 nm with a shoulder at 690 nm and a broad positive feature in the whole spectral region (800-1000 nm) which can be attributed to the cation radical and conduction band electron, respectively. It will be interesting to find out the reason for electron injection from the excited state of the DMACA molecule into ZrO<sub>2</sub> nanoparticles when a structurally similar excited HCA molecule is unable to do so. We have measured the energetics of the ground and excited redox potentials of both DMACA ( $E_{D/D^+} = 1.0 \text{ V}$ ) and HCA ( $E_{D/D^+} = 1.6 \text{ V}$ ) molecules (Scheme 3). The GS redox potential of the dyes has been measured by cyclic voltametry against a Ag/AgCl electrode. The dye oxidations are reversible. The excited redox potentials of the dyes were measured by adding  $E_{00}$  and GS redox potential.  $E_{00}$  has been measured from the crossing point of the excitation and emission spectra of the dye molecules. It is visible from Scheme 3 that the excited redox potential of DMACA  $(E_{D^*/D^+} = -1.9 \text{ V})$  is higher in energy than the conduction band edge of ZrO<sub>2</sub> nanoparticles ( $E_{CB}^{ZrO_2} = -1.8 \text{ V}^{30}$ ). As a result, photoexcited DMACA can easily inject electrons in the CB of ZrO<sub>2</sub> nanoparticles. However, the excited redox potential of HCA ( $E_{D^*/D^+} = -1.6$  V) is lower in energy than the conduction band edge of ZrO<sub>2</sub> nanoparticles. The transient absorption spectrum DMACA/ZrO2 looks very similar to that of DMACA/ TiO<sub>2</sub>. The transient signal in the 630 nm region and also in the near-IR region decay similarly as observed in the DMACA/ TiO<sub>2</sub> system, which has been attributed to charge recombination (CR) or BET with the nanoparticles (Figure 4, inset). The decay kinetics at 630 nm has been fitted with a multiexponential function with the time constants of 2.7 ps (38.1%), 38 ps (50%),



**Figure 5.** Relative magnitude of electron absorption signal at 900 nm in (a) DMACA sensitized  $TiO_2$  nanoparticles and (b) HCA sensitized  $TiO_2$  nanoparticles.

and >400 ps (11.9%) (Table 1). However, for the longer time (>400 ps) residual charge separated (CS) species in DMACA/ ZrO<sub>2</sub> is much less as compared to the situation in the DMACA/ TiO<sub>2</sub> system (Table 1).

(e) Effect of Molecular Structure on Quantum Yield of Electron Injection ( $\phi_{inj}$ ). It will be interesting to find out the effect of molecular structure on the quantum yield of electron injection ( $\phi_{inj}$ ) in these studied systems. We have carried out femtosecond transient absorption measurements of the above systems in similar condition. The optical density of the experimental solutions and the laser intensity was kept the same. At similar laser intensity and the same optical density at excitation wavelength for the samples, the measured change in absorbance can be ascribed to the injection quantum yield relative to one another. Figure 5 shows the kinetic trace of the appearance signal of electrons in the conduction band at 900 nm of DMACA/TiO<sub>2</sub> (Figure 5a), and HCA/TiO<sub>2</sub> system is ~1.6 times higher as compared to that of DMACA/TiO<sub>2</sub> system.

In the present investigation, as the basic molecular structures of both DMACA and HCA are very similar (Scheme 1), the electronic couplings of the dye molecules with the TiO<sub>2</sub> nanoparticle are similar (both the dyes have the same anchoring group with the nanoparticle). Still, we have observed 60% more electron injection in the HCA/TiO2 system as compared to that in the DMACA/TiO<sub>2</sub> system. Solvatochromic measurements reveal that the locally excited state for both the dyes is an intramolecular charge transfer (ICT) state. Emission quantum yield  $(\phi_{em})$  measurements have been carried out for both the dyes with changing polarity of the solvents. It has been observed that  $\phi_{em}$  of HCA monotonically decreases with solvent polarity; however,  $\phi_{em}$  of DMACA decreases drastically in highly polar solvent with a sudden break.33 This observation confirmed that in highly polar solvent, the excited DMACA molecule relaxes very fast to another nonemitting state. This nonemitting state is often attributed to the twisted intramolecular charge transfer (TICT) state.<sup>36-39</sup> Nad et al.<sup>40</sup> have shown the presence of a nonemitting TICT state in the excited states of the coumarin-152 and coumarin-1 molecules, which are structurally very similar to DMACA. However, the transient absorption spectrum of DMACA in both less and more polar solvents looks very similar. From this observation, we can conclude that the TICT state of DMACA does not show any transient absorption. The transient absorption spectrum for DMACA in highly polar solvent is attributed to that of the ICT state only.

In our earlier studies, we have compared electron injection  $(\phi_{inj})$  efficiency of two structurally similar dyes, 7-diethyl amino

coumarin 3-carboxylic acid (D-1421) and coumarin 343 (C-343), adsorbed on TiO<sub>2</sub> nanoparticles.<sup>11</sup> Solvatochromic measurements confirmed that the excited D-1421 molecule exists as both ICT and TICT states and the excited C-343 molecule exists as the ICT state in highly polar solvents. We have observed that  $\phi_{inj}$  in D-1421/TiO<sub>2</sub> system is ~1.5 times higher compared to that in the C-343/TiO<sub>2</sub> system. As the TICT state of D-1421 is a charge-separated state, it can inject electrons more efficiently into TiO<sub>2</sub> nanoparticles. However, in the present investigation we have observed that although excited DMACA exists as a TICT state, still  $\phi_{inj}$  in the DMACA/TiO<sub>2</sub> system is 1.6 times lower than that in the HCA/TiO<sub>2</sub> system. The observed differences can be explained with the following explanation. In the TICT states of both excited D-1421 and DMACA molecules, the electron gets localized on the oxygen atom of the keto group. D-1421 molecules couple with the TiO<sub>2</sub> nanoparticles through phthalate type binding, where the keto group also takes part in the coupling process. As a result, electron injection is very efficient from the TICT state of the D-1421 molecule to TiO<sub>2</sub> nanoparticles. However, on the other hand, in the case of the DMACA/TiO2 system, DMACA couples with TiO<sub>2</sub> nanoparticles through the carboxylic group, where the keto group does not take part in the coupling process with TiO<sub>2</sub> nanoparticles (Scheme 2). As a result, the probability of electron injection from the TICT state of DMACA will be less. However, we have already discussed that excited DMACA molecules exist both in ICT and TICT states. Electron injection from the ICT state of DMACA can be highly possible (Scheme 2). The density of the ICT state will be less in the case of DMACA because of the fact that there is another nonradiative pathway leading to TICT, decreasing the density of ICT states. As excited HCA molecules can exist only in ICT states, whose density will be higher than that of ICT states of DMACA in similar condition (at same excitation intensity), the electron injection yield is higher in the HCA/TiO<sub>2</sub> system as compared to that of the DMACA/TiO<sub>2</sub> system (Figure 5).

(f) Effect of Molecular Structure on ET Dynamics. In addition to the injection quantum yield, it is important to understand the effect of molecular structure on interfacial electron transfer (ET) dynamics (both electron injection and BET). In the present investigation, since both DMACA and HCA molecules have the same electron donating orbital and the same anchoring group to the surface, we can assume that there is very little difference in electronic coupling for the injection process. Shown in Figure 5 is comparison of the electron injection time of TiO<sub>2</sub> nanoparticles sensitized by DMACA and HCA after 400 nm excitation. Electron injection time for all the above systems has been found to be ~100 fs (Table 1).

Now it will be interesting to compare the back electron transfer (BET) dynamics of the above systems and find out the effect of molecular structure. We have already discussed that BET dynamics is multiexponential in both DMACA/TiO<sub>2</sub> (Figure 2, inset) and HCA/TiO<sub>2</sub> (Figure 3, inset) systems and it is found to be faster in DMACA/TiO<sub>2</sub> system (Table 1). According to Marcus semiclassical theory,<sup>41</sup> back electron-transfer rate will be depending on  $\Delta G^{\circ}$ , the overall free energy of reaction ( $\Delta G^{\circ} = E_{\rm C} - E_{\rm S/S}^+$ ), where  $\Lambda$ , the total reorganization energies, and  $H_{\rm AB}$ , the coupling elements of the system, are the same. As the molecular structures of DMACA and HCA are very similar and both the dyes couple with nanoparticles in similar fashion, we can consider that there will be little difference in  $\Lambda$  and  $H_{\rm AB}$  in the above systems. As  $-\Delta G^{\circ}$  in DMACA/TiO<sub>2</sub> is lower (1.5 eV) as compared to that in HCA/



**Figure 6.** Comparison of back electron transfer (BET) dynamics of (a) DMACA sensitized  $TiO_2$  nanoparticles and (b) DMACA sensitized  $ZrO_2$  nanoparticles monitoring the cation radical (DMACA<sup>++</sup>) at 630 nm. [Inset: kinetic decay trace at shorter time scale.]

 $TiO_2$  (2.1 eV), so BET dynamics is expected to be faster (in the inverted regime) in the DMACA/TiO<sub>2</sub> system which has been reflected in our experimental results (Table 1). The inverted behavior of BET dynamics has also been demonstrated by us and others in dye sensitized  $TiO_2^{9,42}$  and  $SnO_2^{43}$  nanoparticle surface.

Similarly, we have compared the BET dynamics of DMACA sensitized on both TiO<sub>2</sub> and ZrO<sub>2</sub> nanoparticles (see Figure 6). As the injection is taking place from the DMACA molecule to both the nanoparticles and it couples with the nanoparticles (both  $TiO_2$  and  $ZrO_2$ ) in a similar fashion, we can assume that there will be little difference in  $\Lambda$  and  $H_{AB}$  for BET reaction. As  $-\Delta G^{\circ}$  in DMACA/TiO<sub>2</sub> is lower (1.5 eV) compared to that in DMACA/ZrO<sub>2</sub> (2.8 eV), so BET dynamics is expected to be faster in the DMACA/TiO<sub>2</sub> system, which has been reflected in our experimental results (Table 1). It may be reasonable to observe Marcus inverted region back ET kinetics in the present investigation, since the fast ET (<100 ps) is from electrons located near the adsorbate where diffusion of electrons is not the rate determining process. A similar argument was suggested by Lian and co-workers<sup>44</sup> in their catechols sensitized TiO<sub>2</sub> nanoparticle systems. It is interesting to see that the rate of charge recombination is slower for the case of the DMACA/ ZrO<sub>2</sub> system as compared to that of the DMACA/TiO<sub>2</sub> system, but the residual absorption of charge separated species is less for the case of ZrO<sub>2</sub> as compared to that of TiO<sub>2</sub>. About 88% of the charge recombination takes place in DMACA/ZrO2 within 460 ps (our detecting limit) whereas only 68% of the CR reaction takes place in the DMACA/TiO2 system. It is very difficult to compare the back ET kinetics in TiO<sub>2</sub> and ZrO<sub>2</sub> because they are highly nonexponential in nature, and we have measured only a small cross-section (up to 460 ps) of the total kinetic process. Still, we have tried to compare the BET process by averaging the first two time constants adopting the following equation.

$$\langle \tau_{\rm av} \rangle = \frac{a_1 \tau_1 + a_2 \tau_2}{a_1 + a_2}$$
(1)

The observed average lifetime depends critically on the time scale region that we are considering. In the present investigation, we have considered the first two time constants (Table 1) to calculate the average time constant where it can give information up to first 100 ps of the total measured kinetics. At this point, it is difficult for us to make any comment on the behavior of the BET process of the above systems at longer time domains

(micro- and millisecond). However, within the time scale region of observation for about 100 ps, back ET is faster in the case of TiO<sub>2</sub> when compared to ZrO<sub>2</sub>. This reason behind the fast back ET (<100 ps) is due to the recombination of the electrons localized near the adsorbate, for which the diffusion into the nanoparticle is so not important where the free energy of back ET plays a significant role. For the >500 ps time scale, the deep trap states and electron diffusion into the nanoparticles can play a major role in back ET dynamics. As the two semiconductors that we are considering are different, the trapping/detrapping rate as well as the diffusion of electrons between the trap states (hopping) may be different, and hence, we can observe different dynamics for the >100 ps time scale region in comparison to <100 ps time domain. Dynamics in longer time domain can be explained by the fact that although photoexcited DMACA can inject electron in the conduction band in both TiO2 and ZrO2 nanoparticles, density of accepting states in  $ZrO_2$  is less as compared to that in  $TiO_2$  at the injecting energy level (-1.9 eV) (Scheme 3). Injected electrons in TiO<sub>2</sub> nanoparticles will be hotter and will possess more energy compared to those in ZrO<sub>2</sub> nanoparticles; as a result diffusivity of the injected electron will be greater within the TiO<sub>2</sub> nanoparticles. So, the availability of injected electrons for the recombination reaction will be greater in ZrO<sub>2</sub> nanoparticles at the injecting site. As a result, the amount of charge recombination is higher in  $ZrO_2$ .

(g) Importance of Molecular Structure in Energy Conversion Implications. In recent years, many researchers have been trying hard to design and develop suitable low cost organic dyes, which can be used in solar cells with higher efficiency. Molecular structure of the organic dyes can be a very important factor to get higher efficiency.<sup>45,24-26</sup> In our previous studies<sup>11</sup> we have observed that a little structural change can increase the injection efficiency in coumarin dye (D-1421 and C-343) sensitized nanoparticles. Among them, excited D-1421 exists in the TICT state, which eventually helps to inject electron efficiently, because an electron localized at the keto group was coupled with the nanoparticles. However, in the present investigation we have observed that although the excited state of DMACA exists as a TICT state, it cannot inject electrons efficiently because its electron localized center is away from the coupling site with the nanoparticles (Scheme 2). As we have observed earlier,<sup>11</sup> the TICT state of dye molecules can be of help to increase the injection efficiency; on the other hand, it can also diminish the same if the molecular structures of the dye molecules are not designed properly.

#### 4. Conclusion

Sub-picosecond transient absorption spectroscopy has been used to study the effect of molecular structure in photoinduced electron-transfer dynamics in 7-N,N-dimethyl amino coumarin 4-acetic acid (DMACA) and 7-hydroxy coumarin 4-acetic acid (HCA) sensitized  $TiO_2$  and  $ZrO_2$  nanoparticles in aqueous solution. The molecular structures of the studied dyes (DMACA and HCA) are very similar with the same anchoring group which binds with the nanoparticles except that HCA has a hydroxy group at the 7-position while DMACA has a dimethyl amino group at the 7-position. Electron injection has been confirmed by direct detection of the conduction band electron in the 800-1000 nm region and a cation radical in the visible region. Electron injection quantum yield is found to be 1.6 times higher in HCA/TiO<sub>2</sub> system as compared to that in DMACA/TiO<sub>2</sub> in similar condition. Solvatochromic measurements indicate that the photoexcited HCA molecule exists in the ICT state; however,

the DMACA molecule exists in both ICT and TICT states. We have observed that the TICT state of DMACA is a less efficient injecting state, because in the TICT state charge is localized in the keto group, which is away from the binding site of the dye (-CH<sub>2</sub>COOH) with the nanoparticle. On the other hand, ICT states of both HCA and DMACA can inject electrons into TiO<sub>2</sub>. The higher density of ICT states in HCA compared to DMACA resulted in a higher quantum yield of electron injection. Another important observation that has been made is that the photoexcited state of DMACA, which lies above the conduction band, can inject electrons into the ZrO<sub>2</sub> nanoparticles, which are normally considered as a noninjecting surface for most photoexcited dyes. However, the photoexcited state of HCA, which lies below, cannot inject electrons in ZrO<sub>2</sub>. Electron injection times have been found to be  $\sim 100$  fs in all the above systems because both the dyes couple with both  $TiO_2$  and  $ZrO_2$  in a similar fashion. However, BET dynamics is found to be slower in the HCA/TiO<sub>2</sub> system compared to the DMACA/TiO<sub>2</sub> system, following the equation of the ET reaction in the Marcus inverted region. In the DMACA/ZrO<sub>2</sub> system, BET dynamics is slower compared to DMACA/TiO<sub>2</sub> system; however, the charge separated species left after 460 ps is less for the case of the ZrO<sub>2</sub> system.

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**Supporting Information Available:** Additional figures and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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