Surface Processes

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Electron Transport in the Long-Range Charge-Recombination Dynamics of Single Encapsulated Dye Molecules on TiO_2 Nanoparticle Films**

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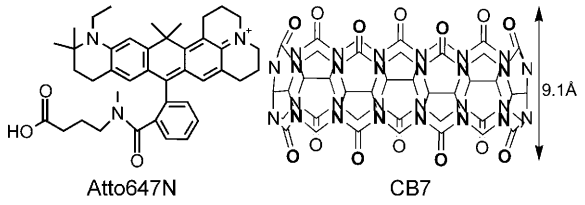
Interfacial electron transfer in dye-sensitized semiconductors, such as TiO_2, has been applied extensively in molecular devices for solar energy conversion. Electron transport in nanocrystalline metal oxides is an important process that is often neglected when describing the charge-recombination dynamics between injected electrons and TiO_2 at the single-molecule level.[1,2] Electron transport is intrinsic to TiO_2 and has been reported to take place on solid-state colloidal TiO_2 films[3] and TiO_2 films filled with electrolytes.[4] It has been proposed that electron transport occurs by a series of charge trapping and detrapping steps, with the trap sites located predominantly on the metal oxide surface.[5] Herein, we examine the role of electron transport in determining the charge-recombination dynamics between single dye molecules and TiO_2.

One of the major drawbacks of molecular devices is the photodegradation of the dyes used. Supramolecular dyes formed by the encapsulation of dye molecules by macrocyclic hosts, such as cucurbituril, are known to be highly thermally stable and photostable.[6] Cucurbit[7]uril (CB7; Scheme 1) effectively complexes rhodamine 6G (R6G); the significant increase in the photostability of R6G upon CB7 encapsulation has been demonstrated at both the bulk and single-molecule levels.[7,8] Furthermore, it is advantageous to study the effects of CB7 on the charge-recombination of single dye molecules. Herein, Atto647N, a rhodamine-type dye (Scheme 1) is used to photosensitize TiO_2 nanoparticles. The binding equilibrium constant of the inclusion complex CB7–Atto647N was determined to be 2290 from UV/Vis measurements (see the Supporting Information).



Scheme 1. Atto647N[9] and cucurbit[7]uril (CB7). The depth of CB7 is 9.1 Å.[16]

The ensemble-averaged fluorescence spectrum of Atto647N is significantly quenched when adsorbed onto TiO_2 nanoparticles in water (see the Supporting Information). This is due to an ultrafast electron-transfer process from the dye to TiO_2, which occurs much faster than the resolution of our time-correlated single-photon counting spectrometer (resolution: ca. 100 ps). The free-energy change $\Delta G°$ for electron transfer is −0.46 V, which indicates an energetically favorable electron-transfer process from the dye to TiO_2 (see the Supporting Information).

Two distinct groups of blinking behavior are observed from the emission intensity time traces of 240 Atto647N molecules on TiO_2 (Figure 1). Of these 240 molecules, 197 (or 82%) displayed temporary off-events that last from tens of milliseconds to a few seconds (see Figure 1a for a typical trace), whilst the rest of the molecules showed constant emission intensity (that is, absence of blinking) before undergoing irreversible photobleaching. The off-events are attributed to the dark oxidized states of Atto647N formed as a result of interfacial electron transfer from the dye molecule to TiO_2 nanoparticle. The transition from "off" to "on" states occurs when the electron injected into the conduction band of TiO_2 recombines with the oxidized dye to form the fluorescent molecule.

A number-density analysis was performed, which showed that the majority of the Atto647N molecules deposited on TiO_2 were probed in the single-molecule experiment (see the Supporting Information). Furthermore, the fluorescence lifetime (τ_f) distribution of single Atto647N on TiO_2 was fitted to a Gaussian distribution with a mean value of 3.9 ns, which is close to the ensemble-averaged emission lifetime of Atto647N in water (ca. 3.6 ns; see the Supporting Information).

In general, ensemble-averaged forward electron-transfer (FET) rates, which were measured by bulk techniques, fall in the ultrafast time domain (that is, fs to ps), and they are much faster than the resolution of the single-molecule experimental set-up.[10] The observation of fluorescence intensity of single dye molecules undergoing rapid electron transfer to metal

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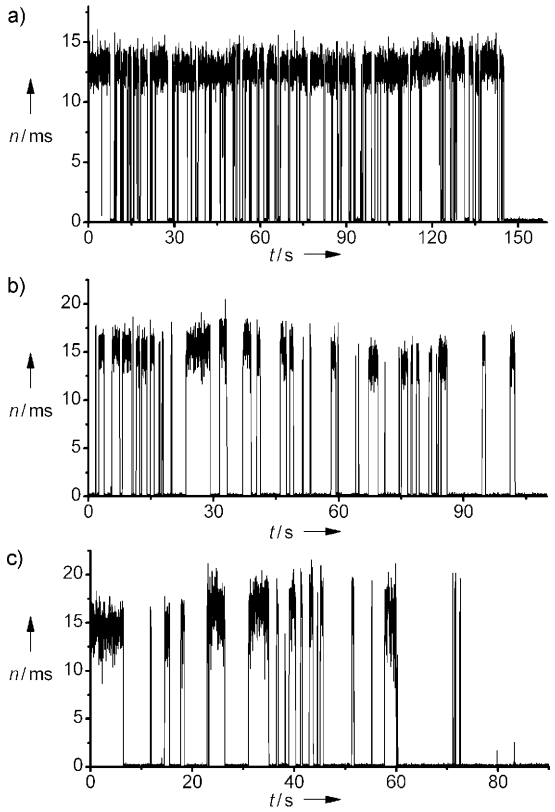


Figure 1. Fluorescence intensity time traces (bin time = 20 ms) of single Atto647N (a) and CB7–Atto647N (b,c) molecules on a TiO_2 surface under ambient conditions. *n* is the emission intensity.

oxides was explained by Lu et al., who reported similar behavior in the interfacial electron-transfer dynamics of single dye molecules (such as cresyl violet, coumarin, and porphyrin) on TiO_2.[2] They proposed that the emission intensity of single molecules, such as that seen in Figure 1 a, is determined by the fraction of time that the FET process dominates the fluorescence, and it is not affected by the rate of the ultrafast FET. In this case, when the reactivity of FET is low (that is, when FET rate is smaller than the radiative rate), the fluorescence quantum yield and fluorescence intensity are high owing to radiative emission from the excited S_1 state of the dye to its ground state ("on" state and unquenched τ_f). The FET then switches to a high reactivity mode (such as when the FET rate is larger than the radiative rate), which leads to electron transfer to TiO_2 followed by a low or zero fluorescence intensity ("off" state). Several factors, such as the dynamic change of the energy gap between dye and TiO_2, electronic coupling between the active species, and the vibrational relaxation energy of the adsorbed dye, have been proposed to be responsible for the changing FET reactivities.[2]

An off-time (τ_{off}) duration histogram was constructed using the threshold method.[11] The linear log–log plot for the combination of blinking Atto647N molecules on TiO_2 nanoparticle (Figure 2) is best described using a power-law distribution [Eq. (1)]:

$$P(\tau_{off}) = P_o \tau_{off}^{-m_{off}} \quad (1)$$

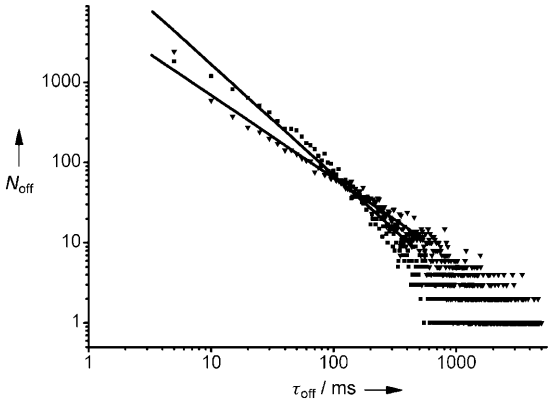
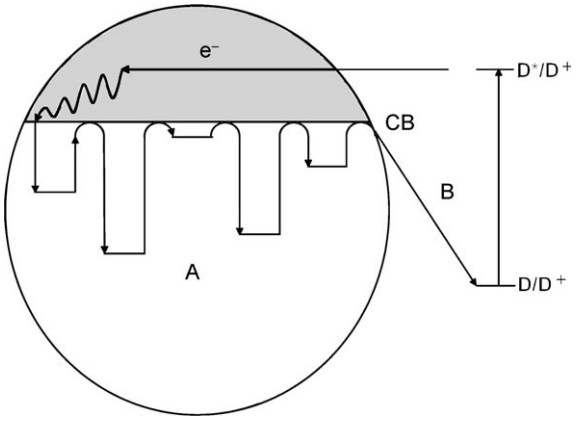


Figure 2. Off-time distributions for a combination of 197 Atto647N (■) and 478 CB7–Atto647N (▼) molecules on TiO_2 nanoparticle film. The linear log–log plots yield m_{off} values of 1.4 for Atto647N and 1.0 for CB7–Atto647N. N_{off} is the number of off-time events and τ_{off} is the off-time.

with the power-law exponent $m_{off} = 1.4$. On the other hand, the on-time histograms do not show a monoexponential decay, thus indicating that the conversion rate from low to high activity does not assume a fixed value (see the Supporting Information).

Following electron injection into the TiO_2 conduction band and fast relaxation, the injected electron undergoes electron transport by moving from trap to trap on the TiO_2 surface by a series of trapping and thermally activated detrapping events. Thereafter, the electron arrives at a suitable reactive site, where it undergoes interfacial back electron transfer (BET) to the oxidized dye (Scheme 2).[12] The classical Marcus equation is commonly used to describe the BET rate k_{bet}.[13] In Figure 1 a, the duration of each off-event (τ_{off}) is equivalent to the total time for electron transport and interfacial BET. As the dye molecules are in direct contact with the TiO_2 nanoparticles, it is assumed that k_{bet} is much faster than the electron detrapping rates at the reactive sites.[12] In such a case, τ_{off} is given by the time taken for the injected electron to visit the traps before arriving at a



Scheme 2. Electron injection and charge recombination. Following electron injection into the conduction band (CB) and fast relaxation, the injected electron undergoes electron transport (A) and then electron transfer (B) back to the oxidized dye.[12]

reactive site (that is, the first passage time). A power-law distribution for the detrapping times of an electron at a trap site, $P(t) = Pt^{-1-\alpha}$, where $0 < \alpha < 1$, is obtained when an exponential distribution of trap energies E_i (depicting the Urbach tail in the conduction band edge) is considered [Eq. (2)]:[14]

$$g(E_i) = \frac{1}{k_B T_0} e^{-(E_c - E_i)/kT_0} \quad (2)$$

where k_B is the Boltzmann's constant and E_c is the conduction band-edge energy. The characteristic temperature T_0, the temperature T, and α are related by $\alpha = T/T_0$. The duration of each off-event is thus the sum of several power-law variables, and follows a power-law distribution with $m_{off} = 1 + \alpha$. Values for α of circa 0.4 were reported for ruthenium-based dye-sensitized TiO_2 using transient absorption spectroscopy, and these values are in good agreement with the α value obtained from the off-time distribution (Figure 2).[14,15]

The emission intensity time traces of 749 CB7–Atto647N molecules on TiO_2 were recorded and their blinking behavior categorized into two groups. 120 molecules (16%) did not show any blinking behavior, whereas the other 629 molecules showed either long-lived off-events in the fluorescence trajectory (478 molecules, see Figure 1b,c) or rapid "on"/"off" intensity fluctuations with "off" states lasting a few ms (151 molecules). The latter process is due to the dark triplet state of the encapsulated molecule (see the Supporting Information).

The intensity time traces of two typical molecules that exhibit long off-events are illustrated in Figure 1b,c. A power-law distribution for the off-times is observed for the collection of blinking molecules with $m_{off} = 1.0$ (Figure 2). The small power-law exponent suggests that there is a higher probability of finding long dark periods when Atto647N molecules are included into CB7 as compared to uncomplexed dyes.

The discrepancy in the observed m_{off} values between Atto647N and CB7–Atto647N on TiO_2 is rationalized by considering a reduced rate k_{bet} when the dye molecule is included into the macrocyclic CB7. In this case, the electronic coupling matrix element H_{el} in k_{bet} diminishes exponentially with increasing distance between the electron donating and accepting states R_e; the relationship is $H_{el}^2 = H_0^2 e^{-\beta R_e}$, where β is the attenuation factor. When Atto647N is included into CB7, the latter increases the spatial separation between the dye molecule and the metal oxide, thus reducing the value of k_{bet} relative to the uncomplexed molecule. In this case, charge recombination is not limited by the first passage time, and the injected electron can visit the reactive sites several times before BET occurs. This results in an increase in the τ_{off} value as observed experimentally.

The above argument is supported by studying the blinking behavior of single CB7–Atto647N molecules surrounded by TiO_2 nanoparticles. In this case, the emission intensity time traces of 240 molecules sandwiched between two layers (top and bottom) of TiO_2 nanoparticle films were recorded. The power-law distribution for the off-time durations, obtained from a combination of 203 blinking molecules, yielded a m_{off} value of 1.4, which is similar to the power-law exponent of uncomplexed Atto647N on TiO_2 nanoparticles. This result means that the probability for faster charge recombination is higher when the oxidized CB7–Atto647N molecule is completely surrounded by TiO_2 nanoparticles than when it is in contact with only a bottom layer of metal oxide. It has been shown that the internal cavity of a CB7 is too small to fully accommodate a R6G molecule by computational chemistry calculations,[8] which suggests that the larger Atto647N molecule is partially encapsulated by CB7. For CB7–Atto647N on a bottom layer of TiO_2, the part of the molecule that is not protected by CB7 is separated from the metal oxide. On the other hand, for CB7–Atto647N surrounded by TiO_2 (that is, by both top and bottom layers), the unprotected part of the dye is in direct contact with the metal oxide, thus enabling interfacial BET to occur without spatial distance effects.

Long off-events may occur when high FET activity persists for a long time.[2] The greater spatial separation between CB7–Atto647N and TiO_2 may result in either unchanged or shorter periods of high FET activity compared to the uncomplexed molecule. Clearly, FET activity alone does not completely describe the off-events, and electron transport plays an important role in the observed fluorescence intermittency.

Computational simulations, based on a continuous-time random walk, were performed to obtain off-time distributions (see the Supporting Information for details).[12] A probability $P_{bet} = k_{bet}/(v_o + k_{bet})$ is introduced to decide if the electron at a reactive site recombines or hops to a neighboring trap with rate v_o (the electron attempt-to-escape frequency). In this case, $P_{bet} = 1$ when fast BET is present ($k_{bet} \gg v_o$), and P_{bet} tends to zero for slow BET (when $v_o \gg k_{bet}$). A value $v_o = 1 \times 10^{10}\ s^{-1}$ that is smaller than the atomic frequency (ca. $10^{12}\ s^{-1}$) is utilized in the simulation. Figure 3 shows the normalized off-time distributions for various P_{bet} values obtained from computational simulations. The off-times follow a power-law distribution with $m_{off} = 1.4$ ($\alpha = 0.4$), 1.3 ($\alpha = 0.3$), 1.1 ($\alpha = 0.1$) and 1.0 ($\alpha = 0$) for $P_{bet} = 1$, 0.01, 0.001, and 0.0005, respectively. When an electron at a reactive site has an increased probability of hopping to a trap, the charge-

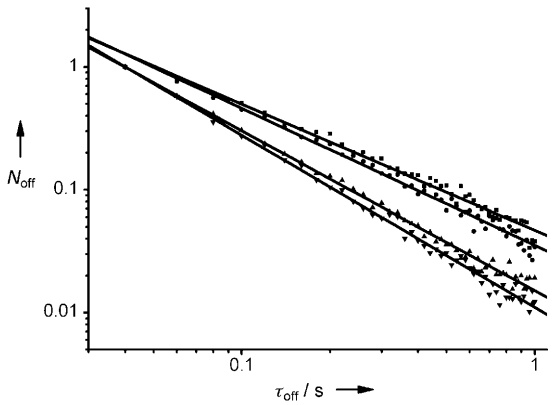


Figure 3. Normalized off-time distributions based on the Monte Carlo simulations. The linear log–log plots yield m_{off} values of 1.4 ($P_{bet} = 1$, ▼), 1.3 (0.01, ▲), 1.1 (0.001, ●), and 1.0 (0.0005, ■). N_{off} is the number of off-time events and τ_{off} is the off-time.

recombination dynamics is no longer limited by the first-passage time. The electron continues to diffuse on the metal oxide surface, and undergoes several encounters with the reactive site before BET occurs. This results in an increase in the probability of finding long off-times, and a concomitant decrease in the α value in accordance with experimental observation. Similar trends are observed when different v_o values are employed in the simulations.

The configuration with the empty portal of CB7 sitting on the nanoparticle will result in a maximum separation between the unprotected portion of the dye and TiO_2 and gives rise to long off-events. In this case, the separation between the unprotected dye and the metal oxide is at least the depth of the macrocyclic CB7 (ca. 9 Å).[16] This is the most important configuration for the long off-events. When $m_{off} = 1.0$, $v_o = 1 \times 10^{10}\ s^{-1}$ and $P_{bet} = 0.0005$, a value of $k_{bet} \approx 5 \times 10^6\ s^{-1}$ is obtained for the back electron-transfer reaction between the inclusion complex and TiO_2. The exact separation R_e between Atto647N and TiO_2 is not known, and by assuming an R_e value of 9 Å (the depth of CB7) and an attenuation factor of $\beta = 1\ Å^{-1}$,[12] a value of $k_{bet} \approx 4 \times 10^{10}\ s^{-1}$ is obtained for the uncomplexed dye. This value is reasonable, as several studies have shown that interfacial BET occurs within a few ps to ns.[17]

In summary, we have detected the presence of long-lived dye cations in the majority of dye molecules on TiO_2, and especially for the encapsulated Atto647N, and have demonstrated that electron transport may play a pivotal role in charge recombination at the single-molecule level, as it adequately describes the power-law dispersion of τ_{off}.

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[1] a) M. W. Holman, R. Liu, D. M. Adams, *J. Am. Chem. Soc.* **2003**, *125*, 12649 – 12654; b) H. P. Lu, X. S. Xie, *J. Phys. Chem. B* **1997**, *101*, 2753 – 2757; c) T. D. M. Bell, C. Pagba, M. Myahkostupov, J. Hofkens, P. Piotrowiak, *J. Phys. Chem. B* **2006**, *110*, 25314 – 25321; d) T. Tachikawa, S. Ciu, S. Tojo, M. Fujitsuka, T. Majima, *Chem. Phys. Lett.* **2007**, *443*, 313 – 318.

[2] a) V. Biju, M. Miodrag, D. Hu, H. P. Lu, *J. Am. Chem. Soc.* **2004**, *126*, 9374 – 9381; b) Y. Wang, X. Wang, S. K. Ghosh, H. P. Lu, *J. Am. Chem. Soc.* **2009**, *131*, 1479 – 1487.

[3] R. Könenkamp, R. Henninger, P. Hoyer, *J. Phys. Chem.* **1993**, *97*, 7328 – 7330.

[4] R. Katoh, A. Furube, A. V. Barzykin, H. Arakawa, M. Tachiya, *Coord. Chem. Rev.* **2004**, *248*, 1195 – 1213.

[5] N. Kopidakis, N. R. Neale, K. Zhu, J. van de Lagemaat, A. J. Frank, *Appl. Phys. Lett.* **2005**, *87*, 202106.

[6] A. L. Koner, W. N. Nau, *Supramol. Chem.* **2007**, *19*, 55 – 66.

[7] J. Mohanty, W. N. Nau, *Angew. Chem.* **2005**, *117*, 3816 – 3820; *Angew. Chem. Int. Ed.* **2005**, *44*, 3750 – 3754.

[8] T. A. Martyn, J. L. Moore, R. L. Halterman, W. T. Yip, *J. Am. Chem. Soc.* **2007**, *129*, 10338 – 10339.

[9] C. Eggeling, C. Ringemann, R. Medda, G. Schwarzmann, K. Sandhoff, S. Polyakova, V. N. Belov, B. Hein, C. von Middendorff, A. Schönle, S. W. Hell, *Nature* **2009**, *457*, 1159 – 1163.

[10] a) D. F. Watson, G. J. Meyer, *Annu. Rev. Phys. Chem.* **2005**, *56*, 119 – 156; b) N. A. Anderson, T. Lian, *Annu. Rev. Phys. Chem.* **2005**, *56*, 491 – 519.

[11] a) E. K. L. Yeow, S. M. Melnikov, T. D. M. Bell, F. C. De Schryver, J. Hofkens, *J. Phys. Chem. A* **2006**, *110*, 1726 – 1734; b) X. Wu, E. K. L. Yeow, *Nanotechnology* **2008**, *19*, 035706.

[12] J. N. Clifford, E. Palomares, M. K. Nazeeruddin, M. Grätzel, J. Nelson, X. Li, N. J. Long, J. R. Durrant, *J. Am. Chem. Soc.* **2004**, *126*, 5225 – 5233.

[13] R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265 – 322.

[14] a) J. Nelson, *Phys. Rev. B* **1999**, *59*, 15374 – 15380; b) J. Nelson, S. A. Haque, D. R. Klug, J. R. Durrant, *Phys. Rev. B* **2001**, *63*, 205321; c) J. Nelson, R. E. Chandler, *Coord. Chem. Rev.* **2004**, *248*, 1181 – 1194.

[15] S. A. Haque, Y. Tachibana, R. L. Willis, J. E. Moser, M. Grätzel, D. R. Klug, J. R. Durrant, *J. Phys. Chem. B* **2000**, *104*, 538 – 547.

[16] J. Lagona, P. Mukhopadhyay, S. Chakrabarti, L. Isaacs, *Angew. Chem.* **2005**, *117*, 4922 – 4949; *Angew. Chem. Int. Ed.* **2005**, *44*, 4844 – 4870.

[17] a) Y. Weng, Y. Wang, J. B. Asbury, H. N. Ghosh, T. Lian, *J. Phys. Chem. B* **2000**, *104*, 93 – 104; b) G. Ramakrishna, H. N. Ghosh, A. K. Singh, D. K. Palit, J. P. Mittal, *J. Phys. Chem. B* **2001**, *105*, 12786 – 12796.

