

## Tuning Electron Transfer Rates via Systematic Shifts in the Acceptor State Density Using Size-Selected ZnO Colloids

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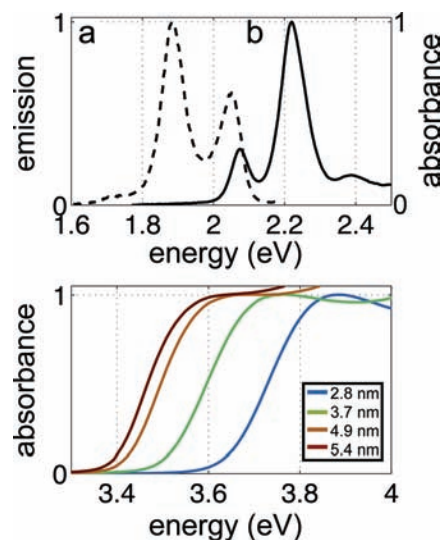
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**Abstract:** We report direct measurements of the influence of the available density of acceptor states on the rate of near-barrierless electron transfer between a dye sensitizer and an oxide semiconductor. The electron donor was the excited state of a zinc porphyrin, and the acceptors were a series of size-selected ZnO nanocrystals. The available density of states was tuned by controlling the relative position of the ZnO band edge using quantum confinement. The resulting change in the rate was consistent with a simple model of the state density as a function of energy above the ZnO band edge.

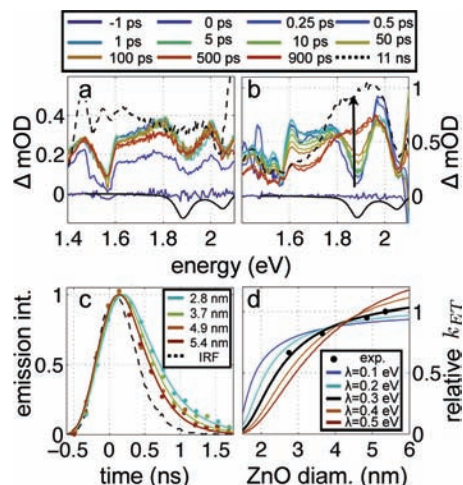
Electron transfer (ET) processes in dye-sensitized solar cells made from nanocrystalline semiconductors have received considerable attention. Rates for ET are typically found to be multifaceted and complicated by film heterogeneity.<sup>1–3</sup> This has motivated measurements of ET in somewhat better defined systems comprising dye molecules bound to colloidal nanocrystals (NCs) dispersed in solution.<sup>4–7</sup> These systems can exhibit single-exponential ET kinetics and provide a platform for more detailed investigations of the ET reaction.<sup>5</sup> One example is the ability to use quantum confinement to tune the energetic alignment of the donor and acceptor without altering the chemistry. By tuning the relative donor potential via size selection of CdSe NCs, Robel et al.<sup>8</sup> demonstrated control over the classical Marcus barrier, thereby changing the ET rate. Here we present the use of size-selected semiconductor electron acceptors to measure the influence of the density of acceptor states on the ET rate. The donor was a zinc porphyrin, and the acceptors were a series of size-selected ZnO NCs. To our knowledge, this is the first reported evidence for modulation of ET rates using quantum confinement to tune the acceptor state density systematically.

The electron donor, 5-(4-carboxyphenyl)-10,15,20-tris(2,4,6-trimethylphenyl)porphyrinatozinc(II) (abbreviated below as ZnP), and size-selected colloidal dispersions of ZnO NCs were synthesized as described elsewhere.<sup>9,10</sup> All of the experiments were performed in methanol at room temperature, and the ZnP concentration was kept under 0.1 mM. Absorption and emission spectra for ZnP are shown in Figure 1a. The absorption spectra for the four size-selected distributions of ZnO NCs used in this study are shown in Figure 1b, and the average NC diameter for each sample, indicated in the figure legend, was assigned on the basis of the absorption onset.<sup>11</sup>

The electron transfer kinetics were measured using a combination of pump–probe and time-resolved fluorescence spectroscopies. Figure 2a shows the pump–probe spectrum for ZnP alone in solution, and Figure 2b presents the same experiment for a ~1:1 ratio of ZnP and 3.7 nm diameter ZnO NCs. ZnP



**Figure 1.** (a) Absorption and emission spectra of ZnP. (b) Absorption spectra of the size-selected colloidal ZnO NC samples.



**Figure 2.** Transient spectra following 2.2 eV excitation of (a) ZnP and (b) a ~1:1 mixture of ZnP and 3.7 nm diameter ZnO NCs. (c) TCSPC at 1.9 eV following excitation at 3.3 eV of ~1:1 ZnP/ZnO NC mixtures. (d) Relative electron injection rates.

has a broad excited-state absorption that shows very little time evolution over the first nanosecond, consistent with the singlet lifetime of 2.3 ns. By 11 ns, the spectrum has shifted to that of the lower-energy triplet absorption. Overlapped with the transient absorption is stimulated emission that appears as a negative contribution to the transient spectrum corresponding to the spontaneous emission spectrum, which is shown as a solid black

**Table 1.** Time Constants for Electron Injection

ZnO NC diameter (nm)	$\tau$ (ps)
2.8	369 $\pm$ 10
3.7	299 $\pm$ 10
4.9	258 $\pm$ 9
5.4	245 $\pm$ 9

line for reference. The ZnP/ZnO NC mixture exhibits an accelerated decay of the stimulated emission feature, and there is a correlated rise of a new transient absorption centered around 1.9 eV. This feature has been identified previously as absorption by the radical cation form of the porphyrin,<sup>12</sup> and our own spectroelectrochemistry measurements provide additional support for this assignment (see the Supporting Information). On the basis of the pump–probe measurements, we have assigned the primary mechanism for excited-state quenching of ZnP by ZnO NCs as ET.

To eliminate complications from the overlapping spectral contributions in the pump–probe transients, time-correlated single photon counting (TCSPC) was used to measure the rate of ET via quenching of spontaneous emission from ZnP. These data were found to fit well to a sum of two exponential decays, one with a time constant matching the unperturbed excited-state dye lifetime of 2.3 ns, corresponding to noninjecting ZnP, and a larger amplitude, faster decay component with a time constant of  $\sim$ 300 ps. Fitting parameters for the faster quenching are shown in Table 1, and normalized TCSPC traces with the noninjecting lifetime component subtracted for clarity are shown in Figure 2c.

The faster fluorescence decay component, which we believe to be dominated by ET, is slower than previous reports for electron injection from ZnP on TiO<sub>2</sub> films.<sup>12,13</sup> The time evolution of the pump–probe measurements at 1.9 eV agree well with the TCSPC results and fail to show evidence for any faster components despite the much higher time resolution ( $\Delta t < 100$  fs). Slower ET from dyes attached to ZnO than from dyes attached to TiO<sub>2</sub> has been observed for many systems. This has been attributed to a number of possible origins, including weaker electronic coupling between the dye and ZnO.<sup>6,14</sup> Rather than on the physical basis of the quantitative value of the rate, the discussion here will focus on the observation that the measured ET rate exhibits a systematic dependence on the average diameter of the ZnO NC acceptor.

Within the assumption of weak coupling (adiabatic), the ET rate coefficient  $k_{ET}$  can be estimated from the classical Marcus expression, as shown in eq 1.<sup>15</sup> The pre-exponential factor has been expanded to include explicitly the density of acceptor states,  $\rho(E)$ , as a function of energy above the acceptor band edge,  $E$ . The electronic coupling is  $H(E)$ ,  $\lambda$  is the reorganization energy,  $f(E, E_F)$  is the Fermi occupancy factor, and  $\Delta G_0$  is the energy difference between the conduction band (CB) edge of the acceptor and the excited state of the donor. Integration over all values of  $E$  accounts for injection into all possible acceptor states.

$$k_{ET} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} dE \rho(E) [1 - f(E, E_F)] |\tilde{H}(E)|^2 \times \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(\lambda + \Delta G_0 + E)^2}{4\lambda k_B T}\right] \quad (1)$$

The exponential term can exert a dramatic influence on the ET rate as a result of changes in the energetic barrier that typically come from changes in the donor–acceptor free-energy

offset.<sup>7</sup> However, in the case of an energetic distribution of available acceptor states, when  $\lambda$  is smaller than  $\Delta G_0$ , acceptor states with barrierless transfer ( $\lambda + E = -\Delta G_0$ ) can dominate the rate.<sup>15</sup> Under such circumstances, it is the pre-exponential terms that control the rate, and this is the case here. At 3.65 eV below the vacuum level, the excited state of ZnP lies well above the ZnO CB edge energetically.<sup>16</sup> The ZnO CB edge ranges from 3.92 to 4.13 eV (below vacuum) for NCs larger than 2.5 nm (see the Supporting Information). Under the assumption that the electronic coupling and Fermi occupancy do not depend significantly on  $E$ , changes in  $k_{ET}$  result primarily from changes in the density of acceptor states for near-barrierless ET,  $\rho(E = -\Delta G_0 - \lambda)$ . Decreasing the size of the ZnO NC acceptor shifts the CB edge up and decreases  $\rho(E = -\Delta G_0 - \lambda)$ . Using a simple model in which  $\rho(E)$  is proportional to  $\sqrt{E}$ ,<sup>15</sup> we compared the prediction of eq 1 to our measured relative ET rates as a function of ZnO NC diameter, as shown in Figure 2d. The best fit was found using  $\lambda = 0.3$  eV, which is comparable to the values of 0.5–0.7 eV reported for analogous zinc porphyrin ET systems.<sup>17,18</sup> The single-exponential ET kinetics and the good agreement with eq 1 when a very simple model for  $\rho(E)$  was employed suggests that states near and below the CB band edge, such as trap states, likely do not play a significant role in the observed charge injection. This reflects the fact that ET predominantly takes place via barrierless transfer well above the CB edge, consistent with the rather subtle influence of particle size on the ET rates.<sup>15</sup> The single-exponential ET kinetics also reflects the relatively homogeneous distribution of donor–acceptor interactions provided by the  $\sim$ 1:1 ZnP/ZnO NC ratio in the colloidal dispersions.

We believe this to be the first experimental observation using the shift in acceptor state density caused by the shift of a semiconductor CB via NC size selection to control electron injection rates in a model dye-sensitized solar cell system. Chakrapani et al.<sup>19</sup> have suggested the influence of  $\rho(E)$  on back-ET with variation of the pH. The present results provide direct experimental evidence to support the predicted influence of  $\rho(E)$  on ET. As the acceptor NC size becomes small, injection becomes heavily weighted by the higher rates at the larger end of a given colloidal sample distribution. Future development of methods to produce narrower distributions of oxide semiconductors within the quantum-confined size regime will improve the prospects for detailed studies of  $\rho(E)$  and its influence on ET.

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**Supporting Information Available:** Synthesis, experimental and analysis procedures, spectroelectrochemistry of ZnP, and additional references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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