Molecular control of photo-induced electron and energy transfer at nanocrystalline semiconductor interfaces

Gerald J. Meyer∗
Department of Chemistry, Johns Hopkins University, Remsen-Hall, Dunning-Hall 3400, N. Charles Street, Baltimore, MD 21218, USA

Received 18 March 2002; received in revised form 20 June 2002; accepted 1 July 2002

Abstract
Some strategies toward the realization of molecular control of photo-induced charge-transfer processes at nanocrystalline semiconductor interfaces are discussed. Supramolecular compounds that efficiently absorb light, promote interfacial electron transfer, and feature additional functions such as intramolecular electron transfer when bound to semiconductor surfaces are of specific interest. Tuning the energetic position of the semiconductor conduction band relative to molecular excited state reduction potentials are also discussed. When utilized as components in photonic devices, these interfaces allow the conversion of light into an electrical response to be controlled at the molecular-level.

Keywords: Molecular compounds, supramolecular compounds, Nanocrystalline semiconductor interfaces

1. Introduction
Molecular compounds have been designed to perform relatively elaborate and useful tasks [1–5]. The design of ‘supramolecular’ compounds capable of functioning as molecular devices is an area of active research. An interesting idea is to join together supramolecular compounds and nanoparticles in what have been called “heterosupramolecular” assemblies [6–12]. Nanoparticles possess solid-state properties that can provide an interface between the molecule and the external world. This brings about interesting possibilities for addressing, modulating, and exploiting supramolecular function in real world devices. The knowledge and control of electronic interactions at the interfaces between molecules and nanometer-sized semiconductors is of fundamental importance for these emerging fields of science and technology [6–12]. Molecular and ‘supramolecular’ compounds have improved our understanding of electron transfer at nanostructured semiconductor surfaces [13,14]. Specifically, novel photo- and redox-active molecular compounds have been positioned on nanocrystalline semiconductor surfaces with high precision and control. Pulsed light excitation of these molecular materials allows fundamental interfacial electron and energy transfer events to be quantified spectroscopically with high signal-to-noise ratios.

∗ Tel.: +1-410-516-7319; fax: +1-410-516-8420.
E-mail address: meyer@jhu.edu (G.J. Meyer).

This short manuscript summarizes examples of how electronic interactions at molecular-semiconductor nanoparticle interfaces may ultimately be controlled with molecular precision. The summary is not meant to be exhaustive and focuses mainly on surface mediated photochemical processes relevant to dye sensitized solar cells, [13,14] with particular emphasis on metal-to-ligand charge-transfer (MLCT) excited states, electron injection, and charge recombination processes with Re(I), Ru(II), and Os(II) coordination compounds, termed sensitizers (S), anchored to ∼20 nm diameter nanocrystalline (anatase) TiO2 particles inter-connected in a mesoporous 10 mm thick film [14].

One theme of this manuscript involves controlling the energetic position of the conduction band edge, Ecb, in the anatase nanocrystals with pH, potential determining cations, solvent, applied potential, and surface chemistry [15–20]. Conditions have identified where the quantum yield for excited state electron injection to TiO2 can be reversibly tuned from zero to unity simply by controlling the interfacial ionic strength [16]. This allows excited states and interfacial electron transfer to be studied on the same material and provides a convenient method for systematically tuning solar conversion efficiencies.

A second theme involves the use of “supramolecular” compounds as sensitizers [20–27]. These compounds have allowed intramolecular ‘hole’ hopping reactions and ‘stepwise’ electron injection processes to be quantified (Fig. 1). In addition, intermolecular energy transfer processes have characterized [28]. In our opinion, the results...
of these studies have implications that extend beyond solar energy conversion toward the realization of devices driven by molecular-level components [6–12].

2. Results and discussion

2.1. Conduction band edge tuning

2.1.1. Cation-induced shifts

Controlling the nature and concentration of cations at the interface has been used to optimize the yield for interfacial electron transfer or long-lived excited states [15,16]. For example, the quantum yield for electron injection from Ru(dcb)(bpy)$_2^{2+}$, where dcb is 4,4′-(COOH)$_2$-2,2′-bipyridine, to titanium dioxide (anatase) can be reversibly tuned from below detection limits, ≈0, to near unity simply by altering the [Li$^+$] concentration in an external acetonitrile bath [16]. A model was proposed to account for this behavior wherein surface adsorption by cations shifts the energy of the semiconductor acceptor states, presumably $E_{cb}$, resulting in more favorable overlap with the donor levels of the molecular excited state (Fig. 2). The reduction potential of the thermally equilibrated excited state also shifts with cation but, apparently to a much lesser extent than the semiconductor. Interestingly, the optical data is most consistent with injection occurring from vibrationally hot excited states, Ru(III/II$^*$), at low Li$^+$ concentrations. Cation promoted electron injection was also observed with other alkali and alkaline earth metals and the magnitude injection yield was correlated with the size-to-charge ratio of the cation [15]. The reversibility of the photoluminescence changes of the sensitizer that accompany surface adsorption/desorption were recently exploited for chemical sensing applications [26].
desorption was absent for carboxylate binding to basic surfaces under the same conditions. The kinetics for binding were faster when the interfacial proton concentration was high however, the saturation surface coverage is about 1/3 lower than for basic surfaces.

Protons, like Li$^+$ cations, enhance the efficiency of excited state electron injection into the semiconductor [15]. Interestingly, they had no measurable affect on the kinetics for recombination of the injected electron with the oxidized dye at open circuit [16]. By varying the light intensity and the cation concentration, to control the yield of interfacial charge separated pairs formed, strong evidence for a bi-second-order kinetic model for charge recombination was reported [16]. Within reasonable experimental error, the abstracted rate constants were independent of the number of interfacial charge separated pairs photo-created. The insensitivity of the abstracted rate constants to the solution ionic strength, incident irradiance, and to the nature of the sensitizer has lead to the suggestion that charge recombination is rate-limited by diffusion of the injected electron [5]. This implies that diffusion is a second-order process and that long-lived charge-separation will be a general feature of these molecular-semiconductor interfaces.

Previous studies have shown that the sensitizers anchored to the nanocrystalline TiO$_2$ films can be reversible oxidized and reduced electrochemically [27]. Recently, it was found that the efficiency for intermolecular Ru(III/II) electron “hopping” between surface bound compounds approaches zero when the proton (or [Li$^+$]) concentration is low [15c]. Protons or lithium cations promote rapid and reversible oxidation-reduction of all the surface bound compounds. The origin of this cation effect was speculative but, was thought to reflect the translational mobility of the surface bound compounds. Small changes in the Ru(III/II) formal reduction potentials, <100 mV, were reported with pH pretreatment. In photoelectrochemical studies, high proton concentrations favor interfacial electron injection and efficient photocurrents, whereas low proton concentrations result in larger open circuit photovoltages but smaller photocurrents.

### 2.1.2. Molecular excited states

Cation-induced shift in the conduction band edge can move it above (toward the vacuum level) the excited state reduction potential of the sensitizer, thereby allowing mechanistic studies of molecular excited states bound to nanocrystalline semiconductor surfaces [16]. In many regards, the photophysical properties of the sensitizers are remarkably similar to that observed in fluid solution when the protonation state of the dcb ligand is taken into consideration [16]. One exception is the sensitizer excited state relaxation dynamics on TiO$_2$ (and ZnO$_2$) surfaces were non-exponential with the appearance of a second-order component attributed to intermolecular energy transfer. A schematic of the proposed model is shown in Fig. 3 [16]. Direct evidence for energy transfer came from studies where both Ru(dcb)(bpy)$_2$(PF$_6$)$_2$ and Os(dcb)(bpy)$_2$(PF$_6$)$_2$ were anchored to the same nanocrystalline TiO$_2$ surface [28]. The Os compound acts as an energy transfer trap and reaction (1) occurs with a quantum yield within experimental error of unity and a rate constant $>$10$^8$ s$^{-1}$. The reactions

$$
\text{TiO}_2 + \text{Ru} + \Delta G^\circ \\
\text{TiO}_2 + \text{Os} \rightarrow \text{TiO}_2 + \text{Ru} + \Delta G^\circ
$$

implications in that it may be possible to sensitize remote catalytic sites on a nanocrystalline semiconductor surface. More fundamentally, energy transfer dynamics can provide direct information on the distance between the surface bound sensitizers [28].

#### 2.2. Supramolecular sensitizers

**2.2.1. Stepwise electron injection**

With the binuclear Rh–Ru compounds shown in Fig. 4 the rhodium unit was bound directly to the semiconductor and the chromophoric ruthenium donor was fixed away from the semiconductor [20]. The energetics of this assembly
were designed such that the Rh acceptor levels lie between the acceptor states in the semiconductor and the Ru MLCT excited state. Light excitation results in an unprecedented electron "hopping" from Ru MLCT excited state to the Rh diimine unit to the semiconductor nanocrystal. This work provides an example of how the principles of stepwise charge-separation, originally developed in the field of supramolecular photochemistry, can be applied to solid-state materials [20]. The systems studied were designed as proof-of-principle heterotriads, without any pretension to compete with the sensitizers commonly used in regenerative solar cells. In fact, the photocurrent efficiency is rather low, mainly because of low charge injection yields. Nevertheless, they suggest a strategy to slow down significantly recombination between the injected electron and oxidized sensitizer.

2.2.2. Hole hopping

The bimetallic sensitizer [Ru(dcb)2(Cl)-bpa-Os(bpy)2]2 (Cl)P(fsc)2, abbreviated Ru-bpa-Os, where bpa is 1,2-bis(4-pyridyl)ethane, were anchored to TiO2 for interfacial electron transfer studies (Fig. 5) [21]. Pulsed 417 or 532.5 nm light excitation of a TiO2|Ru-bpa-Os material immersed in a 1.0 M LiClO4 acetonitrile bath at 25 °C results in rapid interfacial electron transfer and intramolecular electron transfer (Os(II) → Ru(III) to ultimately form an interfacial charge separated state with an electron in TiO2 and an oxidized Os(III) center, abbreviated TiO2(e−)→Ru-bpa-Os(III). This same state an also be generated after selective excitation of the Os(II) moiety with 683 nm light. The rates of intramolecular and interfacial electron transfer are fast, k > 109 s−1, while interfacial charge recombination, TiO2(e−)→Ru-bpa-Os(III) → TiO2|Ru-bpa-Os, requires milliseconds for completion. The results here show a general strategy for promoting rapid intramolecular electron transfer (Os(II) → Ru(III)) after interfacial electron injection and a 'remote' electron injection process that occurs after direct excitation of the Os(II) chromophore. The Os(III) center does not oxidize iodide rapidly and hence, negligible photocurrents were measured in regenerative solar cells with iodide as the donor [21].

Previous studies have also utilized intramolecular "hole" transfer to regenerate the sensitizer [22,23]. The first dyad reported to perform this function was Ru(dcb)24-CH3,4′-CH2-PTZ,-2,2′-bipyridine2+, where dcb is 4,4′-(CO2H)2-2,2′-bipyridine and PTZ is the electron donor phenothiazine, and is shown in Fig. 6. Irradiation of the dyad with visible light results in the creation of the MLCT
excited state that was quenched by electron transfer from the PTZ group in fluid solution. The reductive excited state quenching is moderately exergonic (-0.25 eV) and had an approximate rate constant of $\sim 2.5 \times 10^9$ s$^{-1}$ in methanol. The corresponding charge recombination step was faster than the forward one so that there is no appreciable transient accumulation of the electron transfer product.

When the dyad was attached to TiO$_2$, MLCT excitation can result in a new charge separated state with an excited state quenching more rapidly than the forward one so that there is no appreciable transient accumulation of the electron transfer product.

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With nanosecond time resolution it was not possible to determine whether the TiO$_2$(e$^-$)→Ru(II)-PTZ$^-$ state was formed by interfacial electron transfer from the excited or reduced state. However, electron injection into TiO$_2$ from MLCT excited states can occur on a femto- to pico-second time scale, so pathway 1 is the most probable under the experimental conditions employed [14]. After electron injection, electron transfer from PTZ to the Ru(III) center ($-\Delta G \sim 0.36$ eV) produces the charge separated state TiO$_2$(e$^-$)→Ru(II)-PTZ$^+$. Recombination of the electron in TiO$_2$ with the oxidized PTZ to yield the ground state occurred with a rate constant of $3.6 \times 10^8$ s$^{-1}$. Excitation of a model compound that did not contain the PTZ donor under otherwise identical conditions gave rise to the immediate formation of a charge separated state, TiO$_2$(e$^-$)→Ru(III)$^+$, whose recombination kinetics were complex and analyzed by a distribution model, with an average rate constant of $3.9 \times 10^8$ s$^{-1}$. Therefore, translating the "hole" from the Ru center to the pendant PTZ moiety inhibits recombination rates by about three orders of magnitude decrease in the charge recombination rate of injected electrons with acceptors, $k_i[A_i]$, provided that the electron injection flux into the semiconductor, $I_{inj}$ is constant. Applying the spectrascopically measured rate constants to Eq. (1) gave a predicted increase in $V_{oc}$ of 200 mV, which was in close agreement with the experimentally determined value of 180 mV. It is remarkable that these molecular interfaces behave like ideal diodes over five decades of irradiance with forward electron transfer rates that are at least six orders of magnitude faster than charge recombination.

Grätzel and coworkers have recently reported an interesting study of heterotriads of this type and have emphasized their potential application in photochromic devices [23]. Interestingly, these workers found long-lived charge-separation, like that described for the TiO$_2$–Ru(II)–PTZ system above, in some cases while not in others. More experiments are required before this interesting interfacial behavior can be fully understood.

### 3. Conclusion

It is clear that the interfacial cation concentration for sensitized TiO$_2$ materials has a dramatic effect on surface chemistry, excited states, interfacial electron transfer, and intermolecular electron transfer. This has been exploited to achieve molecular control of excited state processes. Supramolecular sensitizers have provided new insights into interfacial electron transfer processes that could not be gained from bimolecular electron transfer studies alone. It is clear that the marriage of interfacial chemistry and supramolecular chemistry will continue to provide fundamental insights useful for practical applications.

### Acknowledgements

G.J.M. would like to thank the students and post-doctoral associates who have obtained the results described herein. A special thanks to Prof. Carlo A. Bignozzi for a long and valuable collaboration. Financial support from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy and for equipment from the National Science Foundation are gratefully acknowledged.

### References