

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. © 2003 Elsevier Science B.V. All rights reserved.

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.

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 nm thick film [14].

One theme of this manuscript involves controlling the energetic position of the conduction band edge, E_{cb} 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

* Tel.: +1-4105167319; fax: +1-4105168420.
E-mail address: meyer@jhu.edu (G.J. Meyer).

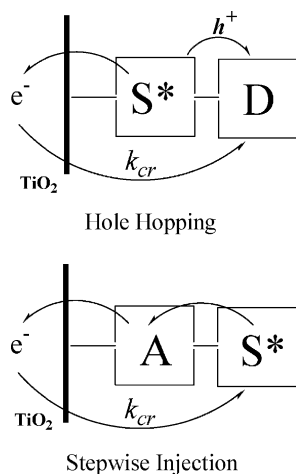


Fig. 1. A simplified diagram of heterosupramolecular assemblies that support photodriven hole hopping and stepwise injection. The molecules were designed to inhibit the rate constant for charge recombination, k_{cr} . Here, S^* is a photoexcited sensitizer, A is an electron acceptor, and D is an electron donor.

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 $\text{Ru}(\text{dcb})(\text{bpy})_2^{2+}$, 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 $[\text{Li}^+]$ 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 better 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, $\text{Ru}(\text{III}/\text{II}^{**})$, 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 [16]. The reversible photoluminescence changes of the sensitizer that accompany surface adsorption/desorption were recently exploited for chemical sensing applications [26].

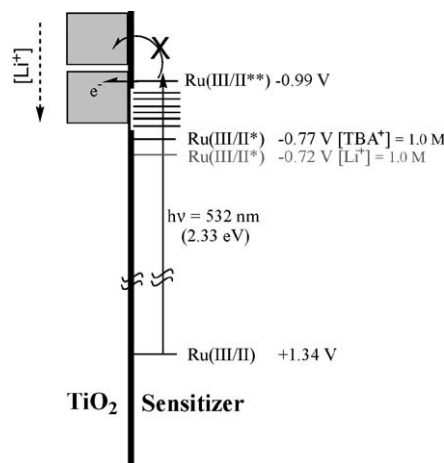


Fig. 2. The cation promoted electron injection model. The acceptor levels in TiO_2 shift positive with increasing Li^+ concentration resulting in more favorable overlap with the excited sensitizer donor states. The sensitizer is $\text{Ru}(\text{dcb})(\text{bpy})_2^{2+}$ where the reduction potentials are given for the ground state, $\text{Ru}(\text{III}/\text{II})$, the Franck–Condon excited state, $\text{Ru}(\text{III}/\text{II}^{**})$, and the thermally equilibrated excited states in 1.0 M tetrabutylammonium and lithium perchlorate, $\text{Ru}(\text{III}/\text{II}^*) [\text{TBA}^+]$ and $\text{Ru}(\text{III}/\text{II}^*) [\text{Li}^+]$. The potentials are vs. SCE.

The surface proton concentration has a profound impact on the interfacial electron injection yield, the chemical nature of the sensitizer-surface linkage, the kinetics for surface binding, and the redox properties of the surface bound sensitizer [15]. The spectroscopic signature of the dyes were excellent reporters of the energetic position of E_{cb} . Furthermore, the photoelectrochemical properties of sensitized TiO_2 in a regenerative solar cell can also be controlled in a rational manner with surface pH [15]. These observations suggest a general approach for controlling molecular excited states bound to semiconductor surfaces.

In one specific study, the excited state and redox properties of $\text{Ru}(\text{deeb})(\text{bpy})_2(\text{PF}_6)_2$, $\text{Ru}(\text{dcb})(\text{bpy})_2(\text{PF}_6)_2$, and $\text{Ru}(\text{bpy})_2(\text{ina})_2(\text{PF}_6)_2$, where deeb is 4,4'-(CO₂Et)₂-bpy, and ina is isonicotinic acid, bound to nanocrystalline TiO_2 and colloidal ZrO_2 films were quantified in acetonitrile at room temperature as a function of the interfacial proton concentration [15c]. The visible absorption and IR data indicate that a high surface proton concentration yields a “carboxylic acid” form of the sensitizer. At low proton concentrations, the spectral data is consistent with a “carboxylate” form. The spectroscopic data did not allow identification of the surface site(s) involved in sensitizer–semiconductor bond. The invariance of the spectroscopic data to the two metal oxide substrates characterized suggested a common surface binding sites or an insensitivity to the Lewis acidic $\text{Ti}(\text{IV})$ or $\text{Zr}(\text{IV})$ metal centers. It was speculated that the carboxylic acid (carboxylate) groups of the $\text{Ru}(\text{II})$ sensitizers interact with intrinsic Bronsted basic (acidic) sites within a hydrated gel-like surface layer [15c,d].

The “carboxylic acid” form of the sensitizers observed on acidic surfaces rapidly desorbed from the surface when Lewis acids such as Li^+ were present in acetonitrile, while

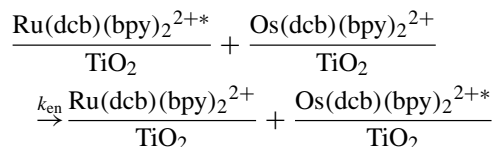
desorption was absent for carboxylate binding to basic surfaces under the same conditions. The kinetics for binding were faster when the interfacial proton concentration was high however, the saturation surface coverage is about 1/3 lower than for basic surfaces.

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 $[\text{Li}^+]$) 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 pre-treatment. 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 ZrO_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 $\text{Ru}(\text{dcb})(\text{bpy})_2(\text{PF}_6)_2$ and $\text{Os}(\text{dcb})(\text{bpy})_2(\text{PF}_6)_2$ 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 $>10^8 \text{ s}^{-1}$. This has practical



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

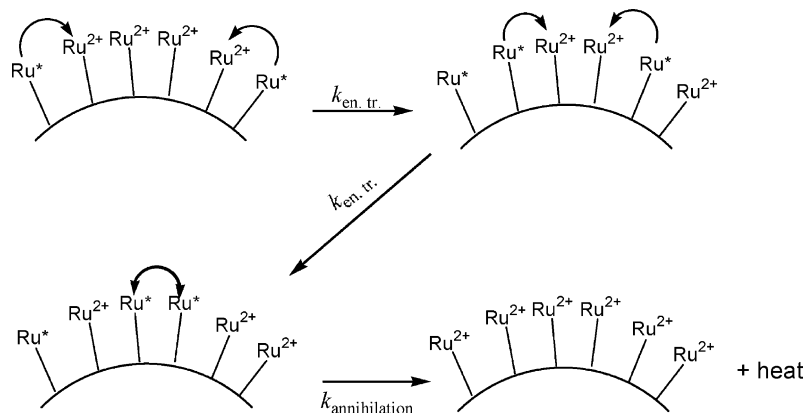


Fig. 3. A parallel first- and second-order kinetic model proposed for excited state relaxation of ruthenium polypyridyl compounds anchored to TiO_2 nanocrystallites. The first-order component predominates at low excitation irradiances and surface coverages. The second-order component is attributed to triplet–triplet annihilation reactions that are rate limited by intermolecular energy transfer across the semiconductor surface.

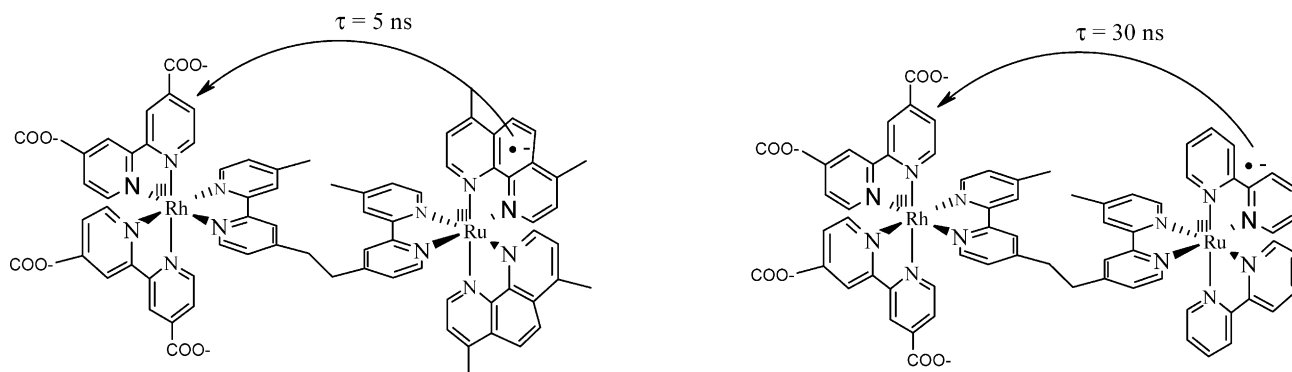


Fig. 4. Bimetallic Ru–Rh compounds designed to undergo stepwise electron injection reactions when anchored to semiconductor surfaces. The Ru MLCT excited state lifetime is quenched (to 5 and 30 ns) by electron transfer to the Rh diimine unit followed by either interfacial electron transfer to TiO_2 or recombination to the Ru(III) center.

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 nanocrystallite. 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 $[\text{Ru}(\text{dcb})_2(\text{Cl})\text{-bpa-Os}(\text{bpy})_2(\text{Cl})](\text{PF}_6)_2$, abbreviated Ru-bpa-Os, where bpa is 1,2-bis(4-pyridyl)ethane, were anchored to TiO_2 for interfacial electron transfer studies (Fig. 5) [21]. Pulsed 417 or 532.5 nm light excitation of a $\text{TiO}_2|\text{Ru-bpa-Os}$ material immersed in a 1.0 M LiClO_4 acetonitrile bath at 25 °C results in rapid

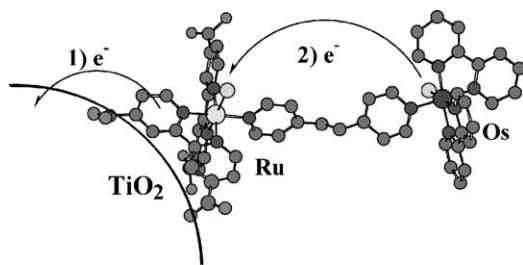


Fig. 5. A bimetallic Ru–Os compound designed to undergo intramolecular Ru(III) \rightarrow Os(II) hole transfer after electron injection. The sequence of electron transfer reactions (1) and (2) were observed after 417 and 532 nm light excitation. A remote injection process from Os^* was observed with 683 nm light excitation.

interfacial electron transfer and intramolecular electron transfer ($\text{Os}(\text{II}) \rightarrow \text{Ru}(\text{III})$) to ultimately form an interfacial charge separated state with an electron in TiO_2 and an oxidized Os(III) center, abbreviated $\text{TiO}_2(\text{e}^-)|\text{Ru-bpa-Os}(\text{III})$. This same state can 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, $k > 10^8 \text{ s}^{-1}$, while interfacial charge recombination, $\text{TiO}_2(\text{e}^-)|\text{Ru-bpa-Os}(\text{III}) \rightarrow \text{TiO}_2|\text{Ru-bpa-Os}$, requires milliseconds for completion. The results here show a general strategy for promoting rapid intramolecular electron transfer ($\text{Os}(\text{II}) \rightarrow \text{Ru}(\text{III})$) 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 $\text{Ru}(\text{dcb})_2\text{-CH}_3\text{-CH}_2\text{-PTZ}$, -2,2' -bipyridine $^{2+}$, where dcb is 4,4'-(CO_2H) $_2$ -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

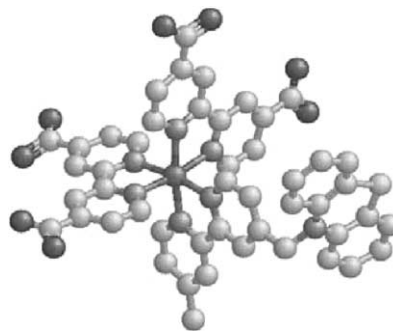


Fig. 6. A Ru(II) polypyridyl compound with a covalently bound phenothiazine group. The compound was designed to support rapid interfacial electron transfer followed by intramolecular hole hopping, Ru(III) \rightarrow PTZ.

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 $\sim 2.5 \times 10^8$ 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 electron in TiO $_2$ and an oxidized PTZ group, abbreviated TiO $_2$ (e $^-$)|Ru-PTZ $^+$. In principle there are two possible electron transfer pathways available to reach this charge separated state. In the first pathway, charge injection is followed by oxidation of the phenothiazine donor by the Ru(III) center, TiO $_2$ |Ru(II)*-PTZ \rightarrow TiO $_2$ (e $^-$)|Ru(III)-PTZ \rightarrow TiO $_2$ (e $^-$)|Ru(II)-PTZ $^+$. In a second possible pathway, reductive quenching by the PTZ group is followed by charge injection into the semiconductor, TiO $_2$ |Ru(II)*-PTZ \rightarrow TiO $_2$ |Ru $^+$ -PTZ $^+$ \rightarrow TiO $_2$ (e $^-$)|Ru(II)-PTZ $^+$. Note that the “Ru $^+$ ” intermediate does not refer to ruthenium in a +1 oxidation state but, rather Ru(II) coordinated to a reduced dcB ligand, i.e. Ru(II)dcB $^-$.

A flash photolysis study of the heterotriad was reported [22]. 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 3.6×10^3 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 3.9×10^6 s $^{-1}$. Therefore, translating the “hole” from the Ru center to the pendant PTZ moiety inhibits recombination rates by about three orders of magnitude [22].

The dyad and model molecules were tested in regenerative solar cells, with iodide as an electron donor. The monochromatic photocurrent efficiency was of the order of 45% for both sensitizers at the absorption maximum. However, the open circuit photovoltage, V_{oc} , was observed to be about 100 mV larger for the heterotriad. The effect was even more pronounced in the absence of iodide with 180 mV larger V_{oc} values over five decades of irradiance [22]. The diode equation (Eq. (1)) predicts a

$$V_{oc} = \left(\frac{kT}{e} \right) \ln \left(\frac{I_{inj}}{n \sum k_i [A]_i} \right) \quad (1)$$

59 mV increase in V_{oc} at room temperature for each order 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 spectroscopically 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.

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