

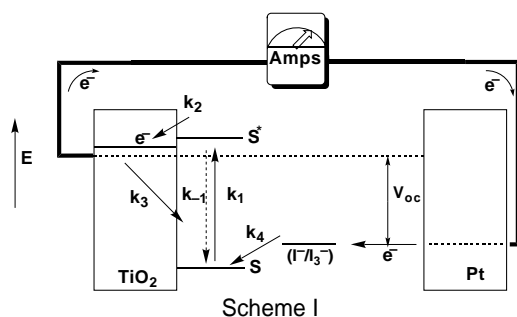
Symposium: Applications of Inorganic Photochemistry

Efficient Light-to-Electrical Energy Conversion:
Nanocrystalline TiO_2 Films Modified with Inorganic Sensitizers

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The use of solid state materials for efficient conversion of sunlight into electricity has long been a goal of inorganic photochemistry (1, 2). A molecular approach has been to sensitize wide-bandgap semiconductors to visible light with inorganic compounds exhibiting charge-transfer excited states. About 20 years ago, electrochemists employed this strategy with single-crystal and polycrystalline films of tin oxide or titanium dioxide in photoelectrochemical cells (3–5). The motivation for this work was to gain insights into electron transfer processes at the semiconductor–electrolyte interface. An accepted model for dye sensitization in regenerative photoelectrochemical cells, shown below, emerged from these studies (6–8).



Scheme I

An excited sensitizer, S^* , injects an electron into the semiconductor with a rate constant k_2 . The oxidized sensitizer accepts an electron from an external donor, such as iodide, present in the electrolyte, with a rate constant k_4 . The net process allows an electrical current to be generated with light of lower energy than the semiconductor bandgap. Note that recombination of the injected electron (k_3) and radiative and nonradiative decay of the excited state (k_1) compete directly with photocurrent production. If the oxidized donor is reduced at the counter electrode, then the solar cell is regenerative, since no net chemical reaction occurs. Many early studies were designed to split water into H_2 and O_2 , and the cells were therefore photoelectrosynthetic. In all cases, however, the solar efficiencies were extremely low and practical devices seemed unlikely.

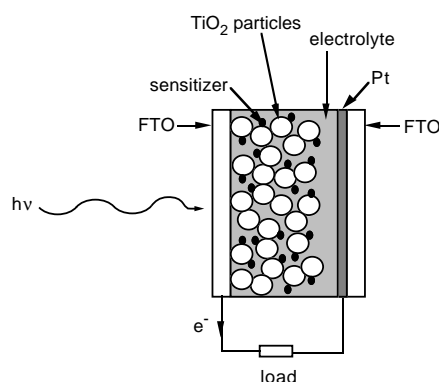
In 1991, a crucial breakthrough that dramatically altered the outlook for practical device applications came from the laboratories of M. Gratzel in Lausanne, Switzerland (9). By replacing the planar semiconductor electrode with a porous nanostructured material, Gratzel increased the solar energy conversion efficiency by an order of magnitude over what had been previously reported. The enhanced efficiency and stability of the new cells suggested an economically practical approach to solar energy conversion. This was indeed an exciting discovery for inorganic photochemists, as it marked the first time that devices operating on a molecular level were competitive with traditional solid-state photovoltaics. In addition, these new materials allow spectro-

scopic characterization of interfacial electron-transfer processes in a manner not previously possible.

The basic features of the efficient sensitized nanostructured solar cells are presented below, followed by a discussion of why these solar cells work so efficiently. It will be apparent that the underlying chemical and physical processes are not always well understood, but the molecular-level electron transfer processes that drive (and inhibit) photocurrent production provide some important clues. Finally, some possible methods for improving the cell and future research directions are presented.

Efficient Sensitized Nanocrystalline Solar Cell

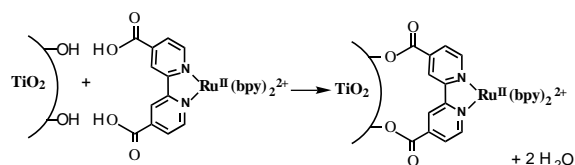
A schematic of a sensitized nanocrystalline regenerative solar cell is shown below.



A key ingredient in these solar cells is the metal oxide electrode, which plays several important roles. It serves as a high-surface-area support for the sensitizer, a pathway for electrical current, and a porous membrane for diffusion of the redox couple. The metal oxide supports are generally prepared by casting a solution of nanometer-sized semiconductor particles onto a transparent fluorine-doped tin oxide (FTO) conductive substrate. The electrode is then given a short heat treatment. Figure 1 displays a metal oxide electrode prepared from commercially available DeGussa P25 TiO_2 . The "necking" between TiO_2 particles shown in this picture lowers the resistivity of the film. The cast TiO_2 films are approximately 10 microns thick and are well described as porous nanocrystalline semiconductor films. Recent materials advances in sol-gel technology allow these films to be prepared with high transparency in the visible region (9). To date, the most efficient solar cells are based on anatase TiO_2 nanocrystallites; however, the use of alternative semiconductor materials is an important area of future research.

A second ingredient is the sensitizer, which acts as a photodriven molecular electron pump. The sensitizer absorbs visible light, pumps an electron into the semiconductor, ac-

cepts an electron from the solution redox couple, and then repeats the cycle. To be useful in solar cells, the sensitizer must meet the following important criteria: (i) high stability in the oxidized, ground, and excited states; (ii) an excited-state oxidation potential that lies at a more negative potential than the semiconductor conduction band edge; (iii) a positive ground state oxidation potential to ensure rapid donor oxidation; (iv) a strong absorber of solar energy; and (v) low cost. The most efficient and stable sensitizers to date are based on Ru(II) polypyridyl coordination compounds. These compounds possess metal-to-ligand charge transfer (MLCT) absorption bands that harvest a large fraction of visible light. The photophysical properties of the parent compound Ru(bpy)₃²⁺, where bpy is 2,2'-bipyridine, have been presented (10). Chemically related sensitizers where one or more of the bpy ligands is replaced by 4,4'-(COOH)₂-2,2'-bipyridine, abbreviated dcb, are anchored to semiconductor surfaces through the reaction of carboxylic acid groups with surface hydroxyl groups to form presumed ester linkages (4), as illustrated below. There now exist some spectroscopic data supporting the presence of ester links (11).



The semiconductor-sensitizer linkage is stable in organic solvents and electrolytes. The sensitizers are rapidly freed from the surface in alkaline solution, which provides a method for quantifying the surface coverage. It is often assumed that dcb-containing Ru(II) compounds coat the nanocrystalline TiO₂ surface in monolayer coverage. This assumption is difficult to verify owing to the unknown surface area of the material. In fact, surface area is ill-defined in Euclidean geometry, and fractal concepts have been applied to these fascinating materials (9b).

A third ingredient is the redox couple, which ferries charge between the two electrodes in the solar cell. Ideally this couple should not absorb visible light and the reduced form must regenerate the sensitizer before recombination (*k*₃), occurs. Iodide/iodine solutions have emerged as the most efficient redox couple. A few drops of a concentrated solution are "sandwiched" between the sensitized nanocrystalline electrode and a Pt-coated FTO counterelectrode. The cell is then clamped shut and sealed to prevent solvent evaporation.

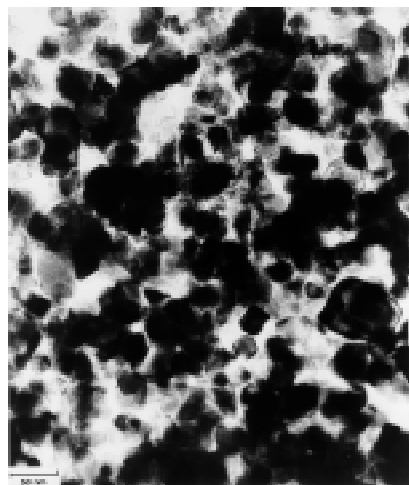


Figure 1. TEM micrograph of a colloidal suspension of TiO₂ prepared from DeGussa P-25 materials and sintered at 450 °C for 15 min.

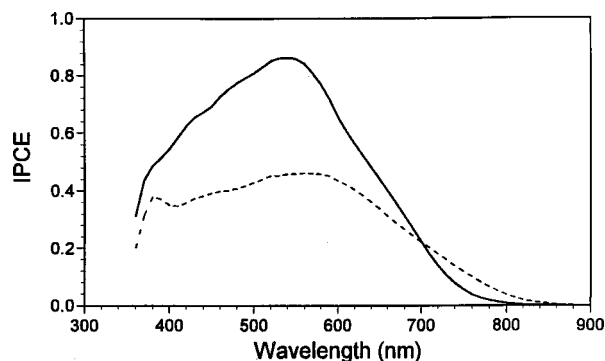


Figure 2. The incident photon-to-current efficiency (IPCE) as a function of excitation wavelength for regenerative nanocrystalline TiO₂ solar cells in 0.5 M NaI, 0.05 M I₂ propylene carbonate. The solid line is for the sensitizer *cis*-Ru(dcb)₂(NCS)₂ and the dashed line is for *cis*-Ru(5,5'-(COOH)₂-2,2'-bipyridine)₂(NCS)₂.

Illumination of the sandwich solar cell at open circuit produces a potential difference between the two electrodes, *V*_{oc}. When the circuit is closed a photocurrent can be measured. The photocurrent production is often reported as the incident photon-to-current efficiency, IPCE, which is the ratio of electrons measured in the external circuit to the photons incident on the solar cell. The IPCE measured as a function of excitation wavelength is called a *photoaction spectrum*. It often resembles the absorption spectrum of the sensitizer (Fig. 2). In the absence of a sensitizer the nanocrystalline TiO₂ films show negligible photocurrents with visible light excitation. *cis*-Ru(dcb)₂(NCS)₂ displays IPCE > 0.7 at individual wavelengths of light as is shown. This sensitizer has emerged as the most efficient to date (11, 12). A solar-to-electrical conversion efficiency of 10% has been reported under simulated sunlight conditions (12).

Why Are These Solar Cells So Efficient?

Several research groups have independently observed the remarkably high photocurrent efficiencies initially reported by Gratzel and coworkers (13–15). When corrections are made for scattered light and competitive absorption, photons are converted to electrons with a quantum yield near unity at single wavelengths of light. A good question is, why? How can these materials be so efficient when early studies of related sensitizers anchored to metal-oxide single crystals or polycrystalline films found efficiencies less than 1%? To answer these questions it is worthwhile to consider the molecular processes by which photons are converted into an electrical current (Scheme 1). The IPCE is the product of three terms: the light-harvesting efficiency (LHE), the quantum yield for electron injection (ϕ), and the efficiency, η , with which electrons are collected in the external circuit (eq 1).

$$\text{IPCE} = (\text{LHE}) (\phi) (\eta) \quad (1)$$

First, the sensitizer must absorb sunlight. The LHE, or absorptance, is simply the fraction of light absorbed by the solar cell. An ideal solar device will have an LHE of unity at any wavelength. The LHE can be directly related to the molar extinction coefficient of the sensitizer and the surface coverage (11). Herein lies a key difference between the nanocrystalline semiconductor films and the planar electrodes studied in the 1970s. A molecular monolayer of a Ru(II) polypyridyl sensitizer on a flat surface will harvest < 1% of the incident light, while the LHE is > 99% for the same dye on a nanocrystalline film as a result of the high surface area and long path length afforded by the complex

three-dimensional structure of the material. This difference is easily seen with the naked eye, since a monolayer of charge transfer sensitizers on a flat surface does not appear colored, whereas the sensitized nanocrystalline films can appear almost opaque.

Electron transfer from the excited sensitizer to the TiO_2 electrode converts the energy stored in the MLCT excited state to an interfacial charge-separated pair consisting of an electron in the solid and the oxidized sensitizer. This charge separation process is similar in some respects to what occurs in natural photosynthetic systems. The quantum yield for electron transfer from the excited sensitizer to the TiO_2 particle occurs with an efficiency of unity for a broad class of Ru(II) sensitizers based on the dcB ligand, $\phi \sim 1$. The electron injection rate constant, k_2 , is currently under debate and likely depends highly on experimental conditions and the specific sensitizer explored. An estimate based on time-resolved photoluminescence studies of Ru(II) polypyridyl sensitizers in operational solar cells indicates a distribution of electron injection rates with peak amplitude $\sim 10^9 \text{ s}^{-1}$ (16), in good agreement with recent time-resolved microwave studies (17).

Once the electron is in the solid it proceeds through the TiO_2 network to the external circuit with an efficiency of η . Perhaps the most fascinating aspect of these materials is the fact that η is near unity under a wide range of experimental conditions. It might naively be expected that recombination of the injected electron with the oxidized sensitizer or donor would be efficient. This clearly is not the case. We and others have found that recombination of the injected electron with the oxidized sensitizer occurs on a microsecond time scale (18–20). Therefore, forward electron transfer is more than a thousand times faster than recombination ($k_2/k_3 > 10^3$). *The high LHE, efficient charge separation, and a dramatic difference in forward and back electron transfer rates underlie the remarkable efficiency of these molecular solar cells.*

The question then naturally arises, why is the back reaction so slow relative to the forward electron transfer rate? Although a clear answer to this question is not known, several possibilities have been suggested. Since different molecular orbitals are involved in the forward and reverse electron transfer processes, different rates are expected. Electron injection occurs from the π^* levels of the bipyridine ligand, while back electron transfer occurs to the t_{2g} orbitals of the Ru(III) center. The thermodynamic driving force for the two processes is not easily calculated because the nature and energetics of the redox active state(s) in TiO_2 remain unknown. However, there is some evidence that the back reaction falls in the Marcus inverted region (21), whereas the forward reaction does not (22). More studies are needed to fully understand this fortuitous difference in interfacial electron transfer rates.

In sensitized single crystal materials, the back reaction is thought to be inhibited by the electric field region at the semiconductor surface (6, 23). More specifically, the semiconductor depletion region sweeps the injected electron toward the bulk and away from the oxidized sensitizer, thereby inhibiting the back reaction. The extent to which similar processes might occur in the nanostructured materials described here is unknown. The application of models developed for bulk semiconductors to colloidal materials is not straightforward, especially when the semiconductor particle is very small (24). The small size severely restricts the magnitude of the electric field a particle can support, and concepts such as depletion or accumulation layers may not be generally applicable. An understanding of the potential distribution (25, 26) and carrier transport mechanisms (27,

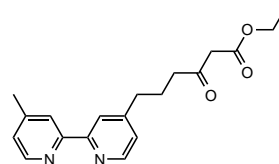
28) in these materials remains a significant challenge in the rapidly growing area of nanostructured photoelectrochemistry (29, 30).

How Do We Make A Better Solar Cell?

The performance of *cis*-Ru(dcb)₂(NCS)₂/ TiO_2 regenerative solar cells is so phenomenal that the hope of marked improvements appears at first glance unlikely. Nevertheless, fine-tuning the semiconductor material, sensitizer, and electrolyte so as to enhance stability and efficiency represent important ongoing research efforts in many labs around the world. More fundamentally, systematic modifications allow the factors that control interfacial electron transfer processes in practical solar cells to be understood on a molecular level.

Figure 2 shows that high monochromatic IPCE *cis*-Ru(dcb)₂(NCS)₂/ TiO_2 is only observed below $\sim 700 \text{ nm}$. Ideally, a solar cell would harvest light through the visible region and into the near IR. The MLCT absorption can be extended to lower energy by appropriate substituent changes on the chromophoric ligands or by decreasing the $d\pi-\pi^*$ backbonding donation to the chromophoric ligands (31). In an attempt to extend the spectral sensitivity toward the red, Ru(II) compounds were prepared based on the ligand 5,5'-(COOH)₂-2,2'-bipyridine, which has π^* acceptor levels below dcB (11). Sensitizers based on this ligand bind to TiO_2 with surface coverages similar to those based on dcB. A comparison of the photoaction spectrum of *cis*-Ru(LL)₂(NCS)₂ is shown in Figure 2, where LL is dcB or 5,5'-(COOH)₂-2,2'-bipyridine. Enhanced spectral sensitivity at long wavelengths is observed, but is offset by poor performance at short wavelengths, which results in an overall less efficient solar cell. Analysis of the photophysical properties of the sensitizer and the photoelectrochemical properties of the solar cell led to the conclusion that the lower efficiency stems in part from less efficient electron transfer to the semiconductor surface. Based on energy gap considerations, the prospect of developing efficient black Ru(II) polypyridyl sensitizers appears dim, since the rate of nonradiative decay will compete even more effectively with electron injection. However, as stated earlier, the rate of electron injection may critically depend on specific factors such as the sensitizer excited state oxidation potential, and efficient black sensitized solar cells may one day be realized.

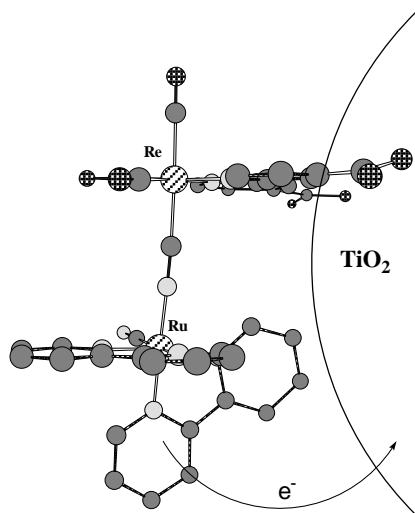
A new chemical bond between the sensitizer and semiconductor surface can enhance electronic coupling and/or alter surface state energetics so that electron injection is faster and more efficient for small energy gap sensitizers. Therefore, an important objective in the next generation of solar cells is to develop new molecular surface linkages. When considering strategies for binding Ru(II) polypyridyl sensitizers to TiO_2 materials we were attracted to acetylacetonate (acac) and its derivatives, which are known to form strong chelate rings with hard transition metal ions (32). The first ligand prepared possessed an *n*-propyl spacer between the bipyridine ring and the acac group, abbreviated bpy-acac as shown.



Surprisingly, the corrected IPCE of a sensitizer based on this ligand was very comparable to related sensitizers with

a carboxylic acid group bound directly to the bpy ring (33). This suggested that intimate electronic coupling between the chromophoric ligand and the surface is not a strict requirement in the design of molecular sensitizers for this application.

In an effort to achieve molecular control of sensitizer orientation, a bimetallic coordination compound was prepared in which the facial geometry of the Re center holds a Ru sensitizer proximate to the TiO_2 surface (34):

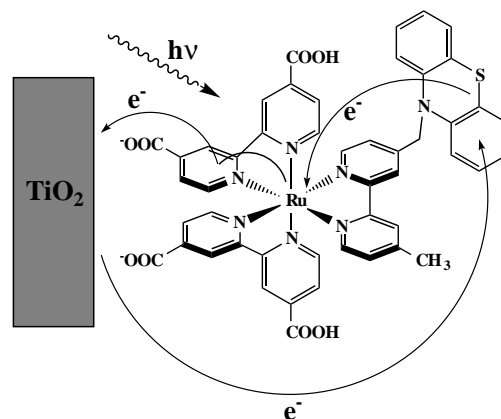


Visible light excitation of this sensitizer bound to TiO_2 leads to efficient photocurrent production in a regenerative solar cell. The $\text{Ru}(\text{bpy})_2$ group absorbs most of the visible light, and since it is not bound directly to the semiconductor surface it can be concluded that direct covalent attachment is not a requirement for efficient solar conversion. While it could be argued that this dimer represents a special case, because intraligand hopping from bpy to dcb is thermodynamically favored, the bpy-acac results presented above (33) and other results (5) indicate that the conclusion is far more general. An important implication of this conclusion is that sensitizers anchored to TiO_2 through nonchromophoric ligands or without a direct chemical bond may also be efficient dyes for sensitization of wide bandgap nanocrystalline semiconductors. The results also suggest that an as-yet undetermined optimum sensitizer orientation exists, wherein interfacial charge separation is still efficient but the back reaction is further inhibited. Such sensitizers will not likely display improved IPCE, but should yield larger open-circuit voltages for reasons discussed below.

An important area for future improvement is in the open circuit photovoltage, V_{oc} , which defines the maximum free energy produced by a solar cell under conditions of constant light irradiance. MLCT sensitizers generally store more than 1.7 eV in their excited states, yet typical V_{oc} values are less than 0.9 eV. The maximum V_{oc} attainable in devices of this type is the energetic difference between the Fermi level of the solid under illumination and the Nernst potential of the redox couple in the electrolyte. However, for these molecular devices this limitation has not been realized and V_{oc} is in general much smaller. It appears that V_{oc} is kinetically limited by electron tunneling through the solid to acceptors at the interface or in the electrolyte (11).

One successful strategy for increasing V_{oc} has been to add pyridine derivatives to the electrolyte (12). Pyridine is thought to adsorb on the TiO_2 surface and inhibit recombi-

nation of injected electrons with I_3^- . An alternative approach is to vectorially translate the hole away from the sensitizer through intramolecular electron transfer. This strategy has been successfully tested with $\text{Ru}(\text{dcb})_2(4\text{-CH}_3, 4'\text{-CH}_2\text{-PTZ}, 2, 2'\text{-bipyridine})$, where PTZ is phenothiazine, anchored to TiO_2 (35):



Visible light excitation results in the formation of the MLCT excited state that rapidly injects an electron into TiO_2 . Intramolecular electron transfer from PTZ to $\text{Ru}(\text{III})$ is then thermodynamically downhill by ~ 360 mV, which yields an interfacial charge-separated pair abbreviated $\text{TiO}_2(e^-) | -\text{Ru}^{\text{II}}\text{-PTZ}^+$. This state recombines to ground state products with a rate constant of $3.6 \times 10^3 \text{ s}^{-1}$ (Fig. 3b, inset). Excitation of a model compound that does not contain PTZ, $\text{Ru}(\text{dmb})_2(\text{dcb})_2^{2+}/\text{TiO}_2$ (where dmb is 4,4'-(CH_3)₂-2,2'-bipyridine), results in the formation of $\text{TiO}_2(e^-) | -\text{Ru}^{\text{III}}$ (Fig. 3a). The kinetics for recombination of this state are complex, presumably reflecting interfacial heterogeneity, and a distribution analysis yields an average rate, $\langle k_3 \rangle = 3.9 \times 10^6 \text{ s}^{-1}$. Therefore, the recombination rate is slowed by $\sim 10^3$ by translating the "hole" from the metal center to the pendant PTZ group.

Both sensitizers efficiently convert light into electricity in regenerative solar cells with NaI/I_2 . With the more transparent TiO_2 films used for excited state absorption spectroscopy, both sensitizers convert light to electricity with a maximum monochromatic efficiency of 0.45 ± 0.05 . However, V_{oc} is consistently 100 mV greater for $\text{Ru}(\text{dcb})_2(\text{bpy-PTZ})/\text{TiO}_2$ than for the model compound. In the absence of iodide, V_{oc} is 180 ± 30 mV larger over 5 decades of irradiance (36). Interestingly, the measured interfacial electron transfer rates applied to a diode equation (37, 38) directly predict the increased V_{oc} . The apparent applicability of the diode equation is surprising, and more studies are needed to test the general applicability. The increased V_{oc} that results from the long-lived interfacial charge-separated pair is encouraging. It should be emphasized, however, that the $\text{Ru}(\text{dcb})_2(\text{bpy-PTZ})/\text{TiO}_2$ assembly is best thought of as a model; it is not sufficiently robust for practical applications. In this regard, a few final comments on the stability of the solar cells is appropriate, because poor long-term stability may ultimately limit applications of these materials for high-current-density solar panels.

The factors governing long-term stability of operational solar cells are not well understood despite considerable discussion and research efforts. The reason for this is simple: the solar cells are quite stable. It is therefore difficult to track down the low-quantum-efficiency side reactions that cause long-term degradation. Two factors that result in a

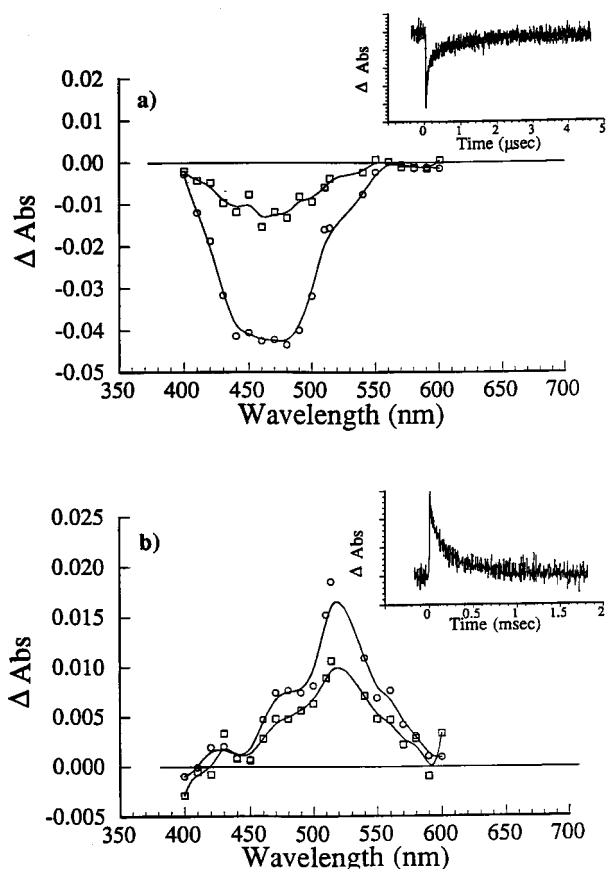


Figure 3. (a) Excited state absorption difference spectra of $\text{Ru}(\text{dcb})_2(\text{dmb})_2^+$ anchored to a transparent TiO_2 film in neat propylene carbonate. Spectra are shown 50 ns (circles) and 500 ns (squares) after excitation with a 10-mJ, 5-ns pulse of 532-nm light. The data represent the average of 10 laser pulses. The absorbance changes at 410 nm are shown in the inset and are assigned to recombination of $\text{TiO}_2(\text{e}^-)-\text{Ru}^{\text{III}}$ to yield ground-state products. Distribution analysis yields an average rate, $\langle k_3 \rangle = 3.9 \times 10^6 \text{ s}^{-1}$. (b) Excited-state absorption difference spectra of $\text{Ru}(\text{dcb})_2(\text{bpy-PTZ})_2^+$ under the same conditions as (a). Spectra are shown at 500 ns (circles) and 5 ms (squares). The inset depicts the kinetics measured at 514 nm with $\sim 2\text{-}\mu\text{s}$ resolution assigned to the recombination of $\text{TiO}_2(\text{e}^-)-\text{Ru}^{\text{II}}-\text{PTZ}$ to yield ground-state products. A first-order kinetic analysis yields $3.6 \times 10^3 \text{ s}^{-1}$.

lower stability in our labs are employment of aqueous electrolytes and failure to remove ultraviolet excitation. The former appears to emanate from hydrolysis of the surface linkage, and the latter from oxidation of the sensitizer by the hole in TiO_2 . It was hoped that the chelate effect would result in more stable solar cells for sensitizers based on bpy-acac discussed above (33). This expectation was not realized. However, a $\text{Ru}(\text{II})$ polypyridyl sensitizer bound to TiO_2 through a phosphonate linkage, which remains bound in water, was recently reported (39). Nevertheless, some photocurrent degradation that cannot be easily accounted for is observed with monochromatic visible light excitation in rigorously dried organic solvents and electrolytes. Preliminary data suggest that the degradation stems from decomposition of the oxidized form of the sensitizer. However, these results are not conclusive. Once all degradation pathways have been identified it is likely that inorganic chemistry can be used to eliminate them.

The prospect for practical molecular solar cells based on this technology therefore appears very bright.

Acknowledgments

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