

Co^{II}(dbbip)₂²⁺ Complex Rivals Tri-iodide/Iodide Redox Mediator in Dye-Sensitized Photovoltaic Cells

Hervé Nusbaumer, Jacques-E. Moser,* Shaik M. Zakeeruddin, Mohammad K. Nazeeruddin, and Michael Grätzel

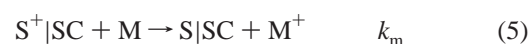
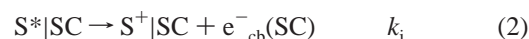
Laboratory for Photonics and Interfaces, Institute of Physical Chemistry, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

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Transient absorption spectroscopy was employed to study charge-transfer dynamics in dye-sensitized nanocrystalline solar cells (DSSC) containing a new one-electron redox mediator, cobalt(II)-bis[2,6-bis(1'-butylbenzimidazol-2'-yl)pyridine]. Photovoltaic cells incorporating this relay have yielded light-to-electricity power conversion efficiencies of up to 5.2%. This rivals the performance of the tri-iodide/iodide couple that is currently almost exclusively used in DSSC. Interception of the dye oxidized state by electron transfer from the Co(II) complex in diluted electrolyte was found to follow a first-order kinetics with a rate constant of $k_m = 5 \times 10^5 \text{ s}^{-1}$. Above a threshold of 10^{-2} M , under which the cationic relay is essentially adsorbed onto the negatively charged particle surface, larger concentrations of the reduced mediator resulted in a linear increase of the apparent rate, yielding a second-order rate constant of $k_m'' = 2.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Dynamics of the recombination reaction between injected conduction band electrons and the oxidized relay species was monitored spectroscopically, and a first-order rate constant of $k_r = 3 \times 10^3 \text{ s}^{-1}$ was determined directly. This kinetic behavior compares approximately with that of the tri-iodide/iodide redox couple. Practical advantages of the Co^{III}/Co^{II} complex mediator, however, make it a promising candidate to replace this widely used system in DSSC.

Introduction

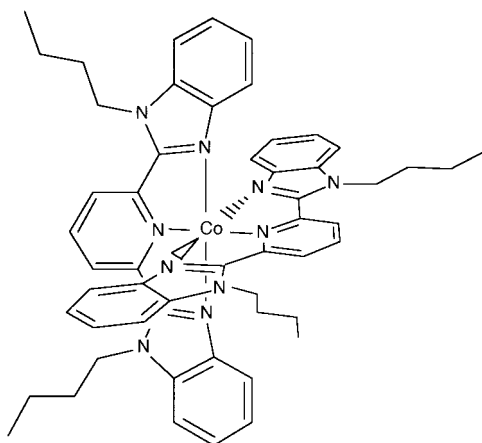
Dye-sensitized nanocrystalline oxide solar cells (DSSC) present an important alternative to current solar technology.^{1–3} High-surface-area mesoporous semiconductor films yield remarkable light-to-electricity energy conversion efficiencies and provide excellent model systems to spectroscopically probe the dynamics of interfacial electron-transfer processes. At the base of the design of the DSSC is a photoanode constituted by a monolayer of a molecular redox dye sensitizer (S) adsorbed onto a layer of nanocrystalline semiconductor (SC) oxide particles. Upon light absorption by adsorbed molecules (eq 1), excited states of the photosensitizer readily inject an electron into the conduction band of the solid (eq 2). Charge injection has been found for numerous efficient systems to occur in the femtosecond time frame,³ thus successfully competing against deactivation of the dye-excited state (eq 3). The electron back transfer from the conduction band to dye cations (eq 4) takes place much more slowly, typically in the microsecond–millisecond domain.^{4,5} In the presence of a redox mediator (M), this interfacial charge recombination competes kinetically with the reaction of the mediator with the oxidized sensitizer (eq 5). Charge transport by the electrolyte in the pores of the semiconductor film to the counter electrode and that of injected electrons within the nanocrystalline film to the back contact should be fast enough to compete efficiently with the electron recapture reaction (eq 6).



Br₂/Br[−] and quinone/hydroquinone redox mediators were successfully used in early DSSC designs.⁶ Interesting results were also obtained with dye-sensitized TiO₂ in conjunction with phenothiazines⁷ and triarylamine donors.⁸ The latter systems provide remarkably long-lived interfacial charge-separated pairs but show somehow deceiving photovoltaic performances.⁸ So far, the tri-iodide/iodide couple has been almost exclusively employed as a redox mediator in DSSCs based on the sensitization of mesoporous titanium dioxide by Ru(II) complexes. Very high incident photon-to-current conversion efficiency (IPCE) approaching unity has been reached. In this case, the dye regeneration reaction is, however, complicated by the fact that the conversion of iodide to tri-iodide involves the transfer of two electrons.⁹ A large driving force is therefore necessary to carry out the primary oxidation step from iodide to atomic iodine atom or I₂^{•−}. The resulting potential mismatch between the redox couples of the sensitizer (S⁺/S) and the mediator (I₃[−]/I[−]) is responsible for large polarization losses (~0.6 V).³ Recently, pseudohalogen couples, (SCN)₂/SCN[−] and (SeCN)₂/SeCN[−], were evaluated for their utilization in dye-sensitized photoelectrochemical cells.¹⁰ Although redox potentials of these mediators

* To whom correspondence should be addressed. Tel: +41 21 693 3628. Fax: +41 21 693 4111. E-mail: je.moser@epfl.ch.

CHART 1



are more positive than that of I_3^-/I^- , no improvement on the open circuit potential of the cells was observed. Moreover, low conversion efficiencies were obtained with these systems, which was attributed to slow interception reaction (eq 5).

Co(II) polypyridine, phenanthroline, and imidazole complexes have been recognized early as potential electron relays and catalysts in photoredox reactions, because they constitute vitamin B12 model compounds.¹¹ $Co(bpy)_3^{2+/3+}$, $Co(phen)_3^{2+/3+}$, and $Co(5\text{-nitro-phen})_3^{2+/3+}$ couples, in particular, were tested in dye-sensitized polycrystalline TiO_2 -based photovoltaic cells, and IPCEs of up to 50% were obtained.¹² In these experiments, however, the reduction of the oxidized Co(III) form of the complex at the conducting glass that serves to support the TiO_2 nanoparticles increased the dark current. Until now, endeavors to increase the photovoltage of dye-sensitized nanocrystalline cells by replacing iodide with a one-electron, outer-sphere redox couple with a more positive oxidation potential have not succeeded, largely because of limitations imposed by dark current and slow diffusion of the alternate mediator. It also has been inferred from intensity-modulated photovoltage spectroscopy experiments that the complex mechanism of the oxidation of iodide could in fact be essential to the energy conversion efficiency of DSSCs and that attempts to use a simple one-electron redox mediator system instead are unlikely to be successful.^{13,14}

Recently, solid-state devices have been described, in which the liquid electrolyte present in the pores of the nanocrystalline oxide film is replaced by a large band gap *p*-type semiconductor acting as a hole transport medium.¹⁵ Parallel to this new promising development, we report here on the use of bis[2,6-bis(1'-butylbenzimidazol-2'-yl)pyridine]cobalt(II) complex ($Co(dbbp)_2^{2+}$) as redox mediator in molecular photovoltaic cells (Chart 1).

$Co^{III}(dbbp)_2^{3+}/Co^{II}(dbbp)_2^{2+}$ couple potential, $\phi_{1/2} = 0.36$ V/SCE, was determined by cyclic voltammetry in acetonitrile using a platinum working electrode. The latter value is comparable with that of the (I_3^-/I^-) couple. Used in conjunction with a blocking TiO_2 underlayer, the function of which is to prevent the short-circuiting reaction and thus minimize dark current, $Co(dbbp)_2^{3+/2+}$ couple appears to rival the performance of the tri-iodide/iodide redox mediator in DSSCs. Also, particularly encouraging is the faint coloration of both oxidation states of the complex. $Co^{II}(dbbp)_2^{2+}$ ($\lambda_{max} = 321$ nm) and $Co^{III}(dbbp)_2^{3+}$ ($\lambda_{max} = 309$ nm, 344 nm) absorption maxima are indeed located in the UV domain. The absorption tail in the visible for both species is fairly weak, allowing for the preparation of concentrated electrolyte solutions: $\epsilon_{450}(Co^{II}) =$

$3.1 \times 10^2 \text{ mol}^{-1} \text{ l cm}^{-1}$, $\epsilon_{450}(Co^{III}) = 1.4 \times 10^3 \text{ mol}^{-1} \text{ L cm}^{-1}$, $\epsilon_{480}(Co^{II}) = 1.3 \times 10^2 \text{ mol}^{-1} \text{ L cm}^{-1}$, $\epsilon_{480}(Co^{III}) = 3.4 \times 10^2 \text{ mol}^{-1} \text{ L cm}^{-1}$. Synthesis and detailed spectroscopic and electrochemical characterization of several derivatives of $Co^{II}(bip)_2^{2+}$ will be reported elsewhere.¹⁶

Experimental Section

Electrolyte Preparation. Electrolyte solutions were prepared by dissolving the cobalt complex redox mediator $Co^{II}(dbbp)_2^{2+}$ in anhydrous acetonitrile/ethylene carbonate (40:60 v/v). This solvent mixture was used throughout all experiments described hereafter. Partial oxidation of Co(II) complex to Co(III) was achieved by adding stoichiometric amounts of solid $NOBF_4$, a strong oxidizer, to the mediator solution.

Laser Flash Photolysis. Transparent mesoporous TiO_2 layers (thickness 5 μm) were prepared on a glass substrate using a previously reported procedure.¹⁷ Dry nanocrystalline titania films were dyed by adsorption of the sensitizer N719, [*cis*- $Ru^{II}(2,2'$ -bipyridyl-4,4'-dicarboxylate- $H)_2(NCS)_2$] $^{2-}$ (TBA $^+$) $_2$, from a $5 \times 10^{-4} \text{ mol l}^{-1}$ solution in acetonitrile/*tert*-butyl alcohol (1:1 v/v). A drop of pure solvent or of the electrolyte was then sandwiched between the sample and a thin microscope coverglass.

Samples were subjected to low-intensity flash photolysis immediately after preparation. Pulsed laser excitation was applied using a broadband optical parametric oscillator (OPO) pumped by a frequency-tripled Q-switched Nd:YAG laser (30 Hz repetition rate, pulse width at half-height of 5 ns). The output of the OPO was tuned at $\lambda = 510$ nm and attenuated by filters. The beam was expanded by a planoconcave lens to irradiate a large cross section ($\sim 1 \text{ cm}^2$) of the sample, the surface of which was kept at a 30° angle to the excitation beam. The analyzer light, produced by a cw Xe arc lamp, was passed through a first monochromator, various optical elements, the sample, and a second monochromator, prior to being detected by a fast photomultiplier tube. Satisfactory signal-to-noise ratios were typically obtained by averaging over several hundred laser shots.

Photoelectrochemical Measurements. Photoelectrodes used in dye-sensitized solar cells consisted of a TiO_2 film of double-layer structure: A compact blocking underlayer of spray-pyrolyzed titania (~ 150 nm thick) was first deposited onto cleaned conducting glass substrate (Nippon Sheet Glass, F-doped SnO_2 , sheet resistance of 10 Ω/sq). A solution of 0.2 mol L^{-1} titanium di-isopropoxide bis(acetylacetonate) in ethanol was sprayed 15 times ($\sim 0.5 \text{ mL cm}^{-2}$) over the conducting glass surface that was maintained at 400 °C. Treated glass plates were fired at 500 °C for 30 min to remove remaining organic traces. Successive depositions of a 2 μm thick transparent layer and of a 4 μm thick light-scattering layer of nanocrystalline TiO_2 and final posttreatment by an aqueous $TiCl_4$ solution were then carried out according to a previously published procedure.¹⁸

Dye sensitization of nanocrystalline oxide films was achieved by immersion of electrodes, heated beforehand under oxygen at 500 °C for 15 min, in solutions of two different compounds: N719 was purchased from Johnson Matthey and used as a $5 \times 10^{-4} \text{ mol L}^{-1}$ solution in acetonitrile/*tert*-butyl alcohol (1:1 v/v); Z316, *cis*- $Ru^{II}(2,2'$ -bipyridyl-4,4'-dicarboxylic acid) (4-methyl-4'-hexadecyl-2,2'-bipyridyl)(NCS) $_2$, was synthesized in our laboratory. Dr. G. Viscardi (University of Torino) kindly provided the ligand carrying the hexadecyl group. This dye was adsorbed from a $3 \times 10^{-4} \text{ mol L}^{-1}$ solution in ethanol. Sensitized semiconductor films were finally pressed against a reflective platinum counter electrode on which a drop of the electrolyte was deposited. A mask limited the photoactive area of such open cells to 0.44 cm^2 . The method used to collect

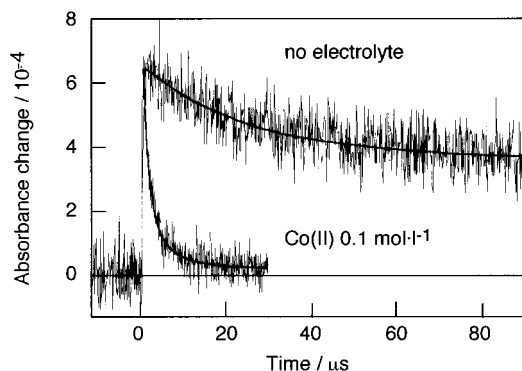


Figure 1. Transient absorbance decay kinetics of the oxidized state of *cis*-Ru(dcbpy)₂(NCS)₂ adsorbed on a TiO₂ nanocrystalline film in the presence and absence of 0.1 M of the Co(II) complex mediator in acetonitrile/ethylene carbonate (40:60 v/v) solvent mixture. Absorbance changes were measured at a probe wavelength of 620 nm, employing 510 nm laser excitation (5 ns fwhm pulse duration, 0.04 mJ cm⁻² pulse fluence).

photoelectrochemical data from these samples was described in a previous publication.¹⁸

Results and Discussion

Figure 1 shows results from nanosecond time-resolved laser experiments. The transient optical signal records the concentration of oxidized ruthenium sensitizer following photoinduced electron injection from the dye into the conduction band of the TiO₂ film.¹⁹ In the absence of the cobalt(II)/(III) redox electrolyte, the decrease of the absorption signal reflects the dynamics of recombination of the conduction band electrons with the oxidized dye (eq 4). The pulsed laser intensity was kept at a very low level ($\leq 40 \mu\text{J cm}^{-2}$ per pulse) to ensure that, on the average, less than one e_{cb}^-/S^+ charge-separated pair was produced per nanocrystalline particle upon pulsed irradiation. Also, the intensity of the monochromatic probe light reaching the sample was attenuated to less than 1 mW cm^{-2} to minimize steady-state carrier concentration. In such conditions, the kinetics of the oxidized dye transient absorption decay could be well fitted by a single exponential, with a rate constant of $k_b = 4.2 \times 10^3 \text{ s}^{-1}$. Increasing the laser fluence above $80 \mu\text{J cm}^{-2}$ caused the gradual appearance of a previously observed fast component in the decay, which could not be reduced to first-order kinetics anymore.^{4,5,20}

In the presence of Co(dbbip)₂²⁺, the decay of the oxidized dye signal was strongly accelerated, indicating that the back reaction is efficiently intercepted by the mediator. The temporal behavior of S⁺ transient absorption was found again to correspond to a simple exponential. In this case, however, an increase of the laser intensity by nearly 2 orders of magnitude did not cause any significant change in the decay rate. From this observation, it is inferred that the kinetics of the interception reaction (eq 5) is clearly decoupled from the back electron-transfer process (eq 4) and is indeed first-order in S⁺ concentration. In the presence of 0.1 mol L⁻¹ Co^{II}(dbbip)₂²⁺, the rate constant for oxidation of the mediator by the oxidized states, S⁺, of the dye-sensitizer was determined to be $k_m = 5.0 \times 10^5 \text{ s}^{-1}$. This value compares approximately with the reciprocal half-life, $1/t_{1/2} = 1.7 \times 10^6 \text{ s}^{-1}$, of the dye ground-state recovery measured with 0.1 mol L⁻¹ *tert*-butylammonium iodide.⁹

Dependence upon the mediator's concentration of the pseudo-first-order rate constant, k_m , for Co^{II}(dbbip)₂²⁺ oxidation by S⁺ is displayed in Figure 2. Two different regimes can be clearly identified. Above a threshold of $10^{-2} \text{ mol L}^{-1}$, larger concentra-

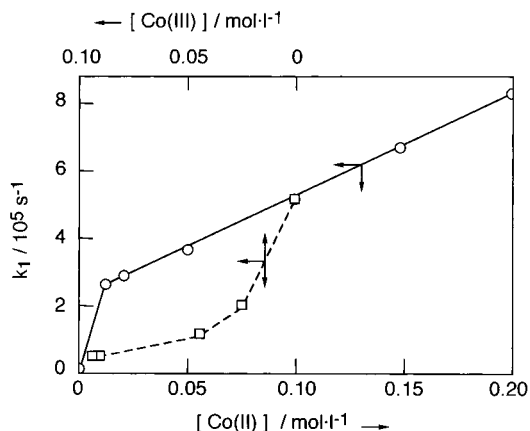


Figure 2. Plot of the first-order rate constant k_m (s^{-1}) fitted from the decay kinetics of the oxidized state of *cis*-Ru(dcbpy)₂(NCS)₂ adsorbed on TiO₂ nanocrystalline films in the presence of an increasing concentration of the Co(II) complex mediator in ethylene carbonate/acetonitrile (O). Partial oxidation of the Co(II) complex to Co(III) by addition of stoichiometric amounts of NOBF₄ (□) caused the kinetics of the interception reaction to decrease markedly.

tions of the mediator resulted in a linear increase of the apparent rate, thus yielding a second-order rate constant for the interception reaction of $k_m'' = 2.9 \times 10^6 \text{ mol}^{-1} \text{ L s}^{-1}$. This value is approximately 1 order of magnitude smaller than that reported for dye ground-state recovery in the presence of sodium iodide ($k_m'' = 2 \times 10^7 \text{ mol}^{-1} \text{ L s}^{-1}$).¹⁹ At mediator concentrations below $10^{-2} \text{ mol L}^{-1}$, static interception appears to take place mainly from species adsorbed at the surface or associated with dye molecules. Because the TiO₂ surface covered by N719 dye is negatively charged,⁹ electrostatic adsorption of the mediator's dications is quite efficient. Contrary to the case of iodide, in which a cooperative effect of adsorbed cations was observed,⁹ addition of 0.1 mol L⁻¹ of Li⁺ClO₄⁻ did not yield any noticeable change in the interception kinetics measured with the cobalt complex. Static interception compensates for the intrinsically slower reduction of S⁺ by Co^{II}(dbbip)₂²⁺, resulting in an observed pseudo-first-order rate similar to that obtained with the tri-iodide/iodide system.

Concomitantly with the decay of the oxidized dye transient absorption, the recovery of the bleached dye ground state was monitored at $\lambda_{\text{obs}} = 480 \text{ nm}$. Beyond a $10 \mu\text{s}$ delay, after which the interception reaction was complete, a weak positive residual absorption was observed at the same wavelength. The latter signal was assigned to the Co^{III} oxidized state of the complex, of which the absorption tail in the visible is characterized by a larger extinction coefficient than that of the reduced species. This long lifetime transient absorption eventually decayed over ca. 1 ms because of the recombination process (eq 6), the first-order rate constant of which was then determined directly as being $k_r = 3 \times 10^3 \text{ s}^{-1}$. For the tri-iodide/iodide system, the two-electron recombination reaction was reported to take place with a pseudo-second-order rate constant of $1.1 \times 10^4 \text{ mol}^{-1} \text{ L s}^{-1}$ at $[\text{I}_3^-] = 5 \times 10^{-2} \text{ mol L}^{-1}$.¹⁴ In a functioning DSSC, in which sufficient charge transport at the counter electrode is ensured by a concentration of the oxidized form of the mediator of typically 0.1 mol L⁻¹, recombination of injected electrons with the Co^{III} complex mediator is therefore expected to be only slightly faster than in the case of tri-iodide.

Figure 2 shows that partial oxidation of the complex slowed significantly the regeneration of the sensitizer. This is attributed to the replacement of the adsorbed Co^{II}(dbbip)₂²⁺ by the Co^{III}(dbbip)₂³⁺ species at the interface next to the sensitizer. The

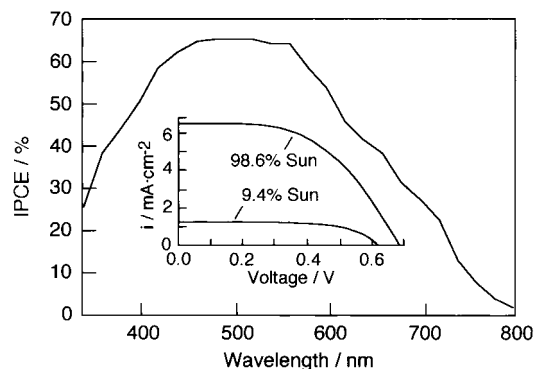


Figure 3. Incident photon-to-current conversion efficiency (IPCE) of a cell based on a 6- μm -thick nanocrystalline TiO_2 film sensitized by dye Z316. The conducting glass substrate was primarily coated with a compact 150-nm-thick TiO_2 blocking underlayer. The exposed area of the photanode was 0.44 cm^2 . The electrolyte solution consisted of 0.18 mol L^{-1} of the Co(II) complex mediator and $2 \times 10^{-2} \text{ mol L}^{-1}$ of NOBF_4 in acetonitrile/ethylene carbonate (40:60 v/v) solvent mixture. The insert displays the photocurrent density/voltage characteristics of the cell. A fill factor of 0.68 and a power conversion efficiency of 5.2% at 9.4% sun irradiation intensity were measured.

electrostatic binding on the negatively charged TiO_2 surface is indeed expected to increase with the positive charge density on the cobalt complex.

To reduce the negative charge density on the semiconductor particle surface, another dye was tried, which contains only two carboxylic groups and is therefore characterized by a neutral charge. The effect of this new sensitizer (Z316) on the photoelectrode was to increase the short-circuit current of the solar cell and therefore the global efficiency. Figure 3 shows the photocurrent action spectrum of a solar cell containing $\text{Co}(\text{dbbip})_2^{2+}$ 0.18 mol L^{-1} and $2 \times 10^{-2} \text{ mol L}^{-1}$ NOBF_4 as redox mediator, in which the incident photon-to-current conversion efficiency is plotted as a function of wavelength. The IPCE value in the plateau region exceeds 65%. The open-circuit potential (V_{oc}) is 670 mV, and the short-circuit photocurrent density (I_{sc}) is 6.8 mA cm^{-2} with the standard global AM1.5 irradiance. The fill factor (ff) was calculated to be 0.46, yielding for the overall solar (1000 W m^{-2}) to electrical power conversion efficiency a value of 2.2%. At a light intensity of 94 W cm^{-2} , the fill factor improved markedly to 0.68 and the efficiency increased to over 5.2%. The nonlinear dependence of the photocurrent on the light intensity and the poor fill factor obtained under full solar irradiance are certainly indicative of deficient diffusive charge transport by the oxidized mediator.

Conclusions

The experiments carried out so far have shown that the $\text{Co}(\text{dbbip})_2^{2+/3+}$ complexes are promising candidates for use as redox mediators in dye-sensitized solar cells. Their kinetic

behavior can rival the performance of the tri-iodide/iodide redox couple. Particularly encouraging is the weak visible light absorption in both oxidation states allowing for the preparation of concentrated redox melts. Also important is the fact that these compounds are expected to be less aggressive than iodine toward silver contact fingers and sealing materials used in solar cells. Further work will focus on the preparation of complexes in which the bip ligands are substituted by suitable groups to increase the solubility of the mediator. This should help to overcome the diffusion problems, which still limit the performance of this couple under full sunlight.

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References and Notes

- O'Regan, B.; Grätzel, M. *Nature* **1991**, *335*, 737.
- Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, *33*, 269–277.
- Grätzel, M.; Moser, J. E. Solar Energy Conversion. In *Electron Transfer in Chemistry*; Balzani, V., Gould, I. R., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. V; pp 589–644.
- Haque, S. A.; Tachibana, Y.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem. B* **1998**, *102*, 1745.
- Haque, S. A.; Tachibana, Y.; Willis, R. L.; Moser, J. E.; Grätzel, M.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem. B* **2000**, *104*, 538–547.
- Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. *J. Am. Chem. Soc.* **1985**, *107*, 2988–2990.
- Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *J. Phys. Chem. B* **1997**, *101*, 2591–2597.
- Bonhôte, P.; Moser, J. E.; Humphry-Baker, R.; Vlachopoulos, N.; Zakeeruddin, S. M.; Walder, L.; Grätzel, M. *J. Am. Chem. Soc.* **1999**, *121*, 1324–1336.
- Pelet, S.; Moser, J. E.; Grätzel, M. *J. Phys. Chem. B* **2000**, *104*, 1791–1795.
- Oskam, G.; Bergeron, B. V.; Meyer, G. J.; Searson, P. C. *J. Phys. Chem. B* **2001**, *105*, 6867–6873.
- Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471.
- Bonhôte, P.; Grätzel, M.; Jirousek, M.; Liska, P.; Pappas, N.; Vlachopoulos, N.; Von Planta, C.; Walder, L. Presented at the 10th International Conference on Photochemical Conversion and Storage of Solar Energy (IPS-10), Interlaken, Switzerland, 1994, Abstract C2.
- Fisher, A. C.; Peter, L. M.; Ponomarev, E. A.; Walker, A. B.; Wijayantha, K. G. U. *J. Phys. Chem. B* **2000**, *104*, 949–958.
- Duffy, N. W.; Peter, L. M.; Rajapakse, R. M. G.; Wijayantha, K. G. U. *J. Phys. Chem. B* **2000**, *104*, 8916–8919.
- Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissörtel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. *Nature* **1998**, *395*, 583.
- Nusbaumer, H.; Zakeeruddin, S. M.; Moser, J. E.; Grätzel, M. *Inorg. Chem.*, manuscript in preparation.
- Barbé, C. J.; Arendse, F.; Comte, P.; Jirousek, M.; Lenzmann, F.; Shklover, V.; Grätzel, M. *J. Am. Ceram. Soc.* **1997**, *80*, 3157–3171.
- Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613–1624.
- Moser, J. E.; Noukakis, D.; Bach, U.; Tachibana, Y.; Klug, D. R.; Durrant, J. R.; Humphry-Baker, R.; Grätzel, M. *J. Phys. Chem. B* **1998**, *102*, 3649.
- Kuciauskas, D.; Freund, M. S.; Gray, H. B.; Winkler, J. R.; Lewis, N. S. *J. Phys. Chem. B* **2001**, *105*, 392–403.