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Short communication

Time-resolved experiments in dye-sensitized solar cells using $[(dcbH_2)_2Ru(ppy)_2](ClO_4)_2$ as a nanocrystalline TiO_2 sensitizer

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Abstract

The complex *cis*-$[(dcbH_2)_2Ru(ppy)_2]^{2+}$, in which $dcbH_2$ is 4,4′-$(CO_2H)_2$-2,2′-bipyridine and ppy is 4-phenylpyridine, was anchored to nanocrystalline TiO_2 films deposited onto FTO substrate. Transient UV–visible absorption spectra with the resulting electrodes were carried out in order to investigate the electron-transfer process across the excited dye/semiconductor interface, as well as the charge recombination and quenching processes.

The formation of the oxidized complex $[(dcbH_2)_2Ru^{III}(ppy)_2]^{3+}$ upon light excitation was monitored by transient absorption difference spectra. The compound performs successful conversion of visible light into electricity as a molecular sensitizer of nanocrystalline n-type TiO_2 in photoelectrochemical solar cells. A fast quenching of the oxidized complex in the presence of iodide emphasizes the importance of a proper concentration of donor species in the redox mediator for the effective regeneration of the oxidized sensitizer. Kinetics data of electron injection obtained by time-resolved experiments are discussed in parallel with photoelectrochemical properties of the dye-sensitized anatase TiO_2.

Keywords: TiO_2 sensitization; 4-Phenylpyridine; Transient absorption spectra

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1. Introduction

Efficient conversion of visible light into electricity is achieved by photoelectrochemical solar cells based on dye sensitization of wide bandgap semiconductors. Dye sensitization presents advantages over direct band to band excitation as in conventional solar cells. It allows electron injection from the photoexcited dye molecule into the semiconductor conduction band (CB) with energy lower than the bandgap and the semiconductor valence band is not involved in the light absorption process. Therefore, the electron–hole pair is separated by the semiconductor–sensitizer interface with the harvesting of a large fraction of sunlight by coordination complexes having a broad absorption band [1–7].

The concept of the dye sensitization was already considered more than 30 years ago [8,9], but the experimental efficiency achieved by the cells was restricted to the low absorptivities presented by monolayers of dyes on electrodes of low surface roughness. Significant improvements have been achieved with the evolution of the synthetic route to effectively bind the molecular sensitizer to the semiconductor surface [10,11] followed by the development of fractal polycrystalline TiO_2 films achieved a decade later [12]. In a porous film, consisting of nanometric semiconductor particles, the active surface area is greatly increased, resulting in an effective light absorption. As a result of these advances, the development of low-cost efficient solar cells became possible [13,14].

n-TiO_2 is widely used as semiconductor material in dye-sensitized photoelectrochemical solar cells, owing to its favorable energetics, stability, low price and simple processing [14–18]. Ruthenium(II) polypyridyl complexes with carboxylated ligands are commonly employed as TiO_2 sensitizers in such cells [19–21] and outstanding results have been achieved using thiocyanate derivatives as ancillary ligands [22–24]. As a result of visible light excitation, dye species are electronically excited resulting in electron transfer through the dye complex to the semiconductor in the femto/sub-picosecond time-domain [2,6,22,25].

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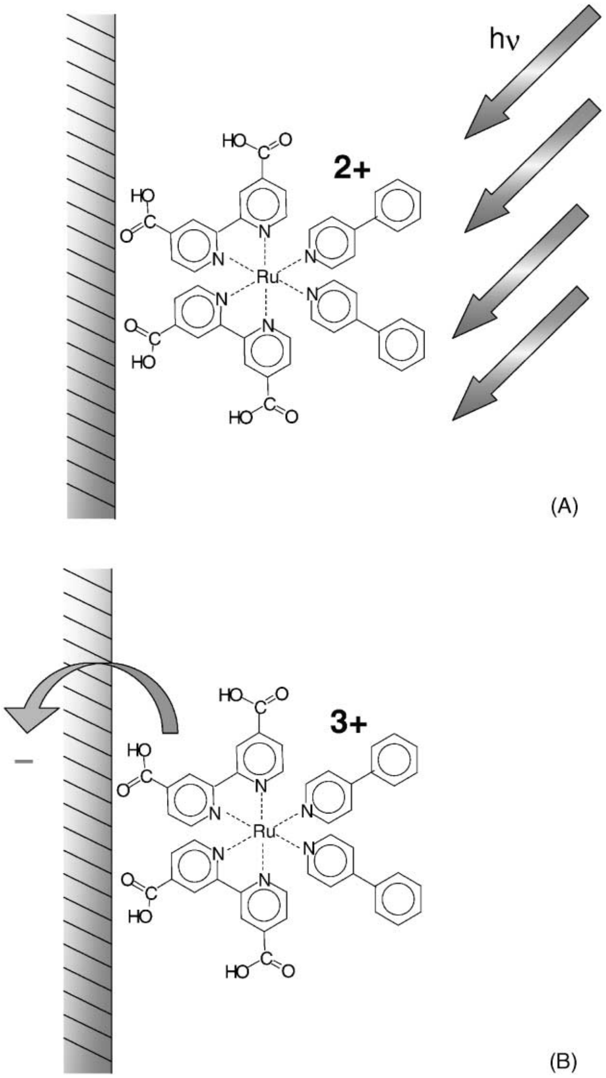
We have been obtaining high incident photon-to-current conversion efficiencies (IPCE) employing a series of *cis*-$[(dcbH_2)_2RuLL']$ species, in which $dcbH_2$ is 4,4′-$(CO_2H)_2$-2,2′-bipyridine and L and/or L′ are substituted pyridines, as n-TiO_2 sensitizers in transparent photoelectrochemical solar cells [26–30]. The results showed that the spectral sensitivity to the visible light, as well as the overall conversion efficiency of the cells, are affected by the nature of ancillary ligands coordinated to the nonattached side of the dye.

In this work, the excited state properties of the complex with 4-phenylpyridine (ppy) as ancillary ligands, *cis*-$[(dcbH_2)_2Ru(ppy)_2](ClO_4)_2$, attached to TiO_2 films, were investigated by means of laser flash-photolysis. Scheme 1 illustrates the interfacial electron transfer following light absorption for the *cis*-$[(dcbH_2)_2Ru(ppy)_2](ClO_4)_2$ dye anchored to TiO_2 surface. Investigation of the electron-transfer process across the excited dye/semiconductor interface, as well as charge recombination and quenching processes, were performed through time-resolved experiments carried out with the sensitizer anchored to nanostructured anatase TiO_2 films.



Scheme 1. Schematic representation of interfacial electron-transfer process (B) following light absorption (A) for the *cis*-$[(dcbH_2)_2Ru(ppy)_2]^{2+}$ complex.

2. Experimental

All chemicals were reagent grade or of the best available purity. HPLC solvents and reagent grade water was always used. Transparent TiO_2 films for photoelectrochemical measurements were obtained following the procedure described in the literature [22,31]. The semiconductor emulsion was deposited on conductive fluorine-doped SnO_2 glass. The molecular sensitizer *cis*-$[(dcbH_2)_2Ru(ppy)_2]$-$(ClO_4)_2$ was synthesized as previously described [27]. Adsorption of the complex into the TiO_2 surface was achieved by immersing the processed electrode for 3 h in ca. 1×10^{-4} M ethanolic solution of the ruthenium complex.

2.1. Methods

Stationary absorption spectra were recorded on a Hewlett Packard HP 8453 UV–visible spectrophotometer. Emission measurements were performed on a SPEX Fluoromax 2 spectrofluorometer equipped with a Hamamatsu R3896 tube.

Transient absorption measurements were performed using a set up and an apparatus that have been previously described [32]. The measurements were performed in 0.3 M $LiClO_4$ in acetonitrile, which is frequently used as the solvent system in photoelectrochemical experiments.

Photoelectrochemical measurements were performed by using a dye-sensitized TiO_2 film incorporated into a thin-layer sandwich-type solar cell as previously described [27,30]. The transparent solar cell consists of two electrodes sandwiching a mediator solution. The photoanode is composed of a fluorine-doped SnO_2 substrate with the TiO_2 film sensitized by the complex. The counter electrode presents a transparent platinum film on its conductive surface. The redox mediator and electrolyte, 0.03 M I_2/0.3 M LiI solution in acetonitrile is placed between the two electrodes.

Preliminary performances of cells were evaluated using a system comprised of a 200 W Hg (Xe) arc lamp and interference filters, as detailed elsewhere [33]. Photocurrent and voltage measurements, as well as photoaction spectra, were obtained as previously described [26,27]. Alternatively, an Oriel system consisting of a 450 W Xe lamp model 6266 coupled to monochromator model 77200 was used. Incident irradiance was measured with a calibrated power meter, model 70260 and the photocurrent was collected on a A.W. Sperry, model DM-8A or a Minipa, model ET-2600, digital multimeters.

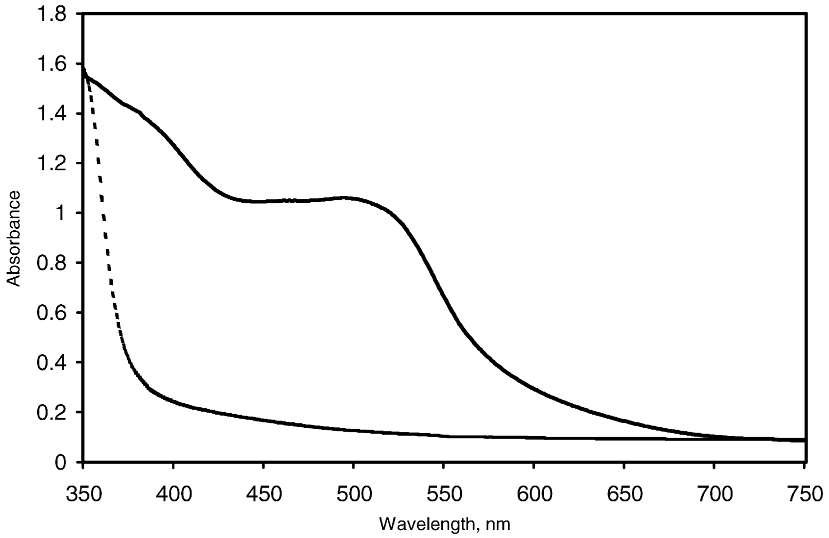


Fig. 1. UV–visible absorption spectra of TiO_2 (dashed line) and $[(dcbH_2)_2Ru(ppy)_2]^{2+}/TiO_2$ (solid line) in acetonitrile (room temperature).

3. Discussion

It has been shown that photophysic and redox properties of compounds of the general formula *cis*-$[(dcbH_2)_2RuLL']$ can be controlled through a convenient selection of the ancillary ligands L and L′. The absorption bands can be adjusted or tuned to lower wavelengths resulting in an enhanced spectral response to the visible light [21–23,26,27,30,34–36].

Efficient sensitization of nanocrystalline n-TiO_2 was achieved employing the species *cis*-$[(dcbH_2)_2Ru(ppy)_2](ClO_4)_2$ as a molecular sensitizer in photoelectrochemical solar cells, resulting in incident monochromatic IPCE values as high as 45% in the 450–550 nm region [27,30].

The electronic absorption spectra of the TiO_2-covered TCO substrate before and after adsorption of *cis*-$[(dcbH_2)_2Ru(ppy)_2](ClO_4)_2$ onto its surface are shown in Fig. 1. The electrode spectrum is similar to the absorption spectrum of the corresponding molecular sensitizer in solution [26] and displays MLCT ($d\pi \rightarrow \pi^*$) bands in the visible region as well as intra-ligand ($\pi \rightarrow \pi^*$) transitions in the UV region [22,23,26,27,34,35,37].

The transient absorbance difference spectra in acetonitrile of the photoanode containing a TiO_2 film covered with *cis*-$[(dcbH_2)_2Ru(ppy)_2](ClO_4)_2$ is presented in Fig. 2. Following light absorption, the electron injection from the excited sensitizer into the semiconductor results in the formation of the oxidized complex *cis*-$[(dcbH_2)_2Ru^{III}(ppy)_2]^{3+}$. This results in a bleach in the region between 350 and 650 nm, which is attributed to the depletion of the ground state MLCT absorption [4,32,38–44]. The absence of a positive absorption in the 350–400 nm region, attributed to intra-ligand absorption of the polypyridine radical-anion in the excited $[(dcbH_2)_2Ru(ppy)_2]$ species, shows that electron injection to the semiconductor is efficient and takes place within the laser pulse (<10 ns) or faster, which is in agreement with earlier reported data [32,39,42–44].

The steady-state emission spectrum of *cis*-$[(dcbH_2)_2Ru(ppy)_2](ClO_4)_2$ in acetonitrile solution exhibits a weak emission centered at 620 nm. The short-lived ($t < 5$ ns) emission could not be resolved with the available equipment.

Fig. 3 shows the absorbance changes of the complex measured at 480 nm obtained by excitation with 3.0 mJ cm^{-2} laser pulse at 532 nm in two conditions. The recovery process observed in Fig. 3A is associated with the reduction of the oxidized species, *cis*-$[(dcbH_2)_2Ru^{III}(ppy)_2]^{3+}$ [32,38,41]. After the fast bleaching observed following light excitation and electron injection, the absorbance of *cis*-$[(dcbH_2)_2Ru(ppy)_2]^{2+}$ in the ground state is regenerated through a multiphasic process, apparently characterized by a comparatively fast step followed by another slower one.

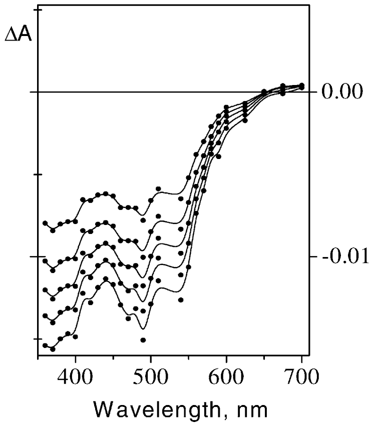


Fig. 2. Time-resolved transient absorption spectra of *cis*-$[(dcbH_2)_2Ru(ppy)_2]^{2+}$ adsorbed in TiO_2 film. MeCN/0.3 M $LiClO_4$, room temperature, $\tau_d = 0$, 50, 250, 1000 and 2000 ns ($\lambda_{exc} = 532$ nm, 3.0 mJ cm^{-2} laser pulse).

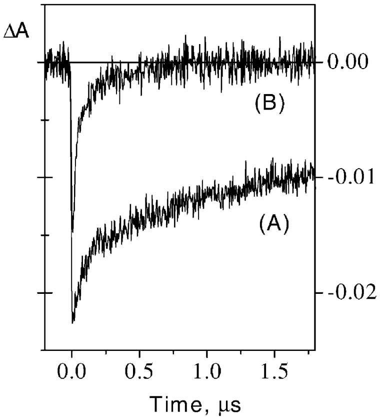


Fig. 3. Absorbance changes measured at 480 nm for *cis*-$[(dcbH_2)_2Ru(ppy)_2]^{2+}$ after 532 nm laser pulse ($3.0\,mJ\,cm^{-2}$) in (A) MeCN/0.3 M $LiOCl_4$ and (B) MeCN/0.3 M LiI.

This behavior is frequently observed in such heterogeneous systems and is attributed to surface defects which could retain temporarily the injected electrons [38,40,42,43,45,46].

Fig. 3B shows the recovery process in the presence of iodide. The concentration employed (0.3 M LiI) is the same as in standard photoelectrochemical solar cell experiments and Li^+ concentration was kept constant with respect to the recombination experiments (0.3 M $LiClO_4$, Fig. 3A). It is observed that the recovery process is much faster in the presence of iodide (Fig. 3B) than in its absence (Fig. 3A). This evidences that the presence of iodide in adequate concentration promotes the fast quenching of the oxidized species as observed in Fig. 3B. This behavior is found to be dependent on the concentration of iodide [45]. A sluggish iodide oxidation was found to be a limiting factor which restricts the conversion efficiencies in photoelectrochemical solar cells [47].

The primary step of electron injection from the excited sensitizer into the semiconductor is extremely fast. After electron injection, the oxidized dye must be rapidly reduced by electrolyte relay in solution in order to prevent both the electronic recombination across the interface and any photodegradation reactions. Reduction of the oxidized dye by iodide regenerates the cromophore to its original state and gives rise to I_3^-,[1] Eq. (1), closing the cycle initiated after light absorption.

$$2[(dcbH_2)_2Ru^{III}(ppy)_2]^{3+} + 3I^- \rightarrow 2[(dcbH_2)_2Ru^{II}(ppy)_2]^{2+} + I_3^- \quad (1)$$

The overall efficiency of the photoelectrochemical conversion process is given by the wavelength dependent IPCE term which is directly related to the fraction of radiant power absorbed by the material (or light harvesting efficiency, LHE), the quantum yield for electron injection into the semiconductor (ϕ) and the efficiency of collecting electrons in the external circuit (η) [20,22,32,48].

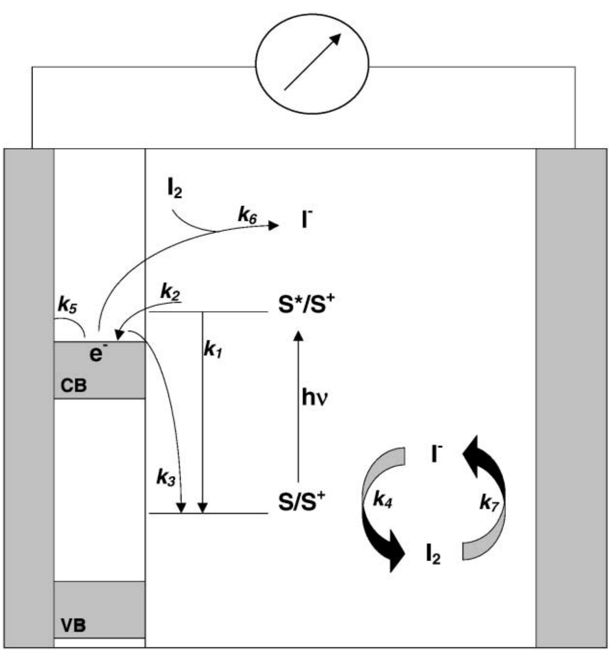


Fig. 4. Schematic representation of the photoconversion process in dye-sensitized solar cell. S is $[(dcbH_2)_2Ru(ppy)_2]^{2+}$, CB and VB are conduction and valence bands.

The η value is related to the fraction of injected charges which percolates through the TiO_2 membrane and reach the back contact of the photoanode [48].

The conventional mechanism of the energy conversion process is shown in Fig. 4. After light absorption, the excited sensitizer (S^*) promotes the electron injection (k_2) into the semiconductor CB. The oxidized sensitizer (S^+) is reduced by an electron donor (k_4) which is regenerated at the counter electrode (k_7). Efficiency loss can take place by radiative and nonradiative decay of the excited state (k_1), by recombination of electrons in the CB with oxidized sensitizer molecules (k_3) and by electrons in TiO_2 which react with oxidants in solution (k_6).

The efficiency of quenching of Ru^{III}, defined as η, most likely reflects in the resulting IPCE values and is evaluated by monitoring the decay of the oxidized sensitizer in the absence (k_3) or presence (k_4) of iodide according to the simplified analytical expressions below [32,48][2]

$$\eta = \frac{k_4}{k_3 + k_4} \quad (2)$$

or

$$\eta = 1 - \frac{k_3}{k_3 + k_4} \quad (3)$$

Eqs. (2) and (3) describe the interplay between the quenching process (k_4) and the recombination of the electrons in the CB with the Ru^{III} center (k_3) [32].

The magnitude of rate constants k_3 and k_4 can be evaluated through the data obtained in time-resolved experiments.

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[1] Shown as I_2 in Fig. 4, representing the process k_4.

[2] See [32] for the full derivation of the kinetic processes.

The η term is then estimated applying Eq. (3). The quenching of Ru^{III} by I^- (Fig. 3B, $k_3 + k_4 = k_{obs}$) was treated as a single exponential. Traces of the recombination between the electron in TiO_2 and the oxidized dye molecule (k_3) were fitted with a bi-exponential function which indicates a fast ($k \approx 5 \times 10^6\,s^{-1}$) and a slow ($k \approx 2 \times 10^5\,s^{-1}$) components. Since the quenching of Ru^{III} is completed within 100 ns, only the fast component is considered. Applying the values obtained in Eq. (3) results in $\eta = 0.67$. Although somewhat high, the value obtained for the quenching efficiency is below that obtained for related species which also resulted in higher IPCE values. Both parameters η and IPCE are interconnected, since the efficiency of the cells is partially attributed to the interplay between the quenching of Ru^{III} by I^- and the recombination of the electrons of the CB with the oxidized dye molecule [32]. Nevertheless, one should be careful while analyzing these values, due to the above mentioned assumptions and simplifications.

There is a difference between the kinetics of charge recombination and the ultrafast electron injection. Such a different behavior among both interfacial electron-transfer processes is a key factor to the successful operation of dye-sensitized photoelectrochemical solar cells [4,41]. Back electron transfer to the oxidized dye S^+ is avoided due to its efficient regeneration by the redox mediator.

4. Conclusion

The process of nanocrystalline n-type TiO_2 sensitization to visible light by $[(dcbH_2)_2Ru(ppy)_2]^{2+}$ in photoelectrochemical solar cells is further examined. The efficient capture of the oxidized dye by the electron relay in solution prevents the recombination, directing the electron transport process to the desired pathway. The regeneration of the oxidized dye provided by the proper concentration of donor species in the redox mediator is critical to the electrical circuit as well as to the stability of the cell.

The kinetics of charge recombination is much slower than the ultrafast electron injection. The difference of several orders of magnitude among these processes is essential to the successful operation of the photoelectrochemical solar cells.

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References

[1] J.R. Bolton, A.F. Haught, R.T. Ross, in: J.S. Connolly (Ed.), Photochemical Conversion Storage of Solar Energy, Academic Press, New York, 1981.

[2] K. Kalyanasundaram, M. Grätzel (Eds.), Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer Academic Publishers, Dordrecht, 1993.

[3] J.A. Bard, M.A. Fox, Acc. Chem. Res. 28 (1995) 141–145.

[4] P.V. Kamat, Inter-Am. Photochem. Soc. Newsletter 19 (1996) 14–23.

[5] G.J. Meyer, J. Chem. Educ. 74 (1997) 652–656.

[6] G.J. Meyer (Ed.), Molecular Level Artificial Photosynthetic Materials, 1997, Interscience, New York, Prog. Inorg. Chem. 44.

[7] C.A. Bignozzi, R. Argazzi, C.J. Kleverlaan, Chem. Soc. Rev. 29 (2000) 87–96.

[8] H. Gerischer, M.E. Michel-Beyerle, F. Rebentrost, H. Tributsch, Electrochim. Acta 13 (1968) 1509–1515.

[9] H. Tributsch, M. Calvin, Photochem. Photobiol. 14 (1971) 95–112.

[10] M.P. Dare-Edwards, J.B. Goodenough, A. Hamnett, K.R. Seddon, R.D. Wright, Faraday Discuss. Chem. Soc. 70 (1980) 285–298.

[11] P.K. Ghosh, T.G. Spiro, J. Am. Chem. Soc. 102 (1980) 5543–5549.

[12] J. Desilvestro, M. Grätzel, L. Kavan, J. Moser, J. Am. Chem. Soc. 107 (1985) 2988–2990.

[13] B. O'Reagan, M. Grätzel, Nature 353 (1991) 737–740.

[14] M. Grätzel, Prog. Photovolt. Res. Appl. 8 (2000) 171–185.

[15] H.O. Finklea (Ed.), Semiconductor Electrodes, Elsevier, Amsterdam, 1988.

[16] P.V. Kamat, Chem. Rev. 93 (1993) 267–300.

[17] A. Hagfeldt, M. Grätzel, Chem. Rev. 95 (1995) 49–68.

[18] A. Mills, S. Le Hunte, J. Photochem. Photobiol. A 108 (1997) 1–35.

[19] O. Horváth, K.L. Stevenson, Charge Transfer Photochemistry of Coordination Compounds, VCH, New York, 1993.

[20] C.A. Bignozzi, J.R. Schoonover, F. Scandola, Prog. Inorg. Chem. 44 (1997) 1–95.

[21] M.K. Nazeeruddin, P. Péchy, M. Grätzel, Chem. Commun. 18 (1997) 1705–1706.

[22] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382–6390.

[23] R. Argazzi, C.A. Bignozzi, T.A. Heimer, F.N. Castellano, G.J. Meyer, Inorg. Chem. 33 (1994) 5741–5749.

[24] M.K. Nazeeruddin, P. Péchy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, J. Am. Chem. Soc. 123 (2001) 1613–1624.

[25] Y. Tachibana, I.V. Rubtsov, I. Montanari, K. Yoshihara, D.R. Klug, J.R. Durrant, J. Photochem. Photobiol. A 142 (2001) 215–220.

[26] C.G. Garcia, N.Y. Murakami Iha, R. Argazzi, C.A. Bignozzi, J. Bras. Chem. Soc. 9 (1998) 13–15.

[27] C.G. Garcia, N.Y. Murakami Iha, R. Argazzi, C.A. Bignozzi, J. Photochem. Photobiol. A 115 (1998) 239–242.

[28] C.G. Garcia, J.F. de Lima, N.Y. Murakami Iha, Coord. Chem. Rev. 196 (2000) 219–247.

[29] N.Y. Murakami Iha, Anais Acad. Bras. Ci. 72 (2000) 67–73.

[30] C.G. Garcia, N.Y. Murakami Iha, I. J. Photoenergy 3 (2001) 131–135.

[31] C.G. Garcia, N.Y. Murakami Iha, I. J. Photoenergy 3 (2001) 137–141.

[32] A.C. Lees, B. Evrard, T.E. Keyes, J.G. Vos, C.J. Kleverlaan, M. Alebbi, C.A. Bignozzi, Eur. J. Inorg. Chem. 12 (1999) 2309–2317.

[33] N.Y. Murakami Iha, J. F de Lima, Inorg. Chem. 30 (1991) 4576–4579.

[34] P. Liska, N. Vlachopoulos, M.K. Nazeeruddin, P. Comte, M. Grätzel, J. Am. Chem. Soc. 110 (1988) 3686–3687.

[35] T.A. Heimer, C.A. Bignozzi, G.J. Meyer, J. Phys. Chem. 97 (1993) 11987–11994.

[36] P. Péchy, F.P. Rotzinger, M.K. Nazeeruddin, O. Kohle, S.M. Zakeeruddin, R.H. Baker, M. Grätzel, J. Chem. Soc., Chem. Commun. (1995) 65–66.

[37] C.G. Garcia, A.K. Nakano, N.Y. Murakami Iha, Sensitization of n-type TiO_2 in transparent thin-layer solar cells with *cis*-$[(dcbH_2)_2RuLL']$ using substituted pyridines as ancillary

ligands, in: Proceedings of the 12th International Conference on Photochemical Conversion and Storage of Solar Energy, Berlin, 1998, p. 1W22.
[38] B. O'Regan, J. Moser, M. Anderson, M. Grätzel, J. Phys. Chem. 94 (1990) 8720–8726.
[39] Y. Tachibana, J.E. Moser, M. Grätzel, D.R. Klug, J.R. Durrant, J. Phys. Chem. 100 (1996) 20056–20062.
[40] P.V. Kamat, I. Bedja, S. Hotchandani, L.K. Patterson, J. Phys. Chem. 100 (1996) 4900–4908.
[41] J.M. Stipkala, F.N. Castellano, T.A. Heimer, C.A. Kelly, K.J.T. Livi, G.J. Meyer, Chem. Mater. 9 (1997) 2341–2353.
[42] T. Hannappel, B. Burfeindt, W. Storck, F. Willig, J. Phys. Chem. B 101 (1997) 6799–6802.
[43] C.J. Kleverlaan, M.T. Indelli, C.A. Bignozzi, L. Pavanin, F. Scandola, G.M. Hasselman, G.J. Meyer, J. Am. Chem. Soc. 122 (2000) 2840–2849.
[44] A. Merrins, C. Kleverlaan, G. Will, S.N. Rao, F. Scandola, D. Fitzmaurice, J. Phys. Chem. B 105 (2001) 2998–3004.
[45] S.G. Yan, L.A. Lyon, B.I. Lemon, J.S. Preiskorn, J.T. Hupp, J. Chem. Educ. 74 (1997) 657–662.
[46] S. Iwai, K. Hara, S. Murata, R. Katoh, H. Sugihara, H. Arakawa, J. Chem. Phys. 113 (2000) 3366–3373.
[47] M. Alebbi, C.A. Bignozzi, T.A. Heimer, G.M. Hasselmann, G.J. Meyer, J. Phys. Chem. B 102 (1998) 7577–7581.
[48] C.A. Bignozzi, M. Alebbi, E. Costa, C.J. Kleverlaan, R. Argazzi, G.J. Meyer, I. J. Photoenergy 1 (1999) 135–142.