

Photoelectrochemical solar cells using $[(dcbH_2)_2RuLL']$, $L, L' =$ substituted pyridines, as nanocrystalline TiO_2 sensitizers

Christian Graziani Garcia[†] and Neyde Yukie Murakami Iha[‡]

Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748 - 05508-900, São Paulo - SP, Brazil

ABSTRACT. The development of thin-layer transparent solar cells based on dye sensitization of nanocrystalline n -type TiO_2 undertaken at the Laboratory of Inorganic Photochemistry and Energy Conversion at the Chemistry Institute of Universidade de São Paulo is presented. Compounds of the formula $cis-[(dcbH_2)_2RuLL']$, $dcbH_2 = 4,4'-(CO_2H)_2-2,2'$ -bipyridine and $L/L' =$ substituted pyridines, have been successfully employed as molecular sensitizers in photoelectrochemical solar cells based on dye-sensitization of n - TiO_2 . This regenerative solar cell consists of a TCO glass with a dye-sensitized TiO_2 semiconductor film as a photoanode, I_2/LiI solution in acetonitrile as a redox mediator and a transparent Pt coated TCO glass as a counter electrode. Efficient conversion of visible light into electricity was achieved with IPCE (Incident Photon-to-Current Conversion Efficiency) as high as 50% between 400 and 550 nm.

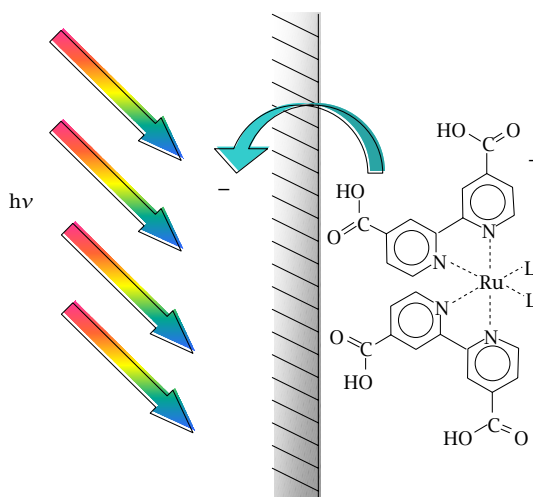
1. INTRODUCTION

Investigation of photoelectrochemical systems for the conversion of solar energy into electricity has found remarkable progress since the development of solar cells based on dye sensitization of wide band-gap semiconductors. Dye sensitization allows electron injection from the excited dye molecule into the semiconductor conduction band with energy lower than the band gap. The processes of light absorption and charge separation are separated minimizing electron recombination [1-6].

Although the dye sensitization conception was already considered more than 30 years ago [7, 8], the progress of the field came with development of covalently bonded sensitizer-semiconductor systems [9, 10] and of fractal polycrystalline TiO_2 films [11]. Due to its favorable energetics, stability, low price and facile processing, n - TiO_2 is conveniently used as semiconductor material in dye-sensitized photoelectrochemical solar cells [12-15]. Ruthenium(II) polypyridyl complexes with carboxylated ligands are commonly employed as TiO_2 sensitizers in such cells. These species present intense visible metal-to-ligand charge transfer bands. The carboxylic groups enable the necessary electronic coupling between the sensitizer and TiO_2 surface. As a result of visible light excitation, dye species are electronically excited resulting in an efficient electron transfer from the carboxylic groups into the semiconductor [16-20].

The Laboratory of Inorganic Photochemistry and Energy Conversion at the Chemistry Institute of

Universidade de São Paulo has developed all the steps involved in the building of regenerative thin-layer solar cells based on dye sensitization of nanocrystalline n - TiO_2 . High incident photon-to-current conversion efficiencies (IPCE) were successfully obtained employing $cis-[(dcbH_2)_2RuLL']$ species, in which $dcbH_2$ is $4,4'-(CO_2H)_2-2,2'$ -bipyridine and L and/or L' are substituted pyridines such as isoquinoline (isq), 4-phenylpyridine (ppy), among others, as photoanode sensitizers [21-24]. Scheme 1 illustrates the inter-



Scheme 1. Schematic representation of interfacial electron transfer after light absorption for $cis-[(dcbH_2)_2RuLL']$ derivatives.

[†] E-mail: cggarcia@iq.usp.br

[‡] E-mail: neydeiha@iq.usp.br

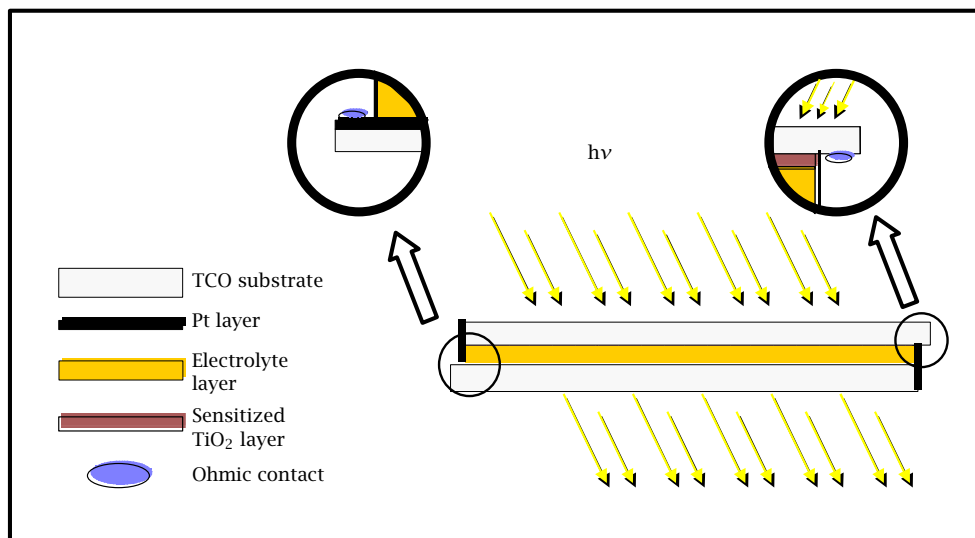


Figure 1. *Thin-layer transparent photoelectrochemical solar cell and its components.*

facial electron transfer after light absorption for *cis*-[(dcbH₂)₂RuLL'] derivatives. The IPCE values showed that the spectral sensitivity to the visible light is affected by the nature of ancillary ligands coordinated to the non-attached side of the dye. In order to further investigate this pattern the complex with one 4-cyanopyridine (CNpy) as an ancillary ligand was synthesized and employed as photoanode sensitizer in the thin-layer solar cell.

2. EXPERIMENTAL

2.1. Materials. All materials were used as supplied without further purification. All chemicals were reagent grade or of the best available purity. Nanopure water was always used.

2.2. Preparation of molecular sensitizers. The molecular sensitizers were synthesized following the procedures described in the literature [21, 22]. Typically, the complexes are obtained starting from the anionic form of [(dcbH₂)₂RuCl₂], dissolving 0.20 mmol of Na₄[(dcb)₂RuCl₂] in methanol and adding 7.0 mmol of the ancillary ligand. The reaction mixture is heated to reflux for 7 h under argon and roto-evaporated. The resulting solid is dissolved in water. After filtration the salt is precipitated by addition of an acid solution. The solid is redissolved in methanol and purified chromatographically on a methanol/sephadex LH-20 column.

2.3. Thin-layer sandwich-type solar cell. Transparent TiO₂ films for photoelectrochemical measure-

ments were obtained following the procedure described in the literature [17]. The complexes were attached to the TiO₂ surface by immersing the processed electrode in a *ca* 10⁻⁴ M ethanolic solution of each dye. Photoelectrochemical experiments were carried out by using the dye-sensitized TiO₂ film arranged as a thin-layer sandwich-type solar cell.

The thin-layer solar cell consists of two electrodes composed by TCO substrates (Asahi) and an intermediary layer. The photoanode is a fluorine-doped SnO₂ substrate with the TiO₂ film sensitized by the complex. The counterelectrode presents a transparent platinum film on its conductive surface. The redox mediator and electrolyte, 0.03 M I₂/0.3 M LiI solution in acetonitrile (or acetonitrile/3-methyl-2-oxazolidinone, vol. 90/10), is placed between the two electrodes. The components of the thin-layer transparent sandwich-type solar cell are depicted in Figure 1.

2.4. Physical measurements. Absorption spectra were recorded on a Hewlett Packard HP 8453 UV-visible spectrophotometer. Preliminary performances of cells were evaluated using an Oriel system with a 200 W Hg (Xe) arc lamp, powered by an universal power supply, and interference filters to select irradiation wavelengths, as detailed elsewhere [25]. Photocurrent and voltage measurements, as well as photoaction spectra, were obtained as previously described [21, 22]. Alternatively, an Oriel system comprised of a 450 W Xe lamp model 6266 coupled to monochromator model 77200 was used. Incident irradiance was measured with a calibrated powermeter, model 70260 and the photocurrent was collected on a A. W. Sperry, model DM-8A or a Minipa, model ET-2600, digital multime-

ters. IPCE values were determined as previously described [21, 22].

3. DISCUSSION

The convenient selection of the ancillary ligands L and L' in $cis-[(dcbH_2)_2RuLL']$ provides the suitable control of the energetic and redox properties of the species. Different compounds with appropriate characteristics can be molecularly engineered enabling the design of new efficient sensitizers. The two ancillary ligands coordinated to the non-attached side of the dye can be conveniently replaced in order to adjust or tune the absorption bands to low energy wavelengths, thus enhancing its spectral response to the visible light.

The $cis-[(dcbH_2)_2RuLL']$ derivatives, in which L and/or L' are substituted pyridines such as isoquinoline (isq), 4-phenylpyridine (ppy), 4-cyanopyridine (CNpy) or water, perform efficient light conversion as molecular sensitizers of wide band-gap semiconductors in photoelectrochemical solar cells. Figure 2 illustrates the main events involved in the photoconversion process. After visible light absorption the sensitizer species $S = cis-[(dcbH_2)_2Ru^{III}LL']$ is promoted to an excited state, S^* . The new species transfers or "injects" an electron into the conduction band of the semiconductor. The redox relay must reduce the oxidized sensitizer S^+ and is regenerated at the counterelectrode in order to complete the cycle. Electron recombination is intercepted due to the fast regener-

ation of the oxidized dye S^+ by the redox mediator. As a result, the electron-hole pair is separated through the semiconductor/sensitizer interface. The system operates as a regenerative electrochemical cell converting visible light into electricity without any permanent chemical change.

The performance of the solar cells is determined by the photoaction spectra, in which incident monochromatic photon-to-current conversion efficiency (IPCE) values are plotted as a function of wavelength. Figure 3 shows the photocurrent action spectra obtained with transparent thin-layer solar cell employing $cis-[(dcbH_2)_2Ru(isq)_2]^{2+}$, $cis-[(dcbH_2)_2Ru(ppy)_2]^{2+}$, $cis-[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$ and $cis-[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ as molecular sensitizers, as well as the electronic absorption spectra of the photoanodes with dye-sensitized transparent TiO_2 films. Each action spectrum closely resembles the spectrum of the related dye adsorbed on the electrode. The electrode spectra are similar to the absorption spectra of the corresponding molecular sensitizers in methanolic solution and display MLCT ($d\pi \rightarrow \pi^*$) bands in the visible region as well as intra-ligand ($\pi \rightarrow \pi^*$) transitions in the UV region [17, 21, 22, 26–28].

High IPCE values were successfully obtained employing the mentioned derivatives, as high as 50% in the 400 to 550 nm region. Although below the values achieved by thiocyanate derivatives, commonly recognized as the best molecular sensitizer to date, the overall efficiency presented by these derivatives is similar to that obtained with related compounds with other ancillary ligands [17, 19, 20, 26–29]. These species present good light harvesting properties and perform efficient charge-transfer sensitization of nanocrystalline n -type TiO_2 .

It is noteworthy that the aqua derivatives with one different ancillary ligand were found to present a broader spectral response at low energy with high IPCE values. The proper substitution of ancillary ligands results in extended spectral sensitivity to the visible light and a consequent enhancement of the solar cell efficiency.

Several properties related to other components of the thin-layer solar cell were found to affect the overall characteristics of the system. Thin-film thickness and transparency, for instance, can be controlled through the appropriate deposition technique and influence the overall efficiency of the cell [30]. The proper concentration of donor species in the redox mediator is fundamental as observed by time-resolved experiments with dye covered TiO_2 films which confirm the formation of the oxidized complex $cis-[(dcbH_2)_2Ru^{III}LL']$ upon light excitation [31].

Sealed modules constituted by transparent thin-layer solar cells with overall active area as high as 25 cm² have also been prepared. Photoconversion per-

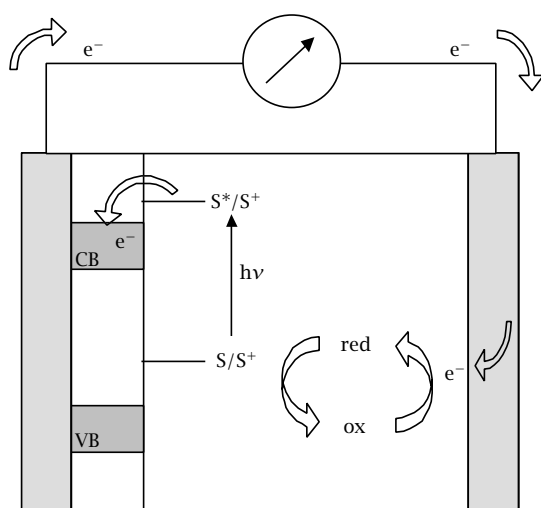


Figure 2. Schematic representation of the photoconversion process in dye-sensitized solar cells. S = molecular sensitizer. Red and ox = the reduced and oxidized forms of the redox mediator. CB and VB = conduction and valence bands.

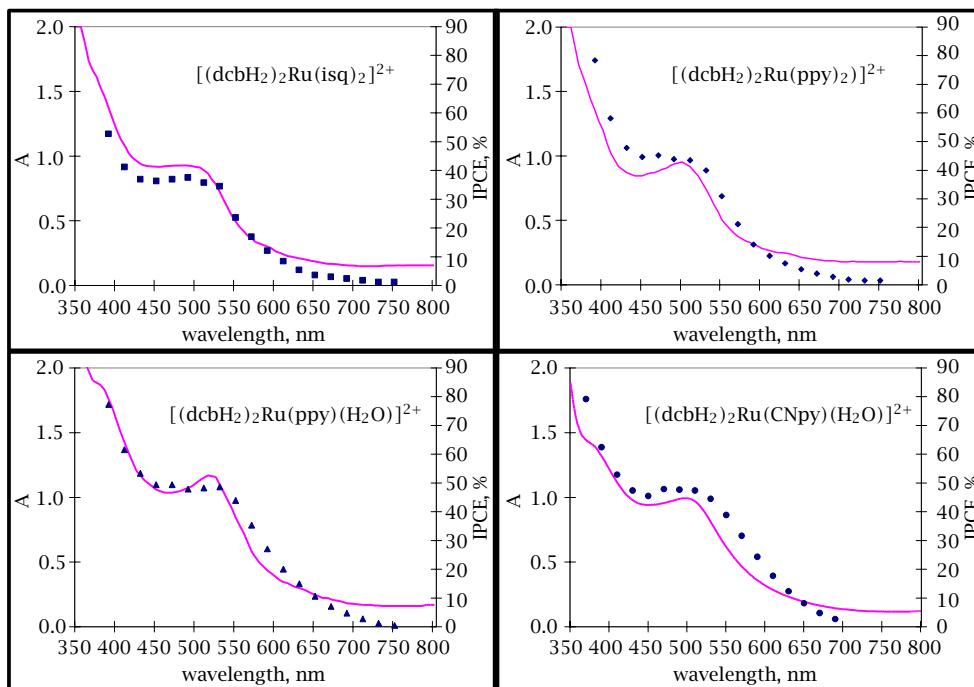


Figure 3. Electronic absorption spectra of photoanodes (—) and photocurrent action spectra of solar cells employing $[(dcbH_2)_2Ru(isq)_2]^{2+}$ (—■—), $[(dcbH_2)_2Ru(ppy)_2]^{2+}$ (—◆—), $[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$ (—▲—) and $[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ (—●—) as molecular sensitizers.

formance of the electrodes is found to be preserved on a long-term basis. The dye cells have also been successfully employed in undergraduate laboratory classes as an illustrative application of molecular devices for energy conversion.

4. CONCLUSION

Enhanced spectral response of TiO_2 to visible light has been successfully accomplished with the use of the sensitizers. The compounds present good light harvesting properties and perform efficient charge-transfer sensitization of nanocrystalline *n*-type TiO_2 . When employed in transparent regenerative solar cells, the complexes convert visible light into electricity effectively. The results confirm that the nature of the ancillary ligands plays an important role in the extension of the spectral sensitivity to the visible light, as well as in tuning the overall properties of the system for the design of molecular-level devices.

ACKNOWLEDGEMENTS

We thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Am-

paro à Pesquisa do Estado de São Paulo (FAPESP) for financial support.

References

- [1] J. R. Bolton, A. F. Haught, and R. T. Ross, *Photochemical Conversion and Storage of Solar Energy*, J. S. Connolly (ed.), Academic Press, N.Y., 1981.
- [2] K. Kalyanasundaram and M. Grätzel (eds.), *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*, Kluwer Academic Pub, Dordrecht, 1993.
- [3] J. A. Bard and M. A. Fox, *Acc. Chem. Res.* **28** (1995), 141.
- [4] P. V. Kamat, *Inter-Amer. Photochem. Soc. Newsletter* **19** (1996), 14.
- [5] G. J. Meyer (ed.), *Prog. Inorg. Chem.* **44** (1997).
- [6] G. J. Meyer, *J. Chem. Educ.* **74** (1997), 652.
- [7] H. Gerischer, M. E. Michel-Beyerle, F. Rebentrost, and H. Tributsch, *Electrochim. Acta* **13** (1968), 1509.
- [8] H. Tributsch and M. Calvin, *Photochem. Photobiol.* **14** (1971), 95.
- [9] M. P. Dare-Edwards, J. B. Goodenough, A. Hamnett, K. R. Seddon, and R. D. Wright, *Faraday Discuss. Chem. Soc.* **70** (1980), 285.

- [10] P. K. Ghosh and T. G. Spiro, *J. Am. Chem. Soc.* **102** (1980), 5543.
- [11] J. Desilvestro, M. Grätzel, L. Kavan, and J. Moser, *J. Am. Chem. Soc.* **107** (1985), 2988.
- [12] H. O. Finklea, *Semiconductor Electrodes*, H. O. Finklea (ed.), Elsevier, Amsterdam, 1988.
- [13] P. V. Kamat, *Chem. Rev.* **93** (1993), 267.
- [14] A. Mills and S. Le Hunte, *J. Photochem. Photobiol. A: Chem.* **108** (1997), 1.
- [15] A. Hagfeldt and M. Grätzel, *Chem. Rev.* **95** (1995), 49.
- [16] O. Horváth and K. L. Stevenson, *Charge Transfer Photochemistry of Coordination Compounds*, VCH, N.Y., 1993.
- [17] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, *J. Am. Chem. Soc.* **115** (1993), 6382.
- [18] C. A. Bignozzi, J. R. Schoonover, and F. Scandola, *Progr. Inorg. Chem.* **44** (1997), 1.
- [19] Md. K. Nazeeruddin, P. Péchy, and M. Grätzel, *Chem. Commun.* **18** (1997), 1705.
- [20] 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, and M. Grätzel, *J. Amer. Chem. Soc.* **123** (2001), 1613.
- [21] C. G. Garcia, N. Y. Murakami Iha, R. Argazzi, and C. A. Bignozzi, *J. Bras. Chem. Soc.* **9** (1998), 13.
- [22] C. G. Garcia, N. Y. Murakami Iha, R. Argazzi, and C. A. Bignozzi, *J. Photochem. Photobiol. A: Chem.* **115** (1998), 239.
- [23] C. G. Garcia, J. F. de Lima, and N. Y. Murakami Iha, *Coord. Chem. Rev.* **196** (2000), 219.
- [24] N. Y. Murakami Iha, *Anais Acad. Bras. Ci.* **72** (2000), 67.
- [25] N. Y. Murakami Iha and J. F. de Lima, *Inorg. Chem.* **30** (1991), 4576.
- [26] R. Argazzi, C. A. Bignozzi, T. A. Heimer, F. N. Castellano, and G. J. Meyer, *Inorg. Chem.* **33** (1994), 5741.
- [27] P. Liska, N. Vlachopoulos, M. K. Nazeeruddin, P. Comte, and M. Grätzel, *J. Am. Chem. Soc.* **110** (1988), 3686.
- [28] T. A. Heimer, C. A. Bignozzi, and G. J. Meyer, *J. Phys. Chem.* **97** (1993), 11987.
- [29] P. Péchy, F. P. Rotzinger, M. K. Nazeeruddin, O. Kohle, S. M. Zakeeruddin, R. H. Baker, and M. Grätzel, *J. Chem. Soc. Chem. Commun.* (1995), 65.
- [30] C. G. Garcia and N. Y. Murakami Iha, *I. J. Photoenergy* **3** (2001), 139.
- [31] C. G. Garcia, C. J. Kleverlaan, C. A. Bignozzi, and N. Y. Murakami Iha, X Brazilian Meeting on Inorganic Chemistry, Florianópolis, 2000, P52 and 14th Intern. Symp. Photochem. Photophys. Coord. Comp., Veszprém, 2001, submitted; manuscript in preparation.

