

4-Phenylpyridine as ancillary ligand in ruthenium(II) polypyridyl complexes for sensitization of n-type TiO₂ electrodes

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Abstract

In this work, the novel molecular sensitizers $cis-[(dcbH_2)_2Ru(ppy)_2]^{2+}$ and $cis-[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$ where $dcbH_2 = 4,4'-(CO_2H)_2-2,2'$ -bipyridine and $ppy = 4$ -phenylpyridine, have been prepared and their effectiveness for sensitization of n-type TiO₂ electrodes in thin-layer transparent solar cells has been investigated. Spectral and photoelectrochemical measurements show that both dyes, when anchored to nanocrystalline TiO₂, present good light harvesting properties and provide enhanced spectral response of the TiO₂ electrodes to visible light in regenerative solar cells. The derivative with one coordinated ppy , $cis-[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$ resulted in considerably higher incident photon-to-current conversion efficiency values, as well as in a broader spectral response in longer wavelengths than the corresponding derivative with two coordinated ppy , $cis-[(dcbH_2)_2Ru(ppy)_2]^{2+}$. The results show that the number of azine ligands coordinated to the non-attached side of the $(dcbH_2)_2RuLL'$ dye can be controlled and plays an important role to extend spectral sensitivity to the visible light, as well as in tuning the overall properties of the system. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photosensitization; Solar cell; Energy conversion; Ru-dye sensitized TiO₂

1. Introduction

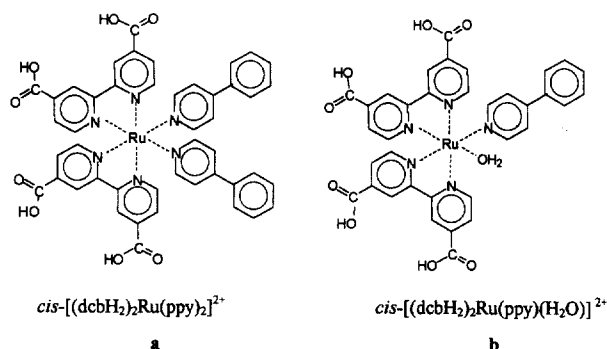
The development of efficient devices for solar energy conversion has been a very active research field. Historically, chemically based systems such as photogalvanic and photoelectrochemical cells have been developed as an alternative for the solid-state silicon-based cells [1–6]. The use of coordination compounds as light absorbers, for instance the well-known $[Ru(bpy)_3]^{2+}$, where bpy is 2,2'-bipyridine, was one of the first approaches to convert low-energy starting materials, such as H₂O, into high-energy products, for instance H₂ and O₂ in homogeneous cells. Although simple and elegant, these systems presented low efficiencies due to fast recombination of the photoredox products in the solution [2,3,7–12]. This limitation was overcome with the semiconductor based photoelectrochemical cells, in which a semiconductor electrode was the light absorber, with the band bending separating the oxidation and reduction sites. These cells displayed low efficiency conversion of visible light into redox energy and were limited to the band-gap of the semiconductors employed [2,9,13]. Dye sensitization was of limited

utility because of sub-monolayer coverage and low absorptivities, although it presented advantages over direct band to band excitation as in conventional solar cells due to the reduction of electron-hole recombination [14,15].

Dye sensitization of wide band-gap semiconductors such as n-type TiO₂ was greatly improved by introduction of high surface area due to a porous nanocrystalline film. This has led to a high absorption of light and efficient conversion of visible photons into electricity in photoelectrochemical devices [16–18]. Among many $cis-[(dcbH_2)_2RuLL']$ complexes, where L and L' = ancillary ligands, studied as sensitizers, the best solar-to-electric power conversion has been achieved by thiocyanate derivatives [19–22]. In the present work, we extend our studies on dye sensitization of n-type TiO₂ with $cis-[(dcbH_2)_2RuLL']$ derivatives [20,23] to Ru(II) complexes containing 4-phenylpyridine, ppy , as the ancillary ligand, based on the properties previously investigated for ruthenium complexes [24] in attempt to improve to improve the efficiency of the solar cells. The novel molecular sensitizers $cis-[(dcbH_2)_2Ru(ppy)_2]^{2+}$ (**a**) and $cis-[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$ (**b**) have been prepared and their effectiveness for the sensitization of n-type TiO₂ elec-

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trodes in thin-layer transparent solar cells has been investigated.



2. Experimental details

2.1. Materials

Ppy = 4-phenylpyridine, dcbH₂ = 4,4'-(CO₂H)₂-2,2'-bipyridine (Aldrich) and RuCl₃ · xH₂O (Aldrich) 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 complexes cis-[(dcbH₂)₂Ru(ppy)₂]²⁺ and cis-[(dcbH₂)₂Ru(ppy)(H₂O)]²⁺

The cis-[(dcbH₂)₂RuCl₂] complex was synthesized following a slight modification of the procedure previously described [19], by adding 53 mg (2.6 mmol) of RuCl₃ · xH₂O to a solution of 37 mg (15 mmol) of dcbH₂ in 10 ml of DMF. The complexes **a** and **b** were obtained starting from the anionic form of [(dcbH₂)₂RuCl₂], dissolving 140 mg (0.20 mmol) of Na₄[(dcb)₂RuCl₂] in 40 ml of methanol and adding 1.1 g (7.1 mmol) of 4-phenylpyridine. The reaction mixture was heated to reflux for 7 h under argon and roto-evaporated. The resulting solid was dissolved in water, the solution filtered and the salt precipitated by addition of a solution of HClO₄. After washing with a pH 1.9 HClO₄ solution, the solid was redissolved in methanol and purified chromatographically on a methanol/sephadex LH20 column. Two fractions were separated, an orange one, assigned to the bis-coordinated species and a red one, assigned to the mono-coordinated one. Anal. Calcd. for [(dcbH₂)₂Ru(ppy)₂](ClO₄)₂, RuC₄₆H₃₄N₆O₁₆Cl₂: C, 50.3; N, 7.7; H, 3.1. Found: C, 50.3; N, 7.0; H, 4.2. Anal. Calcd. for [(dcbH₂)₂Ru(ppy)(H₂O)](ClO₄)₂ · 5H₂O, RuC₃₆H₂₇N₅O₁₇Cl₂ · 5H₂O: C, 40.6; N, 6.6; H, 3.5. Found: C, 39.8; N, 6.1; H, 3.2.

2.3. Thin-layer films

Transparent, nanocrystalline TiO₂ films for photoelectrochemical measurements were prepared using titanium isopropoxide as previously described in the literature [19]. Preliminary experiments were performed using ITO and fluorine-doped SnO₂ glasses supplied by Asahi. The complexes were attached to the TiO₂ surface by immersing the processed electrode in a ~10⁻⁴ M ethanolic solution of each dye. Photoelectrochemical experiments were carried out by using the dye sensitized TiO₂ film incorporated into a thin-layer sandwich-type solar cell. The cell consists of a fluorine-doped SnO₂ glass, with the TiO₂ film sensitized by the complex, as a photoanode, 0.03 M I₂/0.3 M LiI solution in acetonitrile, as the redox relay and electrolyte and a transparent Pt film on a TCO glass as a counter electrode. The components of the thin-layer transparent sandwich-type solar cell are depicted in Fig. 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 200 W Hg (Xe) arc lamp, powered by an Oriel universal power supply and Oriel interference filters to select irradiation wavelengths, as detailed elsewhere [25]. Photocurrent and voltage measurements were performed with an A.W. Sperry digital multimeter, model DM-8A. Photoaction spectra were obtained with an Osram 150 W Xe lamp coupled to a Applied Photo-physics monochromator. Incident irradiance was measured with a calibrated Centronic photodiode, model OSD 100-7Q and the photocurrent was collected on a Kontron digital multimeter, model DMM 4021.

3. Results and discussion

The absorption spectra of complexes **a** and **b** in methanol are shown in Fig. 2. Analogously to similar complexes, they exhibit a π → π* intra ligand transition in the UV region and metal to ligand charge transfer (MLCT), dπ → π* bands in the visible [26,27]. The MLCT bands for the mono-4-phenylpyridine complex are red-shifted with respect to those of the bis-4-phenylpyridine species.

The spectra for the two derivatives adsorbed on TiO₂ in the transparent electrodes are shown in Fig. 3. A comparison between Figs. 2 and 3 shows that the absorption spectra of the dyes in solution is similar to the spectra for the dyes adsorbed on the electrode, but the electrode spectra are slightly red-shifted from the absorbance spectra of the dyes in solution. Red shifted absorptions are related to the stabilization of the π* accepting bipyridine orbitals by the TiO₂ surface accompanied by the adsorption of the dye to the colloidal TiO₂ particle surfaces [27–29].

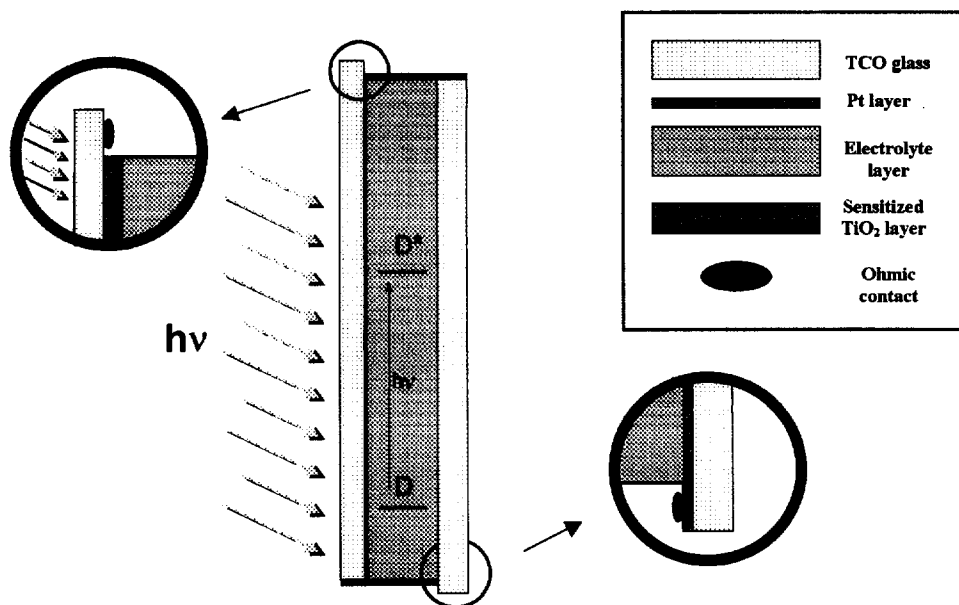


Fig. 1. Thin-layer transparent sandwich-type solar cell and its components.

Fig. 4 presents the photocurrent action spectra of the cells with the two different dyes, where the incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The IPCE values were calculated by using the equation

$$\text{IPCE}\% = \frac{\text{photocurrent density} (\mu\text{A}/\text{cm}^2)}{\text{wavelength (nm)} \times \text{irradiance} (\text{W}/\text{m}^2)} \times 100.$$

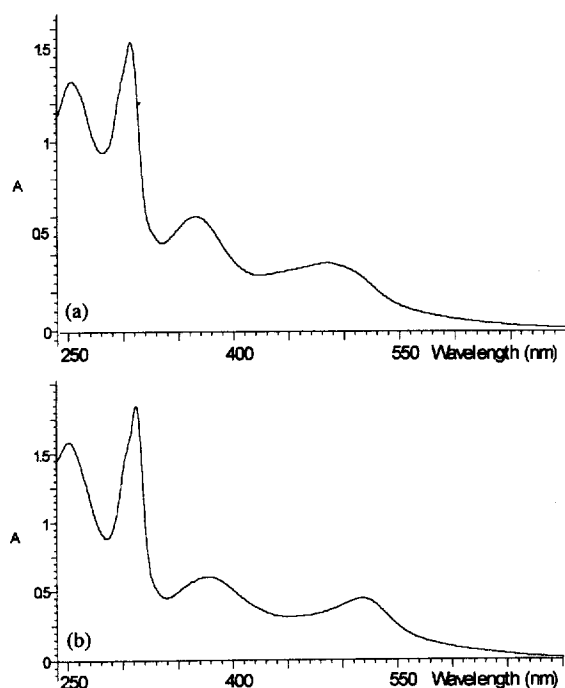


Fig. 2. UV-visible absorption spectra of $[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})_2](\text{ClO}_4)_2$ (a) and $[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (b) in methanolic solution.

A comparison between Figs. 3 and 4 shows that the photocurrent action spectra closely resemble the spectra for the dyes adsorbed on the electrode. The IPCE values obtained for these new complexes are good, ranging up to 50% in the wavelength region between 400 and 550 nm, comparable to or even higher than that obtained by other dyes previously studied by us [20,23].

The result obtained for the derivative with one coordinated ppy, $\text{cis}-[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})(\text{H}_2\text{O})]^{2+}$ is distinct to that obtained for the corresponding derivative with two coordinated ppy, $\text{cis}-[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})_2]^{2+}$. For sensitizers of the type $\text{cis}-[(\text{dcbH}_2)_2\text{RuLL}']$, changes in the co-ligands are expected to affect the properties of the complexes and therefore to influence the overall efficiency in photoelectrochemical devices [20,28,29]. It is noteworthy that the IPCE values obtained for the mono-ppy complex are quite higher than those obtained for the *bis*-coordinated one. This species with two different ancillary ligands presents also a broader spectral

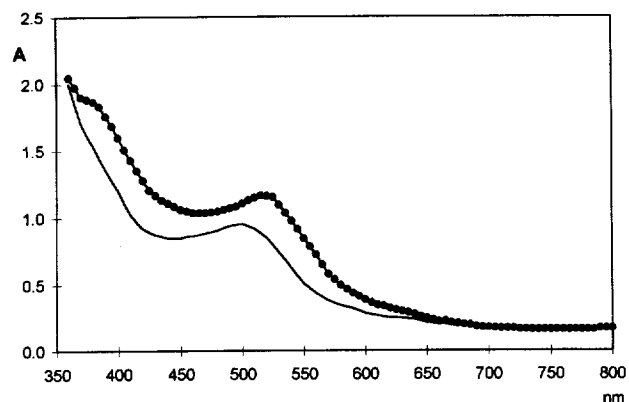


Fig. 3. Absorption of $[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})_2](\text{ClO}_4)_2$ (—) and $[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (- - -) adsorbed on TiO_2 films coated on TCO electrodes.

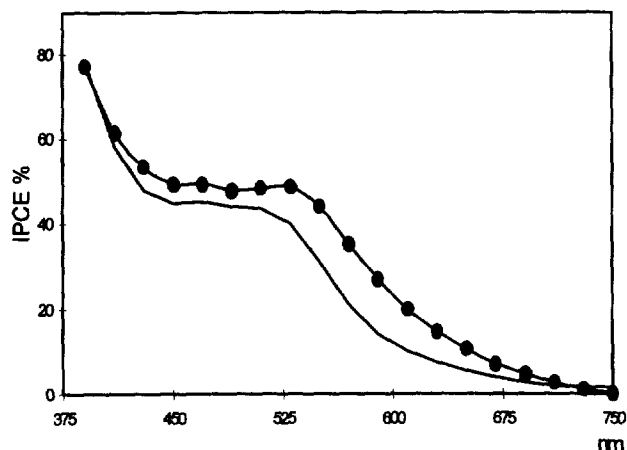


Fig. 4. Photocurrent action spectra obtained for nanocrystalline TiO_2 films coated with $[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})_2](\text{ClO}_4)_2$ (—) and $[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (- - -) as sensitizers in 0.03 M I_2 and 0.3 M LiI in acetonitrile as the redox relay and electrolyte in transparent sandwich-type solar cells.

response in longer wavelengths when compared to the bis-coordinated ppy derivative, as the most interesting feature.

4. Conclusions

Enhanced spectral response of TiO_2 to visible light has been successfully accomplished with the use of *cis*- $[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})_2]^{2+}$ and *cis*- $[(\text{dcbH}_2)_2\text{Ru}(\text{ppy})(\text{H}_2\text{O})]^{2+}$ as sensitizers. These novel compounds with one or two 4-phenylpyridine as ancillary ligands present good light harvesting properties and perform efficient charge-transfer sensitization of nanocrystalline n-type TiO_2 . When employed in regenerative solar cells, the complexes convert light into electricity effectively, with IPCE values ranging ~50% up to 550 nm. The overall efficiency presented is higher than the one obtained by some similar compounds with other ancillary ligands reported in the literature [19,20,23]. The results show that the number of azine ligands coordinated to the non-attached side of the $(\text{dcbH}_2)_2\text{RuLL}'$ dye plays an important role in the extension of the spectral sensitivity to visible light, as well as in tuning the overall properties of the system for the design of molecular-level devices.

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