

Catechol as an efficient anchoring group for attachment of ruthenium–polypyridine photosensitisers to solar cells based on nanocrystalline TiO₂ films

Craig R. Rice,^a Michael D. Ward,^{*a} Mohammed K. Nazeeruddin^b and Michael Grätzel^b

^a School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS.
E-mail: mike.ward@bristol.ac.uk

^b Laboratory for Photonics and Interfaces, Institute of Physical Chemistry, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland

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The Ru(II)–polypyridyl complexes [Ru(H₂L)(terpy)] [PF₆]₂ (**1**) and [Bu₄N][Ru(H₂L)(NCS)₃] (**2**) (H₂L = 4'-(3,4-dihydroxyphenyl)-2,2':6',2''-terpyridine), in which H₂L is coordinated as a terpyridyl fragment with a catechol site pendant from the C4' position, adhere effectively to nanocrystalline TiO₂ (anatase) surfaces *via* the pendant catechol group; incident photon-to-current conversion efficiency values of up to 50% were obtained in their photocurrent action spectra, suggesting that the catechol unit may be a convenient and effective anchoring group for attaching dyes to TiO₂-based photovoltaic cells.

Polypyridine complexes of Ru(II) are well established as photosensitisers for use on photovoltaic cells based on nanocrystalline TiO₂.¹ There are several characteristics of the photosensitiser which need to be optimised, such as a high electron-injection efficiency from the MLCT excited state to the conduction band of the semiconductor; an absorption spectrum which matches as far as possible the solar emission spectrum; and a high affinity for the TiO₂ surface, which is provided by peripheral anchoring groups.

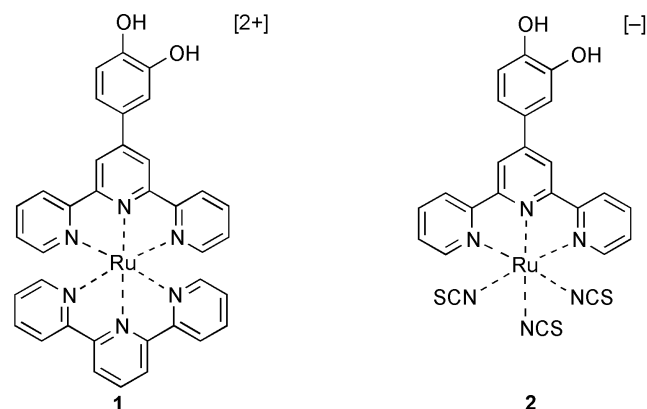
In most of the studies so far these anchoring groups are carboxylate, with the two complexes *cis*-[Ru(4,4'-dcbipy)₂(NCS)₂](4,4'-dcbipy = 2,2'-bipyridine-4,4'-dicarboxylic acid)² and [Ru(4,4',4''-tcterpy)(NCS)₃][−] (4,4',4''-tcterpy = 2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid)³ being the most extensively studied; the latter of these is a particularly effective photosensitiser because its absorption spectrum extends much further into the red region of the spectrum than previous complexes. However, there are two disadvantages to the use of carboxylates as anchoring groups. Firstly their ground state pK_a values are too low to ensure strong binding.⁴ Secondly, in the presence of water, slow desorption of the photosensitisers can still occur which may limit the long-term stability of the cells. For this reason other anchoring groups have been investigated, such as the phosphonate group in the complex [Ru(Me₂bipy)(HP-terpy)(NCS)] (Me₂bipy = 4,4'-dimethyl-2,2'-bipyridine; H₂Pterpy = 2,2':6',2''-terpyridine-4'-phosphonate) which was found to anchor to TiO₂ considerably more effectively than carboxylate-substituted complexes.⁵ The difference in the binding affinity of the complexes containing carboxyl and phosphonate groups is in part due to the differences in the pK_a values of the complexes. The pK_a of the phosphonate group is reported as 6.5, whereas that of carboxylic acid is 3.5.⁶

Here we describe the investigation of ruthenium(II)–polypyridine complexes **1** and **2** (see below), containing a pendant catechol (1,2-dihydroxyphenyl) group, as photosensitisers for

photovoltaic cells. These complexes are based on the terpyridyl–catechol ligand H₂L, which we first prepared a few years ago.⁷ Since it bears a single substituent at the central C-4' position of the terpyridyl unit, it is particularly easy to prepare; and given the known affinity of catecholate for Ti(IV) ions,⁸ and its ability to adsorb onto a TiO₂ surface,⁹ these complexes seemed ideal candidates to investigate as photosensitisers.

Of the complexes, [Ru(terpy)(H₂L)][PF₆]₂ [complex **1**; H₂L = 4'-(3,4-dihydroxyphenyl)-2,2':6',2''-terpyridine] was available from previous work.⁷ [Bu₄N][Ru(H₂L)(NCS)₃] (complex **2**) was prepared by reaction of H₂L with commercial hydrated RuCl₃ in refluxing EtOH for 3 hours, to give a precipitate of [Ru(H₂L)Cl₃]; reaction of this (crude) with excess potassium thiocyanate in aqueous DMF (1 : 1) at reflux for 3 hours afforded a solution containing the purple anion [Ru(H₂L)(NCS)₃][−] which was purified by chromatography on Sephadex-G25 eluting with water, followed by precipitation as the [Bu₄N]⁺ salt. The overall yield was *ca.* 15%, and the complex was characterised on the basis of its negative-ion electrospray mass spectrum [*m/z* 616 (100%, {Ru(H₂L)(NCS)₃})[−] and 557 (50%, {Ru(HL)(NCS)₂})[−]] as well as a correct elemental analysis.

The nanocrystalline TiO₂ (anatase) films, of thickness 14 microns, were prepared on conducting glass using a previously described procedure.^{2,10} The dye solutions were prepared in the concentration range of 1 × 10^{−5} to 2 × 10^{−4} M in ethanol. The electrodes were heated for 10 minutes at 450 °C and then allowed to reach ≈ 50 °C. The hot electrodes were dipped into the dye solution (2 × 10^{−4} M) for 3 hours. However, when the concentration of the dye solution is 1 × 10^{−5} M, then the dipping time was increased to 5 hours.



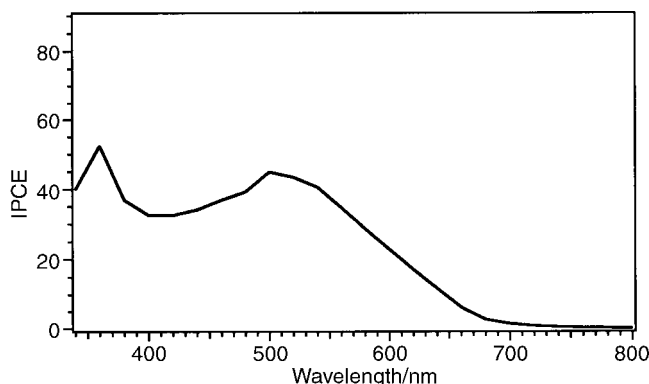


Fig. 1 Photocurrent action spectrum obtained with the complex **1** attached to nanocrystalline TiO_2 films. The incident photon-to-current conversion efficiency is plotted as a function of the wavelength of the exciting light. For further details, see text.

It was noticed that the grafting properties of complexes **1** and **2**, containing catechol functional groups, on to the TiO_2 surface are superior and faster than those of the complexes that contain carboxylic acid groups.

The dark coloured films were tested in a photovoltaic cell† in conjunction with 600 mM dimethylpropylimidazolium iodide and 100 mM of iodine in methoxyacetonitrile as redox electrolyte. Fig. 1 shows the photocurrent action spectrum of such a cell containing complex **1**, where the incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The features are similar to the absorption spectrum.⁷ The incident photon-to-current conversion efficiency value in the peak maximum region is about 50%. The overlap integral of this curve with the standard global AM 1.5 solar emission spectrum yields a measured photocurrent density of 5.5 mA cm^{-2} ; the overall efficiency of **1** is 1.9. The open circuit potential (measured under the same irradiation intensity) is 513 mV and the fill factor is 0.67. Complex **2** under similar conditions shows a broad feature in the photocurrent action spectrum covering the entire visible spectrum up to 800 nm (Fig. 2), consistent with the known absorption properties of the $[\text{Ru}(\text{terpy})(\text{NCS})_3]^-$ chromophore;³ the IPCE value in the plateau region is about 20%. The current measured using complex **2** as sensitizer is 3.25 mA cm^{-2} and the open circuit potential is 617 mV, with a fill factor of 0.75; the overall efficiency of **2** is 1.5.

Despite the very effective anchoring of the complexes **1** and **2** onto the TiO_2 surface, the measured IPCE values are lower than those obtained in related complexes using carboxylate anchor groups. A likely reason for this may be aggregation of

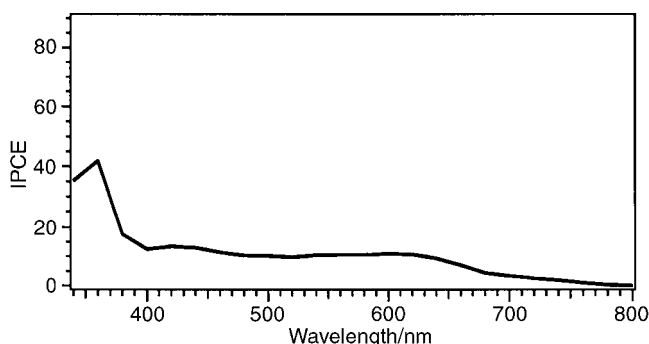


Fig. 2 Photocurrent action spectrum obtained with the complex **2** attached to nanocrystalline TiO_2 films. The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light. For further details, see text.

the dye molecules on the TiO_2 surface. For this reason the results presented here are lower-limit and we are currently trying to improve the IPCE values by preparing the dye solutions in various solvents with different additives such as $3\alpha,7\alpha$ -dihydroxy-5 β -cholic acid (Cheno) and DMSO; we find the presence of Cheno helps to prevent surface aggregation of the sensitizer.

In conclusion it is clear that pendant catechol groups present a synthetically convenient method of anchoring photosensitizer complexes tightly to TiO_2 surfaces, and are therefore of considerable promise for the development of new and more effective photosensitisers.

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Notes and references

† The cells used for the photoelectrochemical experiments had a surface area of 0.7 cm^2 , of which 0.44 cm^2 was illuminated using a 450W Xenon light source focussed to give 1000 W m^{-2} (the equivalent of one sun at AM 1.5) at the surface of the test cell. The spectral output of the lamp was matched in the region of 350 to 750 nm with the aid of a Schott KG-5 sunlight filter so as to reduce the mismatch between the simulated and the true Solar spectrum to less than 2%. The differing intensities were regulated with neutral wire mesh attenuators. The applied potential and measured cell current were determined using a Keithley Model 2400 digital source meter. The counter-electrode used was platinised, fluorine-doped tin oxide glass. The current–voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process is fully automated using Wave-metrics software. A similar data acquisition system is used to control the incident photon-to-current conversion efficiency (IPCE) measurement. Under full computer control, light from a 300W Xe lamp is focussed through a high throughput monochromator onto the photovoltaic cell under test. The monochromator is incremented through the visible spectrum to generate the IPCE (λ) curve as defined by:

$$\text{IPCE}(\lambda) = 1240(I_{\text{sc}}/\lambda\phi)$$

where λ is the wavelength, I_{sc} is the current at short circuit (mA cm^{-2}) and ϕ is the incident radiative flux (W m^{-2}). This curve can be derived from the measured absorption spectrum of the adsorbed photosensitizer for comparison.

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