

Efficient panchromatic sensitization of nanocrystalline TiO₂ films by a black dye based on a trithiocyanato–ruthenium complex

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A black trithiocyanato–ruthenium(II) terpyridyl complex where the terpyridyl ligand is substituted by three carboxyl groups in 4,4',4''-positions achieves very efficient panchromatic sensitization of nanocrystalline TiO₂ solar cells over the whole visible range extending into the near-IR region up to 920 nm.

Dye-sensitized nanocrystalline TiO₂ solar cells are presently under intensive investigation.^{1–3} So far, the best performing charge transfer sensitizer employed for such an application is a *cis*-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) complex,⁴ yielding solar to electric power conversion efficiency of 10% under standard AM 1.5 condition. To improve further the efficiency of such systems, an enhanced spectral response of the sensitizer in the red and near-IR region is required. The present study reports the synthesis and characterization of a new class of trithiocyanato–ruthenium(II) terpyridyl complex. Substitution of the terpyridyl ligand by three carboxyl groups in 4,4',4''-positions yields a black dye displaying very efficient panchromatic sensitization over the whole visible range extending into the near-IR region up to 920 nm.

The oxidation of 4,4',4''-trimethyl-2,2':6',2''-terpyridine^{5,6} (0.32 g, 1.16 mmol) was carried out in sulfuric acid (4 ml), with chromium trioxide (1.05 g, 10.5 mmol) at 75 °C, yielding 4,4',4''-tricarboxy-2,2':6',2''-terpyridine (0.15 g, 41%).[†]

4,4',4''-Tricarboxy-2,2':6',2''-terpyridine (127 mg) was esterified by refluxing in methanol (15 ml) and sulfuric acid (70 mg) for 3 days. The white crystals were filtered, washed with methanol and diethyl ether successively, yielding 4,4',4''-trimethoxycarbonyl-2,2':6',2''-terpyridine L (102 mg, 72%).[‡]

The [RuLCl₃] complex was synthesized by adding a solution of 4,4',4''-trimethoxycarbonyl-2,2':6',2''-terpyridine (40 mg), in dichloromethane (20 ml), to a solution of hydrated ruthenium trichloride (26 mg) in ethanol (30 ml). The reaction mixture was refluxed for 2 h and the solution was concentrated to 20 ml. The precipitated complex was collected and washed thoroughly with ethanol to remove any unreacted ruthenium trichloride (yield 48 mg, 79%).[§]

The complex [NH₄Et₃][RuL(NCS)₃] **1** was obtained by refluxing [RuLCl₃] (48 mg) and ammonium thiocyanate (100 mg) in dmf–water for 3.5 h at 120 °C, in the dark under an argon atmosphere. The ester groups of the terpyridine ligand were hydrolysed by further refluxing for 15 h in the presence of triethylamine (6 ml). The isolated solid was recrystallised from methanol–diethyl ether (yield 39 mg, 69%).[¶]

The UV–VIS absorption spectrum of **1** in ethanol shows an intense metal-to-ligand charge transfer band at 620 nm [Fig. 1(a)], with a molar absorption coefficient of 6500 dm³ mol⁻¹ cm⁻¹. Bands at 291 and 329 nm with a distinct shoulder at 340 nm are assigned to the intraligand π – π^* transition of the 4,4',4''-tricarboxy-2,2':6',2''-terpyridine ligand. The interesting feature of complex **1** is the red-shifted MLCT absorption band in the visible region compared to the [Ru(tpy)₂]²⁺ (tpy = 2,2':6',2''-terpyridine) family.⁷ The three thiocyanato anionic ligands stabilize the excited states by electron donation to Ru causing a red shift in the MLCT bands. The electrochemical data of **1** suggest that the red shift in the MLCT is due to the

decrease in the π^* level of the 4,4',4''-tricarboxy-2,2':6',2''-terpyridine ligand and an increase in the energy of the t_{2g} metal orbital.

The MLCT and the π – π^* bands of **1** were displaced to higher energy (590 nm) upon deprotonation of the carboxyl groups, which could be due to increase in the energy of the π^* orbital of the 4,4',4''-tricarboxy-2,2':6',2''-terpyridine ligand. When excited within the MLCT absorption band, **1** in ethanol solution at 298 K, exhibits a luminescence (measured as described in ref. 4) consisting of a single band with a maximum at 950 nm [Fig. 1(b)] and a lifetime of 18 ± 5 ns.

The cyclic voltammogram of **1** measured in dmf containing 0.1 M [NBu₄][CF₃SO₃] shows one quasireversible wave at 0.6 V (vs. Ag/AgCl), which is attributed to the [Ru^{II/III}L(NCS)₃] redox couple. In the negative potential range two irreversible waves at –1.1 and –1.2 V (vs. Ag/AgCl) are observed which are assigned to ligand reduction. A monolayer of complex **1** was adsorbed from a 2 × 10⁻⁴ M solution in ethanol, containing 40 mM sodium taurodeoxycholate, as a co-adsorbent, onto a 12 nm thick nanocrystalline TiO₂ (anatase) film prepared on conducting glass as previously described.⁴ The black film exhibited striking performance when tested in a photovoltaic cell in

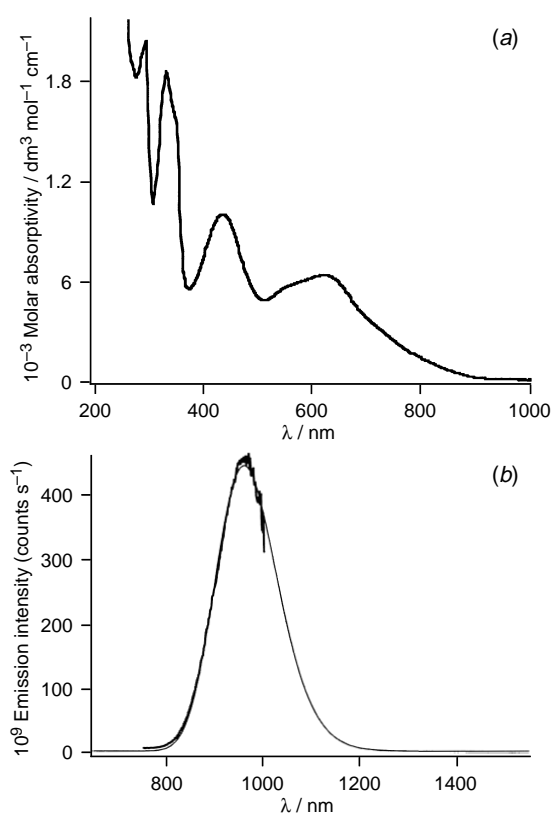


Fig. 1 (a) Absorption spectrum of complex **1** in ethanol solution and (b) emission spectrum in ethanol solution at room temperature. The smoother curve corresponds to a Gaussian fit (instrument limit is 1000 nm).

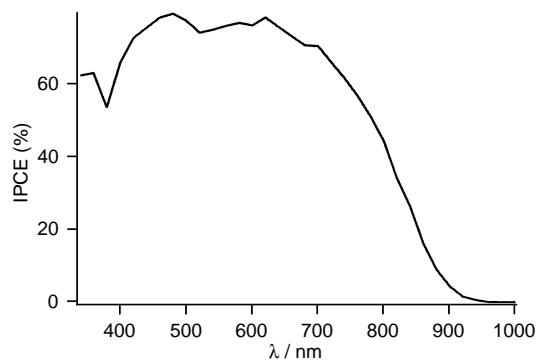


Fig. 2 Photocurrent action spectrum obtained with a nanocrystalline TiO₂ film supported onto a conducting glass sheet and derivatized with complex **1**. The incident photon to current conversion efficiency is plotted as a function of wavelength. A sandwich type cell configuration was used to measure this spectrum.

conjunction with a redox electrolyte such as 0.9 M LiI and 0.1 M LiI₃ in propylene carbonate.

Fig. 2 shows the photocurrent action spectrum of such a cell where the incident photon to current conversion efficiency (IPCE) is plotted as a function of wavelength. Experimental details are described elsewhere.⁴ The broad feature appears covering the entire visible spectrum and extending into the near-IR region up to 920 nm, the IPCE value in the plateau region being *ca.* 80%. Taking the light losses in the conducting glass into account the efficiency of electric current generation is practically 100% over a broad wavelength range extending from 400 to 700 nm. The overlap integral of this curve with the standard global AM 1.5 solar emission spectrum yields a photocurrent density of 20 mA cm⁻² and the first results obtained with these cells in the sun have confirmed these expectations. The discovery of this new black dye exhibiting enhanced light harvesting in the red and near-IR region opens

up the way to improve significantly the overall efficiency of nanocrystalline photovoltaic devices.

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Footnotes and References

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† MS (70 eV, CI, NH₃): *m/z* (rel. int.) 366 (12.2, M + 1), 365 (12.6, M), 322 (16.4), 321 (55.1, M - 44), 293 (4.1), 231 (1.3, M - 3 × 44 + 3), 79 (100). ¹H NMR (D₂O–NaOH): δ 7.52 (2 H, d), 8.13 (2 H, s), 8.31 (2 H, s), 8.43 (2 H, d).

‡ Mp 238–239 °C (MeOH). Anal. for C₂₁H₁₇N₃O₆. Calc.: C, 61.92; H, 4.21; N, 10.31. Found: C, 61.90; H, 4.17; N, 10.30%. MS (thermospray, CI, NH₄OAc): *m/z* (rel. int.): 408 (100; M + 1). ¹H NMR (CDCl₃): δ 4.04 (3 H, s), 4.05 (6 H, s), 7.94 (2 H, d), 8.90 (2 H, d), 9.03 (2 H, s), 9.13 (2 H, s). ¹³C NMR (CDCl₃): δ 165.7 (s), 165.6 (s), 156.5 (s), 156.1 (s), 150.1 (d), 139.9 (s), 138.6 (s), 123.27 (d), 121.1 (d), 120.8 (d), 52.8 (q), 52.7 (q).

§ Anal. for C₂₁H₁₇Cl₃N₃O₆Ru. Calc.: C, 41.02; H, 2.78; N 6.83. Found: C, 40.96; H, 2.75; N, 6.88%.

¶ Anal. for C₂₇H₃₁N₇O₈RuS₃. Calc.: C, 41.64; H, 4.01; N, 12.58. Found: C, 41.85; H, 4.05; N, 12.14%. ¹H NMR (D₂O–NaOH): δ 9.09 (2 H, d), 8.76 (4 H, s), 8.14 (2 H, d), 3.18 (6 H, q), 1.28 (9 H, t).

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