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FULL PAPER

A new efficient photosensitizer for nanocrystalline solar cells: synthesis and characterization of *cis*-bis(4,7-dicarboxy-1,10-phenanthroline)dithiocyanato ruthenium(II)

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Received 27th March 2000, Accepted 3rd July 2000
Published on the Web 31st July 2000

The complexes $[NBu_4]_{2n}$[*cis*-Ru$(H_{2-n}$dcphen$)_2X_2$] ($n = 0$ or 1; H_2dcphen; = 4,7-dicarboxy-1,10-phenanthroline; X = Cl, CN or SCN) were synthesized and spectroscopically characterized as a new class of photosensitizers. The energy levels of the LUMO and HOMO of *cis*-[Ru(H_2dcphen$)_2(NCS)_2$] were estimated to be −1.02 and 0.89 V (*vs.* SCE), respectively, slightly more positive than those of $[NBu_4]_{2n}$[*cis*-Ru$(H_{2-n}$dcbpy$)_2(NCS)_2$] ($n = 0$ or 1; H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridine). A more intense and broader MLCT absorption of $[NBu_4]_{2n}$[*cis*-Ru$(H_{2-n}$dcphen$)_2(NCS)_2$] ($n = 0$ or 1) than that of $[NBu_4]_{2n}$[*cis*-Ru$(H_{2-n}$dcbpy$)_2(NCS)_2$] ($n = 0$ or 1) was observed in ethanol solution at around 525 nm in the visible region. It is demonstrated that the new complexes act as efficient light harvesting antennae for dye-sensitized solar cells. A $[NBu_4]_{2n}$[*cis*-Ru(Hdcphen$)_2(NCS)_2$] sensitized nanocrystalline TiO_2 film shows a remarkable solar light to electrical power conversion efficiency of 6.1% at 100 mW cm^{-2} of AM 1.5.

Introduction

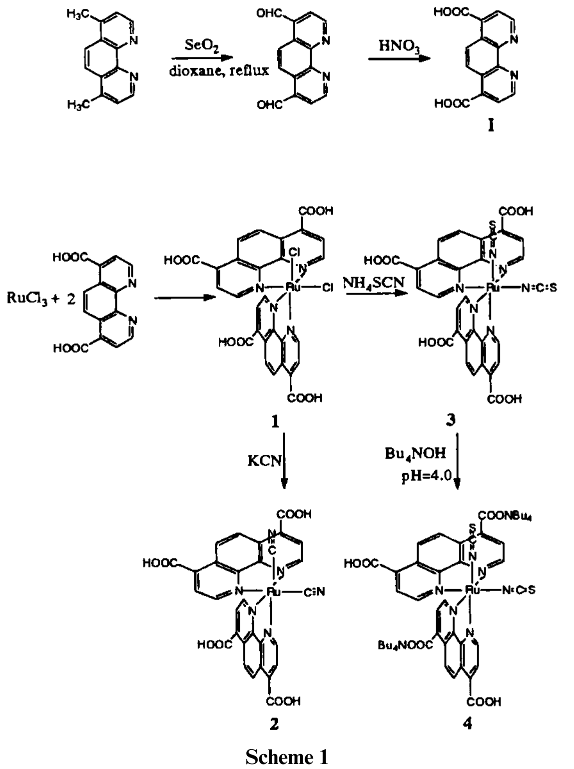
Photosensitization of porous nanocrystalline TiO_2 film electrodes using ruthenium polypyridine complexes has intensively been investigated for solar cell applications.[1–7] An important step for the next generation of solar cells based on this technology is to prepare sensitizers that have an intense response in the solar spectrum *cis*-[Ru(H_2dcbpy$)_2(NCS)_2$] (H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) is one of the most efficient sensitizers for this application reported to date.[5–7]

The chemistry of 1,10-phenanthroline complexes of ruthenium is often very similar to that of corresponding 2,2′-bipyridyl complexes.[8,9] Phenanthroline, however, is structurally more rigid and symmetrical; thus we could expect different optical properties in its complexes. Recently, we reported that a tetrabutylammonium salt of *cis*-bis(1,10-phenanthroline-4,7-dicarboxylate)dithiocyanato ruthenium(II) $[NBu_4]_2$[*cis*-Ru(Hdcphen$)_2(NCS)_2$] shows a remarkable photosensitization when applied to TiO_2 based solar cells.[10] In this paper we would like to report a comparison of the characteristics of $[NBu_4]_{2n}$[*cis*-Ru$(H_{2-n}$dcphen$)_2(NCS)_2$] ($n = 0$ or 1) with those of $[NBu_4]_{2n}$[*cis*-Ru$(H_{2-n}$dcbpy$)_2(NCS)_2$] ($n = 0$ or 1).

Experimental

Materials

All materials were reagent grade and used as received unless otherwise noted. *cis*-Dichlorobis(4,7-dicarboxy-1,10-phenanthroline)ruthenium(II) **1**, *cis*-dicyanobis(4,7-dicarboxy-1,10-phenanthroline)ruthenium(II) **2** and *cis*- bis(4,7-dicarboxy-1,10-phenanthroline)dithiocyanato ruthenium(II) **3** were synthesized with slight modification of the reported procedure (Scheme 1).[10] 4,4′-Dicarboxy-2,2′-bipyridine **II**, *cis*-bis(4,4′-dicarboxy-2,2′-bipyridine)dithiocyanato ruthenium(II) **5** and bis(tetrabutylammonium) *cis*-bis(2,2′-bipyridine-4,4′-dicarboxylato)dithiocyanato ruthenate(II) **6** were synthesized according to the published procedure.[2,11]



Scheme 1

Synthesis

4,7-Dicarboxy-1,10-phenanthroline I.[11] 4,7-Dimethyl-1,10-phenanthroline (3 g, 14 mmol) was dissolved in 200 cm^3 of 1,4-

DOI: 10.1039/b002391o

dioxane containing 4% v/v water. Selenium oxide (7.5 g, 68 mmol) was added, the mixture heated to reflux for 2 h and then filtered through Celite while hot. 4,7-Diformyl-1,10-phenanthroline was separated from the cold filtrate as yellow crystals (2.2 g, 65%) and recrystallized from tetrahydrofuran. The dialdehyde (0.5 g, 2.0 mmol) in 10 cm^3 of 70% nitric acid was heated under reflux for 3 h, then poured onto ice, and the precipitated solid (0.23 g, 43%) recrystallized from methanol (Found: C, 62.57; H, 2.97; N, 10.36. Calc. for $C_7H_4NO_2$: C, 62.69; H, 3.01; N, 10.44%).

***cis*-Dichlorobis(4,7-dicarboxy-1,10-phenanthroline)ruthenium(II) 1.** $RuCl_3 \cdot 3H_2O$ (52 mg) was dissolved in DMF under Ar. To this was added compound **I** as a solid (103 mg). The mixture was refluxed with vigorous stirring, in the dark and an argon atmosphere. After refluxing for 3 h the reaction mixture was allowed to cool to room temperature and filtered. DMF was removed *in vacuo*. The resulting solid was washed with acetone–diethyl ether (1:4) and the solid stirred in 2 M HCl aqueous solution for 2 h and filtered through a membrane filter. After drying, complex **1** (120 mg, 86%) was obtained (Found: C, 47.29; H, 2.24; N, 7.87. Calc. for $C_{28}H_{16}Cl_2N_4O_8Ru$: C, 47.47; H, 2.28; N, 7.91%).

***cis*-Dicyanobis(4,7-dicarboxy-1,10-phenanthroline)ruthenium(II) 2.** A mixture of KCN (183 mg) and complex **1** (100 mg) in 3:1 (v/v) DMF–water was heated to reflux under Ar for 5 h. The solution changed from violet to orange. Then the reaction mixture was allowed to cool and filtered. The filtrate was evaporated to dryness and the resulting solid dissolved in water at pH 10. After addition of dilute $HClO_4$ an orange solid was isolated at pH 2–3, washed with water, ethanol, and anhydrous diethyl ether, and dried in air for 1 day. The compound **2** (69 mg, 70%) was obtained as an orange solid (Found: C, 50.63; H, 2.51; N, 11.28. Calc. for $C_{30}H_{16}N_6O_8Ru \cdot H_2O$: C, 50.92; H, 2.56; N, 11.80%).

***cis*-Bis(4,7-dicarboxy-1,10-phenanthroline)dithiocyanato ruthenium(II) 3.** NH_4NCS (500 mg) was dissolved in 5 cm^3 of water. To this solution 30 cm^3 of DMF were added under Ar followed by 200 mg of complex **1** as a solid. The mixture was refluxed in the dark for 5 h, allowed to cool and then filtered through a membrane filter. DMF and water were removed by rotary evaporation. To the resulting viscous liquid were added 10 cm^3 of 0.05 M NaOH aqueous solution to give a dark purple-red homogeneous solution. This was filtered through a membrane filter and the pH lowered to 3.5 with 0.5 M HNO_3 to give a dense precipitate. The mixture was placed in a refrigerator for 12 hours. After allowing it to reach room temperature the solid was collected on a membrane filter by suction filtration, washed (3×20 cm^3) with water (pH 3.5), and air dried. Purple solid complex **3** (198 mg, 85%) was obtained (Found: C, 47.01; H, 2.15; N, 10.64. Calc. for $C_{30}H_{16}N_6O_8RuS_2$: C, 47.81; H, 2.14; N, 11.15%).

Bis(tetrabutylammonium) *cis*-bis(1,10-phenanthroline-4,7-dicarboxylate)dithiocyanato ruthenate(II) 4. 100 mg of complex **3** were dissolved in 10 ml of a 10% NBu_4OH aqueous solution. This solution was adjusted to pH 4 by the addition of 0.1 M nitric acid and kept in a refrigerator. The flask was allowed to warm to room temperature, and the precipitate was collected on a membrane filter. The yield of compound **4**: 70 mg (47%).

Measurements

^1H NMR spectra were recorded by a Varian 300BB spectrometer. The ratio of tetrabutylammonium cation to the ruthenate anion was estimated from an integration of proton peaks. IR spectra measurements were performed using a JASCO Co. FTIR 5300 spectrophotometer at a resolution of 2 cm^{-1} with the samples in compressed KBr pellets. UV-vis spectra were measured with a Shimadzu UV3101PC spectrometer. An aqueous stock solution (3×10^{-5} M) was prepared, containing 0.1 M $NaClO_4$, and the initial pH was adjusted to 10.4 by adding 0.1 M NaOH solution. The pH dependent UV-vis spectra were measured 5 min after the addition of $HClO_4$ to a solution.

Corrected emission spectra were obtained using a Hitachi Co. F-4500 spectrophotometer. Spectra at 77 K were measured in 4:1 (v/v) ethanol–methanol glasses immersed in liquid N_2. All solutions were prepared to give approximate concentration of 1×10^{-5} M. All samples for emission measurements were purged with nitrogen stream. The emission lifetimes were measured by exciting samples with a 5 ns laser pulse at 500 nm from an optical parametric oscillator (Sirelite OPO) pumped at 355 nm by a Nd:YAG laser (Continum Surelite II). The emission decay was followed on a photomultiplier tube (Hamamatsu R928).

A BAS-100 electrochemical analyzer (Bioanalytical Systems) was used to perform cyclic voltammetry. A conventional three electrodes system was used for the electrochemical measurement with a platinum wire as a counter electrode, a carbon and platinum disk (1.5 mm diameter embedded in Teflon) as a working electrode and Ag–AgCl (saturated aqueous KCl) or Ag–Ag^+ ($AgNO_3$ 0.1 M, tetrabutylammonium perchlorate 0.1 M in acetonitrile) in contact with a KCl salt bridge as reference. Electrode potential values were corrected to the SCE. Scan rates were 10–400 mV s^{-1}. The cyclic voltammetry in water was carried out in 0.1 M $NaClO_4$ aqueous solution at pH 3.5. Dry organic solvents (water < 0.005%) were used as received (Wako Chem.). NBu_4ClO_4 and $NaClO_4$ were purchased from Fluka Corp. and Aldrich Corp., respectively.

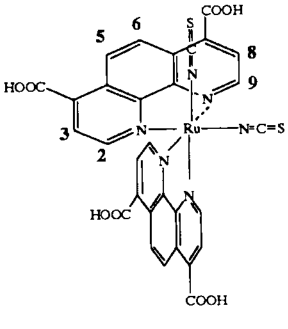
Photoelectrochemical measurements were performed in a two-electrode sandwich cell configuration as previously reported.[2,10,12] The geometric surface area and thickness of the semiconductor film were 0.44 cm^2 and 10 μm, respectively. A solution of complex **4** was prepared in 1:1 (v/v) acetonitrile–*tert*-butyl alcohol at a concentration of 5×10^{-4} M. The electrolyte solution was composed of 0.5 mM 1,2-dimethyl-3-propylimidazolium iodide, 20 mM I_2, 0.5 M 4-*tert*-butylpyridine, 40 mM LiI in methoxyacetonitrile. The amount of adsorbed ruthenium complex was determined by desorbing it from a TiO_2 film into a 0.01 M NaOH 1:1 (v/v) ethanol–water solution and measuring its absorption spectrum.

Results and discussion

NMR spectroscopy

The notation for the aromatic protons of *cis*-bis(4,7-dicarboxy-1,10-phenanthroline)dithiocyanato ruthenium(II) **3** and of *cis*-bis(4,4′-dicarboxy-2,2′-bipyridine)dithiocyanato ruthenium(II) **5** is shown below. The primes are for protons of the pyridine ring not *trans* to SCN. The ^1H NMR spectral data for 4,7-dicarboxy-1,10-phenanthroline **I**, *cis*-dichlorobis(4,7-dicarboxy-1,10-phananthroline)ruthenium(II) **1**, *cis*-dicyanobis(4,7-dicarboxy-1,10-phenanthroline)ruthenium(II) **2**, **3**, 4,4′-dicarboxy-2,2′-

(1)



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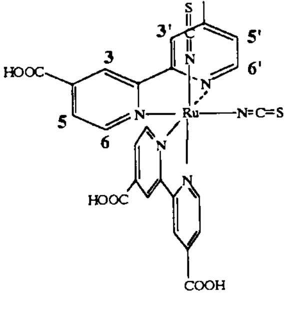

Table 1 Proton NMR spectral data (δ) for ruthenium complexes in D_2O

	4,7-Dicarboxy-1,10-phenanthroline (H_2dcphen)						4,4′-Dicarboxy-2,2′-bipyridine(H_2dcbpy)					
Complex	H(2)	H(9)	H(5)	H(6)	H(3)	H(8)	H(6)	H(6′)	H(3)	H(3′)	H(5)	H(5′)
I H_2dcphen	9.08 (d)		8.18 (s)		7.78 (d)		—	—	—	—	—	—
1 *cis*-[Ru(H_2dcphen)$_2$Cl$_2$]	9.92 (d)	7.90 (d)	9.06 (d)	8.92 (d)	8.50 (d)	7.66 (d)	—	—	—	—	—	—
2 *cis*-[Ru(H_2dcphen)$_2$(CN)$_2$]	9.88 (d)	7.86 (d)	8.46 (d)	8.35 (d)	8.07 (d)	7.45 (d)	—	—	—	—	—	—
3 *cis*-[Ru(H_2dcphen)$_2$-(NCS)$_2$]	9.81 (d)	7.87 (d)	8.55 (d)	8.42 (d)	8.23 (d)	7.37 (d)	—	—	—	—	—	—
II H_2dcbpy	—	—	—	—	—	—	8.76 (d)		8.36 (s)		7.94 (d)	
5 *cis*-[Ru(H_2dcbpy)$_2$(NCS)$_2$]	—	—	—	—	—	—	9.49 (d)	7.75 (d)	8.87 (s)	8.71 (s)	8.15 (dd)	7.45 (dd)

Proton peaks of tetrabutylammonium of $[NBu_4]_{2n}$ [*cis*-RuL$_{2-n}$X$_2$] (n = 1,2) (L = Hdcbpy or Hdcphen, X = CN or NCS) were observed at δ 2.98 (t), 1.47 (m), 1.19 (m) and 0.82 (t). The peak of 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid sodium salt was used as an internal standard.

Table 2 Absorption and luminescence properties of ruthenium complexes

	Absorption max/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1})^a		Emission max/nm		$\tau_{em}{}^d$/ns	
Complex	π–π* band	MLCT band	278 K^b	77 K^c	278 K^b	77 K^c
1 *cis*-[Ru(H_2dcphen)$_2$Cl$_2$]	282 (34)	450 (sh), 534 (7.6)	—	—	—	—
2 *cis*[Ru(H_2dcphen)$_2$(CN)$_2$]	288 (73)	430 (sh), 493 (20)	—	656	—	—
3 *cis*-[Ru(H_2dcphen)$_2$(NCS)$_2$]	278 (71)	450 (sh), 527 (18)	810	755	20	—
4 $[NBu_4]_2$[*cis*-Ru(Hdcphen)$_2$(NCS)$_2$]	280 (86)	450 (sh), 522 (18)	800	740	30	1000
5 *cis*-[Ru(H_2dcbpy)$_2$(NCS)$_2$]	313 (50)	396 (14), 534 (14)	—	—	20	—
6 $[NBu_4]_2$[*cis*-Ru(Hdcbpy)$_2$(NCS)$_2$]	312 (50)	391 (13), 532 (14)	755	735	50	—

^{a} Measured in ethanol. ^{b} Measured in ethanol–methanol (4 : 1 v/v). ^{c} Measured in ethanol–methanol (4 : 1 v/v) glass at 77 K. ^{d} All emission lifetimes were measured at peak maximum.

bipyridine **II** and **5** are shown in Table 1. Three peaks for **I** and **II** were observed. The six peaks of **1**, **2**, **3** and **5** were observed because the coordination-induced chemical shift (CIS) ($\delta_{complex} - \delta_{ligand}$) for the equatorial position appears more positive than for the axial position which is *cis* to SCN, CN or Cl.[13]

IR spectroscopy

The IR absorption peaks of complex **3** and bis(tetrabutylammonium) *cis*-bis(1,10-phenanthroline-4,7-dicarboxylato)dithiocyanato ruthenate(II) **4** at 2105 and 2123 cm^{-1} are ascribed to SCN stretching of the N-co-ordinated ligand. No peak for S-co-ordinated ligand at 1998 cm^{-1} was observed. Absorption at 1713–1715 cm^{-1} is attributed to the C=O stretch mode of the protonated carboxylic acid.[2,14–16] Peaks at 2961, 2933 and 2874 cm^{-1} are attributed to the C–H stretch mode of NBu_4^+. The peaks observed between 1000 and 1600 cm^{-1} were attributed to bands for the framework-stretching mode of phenanthroline ligand. Those between 600 and 1000 cm^{-1} contain the C=S stretching and C–H bending modes.

Electronic absorption spectra

UV-vis absorption spectra of complex **4** and bis(tetrabutylammonium) *cis*-bis(2,2′-bipyridine-4,4′-dicarboxylato)dithiocyanato ruthenate(II) **6** are shown in Fig. 1. The absorption and emission spectral properties of **1**, **2**, **3**, **4**, **5** and **6** are summarized in Table 2. The strong absorption bands of the ruthenium complexes in the region between 250 and 350 nm are due to π–π* transitions. Two MLCT bands at 391 and 532 nm were observed in the spectrum of **6**, an intense and broad MLCT band at 522 nm with a shoulder at 450 nm for **4** and MLCT bands of **1** and **2** at 534 and 493 nm, respectively. The relationship of the MLCT band among **1**, **2** and **3** is similar to that of *cis*-[Ru(H_2dcbpy)$_2$X$_2$] (X = Cl, CN or SCN).[2,14] Compared with two MLCT bands for **5** and **6**, only one broad band for **3** and **4** was observed. A similar relationship is observed between bis(2,2′-bipyridine)ruthenium complexes and their bis(1,10-phenanthroline) analogues.[9] Since complexes **3** and **4** possess broader and more intense absorption peaks than do **5** and **6** in the visible region, **3** is expected to be a more efficient solar light harvesting antenna than **5**.

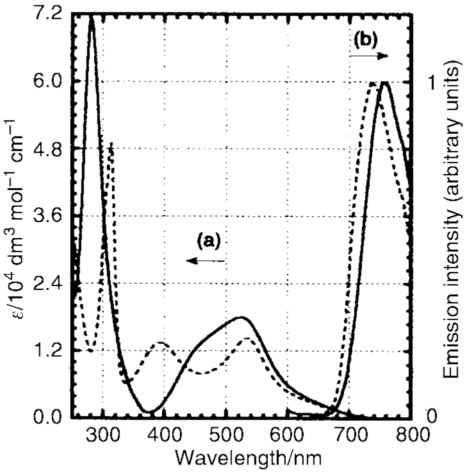

Fig. 1 Absorption and emission spectra of complexes **4** (——) and **6** (– – –). (a) Absorption spectra in ethanol at room temperature. (b) Emission spectra were recorded in 4 : 1 v/v ethanol–methanol at 77 K.

The degree of deprotonation of the carboxylic group affects the photophysical and electrochemical properties of the complexes. Under aprotic conditions, *i.e.* in a dye-sensitized solar cell system, the degree of deprotonation is determined by the stoichiometry of NBu_4^+ in the complex, and under aqueous conditions the degree of deprotonation depends on the pH of the solution. Fig. 2 shows the pH dependence of the MLCT absorption of **3**. The absorption peaks shifted from 273 to 280 nm and from 482 to 500 nm, respectively, when the pH was changed from 10.4 to 2.0. Clean isosbestic points were observed at 285, 362 and 500 nm at pH > 2.7. The protonation of carboxyl groups lowered the π–π* and MLCT transition energy causing a red shift.

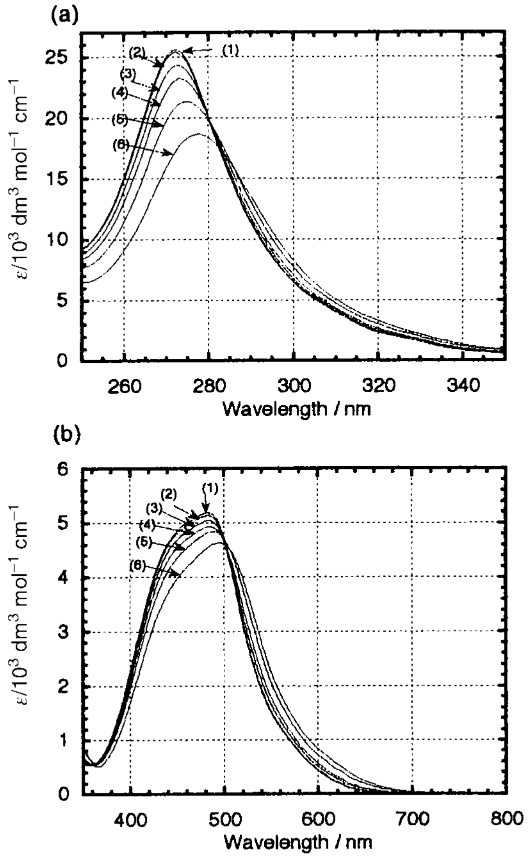

Fig. 2 (a) π–π* and (b) MLCT absorption spectra of complex **3** in 0.1 M $NaClO_4$ at pH values of 10.4 (1), 7.0 (2), 3.5 (3), 3.1 (4), 2.7 (5) and 2.3 (6).

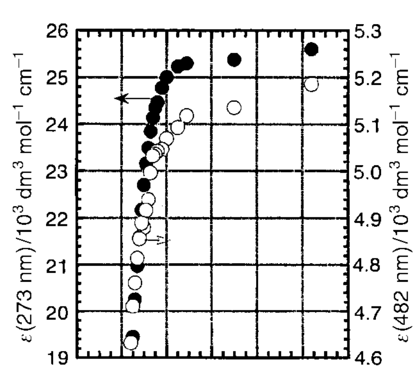

Fig. 3 Absorbance as a function of pH for complex **3** at 273 (●) and 482 nm (○).

Fig. 3 shows the pH dependent absorbance changes at 273 and 482 nm. The pK_a of the carboxyl group of **3** is estimated to be 3. Two stoichiometric points of pH dependent absorbance change due to the protonation of the carboxyl group of **5** have been observed,[2,16] only one for **3**. The completely protonated complex **3** can be obtained when the pH of its aqueous solution is lowered to 3.5 with 0.5 M HNO_3 in the synthesis. The doubly-deprotonated complex **4** can be obtained at pH 4. The completely-deprotonated complex of **3** may be simultaneously protonated between pH 2 and 4.

Emission spectra

Photophysical data of these complexes are summarized in Table 2. The emission spectra are weaker and broader at 298 than at 77 K. Spectra at 77 K of **4** and **6** are shown in Fig. 1. Emission of **4** and **6** was observed at 77 K, maximum being around 755 and 735 nm, respectively, steeply rising at 650 nm (1.91 eV). The 0–0 transition energies (E_{00}) of **4** and **6** were approximately 1.91 eV.[17–19]

Table 3 Oxidation peak potential (E_{op}) of compounds in water(H_2O), methanol(MeOH), acetonitrile(AN) and dimethylformamide(DMF)[a]

Complex	H_2O[b]	MeOH	AN	DMF
3 *cis*-[Ru(H_2dcphen)$_2$(NCS)$_2$]	0.72	0.82	0.89	0.84
5 *cis*-[Ru(H_2dcbpy)$_2$(NCS)$_2$]	0.69	0.82	0.85[c]	0.84

[a] All oxidations were found to be irreversible. Platinum disk used as working electrode. Oxidation peaks (E_{op}) in V *vs.* SCE of the metal based III–II potential. [b] The cyclic voltammetry was carried out in 0.1 M $NaClO_4$ aqueous solution at pH 3.5. [c] Data taken from ref. 2.

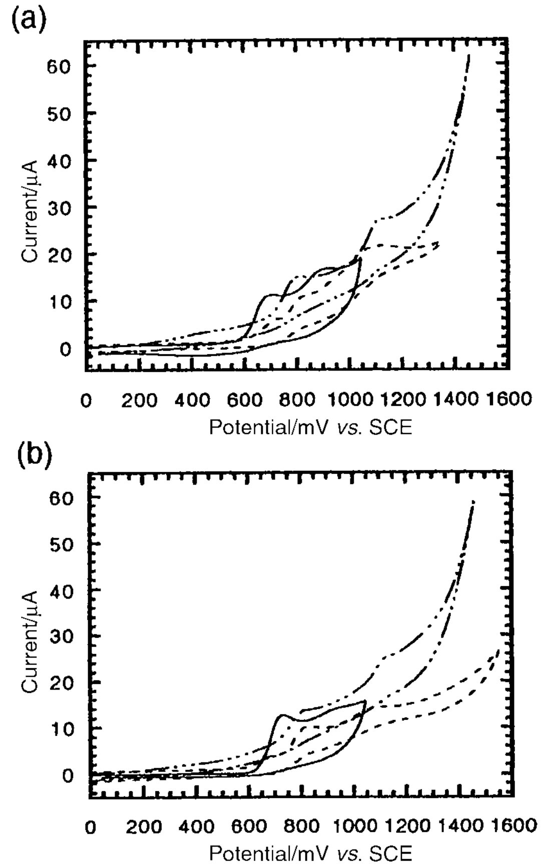

Fig. 4 The cyclic voltammograms of complexes **3** (a) and **5** (b) in DMF (– – –), methanol (– · · · –) and water (——) (pH 3.5) solution.

Electrochemistry

Fig. 4 shows cyclic voltammograms of complexes **3** and **5** in DMF, methanol and water (pH 3.5), respectively. The anodic currents observed between 0.5 and 1.5 V are due to the oxidation from Ru^{II} to Ru^{III}. The irreversible oxidation waves of **3** and **5** have been ascribed to the presence of thiocyanate groups whose oxidation potential is very close to those for $Ru^{II} \longrightarrow Ru^{III}$ of **3** and **5**.[2,10] The oxidation potential of **3** is close to that of **5**, Table 3. The oxidation potential of a ruthenium complex can be predicted by using ligand electrochemical parameters (E_L) of Lever.[20] The E_L of **II** is calculated by eqn. (1) where R, T, F, $\Sigma\sigma$, E_L(2,2′-bipyridine) and ρ(2,2′-bipyridine)$_{\text{RuIII/II}}$ are the gas constant, absolute temperature, Faraday constant, the sum of the Hammett parameters of the carboxylate group, electrochemical parameter of 2,2′-

$$E_L(\mathbf{II}) = 2.303(RT/F)\,\rho(2,2'\text{-bipyridine})_{\text{RuIII/II}}\Sigma\sigma + E_L(2,2'\text{-bipyridine}) \quad (1)$$

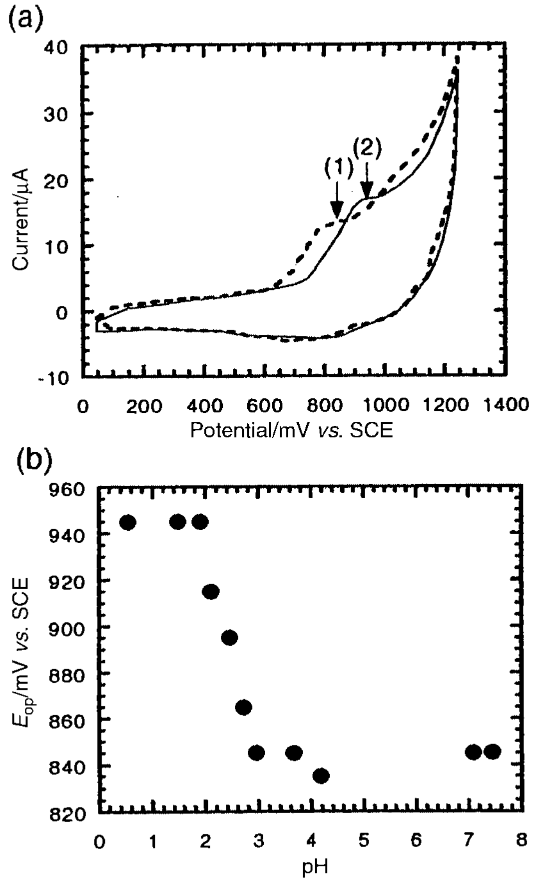

Fig. 5 (a) The cyclic voltammograms of complex **3** in 1 : 1 v/v ethanol–water solution containing 0.1 M $NaClO_4$ at pH 1.9 (——) and 4.2 (– – –). (b) The oxidation peak potential (E_{op}) for **3** as function of pH.

bipyridine and the reaction parameter, respectively. The reaction parameter $\rho(L)_{RuIII/II}$ characterizes the sensitivity of the oxidation potential from Ru^{II} to Ru^{III} for the series of substituents. E_L(**II**) 0.32 was calculated when $\Sigma\sigma = 0.90$, E_L(2,2′-bipyridine) = 0.26 and ρ(2,2′-bipyridine)$_{RuIII/II}$ = 1.2 were substituted into eqn. (1). The oxidation potential E_{ox} of 0.92 V *vs.* SCE was calculated by eqn. (2) when E_L(SCN) = −0.06 was

$$E_{ox} = 0.97\{4E_L(\mathbf{II}) + 2E_L(\mathrm{SCN})\} + 0.04 \qquad (2)$$

used. It is close to the experimental value of 0.85 V *vs.* SCE.[2,21] It is supposed that the E_L(**I**) is almost same as E_L(**II**) since the oxidation potential of **3** also resembles that of **5**. E_L(1,10-phenanthroline) and E_L(4,7-dimethyl-1,10-phenanthroline) are same as E_L(2,2′-bipyridine) and E_L(4,4′-dimethyl-2,2′-bipyridine), respectively.[20] Also that ρ(1,10-phenanthroline)$_{RuIII/II}$ is also similar to ρ(2,2′-bipyridine)$_{RuIII/II}$.

The cyclic voltammetry of complexes **1** and **2** in methanol shows a quasi-reversible and irreversible wave at 0.58 and 1.21 V *vs.* SCE, respectively, which are due to the oxidation from Ru^{II} to Ru^{III}. The relationship of the oxidation potentials among **1**, **2** and **3** is also similar to that of *cis*-$[Ru(H_2dcbpy)_2X_2]$ (X = Cl, CN or SCN).[2,14,21] The oxidation potentials of **1** and **2** calculated by using E_L(Cl) = −0.24 and E_L(CN) = 0.02 are 0.57 and 1.08 V, respectively, which are close to the experimental data.[20]

Fig. 5 shows the cyclic voltammogram of complex **3** in 1 : 1 (v/v) ethanol–water at pH 1.9 and 4.2. The oxidation peak shifted from 0.85 ± 0.02 to 0.95 ± 0.02 V when the pH was changed from 7.2 to 0.5. This can be explained by the electron-withdrawing nature of the carboxyl group which stabilizes the ground state of the metal t_{2g} orbital.[2,21] the pK_a of the carboxyl group of **3** is also estimated to be 2.7 in good agreement with the value from UV data. Deprotonation of these ruthenium complexes at pH 3.5 was observed in UV-vis spectra. On the other hand, the carboxylate group is protonated in 1×10^{-1} M non-aqueous solution. So, the E_{op} in pH 3.5 aqueous solution is most negative in those solutions.

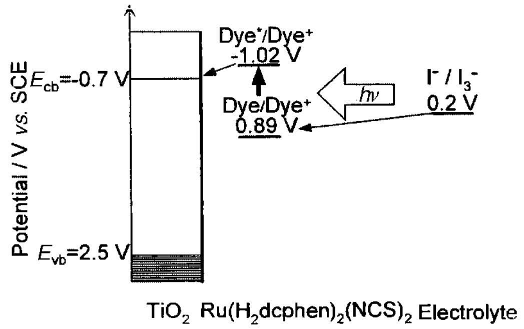

Fig. 6 Schematic diagram of nanocrystalline TiO_2 sensitized with a complex **3**/electrolyte solution interface. The potentials of the conduction band edge (E_{cb}), of valence band (E_{vb}) and of the redox couple (I^-–I_3^-) were taken from ref. 3.

Photovoltaic performance

The energetics of the interface between nanocrystalline TiO_2 sensitized with complex **3** and electrolyte solution containing iodide anion (I^-) as electron donor is described schematically in Fig. 6. The E_{op} of **3** is 0.89 V (*vs.* SCE) in acetonitrile, which is low enough to be reduced by I^-. The 0–0 transition energy (E_{00}) estimated from emission spectra of **3** was *ca.* 1.91 eV. The excited-state oxidation potential (E_{ox}*) was calculated to be −1.02 V, which is high enough to inject an electron into the conduction band of TiO_2 (−0.7 V *vs.* SCE). The energetics of **3** is very similar to that of **5**.

The amount of complex **3** adsorbed per square centimetre of geometrical surface area of TiO_2 film was estimated to be 1.2×10^{-7} mol cm^{-2}. The inner surface of the TiO_2 film is *ca.* 750 cm^2 for each 1 cm^2 of geometric surface. So, the surface coverage of this complex **3** was estimated to be *ca.* 96% when its surface area was assumed to be 100 $Å^2$.

The incident monochromatic photon-to-current efficiency (IPCE) was 70% in the region from 400 to 650 nm.[10] The photocurrent action spectrum of nanocrystalline TiO_2 sensitized with complex **4** showed a more effective photosensitization covering a large part of visible spectrum from 400 to 650 nm than that of TiO_2 sensitized with **6**.[2] The current–voltage characteristic of a solar cell of nanocrystalline TiO_2 sensitized with **4** was measured under illumination by AM 1.5 (100 mW cm^{-2}).[22] The short-circuit photocurrent (J_{sc}), the open-circuit voltage (V_{oc}) and fill factor (ff) were 13.6 mA cm^{-2}, 0.67 V and 0.67, respectively, giving an overall efficiency (η_{global}) of 6.1%. On the other hand, the values for a solar cell of nanocrystalline TiO_2 sensitized with **6** were 15.0 mA cm^{-2}, 0.70 V, 0.74 and 7.8% respectively.

The J_{sc}, V_{oc}, ff and η_{global} for a solar cell of nanocrystalline TiO_2 sensitized with complex **2** were 8.2 mA cm^{-2}, 0.51 V, 0.57 and 2.4% respectively. The IPCE was 70% in the region from 440 to 480 nm. Since the light harvesting efficiency of TiO_2 sensitized with **2** is much lower than that of **4** in the region from 480 to 650 nm, the η_{global} of TiO_2 sensitized with **2** is lower than **4**.

Conclusion

The ruthenium phenanthroline complexes **1**–**4** have been synthesized and characterized as a new class of sensitizer for dye-sensitized solar cells. The energy levels of the oxidized form and the excited state of **3** are favorable enough to oxidize I^- in the electrolyte solution and to inject an electron into the conduction band of TiO_2, respectively. The broad and intense MLCT band of **3** was observed at around 527 nm in visible region. A dye-sensitized solar cell based on these complexes adsorbed onto nanocrystalline TiO_2 film shows a remarkable efficiency in the visible region. Although the optimization for solar cell is still under investigation, an overall solar-to-electrical power conversion efficiency of 6.1% was obtained.

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22 Note added at proof: the AM number characterizes the angle between the incident solar light q and the surface of the earth. AM = 1 cos q. AM 1.5 is solar light at $q = 37°$.