

# Dye-sensitized solar cells based on nanocrystalline TiO<sub>2</sub> sensitized with a novel pyridylquinoline ruthenium(II) complex

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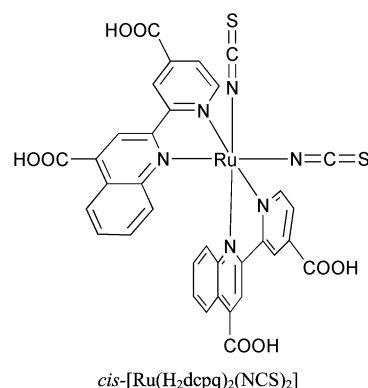
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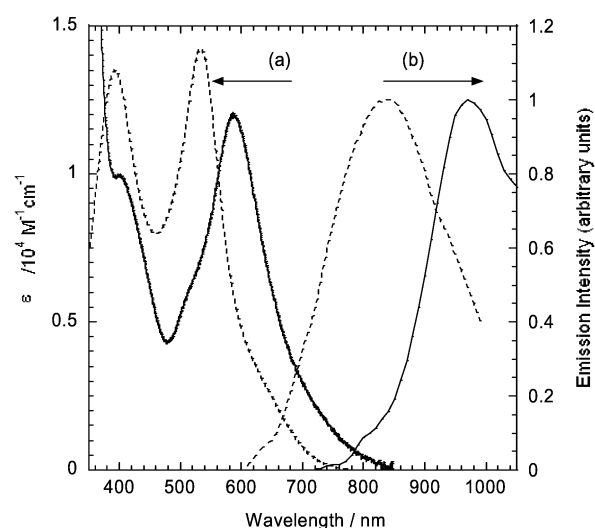
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[NBu<sub>4</sub>]<sub>2n</sub>[*cis*-Ru(H<sub>2</sub>-*n*dcpq)<sub>2</sub>(NCS)<sub>2</sub>] {*n* = 0 or 1; H<sub>2</sub>dcpq = 4-carboxy-2-[2'-(4'-carboxypyridyl)]quinoline} were newly synthesized, and their photophysical and photovoltaic properties were characterized and compared with those of [NBu<sub>4</sub>]<sub>2n</sub>[*cis*-Ru(H<sub>2</sub>-*n*dcbiq)<sub>2</sub>(NCS)<sub>2</sub>] (H<sub>2</sub>dcbiq = 4,4'-dicarboxy-2,2'-biquinoline) and [NBu<sub>4</sub>]<sub>2n</sub>[*cis*-Ru(H<sub>2</sub>-*n*dc bpy)<sub>2</sub>(NCS)<sub>2</sub>] (H<sub>2</sub>dc bpy = 4,4'-dicarboxy-2,2'-bipyridine). The lowest excited-state oxidation potential of *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] was estimated to be −0.72 V *vs.* SCE, which was more positive than that of *cis*-[Ru(H<sub>2</sub>dc bpy)<sub>2</sub>(NCS)<sub>2</sub>], and very close to reported values of the conduction band edge of TiO<sub>2</sub>. [NBu<sub>4</sub>]<sub>2n</sub>[*cis*-Ru(H<sub>2</sub>-*n*dcpq)<sub>2</sub>(NCS)<sub>2</sub>] achieved efficient sensitization of nanocrystalline TiO<sub>2</sub> films over a wide visible and near-infrared wavelength range, generating a large short-circuit photocurrent of 13.2 mA cm<sup>−2</sup> and an open-circuit voltage of 0.53 V with a solar energy conversion efficiency of 5.0% under simulated AM 1.5 solar irradiation (100 mW cm<sup>−2</sup>).

The design of polypyridine ruthenium(II) complexes has attracted great interest for use in dye-sensitized nanocrystalline metal oxide solar cells since a solar cell based on TiO<sub>2</sub> sensitized with [NBu<sub>4</sub>]<sub>2n</sub>[*cis*-Ru(H<sub>2</sub>-*n*dc bpy)<sub>2</sub>(NCS)<sub>2</sub>] (*n* = 0 or 1; H<sub>2</sub>dc bpy = 4,4'-dicarboxy-2,2'-bipyridine) demonstrated a high overall light-to-electric energy conversion efficiency under simulated solar light.<sup>1–3</sup> To improve their efficiencies, enhanced spectral response of the ruthenium complex at lower energies is required.<sup>4–8</sup> The MLCT transition energy of a ruthenium complex can be lowered by introducing a ligand with a low-energy π\* orbital. However, the excited state of the ruthenium complex should maintain sufficient thermodynamic driving force for electron injection from the excited state of the ruthenium complex into the conduction band of TiO<sub>2</sub>. We have investigated TiO<sub>2</sub> nanocrystalline solar cells sensitized with 4,4'-dicarboxy-2,2'-biquinoline (H<sub>2</sub>dcbiq) ruthenium complexes whose π\* orbital is less negative in energy than that of H<sub>2</sub>dc bpy.<sup>8</sup> However, these cells showed only low photocurrent efficiency because the lowest excited state of the ruthenium complex was less negative than the conduction band edge of TiO<sub>2</sub>. The π\* orbital of 2-(2'-pyridyl)quinoline is energetically more negative than that of 2,2'-biquinoline and more positive than that of 2,2'-bipyridine.<sup>9</sup> Thus, the excited state of a 2-(2'-pyridyl)quinoline ruthenium complex is expected to have enough driving force to inject an electron into TiO<sub>2</sub>. [NBu<sub>4</sub>]<sub>2n</sub>[*cis*-Ru(H<sub>2</sub>-*n*dcpq)<sub>2</sub>(NCS)<sub>2</sub>] {*n* = 0 or 1; H<sub>2</sub>dcpq = 4-carboxy-2-[2'-(4'-carboxypyridyl)]quinoline} were newly synthesized and compared with [NBu<sub>4</sub>]<sub>2n</sub>[*cis*-Ru(H<sub>2</sub>-*n*dcbiq)<sub>2</sub>(NCS)<sub>2</sub>] and [NBu<sub>4</sub>]<sub>2n</sub>[*cis*-Ru(H<sub>2</sub>-*n*dc bpy)<sub>2</sub>(NCS)<sub>2</sub>] (*n* = 0 or 1).



UV-vis absorption and emission spectra of *cis*-[Ru(H<sub>2</sub>dc bpy)<sub>2</sub>(NCS)<sub>2</sub>] and *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] are shown in Fig. 1. An intense broad MLCT absorption of *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] was observed in ethanol solution, with an absorption maximum at 590 nm with a shoulder at 400 nm. The energy of the low-energy MLCT transition in these ruthenium complexes decreased in the following order H<sub>2</sub>dc bpy > H<sub>2</sub>dcpq > H<sub>2</sub>dcbiq.<sup>8</sup> Cyclic voltammogram of *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] showed a quasi-reversible wave at



**Fig. 1** Absorption and emission spectra of *cis*-[Ru(H<sub>2</sub>dc bpy)<sub>2</sub>(NCS)<sub>2</sub>] (dashed line) and *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] (solid line). (a) Absorption spectra in ethanol solution; (b) emission spectra in ethanol-methanol (4:1, v/v) at room temperature.

0.86 V *vs.* SCE, which is assigned to the Ru<sup>III</sup>/Ru<sup>II</sup> couple. The redox potential ( $E_{ox}$ ) of the Ru<sup>III</sup>/Ru<sup>II</sup> couple for *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] was almost the same as for *cis*-[Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(NCS)<sub>2</sub>]. Emission of *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] in ethanol-methanol was observed at 298 K, its maximum being around 970 nm. The emission lifetime of the lowest excited MLCT state of *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] in ethanol-methanol was 14 ns at 298 K. The 0-0 transition energy ( $E^0$ ) of *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] is approximately 1.58 eV, which is 0.37 eV less negative than *cis*-[Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(NCS)<sub>2</sub>].<sup>10</sup> The excited-state oxidation potential ( $E_{ox}^*$ ) of *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] was estimated to be -0.72 V, which is 0.11 eV more negative than that of *cis*-[Ru(H<sub>2</sub>dcbiq)<sub>2</sub>(NCS)<sub>2</sub>], 0.34 eV more positive than that of *cis*-[Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(NCS)<sub>2</sub>] and is very close to the conduction band edge ( $E_{cb}$ ) of TiO<sub>2</sub> (-0.7 V *vs.* SCE) under conditions similar to this work.<sup>1,2,8,11</sup>

Fig. 2 shows the incident photon-to-current conversion efficiency (IPCE) spectra of a solar cell sensitized with [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>] where the values are plotted as a function of wavelength. The amount of [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>] adsorbed per square centimeter of geometrical surface area ( $\Gamma$ ) was determined to be  $1.5 \times 10^{-7}$  mol cm<sup>-2</sup> following the method described previously.<sup>11</sup> The  $\Gamma$  value of [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>] is almost the same as that of *cis*-[Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(NCS)<sub>2</sub>] or *cis*-[Ru(H<sub>2</sub>dcbiq)<sub>2</sub>(NCS)<sub>2</sub>]. The short-circuit photocurrent density ( $J_{sc}$ ), open-circuit photovoltage ( $V_{oc}$ ), and fill factor (ff) for a solar cell with [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcbpy)<sub>2</sub>(NCS)<sub>2</sub>] under AM 1.5 (100 mW cm<sup>-2</sup>) light were 14.1 mA cm<sup>-2</sup>, 0.60 V, and 70%, respectively, resulting in an overall efficiency ( $\eta$ ) of 5.9%. The  $J_{sc}$ ,  $V_{oc}$ , ff, and  $\eta$  values for [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>] were 13.2 mA cm<sup>-2</sup>, 0.53 V, 71%, and 5.0%, respectively. The  $J_{sc}$  value for [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>] was comparable with that of [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcbpy)<sub>2</sub>(NCS)<sub>2</sub>]. The IPCE for a cell with [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcbiq)<sub>2</sub>(NCS)<sub>2</sub>] was much lower than for [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>] as the lowest excited state of [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcbiq)<sub>2</sub>(NCS)<sub>2</sub>] is lower than the  $E_{cb}$  of TiO<sub>2</sub>.<sup>8</sup> The IPCE maximum for [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>] was 25% lower than for [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcbpy)<sub>2</sub>(NCS)<sub>2</sub>], probably because the injection yield is lower due to a smaller  $|\Delta G| = |E_{ox}^* - E_{cb}|$  value for [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>], compared with [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcbpy)<sub>2</sub>(NCS)<sub>2</sub>].<sup>6,7,12</sup> However, [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>]

(NCS)<sub>2</sub>] showed an efficient photosensitization covering a large part of the visible and near-infrared region, especially between 700 and 900 nm.

## Experimental

### Syntheses

4-Carboxy-2-[2'-(4'-carboxypyridyl)]quinoline (H<sub>2</sub>dcpq) was prepared from 4-carboxy-2-(4'-methyl-2'-pyridyl)quinoline, which was synthesized from 2,3-indolinedione and 4-methyl-2-acetylpyridine<sup>13</sup> by consecutive SeO<sub>2</sub> and Ag<sub>2</sub>O oxidation without isolation of intermediates.<sup>14</sup> <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O-NaOD):  $\delta$  7.76 (t,  $J$  = 12.0 Hz, 1H), 7.90 (d,  $J$  = 6.0 Hz, 1H), 7.92 (t,  $J$  = 12.0 Hz, 1H), 8.17 (s, 1H), 8.20 (d,  $J$  = 12.0 Hz, 1H), 8.23 (d,  $J$  = 12.0 Hz, 1H), 8.55 (s, 1H), 8.82 (d,  $J$  = 6.0 Hz, 1H). MS (ESI-MS):  $m/z$  292.9 (M - H)<sup>-</sup>, 145.8 (M - 2H)<sup>2-</sup>. Anal. calcd for C<sub>8</sub>H<sub>5</sub>NO<sub>2</sub>: C, 65.31; H, 3.43; N, 9.52; found: C, 64.93; H, 3.37; N, 9.39%.

*cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>Cl<sub>2</sub>] was synthesized by refluxing Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub> (0.47 g), H<sub>2</sub>dcpq (0.57 g) and KCl (0.3 g) in ethylene glycol for 1 h. After cooling, *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>Cl<sub>2</sub>] (0.66 g, 90%) was precipitated by the addition of diluted HNO<sub>3</sub>. *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>(NCS)<sub>2</sub>] was prepared by refluxing *cis*-[Ru(H<sub>2</sub>dcpq)<sub>2</sub>Cl<sub>2</sub>] (0.55 g) with a 16-fold excess of NaNCS (0.96 g) for 5 h in DMF containing 10% v/v water. The reaction mixture was then rotary evaporated to dryness and the solid dissolved in water at pH 10. The solution was acidified with dilute HNO<sub>3</sub> at pH 3.0. The precipitated solid was recrystallized from acetonitrile (50 mg, 10%). IR/cm<sup>-1</sup> (KBr pellet): 2118 (ν<sub>CN</sub>), 1724 (ν<sub>C=O</sub>). <sup>1</sup>H NMR [400 Mz, (CD<sub>3</sub>)<sub>2</sub>SO]:  $\delta$  6.51 (d,  $J$  = 9.0 Hz, 1H), 7.23 (t,  $J$  = 7.0 Hz, 1H), 7.63 (t,  $J$  = 7.0 Hz, 1H), 8.26 (d,  $J$  = 6.0 Hz, 1H), 8.56 (d,  $J$  = 9.0 Hz, 1H), 9.17 (d,  $J$  = 6.0 Hz, 1H), 9.25 (s, 1H), 9.50 (s, 1H). MS (ESI-MS):  $m/z$  804 (M - H)<sup>-</sup>, 401.5 (M - 2H)<sup>2-</sup>, 267.3 (M - 3H)<sup>3-</sup>. Anal. calcd for C<sub>34</sub>H<sub>20</sub>N<sub>6</sub>O<sub>8</sub>RuS<sub>2</sub>: C, 50.68; H, 2.50; N, 10.43; found: C, 50.47; H, 2.58; N, 10.11%.

[NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>] was prepared following a previously reported method.<sup>11</sup>

### Procedures

UV-vis spectra, emission spectra and cyclic voltammograms were measured as previously described.<sup>8</sup>

A TiO<sub>2</sub> film,<sup>15</sup> of which the apparent surface area and thickness was 0.25 cm<sup>2</sup>, and 10 μm, respectively, was dipped in a 0.2 mM methanol or ethanol solution of the ruthenium complexes for 15–48 h. The sandwich-type two-electrode cell for photo-voltaic measurements consisted of a dye-coated TiO<sub>2</sub> film electrode, a polyethylene film spacer, an electrolyte solution, and a Pt film counter electrode. The electrolyte solution of the cell was composed of 0.6 M 1,2-dimethyl-3-propyl imidazolium iodide, 0.05 M I<sub>2</sub> and 0.1 M LiI in acetonitrile.

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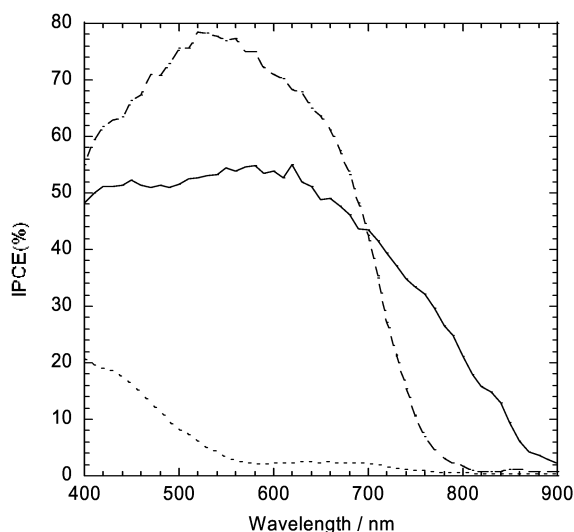


Fig. 2 Photocurrent action spectra of films of TiO<sub>2</sub> dyed with [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcbpy)<sub>2</sub>(NCS)<sub>2</sub>] (dashed line), [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcpq)<sub>2</sub>(NCS)<sub>2</sub>] (solid line) and [NBu<sub>4</sub>]<sub>2</sub>[*cis*-Ru(Hdcbiq)<sub>2</sub>(NCS)<sub>2</sub>] (dotted line).

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