# Synthesis and characterization of dichloro(2,2'-bipyridyl-4,4'dicarboxylate)bis(triphenylphosphine)ruthenium(II) for efficient photosensitization of titanium oxide

Polycarpos Falaras,\*,<sup>a</sup> Antonis P. Xagas<sup>a</sup> and Anne Hugot-Le Goff<sup>b</sup>

<sup>a</sup> Institute of Physical Chemistry, NCSR "Demokritos", 15310 Aghia Paraskevi Attikis, Greece <sup>b</sup> Physique des Liquides et Electrochimie (CNRS UPR 15), Université Pierre et Marie Curie, 75252 Paris cédex 05, France

 $Ru(PPh_3)_2(dcbipy)Cl_2$  (PPh<sub>3</sub> = triphenylphosphine, dcbipy = 2,2'-bipyridyl-4,4'-dicarboxylate) was prepared to use as a TiO<sub>2</sub> sensitizer in wet regenerative photoelectrochemical cells. The complex has been structurally characterized by IR, Raman, ES-MS and NMR spectroscopies. The broad bands in the visible spectrum as well as the reversibility of the redox couple  $Ru^{II}$ - $Ru^{III}$ , established by cyclic voltammetry, make this complex potentially beneficial for the photosensitization process.

The photosensitization of wide bandgap semiconductors (mainly TiO<sub>2</sub> and SnO<sub>2</sub>) with organic dyes or transition metal complexes is being intensively investigated for direct solar to electrical energy conversion.<sup>1–3</sup> Although a large number of complexes have been synthesised and applied as photosensitizers.<sup>2,4,5</sup> the challenge for an efficient redox sensitizer remains. The best efficiencies so far have been achieved by using ruthenium(II) complexes that contain the 2,2'-bipyridyl-4,4'-dicarboxylate ligand (henceforth called dcbipy) on high surface area, nanocrystalline, thin TiO<sub>2</sub> films.<sup>1,2</sup> By keeping the dcbipy ligand and introducing new chromophore groups around the Ru<sup>II</sup> centre, one can alter the light-harvesting characteristics and therefore the photoelectrochemical properties. Ruthenium triphenylphosphine complexes have already been employed in a great variety of chemical and catalytic reactions.<sup>5,6</sup> In this contribution, the preparation and physical characterisation of a new Ru<sup>II</sup> complex, containing both the PPh<sub>3</sub> and the dcbipy ligand, are described.

## **Experimental**

All the solvents was of analytical grade and were dried and degassed before use.  $RuCl_2(PPh_3)_3$  was prepared in accordance with the previously described procedure.<sup>7</sup>  $RuCl_3 \cdot 3H_2O$  and dcbipy were commercially available and were used without further purification.  $PPh_3$  was recrystallized with 95% aqueous ethanol.

#### Synthesis

 $RuCl_2(PPh_3)_3$  (0.191 g, 0.2 mmol) was dissolved in 50 ml of warm deaerated  $CH_2Cl_2$  and 0.049 g (0.2 mmol) of the dcbipy ligand was added. The reaction mixture was heated to reflux under Ar for 5 h. Then the solution was allowed to cool in this inert atmosphere, its volume was reduced to about the onehalf on a rotary evaporator and was left to stand overnight. The dark brown microcrystalline solid that precipitated was filtered, washed thoroughly with a 1 : 1 Et<sub>2</sub>O-pentane mixture and dried in vacuum over CaCl<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> (mp 232–234 °C). The compound is stable in the solid state and in solution. It is soluble in ethanol, acetone and DMF, moderately soluble in dichloromethane and chloroform and insoluble in water and ether. Elemental analysis agreed well with the formulation of the complex. Anal. calcd for C48H38N2O4P2Cl2Ru: C, 61.27; H, 4.04; N, 2.98. Found: C, 61.69; H, 4.45; N, 2.38. IR<sup>8</sup> (KBr) cm<sup>-1</sup>: 3058(m) [v(C-H)], [v(C=O)], 1481(ms)  $[m \ \delta(C-C)]$ , 1434(s) 1724(ms)  $[n \ \delta(C-C)], 1259(m) \ [v_{11}], 1221(m) \ [v_{sym}(COO)], 1159(w) \ [c$  $\delta$ (C-H) in-plane], 1093(m) [q X-sensitive], 1025 [b  $\delta$ (C-H) in-plane or  $v_{15}$ ], 745(s) [(C-H) out-of-plane], 658(ms) [*dcbipy*], 619(ms) [ $\delta$  (C–C) in-plane]. The Raman<sup>9</sup> spectrum contains the bands: 3056(w), 1722(vw), 1478(s), 1436(w), 1257(m), 1162(w), 1099(m), 1029(ms), 658(m), 616(w) and additionally 1615(s)  $[v_5]$ , 1538(s)  $[v_6]$ , 1315(m)  $[v_{sym}(COO)]$ , 997(ms) [ring-breathing], 427(m) [v(Ru-P)].

## **Results and Discussion**

The ES-MS spectrum (positive mode) gave the following fragments (all the m/z values are based on  $^{102}$ Ru, which is the most abundant isotope): [M]<sup>+</sup> (941), [M - Cl]<sup>+</sup> (906), [M - PPh<sub>3</sub>]<sup>+</sup> (679), [M - Cl - PPh<sub>3</sub>]<sup>+</sup> (644), [M - Cl - dcbipy]<sup>+</sup> (662). All these peaks have the appropriate isotopic pattern. The system was also run in the negative mode but no peaks were observed.

The <sup>1</sup>H NMR spectrum (Bruker, 250 MHz) of the complex exhibits a very complex pattern of resonances in the  $\delta$  region of 6.7–7.5, indicative of the presence of the (PPh<sub>3</sub>)<sub>2</sub>Ru<sup>II</sup> moiety.<sup>10</sup> Moreover, there is a doublet at  $\delta$  8.9 (2 H), attributed to the H<sup>6</sup> and a singlet at  $\delta$  8.4 (2 H), attributed to the H<sup>3</sup> of the dcbipy ligand. More structural evidence came from the <sup>31</sup>P NMR spectrum (Varian, 300 MHz, with 85% H<sub>3</sub>PO<sub>4</sub> as external reference), which consists of a singlet at 22.1 ppm. This fact indicates that both PPh<sub>3</sub> are stereochemically equivalent. This leads us, considering also the steric bulk of the two PPh<sub>3</sub>, to assume a *trans* configuration for the PPh<sub>3</sub> (Fig. 1).

Important structural evidence came from infrared and Raman spectroscopic analysis. The most striking feature of the IR spectrum is the strong sharp band at 1724 cm<sup>-1</sup> due to the C=O stretching vibration of the carboxylic group. This band also appears in the Raman spectrum, but with very low intensity. There is also a peak at 1221 cm<sup>-1</sup>, attributed to the C-O stretch. The vibration observed at 3058 cm<sup>-1</sup> is ascribed to the C-H stretching vibration. Comparison with the IR spectra of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> showed that additional bands exist in the fingerprint region, obviously due to the dcbipy ligand (symmetrical C-C and C-N stretches as well as



**Fig. 1** Structure of the Ru(PPh<sub>3</sub>)<sub>2</sub>(dcbipy)Cl<sub>2</sub> complex

in-plane C—H wags).<sup>11</sup> On the other hand, in the Raman spectrum, the coupled symmetrical carbonyl stretch appears at 1315 cm<sup>-1</sup>. The presence of PPh<sub>3</sub> is confirmed by the existence of some characteristic ring vibration modes (the assignment of the characteristic vibration modes of PPh<sub>3</sub> are based upon the classic work of Whiffen on monohalogenobenzenes).<sup>12</sup> The results are in very good agreement with the data reported for (PPh<sub>3</sub>)<sub>3</sub>Ru<sup>II</sup>Cl and other related compounds.<sup>13</sup> Compared to the free phosphine, we note small shifts of the bands, due to complexation. Moreover, there is a band at 427 cm<sup>-1</sup> probably due to a Ru<sup>II</sup>—N stretch.

The electronic spectrum (Perkin-Elmer Lambda 16) of the complex (Fig. 2) displays two broad maxima in the visible region at 521 and 413 nm, with molar extinction coefficients 3400 and 5800  $M^{-1}$  cm<sup>-1</sup>, respectively, and a sharp increase in the near UV region. No spectral changes were observed, even after continuous illumination with visible light for several days. It is now well-established that the two intense low energy-bands are assigned to allowed metal-to-ligand chargetransfer transitions of the type  $d_{\pi}(Ru) \rightarrow \pi^*(dcbipy)$ , which are characteristic of N-heterocyclic complexes of ruthenium(II). Similar assignments have been proposed for analogous complexes.<sup>10,14</sup> In contrast, no emission was detected in the solid state and in ethanolic solutions (Perkin-Elmer LS50B and Jasco FP-777). This may be due to a very short-lived excited state and it is not unexpected for the family of Ru-dcbipy complexes.<sup>2</sup>

The chemical stability and the electrochemical reversibility of the complex are essential for its use as a sensitizer in regenerative photoelectrochemical cells. For this reason, electrontransfer properties of Ru(PPh<sub>3</sub>)<sub>2</sub>(dcbipy)Cl<sub>2</sub> have been studied in DMF solution by cyclic voltammetry. The voltammogram, taken in the region of interest (inset in Fig. 2), shows an oxidation peak whose half-wave potential  $E_{\pm}$  is centered at +0.64 V



**Fig. 2** UV/VIS absorption spectrum of a  $10^{-3}$  M solution of the Ru(PPh<sub>3</sub>)<sub>2</sub>(dcbipy)Cl<sub>2</sub> complex in DMF. Inset: cyclic voltammogram of the same solution (degassed), containing 0.2 M [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]ClO<sub>4</sub>. Scan rate: 50 mV s<sup>-1</sup>, working electrode: Pt wire, counter electrode: planar Pt electrode, reference: saturated calomel electrode (SCE)

vs. SCE. By considering the literature data,  $^{5,15}$  we attribute this wave to the ruthenium(II)-ruthenium(III) couple:

$$\operatorname{Ru}^{II}(\operatorname{PPh}_{3})_{2}(\operatorname{dcbipy})\operatorname{Cl}_{2} \Leftrightarrow \operatorname{Ru}^{III}(\operatorname{PPh}_{3})_{2}(\operatorname{dcbipy})\operatorname{Cl}_{2} + e^{-}$$
 (1)

For this couple, the anodic-cathodic peak current ratio  $(i_{pa}/i_{pc})$  is equal to 1.0, indicating stability of the oxidized complex. The anodic peak current  $i_p$  is proportional to the square root of the scan rate  $(v^{\frac{1}{2}})$  and the peak potential values  $E_{pa}$  and  $E_{pc}$  are independent of the scan rate. The peak-to-peak separation  $(\Delta E_p = E_{pa} - E_{pc})$  as well as the difference  $|E_p - E_{p/2}|$  are both about 60 mV, as expected for a completely reversible one-electron transfer process.

TiO<sub>2</sub> nanocrystalline thin films, prepared by a sol-gel technique, were readily red-colored, after simple immersion in a  $10^{-4}$  M solution of the complex in acetone or ethanol. It is now widely accepted that dcbipy serves as an interlocking group between the molecular 'antenna' (the complex) and the semiconductor's surface through an ester-like linkage between the -COOH group and the surface hydroxyl groups of TiO<sub>2</sub>.<sup>3,16</sup> The characterization of these sensitized cells by in situ resonance Raman spectroscopy,<sup>17</sup> under real photocurrent conditions, confirmed the immutability of the dye Raman spectra and revealed a reversible dependence of the intensities of the bands on the polarization potential. The observed photocurrents are satisfactorily high and very stable while the photocurrent action spectrum matches well the absorption spectrum of the complex. A detailed exploration of the photoelectrochemical properties is now in progress.

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