Letter

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

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$Ru(PPh_3)_2(dcbipy)Cl_2$ (PPh_3 = triphenylphosphine, dcbipy = 2,2′-bipyridyl-4,4′-dicarboxylate) was prepared to use as a TiO_2 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_2 and SnO_2) with organic dyes or transition metal complexes is being intensively investigated for direct solar to electrical energy conversion.[1–3] Although a large number of complexes have been synthesised and applied as photosensitizers,[2,4,5] 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_2 films.[1,2] By keeping the dcbipy ligand and introducing new chromophore groups around the Ru^{II} 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.[5,6] In this contribution, the preparation and physical characterisation of a new Ru^{II} complex, containing both the PPh_3 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.[7] $RuCl_3 \cdot 3H_2O$ 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 one-half 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_2O–pentane mixture and dried in vacuum over $CaCl_2$ and P_2O_5 (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 $C_{48}H_{38}N_2O_4P_2Cl_2Ru$: C, 61.27; H, 4.04; N, 2.98. Found: C, 61.69; H, 4.45; N, 2.38. IR[8] (KBr) cm^{-1}: 3058(m) [ν(C—H)], 1724(ms) [ν(C=O)], 1481(ms) [m δ(C—C)], 1434(s) [n δ(C—C)], 1259(m) [ν_{11}], 1221(m) [ν_{sym}(COO)], 1159(w) [c δ(C—H) in-plane], 1093(m) [q X-sensitive], 1025 [b δ(C—H) in-plane or ν_{15}], 745(s) [(C—H) out-of-plane], 658(ms) [*dcbipy*], 619(ms) [δ (C—C) in-plane]. The Raman[9] 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) [ν_5], 1538(s) [ν_6], 1315(m) [ν_{sym}(COO)], 997(ms) [ring-breathing], 427(m) [ν(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): $[M]^+$ (941), $[M - Cl]^+$ (906), $[M - PPh_3]^+$ (679), $[M - Cl - PPh_3]^+$ (644), $[M - Cl - \text{dcbipy}]^+$ (662). All these peaks have the appropriate isotopic pattern. The system was also run in the negative mode but no peaks were observed.

The ^1H NMR spectrum (Bruker, 250 MHz) of the complex exhibits a very complex pattern of resonances in the δ region of 6.7–7.5, indicative of the presence of the $(PPh_3)_2Ru^{II}$ moiety.[10] Moreover, there is a doublet at δ 8.9 (2 H), attributed to the H^6 and a singlet at δ 8.4 (2 H), attributed to the H^3 of the dcbipy ligand. More structural evidence came from the ^{31}P NMR spectrum (Varian, 300 MHz, with 85% H_3PO_4 as external reference), which consists of a singlet at 22.1 ppm. This fact indicates that both PPh_3 are stereochemically equivalent. This leads us, considering also the steric bulk of the two PPh_3, to assume a *trans* configuration for the PPh_3 (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^{-1} 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^{-1}, attributed to the C—O stretch. The vibration observed at 3058 cm^{-1} is ascribed to the C—H stretching vibration. Comparison with the IR spectra of $RuCl_2(PPh_3)_3$ 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

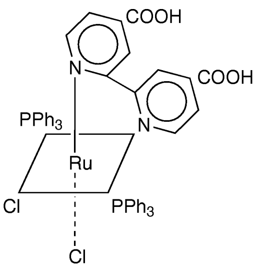

Fig. 1 Structure of the Ru(PPh$_3$)$_2$(dcbipy)Cl$_2$ complex

in-plane C—H wags).[11] On the other hand, in the Raman spectrum, the coupled symmetrical carbonyl stretch appears at 1315 cm^{-1}. The presence of PPh$_3$ is confirmed by the existence of some characteristic ring vibration modes (the assignment of the characteristic vibration modes of PPh$_3$ are based upon the classic work of Whiffen on monohalogenobenzenes).[12] The results are in very good agreement with the data reported for (PPh$_3$)$_3$Ru$^{\mathrm{II}}$Cl and other related compounds.[13] Compared to the free phosphine, we note small shifts of the bands, due to complexation. Moreover, there is a band at 427 cm^{-1} probably due to a Ru$^{\mathrm{II}}$—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^{-1}, 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 charge-transfer transitions of the type $d_\pi(\mathrm{Ru}) \rightarrow \pi^*(\mathrm{dcbipy})$, which are characteristic of *N*-heterocyclic complexes of ruthenium(II). Similar assignments have been proposed for analogous complexes.[10,14] 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.[2]

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, electron-transfer properties of Ru(PPh$_3$)$_2$(dcbipy)Cl$_2$ 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 $E_{\frac{1}{2}}$ is centered at +0.64 V *vs.* SCE. By considering the literature data,[5,15] we attribute this wave to the ruthenium(II)–ruthenium(III) couple:

$$\mathrm{Ru^{II}(PPh_3)_2(dcbipy)Cl_2} \leftrightarrows \mathrm{Ru^{III}(PPh_3)_2(dcbipy)Cl_2} + e^- \quad (1)$$

For this couple, the anodic-cathodic peak current ratio ($i_{\mathrm{pa}}/i_{\mathrm{pc}}$) 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 ($\Delta E_{\mathrm{p}} = E_{\mathrm{pa}} - E_{\mathrm{pc}}$) as well as the difference $|E_{\mathrm{p}} - E_{\mathrm{p/2}}|$ are both about 60 mV, as expected for a completely reversible one-electron transfer process.

TiO$_2$ 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$_2$.[3,16] The characterization of these sensitized cells by *in situ* resonance Raman spectroscopy,[17] 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.

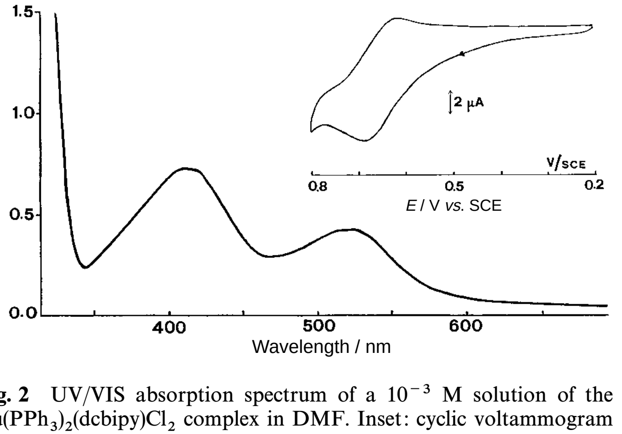

Fig. 2 UV/VIS absorption spectrum of a 10^{-3} M solution of the Ru(PPh$_3$)$_2$(dcbipy)Cl$_2$ complex in DMF. Inset: cyclic voltammogram of the same solution (degassed), containing 0.2 M [(n-C$_4$H$_9$)$_4$N]ClO$_4$. Scan rate: 50 mV s^{-1}, working electrode: Pt wire, counter electrode: planar Pt electrode, reference: saturated calomel electrode (SCE)

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References

1 B. O'Regan and M. Graetzel, *Nature* (*London*), 1991, **353**, 737.
2 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Graetzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382 and references therein.
3 K. Vinodgopal, X. Hua, R. L. Dahlgren, A. G. Lappin, L. K. Patterson and P. V. Kamat, *J. Phys. Chem.*, 1995, **99**, 10883.
4 H. A. Nieuwenhuis, D. J. Stufkens, R. A. McNicholl, A. H. R. Al-Obaidi, C. G. Coates, S. E. J. Bell, J. J. McGarvey, J. Westwell, M. W. George and J. J. Turner, *J. Am. Chem. Soc.*, 1995, **117**, 5579.
5 B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.*, 1978 **17**, 3334.
6 J. Chakravarty and S. Bhattacharya, *Polyhedron*, 1994, **13**, 2671.
7 P. S. Hallman, T. A. Stephenson and G. Wilkinson, *Inorg. Synth.*, 1970, **12**, 237.
8 Italics denote bands from the dcbipy ligand.
9 The Raman spectrum was taken using many different excitation wavelengths. The best results were attained by using the green argon line at 514.5 nm. Since the absorption maximum of the complex lies at 521 nm, we are very near resonance Raman conditions.
10 R. Prasad, *Polyhedron*, 1995, **14**, 2151.
11 T. J. Meyer, G. J. Meyer, B. W. Pfennig, J. R. Schoonover, C. J. Timpson, J. F. Wall, C. Kobusch, X. Chen, B. M. Peek, C. J. Wall, W. Ou , B. Erickson and C. A. Bignozzi, *Inorg. Chem.*, 1994, **33**, 3952.
12 P. F. Whiffen, *J. Chem. Soc.*, 1956, 1350.
13 H. G. M. Edwards, I. R. Lewis and P. H. Turner, *Inorg. Chim. Acta.*, 1994, **216**, 191.
14 H. E. Toma, P. Santos and A. Bolanos, *J. Chem. Res.* (*S*), 1988, 124.
15 M. Haga, Md. M. Ali, S. Koseki, K. Fujimoto, A. Yoshimura, K. Nozaki, T. Ohno, K. Nakajima and D. J. Stufkens, *Inorg. Chem.*, 1996, **35**, 3335.
16 P. Falaras, *Solar Energy Mater. Solar Cells*, in press.
17 A. Hugot-Le Goff, S. Joiret, P. Falaras and A. P. Xagas, *Electrochim. Acta*, submitted.

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