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Ruthenium(II) dichloro or dithiocyanato complexes with 4,4′:2′,2″:4″,4‴-quaterpyridinium ligands: Towards photosensitisers with enhanced low-energy absorption properties

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ABSTRACT

Fourteen new complexes of the form *cis*-$[Ru^{II}X_2(R_2qpy^{2+})_2]^{4+}$ (R_2qpy^{2+} = a 4,4′:2′,2″:4″,4‴-quaterpyridinium ligand, X = Cl^- or NCS^-) have been prepared and isolated as their PF_6^- salts. Characterisation involved various techniques including ^1H NMR spectroscopy and +electrospray or MALDI mass spectrometry. The UV–Vis spectra display intense intraligand $\pi \rightarrow \pi^*$ absorptions, and also metal-to-ligand charge-transfer (MLCT) bands with two resolved maxima in the visible region. Red-shifts in the MLCT bands occur as the electron-withdrawing strength of the pyridinium groups increases, while replacing Cl^- with NCS^- causes blue-shifts. Cyclic voltammograms show quasi-reversible or reversible $Ru^{III/II}$ oxidation waves, and several ligand-based reductions that are irreversible. The variations in the redox potentials correlate with changes in the MLCT energies. A single-crystal X-ray structure has been obtained for a protonated form of a proligand salt, $[(4\text{-}(CO_2H)Ph)_2qpyH^{3+}][HSO_4]_3{\cdot}3H_2O$. Time-dependent density functional theory calculations give adequate correlations with the experimental UV–Vis spectra for the two carboxylic acid-functionalised complexes in DMSO. Despite their attractive electronic absorption spectra, these dyes are relatively inefficient photosensitisers on electrodes coated with TiO_2 or ZnO. These observations are attributed primarily to weak electronic coupling with the surfaces, since the DFT-derived LUMOs include no electron density near the carboxylic acid anchors.

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1. Introduction

The urgent requirement to develop sources of clean and renewable energy has stimulated much interest in dye-sensitised solar cells (DSSCs) [1]. The general field of solar energy conversion is broad and includes many competing but related technologies [1g]. Commonly used silicon solar cells, which exploit photon absorption by a p–n semiconductor junction, require materials of high purity. More recently developed inorganic thin film materials, like cadmium telluride or copper indium gallium selenide, contain toxic or rare elements. In the light of such considerations, the 1991 report by O'Regan and Grätzel of efficient photosensitisation of a wide band-gap semiconductor by a trinuclear ruthenium-based dye [2] inspired much subsequent research. Complexes of Ru and some other metals with polypyridyl ligands such as 2,2′-bipyridyl (2,2′-bpy) typically display intense absorptions in the visible region due to metal-to-ligand charge-transfer (MLCT) transitions.

A DSSC contains a nanoparticulate film of a semiconductor, most commonly TiO_2, coated with a dye monolayer. Most cells are based on a photoanode in which the photoexcited dye injects an electron into the conduction band of the semiconductor. The oxidised dye is then reduced back to its original state by a species in the electrolyte; this is usually an organic solvent containing the I^-/I_3^- couple, but solid 'hole transporting' materials are also attractive. To achieve high power conversion efficiencies, a number of aspects must be considered, but synthetic chemists have naturally focused on the structure of the sensitiser molecule. Amongst the key criteria for potentially useful operation are strong absorption across the entire visible region and the near-UV/IR, appropriate energy matching with and strong electronic coupling to the electrode surface (typically via carboxylate anchors), and high stability over many photoredox cycles.

Ru complexes have featured extensively also in the field of non-linear optical (NLO) compounds [3]. Previously, we have studied complexes of 4,4′:2′,2″:4″,4‴-quaterpyridinium ligands, R_2qpy^{2+} where R = Me, Ph, etc. These compounds include V-shaped dipoles with electron-donating *cis*-$\{Ru^{II}(NH_3)_4\}^{2+}$ centres [4], and octupolar tris-chelates with a $[Ru^{II}(2,2'\text{-bpy})_3]^{2+}$ core [5,6]. The

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MLCT absorption profiles of these complexes are especially broad and intense, with the tris-chelates displaying two well-resolved bands. Pyridinium groups are often used in NLO chromophores [7], and as electron-accepting units in other photoactive molecular assemblies [8]. However, our recent report of *N*-arylstilbazolium species is the first time that pyridinium compounds have been used in DSSCs [9]. These purely organic dyes gave relatively modest efficiencies, but with substantial scope for improvement. In other work of some relevance, TiO_2-based photocathodes incorporating $[Ru^{II}(R_2qpy^{2+})_3]^{8+}$ chromophores (R = 2-carboxyethyl or 2-propylphosphonic acid) have been described [10]. We have investigated also complexes of the form *cis*-$[Ru^{II}(2,2'\text{-bpy})_2(R_2qpy^{2+})]^{4+}$; two carboxylic acid-functionalised derivatives were tested in DSSCs, but showed negligible activities, attributable at least in part to their $[Ru^{II}(2,2'\text{-bpy})_3]^{2+}$-based structures [11]. Here, we describe related complexes that contain the anionic thiocyanate coligand that is present in many of the most effective Ru-based sensitisers, together with analogous chloride species.

2. Experimental

2.1. Materials, procedures and physical measurements

All reactions were performed under an Ar atmosphere. The precursor complex *cis*-$Ru^{II}Cl_2(DMSO)_4$ [12] and the proligand salts *N*″,*N*‴-dimethyl-4,4′:2′,2″:4″,4‴-quaterpyridinium chloride, $[Me_2qpy^{2+}]Cl_2$ [11], *N*″,*N*‴-diphenyl-4,4′:2′,2″:4″,4‴-quaterpyridinium chloride, $[Ph_2qpy^{2+}]Cl_2$ [11], *N*″,*N*‴-di(4-acetylphenyl)-4,4′:2′,2″:4″,4‴-quaterpyridinium chloride, $[(4\text{-AcPh})_2qpy^{2+}]Cl_2$ [11], *N*″,*N*‴-di(2-pyrimidyl)-4,4′:2′,2″:4″,4‴-quaterpyridinium chloride, $[(2\text{-Pym})_2qpy^{2+}]Cl_2$ [11], *N*″,*N*‴-di(3,5-bismethoxycarbonylphenyl)-4,4′:2′,2″:4″,4‴-quaterpyridinium chloride, $[(3,5\text{-}MC_2Ph)_2qpy^{2+}]Cl_2$ [11] and *N*″,*N*‴-di(4-methoxycarbonylphenyl)-4,4′:2′,2″:4″,4‴-quaterpyridinium chloride, $[(4\text{-MCPh})_2qpy^{2+}]Cl_2$ [11], were prepared according to published methods. All other reagents were obtained commercially and used as supplied. Products were dried overnight in a vacuum dessicator ($CaSO_4$) prior to characterisation.

^{1}H NMR spectra were recorded on a Bruker AV-400 or a Bruker AV-500 spectrometer and all shifts are referenced to TMS. The AA′BB′ patterns of pyridyl or phenyl rings are reported as simple doublets, with '*J* values' referring to the two most intense peaks. Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester. IR spectroscopy was performed on solid samples by using an Excalibur BioRad FT-IR spectrometer, and UV–Vis spectra were obtained by using a Shimadzu UV-2401 PC spectrophotometer. Mass spectra were measured by using MALDI on a Micromass Tof Spec 2e or +electrospray on a Micromass Platform II spectrometer with acetonitrile as the solvent. Cyclic voltammetric measurements were carried out with an Ivium CompactStat. An EG&G PAR K0264 single-compartment microcell was used with a silver/silver chloride reference electrode (3 M NaCl, saturated AgCl) separated by a salt bridge from a glassy carbon disk working electrode and Pt wire auxiliary electrode. Acetonitrile was freshly distilled (from CaH_2) and $[NBu^n_4]PF_6$, as supplied from Fluka, was used as the supporting electrolyte. Solutions containing *ca.* 10^{-3} M analyte (0.1 M electrolyte) were deaerated by purging with N_2. All $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 200 mV s^{-1}.

2.2. Syntheses

2.2.1. *N*″,*N*‴-Di(3,5-biscarboxyphenyl)-4,4′:2′,2″:4″,4‴-quaterpyridinium chloride, $[(3,5\text{-}(CO_2H)_2Ph)_2qpy^{2+}]Cl_2$

$[(3,5\text{-}MC_2Ph)_2qpy^{2+}]Cl_2{\cdot}2H_2O$ (250 mg, 0.311 mmol) was added to *tert*-butanol (50 mL) followed by conc. H_2SO_4 (2 mL). The mixture was heated at reflux for 24 h. After cooling, a pale peach-coloured precipitate was filtered off, washed with copious amounts of water and dried. Yield: 227 mg (94%). δ_H (400 MHz, CD_3SOCD_3) 9.64 (4H, d, J = 7.1 Hz, C_5H_4N), 9.12 (2H, d, J = 5.3 Hz, C_5H_3N), 9.08 (2H, d, J = 0.8 Hz, C_5H_3N), 8.94 (4H, d, J = 7.1 Hz, C_5H_4N), 8.74 (2H, t, J = 1.4 Hz, C_6H_3), 8.71 (4H, d, J = 1.5 Hz, C_6H_3), 8.31 (2H, dd, J = 5.2, 1.9 Hz, C_5H_3N). ν(C=O) 1699s cm^{-1}. *Anal.* Calc. for $C_{36}H_{24}Cl_2N_4O_8{\cdot}3.5H_2O$: C, 55.8; H, 4.0; N, 7.2. Found: C, 56.1; H, 3.9; N, 7.1%.

2.2.2. *N*″,*N*‴-Di(4-carboxyphenyl)-4,4′:2′,2″:4″,4‴-quaterpyridinium chloride, $[(4\text{-}(CO_2H)Ph)_2qpy^{2+}]Cl_2$

This compound was prepared in a manner similar to $[(3,5\text{-}(CO_2H)_2Ph)_2qpy^{2+}]Cl_2$ by using $[(4\text{-MCPh})_2qpy^{2+}]Cl_2{\cdot}3.5H_2O$ (250 mg, 0.350 mmol) instead of $[(3,5\text{-}MC_2Ph)_2qpy^{2+}]Cl_2{\cdot}2H_2O$ to afford a cream-coloured solid. Yield: 187 mg (74%). δ_H (400 MHz, CD_3SOCD_3) 9.58 (4H, d, J = 7.1 Hz, C_5H_4N), 9.11 (2H, d, J = 5.3 Hz, C_5H_3N), 9.07 (2H, dd, J = 1.8, 0.8 Hz, C_5H_3N), 8.94 (4H, d, J = 7.1 Hz, C_5H_4N), 8.31–8.27 (6H, $C_5H_3N + C_6H_4$), 8.06 (4H, d, J = 8.6 Hz, C_6H_4). ν(C=O) 1709s cm^{-1}. *Anal.* Calc. for $C_{34}H_{24}Cl_2N_4O_4{\cdot}5.5H_2O$: C, 56.5; H, 4.9; N, 7.8. Found: C, 56.4; H, 4.5; N, 7.6%.

2.2.3. *cis*-$[Ru^{II}Cl_2(Me_2qpy^{2+})_2][PF_6]_4$ (**1**)

cis-$Ru^{II}Cl_2(DMSO)_4$ (30 mg, 0.062 mmol) and $[Me_2qpy^{2+}]Cl_2{\cdot}3.1H_2O$ (51 mg, 0.109 mmol) were added to *n*-propanol (13 mL) and the mixture was heated under reflux for 7 h. A solution of LiCl (53 mg, 1.25 mmol) in water (2 mL) was added, and the deep blue solution heated under reflux for 18 h. After cooling to room temperature, a dark blue precipitate was filtered off, washed with a little *n*-propanol and dried. This solid was dissolved in methanol (~20 mL). Addition of 1 M aqueous NH_4PF_6 afforded a dark blue precipitate which was filtered off, washed with water and dried. Yield: 48 mg (61%). δ_H (400 MHz, CD_3CN) 10.29 (2H, d, J = 6.0 Hz, C_5H_3N), 9.09 (2H, d, J = 1.3 Hz, C_5H_3N), 8.92 (2H, d, J = 1.5 Hz, C_5H_3N), 8.86 (4H, d, J = 6.8 Hz, C_5H_4N), 8.71 (4H, d, J = 6.8 Hz, C_5H_4N), 8.65 (4H, d, J = 6.8 Hz, C_5H_4N), 8.40 (4H, d, J = 6.8 Hz, C_5H_4N), 8.19 (2H, dd, J = 5.8, 1.8 Hz, C_5H_3N), 7.94 (2H, d, J = 6.0 Hz, C_5H_3N), 7.45 (2H, dd, J = 6.0, 1.5 Hz, C_5H_3N), 4.41 (6H, s, Me), 4.31 (6H, s, Me). *Anal.* Calc. for $C_{44}H_{40}Cl_2F_{24}N_8P_4Ru{\cdot}H_2O$: C, 36.4; H, 2.9; N, 7.7. Found: C, 36.5; H, 2.5; N, 7.8%. ES-MS: m/z = 1288 ($[M-PF_6]^+$), 571 ($[M-2PF_6]^{2+}$).

All of the compounds **2**–**6** were prepared in a manner similar to **1**, by using the appropriate proligand salt to give dark blue solids.

2.2.4. *cis*-$[Ru^{II}Cl_2(Ph_2qpy^{2+})_2][PF_6]_4$ (**2**)

Used $[Ph_2qpy^{2+}]Cl_2{\cdot}H_2O$ (66 mg, 0.119 mmol). Yield: 64 mg (60%). δ_H (400 MHz, CD_3CN) 10.34 (2H, d, J = 5.8 Hz, C_5H_3N), 9.26 (2H, d, J = 2.0 Hz, C_5H_3N), 9.20 (4H, d, J = 7.1 Hz, C_5H_4N), 9.10 (2H, d, J = 1.8 Hz, C_5H_3N), 9.05 (4H, d, J = 7.1 Hz, C_5H_4N), 8.88 (4H, d, J = 6.8 Hz, C_5H_4N), 8.64 (4H, d, J = 7.1 Hz, C_5H_4N), 8.26 (2H, dd, J = 6.0, 1.5 Hz, C_5H_3N), 8.03 (2H, d, J = 6.0 Hz, C_5H_3N), 7.90–7.81 (10H, Ph), 7.77 (10H, s, Ph), 7.58 (2H, dd, J = 6.2, 1.6 Hz, C_5H_3N). *Anal.* Calc. for $C_{64}H_{48}Cl_2F_{24}N_8P_4Ru{\cdot}5.5H_2O$: C, 43.2; H, 3.3; N, 6.3. Found: C, 43.1; H, 2.9; N, 6.3%. MALDI-MS: m/z = 1537 ($[M-PF_6]^+$), 697 ($[M-2PF_6]^{2+}$).

2.2.5. *cis*-$[Ru^{II}Cl_2\{(4\text{-AcPh})_2qpy^{2+}\}_2][PF_6]_4$ (**3**)

Used $[(4\text{-AcPh})_2qpy^{2+}]Cl_2{\cdot}1.8H_2O$ (77 mg, 0.118 mmol). Yield: 76 mg (68%). δ_H (400 MHz, CD_3CN) 10.35 (2H, d, J = 6.0 Hz, C_5H_3N), 9.24–9.22 (6H, $C_5H_4N + C_5H_3N$), 9.09–9.06 (6H, $C_5H_4N + C_5H_3N$), 8.87 (4H, d, J = 6.8 Hz, C_5H_4N), 8.64 (4H, d, J = 7.1 Hz, C_5H_4N), 8.35 (4H, d, J = 8.6 Hz, C_6H_4), 8.29–8.27 (6H, $C_5H_3N + C_6H_4$), 8.05 (2H, d, J = 6.0 Hz, C_5H_3N), 8.01 (4H, d, J = 8.8 Hz, C_6H_4), 7.90 (4H, d, J = 8.8 Hz, C_6H_4), 7.60 (2H, dd, J = 6.3, 1.5 Hz, C_5H_3N), 2.72 (6H, s, Me), 2.68 (6H, s, Me). ν(C=O) 1681s cm^{-1}. *Anal.* Calc. for $C_{72}H_{56}Cl_2F_{24}N_8O_4P_4Ru{\cdot}4H_2O$: C, 45.0; H, 3.4; N, 5.8. Found: C, 44.9; H, 2.9; N, 5.9%. MALDI-MS: m/z = 1706 ($[M-PF_6]^+$).

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