Evaluation of polynuclear dendrons as photosensitizers for dye-sensitized solar cells

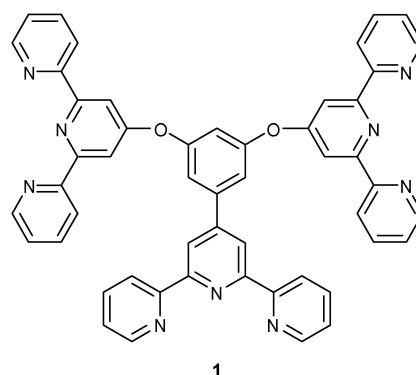Biljana Bozic-Weber, Edwin C. Constable,* Egbert Figgemeier, Catherine E. Housecroft and William Kylberg

Triruthenium dendrons bearing carboxylic acid substituents at the apex have been evaluated as photosensitizers in dye-sensitized solar cells. The disadvantages of a single carboxylate binding site are partially compensated by the higher charges of the trinuclear dendrons. However, the trinuclear units prove to be ineffective photosenstizers compared to mononuclear model compounds.

Introduction

Transition metal complexes are well-established as photosensitizers for photovoltaic cells[1-3] and following the initial proof-of-concept[4] and subsequent extension to nanocrystalline semiconductors,[5] ruthenium-functionalized dye-sensitized solar cells (DSSCs) represent state-of-the-art non-silicon-based photoconversion devices. A wide variety of ruthenium complexes have been evaluated, most of which incorporate one or more oligopyridine ligands. A critical design feature is the incorporation of functionality for covalently attaching the ruthenium complex to the titanium dioxide surface, most often through carboxylate, phosphonate or borate linkers.[2,3,6-8] In parallel studies, the so-called *antenna effect*, in which energy- or electron-transfer between metal centres can lead to multi-photon collection, has been well-established for multinuclear complexes.[9] The direction of energy- or electron-transfer can be precisely controlled through the selection of appropriate metal centre, bridging ligands and terminating ligands. However, there have been surprisingly few studies involving the covalent functionalisation of DSSCs with multinuclear complexes that might act as antenna-type photosensitizers.[10]

The heterotritopic ligand **1** (Scheme 1) is an attractive candidate for the synthesis of metallodendrimers and metallodendrons utilizing either convergent or divergent synthetic strategies. Complexes of **1** are most conveniently obtained directly from reactions of 3,5-dihydroxyphenyl-2,2′:6′,2″-terpyridine or its complexes with 4′-chloro-2,2′:6′,2″-terpyridine (Cltpy)

Department of Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland. E-mail: edwin.constable@unbas.ch; Fax: +41 61 267 1018; Tel: +41 61 267 1008
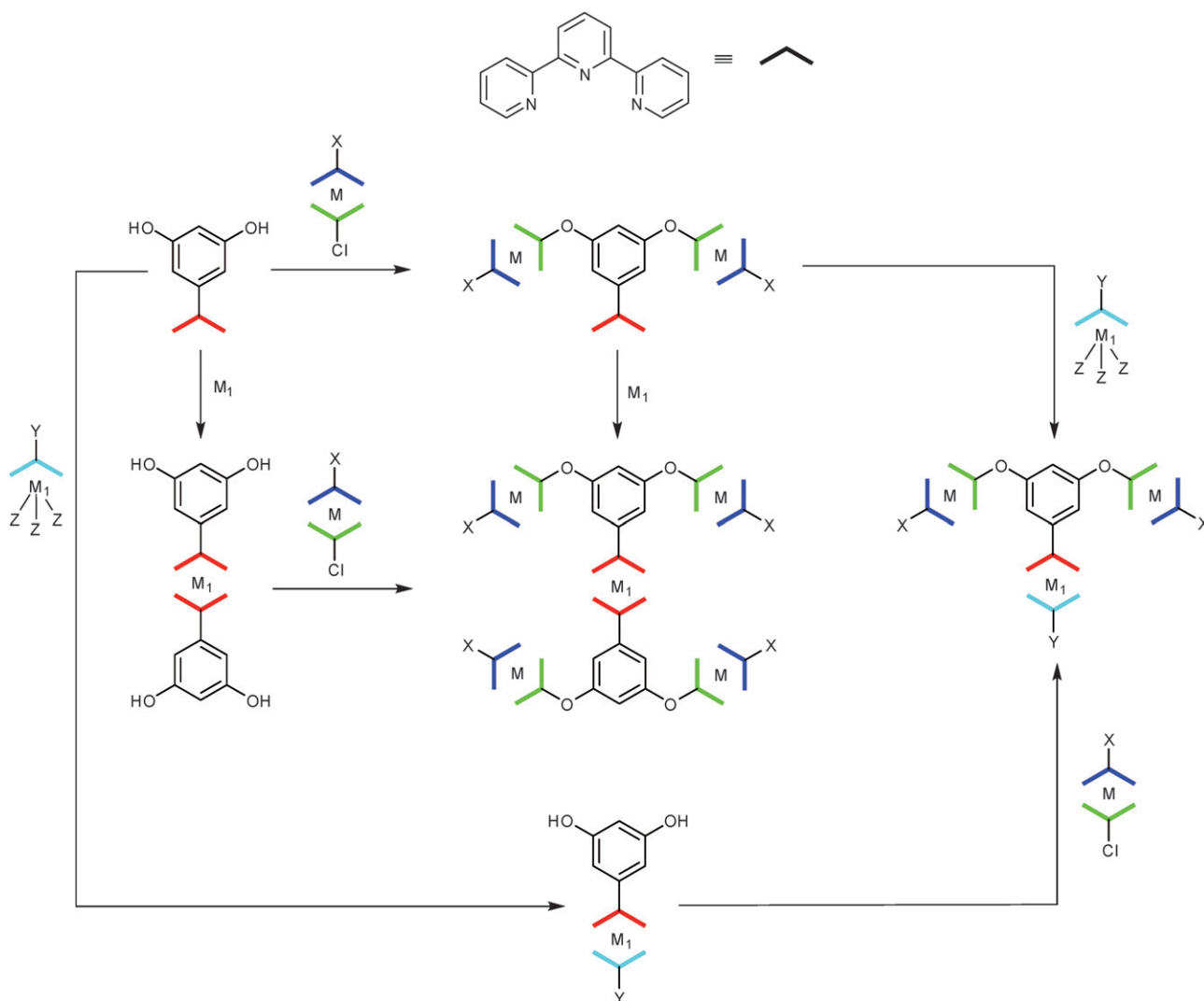

Scheme 1   Structure of ligand **1**.

complexes.[11,12] We have demonstrated the preparation of homo- and hetero- tri- and penta-nuclear complexes using these strategies and have demonstrated that the electron- or energy-transfer may be fine-tuned through the use of pendant substituents on the terminal tpy (tpy = 2,2′:6′,2″-terpyridine) ligands (Scheme 2). Furthermore, we have also shown that the photoinduced electron injection from a surface immobilized complex in a DSSC can be fine tuned by the substituents X on the remote terminal tpy ligands.[13]

We now extend the use of complexes of ligand **1** to the preparation of trinuclear species in which the unique tpy ligand at the focus of the metallodendron is further functionalized with a 4-carboxyphenyl substituent (Y in Scheme 2) to allow attachment to the titanium dioxide of a DSSC. As mentioned above, the terminal ligands can be chemically modified through substituent X (Scheme 2) so as to tune the electronic properties of the complex. In this paper we report the synthesis and properties

Broader context

Dye-sensitized solar cells are an important development in the conversion of solar photons to electrical energy. The dyes should collect as many photons as possible across the entire solar spectrum and inject electrons efficiently into the semiconductor. This paper investigates the use of multinuclear antenna complexes with multiple photon capture sites anchored to the semi-conductor surface. The general conclusion is that there is no significant antenna effect and the investment in synthetic methodology for multinuclear complexes is not merited.

Scheme 2 Synthetic strategies for the synthesis of trinuclear species in which a unique tpy ligand is at the focus of a metallodendron.

of a series of trinuclear metallodendrons based on **1** and report preliminary studies on their use in DSSCs.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer; the numbering scheme adopted for the ligands is shown in the schemes. Chemical shifts for ^{1}H and ^{13}C NMR spectra are referenced to residual solvent peaks with respect to TMS = δ 0 ppm. NMR spectra were assigned by using COSY, NOESY, DEPT, HMQC and HMBC experiments. Electrospray (ESI) mass spectra were recorded using a Finnigan MAT LCQ mass spectrometer. Electronic absorption spectra were recorded on a Varian-Cary 5000 spectrophotometer. Microwave reactions were carried out in a Biotage Initiator 8 reactor. Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer with solid samples on a Golden Gate diamond ATR accessory.

Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 system using platinum working

and auxiliary electrodes with a silver wire as pseudo-reference electrode; purified MeCN was used as solvent and 0.1M [^{n}Bu$_4$N][PF$_6$] as supporting electrolyte; ferrocene was added at the end of each experiment as an internal reference.

Preparation and evaluation of solar cells

DSSCs were prepared using standard methods. The titanium dioxide nanocrystalline films were prepared by "doctor blading" a TiO$_2$ paste (Solaronix Nanooxide-T, Switzerland) onto conducting glass slides (Hartford Glass Co., fluorine-doped tin oxide, TEC8) to give films 6 μm thick. After annealing at 450 °C for 30 min, the slides were dipped into 1 mM solutions of the dye overnight and the cells constructed using 0.1 M LiI, 0.05 M I$_2$, 0.6 M 1-butyl-3-methylimidazolinium iodide and 0.5 M 1-methylbenzimidazole in 3-methoxypropionitrile as electrolyte. The electrolyte was chosen to give the best possible comparison to the state-of-the-art optimized systems based on N719. Cathode electrodes were constructed from FTO glass pieces of the same dimensions as the anodes platinised by treatment with 5 mM H$_2$[PtCl$_6$] in propan-2-ol followed by heating to 280 °C for

300 | *Energy Environ. Sci.*, 2009, **2**, 299–305

This journal is © The Royal Society of Chemistry 2009

15 min. The anode and cathode were assembled using Surlyn (Dupont) plastic and the seal made by heating to 110–120 °C whilst pressing the two together. Measurements were made with irradiation from the rear using a lamp with intensity 100 mW cm^{-2} (1 sun).

Synthesis

Ligands **4**[13] and **5**,[12] and complexes [Ru(tpy)(Cltpy)][PF$_6$]$_2$,[14] [Ru(**6**)(Cltpy)][PF$_6$]$_2$[12] and [Ru(**2**)(tpy)][PF$_6$]$_2$[13] were synthesized as previously reported.

[Ru(4)(5)][PF$_6$]$_2$. Ligand **4** (500 mg, 1.36 mmol) was added to a solution of RuCl$_3\cdot$3H$_2$O (356 mg, 1.36 mmol) in EtOH (10 cm^3). The reaction mixture was heated in a microwave reactor at 140 °C for 15 min. The reaction mixture was cooled to room temperature and the black precipitate was collected and washed with EtOH, H$_2$O and Et$_2$O. Crude [Ru(**4**)Cl$_3$] was left to dry in the air and was used without any further purification or characterization. [Ru(**4**)Cl$_3$] (337 mg, 0.585 mmol) and ligand **5** (200 mg, 0.585 mmol) were added to EtOH (10 cm^3) and after addition of 4 drops of *N*-ethylmorpholine, the reaction mixture was heated in a microwave at 140 °C for 30 min. Upon cooling to room temperature, excess aqueous [NH$_4$][PF$_6$] was added and the red precipitate was collected over Celite. The product was purified by column chromatography (SiO$_2$, MeCN : H$_2$O : aqueous KNO$_3$ 7 : 0.5 : 1). The major red fraction was collected and aqueous [NH$_4$][PF$_6$] was added to the solution to affect [NO$_3$]$^-$/[PF$_6$]$^-$ exchange. [Ru(**4**)(**5**)][PF$_6$]$_2$ was isolated as a red solid (348 mg, 0.316 mmol, 54.0%). ^{1}H NMR (500 MHz, CD$_3$CN) δ (ppm) 9.04 (s, 2H, H^{B3}), 8.95 (s, 2H, H^{E3}), 8.65 (m, 4H, H^{A3+D3}), 8.36 (d$_{AB}$, *J* 8.6 Hz, 2H, H^{C3}), 8.31 (d$_{AB}$, *J* 8.6 Hz, 2H, H^{C2}), 7.95 (m, 4H, H^{A4+D4}), 7.44 (ddd, *J* 5.6, 1.4, 0.7 Hz, 2H, H$^{A6/D6}$), 7.42 (ddd, *J* 5.6, 1.4, 0.6 Hz, 2H, H$^{A6/D6}$), 7.18 (m, 4H, H^{A5+D5}), 7.15 (d, *J* 2.1 Hz, 2H, H^{F2}), 6.60 (t, *J* 2.1 Hz, 1H, H^{F4}), 3.99 (s, 3H, H^{Me}). ^{13}C NMR (125 MHz, CD$_3$CN) δ (ppm) 167.3 (C$^{C=O}$), 160.2 (C^{F3}), 159.2 (C$^{E2/D2}$), 159.1 (C$^{A2/B2}$), 156.7 (C$^{A2/B2}$), 156.3 (C$^{E2/D2}$), 153.5 (C^{A6+D6}), 149.5 (C^{E4}), 147.9 (C^{B4}), 142.2 (C^{C1}), 140.2 (C^{F1}), 139.1 (C^{A4+D4}), 132.8 (C^{C4}), 131.5 (C^{C3}), 129.2 (C^{C2}), 128.6 (C$^{A5/D5}$), 128.5 (C$^{A5/D5}$), 125.7 (C^{A3+D3}), 123.0 (C^{B3}), 122.7 (C^{E3}), 107.6 (C^{F2}), 105.3 (C^{F4}), 53.1 (C^{Me}). ESI-MS *m/z* 952.9 [M − 2H − PF$_6$]$^+$ (calc. 953.1). IR (solid, cm^{-1}): 3348m, 3041m, 1705s, 1605s, 1464w, 1398s, 1389s, 1354s, 1289s, 1252m, 1198w, 1157w, 1113w, 1000w, 833m [PF$_6$]$^-$, 791m, 771s, 752m, 733m. Electrochemical and UV-vis data, see Tables 1 and 2.

[(4)Ru(μ-1){Ru(tpy)}$_2$][PF$_6$]$_6$. [Ru(**4**)(**5**)][PF$_6$]$_2$ (300 mg, 0.269 mmol) and [Ru(tpy)(4′-Cltpy)][PF$_6$]$_2$ (620 mg, 0.683 mmol) were dissolved in MeCN (10 cm^3). K$_2$CO$_3$ (2.83 g, 20 mmol) was added and the reaction mixture was heated in a microwave reactor at 175 °C for 2 h. After cooling to room temperature, excess aqueous [NH$_4$][PF$_6$] was added and the red precipitate was collected over Celite and then redissolved in MeCN. Solvent was removed under reduced pressure and the products were separated by column chromatography (SiO$_2$, MeCN : H$_2$O : aqueous KNO$_3$ 7 : 0.5 : 1). The second, red fraction was collected, aqueous [NH$_4$][PF$_6$] was added to the solution, and the resulting red precipitate was collected by filtration. [(**4**)Ru(μ-**1**){Ru(tpy)}$_2$][PF$_6$]$_6$ was isolated as a red powder (152 mg, 0.0538 mmol,

20.0%). ^{1}H NMR (500 MHz, CD$_3$CN) δ (ppm) 9.25 (s, 2H, H^{B3}), 9.06 (s, 2H, H^{E3}), 8.76 (ddd, *J* 8.1, 1.2, 0.7 Hz, 2H, H$^{A3/D3}$), 8.74 (d, *J* 8.1 Hz, 4H, H^{J3}), 8.67 (ddd, *J* 8.1, 1.2, 0.7 Hz, 2H, H$^{A3/D3}$), 8.64 (s, 4H, H^{H3}), 8.53 (ddd, *J* 8.2, 1.3, 0.8 Hz, 4H, H^{G3}), 8.48 (ddd, *J* 8.2, 1.3, 0.8 Hz, 4H, H^{I3}), 8.46 (d, *J* 2.1 Hz, 2H, H^{F2}), 8.39 (t, *J* 8.1 Hz, 2H, H^{J4}), 8.37 (d$_{AB}$, *J* 8.7 Hz, 2H, H^{C3}), 8.32 (d$_{AB}$, *J* 8.7 Hz, 2H, H^{C2}), 7.99 (t, *J* 2.1 Hz, 1H, H^{F4}), 7.96 (dt, *J* 7.8, 1.5 Hz, 2H, H$^{A4/D4}$), 7.94 (dt, *J* 7.8, 1.5 Hz, 2H, H$^{A4/D4}$), 7.87 (dt, *J* 7.8, 1.5 Hz, 4H, H^{I4}), 7.75 (dt, *J* 7.8, 1.5 Hz, 4H, H^{G4}), 7.53 (ddd, *J* 5.6, 1.4, 0.7 Hz, 4H, H$^{G6/I6}$), 7.48 (m, 4H, H^{A6+D6}), 7.34 (ddd, *J* 5.6, 1.4, 0.6 Hz, 4H, H$^{G6/I6}$), 7.20 (m, 4H, H^{A5+D5}), 7.10 (m, 8H, H^{G5+I5}), 3.99 (s, 3H, H^{Me}). ^{13}C NMR (125 MHz, CD$_3$CN) δ (ppm) 168.4 (C^Q), 167.6 (C$^{C=O}$), 166.4 (C^{H4}), 159.5 (C^Q), 159.4 (C^Q), 159.1 (C^{H2}), 158.1 (coincident signals, C^Q), 157.0 (coincident signals, C^Q), 156.9 (C^Q), 154.1 (C$^{A6/D6/G6/I6}$), 153.9 (C$^{A6/D6/G6/I6}$), 153.8 (overlapping signals, C$^{A6/D6/G6/I6}$), 148.5 (C^{B4}), 147.3 (C^{E4}), 143.3 (C^{C1}), 142.5 (C^{F1}), 139.5 (C$^{A4/D4}$), 139.45 (C$^{A4/D4}$), 139.3 (C$^{G4/I4}$), 139.2 (C$^{G4/I4}$), 136.9 (C^{J4}), 133.1 (C^{C4}), 131.8 (C^{C3}), 129.5 (C^{C2}), 129.0 (overlapping signals C$^{A5/D5/G5/I5}$), 128.8 (C$^{A5/D5/G5/I5}$), 126.1 (overlapping signals, C$^{A3/D3/G3}$), 126.0 (C$^{A3/D3}$), 125.7 (C^{I3}), 125.0 (C^{J3}), 123.3 (C$^{B3/E3}$), 123.25 (C$^{B3/E3}$), 119.7 (C^{F2}), 116.4 (C^{F4}), 114.6 (C^{H3}), 53.5 (C^{Me}). Not all quaternary carbon signals could be unambiguously assigned. ESI-MS *m/z* 1260.2 [M − 2PF$_6$]$^{2+}$ (calc. 1261.1), 791.9 [M − 3PF$_6$]$^{3+}$ (calc. 792.1), 557.7 [M − 4PF$_6$]$^{4+}$ (calc. 557.6), 417.6 [M − 5PF$_6$]$^{5+}$ (calc. 417.3). IR (solid, cm^{-1}): 2924w, 2854w, 1711w, 1674w, 1605m (C=O), 1585w, 1466w, 1448w, 1404m, 1286w, 1202m, 1026w, 1007w, 833s [PF$_6$]$^-$, 789m, 768m, 754m, 604m. Electrochemical and UV-vis data, see Tables 1 and 2.

Found: C, 41.93; H, 3.42; N, 7.51. C$_{104}$H$_{72}$N$_{18}$O$_4$F$_{36}$P$_6$Ru$_3$.13CH$_3$OH·5H$_2$O requires C, 42.36; H, 4.07; N, 7.59%.

[(2)Ru(μ-1){Ru(tpy)}$_2$][PF$_6$]$_6$. [(**4**)Ru(μ-**5**){Ru(tpy)}$_2$][PF$_6$]$_6$ (75 mg, 0.025 mmol) was dissolved in MeCN (2 cm^3) and aqueous NaOH (1 cm^3, 2M) was added slowly as the reaction mixture was being heated to 80 °C. This temperature was maintained for 24 h, after which time, a few drops of HPF$_6$ were added. The product was precipitated by the addition of aqueous [NH$_4$][PF$_6$]. The red solid was filtered through Celite, redissolved in MeCN and the solvent was removed *in vacuo*. [(**2**)Ru(μ-**1**){Ru(tpy)}$_2$][PF$_6$]$_6$ was isolated as a red powder (56 mg, 0.020 mmol, 80%). ^{1}H NMR (500 MHz, CD$_3$CN) δ (ppm) 9.22 (s, 2H, H^{B3}), 9.06 (s, 2H, H^{E3}), 8.74 (ddd, *J* 8.1, 1.2, 0.7 Hz, 2H, H$^{A3/D3}$), 8.73 (d, *J* 8.1 Hz, 4H, H^{J3}), 8.67 (ddd, *J* 8.1, 1.2, 0.7 Hz, 2H, H$^{A3/D3}$), 8.62 (s, 4H, H^{H3}), 8.51 (ddd, *J* 8.2, 1.2, 0.8 Hz, 4H, H^{G3}), 8.48 (ddd, *J* 8.2, 1.2, 0.8 Hz, 4H, H^{I3}), 8.44 (d, *J* 2.1 Hz, 2H, H^{F2}), 8.39 (t, *J* 8.1 Hz, 2H, H^{J4}), 8.37 (d$_{AB}$, *J* 8.7 Hz, 2H, H^{C3}), 8.31 (d$_{AB}$, *J* 8.6 Hz, 2H, H^{C2}), 7.97 (t, *J* 2.1 Hz, 1H, H^{F4}), 7.96 (dt, *J* 7.8, 1.5 Hz, 2H, H$^{A4/D4}$), 7.94 (dt, *J* 7.8, 1.5 Hz, 2H, H$^{A4/D4}$), 7.89 (dt, *J* 7.8, 1.5 Hz, 4H, H^{I4}), 7.76 (dt, *J* 7.8, 1.5 Hz, 4H, H^{G4}), 7.51 (ddd, *J* 5.6, 1.5, 0.7 Hz, 4H, H$^{G6/I6}$), 7.47 (m, 4H, H^{A6+D6}), 7.34 (ddd, *J* 5.6, 1.5, 0.7 Hz, 4H, H$^{G6/I6}$), 7.20 (m, 4H, H^{A5+D5}), 7.10 (m, 8H, H^{G5+I5}). ^{13}C NMR (125 MHz, CD$_3$CN) δ (ppm) 168.4 (C^Q), 167.6 (C$^{C=O}$), 166.4 (C^{H4}), 159.5 (C^Q), 159.4 (C^Q), 159.1 (C^{H2}), 158.1 (coincident signals, C^Q), 157.0 (coincident signals, C^Q), 156.9 (C^Q), 154.1 (C$^{A6/D6/G6/I6}$), 153.9 (C$^{A6/D6/G6/I6}$), 153.8 (overlapping signals, C$^{A6/D6/G6/I6}$), 148.5 (C^{B4}), 147.3 (C^{E4}), 143.3 (C^{C1}), 142.5 (C^{F1}), 139.5 (C$^{A4/D4}$), 139.45 (C$^{A4/D4}$), 139.3 (C$^{G4/I4}$), 139.2 (C$^{G4/I4}$), 136.9 (C^{J4}), 133.1 (C^{C4}), 131.8 (C^{C3}), 129.5 (C^{C2}),
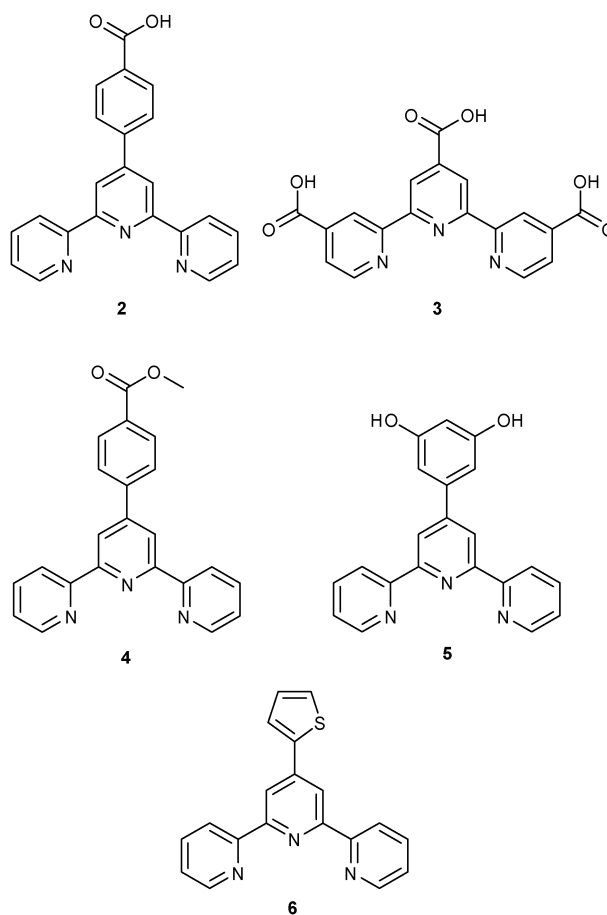
129.0 (overlapping signals $C^{A5/D5/G5/I5}$), 128.8 ($C^{A5/D5/G5/I5}$), 126.1 (overlapping signals $C^{A3/D3/G3}$), 126.0 ($C^{A3/D3}$), 125.7 (C^{I3}), 125.0 (C^{J3}), 123.1 ($C^{B3/E3}$), 123.25 ($C^{B3/E3}$), 119.7 (C^{F2}), 116.4 (C^{F4}), 114.6 (C^{H3}). Not all quaternary carbon signals could be unambiguously assigned. ESI-MS m/z 1254.0 $[M - 2PF_6]^{2+}$ (calc. 1254.1). IR (solid, cm^{-1}): 3659w, 2924w, 2854w, 1605m (C=O), 1587w, 1466w, 1450w, 1435w, 1355w, 1405m, 1389w, 1355w, 1286w, 1245w, 1202m, 1109w, 1028w, 1003w, 829s $[PF_6]^-$, 754w, 740w, 723w. Electrochemical and UV-vis data, see Tables 1 and 2. Found: C, 38.13; H, 4.11; N, 6.11. $C_{103}H_{69}N_{18}O_4F_{36}K-P_6Ru_3.18CH_3OH.(KPF_6)_2$ requires C, 38.45; H, 3.76; N, 6.67%.

[(4)Ru(μ-1){Ru(6)}_2][PF_6]_6. A solution of $[Ru(4)(5)][PF_6]_2$ (300 mg, 0.272 mmol) and $[Ru(6)(4'-Cltpy)][PF_6]_2$ (611 mg, 0.627 mmol) in MeCN (10 cm^3) was treated with dry K_2CO_3 (2.86 g, 21 mmol). The reaction mixture was heated in a microwave reactor at 175 °C for 2 h. After cooling to room temperature, excess aqueous $[NH_4][PF_6]$ was added to precipitate the product. This was collected on Celite, redissolved in MeCN and purified by column chromatography (SiO_2, MeCN : H_2O : aqueous KNO_3 7 : 0.5 : 1). The second red (major) fraction was collected and aqueous $[NH_4][PF_6]$ was added to the solution to precipitate the product. $[(4)Ru(μ-1){Ru(6)}_2][PF_6]_6$ was isolated as a red solid (178 mg, 0.0595 mmol, 22.0%). ^{1}H NMR (500 MHz, CD_3CN) δ (ppm) 9.22 (s, 2H, H^{B3}), 9.07 (s, 2H, H^{E3}), 8.92 (s, 4H, H^{J3}), 8.74 (ddd, J 8.2, 1.2, 0.7 Hz, 2H, $H^{A3/D3}$), 8.68 (ddd, J 8.1, 1.2, 0.7 Hz, 2H, $H^{A3/D3}$), 8.64 (ddd, J 8.2, 1.2, 0.8 Hz, 4H, H^{I3}), 8.63 (s, 4H, H^{H3}), 8.52 (ddd, J 8.2, 1.2, 0.8 Hz, 4H, H^{G3}), 8.45 (d, J 2.1 Hz, 2H, H^{F2}), 8.37 (d_{AB}, J 8.7 Hz, 2H, H^{C3}), 8.32 (d_{AB}, J 8.6 Hz, 2H, H^{C2}), 8.17 (dd, J 3.7, 1.1 Hz, 2H, H^{K3}), 7.94 (m, 6H, $H^{A4 + D4 + F4}$), 7.90 (dt, J 7.7, 1.5 Hz, 4H, H^{I4}), 7.83 (dd, J 5.1, 1.1 Hz, 2H, H^{K5}), 7.78 (dt, J 7.8, 1.5 Hz, 4H, H^{G4}), 7.51 (ddd, J 5.5, 1.5, 0.7 Hz, 4H, $H^{G6/I6}$), 7.47 (m, 4H, $H^{A6 + D6}$), 7.44 (ddd, J 5.7, 1.5, 0.7 Hz, 4H, $H^{G6/I6}$), 7.42 (dd, J 5.1, 3.7 Hz, 2H, H^{K4}), 7.20 (m, 4H, $H^{A5 + D5}$), 7.12 (m, 8H, $H^{G5 + I5}$), 3.99 (s, 3H, H^{Me}). ^{13}C NMR (125 MHz, CD_3CN) δ (ppm) 167.6 ($C^{C=O}$), 166.3 (C^{H4}), 159.4 (C^Q), 159.35 (C^Q), 159.3 (C^Q), 159.1 (C^Q), 158.0 (C^Q), 157.95 (C^Q), 157.1 (C^Q), 157.0 (C^Q), 156.8 (C^Q), 154.0 ($C^{A6/D6/G6/I6}$), 153.8 (overlapping signals, $C^{A6/D6/G6/I6}$), 148.4 (C^{B4}), 147.2 (C^{E4}), 143.3 (C^{C1}), 142.6 (C^{J4}), 142.4 (C^{F1}), 141.2 (C^{K1}), 139.5 ($C^{A4/D4}$), 139.4 ($C^{A4/D4}$), 139.2 (overlapping signals, $C^{G4 + I4}$), 133.0 (C^{C4}), 131.7 (C^{C3}), 131.2 (C^{K5}), 130.8 (C^{K4}), 129.5 (C^{K3}), 129.4 (C^{C2}), 129.0 ($C^{A5/D5/G5/I5}$), 128.9 (overlapping signals, $C^{A5/D5/G5/I5}$), 128.8 ($C^{A5/D5/G5/I5}$), 126.0 (overlapping signals, $C^{A3/D3/G3}$), 125.9 (C^{I3}), 123.3 ($C^{E3/B3}$), 123.2 ($C^{E3/B3}$), 120.9 (C^{J3}), 119.7 (C^{F2}), 116.4 (C^{F4}), 114.5 (C^{H3}), 53.4 (C^{Me}). Not all quaternary carbon signals could be unambiguously assigned. ESI-MS m/z 1343.1 $[M - 2PF_6]^{2+}$ (calc. 1343.6), 847.1 $[M - 3PF_6]^{3+}$ (calc. 846.4). IR (solid, cm^{-1}): 3317w, 1715w, 1605m (C=O), 1587w, 1466w, 1427m, 1402w, 1354w, 1285w, 1202m, 1001m, 956w, 831s $[PF_6]^-$, 787m, 750m, 715m. Electrochemical and UV-vis data, see Tables 1 and 2. Found: C, 40.62; H, 3.19; N, 7.70. $C_{112}H_{76}N_{18}O_4F_{36}P_6Ru_3S_2\cdot18H_2O$ requires C, 40.77; H, 3.41; N, 7.64%.

Results and discussion

Synthetic and design strategy

Our selection of ligand **2** (Scheme 3) for attachment to the surface was based on the ready availability of this ligand[13,15–23] although
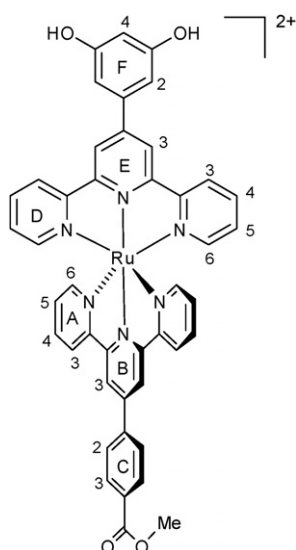

Scheme 3 Structures of ligands **2** to **6**.

we[13] and others[19,20,23] find that it is inferior to polycarboxylic acids such as **3**[24,25] (Scheme 3) for surface functionalization. We have previously demonstrated that the higher positive charges of dendritic and rod-like multinuclear complexes result in an enhanced binding to metal oxide surfaces and we hoped that this effect might compensate for the intrinsically weak binding of **2**.[26]

Synthesis and characterisation
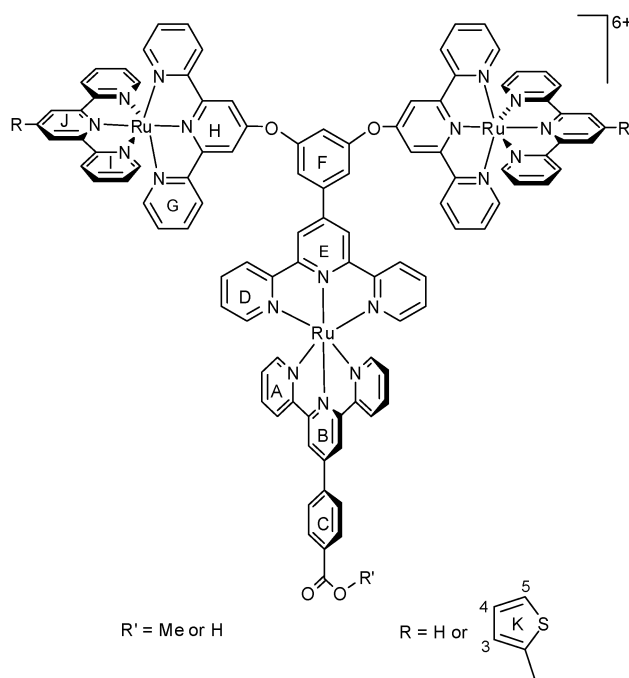
Our synthetic strategy for the modification of the tpy ligand in $[Ru(2)(tpy)][PF_6]_2$ is based on a divergent approach described by us for trinuclear and pentanuclear ruthenium(II)-containing metallorods and metallostars.[12] Central to the procedure is the use of a pendant 4'-(3,5-dihydroxyphenyl)-2,2':6',2''-terpyridine (**5**) ligand to generate phenolate functionalities that readily react with electrophilic metal complexes. Rather than carry out the synthetic steps using the carboxylic acid derivatized complex, it is more efficient to protect the acid functionality and use $[Ru(4)(5)]^{2+}$ (Scheme 4) as the precursor. This was prepared in moderate yield by the stepwise treatment of $RuCl_3\cdot3H_2O$ with **4**, followed by **5** in the presence of N-ethylmorpholine. The product was isolated as the hexafluoridophosphate salt. In the electro-spray mass spectrum, the highest mass peak envelope at m/z 952.9 showed the expected isotope distribution for $[M - 2H - PF_6]^+$. The ^{1}H NMR spectrum revealed the presence of two tpy ligand environments. The singlets for protons H^{E3} and H^{B3} were

302 | *Energy Environ. Sci.*, 2009, **2**, 299–305

This journal is © The Royal Society of Chemistry 2009

Scheme 4 Structure of [Ru(**4**)(**5**)]$^{2+}$ with ring labelling for NMR spectroscopic assignments.

Scheme 5 Structures of [LRu(μ-**1**){Ru(tpy)}$_2$]$^{6+}$ (L = **2** or **4**) and [(**4**)Ru(μ-**1**){Ru(**6**)}$_2$]$^{6+}$ with ring labelling for NMR spectroscopic assignments. Atom numbering is as shown in Scheme 4.

distinguished by the observation of cross peaks in the NOESY spectrum to protons H^{F2} and H^{C2}, respectively. From this starting point, the ^{1}H and ^{13}C NMR spectra were assigned by use of COSY, DEPT, HMQC and HMBC techniques. The presence of the ester group was confirmed by the appearance of a singlet at δ 3.99 ppm (assigned to the Me group) in the ^{1}H NMR spectrum, and a resonance at δ 167.3 ppm (C$^{C=O}$) in the ^{13}C NMR spectrum which showed an HMBC cross peak to the methyl signal.

The presence of the 4′-chloro substituent in [Ru(tpy)(4′-Cltpy)]$^{2+}$ activates the 4′-carbon site towards attack by nucleophiles,[27–29] and we have capitalized upon this behaviour for the divergent synthesis of a range of multinuclear systems.[12,30–36] The reaction of [Ru(**4**)(**5**)][PF$_6$]$_2$ with 2.5 equivalents of [Ru(tpy)(4′-Cltpy)][PF$_6$]$_2$ in the presence of K$_2$CO$_3$ was carried out in a micowave reactor at 175 °C. After chromatographic workup, [(**4**)Ru(μ-**1**){Ru(tpy)}$_2$][PF$_6$]$_6$ was isolated in 20% yield. The electrospray mass spectrum showed a series of peak envelopes arising from sequential loss of [PF$_6$]$^-$ ions, with the highest mass peak coming at m/z 1260.2, assigned to [M − 2PF$_6$]$^{2+}$. The isotope distributions for each peak envelope matched those simulated for the trinuclear complex. Retention of the ester group was confirmed by IR spectroscopic data ($\nu_{C=O}$ 1605 cm^{-1}) and NMR spectroscopic resonances at δ 3.99 ppm (^{1}H) and δ 167.6 ppm (^{13}C) with an HMBC cross peak between the signals. The ^{1}H and ^{13}C NMR spectra were consistent with the presence of four tpy environments in a ratio 1 : 1 : 2 : 2 (Scheme 5). Protons H^{J3} and H^{H3} were easily distinguished from one another by the appearance of the former as a doublet (J 8.1 Hz) and the latter as a singlet. The attachment of the pendant {Ru(tpy)$_2$} groups causes the signals for H^{B3} and H^{E3} to shift to higher frequency (H^{E3} δ 8.95 to 9.06 ppm, and H^{B3} 9.04 to 9.25 pm on going from [Ru(**4**)(**5**)]$^{2+}$ to (**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$). As expected, protons H^{F2} and H^{F4} respond the most to the attachment of the {Ru(tpy)$_2$} moieties (H^{F2} δ 7.15 to 8.46 ppm, and H^{F4} δ 6.60 to 7.99 pm). The ^{13}C NMR spectroscopic signature of ring F is similarly affected, with signals for atoms C^{F2} and C^{F4} shifting

from δ 107.6 to 119.7 ppm, and δ 105.4 to 116.4 ppm, respectively, on going from [Ru(**4**)(**5**)]$^{2+}$ to [(**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$. Protons H^{I3} and H^{G3} could be distinguished only by the response of one of these signals to the attachment of the thienyl group (see below).

The conversion of the ester functionality to carboxylic acid was achieved by treatment with aqueous NaOH at 80 °C for 24 h. With the exception of the disappearance of the signals for the methyl group, the ^{1}H and ^{13}C NMR spectra of [(**2**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$ are essentially identical to those of [(**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$. The highest mass peak at m/z 1254.0 in the electrospray mass spectrum was consistent with [M − 2PF$_6$]$^{2+}$, and the isotope distribution matched that calculated for the trinuclear complex.

The final modification made to the complex was to terminate each pendant {Ru(tpy)$_2$} unit in a 2-thienyl substituent. This was achieved by reaction of [Ru(**4**)(**5**)][PF$_6$]$_2$ with 2.3 equivalents of [Ru(**6**)(4′-Cltpy)][PF$_6$]$_2$[12] under the same conditions used to prepare [(**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$. After column chromatographic purification, [(**4**)Ru(μ-**1**){Ru(**6**)}$_2$][PF$_6$]$_6$ was isolated in 22% yield. The electrospray mass spectrum of the complex exhibited peak envelopes at m/z 1343.1 and 847.1 with the correct isotope patterns for [M − 2PF$_6$]$^{2+}$ and [M − 3PF$_6$]$^{3+}$. ^{1}H NMR spectroscopy was particularly helpful in monitoring the conversion of [(**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$ to [(**4**)Ru(μ-**1**){Ru(**6**)}$_2$]$^{6+}$. The retention of four tpy environments (1 : 1 : 2 : 2) confirmed that both pendant tpy moieties had undergone reaction. The resonance for H^{J3} shifts significantly (δ 8.74 to 8.92 ppm) and collapses to a singlet, while the signal for H^{J4} disappears, consistent with functionalization at the pendant tpy 4′-position. In [(**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$, distinguishing between the H^{I3} and

H^{G3} signals was difficult, but attachment of the thienyl substituent results in a shift to higher frequency for one of the two signals (δ 8.48 to 8.64 ppm, assigned to H^{I3}) while the second signal is unaffected. The thienyl protons appear at δ 8.17, 7.83 and 7.42 ppm, assigned to H^{K3}, H^{K5} and H^{K4}, respectively. Attempts made to deprotect the terminal ester group in [(**4**)Ru(μ-**1**){Ru(**6**)}$_2$]$^{6+}$ by treatment with 2M aqueous NaOH were not successful. Thin layer chromatography showed the formation of four, red products (assumed all to be ruthenium(II)-containing) which could not be cleanly separated by column chromatography or recrystallization. We propose that the presence of the thienyl substituents in [(**4**)Ru(μ-**1**){Ru(**6**)}$_2$]$^{6+}$ makes the complex susceptible to cleavage by HO$^-$ at the ether linkages.

Spectroscopic and electrochemical characterisation

The complexes [Ru(tpy)$_2$]$^{2+}$ and [Ru(**2**)(tpy)]$^{2+}$ act as models with which to compare the electronic spectroscopic (Table 1) and electrochemical properties (Table 2) of the functionalized species. In MeCN solution, each complex exhibits an MLCT band around 480–490 nm diagnostic of a {Ru(tpy)$_2$}$^{2+}$ chromophore, as well as a series of intense, ligand-based absorptions in the UV region. The introduction of a C$_6$H$_4$CO$_2$H substituent results in a red shift of the MLCT band on going from [Ru(tpy)$_2$]$^{2+}$ to [Ru(**2**)(tpy)]$^{2+}$, and a further red shift is observed on going from [Ru(**2**)(tpy)]$^{2+}$ to [Ru(**4**)(**5**)]$^{2+}$. This is consistent with our earlier report that substitution at the 4′-position of ruthenium(II)-coordinated tpy causes a red shift in the MLCT band irrespective of whether the substituent is electron-donating or electron-accepting.[37] Attachment of the pendant arms to [Ru(**4**)(**5**)]$^{2+}$ results in an increase in the intensity of the MLCT band, in keeping with a change from mono- to triruthenium species. The addition of the peripheral thienyl substituents is accompanied by a 5 nm red shift in the MLCT band with little change in intensity.

The MLCT absorptions are typically broad and represent a series of overlapping transitions. The observed red-shifting with [(**4**)Ru(μ-**1**){Ru(**6**)}$_2$]$^{6+}$ is associated with the terminal **6** ligands and the three metal-centred chromo- and lumophores can probably be regarded as decoupled. A similar trend is observed in the electrochemical data (Table 2). These observations lead to the possibility of fine-tuning the "outer" {Ru(tpy)$_2$} moieties such that they formally lie below the conduction band of the TiO$_2$. This could be achieved by cyclometallation (replacing an N,N',N''-donor by a C,N,N'-donor) or changing the metal from ruthenium to osmium and in such a case, the "outer" units would not expected be expected to act as photosensitizers on their own. However, by coupling the "outer" units with an "inner" unit that can act as a photosensitizer, the injection will involve the "inner" centre but the regeneration the "outer" centres (Scheme 6). This offers the intriguing possibility of combining a cascade regeneration step with a formal up-conversion. We are currently extending the dendrons to encompass these new classes of photosensitizers.
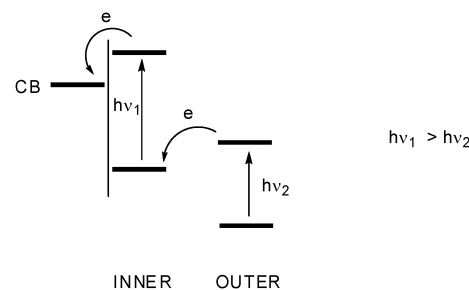
Performance of DSSCs containing dendron photosensitizers

DSSCs have been constructed (see Experimental) using the mononuclear test dye [Ru(**2**)(tpy)]$^{2+}$, the dendron [(**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$ that is not expected to chemisorb to the TiO$_2$ and finally the dendron [(**2**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$ which should bind

Table 1 UV-vis spectroscopic data for complexes (all [PF$_6$]$^-$ salts) in MeCN solution (1.7×10^{-5} mol dm^{-3} for [Ru(**2**)(tpy)][PF$_6$]$_2$, 4.0×10^{-6} mol dm^{-3} for other complexes)

Complex cation	Absorption λ_{max}/nm (ε_{max}/10^3 dm^3 mol^{-1} cm^{-1}) Ligand $\pi^* \leftarrow \pi$	MLCT
[Ru(tpy)$_2$]$^{2+}$ ^{a}	270 (31.6), 307 (50.4)	475 (11.6)
[Ru(**2**)(tpy)]$^{2+}$	274 (57.8), 306 (55.4)	483 (16.0)
[Ru(**4**)(**5**)]$^{2+}$	283 (34.3), 308 (29.0)	491 (12.5)
[(**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$	286 (125), 306 (145.8)	489 (55.3)
[(**2**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$	274 (100.4), 306 (120.0)	488 (40.7)
[(**4**)Ru(μ-**1**){Ru(**6**)}$_2$]$^{6+}$	286 (119.5), 305 (121.5)	494 (59.5)

^{a} ref. 38.

Scheme 6 A formal up-conversion scheme in which the "outer" metal centres of the dendron have ground and excited states below the conduction band of the TiO$_2$. If the excited state of the "outer" metal centres lies above the ground state of the "inner", then absorption of light with energy hν_1 generates a hole at the "inner" metal. Electron transfer from the "outer" excited state leads to regeneration of the "inner" photosensitizer.

to the TiO$_2$. The characteristics of these cells, as measured using our modified scanning electrochemical microscope system, are presented in Table 3. Firstly, we can compare the model compound [Ru(**2**)(tpy)]$^{2+}$ with N719 dye and confirm that the overall efficiency is significantly lower, an observation usually ascribed to the poor binding of the single carboxylate-functionalised dye to the titania.

When we consider the two dendrons a number of interesting features emerge. Firstly, both the ester and the free acid give similar coverage as monitored by the absorbance of the TiO$_2$ films (calculated assuming the absorption coefficients of the solution and chemisorbed material are similar). This could either be due to hydrolysis of the ester at the surface and the generation of identical chemisorbed species or the dominance of the charge effect on physisorption. The latter is shown to be the case by a comparison of the J_{SC} values for the two DSSCs. Only in the case of the covalently linked carboxylic acid species is the injection to the conduction band efficient.

However, the overall set of data indicates that for conventional DSSCs which do not rely on up-conversion, the dendrons offer no significant advantage over conventional mononuclear dyes.

Conclusions

A new class of trinuclear dendrons has been prepared with carboxylic acid functionality at the apex that is utilized for the attachment

Table 2 Cyclic voltammogram data[a] for complexes (all [PF$_6$]$^-$ salts) in MeCN solution.[a]

Complex cation	Metal-centred oxidation/V	Ligand-centred processes/V
[Ru(tpy)$_2$]$^{2+}$ [b]	+0.92	−1.67, −1.92
[Ru(**2**)(tpy)]$^{2+}$	+0.88 (rev)	−1.63 (rev), −1.84 (rev)
[Ru(**4**)(**5**)]$^{2+}$	+0.92 (rev)	+1.39 (irrev phenol oxidation), −1.63, −1.82, −2.30 (irrev tpy reductions)
[(**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$	+0.95 (quasirev)	−1.64 (rev), −1.78 (rev)
[(**2**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$	+0.86 (rev)	−1.62 (rev), −1.82 (rev)
[(**4**)Ru(μ-**1**){Ru(**6**)}$_2$]$^{6+}$	+0.80 (quasirev)	+1.60 (irrev thienyl oxidation), −1.64, −1.80 (rev tpy reductions)

[a] Potentials are *vs.* Fc/Fc$^+$ = 0 V; in 0.1 M [^{n}Bu$_4$N][PF$_6$] at a sweep rate of 100 mV s^{-1}. [b] ref. 38.

Table 3 Current–voltage characteristic data for DSSCs constructed with trinuclear dendrons and model compounds as photosensitizers. Each dye was delivered as a hexafluoridophosphate salt and cells constructed as described in the experimental section

Dye	J_{sc}/mA cm^{-2}	V_{oc}/mV	FF (%)	η (%)	Absorbance TiO$_2$	Coverage/nmol cm^{-2}	J_{sc}/Coverage/mA nmol^{-1}
[Ru(**2**)(tpy)]$^{2+}$	0.64	520	0.67	0.5	2.30	192	0.003
[(**4**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$	0.03	340	0.53	0.01	0.04	0.7	0.04
[(**2**)Ru(μ-**1**){Ru(tpy)}$_2$]$^{6+}$	0.37	390	0.63	0.1	0.07	1.0	0.37
N719	12.64		0.74	0.55	5.2		

of the dyes to TiO$_2$ to give DSSCs. The DSSCs exhibit modest photocurrents but are not competitive with those involving simple mononuclear photosensitizers. Physisorption of the highly charge cationic dendrons appears to be a major factor, although covalent linkage of the carboxylic acid is necessary for charge injection.

Acknowledgements

References

1 V. Balzani, A. Credi and M. Venturi, *ChemSusChem*, 2008, **1**, 26.
2 M. K. Nazeeruddin and M. Grätzel, *Struct. Bonding*, 2007, **123**, 113.
3 M. Grätzel, *Inorg. Chem.*, 2005, **44**, 6841.
4 S. Anderson, E. C. Constable, M. P. Dare-Edwards, J. B. Goodenough, A. Hamnett, K. R. Seddon and R. D. Wright, *Nature*, 1979, **280**, 571.
5 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
6 A. S. Polo, M. K. Itokazu and N. Y. M. Iha, *Coord. Chem. Rev.*, 2004, **248**, 1343.
7 S. Altobelloa, C. A. Bignozzi, S. Caramoria, G. Larramonab, S. Quicic, G. Marzannic and R. Lakhmirid, *J. Photochem. Photobiol., A*, 2004, **166**, 91.
8 O. Schwarz, D. van Loyen, S. Jockusch, N. J. Turro and H. Dürr, *J. Photochem. Photobiol., A*, 2000, **132**, 91.
9 S. Serroni, S. Campagna, F. Puntoriero, C. Di Pietro, N. D. McClenaghan and F. Loiseau, *Chem. Soc. Rev.*, 2001, **30**, 367.
10 (*a*) R. Mosurkal, J.-A. He, J. Kumar, L. Li, J. Walker and L. Samuelson, *Mater. Res. Soc. Symp. Proc.*, 2002, **708**, 367; (*b*) C. A. Bignozzi, R. Argazzi, F. Scandola, J. R. Schoonover and G. J. Meyer, *Sol. Energy Mater. Sol. Cells*, 1995, **38**, 187.
11 E. C. Constable, R. W. Handel, C. E. Housecroft, A. F. Morales, L. Flamigni and F. Barigelletti, *Dalton Trans.*, 2003, 1220.
12 E. C. Constable, R. W. Handel, C. E. Housecroft, A. F. Morales, B. Ventura, L. Flamigni and F. Barigelletti, *Chem.–Eur. J.*, 2005, **11**, 4024.
13 E. Figgemeier, V. Aranyos, E. C. Constable, R. W. Handel, C. E. Housecroft, C. Risinger, A. Hagfeldt and E. Mukhtar, *Inorg. Chem. Commun.*, 2004, **7**, 117.
14 E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher and M. A. M. Daniels, *New J. Chem.*, 1992, **16**, 855.
15 E. C. Constable, E. L. Dunphy, C. E. Housecroft, M. Neuburger, S. Schaffner, F. Schaper and S. R. Batten, *Dalton Trans.*, 2007, 4323.
16 E. C. Constable, C. E. Housecroft and S. Mundwiler, *Dalton Trans.*, 2003, 2112.
17 M. W. Cooke, G. S. Hanan, F. Loiseau, S. Campagna, M. Watanabe and Y. Tanaka, *J. Am. Chem. Soc.*, 2007, **129**, 10479.
18 M. W. Cooke, P. Tremblay and G. S. Hanan, *Inorg. Chim. Acta*, 2008, **361**, 2259.
19 V. Duprez, M. Biancardo and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 230.
20 V. Duprez and F. C. Krebs, *Tetrahedron Lett.*, 2006, **47**, 3785.
21 B.-W. Jing, T. Wu, M.-H. Zhang and T. Shen, *Gaodeng Xuexiao Huaxue Xuebao*, 2000, **21**, 395.
22 F. Neve, D. La, Massimo, F. Puntoriero and S. Campagna, *Inorg. Chim. Acta*, 2006, **359**, 1666.
23 H. Wolpher, S. Sinha, J. Pan, A. Johansson, M. J. Lundqvist, P. Persson, R. Lomoth, J. Bergquist, L. Sun, V. Sundström, B. Åkermark and T. Polívka, *Inorg. Chem.*, 2007, **46**, 638.
24 M. K. Nazeeruddin, P. Pechy and M. Grätzel, *Chem. Commun.*, 1997, 1705.
25 M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi and M. Grätzel, *J. Am. Chem. Soc.*, 2001, **123**, 1613.
26 E. C. Constable, P. Harverson and J. J. Ramsden, *Chem. Commun.*, 1997, 1683.
27 E. C. Constable, *Metals and Ligand Reactivity*, VCH, Weinheim, 1995.
28 E. C. Constable, *Inorg. Chim. Acta*, 1986, **117**, L33.
29 E. C. Constable and T. A. Leese, *Inorg. Chim. Acta*, 1988, **146**, 55.
30 D. Armspach, M. Cattalini, E. C. Constable, C. E. Housecroft and D. Phillips, *Chem. Commun.*, 1996, 1823.
31 E. C. Constable, M. Cattalini, O. Eich, C. E. Housecroft, L. A. Johnson and I. Poleschak, *Polym. Mater. Sci. Eng.*, 1999, **80**, 268.
32 E. C. Constable, C. E. Housecroft and I. Poleschak, *Inorg. Chem. Commun.*, 1999, **2**, 565.
33 E. C. Constable, C. E. Housecroft, M. Neuburger, I. Poleschak and M. Zehnder, *Polyhedron*, 2003, **22**, 93.
34 E. C. Constable, R. Frantz, C. E. Housecroft, J. Lacour and A. Mahmood, *Inorg. Chem.*, 2004, **43**, 4817.
35 E. C. Constable, P. Harveson and C. E. Housecroft, *J. Chem. Soc., Dalton Trans.*, 1999, 3690.
36 E. C. Constable, P. Harveson and M. Oberholzer, *Chem. Commun.*, 1996, 1821.
37 M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. Cargill Thompson, *Inorg. Chem.*, 1995, **34**, 2759.
38 E. C. Constable and A. M. W. Cargill Thompson, *New J. Chem.*, 1996, **20**, 65.