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The 'dendritic effect' on the electrochemical properties of an encapsulated redox center: correlation of size exclusion chromatography data and redox reversibility of electrochemically active homoleptic and heteroleptic ruthenium(II)-bis(terpyridine) metallodendrimers

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Abstract—A series of homoleptic and heteroleptic ruthenium(II)-bis(terpyridine) metallodendrimers bearing an electrochemically active unit encapsulated in a polyether dendritic envelope was prepared. Cyclic voltammetry studies on these dendrimers indicated the decrease of redox reversibility correlated well to the size exclusion chromatography data. The results suggest that electron transfer between the electrode and the buried redox center does not have any orientation preference.

1. Introduction

Since the pioneering works of Diederich[1] and Newkome[2] showing that the electrochemical properties of a metal center could be modified by encapsulation with dendritic appendages, a variety of dendritic scaffoldings had been used to construct a wide array of metallodendrimers possessing novel and interesting electrochemical properties.[3] Generally metallodendrimers can be divided into two categories: those having the redox active center(s) encapsulated within a dendritic envelope[4] and those having multiple redox centers located at or near the dendrimer surface.[5] Most often a clear and measurable "dendritic effect" on the electrochemical properties can be observed in the former category of compounds, while in the latter category the many redox centers usually behave as independent redox units with little electronic communications.

Generally the encapsulation of redox center(s) by dendritic fragments can lead to two observable dendritic effects. The first is a shift of redox potentials upon dendrimerization and the extent and direction of this shift are dependent on the nature of the dendritic appendages and the solvent medium. Details of this effect have been exemplified from studies on a number of dendritic iron-containing porphyrins[1,4a] and on other dendrimers having a core metal unit.[4c,d,g] The second response is a retardation of the redox transfer kinetics and is typified by a gradual increase of the peak-to-peak separation with increasing dendrimer generation in the cyclic voltammograms.[1,2,4] The decrease in rate of electron transfer kinetics with higher generation dendrimers has been attributed to the increasingly long distance between the electroactive core and the electrode surface.[3b,4] While most reported studies have actually been focused on the relationship between electrochemical reversibility and dendrimer generation, few investigations have actually been conducted to correlate the redox reversibility to the molecular size. Although undoubtedly molecular size increases with increasing dendrimer generation, the change of molecular size from one generation to the next, however, can be very substantial and usually an abrupt loss of redox reversibility upon generation increase is often seen. Hence a continuity relationship between redox reversibility and dendrimer size is not often observed. Bearing this in mind, we now report the synthesis, size exclusion chromatographic data and electrochemical properties of a series of ruthenium(II)-bis(terpyridine) dendrimers **1**–**5** in which the dendrimer size increases gradually to allow an evaluation of the size effect on redox reversibility. Unlike the homoleptic iron(II)-bis(terpyridine) dendrimers reported earlier by us,[4b] the present series of dendrimers enables us to fine-tune their molecular sizes by having two terpyridine (terpy) ligands of different generation attached to the ruthenium ion. The relationship between electrochemical reversibility and the molecular size, derived from size exclusion chromatography data, will also be reported (Insert 1).

Keywords: metallodendrimers; cyclic voltammetry.
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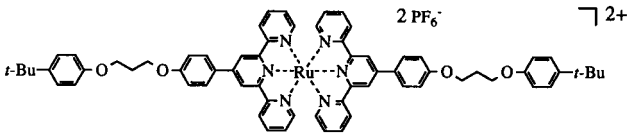
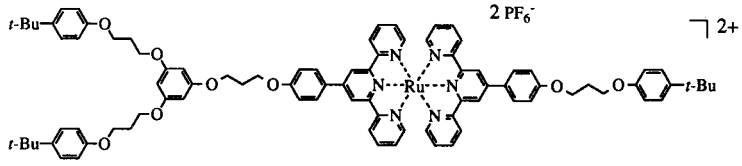
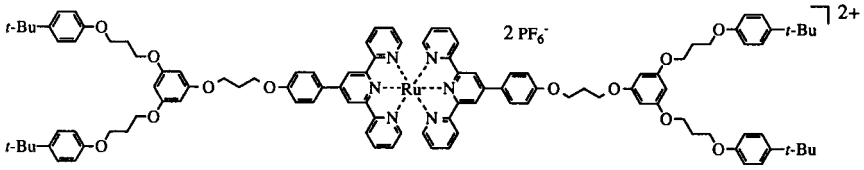


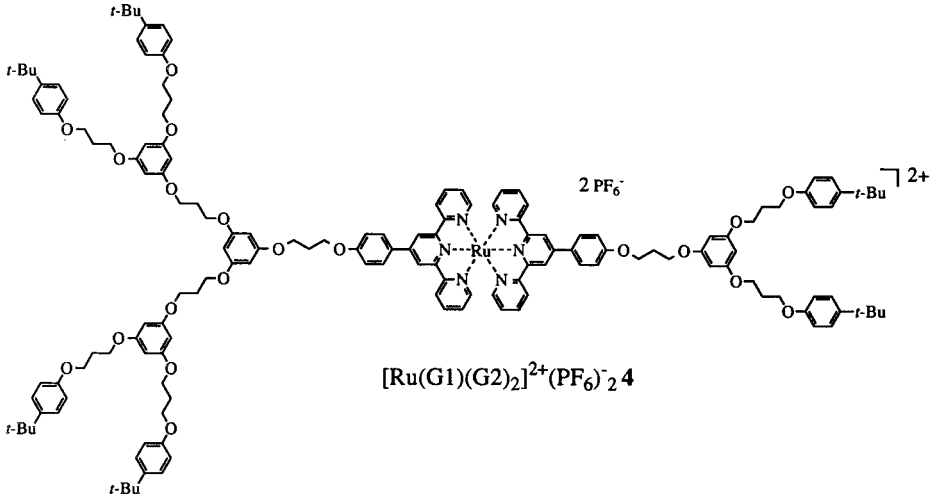
$[Ru(G0)_2]^{2+}(PF_6)^-_2$ **1**



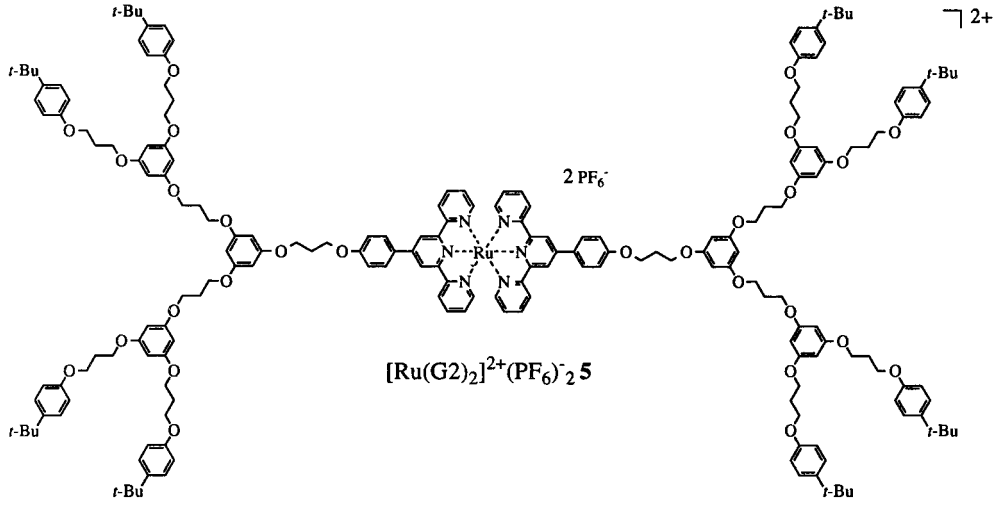
$[Ru(G0)(G1)_2]^{2+}(PF_6)^-_2$ **2**



$[Ru(G1)_2]^{2+}(PF_6)^-_2$ **3**

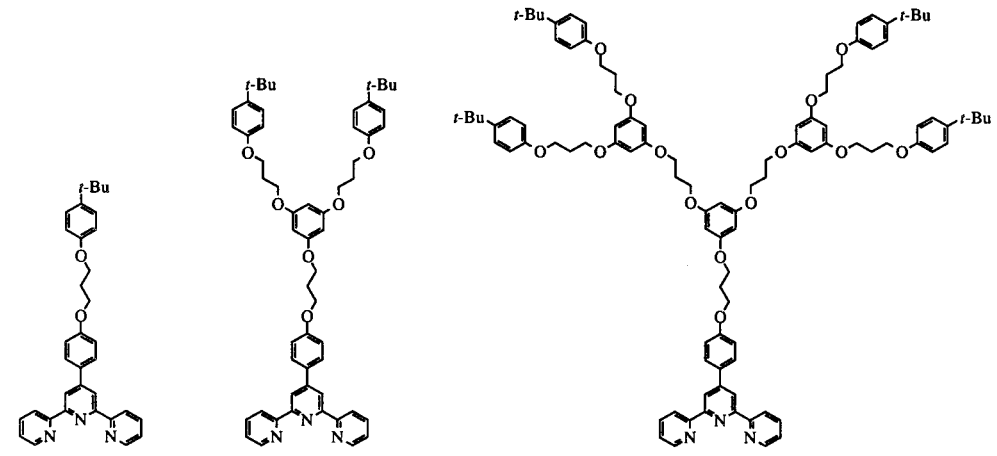


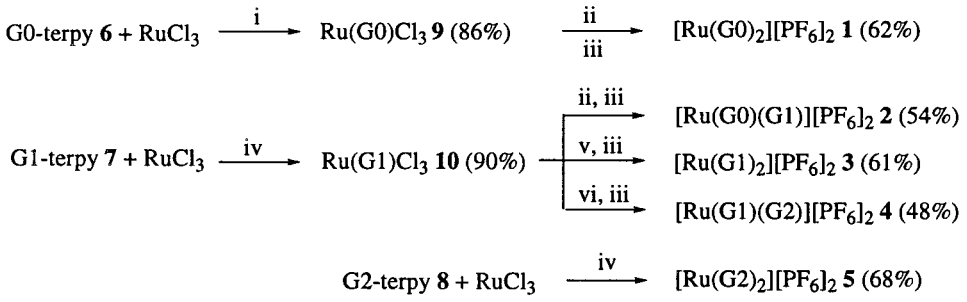
$[Ru(G1)(G2)_2]^{2+}(PF_6)^-_2$ **4**



$[Ru(G2)_2]^{2+}(PF_6)^-_2$ **5**

Insert 1.





Scheme 1. Reagents: (i) MeOH, EtOH, *N*-morpholine; (ii) EtOH, *N*-morpholine, **6**; (iii) NH_4PF_6, EtOH; (iv) $CHCl_3$, EtOH, *N*-morpholine; (v) EtOH, *N*-morpholine, **7**; (iv) EtOH, *N*-morpholine, **8**.

2. Results and discussions

2.1. Synthesis

The target metallodendrimers **1**–**5** were prepared by complexation of the known G0-terpy to G2-terpy ligands **6**–**8**[4b] with ruthenium trichloride following literature procedures (Scheme 1).[6] Among the five target compounds, three of them (**1**, **3** and **5**) are homoleptic and the other two (**2** and **4**) are heteroleptic. Their molecular weights fall into a range from 1400 to 3600 and are evenly spread across this range.

The smallest homoleptic metallodendrimer $[Ru(G0)_2][PF_6]_2$ **1** was synthesized in two steps. Hence, the ligand G0-terpy **6** was treated with 1 mol equiv. of $RuCl_3$ in a boiling mixture of ethanol/methanol to give $Ru(G0)Cl_3$ **9** as a brown precipitate in 86% yield. Due to the paramagnetic nature of the compound, its ^1H NMR signals appeared as broad peaks and therefore compound **9** was used in the next reaction without characterization. Treatment of compound **9** with G0-terpy **6** in the presence of *N*-morpholine in boiling ethanol, followed by precipitation of the cation by ammonium hexafluorophosphate gave the target compound **1** as a reddish brown solid in 62% yield.

Due to the poor solubility of the G1-terpy ligand **7** in alcohol, a mixture of chloroform and ethanol was required to effect the preparation of $Ru(G1)Cl_3$ **10** (90% yield). Similarly, treatment of this brown solid with one mol equiv. of the G0-, G2- and G1-terpy ligands (**6**, **8** and **7**) in the presence of *N*-morpholine, followed by precipitation of the intermediate cation with ammonium hexafluorophosphate produced the heteroleptic $[Ru(G0)(G1)][PF_6]_2$ **2** and $[Ru(G1)(G2)][PF_6]_2$ **4** and homoleptic $[Ru(G1)_2][PF_6]_2$ **3** metallodendrimers in 54, 48 and 61%, respectively.

In a slightly different manner, the homoleptic second-generation dendrimer $[Ru(G2)_2][PF_6]_2$ **5** was synthesized in one step by reacting $RuCl_3$ with 2 mol equiv. of G2-terpy **8** in the presence of *N*-morpholine, followed by precipitation with ammonium hexafluorophosphate. The yield of the product was 68%.

One minor problem encountered in the synthesis was the requirement to further purify the precipitated metallodendrimers by column chromatography. During the complexation reaction, in addition to the desired reddish brown bis(terpy)-Ru(II) metallodendrimer, a purple colored side product whose structure could not be identified was also formed. Fortunately, the side product is much less polar and thus can be removed by column chromatography on alumina. Hence, elution of the product mixture first by hexane/$CHCl_3$/EtOH gave the unknown side product, subsequent elution with acetone/EtOH or $CHCl_3$/EtOH mixture then produced the target metallodendrimers free from any contaminants.

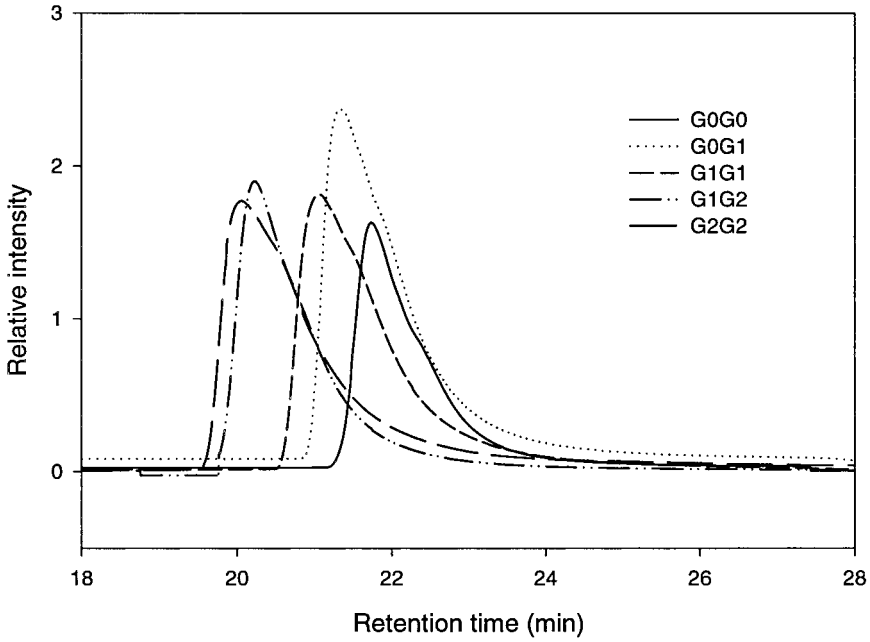


Figure 1. SEC chromatogram of $[Ru(Gm)(Gn)][PF_6]_2$ dendrimers. Columns: styragel HR1, HR2 and HR3 in serial; solvent: THF.

2.2. Characterization

The structural identities of the complexes were confirmed by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The splitting patterns of the ^1H nuclei of the terpy core unit matched well those reported for other structurally related $[Ru(terpy)_2]^{2+}$ ions,[7] and their chemical shift values are independent of the generation of the polyether dendritic fragments. However, for ^1H nuclei belonging to the polyether dendritic fragments, an upfield shift of signals was noted when they are located further away from the Ru metal center. Hence, the ^1H signal of the *t*-butyl group was found to resonate at δ 1.26 for the $[Ru(G0)_2][PF_6]_2$ **1** complex, but was upfield shifted to δ 1.22 for the $[Ru(G1)_2][PF_6]_2$ **3** and further drifted to δ 1.20 for the $[Ru(G2)_2][PF_6]_2$ **5** complex. A similar upfield shift of the ^1H signal of the phloroglucinol branching juncture when it was located further away from the metal center was also noted (δ 6.16→6.11). The result may be rationalized by a through-space inductive effect of the central metal, which exerts a much stronger influence to ^1H nuclei that are in closer proximity than those located further away. The gradual change of chemical shift values within a homologous series of dendrimers had been reported previously by others[8] and us.[9]

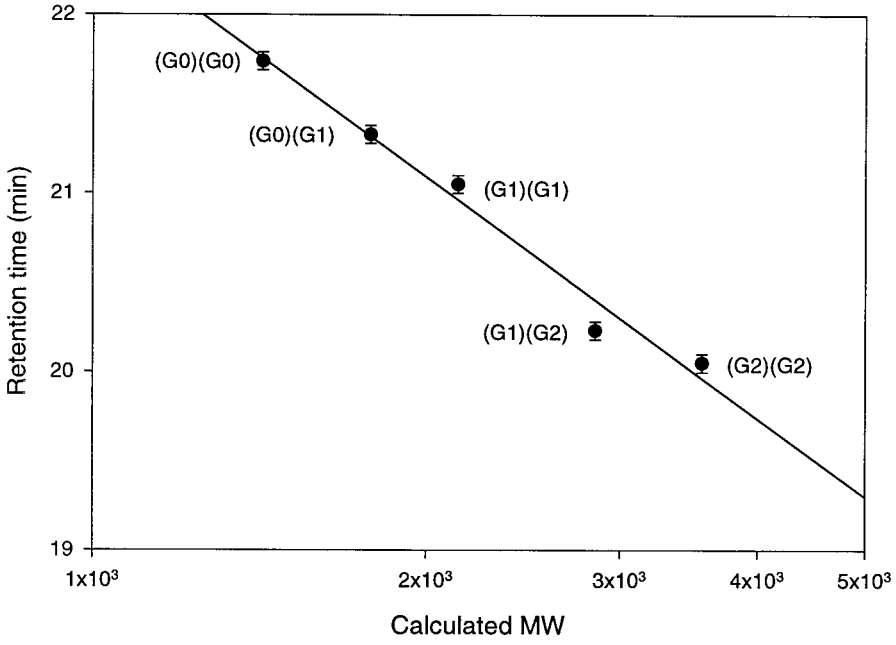


Figure 2. Semi-log plot of calculated molecular weight versus retention time for dendrimers **1**–**5**.

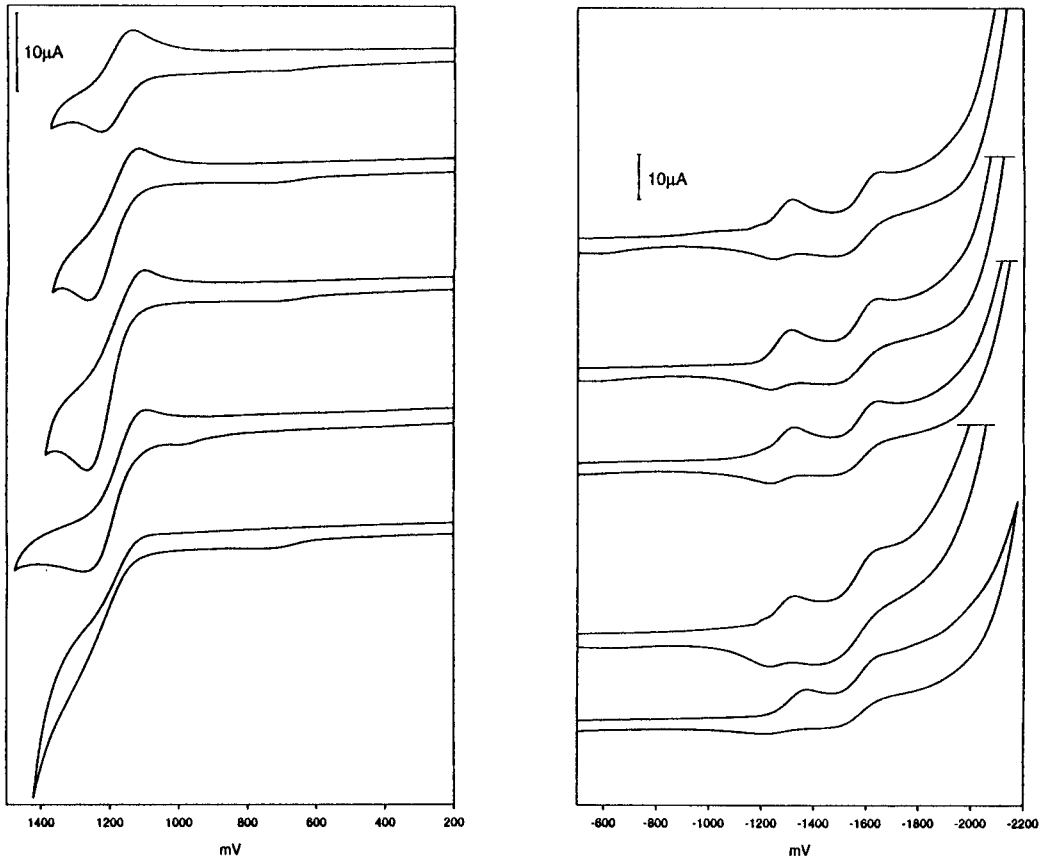


Figure 3. Cyclic voltammograms of dendrimers **1**–**5** (from top to bottom; left: oxidation; right: reduction), scan rate: 100 mV/s. Solvent: CH_2Cl_2.

The molecular weights of the synthesized metallodendrimers were also consistent with their mass spectroscopy data. Using the electrospray ionization technique, the largest molecular peak found always corresponded to the $[M—PF_6]^+$ ion for the lower generation metallodendrimers **1**–**4**. On the other hand, for the higher generation metallodendrimers **3**–**5**, the doubly charged $[M—2PF_6]^{2+}$ ion appeared as one of the prominent species in the mass spectrum.

2.3. Gel permeation chromatography

Owing to the relatively small size of the metallodendrimers, it is difficult to determine their molecular size or hydrodynamic radius accurately using the light-scattering technique. Nonetheless, the retention time data, obtained from gel permeation chromatography, could be used to reflect their relative molecular sizes. Each metallodendrimer exhibited one major peak in its GPC chromatogram in THF as the solvent, thus confirming their structural homogeneity (Fig. 1). Slight tailing of the GPC peak was noted, presumably due to the aggregation of the metallodendrimers in THF solution. The retention time values also correlated well with the calculated molecular weight values on a semi-log plot (Fig. 2).

2.4. Cyclic voltammetry studies

The electrochemical properties of metallodendrimers **1**–**5** were investigated in CH_2Cl_2 using cyclic voltammetry (CV). All compounds, except the largest metallodendrimer $[Ru(G2)_2][PF_6]_2$ **5**, exhibited similar redox patterns and showed one quasi-reversible wave at a positive potential ($+1.18\pm0.01$ V) that corresponded to the one-electron oxidation of the metal center and two quasi-reversible waves at negative potentials (-1.28 ± 0.02 V and -1.55 ± 0.02 V) that corresponded to the reduction processes for the terpy ligands (Fig. 3). A drastic change in the redox behavior was noted for the $[Ru(G2)_2][PF_6]_2$ **5** metallodendrimer, where the ruthenium-based oxidation wave could not be identified and only two irreversible waves for the ligand-centered redox processes were noted. The average peak potentials of the three processes of the various generation dendrimers are comparable to those of $[Ru(terpy)_2][ClO_4]_2$ reported by Morris,[10] and are unperturbed by the dendritic fragments of the different generations. Hence the electron-rich polyether dendritic fragment does not exert any induction effect on the redox processes. This is in contrast to the previous findings by Diederich.[1] As expected, the peak separation of the electron transfer processes increases with increasing dendrimer generation, indicating the shielding effect of the dendritic ligand. To investigate the effect of dendrimer size on redox reversibility, a plot of the peak separation against the GPC retention time data is shown in Fig. 4. Two interesting findings were noted. First, the retention time data correlated relatively well with the reversibility data in a qualitative manner. Hence, a gradual decrease of the peak separation with increasing retention time was noted. Secondly, the sensitivity of the reduction of redox reversibility towards

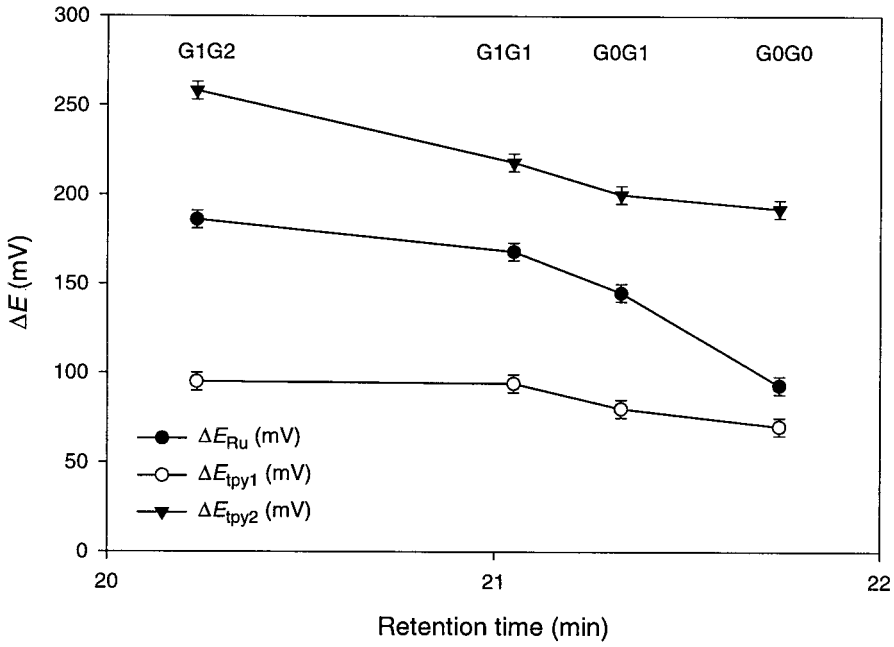


Figure 4. Plot of peak separation versus size exclusion retention time for dendrimers **1**–**4**. ΔE_{Ru}: Ru-based oxidation process; ΔE_{tpy1} and ΔE_{tpy2}: first and second terpyridine-based reduction processes.

increasing dendrimer size is different for the three different electrochemical processes. Hence, the reversibility of the oxidation process of the ruthenium center (ΔE_{Ru}) appears to be highly sensitive to the increase of dendrimer size. On the other hand, the reversibility of the first ligand reduction process (ΔE_{tpy1}) turns out to be the least sensitive.

A recent report by Kaifer demonstrated a molecular orientation effect on the rate of electron transfer kinetics of metallodendrimers having an unsymmetrically disposed 'off center' redox unit.[4h] Hence, when the redox active center was locked in a position that was far away from the electrode by electrostatic interaction, a drastic decrease of electron transfer rate was noted. In the present study, the dependence of the reversibility principally on the retention time data or the hydrodynamic radius of the homoleptic and heteroleptic metallodendrimers suggests that electron transfer between the electrode surface and the buried redox centers does not have any orientation preference and may take place from any direction. If electron transfer were to occur preferentially on the side having a thinner dendritic shell, redox reversibility should have been determined by the generation number of the smallest dendritic fragments for the heteroleptic metallodendrimers. In the present study, the absence of any interfacial interactions between the electrode and the electrically neutral dendritic surface implied that the molecule could tumble freely in solution and hence the efficiency of electron transfer was governed by the hydrodynamic radius of the dendrimer.

In summary, a family of medium-sized metallodendrimers bearing an electrochemically active Ru(II)-bis(terpy) core situated either in the dendrimer center or 'off center' was prepared and their electrochemical property investigated by cyclic voltammetry. The electron-rich polyether dendritic fragments did not exert any induction effect on the redox potentials of the electrochemical active unit. On the other hand, the decrease of redox reversibility correlated to the size exclusion chromatographic data of the metallodendrimers, suggesting that electron transfer between the redox center and the electrode does not have any orientation preference.

3. Experimental

3.1. General

Chemicals were purchased from Aldrich or Acros and used as received. The syntheses of the various G*n*-terpy ligands had been reported before.[4b] Flash column chromatography was conducted on neutral alumina, Merck aluminum oxide 90 active, neutral (70–200 mesh). Melting points were determined on a Reichert Microscope apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Brüker DPX300 spectrometer in d^{6}-DMSO as the solvent. Chemical shifts are reported as parts per million in δ scale downfield from TMS. Coupling constants (J) are reported in hertz. Mass spectra were obtained on a Brüker APEX 47e FTMS spectrometer using an electron spray ionization (ESI) technique. The reported molecular mass (m/z) values were the most abundant monoisotopic mass. Elemental analyses were carried out at MEDAC Ltd., Brunel Science Centre, Copper's Hill Lane, Englefield Green, UK.

3.2. Size exclusion chromatography

Size exclusion chromatography (Styragel HR1, HR2 and HR3 SEC columns; 7.8×300 mm in serial) was carried out with THF as solvent (flow rate=1.0 mL/min) on a Waters HPLC 510 pump equipped with a Waters 486 tunable UV absorbance detector. Polystyrene standards were purchased from Aldrich Chemical Company.

3.3. Cyclic voltammetry measurements

Cyclic voltammetry studies were carried out using a BAS CV50W cyclic voltammeter in anhydrous CH_2Cl_2 (freshly distilled from P_2O_5) with tetrabutylammonium tetrafluoroborate (0.15 M) as supporting electrolyte. Both the sample and the electrolyte were dried under vacuum for one day prior to the experiment. The electrochemical cell was a homemade 5 mL glass cell fitted with a platinum disc working electrode (purchased from Bioanalytical Systems Inc., IN, USA, polished twice with 0.05 micron gamma alumina, purchased from Buehler, IL, USA), a platinum wire auxiliary electrode and a silver reference electrode. Dry nitrogen gas was bubbled carefully through the solution samples (concentration 1.5 mM) for 10 min before the measurements. All the potentials reported were measured against the ferrocene/ferrocenium redox couple with a scan rate of 100 mV/s.

3.4. Synthesis

3.4.1. Ru(G0)Cl_3 (9). An ethanolic solution of $RuCl_3$ (0.40 g, 1.9 mmol) was added to a boiling solution of the terpyridine ligand G0-terpy **6** (1.00 g, 1.9 mmol) in methanol (80 mL). The mixture was refluxed for a further 2 h and cooled to room temperature. The precipitate was filtered and washed with methanol to afford Ru(G0)Cl_3 **9** (1.20 g, 86%) as a brown solid. The product was used immediately in the next step without further purification and characterization.

3.4.2. Ru(G1)Cl_3 (10). An ethanolic solution of $RuCl_3$ (66 mg, 0.32 mmol) was added to a boiling solution of the terpyridine ligand G1-terpy **7** (279 mg, 0.32 mmol) in a mixture of ethanol/chloroform (30 mL, 3/1). The mixture was refluxed for a further 2 h and cooled to room temperature. The precipitate was filtered and washed with methanol to afford Ru(G1)Cl_3 **10** (310 mg, 90%) as a brown solid. The product was used immediately in the next step without further purification and characterization.

3.5. General procedure for the preparation of [Ru(G*m*)(G*n*)][PF_6]$_2$

A mixture of Ru(G*m*)Cl_3 (1.0 mol equiv) and *N*-morpholine (5 drops) was added to a boiling solution of G*n*-terpy (1.0 mol equiv) in EtOH (30 mL) (for n=0) or in EtOH/$CHCl_3$ (30 mL, 10/1) (for n=1 and 2). The mixture gradually turned from a brown suspension to a red solution. After the mixture had been refluxed for 3 h, the hot solution was filtered through celite and an ethanolic solution of ammonium hexafluorophosphate (2.0 mol equiv) was then added. The mixture was cooled with stirring and the precipitate was filtered and washed with methanol. The crude product was then chromatographed on alumina to afford the target compound.

3.5.1. Ru(G0)$_2$][PF_6]$_2$ (1). The product (0.17 g, 62%) was prepared as a reddish brown solid from Ru(G0)Cl_3 **9** (0.14 g, 0.19 mmol) and G0-terpy **6** (0.10 g, 0.19 mmol) and purified by column chromatography (hexane/$CHCl_3$/EtOH=3/1/0.5 gradient to acetone/EtOH=4/1), mp >350°C. ^{1}H NMR: 1.26 (9 H, s, *t*-Bu), 2.27 (4 H, quintet, J=6, CCH_2C), 4.19 (4 H, t, J=6, CH_2O), 4.34 (4 H, t, J=6, CH_2O), 6.92 (4 H, d, J=9, ArH), 7.23–7.36 (12 H, m, ArH and H^5), 7.53 (4 H, d, J=5.4, H^6), 8.05 (4 H, t, J=7.5, H^4), 8.44 (4 H, d, J=8.7, ArH), 9.10 (4 H, d, J=8.1, H^3), 9.44 (4 H, s, H$^{3'}$); ^{13}C NMR: 28.9, 31.6, 34.0, 64.2, 64.9, 114.1, 115.4, 120.4, 124.9, 126.3, 127.9, 128.4, 129.4, 138.1, 143.0, 146.7, 152.4, 155.2, 156.4, 158.3, 160.7; *m*/*z* (ESI) 1277.4 [(M−PF_6)$^+$, 45%]. Anal. Calcd for $C_{68}H_{66}F_{12}N_6O_4P_2Ru$: C, 57.42; H, 4.68; N, 5.91. Found: C, 57.32; H, 4.78; N, 5.73%.

3.5.2. Ru(G0)(G1)][PF_6]$_2$ (2). The product (53 mg, 54%) was prepared as a reddish brown solid from Ru(G1)Cl_3 **10** (60 mg, 0.056 mmol) and G0-terpy **1** (29 mg, 0.056 mmol) and purified by column chromatography (hexane/$CHCl_3$/EtOH=1/1/0.2 gradient to acetone/EtOH=4/1), mp >350°C. ^{1}H NMR: 1.22 (18 H, s, *t*-Bu), 1.25 (9 H, s, *t*-Bu), 2.05–2.20 (4 H, m, CCH_2C), 2.20–2.35 (4 H, m, CCH_2C), 4.03–4.12 (4 H, m, CH_2O), 4.12–4.25 (4 H, m, CH_2O), 4.25–4.37 (4 H, m, CH_2O), 6.16 (3 H, s, ArH), 6.85 (4 H, d, J=8.4, ArH), 6.91 (2 H, d, J=8.1, ArH), 7.23–7.36 (14 H, m, ArH and H^5), 7.52 (4 H, br s, H^6), 8.04 (4 H, t, J=7.8, H^4), 8.43 (4 H, d, J=8.7, ArH), 9.09 (4 H, d, J=8.1, H^3), 9.43 (4 H, s, H$^{3'}$); ^{13}C NMR: 28.9, 31.5, 33.9, 64.2, 64.5, 64.9, 94.2, 114.1, 115.5, 120.4, 124.9, 126.27, 126.34, 127.9, 128.4, 129.4, 138.1, 142.9, 143.0, 146.7, 152.4, 155.2, 156.4, 158.3, 160.6; *m*/*z* (ESI) 1633.6 [(M−PF_6)$^+$, 90%]. Anal. Calcd for $C_{90}H_{94}F_{12}N_6O_8P_2Ru$: C, 60.77; H, 5.33; N, 4.72. Found: C, 60.73; H, 5.17; N, 4.67%.

3.5.3. Ru(G1)$_2$][PF_6]$_2$ (3). The product (130 mg, 61%) was prepared as a reddish brown solid from Ru(G1)Cl_3 **10** (108 mg, 0.10 mmol) and G1-terpy **7** (87 mg, 0.10 mmol) and purified by column chromatography (hexane/$CHCl_3$/acetone/EtOH=10/2/1/1 gradient to $CHCl_3$/EtOH=4/1), mp >350°C. ^{1}H NMR: 1.22 (36 H, s, *t*-Bu), 2.14 (8 H, quintet, J=6, CCH_2C), 2.24 (4 H, quintet, J=6, CCH_2C), 4.00–4.12 (16 H, m, CH_2O), 4.16 (4 H, t, J=6, CH_2O), 4.31 (4 H, t, J=6, CH_2O), 6.16 (6 H, s, ArH), 6.85 (8 H, d, J=8.4, ArH), 7.21–7.35 (16 H, m, ArH and H^5), 7.51 (4 H, d, J=5.4, H^6), 8.04 (4 H, t, J=8.1, H^4), 8.44 (4 H, d, J=8.7, ArH), 9.09 (4 H, d, J=8.4, H^3), 9.43 (4 H, s, H$^{3'}$); ^{13}C NMR: 28.9, 31.5, 33.9, 64.2, 64.5, 64.8, 94.1, 94.2, 114.1, 115.5, 120.4, 125.0, 126.3, 127.9, 128.4, 129.4, 138.1, 142.9, 146.7, 152.4, 155.2, 156.4, 158.3, 160.56, 160.62; *m*/*z* (ESI) 1989.8 [(M−PF_6)$^+$, 10%]. Anal. Calcd for $C_{112}H_{122}F_{12}N_6O_{12}P_2Ru$: C, 63.00; H, 5.76; N, 3.94. Found: C, 62.47; H, 5.85; N, 3.54%.

3.5.4. Ru(G1)(G2)][PF_6]$_2$ (4). The product (107 mg, 48%) was prepared as a reddish brown solid from Ru(G1)Cl_3 **10** (84 mg, 0.078 mmol) and G2-terpy **8** (125 mg, 0.078 mmol) and purified by column chromatography (hexane/$CHCl_3$/acetone/EtOH=10/2/1/1 gradient to $CHCl_3$/EtOH=10/1), mp >350°C. ^{1}H NMR: 1.20 (36 H, s, *t*-Bu), 1.22 (18 H, s, *t*-Bu), 2.05–2.20 (16 H, m, CCH_2C), 2.20–2.35 (4 H, m, CCH_2C), 4.03–4.23 (36 H, m, CH_2O), 4.25–4.37 (4 H, m, CH_2O), 6.11 (6 H, s, ArH), 6.17 (6 H, s, ArH), 6.82 (8 H, d, J=9, ArH), 6.85 (4 H, d, J=9, ArH), 7.21–7.36 (20 H, m, ArH and H^5), 7.52 (4 H, d, J=5.4, H^6), 8.04 (4 H, t, J=7.2, H^4), 8.44 (4 H, d, J=8.7, ArH), 9.10 (4 H, d, J=6.9, H^3), 9.44 (4 H, s, H$^{3'}$); ^{13}C NMR: 28.8, 31.5, 33.9, 64.2, 64.4, 64.8, 94.1, 114.1, 115.4, 120.4, 124.9, 126.2, 127.9, 128.3,

129.4, 138.1, 142.9, 146.8, 152.3, 155.2, 156.4, 158.3, 160.6; *m/z* (ESI) 2702.6 [$(M-PF_6)^+$, 4%]. Anal. Calcd for $C_{156}H_{178}F_{12}N_6O_{20}P_2Ru$: C, 65.79; H, 6.30; N, 2.95. Found: C, 65.39; H, 6.20; N, 2.79%.

3.5.5. Ru(G2)$_2$][PF$_6$]$_2$ (5). A mixture of $RuCl_3$ (36 mg, 0.17 mmol) and *N*-morpholine (5 drops) in ethanol (2 mL) was added to a boiling solution of G2-terpy **8** (540 mg, 0.34 mmol) in ethanol/$CHCl_3$ mixture (30 mL, 4/1). The mixture was refluxed for a further 3 h and was filtered through celite when hot. An ethanolic solution of ammonium hexafluorophosphate (56 mg, 0.34 mmol) was added and the mixture was cooled to room temperature with stirring. The precipitate was filtered and washed with methanol. The crude product was further purified by column chromatography on alumina (hexane/$CHCl_3$/acetone/EtOH=10/2/1/1 gradient to $CHCl_3$/EtOH=10/1) to give the title compound **5** as a reddish brown solid (412 mg, 68%), mp >350°C. ^{1}H NMR: 1.20 (72 H, s, *t*-Bu), 2.00–2.18 (24 H, m, CCH_2C), 2.19–2.30 (4 H, m, CCH_2C), 4.00–4.20 (52 H, m, CH_2O), 4.30 (4 H, t, *J*=6, CH_2O), 6.11 (12 H, s, ArH), 6.16 (6 H, s, ArH), 6.82 (16 H, d, *J*=8.7, ArH), 7.21–7.35 (24 H, m, ArH and H^5), 7.50 (4 H, d, *J*=5.7, H^6), 8.02 (4 H, t, *J*=7.5, H^4), 8.43 (4 H, d, *J*=8.4, ArH), 9.09 (4 H, d, *J*=8.4, H^3), 9.43 (4 H, s, H$^{3'}$); ^{13}C NMR: 28.9, 31.6, 34.0, 64.2, 64.5, 64.9, 94.2, 114.2, 115.5, 120.5, 126.3, 127.9, 128.4, 129.5, 138.2, 143.0, 146.7, 152.4, 155.2, 156.4, 158.4, 160.6; *m/z* (ESI) 1635.1 [$(M-2PF_6)^{2+}$, 100%]. Anal. Calcd for $C_{200}H_{234}F_{12}N_6O_{28}P_2Ru$: C, 67.46; H, 6.62; N, 2.36. Found: C, 67.09; H, 6.73; N, 2.36%.

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