Pulse Radiolysis Studies of Dendritic Macromolecules with Biphenyl Peripheral Groups and a Ruthenium Tris-bipyridine Core

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Abstract: Electron-transfer reactions in Fréchet-type dendrimers with biphenyl peripheral groups and a ruthenium core were investigated by pulse radiolysis techniques. Fast electron-transfer rates found in the two ruthenium dendrimers suggest a very efficient electronic coupling between the peripheral donor groups and the core acceptor.

Introduction

Long-range electron-transfer reactions have been studied extensively because of their importance in redox enzymatic processes[1] and photosynthesis.[2] Recently, the use of dendrimers[3] as light-harvesting antennae,[4−9] fluorescent chemosensors,[10] and organic light-emitting diodes (OLEDs)[11] has been a focus of many groups because of the dendrimers' three-dimensional hyper-branched structure. Even though energy transfer in dendrimers has been studied by many groups, very little has been reported on the study of electron-transfer reactions within a dendrimer framework.[8,12,13] Here we report for the first time a pulse radiolysis study of electron-transfer reactions within a Fréchet-type dendrimer (Chart 1) bearing biphenyl peripheral groups and a ruthenium tris-bipyridine core, and compare their transient absorption spectra with nonmetalated model compounds.

Experimental Section

NMR spectra were recorded with a Varian Gemini 300 MHz instrument. All melting points (uncorrected) were determined with a Melt-Temp apparatus. All chemicals (Aldrich) were used as received. K_2CO_3 was dried in an oven at 130 °C before use. 3,5-Dihydroxybenzyl alcohol was recrystallized from ethyl acetate before use. Methylene chloride (CH_2Cl_2) and tetrahydrofuran (THF) were distilled from CaH_2 and sodium/benzophenone, respectively. All chemicals were dried under vacuum for at least 24 h prior to use.

Pulse Radiolysis. Samples for pulse radiolysis were prepared under Ar in a glovebox (Vacuum Atmospheres). The dendrimer or compound of interest was weighed and dissolved in THF, then placed in cylindrical Suprasil cells of 5, 10, and 20 mm path lengths. Pulse radiolysis experiments were performed at the BNL Laser-Electron Accelerator Facility (LEAF). The electron pulse parameters were the following: duration ∼30 ps, charge 2−4 nC, and energy 8.5 MeV. Transient absoption data were collected by using a pulsed xenon arc lamp, a selection of 10 and 40 nm wide band-pass filters, silicon (FND-100) or germanium photodiodes, and a Tektronix TDS-680C oscilloscope. Kinetic traces were averaged over 2−8 shots.

Preparation of the Benzyl Alcohol Dendrons [Gn-OH] ($n = 1$, 2, 3), Scheme 1. The respective benzyl bromide dendron (2.1 equiv), 3,5-dihydroxy benzyl alcohol (1.0 equiv), K_2CO_3 (2.5 equiv), and 18-crown-6 (0.2 equiv) were heated to reflux in a minimum amount of acetone for 48 h. The solvent was removed under vacuum, dissolved in CH_2Cl_2, and washed with water (3×), then dried over anhydrous $MgSO_4$. The solution was then concentrated under vacuum and applied on a silica gel column, and the product was eluted with CH_2Cl_2. Yield 70−80%.

[G1-OH]: Mp 122−125 °C. ^{1}H NMR ($CDCl_3$) δ 4.67 (d, $J = 4.4$ Hz, 2 H), 5.11 (s, 4 H), 6.61 (d, $J = 1.9$ Hz, 1 H), 6.68 (d, $J = 1.9$ Hz, 2 H), 7.27−7.52 (m, 10 H), 7.59−7.64 (m, 8 H). Calcd. for $C_{33}H_{28}O_3$: C, 83.8; H, 6.0; O, 10.2. Found: C, 83.6; H, 5.9; O, 10.0.

[G2-OH]: Mp 64−66 °C. ^{1}H NMR ($CDCl_3$) δ 4.61 (s, 2 H), 5.00 (s, 4 H), 5.09 (s, 8 H), 6.61 (d, $J = 1.9$ Hz, 1 H), 6.62 (m, 4 H), 6.71 (d, $J = 1.9$ Hz, 4 H), 7.27−7.51 (m, 20 H), 7.58−7.62 (m, 16 H). Calcd. for $C_{73}H_{60}O_7$: C, 83.5; H, 5.8; O, 10.7. Found: C, 83.3; H, 6.1; O, 10.1.

[G3-OH]: Mp 85−90 °C. ^{1}H NMR ($CDCl_3$) δ 4.51 (s, 2 H), 4.94 (s, 4 H), 4.96 (s, 8 H), 5.04 (s, 16 H), 6.52−6.65 (m, 9 H), 6.66 (d, $J = 1.8$ Hz, 4 H), 6.69 (d, $J = 1.9$ Hz, 8 H), 7.27−7.46 (m, 40 H), 7.55−7.58 (m, 32 H). Calcd. for $C_{153}H_{124}O_{15}$: C, 83.4; H, 5.7; O, 10.9. Found: C, 83.2; H, 6.0; O, 10.5.

Preparation of the Benzyl Bromide Dendrons [Gn-Br] ($n = 0$, 1, 2, 3), Scheme 1. To the respective benzyl alcohol dendron (1.0 equiv) in a minimum amount of THF was added CBr_4 (1.2 equiv) and the solution was stirred for 5 min before the addition of PPh_3 (1.2 equiv). For **[G3-Br]** 10.0 equiv of CBr_4 and PPh_3 were required to drive the reaction to completion. The solution was stirred under Ar for 1 h, after which the solvent was removed under vacuum and the remaining solid was dissolved in CH_2Cl_2 and extracted (3×) with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum,

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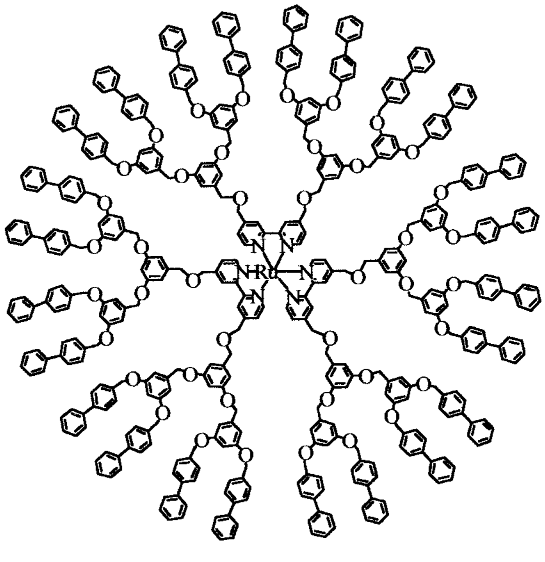
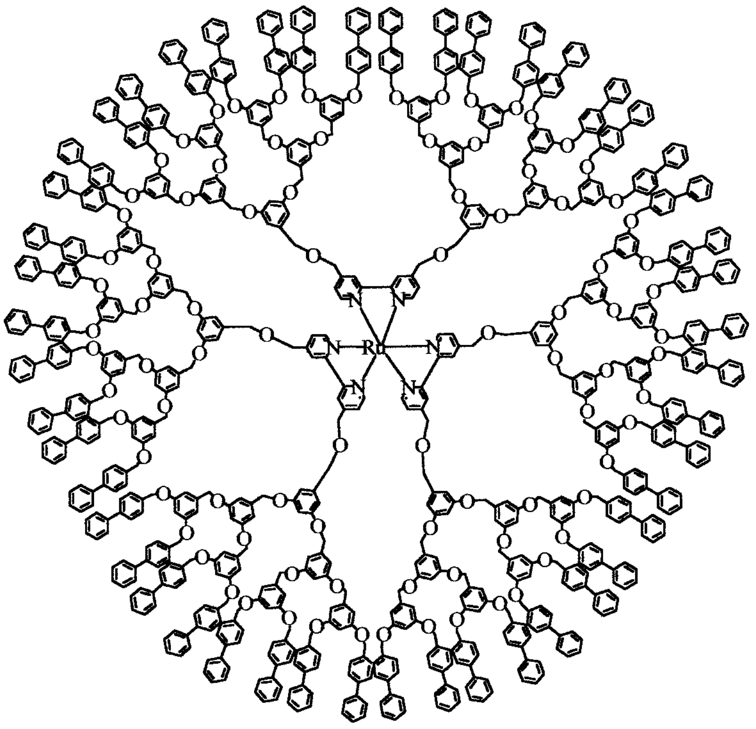
10.1021/ja011615e CCC: $20.00

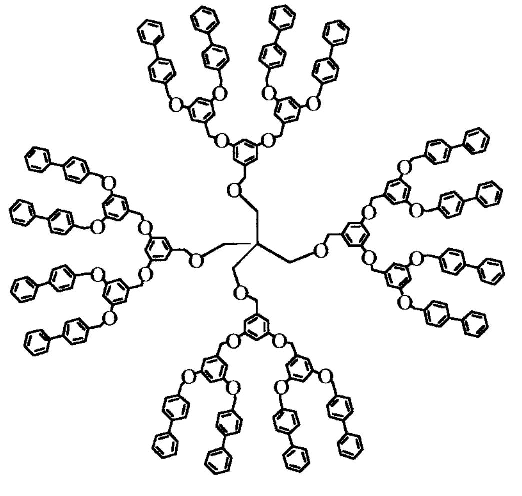
Chart 1. Structures of Ruthenium Dendrimers **[G2-Ru]** and **[G3-Ru]** and Nonmetalated Analog **[G2-D]**



[G2-Ru]



[G3-Ru]



[G2-D]

before being applied to a silica column and eluted with CH_2Cl_2:hexane (4:1). Yield 80−90%.

[G0-Br]: Mp 82−83 °C. ^{1}H NMR ($CDCl_3$) δ 4.57 (s, 2 H), 7.38−7.50 (m, 5 H), 7.58−7.61 (m, 4 H). Calcd. for $C_{13}H_{11}Br$: C, 63.2; H, 4.5; Br, 32.3. Found: C, 63.3; H, 4.6; Br, 32.2.

[G1-Br]: Mp 110−112 °C. ^{1}H NMR ($CDCl_3$) δ 4.54 (s, 2 H), 5.09 (s, 4 H), 6.61 (d, J = 1.9 Hz, 1 H), 6.69 (d, J = 1.9 Hz, 2 H), 7.27−7.52 (m, 10 H), 7.59−7.64 (m, 8 H). Calcd. for $C_{33}H_{27}BrO_2$: C, 74.0; H, 5.1; Br, 14.9; O, 6.0. Found: C, 73.9; H, 5.4; Br, 14.2; O, 5.7.

[G2-Br]: Mp 83−84 °C. ^{1}H NMR ($CDCl_3$) δ 4.40 (s, 2 H), 4.99 (s, 4 H), 5.09 (s, 8 H), 6.55 (s, J = 1.8 Hz, 1 H), 6.63 (m, 4 H), 6.70 (d, J = 1.9 Hz, 4 H), 7.27−7.50 (m, 20 H), 7.58−7.62 (m, 16 H). Calcd. for $C_{73}H_{59}BrO_6$: C, 78.8; H, 5.4; Br, 7.2; O, 8.6. Found: C, 78.3; H, 5.5; Br, 7.6; O, 8.6.

[G3-Br]: Mp 75−77 °C. ^{1}H NMR ($CDCl_3$) δ 4.37 (s, 2 H), 4.93 (s, 4 H), 4.97 (s, 8 H), 5.05 (s, 16 H), 6.52 (d, J = 1.8 Hz, 1 H), 6.56−6.60 (m, 8 H), 6.66 (d, J = 1.9 Hz, 4 H), 6.70 (d, J = 1.9 Hz, 8 H), 7.26−7.47 (m, 40 H), 7.55−7.62 (m, 32 H). Calcd. for $C_{153}H_{123}BrO_{14}$: C, 81.1; H, 5.5; Br, 3.5; O, 9.9. Found: C, 80.1; H, 5.9; Br, 4.7; O, 9.3.

Preparation of [G2-bpy] and [G3-bpy], Scheme 1. 4,4′-Bis(hydroxymethyl)-2,2′-bipyridine[14] (1.0 equiv) was dissolved in anhydrous dimethyl formamide (DMF) and NaH (excess) was added. **[G2-Br]** or **[G3-Br]** (2.5 equiv) was added after H_2 evolution ceased, and the reaction was stirred under Ar for 4 h. Water was added slowly to quench any unreacted NaH, and the solution was extracted with CH_2Cl_2 (3×). The organic layer was dried over anhydrous K_2CO_3, and the solvent was removed under vacuum. The crude product was applied to a silica gel column and eluted with CH_2Cl_2, followed by 2−5% methanol in CH_2Cl_2. Yield 50%.

[G2-bpy]: Mp 76−80 °C. ^{1}H NMR ($CDCl_3$) δ 4.52 (s, 4 H), 4.57 (s, 4 H), 4.98 (s, 8 H), 5.05 (s, 16 H), 6.56 (s, 2 H), 6.60 (s, 4 H), 6.62 (s, 4 H), 6.70 (s, 8 H), 7.26−7.47 (m, 42 H), 7.55−7.58 (m, 32 H), 8.37 (s, 2 H), 8.60 (d, J = 4.9 Hz, 2 H). Calcd. for $C_{158}H_{128}N_2O_{14}$: C, 83.3; H, 5.7; N, 1.2; O, 9.8. Found: C, 82.6; H, 5.6; N, 1.2; O, 9.6.

[G3-bpy]: Mp 85−90 °C. ^{1}H NMR ($CDCl_3$) δ 4.47 (s, 4 H), 4.52 (s, 4 H), 4.92 (s, 16 H), 4.97 (s, 8 H), 5.00 (s, 32 H), 6.54 (s, 2 H), 6.56−6.60 (m, 8 H), 6.65−6.69 (m, 32 H), 7.26−7.44 (m, 82 H), 7.47−7.55 (m, 64 H), 8.35 (s, 2 H), 8.57 (d, J = 5.0 Hz, 2 H). Calcd. for $C_{318}H_{256}N_2O_{30}$: C, 83.3; H, 5.6; N, 0.6; O, 10.5. Found: C, 80.5; H, 5.5; N, 0.7; O, 10.3.

Preparation of [G2-D]. The benzyl bromide dendron **[G2-Br]** (0.50 g, 0.45 mmol), pentaerithrytol (15 mg, 0.11 mmol), and excess NaH (1.0 g, 42 mmol) in 10 mL of anhydrous DMF were stirred under Ar for 18 h. Water (20 mL) was added slowly and the resulting gummy solid was collected by filtration. The solid was then purified by column

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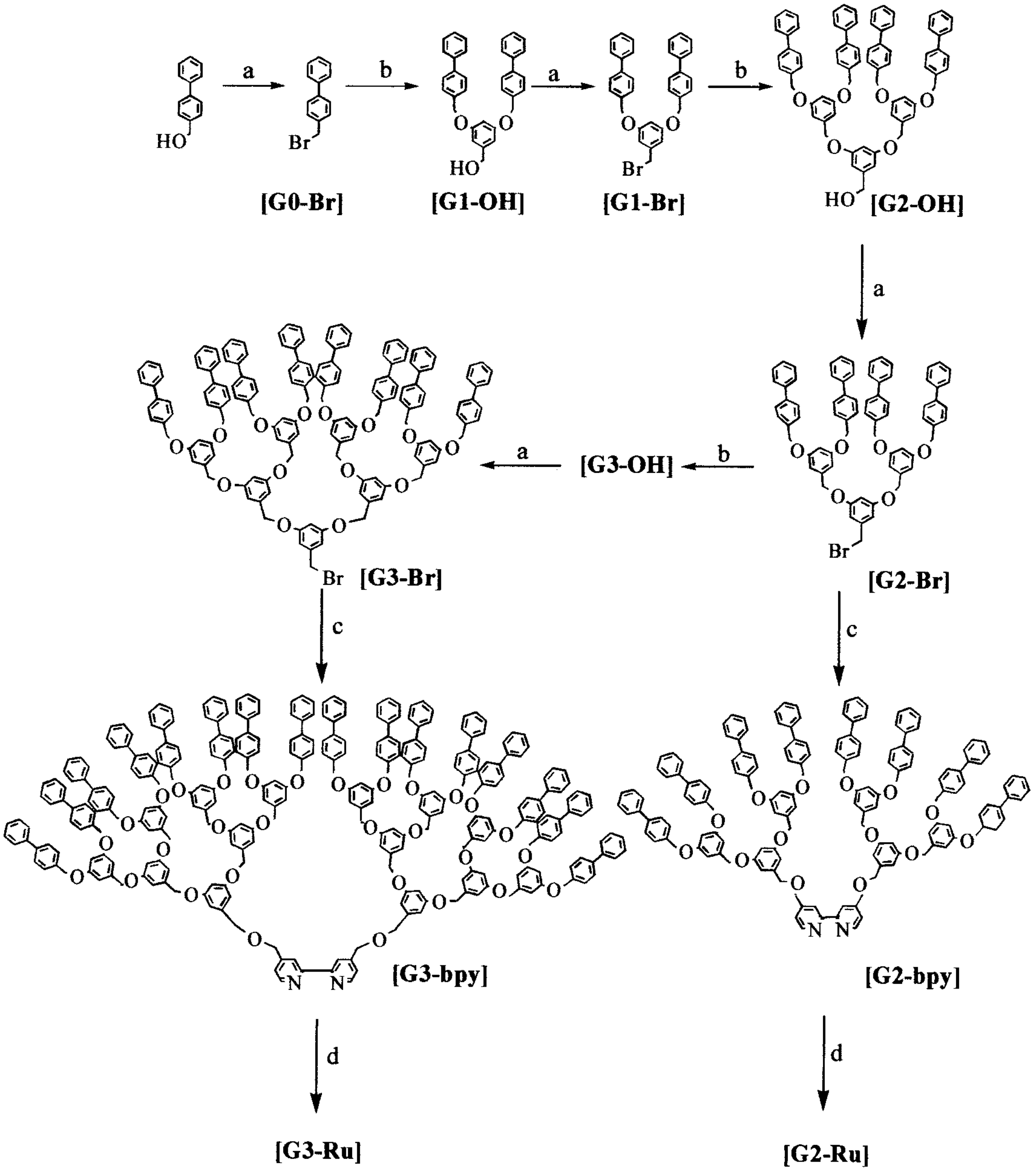
Scheme 1. Synthesis of the Component Aryl Ether Dendrons and the Two Ru-Complexed Dendrimers **[G2-Ru]** and **[G3-Ru]**: (a) CBr_4 and PPh_3, (b) 3,5-Dihydroxybenzyl Alcohol and K_2CO_3, (c) 4,4′-Bis(hydroxymethyl)-2,2′-bipyridine and NaH, and (d) $RuCl_3$



chromatography (silica gel, 17:8 CH_2Cl_2:hexane). The major fraction was collected and the volatiles were removed under vacuum to afford a white crystalline material. Yield 50%. Mp 75−80 °C. ^1H NMR ($CDCl_3$) δ 3.55 (s, 8 H), 4.40 (s, 8 H), 4.84 (s, 16 H), 4.96 (s, 32 H), 6.49−6.55 (m, 20 H), 6.64 (d, $J = 1.5$ Hz, 16 H), 7.27−7.42 (m, 80 H), 7.69−7.74 (m, 64 H). Calcd. for $C_{297}H_{244}O_{28}$: C, 83.7; H, 5.8; O, 10.5. Found: C, 81.8; H, 6.0; O, 10.6.

Preparation of the Ruthenium Dendrimers [Gn-Ru] (*n* = 2 and 3), Scheme 1. The respective dendron **[G2-bpy]** or **[G3-bpy]** (3.0 equiv) and ruthenium trichloride (1.0 equiv) were heated to reflux in 3:1 $CHCl_3$:ethanol under Ar for 3 d. The solvent was then removed under vacuum and the brown solid was flash chromatographed on a silica gel column (10 cm × 3 cm). The solid was first eluted with 3:1 CH_2Cl_2:ethyl acetate (to remove the bis-bipyridine ruthenium complexes), then eluted with 20:1 CH_2Cl_2:methanol. The bright orange solution was collected and the solvent was removed under vacuum to afford the ruthenium dendrimer in 80% yield.

[G2-Ru]: ^1H NMR ($CDCl_3$) δ 4.47 (s, 12 H), 4.67 (s, 12 H), 4.83 (s, 24 H), 5.92 (s, 48 H), 6.47 (s, 6 H), 6.51−6.54 (m, 24 H), 6.60 (s, 24 H), 7.26−7.37 (m, 126 H), 7.48−7.50 (m, 102 H), 8.81 (s, 6 H). Calcd. for $C_{474}H_{384}N_6O_{42}Ru$: C, 82.1; H, 5.6; N, 1.2; O, 9.7; Ru, 1.4. Found: C, 77.5; H, 5.6; N, 1.2; O, 9.7.

[G3-Ru]: ^1H NMR ($CDCl_3$) δ 4.47 (s, 12 H), 4.57 (s, 12 H), 4.77 (s, 16 H), 4.97 (s, 8 H), 5.00 (s, 32 H), 6.50−6.58 (m, 126 H), 7.26−7.39 (m, 246 H), 7.45−7.50 (m, 198 H), 8.55 (s, 6 H). Calcd. for $C_{954}H_{768}N_6O_{90}Ru$: C, 82.7; H, 5.6; N, 0.6; O, 10.4; Ru, 0.7. Found: C, 80.5; H, 5.6; N, 0.6; O, 10.4.

Results and Discussion

First, second, and third generation dendrons with biphenyl units at the periphery were prepared following the general procedure developed by Fréchet et al.[15] by conversion of the alcohol dendrons to the corresponding bromides (Scheme 1). Reaction of the dendritic bromides with 4,4′-bis(hydroxymethyl)-2,2′-bipyridine[14] and sodium hydride in DMF gave the desired bipyridine ligands. The second and third generation

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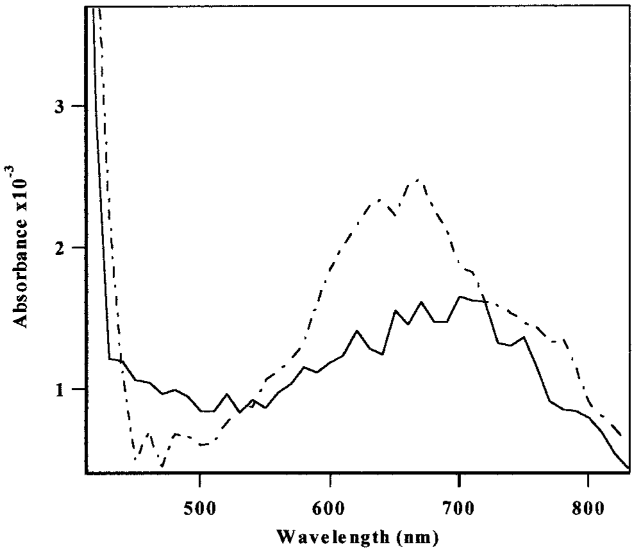

Figure 1. Radical anion spectra of (solid-line) **[G2-D]** (1.0×10^{-3} M) and (dashed-line) 4-ethylbiphenyl (1.6×10^{-2} M).

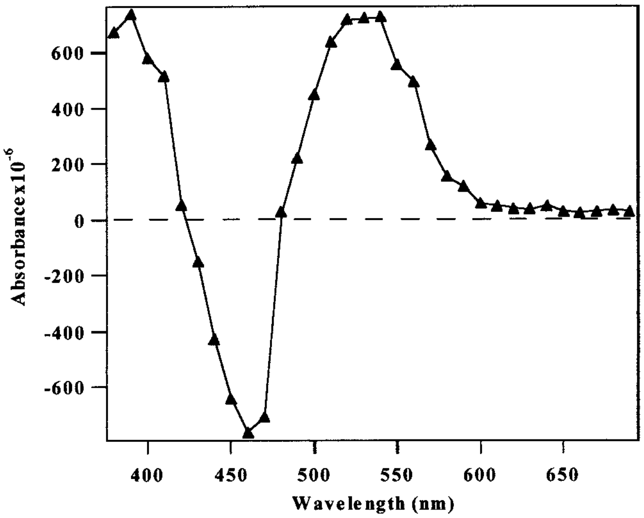

Figure 2. Transient absorption spectrum of **[G2-Ru]** upon the electron attachment (3.9×10^{-4} M).

ruthenium dendrimers, **[G2-Ru]** and **[G3-Ru]** (Chart 1), were prepared by the complexation of ruthenium trichloride and the respective bipyridine ligand in a chloroform:ethanol mixture under reflux for 72 h. The chloride salts of the ruthenium dendrimers were very soluble in CH_2Cl_2 and THF, presumably because of the highly branched organic groups around the ruthenium-metal center.

Pulse radiolysis studies of the chloride salts of the ruthenium-based dendrimers were performed in THF. Electron adducts of the ruthenium-based dendrimers **[G2-Ru]** and **[G3-Ru]** were generated by reaction with solvated electrons in THF formed by 30 ps pulses of 8 MeV electrons.[16] The edge-to-edge distances between the biphenyl groups and the bipyridine were estimated from molecular mechanics calculations to be 14 and 18 Å in the two dendrimers **[G2-Ru]** and **[G3-Ru]**,[17] with a 14 and a 19 bond separation, respectively, as the shortest distance between the biphenyl peripheral groups and the ruthenium core. The $\Delta G°$ values for electron transfer between these parent groups were calculated from literature data[18,19] to be -1.3 eV for the two dendrimers **[G2-Ru]** and **[G3-Ru]**.

The reaction kinetics were measured by monitoring the transient absorption of the reactants between 350 and 1050 nm. Dendrimer **[G2-D]** (Chart 1) was used as a control for checking the dendrimer anion spectrum in THF. The **[G2-D]** anion spectrum was similar to that of 4-ethylbiphenyl (Figure 1), but with a red shift (30 nm) and a smaller extinction coefficient (30%) for the 680 nm band. These small differences may be the result of the restricted geometry of the biphenyl groups within the dendrimer, or may reflect small contributions from exciplex formation between the adjacent biphenyl groups,[20] since the biphenyl radical anion spectrum is very sensitive to the dihedral angle between the two rings.[21] The 680 nm absorption band of the biphenyl anion was not present in the transient absorption spectra of two dendrimers **[G2-Ru]** and **[G3-Ru]** upon reacting with the solvated electrons. No spectral evidence for a biphenyl anion intermediate could be observed, even at the highest possible concentrations ($\sim 10^{-3}$ M) of **[G2-Ru]** and **[G3-Ru]**. The solvated electron disappeared with a rate constant of 5×10^{8} s^{-1}, resulting in an estimated attachment rate of $(5-7) \times 10^{11}$ M^{-1} s^{-1} based on the dendrimer concentration. The simple biphenyl molecule scavenges the solvated electron in THF with a bimolecular rate constant of $\sim 1 \times 10^{11}$ M^{-1} s^{-1}.[22] The dendrimers in question contain 24 and 48 biphenyl groups. These results are consistent with a very fast electron transfer reaction from an initially produced biphenyl anion to the ruthenium tris-bipyridine core. The rates of these electron-transfer reactions from the biphenyl anion to the ruthenium core are thus estimated to be faster than 5×10^{8} s^{-1} in both ruthenium dendrimers. Figure 2 shows the transient absorption spectrum of the **[G2-Ru]**$^-$ anion produced by electron attachment of radiolytically produced solvated electrons, which is a characteristic of a ligand-centered radical "Ru(I)" spectrum. The "Ru(I)" lived for more than 50 ms after its formation in both dendrimers **[G2-Ru]** and **[G3-Ru]**.

Balzani et al.[9] have studied energy transfer in dendrimers similar to the ones reported here, consisting of first- and second-generation dendrimers with a ruthenium core and 12 and 24 naphthyl peripheral units, respectively. Their results are consistent with a very efficient energy-transfer process from the excited state of the naphthalene groups to the ruthenium metal core. No energy-transfer rates were reported, most probably because of the high rate of energy transfer taking place in these dendrimers. Aida et al.[12] reported on photoinduced electron-transfer reactions in water-soluble first- and third-generation dendrimers with a zinc−porphyrin core and noncovalently assembled methyl viologen groups. The rate of electron transfer through the third-generation aryl−ether dendrimer was estimated to be 2.6×10^{9} s^{-1}. The efficient electron transfer observed in all of these systems makes them potentially promising components of the more complex molecular machines,[23,24] so crucial for future advances in nanotechnology.

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In conclusion, pulse radiolysis studies of electron-transfer reactions have been studied in Fréchet-type dendrimers from a singly reduced biphenyl peripheral group to the complexed ruthenium core. The fast electron-transfer rates measured in this rigid dendrimer framework show that electron transfer in such aryl−ether dendrimers is remarkably fast, reflecting the efficiency of these frameworks in facilitating long-range charge-transfer (LRCT) reactions. Efficiencies and rates of electron transfer are being investigated in similar dendritic systems with longer donor−acceptor distances and smaller energetic driving forces. These studies will allow us to determine directly the relevant electronic coupling between disparate chromophores attached to such a framework.

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