Effect of dendrimer generation on electron self-exchange kinetics between metal tris(bipyridine) core dendrimers†

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Here we report the first measurement of homogeneous electron transfer between oxidized and reduced metal tris(bipyridine) core dendrimers by NMR line-broadening; the results indicated that, as the generation of the dendrimer increased, the rate of self-exchange decreased.

Dendrimers with electroactive cores have been studied extensively to understand how this macromolecular architecture can encapsulate (*e.g.* site isolate) its core and how this encapsulation affects electron transfer kinetics.[1–9] These behaviors are relevant to mimicking the functions of electron transfer proteins and potentially, to the trapping of charge on molecules for nanometer scale electronics. In general, one can expect that an increase of the size (generation) of the dendrimer around the electroactive core will lead to a decrease in the rate of electron transfer to/from that core. Further, it has been shown that the primary structure of the dendrimer can have a large effect on its conformational manifold and thus on how the dendrimer encapsulates the core.[8]

To date, all studies on electronic encapsulation of a redox active core by a dendrimer have focused on heterogeneous electron transfer reactions – the electrochemical oxidation and reduction of the core moiety. Electrochemical measurements are convenient, quantitative under the proper conditions and these results are arguably relevant to charge trapping/storage in molecular electronics. However, equally important and interesting is electron transfer between redox active core dendrimers. This bimolecular electron transfer is arguably most relevant in the operation of redox active proteins. Moreover, studying dendrimer–dendrimer electron transfer raises interesting questions as to how the rate will vary with generation and what the relative entropic and enthalpic barriers to this electron transfer will be. Here we report the results of NMR self-exchange experiments on redox active, metal tris(bipyridine) core dendrimers that provide a first evaluation of how the rates and activation parameters of electron transfer between dendrimers change with generation.

We previously reported the synthesis and preliminary electrochemical characterization of metal tris(bipyridine) core dendrimers with zero and one hyperbranching units, *e.g.* $M(G_0Bpy)_3(PF_6)_2$ and $M(G_1Bpy)_3(PF_6)_2$.[10,11] Key to the efficient preparation of these molecules was the deprotonation of 4,4′-dimethyl-2,2′-bipyridine with potassium di-isopropyl amide (KDA) to form a potassium dianion that was sufficiently reactive with dendrons focally substituted with primary alkyl bromides. Here, we have extended that synthetic methodology to the synthesis of $M(G_nBpy)_3$, M = Fe (n = 0 to 3), and M = Ru (n = 0 to 2) (Fig. 1).

Specifically, dendrons with alkyl halide focal groups that we have reported previously[10] were coupled with 4,4′-dimethyl-2,2′-bipyridine (G_0Bpy) in the presence of KDA to form the bis-substituted bipyridine (G_nBpy, n = 1, 2 and 3, Scheme 1). Yields of this procedure were good. The second and third generation dendrons (G_2Bpy and G_3Bpy) were synthesized in 92% and 84% yields, respectively. These molecules were then reacted with iron and ruthenium salts under a variety of conditions to form metal tris(bipyridine) core dendrimers (see ESI for details).

For measurement of self-exchange rates, a partially oxidized/partially reduced solution of the molecule is required. Nitrosonium hexafluorophosphate ($NOPF_6$) was suitable for the partial oxidation of $Fe(G_0Bpy)_3^{2+}$, but it was discovered that addition of this oxidant resulted in some decomposition of the dendrimer for $Fe(G_1Bpy)_3^{2+}$. To overcome this problem, other oxidants were surveyed. Ultimately, $Fe(d_8\text{-bpy})_3(PF_6)_3$ from the known perdeuterio bipyridine was prepared and employed.[12] This molecule was deuterated to $>$ 95%, resulting in a negligible proton NMR signal. Other complexes surveyed had proton NMR signals that

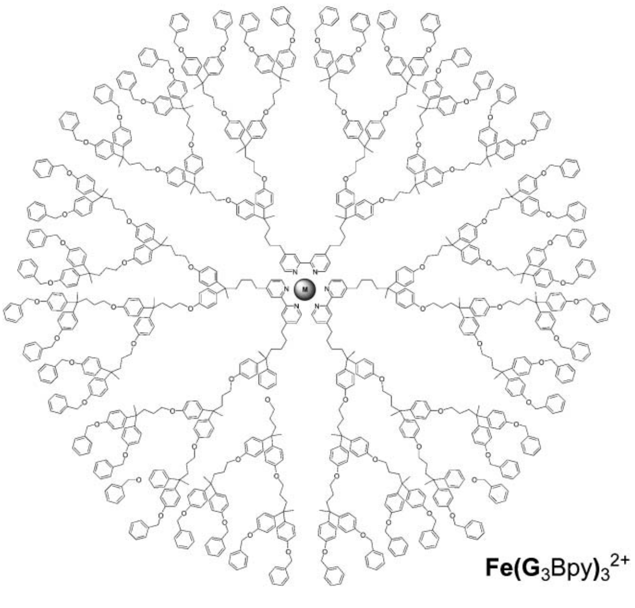

Fig. 1 Representative structure of the metal tris(bipyridine) core dendrimers employed in this study. (M = Fe or Ru, counter ion = PF_6^-).

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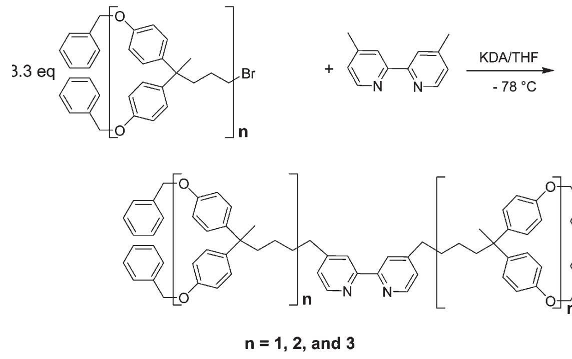

Scheme 1

overlapped with those under observation and were thus unsuitable. Moreover, its redox potential difference with the dendrimers is *ca.* 150 mV and it rapidly and completely oxidized them.

To determine the rate of electron transfer between $M(G_nBpy)_3^{2+}/M(G_nBpy)_3^{3+}$, oxidant was added to a solution of $M(G_nBpy)_3^{2+}$ at different mole fractions, and the shapes of the resulting ^1H NMR lines were observed (Fig. 2). These experiments were performed in the mixed solvent system of CD_2Cl_2–CD_3CN (5/1 v/v) as this mixture was empirically determined to provide adequate solubility for both the oxidized and reduced dendrimers. The approximate Bloch–McConnell equations for the electron self-exchange rate constants in the fast exchange and slow exchange limits were used to calculate the rate constants. (Table 1) The electron self-exchange rate for the zeroth generation iron tris(bipyridine) core dendrimer was found to be in the fast exchange limit (Fig. 2A) as evidenced by the change in chemical shift upon increasing the mole fraction of oxidized material. The electron self-exchange rates for the first through third generation were found to be in the slow exchange limit as determined by a lack of noticeable change in chemical shift over the concentration range examined (Fig. 2B–D). Further details of this procedure are provided in the electronic supporting information.[13–15]

Table 1 Electron self-exchange rate constants in CD_2Cl_2–CD_3CN (5 : 1) at 297 K[a]

	Fe core, k_{ex} (M^{-1} s^{-1})	Ru core, k_{ex} (M^{-1} s^{-1})
G0	$2.59(0.19) \times 10^7$	$3.46(0.23) \times 10^7$
G1	$5.30(1.01) \times 10^4$	$7.26(0.89) \times 10^4$
G2	$2.72(1.03) \times 10^4$	$5.70(0.61) \times 10^4$
G3	$1.14(0.58) \times 10^4$	ND[b]

[a] Values in parentheses represent the magnitude of the 90% confidence interval. [b] Not determined.

The data in Table 1 indicate a large (*ca.* 1000 fold) decrease in k_{ex} from the zeroth to first generation dendrimer and, thereafter, a much smaller decrease with generation. Although the number of data points is small, the decrease in k_{ex} from first to third generation is more linear (*versus* generation and molecular weight) than exponential. This behavior is in contrast with heterogeneous electron transfers to redox-active core dendrimers where the decrease in k_0 with increasing molecular weight is closer to exponential.

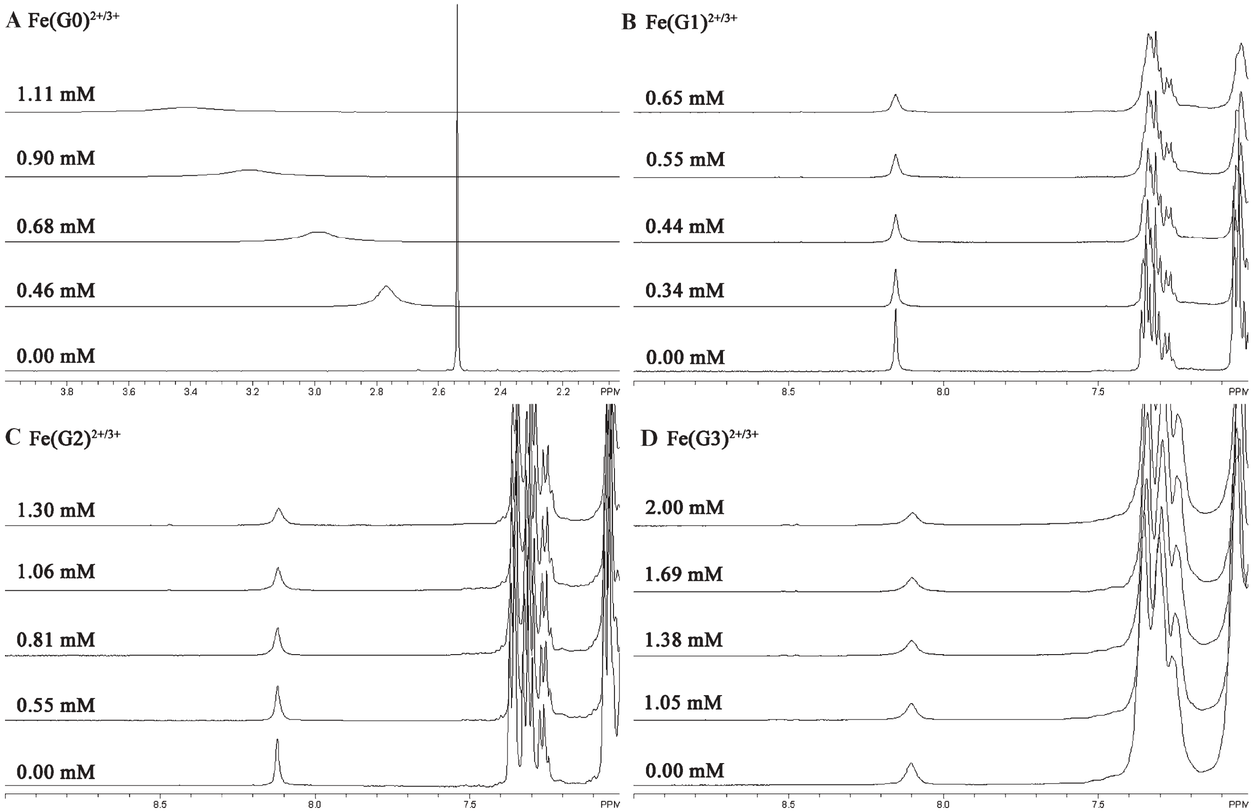

Fig. 2 ^1H NMR spectra of mixtures of $Fe(G_nBpy)_3^{2+}/Fe(G_nBpy)_3^{3+}$ in CD_2Cl_2–CD_3CN (5/1 v/v) mixture at 297 K showing the effect of increasing concentration of oxidized species (total concentration: G0: 11 mM, G1: 2 mM, G2 and G3: 4 mM).

Table 2 Activation parameters and fits to the Marcus equation for $Fe(G_nBpy)_3^{2+/3+}$ self-exchange[a]

Gen.	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})[b]
0	3.09 (0.58)	−14.21 (2.03)	7.33 (0.84)
1	7.75 (1.21)	−10.85 (4.21)	10.98 (1.74)
2	6.37 (1.31)	−16.82 (4.58)	11.38 (1.89)
3	5.19 (1.45)	−22.56 (5.06)	11.91 (2.09)

[a] Values in parentheses represent the magnitude of the 90% confidence interval. [b] Values at 298 K.

This decrease in rate with molecular weight seemed small and led to the question as to what the relative enthalpic and entropic contributions were to the activation barrier for this process. Self-exchange rates were measured as a function of temperature, and Eyring plots showed a good fit to the Eyring equation over the range 278 K to 297 K. Table 2 lists the activation parameters that were determined. The trends in the enthalpy of activation ($\Delta H^{\ddagger}$) and the entropy of activation ($\Delta S^{\ddagger}$) with generation were not the same. Indeed, the entropy of activation increases in magnitude between generations 1 and 3, but the enthalpy of activation decreases in magnitude over this series. The effects leading to these behaviors are hard to generalize from just a few data, but they do indicate that dendritic encapsulation of the redox core affects homogeneous electron transfer kinetics in ways that are more complex than simple shielding effects.

In conclusion, the factors that influence homogeneous electron transfer rate attenuation in dendrimers of increasing generation are quite different than those that have previously been cited when rationalizing analogous heterogeneous electron transfer rate attenuations. The largest rate decrease with generation occurs when the smallest (first generation) ligands are appended to the redox unit. As more dendron layers are added, the rate of self-exchange decreases but only slowly compared to the large decrease between G0 and G1 dendrimers. This decrease is much smaller than what is found in most heterogeneous electron transfer rate attenuation studies, especially considering that the effective distance of electron transfer spans two dendrimer radii (*e.g.* topologically six generations of dendritic spacer between $Fe(G_3Bpy)_3^{2+}$ and $Fe(G_3Bpy)_3^{3+}$, the degree and effect of dendrimer–dendrimer entangling admittedly being unknown). In addition, the several orders of magnitude decrease in the bimolecular electron transfer rate between the G0 and G1 dendrimers coupled with the large changes in both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ between these molecules indicates that encapsulation of the redox core by dendrons must involve important changes in both electronic coupling and outer sphere reorganization energy. The low relative stability of these dendrimers prompts us to continue these types of investigations on other molecules with different redox centers. These studies are underway and will hopefully lead to more insight as to the factors governing the rate and energetics of homogeneous self-exchange on other dendritic and macromolecular redox systems.

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Notes and references

1 K. W. Pollak, J. W. Leon, J. M. J. Fréchet, M. Maskus and H. D. Abruña, *Chem. Mater.*, 1998, **10**, 30.
2 C. B. Gorman, J. C. Smith, M. W. Hager, B. L. Parkhurst, H. Sierzputowska-Gracz and C. A. Haney, *J. Am. Chem. Soc.*, 1999, **121**, 9958.
3 Y. Wang, C. M. Cardona and A. E. Kaifer, *J. Am. Chem. Soc.*, 1999, **121**, 9756.
4 C. B. Gorman and J. C. Smith, *Acc. Chem. Res.*, 2001, **34**, 60.
5 R. Toba, J. M. Quintela, C. Peinador, E. Roman and A. E. Kaifer, *Chem. Commun.*, 2001, 857.
6 P. Ceroni, V. Vicinelli, M. Maestri, V. Balzani, W. M. Müller, U. Müller, U. Hahn, F. Osswald and F. Vögtle, *New J. Chem.*, 2001, **25**, 989.
7 C. S. Cameron and C. B. Gorman, *Adv. Funct. Mater.*, 2002, **12**, 17.
8 T. L. Chasse, R. Sachdeva, C. Li, Z. M. Li, R. J. Petrie and C. B. Gorman, *J. Am. Chem. Soc.*, 2003, **125**, 8250.
9 H. F. Chow, I. Y. K. Chan, P. S. Fung, T. K. K. Mong and M. F. Nongrum, *Tetrahedron*, 2001, **57**, 1565.
10 Y. R. Hong and C. B. Gorman, *J. Org. Chem.*, 2003, **68**, 9019.
11 Y.-R. Hong and C. B. Gorman, in *Metal-Containing and Metallo-Supramolecular Polymers and Materials*, ACS Symposium Series 928, ed. G. R. Newkome, I. Manners and U. S. Schubert, Washington, D. C., 2006.
12 W. R. Browne, C. M. O'Connor, J. S. Killeen, A. L. Guckian, M. Burke, P. James, M. Burke and J. G. Vos, *Inorg. Chem.*, 2002, **41**, 4245.
13 M. S. Chan and A. C. Wahl, *J. Phys. Chem.*, 1978, **82**, 2542.
14 D. M. Triegaardt and A. C. Wahl, *J. Phys. Chem.*, 1986, **90**, 1957.
15 J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982.