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Preparation of a Redox-Gradient Dendrimer. Polyamines Designed for One-Way Electron Transfer and Charge Capture

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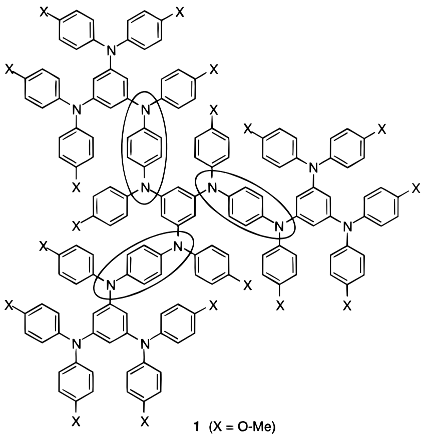
Directional control of electron transfer (ET) within redox-active macromolecules is an important design feature of new molecule-based charge storage materials or charge-transfer devices. Of recent interest in this field have been redox-active dendrimers,[1,2] some of which have been designed for directed energy transfer[3] and for electrical conduction.[4] Here, we present the synthesis and electron-transport properties of a new redox-active polyarylamine dendrimer **1** which possesses a radial redox-gradient. Dendrimer **1** (MW = 2625) contains a benzene core, interior *p*-phenylenediamine groups, and perimeter diarylamino groups. It has nominal C_3 symmetry with nine distinct, meta-linked redox functions. The more difficult to oxidize peripheral arylamino (AA) groups form a partial shell around the more easily oxidized interior phenylenediamino (PD) groups within the dendrimer architecture to afford a radial redox-gradient in the molecule. The surface-to-core potential gradient is hypothesized to support **1**'s core charging (oxidation) but inhibit core discharging (reduction of core cation). Such structures, of which **1** is a first-generation prototype, might serve as three-dimensional charge funnels and as charge storage reservoirs in which core charge is gradient "protected" from neutralization.



1 (X = O-Me)

Dendrimer **1** was prepared via sequential Ullmann reactions as outlined in Scheme 1.[5] Anisidine condensation with phloroglucinol according to the procedure of Buu-Hoï[6,7] gave in good yield tris(arylamino)benzene **A** which was then diarylated under stoichiometric Ullmann conditions to form intermediate **B** in 28% yield after chromatographic purification. Byproducts of this step included hexaaryl and tetraaryl triaminobenzenes which were separated from the mixture for use in other experiments. Treatment of **B** with excess diiodobenzene yielded **C**, which upon Ullmann-coupling with **A** gave dendrimer **1** in 70% purified yield. Compound **1** is a monodisperse, colorless amorphous solid that is soluble in organic solvents.[8]

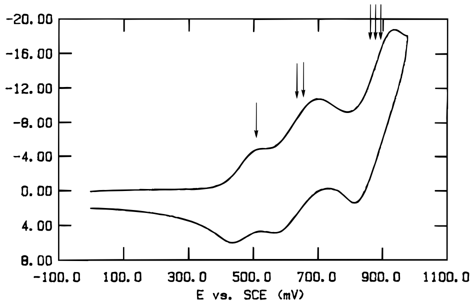


Figure 1. Cyclic voltammogram of **1** in CH_2Cl_2 (0.1 M Bu_4NBF_4) at 200 mV s^{-1} scan at 25 °C.

Electrochemical oxidation of dendrimer **1** by cyclic voltammetry (CV) reveals multiple oxidations as displayed in Figure 1. The first three oxidation peaks are chemically reversible and are assigned as one-, two- and three-electron processes, respectively.[9] The corresponding oxidation potentials are $E_1^{\circ\prime}$ 0.48, $E_2^{\circ\prime} \approx E_3^{\circ\prime}$ 0.63, and $E_4^{\circ\prime} \approx E_5^{\circ\prime} \approx E_6^{\circ\prime}$ 0.88 V vs SCE in CH_2Cl_2. Coulometric analysis confirms that oxidation of **1** at 0.53 V is a one-electron process and of $\mathbf{1}^+$ at 0.75 V is a two-electron event. The CV data of related structures allows the assignment of the first three oxidations as electron removal from interior PD groups. (For example, the anisyl-substituted tris(phenylenediamino)-benzene **2** has $E_1^{\circ\prime}$, $E_2^{\circ\prime}$, $E_3^{\circ\prime}$, and $E_4^{\circ\prime}$ values of 0.41, 0.54, 0.61, and 0.97 V vs SCE in CH_2Cl_2.)[10] The fourth, fifth, and sixth oxidations of **1** at 0.88 V are assigned as electron loss from remote peripheral AA groups. This assignment is consistent with the $E^{\circ\prime}$ values found for 1,3,5-tris(di-*p*-anisylamino)benzene[11] which are 0.65, 0.87, and 0.98 V vs SCE in CH_2Cl_2 for mono-, di-, and trication formation, respectively. As expected, oxidation of the uncoupled peripheral AA groups of $\mathbf{1}^{3+}$ occurs at a single potential because these groups are essentially uncoupled to each other.[12] Subsequent oxidation waves beyond the sixth-electron oxidation are also observed for **1** as chemically quasi-reversible or irreversible waves at room temperature.

Chemical oxidation of **1** with $NOPF_6$ provides isolable $\mathbf{1}^+$, $\mathbf{1}^{2+}$, and $\mathbf{1}^{3+}$ PF_6 salts in high yield.[13] Monocation $\mathbf{1}^+$ gives a broad single-line ESR spectrum at 25 °C in CH_2Cl_2. At lower temperatures (<−20 °C) this spectrum begins to reveal a 5-line pattern with a splitting of roughly 5 G that we assign as a(2N).[14]

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(1) For reviews of organo-metal dendrimers and their properties, see: (a) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26. (b) Gorman, C. B. *Adv. Mater.* **1997**, *9*, 1117.

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(4) Miller, L. L.; Duan, R. G.; Tulley, D. C.; Tomalia *J. Am. Chem. Soc.* **1997**, *119*, 1005.

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(8) ^1H and ^{13}C NMR data is given in the Supporting Information. Analysis for **1** calcd for $C_{168}H_{150}N_{12}O_{18}$: C, 76.88; H, 5.75; N, 6.40. Found: C, 76.74; H, 5.73; N, 6.29.

(9) The CV analysis of isolated $\mathbf{1}^{3+}$ shows that it is electrochemically inert at 0.8 V vs SCE but reduced at potentials below 0.7 V and oxidized at potentials above 0.8 V, consistent with $E_3^{\circ\prime} \approx 0.63$ V but not $E_3^{\circ\prime} \approx 0.88$ V vs SCE.

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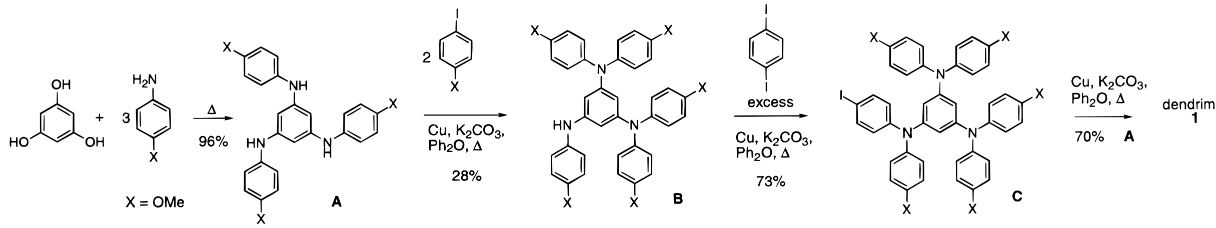
(11) Stickley, K. R.; Blackstock, S. C. *J. Am. Chem. Soc.* **1994**, *116*, 11576.

(12) This behavior has been observed in other polyferrocenyl dendrimers with remote ferrocene groups: Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Lobete, F.; García, B.; Ibisate, M.; Losada, J. *Organometallics* **1996**, *15*, 5278.

(13) Analysis for $\mathbf{1}^+PF_6^-$ calcd for $C_{168}H_{150}N_{12}O_{18}PF_6$: C, 72.85; H, 5.45; N 6.07. Found: C, 72.63; H, 5.40; N 6.02. Analysis for $\mathbf{1}^{2+}(PF_6)_2$ calcd for $C_{168}H_{150}N_{12}P_2F_{12}$: C, 69.22; H, 5.18; N, 5.77. Found: C, 69.25; H, 5.19; N, 5.89. Analysis $\mathbf{1}^{3+}(PF_6)_3$ calcd for $C_{168}H_{150}N_{12}P_3F_{18}$: C, 65.94; H, 4.94; N, 5.49. Found: C, 65.88; H, 4.93; N, 5.59.

10.1021/ja9821091 CCC: $15.00

Scheme 1



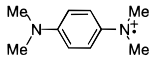
The ESR data, along with the above CV data, suggest that the odd electron of **1**$^+$ is localized on one of the core *p*-phenylenediamine units. For comparison, the observed $E_1^{\circ\prime}$ value of *N*,*N*,*N*′,*N*′-tetra-*p*-anisyl-*p*-phenylenediamine (TAPD) is 0.46 V vs SCE and its a(2N) splitting is 5.75 G.[15]

The redox gradient in dendrimer **1** is estimated to be ∼ 0.2 V, the difference in the $E_1^{\circ\prime}$ values of 1,3,5-tris(di-*p*-anisylamino)benzene[11] and **1**. As mentioned above, this potential gradient should provide a conduit for electron−hole transfer from surface to core and simultaneously impart a barrier to the reverse process to render a degree of electronic "protection" against the reverse charge transport.

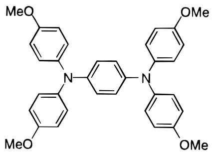
To probe the charge transport properties of **1**$^+$, we have measured its neutral/cation self-electron-exchange reaction rate. For "unprotected" *p*-phenylenediamines such as *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), k_{ET} values for neutral/cation self-electron-exchange (eq 1) are $10^8 - 10^9$ M^{-1} s^{-1}

$$\mathrm{TMPD}^+ + \mathrm{TMPD} \underset{}{\overset{k_{ET}}{\rightleftharpoons}} \mathrm{TMPD} + \mathrm{TMPD}^+ \qquad (1)$$

TMPD$^+$ =



(depending on solvent) and are measurable by ESR line broadening of the TMPD$^+$ signal upon addition of neutral TMPD.[16] For **1**/**1**$^+$ mixtures, no effect on the ESR signal line width is observed, suggesting that the **1**/**1**$^+$ ET reaction is slower than 10^8 M^{-1} s^{-1}. In fact, the **1**/**1**$^+$ electron-exchange is slow enough that its k_{ET} value may be measured by ^{1}H NMR line broadening analysis in the slow exchange limit[17] to give k_{ET} of 1.8×10^5 M^{-1} s^{-1} in CDCl$_3$ at 25 °C. For comparison, neutral/cation k_{ET} values for TAPD and **2** have also been measured.[18] As expected, the latter rates are near the diffusion limit value. The kinetic data is summarized in Table 1.



TAPD

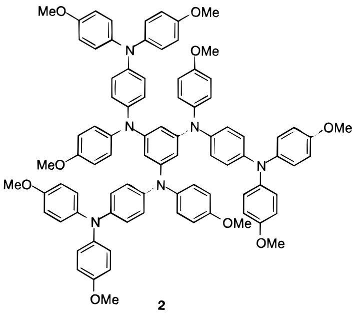


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Table 1. Self-Electron-Exchange Rate Constants (k_{ET}) in CDCl$_3$ for Neutral/Cation Couples

cmpd[a]	k_{ET} (M^{-1} s^{-1})	temp (°C)	method	reference
TMPD/TMPD$^+$	$7.0 \pm 0.7 \times 10^9$	20.0	ESR	ref 13b[b]
TMPD/TMPD$^+$	$4.9 \pm 0.6 \times 10^9$	25.5	NMR[c]	this work
TAPD/TAPD$^+$	$3.5 \pm 0.3 \times 10^8$	25.5	NMR[c]	this work
2/**2**$^+$	$2.8 \pm 1.4 \times 10^9$	25.5	NMR[c]	this work
2/**2**$^+$	$2.1 \pm 0.3 \times 10^9$	25.5	NMR[d]	this work
1/**1**$^+$	$1.8 \pm 0.1 \times 10^5$	25.5	NMR[d]	this work

[a] All cations employed as PF$_6^-$ salts. [b] Solvent is CHCl$_3$. [c] -CH$_3$ NMR signal monitored. [d] Core aryl CH signal monitored.

From Table 1 data, we conclude that the intermolecular PD neutral/cation electron-exchange rate for dendrimer **1** is slowed by a factor of 10^3−10^4 relative to model (unprotected) PD neutral/cation couples. The observed rate retardation for **1**/**1**$^+$ charge transport corresponds to an increase in the effective activation free energy for the PD neutral/cation couple of 4−6 kcal mol^{-1} at 25 °C and is thus consistent in magnitude with a counter-gradient charge-transfer process for **1**/**1**$^+$ electron-exchange.[19] Whether the **1**/**1**$^+$ ET actually occurs through the periphery AA groups or whether the AA groups act more as a steric shield to the close approach of the PD centers cannot be distinguished at this time. It is also possible that the exterior dendrimer generation increases the reorganization energy associated with PD redox changes, thereby slowing ET rates. Further studies will be required to fully elucidate the mechanistic details of **1**'s and **1**$^+$'s electron-transport dynamics. Nevertheless, the current results demonstrate that dendrimer **1** structure imparts a significant kinetic barrier to an otherwise extremely facile PD/PD$^+$ intermolecular exchange reaction. This effect is consistent with the redox-gradient features of **1**, which serves as a prototype for a new class of organic redox systems tailored for controlled charge transport.

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Supporting Information Available: Synthetic procedures and ^{1}H and ^{13}C NMR structure characterization for **A**, **B**, **C**, **1**, and **1**$^+$PF$_6^-$ and experimental details of Table 1 analyses (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(14) The ESR data is consistent with facile intramolecular electron exchange among core PD groups of **1**$^+$ at ambient temperature being frozen out on the ESR time scale at lower temperatures.

(15) TAPD was prepared by Ullmann reaction of *p*-diiodobenzene with di-*p*-anisylamine and its CV and cation-radical ESR and ENDOR properties were measured in our laboratory.

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(18) These rates were measured by ^{1}H NMR line broadening in the fast exchange limit as detailed in the Supporting Information. A complete account of these kinetic measurements will be published elsewhere.

(19) The slow ET kinetics for the **1**/**1**$^+$ exchange are not an inherent result of large molecular size. For spherical particles, the diffusion-limited rate constant k_d is given by $k_d = 2k_bT(r_a + r_b)^2/3\eta r_a r_b$, where k_b is the Boltzman constant, T the absolute temperature, r_a and r_b the radii of the colliding spheres, and η the solvent viscosity. The dependence on particle size is $(r_a + r_b)^2/r_a r_b$ and when $r_a = r_b$, as in the present case, this value is constant and equal to 4. For a detailed treatment of diffusion-limited rates see: Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: Englewood Cliffs, New Jersey; 1989; p 162.