

Synthesis of electrochemically active pyrazine based dendrimers

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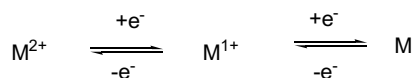
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Abstract—A synthesis of dendrimers with pyrazine as core and *m*-terphenyl as surface end groups has been achieved. The electrochemical behavior of the dicationic pyrazinium dendrimers was also studied by cyclic voltammetry.
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1. Introduction

Radical cations of diquateryary N-heterocycles exhibit a variety of applications in molecular architectures, electro-organic synthesis and material chemistry.^{1–3} Dendrimers are globular monodisperse macromolecules containing branched repeating units emitting from a core unit. Symmetrical building blocks are commonly used to facilitate generational growth due to their easy accessibility and can easily be functionalized. An important focus in the dendrimer field has been the incorporation of functional core molecules that, by their changing properties contribute clearly to the nature of the dendrimers. Dendrimers containing ammonium salts as the peripheral group and a lengthy hydrocarbon chain as the core or as the building blocks trap lipophilic guest molecules such as diphenyl hexatriene, naphthalene and dyes in aqueous solution.⁴ Studies on the electrochemical behavior of dendrimers with a diquateryary nucleus have attracted the attention of synthetic organic chemists during recent times. Electrochemical reduction of the 4,4'-bipyridyl residue in Newkome-type dendrimers encapsulated by cucurbit[7]uril has been reported by Kaifer et al.⁵ The same author has also reported the electrochemical reduction of unsymmetrical viologen based dendrimers⁶ and reduction of the viologen unit present in the host guest complex of Newkome-type dendrimers with crown ethers.⁷ Paired electron transfer reactions in dendrimers with the 4,4'-bipyridyl core and naphthalene surface groups has also been studied.⁸ A deeper understanding of dendritic effects on redox potentials using ferrocene encapsulated within symmetrical dendrimers has been reported by Smith et al.⁹ Den-

drimers with a pyrazine nucleus are dicationic in nature and function as a two-step redox system, which enables various electron transfer processes.¹⁰



Syntheses of permanent fluorescence sensing hyper-branched dendritic architectures,¹¹ novel bactericidal dendrimers¹² and axially chiral enantiopure dendrimers¹³ were reported from our laboratory recently. We report herewith the synthesis and cyclic voltammetry studies of dicationic dendrimers **1a–c** which have pyrazine as the core and *m*-terphenyl as the hydrophobic surface groups (Fig. 1).

Dendrimers **1a–c** were prepared by simple N-alkylation of pyrazine with the corresponding dendritic bromides **2**, **3** and **4**. Reaction of 2.1 equiv of *m*-terphenyl bromide **2** with 1 equiv of pyrazine in DMF in the presence of K₂CO₃ followed by counter ion exchange with NH₄PF₆ afforded dendrimer **1a** in a 48% yield after chromatographic purification (SiO₂) using hexane/CHCl₃, (2:3) as the eluting solvent.¹⁴ Similarly reaction of 2.1 equiv of the first generation dendritic bromide [G₁]-Br **3** with 1 equiv of pyrazine followed by counter ion exchange with NH₄PF₆ afforded dendrimer **1b** in a 52% yield after chromatographic purification (SiO₂) using hexane/CHCl₃, (1:4) as the eluting solvent. The structure of dendrimer **1b** was confirmed from spectral and analytical data.¹⁵ The second-generation dendrimer **1c** was obtained in a 47% yield by the reaction of pyrazine with 2.1 equiv of the second-generation dendritic bromide [G₂]-Br **4** followed by similar counter ion exchange and column chromatographic purification (Scheme 1).

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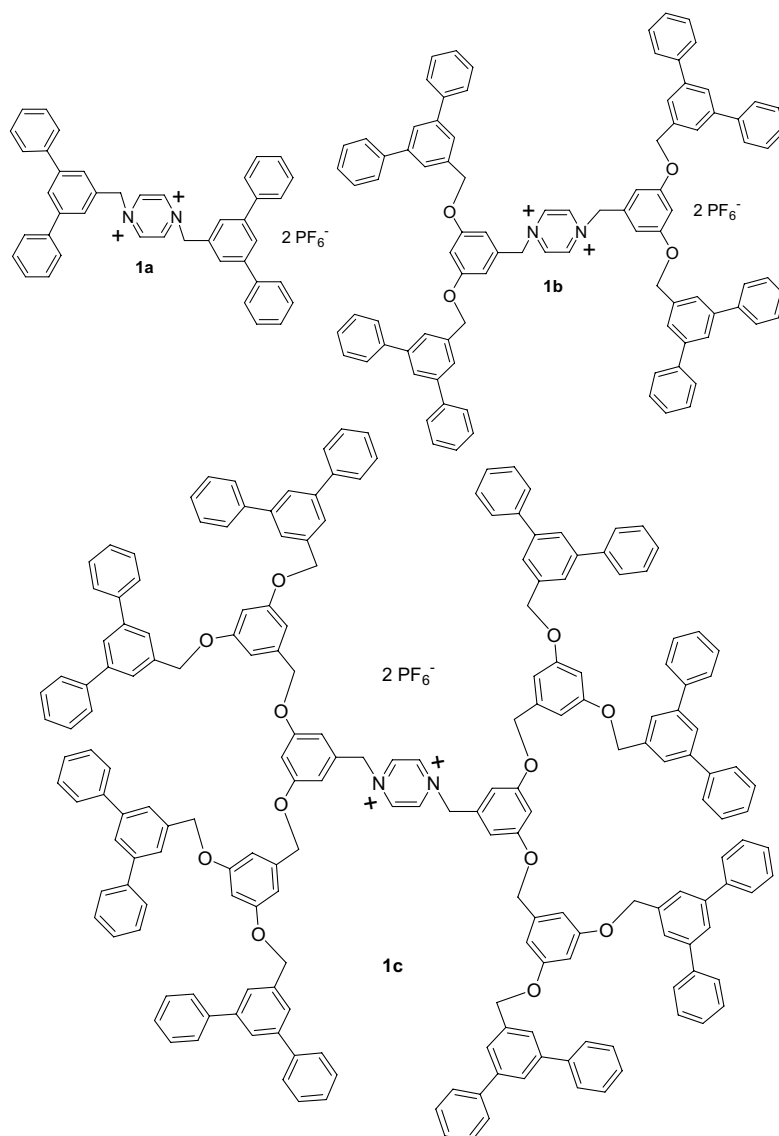


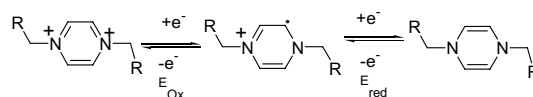
Figure 1.

The structure of the dendrimer **1c** was also confirmed from spectral and analytical data.¹⁶

2. Electrochemical studies

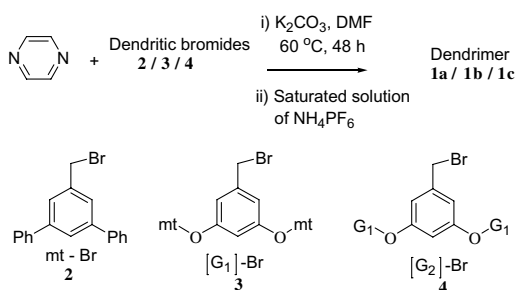
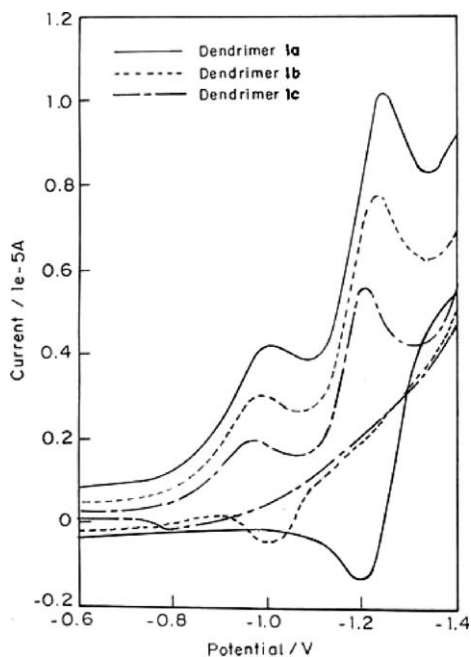
Cyclic voltammetry studies on the dendrimers were carried out in acetonitrile with tetra-*n*-butyl ammonium perchlorate (10^{-1} M) as the supporting electrolyte in the potential range of -0.8 to -1.4 V against Ag/AgCl. Dendrimer **1a** underwent consecutive two-step single electron reduction.¹⁷ The cyclic voltammogram of dendrimer **1a** exhibited a reduction wave in the cathodic potential region at $E_{PC} = -1.12$ V. However, in the second step the reduction product underwent oxidation during the reverse reaction. The dendrimers undergo the following redox reaction under cyclic voltammetric reduction conditions.

A similar cyclic voltammetric response has been recorded for dendrimer **1b**, which showed a simple,



two-step, single electron transfer process. The cyclic voltammogram of dendrimer **1b** showed a reduction wave in the cathodic potential region at $E_{PC} = -1.06$ V. Similarly dendrimer **1c** also exhibited a reduction wave in the cathodic potential region at $E_{PC} = -0.84$ V.

Dendrimers **1a–c** exhibited two-step redox waves corresponding to the formation of a cation radical ($Pz^{2+} > Pz^{1+}$) and a neutral species ($Pz^{1+} > Pz$). In agreement with the results reported for a similar series of dendrimers, the half-wave potential ($E_{1/2}$) values of both the first and second redox processes shift to less negative values as the dendrimer generation increases. The trend observed with respect to the $E_{1/2}$ values of



Scheme 1.

dendrimers **1a–c** could be due to the increased hydrophobic character of the dendrimer core, which makes it progressively harder to solvate the two positive charges of the pyrazinium core effectively.

Similar observations have been reported earlier by Kaifer et al.¹⁷ Therefore, reduction with partial or total elimination of the core charges becomes more favorable with increasing dendrimer generation. The difference between anodic and cathodic potentials (ΔE_p) indicates that the redox processes might be reversible however, the re-oxidation waves do not have similar peak currents corresponding to the reduction wave which clearly indicates the irreversibility of all the redox processes for the dendrimers **1a–c**. Further, the slight distortion observed for the second-generation dendrimer **1c** could be due to precipitation of the one-electron reduced species on the electrode surface as revealed in the voltammogram of **1c**.

From the electrochemical studies, it can be concluded that lower generation dendrimers exhibit clearer electrode reduction potentials than the intermediate generation dendrimer. However, with higher generation dendrimers the redox reaction was slow due to its rapid

deposition on the electrode surface. The synthesis and electrochemical properties of other such related dendrimers and a study on their application as phase transfer catalysts are underway.

3. General procedure for the synthesis of dendrimers **1a–c**

A mixture of pyrazine (1.0 equiv) and the dendritic bromide **2/3/4** (2.1 equiv) was stirred with K_2CO_3 (5.0 equiv) in DMF (20 mL) at 60 °C for 48 h. After completion of the reaction, a saturated solution of NH_4PF_6 (2.5 equiv in 30 mL of H_2O) was added. The reaction mixture was then poured into H_2O and extracted with CH_2Cl_2 (3×150 mL). The combined organic extract was washed with brine and dried over anhydrous $MgSO_4$. Evaporation of the organic layer gave a residue, which was chromatographed over SiO_2 using a mixture of hexane/ $CHCl_3$ to give the corresponding dendrimer.

Acknowledgments

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14. Dendrimer **1a**: Yield: 48% (260 mg); $R_f = 0.32$ (hexane/ CHCl_3 , 2:3); mp: 108–110 °C; ^1H NMR: (500 MHz, CDCl_3) δ 4.94 (s, 4H), 7.13–7.62 (m, 26H) and 9.83 (s, 4H); ^{13}C NMR: (125 MHz, CDCl_3) δ 64.8, 124.1, 124.2, 124.8, 126.7, 127.0, 128.3, 140.4, 141.4 and 141.6; MS (FAB): m/z 566 $[\text{M}-2\text{PF}_6]^+$; Anal. Calcd for $\text{C}_{42}\text{H}_{34}\text{N}_2\cdot 2\text{PF}_6$: C, 58.87; H, 3.97; N, 3.27. Found: C, 58.80; H, 3.89; N, 3.19.
15. Dendrimer **1b**: Yield: 52% (246 mg); $R_f = 0.42$ (hexane/ CHCl_3 , 1:4); mp: 120–124 °C; ^1H NMR: (500 MHz, CDCl_3) δ 5.04 (s, 4H), 5.08 (s, 8H), 7.11–7.66 (m, 58H) and 9.80 (s, 4H); ^{13}C NMR: (125 MHz, CDCl_3) δ 65.3, 70.7, 106.4, 107.1, 125.2, 125.8, 127.2, 127.4, 128.7, 137.7, 139.1, 140.7, 142.0, 159.9 and 160.5; MS (FAB): m/z 1294 $[\text{M}-2\text{PF}_6]^+$; Anal. Calcd for $\text{C}_{94}\text{H}_{74}\text{O}_4\text{N}_2\cdot 2\text{PF}_6$: C, 71.21; H, 4.67; N, 1.76. Found: C, 71.12; H, 4.54; N, 1.68.
16. Dendrimer **1c**: Yield: 47% (126 mg); $R_f = 0.36$ (hexane/ CHCl_3 , 1:4); mp: 86–90 °C; ^1H NMR: (500 MHz, CDCl_3) δ 4.83 (s, 4H), 4.95 (s, 8H), 4.99 (s, 16H), 7.06–7.95 (m, 122H) and 9.79 (s, 4H); ^{13}C NMR: (125 MHz, CDCl_3) δ 65.7, 70.4, 70.7, 107.5, 108.6, 108.9, 125.6, 126.3, 127.5, 127.8, 129.1, 131.2, 137.5, 137.9, 138.7, 141.1, 142.4, 142.5, 160.4, 160.6 and 160.9; MS (MALDI-TOF): m/z 2750 $[\text{M}-2\text{PF}_6]^+$; Anal. Calcd for $\text{C}_{198}\text{H}_{154}\text{O}_{12}\cdot \text{N}_2\cdot 2\text{PF}_6$: C, 78.16; H, 5.06; N, 0.92. Found: C, 78.04; H, 4.83; N, 0.84.
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