

Synthesis of electrochemically active pyrazine based dendrimers

Perumal Rajakumar* and Kilivelu Ganesan

Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India

Received 29 December 2005; revised 25 March 2006; accepted 26 April 2006

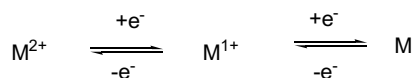
Available online 22 May 2006

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.
© 2006 Elsevier Ltd. All rights reserved.

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).

* Corresponding author. Tel.: +91 44 22351269; fax: +91 44 2352494; e-mail: perumalrajakumar@hotmail.com

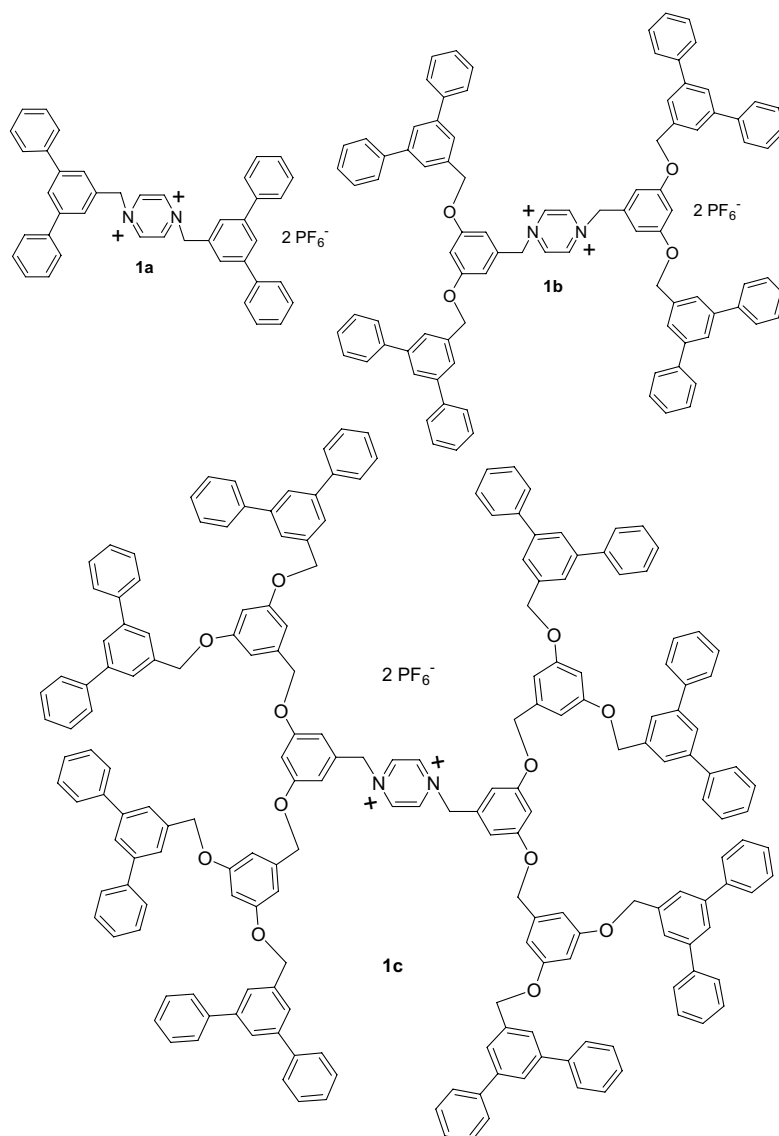


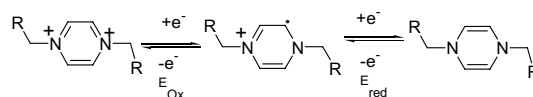
Figure 1.

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

Download English Version:

<https://daneshyari.com/en/article/5289784>

Download Persian Version:

<https://daneshyari.com/article/5289784>

[Daneshyari.com](https://daneshyari.com)