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Dendritic cavitands: preparation and electrochemical properties

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A new series of dendrimers containing a central cavitand core with four appended Fréchet-type dendrons, linked to the core through 4,4′-bipyridinium (viologen) subunits, have been synthesized, characterized and their electrochemical properties investigated using cyclic voltammetric measurements.

Dendrimer chemistry is an area of current research interest.[1] In particular, the investigation of electron transfer reactions in dendrimers containing internal redox active units—partially or completely buried in the dendrimer backbone—has attracted considerable attention.[2] Typically, the electrochemical kinetics of dendrimers with core redox active sites becomes slower with increasing molecular size.[3] Our group[4] and Balzani's[5] have recently reported the synthesis and electrochemical properties of a series of Fréchet-type dendrimers, which constitute the first exception to this general trend. These dendrimers are functionalized with a single 4,4′-bipyridinium (viologen) unit at their core and exhibit fast heterogeneous electron transfer reactions, from the first to the third generation, regardless of their molecular weight. Due to our interest in better understanding the thermodynamics and kinetics of heterogeneous electron transfer reactions of dendrimer-encapsulated redox centers, we have continued our investigation of dendrimers containing internal viologen units. This paper reports the synthesis, characterization and preliminary electrochemical studies of a novel series of Fréchet-type dendrimers that contain four central viologen units covalently attached to a cavitand[6] core.

The synthetic strategy for the preparation of the dendritic cavitands utilized a convergent method. The cavitand precursor containing four bipyridinium subunits (**CAV4**, Fig. 1) was synthesized following a methodology previously reported by us.[7] The benzyl bromide dendrons (**G0–G3**) were prepared according to the procedure reported by Fréchet and Hawker.[8] Menschutkin reaction between **CAV4** and the corresponding dendron bromides (in DMF at 55 °C) afforded, after counterion exchange, the dendritic cavitands with the tetrafunctional core (**CAV4G0–3**, see Fig. 1). All dendrimers were characterized by ^{1}H and ^{13}C NMR spectroscopies, mass spectrometry and elemental analysis.†

The electrochemical reduction of viologen derivatives usually takes place in two sequential, one-electron steps ($V^{2+} \rightarrow V^{+\cdot}$ and $V^{+\cdot} \rightarrow V$). The effect of the dendritic structure on the corresponding reduction potential was investigated by cyclic voltammetry (CV). Since these compounds (**CAV4G0–3**) exhibit very different solubilities from the first to the last generation, the electrochemical studies were performed in two different solvents: pure acetonitrile and dichloromethane/acetonitrile mixtures (see Table 1). In acetonitrile, all compounds showed two separate reduction waves. The observed peak-to-peak potential splittings (ΔE_p) for the first reduction ($4\ V^{2+} \rightarrow 4\ V^+$) indicate that the process is essentially reversible for all four compounds although **CAV4G3** shows some precipitation on the electrode surface. The half-wave potentials ($E^1_{1/2}$) corresponding to this first wave become less negative with increasing dendrimer generation, indicating that the electrochemical reduction is thermodynamically favored with increasing dendrimer size. The second reduction wave ($4\ V^+ \rightarrow 4\ V$) is more strongly affected by precipitation, especially for higher dendrimer generations. Little can be said conclusively about the

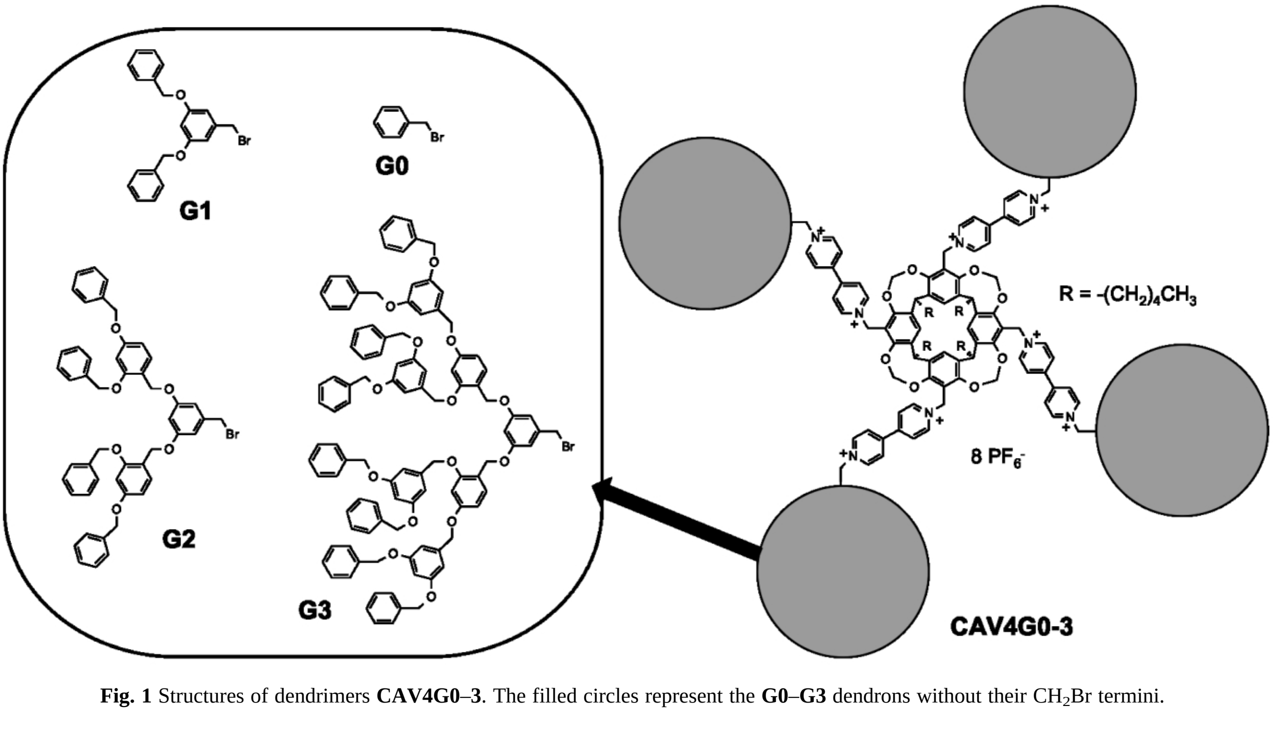

Fig. 1 Structures of dendrimers **CAV4G0–3**. The filled circles represent the **G0–G3** dendrons without their CH$_2$Br termini.

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Table 1 Voltammetric half-wave potentials[a] (V *vs.* Ag/AgCl) and peak-to-peak potential splittings[b] (within brackets, in mV) for the reduction of dendrimers **CAV4G0–3** in solutions also containing 0.1 M TBAPF$_6$ as supporting electrolyte

	Solvent	CAV4G0	CAV4G1	CAV4G2	CAV4G3
$E^1_{1/2}$ (ΔE_p)	CH_3CN	−0.27 (71)	−0.26 (72)	−0.25 (71)	−0.23 (71)
$E^2_{1/2}$ (ΔE_p)	CH_3CN	−0.78 (62)	−0.75 (105)[c]	−0.77 (27)[c]	−0.74 (50)[c]
$E^1_{1/2}$ (ΔE_p)	CH_3CN/CH_2Cl_2 (1:1)	−0.28 (52)[c]	−0.27 (61)	−0.26 (78)	−0.25 (69)
$E^2_{1/2}$ (ΔE_p)	CH_3CN/CH_2Cl_2 (1:1)	−0.77 (31)[c]	−0.77 (56)[c]	−0.78 (54)[c]	−0.76 (63)

[a] Measured on a glassy carbon working electrode. [b] Scan rate = 0.1 V s^{-1}. [c] Values affected by precipitation.

reversibility of this process due to the precipitation effects, but the $E^2_{1/2}$ potentials shift to less negative potentials with increasing molecular weight, maintaining the same trend shown by the first reduction potentials.

In an attempt to minimize the precipitation of the reduced dendrimer forms, CV experiments were also conducted in acetonitrile/dichloromethane mixtures (1:1), a medium of lesser polarity that would increase the solubility of the reduced forms of these dendrimers. In this solvent mixture, the same trend described previously for the $E_{1/2}$ values was observed. In general, precipitation effects were less intense for all four dendrimer generations than they were in acetonitrile solution, although the most polar compound, **CAV4G0**, still exhibited slightly distorted voltammetric waves, especially in its second reduction process.

The electrochemical behavior of all these compounds also reveals the non-interacting character of the viologen units around the cavitand. In other words, all four viologen units are reduced at similar potentials and no significant degree of electronic communication among them was detected in our experiments. Analysis of the ΔE_p values indicates that the electron transfer is essentially reversible, at most quasireversible, at scan rates of 0.1 V s^{-1}, for all compounds, even for the highest generations. Deviations from electrochemical reversibility seem to be associated with precipitation effects, more than to any other factor.

The trends in the $E_{1/2}$ potentials show that the reduced forms of the dendrimers become thermodynamically favored as the dendrimer generation increases, probably because the uptake of electrons gives rise to less charged species, more compatible with the increasing hydrophobicity of the interior of these macromolecules. This is also in agreement with our previously reported results obtained with viologen core Fréchet-type dendrimers.[4] In the present case, the change in the overall molecular charge resulting from electrochemical reduction ($4\ V^{2+} \longrightarrow 4\ V^+ \longrightarrow 4\ V$) is so pronounced that we could not find a suitable solvent that can solubilize each of the four surveyed dendrimers, as electrons are added or taken from the viologen centers. In a polar solvent, such as acetonitrile, the reduced forms of the highest generation dendrimers show partial precipitation on the electrode surface. Addition of dichloromethane reduces the solvent polarity, but also creates solubility problems for the more polar, lower generation dendrimers.

Compounds **CAV4G0–3** constitute the first example of dendrimers with a cavitand core surrounded by four viologen units. The reversible character of their electrochemical behavior is in agreement with the electrochemistry of previously reported viologen-core dendrimers.[4,5] The results reported here further support the notion that internal viologen subunits remain capable of fast heterogeneous electron transfer reactions, even when they are surrounded by a considerable dendritic mass.

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Notes and references

† **CAV4G0**: Yield 90%. ^{1}H-NMR (200 MHz, CD_3CN): 0.89 (t, 12H), 1.20–1.37 (m, 24H), 2.25–2.45 (m, 8H), 4.60–4.80 (m, 8H), 5.66 (s, 8H), 5.85 (s, 8H), 6.34 (d, 4H), 7.53–7.64 (m, 24H), 8.42 (d, 16H), 9.00 (m, 16H) ppm. ^{13}C-NMR (50 MHz, CD_3CN): 14.4, 23.3, 28.1, 30.4, 32.6, 38.5, 56.0, 65.6, 100.4, 120.7, 125.5, 128.1, 128.4, 130.2, 130.5, 133.4, 139.6, 146.4, 146.8, 151.2, 154.3 ppm. MS (ES): *m/z* [int.%] = 1363[10] $(M - 2PF_6^-)^{2+}$, 861[20] $(M3 - PF_6^-)^{3+}$, 609[100] $(M - 4PF_6^-)^{4+}$, 458[72] $(M - 5PF_6)^{5+}$. Anal. Calcd for $C_{124}H_{128}N_8O_8P_8F_{48}$ (3018.14); C: 49.35, H: 4.27, N: 3.71; found: C: 48.89, H: 4.34, N: 3.68%.

CAV4G1: Yield 90%. ^{1}H-NMR (CD_3CN): 0.89 (t, 12H), 1.29–1.47 (m, 24H), 2.33–2.49 (m, 8H), 4.65–4.82 (m, 8H), 5.11 (s, 16H), 5.67 (s, 8H), 5.73 (s, 8H), 6.35 (d, 4H), 6.73–6.76 (m, 12H), 7.32–7.47 (m, 44H), 7.62 (d, 4H), 8.3–8.4 (m, 16H), 8.94–9.00 (m, 16H) ppm. ^{13}C-NMR (CD_3CN): 14.4, 23.2, 28.2, 30.6, 32.8, 38.5, 56, 65.5, 70.9, 100.6, 104.0, 109.5, 121.5, 122.9, 125.5, 127.9, 128.4, 128.6, 129, 129.5, 135.5, 137.6, 139.8, 146.2, 147.0, 151.1, 154.5, 161.5 ppm. MS (ES): *m/z* [int.%] = 1143[38] $(M - 3PF_6^-)^{3+}$, 821[100] $(M - 4PF_6^-)^{4+}$, 628[61] $(M - 5PF_6^-)^{5+}$. Anal. Calcd for $C_{194}H_{188}N_8O_{18}P_8F_{48}$ (3867.13); C: 55.91, H: 4.59, N: 2.90; found: C: 55.81, H: 4.12, N: 2.47%.

CAV4G2: Yield 70%. ^{1}H-NMR (CD_3CN): 0.86 (t, 12H), 1.24–1.42 (m, 24H), 2.3–2.49 (m, 8H), 4.69–4.9 (m, 8H), 5.03 (s, 48H), 5.7 (s, 16H), 6.4 (d, 4H), 6.56–6.69 (m, 36H), 7.25–7.42 (m, 80H), 7.66 (s, 4H), 8.19–8.38 (d, 16H), 8.89 (d, 8H), 9.00 (d, 8H) ppm. ^{13}C-NMR (CD_3CN): 14.3, 23.14, 28.23, 30.5, 32.7, 38.5, 65.5, 70.6, 102.3, 104.4, 107.4, 109.5, 120.7, 127.9, 128.1, 128.5, 128.8, 129.0, 129.4, 135.4, 138.0, 139.6, 140.3, 146.3, 146.63, 150.7, 150.8, 154.3, 160.9, 161.3 ppm. MS (ES): *m/z* [int.%] = 1245[12] $(M - 4PF_6^-)^{4+}$, 967[38] $(M - 5PF_6^-)^{5+}$, 782[80] $(M - 6PF_6^-)^{6+}$. Anal. Calcd for $C_{292}H_{272}N_8O_{32}P_8F_{48}$ (5565.12); C: 63.02, H: 4.93, N: 2.01; found: C: 62.91, H: 4.56, N: 2.23%.

CAV4G3: Yield 63%. ^{1}H-NMR (CD_3CN): 0.80 (t, 12H), 1.05–1.35 (m, 24H), 2.22–2.45 (m, 8H), 4.8–5.12 (m, 112H), 5.62 (s, 16H), 6.38 (d, 4H), 6.49–6.69 (m, 84H), 7.21–7.40 (m, 160H), 7.60 (s, 4H), 8.2 (m, 16H), 8.90 (m, 16) ppm. ^{13}C-NMR (CD_3CN): 14.3, 23.1, 28.2, 30.5, 32.7, 38.6, 65.4, 70.3, 70.6, 102.2, 102.3, 104.1, 107.4, 107.9, 109.4, 122.7, 127.7, 127.9, 128.6, 128.8, 129.1, 129.5, 135.4, 137.9, 139.6, 140.15, 140.6, 146.0, 146.2, 146.5, 152.0, 154.3, 160.7, 160.8, 161.3 ppm. Anal. Calcd for $C_{510}H_{460}N_8O_{63}P_8F_{48}{\cdot}5H_2O$ (8959.07); C: 68.37, H: 5.29, N: 1.25; found: C: 68.33, H: 5.30, N: 1.42%.

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