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A new series of dendrimers with 4,4′-bipyridinium cores capable of fast electron transfer reactions

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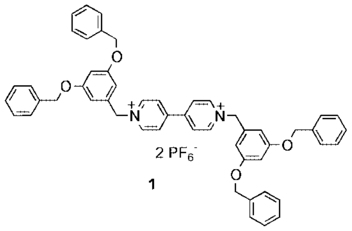
A new series of dendrimers containing a single 4,4′-bipyridinium (viologen) core has been synthesised and characterized that exhibit fast heterogeneous electron transfer reactions from the first to the third generation of dendritic growth.

Dendrimers with redox active cores have been proposed as promising materials for miniaturized information storage circuits.[1] Ideally, injecting/extracting electrons into or from the core of the dendrimer would be a simple way to store and/or read a bit of information in a single molecule. However, the redox active core must be surrounded by a considerable amount of inert material to prevent electronic ‘cross-talk’, that is, self-exchange electron transfer reactions between neighboring dendrimers that would lead to data losses in a two-dimensional storage array. To the best of the authors’ knowledge, the isolation of the redox core by growing dendritic branches has always led to significantly decreased rates of heterogeneous electron transfer.[2] This trend has been clearly demonstrated with dendrimers synthesized around porphyrin,[3] ferrocene[4] and a variety of redox active, metal complex centers.[5] Here, we report the preparation and characterization of a new series of three dendrimers (compounds **1**–**3**, see structures below) containing a single 4,4′-bipyridinium (viologen) core residue covalently attached to two identical Fréchet-type dendrons[6] (first to third generation). The voltammetric behavior of these compounds reveals that the first one-electron reduction of the viologen core is reversible (fast) and rather insensitive to the size of the dendrons throughout the series, an unexpected finding from the available reports on related dendritic systems.[3–5]

The synthetic strategy for the preparation of the dendritic viologens utilized a convergent method. The benzyl bromide dendrons were prepared according to the procedure reported by Fréchet and Hawker.[7] Menschutkin reaction between 4,4′-bipyridine and two equivalents of the corresponding dendron bromides (DMF at 55 °C) afforded, after counterion exchange, the symmetrical dendrimers with a viologen unit at the core.† Their structure was confirmed by ^{1}H and ^{13}C NMR spectroscopies.‡ All compounds yielded satisfactory elemental analyses and exhibited very good correlation with the calculated molecular masses as evidenced by their FAB or MALDI-TOF mass spectra.‡

The influence of the dendritic structure on the electrochemical behavior of the core viologen units was investigated by cyclic voltammetry in acetonitrile solution. Typically, viologen derivatives exhibit two reversible reduction waves that correspond to the formation of a cation radical ($V^{2+} \rightarrow V^+$) and a neutral ($V^+ \rightarrow V$) species.[8] The first reduction is generally very fast, and the second is often coupled to precipitation processes due to the uncharged nature of the fully reduced species, which is insoluble in solvents of intermediate to high polarity.[9] In agreement with the results reported for a different series of bipyridinium-based dendrimers,[10] we found (see Table 1) that the half-wave potentials ($E_{1/2}$) for the first reduction process shift to less negative values as the dendrimer generation increases. Analysis of the peak-to-peak potential splittings (ΔE_p) indicates that this electrochemical process is reversible at moderate scan rates for all dendrimers, even for the third generation compound **3**. However, some distortions associated with precipitation of the one-electron reduced species on the electrode surface are evident in the voltammograms for the



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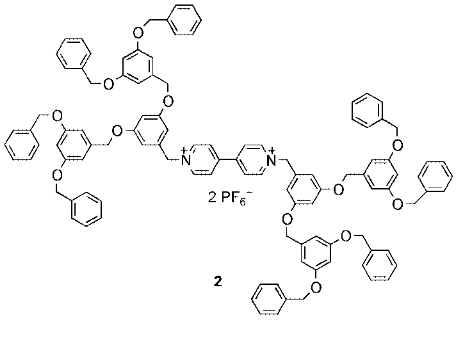

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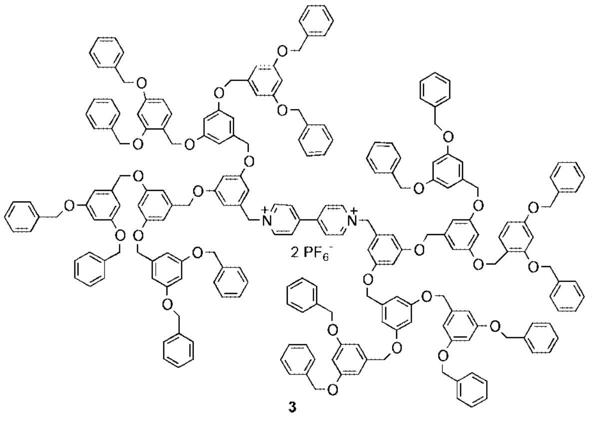

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Table 1 Half-wave potentials ($E_{1/2}$ in V *vs.* Ag/AgCl) and peak-to-peak potential splittings (ΔE_p in mV) for the first and second reduction of dendrimers **1–3** in CH_3CN at 25 °C

	Dendrimer **1**		Dendrimer **2**		Dendrimer **3**	
Electrochemical parameter[a]	$V^{2+} \rightarrow V^+$	$V^+ \rightarrow V$	$V^{2+} \rightarrow V^+$	$V^+ \rightarrow V$	$V^{2+} \rightarrow V^+$	$V^+ \rightarrow V$
$E_{1/2}$	−0.316	−0.754	−0.309	−0.751	−0.274	−0.705
ΔE_p at 0.1 V s^{-1}	65	62	62	65	56	35
ΔE_p at 0.5 V s^{-1}	66	75	65	75	56	42
ΔE_p at 1.0 V s^{-1}	66	81	69	75	60	60
ΔE_p at 2.0 V s^{-1}	74	81	69	71	65	79
ΔE_p at 3.0 V s^{-1}	78	89	78	64	70	85

[a] All electrochemical parameters were measured with a glassy carbon working electrode immersed in 0.25 mM **1–3** + 0.1 M $TBAPF_6$ solutions in acetonitrile. The reported half-wave potential values were measured at 0.1 V s^{-1}.

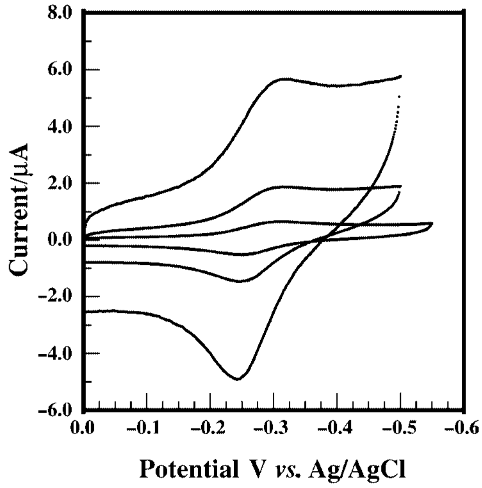

Fig 1 Cyclic voltammetric waves (at scan rates 0.1, 0.5 and 3.0 V s^{-1}) corresponding to the first one-electron reduction of dendrimer **3** (0.25 mM) in 0.1 M $TBAPF_6$–MeCN. Data were recorded with a glassy carbon working, platinum auxiliary and Ag/AgCl reference electrodes.

largest dendrimer (see Fig. 1). At faster scan rates (up to 3 V s^{-1}), our voltammetric data still reveal that the first reduction is quite fast (the largest ΔE_p value measured in these experiments was 78 mV). The distortions mentioned above precluded us from obtaining reliable values for the apparent heterogeneous rates of electron transfer.

The half-wave potentials corresponding to the second electron uptake exhibit the same trend, shifting to less negative values with increasing dendrimer generation. The kinetics of the electron transfer reaction appear to be fast, although very marked precipitation effects were observed. As was the case for the first reduction process, these effects were most visible for the third generation dendrimer **3**. Overall, the trend observed in the $E_{1/2}$ values reveals that the reduction process is thermodynamically more favored as the dendritic structure grows. We attribute this observation to the increasing hydrophobic character of the dendrimer core, which makes it progressively harder to solvate effectively the two positive charges of the viologen core. Therefore, reduction (partial or total elimination of the core charges) becomes more favorable with increasing dendrimer generation.

To our knowledge this is the first example of dendrimers containing a single electroactive core unit that shows relatively fast heterogeneous electron transfer reactions even in the third generation, as measured at scan rates as fast as 3 V s^{-1}. Taken together, these results open some interesting possibilities and suggest that dendrimers with viologen cores are promising in the search for electrochemically active dendrimers with practical applications. We are currently working on methods to immobilize these or similar dendrimers at interfaces in order to obtain electrochemical behavior that will not be affected by precipitation effects.

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Notes and references

† A solution of the dendron bromide (0.06 mmol) and 4,4′-bipyridine (4.7 mg, 0.03 mmol) in DMF (1 ml) was stirred under inert atmosphere at 55 °C for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue dissolved in acetone (1 ml). An aqueous solution of NH_4PF_6 was added. The solvents were removed *in vacuo* and the solid triturated in water. The precipitate was filtered off, washed with water and diethyl ether. The resulting solid was purified by size-exclusion chromatography (Sephadex LH-20), eluting with MeCN to yield the pure dendrimer.

‡ Dendrimer **1**: Yield 90%; ^{1}H NMR (200 MHz, CD_3CN): δ 5.11 (s, 8H), 5.72 (s, 4H), 6.72–6.76 (m, 6H), 7.32–7.49 (m, 20H), 8.36 (d, 4H, ^3J (H, H) 6.8 Hz), 8.95 (d, 4H, ^3J (H, H) 6.8 Hz); ^{13}C NMR (50 MHz, CD_3CN): 65.5, 70.9, 103.9, 109.3, 128.3, 128.6, 128.9, 129.4, 135.5, 137.6, 146.4, 151.1, 161.5; FB MS: *m*/*z* 907 $(M - PF_6^-)^+$, 762 $(M - 2PF_6^-)^+$.

Dendrimer **2**: Yield 86%; ^{1}H NMR (200 MHz, CD_3CN): δ 5.03 (s, 24H), 5.68 (s, 4H), 6.56–6.67 (m, 18H), 7.30–7.38 (m, 40H), 8.18 (d, 4H, ^3J (H, H) 6.8 Hz), 8.82 (d, 4H, ^3J (H, H) 6.7 Hz); ^{13}C NMR (50 MHz, CD_3CN): 65.5, 70.6, 102.3, 104.1, 107.4, 109.4, 128.1, 128.5, 128.8, 129.4, 135.4, 137.9, 140.2, 146.3, 150.7, 160.9, 161.3; FAB MS: *m*/*z* 1756 $(M - PF_6^-)^+$, 1611 $(M - 2PF_6^-)^+$.

Dendrimer **3**: Yield 78%; ^{1}H NMR (200 MHz, CD_3CN): δ 4.84 and 4.95 (each s, 56H), 5.52 (s, 4H), 6.46–6.60 (m, 56H), 7.19–7.33 (m, 80H), 8.04 (d, 4H, ^3J (H, H) 6.7 Hz), 8.72 (d, 4H, ^3J (H, H) 6.8 Hz); ^{13}C NMR (50 MHz, CD_3CN): 65.5, 70.4, 70.7, 102.2, 102.4, 104.1, 107.5, 109.4, 127.9, 128.6, 128.9, 129.4, 135.4, 138.0, 140.2, 140.6, 146.3, 150.5, 160.8, 160.9, 161.4; MALDI-TOF MS: *m*/*z* 3308.4 $(M - 2PF_6^-)^+$.

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