Dendrimers with a 4,4′-bipyridinium core and electron-donor branches. Electrochemical and spectroscopic properties

Letter

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The synthesis, characterization, and electrochemical and spectroscopic properties of a new family of dendrimers comprising a 4,4′-bipyridinium core and 1,3-dimethyleneoxybenzene-type dendrons are described. The electrochemical results show that there is no significant inhibition of electron transfer involving the dendrimer core by the dendrons. The strong fluorescence of the 1,3-dimethyleneoxybenzene units of the branches is completely quenched as a result of charge-transfer interactions with the core.

Dendrimers are currently attracting the interest of a great number of scientists because of their unusual chemical and physical properties and the wide range of potential applications.[1] Particularly interesting classes of dendrimers are those containing photo[2] and/or redox active components.[2a,2d,3] Here, we report the preparation, characterization, and electrochemical and spectroscopic properties of a new family of dendrimers ($MVD1^{2+}$, $MVD2^{2+}$, and $MVD3^{2+}$, Scheme 1) composed of Fréchet-type dendrons[4] appended to a 4,4′-bipyridinium core. Such dendrimers were expected to exhibit interesting properties because (i) 4,4′-dimethylbipyridinium (often known as methylviologen, MV^{2+}) and related compounds (*e.g.* 4,4′-dibenzylbipyridinium, often known as benzylviologen, BZV^{2+}) are well-known electron acceptors[5] extensively used in chemical and electrochemical redox processes,[6] and (ii) the Fréchet-type dendrons D1 (Scheme 1), D2 and D3 contain potentially fluorescent,[4,7] electron-donor[8] dimethyleneoxybenzene units.

The first and second generation $MVD1^{2+}$ and $MVD2^{2+}$ dendrimers were prepared with bromide as counterion by using methods previously applied for nondendritic systems.[9,10] Remarkably, the first two generations precipitated as bromides in acetonitrile, whereas the third generation bromide remained in solution. The isolated crystalline bromides were converted into PF_6^- salts with ammonium hexafluorophosphate in water-free acetonitrile. In the case of the third generation dendrimer ($MVD3^{2+}$), the soluble bromide was isolated from solution by evaporation of the solvent and chromatographed on a reversed phase column with NH_4PF_6 in acetonitrile–dichloromethane. With these new procedures, the dendritic viologen hexafluorophosphates were obtained in analytically pure form.

The electrochemical behavior of $MVD1^{2+}$, $MVD2^{2+}$, $MVD3^{2+}$ was studied in acetonitrile–$[NBu_4]PF_6$ solutions at 298 K. For comparison purposes, the electrochemical behaviour of MV^{2+}, BZV^{2+}, and dendron D1 has also been investigated. The potential values of the observed processes, the diffusion coefficients, and the hydrodynamic radii of the examined compounds are gathered in Table 1. The cyclic voltammetric (CV) curves obtained for dendrimers $MVD1^{2+}$ and $MVD3^{2+}$ are shown in Fig. 1.

The cathodic region shows two one-electron transfer processes, I and II, reversible in all cases, except for $MVD3^{2+}$. For the third generation dendrimer, the first cathodic peak is chemically and electrochemically reversible, while the second cathodic peak and the two anodic counterparts (particularly, the first one) present distorted shapes due to adsorption on the electrode surface. In all cases, the two reduction processes can be straightforwardly assigned to the two successive reductions of the 4,4′-bipyridinium core, on the basis of the comparison with the MV^{2+} and BZV^{2+} model compounds (Table 1). A small positive shift of the cathodic peak potential of the first reduction process is observed in the case of $MVD3^{2+}$, suggesting a destabilization of the dicationic core compared to the first and second generation dendrimers, presumably caused by folding of the two D3 dendrons around the 4,4′-bipyridinium unit.† The electron transfer to the electrode surface is fast for all the dendrimers (in the case of $MVD3^{2+}$, the first cathodic peak shows Nernstian behavior at scan rates up to 10 V s^{-1}), indicating that the site isolation effect on the dendrimer core by the dendrons is not too strong. This result is quite interesting, since the isolation of the redox core by growing dendritic branches usually causes a substantial decrease in the rate of heterogeneous electron transfer.‡[2d,4b–c,11]

The anodic region presents two chemically irreversible oxidation processes (A and B in Table 1; only peak A is shown in Fig. 1). These processes are assigned to the two one-electron oxidations of each 1,3-dimethyleneoxybenzene unit, as shown by the model compound D1. The less positive potential of the E_{pa} value observed for the first oxidation peak of D1 is likely due to the presence of the OH group which, in the dendrimers, is replaced by the electron acceptor 4,4′-bipyridinium unit. The height of the anodic peak of dendrimer $MVD1^{2+}$ is consistent with a two-electron transfer, thus indicating negligible interaction between the two 1,3-dimethyleneoxybenzene units appended at the 4,4′-positions of the bipyridinium core. As the dendrimer generation increases, the width of the anodic peak increases. This behaviour could be due to interactions between 1,3-dimethyleneoxybenzene units attached to the same dendron. The area corresponding to the first oxidation peak of $MVD3^{2+}$ is about 7 times that for $MVD1^{2+}$, as expected on the basis of the number of 1,3-dimethyleneoxybenzene units.

We have determined the diffusion coefficients of all the examined compounds by chronoamperometric experiments

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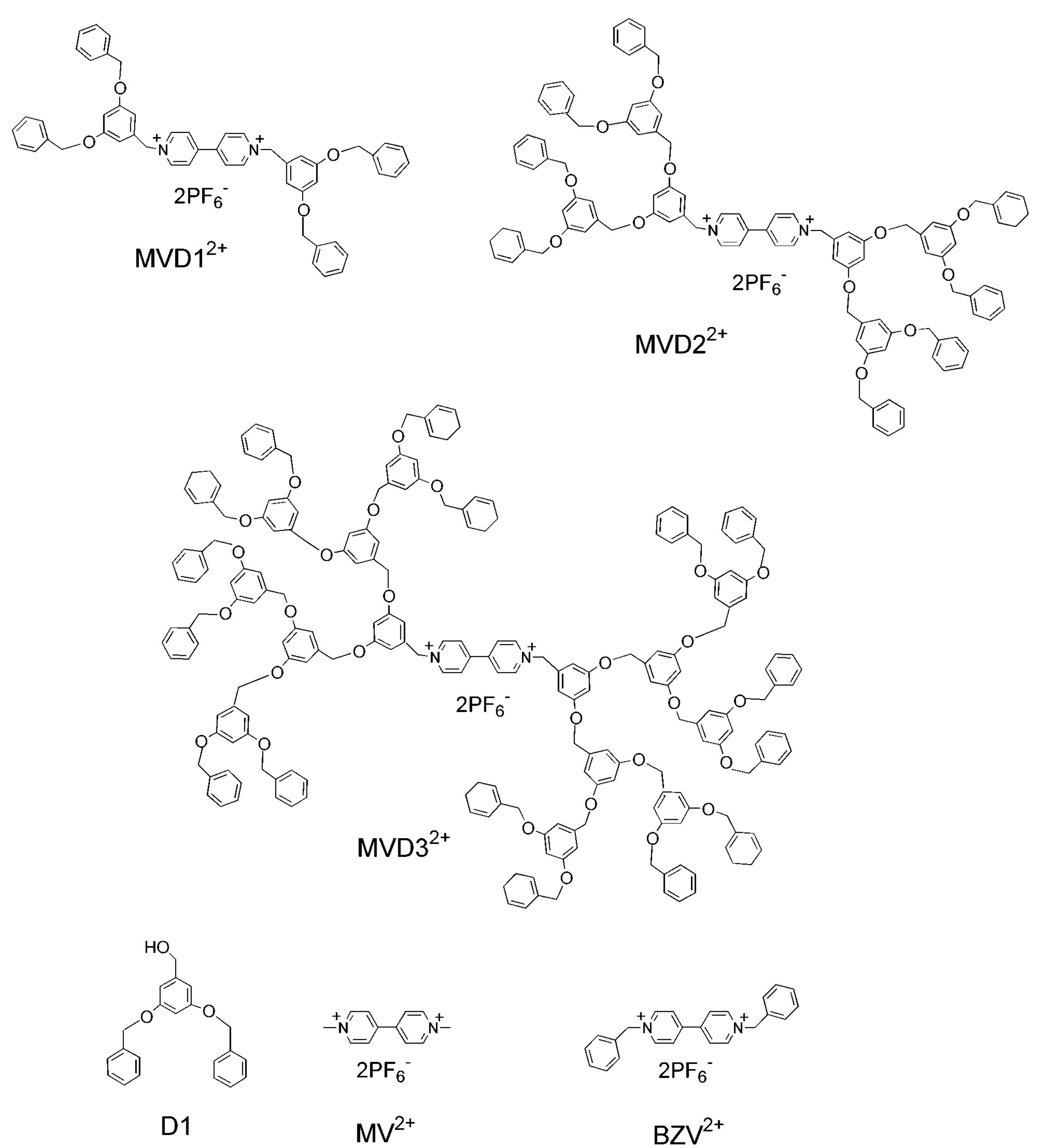

Scheme 1

Table 1 Half-wave potentials ($E_{1/2}$/V *vs.* SCE), diffusion coefficients and hydrodynamic radii in acetonitrile–[NBu$_4$]PF$_6$ solutions

	B	A	I	II	$D/10^{-5}$ cm^2 s^{-1}	$R_H{}^a$/nm
MV^{2+}			−0.44	−0.84	2.0	
BZV^{2+}			−0.35	−0.78	1.5	
D1	+2.31[b]	+1.48[b]				
MVD1^{2+}	+2.26[b]	+1.76[b]	−0.35	−0.77	0.72	0.82
MVD2^{2+}	+2.44[b]	+1.78[b]	−0.34	−0.79	0.50	1.18
MVD3^{2+}	+2.27[b]	+1.76[b]	−0.29[c]	−0.72[c]	0.30	1.97

[a] Hydrodynamic radii calculated by using the viscosity of acetonitrile at 298 K, $\eta = 3.69 \times 10^{-4}$ Pa s. [b] E_{pa} value at 0.1 V s^{-1}, chemically irreversible process. [c] Voltammetric peaks distorted by adsorption on the electrode surface.

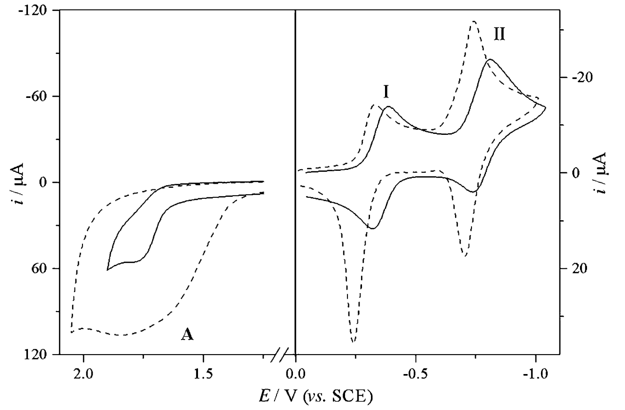

Fig. 1 Cyclic voltammetric curves for $MVD1^{2+}$ (——) and $MVD3^{2+}$ (– – –) in acetonitrile–$[NBu_4]PF_6$ solution. Scan rate $v = 0.2$ V s^{-1}.

with either a standard glassy carbon electrode (Cottrell equation[12]) or a Pt ($r = 5$ μm) ultramicroelectrode[13] as the working electrode. The diffusion coefficients decrease with increasing dendrimer generation, according to the equation $D \propto M^{-a}$, where D is the diffusion coefficient, M is the molecular mass of the compound, and $a = 0.7$ for this dendrimer family. This equation is commonly used for macromolecules; in the approximation of a rigid homogeneous sphere, a is close to 0.3.[14] The experimental value observed indicates a fairly strong deviation from the spherical shape in the case of these dendrimers. Their hydrodynamic radii (R_H) (Table 1) have been calculated by the Stokes–Einstein equation $R_H = kT/(6\pi\eta D)$, where k is the Boltzman constant, T the temperature, and η the viscosity of the solution.

Dendrimers $MVD1^{2+}$, $MVD2^{2+}$ and $MVD3^{2+}$ contain three types of chromophoric units, namely 4,4′-bipyridinium, 1,3-dimethyleneoxybenzene and benzene. The ratios of these three types of units are 1 : 2 : 4 for $MVD1^{2+}$, 1 : 6 : 8 for $MVD2^{2+}$ and 1 : 14 : 16 for $MVD3^{2+}$. The absorption spectrum of $MVD1^{2+}$ in acetonitrile–dichloromethane (1 : 1) solution at 298 K is shown in Fig. 2, where the spectra of its component units (namely 4,4′-dimethylbipyridinium, MV^{2+}, and two equivalents of the first generation dendron D1) are also displayed for comparison purposes. The spectrum is dominated by the strong absorption of 4,4′-bipyridinium (MV^{2+}: $\lambda_{max} = 259$ nm , $\varepsilon = 20\,700$ M^{-1} cm^{-1}; BZV^{2+}: $\lambda_{max} = 259$ nm, $\varepsilon = 22\,700$ M^{-1} cm^{-1}), with some contribution from the 1,3-dimethyleneoxybenzene units around 280 nm. The absorbance of the benzene units ($\lambda_{max} \approx 255$ nm, $\varepsilon \approx 250$ M^{-1} cm^{-1})[15] is negligible above 270 nm. As the dendrimer generation increases, the intensity of the absorption spectrum in the UV region is raised because of the increasing number of 1,3-dimethyleneoxybenzene units.

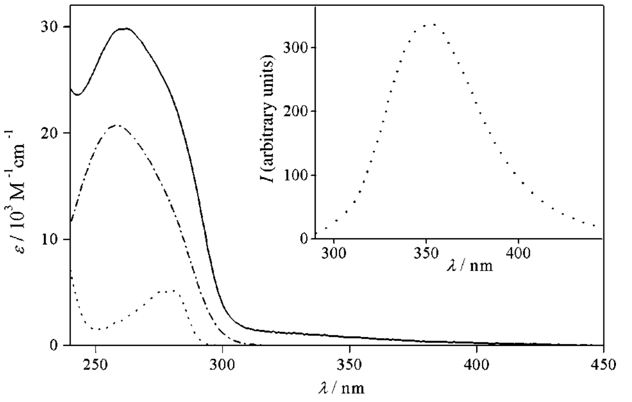

Fig. 2 Absorption spectra of $MVD1^{2+}$ (——), MV^{2+} (·–·–) and D1 (2 equiv., ···) in acetonitrile–dichloromethane (1 : 1) solution at 298 K. Inset shows the fluorescence band of D1 on excitation at 280 nm. $MVD1^{2+}$ does not show any appreciable emission.

As shown in Fig. 3(a), a linear correlation of the molar absorption coefficient at 280 nm, where only 4,4′-bipyridinium and 1,3-dimethyleneoxybenzene absorb, with the number n of 1,3-dimethyleneoxybenzene units is not fully satisfactory, even if it extrapolates to the ε value of the 4,4′-bipyridinium core for $n = 0$. This result suggests that there are interactions between the chromophoric units in the dendrimers, as confirmed by the fact that the dendrimers exhibit a broad and weak absorption tail ($\varepsilon \approx 1350$ M^{-1} cm^{-1} at 320 nm for $MVD1^{2+}$, Fig. 2) which is not present in the spectrum of a mixture of their components. Such an absorption tail is assigned to charge-transfer (CT) transitions from 1,3-dimethyleneoxybenzene electron-donor units to the 4,4′-bipyridinium electron-acceptor core.[16] As shown in Fig. 3(b), the molar absorption coefficient of the CT band is almost the same for the first and second generation dendrimers, and increases for $MVD3^{2+}$. This result suggests that in the third generation dendrimer, part of the donor–acceptor interaction takes place through space, *i.e.* on folding of the dendrons around the core. This picture is consistent with the electrochemical results.

Dimethyleneoxybenzenes are known to exhibit fluorescence.[4,7] Accordingly, in acetonitrile–dichloromethane (1 : 1) solution at 298 K, the Fréchet-type dendrons show a strong emission band (see, for example, Fig. 2, inset) with $\lambda_{max} = 350$ nm and $\tau < 1$ ns. Such a band is no longer present in the $MVD1^{2+}$, $MVD2^{2+}$ and $MVD3^{2+}$ dendrimers, both in acetonitrile–dichloromethane (1 : 1) solution at 298 K and in a rigid butyronitrile–acetonitrile–dichloromethane (2 : 1 : 1) matrix at 77 K. This result shows that the fluorescent excited state of the 1,3-dimethyleneoxybenzene units ($E_{00} \approx 4.1$ eV) is quenched by the 4,4′-bipyridinium core *via* a fast electron-transfer process, as expected from the negative free energy change ($\Delta G \approx -2$ eV).§

In conclusion, the $MVD1^{2+}$, $MVD2^{2+}$ and $MVD3^{2+}$ dendrimers (Scheme 1) exhibit interesting properties. (i) The 4,4′-bipyridinium unit undergoes two distinct and fast one-electron reduction processes at easily accessible negative potentials, regardless of dendrimer generation, indicating that the site isolation effect on the dendrimer core by the dendrons is not too strong. (ii) The 4,4′-bipyridinium unit is reduced at less negative potential in the third generation dendrimer, presumably because of the folding of the two D3 dendrons around the core. (iii) The dimethyleneoxybenzene units (14 in the third generation dendrimer) of the dendrons undergo multi-electron oxidation processes. (iv) The presence of an electron-acceptor core and electron-donor branches causes the appearance of CT absorption bands, with at least part of the CT interaction taking place through space in the third generation dendrimer. (v) The strong fluorescence band of the 1,3-dimethyleneoxybenzene units of the branches is completely

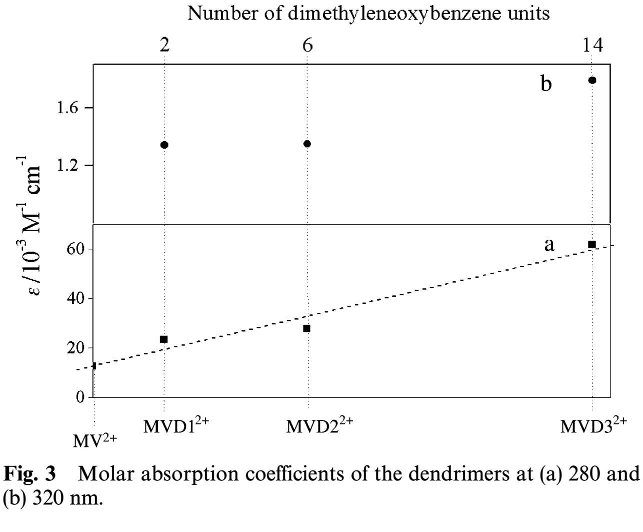

Fig. 3 Molar absorption coefficients of the dendrimers at (a) 280 and (b) 320 nm.

quenched by the presence of the 4,4′-bipyridinium core *via* an excited state electron-transfer process; this means that such dendrimers play the role of light harvesting antennae not for energy,[2] but for electron transfer, a process that could be useful in photochemical energy conversion schemes as well as for information processing.

Experimental

Syntheses

MVD1(PF$_6$)$_2$. 0.122 g (0.78 mmol) of 4,4′-bipyridine in acetonitrile was slowly added dropwise to a solution of 0.600 g (1.57 mmol) D1Br in 10 mL acetonitrile . The resulting yellow solid was filtered off and, after dissolving the product in a mixture of water and acetone (1 : 1), a solution of NH_4PF_6 (50% in water) was added. The crude product was recrystallized from acetone–diisopropyl ether to provide 710 mg of a light yellow solid (yield: 86%). Mp > 320 °C (decomp); R_f (SiO_2; methanol–ammonium chloride–water–nitromethane 7 : 1 : 1 : 1) 0.64; ^{1}H-NMR (400 MHz, Acetone-d$_6$, 25 °C): δ 5.13 (s, 8H, Ar–C*H*$_2$O), 6.02 (s, 4H, Ar–C*H*$_2$N$^+$), 6.82 (t, 2H, $^3J_{HH} = 2.2$, Ar-H), 6.92 (d, 4H, $^3J_{HH} = 2.2$, Ar-H), 7.31–7.48 (m, 20H, Ar-H), 8.80 (d, 4H, $^3J_{HH} = 6.9$, Ar-H), 9.49 (d, 4H, $^3J_{HH} = 6.9$ Hz, Ar-H); ^{13}C-NMR (100.6 MHz, Acetone-d$_6$, 25 °C): δ 65.4 (CH_2N^+), 70.9 (CH_2O), 103.7, 109.4, 128.5, 128.8, 129.0, 129.5, 136.8, 137.9, 147.0, 151.1, 161.7 (Ar-C); FAB-MS: *m/z* 907.4 [$M^{2+} + PF_6^-$].

MVD2(PF$_6$)$_2$. A mixture of 0.487 g (0.45 mmol) D2Br and 0.031 g (0.20 mmol) 4,4′-bipyridine in 15 mL acetonitrile was refluxed under argon for 2 days. The resulting solid was filtered off, washed with warm n-hexane, dissolved in 170 mL hot acetonitrile and 2 g (12.3 mmol) NH_4PF_6 added. The mixture was refluxed for 30 min, filtered and the solvent evaporated. The residue was dissolved in 300 mL $CHCl_3$, washed with water, dried over Na_2SO_4, filtered and the solvent evaporated. The crude product was recrystallized from acetonitrile–diisopropyl ether to provide 213 mg of a dark yellow solid (yield: 37%). Mp 211–213 °C; R_f [RP 18; acetonitrile (containing 0.1 M NH_4PF_6)] 0.67; ^{1}H-NMR (400 MHz, Acetone-d$_6$, 25 °C): δ 5.08 (s, 24H, Ar–C*H*$_2$O), 6.02 (s, 4H, Ar–C*H*$_2$N$^+$), 6.64 (t, 4H, $^3J_{HH} = 2.2$, Ar-H), 6.71 (d, 8H, $^3J_{HH} = 2.2$, Ar-H), 6.80 (t, 2H, $^3J_{HH} = 2.2$, Ar-H), 6.91 (d, 4H, $^3J_{HH} = 2.2$, Ar-H), 7.28–7.47 (m, 40H, Ar-H), 8.67 (d, 4H, $^3J_{HH} = 6.9$, Ar-H), 9.40 (d, 4H, $^3J_{HH} = 6.9$ Hz, Ar-H); ^{13}C-NMR (100.6 MHz, Acetone-d$_6$, 25 °C): δ 65.7 (CH_2N^+), 70.5, 70.6 (CH_2O), 102.1, 104.0, 107.4, 109.4, 128.3, 128.5, 128.8, 129.4, 136.0, 138.2, 140.3, 146.8, 151.2, 161.1, 161.6 (Ar-C); FAB-MS: *m/z* 1756.6 [$M^{2+} + PF_6^-$].

MVD3(PF$_6$)$_2$. A mixture of 0.331 g (0.20 mmol) D3Br and 0.016 g (0.1 mmol) 4,4′-bipyridine in 5 mL *N*,*N*′-dimethylformamide was heated to 60 °C under argon for 2 days. The solvent was evaporated and the residue dissolved in dichloromethane–acetonitrile (3 : 1). The crude product was purified by MPLC [acetonitrile (containing 0.1 M NH_4PF_6)–dichloromethane 7 : 1; solid phase: RP 18 (Merck; 15–25 μm)], dissolved in chloroform, washed with water, dried over Na_2SO_4, filtered and the solvent evaporated to yield 140 mg of a light-red highly viscous oil (yield: 39%). R_f [RP 18; acetonitrile (containing 0.1 M NH_4PF_6)–dichloromethane 7 : 1] 0.41; ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.66 (s, 24H, Ar–C*H*$_2$O), 4.76 (s, 28H, Ar–C*H*$_2$O), 6.28 (s, 4H, Ar–C*H*$_2$N$^+$), 6.33–6.48 (s, 42H, Ar-H), 7.07–7.20 (m, 84H, Ar-H), 7.61 (d, 4H, $^3J_{HH} = 6.5$, Ar-H), 8.00 (d, 4H, $^3J_{HH} = 6.5$ Hz, Ar-H); ^{13}C-NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 64.3 (CH_2N^+), 69.7, 69.9, 70.1 (CH_2O), 101.5, 101.6, 106.4, 106.5, 108.3, 126.7, 127.6, 128.0, 128.6, 128.6, 132.5, 136.7, 138.9, 139.3, 144.3, 149.5, 159.9, 160.1, 160.6 (Ar-C); MALDI-Tof-MS: *m/z* 3309.5 [$M^{2+} + PF_6^-$].

Photophysical and electrochemical experiments

The equipment used for photophysical and electrochemical experiments has been described elsewhere.[17] The diffusion coefficients were determined by chronoamperometric experiments using either a glassy carbon electrode (0.08 cm^2, Amel)[12] or a Pt ultramicroelectrode ($r = 5$ μm)[13] as the working electrode.

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Notes and references

† The peak potential of this process may be slightly affected by the adsorption of MVD3$^+$ on the electrode surface.

‡ Our electrochemical results in the cathodic region are in substantial agreement with those reported by Peinador *et al.* in a communication (R. Toba, J. M. Quintela, C. Peinador, E. Román and A. E. Kaifer, *Chem. Commun.*, 2001, 857) that was published just after the submission of this paper.

§ The free energy change for an oxidative quenching process of the type

$$^*A + B \rightarrow A^+ + B^-$$

can be calculated from the equation

$$\Delta G \sim F[E°(A^+/A) - E°(B/B^-)] - E_{00}(^*A) - w$$

where F is the Faraday constant, $E°(A^+/A)$ and $E°(B/B^-)$ are the standard potentials of the ground state couples, E_{00} is the zero–zero spectroscopic energy of *A and w is the coulombic work term, which can be neglected in polar solvents.

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