The Self Assembly of Controllable [2]Catenanes

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The dynamic and electrochemical properties of two new [2]catenanes, in which bisparaphenylene-34-crown-10 is encircled by a cyclophane incorporating either (i) one bipyridinium and one bis(pyridinium)ethylene unit or (ii) two bis(pyridinium)ethylene units, are investigated in solution.

Increasingly, self assembly[1] can be regarded as one of the most important synthetic tools for the construction of molecular devices[2] based on interlocking molecules such as catenanes and rotaxanes.[3] At present, one of the most fundamental challenges[2] offered by these intriguing molecules is to learn how to effect structural changes between their component parts that are induced either by chemical,[4] electrochemical,[5] or photochemical[6] stimuli. In this regard, viologens **1** are well documented[7] to respond to these stimuli because of their characteristic redox properties and it was partly for this reason that they were identified by us as potential building blocks for the self assembly of controllable catenanes and rotaxanes.[8] Since some vinylogous viologens,[9] such as **2**, have already been synthesised in order to modify the properties and functions of **1**, we were attracted by the idea of incorporating them into a set of new self assembled interlocking molecular structures. Recently, we have reported[10] the template-directed synthesis of a [2]catenane **4**·4PF_6, which incorporates viologen units in one (**3**·4PF_6) of its macrocyclic components. Here, we describe: (*i*) the template-directed synthesis† of two new cyclophanes, **7**·4PF_6 and **11**·4PF_6, containing one and two π-extended viologen units, respectively, (*ii*) the self assembly† of the [2]catenanes, **8**·4PF_6 and **12**·4PF_6, which incorporate bisparaphenylene-34-crown-10 (BPP34C10) and their component cyclophanes, **7**·4PF_6 and **11**·4PF_6, respectively, (*iii*) the characterisation (Table 1) of these tetracationic salts by FAB-MS, (*iv*) the dynamic ^{1}H NMR spectroscopic behaviour of both catenanes in solution, and (*v*) the electrochemical behaviour‡ of the cyclophanes and catenanes.

The cyclophane **7**·4PF_6 was prepared (Scheme 1) in 53% yield from reaction of **5**·2PF_6 with 1,2-bis(4-pyridyl)ethylene **6** in the presence of 1,5-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene (BHEEN) as a template, which proved to be much more efficient than the analogous hydroquinol-containing compound,§ 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene (BHEEB), employed in the template-directed synthesis of cyclobis(paraquat-*p*-phenylene). The preparation (Scheme 2) of **11**·4PF_6 from **9**·2PF_6—prepared from reaction of **6** with **10**—and 1,4-bis(bromomethyl)benzene **10** was successful only in the presence of BHEEN, with BHEEB having no template effect.† The larger π-surface area of BHEEN is presumably necessary in order to complement the relatively weak π–π stacking interactions between the π-electron deficient bis(pyridinium)ethylene units and π-electron rich aromatic systems.¶ The [2]catenanes **8**·4PF_6 and **12**·4PF_6 were self assembled using a template-directing methodology. The instantaneous formation of a complex between BPP34C10 and **5**·2PF_6 was followed by stepwise alkylation of **6** to form (Scheme 1) the [2]catenane **8**·4PF_6 in 23% yield. However, reaction of **10** with **9**·2PF_6 presumably results in a tricationic intermediate,[10,11] which, following complexation with BPP34C10, generates (Scheme 2) the [2]catenane **12**·4PF_6 in 15% yield. Positive-ion FAB-MS of these compounds revealed peaks characteristic of successive loss of PF_6^- counterions from the molecular ion. Table 1 records the key *m/z* values, along with the intensities of the strongest signals.

As in the case of the original[10] [2]catenane **4**·4PF_6, both the new [2]catenanes **8**·4PF_6 and **12**·4PF_6exhibit temperature-dependent behaviour in their ^{1}H NMR spectra. One process (I) involves the degenerate equilibration of the π-electron rich hydroquinol rings between 'inside' and 'alongside' environments with respect to the interlocked cyclophane. In the case of **4**·4PF_6, the circumrotation of BPP34C10 through the cyclophane is slow on the ^{1}H NMR timescale as indicated[10] by the presence of two well-resolved signals at δ 3.45 and 6.16 in the ^{1}H NMR spectrum recorded in CD_3CN at room temperature. In contrast, the ^{1}H NMR spectrum of **8**·4PF_6, recorded under the same conditions, shows that the protons corresponding to the 'inside' and 'alongside' hydroquinol rings in BPP34C10 resonate as broad signals at δ 5.15 and 5.70, respectively, reflecting a faster equilibration for process I as a result of the larger cyclophane and reduced π–π stacking interaction with its π-extended viologen unit. The coalescence of these signals above room temperature allows a $\Delta_c G^{\ddagger}$ value to be obtained (Table 2) for process I in **8**·4PF_6. Another process (II) involves the pirouetting of BPP34C10 macrocycle around the cyclophane. In the case of **4**·4PF_6, this equilibrium

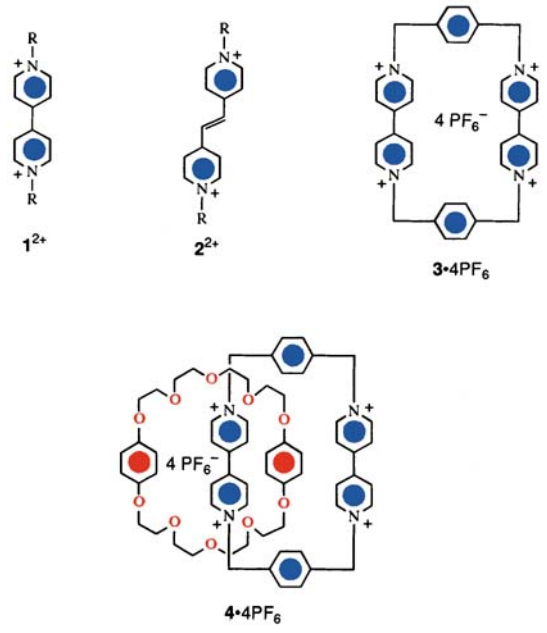


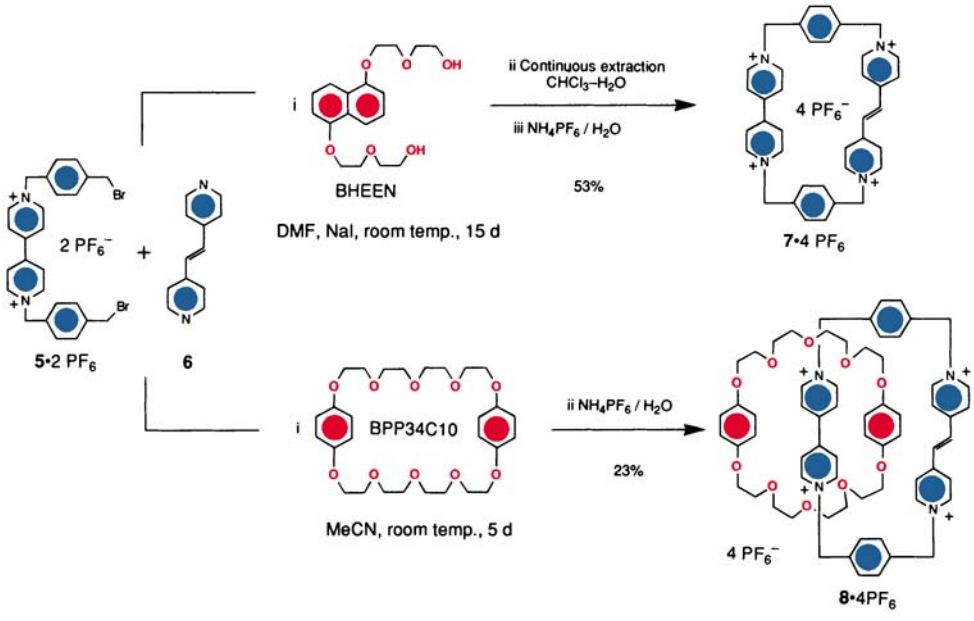
Table 1 FABMS Data[a] for the cyclophanes **7**·4PF_6, **11**·4PF_6 and the [2]catenanes **8**·4PF_6 and **12**·4PF_6

Compound	M^+ (%)	$(M - PF_6)^+$ (%)	$(M - 2PF_6)^+$ (%)	$(M - 3PF_6)^+$ (%)
7·4PF_6	1126 (6)	980 (36)	835 (38)	691 (12)
8·4PF_6	1662 (2)	1517 (80)	1372 (100)	1227 (20)
11·4PF_6	—	1007 (22)	862 (100)	717 (78)
12·4PF_6	1688 (4)	1543 (100)	1398 (60)	1253 (7)

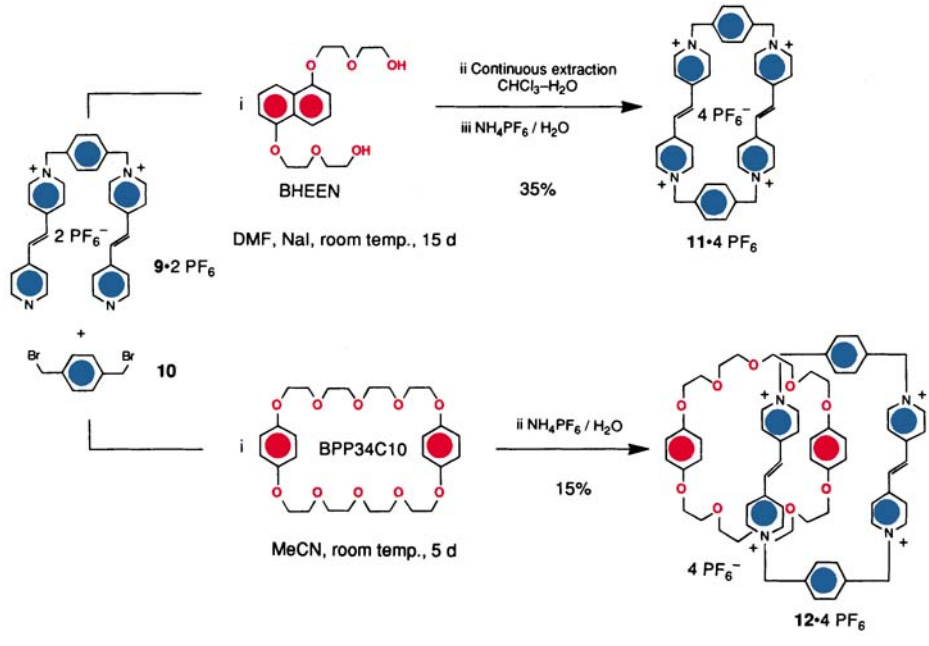
[a] FAB-MS were obtained with a Kratos MS80RF mass spectrometer coupled to a DS90 system. The atom gun (Ion Tech Limited) was operated at 7 keV with a tube current of 2 mA. The primary beam of atoms was produced from research grade krypton. Samples were dissolved in a small amount of 3-nitrobenzyl alcohol that had been coated onto a stainless steel probe and spectra were recorded in the positive ion mode at a scan speed of 30 s per decade.

is a degenerate one, a fact which is reflected in the two sets of signals observed for the bipyridinium protons (both αCH and βCH) and the *N*-methylene protons in the cyclophane when the ^{1}H NMR spectrum is recorded in CD_3COCD_3 at low temperatures, *i.e.* below −30 °C. Not unexpectedly, in **8**·4PF$_6$ with its cyclophane incorporating one *trans*-bis(pyridinium)ethylene unit and in which, therefore, two translational isomers are possible, the different binding abilities¶ of the viologen and π-extended viologen units for the π-electron rich hydroquinol rings manifest themselves in a much higher preference for the BPP34C10 macrocycle encircling the viologen unit at low temperatures in CD_3COCD_3. Thus, at −60 °C, integration of the signals at δ 6.61 and 7.15 for the olefinic protons in the ^{1}H NMR spectrum gives a ratio of 8 : 92 for **8a**·4PF$_6$: **8b**·4PF$_6$ (Scheme 3). In the case of **12**·4PF$_6$, both processes (I and II) are again degenerate ones and both are fast on the ^{1}H NMR timescale at room temperature. The broad signal for the hydroquinol protons centred on δ 5.63 in the ^{1}H NMR spectrum recorded in CD_3COCD_3 separates out into two equal intensity signals resonating at δ 4.81 and 6.32 at −28 °C. This dynamic temperature dependent behaviour associated with process I was accompanied by changes in the ^{1}H NMR spectrum for signals associated with *N*-methylene, αCH bipyridinium, and olefinic protons in the cyclophane component of the [2]catenane **12**·4PF$_6$. Values for $\Delta_c G^{\ddagger}$ were obtained (Table 2) for both these processes.

The cyclophanes **7**·4PF$_6$ and **11**·4PF$_6$ and catenanes **8**·4PF$_6$ and **12**·4PF$_6$ both exhibit interesting electrochemical properties. The results are shown schematically in Fig. 1. Data previously obtained[8] for **3**·4PF$_6$ and **4**·4PF$_6$ are also included



Scheme 1 The template-directed synthesis of the cyclophane **7**·4PF$_6$ and of the [2]catenane **8**·4PF$_6$

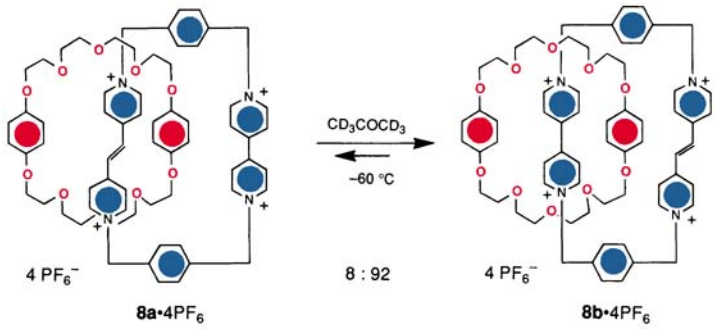


Scheme 2 The template-directed synthesis of the cyclophane **11**·4PF$_6$ and of the [2]catenane **12**·4PF$_6$

Table 2 Kinetic and thermodynamic parameters[a,b] obtained from the temperature-dependent ^{1}H NMR spectra recorded on the [2]catenanes **4**·4PF$_6$ (Ref. 10), **8**·4PF$_6$, and **12**·4PF$_6$

[2]Catenane	Probe protons undergoing site exchange	Process (solvent)	$\Delta\nu$/Hz	k_c/s^{-1}	T_c/°C	$\Delta_cG^{\ddagger}$/kcal mol^{-1}
4·4PF$_6$	OC_6H_4O	I (CD_3CN)	678	1505	81	15.6
	CH_2N^+	II (CD_3COCD_3)	46	102	−25	12.1[c]
8·4PF$_6$	OC_6H_4O	I (CD_3CN)	832	1848	27	13.1
12·4PF$_6$	OC_6H_4O	I (CD_3COCD_3)	612	1359	12	12.6
	CH_2N^+	II (CD_3COCD_3)	44	98	−47	11.1[c]

[a] The coalescence method was employed to obtain kinetic and thermodynamic data: values for the rate constant k_c at the coalescence temperature (T_c) were obtained[13] from the approximate expression, $k_c = \pi(\Delta\nu)/(2)^{1/2}$, where $\Delta\nu$ is the limiting chemical shift difference (in Hz) between the signals observed below T_c for the protons undergoing site exchange. The Eyring equation was used to calculate $\Delta_cG^{\ddagger}$ values at T_c. [b] ^{1}H NMR Spectra were recorded on a Bruker AMX (400 MHz) spectrometer. [c] Similar $\Delta_cG^{\ddagger}$ values were obtained from data arising from other probe protons such as the αCH and βCH bipyridinium protons, and in the case of **12**·4PF$_6$, from the olefinic protons.



Scheme 3 The equilibration of translational isomers for the [2]catenane **8**·4PF$_6$ at −60 °C in CD_3COCD_3

for comparison purposes. Good correlations exist amongst the three cyclophanes (dashed lines), the three catenanes (dotted lines), and between each cyclophane and its catenane (solid lines). In both **3**·4PF$_6$ and **11**·4PF$_6$, the two equivalent units respond independently of each other as shown by the fact that they are reduced at the same potential. Since each bipyridinium and bis(pyridinium)ethylene unit can undergo two separate reduction processes, two two-electron waves are observed for each compound. The first reduction wave for **3**·4PF$_6$ occurs at more positive potentials than the first reduction wave for **11**·4PF$_6$. However, the opposite is the case for the second reduction wave. In the asymmetrical cyclophane **7**·4PF$_6$, four reduction waves are observed. Spectrochemical experiments have shown that the first one corresponds to reduction of the bipyridinium unit. Assignment of the second and third waves to the first and second reduction, respectively, of the bis(pyridinium) ethylene unit, and of the fourth wave to the second reduction of the bipyridinium unit is straightforward (the dashed lines in Fig. 1). In comparing the two symmetrical cyclophanes **3**·4PF$_6$ and **11**·4PF$_6$ with their respective catenanes (solid lines at the top and bottom of Fig. 1), the first two-electron reduction wave moves to more negative potential and divides into two components because the two units are stabilised by charge-transfer interactions, with the 'inside' unit being more stabilised than the 'alongside' one. The wave corresponding to the second reduction of the two units does not undergo a measurable splitting since the charge-transfer interaction no longer plays a role in the reduced species. As a consequence, the 'inside' and 'alongside' positions—as well as any other position—become substantially equivalent. In the asymmetrical catenane **8**·4PF$_6$, the four reduction waves are separated, as indeed they are in the corresponding cyclophane **7**·4PF$_6$. The first wave, which corresponds to the reduction of the bipyridinium unit (as shown by spectroelectrochemical experiments), appears with a potential close to that of the 'inside' unit of **4**·4PF$_6$. This result suggests that, in MeCN solution at room temperature, the equilibrium between the two translational isomers is displaced towards the one in which the BBP34C10 macrocycle

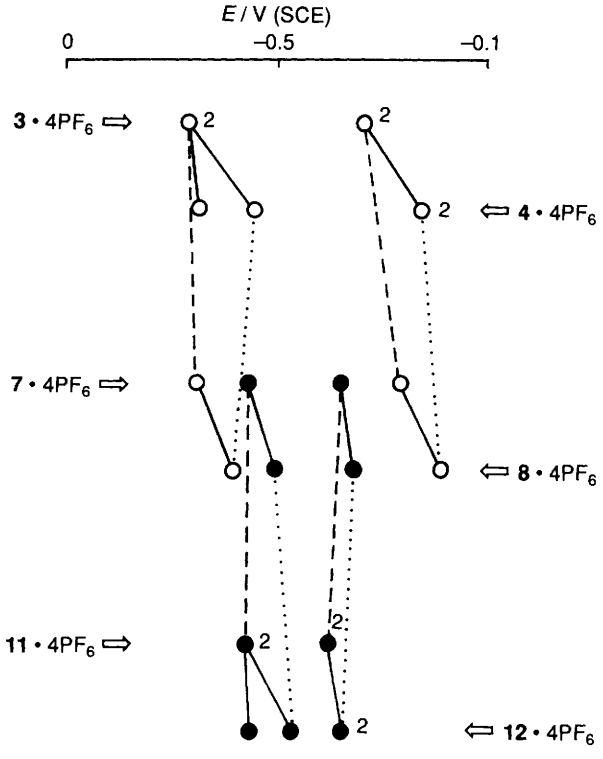


Fig. 1 Correlations between the reduction half-wave potentials of the cyclophanes **3**·4PF$_6$, **7**·4PF$_6$ and **11**·4PF$_6$ (dashed lines), the catenanes **4**·4PF$_6$, **8**·4PF$_6$, and **12**·4PF$_6$ (dotted lines), and each cyclophane with the respective catenane (solid lines). The empty circles and solid dots correspond to reduction of bipyridinium and bis(pyridinium)ethylene units, respectively. Two-electron reduction processes are labelled with the number 2. The first reduction wave of **8**·4PF$_6$ is correlated with the second reduction wave of **4**·4PF$_6$ because, in **8**·4PF$_6$, the bipyridinium unit occupies the 'inside' position preferentially.

encircles the bipyridinium unit (*cf.* Scheme 3). The second reduction wave of **8**·4PF_6, which must involve the bis(pyridinium)ethylene unit, lies close to the second reduction wave of **12**·4PF_6. This result is to be expected since, once the bipyridinium unit has been reduced, the bis(pyridinium)ethylene one is obliged to occupy the 'inside' position in **8**·4PF_6.

The potential for the two [2]catenanes **8**·4PF_6 and **12**·4PF_6 —as well as their component cyclophanes **7**·4PF_6 and **11**·4PF_6 —to undergo *cis–trans* photoisomerisation is now under active investigation. Since the bis(pyridinium)ethylene units are primary recognition sites in all these compounds, they complement analogues where, for example, the spacers between standard bipyridinium units in the cyclophane (component) contain photoisomerisable azo-benzene units.[12]

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Footnotes

† *Experimental and spectroscopic data* for **9**·2PF_6: A solution of **10** (570 mg, 2.16 mmol) in dry MeCN (60 ml) was added over 6 h to a solution of **6** (940 mg, 5.18 mmol) in dry MeCN (20 ml) and the reaction mixture was heated under reflux for 18 h after which the suspension was cooled to room temp. before the yellow precipitate was filtered off and washed with MeCN (2 × 5 ml). The residue was subjected to chromatography [SiO_2: MeOH–2 mol dm^{-3} NH_4Cl–$MeNO_2$ (5 : 2 : 3)]. The fractions containing the product were concentrated to give a residue, which was dissolved in hot water (250 ml). Then, a saturated aqueous NH_4PF_6 solution was added until no further precipitation was observed. The precipitate was filtered off and dried to give **9**·2PF_6 (1.26 g, 77%) as a white solid, mp 209 °C: FAB-MS: *m/z* 613 $(M\text{-}PF_6)^+$. ^1H NMR (CD_3CN): δ 5.68 (s, 4H), 7.52 (s, 4H), 7.56 (d, 2H, *J* 16.3 Hz), 7.57 (d, 4H, *J* 5.0 Hz), 7.75 (d, 2H, *J* 16.3 Hz), 8.10 (d, 4H, *J* 6.5 Hz), 8.64 (d, 4H, *J* 6.5 Hz), 8.68 (d, 4H, *J* 5.0 Hz); for **7**·4PF_6: **6** (22.5 mg, 0.12 mmol) and NaI (5 mg) were added to a solution of **5**·2PF_6 (100 mg, 0.12 mmol) and BHEEN (125 mg, 0.36 mmol) in dry DMF (5 ml). A red precipitate was formed in the reaction mixture. After stirring at room temp. for 15 days, Et_2O (20 ml) was added and the precipitate was filtered off and dried *in vacuo*. Decomplexation was effected by continuous extraction of an aqueous solution (250 ml) with $CHCl_3$ for 5 days. The aqueous solution was concentrated to 5 ml and a saturated solution of NH_4PF_6 was added until no further precipitation was observed. The suspension was filtered off and the solid was recrystallised from $MeNO_2$–EtOAc and then from Me_2CO–H_2O to give **7**·4PF_6 (73 mg, 53%) as a yellow crystalline solid, mp 285 °C (decomp.); ^1H NMR (CD_3CN): δ 5.73 (s, 4H), 5.84 (s, 4H), 7.56 (s, 8H), 7.83 (s, 2H), 8.18 (d, 4H, *J* 7.0 Hz), 8.39 (d, 4H, *J* 6.6 Hz), 8.73 (d, 4H, *J* 7.0 Hz), 8.95 (d, 4H, *J* 6.6 Hz); for **11**·4PF_6: A template-directed reaction and work-up similar to that described above for the synthesis of **7**·4PF_6 was carried out between **10** (35 mg, 0.13 mmol), NaI (5 mg), **9**·2PF_6 (100 mg, 0.13 mmol), and BHEEN (133 mg, 0.39 mmol) in dry DMF (5 ml) to afford **11**·4PF_6 (53 mg, 35%) as a white crystalline solid, mp 263 °C, after recrystallisation from MeCN–H_2O; ^1H NMR (CD_3CN): δ 5.64 (s, 8H), 7.57 (s, 4H), 7.59 (s, 8H), 7.98 (d, 8H, *J* 7.0 Hz), 8.75 (d, 8H, *J* 7.0 Hz); for **8**·4PF_6: **5**·2PF_6 (200 mg, 0.25 mmol) and **6** (50 mg, 0.27 mmol) were added to a solution of BPP34C10 (330 mg, 0.61 mmol) in dry MeCN (20 ml). The reaction mixture, which turned red immediately, was stirred at room temp. during 5 days. The solvent was then evaporated off to afford a red solid which was subjected to chromatography [SiO_2: MeOH–2 mol dm^{-3} NH_4Cl–$MeNO_2$ (7 : 2 : 1)]. The fractions containing the product were concentrated and the residue dissolved in water (2 ml) before a saturated aqueous NH_4PF_6 solution was added until no further precipitation occurred. The suspension was filtered off and the solid recrystallised from MeCN–H_2O to give **8**·4PF_6 (93 mg, 23%) as a red solid, mp >300 °C; ^1H NMR (CD_3CN): δ 3.41–3.47 (m, 8H), 3.62–3.68 (m, 8H), 3.78–3.88 (m, 16H), 5.15 (br s, 4H), 5.64 (s, 4H), 5.70 (br s, 4H), 5.73 (s, 4H), 6.63 (s, 2H), 7.53 (d, 4H, *J* 6.5 Hz), 7.59 (d, 4H, *J* 7.2 Hz), 7.68 (d, 4H, *J* 8.5 Hz), 7.79 (d, 4H, *J* 8.5 Hz), 8.71 (d, 4H, *J* 6.5 Hz), 8.88 (d, 4H, *J* 7.2 Hz); for **12**·4PF_6: A template-directed reaction and work-up similar to that described above for the synthesis of **8**·4PF_6 was carried out between **9**·2PF_6 (113 mg, 0.15 mmol), **10** (43 mg, 0.16 mmol), BPP34C10 (200 mg, 0.37 mmol) in dry MeCN (20 ml) to afford **12**·4PF_6 (38 mg, 15%) as an orange solid, mp >300 °C; ^1H NMR (CD_3CN): δ 3.14–3.22 (m, 8H), 3.49–3.55 (m, 8H), 3.72–3.77 (m, 8H), 3.78–3.83 (m, 8H), 5.50 (br s, 8H), 5.60 (s, 8H), 6.61 (s, 4H), 7.49 (d, 8H, *J* 6.5 Hz), 7.68 (s, 8H), 8.72 (d, 8H, *J* 6.5 Hz).

Satisfactory elemental analyses are available on all new compounds.

‡ Electrochemical measurements were carried out at room temp. with a Princeton Applied Research 273 multipurpose instrument interfaced to a personal computer. A glassy carbon electrode (0.08 cm^2, Amel) was used as the working electrode. The counter electrode was a Pt flag and the reference electrode was an SCE (saturated calomel electrode) separated with a fine glass frit. The concentration of the examined compounds was 5.0×10^{-4} mol dm^{-3}. Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte. The solutions were purged with argon. The scan rate was 100 mV s^{-1}. Complete reversibility characterised the voltammograms.

§ Using 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene (BHEEB), only a 12% yield of **7**·4PF_6 was obtained.

¶ Using a spectrophotometric titration procedure (Ref. 10)—by employing the charge-transfer band as a quantitative spectroscopic probe (λ_{max} 424 nm) at 25 °C and subjecting the data to a Benesi–Hildebrand treatment (H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703)—1 : 1 stoichiometry was established in MeCN solution for the interaction between BPP34C10 and the vinylogous viologen **2** (R = CH_2Ph). The value of 86 ± 3 dm^3 mol^{-1} obtained for K_a corresponds to a ΔG^0 value of −2.6 kcal mol^{-1} (1 cal = 4.184 J). The inclusion nature of the 1 : 1 complex was confirmed by FAB-MS and ^1H NMR spectroscopy. Relative to spectra recorded in CD_3CN for free BPP34C10 and free **2**·2PF_6 (R = CH_2Ph), the olefinic protons experience an upfield shift of 0.32 ppm in the complex. However, the remainder of the signals were considerable less shielded than those observed (Ref. 10) in the corresponding 1 : 1 complex formed between BPP34C10 and Paraquat **1**·2PF_6 (R = Me) where the K_a value in Me_2CO is 730 dm^3 mol^{-1} corresponding to a ΔG^0 value of −3.9 kcal mol^{-1}.

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