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Towards Molecular Scale Mechano–Electronic Devices: Porphyrin Catenanes

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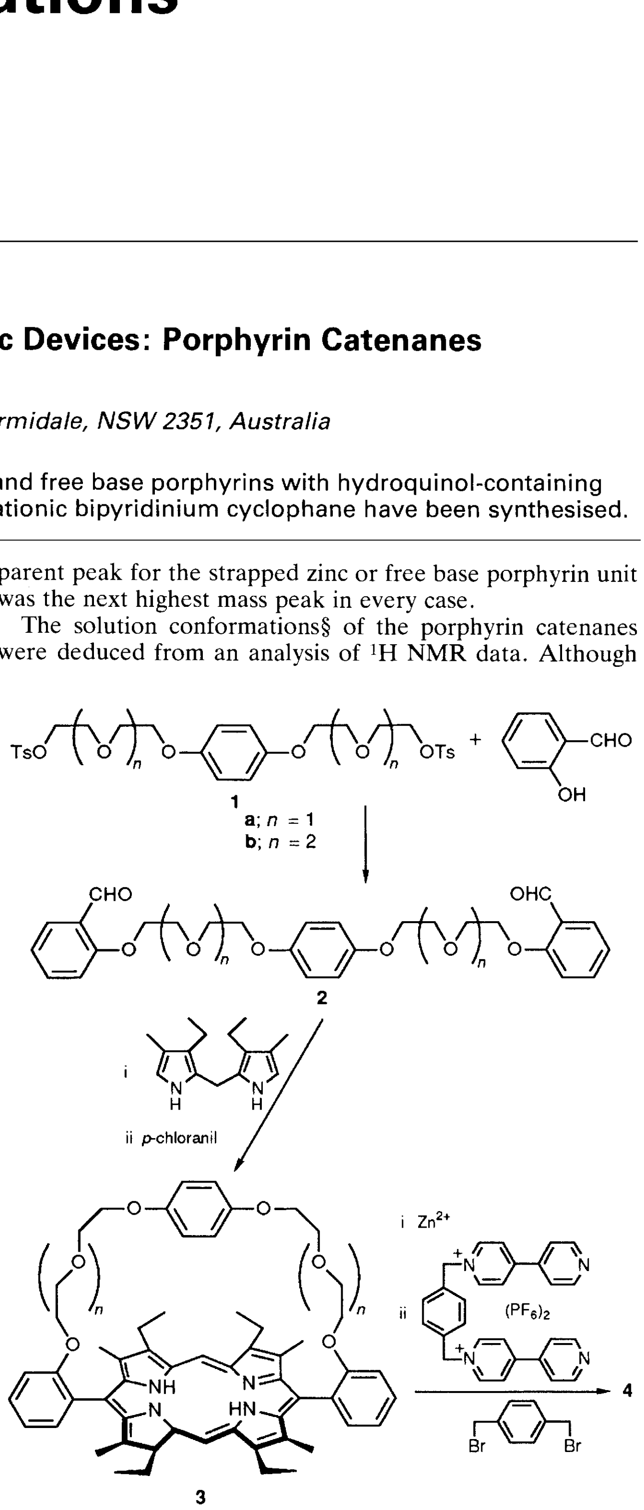
Using self-assembly strategies, catenanes consisting of zinc and free base porphyrins with hydroquinol-containing polyether straps of different lengths interlinked with a tetracationic bipyridinium cyclophane have been synthesised.

Electron donor–acceptor interactions have been exploited by Stoddart and coworkers[1] to achieve efficient template-directed synthesis of a series of mechanically linked molecular assemblies. We now report the successful synthesis and characterisation of porphyrin-containing catenanes utilising these concepts. This represents the first stages in establishing the methodological basis for more elaborate porphyrinic molecular devices which may be designed to function in a predictable and controllable manner.

Thus, 1,4-bis[2-{2-(2-tosyloxyethoxy)ethoxy}ethoxy]benzene[1] **1b** was allowed to react with salicylaldehyde (K_2CO_3, MeCN, 80 °C, 30 h) to give **2b** (quantitative yield). Condensation with 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane[2] (MeCN, CCl_3CO_2H, room temp., 5 h)[3] followed by oxidation of the porphyrinogen [*p*-chloranil, tetrahydrofuran (THF), 12 h][4] gave the strapped porphyrin **3b**, after chromatography (15%). The catenane **4b** was produced by reaction of the zinc derivative of **3b** with 1,1′-[1,4-phenylenebis(methylene)] bis-(4,4′-bipyridinium) bis(hexafluorophosphate) ([BBIPYXY]-$[PF_6]_2$)[1] and 1,4-bis(bromomethyl)benzene in dimethylformamide (room temp., 14 days) containing NaI and NH_4PF_6, followed by extraction, chromatography [SiO_2, MeOH–NH_4Cl (2 mol dm^{-3})–nitromethane 7 : 2 : 1] and anion exchange (28%).† The catenane **4a** was prepared from **1a** in an analogous manner. The metal-free derivatives **5** were obtained by treatment of the zinc derivatives with aqueous hydrochloric acid, neutralisation and subsequent anion exchange.

Analysis of the catenanes **4a**, **4b**, **5a** and **5b** by positive ion FAB-MS (fast atom bombardment mass spectrometry) revealed peaks for the parent ions, as well as peaks for the loss of one, two and three PF_6^- counterions in each case,‡ typical of the behaviour of the non-porphyrinic catenanes.[5,6] The parent peak for the strapped zinc or free base porphyrin unit was the next highest mass peak in every case.

The solution conformations§ of the porphyrin catenanes were deduced from an analysis of ^1H NMR data. Although



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† *Spectroscopic data* for **5b**: FAB-MS: 2101 (M^+), 1956 ($M^+ - PF_6$), 1811 ($M^+ - 2PF_6$), 1666 ($M^+ - 3PF_6$). ^1H NMR (MeCN, 298 K): 9.87 (2 H, s, *meso*), 7.99 (2 H, t, *J* 7 Hz, 2-H), 7.88 (2 H, d, *J* 7 Hz, 4-H), 7.84 (8 H, br s, α-BIPY), 7.68 (2 H, d, *J* 8 Hz, 1-H), 7.52 (2 H, t, *J* 7 Hz, 3-H), 7.39 (8 H, s, C_6H_4), 5.63 (8 H, br s, β-BIPY), 5.34 (8 H, s, CH_2N^+), 4.46 (4H, br s, $PhOCH_2$), 4.28 (4 H, q, *J* 7 Hz, CH_2–Me), 3.84 (4 H, q, *J* 7 Hz, CH_2–Me), 3.64 (4 H, br s, $-OCH_2$), 3.46 (4 H, br s, $-OCH_2$), 3.39 (8 H, br s, $-OCH_2$), 2.93 (4 H, br s, α-OCH_2), 2.67 (12 H, s, Me), 2.51 (4 H, s, hydroquinol), 1.80 (12 H, t, *J* 7 Hz, *Me*–CH_2), −3.67 (2 H, br s, pyrrolic NH).

‡ For the derivatives **4**, smaller peaks also were apparent for the loss of Zn, in addition to loss of the counterions.

§ There exist two possible extremes for the relative orientations of the aromatic rings in these catenanes: if the hydroquinol is orthogonal to the porphyrin, then the bipyridyl moiety of the macrocycle will be closest to the porphyrin. On the other hand, if the hydroquinol and porphyrin are parallel then the phenylene moiety is closest to the porphyrin ring. An X-ray crystal structure of the strapped porphyrin precursor **3a** indicates that the hydroquinol ring is in fact orthogonal to the porphyrin plane, within an edge-to-face interaction distance (M. J. Gunter, M. R. Johnston, A. H. White and B. W. Skelton, unpublished observation).

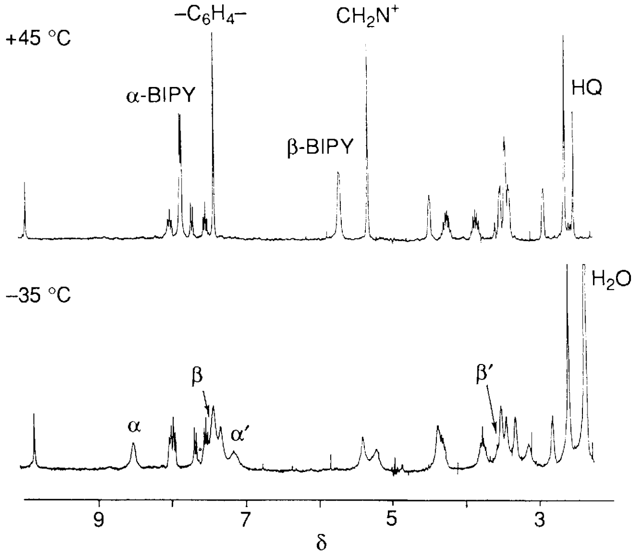


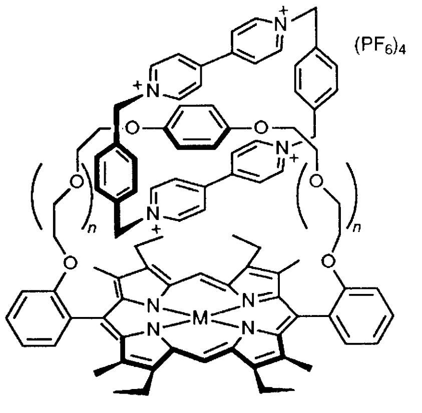
Fig. 1 Partial ^1H NMR spectra at 300 MHz for **5b** in acetonitrile at +45 and −35 °C. At −35 °C β and β′ bipyridyl resonances are masked by $-C_6H_4-$ and $-OCH_2-$ peaks, respectively.

these catenanes lack the symmetry of those previously reported, the temperature dependent processes that can be observed in the ^1H NMR spectra are in some respects simpler; while rotation of the tetracationic macrocycle around the central hydroquinone is an allowed and observable process, the threading of the bulky porphyrin-containing moiety through the tetracation (or 'pirouetting' of the bipyridinium macrocycle[1]) is clearly disallowed. Additionally, the strong shielding effects of the aromatic ring current of the porphyrin induce large shifts in those regions of the tetracationic cyclophane which are closest to it.

Representative ^1H NMR spectra of **5b** in acetonitrile at two temperatures are shown in Fig. 1. Assignments were carried out using a combination of nuclear Overhauser effect (NOE) difference, saturation transfer, and COSY 45 experiments. At 45 °C, sharp peaks for the tetracationic macrocycle indicate its fast rotation on the NMR timescale. Selected macrocycle resonances are recorded in Table 1, along with data from a typical non-porphyrinic [2]-catenane, {[2]-[BPP34C10] [BBIPYBIXYCY]catenane}$[PF_6]_4$ in Stoddart's nomenclature.[1] For all resonances increased changes in chemical shifts between the free bipyridinium cyclophane and the catenane are evident for **5b** compared to those for the hydroquinol catenane,[1] owing to the large magnetic anisotropy of the porphyrin ring. However, the shifts observed for the complexed hydroquinol upon catenane formation indicate a similar inclusion geometry to that previously observed, and little affected by the porphyrin.

By comparison, the spectrum of **5b** at −35 °C shows slow rotation of the tetracationic macrocycle, with a splitting of the resonances into two sets of equal intensity signals. Slow rotation is, however, evident in **4a** at ambient temperatures, with heating to +105 °C in $[^2H_6]$dimethyl sulfoxide necessary to observe fast rotation.

The conformation of **5b** shown in Fig. 2, with the bipyridinium rings, the hydroquinol, and the porphyrin co-parallel is consistent with the ^1H NMR data. From Table 1 it is evident that the β-bipyridyl resonances are the most shifted on catenane formation (Δδ −2.42 ppm). Additionally, spectra recorded under conditions of slow exchange show this resonance to be split into two peaks with a remarkably large separation (Δδ 3.78 ppm); the most upfield resonance at δ 3.56 is assigned to the β-proton of the 'inside' bipyridinium ring strongly shielded by the porphyrin, while the 'outside' β-proton (δ 7.33) is not significantly shifted from its position in the non-porphyrinic catenanes.[1] The α- and methylene protons on the 'inside' position are likewise shielded, but to a lesser extent. This indicates a conformation with significant face-to-face interaction between the bipyridinium rings and the porphyrin,¶ as well as interactions between the electron-



4a; *n* = 1, M = Zn
4b; *n* = 2, M = Zn
5a; *n* = 1, M = 2H
5b; *n* = 2, M = 2H

Fig. 2

Table 1 Selected ^1H NMR chemical shifts of catenane components in CD_3CN at 298 K[a]

	α-H	β-H	C_6H_4	CH_2N^+	Hydroquinol-H
Free macrocycle[b]	8.86	8.16	7.52	5.74	6.73[c]
[2]-Catenane[b]	8.85 (−0.01)	7.66 (−0.50)	7.79 (+0.27)	5.67 (−0.07)	3.45 (−3.28)
3b					5.48[d]
5b[e]	7.86 (−1.0)	5.74 (−2.42)	7.40 (−0.12)	5.34 (−0.40)	2.57 (−2.91)

[a] Values in parenthesis indicate the difference in chemical shift (ppm) between the free macrocycle and catenane macrocycle. [b] Chemical shift data obtained from ref. 1. [c] Hydroquinol chemical shift before catenane formation is from BPP34C10 (1,4,7,10,17,20,23,26,28,32-decaoxa[13.13]paracyclophane) crown ether from ref. 1. [d] In $CDCl_3$ at 25 °C. [e] Spectrum recorded at +45 °C under conditions of fast rotation; at lower temperatures exchange broadening alters peak positions.

¶ That there is some charge-transfer interaction between the bipyridinium ring of the macrocycle and the porphyrin constrained in the catenane is evidenced by a shift of the Soret band in both **4a** and **4b** from 414 to 422 nm, compared to the zinc derivatives **3a** and **3b**. In related structures in which bipyridinium cations have been shown to bind to aromatic crown ether-strapped porphyrins,[7] or in benzo-crown ether 'tweezer' porphyrins,[8] there has been no evidence of any π-sandwich type interactions between a bipyridinium ring and a porphyrin. Indeed, there is no significant change in the electronic spectra of the strapped porphyrin precursor molecules **3** (M = Zn or 2H) on addition of even a large excess of the separately synthesized tetracationic bipyridium cyclophane, of paraquat (4,4′-bipyridinium) dication, or of $[BBIPYXY][PF_6]_2$ (likewise, no complexation has been detected between bipyridinium cations and a tetraalkyl porphyrin derivative[9]). The same magnitude in shift of the Soret in both **4a** and **4b** is indicative of an interplanar separation of the phenylene and porphyrin rings of similar proportion. Examination of molecular models indicate that there is no restriction within an interplanar separation of 3.5 to 4.0 Å for either molecule; the limiting distance is defined by the 'tightness' of the shorter strap in **4a**. Although the strong porphyrin B-bands obscure the region in which the much weaker charge transfer bands associated with the bipyridinium rings and the hydroquinol in the catenane are expected, a weakly defined shoulder is apparent in the spectra of **4a** and **4b** at 485 nm.

rich hydroquinol and the electron-deficient bipyridiniums, common to all the catenanes and rotaxanes reported to date by the Stoddart group.

The methylene resonances (δ 5.34) provide the most accessible probe in determining cyclophane rotation rates.[||] In acetone solutions of **4b** a $\Delta\nu = 47$ Hz and coalescence temperature of -21 °C gave $k_c = 104$ s^{-1} and $\Delta G_c^{\ddagger} = 12.9$ kcal mol^{-1} (1 cal = 4.184 J). By comparison for **4a** a $\Delta\nu = 200.5$ Hz and $T_c = +43$ °C corresponds to a $k_c = 445$ s^{-1} and $\Delta G_c^{\ddagger} = 14.4$ kcal mol^{-1}. The value of $\Delta G_c^{\ddagger}$ for **4b** is similar to those reported for the non-porphyrinic hydroquinol-derived catenanes;[1] this, together with the fact that there appears to be little difference between **4a** and **4b** in the electronic interactions of the bipyridinium units of the macrocycle and the porphyrin would indicate that the rate and free energy differences are dominated by steric constraints, and that the porphyrin subunits in these catenanes contribute about the same degree of 'drag' to macrocycle rotation as does a second hydroquinol unit in the non-porphyrinic catenanes.[1]

The way is now open for more elaborate structures with intriguing dynamic properties. A photo-driven molecular 'shuttle' with several hydroquinol units in a strapped porphyrin is an obvious target. We are currently investigating these and other approaches.

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[||] Rotation rates were measured by the coalescence method (J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, London, 1982, ch. 6) with frequency separation ($\delta\nu$) being measured in the slow exchanged region and extrapolated to T_c. Rates were then calculated at T_c using $k_c = \pi(\delta\nu)/(2)^{1/2}$, followed by the Eyring equation to determine $\Delta G_c^{\ddagger}$. Conversion of the calculated rates to a common temperature (298 K) allows a more readily visualised comparison; the values of k_{298} are 110 and 5570 s^{-1} for **4a** and **4b**, respectively.

References

1 P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent and D. J. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 193 and references cited therein.

2 R. Young and C. K. Chang, *J. Am. Chem. Soc.*, 1985, **107**, 898.

3 A. Osuka, T. Nagata, F. Kobayashi and K. Maruyama, *J. Heterocycl. Chem.*, 1990, **27**, 1657.

4 M. J. Gunter and L. N. Mander, *J. Org. Chem.*, 1981, **46**, 4792.

5 P. R. Ashton, T. T. Goodnow, A. E. Kaifer, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1396.

6 P. R. Ashton, C. L. Brown, E. J. T. Chrystal, T. T. Goodnow, A. E. Kaifer, K. P. Parry, D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 634.

7 M. J. Gunter and M. R. Johnston, *Tetrahedron Lett.*, 1990, **31**, 4801.

8 M. J. Gunter and M. R. Johnston, *Tetrahedron Lett.*, 1992, **33**, 1771.

9 P. Leighton and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1984, 856.