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Amide-appended porphyrins as scaffolds for catenanes, rotaxanes and anion receptors

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The synthesis of a porphyrin with an over-arching strap incorporating an isophthalamide unit produced both a porphyrin monomer with a potentially H-bonding receptor site, and a [2]catenane. Although both compounds exhibit fluxional behaviour, ^{1}H NMR and MS data was used to distinguish them, and was interpreted in terms of the dynamics of each system. The self-complementarity of the isophthalamide unit provides an ideal building block for assembling [2]pseudorotaxanes with similarly functionalised threads. This was illustrated by the self-assembly of a ruthenium–porphyrin stoppered rotaxane under thermodynamically controlled conditions, by simple mixing of the strapped porphyrin, a complementary thread unit containing an isophthalamide central unit and pyridine-attached ends, and a ruthenium carbonyl porphyrin. The strapped porphyrin was also shown to act as a receptor for chloride ion, and its binding ability with other H-bonding isophthalamide guests was found to be modulated by the presence of chloride ion. Chloride complexation was observed in both metallated and free base porphyrin monomers as well as the rotaxanes counterparts, but no anion binding was observed for the catenane.

Introduction

Incorporation of the porphyrin macrocycle into components for molecular machinery[1] and molecular scale electronic devices[2] allows for a variety of stimuli that are necessary for the control of specific mechanical motion. This has been successfully demonstrated in at least several catenane and rotaxane systems.[3–6] We have utilised various strapped and superstructured porphyrins for catenane and rotaxane production, including bipyridinium and diimide moieties.[7–9] By exploiting the inherent properties of the inbuilt porphyrin, we have shown that the dynamic behaviour of these systems can be controlled by such factors as temperature,[6,9,10] chemical change[5,6,11] (*e.g.*, protonation, metallation *vs.* free base), photophysical stimuli and electrochemistry.[4,12] We had recognised the alternatives offered by the neutral diimides compared to the charged bipyridinium systems,[8,13] especially in the assembly of (pseudo)rotaxanes under thermodynamically controlled conditions.[14,15]

Since the advent of the hydrogen-bonded amide-based rotaxanes and catenane synthetic methodology,[16] we have been intrigued by the possibility of incorporating this motif into porphyrinic assemblies. Apart from their inherent chemical novelty, we were particularly interested in the possibility of an expected solvent- and anion-dependent behaviour which might present yet further means by which the dynamic properties of the systems could be modified. Furthermore, an additional binding motif allows for more flexibility in the design of future addressable multi-station rotaxanes and catenanes. We now demonstrate how the concepts of hydrogen-bonded amide-based catenanes, rotaxanes and anion receptors can indeed be applied to produce a new series of dynamic porphyrin supramolecules with exciting potential.

The design was based on analogous ditopic receptors containing an overarching diamide as a H-bonding receptor module.[17–19] The isophthalamide subunit has formed the basis for numerous rotaxane and catenane structures, particularly more recently with the elegant work of Leigh,[20] Beer,[21,22] Smith[17,18,23] and Schalley,[24] amongst others. Of particular relevance are those which are receptors for anions,[21,22] especially chloride, and where the anion has been incorporated as a template in the molecular assembly.

The target fundamental unit in our case was a porphyrin strapped with a potential hydrogen-bonding amide component, exemplified by **A** (Fig. 1). Such a superstructure over the porphyrin macrocycle could then form a scaffold for complementary H-bond-capable guests in the form of pseudorotaxanes, which might be then capped with appropriate end-groups to produce functional rotaxanes. Alternatively, depending on the synthetic route chosen to the strapped porphyrin, [2]catenane production might be optimised. In any case, the strapped porphyrins offer an anion receptor geometrically constrained to be adjacent to a porphyrin subunit. The possibilities offered by such an arrangement are numerous. For example: the anion binding can be modulated by the nature of the positively charged metal ion in the porphyrin; the binding of trivalent metal ions (*e.g.* Fe^{3+}, Rh^{3+}) with anionic axial ligands might be enhanced and geometrically enforced; anion binding can be monitored by a change in fluorescence of a suitably chosen metalloderivative; binding of H-bonding guests can be attenuated by the presence of anions; and metal-ion dependent anion selectivity can be anticipated. A viable synthetic pathway to such a base system was thus required, so that its potential within these and perhaps other roles could be assessed.

Results and discussion

The preparation of the precursor dialdehyde **1** was straightforward, by condensation of 3-*t*-butyl*iso*phthaloyl dichloride and *m*-hydroxyaniline, followed by chain extension with 2-(2-chloroethoxy)ethanol and subsequent reaction with salicylaldehyde. Condensation with the dipyrromethane **2** under standard conditions (Scheme 1) produced two major isolable porphyrinic components which were identified by mass spectral and NMR

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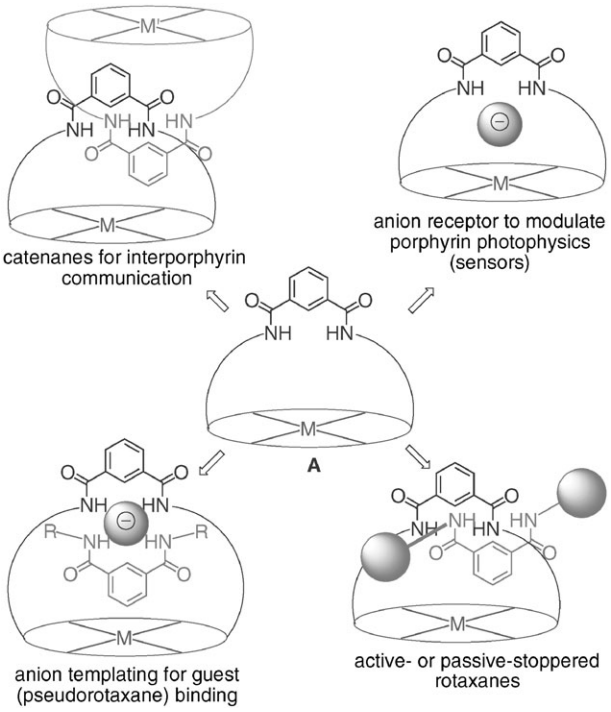
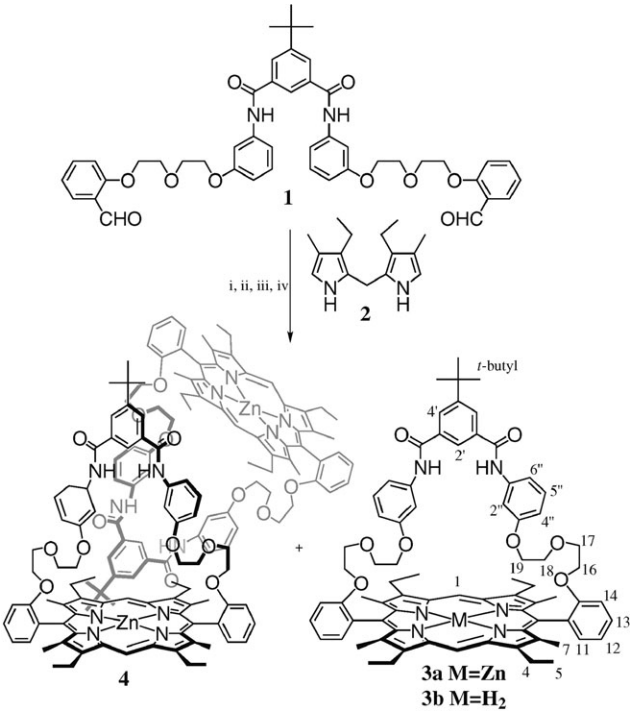


Fig. 1 Diagram indicating possible roles for amide strapped porphyrin **A** as a component for supramolecular assemblies and anion receptor systems.



Scheme 1 *Reagents and conditions:* (i) trichloroacetic acid, THF, rt, N_2, 5 h; (ii) *o*-chloranil, rt, N_2, 18 h; (iii) **3a** $Zn(OAc)_2$, $MeOH/CHCl_3$; (iv) for **3b**: 2 *M* HCl/H_2O wash.

techniques as the amide strapped porphyrin **3a** (11%) and the [2]catenane **4** (5%).

ESI and FAB mass spectrometry allowed easy distinction between the monomeric structure **3a** and the catenated dimer **4**; while both showed mass peaks at *m*/*z* 1269.7 [M + H^+] and 1204 [M–Zn], the catenane **4** also showed a significant peak at 2539.6 [M′ + H^+] indicative of a dimeric structure, and demonstrated no significant fragmentation between this peak and the monomer peak at 1269.7, a feature characteristic of interlocked molecules.

The NMR spectrum of **3a** (Fig. 2) is consistent with its strapped structure, where the shielding of the protons in the strap is attenuated as a function of distance from the porphyrin. The resonances associated with the *t*-butyl (1.33 ppm) and H-4′ (8.06 ppm)† positions are similar to those of the analogous, non-porphyrinic system synthesised by Smith,[17,23] and thus are clearly removed from any shielding by the porphyrin.‡ There were no NOE interactions detected between the porphyrin subunit and resonances such as the *t*-butyl or H-4′, which is also indicative of a monomeric species rather than an interlocked dimer.

Compound **4** displayed some particularly diagnostic resonances in its ^1H NMR compared to **3a** (Fig. 2). The protons at position H-2′ and H-4′ have been significantly deshielded ($\Delta\delta$ 0.85 and 0.15 ppm respectively) when compared to the monomeric species **3**, analogous to the deshielding of the corresponding resonances of the more symmetrical benzylic system synthesised by Leigh and co-workers.[25] Protons H-18 and H-19 are also shifted upfield in **4** compared to **3a**, as a result of shielding by the isophthaloyl group of the second ring. The observed diastereotopicity in the protons H-4 on the periphery of the porphyrin is much larger in **4** at 150 Hz (*cf*. 20 Hz in **3a**), indicative of greater facial discrimination of the porphyrin subunits.

Conversely, the *t*-butyl resonance has also been deshielded ($\Delta\delta$ 0.18 ppm) in **4** which would be expected if the interlocking porphyrins adopt the conformation shown in Scheme 1 with the rings of the [2]catenane offset with respect to each other. This is analogous to non-porphyrinic amide [2]catenanes which have been shown to have a similar offset orientation in order to maximise hydrogen bonding interactions. This results in an unsymmetrical structure where the axis through the isophthaloyl groups of each of the interlocked rings are angled to each other. Furthermore, the flexible straps in these systems allow further conformational mobility with respect to positional orientation and dihedral angles between the amide and porphyrin planes. Significant NOE interactions were observed between the protons at position H-4′ and H-4 of the porphyrin, and between H-2′ and H-2″ which are consistent with inter-ring interactions in the structure depicted in Scheme 1. No such correlations were observed for the monomeric structure **3a**.

The *meso*-hydrogen H-1 on the porphyrin in **4** is also deshielded and somewhat broadened compared to that in **3a** which suggests a dynamic process. At low temperatures (238 K), this signal splits into two, and other porphyrinic and strap resonances also show signs of separated environments at lower temperatures. This is indicative of a dynamic process which could involve either 'rocking' of one amide ring relative to the other, or a 'flipping' of the second interlocked ring from one side of the first porphyrin to the other. It is also significant that no analogous dynamic processes were observed for **3a** over the same temperature range.

The amide-strapped porphyrin **3a**, as well as functioning as a component of the symmetrical [2]catenane **4**, is a versatile building block for more elaborate systems. For example, unsymmetrical [2]catenanes are now available by known synthetic procedures using pre-formed **3a** or **3b** and other porphyrinic or non-porphyrinic macrocycle precursors for the second link of the catenane. Alternatively, **3a** or **3b** can also function as the loop component for rotaxanes assembled by hydrogen-bonding motifs. We illustrate this by the reversible

† Non-systematic numbering for NMR assignments is shown in Scheme 1.

‡ It should be noted that the length and flexibility of the ethyleneoxy linkages allows considerable conformational freedom in the molecule, with the amide moiety free to lay over laterally, and not restricted to a vertical alignment as might be implied by the drawing in Scheme 1.

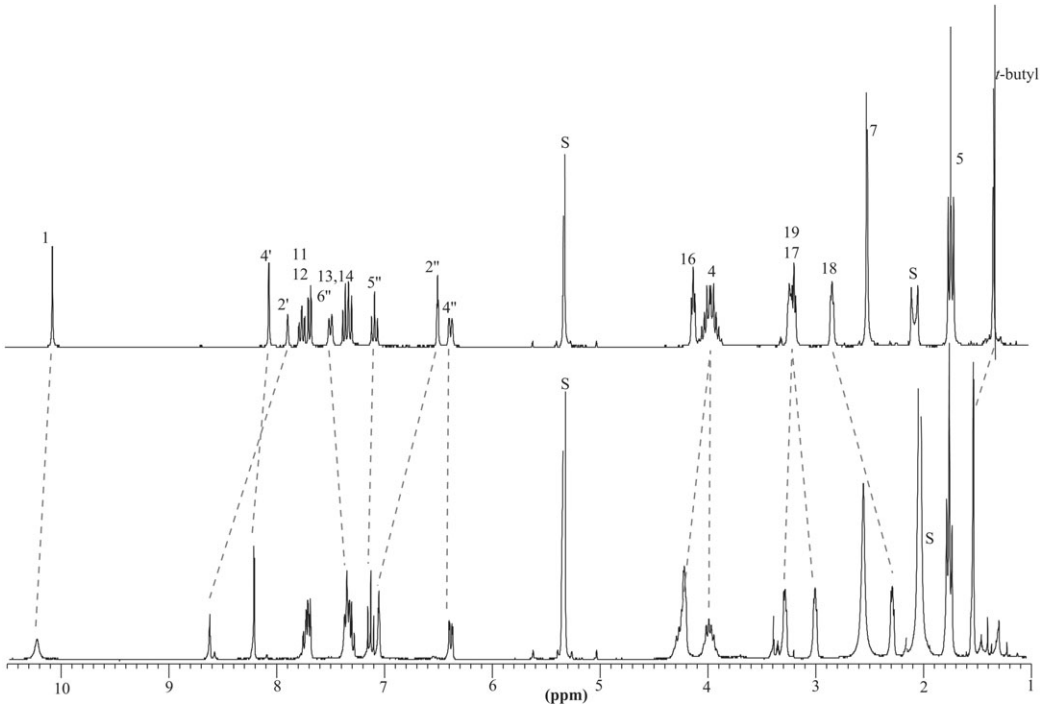
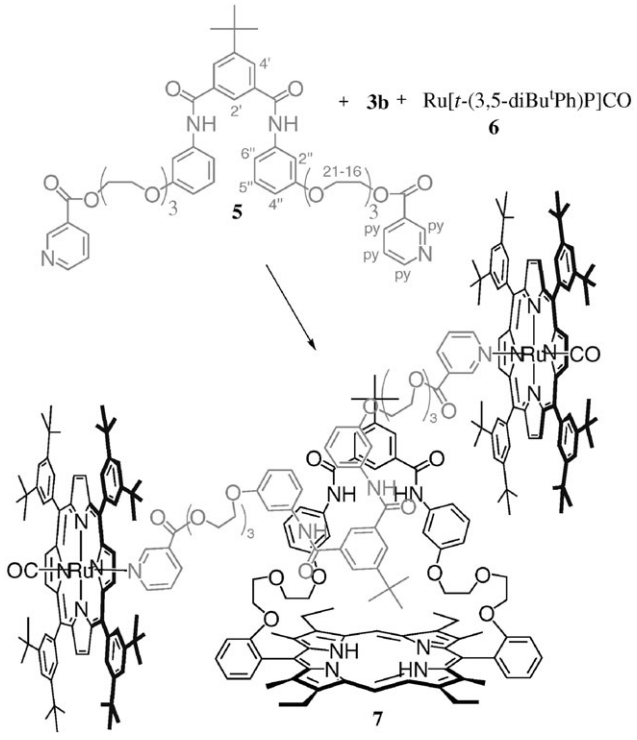


Fig. 2 ^{1}H NMR spectra in CD_2Cl_2 at 303 K of amide-strapped porphyrin **3a** (top) and catenane **4** (bottom). Lines indicate significant shifts of important resonances.

assembly of a metalloporphyrin-stoppered, porphyrin-looped, rotaxane. The successful assembly of this system also confirms the monomeric nature of **3**, compared to the catenane **4**, which showed no evidence of pseudorotaxane or stoppered rotaxane formation under similar conditions.

The thread component **5** for this thermodynamically assembled rotaxane was easily synthesised by condensation of the homologue of the hydroxy-precursor of **1** with nicotinic anhydride. The protocol for the formation of the rotaxane was the same as we have used previously for the self-assembly of dibenzo-crown ethers with diimide thread components and metalloporphyrin stoppers[14] (Scheme 2). Thus, admixing **3b** with **5** in 1 : 1 stoichiometric ratio produced changes in the ^{1}H NMR spectrum indicative of a rapidly exchanging system, and consistent with reversible binding of the thread within the loop of **3b**. At lower temperatures, the equilibrium is shifted towards pseudorotaxane formation, and exchange becomes slower.



Scheme 2 *Reagents and conditions:* mix stoichiometric quantities, CD_2Cl_2.

This pseudo-rotaxane formation is also solvent dependent; the presence of even trace amounts of methanol precludes significant binding of the thread, presumably because of competing H-bonding with solvent. Chloroform is also suitable as a solvent, but the spectra are somewhat broadened compared to those in dichloromethane. It should also be noted that the spectra are broadened by aggregation at too high a concentration. An additional problem encountered with solutions in dichloromethane or chloroform is a slow change of the spectrum over time (hours to days), which we attribute to an effect of chloride ion from slow solvent decomposition (the effect of chloride binding from added chloride is discussed below).

Addition of two equivalents of carbonyl-*meso*-tetrakis(3,5-di-*t*-butylphenyl)porphyrinatoruthenium(II) **6** to the pseudorotaxane system of **3b** plus **5** resulted in a spectrum characteristic of the more slowly exchanging rotaxane **7** (Fig. 3). The assignment of the NMR spectrum was aided by the usual 2-D techniques, but most importantly, the shifts associated with the central units of the rotaxane (*i.e.* protons 2′, 4′ and NH) correspond closely to those of the [2]catenane **4**.

In particular the NH protons have broadened under the baseline and the 2′ protons have shifted downfield of the 4′ protons ($\Delta\delta$ 0.77 for 2′ of the thread unit, and 0.55 for 2′ of the porphyrin strap). Significant shifts are also seen in the protons 20 and 21 as a result of shielding by the isophthaloyl group in the porphyrin. All of these effects are mirrored in the catenane **4**.

As a result of the Ru porphyrin coordination, the resonances of the terminal pyridine units are all shifted well upfield and are hidden under other resonances. By analogy with previously reported coordinatively assembled rotaxanes,[14] these peaks would be expected to be in the regions 6.7, 5.3, 2.2 and 1.8 ppm, and they could be identified by COSY techniques. No other significant shifts were detected in the polyether chains of the thread unit,

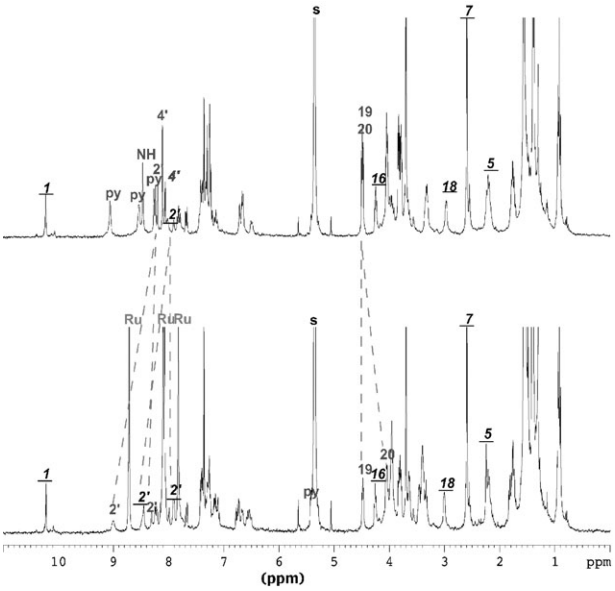
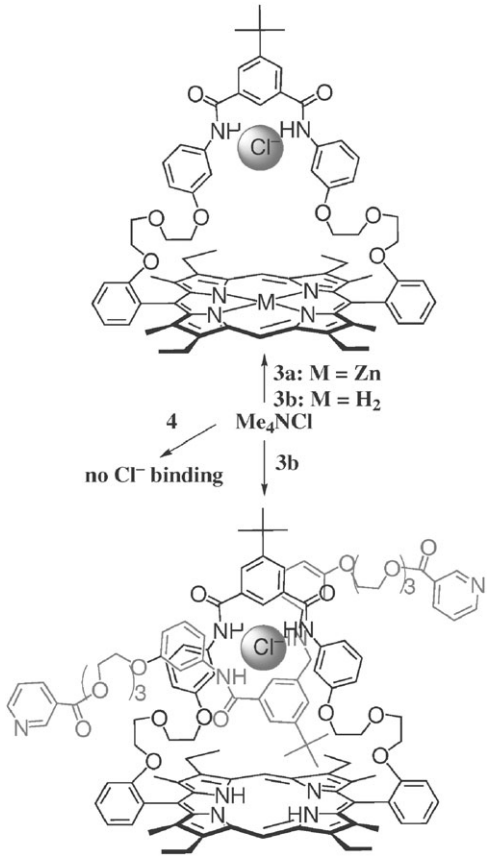


Fig. 3 Partial ^{1}H NMR spectra in CD_2Cl_2 at 303 K for **3b** + **5** (top), **7** (bottom). Lines indicate shifts of selected resonances. Numbers in bold correspond to **5**, those underlined to **3**, and Ru porphyrin and pyridine resonances are indicated Ru and py.



Scheme 3 *Reagents and conditions:* CD_2Cl_2, excess Me_4NCl (solid), sonication.

as these are too far removed from the shielding influence of the Ru porphyrin.

Having obtained the catenane, porphyrin monomer and both a pseudorotaxane and a reversibly coordinated rotaxane, a preliminary investigation of the capacity for anion binding and templating was undertaken. The effect of chloride ion was examined by the addition of tetramethylammonium chloride to

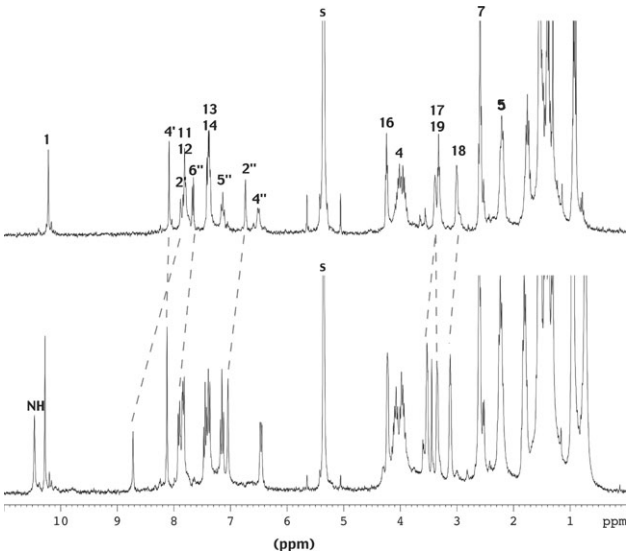


Fig. 4 Partial ^{1}H NMR spectrum in CD_2Cl_2 at 303 K for **3b** (top) and **3b** + Cl^- (bottom). Lines indicate shifts of selected resonances.

the previously prepared solutions of the catenane, metallated and free base porphyrin monomer, the pseudorotaxane (**3b** + **5**) and rotaxane **7** (Scheme 3). All experiments were performed in dry, non-protic CD_2Cl_2 as the solvent. The samples were briefly sonicated in the presence of excess (insoluble) ammonium salt and allowed to equilibrate until there was no further change in the NMR spectrum (1–3 h).

The zinc and free base porphyrins **3a** and **3b** showed clear evidence of chloride binding, with significant shifts analogous to those observed in Beer's systems[22] (Fig. 4). Obvious downfield shifts of the 2′, and 2″ protons ($\Delta\delta$ 0.84 and 0.30 ppm respectively) and the reappearance of the NH proton signal in a highly deshielded position (δ 10.46 ppm) are symptomatic of anion binding. Analogous shifts for both the porphyrin and thread protons were also observed when a mixture of the thread component **5** and the free base porphyrin **3b** was treated with chloride. The spectrum was different to the sum of the individual spectra of chloride-bound thread component **5** and porphyrin **3b**, indicating that pseudorotaxane formation of **3b** with **5** is templated by chloride ion. Rotaxane **7** also showed evidence of similar anion-induced shifts after being exposed to chloride anions.

Somewhat surprisingly, the catenane **4** showed no evidence for anion binding under similar conditions. This indicates a steric constraint of the covalently interlocked species which presumably precludes the conformation required for anion binding. Thus, whether chloride ion can act as a template in the formation of the catenane during the porphyrin forming reaction warrants further investigation, but the prognosis is poor.§

Conclusion

Porphyrins strapped with potential H-bonding amide superstructures based on isophthalamide units are clearly versatile components for a variety of new structures. Here we have demonstrated that much of the corresponding chemistry that is available for simpler analogues is readily transferable to these porphyrinic systems, and thus routes to porphyrin-containing catenanes, psuedo-rotaxanes, rotaxanes, and anion receptors of various types has now become available. The advantages of the in-built porphyrin sub-units are self-evident, in that it

§ Although the product catenane may not be stabilised by chloride, there is a distinct possibility that a transition state towards it may well be, given that the pseudorotaxane structure shows evidence for chloride ion templation.

allows provision for both a detection and trigger functionality, depending on the chosen system. The dynamics of the system can be modified by a wide variety of factors, including temperature, solvent, anion, and metallation state. Within these sets, the porphyrin moiety allows additional stimulation by photophysical, electrochemical or chemical means. A modification of the synthesis of the catenane, by initial synthesis of the monomeric unit **3** and subsequent stepwise catenation with the components of a *different* porphyrinic unit, allows for a route to unsymmetrical catenanes where inter-porphyrin communication and stimulation could be examined. The scope for these versatile systems is considerable.

Experimental

General

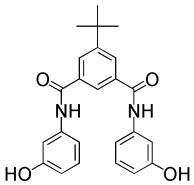
All solvents were distilled before use, using standard procedures: tetrahydrofuran (THF) was distilled over benzophenone and sodium under N_2; triethylamine (Et_3N) was distilled over CaH_2; dimethylformamide (DMF) was dried over type 4 Å molecular sieves. Column chromatography used Aldrich silica gel (grade 9385, 230–400 mesh).

^{1}H NMR spectra were acquired using a 300 MHz Bruker Avance 300 spectrometer at 303 K, unless otherwise stated. Chemical shifts (δ) are reported in parts per million relative to residual solvent. Coupling constants (J) are reported in Hz. Deuterated solvents were purchased from Aldrich and stored over type 3 Å molecular sieves after opening. COSY-45, gradient COSY, one-bond C–H correlation (HMQC), long-range C–H correlation (HMBC), NOESY, gradient NOESY two-dimensional NMR experiments employed the standard Bruker parameters. DEPT, NOE difference and saturation transfer experiments, as well selective gradient NOE experiments utilised standard Bruker pulse programs. ^{1}H NMR assignments of porphyrin-based molecules use the non-systematic numbering displayed in Scheme 1; for the pseudorotaxane **3** + **5**, rotaxane **7** and related compounds, the protons of the thread component polyether chain are numbered from the carbon adjacent to the nicotinic ester group (C16) to C21 at the phenoxy end.

Melting points were determined using a Reichert microscopic hot-stage apparatus.

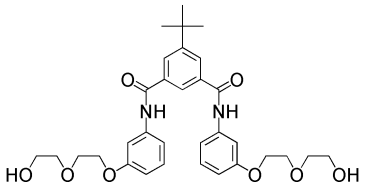
FAB and ESI mass spectrometry was carried out by CSIRO Molecular Science at the Ian Wark Laboratory, Clayton, and high resolution ESI was performed at the Centre for Molecular Architecture, Rockhampton.

5-*tert*-Butyl-*N*,*N*′-*bis*-(3-hydroxyphenyl)-1,3-benzenediamide (8)



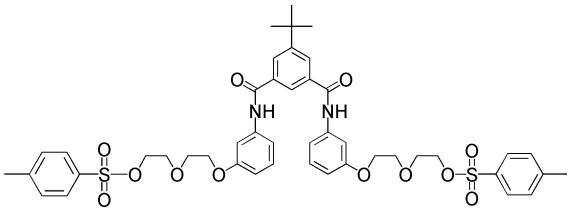
3-Aminophenol (1 g, 9.16 mmol), 5-*tert*-butyl-isophthaloyl dichloride (1.08 g, 4.17 mmol) and MeCN (dry, 50 ml) were stirred together under N_2 (30 min). Et_3N (1.37 ml, 9.88 mmol) was then added *via* syringe and the mixture was left to stir overnight. The mixture was then filtered and the remaining solution was then added to EtOAc (100 ml) and washed with dilute HCl (2 × 50 ml), water (50 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo* to yield **8** as a white solid (1.6 g, 95%); mp 160–161 °C; δ_H (300 MHz, d_6-acetone) 9.56 (2H, s, NH), 8.29 (1H, t, J 1.5, isophthal H-2), 8.15 (2H, d, J 1.5, isophthal H-4), 7.50 (2H, t, J 2, Ar H-2), 7.20 (2H, d, J 8, Ar H-6), 7.15 (2H, t, J 8, Ar H-5), 6.60 (2H, d, J 8, Ar H-4), 2.9–2.7 (2H, bs, OH); m/z (EI) 404.1736 [M^+ requires 404.1736], 296.13 [M-$C_6H_6NO^+$ requires 296.35].

5-*tert*-Butyl-*N*,*N*′-*bis*-{3-[2-(2-hydroxyethoxy)ethoxy]phenyl}-1,3-benzenediamide (9)



A mixture of diol **8** (1 g, 2.5 mmol) and K_2CO_3 (1.59 g, 11.48 mmol) in MeCN (dry, 100 ml) was heated, with stirring, under N_2 (30 min). 2-(2-Chloroethoxy)ethanol (800 mg, 6.42 mmol) was then added and the mixture was refluxed for 5 days. The mixture was then cooled to room temperature and filtered to remove potassium salts. The solvent was then evaporated and the residue was taked up in EtOAc (100 ml), washed with HCl (dilute, 2 × 50 ml), water (50 ml) and dried (Na_2SO_4). The solvent was then removed *in vacuo* to yield **9** as an oily yellow solid (1.3 g, 95%); mp 66 °C; δ_H (300 MHz, d_6-acetone) 9.69 (2H, s, NH), 8.29 (1H, t, J 1.5, isophthal H-2), 8.15 (2H, d, J 1.5, isophthal H-4), 7.58 (2H, t, J 2, Ar H-2), 7.36 (2H, d, J 8, Ar H-6), 7.21 (2H, t, J 8, Ar H-5), 6.68 (2H, d, J 8, Ar H-4), 4.10 (4H, t, J 5, OCH_2), 3.80 (4H, t, J 5, OCH_2), 3.66–3.57 (8H, m, 2 × OCH_2), 3.1–2.9 (2H, bs, OH), 1.35 (9H, s, t-butyl); m/z (EI) 580.2783 [M^+ requires 580.2785], 384 [(M^- $C_{10}H_{14}NO_3$)$^+$ requires 384.46].

5-*tert*-Butyl-*N*,*N*′-*bis*-[3-{2-[2-(4-toluenesulfonyloxy)ethoxy]ethoxy}phenyl]-1,3-benzenediamide (10)



The extended diol **9** (2 g, 3.75 mmol) in CH_2Cl_2 (50 ml) and Et_3N (2 ml) was stirred at room temperature for 30 min. *p*-Toluenesulfonyl chloride (1.79 g, 9.39 mmol) in CH_2Cl_2 (50 ml) and Et_3N (2 ml) was then added and the whole was stirred for 40 h. The solution was then poured onto ice and washed with HCl (dilute, 50 ml), water (50 ml), dried (Na_2SO_4) and finally dried *in vacuo* to yield the product **10** as an oily, pale yellow solid (2 g, 63%) which was used crude in the subsequent reaction; δ_H (300 MHz, d_6-acetone) 9.69 (2H, s, NH), 8.34 (1H, t, J 1.5, isophthal H–2), 8.20 (2H, d, J 1.5, isophthal H-4), 7.79 (4H, d, J 8, tosyl-H), 7.58 (2H, t, J 2, Ar H-2), 7.43 (4H, d, J 8, tosyl-H), 7.36 (2H, d, J 8, Ar H-6), 7.21 (2H, t, J 8, Ar H-5), 6.68 (2H, d, J 8, Ar H-4), 4.20 (4H, t, J 5, OCH_2), 4.05 (4H, t, J 5, OCH_2), 3.76–3.69 (8H, m, 2 × OCH_2), 2.42 (6H, s, tosyl-CH_3), 1.35 (9H, s, t-butyl).

5-*tert*-Butyl-*N*,*N*′-*bis*-[3-{2-[2-(2-formylphenoxy)ethoxy]ethoxy}phenyl]-1,3-benzenediamide (1)

Salicylaldehyde (725 mg, 5.93 mmol), K_2CO_3 (2 g, 14.4 mmol) and MeCN (dry, 100 ml) were heated together, with stirring, under N_2 (30 min). The tosylate **10** (2 g, 2.37 mmol) was then added and the mixture was refluxed for 2 days. The mixture was then cooled to room temperature, dried *via* rotary evaporator and partitioned between CH_2Cl_2 (100 ml) and water (100 ml). The organic layer was washed with HCl (dilute, 50 ml), water (3 × 50 ml). The solvent was then removed *in vacuo* to yield **1** as a slightly oily yellow solid (1.88 g, 100%); mp 68 °C; δ_H (300 MHz, $CDCl_3$) 10.46 (2H, s, CHO), 9.10 (2H, s, NH), 8.12 (1H, s, isophthal H-2), 7.99 (2H, s, isophthal H-4), 7.70 (2H, d, J 6, Ar ald H-3), 7.44 (2H, t, J 6, Ar ald H-4), 7.37 (2H, t, J 1.5, Ar H-2), 7.26 (2H, d, J 6, Ar H-6), 7.10 (2H, t, J 9,

Ar H-5), 6.91 (4H, m, Ar ald H-5, Ar ald H-6), 6.59 (2H, d, *J* 6, Ar H-4), 4.17 (4H, t, *J* 5, OCH_2), 4.05 (4H, t, *J* 5, OCH_2), 3.88 (4H, t, *J* 5, OCH_2), 3.82 (4H, t, *J* 5, OCH_2), 1.23 (9H, s, *t*-butyl); δ_C (75 MHz, $CDCl_3$) 31.0, 35.0, 67.4, 68.2, 69.8, 106.9, 111.0, 113.0, 121.0, 121.9, 125.0, 128.3, 129.7, 134.8, 136.1, 139.5, 152.6, 159.1, 161.3, 166.0, 190.5; *m*/*z* (ESI) 811 [$(M + Na)^+$ requires 811.89], 789.33 [$(M + H)^+$ requires 789.91]; *m*/*z* (EI) 788.3311 [M^+ requires 788.3309].

[2]-*bis*-{2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15[2,2-{2-[2-[3-*N*,*N*′-(5-*tert*-butyl-1,3-benzenediamido)phenyl]ethoxy]ethoxy}diphenyl] porphyrinato}-zinc(II) [2]catenane (4)

and

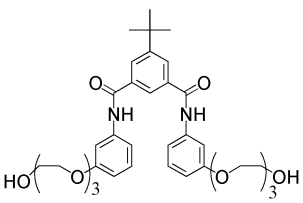
{2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15[2,2-{2-[2-[3-*N*,*N*′-(5-*tert*-butyl-1,3-benzenediamido)phenyl]ethoxy] ethoxy}diphenyl]porphyrinato}-zinc(II) (3a)

The dialdehyde **1** (0.43 g, 0.54 mmol) and 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane **2** (0.25 g, 1.1 mmol) were added to a degassed solution of MeCN (50 ml). Trichloroacetic acid (~20 mg) was then added and the mixture was left to stir (in the dark, under N_2) for 5 h. *o*-Chloroanil (0.75 g, 3 mmol) in THF (20 ml) was added all at once and the mixture was taken to dryness *via* rotary evaporator. The residue was run through a plug of silica using EtOAc as the solvent followed by insertion of zinc in the usual manner (excess $Zn(OAc)_2$, MeOH/$CHCl_3$). The residue was then purified *via* silica column chromatography using CH_2Cl_2, CH_2Cl_2/MeOH (1%) and CH_2Cl_2/MeOH (5%) as the eluants to give two major fractions. These fractions were recrystallised from acetone/MeOH to yield bright purple solids **3** and **4**.

4 (35 mg, 5%); δ_H (300 MHz, CD_2Cl_2/d_3-MeOD) 10.24 (2H, s, H-1), 8.63 (1H, s, H-2′), 8.21 (2H, s, H-4′), 7.75–7.69 (4H, m, H-11, H-12), 7.36–7.28 (6H, m, H-6″, H-13, H-14), 7.12 (2H, t, *J* 9, H-5″), 7.05 (2H, m, Ar–H), 6.37 (2H, d, *J* 9, H-4″), 4.24 (4H, m, H-4), 4.20 (4H, m, H-16), 3.95 (4H, m, H-4), 3.26 (4H, m, H-17), 2.97 (4H, m, H-19), 2.52 (12H, s, H-7), 2.25 (4H, m, H-18), 1.72 (12H, t, *J* 6, H-5), 1.50 (9H, s, *t*-butyl); *m*/*z* (ESI) 1269.7 [$(M/2 + H)^+$ requires 1269.5], 1207.6315 [$(M/2-Zn + H)^+$ requires 1207.6272]; *m*/*z* (FAB) 2538.6 [M^+ requires 2537.066].

3a (75 mg, 11%), δ_H (300 MHz, CD_2Cl_2/d_3-MeOD) 10.06 (2H, s, H-1), 8.06 (2H, s, H-4′), 7.88 (1H, s, H-2′), 7.75 (2H, t, *J* 6, H-12), 7.67 (2H, d, *J* 6, H-11), 7.49 (2H, d, *J* 9, H-6″), 7.47–7.29 (4H, m, H-13, H-14), 7.07 (2H, t, *J* 9, H-5″), 6.49 (2H, m, H-2″), 6.37 (2H, d, *J* 9, H-4″), 4.12 (4H, m, H-16), 3.95 (8H, m, H-4), 3.22–3.16 (8H, m, H-19, H-17), 2.84 (4H, m, H-18), 2.52 (12H, s, H-7), 1.72 (12H, t, *J* 6, H-5), 1.33 (9H, s, *t*-butyl); δ_C (75 MHz, $CDCl_3$) 13.5, 17.5, 31.4, 34.1, 66.6, 69.6, 70.7, 96.1, 103.6, 110.9, 111.8, 113.6, 118.0, 121.0, 122.6, 127.5, 130.0, 134.6, 135.7, 138.7, 144.3, 158.8, 159.3; *m*/*z* (ESI) 1291.5285 [$(M + Na)^+$ requires 1291.5227], 1270 [$(M + H)^+$ requires 1269.5], *ca.* 1207 [$(M^- Zn + 3H)^+$ requires 1207.1].

5-*tert*-Butyl-*N*,*N*′-*bis*-[3-{2-[2-(2-hydroxyethoxy) ethoxy] ethoxy}phenyl]-1,3-benzenediamide (11)



The diol **8** (5 g, 12.4 mmol) and K_2CO_3 (7.95 g, 57.5 mmol) were suspended in MeCN (dry, 200 ml) and heated, with stirring, under N_2 for 30 min. 2-[2-(2-Chloroethoxy)ethoxy] ethanol (4 g, 23.7 mmol) was then added and the mixture was refluxed for 5 days. The mixture was then cooled to room temperature and filtered to remove potassium salts. The solvent was then evaporated, and the residue was taked up in EtOAc (100 ml), washed with HCl (dilute, 2 × 50 ml), water (50 ml) and dried (Na_2SO_4). The solvent was then removed *in vacuo* to yield **11** as a thick yellow oil (3.25 g, 40%); δ_H (300 MHz, d_6-acetone) 9.64 (2H, s, NH), 8.29 (1H, t, *J* 1.5, isophthal H–2), 8.15 (2H, d, *J* 1.5, isophthal H–4), 7.58 (2H, t, *J* 2, Ar H-2), 7.36 (2H, d, *J* 8, Ar H-6), 7.21 (2H, t, *J* 8, Ar H-5), 6.68 (2H, d, *J* 8, Ar H-4), 4.12 (4H, t, *J* 5, OCH_2), 3.83 (4H, t, *J* 5, OCH_2), 3.66–3.57 (8H, m, 2 × OCH_2), 3.5 (8H, t, *J* 5, 2 × OCH_2), 3.1–2.9 (2H, bs, OH), 1.35 (9H, s, *t*-butyl); *m*/*z* (EI) 668.3313 [M^+ required 668.3309], *ca.* 637 [$(M-CH_3O)^+$ requires 637.76], *ca.* 427 [$(M-C_{12}H_{18}NO_5]^+$ requires 427.52.

5-*tert*-Butyl-*N*,*N*′-*bis*-[3-{2-[2-(2-nicotinoyloxy)ethoxy] ethoxy}phenyl]-1,3-benzenediamide (5)

The extended diol **11** (200 mg, 0.299 mmol), nicotinic acid (148 mg, 1.2 mmol), *N*-hydroxybenzotriazole (HOBT, 162 mg, 1.2 mmol) and 1-[(3-dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) (172 mg, 0.90 mmol) were dissolved in CH_2Cl_2 (30 ml) before triethylamine (90.8 mg, 0.90 mmol) was added *via* a syringe and the solution was stirred at room temperature under nitrogen in the dark for 4 days. The solvent was evaporated and the residue was taken up in 6 M HCl and chloroform. The aqueous layer was separated and neutralised with $NaHCO_3$ (sat'd. aq.). The product was extracted with chloroform, dried (Na_2SO_4) and the solvent removed to yield a yellow/brown oil which was subjected to column chromatography using CH_2Cl_2, CH_2Cl_2/MeOH (1%) and CH_2Cl_2/MeOH (5%) as the eluents to give the product **5** as a dark yellow oil (150 mg, 57%); δ_H (300 MHz, CD_2Cl_2) 9.19 (2H, s, NH), 8.86 (2H, s, H-py), 8.70 (2H, d, *J* 1, H-py), 8.27 (2H, d, *J* 2, H-py), 8.22 (1H, s, H-2′), 8.09 (2H, s, H-4′), 7.39–7.23 (8H, m, H-6″, H-5″, H-2″, H-py), 6.69 (2H, dm, *J* 8, H-4″), 4.50 (8H, m, H-19, H-21), 4.09 (4H, m, H-20), 3.85 (12H, m, H-18, H-17, H-16), 1.36 (9H, s, *t*-butyl); *m*/*z* (ESI-APCI) 879.4 [$(M + H)^+$ requires 879.4].

Pseudorotaxane (3b + 5)

An equimolar mixture of porphyrin **3b** and thread **5** were combined in a NMR tube and allowed to reach equilibrium. The porphyrin (H_p) and thread (H_t-) resonances were monitored. δ_H (300 MHz, CD_2Cl_2) 10.23 (2H, s, H_p-1), 9.06 (2H, br s, H_t-py), 8.53 (2H, br s, H_t-py), 8.47 (2H, br s, H_t-NH), 8.25 (2H, d, *J* 6, H_t-py), 8.20 (2H, s, H_t-2′), 8.11 (2H, s, H_t-4′), 8.06 (2H, s, H_p-4′), 7.90 (1H, s, H_p-2′), 7.80 (4H, t, *J* 6, H_p-11, H_p-12), 7.68 (2H, d, *J* 9, H_p-6″), 7.42–7.21 (12H, m, H_p-13, H_p-14, H_t-2″, H_t-5″, H_t-6″, H_t-py), 7.14 (2H, t, *J* 9, H_p-5″), 6.71 (2H, m, H_p-2″), 6.65 (2H, d, *J* 9, H_t-4″), 6.37 (2H, d, *J* 6, H_p-4″), 4.49 (8H, m, H_t-19, H_t-20), 4.25 (4H, m, H_p-16), 4.06–4.03 (8H, m, H_t-18, H_t–21), 3.85–3.77 (8H, m, H_t-16, H_t-17), 3.33 (8H, m, H_p-17, H_p-19), 2.95 (4H, m, H_p-18), 2.6 (12H, s, H_p-7), 2.21 (12H, t, *J* 6, H_p-5), 1.30 (9H, s, H_p-*t*-butyl, H_t-*t*-butyl).

Metalloporphyrin-stoppered rotaxane (7)

An equimolar mixture of strapped porphyrin **3b**, thread **5** were combined in an NMR tube. Two equivalents of ruthenium carbonyl porphyrin **6** was added and the solution was allowed to equilibrate (10 min). The porphyrin (H_p), thread (H_t−) and ruthenium porphyrin (H_{RuP}−) resonances were monitored. δ_H (300 MHz, CD_2Cl_2) 10.22 (2H, s, H_p-1), 8.97 (1H, br s, H_t-2″), 8.72 (16H, s, H_{RuP}-Ru), 8.45 (3H, br s, H_t-NH, H_p-2′), 8.30 (1H, s, H_t-2′), 8.23 (4H, m, H_t-4′, H_p-4′), 8.10 (18H, m, H_t-4′, H_{RuP}-Ru), 8.01 (2H, m, H_p-4′), 7.90 (5H, m, H_p-2′, H_p-11, H_p-12), 7.82 (8H, s, H_{RuP}-Ru), 7.67 (2H, d, *J* 6, H_p-6″),

7.42–7.11 (23H, m, H_p-13, H_p-14, H_p-2′, H_p-6″, H_p-5″, H_p-5″, H_p-4″, H_t-2″, H_t-2″, H_t-5″, H_t-5″, H_t-6″, H_t-6″), 6.78–6.55 (9H, m, H_p-4″, H_t-py, H_t-2″, H_t-4″, H_t-4″), 4.47 (4H, m, H_t-19), 4.26 (4H, m, H_p-16), 4.06 (4H, m, H_t-20), 3.95 (12H, m, 4, H_t-21), 3.79 (4H, m, H_t-18), 3.65 (4H, m, H_t-17), 3.48–3.33 (12H, m, H_p-17, H_p-19, H_t-16), 2.97 (4H, m, H_p-18), 2.59 (12H, s, H_p-7), 2.23 (12H, m, H_p-5), 1.54 (72H, s, H_{RuP}-*t*-butyl), 1.42 (9H, s, H_p-*t*-butyl, H_t-*t*-butyl). As previously observed for coordinatively stoppered rotaxanes,[14] only mass peaks corresponding to the component entities were observed in ESI mass spectra: *m*/*z* (ESI) 1207.6 [**3b** $(M + H)^+$ requires 1207.6], 879.4 [**5** $(M + H)^+$ requires 879.4], 1191 [**6** $(M + H)^+$ requires 1191.6].

General procedure for chloride binding

A small crystal of tetramethylammonium chloride was added to NMR samples of the host molecules in CD_2Cl_2. In each case the sample was sonicated for 2 min and then allowed to equilibrate (5 min–several h) until there was no further change in the spectrum. Spectral shifts are shown in Fig. 4 and discussed in the text.

Acknowledgements

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