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Neutral π-associated porphyrin [2]catenanes

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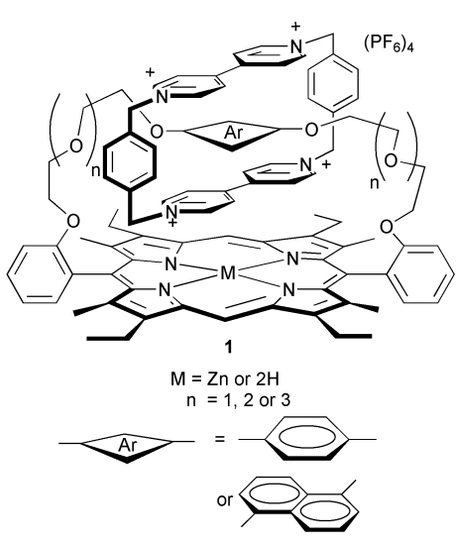
A series of neutral porphyrin-containing catenanes has been synthesised, consisting of a zinc porphyrin strapped by a polyethylene glycol chain containing four or six ethylenoxy-units and incorporating a central naphthoquinol unit, interlinked with a naphthalene diimide macrocycle. The napthalene diimide precursor units exhibit only weak binding with the strapped porphyrins (K_a between 8 and 0.02 M^{-1}), but good yields of the catenanes were obtained by Glaser coupling of the alkynyl napthalene diimide precursors in the presence of the porphyrins. Structures and solution conformations were determined by mass spectral and detailed ^{1}H NMR studies. For the longer strapped porphyrins, the diimide macrocycle rotates around the central naphthoquinol unit at 420–450 times per second, while rotation is virtually prevented in the tighter strapped derivatives. A second dynamic process occurring in both sets of catenanes and described as 'yawing' leads to inequivalence in the naphthalene moieties. UV-Visible spectra indicate charge transfer interactions and electronic communication between the two components of the catenane.

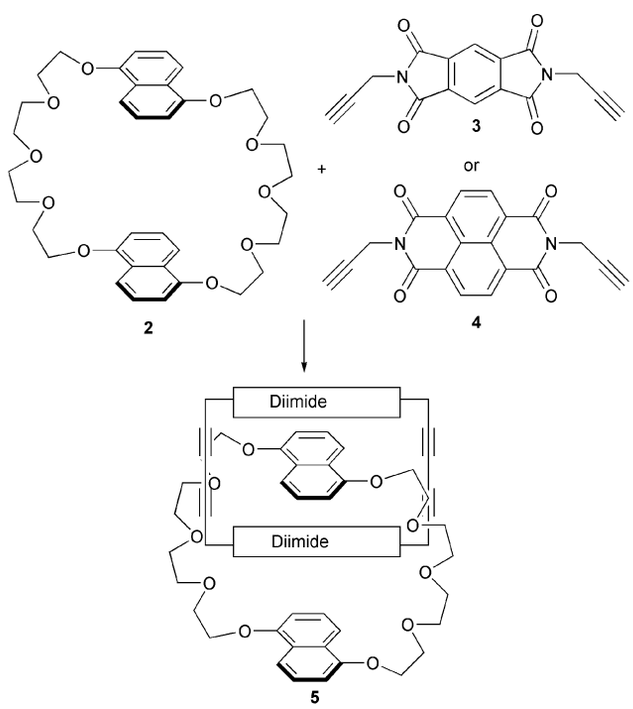
Introduction

Adressable functionality in components of supramolecular systems such as catenanes and rotaxanes provides a means for controlling their dynamics, photochemical, electrochemical, chemical and physical properties. Porphyrins are ideal trigger units, and there have been several approaches to their incorporation into multicomponent linked systems.[1–4]

We have previously shown that porphyrins strapped across one face with polyethylene glycol straps of various lengths including hydroquinol or naphthoquinol units form relatively stable pseudo-rotaxane type complexes with substituted 4,4′-bipyridinium derivatives,[5,6] analogous to those formed with the non-porphyrinic crown ethers which have been extensively studied by Stoddart and co-workers.[7] Furthermore, we have demonstrated that these systems can be used to form charged catenanes **1** incorporating the cyclobis(paraquat-4,4′-biphenylene) macrocycle interlinked with a strapped porphyrin.[2,3] The dynamics of these systems have been reported by us previously, and we have studied their behaviour under protonation,[8] and their photophysical and electrochemical properties have been investigated in some detail.[9–11]



Sanders and co-workers[12–16] have also shown that hydroquinol and naphthoquinol crown ethers such as DN38C10 **2** form pseudorotaxanes with substituted napthodiimides and pyromellitimides, and that it is possible to form neutral catenanes using a variety of approaches for assembling diimide-containing macrocycles of various dimensions and constitutions interlinked with the crown ether (Scheme 1). In particular, Cu(I) mediated Glaser coupling of propynyl substituted diimides **3** or **4** in the presence of **2** led to excellent yields of the catenanes **5**.



Scheme 1 Neutral diimide/crown ether catenanes prepared by Glaser coupling methods as used by Sanders *et al.*[10–12]

Thus it was logical for us to extend the concepts of our charged porphyrin-containing catenanes of the Stoddart type to those of the Sanders type. Such neutral catenanes retain the inherent interest and potential of the charged analogues, but now provide an entry into non-charged systems which can be studied in a wider variety of solvents, and which allow variation in photophysical and photochemical studies by virtue of the

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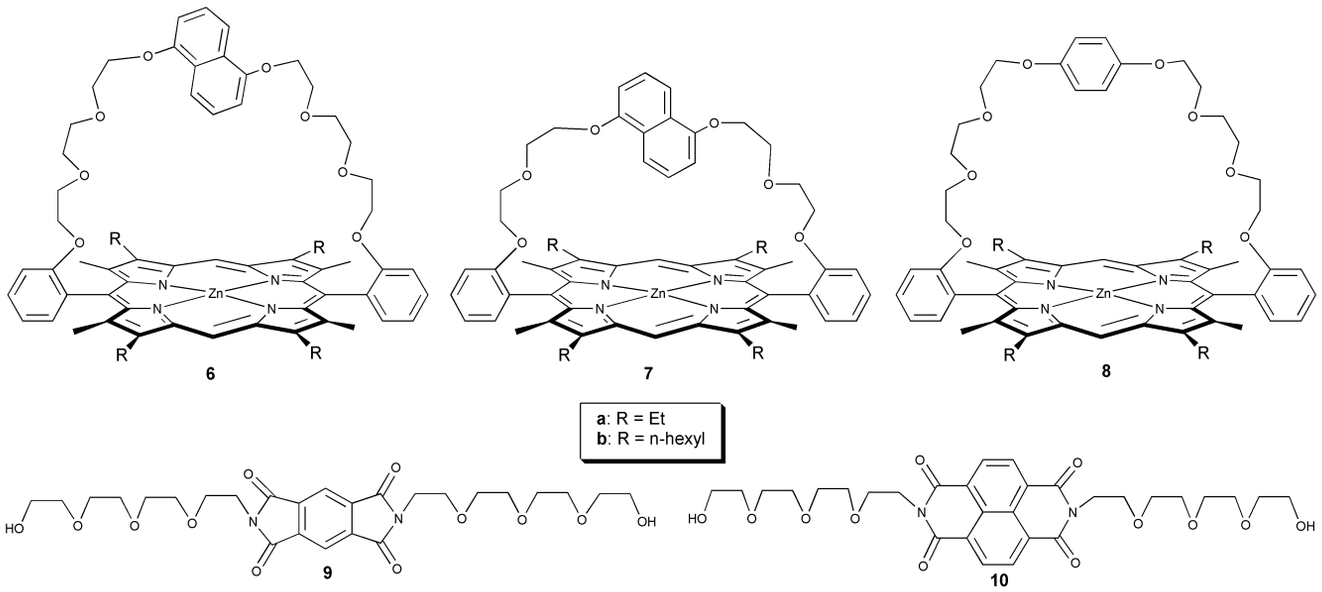


diimide subunits. The successful synthesis of a porphyrin containing [2]catenane would also establish a methodological basis for the construction of more elaborate porphyrinic molecular assemblies.

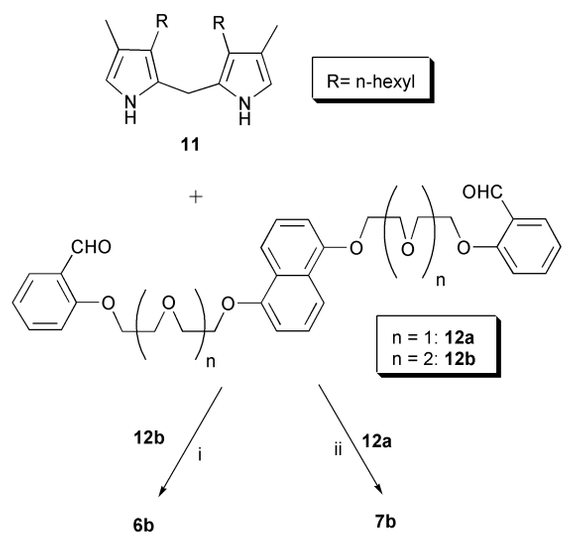
Results and discussion

A number of preliminary NMR binding studies were undertaken with the strapped tetraethyl porphyrins **6a**, **7a** and **8a** with bis-*N*,*N*′-tetraethylene glycol substituted pyromellitic **9** and naphthalene diimides **10**[17] in order to establish which systems would be likely to form catenated compounds. These particular disubstituted diimides were used for the binding studies because of their good solubility characteristics.

Studies which involved the pyromellitic diimide **9** indicated that there was no significant interaction with any of the porphyrin hosts, whereas the disubstituted naphthalene diimide **10** was found to bind only with the naphthalene-strapped porphyrin **7a** under conditions of slow exchange on the ^{1}H NMR timescale at 300 MHz and 303 K, and with **6a** under fast exchange. Binding constants were determined by direct integration (for **7a**) or by the titration method[18] (for **6a**).

The association constants (K_a) for the porphyrins **6a** and **7a** in $CDCl_3$ at 303 K were calculated to be 0.1 M^{-1} and 8 M^{-1} respectively which were significantly lower than those observed for the charged bipyridinium paraquat in these same cavities (≈2300 and 5600 M^{-1} respectively).[5] The hydroquinol triethylene glycol strapped porphyrin **8a** exhibited only very weak binding with **10** (K_a < 0.02 M^{-1}), in keeping with previous studies using paraquat as the guest where it was found that the hydroquinol strapped porphyrins exhibited a K_a that was, on average, an order of magnitude lower than those of the corresponding naphthoquinol porphyrins.[10] The results indicated that attempts to catenate the hydroquinol strapped porphyrins with either the pyromellitic or naphthodiimide precursors might be unsuccessful and indeed subsequent attempts at the synthesis of a number of these [2]catenanes proved to be fruitless; catenanes were successfully synthesised only in the case of naphthalene-strapped porphyrins and naphthalene diimides.

In the first instance, the known tetraethyl strapped porphyrin **6a**,[3] and the shorter strapped analogue **7a** were utilised for the [2]catenane syntheses. Nevertheless, because of limited solubility of the product materials, the corresponding tetrahexyl derivatives **6b** and **7b** proved more satisfactory.[19] Scheme 2 describes the synthetic pathway for the naphthoquinol diethylene glycol strapped hexyl porphyrins and follows a similar route to that which has been shown to be successful for many other related strapped porphyrins. The dihexyl

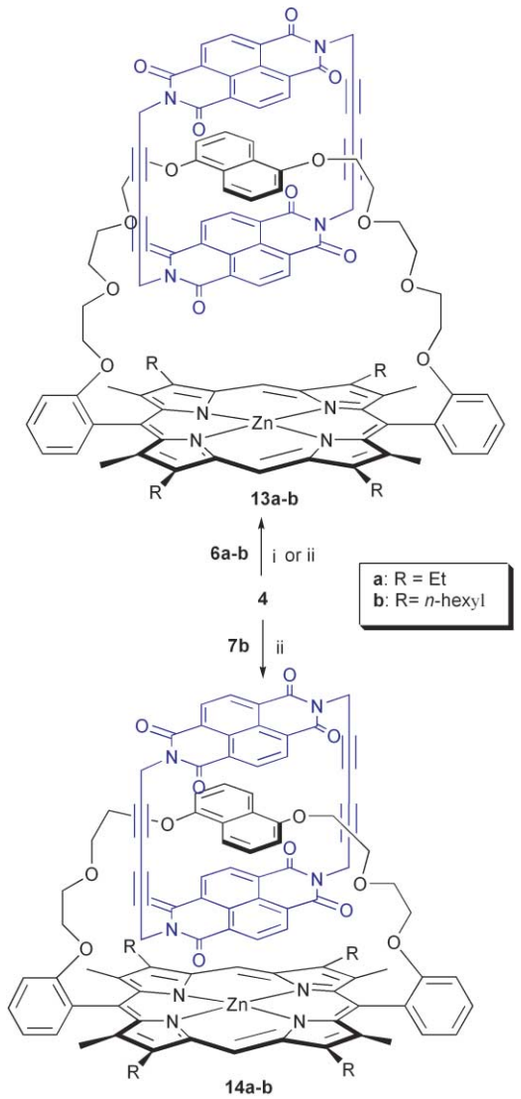


Scheme 2 Synthesis of the tetrahexyl porphyrins **6b** and **7b**. *Reagents and conditions*: i) *p*-toluensulfonic acid, acetonitrile under N_2, 48 h followed by *o*-chloranil, 18 h; ii) trichloroacetic acid, acetonitrile under N_2, 5 h followed by *o*-chloranil, 18 h.

dipyrromethane **11** was obtained by hydrogenolysis of the benzyl ester,[20] followed by decarboxylation using trifluoroacetic acid. The significant shielding of the α, β and γ naphthalene protons, amongst others in the polyethylene glycol chains in both **6b** and **7b**, is as expected and is consistent with the structure shown with the naphthoquinol unit strapped over the face of the porphyrin.

The catenane synthesis employed the same Glaser coupling conditions which were used by the Sanders group[12,13] for the non-porphyrinic analogues (Scheme 3). The Zn(II) metallated derivative was used in an attempt to obviate transmetallation with Cu(II), but about 10% of the starting porphyrin in this reaction was converted to the copper species. Separation from the Cu(II) species by chromatography was possible however, and the isolated yield of the target compound **13a** was 12%. Alternatively, by using palladium dichlorobis(triphenylphosphine) as the coupling reagent[21] the isolated yield (16%) was marginally higher than that afforded by the Glaser method although purification was simplified. As expected, there was a large amount of higher molecular weight insoluble material accompanying the products.

Using the tetrahexyl porphyrin **6b** the yield of the catenated species **13b** was now 60%. The improved yield could only be attributed to the increased solubility of both the porphyrin and



Scheme 3 Synthesis of the catenanes **13a**–**b** and **14a**–**b**. *Reagents and conditions*: i) DMF, dry air and $CuCl/CuCl_2$, 50 °C; ii) DMF, dry air and $[Pd(PPh_3)_2]Cl_2$, 50 °C.

the product catenane under the reaction conditions. Due to the observed solubility problems with the tetraethyl porphyrin catenane **13a**, no attempt was made to synthesise a [2]catenane using the shorter strapped porphyrin **7a**, but catenation of the diethylene glycol strapped hexyl porphyrin **7b** gave the [2]catenane **14b** in 54% yield.

Mass spectral data were consistent with the catenated structures; fast-atom bombardment (FAB) mass spectrometry of catenane **13a** revealed a molecular ion at *m*/*z* 1792.62, and ESI spectrometry showed expected molecular ion peaks at *m*/*z* 2017.8 for $[M + H]^+$ and 2039.8 for $[M + Na]^+$ for **13b**, and *m*/*z* 1929.8 for $[M + H]^+$and *m*/*z* 1951.7 for $[M + Na]^+$ for **14b**.

The ^{1}H NMR spectrum of the catenane **13b** shown in Fig. 1 shows the resonances of the catenated species compared to those of the starting porphyrin (non-systematic numbering used for the spectral assignments are given below in Fig. 2). Proton assignments were carried out with the aid of gradient NOESY and COSY experiments. The most surprising aspect of the spectrum at first sight is the complete absence of a resonance for the diimide aromatic protons. Nevertheless, variable temperature and gradient NOESY experiments (discussed further below) indicated that the diimide resonance was broadened and hidden under the baseline in the region between 7.8 and 6.5 ppm. The observed shifts of the other resonances are consistent with a catenated structure, and the spectrum

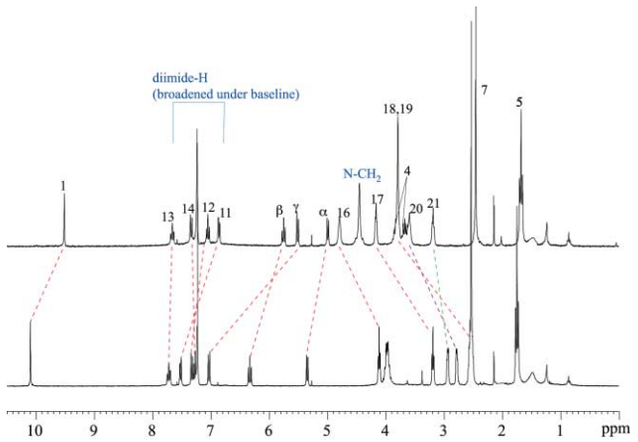


Fig. 1 ^{1}H NMR spectra of the strapped porphyrin **6b** (bottom) and its catenane **13b** (top). Numbering used for the assignments is shown in Fig. 2.

provides useful information about the solution conformation of the catenane.

The figure shows the shielding of the *meso*-hydrogens indicated by an upfield shift of 0.57 ppm consistent with a structure in which the diimide is located co-facially over the porphyrin. The protons associated with the naphthoquinol unit (α, β and γ) have also been shifted significantly upfield which is consistent with additional shielding from the bis(diimide) macrocyclic moiety in a co-facial arrangement which more than effectively replaces the shielding by the porphyrin in the strapped porphyrin starting material **6b**. Proton γ has the greatest upfield shift, which would suggest that it is located more or less centrally over the aromatic ring of the diimide. The upfield shifts of protons H-4, H-5 and H-7 also show the effects of shielding by the diimide moiety, and the methylene protons H-4 are now diastereotopic, as expected from a structure in which the facial differentiation of the porphyrin is enhanced.

Conversely, the ethylene resonances of the strap are all deshielded to varying degrees. Protons associated with positions H-18 and H-19 have been deshielded significantly ($\Delta\delta$ 1.23 ppm). Above and below these positions, the deshielding effect lessens somewhat, although it is still significant for protons H-16, H-17 and H-20 ($\Delta\delta$ 0.8–1.0 ppm). The protons least affected are those associated with position H-21. A co-facial orientation of the diimide with the porphyrin places H-18 and H-19 directly in the deshielding region (edge) of the diimide, and H-21 over the shielding region (face), effectively replacing the shielding of the porphyrin in **6b** with that of the naphthodiimide in **13b**.

The free diimide macrocycle has not been synthesised and thus direct comparison of shifts with this compound is not possible. However, comparison of the spectrum with that of the acyclic unit **4** shows significant upfield shifts for the N-methylene resonances ($\Delta\delta$ 4.46 ppm). The broadened resonance underlying the aromatic signals was assigned to the aryl hydrogens on the diimide macrocycle (absolute assignments were completed with the aid of dynamic NMR described below). The diimide resonances at this temperature are in a fast exchange between 'inside' and 'outside' environments, but are close to coalescence and have broadened almost to disappearance.

The proton NMR spectrum for the less soluble catenane **13a** is very similar to that of the more soluble hexyl catenane **13b**, and again shows a broadened baseline resonance for the aromatic protons on the naphthalene diimide unit. In all other respects the spectra are virtually identical except for the resonances of the hexyl *vs.* ethyl groups of the side chains.

The spectrum of **14b** (Fig. 3) clearly shows significant differences to those of the [2]catenanes from the looser triethylene

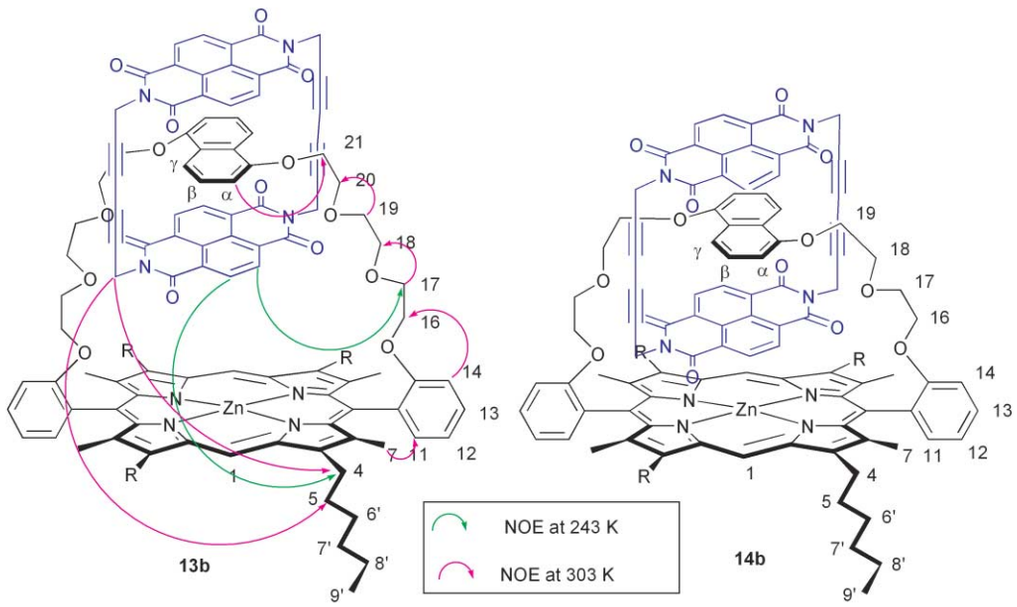


Fig. 2 The numbering system used to describe the NMR spectra of the catenanes **13b** and **14b** and their porphyrin precursors. Also indicated are significant NOE correlations in catenane **13b** at high and low temperatures.

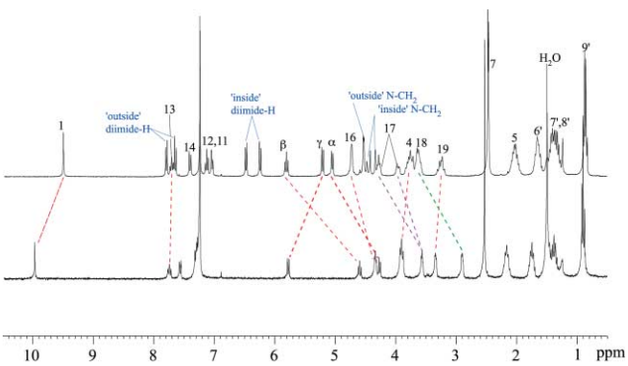


Fig. 3 ^{1}H NMR spectra ($CDCl_3$ at 303 K) of the starting porphyrin **7b** (bottom) compared to that of the catenated species **14b** (top). Numbering used for the assignments is shown in Fig. 2.

glycol strapped porphyrins. An upfield shift of 0.45 ppm of the *meso*-hydrogens, the shielding of the porphyrin methyl H-7, methylenes H-4 and H-5, and the γ proton on the naphthoquinol unit ($\Delta\delta$ 0.50 ppm), are all indicative of a cofacial arrangement between the porphyrin and the naphthoquinol moieties in a catenated structure. However, in this case the protons α and β on the naphthoquinol moiety are significantly deshielded ($\Delta\delta$ 0.84 and 1.27 ppm respectively). This can be explained by replacement of the strong shielding of the large π-cloud of the porphyrin by that of the smaller diimide units.[22]

What is most obvious however is the sharpness and multiplicity of the diimide protons which indicate that the dynamics of the system must be quite different to those of **13a** and **b** at this temperature. Not only are there 'inside' and 'outside' environments in evidence indicating a slow exchange process (or indeed a locked structure), but these protons are also non-equivalent in themselves. The NOESY spectrum of **14b** shows cross-peaks for the interchange of the two naphthalene diimide components which implies that whilst this process is slow on the chemical shift time scale it is fast on the NOESY time scale. This AB spin system which is apparent for the diimide aromatic protons can be explained in terms of the geometry of the catenane and the asymmetric orientation of the aromatic subunit relative to the porphyrin as shown in Fig. 4. Such an orientation is supported by gradient NOESY and ROESY 2D experiments: proton (**b**) shows an NOE to the methyl protons H-7, whereas (**a**) shows an NOE to the hexyl protons at H-6′. This reasoning can also be applied to the 'outside' diimide

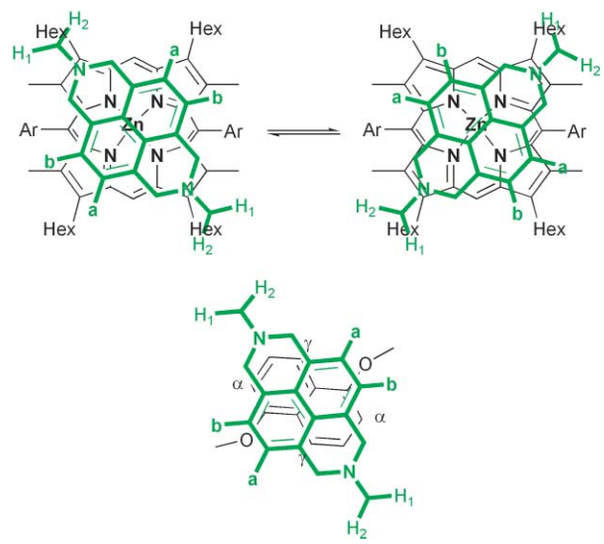


Fig. 4 Orientations giving rise to the observed asymmetry in the aromatic and methylene protons of the diimide in **14b**. Also shown is the dynamic behaviour of the naphthalene diimide within the porphyrin cavity which causes the asymmetry observed (at different temperatures) in all of the [2]catenanes **13a**, **13b** and **14b**. This translational motion is described as 'yawing'.

protons and their asymmetric positioning over the naphthoquinol unit as indicated.

The resonances associated with the N–CH_2 protons (both inside and outside) are also non-equivalent showing AB spin systems with a coupling $J_{geminal}$ of 16.8 Hz. The 'outside' N–CH_2 protons are in a very tight AB system ($J_{vicinal}$ 3 Hz), whereas the 'inside' N–CH_2 protons are obviously in quite different environments ($J_{vicinal}$ 27 Hz). Fig. 4 can also be used to note that each of these 'inside' protons would also be either positioned closer to the hexyl ($\mathbf{H_2}$) or the methyl ($\mathbf{H_1}$) group on the porphyrin. It is also interesting to note that the methyl protons (H-7) on the porphyrin are both shielded to some extent as well as split into two singlets. This also supports the proposed structure in the figure above where the different environments for each pair of methyls is obvious and inequivalence is clearly discerned in the complex splitting pattern for the chain, especially for H-4.

Another striking characteristic of the ^{1}H NMR of **14b** is the diastereotopicity (84 Hz) observed for the protons on position

H-17. There is an NOE between proton (**b**) of the imide and the most downfield multiplet for H-17 with the upfield multiplet for H-17 showing a weak NOE to (**a**). Perusal of molecular models indeed indicates the expected closest proximity of H-21 to the diimide unit in a catenane structure with an approximate 3.5 Å separation between diimide and porphyrin planes.

Dynamic NMR experiments (both high and low temperature) are particularly revealing about the solution conformations of the catenanes. For the [2]catenanes **13a** and **13b** the diimide resonances sharpen as the temperature is raised to 383 K. However for compound **14b** the separate diimide aromatic protons did not coalesce up to 458 K, indicating that the macrocycle does not spin at a rate within the limits of the NMR time scale. There was also no evidence of decomposition at this temperature which gives some indication of the thermal stability of this compound.

For **13b** at fast exchange (373 K) there are only two peaks for the diimide macrocyclic component, one for the diimide protons, and one for the N-methylene protons (Fig. 5). At low temperature (253 K) however, not only were these peaks split into both 'inside' and 'outside' environments, but each of these resonances were further split, giving four peaks. This behaviour at low temperature is the same as that displayed by **14b** at 303 K and so the assignments made on the latter could be confirmed by the results of 2D experiments carried out on **13b**.

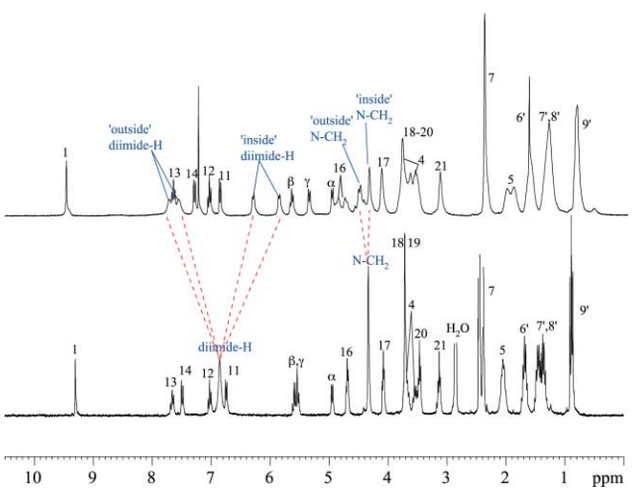


Fig. 5 ^{1}H NMR spectra of **13b** at 253 K in $CDCl_3$ (top) and 373 K in dimethyl sulfoxide-d^6 (bottom). Numbering used for the assignments is shown in Fig. 2.

Fig. 2 demonstrates some of the more significant NOE interactions observed at both fast and slow exchange for **13b**. The NOESY spectra of both compounds showed correlations between the N-methylene resonance and the most downfield multiplet of proton H-4 and the triplet or multiplet associated with protons at position H-5 on the periphery of the porphyrin. Due to the broadened nature of the aromatic protons of the diimide, there were no observable interactions with any of the porphyrin resonances at this temperature, but there were clear corellations at lower temperatures under conditions of slow exchange.

From this dynamic NMR data, it is evident that there are two distinct processes operative in these compounds. The first process is the 'rotation' of the diimide macrocycle described by exchanging 'outside' and 'inside' environments (Fig. 6).[23]

The second process under slow exchange yields the non-equivalence observed for the diimide aromatic and N-methylene protons. This translational switching of the diimide across the face of the porphyrin as demonstrated in Fig. 3 indicates a motion which is described as 'yawing'. When this process is sufficiently slow, the asymmetry of the protons (**a**) and (**b**) is clearly defined with an AB spin system for both 'inside' and 'outside' environments (as seen in the NMR spectra of **13b** and **14b**).

By using the coalescence method, rates for both the spinning of the diimide macrocycle and its yawing were estimated using the Eyring and van't Hoff equations. The coalescence temperature (T_c) for the N-methylene resonances of **13a** was found to be 274 K with a k_c of 106 s^{-1} and a free energy of activation $\Delta G_c^{\ddagger}$ of 56.1 kJ mol^{-1}; an estimation of the rotation rate of the diimide macrocycle at 298 K was 420 s^{-1}. For **13b** k_c at 274 K was found to be 120 s^{-1} with a free energy of activation $\Delta G_c^{\ddagger}$ of 56.1 kJ mol^{-1}, giving a similar rotation rate of the diimide macrocycle of about 450 s^{-1} at 298 K, indicating no more interference of a hexyl chain compared to an ethyl group. It is interesting to note by comparison that the analogous charged [2]catenane of the Stoddart type **1** (n = 2, Ar = naphthyl) gave a tetracationic macrocycle spinning rate of around 400 s^{-1} at 298 K,[3] which demonstrates similarities of size and other criteria that determine the interplanar interactions between the two different electron deficient macrocycles with similar strapped porphyrin compounds.

The spinning rate for **14b** could not be determined as the coalescence temperature for this process could not be reached. However the k_c for the 'yawing' process of **14b** at 383 K was found to be 135 s^{-1} with a free energy of activation $\Delta G_c^{\ddagger}$ of 81.2 kJ mol^{-1} and a yawing rate of the diimide macrocycle of 0.02 s^{-1} at 298 K. The relatively slow rate of yawing indicates that the diimide is severely restricted in the porphyrin cavity which gives some insight into the steric constraints of this system.

UV-Vis spectra of this series of porphyrin [2]catenanes (Fig. 7 and Table 1) indicate some electronic interaction between the porphyrin and the naphthalene diimide. As with the charged bipyridinium porphyrin [2]catenanes,[3] red shifts ($\Delta\lambda \approx 6$ nm) of the porphyrin Soret band are observed upon catenation. The Soret band also has a broad shoulder at 380 nm which is associated with the diimide subunit. The catenanes display Soret and Q bands which are typical for the porphyrins,[11] but with the Q bands somewhat broader, and shifted to *higher* energies with lower molar extinction coefficients.

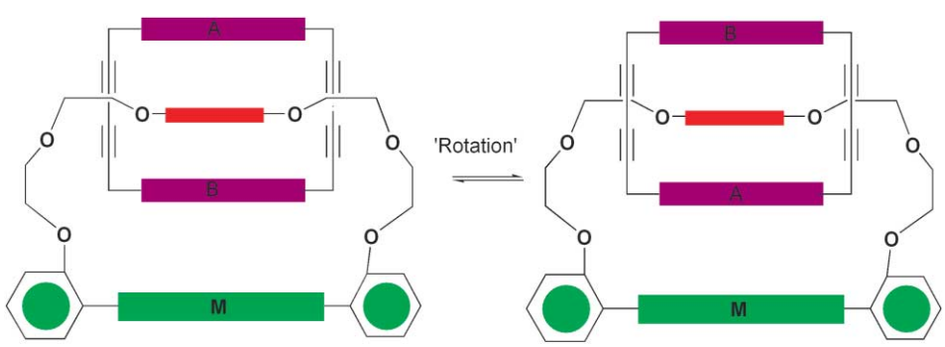


Fig. 6 Schematic representation of the dynamic behaviour of the diimide macrocycle in the [2]catenanes **13** and **14**. The exchange of rings A and B between 'inside' and 'outside' environments may be regarded as rotation (green: porphyrin, red: naphthalene, magenta: naphthodiimide).

Table 1 Ground state absorption properties of the porphyrins and their corresponding catenanes at 298 K in chloroform solution[a]

Compound	Soret λ_{max}/nm ($10^{-5}\varepsilon$)	Q Bands λ_{max}/nm ($10^{-4}\varepsilon$)	Q Bands λ_{max}/nm ($10^{-3}\varepsilon$)	CT Bands λ_{max}/nm ($10^{-2}\varepsilon$)
7b	412 (3.50)	542 (2.23)	577 (12.0)	
6b	413 (2.45)	544 (1.40)	576 (6.3)	
6a[b]	414 (3.0)	542 (1.80)	576 (6.0)	
14b	419 (2.50)	538 (1.62)	570 (9.30)	687 (6.5)
13b	418 (2.16)	538 (1.28)	570 (7.6)	686 (5.5)
13a	417 (2.45)	537 (1.43)	569 (8.6)	687 (6.0)

[a] ε/dm^3 mol^{-1} cm^{-1}; [b] spectrum in acetonitrile.

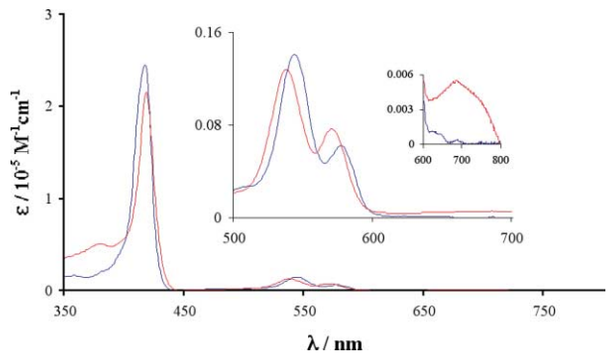


Fig. 7 Soret and Q band (bottom inset) region for the porphyrin **6b** (blue) and its catenane **13b** (red) demonstrating the observed shifts and the CT band (top inset) with a maximum at 686 nm.

Conversely, the Q bands for the charged porphyrin catenanes were shifted to *lower* energies (longer wavelength). The reason for the blue shift of the Q bands in these catenanes is not obvious but may be induced by conformational constraints. Nevertheless, it is interesting to note that the shifts are similar for both the 'looser' **13** and the more constrained catenane **14b**. Thus it would seem unlikely that the porphyrin ring is forced to distort in the catenanes. Furthermore, distortions in the form of puckering or saddling of the porphyrin have been shown to lead to red shifts in both the Soret and Q bands.[24] A more detailed study of these factors must await further investigations into the photophysical and structural properties of these systems.

A feature of the catenane absorptions is the appearance of a broad band with a maximum in the region of 670–700 nm with a molar extinction coefficient in the range 10^2–10^3 dm^3 mol^{-1} cm^{-1}, which is assigned to CT bands originating from the interaction between the porphyrin component and the diimide units of the macrocycle. Similar CT bands have been observed in spectroscopic studies on the charged porphyrin catenanes, although the maxima of these bands appeared at longer wavelengths (720–760 nm).[10] The neutral π-associated catenanes containing the dinaphtho-crown of the Sanders group had a broad CT band (ε_{max} = 400 dm^3 mol^{-1} cm^{-1}) for the charge transfer interaction between the naphthoquinol of the crown and the diimide unit in the 480–650 nm region,[13] but such a band would be masked by the strong porphyrin absorptions here; nevertheless the slight broadening of the Q bands in the catenanes may be an indication of the presence of an underlying band. The small broad absorption at ≈380 nm is assigned to a diimide based transition, as naphthalene diimide itself has bands in this region.

Conclusion

We have demonstrated that neutral π-associated porphyrin catenanes can be produced readily and in high yields using Glaser coupling methodology with the approriate propynyl substituted naphthalene diimides, assembled around naphthoquinol-strapped porphyrins. It should now be possible to extend these concepts to other established coupling procedures that have been utilised for a series of non-porphyrinic analogues, including Mitsonobu alkylations[17] and assembly under thermodynamic control with olefin metathesis,[15] and related methods.[14] Furthermore, similar principles can now be applied to porphyrinic rotaxanes and rotacatenanes, both in solution[4] and attached to polymeric supports.[25] The photochemical and electrochemical properties of these assemblies remain to be explored in detail, as has been done for the non-porphyrinic analogues,[13] and for the corresponding bipyridinium-based porphyrin catenanes[10,11] and these experiments are continuing in our laboratories.

Experimental

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 4 Å molecular sieves. Column chromatography used Aldrich silica gel (grade 9385, 230–400 mesh). Chromatotron chromatography was carried out on a model 7924T Chromatotron using plates coated with 2 mm thick Merck silica gel 60 PF_{254} containing gypsum. Preparative TLC was performed on 20 × 20 cm plates coated with 0.5 mm thick Art. 7731 Kieselgel 60 G Merck silica. Analytical TLC was carried out on Merck Silica Gel 60 G_{254} pre-coated aluminium sheets.

^{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 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 as selective gradient NOE experiments utilised standard Bruker pulse programs. ^{1}H NMR assignments of porphyrin-based molecules use the non-systematic numbering displayed in Fig. 2.

UV-Vis spectra were recorded on a Varian Cary IE UV-VIS spectrophotometer. 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 the Australian National University, Canberra, and high resolution ESI was performed at the Centre for Molecular Architecture, Rockhampton.

1,5-Bis[2-[2-(*o*-formylphenoxy)ethoxy]ethoxy]naphthalene 12a

Salicylaldehyde (1.67 g, 13.7 mmol) and K_2CO_3 (3.44 g, 24.9 mmol) were stirred in dry acetonitrile (55 mL) with heating under an atmosphere of N_2 for 1 h. Then 1,5-naphthoquinol bistosylate[26] (4.01 g, 6.22 mmol) in dry CH_3CN (190 mL) was added all at once, and the resulting solution

refluxed under N_2 for 4 days. On cooling, the solvent was removed by rotary evaporation, and the residue partitioned between CH_2Cl_2 and H_2O. The organic layer was separated, washed (H_2O), and dried ($MgSO_4$). The product was purified using column chromatography (silica) by eluting first with CH_2Cl_2 and then CH_2Cl_2/petroleum spirit (5%) to remove impurities, followed by CH_2Cl_2/Et_2O (2%) to give a yellow solid, which was recrystallised to yield the dialdehyde **12a** as a beige solid (2.69 g, 79%), mp 121–123 °C (from $CHCl_3$/ethyl acetate) (Found: C, 70.05; H, 5.96. $C_{32}H_{32}O_8$ requires C, 70.58; H, 5.92%); δ_H (300 MHz; $CDCl_3$) 10.53 (2H, s, CHO), 7.83 (4H, dt, *J* 7, 2, Ar–H), 7.50 (2H, dt, *J* 8, 2, Ar–H), 7.32 (2H, t, *J* 8, Ar–H), 7.00 (2H, dt, *J* 8, 2, Ar–H), 6.98 (2H, d, *J* 8, Ar–H), 6.83 (2H, d, *J* 8, Ar–H), 4.33–4.27 (8H, m, OCH_2), 4.08–4.04 (8H, m, OCH_2).

{2,8,12,18-Tetrahexyl-3,7,13,17-tetramethyl-5,15[2,2′-{2″-[2‴-(1⁗,5⁗-naphthoxy)ethoxy]ethoxy}diphenyl]porphinato}zinc(II) 7b

The dipyrromethane dicarboxylate[20] (600 mg, 1.39 mmol) was added to degassed trifluoroacetic acid (5 mL) and stirred with regular degassing, under N_2 for 1 h. The mixture was then diluted with CH_2Cl_2 (50 mL) and the whole was washed with $NaHCO_3$ (sat'd aq, 2 × 50 mL), water (50 mL) and dried over Na_2SO_4. The CH_2Cl_2 was removed *in vacuo*, the residue dissolved in dry tetrahydrofuran (THF, 50 mL) and saturated with N_2. **12a** (360 mg, 0.7 mmol) in THF (30 mL) and added to the stirred solution. A catalytic amount of *p*-toluenesulfonic acid (30 mg) was then added and the mixture was stirred under N_2 for 48 h. *o*-Chloranil (176 mg, 0.7 mmol) was then added and the mixture stirred overnight. Triethylamine (Et_3N, 4 mL) was added and the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and run through a short plug of silica using EtOAc as the eluant. Zinc was then inserted *via* the usual method.[6] The product was purified by column chromatography (CH_2Cl_2/hexane, 1 : 1) followed by CH_2Cl_2 to produce **7b** (40 mg, 5%) as fine purple crystals, mp > 350 °C (from CH_2Cl_2/methanol); δ_H (300 MHz; $CDCl_3$) 9.96 (2H, s, H1), 7.75 (2H, t, H13), 7.55 (2H, d, H14), 7.30 (4H, m, H11, H12), 5.70 (2H, d, *J* 9, γH;), 4.54 (2H, t, *J* 8, βH), 4.20 (2H, d, *J* 9, αH), 4.12 (4H, t, *J* 6, H16), 3.89 (8H, m, H4), 3.30 (4H, t, *J* 6, H17), 3.06 (4H, m, H19), 2.73 (4H, m, H18), 2.50 (12H, s, H7), 2.16 (8H, m, H5′), 1.76 (8H, m, H6′), 1.50–1.41 (16H, m, H7′, H8′), 0.92 (12H, t, H9′); *m*/*z* (ESI) 1249.6630, $C_{78}H_{96}N_4O_6Zn$ requires 1249.6621 $[M + H]^+$.

[2,8,12,18-Tetrahexyl-3,7,13,17-tetramethyl-5,15{2,2′-[2″-{2‴-[2⁗-(1⁗⁗,5⁗⁗-naphthoxy)ethoxy]ethoxy}ethoxy]diphenyl}porphyrinato]zinc(II) 6b

The dipyrromethane dicarboxylate[20] (600 mg, 1.39 mmol) was added to degassed trifluoroacetic acid (5 mL) and stirred with regular degassing, under N_2 for 1 h. The mixture was then diluted with CH_2Cl_2 (50 mL) and the whole was washed with $NaHCO_3$ (2 × 50 mL), water (50 mL) and dried over Na_2SO_4. The CH_2Cl_2 was removed *in vacuo*, the residue dissolved in methanol (60 mL) and saturated with N_2. Dialdehyde **12b**[3] (360 mg, 7×10^{-1} mmol) in THF (20 mL) was added together with a catalytic amount of trichloroacetic acid (30 mg) and the mixture was left to stir under N_2 for 5 h. *o*-Chloranil (176 mg, 0.7 mmol) was then added and the mixture stirred for 14 h. Et_3N (4 mL) was added and the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and passed through a short plug of silica using EtOAc as the eluant. Zinc was then inserted *via* the usual method. The product was purified by column chromatography (CH_2Cl_2/hexane, 1 : 1) and CH_2Cl_2 to yield porphyrin **6b** (200 mg, 21%) as a glassy purple solid, mp 331–333 °C (from CH_2Cl_2/methanol); δ_H (300 MHz; $CDCl_3$) 10.08 (2H, s, H1), 7.70 (2H, t, *J* 8, H13), 7.53 (2H, d, *J* 6, H14), 7.31 (4H, m, H11, H12), 7.02 (2H, d, *J* 9, γH), 6.34 (2H, t, *J* 8, βH), 5.35 (2H, d, *J* 9, αH), 4.09 (4H, t, *J* 6, H16), 3.94 (8H, m, H4), 3.16 (4H, t, *J* 6, H17), 2.90 (4H, m, H21), 2.73 (4H, m, 20), 2.54 (16H, bs, H19, H7), 2.47 (4H, m, H18), 2.15 (8H, m, H5), 1.74 (8H, m, H6′), 1.50–1.33 (16H, m, H7′, H8′), 0.90 (12H, t, H9′); *m*/*z* (ESI) 1337.7128, $C_{82}H_{104}N_4O_8Zn$ requires 1337.7145 $[M + H]^+$.

[2]{[2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-[2,2′-{2″-[2‴[2⁗-(1⁗⁗,5⁗⁗-naphthoxy)ethoxy]ethoxy}diphenyl]porphyrinato]zinc(II)}{cyclobis(1,4,5,8-naphthalenetetracarboxylic diimide-hexa-2,4-diyne)}catenane 13a

Glaser oxidative coupling. To dry dimethylformamide (DMF, 8 mL) were added **6a** (75 mg, 53 μmol) and bis-*N*,*N*′-(prop-2-ynyl)-naphthodiimide[16] (47 mg, 107 mmol) in an atmosphere of dry air. The stirred mixture was heated to 55 °C, anhydrous CuCl (741 mg, 7.5 mmol) and anhydrous $CuCl_2$ (173 mg, 1.3 mmol) were then added and the reaction was stirred for 2 days. The mixture was then diluted with $CHCl_3$ (100 mL), extracted with water (2 × 50 mL), dried over $MgSO_4$ and evaporated *in vacuo*. The residue was purified by Chromatotron (2 mm silica plate) using CH_2Cl_2, $CH_2Cl_2/CHCl_3$ (50%), $CHCl_3$ as the eluants. The product was recrystallised from $CHCl_3$/MeOH to yield the catenane **13a** (20 mg, 10%) as a fine purple solid, mp > 350 °C; δ_H (300 MHz; $CDCl_3$) 9.52 (2H, s, H1), 7.67 (2H, t, *J* 7, H13), 7.34 (2H, d, *J* 9, H14), 7.06 (2H, t, *J* 7, H12), 6.87 (2H, d, *J* 7, H11), 5.76 (2H, t, *J* 8, βH), 5.51 (2H, d, *J* 8, γH), 4.99 (2H, d, *J* 8, αH), 4.80 (4H, m, H16), 4.46 (8H, m, N–CH_2), 4.17 (4H, m, H17), 3.80 (8H, m, H18, H19), 3.86, 3.68 (8H, m, H4), 3.60 (4H, m, H20), 3.19 (4H, m, H21), 2.46 (12H, s, H7), 1.68 (12H, t, H5). *m*/*z* (FAB) 1792.620, $C_{106}H_{88}N_8O_{16}Zn$ requires 1792.561 $[M]^+$, 1112.460 $C_{66}H_{72}N_4O_8Zn$ requires 1112.464 $[Porphyrin]^+$.

Palladium catalysed coupling. 6a (1.35×10^{-1} mmol), bis-*N*,*N*′-(prop-2-ynyl)-1,4,5,8-naphthalene-tetracarboxylic diimide[16,27] (47 mg, 1.35×10^{-1} mmol) and $Pd(PPh_3)_2Cl_3$ (94 mg, 1.35×10^{-1} mmol) together with Et_3N (5 mL) and dry DMF (25 mL) were heated, with stirring, at 50 °C for 24 h. The solvent was then removed under high vacuum and the residue was dissolved in $CHCl_3$ (50 mL). The solution was then filtered to remove any insoluble material. The filtrate was then purified by Chromatotron (2 mm silica plate) using CH_2Cl_2, $CH_2Cl_2/CHCl_3$ (50%), $CHCl_3$ as the eluants. The first fraction was found to be starting porphyrin (73 mg), the second fraction was the catenane **13a** (29 mg) with a small band of soluble higher molecular weight material eluting with the addition of MeOH to the elution solvent. The insoluble material contained both palladium compounds and polymeric material. The product was recrystallised from $CHCl_3$/MeOH to yield **13a** as a fine purple solid (29 mg, 16%), identical in all respects to that obtained above.

[2]-{[2,8,12,18-Tetrahexyl-3,7,13,17-tetramethyl-5,15-{2,2′-[2″-{2‴-(1⁗,5⁗-naphthoxy)ethoxy]ethoxy}ethoxy]diphenyl}porphyrinato]zinc(II)}{cyclobis(1,4,5,8-naphthalenetetracarboxylic diimide-hexa-2,4-diyne)}catenane 14b

Porphyrin **7b** (70 mg, 4.8×10^{-2} mmol), bis-*N*,*N*′-(prop-2-ynyl)-1,4,5,8-naphthalenetetracarboxylic diimide[27] (10 mg, 2.88×10^{-2} mmol), $Pd(PPh_3)_2Cl_3$ (20 mg, 2.88×10^{-2} mmol) and dry DMF (5 mL) were mixed and freshly distilled Et_3N (1 mL) was added to the reaction mixture, which was then heated, with stirring, at 50 °C for 24 h. The solvent was then removed under high vacuum and the residue was dissolved in $CHCl_3$ (50 mL). The solution was then filtered to remove any insoluble material. The filtrate was then purified by column chromatography using CH_2Cl_2/hexane (9 : 1), CH_2Cl_2, $CH_2Cl_2/CHCl_3$ (1 : 1), and $CHCl_3$ as the eluants. The product was recrystallised from $CHCl_3$/MeOH to yield the catenane **14b** (15 mg, 54%) as a fine

purple solid, mp > 350 °C; δ_H (300 MHz; $CDCl_3$) 9.49 (2H, s, H1), 7.78 (2H, d, *J* 8, 'outside' diimide-H), 7.71 (2H, t, *J* 7, H13), 7.64 (2H, d, *J* 8, 'outside' diimide-H), 7.39 (2H, d, *J* 8, H14), 7.13 (2H, t, *J* 7, H12), 7.03 (2H, d, *J* 6, H11), 6.47 (2H, d, *J* 8, 'inside' diimide-H), 6.24 (2H, d, *J* 8, 'inside' diimide-H), 5.81 (2H, t, *J* 8, βH), 5.21 (2H, d, *J* 9, γH), 5.05 (2H, d, *J* 8, αH), 4.73 (4H, m, H16), 4.53 (2H, d, *J* 16.8, 'outside' N–CH_2), 4.52 (2H, d, *J* 16.8, 'outside' N–CH_2), 4.44 (2H, d, J 16.8, 'inside' N–CH_2), 4.33 (2H, d, J 16.8, 'inside' N–CH_2), 4.28 (2H, t, H17), 3.95 (2H, t, H17), 3.76 (12H, m, H4), 3.63 (4H, m, H18), 3.24 (4H, m, H19), 2.47 (12H, d, *J* 3.5, H7), 2.02 (8H, m, H5), 1.65–1.60 (8H, m, H6′), 1.48–1.32 (16H, m, H7′, H8′), 0.86 (12H, m, H9′); *m/z* (ESI) 1951.750, $C_{118}H_{112}N_8O_{14}Zn$ requires 1951.749 $[M + Na]^+$, 1929.76 $[M + H]^+$, 1207.3 [Porphyrin − Zn + $Na]^+$.

[2]-{[2,8,12,18-Tetrahexyl-3,7,13,17-tetramethyl-5,15-{2,2′-[2″-{2‴-[2⁗-(1⁗″,5⁗″-naphthoxy)ethoxy]ethoxy}ethoxy]diphenyl}-porphyrinato]zinc(II)}{cyclobis(1,4,5,8-naphthalenetetracarboxylic diimide-hexa-2,4-diyne)}catenane 13b

Porphyrin **6b** (100 mg, 7.47×10^{-2} mmol), bis-*N*,*N*′-(prop-2-ynyl)-1,4,5,8-naphthalene-tetracarboxylic diimide[27] (20 mg, 5.6×10^{-2} mmol), $Pd(PPh_3)_2Cl_2$ (40 mg, 5.6×10^{-2} mmol) and dry DMF (5 mL) were mixed and freshly distilled Et_3N (1 mL) was added to the reaction mixture, which was then heated, with stirring, at 50 °C for 24 h. The solvent was then removed under high vacuum and the residue was dissolved in $CHCl_3$ (50 mL). The solution was filtered to remove any insoluble material. The filtrate was then purified by column chromatography using CH_2Cl_2/hexane (9 : 1), CH_2Cl_2, CH_2Cl_2/$CHCl_3$ (1 : 1), and $CHCl_3$ as the eluants, to give the catenane **13b** (35 mg, 60%), mp > 350 °C; δ_H (300 MHz; $CDCl_3$) 9.49 (2H, s, H1), 7.66 (2H, t, *J* 7, H13), 7.32 (2H, d, *J* 8, H14), 7.06 (2H, t, *J* 7, H12), 6.86 (2H, d, *J* 6, H11), 5.74 (2H, t, *J* 8, βH), 5.52 (2H, d, *J* 9, γH), 4.97 (2H, d, *J* 8, αH), 4.77 (4H, m, H16), 4.44 (8H, m, N–CH_2), 4.15 (4H, t, *J* 4.5, H17), 3.76 (12H, m, 4, H19), 3.59 (8H, m, H18, H20), 3.17 (4H, m, H21), 2.44 (12H, s, H7), 2.04 (8H, m, H5), 1.67 (8H, m, H6′), 1.47–1.33 (16H, m, H7′, H8′), 0.90 (12H, t, H9′); *m/z* (ESI) 2039.796, $C_{122}H_{120}N_8O_{16}Zn$ requires 2039.801 $[M + Na]^+$, 2017.819 requires 2017.819 $[M + H]^+$, 1956 requires 1955.4 $[M - Zn + H]^+$, *ca.* 701 requires 702.1 [diimide macrocycle + $Na]^+$, *ca.* 657 requires 656.1 [diimide macrocycle-$C_2]^+$.

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