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Neutral Donor–acceptor Porphyrin-stoppered [2]Rotaxanes

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A series of porphyrin-stoppered [2]rotaxanes incorporating neutral naphthodiimide and dinaphtho-crown ether subunits have been assembled using Pd-catalysed coupling reactions and by acylations of hydroxy and amino functions on the porphyrin stopper units. This establishes the methodology for the production of more complex systems which can be addressed by the porphyrin components.

Keywords: Porphyrin-stoppered [2]rotaxanes; Naphthodiimide; Dinaphtho-crown ether; Catenanes; Rotaxanes 2

INTRODUCTION

For the fabrication of a variety of mechanically interlocked molecules including rotaxanes and catenanes, templating by non-covalent interactions has been the underlying principle of the process of self assembly [1]. In many of these syntheses, donor–acceptor interactions (D → A) of the charged and neutral types are incorporated as recognition factors, usually supplemented by other interactions such as dipole–dipole, H-bonding, metal ion coordination or electrostatics. A donor–acceptor pair of suitable geometric and interactive complementarity [2] can lead to pseudorotaxanes, potential precursors for the synthesis of variety of [*n*]catenanes and [*n*]rotaxanes. The Stoddart group has pioneered the use of charged donor–acceptor interactions [3–8], while Sanders and co-workers have concentrated on the use of neutral donor–acceptor interactions [9–12] invariably incorporating pyromellitic and naphthalene diimides and naphtho-crown ethers for the synthesis of a number of [2]catenanes and [2]rotaxanes.

For functional and dynamic systems, an addressable unit needs to be incorporated into the design. In many instances porphyrins have been utilised as this unit, allowing for a variety of possible stimuli as trigger functions [13–21]. Indeed several porphyrin-diimide systems have been designed to take advantage of the complementary donor–acceptor interactions of the two types of sub-units, and the photoelectron and energy transfer characteristics of these systems have been studied especially with respect to photoinduced charge-separation and charge-recombination processes [11,22–24].

RESULTS AND DISCUSSION

Following our successful synthesis of both charged and neutral porphyrin-containing catenanes utilising both the Stoddart and Sanders methodology [21,25–30], it was of interest to extend these concepts to the construction of porphyrinic [2]rotaxanes. The donor–acceptor pair of an electron-deficient naphthalene diimide derivative **ND** and an electron-rich DN38C10 crown ether **1**, was incorporated into the fundamental design principles relying on charge-transfer (CT) interaction between the π-donor and π-acceptor [31] complementary components. Diimide **2** has been employed by Sanders et al. [11] as a component of catenanes of type (i) (Fig. 1) and we have extended this to the synthesis of novel porphyrin-containing catenanes of type (ii) (Fig. 1) [30]. In the present study, we report the formation of neutral porphyrin-based [2]rotaxanes incorporating a naphthalene diimide as the central recognition unit of the linear components of the rotaxane with a crown ether encircling it and with two free-base porphyrinic groups at the terminals as stoppers (iii) (Fig. 1).

The ring closing reactions for both catenanes (i) [11] and (ii) [30] (Fig. 1) were carried out via either the Glaser oxidative coupling or Pd-mediated

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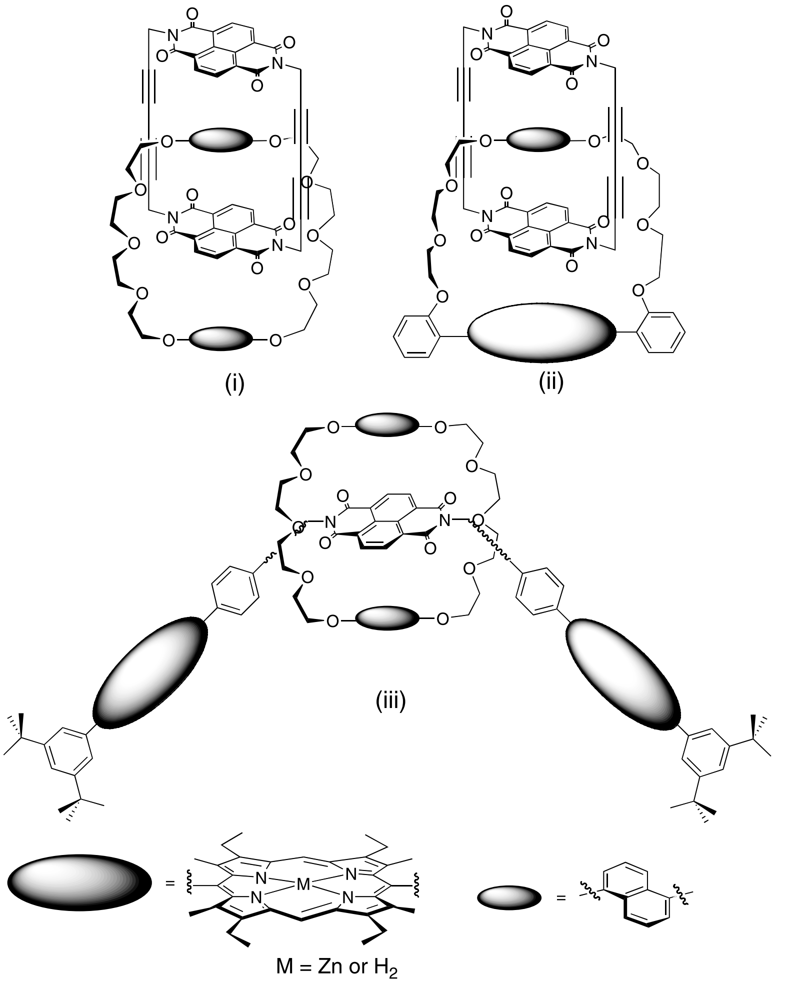
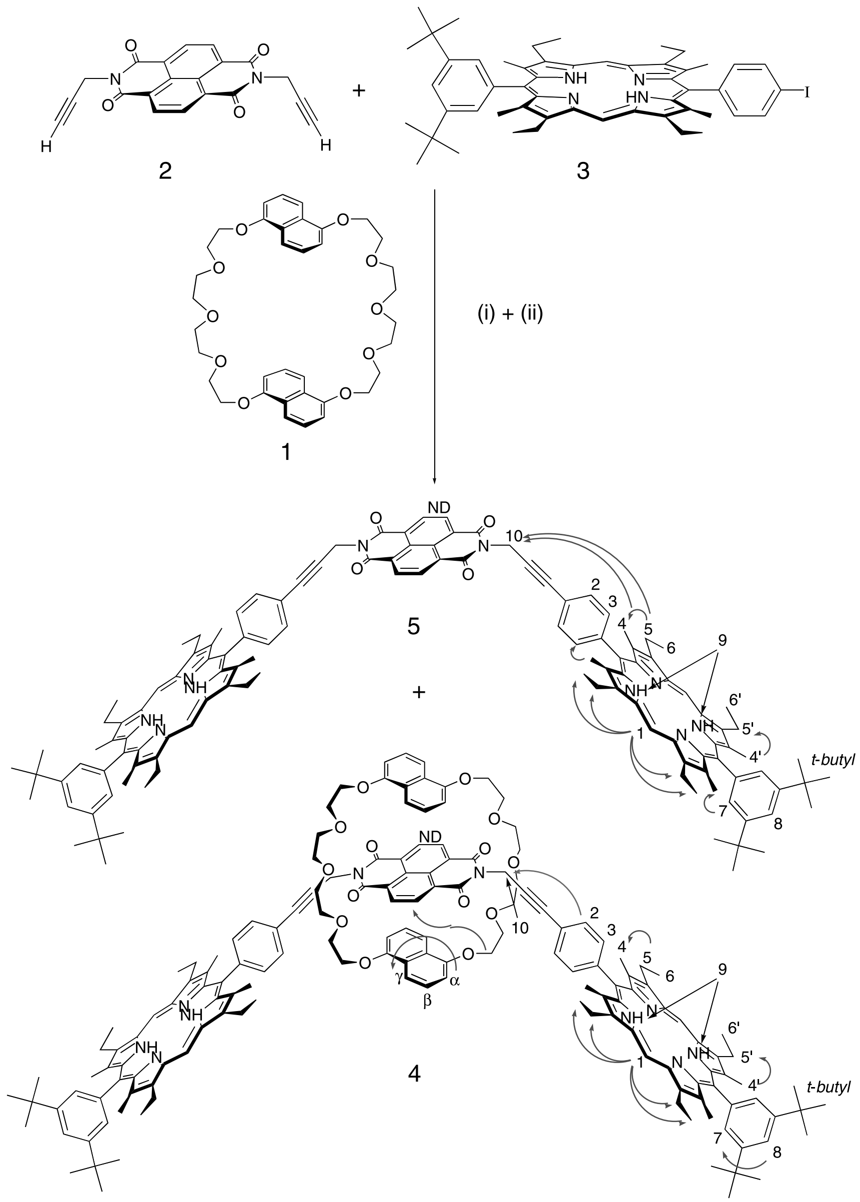


FIGURE 1 Conceptual evolution of the porphyrin-stoppered rotaxanes (iii) described in this work from previous neutral donor–acceptor catenanes incorporating naphthodiimide and naphthoquinol-crown ethers employed by Sanders [5] (i) and subsequently extended by us [9] to incorporate a porphyrin sub-unit (ii).

coupling reactions [32]. We have found that the latter procedures are preferable for our porphyrinic systems, and thus rotaxane **4** was prepared by the cross-coupling (DMF, Et_3N, $AsPh_3$, $Pd_2(dba)_3$) between a *meso*-substituted porphyrin aryl halide **3** with propynyl naphthalene diimide **2** in the presence of an excess of the crown DN38C10 **1** (Scheme 1) [32].

Although the coupling reactions under a variety of conditions invariably produced much intractable material, rotaxane **4** and thread component **5** were isolated (4% and 8% respectively). The ES mass spectrum of **5** clearly indicated a parent ion peak $[M + H]^+$ ($m/z = 1824.034$, calcd. 1824.035) and $[M + 2H]^{2+}$ (m/z 913.5, calcd. 913.5), while the rotaxane **4** revealed a peak corresponding to the doubly charged ion, $[M + 2H]^{2+}$ ($m/z = 1231.672$, calcd. 1231.660).

Comparison of the ^{1}H NMR spectra of all components of the rotaxane including the crown, the stopper moieties and the capped thread unit with the complete rotaxane reveals some interesting phenomena. The spectra are compared in Figs. 2 and 3. For the open stoppered thread unit **5**, shifts in the porphyrin resonances might be explained in terms of replacing an iodide with the propargyl group. However, the diimide (ND), propargyl methylene (H10) and the inner porphyrin NH (H9) all show significant shielding. The chemical shifts for these protons are also concentration-dependent, moving downfield towards their more expected positions on dilution. Further, for more concentrated solutions, besides the expected NOE and ROESY correlations at the porphyrin (for example betweeen the *meso* (H1) and adjacent ethyl group protons, and between methyl and ethyl substituents), there is a significant NOE correlation between the propargyl methylene (H10) and the methyl (H4) and ethyl methylene (H5) of the porphyrin (Scheme 1). This indicates an intermolecular interaction in solution for **5**, and is consistent with a conformation in which either U-shaped or step-like molecules mutually interact by stacking so that the diimide unit of one shields the



SCHEME 1 Reagents and conditions: i) DMF:Et$_3$N (5:1), N$_2$ atm, 40°C, 30 mins; ii) AsPh$_3$, Pd$_2$(dba)$_3$, N$_2$ atm, 12 h. Arrows indicate significant NOESY and ROESY correlations.

porphyrin unit of the next molecule (the rigid nature of the propargyl, porphyrin and diimide units would prevent any possibility of intramolecular interactions through folding). This places the H10 methylenes close to the porphyrin periphery of the adjacent molecule, resulting in the observed NOE, and explains the mutual shielding of the ND and H9 protons. Smaller shifts of the other protons are also consistent with such a stacked arrangement.

On formation of the rotaxane, any intermolecular stacking interactions between thread units is now prevented, and the chemical shifts of rotaxane **4** are more as expected, and are not concentration-dependent. For instance, the chemical shift differences of the resonances for the α, β, γ crown protons ($\Delta\delta$ -0.17, -0.20 and -0.74 ppm respectively) and the ND rotaxane protons ($\Delta\delta$ -0.31 ppm) reflect the shielding of the diimide ring by the crown naphthoquinol units, which is also consistent with a structure in which the diimide is co-facially stacked with the latter. The propargyl methylenes (H10) are now moved downfield by $+0.33$ ppm, and there is now no detectable NOE correlations with any other protons. The chemical shifts of the porphyrin inner NH protons have now returned to a similar value to the component stopper units. Importantly, there are now inter-component NOE correlations between the crown methylene protons closest to the naphthalene rings and the diimide ND protons (Scheme 1).

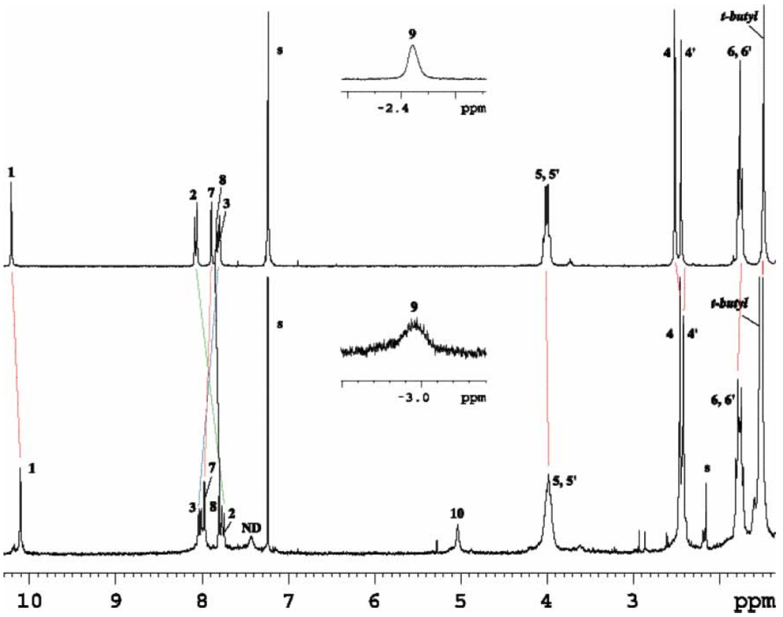


FIGURE 2 ^{1}H NMR spectra ($CDCl_3$) of porphyrin aryl iodide precursor **3** (top) and thread component **5** (bottom) (303 K, 300 MHz).

Because of its limited solubility and the low yields of the rotaxane **4** obtained by this route which might be due to steric crowding between the pre-formed pseudorotaxane and the stopper reactants, a more generally applicable route to these types of rotaxanes was investigated. Certainly the compact nature of **4** would preclude any useful dynamic studies, although the methodology could be utilised in the production of more extended and multifunctional molecular nanostructures, which was the main aim of this synthetic study. Thus, the axle component was modified to incorprate a longer tetraethyleneoxy unit with a view to enhanced solubility and a longer chain **6** (Scheme 2). Attachment of the stoppers was then via ester or amide linkages.

For the preparation of [2]rotaxanes **9** and **10**, acyl chloride condensations of **6** and either *m*-hydroxyphenylporphyrin **7** or *p*-aminophenylporphyrin **8** were carried out in the presence of crown ether DN38C10 **1** at −45°C (Scheme 2).

Purification of the crude mixtures[†] afforded rotaxanes **9** and **10** in 4% and 5% yields, respectively. They were characterised in a similar fashion to **4** and **5**. ES mass spectrometry yielded mass peaks corresponding to the doubly charged ions for the intact rotaxanes in each case. The low yields of the rotaxanes in these and the previous systems are indicative perhaps of a weak interaction between the precursor diimide strap units and the crown which is necessary for effective preorganisation of the components prior to the capping by the porphyrins. This may be due in part to a competitive stacking interactions between the diimides and porphyrin units in the reaction mixture, which might hinder complexation by the crown. Indeed, a more detailed study of the folding of the porphyrin-terminated strap units as a result of relatively strong diimide–porphyrin interactions is the subject of an on-going study to be reported elsewhere.

As for the propyne-linked rotaxane **4**, the observed ^{1}H NMR shifts in the spectrum of rotaxane **9** (Fig. 3) are consistent with the expected rotaxane structure (Scheme 2) reflecting the mutual shielding of the diimide and crown naphthoquinol units. In comparison to rotaxane **4**, however, the crown aromatic protons of **9** and **10** were shifted further upfield relative to those of **4**. Further evidence for the formation of the rotaxanes are ^{1}H NMR NOE and ROESY correlations between the ND protons and the crown methylenes (Scheme 2) as well as between axle methylene protons and crown macrocycle H-26 protons and to the H-32 and 33 protons. In these cases there were no NOE cross-peaks observed between any of the porphyrin resonances and those of the crown, indicating an extended conformation in solution.

Upfield shift of the bound naphthodiimide (ND) protons ($\Delta\delta$ −0.54 and −0.50 ppm for the two rotaxanes compared to the non-rotaxane thread) and for the α, β, γ crown protons in **9** and **10** ($\Delta\delta$ −0.47, −0.53 and −0.95 ppm for **9** and −0.45, −0.50 and

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[†] Other products from the the rotaxane **9** and **10** mixtures were the crown-free bis- and mono- ester- and amide-linked porphyrin stoppered adducts, together with a quantity of intractable and unidentified material. We were not able to isolate any fractions which showed evidence of any higher level rotaxanes or isolable porphyrinic components.

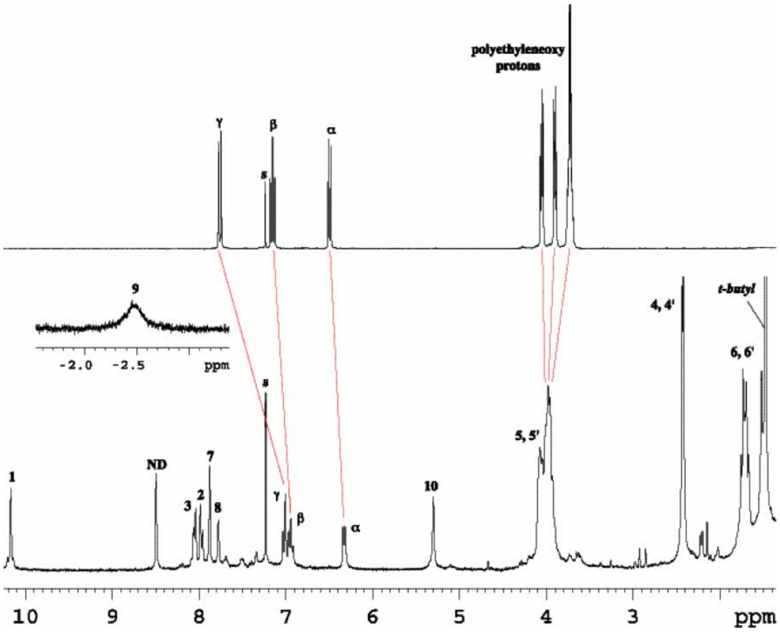


FIGURE 3 ^{1}H NMR spectra ($CDCl_3$) of DN38C10 **1** (top) and propyne-linked [2]rotaxane **4** (bottom) (303 K, 300 MHz).

−0.92 ppm for **10**) are indicative of the assigned structures. The shifts in the methylene protons are also as expected (Fig. 4). The spectra are not concentration-dependent, indicating the absence of any significant porphyrin–porphyrin φ-stacking in the rotaxanes.

Having established these methodologies for the construction of porphyrin-stoppered rotaxanes, albeit in low yields at this stage, we are now in a position to take steps to improve the efficiency and to assemble more complex systems, including multi-porphyrinic and polymer-attached assemblies, which can be driven dynamically by the repetoire of chemistry available in the porphyrin components.

EXPERIMENTAL

Rotaxane 4 and Porphyrin-stoppered Thread Unit 5

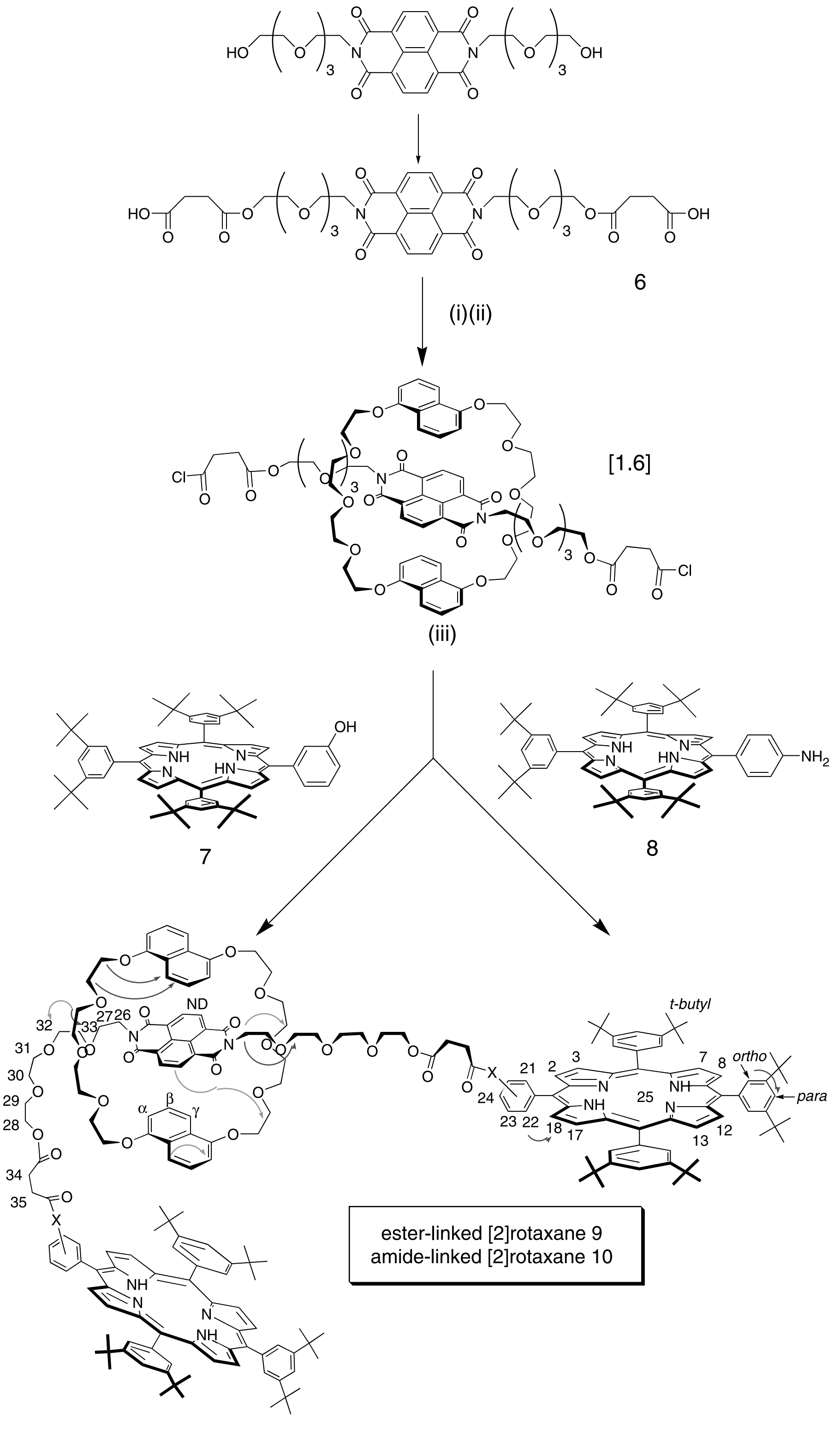
Propynyl naphthalene diimide **2** (9.84 mg, 2.88×10^{-5} mol), DN38C10 **1** (50 mg, 5.75×10^{-5} mol) were dissolved in dry DMF (13.7 mL) and Et_3N (2.7 mL). The red colour of the solutuion was indicative of a charge transfer complex formation. The solution was then warmed to 35°C and was deaerated by gently bubbling nitrogen for 30 min before $Pd_2(dba)_3$ (7.94 mg, 8.64 μmol), $AsPh_3$ (17.6 mg, 5.75×10^{-5} mol) and porphyrin **3** (73.2 mg, 11.50×10^{-5} mol) were added and the reaction was allowed to proceed under N_2 atm for 14 h. Excess DMF was removed *in vacuo*. The crude product was washed with HCl (2*M*), water and dried (Na_2SO_4), and the resulting solution was evaporated to dryness. The crude residue was initially purified by flash column chromatography (SiO_2, DCM to 5% MeOH/DCM eluants) to give (in order of elution): the phosphine by-product, excess crown **1** and other porphyrin containing fractions. A multiple purification using preparative TLC (SiO_2) was carried out to further purify the porphyrinic fractions which gave (in order of elution): rotaxane **4** (50% hexane/EtAc) and bis-adduct **5** (1% MeOH/DCM). Both products were recrystallised from MeOH/$CHCl_3$.

4: Purple solid. Yield: 2.7 mg (3.8%); Decomp. 228–232°C; m/z (ES–MS) ($C_{160}H_{174}N_{10}O_{14}$): $[M + 2H]^{2+}$ 1231.672 (calcd. 1231.660); δ_H: 10.17 (2H, s, H1), 8.50 (4H, s, ND), 8.07 (4H, d, H3), 7.99 (4H, d, H2), 7.88 (4H, s, H7), 7.78 (2H, s, H8), 7.01 (4H, d, Hγ), 6.95 (4H, t, Hβ), 6.51 (4H, d, Hα), 5.30 (4H, s, H10), 4.08 (16H, m, H5,5′), 3.98 (32H, m, OCH_2), 2.44 (12H, s, H4), 2.42 (12H, s, H4′), 1.76 (24H, m, H6,6′), 1.48 (36H, s, *t-butyl*), −2.43 (4H, br, H9).

5: Purple solid. Yield: 4.5 mg (8.4%); M.p. >350°C; m/z (ES–MS) ($C_{124}H_{130}N_{10}O_4$): $[M + H]^+$1824.034 (calcd. 1824.035); δ_H: 10.10 (2H, s, H1), 8.04 (4H, d, H3), 7.97 (4H, s, H7), 7.80 (2H, s, H8), δ 7.77 (4H, d, H2), 7.45 (4H, br, ND), 5.03 (4H, s, H10), 3.98 (16H, m, H5,5′), 2.45 (12H, s, H4), 2.41 (12H, s, H4′), 1.81 (24H, m, H6,6′), 1.52 (36H, s, *t-butyl*), −2.95 (4H, br, H9).

Naphthalene Diimide Succinic Acid Derivative 6

To the tetraethyleneoxy diol thread unit [12] (Scheme 2) (0.16 g, 2.61×10^{-4} mol) were added DMAP (3.2 mg, 2.62×10^{-5} mol), freshly distilled Et_3N (78.4 mg, 7.74×10^{-4} mol) and DCM (16 mL). Succinic anhydride (0.31 g, 3.10×10^{-3} mol) in dry THF (3–4 mL) was then added to the mixture. The mixture



SCHEME 2 Reagents and conditions: (i) $SOCl_2$ reflux, 45 min *or* $(COCl)_2$, $CHCl_3$, RT, 45 min; (ii) $CHCl_3$, Et_3N, DN38C10 **1**, N_2 atm, −45°C; (iii) porphyrin **7** or **8**, N_2 atm, dark, −45°C, 4 h. Arrows indicate significant NOESY and ROESY correlations.

was stirred for 3–4 days depending on the course of the reaction (monitored by analytical TLC). Upon completion of the reaction, excess solvent was removed and the crude product mixture was acidified (2*M* HCl), washed with water and dried over Na_2SO_4. Excess solvent was removed *in vacuo* to afford a light yellow oil, sufficiently pure for further reaction. Yield: 0.21 g (quantitative); m/z (ES–MS) ($C_{38}H_{46}N_2O_{18}$): $[M + Na]^+$841.263 (calcd. 841.264); δ_H: 8.73 (4H, s, ND), 4.44 (4H, t, H26), 4.16 (4H, t, H33), 3.84 (4H, t, H27), 3.70 (4H, t, H30), 3.62–3.58 (8H, m, H31,32), 3.56–3.51 (8H, m, H28,29), 2.55 (8H,

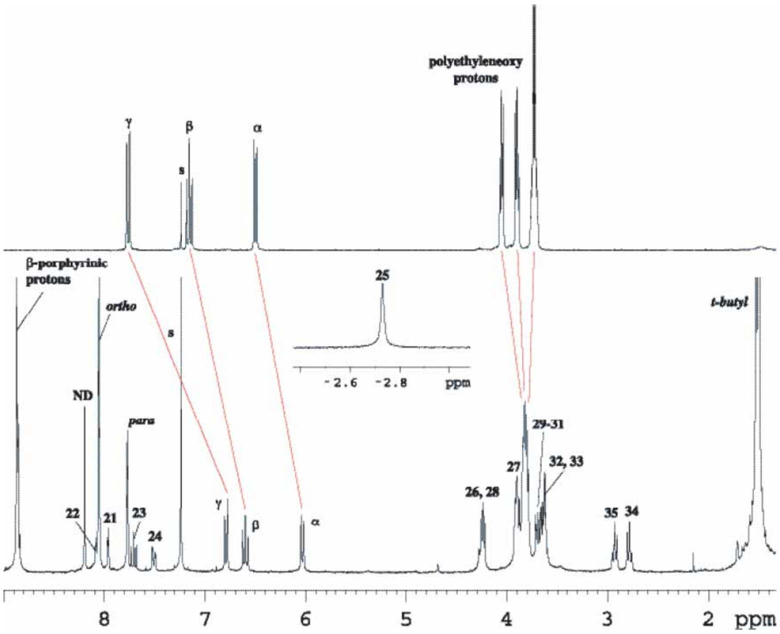


FIGURE 4 ^{1}H NMR ($CDCl_3$) spectrum of ester-linked rotaxane **9** (bottom) compared to DN38C10 **1** (top) (303 K, 300 MHz).

s, H34,35); δ_C: 176.0, 172.0, 162.9, 131.0, 126.7, 126.6, 70.6, 70.4, 70.1, 68.9, 67.8, 63.8, 39.6, 29.1, 28.9.

General Procedure for Rotaxanes 9 and 10

To dicarboxylic acid axle **6** (8.5 mg, 10.33 μmol) in $CHCl_3$ (2 mL) was added oxalyl chloride (2 mL). The reaction was stirred at RT for 45–60 min. The conversion to the acyl chloride derivative was monitored by infrared spectroscopy after removal of excess oxalyl chloride [IR ($CHCl_3$): 1788 cm^{-1} (med, C = O *str*)].

To the diacyl chloride thread formed *in situ* in dry $CHCl_3$ (3 mL) was added DN38C10 **1** and dry Et_3N (0.1 mL). The mixture was then equilibrated for 30 min while stirring at −45° C in an acetone-dry ice bath. The complexation of axle component and the crown was indicated by the typical observable bright red colour. A solution of a hydroxyphenyl or aminophenyl porphyrin (**7** or **8**) in dry $CHCl_3$ was added dropwise at −45°C and stirred for a further hour at −45° C and a further 4 hr (in the case of **9**) or 2 days (in the case of **10**) at RT. Excess solvent was removed and purification was carried out using a radial chromatotron or preparative TLC silica plates.

Rotaxane 9

Diacyl chloride of axle component **6**, DN38C10 **1** (7 mg, 10.33 μmol) and *m*-hydroxyphenyl porphyrin **7** (20 mg, 20.66 μmol). Multiple purifications were performed on radial chromatotron plates (3–5% MeOH/DCM) to afford rotaxane **9**. The rotaxane was recrystallised from MeOH/$CHCl_3$ to give a purple solid. Yield: 1.4 mg (4%); M.p. 98–99 °C; *m/z* (ES–MS) ($C_{210}H_{242}N_{10}O_{28}$): $[M + 2H]^{2+}$1677.905 (calcd. 1677.902); δ_H: 8.87–8.85 (16H, m, H2,3, 7,8,12,13,17,18), 8.19 (4H, s, ND), 8.06 (2H, d, H22), 8.05 (12H, s, H*ortho*), 7.96 (2H, s, H21), 7.78 (6H, s, H*para*), 7.71 (2H, t, H23), 7.55 (2H, d, H24), 6.80 (4H, d, Hγ), 6.62 (4H, t, Hβ), 6.04 (4H, d, *J* 6, Hα), 4.25–4.23 (8H, m, H26,33), 3.90–3.88 (4H, m, H27), 3.84–3.79 (32H, m, 16 × OCH_2), 3.72–3.64 (12H, m, H30,31,32), 3.63–3.62 (8H, m, H28,29), 2.93 (4H, t, H35), 2.80 (4H, t, H34), 1.50 (108H, s, *t-butyl*), −2.73 (4H, s, H25).

Rotaxane 10

Diacyl chloride of axle component **6**, DN38C10 **1** (9.90 mg, 15.50 μmol) and *p*-aminophenyl porphyrin **8** (30 mg, 31.10 μmol). Initial purification was carried out on a preparative plate (5% MeOH/DCM) to afford rotaxane **10**. Subsequent purification of the rotaxane mixture on preparative silica plates led to some product decomposition. Yield: 5.2%; *m/z* (ES–MS) ($C_{210}H_{244}N_{12}O_{26}$): $[M + 2H]^{2+}$1676.909 (calcd. 1676.918); δ_H: 8.85–8.83 (16H, m, H2,3,7,8,12,13,17,18), 8.31 (2H, br, H23), 8.23 (4H, s, ND), 8.18 (4H, d, H21), 8.05 (12H, s, H*ortho*), 7.95 (4H, d, H22), 7.76 (6H, s, H*para*), 6.83 (4H, d, Hγ), 6.65 (4H, t, Hβ), 6.06 (4H, d, Hα), 4.33 (8H, m, H26,33), 3.94 (4H, m, H27), 3.83–3.76 (32H, m, 16 × OCH_2), 3.73–3.64 (12H, m, H30,31,32), 3.57 (8H, m, H28,29), 2.89 (4H, t, H34), 2.85 (4H, t, H35), 1.49 (108H, s, *t-butyl*), −2.74 (4H, br, H25).

Acknowledgements

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