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Axially coordinated porphyrins as new rotaxane stoppers

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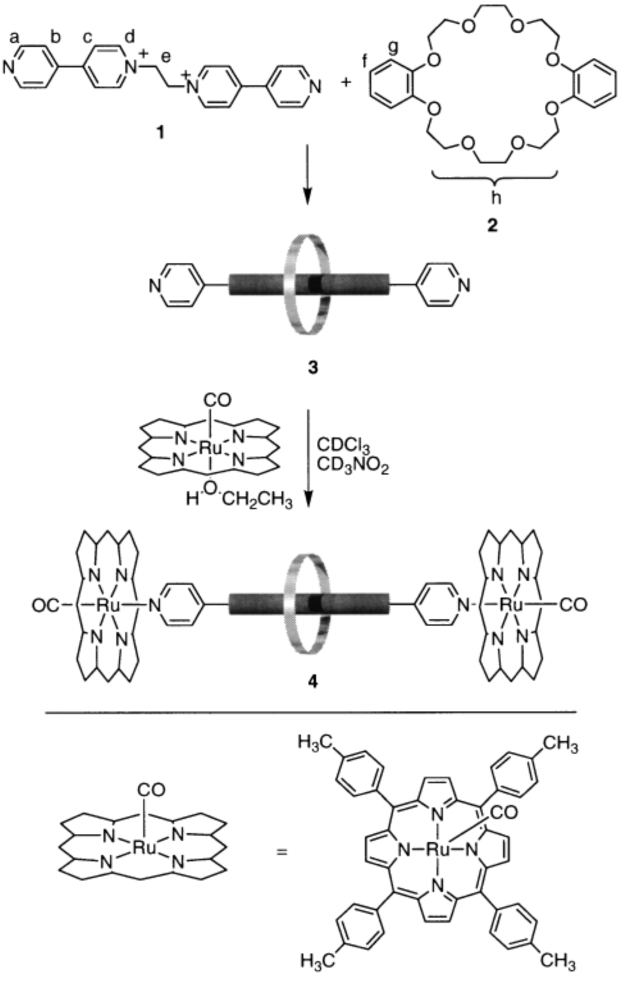
Coordination to the axial position of the metalloporphyrin Ru(TTP)(CO) is an effective means to end-cap the 1,2-bis(4,4′-dipyridinium)ethane dication·dibenzo[24]-crown-8 [2]pseudo-rotaxane and generate the stable porphyrinic [2]rotaxane 4.

In order for rotaxanes to be used effectively as architectures when building nanoscale machines and new materials, the macrocyclic wheel, once threaded onto the molecular axle, must be held there to prevent the components from disassembling.[1] This task is typically carried out by covalently fastening bulky stoppers onto the two ends of the axle. Using this strategy, pseudo-rotaxanes are transformed into permanently interlocked rotaxanes.[2] An alternative approach (slippage), which is a thermodynamically driven self-assembly process, involves the threading of a presynthesized axle through the macrocyclic wheel under the influence of appropriate heating.[3] However, the harsh reaction conditions that tend to accompany the first strategy may not be conducive for synthesizing rotaxanes containing highly sensitive molecular components. The slippage strategy is also limiting in that rotaxanes can only be prepared from axles small enough to allow for the wheel to pass over them. A recently reported solution to these problems utilizes the dynamic nature of the imine bond to end-cap pseudo-rotaxanes under thermodynamic control.[4] An alternative to using reversible carbon–heteroatom bond formation is to exploit metal-directed self-assembly synthesis, which again has the advantage of being thermodynamically driven but is accomplished more rapidly and under milder conditions. Despite its being introduced almost two decades ago, there are few examples that utilize this approach to generate interlocking structures.[5]

The growing interest in rotaxanes containing chromophores as stoppers[6] prompted us to develop mild porphyrin-based end-capping methods. Porphyrins are particularly attractive stoppers not only because of their bulkiness, but also because of their rich electro- and photo-physical properties, which have played important roles in synthetic electron and energy transfer systems.[6] In this study, we continue to use axial coordination to the central metal of Ru(TTP)(CO)† as a means to self-assemble porphyrin arrays in light of our recent success in rapidly generating thermodynamically controlled multicomponent arrays.[7] What we sought was a pseudo-rotaxane displaying divergent Lewis-basic sites appropriately distanced from the threaded wheel so as not to interfere with the self-assembly process. The 1,2-bis(4,4′-dipyridinium)ethane dication·dibenzo[24]crown-8 [2]pseudo-rotaxane **3** recently spot-lighted by Loeb and Wisner[5] provided the suitable model rotaxane for our purpose (Scheme 1).

Dissolving equimolar amounts of **1** and **2** in a 1 : 1 mixture of $CDCl_3$ and CD_3NO_2‡ immediately generated [2]pseudo-rotaxane **3** as apparent by ^1H NMR spectroscopy. A comparison of the integrals of the signals for free and bound **1** and **2**, both of which were clearly separated in the ^1H NMR spectrum, allows for facile determination of the association constant (K_a) in the slow-exchange threading process. This value was measured to be in the range of 3000–10000 M^{-1} in the mixed-solvent system (1–3 mM solutions). We prefer to report K_a as being within a range because we found that the extent of threading was sensitive to the concentration of **1** and **2** in the sample, with the magnitude of the association constant increasing as the concentration of both components are raised.§ We attribute this unexpected concentration dependency to the trace amount of residual water in the solvents. Because the solvent shells surrounding all species (**1**–**3**) certainly can include water, it is reasonable to assume that the concentration of free and bound water would change throughout the complexation reaction at the low water concentrations found in these solutions. The result is that water cannot be eliminated from the thermodynamic equilibrium equation and will thus have a great effect on the ability to form the [2]pseudo-rotaxane **3**. In this way, the slightly hydrous nature of the solvents used affects the precision of our measurements. Our support for this suggestion comes in the observed lowering of K_a for solutions at any concentration when additional water was added to the sample. The association constants leveled out to 800–1000 M^{-1} when enough water (200–300 equivalents) was added so that its concentration remains unchanged during the threading process. Despite this, the strength of the interactions holding the interlocked components together compensates for the presence of such a competitive solvent like water.



Scheme 1 PF_6^- counter ion.

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^{1}H NMR analysis of **3** also revealed the C–H···O hydrogen bonds and π–π stacking interactions responsible for driving the threading process.[5] When 2 mol equivalents of Ru(TTP)(CO)(EtOH) are added directly to the NMR sample, signals for the hydrogen atoms of both **1** and **2** shift significantly upfield, as would be expected for protons that reside within the additive shielding cones of the porphyrin stoppers.¶ The hydrogen atoms immediately adjacent to the coordinating nitrogen are closest to the end-caps (2.7 Å average nitrogen-to-porphyrin distance) and are the most affected by the anisotropic effect (Table 1). The shielding is minimally felt by the methylene (CH_2) protons of the dication axle which are as far as 10.2 Å from the stoppers, although it is still significant ($\Delta\delta$ = 0.72 ppm). All protons on the crown ether are also shielded, the most effected being those on the phenyl ring which are 3.0 and 5.1 Å from the mean centre of the porphyrin planes.

Table 1 Selected ^{1}H NMR data (500 MHz) of **4** in $CDCl_3$–CD_3NO_2 (1:1)

	Axle fragment				Wheel fragment			
	H(a)[a]	H(b)	H(c)	H(d)	H(e)	H(f)	H(g)	H(h)
δ	1.65	5.36	6.91	8.60	5.01	5.33	5.94	3.67–3.59
$\Delta\delta^b$/ppm	−7.18	−2.14	−1.17	−0.72	−0.72	−1.37	−0.76	−0.48

[a] Atom numbering scheme refers to Scheme 1. [b] Refers to upfield shifts of the protons relative to those in the spectrum of [2]pseudo-rotaxane **3**.

Addition of an excess of a competitive Lewis basic solvent such as pyridine to solutions of **4** resulted in the quantitative displacement of the stoppers as Ru(TTP)(CO)(py) and the regeneration of the dynamic mixture of pseudo-rotaxane **3** and the non-threaded wheel and axle. This study reveals the dynamic nature of the end-capping process.

Crystals of [2]rotaxane **4** suitable for structure determination were obtained by treating acetone solutions of **1** with excess **2**, end-capping the quantitatively formed [2]pseudo-rotaxane **3** with 2 mol equivalents of Ru(TTP)(CO)(EtOH), followed by slow evaporation. The crystal structure‖ (Fig. 1) is consistent with the binding interactions observed in the ^{1}H NMR spectrum. All methylene protons of **1** are within hydrogen bond distances to the oxygen atoms of the crown ether (average C···O distance = 3.54 Å). Also, the phenyl rings of the crown ether wheel are lying parallel to the heterocycles of the axle within π–π stacking range (mean Ar–Ar distance = 3.4 Å). The crystal structure shows that the distance between the porphyrin walls [Ru(1)···Ru(2) 21.692(3) Å] is just enough to accommodate the entire crown ether fragment without sacrificing any of the favourable π–π stacking interactions between the wheel and the axle.

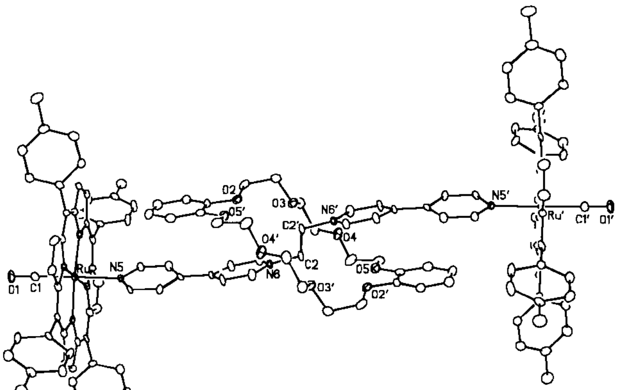

Fig. 1 Molecular structure of [2]rotaxane **4** in the crystal. The thermal ellipsoids are drawn at the 20% probability level.

We have shown that axial coordination is an effective self-assembly method to convert dynamic [2]pseudo-rotaxanes into stable interlocked [2]rotaxanes. The stoppers can be removed under mild conditions by treating **4** with the appropriate solvent. This end-capping strategy will be useful when removable stoppers are desired. Photochemical studies are underway in order to evaluate the influence the porphyrins have on the charge transfer process that has already been observed in the [2]pseudo-rotaxane.[5]

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Notes and references

† TTP = 5,10,15,20-tetratolylporphyrinato dianion.

‡ Although the [2]pseudo-rotaxane is soluble in single-solvent systems such as nitromethane and acetonitrile, the poor solubility of Ru(TTP)(CO)(EtOH) in nitromethane alone eliminated the possibility of using this solvent. Acetonitrile was avoided as its nitrogen atom effectively competes as a Lewis base with those on **1** for coordinating to the transition metal. Once formed, however, the [2]rotaxane **4** is freely soluble in organic solvents alone such as $CHCl_3$ and CH_2Cl_2.

§ Representative K_a values were measured to be 4161 M^{-1} (1.2 mM solution), 4647 M^{-1} (2.2 mM solution) and 9356 M^{-1} (3.3 mM solution).

¶ Rotaxane **4** was also characterized by IR and ES-MS.

‖ *Crystal data* for **4**: $C_{166.5}H_{169}F_{12}N_{12}O_{17.5}P_2Ru_2$, M = 3110.22, monoclinic, space group $P2_1/n$ (a non-standard setting of $P2_1/c$ (no. 14)], a = 11.655(2), b = 30.385(5), c = 24.340(4) Å, β = 103.745(3)°, V = 8373(2) Å^3, T = −80 °C, Z = 2, μ = 0.276 mm^{-1}, number of reflections = 41325; number of independent reflections = 17184, $R_1(F)$ = 0.0877 [for 4929 data with $F^2 \geqslant 2\sigma(F^2)$], $wR_2(F^2)$ = 0.2673 (all data).

CCDC 182/1594. See http://www.rsc.org/suppdata/cc/b0/b001259i/ for crystallographic files in .cif format.

1 L. Flamigni, N. Armaroli, F. Barigelletti, J.-C. Chambron, J.-P. Sauvage and N. Solladie, *New J. Chem.*, 1999, **23**, 1151 and references therein.
2 Previously employed stoppers include: phosphines, S. J. Rowan and J. F. Stoddart, *J. Am. Chem. Soc.*, 2000, **122**, 164; calixarenes, C. Fischer, M. Nieger, O. Mogck, V. Bohmer, R. Ungaro and F. Vogtle, *Eur. J. Org. Chem.*, 1998, 155; fullerenes, N. Armaroli, F. Diederich, C. O. Dietrich-Buchecker, L. Flamigni, G. Marconi, J.-F. Nierengarten and J.-P. Sauvage, *Chem. Eur. J.*, 1998, **4**, 406; ferrocene, A. C. Benniston, A. Harriman and V. M. Lynch, *J. Am. Chem. Soc.*, 1995, **117**, 5275; saccharides, C. Kauffmann, W. M. Muller, F. Vogtle, S. Weinman, S. Abramson and B. Fuchs, *Synthesis*, 1999, 849; T. Schmidt, R. Schmieder, W. M. Muller, B. Kiupel and F. Vogtle, *Eur. J. Org. Chem.*, 1998, 2003; dendrimers, D, B. Amabilino, P. R. Ashton, V. Balzani, C. L. Brown, A. Credi, J. M. J. Frechet, J. W. Leon, F. M. Raymo, N. Spencer, J. F. Stoddart and M. Venturi, *J. Am. Chem. Soc.*, 1996, **118**, 12 012; trityl, C. Heim, A. Affeld, M. Nieger and F. Vogtle, *Helv. Chim. Acta.*, 1999, **82**, 746.
3 F. M. Raymo, K. N. Houk and J. F. Stoddart, *J. Am. Chem. Soc.*, 1998, **120**, 9318.
4 S. J. Rowan and J. F. Stoddart, *Org. Lett.*, 1999, **1**, 1913; S. J. Cantrill, S. J. Rowan and J. F. Stoddart, *Org. Lett.*, 1999, **1**, 1363.
5 For examples of using coordination chemistry to interlock rotaxanes, see: S. J. Loeb and J. A. Wisner, *Chem. Commun.*, 1998, 2757; S. J. Loeb and J. A. Wisner, *Angew. Chem., Int. Ed.*, 1998, **37**, 2838; D. J. Cárdenas, P. Gaviña and J.-P. Sauvage, *Chem. Commun.*, 1996, 1915; A. P. Lyon and D. H. Macartney, *Inorg. Chem.*, 1997, **36**, 729 and references therein. For examples to interlock catenanes, see: M. Fujita, *Acc. Chem. Res.*, 1999, **32**, 53; A. C. Try, M. M. Harding, D. G. Hamiltion and J. K. M. Sanders, *Chem. Commun.*, 1998, 723. For examples to link rotaxanes into oligomers and necklaces, see: S.-G. Roh, K.-M. Park, G.-J. Park, S. Sakamoto, K. Yamaguchi and K. Kim, *Angew. Chem., Int. Ed.*, 1999, **38**, 638; D. Whang, K.-M. Park, J. Heo, P. Ashton and K. Kim, *J. Am. Chem. Soc.*, 1998, **120**, 4899.
6 N. Solladie, J.-C. Chambron and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1999, **121**, 3684; M.-J. Blanco, M. C. Jimenez, J.-C. Chambron, V. Heitz, M. Linke and J.-P. Sauvage, *Chem. Soc. Rev.*, 1999, **28**, 293; F. Vogtle, F. Ahuis, S. Baumann and J. L. Sessler, *Liebigs Ann. Rec.*, 1996, 921; R. Ishin and A. E. Kaifer, *J. Am. Chem. Soc.*, 1991, **113**, 8188.
7 K. Chichak and N. R. Branda, *Chem. Commun.*, 1999, 593.