Thermodynamically self-assembling porphyrin-stoppered rotaxanes

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A variety of porphyrin-stoppered rotaxanes has been assembled under conditions of thermodynamic reversibility by judicious choice of components and temperatures. An admixture of a thread unit comprising a central naphthodiimide with terminal pyridines (**2a**), a ring unit dinaphtho-38-crown-10 (**1**) and either Zn^{II} (**3a**), Ru^{II} (CO) (**3b**) or Rh^{III} I (**3c**) as stoppers was shown to form an equilibrating mixture of pseudorotaxanes and the porphyrin-stoppered rotaxanes. The intact rotaxane could be crystallised from solution and chromatographed at low temperatures; at higher temperatures only a mixture of the components separated on chromatography. ^{1}H NMR revealed NOE correlations between all three components for the rotaxane, and exchange peaks for related free and complexed species. The temperature and concentration dependence of the equilibria were studied by NMR methods, and van't Hoff plots for the Ru(CO) stoppered system enabled an estimation of ΔH° and ΔS°, -41.4 kJ mol^{-1}, and -95 J K^{-1} mol^{-1}, respectively, and a K_a at 273 K of 790 M^{-1}, rising to 5.39×10^4 M^{-1} at 223 K. For the unstoppered pseudorotaxane systems **1**–**2a** and **1**–**2b**, the $R \ln K$ *vs.* $1/T$ plots were not linear, implying a temperature-dependent ΔH and a non-zero ΔC_p, indicative of a folding/unfolding of the extended thread unit on complexation. Nevertheless, although the thermodynamic stability of the overall rotaxane is expected to be comparable to that of the pseudorotaxane, there is clearly an enhanced kinetic barrier for formation of the metalloporphyrin-stoppered rotaxanes, but not for the more labile zinc analogue. While mixing of all three components of the rotaxanes at room temperature resulted in rapid rotaxane assembly irrespective of the order of addition (thermodyamic control), it was shown that at low temperatures it was possible to "lock out" or "lock on" the central thread unit under conditions of kinetic control. These concepts were further extended to the assembly of more complex multi-porphyrin arrays, where the central ring unit is a naphthocrown-strapped zinc porphyrin. It is therefore possible to use the kinetics of the remote event (metal ligation/coordination) to control the overall kinetics of rotaxane formation.

Introduction

As the sophistication and complexity of supramolecular systems increase, simplicity in assembly and synthesis assumes an ever more important role; this has been matched by moves towards the production of modular components that can be assembled readily and predictably. Product selection through thermodynamic preference is a key concept in these approaches and there have been many examples where these principles have been demonstrated, such as in helicates,[1] macrocyclic synthesis,[2,3] thermodynamic templating for cyclic oligomer formation,[4] molecular amplification in a dynamic combinatorial library,[5] cyclic porphyrin dimers,[6] large polyhedral capsules,[7,8] and catenane formation.[9–11] Porphyrin-containing systems of increasing complexity can also be assembled through self-assembling, reversible processes to produce intricate shapes and motifs, including squares,[12] three-dimensional arrays and tapes,[13–15] ladders,[16,17] wires[18] and various multi-metal assemblies;[19–22] and more recently an elegant application of non-covalent assembly through a combination of hydrogen bonding and porphyrin coordination has resulted in the guest-templated selection of an intricate receptor in a thermodynamically equilibrating combinatorial mixture.[23] We now illustrate how similar principles can be applied to rotaxane assembly as an efficient and rapid route to porphyrin-based multicomponent systems that have particular relevance to photophysical electron and energy-transfer systematics.[24,25] We also show how the kinetics of rotaxane assembly can be influenced by remote metal complexation/decomplexation events.

Pseudorotaxane formation inherently involves non-covalent and thus reversible assembly of the components. Conversion into a more or less permanently interlocked rotaxane *via* the stoppering approach is usually achieved under kinetic control for covalent attachment of the required bulky end-groups. On the other hand, an alternative so-called slippage approach is based on thermodynamic control with heating necessary to overcome the forward kinetic barrier while preventing dethreading through the reverse process with its higher activation barrier. Obviously, the success of this approach relies critically on the size selection process that matches the dimensions of the ring with the stoppers. This is a serious limitation for systems in which porphyrins are to be used as potentially photo- and electro-active stoppers. More recently, an alternative approach to self-assembly of rotaxanes under conditions of thermodynamic reversibility using imine chemistry has been reported;[26] in the resulting rotaxane it was demonstrated that exchange of stoppers could be effected under kinetic control without dethreading.[27] On the other hand, metal–ligand coordination can be employed for thermodynamic control[26] and this has been a successful strategy for a variety of pseudorotaxane and rotaxane-like structures, either as a method for

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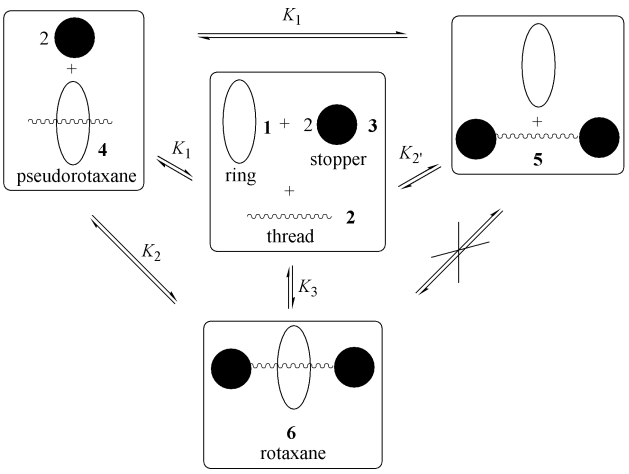
attaching stoppers in cyclodextrin-based[28–30] and other systems,[31,32] or for assembling the ring unit around a pre-formed thread in a clipping approach.[33] Sauvage and co-workers have extensively used templating metal ions around a central coordination site to assemble porphyrin-stoppered rotaxanes and catenanes.[34–37] Nevertheless, the stoppering of a pre-formed pseudorotaxane *via* porphyrin axial coordination chemistry had not been described until very recently, when Branda and co-workers[38] reported such a system at the same time that we had independently been investigating similar strategies.

However, in all of these processes, the distinction between rigorously defined terms rotaxane and pseudorotaxane becomes blurred, and to some extent such a definition requires inclusion of a time-frame; these factors have been recognised previously,[39] where for example a pseudorotaxane in solution can be considered a rotaxane in its corresponding solid state structure. It is also interesting that for the ionic rotaxane structures reported by Branda and co-workers[38] there was an added complication of a solvent dependence of the equilibrium constant for the pseudorotaxane, but no corresponding values were reported for the porphyrin-stoppered system. Hence no comparison of the thermodynamic parameters for the two systems was presented, and the solution state dynamics was not discussed. We intended to investigate more fully the solution dynamics of the self-assembly process of rotaxanes using axial coordination chemistry of a variety of metalloporphyrins as stoppers, and the results are reported here.

Results and discussion

For a modular thermodynamic approach to self-assembled rotaxane structures the equilibria in Scheme 1 need to be considered, where both threading and stoppering are reversible processes. We have chosen components with dimensions such that it can reasonably be assumed that $K_{2'}$ and K_2 (coordination at the termini of the thread unit) would not be significantly different; this implies the absence of any cooperativity or repulsive interactions between coordination of the porphyrin stoppers within the pseudorotaxane structure compared to the uncomplexed thread.[40] In this case it can easily be shown by manipulation of the equilibrium expressions that the overall formation constant $K_3 = K_1$. Nevertheless, the kinetic barriers for each process will be very different, as it is clear that direct complexation/decomplexation of the pre-stoppered thread cannot take place, and can only occur *via* the stepwise process of coordination/decoordination of the thread and the metalloporphyrin; this is a classic case of the distinction between thermodynamic stability *vs.* kinetic lability, and is illustrated schematically in Fig. 1.



Scheme 1

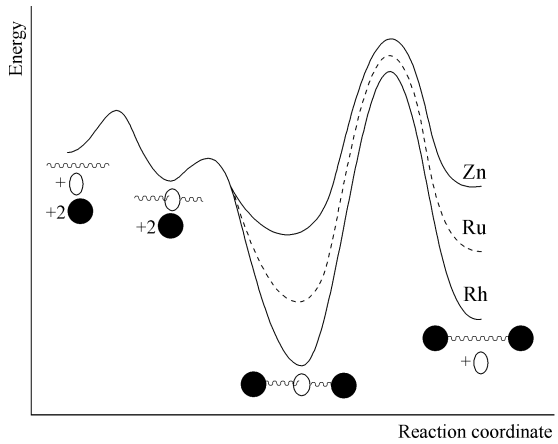
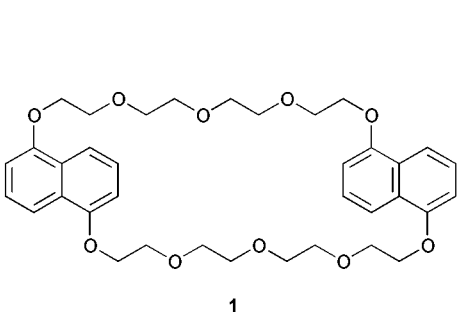


Fig. 1 Schematic energy profiles for the processes depicted in Scheme 1, illustrating the essential differences between the Zn, Ru(CO), and RhI porphyrin stopper units in the assembly of the rotaxanes **6**.

For our purposes we chose a thread **2a** with a naphthodiimide as a central recognition component and pyridines as terminal ligands,[41] while the ring **1** was the naphthocrown ether dinaphtho-38-crown-10 (DN38-C-10). **2a** was synthesized from the corresponding substituted naphthodiimide and nicotinic acid chloride.[41] It has been well established that neutral diimides of the type **2** bind effectively to DN38-C-10 through a combination of electrostatic, hydrogen-bonding and donor–acceptor interactions resulting from π–π stacking, and these components have been employed for a variety of interlocked systems.[9,10,41,42] For the detachable stoppers **3** the choice was between zinc **3a**, Ru^{II}(CO) **3b** and Rh^{III}I **3c** complexes of the readily soluble and sterically demanding *meso*-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin. Thus the target rotaxanes were **6a–6c**.

Zinc porphyrins form five-coordinate labile complexes with nitrogen donor ligands, while the six-coordinate Ru(CO) and RhI nitrogen donor complexes are comparatively much more stable and inert.[43] For typical pyridine zinc *meso*-tetraarylporphyrins at room temperature, ligand exchange is fast on the NMR chemical shift timescale, with on-rates of more than 10^8 M s^{-1} and off-rates around 10^5 s^{-1}, giving an overall K_a ($K_{2'}$ in Scheme 1) of 10^3–10^4 M^{-1}. On the other hand ruthenium(II) carbonyl porphyrins exhibit a rapid on-rate and slow off-rate (*ca.* 0.1 s^{-1}) with K_a values of 10^7 to 10^8 M^{-1} for typical pyridine ligands, and exchange is slow on the NMR timescale. Rhodium(III) iodo complexes are more stable still, with K_a estimated at $>10^9$ M^{-1}.[43] By comparison, the stability constants (K_1 in Scheme 1) for naphthodiimide binding to dinaphtho-38-crown-10 are of the order of 10^3 M^{-1},[42] and this exchange is rapid on the NMR timescale at room temperature. Thus, in the first instance, variation of the metalloporphyrin stoppers while maintaining constant DN38-C-10 and naphthodiimide thread components **1** and **2a** allowed us to establish a useful basis set for timescale and temperature dependence of the overall rotaxane self-assembly process, K_3 (Scheme 1).

Simply mixing the components in the required stoichiometry for rotaxane formation at room temperature in deuteriochloroform at millimolar concentrations produced a new set of peaks in the NMR spectrum, distinct from those of the individual components (Fig. 2). The same result was obtained irrespective of the order of the addition, and the spectra did not change over time when the solutions were maintained at ambient temperature. However, variation in the temperature or the overall concentration changed the relative ratios of the peaks, which is consistent with a dynamic and rapid equilibration. The results of two-dimensional NMR experiments (COSY, NOESY and C–H correlation) were consistent with



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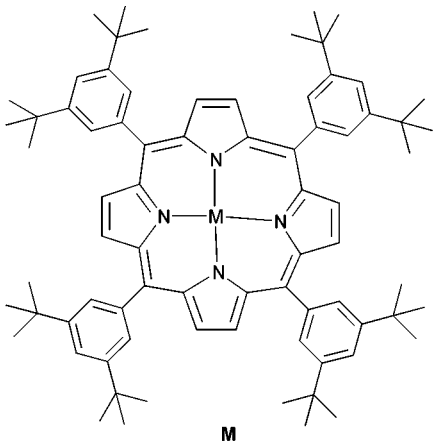
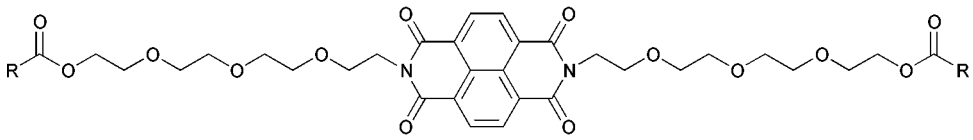


M

3 a: Zn
b: Ru(CO)
c: RhI



R

2 a:

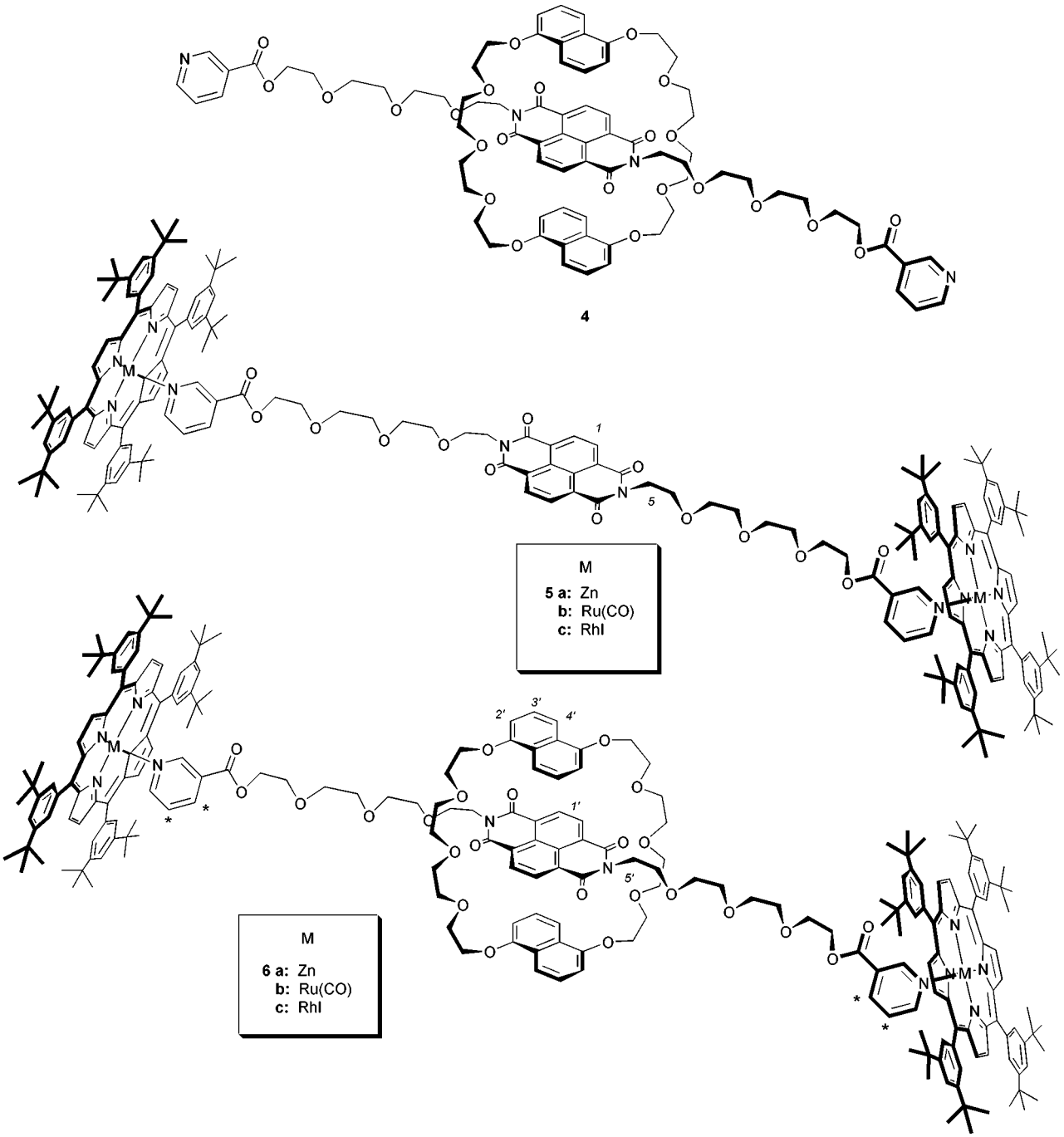
b: —CH_3

the new set of upfield shifted peaks arising from the rotaxane structure **6**, and both exchange-related and coupled peaks indicated an equilibrium with the individual components. In the case of the Zn–porphyrin stoppered systems all components (thread, stoppers, ring, unstoppered pseudorotaxane and intact rotaxane) were observed in fast exchange on the NMR chemical shift timescale at room temperature, whereas the Ru(CO) and RhI analogues showed only stoppered thread **5b** and **5c**, ring **1**, and rotaxane **6b** and **6c** in equilibrium (reflecting the large stability constant of the pyridine ligands for these metallo-derivatives; for a 1 : 2 bidentate ligand : metalloporphyrin ratio at these concentrations, more than 99% of the ligand is coordinated).

Nevertheless, in all cases the intact rotaxane could be crystallised from solution by slow infusion of methanol into chloroform solutions of the admixed components. Although at this stage none of the crystals has yielded to X-ray structural analysis, redissolution of the isolated needle-like crystals reproduced the original NMR spectra of the equilibrating mixture in an identical stoichiometric ratio; neither the thread nor the ring crystallises independently under these conditions. It is also interesting that Branda and co-workers were able to isolate single crystals of X-ray quality of a related rotaxane, albeit with quite different thread, ring and stopper components.[38]

Variable temperature ^{1}H NMR experiments were particularly enlightening. In all cases as the temperature was lowered the peaks due to the rotaxane grew at the expense of those of the individual components. Equilibrium was established fairly rapidly down to about 0 °C for the RhI derivatives, and about −20 °C for the Ru(CO) derivatives, but was noticeably slower at lower temperatures; it remained rapid for the zinc derivatives down to −65 °C. For the slowly exchanging systems it was possible to determine the K_a as a function of temperature, and thus in principle thermodynamic parameters from van't Hoff plots. For the Ru(CO) stoppered system **6b** the linear relationship between R ln K and $1/T$ over the available temperature range enabled an estimation of ΔH° and ΔS°, −41.4 kJ mol^{-1}, and −95 J K^{-1} mol^{-1}, respectively, and a K_a at 273 K of 790 M^{-1}, rising to 5.39 × 10^4 M^{-1} at 223 K. Comparable values were to be expected for the simple unstoppered complex of **1 · 2a**. However, although the K_a at 273 K was 448 M^{-1}, a van't Hoff plot for this system was not linear (Fig. 3) and a direct comparison of the ΔG° and ΔS° values with those of **6b** was not possible. Such a non-linear dependence is indicative of a temperature-dependent ΔH, and hence a non-zero heat capacity term ΔC_p. A negative ΔC_p is typically indicative of temperature dependent solvation of polar functional groups in a host and/or guest,[44,45] whereas a positive value generally accompanies phenomena such as protein folding or dissolution of organic molecules in water.[44,46,47] Given the conditions of these experiments (water-free $CDCl_3$ solvent), it is reasonable to assume that the ΔC_p term in this instance is positive, and reflects perhaps an inter- or intra-molecular interaction (such as π–π stacking) of the terminal pyridine groups on the thread with the dinaphtho crown and its included central diimide moiety. Clearly, such an interaction is prohibited in **6** when the pyridines are axially coordinated to the ruthenium porphyrin. We reasoned that a test for these types of interactions would be to replace the nicotinoyl moieties with non-aromatic acetyls, in compound **2b**. However, contrary to our expectations, the acetyl derivative **2b** showed virtually identical behaviour to that of the nicotinyl **2a** (Fig. 3c). Thus we are led to conclude that the non-zero ΔC_p term arises from a more subtle, but undefined, effect as a result of the rather flexible tetra(ethyleneoxy) arms, which is removed when these are restricted by terminal coordination to the ruthenium porphyrin stoppers.[48]

As the unstoppered pseudorotaxane **1 · 2a** exhibits fast exchange at room temperature, it was possible to extract the free enthalpy of activation for the complexation from the coalescence temperature T_C, 290 K, so that $\Delta G^\ddagger = 58 \pm 1$ kJ mol^{-1}. On introduction of the Ru–porphyrin stoppers in **6** the system now exhibits slow exchange at room temperature, and no coalescence could be observed up to the temperature limit of the solvent (320 K). Thus although it was not possible to



determine a corresponding $\Delta G^{\ddagger}$ for the exchange process here, clearly it must be significantly higher than about 65 kJ mol^{-1}, consistent with the kinetic barrier introduced by the stoppering. On the other hand, for the zinc porphyrin stoppered system which remains fast at room temperature, $\Delta G^{\ddagger}$ is constant (59 $\pm$ 1 kJ mol^{-1}), which is to be expected for such a system where the complexation and coordination rates (and the K_a) are of the same order of magnitude.

As further evidence for discrete rotaxane formation in solution, the ^{1}H NMR spectra of compound **6b** exhibited significant NOE connectivities, among others, between the diimide aromatic and N–CH_2 protons and those of the crown aromatic rings and adjacent methylenes. In addition for the equilibrating mixture at 30 °C, NOE cross-peaks could only be detected within the resonances for the rotaxane, and not between the uncomplexed components; instead, these showed exchange peaks with their rotaxane counterparts. No NOE cross-peaks were detected between any of the porphyrin stopper resonances and those of the ring, indicating that the stopper units are remote from the central ring, and that the molecule most likely adopts an extended conformation in solution.

The temperature-dependent NMR behaviour suggested that it might be possible to perform experiments at low temperatures either to form the rotaxane more or less irreversibly and in high yield by prior threading and then stoppering ("locking on"), or alternatively to "lock out" rotaxane formation by stoppering before threading. This relies on the principle that K_1 for complexation of the diimide within the dinaphthocrown is significantly smaller than that for coordination of the ligands with the metal ion (K_2 or $K_{2'}$), or alternatively that there is a significant difference in the limiting off-rates for the two processes. This is clearly the case for the Ru(CO) and RhI derivatives, but not necessarily so for that of Zn.

In the first instance it could be shown that the Ru(CO) and RhI rotaxanes can be chromatographed intact at low temperatures. By applying a stoichiometric mixture of the com-

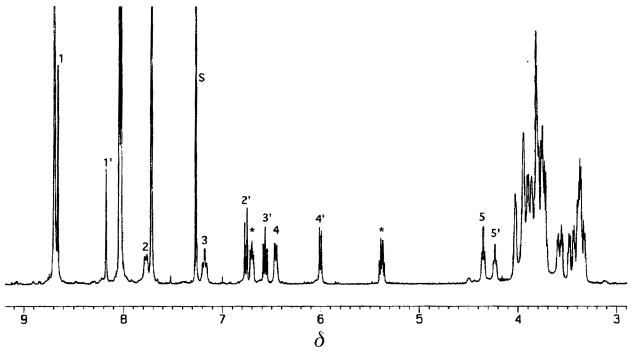


Fig. 2 Partial ^{1}H NMR (400 MHz) spectrum of an admixture of compounds **1**, **2a** and **3b** (1 : 1 : 2 molar ratio) in $CDCl_3$ at 0 °C. Numbered peaks are those of the uncomplexed **1** and coordinated thread component **5b**, and the dashed numbers are their corresponding positions in the rotaxane **6b**. Larger unnumbered peaks are for porphyrin β-pyrrole and meso-aryl (S is solvent). The peaks between δ 3 and 4 are due to crown ether methylenes. Peaks 1–5 are due to naphthodiimide, DN38-C-10 and crown methylenes, respectively, as indicated in the structures. Peaks marked with asterisks (*) are assigned to H4 and H5 of the coordinated pyridines (H6 and H2 appear at δ 2.21 and 1.76, respectively).

ponents to a 2-D TLC plate, and thence developing the plate in a suitable solvent (10% MeOH in CH_2Cl_2) at −30 °C (in a freezer compartment), a major spot for the rotaxane could clearly be identified, in addition to smaller spots for each of the components. Re-development in an orthogonal direction, but at ambient temperature, showed spots *only* for the individual components, with no rotaxane. This is shown in Fig. 4.[49] On the other hand, the system utilising the zinc porphyrin stoppers could not be chromatographed intact, and only the individual components separated even at −40 °C.

This temperature dependence was probed spectroscopically. For an increased yield of rotaxane, an equimolar mixture of the thread **2a** and the ring **1** was cooled to −40 °C and maintained at this temperature while a pre-cooled solution of the appropriate metalloporphyrin was added ("locked-on" experiment). After thorough mixing, the sample was rapidly transferred without warming to an NMR spectrometer kept at −40 °C. The spectrum was then monitored as the temperature was stepped up to +30 °C, and as it was re-cooled to −40 °C.

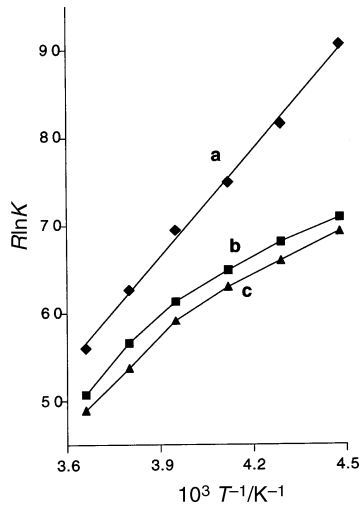


Fig. 3 van't Hoff plots for (a) the Ru(P) stoppered rotaxane/pseudorotaxane system **6**, (b) the pseudorotaxane system resulting from an equimolar mixture of compounds **1** and **2a**, and (c) the pseudorotaxane from **1** and **2b**. The symbols are the measured data, and the solid line in (a) represents the fit for $\Delta H^\circ = -41.4$ kJ mol^{-1} and $\Delta S^\circ = -95$ J K^{-1} mol^{-1}; in (b) and (c) the solid lines are a guide to the eye.

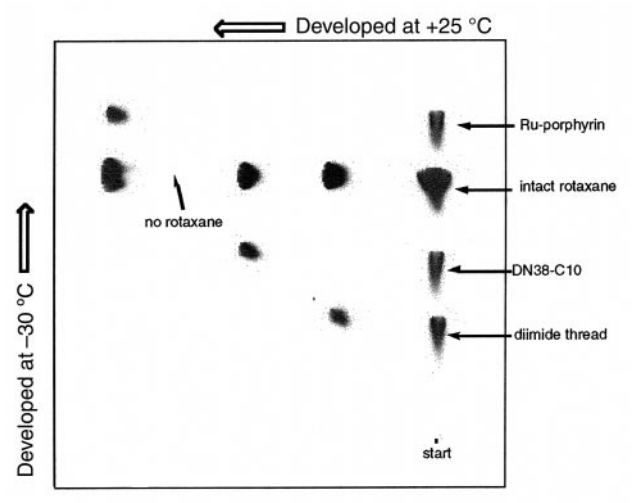


Fig. 4 The two dimensional TLC experiment described in the text. A stoichiometric mixture (1 : 1 : 2 mol ratio) of components **1**, **2a** and **3b** was applied to the silica-coated plate at the start. The plate was cooled to −30 °C and developed at this temperature in a pre-cooled CH_2Cl_2–MeOH (10 : 1) solvent mixture. Subsequently, the plate was developed in an orthogonal direction in the same solvent mixture at +25 °C. The spots for **1** and **2a** were visualised under UV light, and are traced, while the rotaxane and ruthenium porphyrin spots were visible to the naked eye.

The results are illustrated in Fig. 5, where it is shown that rotaxane construction by prior threading, and subsequently stoppering at low temperatures, resulted in a significantly increased yield, more so than the fully equilibrated mixture (shown by the warmed, then re-cooled sample). Thus, by enhancing complexation of **1** and **2a** by use of low temperatures, and then "locking on" the thread by even stronger coordination of the stoppers at a temperature where the off-rate of the ligand-to-metal bonding was sufficiently slow, a high yield of rotaxane **6** could be achieved. Note, however, that in the zinc case **6a**, equilibration is still rapid at −40 °C, and the same equilibrium distribution is obtained whether the reaction is performed at −40 or at +30 °C and then cooled.

As a corollary to this procedure, a "locking out" experiment was performed, and the results are also shown in Fig. 5. In this case the ligand thread and the metalloporphyrin were

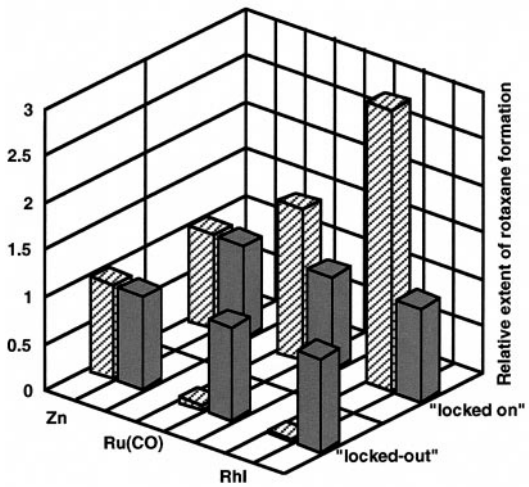


Fig. 5 Normalised relative ratios of rotaxane *vs.* uncomplexed components **1** and **5** for the two experiments described in the text. The hatched bars represent the proportion of rotaxane formed at −40 °C: in the case of the "locked on" experiment by mixing **1** and **2a**, followed by **3b** at −40 °C, and in the "locked out" case by mixing **2** and **3b**, followed by **1** at −40 °C. The solid bars are the relative ratios of the same mixtures equilibrated at +30 °C followed by re-cooling to −40 °C.

mixed and pre-cooled, thus ensuring a "fixed" stoppered thread **5**. Now addition of the ring **1** at −40 °C resulted in only minimal production of rotaxanes **6b** and **6c**. Again, warming to +30 °C and re-cooling resulted in the same equilibrated mixture as before. Equilibration began at a reasonable rate at about −20 °C for the Ru(CO) derivative, whereas for the RhI analogue this did not happen until about 0 °C, consistent with the previous observations. As previously, only the Ru(CO) and RhI stoppers showed this behaviour; the zinc stopper is still equilibrating too fast at −40 °C for effective "locking out" in the case of **6a**.

As a further indication of the utility of this procedure for the ready assembly of complex systems under reversible conditions we were able to investigate the properties of the more complex assemblies **8**, containing zinc, free-base, ruthenium and rhodium porphyrins with a potential communication pathway between them *via* the naphthodiimide and the thread. Therefore, in place of the DN38-C-10 ring, we substituted the naphthoquinol-strapped zinc or free-base porphyrin **7**,[50] and in a similar manner by simply mixing the components we could easily establish the existence of the various rotaxanes **8** in solution. In all cases at low temperatures at millimolar concentrations it was apparent that the rotaxane was the major component. In principle, it should now be possible to investigate the photophysical behaviour of such systems at low temperatures. Furthermore, it is a simple matter of varying the components by judicious choice of metal ion for both the central and stopper components, for a ready entry into a regular series of differently metallated species for a systematic study of their appropriate properties.

Conclusion

By appropriate choice of components, we have shown that it is feasible to fine tune the conditions necessary for porphyrin-stoppered rotaxane self-assembly by simple mixing of the constituent parts. It is clear that this choice can be extended to a range of threads, rings and stoppers where the appropriate combinations can be guided by the relative values of the kinetic and stability constants, and we have applied these procedures for the synthesis of related rotaxanes where the ring unit is a crown-strapped metalloporphyrin. Furthermore, the principles established in the reversible and thermodynamically controlled assembly of these rotaxanes should facilitate the construction of more complex structures, and indeed may form the basis for combinatorial libraries of supramolecular interlocked structures.

Experimental

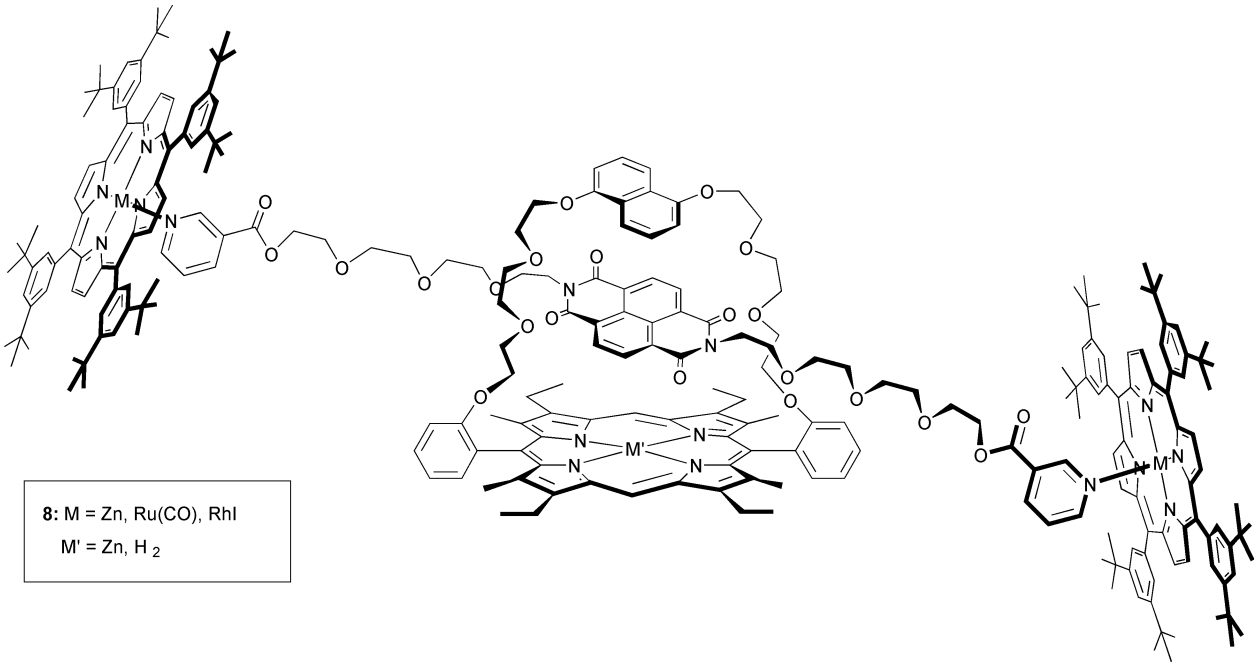
^{1}H NMR spectra were recorded in $CDCl_3$ solutions on Bruker AM or DRX-400 and DRX-500 and 800 MHz spectrometers using standard pulse sequences, and the residual solvent peak as reference. All spectra were assigned using a combination of COSY, NOESY, ROESY (rotating frame Overhauser enhancement spectroscopy) and C–H correlation techniques. Concentrations were typically 10–15 mM. Measurements at various temperatures were performed after at least 5 minutes equilibration (longer for lower temperatures). As a check that equilibria had been established, representative samples were held for up to 2 hours at the desired temperature, and the spectra periodically monitored. It was confirmed that no further change had taken place after this time. Additionally, sample spectra were checked for consistency after approaching the same temperature from either higher or lower values.

For spectra showing slow exchange, K values were calculated from integrated values of the separate peaks and averaged over several values. Uncertainty in K values is estimated at ±10%. Rate constants for the exchange process at the coalescence temperature were calculated using standard methods.[51]

Low temperature experiments were performed by mixing pre-cooled solutions and the resulting mixture was also maintained at the desired temperature in an acetone–solid CO_2 bath. For NMR experiments, pre-cooled solutions in NMR tubes were rapidly transferred without warming to the NMR probe previously cooled to the desired temperature.

Low temperature TLC experiments were conducted by applying the stoichiometric mixture of the components at room temperature, then cooling the plate to −35 °C in a freezer, and finally developing the plate in a pre-cooled solvent mixture (10% methanol in chloroform) in a tank in the same freezer. Colourless components were visualised under UV light.

We were unable to obtain suitable mass spectra of the intact rotaxanes **6**, using FAB, electrospray or matrix-assisted laser desorption–ionisation (MALDI) techniques; in all instances only the components were identified, and in most



cases even the coordinated thread units **5** were not identified, but only the unligated metalloporphryins.

Syntheses

Dinaphtho-38-crown-10 **1** was synthesized as previously described,[52] as were the zinc, Ru(CO) and RhI derivatives of *meso*-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin.[43] Compounds **2a** and **2b** were available from treatment of the corresponding hydroxy compound[41] with either nicotinoyl chloride (for **2a**) or acetyl chloride (for **2b**) in excess in dry tetrahydrofuran containing at least a 10-fold excess of triethylamine. Aqueous work-up afforded both as viscous oils, which were purified further by column chromatography (SiO_2, eluting with 5% MeOH in CH_2Cl_2). Both samples were shown to be pure by TLC in at least two different solvent systems.

***N,N′*-Bis[13-(nicotinoyl)-4,7,10,13-tetraoxatridecyl)]-1,4,5,8-naphthalenedicardoxiimide (2a).** ^{1}H NMR ($CDCl_3$): δ 3.52 (12H, m), 3.63 (4H, m), 3.68 (8H, m), 4.46 (8H, m), 7.37 (2H, dd, $J = 8.5$), 8.28 (2H, dd, $J = 8.5$), 8.75 (4H, s), 8.75 (2H, d, $J = 8.5$ Hz) and 9.20 (2H, s). HRMS (EI): *m/z* calc. for $[M]^+$ ($C_{42}H_{44}N_4O_{14}$) 828.2854, found 828.2862.

***N,N′*-Bis[13-acetyl-4,7,10,13-tetraoxatridecyl)]-1,4,5,8-naphthalenedicarboxiimide (2b).** ^{1}H NMR ($CDCl_3$): δ 2.06 (6H, s), 3.63 (16H, m), 3.70 (4H, m), 3.85 (4H, m), 4.18 (4H, m), 4.46 (4H, m) and 8.75 (4H, s). HRMS (EI): *m/z* calc. for $[M]^+$ ($C_{34}H_{42}N_2O_{14}$) 702.2636, found 702.2642.

Spectra

Mixture of compounds 1 + 2a + 3b (rotaxane 6b). ^{1}H NMR ($CDCl_3$, 10 mM **1** and **2a**, 20 mM **3b**, 800 MHz, 270 K, primes indicate resonances due to **6b**, others to **5b**, or **5b** and **6b** where these occur at the same chemical shifts; the numbering for the naphthoquinol protons is as indicated in the structure): δ 1.54 (br s, *meso*-Ar t-butyl), 1.85 (d, py CH5), 2.29 (br s, py CH1), 3.35 (m, OCH_2), 3.40 (m, OCH_2), 3.42 (m, OCH_2'), 3.45 (m, OCH_2), 3.52 (m, OCH_2'), 3.57 (m, OCH_2), 3.62 (m, OCH_2'), 3.74 (m, OCH_2), 3.79 (m, OCH_2), 3.85 (m, OCH_2'), 3.89 (m, OCH_2'), 3.94 (m, OCH_2), 3.96 (m, OCH_2'), 4.07 (m, OCH_2), 4.26 (t, OCH_2'), 4.37 (t, OCH_2), 5.39 (br t, py CH4), 6.04 (d, naphthoquinol CH4′), 6.51 (d, naphthoquinol CH4), 6.60 (t, naphthoquinol CH3′), 6.73 (br d, py CH3), 6.80 (d, naphthoquinol CH2′), 7.19 (t, naphthoquinol CH3), 7.76 (s, *meso*-aromatic CH), 7.78 (d, naphthoquinol CH2), 8.03 (s, *meso*-aromatic CH), 8.08 (s, *meso*-aromatic CH), 8.21 (s, naphthodiimide CH′), 8.68 (s, naphthodiimide CH) and 8.70 (s, β-pyrrole CH).

Mixture of compounds 1 + 2a + 3c (rotaxane 6c). ^{1}H NMR ($CDCl_3$, 10 mM **1** and **2a**, 20 mM **3c**, 400 MHz, 300 K, primes indicate resonances due to **6c**, others to **5c**, or **5c** and **6c** where these occur at the same chemical shifts): δ 1.38 (d, py CH5), 1.54 (br s, *meso*-Ar t-butyl), 1.80 (br s, py CH1), 3.30–4.08 (overlapping m, OCH_2 and OCH_2'), 4.22 (t, OCH_2'), 4.33 (t, OCH_2'), 5.33 (br t, py CH4), 6.00 (d, naphthoquinol CH4′), 6.51 (d, naphthoquinol CH4), 6.57 (t, naphthoquinol CH3′), 6.68 (br d, py CH3), 6.76 (d, naphthoquinol CH2′), 7.19 (t, naphthoquinol CH3), 7.76 (s, *meso*-aromatic CH), 7.77 (d, naphthoquinol CH2), 8.06 (s, *meso*-aromatic CH), 8.12 (s, *meso*-aromatic CH), 8.19 (s, naphthodiimide CH′), 8.64 (s, naphthodiimide CH) and 8.90 (s, β-pyrrole CH).

Mixture of compounds 1 + 2a + 3a (rotaxane 6a). ^{1}H NMR ($CDCl_3$, *ca.* 12 mM **1** and **2a**, 24 mM **3a**, 400 MHz, 300 K; peaks are broad and represent average values for **1**, **2a**, **5a**, and **6a** in slow exchange): δ 1.54 (br m, *meso*-Ar t-butyl), 3.50–4.30 (overlapping m, OCH_2), 6.46 (br s, naphthoquinol CH4), 6.70 (br t, py CH3), 7.13 (br s, naphthoquinol CH3), 7.74 (br s, naphthoquinol CH2), 7.77 (s, *meso*-aromatic CH), 8.10 (s, *meso*-aromatic CH) and 8.35 (s, naphthodiimide CH), 8.98 (s, β-pyrrole CH) (resonances for the pyridine protons are unresolved in the baseline, and slowly resolve and move as the temperature is lowered; at 203 K they appear as broad singlets at δ 2.77, 2.90, 5.66 and 6.99).

Mixture of compounds 7 + 2a + 3b (rotaxane 8, M = Ru(CO), M′ = Zn). ^{1}H NMR ($CDCl_3$, 8 mM **7** and **2a**, 16 mM **3b**, 400 MHz, 270 K, dashes indicate resonances due to **8**, others to **5b**, or **5b** and **8** where these occur at the same chemical shifts): δ 1.54 (br s, *meso*-Ar t-butyl), 1.66 (t, CH_2CH_3'), 1.75 (t, CH_2CH_3), 1.82 (d, py CH5), 2.25 (br s, py CH1), 2.46 (m, OCH_2), 2.47 (m, OCH_2), 2.55 (s, CH_3), 2.75 (m, OCH_2), 2.93 (m, OCH_2), 3.14 (m, OCH_2), 3.30–4.27 (m, OCH_2 and OCH_2'), 4.81 (t, zinc porphyrin naphtho CH′), 5.36 (t, zinc porphyrin naphtho CH), 5.41 (t, py CH5), 5.90 (t, zinc porphyrin naphtho CH′), 6.36 (t, zinc porphyrin naphtho CH), 6.70 (d, py C4), 6.84 (zinc porphyrin naphtho CH′), 7.05 (zinc porphyrin naphtho CH), 7.34 (m, zinc porphyrin *meso*-Ar H), 7.67 (m, zinc porphyrin *meso*-Ar H), 7.69 (s, ruthenium porphyrin *meso*-Ar H), 7.71 (m, zinc porphyrin *meso*-Ar H), 8.00 (s, ruthenium porphyrin *meso*-Ar H), 8.04 (s, ruthenium porphyrin *meso*-Ar H), 8.05 (s, naphthodiimide CH′), 8.41 (naphthodiimide CH), 8.68 (s, porphyrin β-pyrrole CH), 9.63 (zinc porphyrin *meso*-CH′) and 10.08 (zinc porphyrin *meso* CH). Other resonances due compound to **8** are unassigned and/or hidden.

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