Crown-ether- and porphyrin-attached gel-phase resins in thermodynamically controlled rotaxane assembly

Kathleen M. Mullen, Ken D. Johnstone, Dilip Nath, Nick Bampos, Jeremy K. M. Sanders and Maxwell J. Gunter*

Supplementary Information

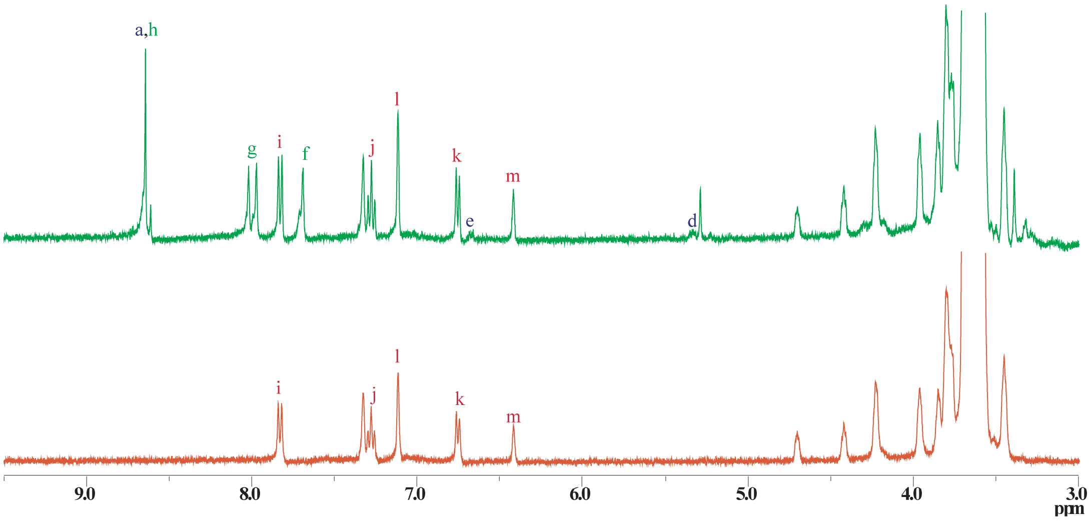

Figure S1 HR MAS proton NMR spectra of **6** (bottom) and the mixture of **6**, **3** and **2a** (top) in $CDCl_3$ at 30 ºC. The spectrum of the mixture of **6** and **3** in $CDCl_3$ did not exhibit any crown-diimide threading interaction and thus is not shown here.

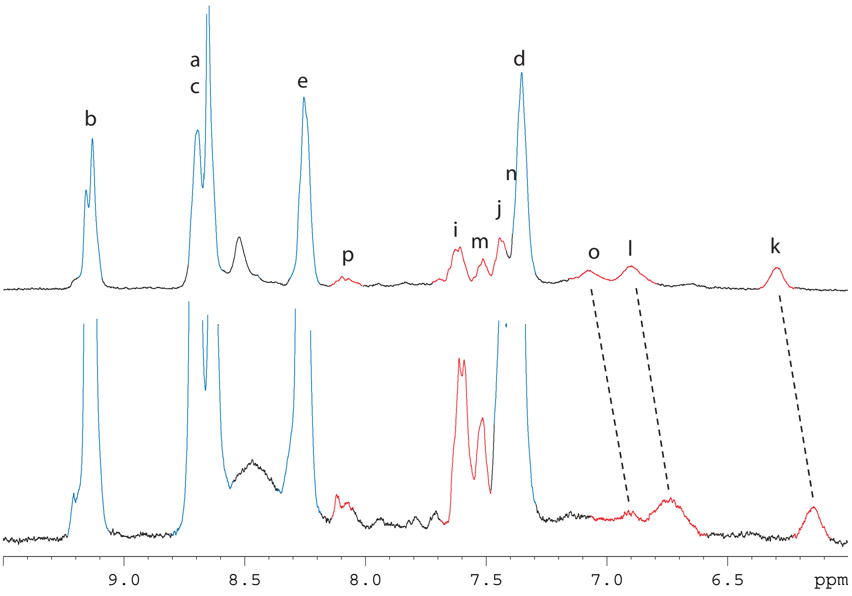

Figure S2 HR MAS spectra of a mixture of tethered crown **10**, diimide thread **3** and LiI at 27˚C (top) and –10 ˚C (bottom).

Possible alternative structural types for Series III structure

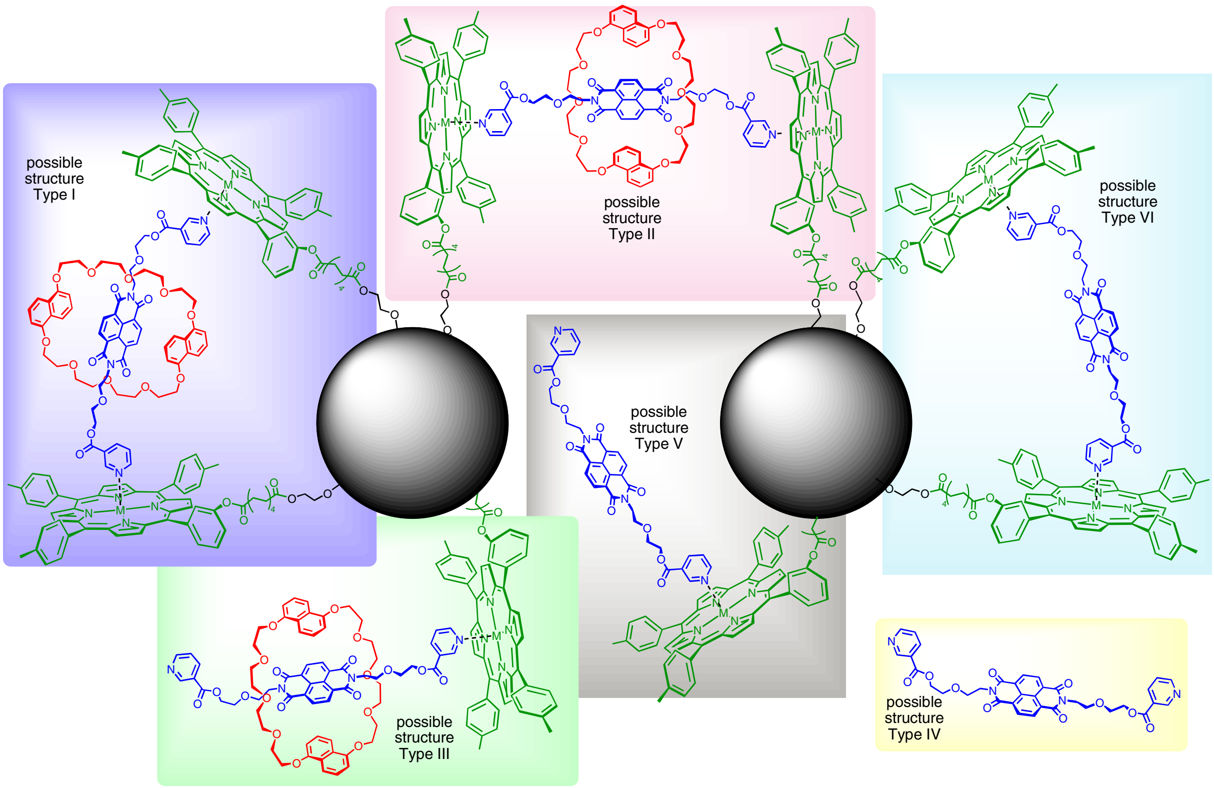

Figure S3 Possible rotaxane structural types resulting from metalloporphyrin-tethered beads, with thread **3** and shuttle **1** units in the surrounding solution phase.

In the self assembly of rotaxanes incorporating a porphyrin-attached polymer bead, there are several possibilities (Figure S3). For the Type I structure, shown in Figure 4 which corresponds to the Series III structure cartooned in Figure 1, the *bis*-pyridyl diimide thread **3** in the solution phase coordinates to two adjacent tethered porphyrin molecules on a single bead, and the crown completes the rotaxane formation in a fully reversible thermodynamically controlled assembly. However, alternative structures of Types II, III, IV, V and VI are also possible, although structure Type II, in which the diimide thread is coordinated to porphyrins on two separate beads is considered unlikely due to the size incompatibilities between the polymer beads and the rotaxane components. Conversely, it is very probable that a proportion of the equilibrating structures would include structure Types III and V where the spacing of adjacent porphyrins might preclude a bridging structure of Type I. Furthermore due to the experimental limitations, large excesses of the added thread **3** (accounting for structure Type IV) would influence the equilibrium in favour of structure Types III and V over Types I and VI even for suitably spaced porphyrin pairs. Likewise, excess crown would disfavour Types V and VI over I and III.

Differentiating between these species using HR MAS NMR is not trivial. Unfortunately, no distinction between the resonances of the coordinated pyridine protons of the mono-bound (of Types III and V) and the di-bound (of Types I and VI) pyridine protons can be made as they would be expected to appear at the same chemical shifts. Likewise signals of the free pyridine protons in the mono-bound Types III and V and unbound Type IV would also be indistinguishable. Another significant problem is the limitations of the technique in that precise quantitation (either by integration, or uncertainty in the precise molar ratio of the added crown with respect to the thread components; see the Experimental Section) is not possible with HR MAS NMR.