A self-assembling polymer-bound rotaxane under thermodynamic control

Ken D. Johnstone,[a] Nick Bampos,[b] Jeremy K. M. Sanders[b] and Maxwell J. Gunter*[a]

[a] *Chemistry, School of Biological, Biomedical and Molecular Sciences, University of New England, Armidale, N.S.W. 2351, Australia. E-mail: mgunter@metz.une.edu.au; Fax: +61 2 6773 3268; Tel: +61 2 6773 2767*

[b] *University Chemical Laboratory, Lensfield Rd, Cambridge, UK CB2 1EW*

The thermodynamically controlled self-assembly of a neutral donor–acceptor rotaxane, stoppered *via* porphyrin coordination and bound to polystyrene beads is described, and the dynamic equilibrium between solid and solution phases has been examined by HR MAS nmr spectroscopy.

The use of catenane and rotaxane systems as components of potential molecular electronic devices has been extensively reported. Recently there has been an increased interest in attaching these systems to solid surfaces in order to optimise their ability to work in a practical sense.[1] However, it is often difficult to study such systems in their solid form. We have utilised HR MAS nmr techniques to analyse a rotaxane and various other supramolecular systems bound to polystyrene beads.[2] We also recently reported a solution phase self-assembling rotaxane system under thermodynamic control[3] that we have now adapted to the immobilised phase and where the solution–solid phase dynamics are probed using high-resolution magic angle spinning (HR MAS) nmr spectroscopy.

The synthesis of rotaxane **5** tethered to ArgoGel™-OH polystyrene resin beads *via* terminal polyethylene glycol groups was accomplished according to Scheme 1. The complete rotaxane has three components: a polystyrene bead-bound naphthodiimide thread with terminal pyridine group **4**, a dinaphtho 38-crown-10 loop component **2** and a ruthenium carbonyl porphyrin stopper with bulky tertiary butyl groups **3**. The polystyrene bead acts as a permanent stopper at one end of the thread, while at the other end the pyridine group coordinates to the ruthenium porphyrin stopper. In solution the crown macrocycle **2** forms a charge transfer complex with a naphthodiimide thread such as **1**.[3,4] When the components of the rotaxane (**2** + **3** + **4**) are mixed in a suitable solvent in which the beads swell, both the loop and stopper components freely exchange between the solution phase and the immobilised phase complexed to the thread **4**, resulting in an equilibrium between a number of states, with the complete rotaxane being the most stable thermodynamically.

The assembly process can be observed by optical microscopy. The beads are white (Fig. 1a), but yellow with the attached thread (Fig. 1b). Mixing the thread-attached bead **4** with a solution of the crown component **2** produces a light red colour in the beads (Fig. 1c), indicative of the charge transfer interaction between the components; this can be removed by filtering and washing the beads.† Addition of the stopper component **3** colours the beads a deep red (Fig. 1d) which does not wash off, due to the strong binding between the terminal pyridine and ruthenium porphyrin,‡ trapping both **2** and **3** on the beads after filtration. Prolonged re-solvation of the complex **5** enables re-equilibration, reducing the percentage of complexed crown component on the beads.

Of great importance in such a rotaxane system, yet difficult to determine, is the relative loading of thread sites on the bead surface. Little is known about the surface architecture and binding site environment of ArgoGel™ beads. UV studies were performed to calculate the change in concentration of a solution of ruthenium porphyrin **3** before and after the incorporation of a sample of thread-attached bead **4**. The reverse experiment was also performed by mixing ruthenium porphyrin coordinated beads with a solution of pyridine, thus displacing the stopper groups and allowing quantification of their resulting concentration. The loading on the beads for both experiments was calculated to be 0.01 mmol g^{-1}. The unreacted ArgoGel™-OH
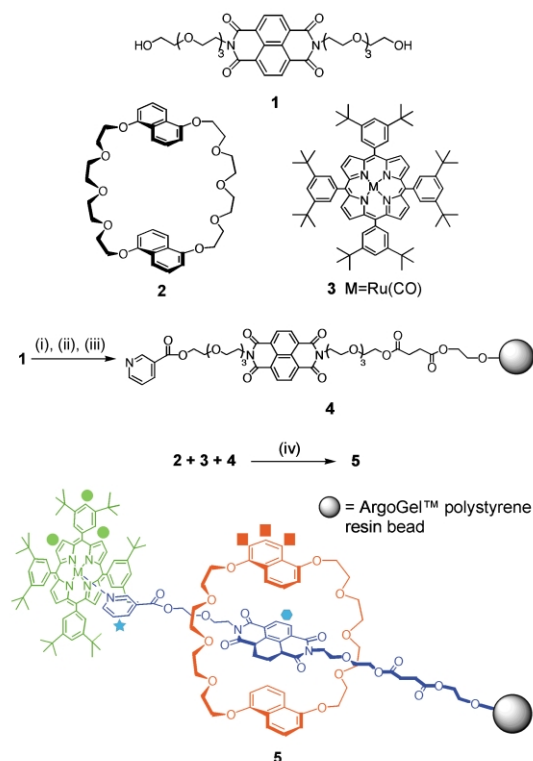
Scheme 1 *Reagents and conditions:* (i) nicotinic acid, HOBT, EDC, NEt$_3$, CHCl$_3$, r.t., 2 days, 33%; (ii) succinic anhydride, NEt$_3$, DMAP, CHCl$_3$, 5 days, 81%; (iii) ArgoGel™-OH, HOBT, EDC, NEt$_3$, CHCl$_3$, 50 °C, 7 days; (iv) CDCl$_3$, r.t.
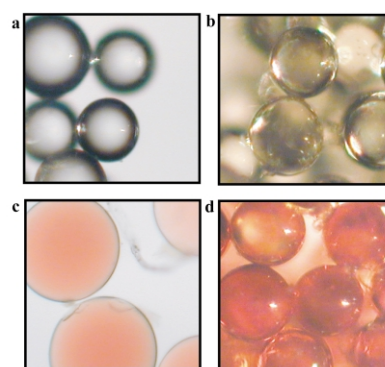

Fig. 1 10x Magnification optical microscope images: (a) ArgoGel™-OH beads, (b) **4**, (c) **4** + **2**, (d) **4** + **2** + **3**. (a), (b) and (d) are dried beads; in (c) the beads are swollen in CHCl$_3$.

beads have a typical loading of 0.4–0.5 mmol g^{-1}, thus only 2–2.5% of all sites are accessible for both the thread and bulky stopper components.§

HR MAS nmr proved to be the best technique for analysing this exchanging rotaxane system as it allows both solution and solid-bound components to be studied concurrently. The HR MAS ^{1}H nmr spectra of **4** showed typical pyridine (δ 9.2, δ 8.7, δ 8.3 and δ 7.4; ★) and diimide (δ 8.7; ⊗) aromatic peaks (Fig. 2a). Upon addition of a solution of **2** the diimide peak shifts upfield (δ 8.2; ⬢) due to the shielding effect of the crown naphthalene groups (Fig. 2b). The diimide (⬢) and crown (⊠) peaks are an average between the threaded and dethreaded states due to their fast exchange rate on the chemical shift timescale. In this respect, the system is comparable to the analogous solution state system.[3] Addition of a solution of **3** results in a large shift upfield of the pyridine protons (δ 6.7, δ 5.4, δ 2.2 and δ 1.8; ★) as the pyridine groups coordinate to the ruthenium porphyrin (●) (Fig. 2c). Stoppering the system also slows down the threading–dethreading complexation between the crown and diimide thread, resulting in observable bound and unbound crown (■, ⊠) and diimide (⬢, ⊗) peaks in an approximate 1 : 1 ratio.¶ However, a set of three aromatic peaks (δ 6.3, δ 7.0 and δ 7.5; □) absent in the solution analogue system (bis-terminal pyridine diimide thread with **2** and **3**)[3] was found in the HR MAS nmr ^{1}H spectra of the solid-bound rotaxane **5**. The HR MAS nmr COSY spectra (Fig. 3) showed coupling between all three peaks and this, added to their relative shifts, suggests the presence of a third crown environment, upfield of the uncomplexed set and downfield of the complexed set of aromatic crown peaks. The third set of peaks remained after filtering and washing the beads, indicating a third environment in which one or more crowns are threaded on the terminal polyethylene glycol groups of the ArgoGel™ beads, still stoppered by the porphyrin complexation. This polyethylene glycol-type environment would be sufficiently different to the solvated uncomplexed crown environment to account for the slight upfield shift. We have previously reported a rotaxane system with a loop component which complexed with the terminal polyethylene glycol groups of ArgoGel™ beads.[2]

Solid-state on-bead IR investigations into **5** using ATR techniques were performed in expectation that a diimide IR carbonyl shift might be evident on binding. Such a shift was observed, but was too small‖ to be a useful tool for investigating the inter-component interactions of the solid-bound rotaxane. However, solid-state IR is a useful tool for further character-
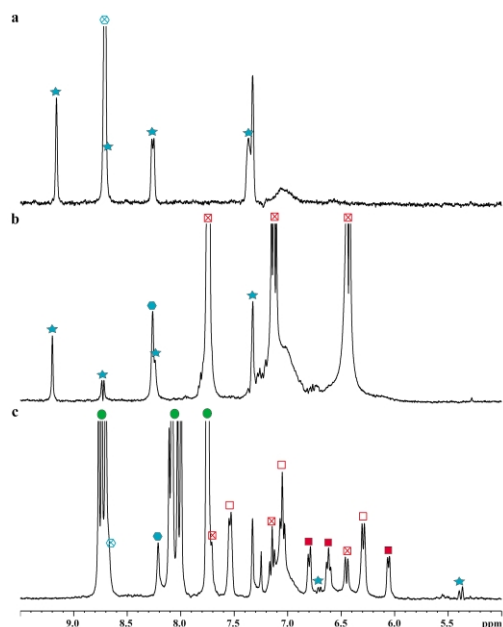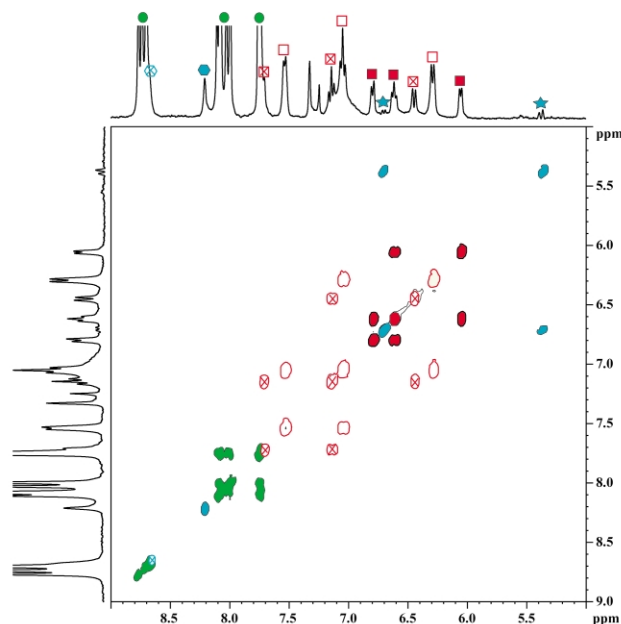

Fig. 3 HR MAS COSY data for **4** + **2** + **3**. The sets of coupled peaks for the different diimide, crown and porphyrin environments are indicated by blue, red and green cross-peaks respectively.

isation of such systems, as functional group resonances can be observed easily.

HR MAS nmr has proven to be an invaluable technique for characterising and probing the inter-component interactions of our thermodynamically controlled, self-assembling solid-bound rotaxane. We intend to utilise this methodology to develop and study a series of higher-order solid-bound supramolecular systems in the future.

Notes and references

† The crown-thread complexation has a binding constant of ~ 700 M^{-1} at 273 K as calculated from analogous solution rotaxane studies.
‡ Pyridine–ruthenium porphyrin complexation has a binding constant of ~ 10^8 M^{-1}.
§ This result implies a total percentage nitrogen composition of ~ 0.04% by mass; too low for meaningful quantitation by microanalysis or atomic absorption spectroscopy.
¶ Due to the nature of the experiment, adding exact stoichiometric quantities of each component was impractical; approximate excesses can be estimated from the relative peak heights in the nmr spectra.
‖ IR shifts from 1712 to 1710 cm^{-1} for unbound and bound diimide carbonyls were observed.

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Fig. 2 HR MAS ^{1}H nmr data for: (a) **4**, (b) **4** + **2**, (c) **4** + **2** + **3**. The symbol colours correspond to the protons indicated in Scheme 1.