

## CHAPTER 4

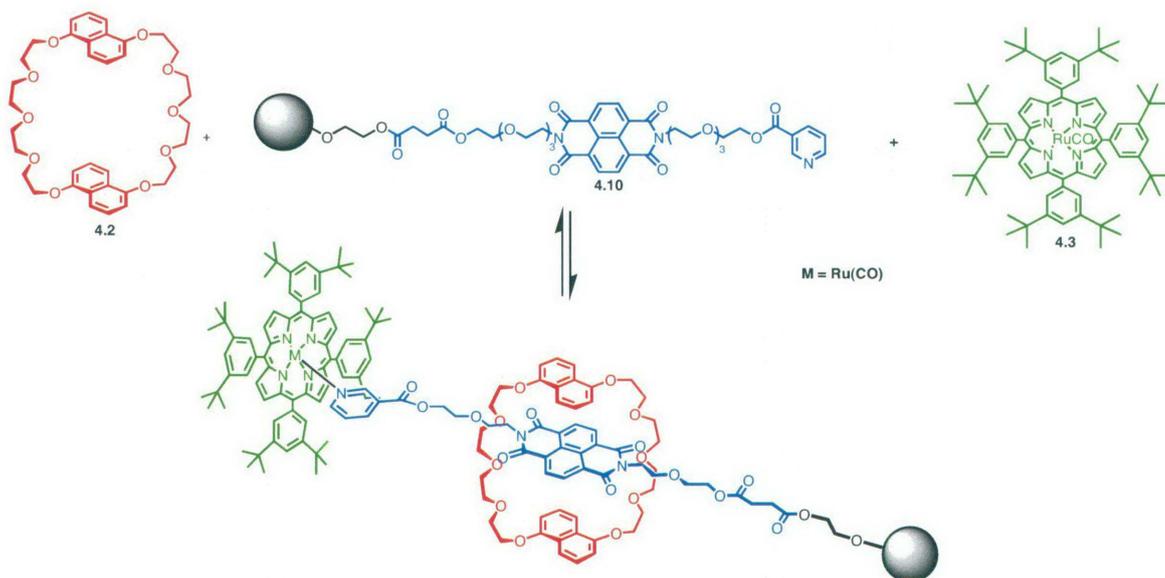
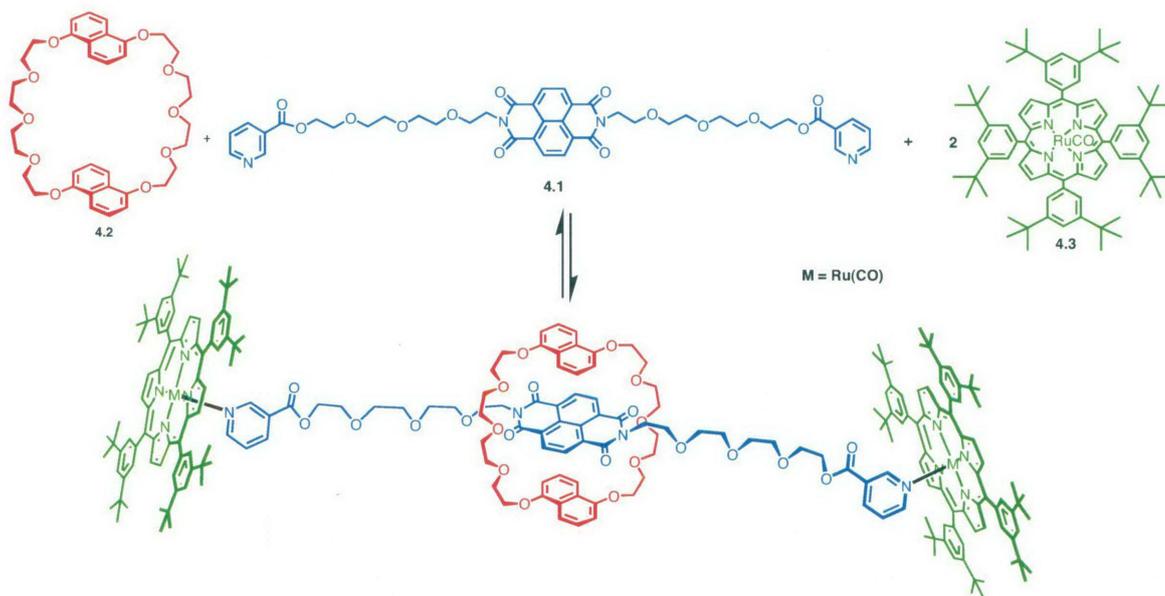
### SELF-ASSEMBLING POLYMER BOUND ROTAXANES UNDER THERMODYNAMIC CONTROL

#### 4.1 INTRODUCTION

As discussed in Chapter 1, there have been numerous reported examples of the attachment of supramolecular systems to solid surfaces such as glass and gold.<sup>1</sup> Whilst these surfaces have the advantage of having useful electro- and photochemical capabilities<sup>2</sup>, there is a serious disadvantage in the number of available techniques that allow solid supported systems to be directly compared to their solution analogues. Particularly, NMR techniques that can give so much structural and dynamic information about molecules and systems in solution are generally not available for solid-tethered analogues. However, the use of high resolution magic angle spinning (HR MAS) NMR on systems tethered to swollen polymer resin beads allows the possibility of obtaining NMR spectra comparable to solution state spectra.<sup>2, 3</sup> Hence direct comparison can be made between solution and solid-tethered self-assembly and dynamics of complex supramolecular systems.

Gunter *et al.* have previously reported on a series of neutral rotaxane and catenane systems and have compared their synthesis, behaviour and properties in solution with those of analogous systems tethered to solid phase polystyrene supports.<sup>4-6</sup> The fundamental components of these systems in both solution and solid-phase studies are the neutral naphthodiimide thread **4.1**, the dinaphtho 38-crown-10 macrocycle **4.2**, and the ruthenium carbonyl porphyrin **4.3**. In a typical rotaxane system illustrated in Scheme 4.1, the thread unit is encircled by the crown ether through a combination of dipolar,  $\pi$ - $\pi$  and charge transfer intermolecular forces, and the rotaxane is completed by stoppering as a result of coordination of the terminal pyridine units of the thread with the ruthenium carbonyl porphyrin. The assembly of this system is completely reversible and the

thermodynamically most stable product, the rotaxane, self-assembles in solution by simple mixing of the components in a suitable solvent.<sup>7, 8</sup>



Based on the same principles, the self-assembly of analogous rotaxanes on solid supports could also be studied (see Scheme 4.2). A naphthodimide thread terminated with a single pyridine group was tethered at the opposite end to polystyrene beads. The functionalised beads were then allowed to swell in solutions containing the crown and porphyrin stopper components, and the system was analysed by HR MAS NMR. This allowed the dynamic equilibrium between the solid and solution phases to be easily monitored as the polymer-

bound rotaxane assembled in real time.<sup>4, 5</sup> Gunter *et al.* have also reported the non-equilibrium counterparts to these systems, where rotaxane and catenanes were covalently attached to these beads under kinetically controlled conditions.<sup>6</sup>

This chapter describes the extension of concepts established in these preliminary studies, where each of the other two components of this three-component system are attached to the beads in turn, and the assembly of the rotaxanes is again studied under conditions of dynamic equilibrium between solution and solid-phase components. For the naphthodiimide-attached system, a further extension is introduced by replacement of the crown ether macrocycle by a strapped porphyrin resulting in novel multi-porphyrin arrays assembled on solid supports, with unique structures and exciting potential. In-depth solution and solid-state studies into the dynamic behaviour of these systems will be discussed. Furthermore, parallel solution-phase studies of entirely analogous systems with the polystyrene support replaced by a discrete bulky molecular entity are described, to confirm a direct correspondence between solution-phase behaviour and that observed in the solid state.

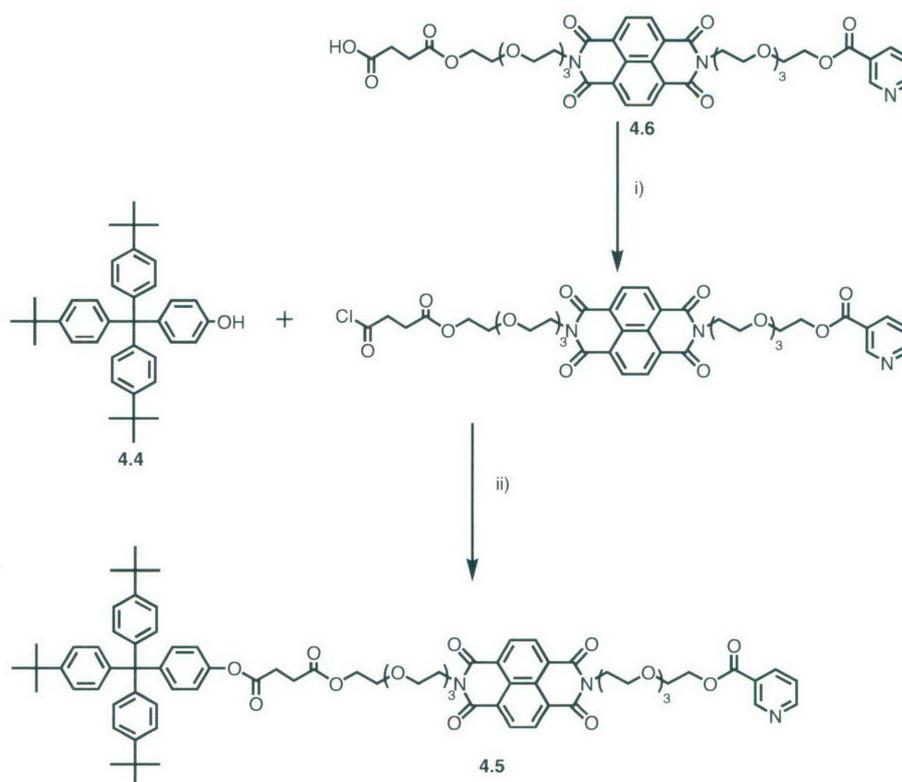
## **4.2 NAPHTHALENE DIIMIDE TETHERED SYSTEM**

### **4.2.1 Solution studies into the binding of a mono-stoppered naphthodiimide thread to a crown ether macrocycle**

Previous solution studies of this three component system described above have involved the use of a *bis*-pyridine functionalised thread **4.1** in which two equivalents of porphyrin are required for successful rotaxane stoppering.<sup>4, 7</sup> However when this system is tethered on solid supports, one end of the thread is effectively stoppered by the bead and thus only one porphyrin equivalent is needed for rotaxane formation. A better solution analogue was reasoned to be one in which one end of the thread is stoppered by a bulky, non-porphyrinic entity designed to prevent slippage of the macrocycle from one end of the thread. It was deemed important to establish whether restricting the number of threading/dethreading pathways has any impact on the binding or stability of the

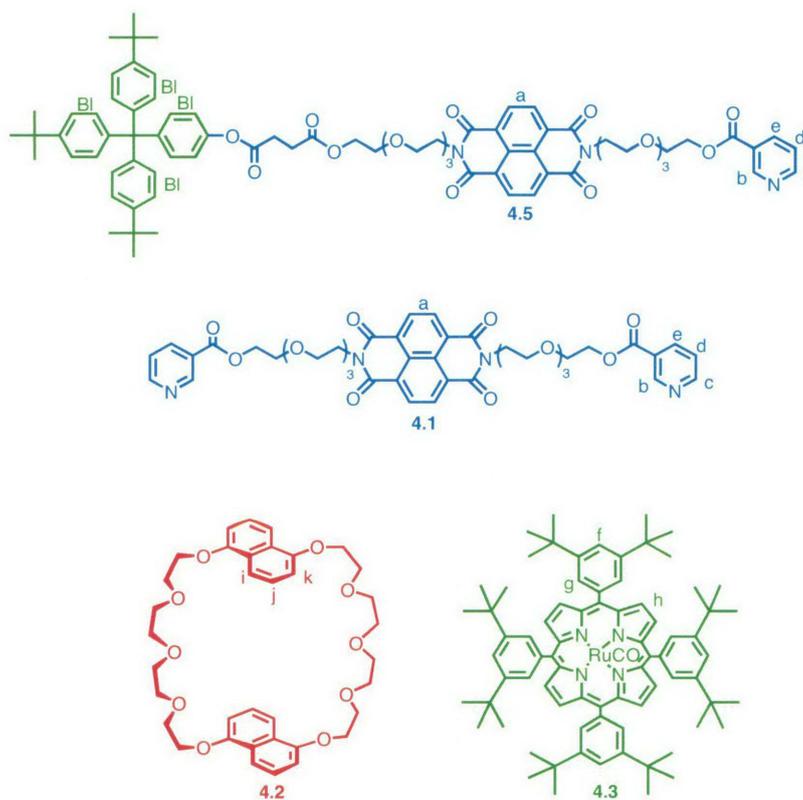
subsequent rotaxane complex. It was thus decided that the “Stoddart type” stopper group **4.4** would be an ideal candidate as it has previously been reported to be sufficiently bulky to prevent deslippage of the crown ether macrocycle in related bipyridinium based rotaxanes.<sup>9</sup>

Thus the mono-stoppered naphthodiimide thread **4.5** was synthesised *via* an acid chloride reaction between **4.4** and **4.6** (Scheme 4.3).



**Scheme 4.3:-** Reagents and conditions i) oxalyl chloride, toluene, quantitative yield; ii) dry DCM, room temperature, 12 hours, 81%.

As with the previous solution and solid-tethered systems, NMR spectroscopy was crucial for analysing the diimide crown porphyrin rotaxane systems. The non-schematic labelling and colouring system used in the NMR analysis of these systems is shown in Figure 4.1.



**Figure 4.1:-** Non-systematic aromatic group labelling and colouring system used for the NMR analysis of **4.1**, **4.2**, **4.3** and **4.5** and their related supramolecular systems.

The binding of the crown ether macrocycle **4.2** to the mono-stoppered thread **4.5** was monitored by  $^1\text{H}$  NMR spectroscopy in 2%MeOD/ $\text{CDCl}_3$ . Upon addition of one equivalent of **4.2** to **4.5**, the resonances for the diimide protons shifted slightly upfield from 8.72 to 8.59 ppm due to shielding by the crown, indicating successful binding of the macrocycle. The crown aromatic protons also shifted slightly to the more upfield positions of 7.54 ( $\Delta\delta = -0.16$  ppm), 7.05 ( $\Delta\delta = -0.13$  ppm) and 6.42 ppm ( $\Delta\delta = -0.08$  ppm). Only one set of broadened resonances for both the diimide and the crown protons were observed indicating the system was in fast exchange on the NMR chemical shift time scale as previously observed for the analogous system with the *bis*-pyridyl-substituted naphthodiiimide thread **4.1**. The magnitude of the shifts were also consistent with those observed previously albeit with small variations (see Figure 4.2).

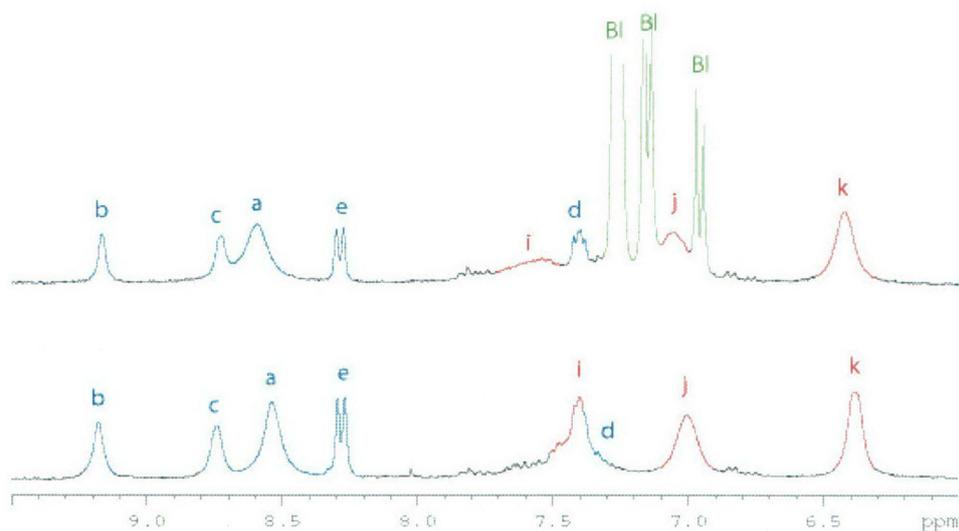


Figure 4.2:- Aromatic region of  $^1\text{H}$  NMR of equimolar solutions of **4.5** + **4.2** (top) and **4.1** + **4.2** (bottom).

Variable temperature NMR experiments were performed and, as with the binding of **4.1**<sup>7</sup>, at temperatures below 0 °C two sets of peaks became evident for both the diimide and crown resonances indicating the change in dynamics from a fast to a slow exchanging system on the NMR chemical shift timescale (see Figure 4.3).

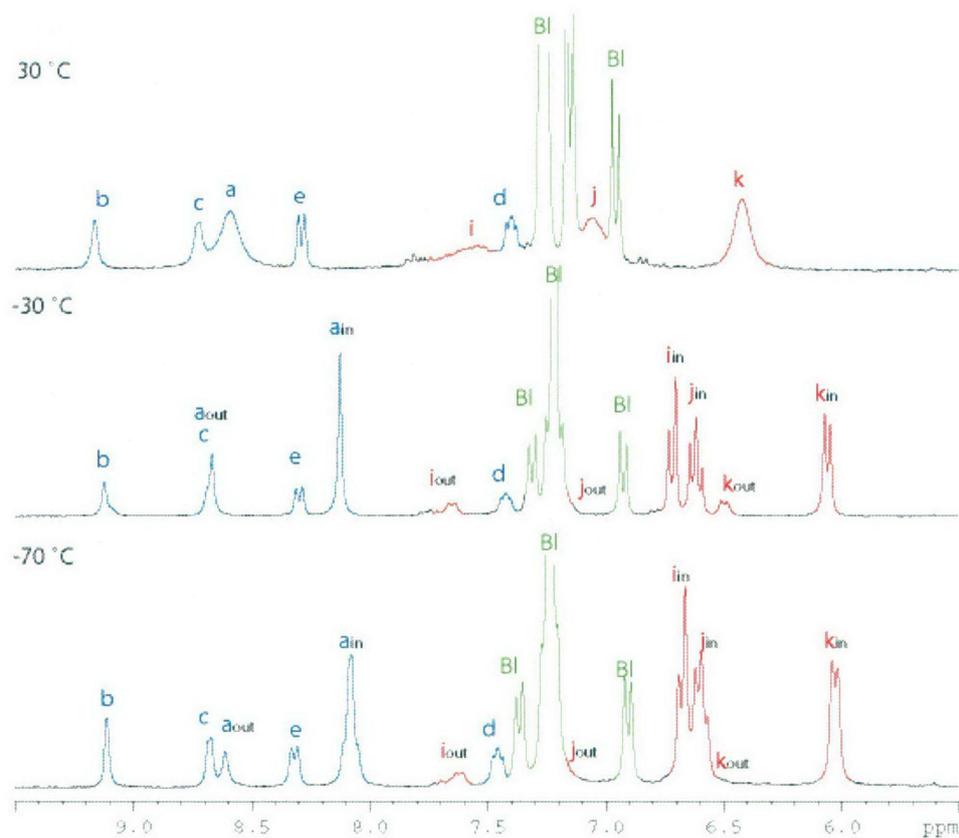
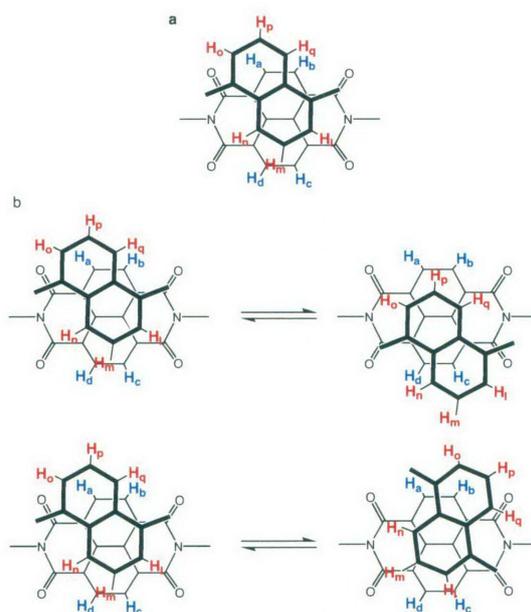


Figure 4.3:-  $^1\text{H}$  NMR temperature comparison of equimolar mixtures of **4.5** and **4.2**. Numbering and colours refer to Figure 4.1.

The time-averaged diimide proton resonance (a) at 8.59 ppm split into unbound ( $a_{\text{out}}$ , 8.61 ppm) and bound ( $a_{\text{in}}$ , 8.08 ppm) resonances with the bound resonance increasing in proportion relative to the unbound resonance as the temperature decreased. Likewise two sets of crown peaks (i, j, k) were observed with those belonging to unbound crown appearing at 7.62, 7.18 and 6.54 ppm, and those belonging to its bound partner appearing at 6.67, 6.59, 6.03 ppm. Again the temperature at which slow exchange was reached, and the proportions of bound versus unbound crown at different temperatures were comparable to studies of the binding of the *bis*-pyridine thread **4.1**. This indicates that any effect on the binding or stability of having one end of the thread stoppered is negligible in this time frame and concentration range. At  $-70$  °C fine structure around the bound diimide peak ( $a_{\text{in}}$ ) was evident. This has been seen in similar systems involving crowns complexed with diimides and has been shown to be due to rocking back and forth and “yawing” from side to side of the diimide inside the crown (see Figure 4.4).<sup>8</sup>



**Figure 4.4:-** (a) Exaggerated depiction of the offset face-to-face  $\pi$ -stacking between naphtho-crown (above) and naphthodiimide (below) aromatics as evidenced by low temperature NMR experiments; (b) Some possible dynamic processes in the crown naphthodiimide interaction include rocking back and forth (top) and “yawing” from side to side (below). Carbon-carbon double bonds and adjoining functional groups are omitted for clarity.<sup>8</sup>

This effect is not seen when the same system is studied in  $\text{CDCl}_3$  rather than the 2%MeOD/ $\text{CDCl}_3$  solvent system, indicating that the presence of methanol is stabilising this complex in some way. The exact nature of this effect is not defined at this stage, but it may possibly be the result of a hydrogen bonding network between the carbonyls of the

diimide and the ethoxy protons in the crown, which is interrupted by completing hydrogen-bonding to the added hydroxylic methanol solvent.

Addition of one equivalent of ruthenium carbonyl porphyrin **4.3** to the 1:1 mixture of **4.5** and **4.2** completed the rotaxane formation through stoppering of the single pyridine terminus of the thread *via* a coordinate covalent bond. Again the system was studied by NMR to compare the dynamics of the dipyridine thread **4.1** with the mono-stoppered thread **4.5**. As expected, the NMR showed dramatic upfield shifts of the pyridine proton resonances from their unbound positions of 9.17, 8.73, 8.29 and 7.40 ppm to typical coordinated positions of 6.74, 5.39, 2.20 and 1.78 ppm indicating successful stoppering of the rotaxane. Notably, even at room temperature two sets of resonances for the crown and diimide protons were observed indicating the system was now in slow exchange on the NMR chemical shift timescale. Variable temperature NMR experiments were performed and again similar ratios of bound versus unbound crown were obtained compared to the symmetrical diimide thread **4.1**.<sup>7</sup>

Thus it was established that the covalent stoppering of one end of the diimide thread, whether it be by a covalently linked molecular stopper or a polymer support, should have no effect on the dynamic self-assembly of this system.<sup>†</sup>

#### **4.2.2 Enhancing the crown-diimide interaction using cations**

Despite the successful formation of rotaxanes using this three component system of thread **4.1**, crown **4.2** and porphyrin stopper **4.3**, the interactions between the crown and the naphthodiimide are relatively weak, and in equimolar mixtures there are inevitably bound and unbound species present. It has been reported that the addition of some cations such as Na<sup>+</sup> and Li<sup>+</sup> can not only enhance the interactions between crown ethers and

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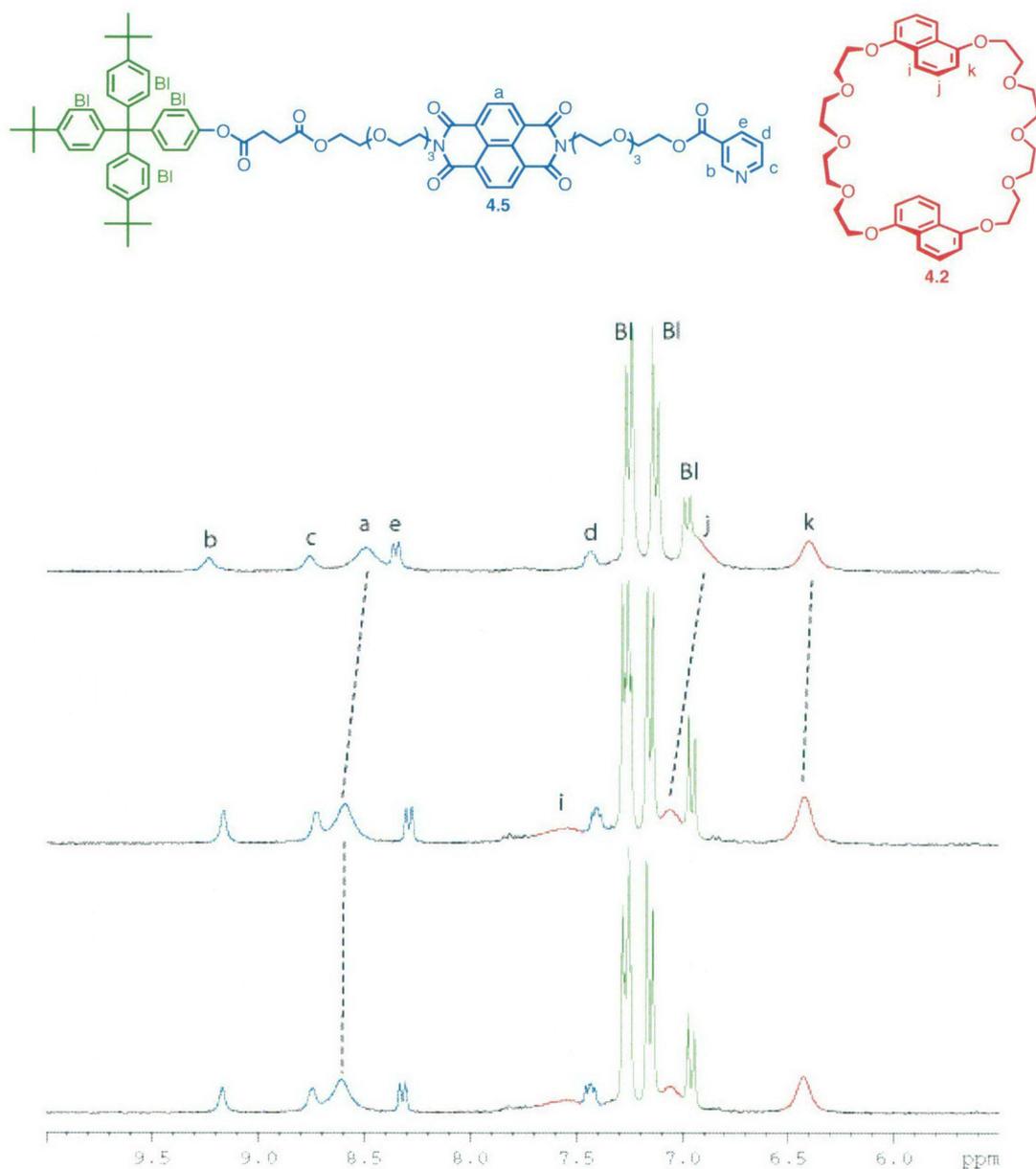
<sup>†</sup> This is to be expected as stoppering of one end of the thread, instead of both ends, alters both the on and off rates equally (by a factor of 1/2), having no net effect on the overall  $K_a$ . However, this would not be the case in situations in which the stopper directly interacts with the binding either positively or negatively, and so this possibility needed to be discounted.

diimides through a cation-induced effect but can also be used to drive molecular motion in [2]-rotaxanes incorporating these components.<sup>10, 11</sup> Thus it was reasoned that the addition of such alkali metals to our self-assembling rotaxane system may have a similar positive effect on the binding interaction between the crown and the diimide thread, and thus increase the proportion of intact rotaxane in any given mixture of components.

Two alkali metal salts were chosen for study, these being LiI and NaI, since these have had previously reported success in enhancing similar crown-diimide interactions in related systems.<sup>10, 11</sup> All NMR studies were performed in the mixed solvent 2%MeOD/CD<sub>2</sub>Cl<sub>2</sub> to assist in partially solubilizing the alkali metal salts which were added in large excess.

To two separate NMR tubes containing equimolar mixtures of mono-stoppered thread **4.5** and dinaphtho-crown **4.2** in 2%MeOD/CD<sub>2</sub>Cl<sub>2</sub> were added solid LiI or NaI respectively. The mixtures were sonicated to ensure sufficient solubilisation of the salts and <sup>1</sup>H NMR spectra were recorded (see Figure 4.5). The fast-exchanging resonances for the diimide and the crown protons had shifted upfield in the Na<sup>+</sup> addition experiment, indicating an enhanced complexation of the crown to the naphthodiimide moiety.

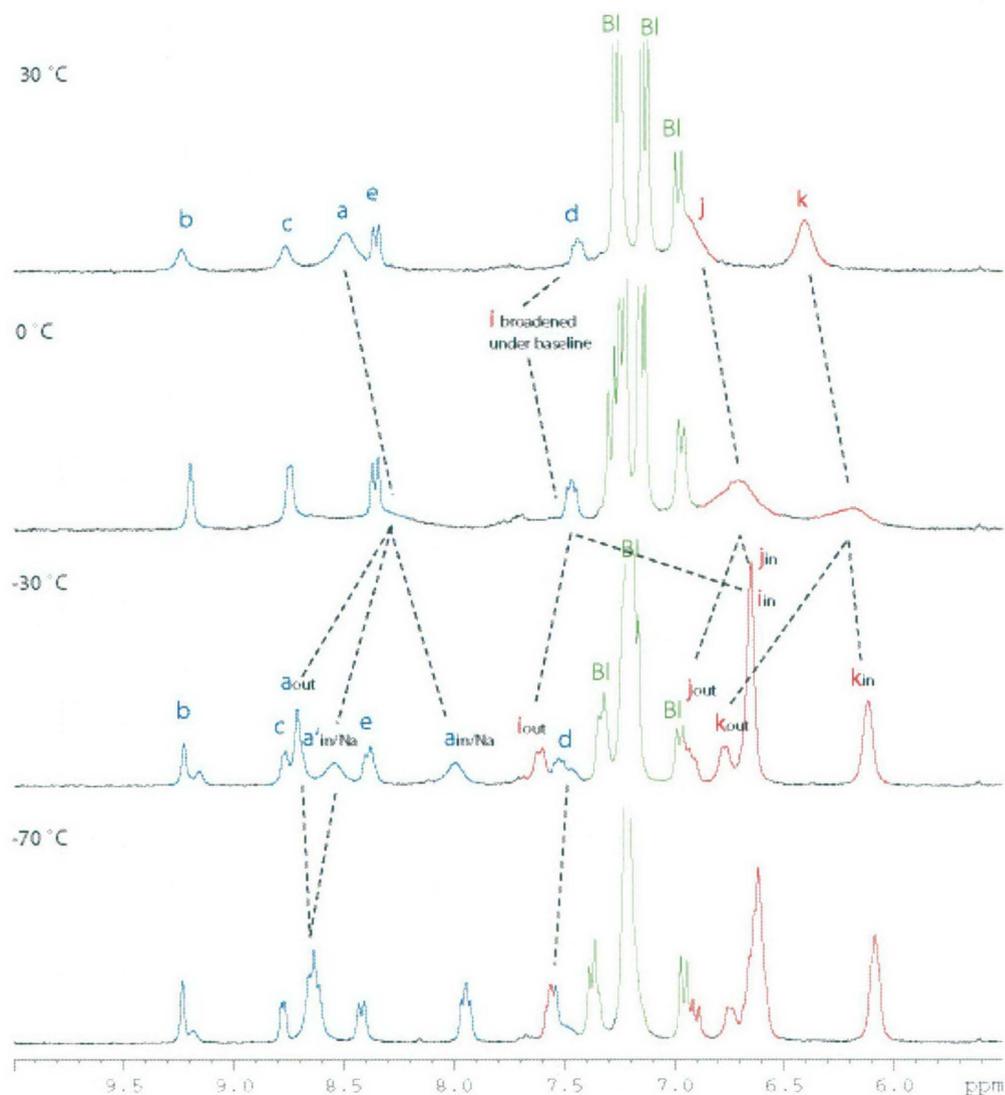
In the case where LiI had been added, the resonance for the diimide protons had initially remained unshifted at 8.59 ppm and each of the crown resonances had negligible shifts of 0.01 ppm. As the temperature was lowered the diimide proton peak gradually shifted upfield (to a greater extent than in the absence of Li<sup>+</sup>) indicating that LiI does enhance binding, albeit minimally. Previous reported studies had shown that stabilisation due to the addition of lithium salts was more effective for the smaller pyromellitic diimide than the naphthalene diimides, and this could explain the less than desired cooperative binding effect in our case.<sup>10</sup>



**Figure 4.5:-**  $^1\text{H}$  NMR comparison at 30 °C of diimide thread **4.5** binding equimolar proportion of crown ether **4.2** in the presence of NaI (top), no added salt (middle) and LiI (bottom). All spectra were run in 2%MeOD/ $\text{CD}_2\text{Cl}_2$ .

The results for the addition of NaI however, were far more promising. The analogous experiment with NaI shifted the diimide resonances to a far greater extent, from 8.59 to 8.50 ppm at 30 °C. The crown resonances also were more shielded with the most downfield proton moving to become hidden under other peaks, and the remaining two protons appearing at 6.90 and 6.40 ppm from their original positions of 7.05 and 6.42 ppm. It was therefore decided that all future experiments should be performed using NaI as the salt rather than LiI as the changes in the shifts of the resonances in the NMR

spectra at 30 °C were more informative. A more in-depth study of cation induced binding enhancement using NaI was thus carried out.



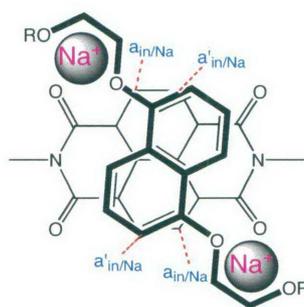
**Figure 4.6.-**  $^1\text{H}$  NMR temperature comparison for the binding of crown **4.2** to diimide thread **4.5** in the presence of NaI.<sup>‡</sup>

Variable temperature NMR experiments were conducted on an equimolar mixture of crown **4.2** and thread **4.5** in the presence of excess NaI (see Figure 4.6). A change from fast exchange to slow exchange on the NMR chemical shift timescale was observed as the temperature was lowered. Clear sets of peaks for bound (6.62 ppm i & j, and 6.09 ppm k) and unbound crown (7.55 i, 6.89 j and 6.76 k ppm) could be seen at low temperatures.<sup>§</sup> At

<sup>‡</sup> Bound crown and diimide peaks are depicted as  $i_{\text{in}}$ ,  $j_{\text{in}}$  etc, while unbound peaks are depicted as  $i_{\text{out}}$ ,  $j_{\text{out}}$  etc.

<sup>§</sup> It is important to note that the position of the unbound crown is slightly different from analogous experiments in the absence of NaI due to the unbound crown binding excess NaI present in solution.

-30 °C in addition to the two sets of resonances for the diimide protons representing bound and unbound conformations, a third set had appeared. As well as the typical unbound peak at 8.64 ppm ( $a_{out}$ ), and the typical bound peak at 7.97 ppm (designated  $a_{in/Na}$ ), there was now a new peak with the same intensity as the bound peak at 8.57 ppm (designated  $a'_{in/Na}$ ). It has been reported that in analogous systems sodium cations bind in the region of the polyether chain adjacent to the aromatic group and the naphthalene groups are then offset over the face of the diimide to maximise electrostatic interactions between the  $Na^+$  cation and the carbonyls of the diimide.<sup>11</sup> This offset geometry, shown in Figure 4.7, would result in two inequivalent diimide protons as is seen in the variable temperature experiments.



**Figure 4.7:-** Schematic drawing depicting the inequivalence of the diimide protons created through the binding of sodium ions, as previously reported.<sup>11</sup>

The peak at 7.97 ppm is the diimide proton closest to the complexed  $Na^+$  ion (designated  $a_{in/Na}$ ) while the other proton is at 8.57 ppm (designated  $a'_{in/Na}$ ). This is similar to results reported in the literature for the complexation of pyromellitic diimides to crown ethers where it was found that in the mono- $Na^+$  adducts, the pyromellitic diimide proton closest to the cation was significantly shielded in the NMR, whereas the other was significantly deshielded relative to their positions in pyromellitic diimide:crown complexes in the absence of added cations.<sup>11</sup>

In addition to this, as seen in the low temperature spectra of the experiments without addition of NaI (Figure 4.3), at -70 °C fine structure is seen appearing around these diimide resonances which is again indicative of rocking and yawing of the diimide inside

the crown (see Figure 4.4).\*\* Thus, it is clear that NaI has a significant positive effect on the binding of crown **4.2** to diimide thread **4.5**, an effect that can be utilised to advantage in the solid phase as well as in these solution studies.

The ruthenium porphyrin stopper **4.3** was subsequently added to the equimolar mixture of diimide **4.5** and crown **4.2** in the presence of NaI. As in the case where no NaI was added this system was now in slow exchange on the NMR chemical shift timescale and clear bound (6.64 ppm for protons i and j overlapping, and 6.14 ppm) and unbound (7.58, 6.86, 6.79 ppm) resonances for the crown, and similarly bound (8.05 ppm) and unbound (8.69 ppm) diimide peaks were observed. An increase in the proportion of bound versus unbound crown was clear evidence of enhanced stabilisation of the crown-diimide complex by the Na<sup>+</sup> cation. Again at low temperatures the appearance of the a'<sub>in/Na</sub> peak due to the asymmetry resulting from binding of the sodium cations was observed at 8.50 ppm, as was the fine structure around both bound diimide peaks due to the “yawing” and “rocking” phenomena described in Figure 4.4.

In summary, it was established that the stoppering of one end of the diimide thread did not significantly alter the thermodynamic behaviour of this system. More importantly it is apparent that the addition of NaI enhances the crown-diimide interaction and it can be anticipated that subsequent experiments on solid surfaces will be able to incorporate this to advantage.

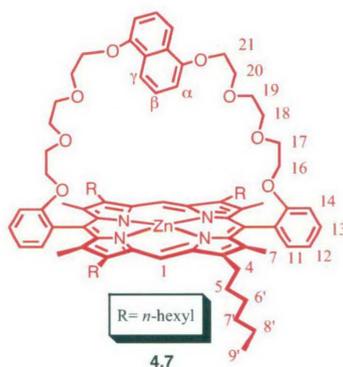
### **4.2.3 Solution studies of the use of strapped porphyrins as shuttle units of the rotaxanes**

As an extension to using the simple crown ether macrocycle **4.2**, the use of a strapped porphyrin such as **4.7** was investigated as an alternative shuttle unit in these rotaxane systems. The advantages of incorporating porphyrins in supramolecular systems have been described in some detail in section 1.3.1. In this case, an additional porphyrin shuttle

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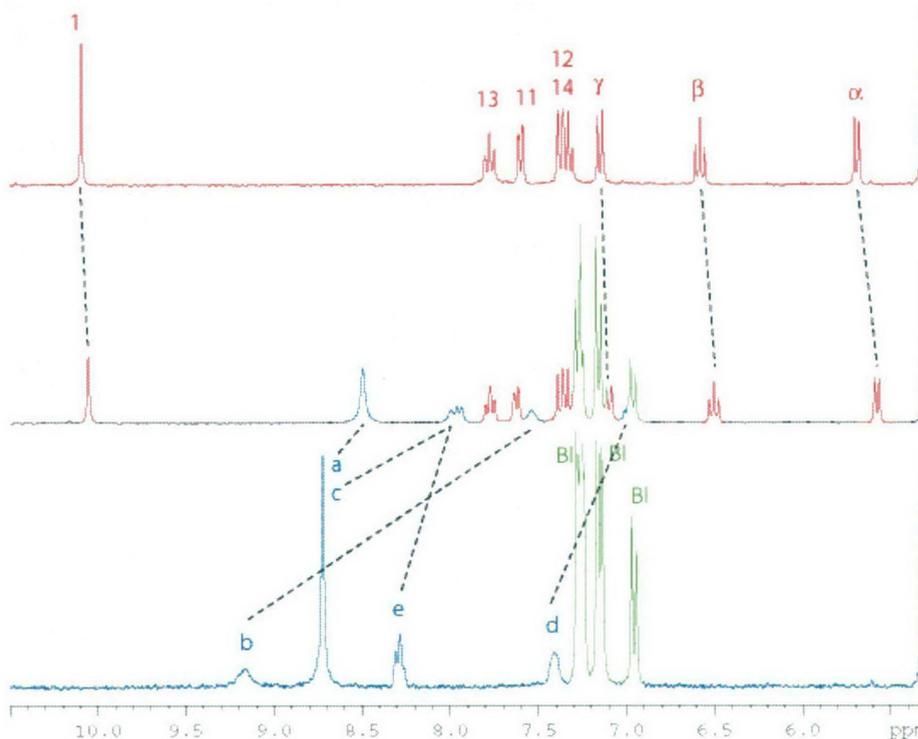
\*\* It was noted that at low temperature (-30 °C) a small peak at 9.23 ppm appeared. Various experiments proved that this peak was due to a small impurity of diimide thread **4.1** produced in the reaction to make **4.6** and in which the complete separation of these compounds is difficult by column chromatography.

unit can add considerably to the dimensions and potential of these types of rotaxanes, acting as it can as an addressable trigger unit or stimulus to “drive” the rotaxane. Such porphyrins have been incorporated into catenanes using diimide templates<sup>4, 12</sup> and the same principles should apply here to allow self-assembly of thermodynamically stable multi-porphyrin rotaxanes.



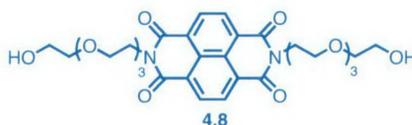
**Figure 4.8:-** Non-systematic numbering and colour coding of porphyrin **4.7** used in subsequent NMR assignment.

Binding of porphyrin **4.7** to diimide thread **4.5** was monitored by <sup>1</sup>H NMR in 2%MeOD/CD<sub>2</sub>Cl<sub>2</sub> (Figure 4.9).

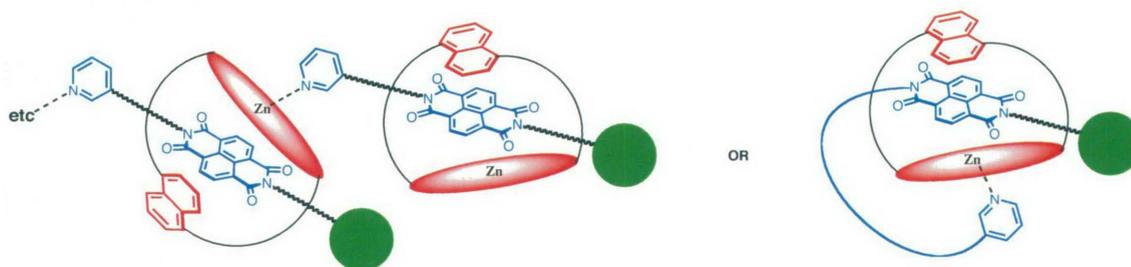


**Figure 4.9:-** Aromatic proton region of the NMR spectra of **4.7** (top), an equimolar mixture of **4.7** and **4.5** (middle) and diimide thread **4.5** (bottom). Numbering and colours refer to Figures 4.1 and 4.8.

Addition of an equimolar amount of porphyrin **4.7** to the diimide thread **4.5** resulted in an upfield shift for the diimide protons from 8.72 to 8.49 ppm caused by the shielding effects of the strapped porphyrin in a pseudo-rotaxane structure. Likewise, the porphyrin *meso* proton was shifted upfield ( $\Delta\delta$  -0.01) as were the naphthalene proton peaks ( $\alpha$   $\Delta\delta$  = -0.11;  $\beta$   $\Delta\delta$  = -0.08; and  $\gamma$   $\Delta\delta$  = -0.05 ppm). The pyridine protons from the diimide thread **4.5** were also substantially shielded and broadened, with proton b shifting from 9.16 to 7.60 ppm, proton c from 8.72 to 7.97 ppm, proton e from 8.29 to 7.96 ppm and proton d from 7.41 to 7.01 ppm indicating coordination (in typical fast exchange) of the terminal pyridines to the zinc atom in the strapped porphyrin moiety, in either the same or different molecular assembly. However, it is clear that the coordination of the pyridine does not prevent diimide binding and in fact enhances it, as adjudged from the larger upfield shift compared to other non-pyridine containing threads such as **4.8** (8.56 ppm).



Thus there is clearly some cooperativity between the binding of the pyridine unit to the metallated porphyrin and diimide complexation, which enhances the formation of the pseudorotaxane. Positive cooperativity for pyridine binding has also been seen in other strapped porphyrin systems involving viologen guests.<sup>13</sup> Inter- or intra-molecular pyridine-zinc coordination motifs are possible, as cartooned in Figure 4.10. While inter-molecular coordination leads to polymeric species (Figure 4.10, left), an intramolecular interaction may be favoured by principles similar to the chelate or macrocyclic effect (Figure 4.10, right).

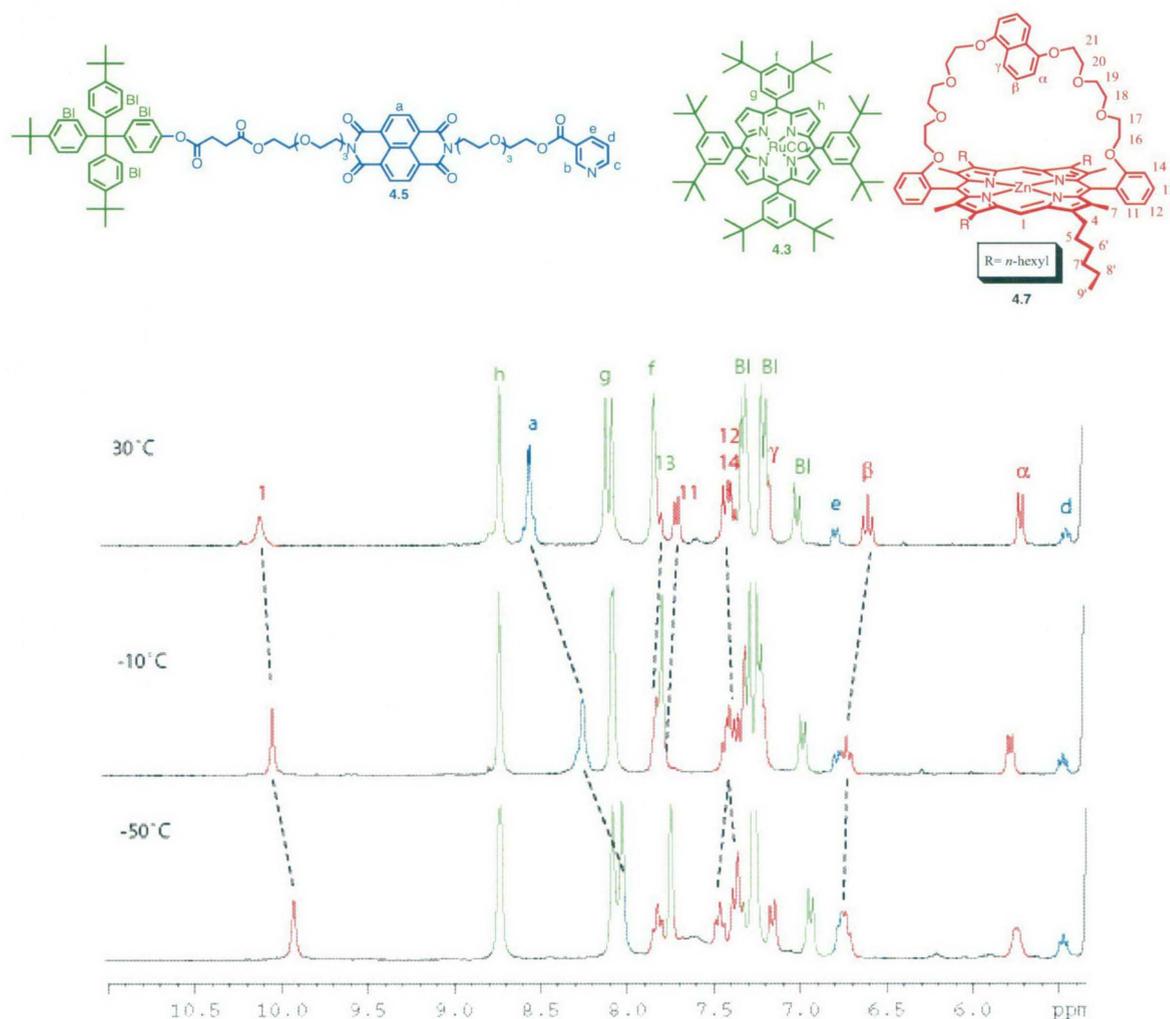


**Figure 4.10**:- Cartoon representation of pseudorotaxane geometries that would enable cooperative binding between the pyridine and diimide in mixtures containing **4.7** and **4.5**.

Addition of one equivalent of **4.3** results in a larger upfield shift of the pyridyl protons ( $\delta$  2.20 (b), 1.79 (c), 5.35 (d) and 6.72 (e) ppm) as the pyridine groups now coordinate to

the ruthenium porphyrin stopper in preference to the inherently weaker pyridine-zinc porphyrin coordination. However in doing so the cooperative binding that was observed in the mixture of **4.7** and **4.5** is disrupted and the diimide and porphyrin *meso* and naphtho peaks are shifted downfield (deshielded) into positions more typical of simpler diimide threads, such as **4.8**, binding to the porphyrin. This strongly suggests that the cooperative binding is indeed intramolecular (Figure 4.10, right) since if it were due to an intermolecular polymeric type geometry (Figure 4.10, left) little difference in diimide-porphyrin interactions would be expected whether the pyridine is binding to a remote zinc strapped porphyrin or to the ruthenium porphyrin stopper.

Surprisingly, the addition of ruthenium porphyrin **4.3** to an equimolar mixture of diimide **4.5** and porphyrin **4.7** did not result in a system in slow exchange on the NMR chemical shift timescale as it did when crown **4.2** was used as the macrocycle (see Figure 4.11).



**Figure 4.11:**  $^1\text{H}$  NMR temperature comparison for a mixture of **4.5**, **4.7**, and **4.3**.

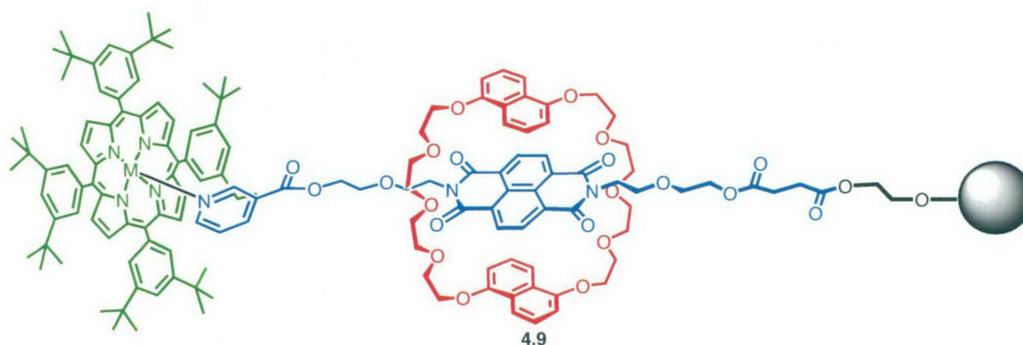
Variable temperature studies revealed that as the temperature was decreased the diimide proton peak steadily shifted upfield from 8.53 ppm to 8.01 ppm at  $-50^{\circ}\text{C}$ . This is consistent with the diimide becoming more bound (hence more shielded by the strapped porphyrin) at lower temperatures, a behaviour consistent with experiments carried out using crown as the macrocycle. However even at  $-50^{\circ}\text{C}$ , the diimide proton peak is not split into bound and unbound environments; rather the peak remains in fast exchange on the NMR chemical shift timescale. Similarly the *meso* protons of the strapped porphyrin **4.7** and the naphthoquinol  $\gamma$  proton are shifted further upfield with decreasing temperature indicating that the diimide is in a cofacial arrangement with the porphyrin and the naphthoquinol moieties. Conversely the naphthoquinol protons  $\alpha$  and  $\beta$  are shifted downfield (deshielded) as the temperature decreases. This can be explained by the fact that as the binding of the diimide increases, the strong shielding by the large  $\pi$ -cloud of the porphyrin on the naphthoquinol aromatic is replaced by the shielding of the smaller diimide moiety, resulting in a net deshielding effect. Similar examples of such overall deshielding effects on these protons despite the binding of shielding guests has been observed and reported previously.<sup>12, 14</sup>

NaI and LiI were added separately to equimolar mixtures of diimide **4.5** and porphyrin **4.7** and the subsequent solutions examined by NMR to ascertain whether these cations might stabilise the diimide-porphyrin interaction in a similar manner to that observed for the crown **4.2** system. However, it was apparent that both salts caused destabilisation of the diimide-porphyrin interaction, due at least in part to a disruption of the pyridine binding which led to the cooperativity. For the case where NaI was added the diimide proton peak shifted from 8.49 to 8.68 ppm and for addition of LiI from 8.49 to 8.61 ppm. These new diimide positions are still shifted upfield from their starting material indicating that binding still occurs, but clearly to a much lesser extent than in the absence of salt. Similarly, in the presence of both NaI and LiI the pyridine protons are substantially deshielded compared to the case without added salts, indicating decreased binding. Addition of ruthenium stopper **4.3** does not alter these observations, and it is clear that the diimide binding is diminished by addition of either salt. Thus, it was concluded that although the diimide binds under the strap of the porphyrin in the presence of added cations, it does so to a much lesser extent; therefore there was no advantage in using these salts in future experiments (both in solution and on solids).

#### 4.2.4 HR MAS NMR studies into the binding of a polymer tethered naphthodiimide thread to a crown ether macrocycle

Having established the principles of the binding and dynamic behaviour of crown ether **4.2** to a mono-stoppered diimide thread **4.5** in solution, attention was turned to examining the analogous system on solids supports, in this case polystyrene beads. This work was started by Johnstone *et al.*<sup>5</sup> but more detailed studies into the reproducibility and dynamic behaviour were required.

As discussed in Section 1.4 Johnstone *et al.*<sup>5</sup> reported the thermodynamic self assembly of the pseudorotaxane **4.9** on solid supports. It was expected that two crown peaks representing bound and unbound crown would be evident in the HR MAS NMR spectra; however he reported the appearance of a third set of crown peaks, not seen in solution studies. This was attributed to some crown macrocycles bound around the inner polyethylene glycol linkers on the ArgoGel beads.<sup>5</sup>



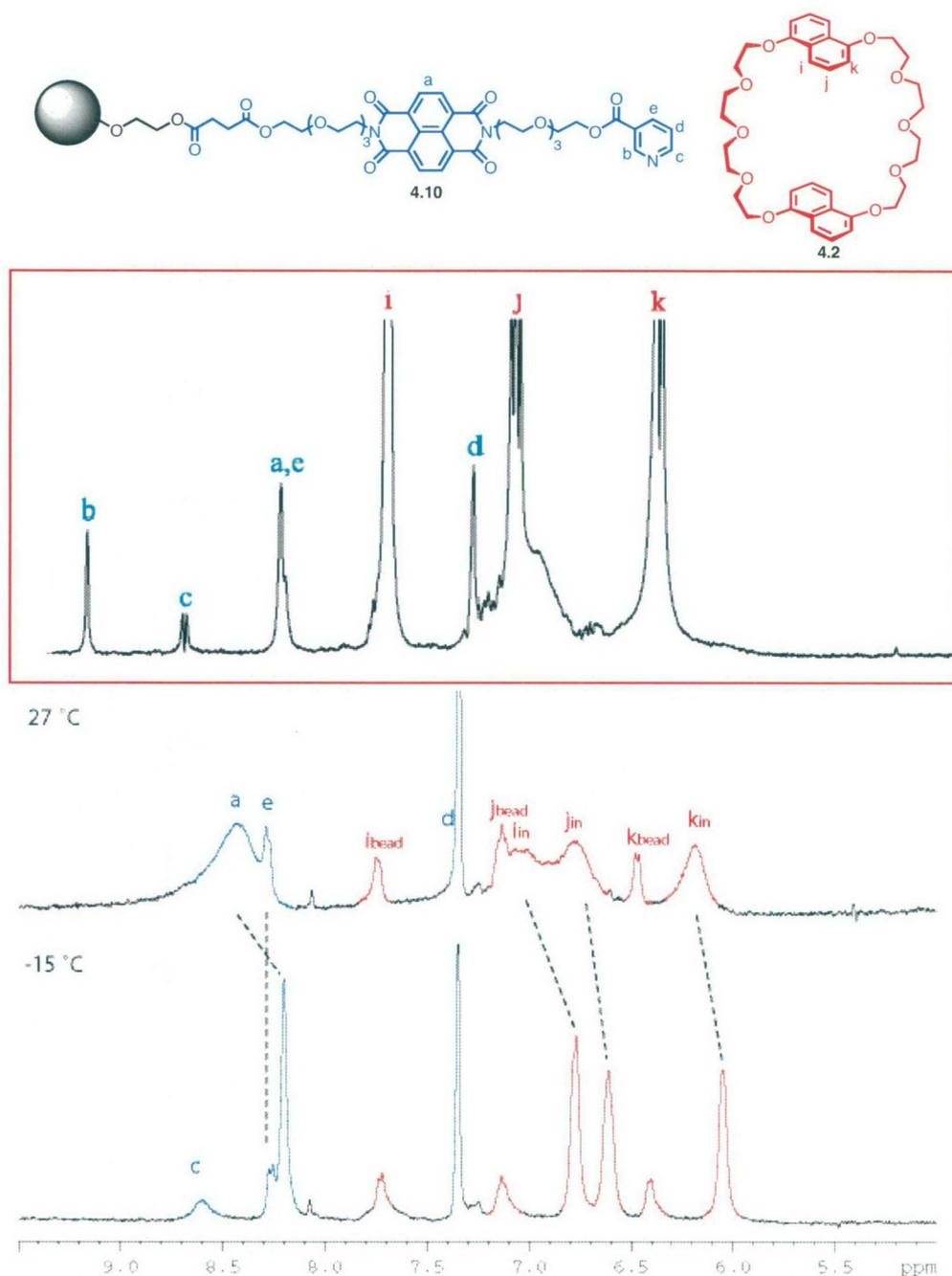
This complicates the NMR spectra obtained, and thus it was reasoned that decreasing the amount of crown added<sup>††</sup> to the diimide tethered beads would eliminate this third set of polyethylene glycol bound crown peaks. As well as adding evidence for the identity of this set of peaks, this would also simplify interpretation of future work involved in examining the dynamic behaviour of this system using variable temperature HR MAS NMR.

<sup>††</sup> Due to the nature of the experiment monitoring exact stoichiometric quantities of each component is not practical.

Attachment of the diimide thread to ArgoGel-OH beads to produce tethered bead **4.10** was carried out according to the procedures of Johnstone *et al.*<sup>15</sup> HR MAS NMR analysis of these beads indicated successful attachment of the diimide thread as evidenced by the expected pyridyl (9.16, 8.72, 8.28, 7.39 ppm) and diimide (8.72 ppm) aromatic peaks visible in the NMR spectrum.

Investigations to determine the loading of the diimide thread on the polystyrene beads by UV Vis and elemental analysis were undertaken. Details of the procedures and the results are described in Appendix 5. The loading of the naphthodiimide tethered beads **4.10** was determined to be approximately 0.19 mmol/g (taken as an average of the three methods) which is approximately 40% of the theoretical loading (0.46 mmol/g) reported by the manufacturer. Despite the lower than theoretical loading it is clear that the tethering process is still more than adequate for HR MAS NMR analysis yielding good quality spectra.

Addition of a solution of crown **4.2** to the diimide tethered beads **4.10** resulted in an upfield shift in the diimide protons to 8.43 ppm caused by the shielding effects of the bound crown naphthalene groups. However, with this less concentrated crown solution, two new sets of crown peaks were apparent in the HR MAS NMR proton spectrum (see Figure 4.12). This second set of crown peaks is absent both in the solution analogues discussed in Section 4.2.1 and Johnstone's work<sup>5</sup> and represents an average set of peaks present in fast exchange on the NMR chemical shift timescale.



**Figure 4.12:-** HR MAS proton NMR temperature comparison of a mixture of diimide tethered bead **4.10** with crown **4.2** in 2%MeOD/ $\text{CDCl}_3$ .<sup>††</sup> The top figure (in red box) is the original HR MAS proton spectrum of a mixture of diimide tethered beads **4.10** and crown **4.2** obtained by Johnstone. Differences in the HR MAS spectrum is due to both a different solvent system (Johnstone's work being performed in  $\text{CDCl}_3$ ) and a different concentration range, in that Johnstone added a higher concentration of added crown resulting in stronger diimide complexation (as evident by a higher field diimide proton a chemical shift).<sup>5</sup>

<sup>††</sup> Some pyridine protons are not visible in this spectra due to filtering out as a result of a 2K CPMG loop pulse sequence used to filter out core bead proton resonances. All such samples are routinely run with 0, 32, and 2K CPMG loop pulse sequences to ensure visualisation of all components. Clear NMR signals for the pyridine protons b-e can be visualised in the basic proton pulse acquisition where no CPMG sequences are used.

It was initially thought that in this case the binding of crown on the beads was in slow exchange on the NMR chemical shift timescale and that the two sets of crown peaks represented bound and unbound configurations. Variable temperature HR MAS studies were thus performed to decipher any dynamic behaviour. If the system were in slow exchange no upfield or downfield shifts in the crown peaks should be observed with changing temperature, but a change in the ratio of bound to unbound peaks would be expected. Inspection of this system at different temperatures however, revealed that one set of crown peaks did move upfield (from 6.92, 6.77 and 6.19 ppm to 6.77, 6.61 and 6.05 ppm at  $-15\text{ }^{\circ}\text{C}$ ) indicating that this set of peaks is indeed involved in an equilibrium. The diimide peak also shifted upfield from 8.43 to 8.21 ppm indicating that it is involved in the equilibrium with the set of crown peaks most upfield.

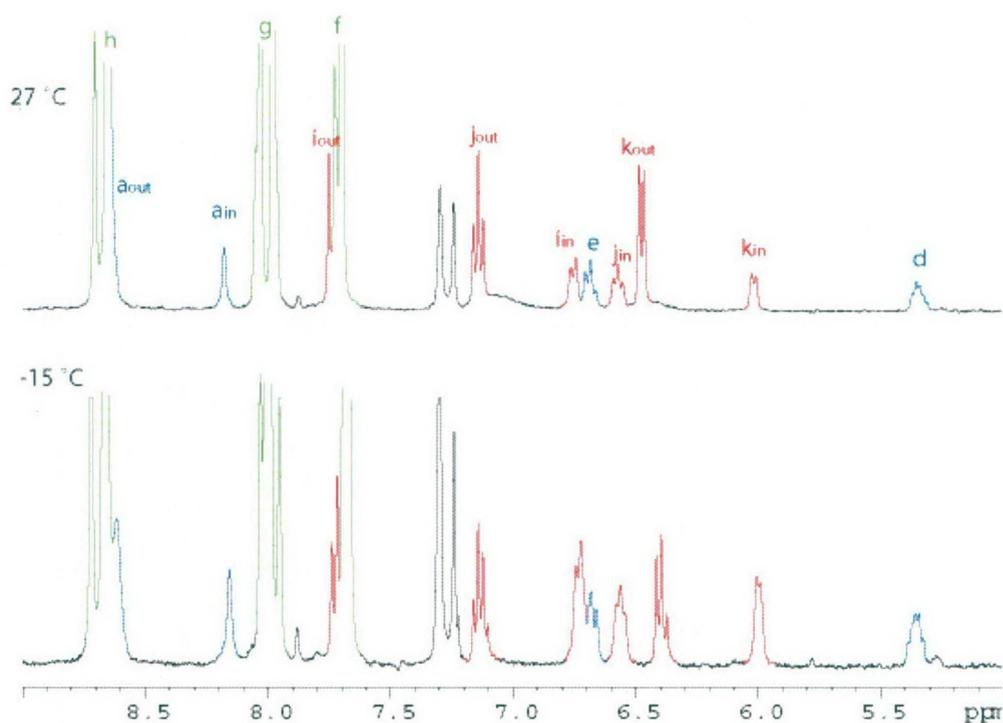
The other set of crown peaks at 7.75, 7.14, 6.47 ppm did not shift as temperature decreased indicating a fixed, non-equilibrating component. This suggests that this downfield set of crown peaks is not involved in the binding of crown to diimide and is “entrapped” or “intertwined” in the bead core and thus unable to access the diimide<sup>§§</sup>; the more upfield set is involved in binding to the diimide, and as the temperature decreases, pseudorotaxane formation is favoured. This is not seen in Johnstone’s previous studies as when a large excess of crown is added, the peaks seen are in the typical unbound region of the NMR, overlapping and obscuring the region where the entrapped crown peaks appear. Thus it is important to ensure that analysis of these and future systems is done with both concentrated and more dilute solutions so that the different behaviour can be monitored. It is also clear that the use of variable temperature HR MAS can be of considerable utility in understanding the dynamic behaviour of these systems on solid supports.

Under similar concentration conditions, addition of an equimolar solution of **4.2** and **4.3** to the diimide tethered beads **4.10** resulted in a large upfield shift of the pyridyl protons

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<sup>§§</sup> The crown may be threaded on the polyether chains (as is the case in similar systems incorporating these functionalities<sup>16</sup>), or more simply entangled in them; the spectra are unable to distinguish between these possibilities. In either case, the environment provided by the polyethylene glycol chains would be sufficiently different to that of the solvated uncomplexed crown to account for the slight upfield shifts.

(to 6.68, 5.35, 2.18 and 1.76 ppm) as the pyridine group coordinated to the ruthenium porphyrin. Stopping by this porphyrin slows the dynamics of this system from fast to slow exchange on the NMR chemical shift timescale, resulting in observable bound (6.75, 6.57, 6.02 ppm) and unbound (7.70, 7.14, 6.48 ppm<sup>\*\*\*</sup>) crown, and likewise bound (8.18 ppm) and unbound (8.71 ppm) diimide peaks (Figure 4.13). Unlike Johnstone's work however, no third set of crown peaks due to polyethylene glycol bound crown around the polyethyleneglycol tentacles of the ArgoGel beads were observed under these more dilute conditions. Variable temperature experiments showed that as the temperature decreased the proportion of bound versus unbound crown increased indicating that rotaxane formation is thermodynamically favoured at lower temperatures, which is comparable behaviour to that observed on analogous solution rotaxanes (see Section 4.2.1).



**Figure 4.13:-** HR MAS NMR proton temperature comparison of diimide tethered bead **4.10** with equimolar mixture of crown **4.2** and porphyrin stopper **4.3** added.

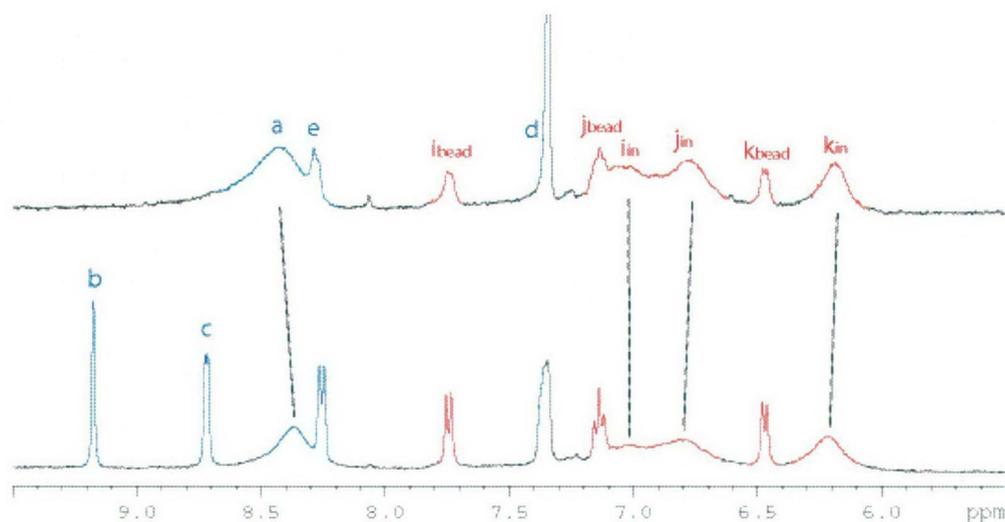
As these results were different to those obtained to Johnstone's work it was considered necessary to determine the reproducibility of this technique. More concentrated solutions of crown **4.2** and equimolar mixtures of crown **4.2** and porphyrin **4.3** were added to bead

<sup>\*\*\*</sup> It should be noted that this unbound crown set will include both crown "entrapped" in the bead core which is not involved in the equilibrium with the diimide, and unbound crown which is involved in the binding with diimide.

samples and their HR MAS NMR spectra recorded. The spectra obtained were now identical to Johnstone's work, with the mixture containing crown showing only one set of peaks, and the sample containing both crown and porphyrin revealing the third set of crown peaks representing polyethylene glycol-bound crown which was absent in our initial measurements. This confirms that the technique is indeed reproducible and the differences seen in this work were a function of the ratio of diimide to crown and porphyrin, and not to any anomaly in either the synthesis/loading of the beads or an experimental artefact of the HR MAS technique.

We had previously observed in solution-phase studies, that the addition of sodium cations had a positive impact on the binding of crown **4.2** to the diimide thread **4.5** (see Section 4.2.2). It was of interest to determine whether this effect could be seen in the analogous systems tethered to solid polystyrene beads. However as quantitation is difficult in this technique, care must be taken to ensure that any increase in binding that might be detected is due to the addition of sodium cations, and not simply due to more or less crown being added to the bead samples during their preparation for HR MAS analysis.

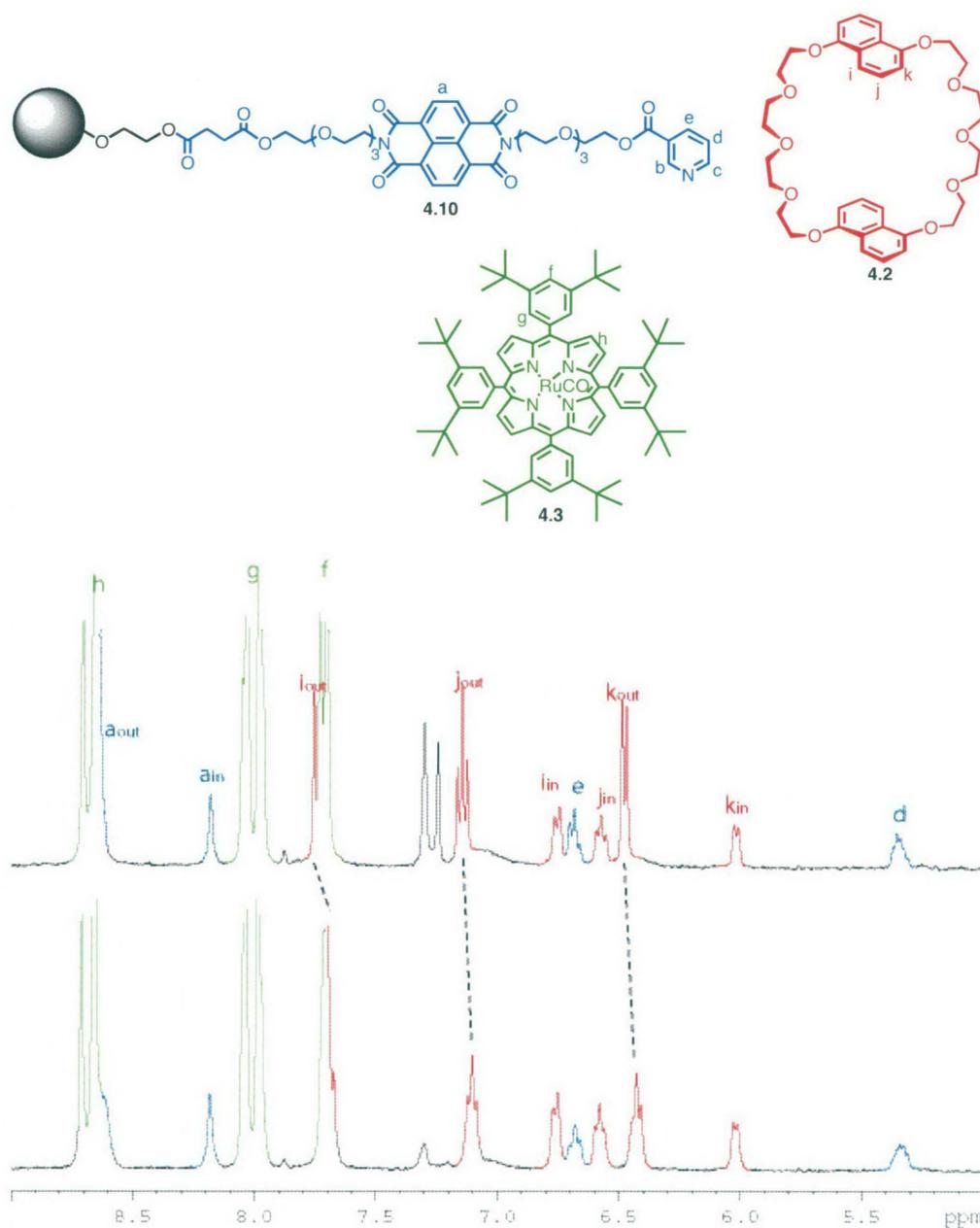
Thus, a solution of crown **4.2** and NaI in 2%MeOD/ $\text{CDCl}_3$  was sonicated for several minutes to ensure solubilisation of the sodium iodide and then this solution was added to the diimide tethered beads **4.10** and HR MAS NMR recorded (Figure 4.14).



**Figure 4.14:-** HR MAS NMR comparison of pseudorotaxane with and without NaI at 300 K. Top spectrum is tethered diimide **4.10** plus crown **4.2**. Bottom spectrum is tethered diimide **4.10** plus crown **4.2** plus NaI.

When compared to the NMR spectra recorded in the absence of NaI it is immediately obvious that the spectrum with NaI shows much sharper peaks. Indeed, in this case, the pyridine protons are visible; they are not filtered by the application of the CPMG pulse sequence, presumably due to different relaxation effects caused by the presence of the NaI. The diimide proton has shifted from 8.43 ppm in the system without NaI to 8.37 ppm with NaI. In this case however, the crown peaks are seen to be deshielded slightly, moving from 6.92, 6.77 and 6.19 ppm to 7.01, 6.79 and 6.22 ppm. This suggests an excess of crown added to the beads, and thus the upfield shift of the diimide peak could be a result of additional crown causing a shift in the equilibrium to more bound species. Nevertheless the sharpening of the spectra suggests that the exchange process is slower and that the formation of pseudorotaxane is indeed stabilised. This is evidence that addition of NaI is effective, although the relative magnitudes of the shifts of the peaks in this case is not definitive.

Addition of a solution containing the same crown **4.2**, but now with added porphyrin stopper **4.3** and NaI, showed far more promising evidence of the sodium ion positively influencing the binding of the tethered diimide **4.10** to the crown (see Figure 4.15). In this case, addition of NaI increased both the proportion of bound diimide and bound crown relative to their unbound counterparts. This is not due to excess crown being added, as otherwise the spectrum would show an increase in bound diimide but a decrease in bound crown. Conversely it cannot be due to a lower amount of crown added, which would result in increased bound crown peaks but a reduction of bound diimide. Thus it is clear that the sodium cation enhances the rotaxane formation on solid supports just as it does in solution (see Section 4.2.2).



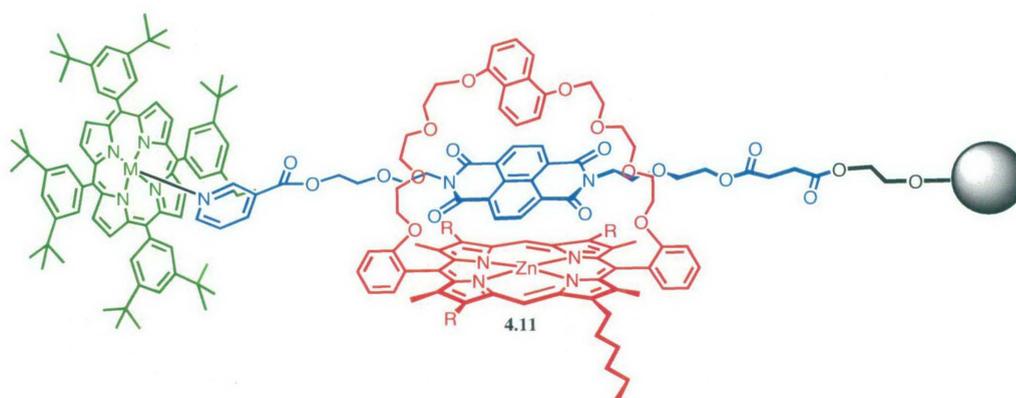
**Figure 4.15:-** HR MAS NMR comparison of pseudorotaxane with and without NaI at 300 K. Top spectrum is tethered diimide **4.10** plus crown **4.2** plus porphyrin stopper **4.3**. Bottom spectrum is tethered diimide **4.10** plus crown **4.2** plus porphyrin stopper **4.3** plus NaI.

The results presented here show that there is no significant difference in the behaviour of the solid-tethered diimide thread system compared to that observed in their solution phase analogues. The enhancement of rotaxane formation by addition of  $\text{Na}^+$  ions observed in solution is also paralleled in the gel-phase system. We have also confirmed that previous work by Johnstone *et al.* is reproducible, which shows that this technique is reliable and

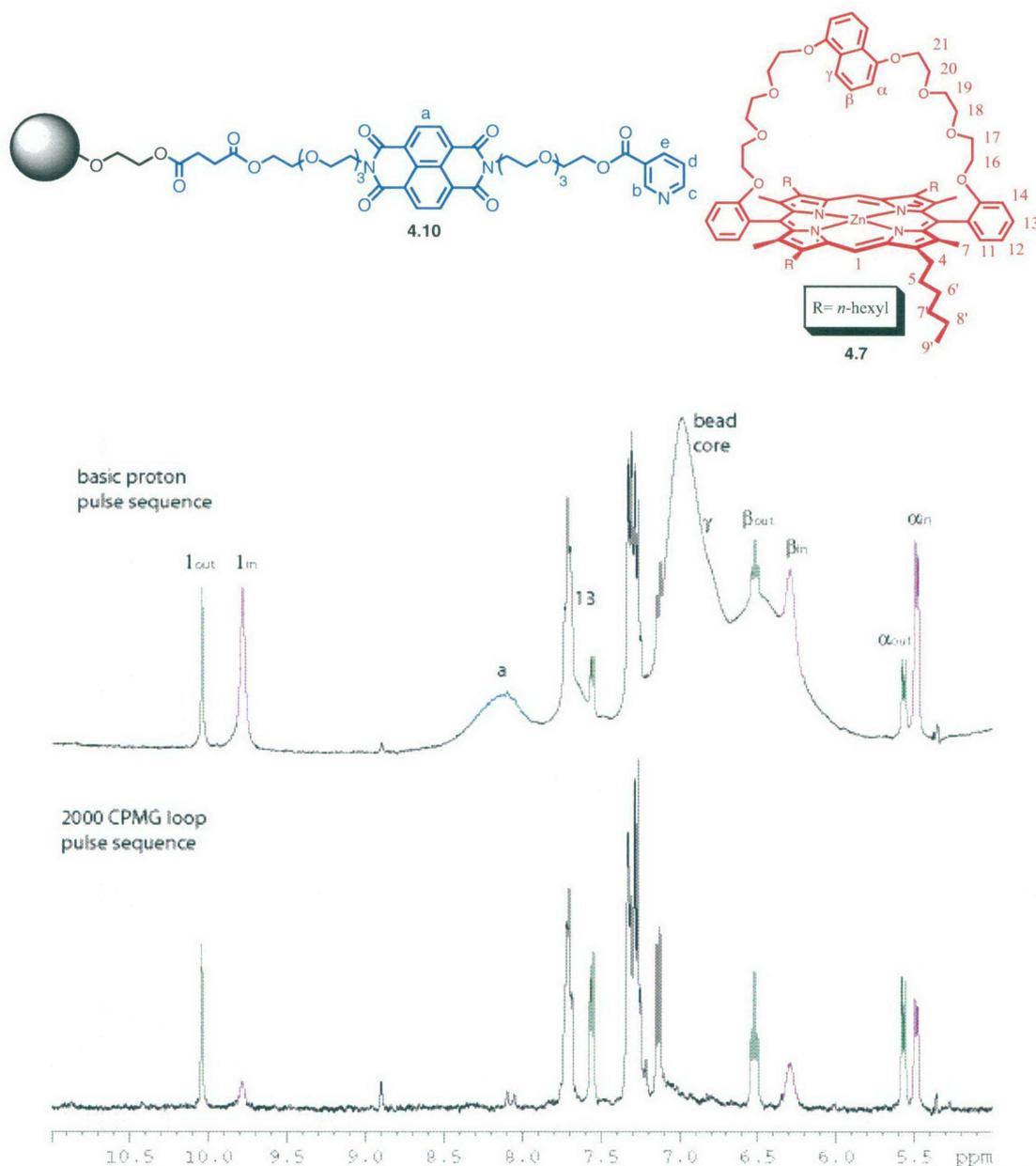
robust. The ability to use variable temperature makes this a very versatile technique and extends its potential considerably.

#### 4.2.5 HR MAS NMR studies into the binding of polymer tethered naphthodiimide thread to a strapped porphyrin macrocycle.

Having established the important principles described thus far, studies were now extended to incorporate strapped porphyrin **4.7** rather than the crown **4.2** into these systems, and to examine its binding behaviour and ability to self assemble into rotaxanes on solid supports.



Thus a solution of strapped porphyrin **4.7** was added to the diimide tethered beads **4.10** and the HR MAS NMR spectra recorded. However upon application of the standard 2K CPMG pulse sequence (used to filter out the bead core resonances) many of the pseudorotaxane signals that are present in the basic proton spectrum were also filtered out (see Figure 4.16). This is due to the fact that the CPMG pulse program is not discriminative and filters out all broad signals, in this case not only those due to the bead core, but also the broad pseudorotaxane signals arising from the weaker binding of the strapped porphyrin in fast exchange on the NMR chemical shift timescale. Despite the broadness (and added complication of the bead core resonances) in the basic proton HR MAS spectra obtained for this system, the binding of the strapped porphyrin macrocycle to the tethered diimide could still be examined.



**Figure 4.16:-** HR MAS NMR comparison of a mixture of diimide tethered bead **4.10** and strapped porphyrin **4.7** upon application of different pulse sequences (top being a standard proton spectrum, bottom being a spectrum obtained after application of a 2K CPMG pulse sequence). Purple colouring refers to those resonances resulting from the porphyrin diimide binding. Green colouring refers to those resonances resulting from unbound porphyrin (present due to the large excess of porphyrin added).

At room temperature, the addition of strapped porphyrin resulted in an upfield shift in the diimide protons a from 8.72 to 8.11 ppm caused by the shielding effects of the bound strapped porphyrin. The pyridine protons of the diimide tethered thread have also shifted

upfield to 7.70, 7.55, and 7.29<sup>†††</sup> indicating some degree of coordination to the metallated porphyrin; however whether this is through an intramolecular or intermolecular interaction can not be determined.<sup>†††</sup> Nevertheless, two sets of porphyrin *meso* and naphthalene aromatic peaks were evident, indicated by green and purple colouring in Figure 4.16. The more downfield (green) set of porphyrin protons displayed a *meso* proton peak at 10.05, and naphthalene proton peaks at 7.12, 6.52 and 5.56 ppm. The other (more upfield) set of porphyrin protons (purple) has a *meso* proton peak at 9.79 ppm and naphthalene protons at 6.30 ( $\beta$ ) and 5.48 ( $\alpha$ ) ppm with the  $\gamma$  naphthalene obscured by the core bead proton peaks. Variable temperature studies showed that these two species were in slow exchange on the NMR chemical shift timescale and that pseudorotaxane formation is favoured at lower temperatures as evident by a decrease in the proportion of the unbound (green) set of porphyrin protons relative to the bound set (purple). Interestingly no unbound diimide is evident which suggests that it is fully bound even at room temperature due to the excess porphyrin added.

This observation is contrary to that seen in the solution analogues as even at  $-50\text{ }^{\circ}\text{C}$  the pseudorotaxane remains in fast exchange. This is the first significant difference in the dynamic behaviour of pseudorotaxanes on solid supports compared to their solution counterparts, but the reason for the change to slow exchange is unknown. It does however emphasise the importance of this technique in the easy visualisation of such subtle (yet important) differences in the dynamic behaviour of these systems that other surface techniques would be unable to detect.

The relaxation properties of the porphyrin make HR MAS NMR spectra difficult to obtain as the standard CPMG pulse sequence used for filtering bead signals cannot be used due to filtering of important porphyrin signals. This makes it more difficult to interpret the spectra. As the binding is not as strong as with the non-porphyrinic crown, it

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<sup>†††</sup> These protons although masked by other resonances were identified by their typical coupling patterns in a COSY experiment. Pyridine proton b is presumably hidden underneath the porphyrin resonances, but cannot be located with certainty- due to its singlet nature it is not detectable in COSY experiments.

<sup>†††</sup> The extent of shielding of the diimide suggests that as in the solution analogues (see section 4.2.3) that cooperative binding is occurring but this cannot be concluded in this case as excess porphyrin is added and the dynamic behaviour on the beads is different to that in solution.

is suggested that it may be more beneficial at this stage to continue using the crown ether as the macrocyclic component rather than the strapped porphyrin until the porphyrin diimide interaction can be enhanced, or until these particular problems associated with spectral acquisition and processing can be overcome.

### 4.3 CROWN TETHERED SYSTEMS

For an understanding of the self assembly of more complex (ie multiple component) tethered rotaxane systems it is important that attachment on solid supports and subsequent rotaxane formation of each of the individual components in this system is understood in some detail. Thus having established the principles of self assembly of rotaxanes on solid supports using the diimide tethered component **4.10**, the concept was extended to examine rotaxane formation using the tethered crowns. Preliminary studies into the attachment of crown ether macrocycles to solid polystyrene supports and subsequent rotaxane formation was initiated by Johnstone *et al.*<sup>15</sup> Johnstone developed methods for the synthesis of mono-functionalised crown ethers and subsequently the tethering of mono-functionalised crown ethers to the gel-phase polystyrene supports. Preliminary investigations into the binding of naphthodiimides to a series of three mono-functionalised crown ethers (Figure 4.17) were undertaken to determine the optimum crown for bead attachment and HR MAS NMR analysis.

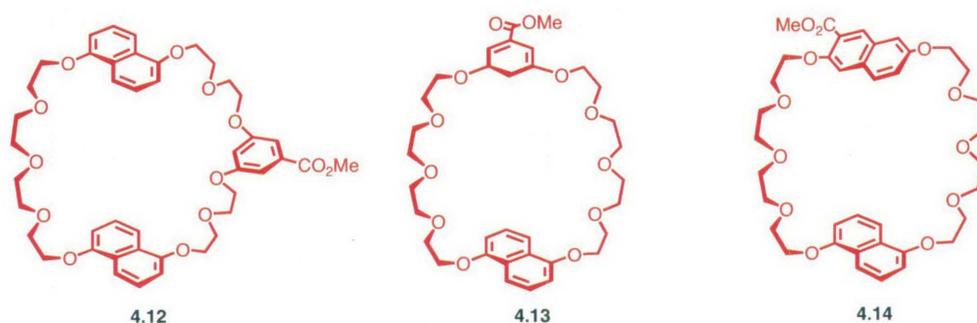


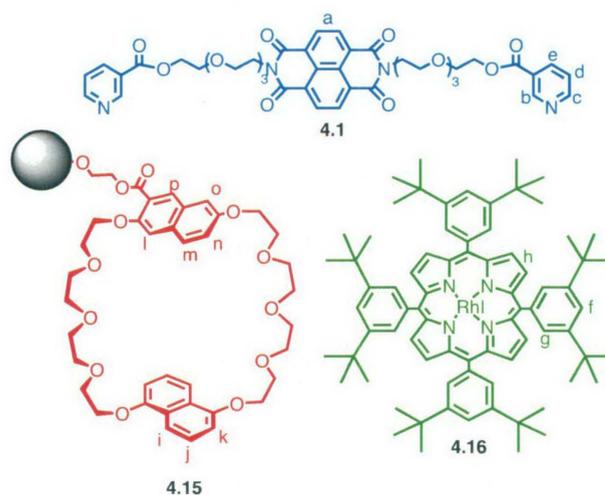
Figure 4.17:- Crown ethers used in Johnstone *et al.* studies.<sup>15</sup>

Johnstone determined that all three mono-functionalised crown ethers did not bind well to naphthodiimides in solution as indicated by little to no shifts in the crown or diimide proton peaks in equimolar mixtures of crown and diimide **4.8**. It was calculated that all three crowns had binding constants with the diimide **4.8** of about  $12 \text{ M}^{-1}$ ,<sup>15</sup> which was

deemed inadequate for effective rotaxane formation either in solution or on solid surfaces. However, it was discovered that addition of LiI to equimolar mixtures of crown **4.14** and diimide **4.8** dramatically improved the association between crown and diimide and resulted in significant upfield shifts in both the diimide and crown resonances. This crown was selected as the ideal candidate for subsequent tethering to ArgoGel beads.<sup>15</sup>

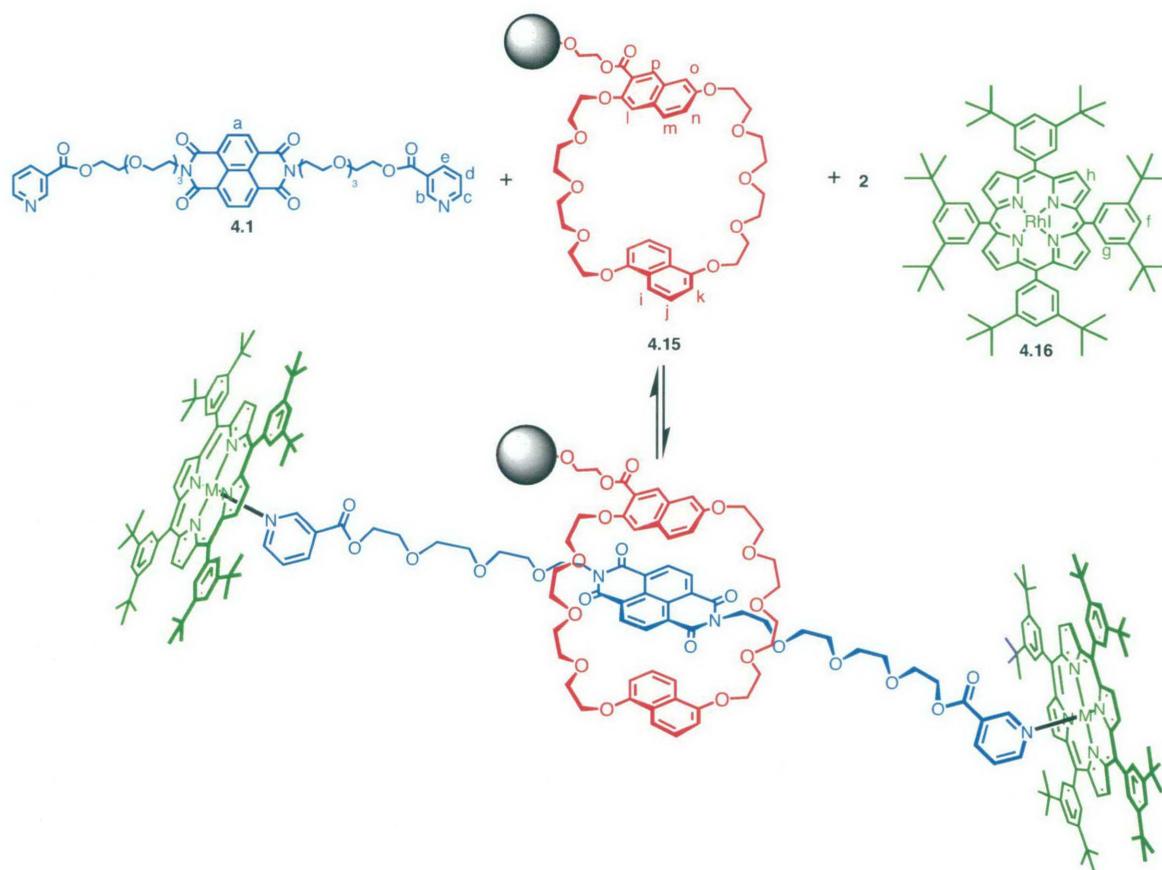
Tethering of the crown macrocycle **4.14** was successful as were initial HR MAS NMR studies on the tethered crown. However subsequent rotaxane formation studies in the presence of LiI were not conclusive. Thus the work described in this thesis re-visits the analysis of the self assembly of rotaxanes using tethered crown beads under conditions of dynamic equilibrium between solution and solid phase components, with and without the addition of added salts.

HR MAS NMR was thus used to analyse the ArgoGel tethered dinaphtho 38-crown-10 **4.15** and its associated supramolecular systems.<sup>§§§</sup> The non-systematic aromatic numbering and colouring system used in the HR MAS NMR discussion are shown in Figure 4.18.



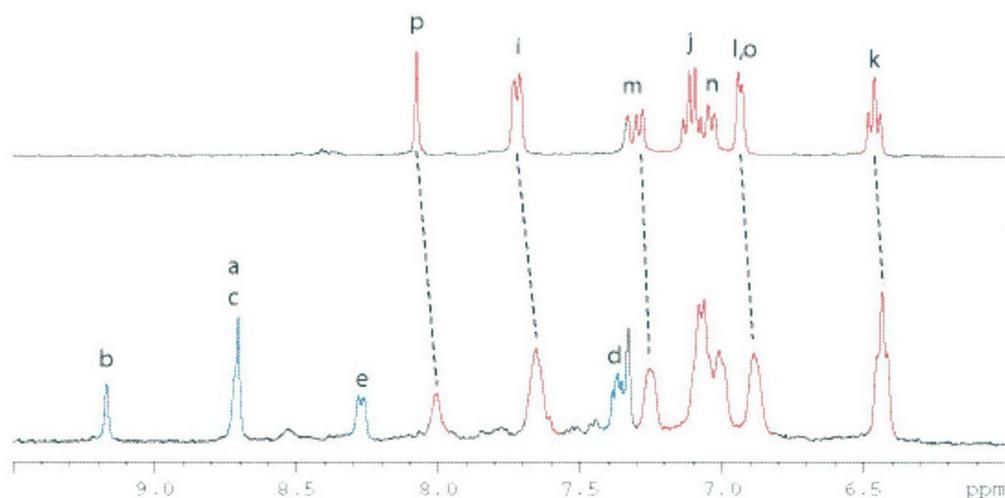
**Figure 4.18:-** The non-systematic numbering and colouring system used for HR MAS NMR analysis of **4.15** and its related supramolecular systems.

<sup>§§§</sup> The crown tethered beads used in these studies were synthesised by Dilip Nath according to procedures reported by Johnstone et al.<sup>15</sup>



**Scheme 4.4:**- Schematic diagram showing the possible assembly of the tethered crown rotaxane.

The  $^1\text{H}$  HR MAS NMR spectrum showed expected crown peaks at 8.08, 7.72, 7.33, 7.29, 7.10, 7.03, 6.94 and 6.46 ppm in 2%MeOD/ $\text{CDCl}_3$ . These shifts are consistent with solution studies and with previous bead attached systems reported by Johnstone *et al.*<sup>15</sup> Furthermore, the intensity and signal to noise ratio in the spectra of these beads indicate good loading onto the ArgoGel polystyrene supports. Addition of a solution of the bis-pyridyl-substituted diimide thread **4.1** resulted in small upfield shifts in the crown proton positions to 8.01, 7.65, 7.32, 7.25, 7.07, 7.01, 6.88 and 6.43 ppm (Figure 4.19). Due to the addition of excess diimide thread, the extent of these shifts is slightly larger than the weak binding observed in solution (by Johnstone) in the absence of any  $\text{Li}^+$  ions.



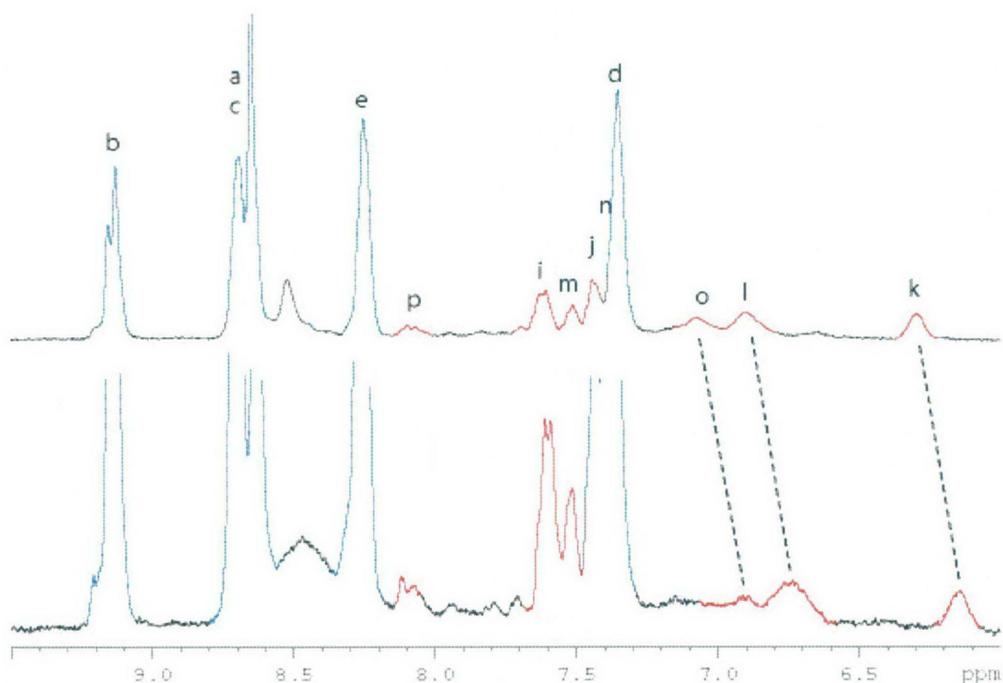
**Figure 4.19:-** HR MAS NMR spectra of **4.15** (top) and a mixture of **4.15** and **4.1** (bottom). Colours and labelling follow those described in Figure 4.18.

As solution studies had shown that the addition of LiI substantially increased the binding of diimide threads to this crown, it was of interest to determine whether this effect could be observed in the analogous tethered systems. Thus, a solution of diimide thread **4.1** in 2%MeOD/ $\text{CDCl}_3$  and excess solid LiI was sonicated for several minutes to solubilise the lithium iodide and then this solution was added to the crown tethered beads **4.15** and the HR MAS NMR spectrum recorded.

The addition of LiI resulted in further small upfield shifts in the crown and diimide peaks. The diimide proton peak shifted from 8.71 to 8.69 ppm indicating a slight increase in its binding to the crown; however such a minimal shift is expected because of the excess thread **4.1** added to the solution. The crown peaks had upfield shifts of between 0.01 and 0.06 ppm, again indicating a more shielded environment due to a slight increase in the binding of diimide to the crown tethered beads. However the extent of these upfield shifts is far less than that seen in analogous solution studies.

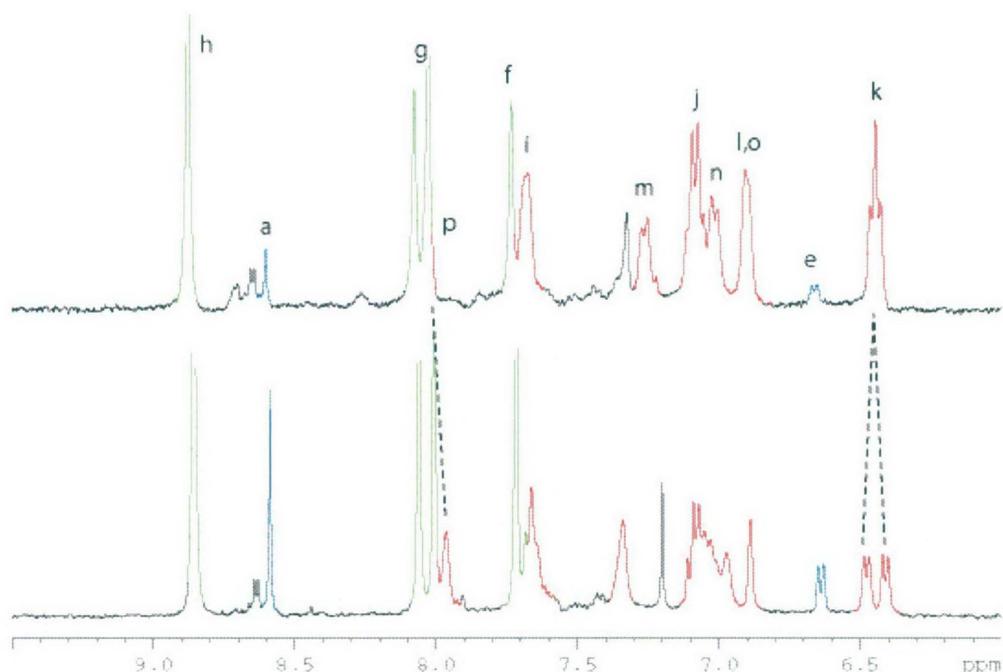
Subsequently a more concentrated solution of diimide thread **4.1** and LiI was added to the crown tethered beads **4.15** in order to determine the effects of concentration. As expected the crown resonances shifted further upfield in the presence of excess thread and LiI although in this case the crown resonances were broadened, as expected for the fast

exchanging system. Variable temperature experiments were performed on this system to examine the dynamic behaviour of the rotaxane formation (See Figure 4.20). It was clear that as the temperature decreased the resonances associated with the tethered crown shifted further upfield with the most substantial shifts being in proton k, moving from 6.30 to 6.15, proton l from 6.90 to 6.74 and proton o from 7.08 to 6.92 ppm. This clearly shows pseudorotaxane formation is more favoured at lower temperatures, a result consistent with solutions studies and analogous bead experiments on the tethered diimide thread.



**Figure 4.20:-** Temperature comparison of a mixture of tethered crown **4.15**, diimide thread **4.1** and LiI at 27°C (top) and -10 °C (bottom).

Stoppering of this crown tethered rotaxane can be achieved with the addition to beads **4.15** of a mixture containing diimide thread **4.1** with two equivalents of rhodium porphyrin **4.16**. The addition of this mixture results in typically large upfield shifts of the terminal pyridine protons on the diimide thread (6.66, 5.31, 2.16 and 1.74 ppm) as a result of coordination to the metal ion. Only one set of peaks for the crown and diimide protons can be seen in the <sup>1</sup>H HR MAS spectrum indicating that, as in solution, this system is still in fast exchange (See Figure 4.21). This is due to the inherently weak interaction between the diimide and crown.



**Figure 4.21**:- HR MAS NMR spectra obtained with mixtures of tethered crown **4.15**, porphyrin **4.16** and diimide thread **4.1** (top), and mixture of tethered crown **4.15**, porphyrin **4.16** and diimide thread **4.1** plus LiI (bottom). All spectra recorded in 2%MeOD/ $\text{CDCl}_3$ .

The crown peaks were again shifted slightly upfield by between 0.01 and 0.07 ppm (8.00, 7.68, 7.33, 7.26, 7.09, 7.02, 6.91, 6.45 ppm) due to the shielding of the weakly bound diimide. The resonances for the diimide and terminal pyridine protons have low intensity despite excess thread having been added and indeed spectra run on this sample without employing a CPMG pulse sequence showed much higher proportions of the diimide **4.1**. It has been previously shown that the application of the CPMG sequence, while effectively filtering out the broad proton peaks of the ArgoGel beads, can in some cases also filter out “non-bead” resonances.<sup>15</sup>

Again, LiI was added to this system (in the same manner as described above) in order to see if its addition results in an increased binding of the diimide to the tethered crown (Figure 4.21). What is immediately noticeable is the increase in intensity of the diimide and terminal pyridine proton peaks of thread **4.1**. This is however not a result of additional thread as not only was the same concentration of thread added, but also if an increased amount of thread had been added it would result in a downfield shift in the NMR spectrum rather than the observed slight upfield shift observed. Furthermore small upfield shifts in the crown resonances are evident due to a slight increase in the binding of

the diimide to the crown. Of particular interest was the splitting of the crown resonance k into two peaks, which is indicative of a loss of symmetry of the naphthalene moiety as a result of the crown-diimide interaction (an effect which has been seen in analogous solution studies).

Despite the addition of LiI to the tethered crown pseudorotaxane systems showing small increases in the binding of this crown to the diimide thread **4.1**, the extent of the LiI effect is far less than that observed in solution. This could be due to insufficient LiI being solubilised in solutions made up in the absence of crown, as it is known that the presence of crown facilitates LiI solubilisation. One attempt to overcome this was to add solid LiI to the rotor containing crown beads in the expectation that the presence of crown will enhance the availability of the LiI to the system. HR MAS NMR analysis showed that, whilst slightly further upfield shifts in both the crown and diimide resonances were observable, indicating some enhancement of the binding by the addition of the LiI (presumably due to more being solubilised by the crown), nevertheless its effect remained less than that observed in solution. It is unlikely that the full effect of the addition of LiI can be achieved in these types of HR MAS NMR experiments due to the limitations of the experimental procedure.

Despite the difficulties in successfully inserting lithium iodide into tethered crown systems it is clear that the tethered crown is able to bind to the diimide thread, and that factors such as increasing the concentration of thread and lowering the temperature increases the pseudorotaxane formation. These factors may be harnessed in the design, synthesis and subsequent analysis of rotaxane formation in future multi-component bead systems.

#### **4.4 PORPHYRIN TETHERED SYSTEMS**

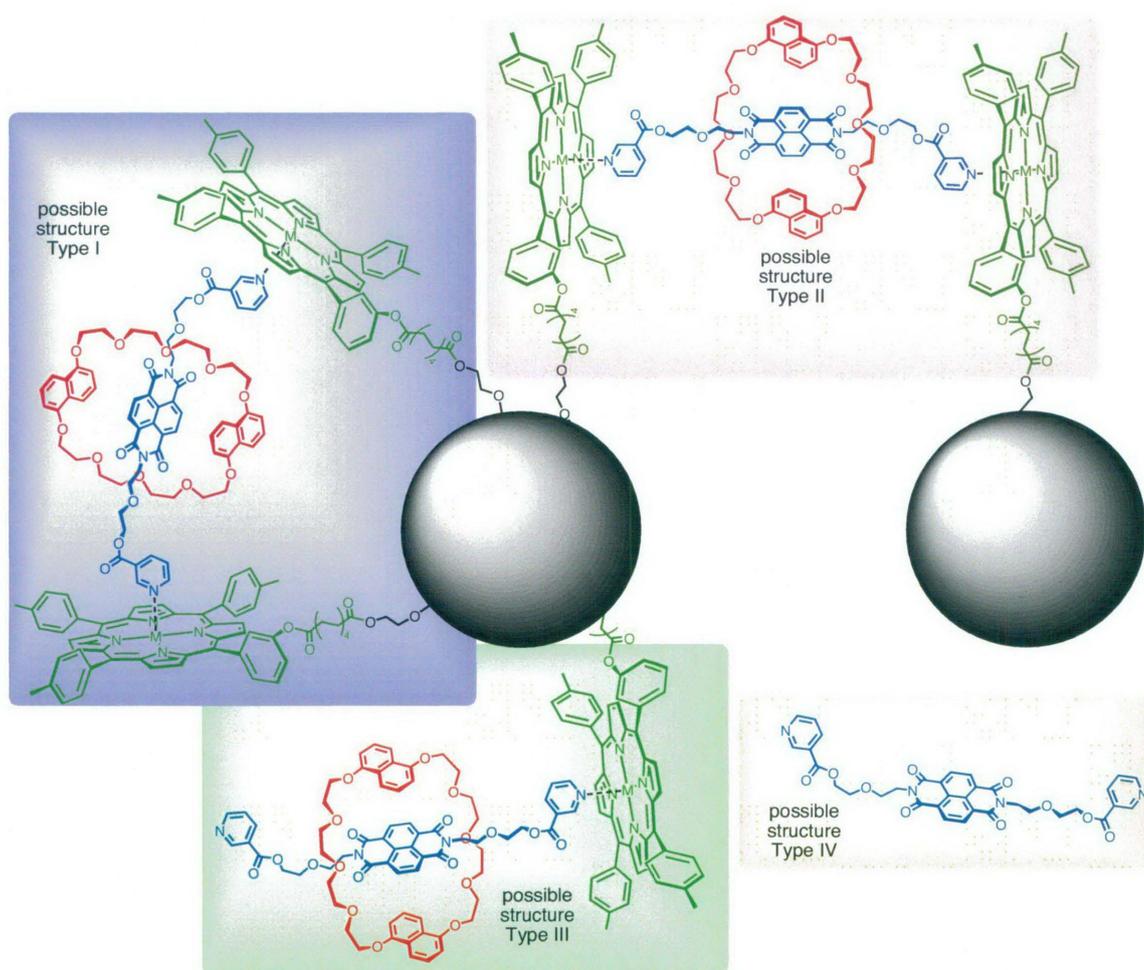
To further extend the concept of the self-assembly of these types of systems on solid supports with a view to more complex multi-component assemblies on solid supports, work was extended to examine rotaxane formation using the tethered porphyrins in place

of the diimide and crown tethered components **4.10** and **4.15**. Preliminary studies into the attachment of ruthenium porphyrin **4.17** to solid polystyrene supports and subsequent rotaxane formation were started by Johnstone *et al.*<sup>15</sup> While Johnstone developed methods for the synthesis of mono-functionalised porphyrins, the subsequent tethering of mono-functionalised ruthenium porphyrins to solid supports proved problematic. Johnstone *et al.* proposed that this was due to the fact that the acid group on the tethered porphyrin chain was coordinating to the ruthenium, thus interfering with the bead attachment reaction, resulting in decreased loading and poor quality HR MAS spectra.<sup>15</sup> This however needed more detailed investigation.

The original target rotaxane utilising porphyrin tethered beads, proposed by Johnstone, was the possible structure Type I, shown in Figure 4.22. Johnstone proposed that the addition of the *bis*-pyridyl diimide thread **4.1** in the solution phase, may be able to coordinate to two adjacent tethered porphyrin molecules on the bead, and hence that the addition of crown would complete the rotaxane formation in a fully reversible thermodynamically controlled assembly.<sup>15</sup> It should be noted that this structure may in fact be formally termed a catenane, as the connection between the thread and the tethered porphyrins creates a pseudo-macrocycle. However, identification and structural confirmation of this species by HR MAS NMR is not trivial. Addition of a solution of *bis*-pyridyl thread **4.1** could result in a variety of structures as depicted in Figure 4.22. The proposed structure Type II, in which the diimide thread is coordinated to porphyrins on two separate beads is extremely unlikely due to the vast size difference between the polymer beads, and the rotaxane components. Conversely, it is very probable that a proportion of the equilibrating structures would include structure Type III where the spacing of adjacent porphyrins might preclude a bridging structure I. Furthermore due to the experimental limitations, large excesses of the thread **4.1** are added (accounting for structure Type IV) which would push the equilibrium in favour of structure Type III over Type I even for suitably spaced porphyrin pairs.

Furthermore, despite predicting the possible structures, the assignment of these species using HR MAS NMR is not trivial. Unfortunately, no distinction between the mono-bound (of Type III) and the di-bound (of Type I) pyridine protons can be made as they would appear in identical chemical shift positions. Likewise mono-unbound (of Type III)

and di-unbound (of Type IV) pyridine protons would also have identical chemical shifts. Therefore, differentiation of the possible rotaxane species present in these systems based simply on a comparison of their chemical shifts is not possible in this case. Another significant problem is that no quantitation (either by integration\*\*\*\*, or the ability to know the precise concentration of the added crown with respect to the thread components) is possible with HR MAS NMR, thus rendering it impractical to identify the different structures present in the bead-solution equilibrium. Thus, to circumnavigate these problems, it was proposed that the mono-stoppered mono-pyridine diimide thread **4.5** be used as this can only result in one type of rotaxane, and hence the assembly of rotaxanes using porphyrin tethered beads can be more fully understood.



**Figure 4.22:-** Species possibly formed by the addition of crown **4.2** and thread **4.1** to porphyrin tethered beads.

\*\*\*\* As discussed previously, due to relaxation effects, and their implication in the NMR pulse sequences used in this method, relative signal integrations are an unreliable quantitative measure even within a single tethered molecular species, and certainly cannot be used to quantify differently structured components.

Thus a series of porphyrin tethered beads containing different metals (those being free base, Zn, Ru and Rh porphyrins) were synthesised and their HR MAS NMR spectra recorded. Since any interference in the condensation reaction caused by metal ion coordination is avoided, it was expected that good bead loading could be achieved in the synthesis of the free base tethered porphyrin beads **4.18**. Subsequent insertion of zinc post synthesis to produce the zinc tethered porphyrin beads **4.19** with identical loading should then be possible. This avoids any confusion due to different bead loading resulting from the condensation reactions on the beads. It should be noted that post-synthesis insertion of Ru or Rh into the free base porphyrin beads **4.18**, to obtain beads **4.20** and **4.21** respectively is not a viable option as both ruthenium and rhodium insertion reactions yield black decomposition solid by-products which can not be separated from the beads due to their insolubility.

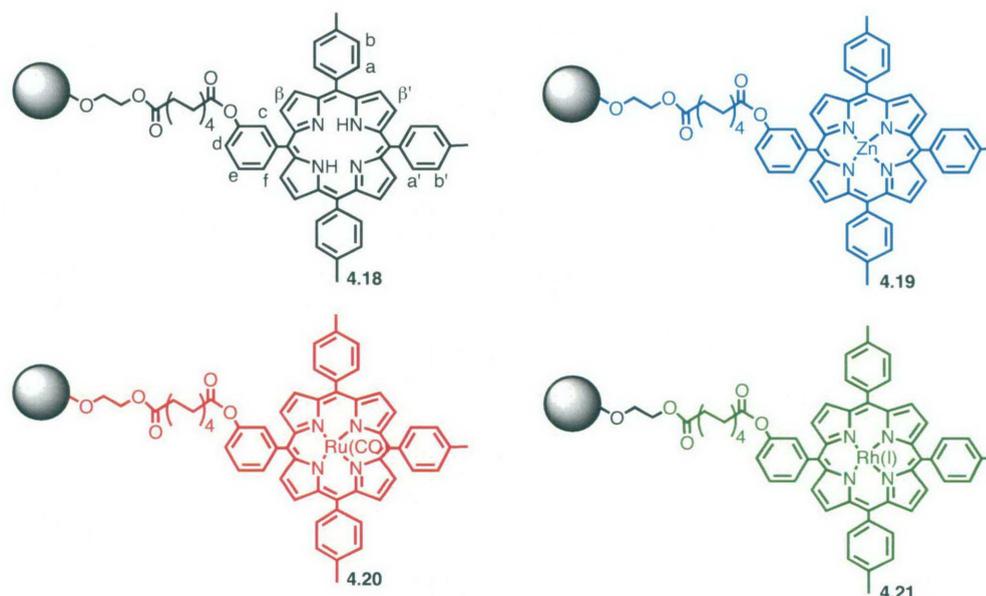
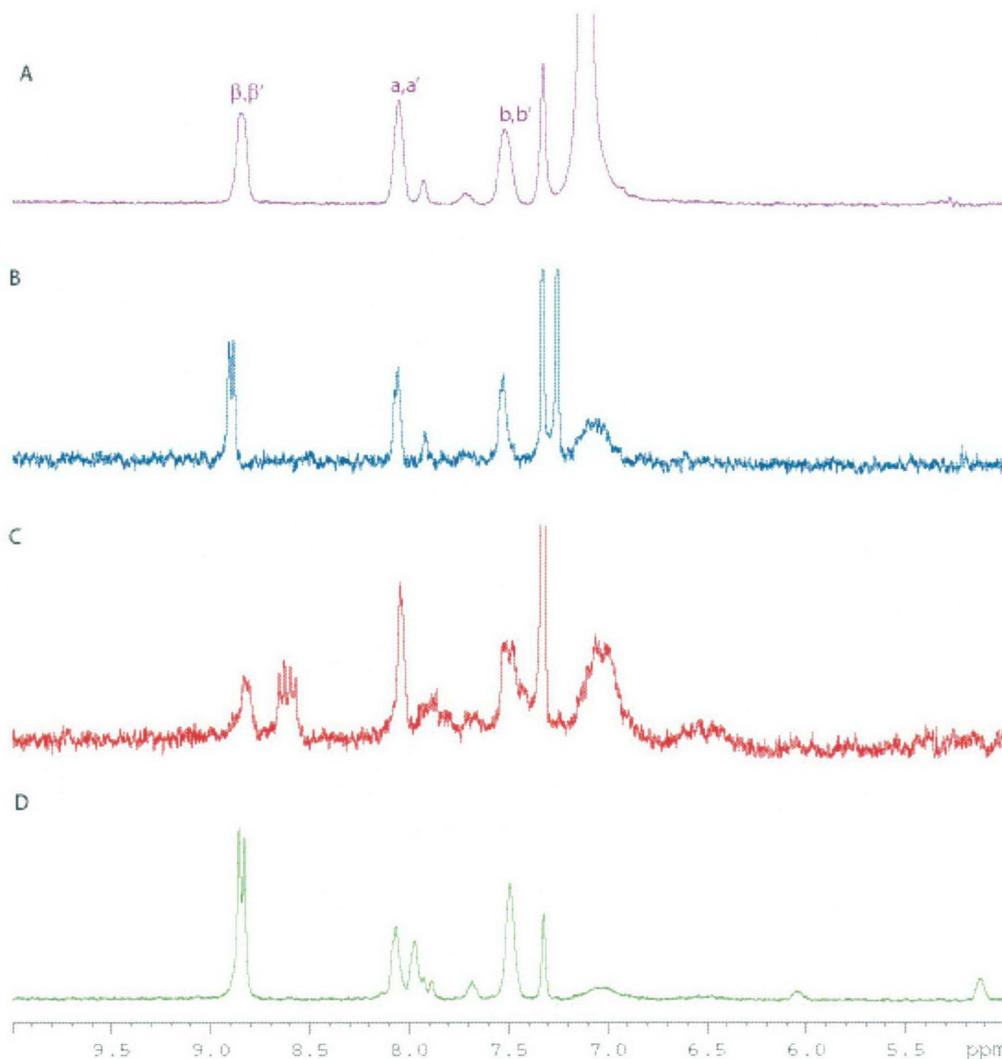


Figure 4.23:- Porphyrin tethered beads synthesised in this work.

The free base tethered beads **4.18** were produced by an EDC condensation between mono-sebacoyloxy tetratolyl porphyrin and the ArgoGel polymer beads. The HR MAS spectrum of the free base tethered porphyrin beads **4.18** was of good quality, showing good signal to noise ratios. Shifts for the porphyrin protons were as expected with the β and β' protons appearing at 8.82 ppm and the other porphyrin protons at 8.04 (a, a') and 7.51 ppm (b, b'). From COSY spectra, protons (c-f) could be easily identified as having chemical shifts of 8.03, 7.92, 7.70, 7.51 ppm. This is a dramatic improvement in the quality of spectra obtained for these types of tethered porphyrins compared to Johnstone's

work indicating that the method of attachment is satisfactory, and that the low quality in the previous ruthenium porphyrin examples is probably not due to limited access to the functional sites on the bead due to the steric bulk of the porphyrin units.



**Figure 4.24:-** HR MAS NMR spectra obtained on porphyrin tethered beads, A) is the spectrum of free base porphyrin beads **4.18**, B) is the spectrum of zinc porphyrin tethered beads **4.19**, C) is the HR MAS NMR spectrum of tethered ruthenium porphyrin beads **4.20**, and D) is the HR MAS NMR spectrum for rhodium porphyrin beads **4.21**.

Zinc insertion was then attempted on these free base porphyrin tethered beads to determine firstly whether post synthesis modifications were possible, and secondly whether the insertion of a metal into the porphyrin core has any effect on the signal to noise ratio of the HR MAS spectrum. Zinc insertion was indeed successful, as evident by the disappearance of the free base NH proton peak at  $-2.84$  ppm in the HR MAS spectrum of the resultant beads **4.19**. However, despite having the identical porphyrin loading as the free base beads **4.18**, the signal to noise ratio in the HR MAS NMR

spectrum is reduced. This strongly suggests that metallation of the porphyrin does impact on the quality of the NMR spectrum, and therefore lower quality spectra of metalloporphyrin beads is not necessarily indicative of poor loading.

Ruthenium tethered beads **4.20** were also synthesised using identical concentration conditions as for the free base derivatives used in this and Johnstone's previous work, but in the presence of 1 equivalent of pyridine per mole of Ru porphyrin to obviate any complication due to carboxylic acid coordination to the ruthenium porphyrin. Unfortunately poor quality HR MAS spectrum were again obtained. Despite this the beads themselves are highly coloured and it is proposed, that similar to the zinc tethered beads, the low signal to noise ratio is an inherent function of the ruthenium porphyrin<sup>††††</sup>, rather than due to poor loading.

Although free base and zinc tethered porphyrin beads provide reasonable NMR spectra, they are not suitable for assembling rotaxanes on solid supports using pyridine coordination as stoppers (the lability of the zinc-pyridine coordination renders them unsuitable for these thermodynamically assembled systems). Also, having ruled out ruthenium porphyrins as a viable option due to the poor quality of the NMR spectrum obtained, attention was turned to the attachment of rhodium porphyrins to the beads as an alternative. The rhodium porphyrin beads **4.21** were synthesised using the same procedure, and in the presence of pyridine (to negate any competitive acid group coordination to the rhodium).

HR MAS NMR spectra of the rhodium tethered beads **4.21** showed better signal to noise ratios than those of the ruthenium derivatives. The  $\beta$ ,  $\beta'$  porphyrin protons appeared in the typical position of 8.83 ppm. The porphyrin protons a and a' had split into two broad doublets at 8.06 and 7.97 ppm, an effect indicative of the facial differentiation of the rhodium iodide porphyrin which has been commonly seen. The porphyrin protons b and

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<sup>††††</sup> Possibly due to restricted flexibility, which itself may be caused by intra-bead substituent aggregation, (metallo-porphyrins including zinc porphyrins are known to aggregate in solution). This may introduce a paradoxical situation, in that a higher loading could lead to a decrease in the signal to noise ratio through more aggregation.

b', and the aromatic protons (c-f) again showed characteristic chemical shifts of 7.49 (b, b') and 8.06, 7.97, 7.69 respectively.

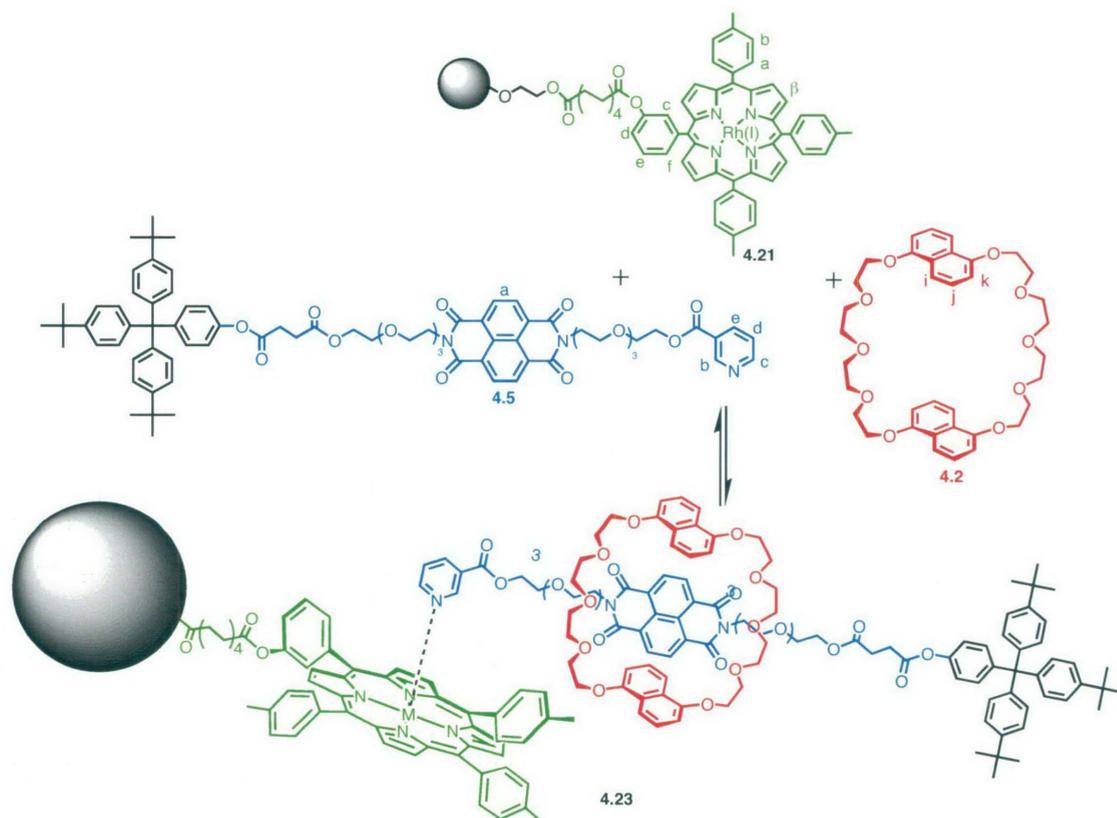
Unfortunately, residual bound pyridine (from the synthetic procedure) was also apparent in the NMR spectrum at 6.05, 5.12 and 1.99 ppm. Despite having washed the beads extensively with dilute HCl, the pyridine remained coordinated.<sup>††††</sup> This provides an additional limitation in the designed use of these beads for the assembly of supramolecular systems, as any additional coordinating component might not be able to displace the pyridine effectively.

Nevertheless, an equimolar solution of diimide thread **4.5** and crown ether **4.2** was added in large excess to the beads and the HR MAS NMR spectrum was recorded. It was reasoned that the large excess of the added pyridine diimide thread would compete with the pyridine on the beads for coordination, and rotaxane formation on the porphyrin beads would be successful.

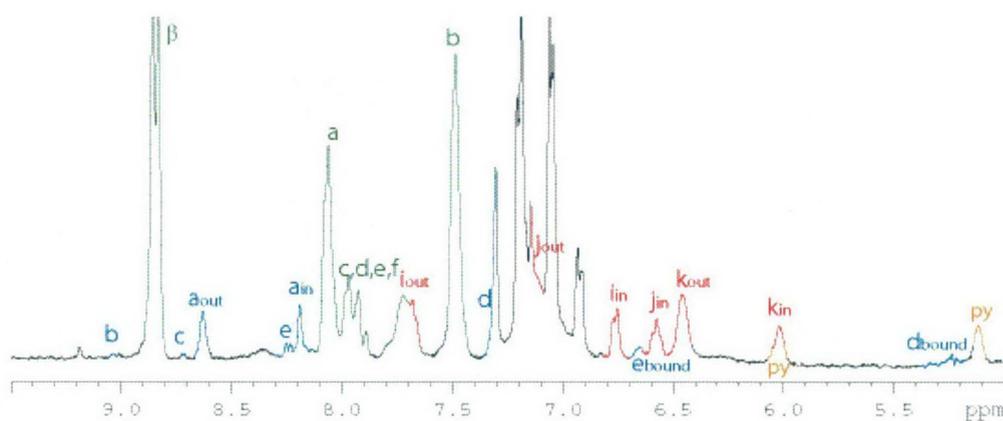
Despite pyridine itself being already coordinated to the rhodium porphyrin, the HR MAS NMR spectrum showed that the tethered pyridine diimide thread **4.5** could coordinate to the rhodium porphyrin as evident by the appearance of bound pyridine resonances at 6.65, 5.23, 2.16 and 1.74 ppm. Counterpart unbound pyridine peaks were also evident at 9.19, 8.71, 8.24, 7.31 ppm due to the excess diimide thread added. Interestingly, application of the 2K CPMG pulse sequences during the spectral acquisition significantly decreases the intensity of these tethered pyridine peaks, an effect seen previously for the diimide tethered beads **4.10** (see Figure 4.12).

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<sup>††††</sup> These beads were also washed with neat TFA which, although it successfully removed the pyridine ligand, also caused some decomposition of the porphyrin. This was thought to be either demetallation of the porphyrin or ligand exchange of the iodide anion, for trifluoroacetate. Similar effects have been seen in solution when using TFA in large excesses.



**Figure 4.25:-** The non-systematic aromatic labelling used for the NMR analysis of tethered porphyrin **4.22** and the subsequent assembly of porphyrin tethered rotaxane **4.23**.



**Figure 4.26:-** HR MAS NMR spectrum of rhodium porphyrin beads **4.21** plus addition of an equimolar mixture of diimide **4.5** and crown **4.2**. Colouring and number refer to Figure 4.25. Bound crown, diimide and pyridine beaks are depicted as  $j_{in}$ ,  $a_{in}$ , etc, while unbound peaks are depicted as  $i_{out}$ ,  $a_{out}$  etc.

Coordination of the mono-pyridine diimide thread to the rhodium porphyrin beads resulted in a slowing of the equilibrium for the binding of the crown to the diimide from fast to slow exchange on the NMR chemical shift timescale. This was evident by the presence of both bound (8.19 ppm  $a_{in}$ ) and unbound (8.63 ppm  $a_{out}$ ) diimide proton peaks as well as bound (6.02, 6.57 and 6.76 ppm) and unbound (6.45, 7.14, and 7.71 ppm)

crown peaks (k,j,i). This parallels the solution behaviour where addition of rhodium or ruthenium porphyrin to an equimolar mixture of crown and diimide in solution results in a change from fast to slow exchange on the NMR chemical shift timescale and gives a similar pattern in the NMR spectrum as seen here.

This shows that the attachment of rhodium porphyrins to polystyrene supports indeed has great potential. The signal to noise ratio of the HR MAS NMR spectra obtained is more than adequate for a detailed interpretation of the behaviour and spectra of these systems. Despite residual pyridine being present on the beads it appears that rotaxane assembly is still possible, and future multi-component bead synthesis can be designed utilising a weaker coordinating pyridine ligand in the added components.

#### **4.5 SUMMARY AND CONCLUSIONS**

The work described in this chapter is vital in the understanding of how the tethering of molecules on beads affects subsequent assembly of rotaxanes on solid supports under thermodynamic control. Three equilibrium components, those being the diimide thread, a crown ether macrocycle and a variety of metallo-porphyrins were tethered to gel-phase cross-linked polystyrene solid supports and the subsequent rotaxane formation was analysed by HR MAS NMR. In addition, solution studies of the effect of stoppering one end of the diimide thread unit and its subsequent binding to macrocycles was investigated. Solution studies of the extension of this system to incorporate different alkali salts (eg NaI or LiI) to enhance complexation and to incorporate different macrocycles were also conducted.

HR MAS NMR analysis of the diimide tethered beads, showed that the binding of the crown macrocycle can be affected by concentration of the surrounding solution-phase components, and the addition of sodium salts (specifically NaI). In addition to this, studies involving the binding of strapped porphyrin macrocycles as the macrocycle component (replacing the crown ether) on solid supported diimide threads were carried out. Unfortunately the resonances associated with the porphyrin binding are broad and the

CPMG pulse sequences that are used in the spectral acquisition also filter many signals of the assembled system out. The adaptation of this technology to allow variable temperature studies on these dynamic binding systems proved very useful, and aided in the spectral interpretation of both structure and dynamics. Unfortunately at this stage the technology is limited to  $-10\text{ }^{\circ}\text{C}$  and many of the systems used here would benefit from much lower temperatures in order to fully resolve the typically broad peaks.

In a repeat of earlier work, attachment of the crown macrocycle to the polystyrene beads was again successful; in this case the analysis of the binding of the diimide thread was able to be completed. It was shown that the diimide thread did bind to the tethered crown, although weakly, and that, as expected, decreasing the temperature favoured complexation. Unfortunately addition of alkali metal salts to improve the complexation proved difficult due to technical problems.

Investigations into the attachment of metalloporphyrins to the solid supports were also undertaken. It appears that a decrease in the signal to noise ratio of the HR MAS NMR spectra obtained is evident for some metallo-porphyrins. Whether this is through fast exchanging coordination of the porphyrin to the polyethylene glycol chains, which broadens the peaks and in turn reduces the NMR signal or more simply due to relaxation effects and signal broadening, is not clear. Despite this, it was found that the attachment of rhodium porphyrins gave ideal quality spectra and that rotaxane assembly is possible using these beads.

Thus it is now possible to not only successfully tether all three components to solid surfaces, but to also understand the factors affecting the assembly of rotaxanes on solid supports for each of the tethered components. This leads the way to synthesising more complex tethered systems involving two or three of these components attached to the one bead to see whether components on the same bead can assemble into rotaxanes. This work is discussed in Chapter 5.

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