Gel-phase HR-MAS ^{1}H NMR spectroscopy as a probe for solid-tethered diimide rotaxanes and catenanes

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

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The design and kinetically-controlled construction of a series of solid-tethered supramolecular systems utilising crown ether–naphthalene diimide host–guest chemistry are described. Functionalised polystyrene beads (ArgoGel-OH™) were utilised as the gel-phase solid support for the assembly of an appended diimide-crown catenane, and for a porphyrin-stoppered diimide-crown rotaxane. The structures of the resulting solid-tethered systems were probed using gel-phase high-resolution magic-angle spinning (HR-MAS) ^{1}H NMR spectroscopy. The advantages of using this spectroscopic tool in conjunction with optical microscopy to probe solid-tethered supramolecular systems are discussed.

Introduction

In the context of the new era of nanotechnology, the design and construction of molecular scale electronic components have assumed an increasing priority in research directed towards nanoscale machines and electronic devices.[1–4] Of particular interest have been rotaxane and catenane supramolecular systems[5–9] because of their intriguing mechanically interlocked topologies and their potential dynamic switching characteristics. Indeed, an understanding of the behaviour and dynamics of these systems in solution is well advanced, as a consequence of the large number of modern solution analytical techniques available. Successful single and multi-state systems designed to switch between co-conformations under the application of various chemical, electrochemical and photochemical stimuli have been described and their behaviour comprehensively analysed in solution.[3,9,10]

The next phase in the development of these systems is to produce useful work from ordered solid-state assemblies. This involves their physical connection at appropriate input and output points in order to utilise their signalling mechanisms. In many instances this involves modifying the supramolecular systems so that they can be attached to a suitable solid surface. While there are many examples of supramolecular systems that have been successfully immobilised on various surfaces or solid phase supports,[2,11,12] the most developed solid-tethered supramolecular systems to date are those constructed under irreversible, kinetically controlled conditions.[1,2] More detailed analysis of these and related systems on the solid phase is vital for further development. However, the available techniques that can be employed to study the solid-state systems are severely limited when compared to their solution prototypes.

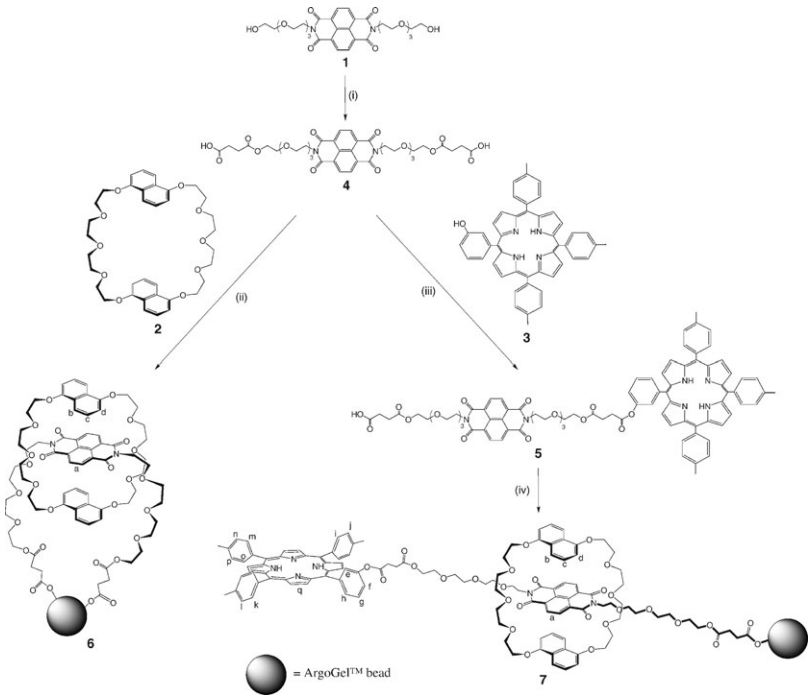
Recent developments in gel-phase HR-MAS spectroscopy have provided a useful tool for examining the behaviour of supramolecular systems that are tethered to solid surfaces. Now it is possible to obtain ^{1}H solid-phase NMR spectra with peak resolutions comparable to solution-phase measurements.[13]

We have previously reported extensions to our diimide-based rotaxanes and catenane supramolecular systems by tethering them to ArgoGel™ beads. These cross-linked polystyrene-based beads are armed with long end-functionalised polyethylene glycol chains which allow them to swell in a variety of solvents. The flexible nature of the chains and the gel-like properties render them suitable for analysis by HR-MAS NMR spectroscopy.[12,14] Furthermore, since resonances can be observed within the same spectrum for both the solid-tethered components and those in the surrounding solution, dynamic equilibrium processes between solution and solid-phase components can be monitored easily.

In our diimide–crown ether–porphyrin systems we reported[14] on the dynamics of the equilibrating self-assembly process, observable on the NMR timescale, as the solution-phase stopper and ring components assemble on the bead-attached thread unit of a potential rotaxane. We now describe the non-equilibrium counterparts to these experiments, where rotaxanes and catenanes are assembled under conditions of *kinetic* control onto the surface of the beads.

In this paper we describe the design of two systems, both utilising the host–guest interactions between π-electron rich aromatic crown ether macrocycles and π-electron deficient naphthalene diimides. The first uses the ArgoGel™ bead surface to attach both ends of a naphthalene diimide-containing thread unit to 'trap' the macrocyclic component, thus forming the catenane **6**. The second system incorporates a porphyrin stopper covalently affixed to one end of the naphthalene diimide thread component; tethering this to the ArgoGel™

[a] *School of Biological, Biomedical and Molecular Sciences, University of New England, Armidale, N.S.W. 2350, Australia. E-mail: mgunter@une.edu.au; Fax: +612 6773 3268; Tel: +612 6773 2767*
[b] *University Chemical Laboratory, University of Cambridge, Lensfield Rd, Cambridge, UK CB2 1EW. E-mail: jkms@cam.ac.uk; Fax: +44 1223 336017; Tel: +44 1223 336411*



Scheme 1 Reagents and conditions: (i) succinic anhydride, DMAP, NEt_3, DCM, 98%; (ii) ArgoGel™-OH beads, **2**, HOBT, EDC, NEt_3, $CHCl_3$, 50 °C; (iii) HOBT, EDC, **4**, NEt_3, DCM, 31%; (iv) ArgoGel-OH™, **2**, HOBT, EDC, NEt_3, DCM, 50 °C. The aromatic labelling system used for the HR MAS NMR analysis of both **6** and **7** is shown.

beads in the presence of the crown ether utilises the bead as the other stopper, effectively 'fixing' the pre-formed pseudo-rotaxane to form the rotaxane **7**.

Results and discussion

Synthesis

The synthesis of the target solid-tethered catenane **6** was achieved by first modifying the terminal hydroxy groups of **1** with succinic anhydride, 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and triethylamine in dichloromethane to afford the terminal carboxylic acid thread **4** (Scheme 1). This was subsequently reacted with ArgoGel-OH™ beads, using *N*-hydroxybenzotriazole (HOBT), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDC) and triethylamine in chloroform, in the presence of an excess of dinaphtho-38-crown-10 **2** (Scheme 1). The reaction aimed to attach the thread at both ends to the bead surface while trapping the crown to form the target catenane **6**.

The solid-tethered rotaxane target compound **7** was synthesised by coupling the terminal carboxylic acid thread **4** to the porphyrin sub-unit **3** *via* an ester linkage using HOBT, EDC and triethylamine in dichloromethane to afford a mixture of mono- and bis-porphyrin substituted threads. Column chromatography was used to separate and purify the mono-porphyrin substituted thread species **5**, which was then allowed to form a pseudo-rotaxane-like complex with an excess of the crown **2** before being tethered to the ArgoGel-OH™ beads using HOBT, EDC and triethylamine in dichloromethane to form the target compound **7**.

HR-MAS NMR analysis

We were then able to examine the two supramolecular systems using HR-MAS ^{1}H NMR spectroscopy. The non-systematic aromatic labelling system used for the HR-MAS NMR analysis of the solid-tethered catenane **6** and rotaxane **7** and solution NMR analysis of their precursors is depicted in Scheme 1. All peaks were assigned using COSY spectra.

The HR-MAS ^{1}H NMR spectrum of **6** (Fig. 1) showed a major diimide peak at δ 8.72 (H_a), with a much smaller set of peaks further upfield, including a diimide peak at δ 8.21 (H_a) and three crown peaks at δ 6.76 (H_b), 6.58 (H_c) and 6.03 (H_d). These crown peaks were shifted significantly upfield when compared to the free crown aromatic shifts (δ 7.80 (H_b), 7.19 (H_c), 6.53 (H_d)), while the minor diimide peak was upfield shifted when compared to the spectrum of its precursor **4** (δ 8.76 (H_a)).

The HR-MAS NMR proton spectrum of **6** indicates the presence of at least two different components tethered to the beads. The major product system is most likely a non crown-complexed diimide thread **8**, tethered at both ends to the ArgoGel™-OH beads, while the spectrum of the minor product is indicative of the target bead-tethered catenane **6** (Fig. 2). Some single-linked linear chains with free carboxyl ends are also likely, although diagnostic methylene peaks identifying these species could not be detected in the crowded methylene proton region of the spectra. While it is not possible to quantify the proportion of uncatenated cyclised *vs.* single-linked species, the fact that catenated species are formed is indicative of bis-linked attachment. Integration of the HR-MAS NMR spectral peaks indicates that approximately

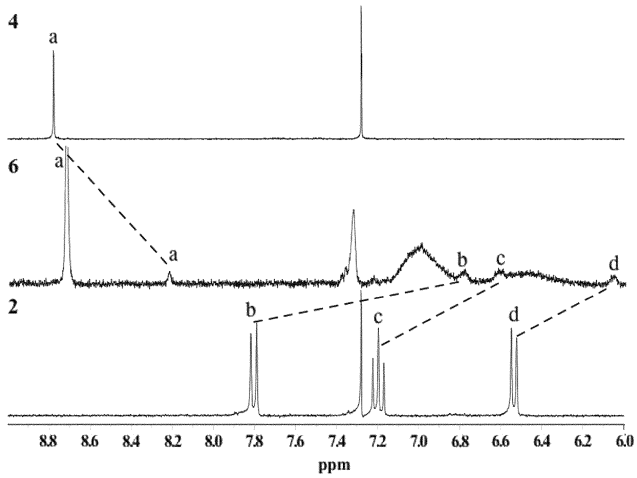


Fig. 1 HR-MAS NMR aromatic region proton spectrum of **6** (centre) compared with the solution NMR proton spectra of precursors **2** (bottom) and **4** (top). All spectra were obtained at 30 °C in $CDCl_3$. Large chemical shift differences are highlighted with dotted lines. Note: the broad region of the HR-MAS NMR spectrum of **6** (6.1–7.1 ppm) is caused by the low number of π-pulses† in the CPMG pulse sequence during acquisition. This was necessary to prevent loss of the small complexed-crown aromatic peaks.

6% of the total bead-tethered supramolecular systems are the target catenane **6**.‡

Although there is some broadening of the resonances of the catenated component **6** which might be indicative of restricted flexibility of the attached structures, the peaks of the uncomplexed tethered thread **8** were typically sharp and well-resolved. This indicates that cross-linking of the doubly-functionalised thread does not significantly restrict the solution-like flexibility that is required for high resolution spectra using this technique; indeed, the long polyethylene glycol chains of the tether and the thread act to increase the surface-attached molecular freedom of movement for sharp spectra. Extensive washing through shrinking/re-swelling processes ensured as much as possible removal of non-covalently bound, physically entrapped species; only catenated species could account for the upfield diimide and crown resonances observed. Likewise there was no evidence of any unbound crown resonances in their normal (unshifted) positions (Fig. 1). Furthermore, any pseudo-rotaxane-like species from threading of the crown onto linear chains would not be expected to survive the washing process.

The solution NMR of the rotaxane precursor **5** (Fig. 3) showed aromatic peaks at δ 8.84 (H_q), 8.47 ($H_{I,m}$), 8.38 (H_e), 7.91 ($H_{h,k,o}$), 7.71 ($H_{g,j,n}$), 7.54 ($H_{f,l,p}$) and an upfield shifted naphthalene diimide peak multiplet,§ indicative of a porphyrin–naphthalene diimide folding interaction similar to that which we have observed previously in related systems.[4]

† The HR-MAS spectrum of **6** used 32 π-pulses in its CPMG pulse sequence. All other HR-MAS spectra in this report utilise 2000 π-pulses.

‡ The application of a CPMG pulse sequence in the HR-MAS NMR experiment limits the accuracy of the integration of the resultant peaks.

§ The loss of symmetry in **5** gives rise to the non-equivalent H_a protons when compared to the corresponding singlet H_a peak in **4** (Fig. 1).

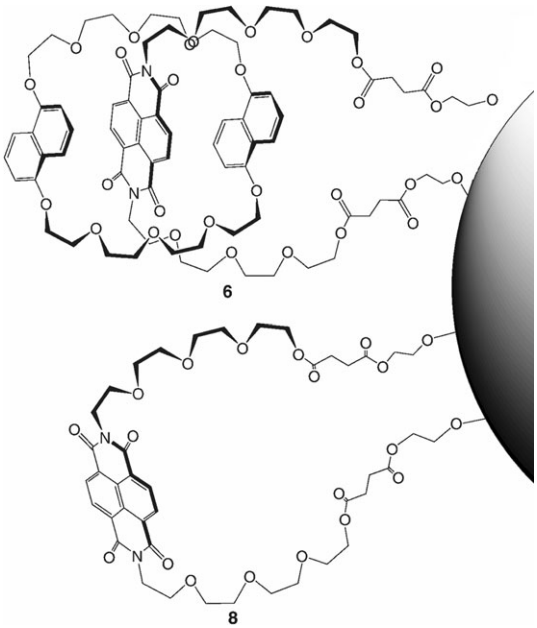


Fig. 2 The most probable bead-tethered supramolecular systems, formed when **4** is tethered to ArgoGel™-OH beads in the presence of crown **2**, include the crown-complexed solid-tethered catenane **6** and uncomplexed solid-tethered thread **8**.

The bead-attached rotaxane target compound **7** showed a high bead loading (Fig. 3). Although all peaks in the HR-MAS NMR spectrum were broadened by exchange or relaxation factors, it was clear that **7** exhibited two different sets of aromatic proton peaks. The first set was almost identical to that of its precursor, with peaks at δ 8.79 (H_q), 8.42 ($H_{I,m}$), 8.32 (H_e), 7.93 ($H_{h,k,o}$), 7.67 ($H_{g,j,n}$), 7.51 ($H_{f,l,p}$) and even further upfield shifted broadened naphthalene diimide peaks at δ 7.03 (H_a). The second set had peaks at δ 8.79 (H_q), 8.32 (H_e), 8.17 ($H_{m,o}$), 8.09 ($H_{I,k}$), 7.93 (H_h), 7.67 (H_g), 7.51

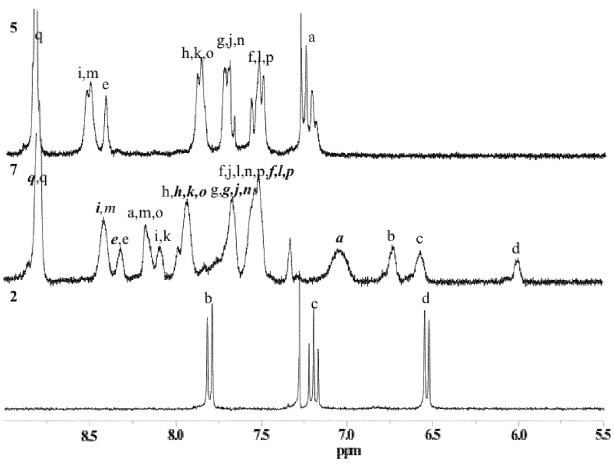


Fig. 3 Comparison of the HR-MAS proton NMR spectrum of **7** (middle) in $CDCl_3$ at 30 °C with the solution proton NMR spectra of its precursors, **5** (top) and **2** (bottom), in $CDCl_3$ at 30 °C. The two sets of aromatic peaks found in the spectrum of **7** are distinguished by italicised and non-italicised labels.

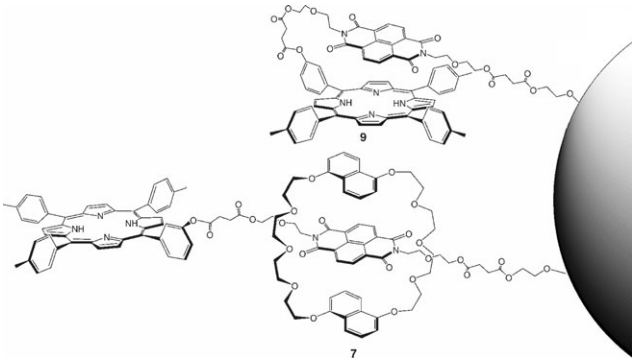


Fig. 4 The two bead-tethered supramolecular systems formed when **5** is tethered to ArgoGel™-OH beads in the presence of crown **2**. **7** is the complete target rotaxane and **9** the non-crown complexed product.

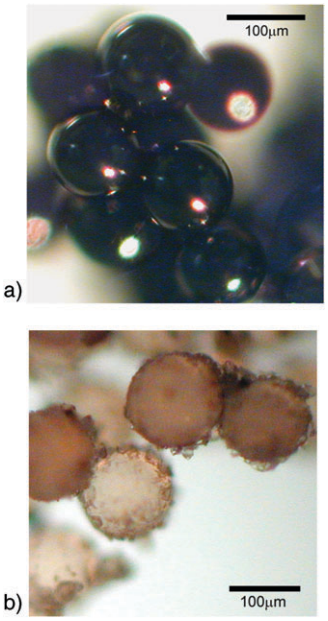


Fig. 5 10x magnification optical microscopy images of **7** (above) and **6** (below). ArgoGel™-OH beads are initially colourless before compound attachment.

($H_{f,j,l,n,p}$) and naphthalene diimide peaks at δ 8.17 (H_a). There were also a set of naphthalene diimide-bound crown aromatic peaks at δ 6.72 (H_b), 6.57 (H_c) and 5.99 (H_d) that were significantly upfield shifted when compared to the free crown **2** spectrum (Fig. 3).

These two sets of aromatic protons in **7** indicate the presence of two different types of supramolecular systems attached to the ArgoGel-OH™ beads. The first set of aromatic peaks, with shifts similar to the precursor **5**, possess an extreme upfield shifted naphthalene diimide peak. This is consistent with a structure in which **5** is tethered to the beads without crown complexation, depicted in Fig. 4 by structure **9**; the intramolecular diimide–porphyrin interaction in a preferred foldamer conformation which is observed in solution[4] is maintained in this polymer-bound species. The second set of aromatic peaks, with its naphthalene diimide peak at δ 8.17, is assigned to the complete rotaxane structure **7**, with its naphthalene diimide permanently complexed within the crown. In this case, the encircling crown in **7** prohibits any porphyrin–naphthalene diimide interaction, and hence the diimide resonances occur at their ''normal'' bound position. There are no unbound crown peaks, as any such crown species would have been removed in the extensive shrinking/swelling bead washing purification steps. NMR peak integration indicates that target crown-bound species **7** was 34% of the total bead-tethered population.

Optical microscopy

Both bead-tethered supramolecular systems were investigated by optical microscopy (Fig. 5). The ArgoGel-OH™ tethered rotaxane beads appeared deep purple, a colour characteristic of the attached free-base porphyrin stoppering components. The intense bead colour is consistent with the high bead loading observed in the HR-MAS spectrum.

It is particularly noteworthy that the relative quantities and structures of the non-crown complexed component **9** and its rotaxane counterpart **7** could not have been determined without HR-MAS NMR spectroscopy. This result highlights the importance of this technique for the analysis of the microscopic environment of solid-tethered supramolecular systems in contrast to the tools currently most commonly used for such systems, including optical microscopy, that are limited to analysing the macroscopic properties of the solid-tethered systems.[15]

For the non-porphyrinic potential catenane system, optical microscopy showed pink coloured beads characteristic of charge transfer interactions between crown and diimide[6,7] in the solid-tethered catenane **6** (Fig. 5). Visually, the weak intensity of the pink colour is consistent with the HR-MAS evidence indicating that only a small proportion of the attached naphthalene diimide species is complexed with the crown **2**, although no attempts were made in this study to quantify bead loading in relation to colour intensity.[16]

The roughened nature of the bead surfaces in this instance is noteworthy. The dual-functionality of the carboxylic acid naphthalene diimide thread precursor **4** could result in a variety of by-products during the formation of the bead-tethered catenane. As well as mono bead-attached naphthalene diimide thread species **6** and **8**, there is also the possibility of the di-functional thread **4** bridging between two separate ArgoGel-OH™ beads to produce species such as **10**, and the associated crown-complexed inter-bead rotaxane system **11** (Fig. 6).

Although intact bead clusters resulting from such inter-bead attachment is thought to be unlikely, given the low bead functionalisation and loadings, and the vastly mismatched nm scale molecular size and surface area of **4** compared to the μm size of the beads, the optical image of the beads (Fig. 5) show fragments on the surface of each bead. This phenomenon occurs on all of the beads and is unusual; indeed, of all the other bead-tethered systems we have investigated, no others have exhibited similar effects.[14] Although some amount of physical bead crushing can occur through handling, it is

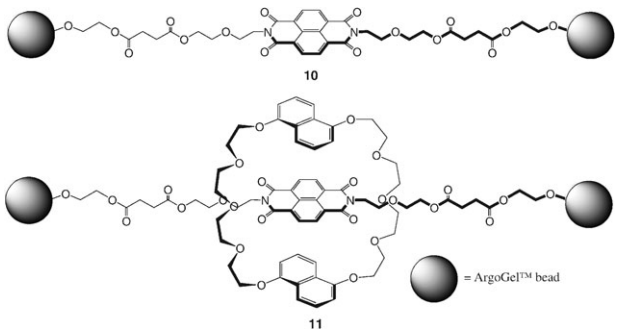


Fig. 6 Possible side-product solid-tethered supramolecular systems associated with the formation of **6**, involving the linking of two separate ArgoGel™-OH beads, include a naphthalene diimide thread-linked system **10** and the corresponding crown-complexed rotaxane system **11**.

normally random, leaving a variety of various sized bead remnants quite unlike those seen here. This could be the result of several factors including surface charge of the attached species, or it may be that the unusual small surface-attached bead fragments on the solid-tethered catenane beads **6** result from effects of some incipient inter-bead cross-linking which disposes them to fragmentation. Unfortunately, inter-bead attachment cannot be distinguished from intra-bead attachment using normal solid-phase analytical methods, such as HR-MAS NMR spectroscopy and at this time the authors are aware of only one other reported example of a reaction resulting in some evidence for inter-bead attachment.[17]

Conclusions

We have thus shown that it is possible to construct a bead-tethered catenane system such as **6**, by attaching a naphthalene diimide thread **4** at both ends to ArgoGel-OH™ beads in the presence of an excess of crown **2**. HR-MAS NMR spectroscopy showed that although the naphthalene diimide thread catenane component had a high bead-loading, only 6% of the bead-tethered thread was complexed with the crown in the form of the catenane **6**. Optical microscopy showed that the beads were pink, indicative of the charge-transfer resulting from crown–naphthalene diimide interaction. The di-functional nature of the naphthalene diimide thread precursor in this system allows for a variety of possible interesting by-product supramolecular structures, involving inter-bead attachment. However, these could not be specifically identified using HR-MAS NMR spectroscopy, but interesting bead fragmentations observed with optical microscopy suggest their possible involvement.

The bead-tethered rotaxane **7** was successfully constructed under kinetic control by attaching a covalently mono-stoppered naphthalene diimide thread **5** to ArgoGel-OH™ beads in the presence of excess crown **2**. The total loading on the bead was found to be high as indicated by HR-MAS NMR spectroscopy and optical microscopy, while 34% of the total bead-tethered naphthalene diimide thread was crown-complexed in the rotaxane structure **7**; the remaining fraction was the simple tethered thread unit **9**.

These solid-tethered systems, formed under kinetic control, could be developed in the future into more complex systems with multiple binding sites, with the ability to function as molecular switching devices. The ease of synthesis under mild conditions, together with the solid-phase synthesis advantage of product isolation by simple filtration and washing steps allows for easy synthetic strategies to afford quite complex systems. Because of their increased complexity, HR-MAS NMR spectroscopy will prove vital in identifying and characterising expected and unexpected component behaviour for the solid-attached supramolecular systems. We predict that it will increasingly become an indispensable diagnostic tool for supramolecular chemists modifying their solution systems for solid-phase development.

Experimental

Methods and materials

All solvents were dried and distilled using standard procedures before use: chloroform (AR grade) was passed through an alumina column to remove the ethanol before being distilled over K_2CO_3; dichloromethane (AR grade) and triethylamine were distilled over calcium hydride. ArgoGel-OH™ beads with resin loading 0.4–0.5 mmol g^{-1} were purchased from the Aldrich chemical company. Column chromatography on silica was carried out using Aldrich silica gel (grade 9385, 230–400 mesh). Preparative TLC was performed on 20 × 20 cm glass plates coated with 1.0 mm thick Art. 7731 Kieselgel 60 G Merck silica. Solution NMR spectra were acquired on a 300 MHz Bruker AC-300P FT spectrometer at 303 K. HR-MAS NMR spectra were acquired on a Bruker DRX400 spectrometer at room temperature using a Bruker HR-MAS probe at the Cambridge University Chemical Laboratory. Rotors containing a suspension of the beads in $CDCl_3$ were spun at 4 kHz. One-dimensional HR-MAS spectra were obtained with 64 scans. CPMG pulse sequence contained 32 or 2000 π-pulses with a repetition time of 30 ms. Chemical shifts (δ) are reported in parts per million relative to residual solvent. Deuterated solvents were stored over type 3 Å molecular sieves and used without any further purification. Coloured bead images were taken with a Leica DME light microscope with a Nikon Coolpix 950 digital camera mounted at 10x magnification. UV-Vis spectra were performed on a Varian Cary IE UV-Vis spectrophotometer or a Hewlett Packard 8452A diode array spectrometer. Melting points were determined using a Reichert microscopic hot-stage apparatus. Electrospray mass spectrometry was performed by the mass spectrometry service at Central Queensland University.

Syntheses

2,7-*Bis*[2-(2-{2-[2-(3-carboxypropionyloxy)ethoxy]ethoxy}ethoxy)ethyl] benzo[lmn]-[3,8]phenanthroline-1,3,6,8-tetraone (4). 2,7-*Bis*-[2-(2-{2-[2-hydroxyethoxy]ethoxy}ethoxy)ethyl]-benzo[lmn]-[3,8]phenanthroline-1,3,6,8-tetraone[6] (**1**) (20 mg, 32.4 μmol), triethylamine (9.8 mg, 97.2 μmol), succinic anhydride (9.7 mg, 97.2 μmol) and 4-(dimethylamino)pyridine (DMAP, 0.4 mg, 3.2 μmol) were dissolved in dichloromethane (DCM, 5.0 mL) and left to stir at room temperature under

nitrogen for two days. The solvent was then evaporated under reduced pressure and the residue taken up in DCM–HCl (aq, 2 M). The organic layer was separated, washed with water, dried ($MgSO_4$) and the solvent evaporated. The crude mixture was subjected to preparative TLC (SiO_2: 8% MeOH–DCM) to afford the product as a yellow oil (26 mg, 98%); *m*/*z* (ES-MS) $[M + Na]^+$ 841.2633 $C_{38}H_{46}N_2O_{18}Na_1$ (calc. 841.2643); ^1H NMR (300 MHz, $CDCl_3$) δ 8.76 (4H, s, Ar–H), 4.48 (4H, t, OCH_2), 4.20 (4H, t, OCH_2), 3.87 (4H, t, OCH_2), 3.72 (4H, m, OCH_2), 3.58–3.66 (16H, m, OCH_2), 2.60 (8H, s, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 171.9, 163.0, 131.0, 126.8, 126.7, 70.7, 70.5, 70.4, 70.1, 68.9, 67.8, 63.8, 53.4, 39.6, 29.3, 29.0.

2-[2-(2-{2-[2-(3-Carboxypropionyloxy)ethoxy]ethoxy}ethoxy)ethyl]-7-[2-(2-{2-[2-(3-{5-[phen-3-yl]10,15,20-*tris*-[*p*-tolyl]-porphyrinyl}carboxypropionyloxy) ethoxy]ethoxy}ethoxy) ethyl]benzo[lmn]-[3,8]phenanthroline-1,3,6,8-tetraone (5). 2,7-*Bis*[2-(2-{2-[2-(3-carboxypropionyloxy)ethoxy]ethoxy}ethoxy) ethyl]benzo[lmn]- [3,8]phenanthroline-1,3,6,8-tetraone (**4**) (361 mg, 441 μmol), *N*-hydroxybenzotriazole (HOBT, 122 mg, 900 μmol), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC, 173 mg, 900 μmol) and triethylamine (125 μL, 900 μmol) were dissolved in DCM (50 mL) and stirred at room temperature under nitrogen. 5-[*m*-Hydroxy phenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin[4] (**3**) (300 mg, 441 μmol) dissolved in DCM (50 mL) was added dropwise over 30 min. The reaction was stirred for four days at room temperature. The solvent was then removed and the residue taken up in a water–DCM mixture. The organic layer was separated, dried over sodium sulfate and the solvent evaporated to yield the crude product. This was subjected to column chromatography (SiO_2: DCM to 3% MeOH–DCM) to afford the pure product as a purple solid, 202 mg (31%), mp 95–98 °C; (ES-MS) $[M + H]^+$ 1473.5644 $C_{85}H_{81}N_6O_{18}$ (calc. 1473.5607); ^1H NMR (300 MHz, $CDCl_3$) δ 8.84 (8H, m, β-H), 8.47 (3H, d, Ar–H), 8.38 (1H, s, Ar–H), 7.91 (3H, d, Ar-H), 7.91 (1H, dd, Ar–H), 7.71 (1H, dd, Ar–H), 7.71 (3H, d, Ar–H), 7.54 (1H, dd, Ar–H), 7.54 (3H, d, Ar–H), 7.24 (4H, s, Ar–H), 4.28 (2H, m, OCH_2), 4.15 (2H, m, OCH_2), 4.02 (4H, m, OCH_2), 3.65 (2H, m, OCH_2), 3.52–3.48 (20H, m, OCH_2), 3.09 (2H, t, CH_2), 2.94 (2H, t, CH_2), 2.74 (9H, s, Ar–CH_3), 2.50 (4H, m, CH_2), −3.89 (2H, s, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 161.4, 161.2, 149.4, 143.3, 139.1, 139.0, 137.4, 135.1, 134.1, 132.6, 131.2, 130.5, 128.1, 127.7, 127.4, 123.7, 123.5, 120.6, 120.4, 120.2, 118.0, 70.9, 70.5, 70.3, 70.1, 69.9, 68.9, 67.7, 67.5, 63.9, 63.5, 39.2, 30.8, 29.7, 29.6, 29.4, 29.0, 21.5; UV (λ nm (ε M^{-1} cm^{-1}), CH_2Cl_2) 419 (8.64×10^4), 516 (9.42×10^3), 551 (6.18×10^3), 592 (4.27×10^3), 647 (4.12×10^3).

ArgoGel-OH™ tethered catenane (6). 2,7-*Bis*[2-(2-{2-[2-(3-carboxypropionyloxy)ethoxy]ethoxy}ethoxy)ethyl]benzo[lmn]-[3,8]phenanthroline-1,3,6,8-tetraone (**4**) (61.4 mg, 75 μmol), dinaphtho-38-crown-10[8] (**2**) (95.5 mg, 150 μmol) and ArgoGel-OH™ beads (10 mg) in $CHCl_3$ (1.0 mL) were stirred at 50 °C under nitrogen for 30 min. HOBT (40.5 mg), EDC (60 mg) and triethylamine (31 μL) were added and the mixture was stirred for 6 days. Then the beads were filtered and washed successively with $CHCl_3$ (5.0 mL), acetone (5.0 mL), water (5.0 mL), acetone (5.0 mL), hexane (5.0 mL) and $CHCl_3$ (5.0 mL), with partial drying and shrinking between wash cycles. The pale pink coloured product beads were then dried under high vacuum. ^1H HR-MAS NMR (400 MHz, $CDCl_3$) δ 8.75 (4H, s, Ar–H), **8.10** (4H, s, Ar–H), **6.80** (4H, dd, Ar–H), **6.61** (4H, dd, Ar–H), **6.12** (4H, dd, Ar–H), 3.0–4.7 (32H, m, OCH_2), **3.0–4.7** (64H, m, OCH_2), 2.50 (8H, m, CH_2), **2.50** (8H, m, CH_2). Note: crown-complexed system proton peaks are highlighted in bold.

ArgoGel-OH™ tethered rotaxane (7). 2-[2-(2-{2-[2-(3-Carboxypropionyloxy)ethoxy]ethoxy}ethoxy)ethyl]-7-[2-(2-{2-[2-(3-{5-[phen-3-yl]10,15,20-*tris*-[*p*-tolyl]porphyrinyl}carboxypropionyloxy)ethoxy] ethoxy}ethoxy)ethyl]benzo[lmn]-[3,8] phenanthroline-1,3,6,8-tetraone (**5**) (188 mg, 128 μmol), dinaphtho-38-crown-10[8] (**2**) (122 mg, 192 μmol) and ArgoGel-OH™ beads (20 mg) in $CHCl_3$ (2 mL) were stirred at 50 °C under nitrogen for 30 min. HOBT (81 mg), EDC (115 mg) and triethylamine (61 μL) were added and the mixture was stirred for 6 days. Then the beads were filtered and washed successively with $CHCl_3$ (5.0 mL), acetone (5.0 mL), water (5.0 mL), acetone (5.0 mL), hexane (5.0 mL) and $CHCl_3$ (5.0 mL) with partial drying and shrinking between wash cycles. The purple coloured product beads were then dried under high vacuum. ^1H HR-MAS NMR (400 MHz, $CDCl_3$) δ **8.79** (8H, m, β-H), 8.79 (8H, m, β-H), 8.42 (3H, d, Ar–H), **8.32** (1H, s, Ar–H), 8.32 (1H, s, Ar–H), **8.17** (4H, s, Ar–H), **8.17** (2H, m, Ar–H), **8.09** (4H, m, Ar–H), 7.93 (3H, dd, Ar–H), 7.93 (1H, dd, Ar–H), **7.93** (1H, dd, Ar–H), 7.66 (3H, dd, Ar–H), 7.66 (1H, dd, Ar–H), **7.66** (1H, dd, Ar–H), 7.51 (1H, dd, Ar–H), 7.51 (3H, d, Ar–H), **7.51** (6H, m, Ar–H), **7.51** (1H, dd, Ar–H), 7.03 (4H, s, Ar–H), **6.72** (4H, dd, Ar–H), **6.57** (4H, dd, Ar–H), **5.99** (4H, dd, Ar–H), **3.45–4.21** (64H, m, OCH_2), 3.45–4.21 (32H, m, OCH_2), **3.06** (4H, t, CH_2), **2.89** (4H, t, CH_2), 2.95 (4H, t, CH_2), 2.80 (4H, t, CH_2), **2.70** (9H, s, Ar–CH_3), 2.61 (9H, s, Ar–CH_3), −3.06 to −3.82 (2H, broad-s, NH), −**4.22** (2H, broad-s, NH). Note: the crown-complexed system proton peak assignments are highlighted in bold.

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