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## PAPER

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## 'Click' functionalised polymer resins: a new approach to the synthesis of surface attached bipyridinium and naphthalene diimide [2]rotaxanes†

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Herein we describe the design and synthesis of a series of solid-tethered [2]rotaxanes utilising crown ether-naphthalene diimide or crown ether-bipyridinium host guest interactions. TentaGel polystyrene resins were initially modified in a two-stage procedure to azide functionalised beads before the target supramolecular architectures were attached using a copper catalysed "click" procedure. The final assembly was examined using IR spectroscopy and gel-phase <sup>1</sup>H High Resolution Magic Angle Spinning (HR MAS) NMR spectroscopy. The HR MAS technique enabled a direct comparison between the solid-tethered architectures and the synthesis and characterisation of analogous solution-based [2]rotaxanes to be made.

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### Introduction

Developments in fundamental concepts such as self-assembly, template directed synthesis and dynamic covalent synthesis have transformed the field of supramolecular chemistry, allowing for the design and operation of more elaborate interlocked architectures and molecular machines than would have been thought possible at its inception. Early statistical approaches to isolate rotaxanes or catenanes in <5% yield, have been abandoned in light of these developments allowing [n] rotaxanes, [n]catenanes and even more complex molecular knots and links to be made reliably and in much higher yields.<sup>1-4</sup> Greater understanding of the inherent dynamic nature of such interlocked systems has also led to the development of a range of molecular switches or shuttles, ratchets, and molecular motors.<sup>5</sup> However, in order to realise the potential these systems hold in transforming modern technologies, they need to be incorporated into functionalised materials or deposited onto surfaces.6 These objectives present several challenges. Firstly, the chemistry used for surface attachment needs to be compatible with the synthetic requirements of the interlocked assemblies. Secondly, the characterisation of such surface

confined systems is more difficult, particularly in the absence of an appropriate redox probe. Various methods including X-ray photoelectron spectroscopy (XPS), electrochemical techniques, steady state fluorescence, surface probe microscopy (STM, AFM) and solid-state FT-IR have all been used to analyse solid tethered supramolecular systems.<sup>7,8</sup> However, many of these techniques do not provide direct comparisons with solution based systems. Finally, but perhaps most importantly, fundamental questions remain as to the full effect surface confinement has on the dynamic nature of complex molecular machines.

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Research attempting to answer many of these questions has been ongoing, with notable examples by the groups of Stoddart, Leigh, and Sauvage, amongst others demonstrating the successful assembly of interlocked architectures on a variety of substrates including Langmuir Blogett films,9-12 embedded polymer matrixes,<sup>13-15</sup> sol gel glass surfaces<sup>6</sup> and self assembled monolayers (SAMs) on gold or other surfaces.<sup>16–29</sup> Furthermore, for a series of surface bound multi-station rotaxanes, Stoddart et al. have demonstrated that while the rate of shuttling is dependent on the surface medium, the mechanism for switching between stations is consistent for all molecules, regardless of whether they are in solution, tethered to solid surfaces (such as gold) or embedded in polymer matrixes.<sup>13</sup> In contrast, Sauvage et al. showed that while redox activated ring circumrotation is observed in solution for a series of Cu(I)/Cu(II) catenanes, when such systems are deposited on gold, intramolecular motion is markedly slowed if not completely frozen.<sup>23,30</sup> These examples highlight the need to be able to accurately characterise and understand the dynamic behaviour of supramolecular architectures deposited

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on surfaces, as solution behaviour is not always directly comparable.

As the complexity of supramolecular architectures in solution increases, <sup>1</sup>H NMR is vitally important in understanding the dynamic behaviour characteristic of interlocked architectures. Attachment of these systems to surfaces such as gold, prevents investigation of dynamic behaviour by <sup>1</sup>H NMR. However, when using swelling polystyrene resins as the solid support, <sup>1</sup>H NMR spectra can be obtained using HR MAS (High Resolution Magic Angle Spinning) NMR techniques, thus providing a direct comparison between solid and solution dynamics. Previous work has allowed us to monitor the reversible assembly of a range of pseudorotaxanes incorporating neutral naphthalene diimide threads, crown ether macrocycles and ruthenium stoppered porphyrins on polystyrene resins (such as ArgoGel or TentaGel resins).<sup>31-34</sup> In some of these studies it was found that although pseudorotaxane assembly is fast relative to the chemical shift timescale in solution, the binding process was in slow exchange on the polymer surface.<sup>34</sup> Additional binding interactions between the macrocycle and the polymer tethers were also observed, which highlights the importance of this technique in identifying key differences between solution and surface based supramolecular chemistry. Preliminary studies into the assembly of kinetically trapped rotaxanes on polymer resins was also undertaken; however, to date surface functionalisation has been limited to ester condensation reactions.<sup>32</sup> Herein we report the use of the Cu(1) catalyzed Huisgen 1,3-dipolar cycloaddition or "click" reaction between azides and alkynes as a means of functionalising polymer resins with [2]rotaxane architectures and their subsequent characterisation by <sup>1</sup>H HR MAS NMR spectroscopy (see Fig. 1).



Fig. 1 Target surface bound bipyridinium and diimide [2]rotaxanes, 1 and 2 respectively.



Scheme 1 Synthesis of mono-stoppered bipyridinium thread 5. Reagents and conditions: (i) TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, acetone, 48 h, RT.



#### **Results and discussion**

#### Synthesis of mono-stoppered threads

In this study two electron deficient motifs, one containing the charged bipyridinium motif and another containing the neutral naphthalene diimide moiety, were investigated as suitable thread components for the assembly of [2]rotaxanes on polymer supports. The synthesis of the alkyne functionalised mono-stoppered bipyridinium thread 5 necessary for surface functionalisation using a click methodology is outlined in Scheme 1. Bipyridinium 5 was synthesised according to a modified literature procedure<sup>35</sup> in which stopper azide 3 was reacted with an excess of bipyridinium bis-alkyne 4, in the presence of Cu(MeCN)<sub>4</sub>PF<sub>6</sub> and TBTA. Purification by reverse phase medium pressure liquid chromatography (MPLC) afforded the target mono-stoppered thread in good yield.

A similar strategy was initially employed for the synthesis of the neutral mono-stoppered naphthalene diimide thread 7 (Scheme 2). However, despite using an excess of diimide bisalkyne **6**, all attempts to synthesise 7 were unsuccessful with only the di-stoppered thread and unreacted diimide bis-alkyne being isolated from the reaction mixtures. This can be attributed to the insolubility of the diimide bis-alkyne **6** in almost all organic solvents. Although the first cycloaddition between the diimide bis-alkyne and stopper azide is inherently slow, upon formation, the *soluble* mono-stoppered naphthalene diimide thread immediately reacts with the remaining stopper azide in solution to yield exclusively the di-stoppered thread.

An alternative strategy involving the initial synthesis of unsymmetrical naphthalene diimide was ultimately used to synthesise the desired mono-stoppered naphthalene diimide thread **9** (see Scheme 3). Propargyl amine and 5-amino-1pentanol were slowly added to a heated suspension of



**Scheme 3** Synthesis of mono-stoppered diimide thread **9**. Reagents and conditions: (i) DMF, 120 °C, 2 h; (ii) 4-(tris(4-(*tert*-butyl)phenyl)methyl)phenol, PPh<sub>3</sub>, DBAD, CHCl<sub>3</sub>, 50 h, RT.

1,4,5,8-naphthalenetetracarboxylic dianhydride in dry DMF, to provide the unsymmetrical diimide **8** in statistical yield following purification by column chromatography. A Mitsunobu reaction between **8** and 4-(tris(4-(*tert*-butyl)phenyl)methyl)phenol<sup>36</sup> subsequently afforded the desired mono-stoppered thread **9** in 61% yield.

#### Control solution based rotaxane experiments

Having obtained both the mono-stoppered bipyridinium 5 and the mono-stoppered naphthalene diimide 9 threads, conditions for rotaxane formation using dinaphtho-38-crown-10 10 as the macrocycle component were investigated. Whilst similar rotaxanes using these components have been previously reported, these experiments were important not only to establish ideal conditions for the surface click reactions, but were also necessary in order to ensure that the increased solubility of the thread did not significantly affect the yield of rotaxane as has been seen in related systems.<sup>37</sup> A solution of mono-stoppered thread 5 or 9, was reacted with stopper azide 3 in the presence of one equivalent of dinaphtho-38-crown-10 10. Following purification via column chromatography the desired bipyridinium rotaxane 11 and the naphthalene diimide rotaxane 12 were isolated in 25% and 23% yields, respectively (see Schemes 4 and 5). The reactions were then repeated using five equivalents of crown 10 and as expected the yield of interlocked products increased to 36% and 33% respectively. Both rotaxanes were characterised by <sup>1</sup>H NMR,  $^{13}$ C NMR, UV-Vis and ESI-MS (mass peak at m/z 1066.6174  $[M - 2PF_6]^{2+}$  for **11** and 2130.1467  $[M]^+$  for **12**). The yields of the [2]rotaxanes were not significantly different to the yields expected using double click strategies, indicating that the use of a more soluble thread should still give reasonable yields of interlocked products on polymer bead surfaces.

Unlike the dumbbell and macrocycle non-interlocked counterparts which are either off-white or pale yellow in



Scheme 4 Synthesis of solution phase bipyridinium [2]rotaxane 11. Reagents and conditions: (i) TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), 4 days, RT.



Scheme 5 Synthesis of solution phase naphthalene diimide [2]rotaxane 12. Reagents and conditions: (i) TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95 : 5), 4 days, RT.



**Fig. 2** <sup>1</sup>H NMR spectra of the mono-stoppered bipyridinium thread **5** (top), bipyridinium rotaxane **11** (middle) and dinaphtho-38-crown-10 **10** (bottom) in CDCl<sub>2</sub> at 303 K.

colour, both rotaxanes are highly coloured (red/pink). This is attributed to a charge transfer interaction which in the UV can be seen at 517 nm ( $\varepsilon$  1710 M<sup>-1</sup> cm<sup>-1</sup>) and 491 nm ( $\varepsilon$  1040 M<sup>-1</sup> cm<sup>-1</sup>) for the bipyridinium rotaxane **11** and the diimide rotaxane **12** respectively (see Fig. S1†). This is indicative of the strong complexation in the mechanically interlocked systems and has been observed in related bipyridinium-crown and diimide-crown rotaxanes and catenanes.<sup>37,38</sup>

The partial <sup>1</sup>H NMR spectra of **11** and **12** in CDCl<sub>3</sub> are displayed in Fig. 2 and S2.<sup>†</sup> For the bipyridinium rotaxane **11**, significant upfield shifts in the bipyridinium protons a and b ( $\Delta\delta = 1.86$  ppm and 0.88 ppm respectively), and crown protons  $\beta$  and  $\gamma$  ( $\Delta\delta = 0.10$  ppm and 0.80 ppm respectively) were observed due to  $\pi$ - $\pi$  stacking interactions between the crown ether macrocycle and bipyridinium thread, indicative of successful rotaxane formation (see Fig. 2).

<sup>1</sup>H NMR analysis of the neutral [2]rotaxane **12** also revealed significant upfield shifts in both the naphthalene diimide and macrocycle protons (see Fig. S2<sup>†</sup>). The naphthalene diimide proton a is shifted from 8.81 ppm to 8.28 ppm, indicative of the shielding effect from the aromatic protons in the

macrocycle. Similarly, the crown aromatic protons  $\alpha$ ,  $\beta$  and  $\gamma$  have been shifted upfield, appearing at 5.98, 6.43 and 6.84 ppm in the bound rotaxane, as compared to their typical shifts when unbound of 6.52, 7.20 and 7.80 ppm. These changes in chemical shifts are characteristic of the interlocked nature of this structure, and are consistent with literature reports of related [2]rotaxanes.<sup>37</sup>

#### Surface attachment and HR MAS analysis

Having established suitable reaction conditions for the synthesis of diimide and bipyridinium [2]rotaxanes in solution, attention turned to the attachment of these [2]rotaxanes to polymer resins. Previous surface attachment has involved using EDC catalysed ester condensation reactions to successfully attach individual rotaxane components to either TentaGel or ArgoGel beads and monitor the subsequent rotaxane assembly process under thermodynamic control.<sup>31,33,34</sup> In addition, there has been one reported attempt to attach kinetically stable interlocked architectures to ArgoGel beads using the same ester condensation reaction, with modest success.<sup>32</sup> In this study we extended the bead attachment protocol to the Cu(I) catalysed Huisgen 1,3-dipolar cycloaddition 'click' reaction between azides and alkynes (see Scheme 6).

Given the mild reaction conditions and typically high yields, this reaction has gained favour in the synthesis of supramolecular systems such as catenane and rotaxanes.<sup>39–42</sup> Our objective was to attain high loading efficiency of rotaxane components and a significant proportion of the interlocked architectures on the bead using this reaction.

The synthesis of azide functionalised TentaGel resins was achieved *via* an initial reaction of TentaGel HL-OH beads with tosyl chloride to generate the tosylated resin **13**. This was subsequently reacted with sodium azide to give the desired azide functionalised beads **14**. In both reactions, a large excess of either tosyl chloride or sodium azide was used in order to maximise functional group conversion. As a control, the azide functionalised beads **14** were initially reacted with the monostoppered threads **5** and **9** to give the bipyridinium and diimide thread functionalised beads **15** and **16** (see Scheme 6).

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Scheme 6 Synthesis of polymer bound [2]rotaxanes. Reagents and conditions: (i) tosyl chloride, Et<sub>3</sub>N, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, RT, 7 days; (ii) NaN<sub>3</sub>, H<sub>2</sub>O, RT, 7 days; (iii) 5, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (v) 5, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (v) 5, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (v) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (vi) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (vi) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (vi) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (vi) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (vi) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (vi) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (vi) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (vi) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days; (vi) 9, 10, TBTA, Cu(MeCN)<sub>4</sub>PF<sub>6</sub>, CHCl<sub>3</sub>: MeOH (95:5), RT, 7 days.



Fig. 3 IR spectra of TentaGel-OH beads (blue), azide functionalised TentaGel beads 14 (red) and diimide thread functionalised beads 16 (green).

IR spectroscopy was used initially to qualitatively monitor the success of the 'click' reaction (see Fig. 3 and S3–S5<sup>†</sup>). After conversion of the starting TentaGel-OH beads to the azide functionalised resin 14, a new peak at 2108 cm<sup>-1</sup> was observed which is characteristic of the N<sub>3</sub> moiety.<sup>43</sup> Upon 'click' reaction with either the bipyridinium mono stoppered thread 5 or the diimide mono stoppered thread 9, this resonance disappeared indicating that the bead functionalisation reaction to give 15 and 16 was successful.

<sup>1</sup>H HR MAS NMR analysis of these beads also indicated successful attachment of the thread components (see Fig. 4 and S8<sup> $\dagger$ </sup>), as evidenced by the expected bipyridinium (8.93 and 8.38 ppm) and triazole (7.68 ppm) aromatic peaks for the bipyridinium functionalised resin **15**, and the diimide



Fig. 4 Comparison of the effect of the number of CPMG loops on the quality of the HR MAS <sup>1</sup>H NMR spectrum of **15**. Beads were swollen in CDCl<sub>3</sub>.

(8.73 ppm) and triazole (7.78 ppm) aromatic peaks for the diimide functionalised resin **16** visible in the NMR spectra. In both cases peaks for the tetraphenyl stopper group were observed at 7.22, 7.08 and 6.72 ppm. Good signal to noise was achieved when running the basic 1D NMR experiments; however, for bipyridinium functionalised resins **15**, application of a standard 32  $\pi$ -pulse CPMG sequence (used previously to improve the quality of the <sup>1</sup>H spectrum by removing the broad aromatic resonances arising from the polystyrene bead core) also resulted in the removal of the broad bipyridinium aromatic proton peaks (see Fig. 4). This is due to the fact

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Fig. 5  $4 \times$  Magnification optical microscope photos of (a) 15, (b) 16, (c) 1, and (d) 2.

that while the CPMG pulse sequence successfully filters out any broad resonances due to the bead core, it is an indiscriminate process and the intensity of signals arising from the tethered components can also be suppressed, depending on their relaxation properties. As such, shorter CPMG pulse sequences with only 8  $\pi$ -pulses were acquired to identify the balance between suppression of the bead core resonances without significantly affecting the proton peaks attributed to the bipyridinium thread. From these experiments it was clear that the click reaction was indeed successful in functionalising the beads with a loading sufficient to record good quality <sup>1</sup>H HR MAS NMR spectra.

The bead functionalisation reaction was then repeated in the presence of dinaphtho-38-crown-10 **10** to generate the desired rotaxane functionalised beads **1** and **2** (see Scheme 6). IR spectroscopy revealed that the peak characteristic of the azide functionality on resin **14** (2108 cm<sup>-1</sup>) was absent in the IR spectra for rotaxane functionalised beads **1** and **2** indicating good bead loading. Visual inspections of the rotaxane functionalised beads **1** and **2** were also promising as unlike the thread functionalised beads **15** and **16** which were yellow in appearance, both the rotaxane functionalised beads had a strong reddish appearance (see Fig. 5). This colouration (which was also observed in the solution based rotaxanes **11** and **12**) is indicative of donor-acceptor complex formation between crown macrocycles and diimide or bipyridinium threads resulting in this characteristic charge transfer phenomenon.

Further definitive evidence of rotaxane formation on the polymer surface was provided by <sup>1</sup>H HR MAS NMR spectroscopy (see Fig. 6 and 7). For the bipyridinium rotaxane functionalised beads **1**, two sets of bipyridinium peaks (a and b) were observed with those belonging to the uncomplexed thread appearing at 9.21 and 8.60 ppm, while those indicative of rotaxane formation appeared in the upfield position at 8.19 and 6.78 ppm. Likewise peaks for the crown ether macrocycle were observed at 6.78 and 6.56 ppm. Integration of the basic 1D NMR spectrum suggests that the target bipyridinium rotaxane species **1** was approximately 40% of the total bead tethered population with the remaining surface functionalised by the uncomplexed bipyridinium thread.

For diimide rotaxane functionalised beads 2, again two sets of naphthalene diimide peaks were observed, with those



**Fig. 6** HR MAS <sup>1</sup>H NMR spectra of bipyridinium rotaxane functionalised beads **1** (top) and solution based bipyridinium rotaxane **11** (bottom) in CDCl<sub>3</sub>.



Fig. 7 HR MAS <sup>1</sup>H NMR spectra for diimide functionalised beads **16** (top), diimide rotaxane functionalised beads **2** (middle) and solution based diimide rotaxane (bottom) in CDCl<sub>3</sub>.

corresponding to unbound diimide appearing at 8.70 ppm, and those resulting from the complexed rotaxane diimide appearing upfield at 8.21 ppm (see Fig. 7). In addition, peaks corresponding to the crown ether aromatic protons were identified at 6.81, 6.36 and 5.89 ppm. This clearly indicates that a mixture of diimide thread and diimide rotaxane were attached to the bead, and based on proton integration of the basic 1D NMR spectrum, the percentage of rotaxane was determined to be approximately 20%.

Attempts to improve the proportion of interlocked architectures on the surface by using an excess of crown **10** (five equivalents) were surprisingly unsuccessful. IR and HR MAS NMR spectroscopy showed a drop in the efficiency of the click reaction as evidenced by the appearance of a residual azide peak in the IR at 2108 cm<sup>-1</sup>, and poor quality HR MAS NMR spectra. This is contrary to the solution based control studies in which increasing the macrocycle concentration had no effect on the overall reaction efficiency. Addition of more copper catalyst did not improve reaction efficiency.

#### Conclusion

This study has shown that the Cu(I) catalyzed Huisgen 1,3dipolar cycloaddition or "click" reaction between azides and alkynes is an effective reaction for synthesising interlocked architectures both in solution and on solid supports. The synthesis of mono-stoppered rotaxane thread components was achieved in good yields, and subsequent attempts to synthesise rotaxanes in solution proceeded smoothly with interlocked architectures being isolated in yields of 33-36%. These yields are comparable to related literature reports indicating that the stoppering of one end of each thread had no significant effect on its binding to the macrocycle or subsequent rotaxane formation. Analogous "click" reactions to functionalise polymer resins with interlocked architectures were also attempted. Initial screening of the azide bead functionalisation and subsequent reaction with the mono-stoppered diimide or bipyridinium threads was followed using IR spectroscopy. Clear (qualitative) evidence of the appearance and subsequent disappearance of the azide resonance at 2108 cm<sup>-1</sup> suggested that the click reactions were highly efficient. <sup>1</sup>H HR MAS NMR spectroscopy demonstrated that the reactions to functionalise the beads with individual stoppered thread components were successful with bead loading at a sufficient level to allow high quality <sup>1</sup>H spectra to be recorded. However, given the inherent broadness in these systems (particularly for the bipyridinium thread) attempts to selectively remove the broad polystyrene resonances also resulted in the removal of characteristic bipyridinium aromatic proton peaks. This is due to the non-discriminant nature of the CPMG pulse sequences used and thus a careful balance needed to be found such that the quality of the NMR spectra was improved by removing some of the broadness associated with the polystyrene core without impacting significantly on the attached thread or rotaxane resonances. When repeating the bead reactions in the presence of crown, significant proportions of both the bipyridinium rotaxane 1 (40%) and the diimide rotaxane 2 (20%) were evident in the HR MAS <sup>1</sup>H NMR spectra. Attempts to increase the proportion of rotaxane on the bead by using an excess of crown were not successful. In fact the excess crown impeded the bead functionalisation reaction, as evidenced by the residual azide peak in the IR spectrum and the poor signal to noise ratios observed in the <sup>1</sup>H HR MAS spectra. This is surprising given the fact that the use of excess crown did not negatively impede the rate of reaction or yield in our solution control studies. Addition of higher equivalents of copper catalyst also failed to improve reaction efficiency suggesting that the poor reaction efficiency is not due to problems with the copper catalysts (i.e. the excess crown sequestering the copper) as this would have been either observed in solution control studies or overcome upon addition of excess copper to the bead reactions. Whether the excess crown ether

macrocycle is binding to the polyether tethers in such a way as to inhibit the reaction with the diimide or bipyridinium thread remains unclear. Repeated "click reactions" of these beads in the presence of excess crown may ultimately lead to complete bead functionalisation, however more efficient syntheses will be the focus of future work. Nevertheless this is a clear example of a situation in which solution chemistry has not been directly transferred to the chemistry of solid supports, therefore highlighting the need to use surfaces and techniques that allow such direct comparison between solution and surface processes. Future work will investigate these observations using dynamic covalent chemistry as a strategy to increase the percentage of interlocked architectures on these polymer surfaces.

#### Experimental

#### General considerations

Unless otherwise stated, reagents were purchased from commercial sources and used without further purification. All solvents were dried before use over type 3 Å or 4 Å molecular sieves according to standard procedures. Triethylamine was dried over KOH. Silica gel column chromatography was carried out using Merck Silica Gel 60 (grade 9385, 230–400 mesh). Analytical TLC was carried out on Merck Silica Gel 60  $F_{254}$  precoated aluminium sheets. Reverse phase chromatography was carried out using an Agilent SuperFlash C18n (SF 25–55 g) column.

Solution NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer and referenced to the relevant solvent peak. TentaGel<sup>TM</sup>-HL-OH resins were purchased from Peptides International with a quoted loading of 0.43 mmol g<sup>-1</sup> and a particle size of approximately 90 µm. HR MAS NMR spectra were acquired on a Bruker DRX400 spectrometer at room temperature using a Bruker HR MAS probe. Rotors containing a suspension of the beads in CDCl<sub>3</sub> were spun at 4 kHz. One-dimensional HR MAS spectra were obtained with 64 scans. Unless otherwise stated, the CPMG pulse sequence contained 0, 8, 32 or 64  $\pi$ -pulses with a repetition time of 30 ms.

ESI high-resolution mass spectra were obtained using a QTOF LC mass spectrometer which utilised electrospray ionization. Melting points were measured on a variable-temperature apparatus by the capillary method and are uncorrected. IR spectra were obtained using a Thermo Nicolet Nexus 870 esp spectrometer equipped with a  $45^{\circ}$  Ge ATR accessory at 4 cm<sup>-1</sup> resolution using 64 scan averaging.

Coloured bead images were taken using a Leica MZ6 modular stereomicroscope with a Leica CLS 150 light source and Leica camera mounted at 4× magnification.

#### Synthetic procedures

The stopper azide 3,<sup>37</sup> the bipyridinium alkyne 4,<sup>44</sup> the NDI alkyne 6,<sup>45</sup> and the dinaphtho-38-crown-10 10,<sup>46</sup> were synthesised according to literature procedures. Full <sup>1</sup>H and

<sup>13</sup>C NMR spectra for all key compounds are provided in the ESI (see Fig. S9–S18<sup>†</sup>).

#### Mono-stoppered BIPY-2PF<sub>6</sub> thread (5)

Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA) (0.21 g, 0.40 mmol) and bipyridinium alkyne 4 (2.20 g, 4.0 mmol) and Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (0.15 g, 0.39 mmol) were dissolved in dry acetone (90 mL). Stopper azide 3 (0.61 g, 0.99 mmol) dissolved in dry acetone (100 mL) was then added dropwise over a period of 60 minutes. The reaction mixture was stirred under argon at room temperature for 48 hours, before the solvent was removed in vacuo. The crude product was purified by RP MPLC using a gradient of 100% H<sub>2</sub>O to 100% MeCN over 40 min to give the pure product as a pale brown solid (0.66 g, 76%); m.p. 246–248 °C; m/z (ESI-MS)  $[M]^{2+}$  440.2766 C<sub>59</sub>H<sub>70</sub>N<sub>5</sub>O<sub>2</sub> (calc. 440.2759); <sup>1</sup>H NMR (400 MHz, Acetone-d<sub>6</sub>)  $\delta$  9.44 (4H, d, J = 5.6 Hz, b-H), 8.82 (4H, d, J = 4.0 Hz, a-H), 7.89 (1H, s, c-H), 7.34 (6H, d, J = 8.0 Hz, Ar-H), 7.17-7.13 (8H, m, Ar-H), 6.83 (2H, d, J = 8.0 Hz, Ar-H), 5.29 (2H, m, CH<sub>2</sub>), 5.15 (2H, m,  $CH_2$ ), 4.59 (2H, t, J = 5.0 Hz,  $CH_2$ ), 4.08  $(2H, t, J = 4.0 Hz, CH_2), 3.94 (2H, t, J = 5.0 Hz, OCH_2),$ 3.82 (2H, t, J = 4.0 Hz, OCH<sub>2</sub>), 3.62 (2H, m, CH<sub>2</sub>), 3.19 (2H, m, CH<sub>2</sub>), 2.72 (1H, s, CH), 1.31 (27H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, Acetone-d<sub>6</sub>)  $\delta$  156.7, 150.3, 149.9, 148.3, 146.3, 144.3, 139.6, 131.9, 130.4, 127.0, 126.9, 124.2, 123.6, 113.2, 78.1, 74.1, 69.2, 69.1, 67.1, 63.0, 61.3, 60.1, 49.7, 33.9, 30.7, 29.5, 26.9, 20.7.

#### **Unsymmetrical NDI thread (8)**

Naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (490 mg, 1.8 mmol) was dissolved in dry, degassed DMF (2 mL). A solution of 5-amino-1-pentanol (200 mg, 1.9 mmol) and propargyl amine (200 mg, 1.9 mmol) dissolved in dry, degassed DMF (3 mL) was added dropwise under argon. The reaction mixture was stirred under argon at 120 °C for 2 hours. The solvent was evaporated to yield a crude purple solid which was purified by column chromatography using 20% EtOAc: 80% DCM as the eluent to give the pure product as a cream solid (230 mg, 32%); m.p. 206–208 °C; m/z (ESI-MS)  $[M]^+$  390.1247  $C_{22}H_{18}N_2O_5$  (calc. 390.1215); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.81 (4H, m, a-H), 5.00 (2H, s, CH<sub>2</sub>), 4.24 (2H, t, J = 7.4 Hz, CH<sub>2</sub>), 3.69 (2H, m, CH<sub>2</sub>), 2.25 (1H, s, OH), 1.81 (2H, m, CH<sub>2</sub>), 1.68 (2H, m, CH<sub>2</sub>), 1.55 (2H, m, CH<sub>2</sub>), 1.31 (1H, s, CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.7, 162.0, 131.3, 131.0, 126.9, 126.7, 126.2, 77.8, 77.2, 71.2, 62.7, 40.8, 32.3, 29.8, 27.8, 23.2.

#### Mono-stoppered NDI thread (9)

Unsymmetrical NDI thread **8** (80 mg, 0.21 mmol), 4-(tris-(4-(tert-butyl)phenyl)methyl)phenol<sup>36</sup> (103 mg, 0.21 mmol) and PPh<sub>3</sub> (82 mg, 0.31 mmol) were dissolved in dry, degassed CHCl<sub>3</sub> (8 mL). Di-*tert*-butyl azodicarboxylate (105 mg, 0.46 mmol) in dry, degassed CHCl<sub>3</sub> (3 mL) was then added dropwise at 0 °C and the reaction mixture was left to stir under argon at room temperature for 50 hours. The reaction mixture then was filtered through a short plug of silica and the filtrate evaporated. The crude material was purified by column

chromatography using 100% CHCl<sub>3</sub> to 80% CHCl<sub>3</sub> : 20% EtOAc as the eluent followed by recrystallisation from CHCl<sub>3</sub> and MeOH to give the pure product as a cream solid (110 mg, 61%); m.p. 275–277 °C; m/z (ESI-MS) [M]<sup>+</sup> 876.4587 C<sub>59</sub>H<sub>60</sub>N<sub>2</sub>O<sub>5</sub> (calc. 876.4502); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.81 (4H, m, a-H), 7.24 (6H, d, J = 8.0 Hz, Ar-H), 7.10–7.09 (8H, m, Ar-H), 6.75 (2H, d, J = 8.0 Hz, Ar-H), 5.00 (2H, s, CH<sub>2</sub>), 4.25 (2H, t, J = 7.4 Hz, CH<sub>2</sub>), 3.97 (2H, m, OCH<sub>2</sub>), 1.85 (2H, m, CH<sub>2</sub>), 1.64 (2H, m, CH<sub>2</sub>), 1.53 (2H, m, CH<sub>2</sub>), 1.31 (28 H, s, CH and CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.7, 162.0, 156.7, 148.2, 144.1, 139.4, 132.1, 131.3, 131.0, 130.6, 126.9, 126.7, 126.2, 124.0, 112.8, 77.8, 77.2, 71.2, 67.3, 63.0, 40.8, 34.2, 31.3, 29.8, 29.0, 27.8, 23.7.

#### BIPY rotaxane (11)

Mono-stoppered BIPY·2PF<sub>6</sub> thread 5 (50 mg, 0.057 mmol), dinaphtho-38-crown-10 (10) (185 mg, 0.29 mmol), TBTA (3 mg, 0.006 mmol) and Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (2 mg, 0.006 mmol) were dissolved in a dry, degassed mixture of 5% MeOH: 95% CHCl<sub>3</sub> (5 mL). The stopper azide 3 (35 mg, 0.057 mmol) was then added and the reaction mixture was stirred under argon at room temperature for 4 days. After this time the solvent was evaporated and the residue purified by column chromatography using 5% MeOH: 95% CHCl<sub>3</sub> as the eluent to give the desired rotaxane as an orange solid (50 mg, 36%); m.p. 223–225 °C; m/z (ESI-MS)  $[M - PF_6]^{2+}$  1066.6174  $C_{136}H_{164}F_{12}N_8O_{14}P_2$  (calc. 1066.6184); <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.56 (4H, d, J = 8.0 Hz, b-H), 7.98 (2H, s, c-H), 7.21 (12H, d, J = 8.0 Hz, Ar-H), 7.11–7.00 (24H, m,  $\gamma$ -H, Ar-H and  $\beta$ -H), 6.96 (4H, d, J = 8.0 Hz, a-H), 6.79 (4H, d, J = 8.0 Hz, Ar-H), 6.51 (4H, d, J = 7.9 Hz,  $\alpha$ -H), 5.01 (4H, m, CH<sub>2</sub>), 4.62 (4H, t, J =4.0 Hz, CH<sub>2</sub>), 4.12 (4H, m, OCH<sub>2</sub>), 3.99 (2H, m, OCH<sub>2</sub>), 3.92-3.87 (36H, m, OCH<sub>2</sub>), 3.53 (4H, m, CH<sub>2</sub>), 1.30 (54H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.3, 153.0, 148.2, 144.4, 144.0, 143.9, 141.2, 139.8, 132.2, 130.6, 126.0, 125.3, 124.0, 123.9, 123.5, 113.7, 113.0, 105.8, 77.2, 71.1, 71.0, 70.1, 69.6, 69.3, 67.9, 67.2, 63.0, 60.5, 50.2, 34.2, 31.3, 27.3.

#### NDI rotaxane (12)

Mono-stoppered NDI thread 9 (50 mg, 0.055 mmol) and dinaphtho-38-crown-10 (10) (180 mg, 0.28 mmol) were dissolved in a dry, degassed mixture of 5% MeOH: 95% CHCl<sub>3</sub> (6 mL). A solution of  $Cu(MeCN)_4PF_6$  (2 mg, 0.006 mmol) and TBTA (3 mg, 0.006 mmol) dissolved in a dry, degassed mixture of 5% MeOH: 95% CHCl<sub>3</sub> (0.2 mL) was added to the reaction mixture, followed by a solution of stopper azide 3 (34 mg, 0.056 mmol) dissolved in dry, degassed 5% MeOH:95% CHCl<sub>3</sub> (0.6 mL). The reaction mixture was then stirred under argon at room temperature for 4 days. After this time the solvent was evaporated and the crude material was purified by column chromatography using 50% EtOAc: 50% hexane to 100% EtOAc as the eluent to give the desired rotaxane as a red solid (39 mg, 33%); m.p. 166–168 °C; m/z (ESI-MS) [M]<sup>+</sup> C136H155N5O7 2130.1467 (calc. 2130.1418); <sup>1</sup>H NMR (400 MHz, CDCl3)) & 8.28 (4H, m, a-H), 8.09 (1H, s, c-H), 7.23 (12H, d, J = 8.0 Hz, Ar-H), 7.09–7.06 (16H, m, Ar-H), 6.84–6.80 (6H, m, γ-H

and Ar-H), 6.73 (2H, d, J = 8.0 Hz, Ar-H), 6.43 (4H, m,  $\beta$ -H), 5.98 (4H, m,  $\alpha$ -H), 5.41 (2H, s, CH<sub>2</sub>), 4.64 (4H, m, CH<sub>2</sub>), 4.08 (4H, m, OCH<sub>2</sub>), 4.00 (12H, m, OCH<sub>2</sub>), 3.91–3.86 (26H, m, OCH<sub>2</sub>), 3.77 (4H, m, OCH<sub>2</sub>), 2.05–1.94 (4H, m, CH<sub>2</sub>), 1.31 (54H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.9, 162.6, 156.8, 156.2, 154.1, 152.8, 148.2, 148.2, 144.1, 144.0, 139.8, 139.4, 132.2, 130.6, 130.6, 130.4, 126.5, 124.9, 124.6, 124.0, 123.9, 123.4, 114.4, 114.0, 112.9, 112.9, 105.4, 103.3, 71.3, 71.1, 70.9, 69.8, 69.7, 67.7, 67.2, 66.8, 62.9, 34.2, 34.2, 33.8, 31.8, 31.3, 29.6, 29.4, 29.3, 29.2, 29.1, 27.8, 24.1, 22.6, 14.1.

#### Tosyl functionalised TentaGel resins (13)

Under argon TentaGel-OH beads (103 mg, 0.43 mmol g<sup>-1</sup> OH loading), tosyl chloride (103 mg, 0.54 mmol) and a catalytic amount of 4-dimethylaminopyridine were suspended in dry DCM (3 mL). To this mixture  $Et_3N$  (100  $\mu$ L) was added and the reaction was left for one week with occasional stirring. After this time the beads were filtered and washed sequentially with DCM and hexane several times (5 × 5 mL each), followed by a final wash with acetone (5 mL), water (5 mL) and acetone (5 mL). The resulting off white beads were dried *in vacuo*.

#### Azide functionalised TentaGel resins (14)

The tosyl functionalised TentaGel beads 13 were suspended in water (3 mL) and sodium azide (351 mg, 5.4 mmol) was then added. The reaction was left for one week with occasional stirring, before the beads were filtered, washed with water (10 × 5 mL), acetone (5 mL) and sequential rinsing with DCM and hexane (5 × 5 mL each). The off white beads were then dried *in vacuo*.

#### Bipyridinium functionalised TentaGel resins (15)

A solution of mono-stoppered BIPY-2PF<sub>6</sub> thread 5 (250 mg, 0.28 mmol) dissolved in dry, degassed acetone (2 mL) was added to a round bottomed flask containing the azide functionalised TentaGel resins 14 (40 mg) under argon. TBTA (15 mg, 0.029 mmol) and Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mg, 0.029 mmol) dissolved in dry, degassed acetone (1 mL) was then added to the beads and the reaction was kept under argon at room temperature for 7 days. The beads were collected by filtration and washed with acetone (10 mL), water (10 mL), sat. NH<sub>4</sub>Cl (10 mL), CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and hexane (10 mL). The off white beads were then dried under vacuum. <sup>1</sup>H HR MAS NMR (400 MHz, CDCl<sub>3</sub>) δ 8.93 (4H, br m, b-H), 8.38 (4H, br m, a-H), 7.68 (2H, br s, c-H), 7.22-7.20 (6H, m, Ar-H), 7.08-7.06 (8H, m, Ar-H), 6.72–6.70 (2H, m, Ar-H), 5.01 (2H, br m, CH<sub>2</sub>), 4.47 (4H, br m, CH<sub>2</sub>), 4.02 (2H, br m, CH<sub>2</sub>), 3.88 (2H, m, OCH<sub>2</sub>), 3.76 (4H, br m, OCH<sub>2</sub>), 2.74 (2H, m, CH<sub>2</sub>), 1.29 (27H, s, CH<sub>3</sub>).

#### Diimide Functionalised TentaGel resins (16)

A solution of mono-stoppered NDI thread **9** (253 mg, 0.29 mmol) dissolved in dry, degassed 5% MeOH : 95% CHCl<sub>3</sub> (2 mL) was added to a round bottomed flask containing the azide functionalised TentaGel resins **14** (53 mg) under argon. A solution of TBTA (15 mg, 0.029 mmol) and Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mg, 0.029 mmol) dissolved in dry, degassed 5%

MeOH: 95% CHCl<sub>3</sub> (1 mL) was then added to the beads, and the reaction mixture was kept under argon at room temperature for 7 days. The beads were collected by filtration and washed with CHCl<sub>3</sub> (10 mL), acetone (10 mL), water (10 mL), sat. NH<sub>4</sub>Cl (10 mL), CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and hexane (10 mL) to give the pale yellow diimide functionalised beads. <sup>1</sup>H HR MAS NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.73 (4H, m, a-H), 7.78 (1H, br s, c-H), 7.22 (6H, br m, Ar-H), 7.08 (8H, br m, Ar-H), 6.72 (2H, m, Ar-H), 5.50 (2H, br s, CH<sub>2</sub>), 4.50 (2H, br m, CH<sub>2</sub>), 4.21 (2H, m, OCH<sub>2</sub>), 2.75 (2H, m, CH<sub>2</sub>), 1.63 (4H, m, CH<sub>2</sub>), 1.29 (27 H, s, CH<sub>3</sub>).

#### Bead tethered bipyridinium rotaxane (1)

A solution of mono-stoppered BIPY-2PF<sub>6</sub> thread (254 mg, 0.29 mmol) and dinaphtho-38-crown-10 (10) (915 mg, 1.4 mmol) dissolved in dry, degassed 5% MeOH: 95% CHCl<sub>3</sub> (3 mL) was added to a round bottomed flask containing the azide functionalised TentaGel resin 14 (49 mg) under argon. TBTA (15 mg, 0.029 mmol) and Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mg, 0.028 mmol) dissolved in dry, degassed 5% MeOH:95% CHCl<sub>3</sub> (0.5 mL) were then added and the reaction mixture was kept under argon at room temperature for 7 days. The beads were collected by filtration and washed with acetone (10 mL), water (10 mL), sat. NH<sub>4</sub>Cl (10 mL), CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and hexane (10 mL). The resulting orange beads were dried in vacuo. <sup>1</sup>H HR MAS NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.21 (m, b-H), 8.60 (m, a-H), 8.19 (m, b-H), 7.68 (br s, c-H), 7.22 (m, Ar-H), 7.08 (m, γ-H and Ar-H), 6.78 (m, a-H), 6.70 (m, Ar-H), 6.56 (m, α-H), 5.15 (m, CH<sub>2</sub>), 4.61 (m, CH<sub>2</sub>), 4.48 (m, CH<sub>2</sub>), 4.19 (m, CH<sub>2</sub>), 4.00 (m, CH<sub>2</sub>), 3.96 (m, CH<sub>2</sub>), 3.85 (m, OCH<sub>2</sub>), 3.50 (m, OCH<sub>2</sub>), 3.40 (m, OCH<sub>2</sub>), 2.83 (m, CH<sub>2</sub>), 2.25 (m, CH<sub>2</sub>), 1.30 (s,  $CH_3$ ). Note: The characteristic crown-complexed proton peak assignments are highlighted in bold.

#### Bead tethered naphthalene diimide rotaxane (2)

A solution of mono-stoppered NDI thread (250)mg, 0.29 mmol) and dinaphtho-38-crown-10 (10) (907 mg, 1.4 mmol) dissolved in dry, degassed 5% MeOH: 95% CHCl<sub>3</sub> (4 mL) was added to a round bottomed flask containing the azide functionalised TentaGel resin 14 (52 mg) under argon. TBTA (15 mg, 0.029 mmol) and Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mg, 0.029 mmol) dissolved in dry, degassed 5% MeOH:95% CHCl<sub>3</sub> (0.5 mL) were then added and the reaction mixture was kept under argon at room temperature for 7 days. The beads were collected by filtration and washed with CHCl<sub>3</sub> (10 mL), acetone (10 mL), water (10 mL), sat. NH<sub>4</sub>Cl (10 mL), CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and hexane (10 mL). The resulting red beads were dried under vacuum. <sup>1</sup>H HR MAS NMR (400 MHz, CDCl<sub>3</sub>) δ 8.70 (m, a-H), 8.21 (m, a-H), 7.78 (br s, c-H), 7.22 (br m, Ar-H), 7.08 (br m, Ar-H), 6.81 (m, γ-H), 6.73 (m, Ar-H), 6.36 (m, β-H), 5.89 (m,  $\alpha$ -H), 5.50 (br m, CH<sub>2</sub>), 5.15 (m, CH<sub>2</sub>), 4.66 (m, CH<sub>2</sub>), 4.51 (m, CH<sub>2</sub>), 4.20 (m, OCH<sub>2</sub>), 4.07 (m, CH<sub>2</sub>), 3.93 (m, OCH<sub>2</sub>), 3.84 (m, OCH<sub>2</sub>), 3.47 (m, OCH<sub>2</sub>), 3.33 (m, OCH<sub>2</sub>), 2.76 (m, CH<sub>2</sub>), 2.30 (m, CH<sub>2</sub>), 1.60 (m, CH<sub>2</sub>), 1.29 (s, CH<sub>3</sub>). Note: the characteristic crown-complexed proton peak assignments are highlighted in bold.

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