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Due to potential applications in the biological and material sciences there is considerable interest in the development of mechanically interlocked ligands (MILs). The mild functional-group tolerant copper(I)-catalysed azide-alkyne cycloaddition active-metal-template (CuAAC-AMT) method has been exploited to generate mono- and bi-functionalised [2]rotaxanes by interlocking an exo-alcohol functionalised macrocycle and functionalised triphenylmethyl (trityl) stoppers. These [2]rotaxanes were post-synthetically conjugated to either one or two 2,2',6',2''-terpyridine (terpy) coordinating units to generate mechanically interlocked “super” ligands. Addition of Fe(II) ions to the mono-terpy ligand leads to the formation of a metallo-bis-[2]rotaxane. At high dilution the bi-terpy [2]rotaxane ligand forms a [2]rotaxane metallo-macrocycle, in the presence of Fe(II) ions. Conversely, at high concentration self-assembly of the bi-terpy [2]rotaxane ligand with Fe(II) ions results in the generation of a metallo-supramolecular poly-[2]rotaxane oligomer. The [2]rotaxane ligands and corresponding Fe(II) complexes have been characterised with \(^1\)H and \(^{13}\)C NMR and UV-vis spectroscopies, high resolution electrospray ionisation mass spectrometry (HR-ESMS), and elemental analyses. Additionally, \(^1\)H DOSY NMR spectroscopy and GPC analysis were used to provide evidence for the constitution of the self-assembled metallo-supramolecular mechanically-interlocked architectures.

Introduction

With the strategies for their synthesis now well understood, there has been considerable interest in the use of mechanically interlocked (MIAs)\(^1\) and metallo-supramolecular architectures\(^2\) for the development of a range of nanotechnologies.\(^3\) Encouraged by these potential applications a number of groups have begun to merge these two distinct areas of supramolecular chemistry and develop mechanically interlocked ligands (MILs).\(^4\) The Loeb,\(^5\) and Stoddart and Yaghi groups,\(^6\) amongst others have synthesised a range of MILs (mostly based on [2]rotaxanes) and incorporated them into metal-organic frameworks (MOFs) generating a new class of materials, metal-organic rotaxane frameworks (MORFs).\(^4\), \(^7\) Loeb and co-workers have elegantly demonstrated that the interlocked component retains its inherent dynamic motions once incorporated in the MORF.\(^8\) Other MIL systems have been used to integrate MIAs into condensed phases (onto nanoparticles and surfaces).\(^9\) MILs have also been used to generate metallo-supramolecular polymers\(^10\) and discrete architectures.\(^11\) Of note, Giuseppone and co-workers synthesised a daisy chain polymer architecture that extends or contracts in response to pH changes in the system.\(^12\) While impressive, the systems developed to date for the most part have exploited supramolecular forces (mainly hydrogen bonding or \(\pi-\pi\) interactions) to template the formation of interlocked ligand architectures. This limits both the functional diversity and potential applications of these MILs.

The ‘active’ metal template (AMT) strategy,\(^13\) established by the Leigh group in 2006,\(^14\) has emerged as a convenient technique to efficiently construct MIAs. In the AMT strategy the metal ion plays a dual role; templating the formation of the MIA and mediating (or catalysing) the formation of the covalent bond that captures the interlocked architecture. The strategy is quite general and a range of metal ions and bond forming reactions have been exploited to generate MIAs.\(^15\) Due to its mild reaction conditions, which are tolerant to a wide range of functional groups, the copper(I)-catalysed azide and alkyne cycloaddition active metal template (CuAAC-AMT)\(^14,16\) method has become the most popular strategy to generate
functional MIAs. Rotaxanes,\textsuperscript{14, 16-17} catenanes,\textsuperscript{18} knots,\textsuperscript{19} mechanically planar chiral [2]rotaxanes\textsuperscript{17d} and molecular machines\textsuperscript{20} have all been generated using the CuAAC-AMT approach.

Combining our interests in the development of mechanically interlocked and metallo-supramolecular architectures herein, we show that the “click” CuAAC-AMT strategy can be exploited to develop new mono- and bifunctionalised [2]rotaxanes. These rotaxanes can be post-synthetically conjugated to coordinating units (2,2',6',2''-terpyridine) and used to self-assemble metallo-bis-([2]rotaxanes), macrocycles and oligomers with Fe(II) ions.

Results and discussion

Design strategy and component synthesis

The presence of coordinating units/ligands in the [2]rotaxane precursors could potentially interfere with the AMT reaction. As such we designed a two-step AMT post-synthetic conjugation approach to the MILs. This strategy requires reactive functionality in the macrocycle and stopper components of the rotaxane which could be used to attach the ligands after the AMT reaction. Tridentate 2,2',6',2''-terpyridine was chosen as the ligating motif because the “click” [2]rotaxanes feature a bidentate pyridyl triazoyl binding pocket which could compete for the metal ions\textsuperscript{14, 16} that would be used for the self-assembly reactions. The 2,2',6',2''-terpyridine based ligands\textsuperscript{21} have been shown to bind a wide variety of metal ions and this motif has been extensively exploited in the generation of both discrete\textsuperscript{22} and polymeric\textsuperscript{23} metallo-supramolecular architectures.

Macrocycles containing the 2,6-bis(alkyloxy)methyl)pyridine subunit have been successfully used in the CuAAC-AMT synthesis of a range of MIAs,\textsuperscript{14, 16-17, 18-19} therefore we targeted theexo-alcohol functionalised macrocycle 1 containing that motif (Scheme 1). Macrocycle 1 was readily prepared in 35% yield, using similar conditions to those exploited for the synthesis of the unfuctionalised parent macrocycle (Scheme S1, ESI†).\textsuperscript{14, 16} The molecular structure of 1 was confirmed by X-ray crystallography (ESI†). Vapour diffusion of diethyl ether into a chloroform/methanol (1:1) solution of 1 produced small colourless X-ray quality crystals. The structure of 1 was as expected (Figure 1a), a large (N1-\textsuperscript{exo}-C16 9.130(3) Å, C11-\textsuperscript{exo}-C27 9.203(4) Å) 30-membered pyridyl macrocycle with anexo-alcohol functional group. Interestingly, a hydrogen bonding interaction (N1-\textsuperscript{exo}-O5' 2.808(2) Å) between theexo-alcohol functional group and the pyridyl unit on a second macrocycle leads to the formation of dimers in the solid state (ESI†). This hydrogen bonding interaction could potentially interfere with the metal ion coordination required for the AMT “click” reaction. As such we examined the ability of the macrocycle to coordinate to both Cu(I) and the larger isoelectronic Ag(I) ions. \textsuperscript{1}H NMR and HR-ESMS experiments on 1:1 mixtures of either [Cu(CH\textsubscript{3}CN)\textsubscript{3}](PF\textsubscript{6}) (1 equiv.) or AgOTf (1 eq.) and the macrocycle 1 confirmed the formation of 1-M (Cu' or Ag') macrocycle complexes in solution (ESI†).\textsuperscript{24}

The triphenylmethyl (trityl) stoppers with the terminal azide 2 and alkyne 3a-b functionalities were prepared in good to excellent yield by modification of literature procedures (Scheme S2, ESI†). Molecular modelling (MMFF, SPARTAN '08, ESI†) indicated that these trityl stoppers would be large enough to prevent the macrocycle dethreading.

“Click” AMT [2]rotaxane synthesis

Having confirmed that macrocycle 1 would coordinate metal ions, the synthesis of the alcohol functionalised [2]rotaxane was attempted using standard CuAAC “click” AMT conditions.\textsuperscript{14, 16} The macrocycle 1 (1 equiv.), [Cu(CH\textsubscript{3}CN)\textsubscript{3}](PF\textsubscript{6}) (1 equiv.), azide 2 (1 equiv.) and alkyne 3a (1 equiv.) stopper were stirred in dichloromethane at room temperature for 24 hours (Scheme 1). Thin layer chromatography (TLC) and HR-ESMS (m/z = 1703.0100 [4a+H]\textsuperscript{+}) indicated that the desired [2]rotaxane 4a was present in the reaction mixture but the product was only isolated in 26% yield. After optimisation (raising the reaction temperature...
to 40 °C and using 5 equiv. of the azide and alkyne stoppers) of the “click” AMT conditions it was found that the [2]rotaxanes 4a-b could be isolated in 78% and 72% yield, respectively (Scheme 1).

The alcohol functionalised [2]rotaxanes 4a-b were post-synthetically conjugated to the 2,2',6',2'”-terpyridine coordinating motif using standard ether formation conditions.26 One of the [2]rotaxanes either 4a or 4b (1 equiv.), 4’-(4-(chloromethyl)phenyl)-2,2',6',2’”-terpyridine (1.5 or 3 equiv.), and NaH (5 equiv.) were stirred at room temperature in DMF for 48 hours (Scheme 1). TLC and HR-ESMS of the reactions mixtures confirmed the formation of the 2,2',6',2'”-terpyridine functionalised [2]rotaxanes 5a (m/z = 2024.1366 [5a+H]+) and 5b (m/z = 1182.1142 [5b+2H]2+). These rotaxane ligands were isolated as colourless solids in 62% and 42% yield, respectively.

The 1H and DOSY NMR spectra of the “click” [2]rotaxanes provided further evidence for the formation of the interlocked structures. All proton signals due to the macrocyclic and thread components of the individual [2]rotaxanes 4a-b and 5a-b displayed the same diffusion coefficient indicating that they are part of the same molecular species (ESI†). Furthermore, the diffusion coefficients of the larger terpy conjugated 5a-b were smaller than those of the alcohol functionalised [2]rotaxanes 4a-b consistent with the larger molecular size of the [2]rotaxane terpy ligands. Furthermore, by using an external polystyrene calibration curve27 the molecular weights of the [2]rotaxanes could be estimated from the DOSY experiments (Table 1) and these values were in agreement to those found from ESMS experiments.

The 1H NMR spectra of 4a-b (CDCl3) and 5a-b (acetone-d6) were similar to that of previously reported “click” AMT [2]rotaxanes (Figure 1b, Figure 2a and ESI†).14, 16-17, 20 Large upfield shifts, with respect to its non-interlocked triazole thread (the labels correspond to those shown in Scheme 2).

The 1H NMR spectra (500 MHz, d6-acetone, 298K) of [Fe(H2O)6](BF4)2 and [Fe5a]2(BF4)2; (i) [Fe(H2O)6](BF4)2, acetonitrile, RT, 30 mins.

Self-assembly of discrete architectures with Fe(II) ions.

Mixing the mono-terpy (5a) or di-terpy (5b) ligands with [Fe(H2O)6](BF4)2 in dilute acetonitrile solution at room temperature leads to the formation of discrete self-assembled metalloc-supramolecular mechanically-interlocked architectures [Fe(5a)2](BF4)2 (Scheme 2) and [Fe(5b)2](BF4)2 (Scheme 3). The formation of the diamagnetic low-spin iron(II) complexes was immediately signalled upon mixing the terpy ligands and the [Fe(H2O)6](BF4)2 by the appearance of a deep purple colour (λmax = 570 nm, ESI†).
coordination of the metal ions within the terpy binding pocket(s). Large downfield shifts of the proton resonances associated with the terpy units (H_p and H_q, \( \Delta \delta(H_p) = 0.79 \) ppm), relative to the free terpy ligands (Fig. 3 and ESI†) are observed. Additionally, there is a characteristic upfield shift of 6,6'-proton resonances (H_t) of the the terpy units upon complex formation. Furthermore, only the proton signals due terpy unit(s) experience significant shift changes on complexation, the protons resonances associated with the macrocycle and linear thread components of the rotaxanes do not show significant shifts in the aryl region. These observations strongly suggest that only the terpy coordinating units of the rotaxanes are involved in metal ion complexation (i.e. the pyridyl and 1,2,3-triazolyl units are not participating in metal complexation).

HR-ESMS of the rotaxane complexes \([\text{Fe} (5\text{a})_2] (\text{BF}_4)_2\) and \([\text{Fe} (5\text{b})] (\text{BF}_4)_2\) provided evidence of the stoichiometry of the self-assembled metallosupramolecular architectures. The mass spectrum of \([\text{Fe} (5\text{a})_2] (\text{BF}_4)_2\) displayed a major peak at m/z 2051 corresponding to the \([\text{Fe} (5\text{a})_2]^{2+}\) ion, along with additional peaks due to fragmentation (ESI†). The mass spectrum \([\text{Fe} (5\text{b})] (\text{BF}_4)_2\) displayed only a single major signal at m/z 1209 corresponding to the \([\text{Fe} (5\text{b})]^{2+}\) ion. The isotope patterns of the observed peaks matched well with the simulated patterns, further supporting the formation of the proposed metallosupramolecular species (ESI†). The collected NMR and ESMS data indicate that the ligand 5a assembles into a bis([2]rotaxane)5i, 28 (Scheme 2) while 5b forms a [1+1] metallo-macrocyclic architecture28, 30 (top), and the iron(II) bis([2]rotaxane) \([\text{Fe} (5\text{a})_2] (\text{BF}_4)_2\) (bottom). The lettering corresponds to that shown in Scheme 2.

Despite numerous efforts all attempts to grow X-ray quality crystals30 of the complexes proved unsuccessful so molecular modelling (MMFF, SPARTAN '08, ESI†) was used to obtain...
an estimation of the size and shape of the architectures. Figure 3 shows low energy conformations for \([\text{Fe}(5a)_2](\text{BF}_4)_2\) and \([\text{Fe}(5b)](\text{BF}_4)_2\). The model of \([\text{Fe}(5a)_2](\text{BF}_4)_2\) indicates that a large, approximately 4 nm across, architecture is readily formed with no steric impediments. The model of the smaller (~ 2 nm across) \([\text{Fe}(5b)](\text{BF}_4)_2\) complex also indicated the system can easily form the \([1+1]\) metallo-macrocycle without any steric clashes or strain due to the conformational freedom that is inherent in the ligand 5b (Figure 4a). Because of this flexibility the system can readily form the entropically favoured \([1+1]\) metallo-macroyclic architecture.

Table 1. Molecular weights of \([2]\)rotaxane ligands and iron(II) complexes estimated from HR-ESMS, \(^1^H\) DOSY NMR and GPC data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Expected molecular weight (M_e)</th>
<th>HR-ESMS ions (m/z)</th>
<th>Calculated molecular weight (MOSY)</th>
<th>Calculated molecular weight (M_e) (GPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>1702</td>
<td>1703 [4a+H] (^+^)</td>
<td>1640 ± 160</td>
<td>n.d.</td>
</tr>
<tr>
<td>4b</td>
<td>1720</td>
<td>1721 [4a+H] (^+^)</td>
<td>1800 ± 180</td>
<td>n.d.</td>
</tr>
<tr>
<td>5a</td>
<td>2022</td>
<td>2023 [5a+H] (^+^)</td>
<td>2260 ± 220</td>
<td>n.d.</td>
</tr>
<tr>
<td>5b</td>
<td>2363</td>
<td>1182 [5b+2H] (^2^+)</td>
<td>2500 ± 250</td>
<td>n.d.</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Fe}(5a)_2</a>_2)</td>
<td>4276</td>
<td>2051 [Fe(5a)] (^2^+)</td>
<td>4400 ± 440</td>
<td>n.d.</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Fe}(5b)</a>_2)</td>
<td>2592</td>
<td>1209 [Fe(5b)] (^2^+)</td>
<td>2400 ± 250</td>
<td>n.d.</td>
</tr>
<tr>
<td>([\text{Fe}(5b)]_4(\text{PF}_6)_2)</td>
<td>29788 (n=11)</td>
<td>1209 [Fe(5b)] (^2^+) (fragment ion)</td>
<td>27600 ± 2700</td>
<td>31400</td>
</tr>
</tbody>
</table>

Self-assembly of a polymeric architecture with Fe(II) ions.

Whilst the ditopic terpy ligand 5b formed a \([1+1]\) metallo-macroyclic architecture under dilute assembly conditions, similar di-terpy ligands have been extensively exploited for the generation of metallosupramolecular polymers.

Using a protocol previously exploited for the synthesis of linear non-interlocked terpy containing metallosupramolecular polymers we attempted to generate a metallo-[2]rotaxane polymer (Scheme 3). A concentrated (32 mM) solution (1:1 CH\(_3\)OH:HCl) of ligand 5b and FeCl\(_2\) were stirred at room temperature for 10 minutes then a methanolic solution of NH\(_4\)PF\(_6\) was added to precipitate the metallosupramolecular polymer/oligomer [Fe(5b)]\(_n\)(PF\(_6\))\(_{2n}\) as a purple solid. UV-vis and \(^1^H\) NMR spectroscopic analysis indicated that iron(II) complex had formed. The purple material (\(\lambda_{\text{max}} = 570 \text{ nm}\)) contained the same MLCT band that was observed for the discrete metallosupramolecular architectures while the \(^1^H\) NMR spectrum of the complex displayed large downfield shifts, relative to the free ligand, for many of the proton resonances associated with the terpy units (ESI†). Additionally, the broad nature \(^1^H\) NMR spectrum of [Fe(5b)]\(_n\)(PF\(_6\))\(_{2n}\) suggested the formation of a oligo-/poly-meric rather than a discrete material.

Efforts to gain insight into the size of the polymer using mass spectrometry were unsuccessful. Under HR-ESMS conditions a signal peak was observed at m/z 1209 corresponding to the doubly charged [Fe(5b)]\(^{2+}\) ion suggesting that the metallo-polymer was fragmenting. Matrix-assisted laser desorption/ionization (MALDI)-MS produced similar results. Due to these difficulties gel permeation chromatography (GPC) and \(^1^H\) DOSY NMR were used to estimate the molecular weight of [Fe(5b)]\(_n\)(PF\(_6\))\(_{2n}\) (Table 1).

\(^1^H\) DOSY NMR spectrum of the [Fe(5b)]\(_n\)(PF\(_6\))\(_{2n}\) complex gave a diffusion coefficient of \(1.9 \times 10^{-10} \text{ m}^2\text{ s}^{-1}\) for the polymeric material indicating that this system formed a complex that was much larger than the discrete iron(II) complexes Fe(5a)\(_2\)(BF\(_4\))\(_2\) and [Fe(5b)](BF\(_4\))\(_2\). Using the external polystyrene calibration curve\(^2^7\) the molecular weight of the metallo-supramolecular [2]rotaxane polymer was estimated to be \(M_w = 29000 \pm 2900\) and this value agreed well that obtained from GPC analysis. The [Fe(5b)]\(_n\)(PF\(_6\))\(_{2n}\) complex, gave a retention time of 35 minutes in the GPC with the molecular weight and PDI of the metallo-polymer estimated to \(M_w = 31400\) and 1.26, respectively. Whilst the molecular weight of the metallo-polymer is reasonably high the degree of polymerisation is modest. The observed molecular weights indicate that the metallo-polymers [Fe(5b)]\(_n\)(PF\(_6\))\(_{2n}\) only incorporate eleven to thirteen 5b monomer units (i.e \(n = 11-13\)). There are probably two main reasons for this. The high molecular weight of the precursor 5b makes accurate addition of an equivalent molar amount of iron difficult on such a small scale, even assuming full complexation. According to Carothers,\(^2^2\) this would lead to an excess of one end-group and corresponding large drop in molecular weight. The large size and conformation flexibility of 5b also would promote the formation of cyclic oligomers\(^2^2\) which prevent the formation of...
high molecular weight polymers. For a reversibly coordinating system this could be estimated by using the Jacobsen-Stockmayer theory\(^{35}\) which takes into account chain length, concentration and flexibility. As the molecular weight does not change on dilution over several hours, this suggests that the iron coordination is irreversible over this time-scale and making the modelling of the polymerization difficult.

**Conclusions**

The mild functional-group tolerant copper(I) catalysed azide-alkyne cycloaddition active metal template (CuAAC-AMT) method has been exploited to generate mono- and bifunctional [2]rotaxanes by interlocking an exo-alcohol functionalised macrocycle and functionalised triptyl stoppers. These [2]rotaxanes were post-synthetically conjugated to either one or two terpy coordinating units to generate mechanically interlocked ligands. Reaction of the ligands with iron(II) ions resulted in the self-assembly of small [1+1] macrocycles and large size and conformation flexibly of the [2]rotaxanes studied. The functional group tolerance of the CuAAC-AMT should allow for the generation of a wide range of substituted [2]rotaxanes, including switchable systems. Furthermore, the ligating motif can be readily changed from terpy to almost any conceivable ligand. Access to this functional diversity should enable these types of [2]rotaxane ligands to be exploited to generate a range of interlocked systems which could be used to create novel MORFs, metallosupramolecular architectures, light harvesting systems,\(^{36}\) drug-delivery agents, and magnetic materials.\(^{36}\) Efforts in these directions are currently underway.

**Acknowledgements**

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**Notes and references**

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†Electronic Supplementary Information (ESI) available: the supplementary information contains the experimental procedures, \(^{1}H, ^{13}C\) and DOSY NMR, ESI-MS, UV-vis, molecular models and crystallographic data. CCDC reference numbers 1002573-1002575. See DOI: 10.1039/b000000x/


30. While we were unable to crystallise the large MIL-8, we did obtain an X-ray crystallography (ESI†). Vapour diffusion of diethyl ether into a methanol solution of the Ag(I) complex 1-Ag produced small X-ray quality crystals. Like the parent macrocycle 1 the 1-Ag complex forms a dimer, with the formulation [(1H2Ag(CH2OH)2O]3]. This solid state conformation is driven by crystal packing forces.


32. The solid state structure of the 1-Ag macrocycle complex was obtained by X-ray crystallography (ESI†). Vapour diffusion of diethyl ether into a methanol solution of the Ag(I) complex 1-Ag produced small X-ray quality crystals. Like the parent macrocycle 1 the 1-Ag complex forms a dimer, with the formulation [(1H2Ag(CH2OH)2O]3]. This solid state conformation is driven by crystal packing forces.


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37. The solid state structure of the 1-Ag macrocycle complex was obtained by X-ray crystallography (ESI†). Vapour diffusion of diethyl ether into a methanol solution of the Ag(I) complex 1-Ag produced small X-ray quality crystals. Like the parent macrocycle 1 the 1-Ag complex forms a dimer, with the formulation [(1H2Ag(CH2OH)2O]3]. This solid state conformation is driven by crystal packing forces.


39. While we were unable to crystallise the large MIL-8, we did obtain an X-ray crystallography (ESI†). Vapour diffusion of diethyl ether into a methanol solution of the Ag(I) complex 1-Ag produced small X-ray quality crystals. Like the parent macrocycle 1 the 1-Ag complex forms a dimer, with the formulation [(1H2Ag(CH2OH)2O]3]. This solid state conformation is driven by crystal packing forces.

40. While we were unable to crystallise the large MIL-8, we did obtain an X-ray crystallography (ESI†). Vapour diffusion of diethyl ether into a methanol solution of the Ag(I) complex 1-Ag produced small X-ray quality crystals. Like the parent macrocycle 1 the 1-Ag complex forms a dimer, with the formulation [(1H2Ag(CH2OH)2O]3]. This solid state conformation is driven by crystal packing forces.