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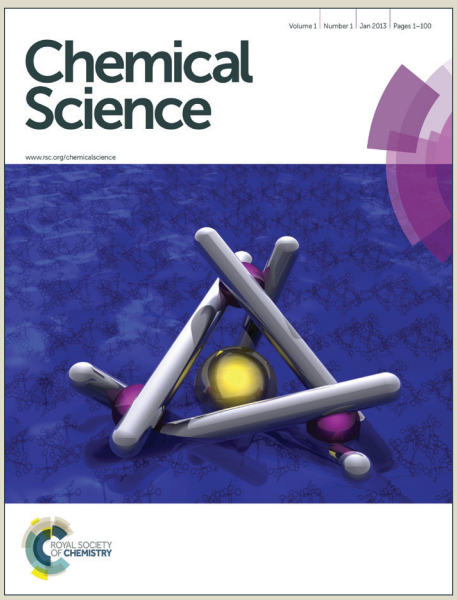

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Active-Template Synthesis of "Click" [2]Rotaxane Ligands: Self-Assembly of Mechanically Interlocked Metallo-Supramolecular Dimers, Macrocycles and Oligomers.

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Asif Noor,[a] Stephen C. Moratti,[a] and James D Crowley*[a]

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).[3g, 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 π-π 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,[14, 16-17] catenanes,[18] knots,[19] mechanically planar chiral [2]rotaxanes[17d] and molecular machines[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 bi-functionalised [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.

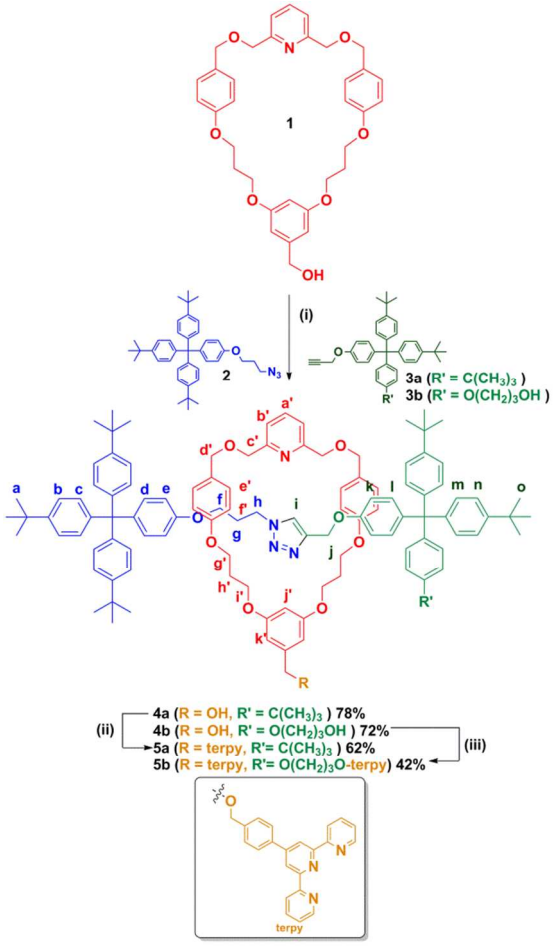
Results and discussion

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 metals ions[14, 16] that would be used for the self-assembly reactions. The 2,2′,6′,2″-terpyridine based ligands[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[22] and polymeric[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, [14, 16-17, 18-19] therefore we targeted the *exo*-alcohol functionalised macrocycle **1** containing that motif (Scheme 1). Macrocycle **1** was readily prepared in 35% yield, using similar condition to those exploited for the synthesis of the unfunctionalised parent macrocycle (Scheme S1, ESI†).[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---C16 9.130(3) Å, C11---C27 9.203(4) Å) 30-membered pyridyl macrocycle with an *exo*-alcohol functional group. Interestingly, a hydrogen bonding interaction (N1---O5' 2.808(2) Å) between the *exo*-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. ^{1}H NMR and HR-ESMS experiments on 1:1 mixtures of either $[Cu(CH_3CN)_4](PF_6)$ (1 eq.) or AgOTf (1 eq.) and the macrocycle **1** confirmed the formation of **1-M** (Cu^+ or Ag^+) macrocycle complexes in solution (ESI†).[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[14, 16, 25] (Scheme S2, ESI†). Molecular modelling (MMFF, SPARTAN '08, ESI†) indicated that these trityl stoppers would be large enough to prevent the macrocycle dethreading.



Scheme 1. Synthesis of functionalised [2]rotaxanes **4a-b** and **5a-b**: (i) $[Cu(CH_3CN)_4](PF_6)$ (1 eq.), azide stopper **2** (5 eq.), alkyne stopper (either **3a** or **b**, 5 eq.), CH_2Cl_2, 40 °C, 48 h; (ii) 4′-(4-(chloromethyl)phenyl)-2,2′,6′,2′′-terpyridine (1.5 eq.), NaH, DMF, RT, 48h; (ii) 4′-(4-(chloromethyl)phenyl)-2,2′,6′,2′′-terpyridine (3 eq.), NaH, DMF, RT, 48h.

"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.[14, 16] The macrocycle **1** (1 equiv.), $[Cu(CH_3CN)_4](PF_6)$ (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]$^+$) 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.

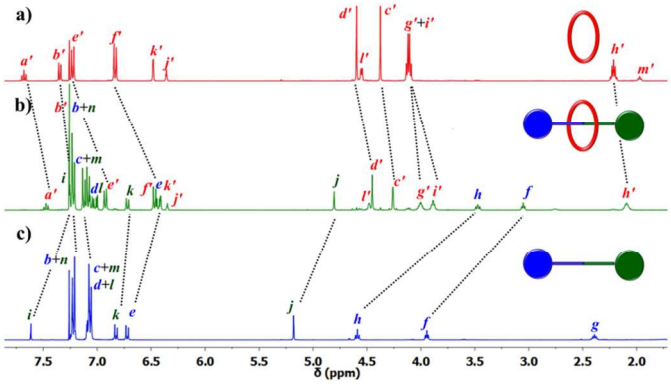


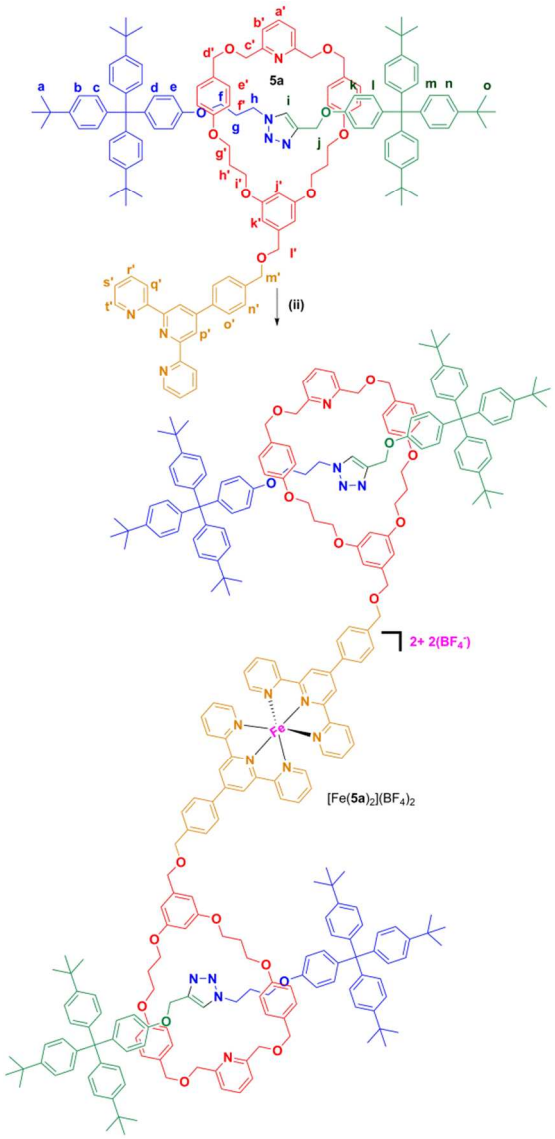
Fig. 1 Partial stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of a) macrocycle **1**, b) [2]rotaxane **4a**, c) the non-interlocked triazole thread (the labels correspond to those shown in Scheme 2.

The ^{1}H 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 curve[27] 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 ^{1}H NMR spectra of **4a-b** ($CDCl_3$) and **5a-b** (acetone-d_6) 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 components (Figure 1a and c, respectively) are observed for several non-stopper proton resonances ($H_{f,g,h \text{ and } j}$). This shielding is consistent with the thread component of the [2]rotaxanes being sandwiched face-on between the two aromatic groups of the macrocyclic unit and indicates that the macrocycle can access the full length of the thread. In addition to the proton resonances due the macrocyclic and thread components, [2]rotaxanes **5a-b** also displayed signals due to the terpy units (Fig. 2a and ESI†).

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

Mixing the mono-terpy (**5a**) or di-terpy (**5b**) ligands with $[Fe(H_2O)_6](BF_4)_2$ in dilute acetonitrile solution at room temperature leads to the formation of discrete self-assembled metallo-supramolecular mechanically-interlocked architectures $[Fe(\mathbf{5a})_2](BF_4)_2$ (Scheme 2) and $[Fe(\mathbf{5b})](BF_4)_2$ (Scheme 3). The formation of the diamagnetic low-spin iron(II) complexes was immediately signalled upon mixing the terpy ligands and the $[Fe(H_2O)_6](BF_4)_2$ by the appearance of a deep purple colour (λ_{max} = 570 nm, ESI†).



Scheme 2. Synthesis of the iron(II) bis([2]-rotaxane), $[Fe(\mathbf{5a})_2](BF_4)_2$; (i) $[Fe(H_2O)_6](BF_4)_2$, acetonitrile, RT, 30 mins.

The ^{1}H NMR spectra (500 MHz, d_6-acetone, 298K) of $[Fe(\mathbf{5a})_2](BF_4)_2$ and $[Fe(\mathbf{5b})_2](BF_4)_2$ are consistent with the

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).

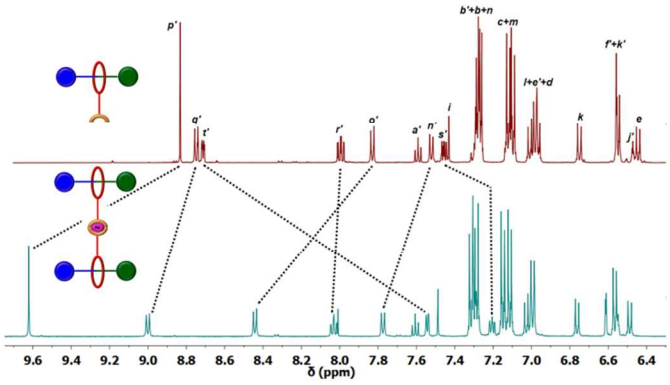
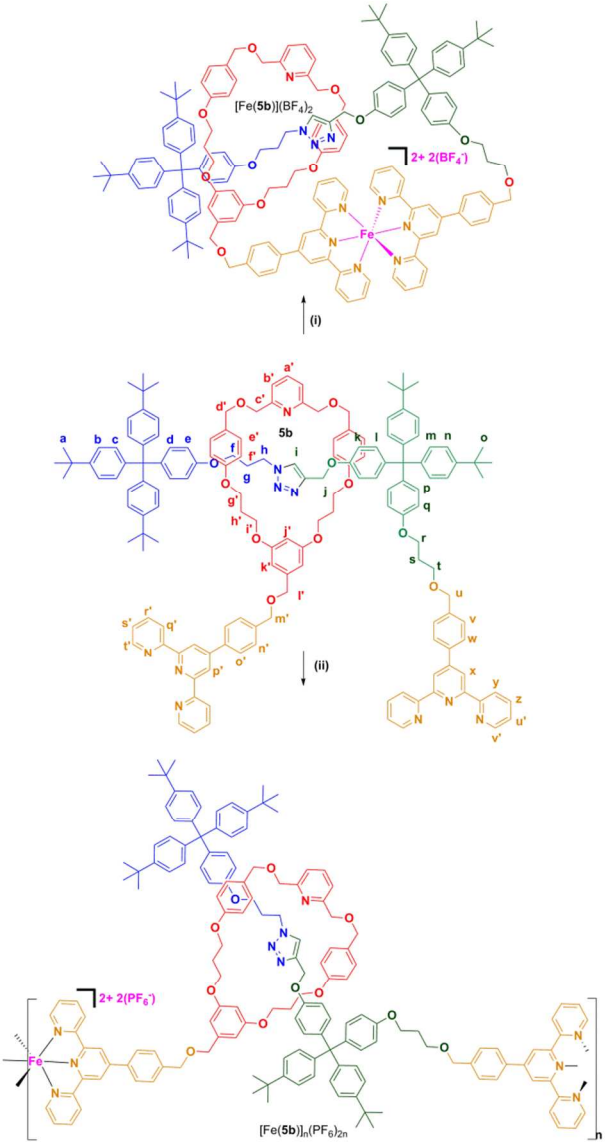


Fig. 2 Partial ^{1}H NMR spectra (500 MHz, acetone-d_6, 298 K) of the mono-terpy [2]rotaxane **5a** (top), and the iron(II) bis([2]rotaxane) [Fe(**5a**)$_2$](BF$_4$)$_2$ (bottom). The lettering corresponds to that shown in Scheme 2.

HR-ESMS of the rotaxane complexes [Fe(**5a**)$_2$](BF$_4$)$_2$ and [Fe(**5b**)](BF$_4$)$_2$ provided evidence of the stoichiometry of the self-assembled metallosupramolecular architectures. The mass spectrum of [Fe(**5a**)$_2$](BF$_4$)$_2$ displayed a major peak at *m/z* 2051 corresponding to the [Fe(**5a**)$_2$]$^{2+}$ ion, along with additional peaks due to fragmentation (ESI†). The mass spectrum [Fe(**5b**)](BF$_4$)$_2$ displayed only a single major signal at *m/z* 1209 corresponding to the [Fe(**5b**)]$^{2+}$ ion. The isotope patterns of the observed peaks matched well with the simulated patterns, further supporting the formation of the proposed metallo-supramolecular 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-macrocycle[22m, 22q, 29] structure (Scheme 3), similar assemblies have been observed in the literature.

Additional support for the formulations obtained from HR-ESMS data was obtained using ^{1}H DOSY NMR spectroscopy (500 MHz, d_6-acetone, 298K). The DOSY experiments confirm the presence of single species in solution for both Fe(**5a**)$_2$](BF$_4$)$_2$ and [Fe(**5b**)](BF$_4$)$_2$ with diffusion coefficients of 4.5×10^{-10} m^2 s^{-1} and 5.8×10^{-10} m^2 s^{-1} , respectively. The larger diffusion coefficient observed for [Fe(**5b**)](BF$_4$)$_2$ system is consistent with the formation of the smaller [1+1] metallo-macrocyclic architecture proposed from the ESMS data. The bis([2]-rotaxane) [Fe(**5a**)$_2$](BF$_4$)$_2$ has a smaller diffusion coefficient than [Fe(**5b**)](BF$_4$)$_2$ as this larger species moves more slowly through solution. Furthermore, by using an external polystyrene calibration curve[27] the molecular weights of the [2]rotaxanes and their iron(II) complexes can be estimated from the DOSY experiments (Table 1). The values obtained using this method show excellent agreement with the expected values, despite chemical differences between the polystyrene standards and the metallo-rotaxanes systems, providing additional strongly support for the proposed stoichiometries.



Scheme 3. Synthesis of the iron(II) metallo-macrocycle [Fe(**5b**)](BF$_4$)$_2$ and metallo-polymer, [Fe(**5b**)]$_n$(PF$_6$)$_{2n}$; (i) [Fe(H$_2$O)$_6$](BF$_4$)$_2$, acetonitrile, RT, 1 h; (ii) FeCl$_2$, NH$_4$PF$_6$, CHCl$_3$/CH$_3$OH (1:1, 32 mM) RT, 20 h.

Despite numerous efforts all attempts to grow X-ray quality crystals[30] 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 [Fe(**5a**)$_2$](BF$_4$)$_2$ and [Fe(**5b**)](BF$_4$)$_2$. The model of [Fe(**5a**)$_2$](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) [Fe(**5b**)](BF$_4$)$_2$ complex also indicated the system can easily form the [1+1] metallo-macrocycle[22m, 22q, 29] structure 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-macrocyclic architecture.

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

Compound	Expected molecular weight (M_w)	HR-ESMS ions (*m/z*)	Calculated molecular weight (M_w) (DOSY)	Calculated molecular weight (M_w) (GPC)
4a	1702	1703 [**4a**+H]$^+$	1640 ± 160	n.d.
4b	1720	1721 [**4a**+H]$^+$	1800 ± 180	n.d.
5a	2022	2023 [**5a**+H]$^+$	2260 ± 220	n.d.
5b	2363	1182 [**5b**+2H]$^{2+}$	2500 ± 250	n.d.
[Fe(**5a**)$_2$](BF$_4$)$_2$	4276	2051 [Fe(**5a**)$_2$]$^{2+}$	4400 ± 440	n.d.
[Fe(**5b**)](BF$_4$)$_2$	2592	1209 [Fe(**5b**)]$^{2+}$	2400 ± 250	n.d.
[Fe(**5b**)]$_n$(PF$_6$)$_n$	29788 (n =11)	1209 [Fe(**5b**)]$^{2+}$ (fragment ion)	27600 ± 2700	31400

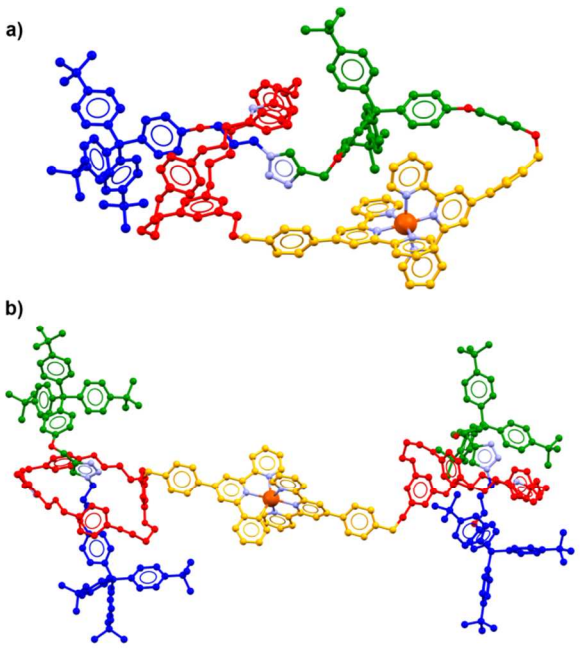


Fig. 3 Ball-and-stick molecular models of the cations [Fe(**5b**)] (a) and [Fe(**5a**)$_2$] (b) showing one of many low-energy conformations of the systems (MMFF, SPARTAN '08, ESI†). Hydrogen atom are omitted for clarity, colours correspond to those shown in Scheme 2 and 3.

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

Whilst the ditopic terpy ligand **5b** formed a [1+1] metallo-macrocyclic architecture under dilute assembly conditions, similar di-terpy ligands have been extensively exploited for the generation of metallosupramolecular polymers.[21a, 21d, 23a-f, 31]

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_3OH:$CHCl_3$) of ligand **5b** and $FeCl_2$ were stirred at room temperature for 10 minutes then a methanolic solution of NH_4PF_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 (λ_{max} = 570 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 × 10^{-10} m^2 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[27] the molecular weight of the metallo-supramolecular [2]rotaxane polymer was estimated to be M_w = 29000 ± 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,[32] 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[22] which prevent the formation of

high molecular weight polymers. For a reversibly coordinating system this could be estimated by using the Jacobsen-Stockmayer theory[33] 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 bi-functionalised [2]rotaxanes by interlocking an exo-alcohol functionalised macrocycle and functionalised trityl 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 generates either discrete or polymeric metallosupramolecular structures. 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 [1+1] [2]rotaxane metallo-macrocycle, in the presence of Fe(II) ions. Conversely, at high concentration, the bi-terpy [2]rotaxane self-assembles into a metallo-supramolecular polyrotaxane oligomer when exposed to Fe(II) ions. The [2]rotaxane "super" ligands and corresponding Fe(II) complexes have been characterised with ^{1}H and ^{13}C NMR and UV-vis spectroscopies, 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. The large size and conformation flexibly of the [2]rotaxanes studied resulted in the self-assembly of small [1+1] macrocycles and low molecular weight oligomeric metallo-supramolecular systems. Therefore, we are currently targeting the synthesis of smaller, more rigid macrocycles and rotaxanes[17b-d, 34] to afford greater control over the resulting metallosupramolecular architectures.

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,[5h, 35] drug-delivery agents, and magnetic materials.[36] Efforts in these directions are currently underway.

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Notes and references

[a] *Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. Fax: +64 3 479 7906; Tel: +64 3 479 7731; E-mail: jcrowley@chemistry.otago.ac.nz*

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

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