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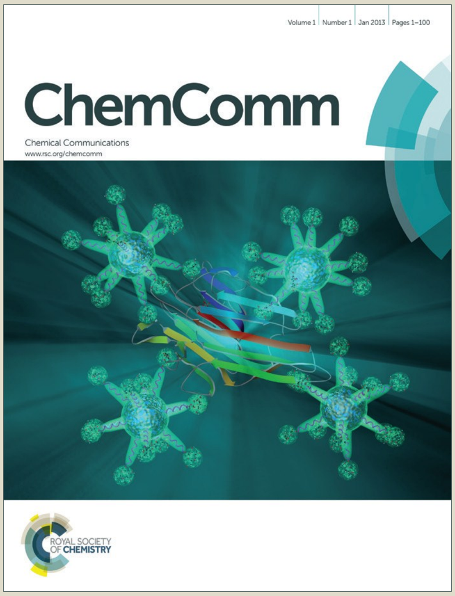

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ARTICLE TYPE

Facile Thermodynamic Conversion of a Linear Metallopolymer into a Self-assembled Hexameric Metallomacrocycle

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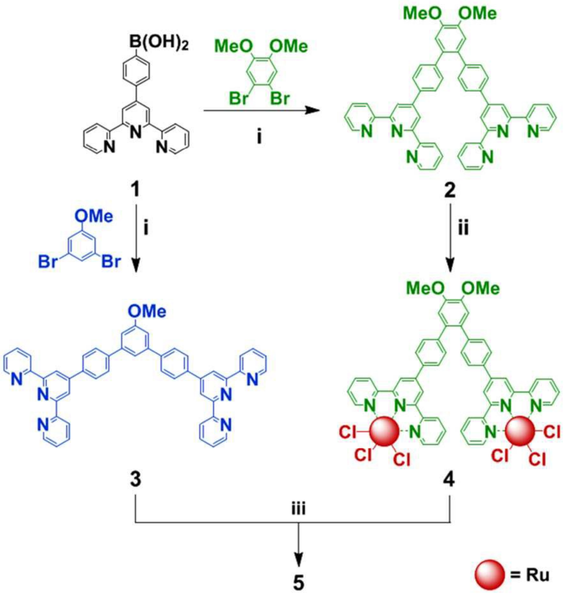
The initial metallopolymer, which was derived from two different organic building blocks, is a kinetic intermediate to the final stable *hexa*nuclear (bearing $4Ru^{2+}$ and $2Fe^{2+}$) metallomacrocycle transforming through a thermodynamic self-assembly route. The heteroleptic metallomacrocyclic architecture was characterized by NMR, UV, IR, CV, 2D-ROESY, DOSY, and ESI-MS.

Recently, numerous advances in the utilization of terpyridine-M^{2+}-terpyridine (<typ-M^{2+}-tpy>) connectivity have been reported that have ramifications in the fields of electrochemistry, photophysics,[1] catalysis and red-ox chemistry,[2] to mention but a few. Due to the ability of <typ-M^{2+}-tpy> to readily incorporate diverse metals, this mode of connectivity is widely used as a building block in metallo-macromolecular syntheses. In general, these novel pyridine or *poly*pyridine contained metallo-organic architectures[3] possess a high degree of symmetry and are synthesized through a simple, high yield one-step self-assembly utilizing predominately Fe^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ru^{2+}, as well as to a lesser extent, ca. 50 other metals.[3] Directed, step-wise assembly has also been used to achieve highly ordered, Ru^{2+}-based, dimetallic macromolecular architectures.[4] Terpyridine containing heterophane ligands were designed for the construction of 3D dimensional supramolecules by a one-pot self-assembly.[5] Newkome et al.[6] have recently employed the staggered tristerpyrdine ligands to achieve 3D metallo-organic wheel construction via a self-assembly protocol. Utilizing a *bis*Ru^{2+} trimer possessing two, uncomplexed, free terpyridine end groups that was derived from the connection of three, 120°-oriented, 1,3-bisterpyridines, hexanuclear and nonanuclear macrocyclic rings were obtained in 49 and 14%, respectively, upon treatment with Fe^{2+}. Advisable reaction condition are capable of controlling the product of self-assembly, besides concentration,[7] temperature can also be the key to some specific self-assembly systems.[8]

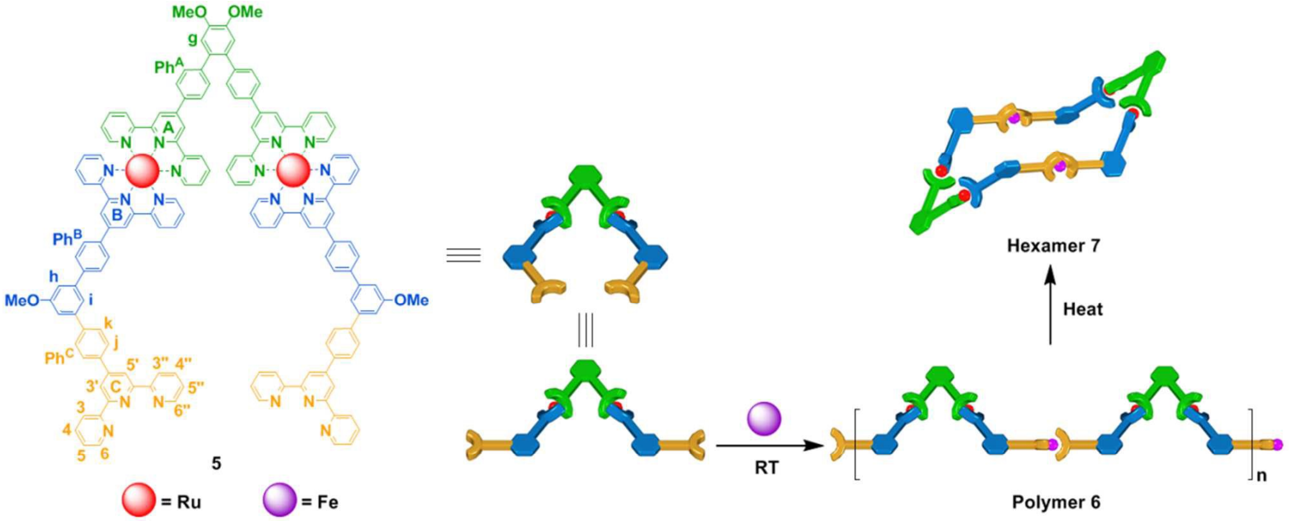
Herein, we report the generation of chair-like metallomacrocycle **7** comprised of 4<typ-Ru^{2+}-tpy> and 2<tpy-Fe^{2+}-tpy> linkages (Figure **1**) via the assembly-disassembly of metallo-ligand **5** (constructed from terpyridine building blocks **2** and **3** and $2Ru^{2+}$ metal ions, Scheme **1**). The initial metallo-ligand **5** spontaneously generated linear polymer **6** when treated with Fe^{2+} at 25 °C, however, increasing the reaction temperature to 80°C readily fragmented polymer **6** via cleavage of the more labile <tpy-Fe^{2+}-tpy> bond to generate in near quantitative yield the more stable 2D cyclic structure **7**.

Initially, 60°-based bisterpyridine ligand **2** was synthesized according to a known literature procedure.[9] Ligand **3** possessing 120° directionality was prepared through a Suzuki cross-coupling reaction[10] with 4'-boronatophenyl-[2,2':6',2"]terpyridine (**1**) and 1,3-dibromo-5-methoxybenzene, to generate (75%) **3** after column chromatography ($Al_2O_{3,}$) eluting with CH_2Cl_2. The ^1H NMR of **3** (Figure **1**) displayed a singlet at 8.83 ppm assigned to the $H^{3',5'}$ and the characteristic methoxy signals at 4.01 ppm; all other expected resonances were readily assigned. A mixture of **2** and $RuCl_3{\cdot}3H_2O$ (1:2) was refluxed in MeOH for 18h to generate (65%) the paramagnetic *bis*Ru^{3+} adduct **4** that was used without further purification.



Scheme 1. The construction of *bis*Ru^{2+} trimer **5** via a step-wise manner [reagents and conditions: i) $Pd(PPh_3)_4$, NaOH, THF, reflux, 24h; ii) $RuCl_3{\cdot}H_2O$, MeOH, reflux, 18h; iii) MeOH/$CHCl_3$ reflux, 18h].

Metallo-ligand **5** with two free-terpyridine ligands was generated (55%) by reacting two equivalents of bisterpyridine **3** with the paramagnetic *bis*Ru^{3+} adduct **4**. The key *bis*metallic complex **5** possesses two different vertices - one possessing a 60° orientation and two possessing 120° orientations exhibited in the ^1H NMR spectrum where three representative singlets are attributed to the tpyH$^{3',5'}$s (1:1:1 ratio, Figure **1**). Two of these exhibit expected down-field shifts at 9.38 and 9.34 ppm corresponding to the complexed terpyridines of H$^{3',5'}$-tpy-A and H$^{3',5'}$-tpy-B, respectively. A singlet at 8.82 ppm was assigned to the uncomplexed tpyH$^{3',5'}$s. All ^{1}H NMR peak assignments were confirmed based on 2D ROESY NMR spectra.



Scheme 2. Schematic illustration of synthesizing hexamer **7** from a free terpyridine contained metallo-ligand **5**.

Treatment of **5** in a stirred MeOH/CHCl$_3$ (1:1 v/v) solution with FeCl$_2$·4H$_2$O (dissolved in MeOH) at 25 °C for 8 h gave polymer **6**, as a violet solution, as evidenced by its ^{1}H NMR spectrum that showed a typical polymer-based, broadened spectrum (Figure. **2**-Aa). Upon heating **6** at 80°C for 8 hours, the ^{1}H NMR spectrum exhibited initial sharpening (Figure. **2**-Ab) and after continued heating for a total of 16 hours, **6** was quantitatively transformed to the macrocyclic hexamer **7** (Figure **2**-Ac) as shown by the now well-resolved spectrum.

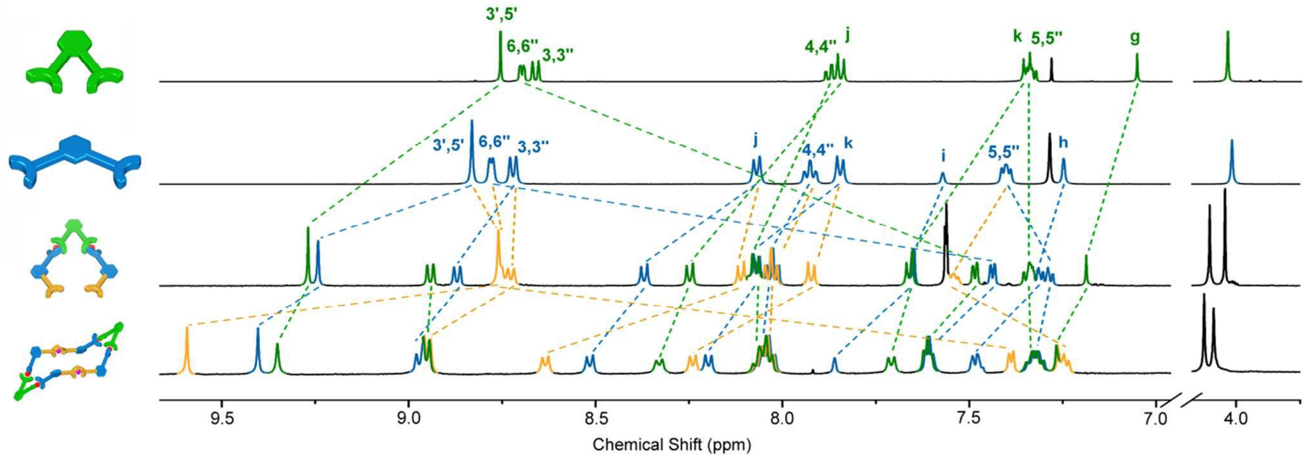


Fig. 1. ^{1}H NMR (500 MHz) of **2**, **3** in CDCl$_3$ and **5**, **6** in CD$_3$OD.

The ^{1}H NMR spectrum of macrocycle **7** showed three characteristic tpy$H^{3',5'}$ singlets with one occurring at 9.60 ppm attributed to the new <tpy-Fe^{2+}-tpy> complexes and two observed peaks at 9.41 and 9.36 ppm attributed to the macrocyclic <tpy-Ru^{2+}-tpy> complexes; a 1:1:1 integration ratio was observed. The spectra displayed no evidence for free terpyridine. As well, in contrast to the *di*nuclear complex **5**, macrocycle **7** displayed the two expected resonance signals, upfield ($\Delta\delta$=+0.83) and downfield ($\Delta\delta$= −1.33), corresponding to the tpy$H^{6,6''}$s and tpy$H^{3',5'}$s, respectively. The observation of a peak at 9.36 ppm attributed to the 60°-based tpy$H^{3',5'}$s corresponds well with a previously reported, 60°-based hexamer.[11] Notably, a 2D DOSY NMR experiment (CD$_3$CN, 298 K) revealed macrocycle **7** to be a single component (Figure 2B) yielding a diffusion coefficient D = 2.78×10^{-10} m^2/s that also corresponds well to similar metallomacrocycles.[12]

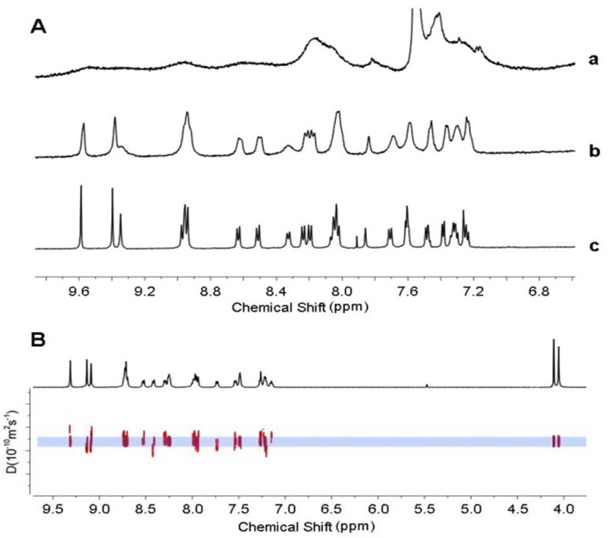


Fig. 2. A) ^{1}H NMR of the thermodynamic macrocyclic hexamer **7** from metallo-polymer **6**: a) mixing **5** with $FeCl_2$ in CD_3OD, without heating; b) after 8h heating at 80°C; c) after 16h heating at 80 °C; B) the 2D DOSY NMR spectra of macrocycle **7**.

Electrospray ionization mass spectroscopy (ESI-MS, Figure **3**) exhibited peaks at mass/charge (m/z) ratios 520.0 $(7\text{-}10PF_6^{-})^{10+}$ and 459.8 $(7\text{-}11PF_6^{-})^{11+}$ further supporting structure **7**. Additional peaks, confirmed as fragments of **7**, provide further evidence for the assigned structure.

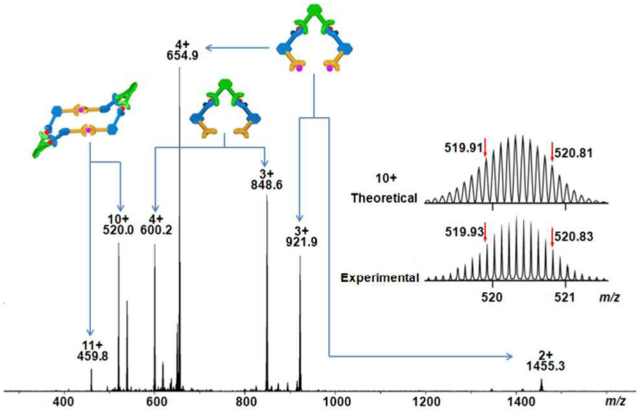


Fig. 3. ESI mass spectra for hexamer **7**.

Ultraviolet-visible (UV-vis) spectroscopy (DMF) verified the coordination between *bis*Ru^{2+} trimer **5** and Fe^{2+} (Figure **4**-A). The expected absorbance position at 498 nm was attributed to the metal-to-ligand-charge transfer (MLCT) band of the <tpy-Ru^{2+}-tpy> complex. With the introduction of Fe^{2+}, a new absorption was observed at 574 nm attributed to the characteristic MLCT band of the <tpy-Fe^{2+}-tpy> complex. Notably, this absorption lies in the visible region and is responsible for the color change (from red to violet).

Further evidence for macrocycle **7** is provided by cyclic voltammetry (CV) experiments using *bis*Ru^{2+} trimer **5** and macrocycle **7** (Figure 4B-a). Both complexes exhibited a wave at *ca*. 1.35 V corresponding to the quasi-reversible oxidation of a Ru^{III}/Ru^{II} couple. Observation of absorption at *ca.* 1.2 V (Figure 4B-b) assigned to the quasi-reversible oxidation process associated with the Fe^{III}/Fe^{II} couple was expected for the heterometallic **7**.

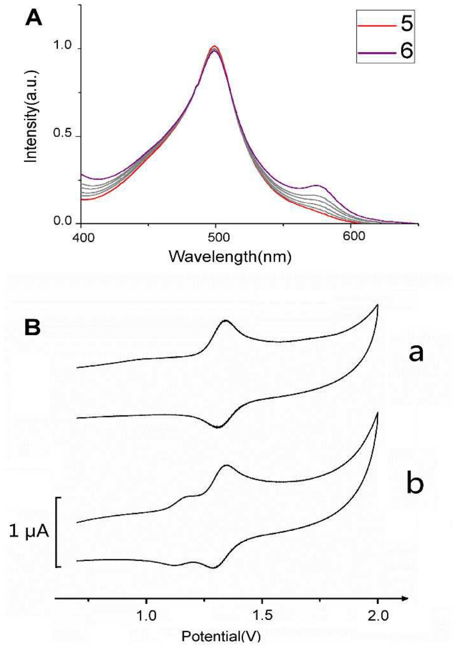


Fig. 4. A) Evolution of the absorption spectra of adding $FeCl_2$ solution to **5**; B) Cyclic voltammograms (CV) of solutions of: a) *bis*Ru^{2+} trimer **5** and b) macrocycle **7** (performed in 0.1M $n\text{Bu}_4\text{NBF}_4$ in MeCN at 298 K with a scan rate of 100 mVs^{-1}).

Transmission electron microscopy (TEM) also confirms the transformation of polymer **6** to macrocycle **7**, as evidenced by images of rod-like patterns for the metallo-polymer (**6**, Figure 5A) and a field of dots that when viewed at higher magnification appear as rings (**7**, Figure 5B). Molecular modeling of the polymeric and cyclic structures supports the sizes of the two differing architectures.

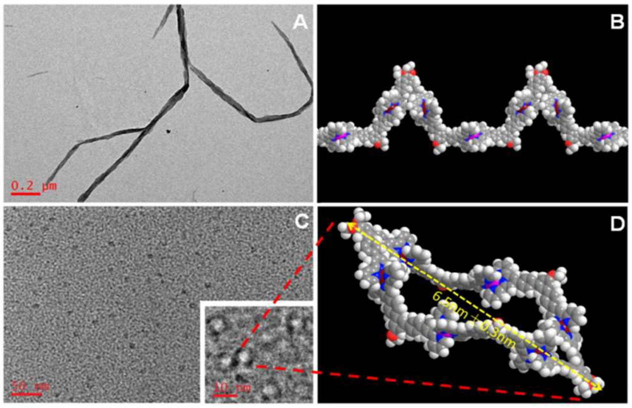


Fig. 5. A) TEM images of polymer **6** on a carbon-coated Cu grid. B) Computer-generated image of the self-assembled polymer 6. C) TEM images of hexamer **7** on a carbon-coated Cu grid. D) Representative energy-minimized structure of **7** [prepared by casting a dilute solution of **6** or **7** onto a carbon-coated Cu grid].

Conclusions

In conclusion, the self-assembly to the Fe^{2+}- and *bis*Ru^{2+}-based trimer **5** at 25 °C generated an intermediate polymer **6**, which was quantitatively transformed by warming (80 °C) to the 2D metallomacrocyclic hexamer **7**. Transformation between the polymer and metallomacrocyclic hexamer **7** proceeds by a thermodynamic self-assembly process. This conversion offers a new protocol for the construction of complex 2D supramolecular architectures demonstrating the potential to employ different <tpy-metal^{2+}-tpy> modes of connectivity, as masking groups, to give access to more thermodynamically stable architectures. The transformation is also meaningful to anticipate self-assembly architectures *via* appropriate temperatures.

Notes and references

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† Electronic Supplementary Information (ESI) available: Full experimental details give the^{1}H NMR, ^{13}C NMR, COSY, REOSY, and DOSY spectra of the new compounds, and IR and ESI-MS spectra of related compounds. See DOI: 10.1039/b000000x/

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