CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200902988

Unexpected Isolation of a Pentameric Metallomacrocycle from the Fe^{II}-Mediated Complexation of 120° Juxtaposed 2,2′:6′,2″-Terpyridine Ligands

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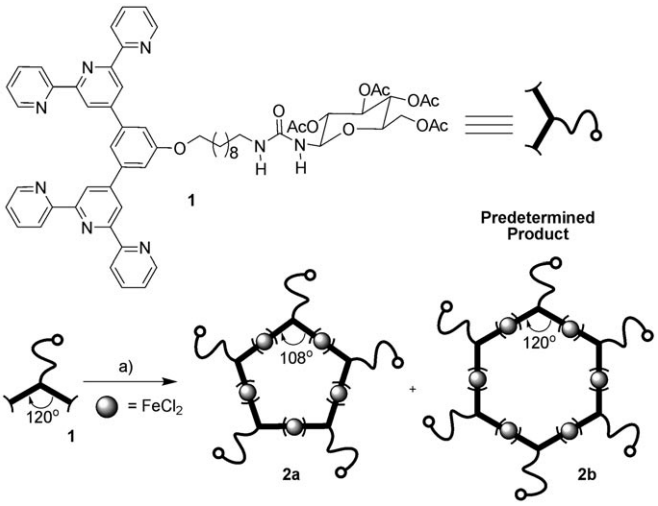
Self-assembly of specially designed building blocks has been widely employed in the construction of rigid supramolecular structures.[1] Towards this goal, many successful strategies have been developed for the synthesis of metallomacrocycles, such as for trigonal,[2] rectangular,[3] hexagonal,[4] heptagonal,[5] and octagonal[6] structures. In contrast, only a limited number of pentagonal[7] shapes have been reported in the literature. Accordingly, building blocks require a suitable angle to generate five-sided motifs. For example, a carbazole unit that introduced a 105° angle between two terpyridine ligands was readily self-assembled to give metallopentacycles.[7b]

Tetragonal and trigonal metallomacrocycles formed by 60° juxtaposed bis(terpyridine) ligands possessing bendable alkyne spacers have been documented.[8] However, the formation of unexpected products by using rigid linkers is rare.[2c] Herein, we report the isolation and characterization of a unique pentameric macrocycle, along with its anticipated hexameric homologue, generated from an Fe^{II}-mediated complexation of functionalized bis(terpyridine) ligands with a 120° angle relative to the coordination sites.

Reaction of **1**[9] (Scheme 1) with 1.05 equivalents of $FeCl_2{\cdot}4H_2O$ in MeOH at 25 °C for 24 h gave the pentamer $[Fe_5(\mathbf{1})_5(NO_3)_{10}]$ (**2a**; 4.3%) and the hexamer $[Fe_6(\mathbf{1})_6(NO_3)_{12}]$ (**2b**; 11.9%), which were isolated by gradient column chromatography eluting with H_2O/MeCN/sat. $KNO_{3(aq)}$ (from 1:20:1 to 1:15:1; v/v/v). The ^{1}H NMR spectrum of pentamer **2a** revealed sharp singlets at 8.22 and 8.75 ppm for 2,6-Ar*H*s and 4-Ar*H* respectively, supporting the presence of the symmetric macrocycle, in contrast to linear oligomers that exhibit more complicated patterns.[4a,c,10] Other supportive data (^{1}H NMR spectroscopy) included an expected upfield shift for 6,6″-tpy*H*s ($\delta =$ 7.41 ppm, $\Delta\delta = -1.34$ ppm) and a downfield shift for 3′,5′-tpy*H*s ($\delta = 9.65$ ppm, $\Delta\delta = +0.86$ ppm) relative to the corresponding peaks in the uncomplexed ligand **1** (Figure 1). The ^{1}H NMR spectrum of hexamer **2b** exhibited a similar pattern, but the peaks of terpyridine part showed a slight downfield shift relative to the corresponding peaks in **2a** presumably due to the additional metal centers in **2b** resulting in added electron deficiency. In comparison with **2b**, notably the 4-Ar*H* peak of **2a** has an upfield shift ($\Delta\delta = -0.2$ ppm) due to the enhanced crowded inner space. This proved to be a key discernable feature in recognizing, isolating and characterizing the otherwise remarkably similar five- and six-membered ring structures. The 2D COSY NMR spectra of the bis(terpyridine) ligand **1** and the self-assembled macrocycle **2a** also ensured the proper assignments. Notably, at



Scheme 1. Unexpected and predetermined products **2a** and **2b** obtained by self-assembly of **1**. a) $FeCl_2{\cdot}4H_2O$, MeOH, 25 °C, 24 h (each Fe^{II} macrocycle isolated as the polyNO_3^- salt; see Experimental Section).

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902988.

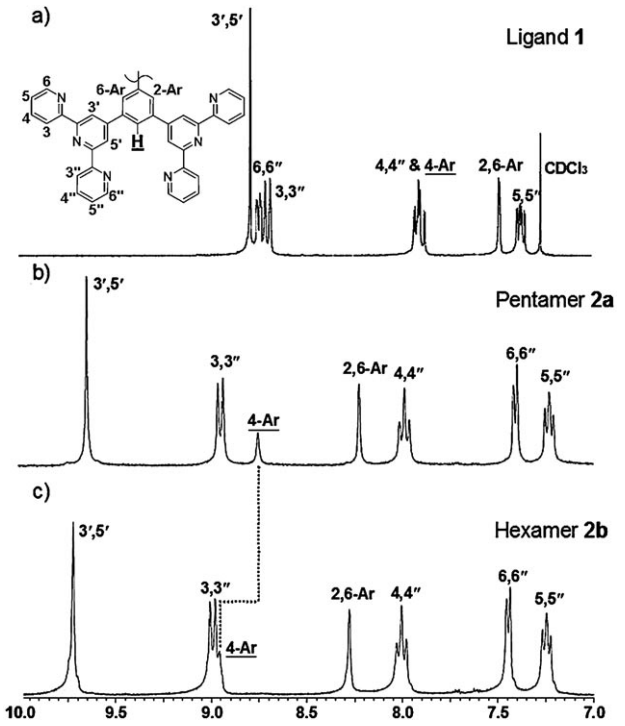


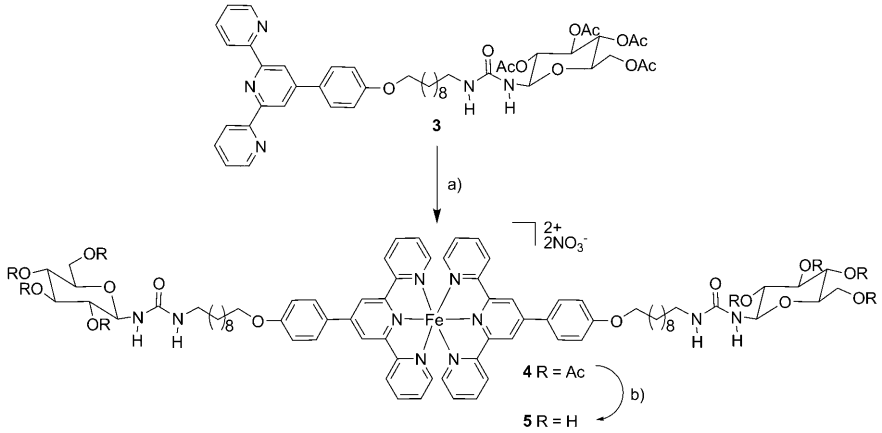
Figure 1. Aromatic region of the ^{1}H NMR spectra for a) ligand **1**, and b) the five- and c) six-sided metallomacrocycles **2a** and **2b**. The key, distinguishing central 4-Ar*H* and its chemical shifts assignments in the ligand and corresponding macrocycles are underlined.

25 °C no equilibrium between **2a** and **2b** was observed as would be expected in refluxing solvent.[10b] The cyclic structures **2a** and **2b** were further confirmed by ESI-MS (Figures S1 and S2 in the Supporting Information) peaks of multiple-charged entities of **2a** at 1518.9 $[M-4NO_3]^{4+}$ (calcd m/z: 1518.5), 1202.9 $[M-5NO_3]^{5+}$ (calcd m/z: 1202.4), 992.2 $[M-6NO_3]^{6+}$ (calcd m/z: 991.7), and 841.7 $[M-7NO_3]^{7+}$ (calcd m/z: 841.1), which resulted from the loss[11] of nitrate counterions. Similarly, the ESI mass spectrum of **2b** confirmed the hexameric structure with signals at m/z 1455.6, 1202.8, 1022.2, 886.8, and 781.3 for the species in charge states +5 to +9, respectively.

For comparison, the monocoordinating ligand **3** was synthesized according to the previous procedure.[9] Monoterpyridine **3** (Scheme 2) was treated with 0.6 equivalents of $FeCl_2\cdot 4H_2O$ in MeOH at 25 °C for 18 h to give mono-iron(II) complex **4** (72 % yield), as a deep purple solid. As in the case of pentamer **2a**, complex **4** exhibited an upfield shift for 6,6″-tpy*H*s ($\delta = 7.32$ ppm, $\Delta\delta = -1.42$ ppm) and a downfield shift for 3′,5′-tpy*H*s ($\delta = 9.40$ ppm, $\Delta\delta = +0.68$ ppm), when compared to the corresponding signals in the uncomplexed ligand **3**. The acetylated complex **4** was deprotected by using triethylamine in MeOH to give (≈64 %) the sugar-functionalized iron dimer **5**. The crude ^{1}H NMR spectrum of the deprotected material showed 26 % of the iron complex was decomplexed under these basic conditions.[12] Notably, strong basic conditions lead to both deacetylation and demetalation of **4** to generate the deprotected starting material (**3**).

UV/Vis spectra (see Supporting Information and Table S1) of pentamer **2a**, hexamer **2b**, and model complex **4** in a dilute MeOH exhibited the expected absorption transition; in the case of **2a**, the peaks at 286 ($\varepsilon = 2.68\times 10^5\,\text{M}^{-1}\text{cm}^{-1}$) and 323 nm ($\varepsilon = 2.15\times 10^5\,\text{M}^{-1}\text{cm}^{-1}$) are attributed to the π–π* transition and the peak at 571 nm ($\varepsilon = 1.14\times 10^5\,\text{M}^{-1}\text{cm}^{-1}$) is attributed to the metal-to-ligand charge-transfer (MLCT) transition;[13] the peaks at 287 ($\varepsilon = 3.14\times 10^5$), 323 ($\varepsilon = 2.57\times 10^5\,\text{M}^{-1}\text{cm}^{-1}$), and 572 nm ($\varepsilon = 1.43\times 10^5\,\text{M}^{-1}\text{cm}^{-1}$) were observed for hexamer **2b**. Similarly, complex **4** exhibited two π–π* transitions and an MLCT at $\lambda_{max} = 285$ ($\varepsilon = 4.5\times 10^4\,\text{M}^{-1}\text{cm}^{-1}$), 321 ($\varepsilon = 5.1\times 10^4\,\text{M}^{-1}\text{cm}^{-1}$), and 572 nm ($\varepsilon = 2.4\times 10^4\,\text{M}^{-1}\text{cm}^{-1}$), respectively. The UV extinction coefficients (ε) of **2a** showed 6.0-, 4.2-, and 4.8-fold increases for λ_{max} at 286, 323, and 571 nm respectively, relative to the analogously measured coefficients for the model complex **4**. In the case of **2b**, the coefficients revealed 7.0-, 5.0-, and 6.0-fold increases for λ_{max} at 287, 323, and 572 nm, respectively.

The electrochemical potentials of the family of Fe^{II} complexes **2a**, **2b**, and **4** were examined using cyclic voltammetry (CV). These complexes exhibited two quasi-reversible one-electron reduction processes assigned to the terpyridine ligands and one quasi-reversible oxidation due to the iron centers[13] (Table 1). For complexes **2a** and **2b**, the presence of a single quasi-reversible oxidation process (Fe^{II}/Fe^{III}) (see Table S2 in the Supporting Information) suggests that all iron centers in the macrocycle are oxidized at the same potential as expected in identical environments. The slight potential difference between compounds **4** and **2a** or **2b** is pre-



Scheme 2. Model complexes **4** and **5**. a) $FeCl_2\cdot 4H_2O$, MeOH, 25 °C, 18 h; b) Et_3N, MeOH, 35 °C, 24 h.

Table 1. Redox potentials ($E_{1/2}$) of complexes **2a**, **2b**, and **4**.[a]

Complex	E_{red} (I) [V]	E_{red} (II) [V]	E_{ox} (I) [V]
2a	−1.59	−1.74	0.65
2b	−1.60	−1.75	0.65
4	−1.67	−1.77	0.57

[a] Conditions: Redox potentials (V vs Fc/Fc^+) were measured in dry DMF at 25 °C containing 0.1 M $TBAPF_6$ as supporting electrolyte; scan rate = 100 m Vs^{-1}.

sumably due to the different electron-donating abilities of mono- and bis(terpyridine) ligands.

The self-assembled nanofibers of **2a** and **2b** were generated by slowly diffusing hexane into macrocycle solutions (3 mg mL^{-1}) in a mixed solvent ($CHCl_3$/MeOH/MeCN, 8:3:1 in volume). TEM images were obtained by casting a dilute suspension (diluted with hexane) of the fibers onto a 200-mesh carbon-coated Cu grid. Figure 2 shows branched and

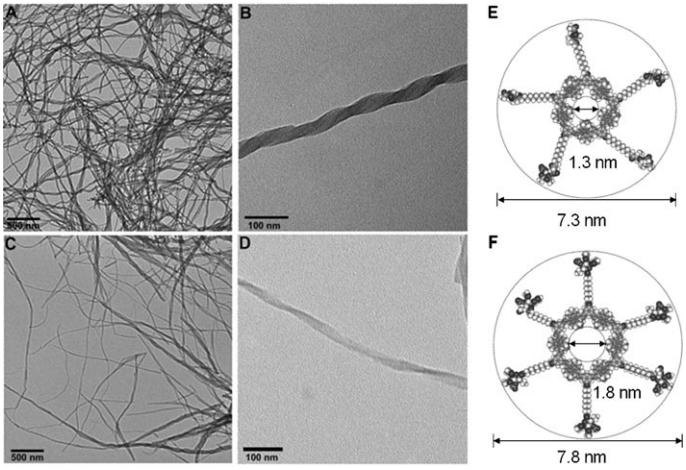


Figure 2. TEM images of self-assembled pentamer **2a** (A: scale bar 500 nm, B: scale bar 100 nm) and hexamer **2b** (C: scale bar 500 nm, D: scale bar 100 nm); and space-filling models of **2a** (E) and **2b** (F).

intertwined networks of fibrous assemblies with the lengths of several micrometers and diameters ranging from 10–80 nm (most fibers possessed diameters of 20–30 nm). Molecular modeling of the pentamer and hexamer revealed inner cavity diameters of about 1.3 (**2a**) and 1.8 nm (**2b**) and elongated outer diameters of approximately 7.3 (**2a**) and 7.8 nm (**2b**). Preliminary calculations show the total energy of **2b** possesses ≈6 kcal mol^{-1} per bis(terpyridine) less than the pentamer **2a** presumably due to the less ring strain in the hexagonal structure.

Notably, fibers prepared from both the five- and six-sided motifs show twisting architectures with diameters greater than the measured molecular diameters. Inherent packing parameters should include electrostatic, hydrogen-bonding (from the urea moieties), lipophilic–hydrophilic, and HOMO–LUMO interactions; investigations of these effects are ongoing.

In conclusion, we have successfully isolated and characterized an unexpected and unique pentameric metallomacrocycle, as well as its predesigned hexameric cousin from the Fe^{II}-mediated complexation of functionalized 3,5-bis(terpyridinyl)arene ligands. Structural characterization of the pentameric and hexameric macrocycles was achieved by ^1H NMR, ^{13}C NMR, and UV/Vis spectroscopy, cyclic voltammetry; and mass spectrometry. The self-assembled nanofibers of both macrocycles were generated by slowly diffusing the nonpolar solvent hexane into a homogeneous solution of macrocycles. The minor product, pentamer, which we believe to result from the initially formed kinetic product, suggests that there are likely exceptions to the coordination-driven self-assembly of bis(terpyridine) ligands.

Experimental Section

$[Fe_5(1)_5(NO_3)_{10}]$ (2a): A solution of $FeCl_2{\cdot}4H_2O$ (15.4 mg, 77 μmol) in MeOH (200 mL) was slowly added to a stirred solution of **1** (80 mg, 74 μmol) in MeOH (200 mL). After stirring at 25 °C for 24 h, the solvent was evaporated and the deep purple residue was subjected to column chromatography (SiO_2) by eluting with H_2O/MeCN/sat. $KNO_{3(aq)}$ (from 1:20:1 to 1:15:1; v/v/v) to afford **2a**, as a purple solid. Yield: 4 mg, 4.3% (the diminished yields were due to multiple column chromatographs to separate the two pure compounds); m.p. > 400 °C; ^1H NMR (300 MHz, CD_3OD): δ = 9.65 (s, 20H; Py$H^{3',5'}$), 8.95 (d, J = 7.8 Hz, 20H; Py$H^{3,3''}$), 8.75 (s, 5H; ArH^4), 8.22 (s, 10H; Ar$H^{2,6}$), 7.99 (dd, J = 7.5 Hz, 20H; Py$H^{4,4''}$), 7.41 (d, J = 5.4 Hz, 20H; Py$H^{6,6''}$), 7.23 (dd, J = 6.5 Hz, 20H; Py$H^{5,5''}$), 5.29 (t, J = 9.6 Hz, 5H; GluH^3), 5.13 (d, J = 9.6 Hz, 5H; GluH^1), 5.00 (t, J = 9.3 Hz, 5H; GluH^4), 4.92 (t, J = 9.6 Hz, 5H; GluH^2), 4.57 (t, J = 6.0 Hz, 10H; OCH_2), 4.24 (dd, J = 12.0, 4.8 Hz, 5H; GluH^6), 4.06 (dd, J = 12.6, 2.7 Hz, 5H; GluH^6), 3.85 (m, 5H; GluH^5), 3.14 (t, J = 6.6 Hz, 10H; CH_2NH), 2.10 (m, 10H; CH_2), 2.01 (s, 15H; Ac), 2.00 (s, 15H; Ac), 1.98 (s, 15H; Ac), 1.96 (s, 15H; Ac), 1.76 (m, 10H; CH_2), 1.62–1.20 ppm (br, 60H; CH_2); ^{13}C NMR (125 MHz, CD_3OD): δ = 172.4, 171.7, 171.6, 171.4, 163.0, 162.2, 159.8, 154.3, 154.2, 152.5, 141.7, 140.3, 129.0, 125.7, 123.9, 123.0, 116.7, 81.2, 75.0, 74.4, 72.1, 70.3, 70.0, 63.4, 41.1, 31.2, 30.9, 30.8, 30.7, 30.6, 28.0, 27.5, 20.8, 20.7 ppm; ESI-MS: m/z: 1518.9 $[M-4NO_3]^{4+}$ (calcd m/z: 1518.5), 1202.9 $[M-5NO_3]^{5+}$ (calcd m/z: 1202.4), 992.2 $[M-6NO_3]^{6+}$ (calcd m/z: 991.7), 841.7 $[M-7NO_3]^{7+}$ (calcd m/z: 841.1).

$[Fe_6(1)_6(NO_3)_{12}]$ (2b): Compound **2b** was obtained from the same reaction of **2a**. Yield: 11 mg, 11.9%; m.p. > 400 °C; ^1H NMR (300 MHz, CD_3OD): δ = 9.72 (s, 24H; Py$H^{3',5'}$), 8.99 (d, J = 8.1 Hz, 24H; Py$H^{3,3''}$), 8.95 (s, 6H; ArH^4), 8.27 (s, 12H; Ar$H^{2,6}$), 8.01 (dd, J = 7.5 Hz, 24H; Py$H^{4,4''}$), 7.44 (d, J = 5.4 Hz, 24H; Py$H^{6,6''}$), 7.25 (dd, J = 6.6 Hz, 24H; Py$H^{5,5''}$), 5.29 (t, J = 9.6 Hz, 6H; GluH^3), 5.13 (d, J = 9.6 Hz, 6H; GluH^1), 5.00 (t, J = 9.3 Hz, 6H; GluH^4), 4.92 (t, J = 9.6 Hz, 6H; GluH^2), 4.59 (br, 12H; OCH_2), 4.24 (dd, J = 12.0, 4.8 Hz, 6H; GluH^6), 4.06 (dd, J = 12.6, 2.7 Hz, 6H; GluH^6), 3.85 (m, 6H; GluH^5), 3.13 (t, J = 6.9 Hz, 12H; CH_2NH), 2.09 (m, 12H; CH_2), 2.01 (s, 18H; Ac), 2.00 (s, 18H; Ac), 1.98 (s, 18H; Ac), 1.96 (s, 18H; Ac), 1.76 (m, 12H; CH_2), 1.62–1.20 ppm (br, 72H; CH_2); ^{13}C NMR (125 MHz, CD_3OD): δ = 172.4, 171.7, 171.6, 171.4, 163.0, 162.2, 159.9, 154.3, 154.2, 152.1, 141.4, 140.3, 129.0, 126.2, 125.7, 123.6, 117.1, 81.2, 75.0, 74.4, 72.1, 70.3, 70.0, 63.4, 41.1, 31.2, 30.9, 30.8, 30.7, 30.6, 28.0, 27.5, 20.8, 20.7 ppm; ESI-MS: m/z: 1455.6 $[M-5NO_3]^{5+}$ (calcd m/z: 1455.3), 1202.8 $[M-6NO_3]^{6+}$ (calcd m/z: 1202.4), 1022.2 $[M-7NO_3]^{7+}$ (calcd m/z: 1021.8), 886.8 $[M-8NO_3]^{8+}$ (calcd m/z: 886.3), 781.3 $[M-9NO_3]^{9+}$ (calcd m/z: 780.9).

Acknowledgements

The authors gratefully thank the National Science Foundation (DMR-0812337, DMR-0705015) and the Ohio Board of Regents for financial support.

Keywords: carbohydrates · iron · macrocycles · self-assembly · tridentate ligands

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Received: October 28, 2009
Published online: January 11, 2010

