COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Coordination polymers with macrocyclic cages and pockets within their backbones†

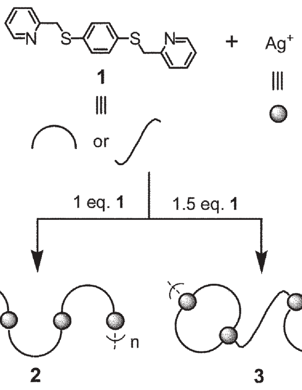
Moonhyun Oh, Charlotte L. Stern and Chad A. Mirkin*
Department of Chemistry and the Center for Nanofabrication and Molecular Self-Assembly, Northwestern University, Evanston, IL, 60208-3113, USA. E-mail: chadnano@northwestern.edu

Received (in Columbia, MO, USA) 27th May 2004, Accepted 12th August 2004
First published as an Advance Article on the web 8th October 2004

The reaction between the flexible ligand 1 (1,4-bis(pyridine-2-yl-methanethio)benzene) and Ag^+ produces two novel coordination polymers with macrocyclic cages or pockets contained within their backbones, depending upon the ratio of starting materials.

Reactions developed for assembling modular building blocks into supramolecular nanostructures is one of the most active areas of chemical research, not only because of the interesting structural diversity[1] associated with this class of complexes, but also because of the potential applications of such structures in optics,[2] catalysis,[3,4] sensing,[4,5] and host–guest chemistry.[4–8] Most structures investigated thus far have been molecular systems or networks of molecular systems contained within a crystalline lattice. In addition, several examples of polymeric versions of macrocycles[9] and coordination polymers with Ag^+ and pyridyl-type ligands have been reported.[10] Herein, we report a novel reaction that allows one to generate polymers with three-dimensional supramolecular cages contained within the backbone through the use of flexible ligand **1** and Ag^+. Two types of polymers can be generated, depending upon the ratio of starting materials used, one where ligand **1** adopts a folded conformation (**2**) and another where it adopts both linear and folded conformations within the structure (**3**) (Scheme 1).

Colorless single crystals of one-dimensional polymer **2**, $\{[Ag(L)]CF_3SO_3\}_n$ (L = **1**), were obtained by the reaction of **1** and $AgCF_3SO_3$ in a 1 : 1 ratio in acetone at room temperature.† Coordination polymer **2** exhibits a repeat unit where **1** adopts a folded conformation with the pyridine moieties pointed away from the central arene linker and towards one another (Fig. 1a).‡ Ligand **1** acts as a bis-bidentate ligand to link two Ag ions. This repeat unit generates one-dimensional zig-zag networks,[11] in which the silver metal ions are coordinated in distorted square planar geometries to two nitrogen and two sulfur atoms (Fig. 1b). The Ag–N distance is 2.21 Å, indicative of a bonding interaction. In contrast, there are comparatively weak bonding interactions between the silver and sulfur atoms as evidenced by an average bond distance of 2.93 Å. An interesting feature of the structure is the presence of pockets (7 × 6 × 5 Å), a result of the folded geometry of ligand **1** within the polymer structure (Fig. 1c, encapsulated triflate ion is shown in dark blue).



Scheme 1

In contrast, if the amount of ligand **1** is increased to 1.5 equivalents, the reaction with $AgCF_3SO_3$ yields a novel polymeric structure $\{[Ag(L)_{1.5}]CF_3SO_3\}_n$ (**3**, L = **1**) containing macrocyclic cages along the backbone (Scheme 1). The ligand in polymer **3** adopts two different conformations (Fig. 2). In the first conformational type, ligand **1** coordinates to Ag^+ through nitrogen and sulfur atoms, adopting a folded geometry similar to that seen in polymer **2** (Fig. 2a). The second conformational type involves coordination to Ag^+ only through nitrogen atoms, resulting in a more linear geometry (Fig. 2b).‡ The distance between the two nitrogen atoms in the type 1 conformation is 6.94 Å and much shorter than 12.06 Å observed for the type 2 conformation.

Each Ag^+ ion in **3** is coordinated to three nitrogen atoms, two from the ligand in the type 1 conformation and one from the ligand in the type 2 conformation. In addition, both sulfur atoms from the ligand in the type 1 conformation coordinate to Ag^+ ions. This results in the formation of macrocyclic cages along the polymer backbone (Fig. 3). This unusual structure is a result of the folded

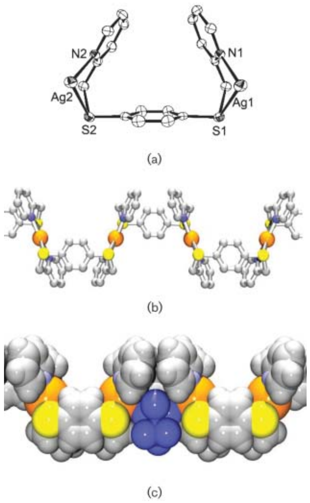


Fig. 1 Structure of **2** showing (a) a folded conformation of **1**, (b) ball and stick, and (c) space filling representation of one-dimensional polymer. Note that triflate anion is encapsulated, as shown. (Ag, orange; N, light blue; S, yellow; C, gray; CF_3SO_3, dark blue.)

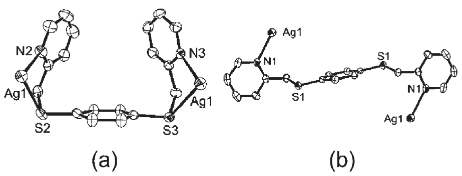


Fig. 2 (a) Type 1 folded conformation and (b) type 2 linear conformation in polymer **3**.

---

† Electronic supplementary information (ESI) available: synthesis of ligand **1** and coordination polymers **2** and **3**. See http://www.rsc.org/suppdata/cc/b4/b408084j/.

DOI: 10.1039/b408084j

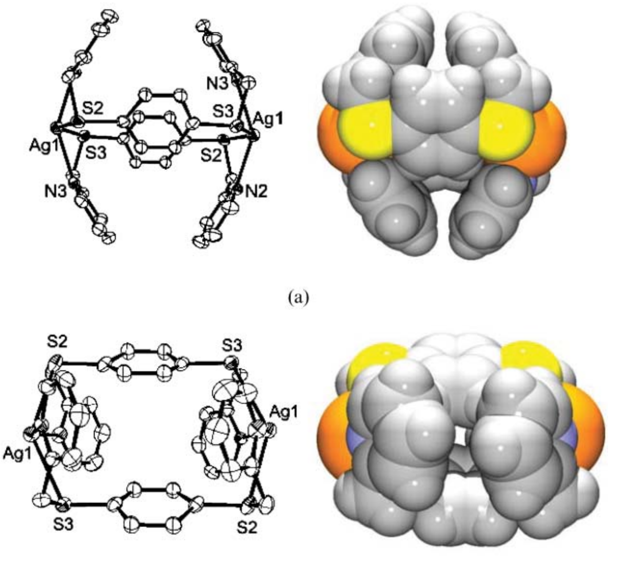


Fig. 3 ORTEP and space filling representations of the macrocyclic cage in **3** (a) with top view and (b) with side view. (Ag, orange; N, light blue; S, yellow; C, gray.)

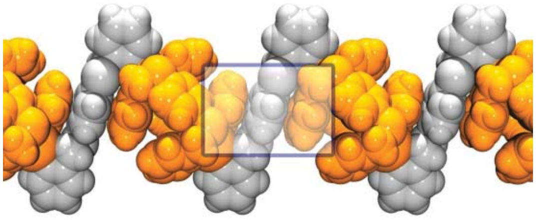


Fig. 4 Space filling representation of **3**. Note that the type 2 ligand (gray) connects two macrocyclic cages (orange). The disordered central arene ring in the type 1 ligand is not described. The boxed area shows the close contact between the pyridine groups of the type 1 ligand and the central arene of the type 2 ligands, consistent with strong π–π stacking interactions.

conformation of the ligand, where the pyridine groups act as the walls of each cage. The dimensions of the macrocyclic cage are approximately 9 × 8 × 5 Å. The ligand in the type 2 conformation within polymer **3** connects adjacent macrocyclic cages generating the repeat structure (Fig. 4). One silver center and three nitrogen atoms coordinated to silver metal are almost all in one plane with a torsion angle of 168.5°. The Ag–N bond distance for the complex formed with the ligand in the type 2 conformation (2.37 Å) is slightly shorter than that the Ag–N distances for the complex formed from the ligand in the type 1 conformation (average 2.43 Å). The average Ag–S distance of 2.79 Å indicates a weak bonding interaction. The π–π stacking interactions between the central arene rings for the type 2 ligands and the pyridine groups in the type 1 ligands are significant as evidenced by the very short ring–ring distance of 3.3 Å and likely contribute to the assembly process and stabilization of the supramolecular polymeric structure (Fig. 4).

In conclusion, this work describes the formation of novel Ag(I) coordination polymers based on the flexible ligand **1** which acts as a spacer with two different conformations. The resulting polymers contain unique macrocyclic pockets or cages in their backbones. These polymers may exhibit unusual molecular sieving and separation properties as a result of their unusual structures much like the non-covalent crystalline lattices formed by molecular squares.[12] Efforts to explore such properties are underway.

C. A. M. acknowledges the National Science Foundation and Air Force Office of Scientific Research for generous financial support.

Notes and references

‡ Crystal data for **2**: formula $C_{19}H_{16}AgF_3N_2O_3S_3$, $M = 581.39$, monoclinic, space group $P2_1/c$, $a = 15.1464(12)$, $b = 8.7729(7)$, $c = 16.6884(13)$ Å, $\beta = 105.0870(10)°$ $V = 2141.1(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.804$ g cm^{-3}, $\mu = 1.285$ mm^{-1}, $F(000) = 1160$, θ range 1.39–28.75°, 283 variables refined with 5219 independent reflections to final R indices $[I > 2\sigma(I)]$ of $R1 = 0.0363$ and $wR2 = 0.0889$, and GOF = 1.043. Crystal data for **3**: formula $C_{28}H_{24}AgF_3N_3O_3S_4$, $M = 743.61$, triclinic, space group $P\bar{1}$, $a = 7.9335(6)$, $b = 12.9848(10)$, $c = 14.9460(11)$ Å, $\alpha = 86.7800(10)°$, $\beta = 80.9040(10)°$, $\gamma = 75.8630(10)°$ $V = 1474.01(19)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.675$ g cm^{-3}, $\mu = 1.022$ mm^{-1}, $F(000) = 750$, θ range 1.38–28.84°, 374 variables refined with 6932 independent reflections to final R indices $[I > 2\sigma(I)]$ of $R1 = 0.0328$ and $wR2 = 0.0804$, and GOF = 1.031. X-ray data collection with Mo Kα radiation was carried out at 153 K using a Bruker Smart-1000 diffractometer equipped with a CCD area detector. Structures were determined by direct methods and refined on F^2. CCDC 240741 and 240742. See http://www.rsc.org/suppdata/cc/b4/b408084j/ for crystallographic data in .cif or other electronic format.

1 (*a*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*b*) L. R. MacGillivray and J. L. Atwood, *Angew. Chem., Int. Ed.*, 1999, **38**, 1018; (*c*) R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735; (*d*) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; (*e*) M. Oh, G. B. Carpenter and D. A. Sweigart, *Acc. Chem. Res.*, 2004, **37**, 1.

2 O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511.

3 N. C. Gianneschi, P. A. Bertin, S. T. Nguyen, C. A. Mirkin, L. N. Zakharov and A. L. Rheingold, *J. Am. Chem. Soc.*, 2003, **125**, 10508.

4 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.

5 J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim and K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621.

6 B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021.

7 F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *Angew. Chem., Int. Ed.*, 2001, **40**, 1529.

8 K. Kasai, M. Aoyagi and M. Fujita, *J. Am. Chem. Soc.*, 2000, **122**, 2140.

9 V. J. Catalano, M. A. Malwitz, S. J. Horner and J. Vasquez, *Inorg. Chem.*, 2003, **42**, 2141.

10 (*a*) A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schröder, *Coord. Chem. Rev.*, 2001, **222**, 155; (*b*) T. J. Burchell, D. J. Eisler and R. J. Puddephatt, *Chem. Commun.*, 2004, 944; (*c*) D. M. Shin, I. S. Lee, Y.-A. Lee and Y. K. Chung, *Inorg. Chem.*, 2003, **42**, 2977; (*d*) H.-F. Zhu, L.-Y. Kong, T.-a. Okamura, J. Fan, W.-Y. Sun and N. Ueyama, *Eur. J. Inorg. Chem.*, 2004, 1465; (*e*) R. Horikoshi, T. Mochida, N. Maki, S. Yamada and H. Moriyama, *J. Chem. Soc., Dalton Trans.*, 2002, 28.

11 C. M. Hartshorn and P. J. Steel, *J. Chem. Soc., Dalton Trans.*, 1998, 3927.

12 C. R. Graves, M. L. Merlau, G. A. Morris, S.-S. Sun, S. T. Nguyen and J. T. Hupp, *Inorg. Chem.*, 2004, **43**, 2013.