

Folding of Coordination Polymers into Double-Stranded Helical Organization

Ho-Joong Kim, Eunji Lee, Myongsoo Lee*

Center for Supramolecular Nano-Assembly and Department of Chemistry, Yonsei University, Seoul 120-749, Korea
mlee@yonsei.ac.kr

Introduction

One of the most significant recent highlights in the field of supramolecular polymer chemistry is the development of folded helical structures which are important modules in the engineering of functional nanoobjects such as nanotubes, nanowires and chiral materials.¹ In most cases, however, the supramolecular interactions lead to the formation of polymeric strands that fold into single helical conformations. Because only a few supramolecular polymers have been reported to form infinite double-stranded helices, the development of supramolecular double helices structurally comparable to those of DNA is a challenging topic of current research.² We present here the formation of DNA-like double-stranded helical polymers with regular grooves along the helical axis, driven by unique interstranded metal-ligand interactions (Figure 1).

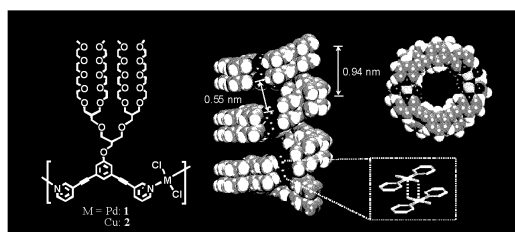


Figure 1. Molecular structure and schematic representation of the double-stranded helical structure of **2**.

Experimental

The synthesis of the bispyridine ligand started with a stepwise fashion according to the procedures described previously.³ The resulting ligand was complexed with $\text{PdCl}_2(\text{PhCN})_2$ or CuCl_2 to afford the Pd(II) or Cu(II) coordination polymers, respectively. Small-angle X-ray scattering (SAXS) measurements of **1** showed several sharp reflections corresponding to a 1-D lamellar structure with in-plane 2D order with a layer thickness of 3.6 nm. The lamellar structure with this dimension indicates that the coordination polymer backbone of **1** adopts an unfolded zigzag conformation that organizes into a layered structure. Bridging bispyridine ligands connected in a *trans* position of the square planar coordination geometry of Pd(II) ion seems to generate unfolded polymer chains. In contrast to that of polymer **1** based on a Pd(II) ion, Cu(II) coordination polymer **2** showed to self-assemble into a 2-D oblique columnar structure with lattice constants of $a = 4.9$ nm, $b = 4.2$ nm and $\gamma = 122^\circ$, as identified by SAXS patterns (Figure 2a). The evidence for the formation of the 2-D oblique columnar structure was also provided by TEM (Figure 2c).

Another interesting point to be noted is the presence of two sharp reflections at the wide angles, corresponding to d spacings of 0.88 and 0.55 nm, respectively (Figure 2a, inset). As shown in Figure 2b, these reflections were diffracted at an angle of 70° with respect to a meridian, indicative of the presence of a periodicity together with an additional order along the direction of the column axis. To further corroborate the structural features of the coordination polymer, EXAFS experiments were performed with **2** at ambient temperature. As shown in Figure 2d, the profile revealed several peaks at 2.2, 3.5, and 4.4 Å, that can be indexed as Cu(1)-Cl(1), Cl(1)-Cu(2), and Cu(1)-Cu(2) scatterings. In particular, the Cu-Cu distance at 4.4 Å was also identified by the WAXS pattern. All of these scattering peaks are consistent with the values for the pseudo-square planar chloro-bridged dimers formed through weak axial coordination to one copper center by a chloride ligand located at the adjacent copper atom.⁴ It is worth noting that, considering the Cl(1)-Cu(2) distance (0.35 nm) together with the WAXS peak at 0.88 nm associated with a pitch, an

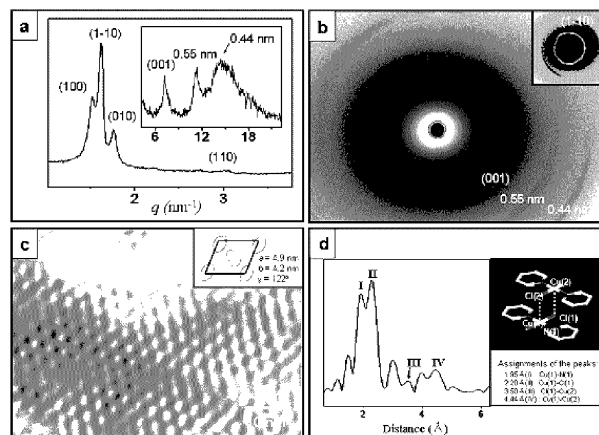


Figure 2. (a) X-ray diffraction patterns, and (b) 2-D X-ray diffraction patterns of **2**. The inset image shows the 2-D small angle X-ray diffraction pattern. (c) TEM image of ultramicrotomed film of **2** revealing 2-D oblique columnar array of aromatic core, and (d) EXAFS profile of **2** and the peak assignments.

additional X-ray diffraction peak at 0.55 nm can be described as the width of a groove along the direction of column axis. By using the lattice constants and a density, the number of repeating units per pitch was calculated to be 4.2 units. Considering the interstrand copper-chloride dimeric interactions, this calculated number indicates that the columns are based on double-stranded helical chains.

Results and discussion

On the basis of the results described thus far, it can be concluded that the Cu(II) coordination polymer chains adopt a double-stranded helical conformation with a regular pitch of 0.94 nm (deduced from $0.88 \text{ nm} / \sin 70^\circ$) together with a groove of 0.55 nm in width along the helical axis (Figure 1). Subsequently, the double-stranded helices self-organize into a 2-D oblique columnar structure. These results strongly support that the complexation of the bent-shaped bispyridine ligand with a Cu(II) metal ion with a pseudo-square planar coordination geometry could lead to folded double-stranded helical polymers through complementary dimeric interactions. Considering that **1** with absence of the metal-chloride bridging interactions self-assembles into a layered structure consisting of an unfolded zigzag conformation, the dimeric association through metal-chloride bridging interactions in the Cu(II) coordination polymer seems to be essential for the formation of a double-stranded helical structure.

Conclusions

The notable feature of the Cu(II) coordination polymer investigated here is its ability to self-assemble into a double-stranded helical structure with regular grooves along the helical axis, through the combination of metal-chloride dimeric interactions and repulsive interactions, as an organizing force. It is also remarkable that the double-stranded helices self-organize into a 2-D columnar structure in both the bulk state and aqueous solution. These results represent a unique example that weak metal-ligand bridging interactions can provide a useful strategy to construct stable double-stranded helical nanotubes.

References

- [1] Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013-4038.
- [2] (a) Krämer, R.; Lehn, J.-M.; Marquis-Rigault, A. *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394-5398. (b) Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Angew. Chem. Int. Ed.* **2005**, *44*, 3867-3870.
- [3] (a) Kim, H.-J.; Zin, W.-C.; Lee, M. *J. Am. Chem. Soc.* **2004**, *126*, 7009-7014. (b) Kim, H.-J.; Lee, J.-H.; Lee, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 5810-5814.
- [4] (a) Marsh, W. E.; Hatfield, W. E.; Hodgson, D. *J. Inorg. Chem.* **1982**, *21*, 2679-2684. (b) Estes, E. D.; Estes, W. E.; Hatfield, W. E.; Hodgson, D. *J. Inorg. Chem.* **1975**, *14*, 106-109.