DOI: 10.1002/chem.200800056

Folding of Coordination Polymers into Double-Stranded Helical Organization

Ho-Joong Kim,[a] Eunji Lee,[a] Min Gyu Kim,[b] Min-Cheol Kim,[a] Myongsoo Lee,*[a] and Eunji Sim*[a]

Abstract: Self-assembling coordination polymers based on Pd^{II} and Cu^{II} metal ions were prepared from complexation of a bent-shaped bispyridine ligand and a corresponding transition metal. These coordination polymers were observed to self-assemble into supramolecular structures that differ significantly depending on the coordination geometry of the metal center. The polymer based on Pd^{II} self-assembles into a layer structure formed by bridging bispyridine ligands connected in a *trans*-position of the square-planar coordination geometry of metal center. In contrast, the polymer based on Cu^{II} adopts a double-helical conformation with regular grooves, driven by interstranded, copper–chloride dimeric interaction. The double-stranded helical organization is further confirmed by structure optimization from density functional theory with aromatic framework, showing that the optimized double-helical structure is energetically favorable and consistent with the experimental results. These results demonstrate that weak metal–ligand bridging interactions can provide a useful strategy to construct stable double-stranded helical nanotubes.

Keywords: coordination polymers · helical structures · self-assembly · supramolecular chemistry

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 nano-sized objects, 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.[2] Because only a few supramolecular polymers have been reported to form infinite double-stranded helices,[3] the development of supramolecular double helices structurally comparable to those of DNA is a challenging topic of current research. Double-stranded helical structures can be constructed by the complexation of two oligomeric ligands twisted around metal ions,[4] attractive π–π interactions between two single strands,[5] and complementary interactions between two different strands.[6]

Previous publications from our laboratory have shown that extended polymeric chains formed from complexation between bent-shaped ligands and silver cations with a linear coordination geometry can give rise to a helical secondary structure depending on the size of the counter anion.[7] In addition, these helical polymers showed the dynamic conformational change from the nonfluorescent compressed state to the fluorescent stretched state, triggered by temperature.[8] One can envision that the coordination geometry of the metal center has influence on the secondary structure of coordination polymers.[9] With this in mind, we have prepared coordination polymers based on Pd^{II} and Cu^{II} ions, which are known to adopt a square-planar coordination geometry.[9a,10]

In this article, we present the formation of a double-stranded helical structure from coordination polymers, driven by interstranded metal–ligand dimeric interactions. The coordination polymers are based on Pd^{II} (**1**) and Cu^{II} (**2**) metal ions, prepared from complexation of a conformationally flexible, *meta*-linked bispyridine ligand containing a flexible dendritic side group and a corresponding transition metal. The polymer based on Pd^{II} self-assembles into an un-

[a] H.-J. Kim, E. Lee, M.-C. Kim, Prof. Dr. M. Lee, Prof. Dr. E. Sim
Center for Supramolecular Nano-Assembly and
Department of Chemistry
Yonsei University, Seoul 120-749 (Korea)
Fax: (+82) 2-393-6096
E-mail: mslee@yonsei.ac.kr
esim@yonsei.ac.kr

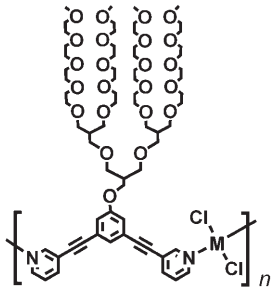
[b] Dr. M. G. Kim
Pohang Accelerator Laboratary
Pohang University of Science and Technology
Pohang 790-784 (Korea)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

folded zigzag conformation that organizes into a layered structure. In contrast, the polymer based on Cu^{II} adopts a double-helical conformation that organizes into a two-dimensional lattice, even though the coordination geometry of Cu complex is an essentially similar square-planar structure to that of Pd complex.

Results and Discussion

Synthesis and characterization: The synthesis of a bispyridine ligand containing a dendritic side chain started with a stepwise fashion according to the procedures described previously.[7] The resulting ligand was treated with $[PdCl_2(PhCN)_2]$ or $CuCl_2$ to afford the Pd^{II} (**1**) or Cu^{II} (**2**) coordination polymers, respectively. They were characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and were shown to be in full agreement with the structures presented.



M = Pd: **1**
Cu: **2**

Both polymers were birefringent waxy solids that are readily soluble in common organic solvents such as CH_2Cl_2, THF, EtOH and water. The solid-state structures of the polymers were investigated by X-ray scattering. Small-angle X-ray scattering (SAXS) measurements of **1** showed several sharp reflections corresponding to a 1D lamellar structure with in-plane 2D order with a layer thickness of 3.6 nm (Figure 1, top). This structural identification was further confirmed by transmission electron microscopy (TEM) experiments that showed dark organized aromatic layers with a lattice dimension of approximately 4 nm (Figure 1, bottom). 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 (Figure 2). Bridging bispyridine ligands connected in the *trans*-position of the square-planar coordination geometry of Pd^{II} generates unfolded polymer chains.[9a,11]

In great contrast to polymer **1**, Cu^{II} coordination polymer **2** self-assembles into a 2D oblique columnar structure with lattice constants of $a=4.9$ nm, $b=4.2$ nm and $\gamma=122°$, as identified by SAXS patterns (Figure 3, top). The evidence for the formation of the 2D oblique columnar structure was also provided by a TEM image that shows a 2D array of dark domains in a matrix of light aliphatic segments with dimensions of 4 and 5 nm, which is consistent with the results obtained from the SAXS (Figure 3, bottom). 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 3, top inset). Additional

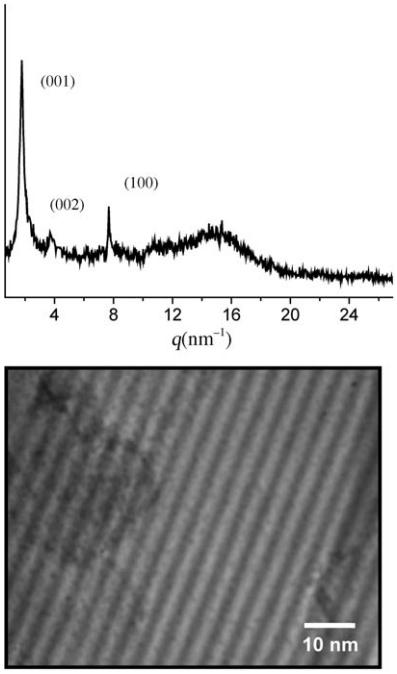


Figure 1. Top: X-ray diffraction pattern of **1**. Bottom: TEM image of an ultramicrotomed film of **1** revealing layered structures of alternating light-colored dendritic, and dark aromatic layers.

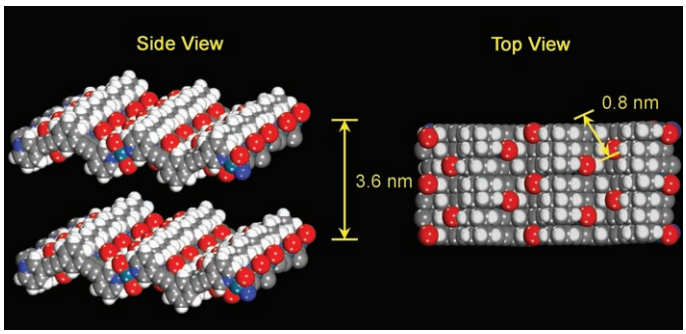


Figure 2. Schematic representation for the formation of the lamellar structure of **1**.

information on the structural dimensionality of **2** was obtained by 2D X-ray diffraction with a sheared sample exhibiting macroscopic orientation. As shown in Figure 4, the reflections at wide angles were diffracted at an angle of 70° with respect to the SAXS scattering, 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, extended X-ray absorption fine structure (EXAFS) experiments were performed with **2** at ambient temperature. As shown in Figure 5, 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, respectively. In particular, the Cu–Cu distance at 4.4 Å was also identified by the WAXS pattern.[12] All of these scattering peaks are consistent with the values for the pseudo-

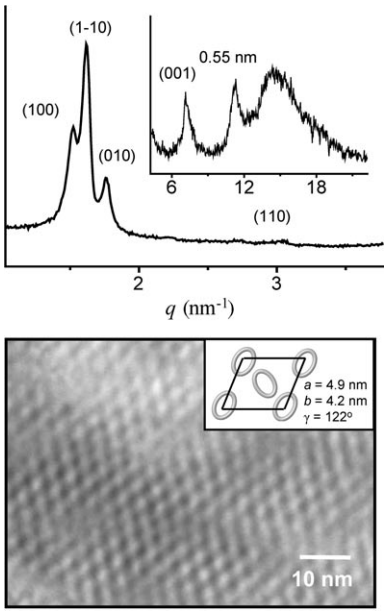


Figure 3. Top: X-ray diffraction patterns of **2**. Bottom: TEM image of ultramicrotomed film of **2** revealing 2D oblique columnar array of aromatic core.

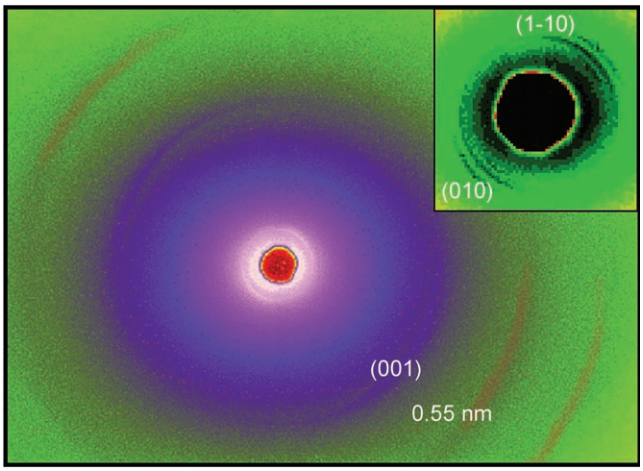


Figure 4. 2D X-ray diffraction patterns of **2**. The inset image shows the 2D small angle X-ray diffraction pattern.

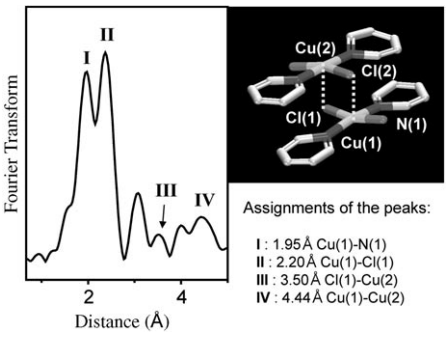


Figure 5. EXAFS profile of **2** and the peak assignments.

square-planar, chloro-bridged dimers formed through weak axial coordination to one copper center by a chloride ligand located at the adjacent copper atom.[13] 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 additional X-ray diffraction peak at 0.55 nm can be described as the width of a groove along the direction of column axis. From the lattice constants and the density, the number of repeating units per pitch was calculated to be 4.2 units.[7a,14] Considering the interstrand, copper–chloride dimeric interactions, this calculated number indicates that the columns are based on double-stranded helical chains.

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 nm/sin 70°) together with a groove of 0.55 nm in width (Figure 6). Subsequently, the

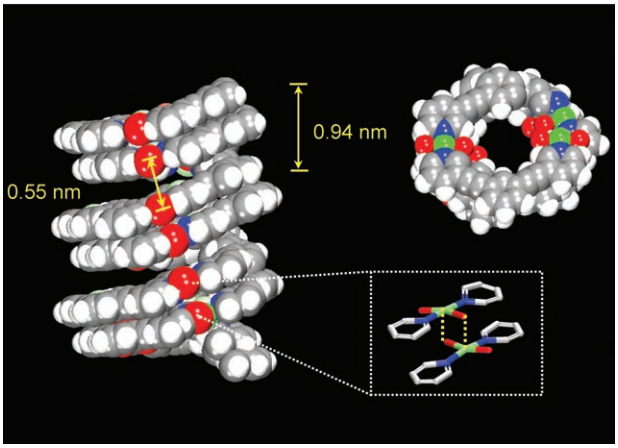


Figure 6. Schematic representation of the double-stranded helical structure of **2**.

double-stranded helices self-organize into a 2D oblique columnar structure. These results show how the complexation of the bent-shaped bispyridine ligand with a Cu^{II} metal ion and a pseudo-square-planar coordination geometry could lead to folded double-stranded helical polymers through complementary dimeric interactions. Considering that in the absence of the metal–chloride bridging interactions compound **1** 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. Indeed, inspection of CPK models revealed that a *cisoid* double-helical conformation of two polymer chains maximizes these dimeric interactions (see Figure S4 in the Supporting Information).

In an effort to provide further evidence for the key influence of the dimeric association on the formation of a double-helical structure, we synthesized homologous Cu^{II} complex **3** containing a methyl group on the *ortho*-position of pyridyl unit that is expected to prevent the copper–chlo-

ride dimeric association due to steric crowding (Figure 7).[15] In contrast to **2**, the resulting coordination polymer showed to self-assemble into a layered structure (Figure 7 and

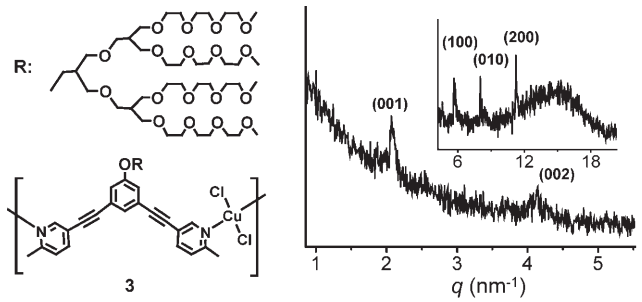


Figure 7. Molecular structure and X-ray diffraction patterns of **3**.

Figure 8, bottom), suggesting that the coordination geometry of Cu^{II} consists of a separated square-planar structure. Furthermore, the EXAFS profile showed no peak corre-

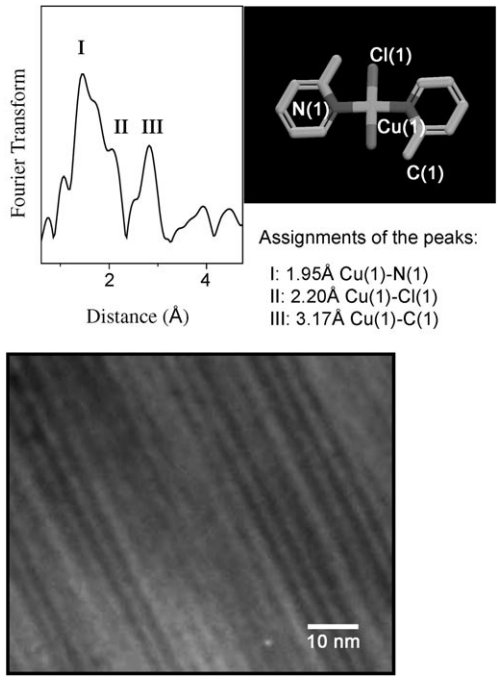


Figure 8. Top: EXAFS profile of **3** and the peak assignments. Bottom: TEM image of ultramicrotomed film of **3** revealing layered structures of alternating light dendritic, and dark aromatic layers.

sponding to a Cu(1)–Cl(2) scattering at 3.5 Å (Figure 8, top). These results further support that the double-helical conformation is attributed to the metal–chloride bridging dimeric association.

Computational structure modeling: To provide further information on the formation of a double-stranded helical organization, computational modeling was performed with model complex **4**.[16] It should be noted that, similar to **2**, the model complex exhibited the three strong reflections at the wide angles, corresponding to helical pitch of 0.88, groove width of 0.55, and π–π stacking distance of 0.35 nm, respectively, demonstrating that model complex **4** also adopt a double-helical conformation with the same dimensions as those of **2** (Figure 9). Structural modeling was performed by density

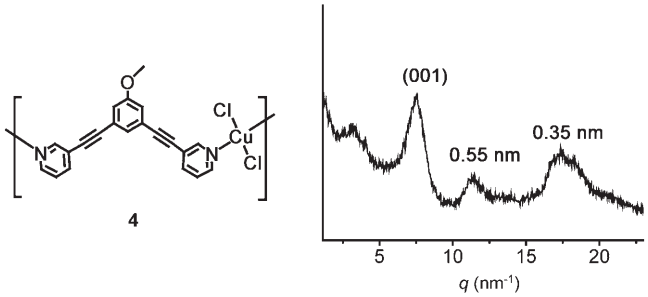


Figure 9. Molecular structure and X-ray diffraction pattern of **4**.

functional theory (DFT) by using SIESTA (Spanish Initiative for Electronic Simulation of Thousands of Atoms).[17] To mimic periodic structure, the computation unit cell was chosen to contain two turns of double-stranded helix composed of eight monomers with 296 atoms. Atom-centered and strictly confined numerical functions were used as a basis set for solving the Kohn–Sham equations.[18] Norm-conserving pseudopotentials were constructed within improved Troullier-Martins scheme.[19] The electron configurations of used pseudopotentials with pseudoionization radii are given in Table 1 (given in Bohr). We used a double-ζ

Table 1. Pseudoionization radii used for pseudopotentials.

Atom	Pseudoionization radius [Bohr]
Cu	$4s^1$ (2.05) $4p^0$ (2.30) $3d^{10}$ (2.05) $4f^0$ (2.05)
Cl	$3s^2$ (1.74) $3p^5$ (1.74) $3d^0$ (1.74) $4f^0$ (1.74)
C	$2s^2$ (1.25) $2p^2$(1.25)
N	$2s^2$ (1.24) $2p^3$(1.24)

basis set for all atoms except Cu and Cl. While double-ζ polarization orbitals were used for both Cu and Cl, relativistic effects were taken into account only for Cu. The exchange-correlation was treated in GGA-PBE.[20] We performed a full optimization of the double-stranded helical structure by means of conjugate gradients allowing unit cell variation. The optimized structure is consistent with the double-stranded helical conformation predicted experimentally as shown in Figure 10. Table 2 shows that the geometric parameters for the double-helical system obtained from our simulations are in good agreement with the experimental profiles. In particular, the Cu(1)–Cl(2) dimeric interaction distance was reproduced excellently as well as the Cu(2)–Cu(1)′ groove with respect to the values obtained from the X-ray diffraction pattern given in Figure 9.

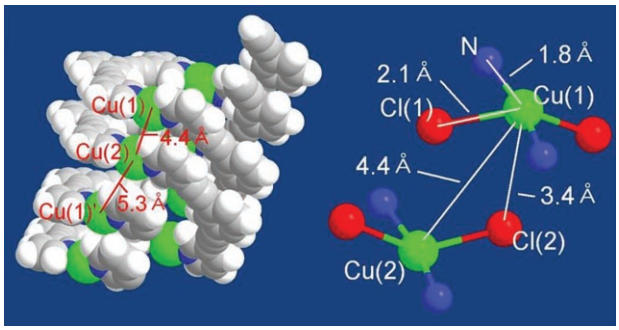


Figure 10. Left: Optimized structure of double-stranded helix unit cell (Cl atoms are not shown for clarity). Right: dimeric unit of **4**.

Table 2. Comparison of relevant geometrical parameters [Å].

Bond length	Calculated[a] [Å]	Experimental [Å]
Cu(1)–N(1)	1.8	1.9
Cu(1)–Cl(1)	2.1	2.2
Cu(1)–Cu(2)	4.4	4.4
Cu(1)–Cl(2)	3.4	3.5
Cu(2)–Cu(1)′	5.3	5.5

[a] Average values.

Conclusion

A bent-shaped bipyridine ligand containing a dendritic aliphatic side chain has been synthesized and forms complexes with Pd^{II} and Cu^{II} through a self-assembly process. These complexes were observed to self-assemble into ordered structures that differ significantly depending on the coordination geometry of the metal center in the solid state. The polymer based on Pd^{II} self-assembles into layer structure formed by bridging bispyridine ligands connected in a *trans*-position of the square-planar coordination geometry of metal center. In contrast, the polymer based on Cu^{II} adopts double-helical conformations with regular grooves along the helical axis, through the metal–chloride dimeric interactions. These notable conformations are attributed to 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. It is also notable that the double-stranded helices self-organize into a 2D columnar structure in the bulk state. These results represent a unique example that weak metal–ligand bridging interactions can provide a useful strategy to construct stable double-stranded helical nanotubes.

Experimental Section

Materials: NaH (60%), and *p*-toluenesulfonyl chloride (98%) from TCI and Tokyo Kasei were used as received. 3-Ethynylpyridine (98%) from Aldrich was used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, TCI, etc.) and were used without purification. Dichloromethane and ethyl acetate were distilled before use. Flash chromatography was carried out with Silica Gel 60 (230–400 mesh) from EM Science. Dry triethylamine was obtained by vacuum transfer from calcium hydride. Dry THF was obtained by vacuum transfer from sodium and benzophenone.

Techniques: ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM 250 spectrometer. The purity of the products was checked by thin-layer chromatography (TLC; Merck, silica gel 60); visualization was achieved with UV light and iodine vapor. A Nikon optical polarized microscopy (magnification: 100) equipped with a Mettler FP 82 hot-stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze anisotropic texture. Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at Organic Research Center, Sogang University. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 and 10C1 X-ray beam line at the Pohang Accelerator Laboratory (Korea). The scattered X-rays were detected on imaging plates for better 2D-XRD resolution. The orientationally ordered domain of complex **2** was obtained by shearing the sample on a kapton film. The long axis of resulting columns was aligned in the direction of shear. To reduce air-scattering, a vaccum chamber made of kapton film was placed between sample and detector. Extended X-ray absorption fine structure (EXAFS) spectra were performed at the 7C1 beam line at the Pohang Accelerator Laboratory (Korea). MALDI-TOF mass spectra were performed on Perceptive Biosystems Voyager-DE STR by using a 2,5-dihydroxy benzoic acid matrix. The transmission electron microscope (TEM) was performed at 120 kV using JEOL-JEM 2010. Ultrathin sectioning of specimens was performed by cryoultramicrotomy using a RMC PowerTome-XL. Before the ultrathin sectioning, the samples were aligned by annealing at 80 °C for 10 h. Thin sections of the specimen were transferred to a carbon-coated copper grid. Compounds were synthesized according to the procedure described Scheme S1 and S2 in the Supporting Information and then purified by silica gel column chromatography and preperative HPLC (Japan Analytical Instrument). CPK models were computed with Materials Studio Modeling 3.0 (Accelrys Inc.) software.

Acknowledgements

This work was supported by the National Creative Research Initiative Program of the Korean Ministry of Science and Technology. Partial support was provided by the Korea Science and Engineering Foundation (KOSEF-R01-2007-000-11831-0, E.S.). E.L. thanks the Seoul Science Fellowship Program, H.-J.K. and E.L. acknowledge a fellowship of the BK21 program from the Ministry of Education and Human Resources Development.

[1] a) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, J. S. Moore, *Chem. Rev.* **2001**, *101*, 3893–4013; b) T. Nakano, Y. Okamoto, *Chem. Rev.* **2001**, *101*, 4013–4038; c) J. P. Hill, W. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii, T. Aida, *Science* **2004**, *304*, 1481–1483; d) L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071–4097; e) W.-Y. Yang, E. Lee, M. Lee, *J. Am. Chem. Soc.* **2006**, *128*, 3484–3485; f) K. Okoshi, S.-I. Sakurai, S. Ohsawa, J. Kumaki, E. Yashima, *Angew. Chem.* **2006**, *118*, 8353–8356; *Angew. Chem. Int. Ed.* **2006**, *45*, 8173–8176; g) T. Miyagawa, A. Furuko, K. Maeda, H. Katagiri, Y. Furusho, E. Yashima, *J. Am. Chem. Soc.* **2005**, *127*, 5018–5019.

[2] a) R. B. Prince, J. G. Saven, P. G. Wolynes, J. S. Moore, *J. Am. Chem. Soc.* **1999**, *121*, 3114–3121; b) J. C. Nelson, J. G. Saven, J. S. Moore, P. G. Wolynes, *Science* **1997**, *277*, 1793–1796; c) A. E. Rowan, R. J. M. Nolte, *Angew. Chem.* **1998**, *110*, 65–71; *Angew. Chem. Int. Ed.* **1998**, *37*, 63–68; d) C. Schmuck, *Angew. Chem.* **2003**, *115*, 2552–2556; *Angew. Chem. Int. Ed.* **2003**, *42*, 2448–2452; e) A. Petitjean, L. A. Cuccia, J.-M. Lehn, H. Nierengarten, M. Schmutz, *Angew. Chem.* **2002**, *114*, 1243–1246; *Angew. Chem. Int. Ed.* **2002**, *41*, 1195–1198.

[3] a) M. Ikeda, Y. Tanaka, T. Hasegawa, Y. Furusho, E. Yashima, *J. Am. Chem. Soc.* **2006**, *128*, 6806–6807; b) L. Carlucci, G. Ciani, D. W. v. Gudenberg, D. M. Proserpio, *Inorg. Chem.* **1997**, *36*, 3812–3813; c) X.-M. Chen, G.-F. Liu, *Chem. Eur. J.* **2002**, *8*, 4811–4817.
[4] a) R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394–5398; b) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; c) V. Maurizot, G. Linti, I. Huc, *Chem. Commun.* **2004**, 924–925.
[5] a) V. Berl, I. Huc, R. G. Khoury, M. J. Krische, J.-M. Lehn, *Nature* **2000**, *407*, 720–723; b) C. Brotschi, A. Häberli, C. J. Leumann, *Angew. Chem.* **2001**, *113*, 3101–3103; *Angew. Chem. Int. Ed.* **2001**, *40*, 3012–3014; c) H. Goto, H. Katagiri, Y. Furusho, E. Yashima, *J. Am. Chem. Soc.* **2006**, *128*, 7176–7178.
[6] Y. Tanaka, H. Katagiri, Y. Furusho, E. Yashima, *Angew. Chem.* **2005**, *117*, 3935–3938; *Angew. Chem. Int. Ed.* **2005**, *44*, 3867–3870.
[7] a) H.-J. Kim, W.-C. Zin, M. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 7009–7014; b) H.-J. Kim, J.-H. Lee, M. Lee, *Angew. Chem.* **2005**, *117*, 5960–5964; *Angew. Chem. Int. Ed.* **2005**, *44*, 5810–5814.
[8] H.-J. Kim, E. Lee, H.-s. Park, M. Lee, *J. Am. Chem. Soc.* **2007**, *129*, 10994–10995.
[9] a) H. Ohi, Y. Tachi, S. Itoh, *Inorg. Chem.* **2004**, *43*, 4561–4563; b) Z. Zhang, S. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 9204–9205.
[10] T. Kawamoto, B. S. Hammes, R. Ostrander, A. L. Rheingold, A. S. Borovik, *Inorg. Chem.* **1998**, *37*, 3424–3427.
[11] M. T. Stone, J. S Moore, *J. Am. Chem. Soc.* **2005**, *127*, 5928–5935.
[12] The broad reflection is attributed to overlap with (002) reflection and halo corresponding to liquid-like correlation of aliphatic chains.
[13] a) W. E. Marsh, W. E. Hatfield, D. J. Hodgson, *Inorg. Chem.* **1982**, *21*, 2679–2684; b) E. D. Estes, W. E. Estes, W. E. Hatfield, D. J. Hodgson, *Inorg. Chem.* **1975**, *14*, 106–109.
[14] a) See Supporting Information; b) M. Peterca, V. Percec, A. E. Dulcey, S. Nummelin, S. Korey, M. Ilies, P. A. Heiney, *J. Am. Chem. Soc.* **2006**, *128*, 6713–6720; c) L.-L. Lai, C.-H. Lee, L.-Y. Wang, K.-L. Cheng, H.-F. Hsu, *J. Org. Chem.* **2008**, *73*, 485–490.
[15] a) P. Singh, D. Y. Jeter, W. E. Hatfield, D. J. Hodgson, *Inorg. Chem.* **1972**, *11*, 1657–1661; b) J. A. Campbell, C. L. Raston, J. N. Varghese, A. H. White, *Aust. J. Chem.* **1977**, *30*, 1947–1953.
[16] For computational simplicity, methoxy side groups are omitted in the computational modeling.
[17] a) J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, *J. Phys. Condens. Matter* **2002**, *14*, 2745–2779; b) P. Ordejón, E. Artacho, J. M. Soler, *Phys. Rev. B* **1996**, *53*, R10441-R10444; c) SIESTA homepage: http://www.uam.es/siesta.
[18] a) D. Sánchez-Portal, E. Artacho, J. M. Soler, *J. Phys. Condens. Matter* **1996**, *8*, 3859–3880; b) J. Junquera, Ó. Paz, D. Sánchez-Portal, E. Artacho, *Phys. Rev. B* **2001**, *64*, 235111.
[19] N. Troullier, J. L. Martins, *Phys. Rev. B* **1991**, *43*, 8861–8869.
[20] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

Received: January 11, 2008
Published online: April 7, 2008

