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Copper(I) Ion Mediated Self-Organization of Molecular Rectangular Boxes from 1,2-Bis(2-pyridylethynyl)benzene Ligands with Bulky Substituents

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The reaction of chiral 1,2-bis(2-pyridylethynyl)benzene ligands with copper(I) ions in dichloromethane at room temperature gives rise to the formation of molecular rectangular boxes in high yields. The structures of these complexes were confirmed by X-ray crystallographic analysis. The compound **CL1** crystallizes in the triclinic space group $P1$, with $a = 13.707(4)$ Å, $b = 14.891(3)$ Å, $c = 12.030(1)$ Å, $\alpha = 101.65(2)^\circ$, $\beta = 115.08(2)^\circ$, $\gamma = 97.66(1)^\circ$, $V = 2110.8(2)$ Å^3, $Z = 1$ ($T = 288$ K). The compound **CL2** crystallizes in the triclinic space group $P1$, with $a = 13.539(4)$ Å, $b = 14.755(2)$ Å, $c = 11.951(2)$ Å, $\alpha = 101.70(1)^\circ$, $\beta = 115.11(1)^\circ$, $\gamma = 97.44(2)^\circ$, $V = 2053.8(8)$ Å^3, $Z = 1$ ($T = 198$ K). The formation of box-type structure is caused by steric hindrance between bulky substituents of the ligands.

The metal ion mediated self-organization of functionalized higher-order supramolecular structures is of current interest in the field of supramolecular chemistry.[1] Over the past decade, various reports have been published on the self-organization of higher-order supramolecular structures such as helicates,[2] knots,[3] catenanes,[4] rotaxane,[5] and molecular boxes[6] from suitably designed ligands and metal ions. However, far less attention has been devoted to the metal ion assisted self-organization of higher-order supramolecular structures from enediyne-type nitrogen ligands.[7] We recently reported that the enediyne-type nitrogen ligand 1,2-bis(2-pyridylethynyl)benzene having small substituents, such as a methoxymethyl group, at the 6-position of the pyridine ring coordinates with copper(I) ions to yield two-coordinate copper(I)-mediated planar complexes.[8] Instead of the use of such a small substituent, the introduction of a bulky substituent would lead to the self-organization of higher-order supramolecular structures because of steric hindrance between the substituents. Furthermore, enediyne compounds are, in general, known to possess attractive properties, such as DNA-damaging activity[9] or cycloaromatization.[10] Therefore, supramolecular structures derived from enediyne-type nitrogen ligands in this study would also be expected to exhibit more remarkable properties. Herein, we report the copper(I) ion mediated self-organization of molecular rec-

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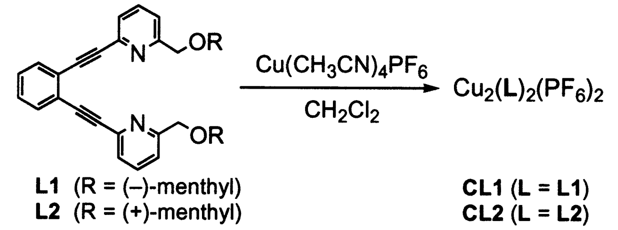
Scheme 1. Coordination of Ligands with Copper(I) Ions



tangular boxes from enediyne-type nitrogen ligands, 1,2-bis(2-pyridylethynyl)benzenes with optically active (menthyloxy)methyl substituents (**L1** and **L2**).

The ligand (**L1**) was obtained from the palladium(0)-catalyzed cross-coupling reaction of readily accessible 1,2-bis(ethynyl)benzene[11] with 2 equiv of 2-bromo-6-((−)-menthyloxy)pyridine in diethylamine at 60 °C. The synthesis of **L2** was also accomplished in a similar manner using the (+)-menthyl derivative. No racemization of the chiral centers took place under the conditions employed. The resulting ligands exhibited equal and opposite optical rotations in chloroform (**L1**, $[\alpha]_D$ −69.1° (*c* 1.94); **L2**, $[\alpha]_D$ +69.4° (*c* 1.98)). The structures of **L1** and **L2** were completely characterized by spectroscopy (^{1}H NMR, IR, UV, and FAB mass) and elemental analysis.

The reaction of **L1** with $Cu(CH_3CN)_4PF_6$ in dichloromethane at room temperature led to the formation of copper(I) complex **CL1** as yellow blocks in 85% yield. Similarly, copper(I) complex **CL2**, which was derived from **L2**, was also obtained as yellow blocks in 71% yield. The structures of **CL1** and **CL2** were unambiguously assigned on the basis of ^{1}H NMR, UV, mass spectroscopy, and X-ray crystallography. The molecular formulas for **CL1** and **CL2**, calculated from elemental analysis and FAB mass evidence, were determined to be $[Cu_2(\mathbf{L1})_2][PF_6]_2$ and $[Cu_2(\mathbf{L2})_2][PF_6]_2$, respectively (Scheme 1). The ^{1}H NMR spectrum of **CL1** showed the same number of lines as in **L1**. The ^{1}H NMR spectra of **L2** and **CL2** showed changes similar to those of **L1** and **CL1**.[12] The UV electronic spectra of **CL1** showed a new absorption at 358 nm, which was assigned to a metal-to-ligand charge-transfer band. The UV spectrophotometric titration of **L1** with $Cu(CH_3CN)_4PF_6$ in dichloromethane shows clear isosbestic points, indicating that a single species was exclusively formed. Figure 1 shows the circular dichroism spectra of **CL1** and **CL2**, respectively. The spectra are mirror images of each other. Additionally, a significant change in the optical rotations of the complexes in chloroform (**CL1**, $[\alpha]_D$ −446.9° (*c* 1.62); **CL2**, $[\alpha]_D$ +418.4° (*c* 1.47)) implies that the reaction of the present ligands with the copper(I) ions proceeded enantioselectively to afford the enantiomerically pure complexes in solution.

The molecular structures of **CL1** and **CL2** were determined by single-crystal X-ray crystallographic analysis. Both **CL1** and **CL2** consist of two copper(I) ions, two ligands, and two uncoordinated hexafluorophosphate. Each crystal system of **CL1** and **CL2** was assigned to be triclinic *P*1, which is in a chiral space group. This result indicates that enantioselective self-assembly is also achieved in the solid state, and that this stereoselectivity is attributable to the chirality of the ligand itself. The absolute configurations of both **CL1** and **CL2** were completely determined on the basis of each ligand's chirality.

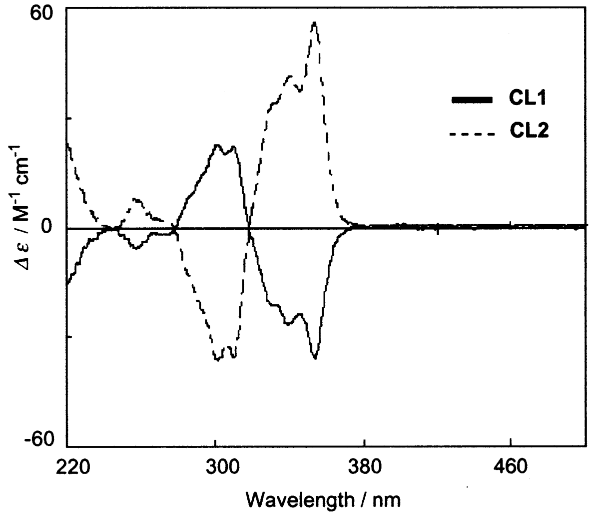


Figure 1. CD spectra of **CL1** and **CL2** in chloroform.

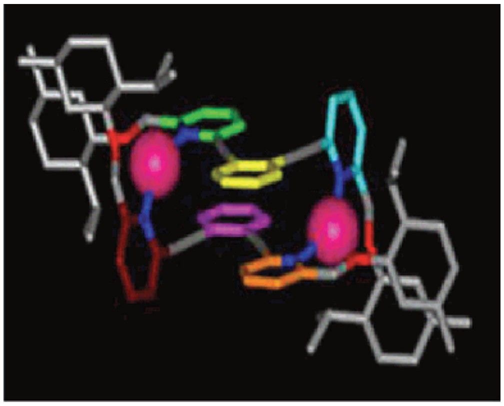


Figure 2. Crystal structure of **CL2**. Counterions and hydrogen atoms are omitted for clarity.

Figure 2 shows the structures of the cation of **CL2**.[13] Each copper(I) ion of **CL2** has a distorted tetrahedral (N_2O_2) coordination. However, oxygen atoms weakly coordinate to copper(I) ion. The two ligands of **CL2** are stacked coplanar above each other, with an interplane distance of about 3.5 Å, indicative of the presence of a $\pi-\pi$ interaction. The slight bending of the triple bond is also observed (about 173°). The structure of **CL1**[14] is a complete mirror image of **CL2**.

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(13) Crystal data for $Cu_2(\mathbf{L2})_2(PF_6)_2$: $C_{84}H_{104}N_4O_4P_2F_{12}Cu_2$, $M_r = 1650.79$, triclinic, space group *P*1 (No. 1), $a = 13.539(4)$ Å, $b = 14.755(2)$ Å, $c = 11.951(2)$ Å, $\alpha = 101.70(1)°$, $\beta = 115.11(1)°$, $\gamma = 97.44(2)°$, $V = 2053.8(8)$ Å^3, $Z = 1$, $D_{calc} = 1.34$ g cm^{-3}, $T = 198$ K, R (R_w) = 0.052 (0.053) for 5966 reflections with $I > 3.0\sigma(I)$. The X-ray diffraction data were collected on a Rigaku AFC5R difflactometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 198 K. Calculations were carried out on an SGI Indy using the teXsan[15] crystallographic software package from Molecular Science Corp. The structure was solved by direct methods of SIR92[16] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The refinement of the structure was performed by full-matrix least-squares methods.

Table 1. Relevant Dihedral Angle (deg) between Aromatic Rings of **CL2**[a]

	benzene [A]	pyridine [B]	pyridine [C]	benzene [D]	pyridine [E]
pyridine [B]	4.14				
pyridine [C]	76.72	79.84			
benzene [D]	176.67	176.10	100.16		
pyridine [E]	101.58	98.31	176.45	81.48	
pyridine [F]	2.78	1.96	77.88	175.81	100.28

[a] [A], yellow; [B], green; [C], blue; [D], purple; [E], brown; [F], orange.

Table 1 shows the dihedral angles between aromatic rings of **CL2** on the basis of Figure 2. In one ligand of **CL2**, the pyridyl and the remaining 1-ethynyl-2-(2-pyridylethynyl)-phenyl binding domains are twisted with respect to each other (average twist angle: 84.5°), and therefore, the coordination of the two ligands with the two copper(I) ions produces a hollow cavity. This fact demonstrates clearly that steric hindrance between the terminal bulky substituents in the ligand has a large effect on the formation of such a higher-order supramolecular structure. The role of ethereal oxygens coordinated to metal ions may not be neglected.

To probe the possible thermal reactivity of our system, we examined their behavior by differential scanning calorimetry (DSC). Figure 3 illustrates the DSC traces for the thermal cyclization of the ligand **L1** and its copper(I) complex **CL1**. The ligand **L1** exhibits a sharp endothermic peak at about 118 °C followed by a broad exothermic peak at above 300 °C. On the other hand, the complex **CL1** exhibits a sharp endothermic peak at about 250 °C followed by a broad exothermic peak at about 275 °C. It indicates that metal-binding enediyne ligands in our system also make possible modulating thermal Bergman cyclization temperatures.

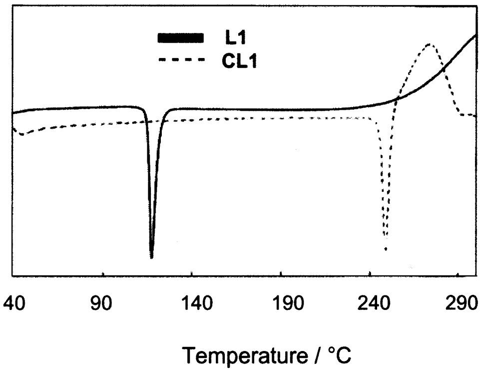

Figure 3. DSC traces for the thermal cyclization of **L1** and **CL1**.

In conclusion, we have demonstrated that the reaction of 1,2-bis(2-pyridylethynyl)benzene ligands having bulky substituents with copper(I) ions led to the self-organization of molecular rectangular boxes in high yields. The encapsulation of guest molecules by adjustment of the box cavity would be expected. Furthermore, detailed studies of the biological activity of these complexes and their reactivity for the cycloaromatization are now in progress.

Acknowledgment. We thank the Material Analysis Center of our institute for assisting with elemental analysis.

Supporting Information Available: Description of experimental procedures for **L1** and **CL1**, ORTEP representations of **CL1** (PDF), and X-ray crystallographic files for **CL1** and **CL2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Crystal data for $Cu_2(\mathbf{L1})_2(PF_6)_2$: $C_{84}H_{104}N_4O_4P_2F_{12}Cu_2$, $M_r = 1650.79$, triclinic, space group $P1$ (No. 1), $a = 13.707(4)$ Å, $b = 14.891(3)$ Å, $c = 12.030(1)$ Å, $\alpha = 101.65(2)°$, $\beta = 115.08(2)°$, $\gamma = 97.66(1)°$, $V = 2110.8(2)$ Å^3, $Z = 1$, $D_{calc} = 1.30$ g cm^{-3}, $T = 288$ K, R (R_w) = 0.054 (0.092) for 4679 reflections with $I > 3.0\sigma(I)$. The X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at 288 K. Calculations were carried out on an SGI Indy using the teXsan[15] crystallographic software package from Molecular Science Corp. The structure was solved by direct methods of SIR92[16] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The refinement of the structure was performed by full-matrix least-squares methods. See Supporting Information.

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