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Supramolecular macrocycles self-assembled by phenanthroline–Cu(I) and sugar–boronic acid interactions

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Abstract

Two kinds of ligand which have two phenanthroline groups linked by a C_2-symmetrical chiral tetrol were synthesized by a boronic acid–diol interaction. It was shown that these ligands form unique dinuclear chiral macrocycles by a Cu(I)–phenanthroline interaction. The results indicate that a novel supramolecular system can be exploited by combination of the Cu(I)–phenanthroline interaction with the boronic acid–diol interaction.

It is known that molecular aggregation programmed by metal–ligand interactions can generate various supramolecular structures such as network,[1] cylinder,[2] etc.[3] In particular, when a ligand involves chiral carbons, the resultant metal complex can create unique metal-linked macrocycles with a helical structure.[4] However, such examples are still very limited probably because of the difficulty to design and synthesize well-programmed chiral ligands which can form such helical macrocycles. We recently demonstrated that a saccharide family is utilizable as combinatorial chiral resources for designing supramolecular structures because they can be readily inserted into the boronic acid-appended sites owing to the boronic acid–diol interaction.[5–7] This idea has been applied to designs of helical polymers,[5] control of the angle and the distance between two porphyrins,[6] stabilization of organogels,[7] etc. It thus occurred to us that if a well-programmed ligand bearing both a metal-binding ligand site and a saccharide-binding boronic acid site could be synthesized, it would be linked both by metal–ligand and boronic acid–diol interactions to form a unique helical macrocycle. With this object in mind, we synthesized compound **1** bearing a phenanthroline moiety as a metal-binding site and a 2-aminomethylboronic acid moiety as a saccharide-binding site.[8] Since the saccharide offers the different angle and the different chirality as a connector, the resultant macrocycle (if it is formed) should represent the different helical structure (Scheme 1).

Compound **1** (mp 179–183°C) was synthesized from 2-*p*-anisyl-9-*p*-tolyl-1,10-phenanthroline[9] according to the literature[10] and identified by IR and ^{1}H NMR spectral evidence and elemental analysis.

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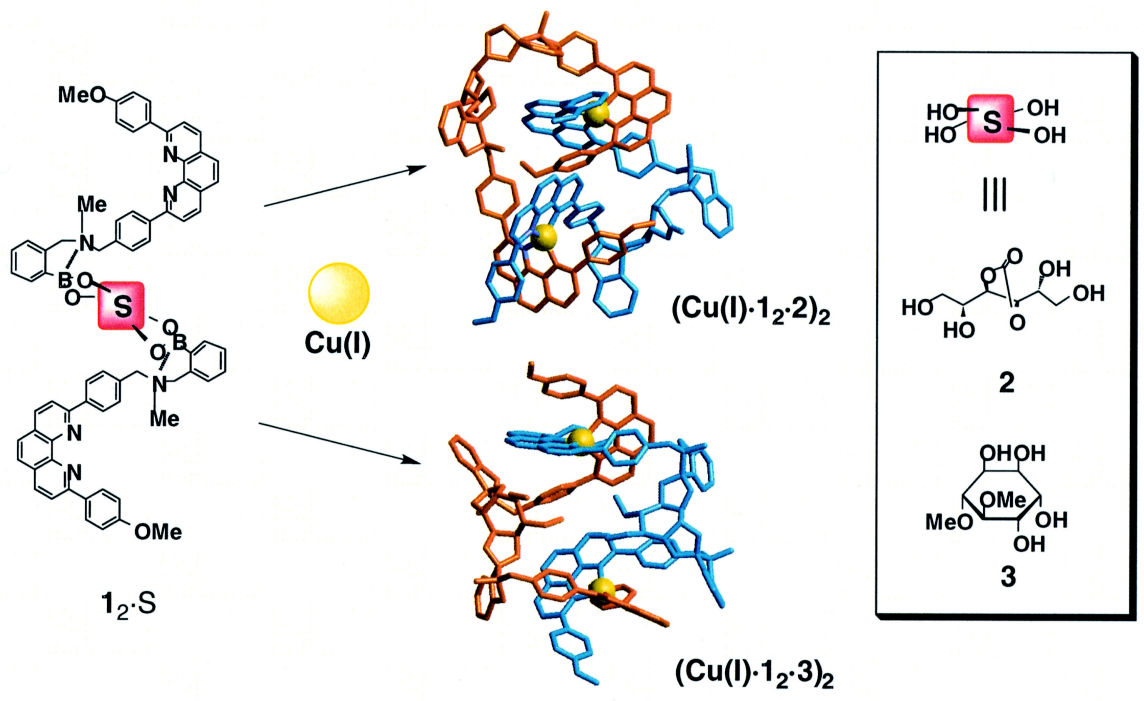

Scheme 1. Scheme of self-assembled supramolecular macrocycles by phenanthroline–Cu(I) and sugar–boronic acid interactions; (Cu(I)·**1**$_2$·**2**)$_2$ macrocycle and (Cu(I)·**1**$_2$·**3**)$_2$ macrocycle are energy-minimized structures

To avoid the head-to-tail disorder which makes the structural analysis complex we here employed D-mannitol-3,4-carbonate (**2**)[11] and 1,2-*O*-dimethyl-D-inositol (**3**)[12] with C_2 symmetry. The 2:1 ligands (i.e. **1**$_2$·**2** and **1**$_2$·**3**) were synthesized from **1** and **2** (or **3**) in refluxing dichloromethane in the presence of molecular sieve 4 Å. The products (**1**$_2$·**2**, yield 91%, mp 180–182°C; **1**$_2$·**3**, yield 71%, mp 157–159°C) were identified by ^{1}H NMR and mass (MALDI-TOF) spectral evidence.

Firstly, the stoichiometry between the 2:1 ligands and Cu(I) (added as Cu(MeCN)$_4$ClO$_4$) was estimated by absorption spectroscopy. For the **1**$_2$·**2** ligand, the absorption spectrum with λ_{max} at 282 and 318 nm changed to new absorption spectra with λ_{max} at 319 and 440 nm and isosbestic points at 261 and 373 nm with increasing Cu(I) concentration. The absorbances plotted against [Cu(I)]/[**1**$_2$·**2**] gave a sharp break point at [Cu(I)]/[**1**$_2$·**2**]=1:1, indicating that the typical Cu(I)·(phenanthroline)$_2$ complex is formed from Cu(I) and the **1**$_2$·**2** ligand. Similar results were also obtained from Cu(I) and the **1**$_2$·**3** ligand. Thus, one can conclude that the Cu(I) complexes have a 1:1 stoichiometry between Cu(I) and the **1**$_2$·**2** (or **1**$_2$·**3**) ligand.

The 1:1 mixture of Cu(I) and the **1**$_2$·**2** (or **1**$_2$·**3**) ligand have a possibility of either the linear oligomer or the macrocycle. Molecular weights of such macromolecules can be conveniently estimated by TOF-MS spectrometric methods (MALDI-TOF or ESI-TOF). MALDI-TOF-MS for a 1:1 mixture of Cu(I) and the **1**$_2$·**3** ligand gave only a monocationic *m/z*=2656 peak and a dicationic *m/z*=1278 peak (i.e. [(Cu(I)·**1**$_2$·**3**)$_2$-ClO$_4$]$^+$ and [(Cu(I)·**1**$_2$·**3**)$_2$-2ClO$_4$]$^{2+}$, respectively), which support the formation of a dinuclear macrocycle. In ESI-TOF-MS, the monocationic peak was observed only very weakly whereas the dicationic peak appeared as a sole, strong peak. The observed peak intensities at around the dicationic *m/z*=1278 peak can be well simulated by the theoretical computation. Similarly, for a 1:1 mixture of Cu(I) and the **1**$_2$·**2** ligand MALDI-TOF-MS gave a monocationic *m/z*=2659 peak and a dicationic *m/z*=1278 peak whereas ESI-TOF-MS gave the dicationic peak. In addition, both MALDI-TOF-MS and

ESI-TOF-MS gave a weak peak at *m/z*=1487 which is assignable to a monocationic fragment species $[(Cu(I)\cdot(\mathbf{1}\cdot\mathbf{2})_2\text{-}ClO_4]^+$. This finding suggests that the Cu(I) complex obtained from the $\mathbf{1}_2\cdot\mathbf{2}$ ligand is less stable than that obtained from the $\mathbf{1}_2\cdot\mathbf{3}$ ligand. Anyhow, these mono- and dicationic peaks cannot be generated by linear oligomers but only by dimeric, dinuclear complexes. Thus, the foregoing mass spectral data consistently support the view that 2 mols of Cu(I) and 2 mols of the $\mathbf{1}_2\cdot\mathbf{2}$ (or $\mathbf{1}_2\cdot\mathbf{3}$) ligand yield a 'chiral' macrocycle by the Cu(I)–phenanthroline interaction at two sites.

When the phenanthroline ligand is asymmetrically substituted, the resultant Cu(I) complex becomes a racemic mixture of *P*- and *M*-isomers. The ratio is affected by the chirality in the substituent.[13] When Cu(I) and the $\mathbf{1}_2\cdot\mathbf{2}$ (or $\mathbf{1}_2\cdot\mathbf{3}$) ligand was mixed in a 1:1 ratio, the CD (circular dichroism)-active spectra appeared gradually, which reached the saturation value after 6 h in the $\mathbf{1}_2\cdot\mathbf{2}$ ligand and after 1 h in the $\mathbf{1}_2\cdot\mathbf{3}$ ligand (Fig. 1). The slow CD appearance implies that even though the racemic Cu(I) complexes are formed immediately after mixing under the kinetic control, slow equilibration between *P*- and *M*-isomers subsequently occurs under the thermodynamic control.

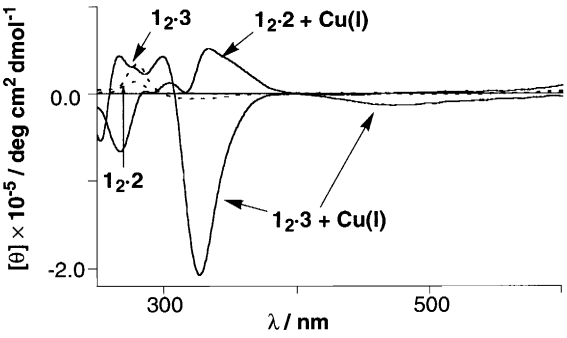

Fig. 1. Final CD spectra obtained from a mixture of $\mathbf{1}_2\cdot\mathbf{2}$+Cu(I) or $\mathbf{1}_2\cdot\mathbf{3}$+Cu(I) (1.00 mmol dm^{-3}): the dotted curves indicate the CD spectra in the absence of Cu(I)

It is known that the helicity of the Cu(I)·(phenanthroline)$_2$ complex can be judged with the CD signs at π–π* region (at around 300 nm) and MLCT region (at around 500 nm).[13,14] It is seen from Fig. 1 that the CD signs of both π–π* region and MLCT region for the Cu(I) complex obtained from the $\mathbf{1}_2\cdot\mathbf{3}$ ligand are negative, indicating that the two Cu(I)·(phenanthroline)$_2$ moieties adopt a left-handed *M*-helicity (i.e. homohelicity). On the other hand, the CD sign of the π–π* region for the Cu(I) complex obtained from the $\mathbf{1}_2\cdot\mathbf{2}$ ligand is positive and much weaker (about 1/5 of the $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{3})_2$ complex) and MLCT region is almost CD-silent. These results suggest that the two Cu(I)·(phenanthroline)$_2$ moieties in this complex adopt the opposite *M*/*P* helicities, offsetting the CD bands each other (i.e. heterohelicity). In fact, the ^{1}H NMR spectrum of the $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{3})_2$ complex was assignable assuming the symmetrical structure whereas that of the $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{2})_2$ complex was very complicated (400 MHz, CD_2Cl_2:CD_3CN=50:1 v/v): the six phenanthroline protons of the $\mathbf{1}_2\cdot\mathbf{2}$ ligand appeared at 8.35 (J_H=8.5 Hz), 8.32 (J_H=8.5 Hz), 8.14 (J_H=8.5 Hz), 8.13 (J_H=8.5 Hz), 7.82 (J_H=8.5 Hz), and 7.79 (J_H=8.5 Hz) ppm (doublet each) and those of the $\mathbf{1}_2\cdot\mathbf{3}$ ligand appeared at 8.39 (J_H=8.5 Hz), 8.33 (J_H=8.5 Hz), 8.20 (J_H=8.5 Hz), 8.14 (J_H=8.5 Hz), 7.85 (J_H=8.9 Hz), and 7.83 (J_H=8.9 Hz) ppm (doublet each). In the $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{3})_2$ complex, which still retains high symmetry because of the homohelical macrocyclic structure, the chemical shifts moved to either lower or higher magnetic field but the splitting pattern was not changed [8.64 (J_H=8.5 Hz), 8.38 (J_H=8.5 Hz), 8.04 (m, 2H), 7.95 (J_H=8.5 Hz), and 7.60 (J_H=8.5 Hz) ppm (doublet each except the peak at 8.04 ppm which corresponds to the integral intensity of two protons)]. On the other hand, in the $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{2})_2$ complex which loses high symmetry because of the heterohelical macrocyclic structure, the ^{1}H NMR spectrum has the several additional peaks.[15]

Taking these lines of information into account, the energy-minimized structures for the two macrocycles were generated by a computational method (Discover 97.0, MSI). As shown in Scheme 1, the homohelical $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{3})_2$ macrocycle has a highly-symmetrical structure: that is, the ring is twisted twice toward the left-handed direction. In contrast, the structure of the heterohelical $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{2})_2$ macrocycle is disordered because the ring is twisted twice toward the opposite direction. This disorder may be related to the unstability of the $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{2})_2$ macrocycle observed in the mass spectral studies.

In conclusion, the present study has demonstrated that a novel supramolecular system can be exploited by combining a Cu(I)–phenanthroline interaction with a boronic acid–diol interaction. Taking advantage of the availability of various chiral tetrols (including saccharides), one can readily introduce chiral factors into the present supramolecular system and create even unique macrocycles with a helical structure.

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15. In the ^{1}H NMR spectra, the minor weak peaks sometimes appeared (~10% intensity) when $Cu(MeCN)_4ClO_4$ was added. These are assigned to the products decomposed by water concomitant in the Cu(I) salt or to the cyclic compounds larger than $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{2})_2$ or $(Cu(I)\cdot\mathbf{1}_2\cdot\mathbf{3})_2$.