

論文内容の要旨

論文題目

Construction of Metallo-Supramolecular Architectures with Bisphenanthroline Macrocycles

(ビスフェナントロリン骨格を有する大環状化合物を用いた金属内包超分子構造の構築)

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This thesis describes metal arrangement abilities and aggregation behaviors of rigid macrocycles with two inward phenanthroline coordination sites directed toward the construction of novel supramolecular architectures containing multiple metal ions. The thesis is composed of four chapters as summarized below.

[Chapter 1: General Introduction]

Constrained nanoscopic spaces surrounded by multiple functional sites have specific chemical environments to provide a platform for molecular recognition and transformation. Macrocyclic compounds can be appropriately designed so as to have a variety of functional groups directing inward for their cooperative characteristics within the inner spaces. Furthermore, when these macrocycles are stacked in a face-to-face manner, they would form a laminate structure with a multifunctional channel (Figure 1).

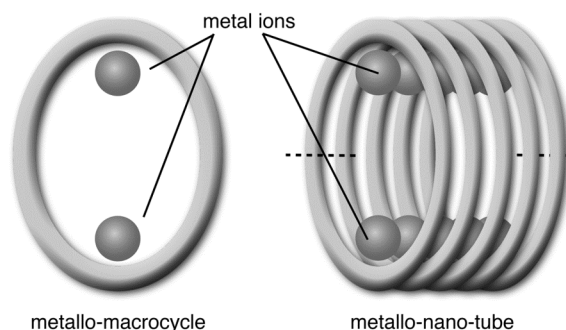


Figure 1. Schematic illustration of aggregation of metallo-macrocycles.

In this work, novel rigid macrocycles have been constructed which possess two chemically-equivalent metal binding sites within their cavity. These macrocyclic ligands form various dinuclear metal complexes (Figure 1 left). Since metal ions have specific chemical and physical properties with regard to geometrical and dynamic coordination behaviors, oxidation-reduction, magnetism, and conductivity, such endohedral metallo-macrocycles would provide functional inner spaces based on the kind of metals and how they stay inside. Furthermore, self-assembly of these macrocycles is expected to lead to the metal-assembled, higher-order structures. For example, layer-by-layer accumulation of metallo-macrocycles would result in the formation of polymetallo-nano-tubes (Figure 1 right), which may exhibit metal clustered-centered functions in the micron-scale

range.

[Chapter 2: Homo and Heterodinuclear Metal Arrangements within a Bisphenanthroline Macrocycle]

A macrocyclic ligand **1** (Figure 2a left), which possesses a rigid aromatic cyclic skeleton and two inward phenanthroline coordination sites, was newly designed and synthesized aiming at well-defined metal arrangement within the cavity, and its metal complexation behaviors were examined.

Firstly, the addition of $\text{Zn}(\text{CF}_3\text{CO}_2)_2$ (2.0 eq) to **1** in $\text{CDCl}_3/\text{CD}_3\text{CN} = 10/1$ resulted in the formation of a dinuclear $\text{Zn}(\text{II})$ complex. In ^1H NMR titration study, a complex with C_{2v} symmetry was firstly observed, followed by a complex with D_{2h} symmetry. The signals of protons around phenanthroline coordination sites showed down-field shift, which indicates metal coordination of phenanthroline (Figure 2b-2). Thus, it is suggested that a D_{2h} dinuclear $\text{Zn}(\text{II})$ complex, in which two $\text{Zn}(\text{II})$ ions are bound to the phenanthroline coordination sites, is formed *via* a C_{2v} mononuclear $\text{Zn}(\text{II})$ complex. This dinuclear $\text{Zn}(\text{II})$ -macrocycle formation was also supported by electrospray ionization-time-of-flight (ESI-TOF) MS (m/z 1619.4 as $[\text{Zn}_2\mathbf{1}(\text{CF}_3\text{CO}_2)_4 + \text{Na}]^+$) and the single-crystal X-ray analysis (Figure 2c). In the crystal structure, it turned out that two $\text{Zn}(\text{II})$ ions are bound by the phenanthroline site and two CF_3CO_2^- ions to result in a tetrahedral coordination geometry.

Next, $\text{Cu}(\text{I})$ ions, in stead of $\text{Zn}(\text{II})$ ions, which also prefer a tetrahedral coordination geometry, were examined for macrocycle **1**. Upon the addition of $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ (2.3 eq) to **1** in $\text{CDCl}_3/\text{CD}_3\text{CN} = 10/1$, the ^1H NMR signals of phenanthroline protons showed down-field shift (Figure 2b-3). The formation of dinuclear $\text{Cu}(\text{I})$ -macrocycle was also confirmed by ESI-TOF MS (m/z 1268.4 as $[\text{Cu}_2\mathbf{1}\text{BF}_4(\text{CH}_3\text{CN})]^+$).

Based on these results, heterodinuclear complexation was then examined. The addition of both $\text{Zn}(\text{CF}_3\text{CO}_2)_2$ (1.0 eq) and $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ (1.0 eq) to **1** in $\text{CDCl}_3/\text{CD}_3\text{CN} = 10/1$ resulted in the formation of a heterodinuclear $\text{Zn}(\text{II})$ - $\text{Cu}(\text{I})$ -complex in which each metal ion binds to one of the two chemically-equivalent phenanthroline sites. Its ^1H NMR spectrum showed a lower symmetrical pattern compared with those of homodinuclear $\text{Zn}(\text{II})$ - and $\text{Cu}(\text{I})$ -macrocycles, that is, two sets of signals for phenanthroline protons were observed (Figure 2b-4). ESI-TOF MS measurement also

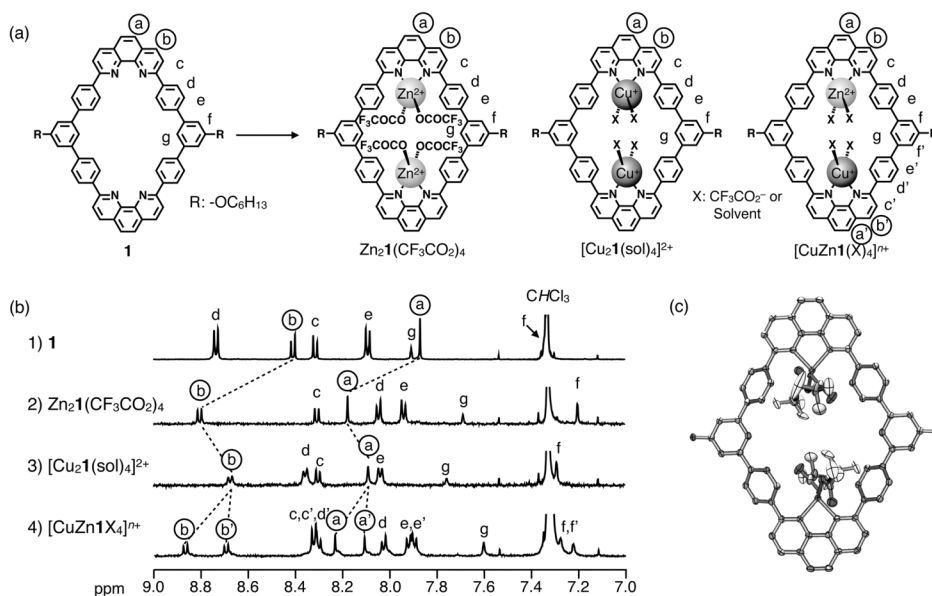


Figure 2. Dinuclear metal arrangement within the macrocycle **1**; (a) Scheme of metal complexation; (b) ^1H NMR spectra of **1** and its complexes (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN} = 10/1$, 293 K) 1) **1**] = 0.30 mM, 2) **1**] = 0.13 mM, $[\text{Zn}(\text{CF}_3\text{CO}_2)_2] = 0.26$ mM, 3) **1**] = 0.13 mM, $[\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4] = 0.29$ mM, 4) **1**] = $[\text{Zn}(\text{CF}_3\text{CO}_2)_2] = [\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4] = 0.24$ mM; (c) X-ray structure of the dinuclear $\text{Zn}(\text{II})$ -macrocycle, $\text{Zn}_2\mathbf{1}(\text{CF}_3\text{CO}_2)_4$ (hydrogen atoms, side chains, solvent molecules are omitted for clarity.).

supported the formation of this heterodinuclear Zn(II)-Cu(I)-macrocycle ($m/z = 1408.1$ as $[\text{CuZn1}(\text{CF}_3\text{CO}_2)_2(\text{CH}_3\text{CN})]^+$). This heterodinuclear Zn(II)-Cu(I) complex was formed with high efficiency (> 90%). Evaluation of binding constants of stepwise metal complexation well explained this high selectivity of the heterodinuclear complex formation due to the relatively low stability of the homodinuclear Cu(I) complex. Thus, a homodinuclear Zn(II)-macrocycle, a homodinuclear Cu(I)-macrocycle, and a heterodinuclear Zn(II)-Cu(I)-macrocycle were efficiently formed using macrocycle **1** with two chemically-equivalent metal binding sites within the molecule (Figure 2a).

[Chapter 3: Aggregation Behaviors of Bisphenanthroline Macrocycles]

With a view to the aggregation of macrocycles, macrocycle **2**, which has the same cyclic skeleton as **1** and six long alkyl side chains (Figure 3a left), was synthesized. In general, compounds with a rigid aromatic core and long alkyl chains tend to stack in a low polar solvent due to their different affinities to the solvent. Thus, macrocycle **2** with these peripheral side chains was expected to form aggregates in a solvent-dependent manner.

In fact, macrocycle **2** was found to stack in low polar solvents such as cyclohexane to form fibrous structures. The

^1H NMR spectrum of **2** in cyclohexane- d_{12} was extremely broadened whereas that of **2** in CDCl_3 showed sharp signals. This suggests that self-aggregates are formed in the low polar cyclohexane (Figure 3b). Furthermore, atomic force microscope (AFM) measurements of mica surfaces, on which a cyclohexane solution of **2** was dropped and dried, gave fibrous images with up to micrometer-scale length and a height of about 6 nm corresponding to the diameter of **2** (Figure 3a right). This suggests the face-to-face self-stacking of **2**.

For the purpose of construction of supramolecular structures with multiple metal ions, aggregation behaviors of mixtures containing **2** and metal ions were examined. For example, aggregation of the complex composed of **2** and ZnCl_2 in a mixture of CHCl_3 -cyclohexane was suggested by ^1H NMR signal broadening. AFM measurements on the mica surface eventually revealed that the aggregation is due to the formation of particle-like structures.

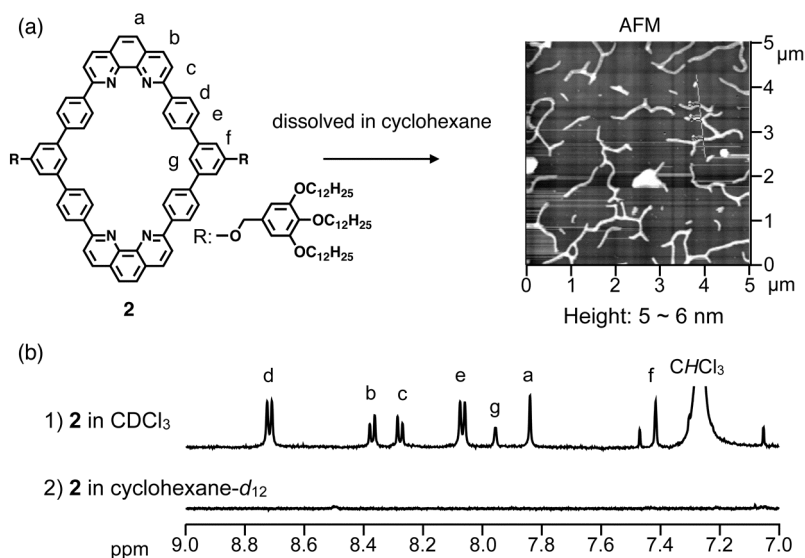


Figure 3. Aggregation behaviors of macrocycle **2** in cyclohexane; (a) chemical structure of **2** and an AFM image of a mica surface on which cyclohexane solution of **2** was dropped and dried; (b) the comparison of ^1H NMR spectra of **2** in CDCl_3 and cyclohexane- d_{12} (500 MHz, 293 K, $[\mathbf{2}] = 0.05$ mM).

Meanwhile, fibrous structures with up to micrometer-scale length were observed by AFM and transmission electron microscope (TEM) measurements of a CHCl_3 solution containing **2** and FeCl_3 (Figure 4a). To estimate the association structure, a model study was performed using FeCl_3 and a ligand 2,9-diphenyl-1,10-phenanthroline (**17**), a partial structure of macrocycle **2**. As the result, no Fe(III)-coordinating complexes of **17** were formed but a salt

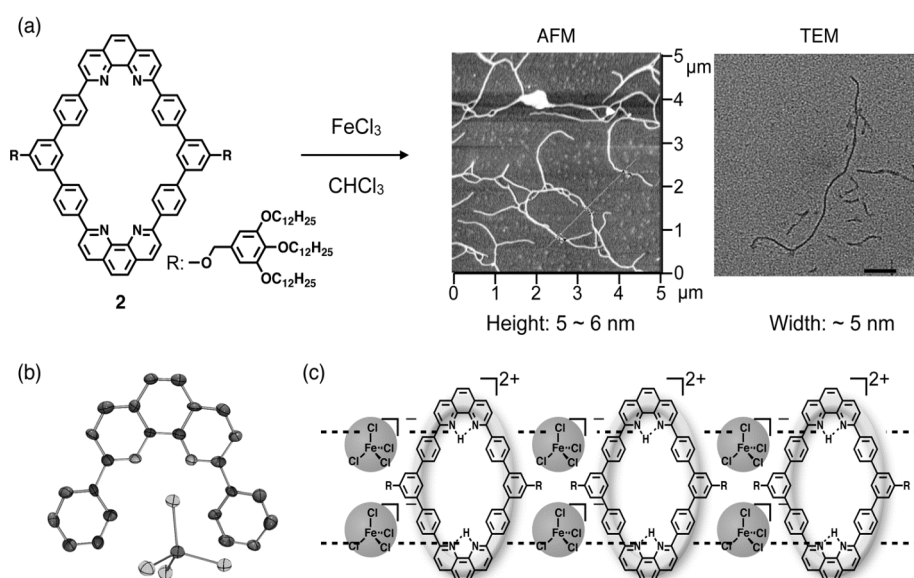


Figure 4. Aggregate formation from macrocycle **2** and FeCl_3 ; (a) chemical structure of **2** and an AFM image of a mica surface on which a CHCl_3 solution containing **2** and FeCl_3 (4.0 eq) was dropped and dried, and a TEM image (black bar: 100 nm) of support membrane on which a CHCl_3 solution containing **2** and FeCl_3 (4.0 eq) was dropped and dried; (b) X-ray structure of a salt formed from the protonated model ligand **17** and FeCl_4^- , $[\text{H}\cdot\mathbf{17}][\text{FeCl}_4]$ (hydrogen atoms are omitted for clarity.); (c) a plausible laminate structure consisting of the salt formed from protonated **2** and FeCl_4^- .

containing protonated **17** and FeCl_4^- was obtained (for the X-ray structure, see Figure 4b). This may be a result of the self-disproportionation followed by deprotonation of some Fe(III) species aquated by contaminated water, leading to the protonation of phenanthroline moieties. Thus, it is most likely that the formation of fibrous structures are not due to aggregation of endohedral Fe(III)-macrocycles but to a salt formation from protonated **2** and FeCl_4^- leading to a laminated structure (Figure 4c).

[Chapter 4: Conclusions and Perspectives]

For the purpose of constructing endohedral metallo-macrocycles and their supramolecular aggregates, I have synthesized novel macrocyclic ligands which have two chemically-equivalent, inward phenanthroline parts as metal binding sites. As the result, homo- and heterodinuclear endohedral metallo-macrocycles were efficiently and selectively constructed. Furthermore, the metal-free macrocycle was found to stack in a low polar solvent. Meanwhile, the reaction of the macrocyclic ligand and FeCl_3 provided fibrous structures, as shown in AFM and TEM measurements, which is considered from the model study to be a salt type laminate. Thus, this study demonstrates the ability of bisphenanthroline macrocycles to construct discrete and polymeric structures containing multiple metal ions from nanometer- to micrometer-scale. These supramolecular architectures would provide a clue to multi-point molecular recognition or electron conduction based on the multiple metal centers.