

## 論文の内容の要旨

# **Bisphenanthroline Macrocyclic Scaffolds for Anisotropic Metallonanofibers and Chiral Heterodinuclear $\text{Pt}^{\text{II}}\text{Cu}^{\text{I}}$ Complexes** (ビスフェナントロリン大環状分子を基盤とした 異方性金属ナノファイバーおよび キラルなヘテロ二核 $\text{Pt}^{\text{II}}\text{Cu}^{\text{I}}$ 錯体の構築)

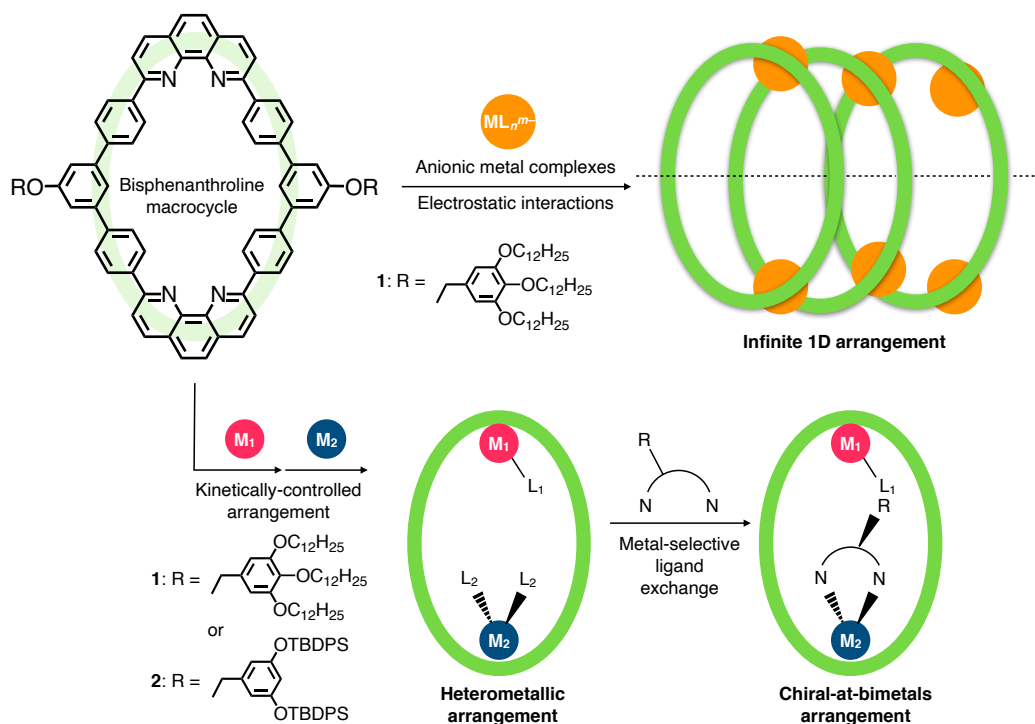
清水 駿

### **1. General introduction**

Arrangement of metal ions is the essential factor for properties and functions of natural and artificial multinuclear metal complexes. In this context, macrocyclic molecules are fascinating structural motifs in supramolecular chemistry and materials science today because of the advantages of their well-defined cavities for precise molecular arrangement and the resulting metal-surrounded confined space for unique molecular recognition and reaction fields. In general, such macrocycles are highly symmetric, and therefore their properties and self-assembling structures tend to be non-directional or isotropic. On the other hand, from the viewpoint of metal-based functional materials such as electrical nanowires and asymmetric catalysts, it is necessary to establish a general method for inducing anisotropy or asymmetry in macrocyclic metal complexes.

Our group has previously reported a bisphenanthroline macrocycle with two inward phenanthroline moieties for entrapping two metal ions in the rigid macrocyclic cavity. By utilizing the two coordination sites, a series of homometallic or heterometallic dinuclear complexes have been synthesized in thermodynamic control. For instance, the homodinuclear  $\text{Ag}^{\text{I}}$  complex was prepared to show its guest-specific molecular recognition ability,<sup>1</sup> and the homodinuclear  $\text{Pd}^{\text{II}}$  complexes were found to one-dimensionally self-assemble into  $\text{Pd}^{\text{II}}$ -assembled nanofibers.<sup>2</sup> However, the applicable metal ions were limited especially in the case of heterometallic and one-dimensional arrangement.

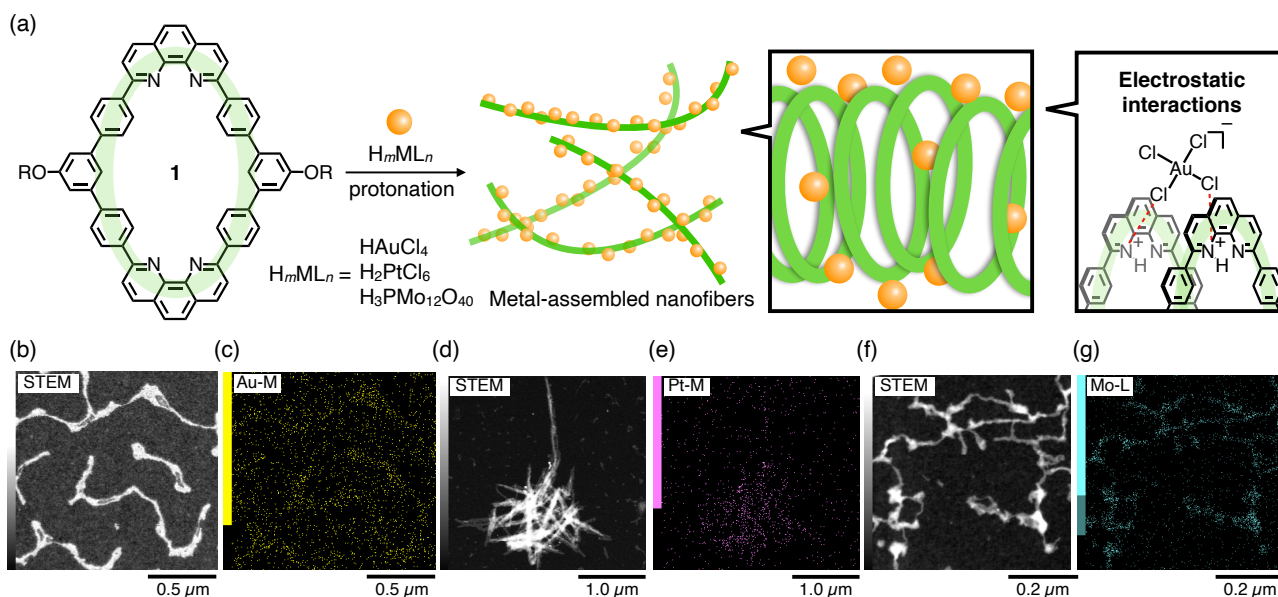
The purpose of this study was to develop a methodology for anisotropic or asymmetric arrangement of metal ions by fully utilizing the bisphenanthroline macrocycles. Here I report three systems: protonation-induced one-dimensional assembly of macrocycles arranged with metal ions, kinetically-controlled syntheses of macrocyclic heterodinuclear metal complexes, and arrangement of two different metal ions with chirality at both metal centers (Figure 1).



**Figure 1.** Outline of this research: infinite one-dimensional arrangement of anionic metal complexes, kinetically-controlled synthesis of heterodinuclear metal complexes, and construction of chiral-at-bimetals heterodinuclear complexes.

## 2. Protonation-induced self-assembly of bisphenanthroline macrocycles into metal-assembled nanofibers

Metal-assembled nanofibers were constructed by mixing bisphenanthroline macrocycle **1** and protic acids of anionic metal complexes. Studies on  $Au^{III}$ -assembled nanofibers composed of **1** and  $HAuCl_4$  revealed that two phenanthroline moieties of **1** are protonated, and electrostatic interaction between the protonated **1** and  $AuCl_4^-$  is the driving force for one-dimensional self-assembly (Fig. 2a). Their fiber structure and the alignment of  $Au^{III}$  ions along it were confirmed by the STEM-EDS analysis (Fig. 2b,c). The protonation-induced assembly was further applied to other metal-containing anions with different sizes and charge numbers, such as  $H_2PtCl_6$  and  $H_3PMo_{12}O_{40}$  as observed by STEM-EDS analyses (Fig. 2d-g).

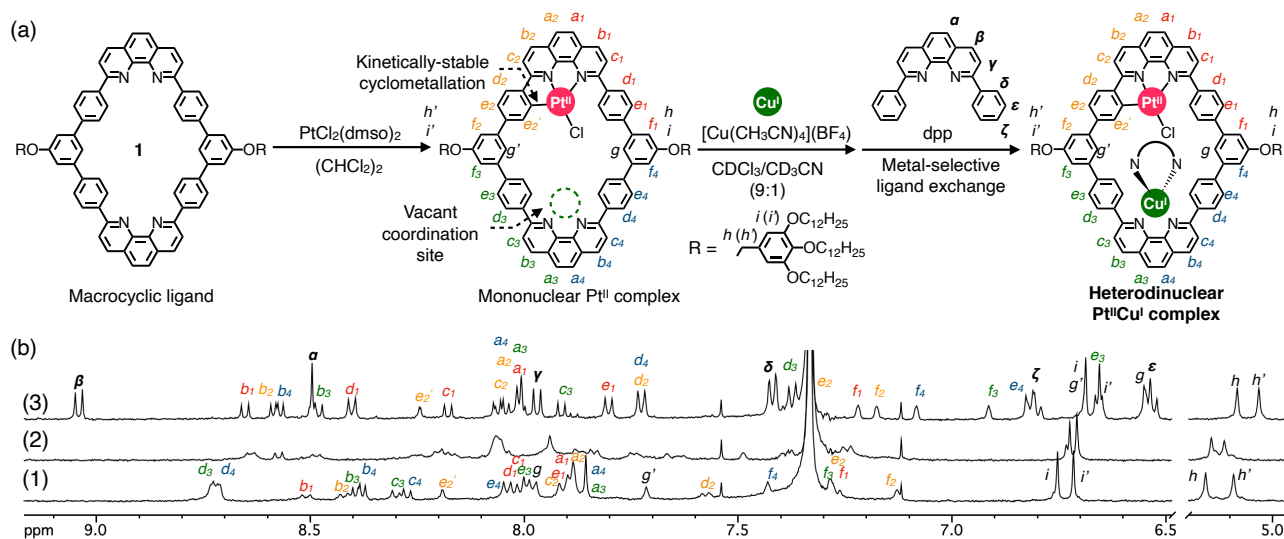


**Figure 2.** Protonation-induced one-dimensional assembly of **1** arrayed with metal ions: (a) schematic representation of the fiber formation; (b,c) a dark-field STEM image and an EDS-map for Au (M-peak) of the  $Au^{III}$ -assembled nanofibers; (d,e) a dark-field STEM image and an EDS-map for Pt (M-peak) of the  $Pt^{IV}$ -assembled nanofibers; (f,g) a dark-field STEM image and an EDS-map for Mo (L-peak) of the  $Mo^{VI}$ -assembled nanofibers.

Since the nanofibers were expected to exhibit properties derived from accumulated metal ions, chemical reduction was conducted as an application of the nanofibers. For instance, the accumulated Au<sup>III</sup> ions could be chemically reduced by NaBH<sub>4</sub> to Au nanoparticles with a relatively controlled size and dispersibility in organic solvents. On the other hand, the Mo<sup>VI</sup>-assembled nanofibers could be partially reduced by L-ascorbic to afford Mo<sup>VI</sup>/Mo<sup>V</sup> mixed-valence nanofibers. Their chemical state and fiber structures were confirmed by UV-vis spectroscopy and AFM measurements, respectively. These results suggest that the protonation-induced assembly method can be applied to various metal ions regardless of their coordination geometries, and the accumulated metal ions can show array-specific reduced states.

### 3. Kinetically controlled synthesis of bisphenanthroline macrocyclic heterodinuclear metal complexes

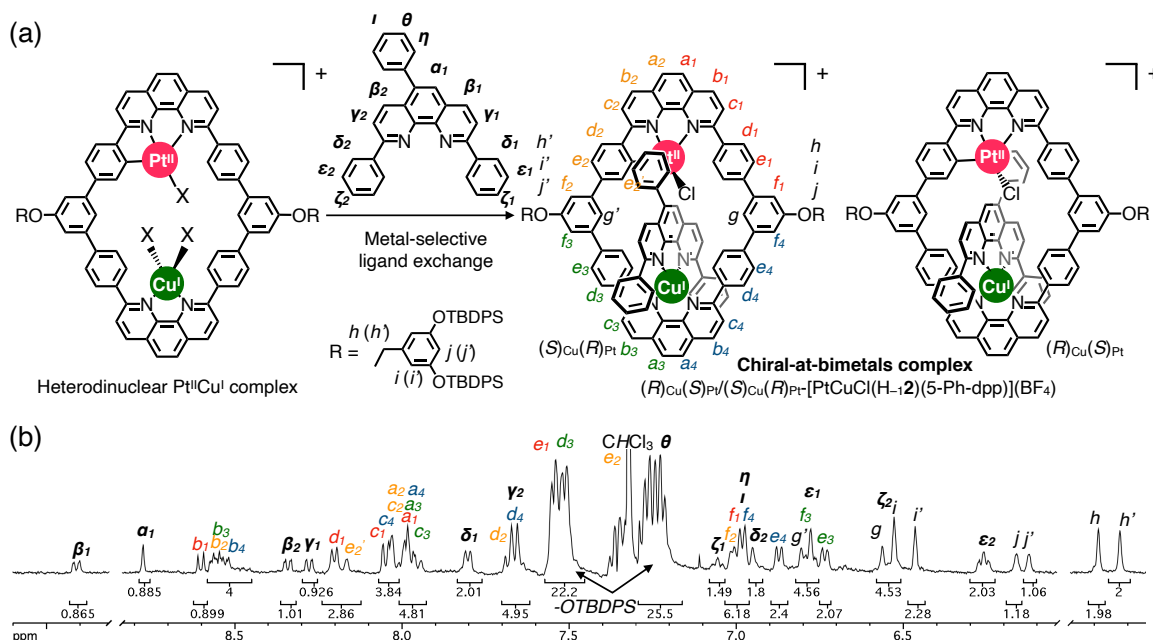
The bisphenanthroline macrocyclic ligands have been widely studied as a platform for the placement of two homogeneous metal ions, but precise synthesis of heterogeneous dinuclear metal complexes remains unexplored.<sup>3</sup> From this viewpoint, a mononuclear Pt<sup>II</sup> complex was an attractive scaffold because the kinetically stable nature of the cyclometalated Pt<sup>II</sup> center was expected to allow coordination at the vacant phenanthroline site without undergoing transmetalation (Fig. 3a). A mononuclear Pt<sup>II</sup> complex of bisphenanthroline macrocyclic ligand was prepared by reaction with PtCl<sub>2</sub>(dmsO)<sub>2</sub> and repetitive column chromatography to separate the dinuclear Pt<sup>II</sup> complexes. The binding behavior of the mononuclear [PtCl(H<sub>1</sub>1)] complex to metal ions was examined by titration experiments using Zn<sup>II</sup> or Cu<sup>I</sup> sources monitored by <sup>1</sup>H NMR spectroscopy, UV-vis spectroscopy, and ESI-MS spectrometry. In particular, it was revealed that addition of equimolar amount of [Cu(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>) in CHCl<sub>3</sub>/CH<sub>3</sub>CN (9:1) smoothly afforded a Pt<sup>II</sup>Cu<sup>I</sup> heterodinuclear complex, while signals spread indicating fast ligand exchange around the Cu<sup>I</sup> center. Therefore, the heterodinuclear structure was stabilized by the second bidentate ligands. <sup>1</sup>H NMR spectroscopy and ESI-TOF MS spectrometry showed that 1,10-phenanthroline derivatives with phenyl substituents at the α-position of the nitrogen atoms, 2,9-diphenyl-1,10-phenanthroline (dpp), could serve as stabilizer of the Cu<sup>I</sup> center against both ligand exchange and oxidation to Cu<sup>II</sup> by molecular oxygen to yield the desired heterodinuclear Pt<sup>II</sup>Cu<sup>I</sup> complex [PtCuCl(H<sub>1</sub>1)(dpp)](BF<sub>4</sub>) that is stable in air for several weeks as confirmed by <sup>1</sup>H NMR spectroscopy (Fig. 3b) and ESI-TOF MS spectrometry (*m/z* = 2756.534 for [PtCuCl(H<sub>1</sub>1)(dpp)]<sup>+</sup>).



**Figure 3.** The kinetically controlled synthesis of macrocyclic heterodinuclear complexes: (a) Synthetic scheme of macrocyclic heterodinuclear Pt<sup>II</sup>Cu<sup>I</sup> complexes; (b) <sup>1</sup>H NMR spectrum (500 MHz, 300 K, CDCl<sub>3</sub>/CD<sub>3</sub>CN = 9:1) for (1) [PtCl(H<sub>1</sub>1)], (2) [PtCuCl(H<sub>1</sub>1)(X)<sub>2</sub>](X) (X = Cl, CH<sub>3</sub>CN or CD<sub>3</sub>CN) and (3) [PtCuCl(H<sub>1</sub>1)(dpp)](BF<sub>4</sub>).

#### 4. Diastereoselective synthesis of chiral-at-bimetal heterodinuclear Pt<sup>II</sup>Cu<sup>I</sup> complexes

The less symmetrical Pt<sup>II</sup>Cu<sup>I</sup> complexes could be further applied to the synthesis of chiral-at-bimetals complexes by asymmetrically placing only achiral ligands. In other words, the effect of asymmetric induction at the tetrahedral Cu<sup>I</sup> center on the square-planar Pt<sup>II</sup> center was investigated to diastereoselectively synthesize chiral-at-bimetals heterodinuclear Pt<sup>II</sup>Cu<sup>I</sup> complexes (Fig. 4a). For this purpose, a *C<sub>s</sub>* symmetrical derivative of the dpp ligand with a phenyl group at the 5-position, 5-Ph-dpp, was introduced to the *C<sub>s</sub>* symmetrical heterodinuclear Pt<sup>II</sup>Cu<sup>I</sup> complex of a bisphenanthroline macrocyclic ligand **2** with bulky side chains. The metal-selective ligand exchange reaction could be carried out by adding 1.0 eq of 5-Ph-dpp as a secondary ligand, resulting in the complicated <sup>1</sup>H NMR signals of the chiral-at-bimetals heterodinuclear [PtCuCl(H-**2**)(5-Ph-dpp)](BF<sub>4</sub>) complex (Fig. 4b). Furthermore, the crystal structure of this complex not only showed chirality at the distorted tetrahedral Cu<sup>I</sup> center, but also at the distorted square-planar Pt<sup>II</sup> center, indicating diastereoselective formation of (*R*)<sub>Cu</sub>(*S*)<sub>Pt</sub>/(*S*)<sub>Cu</sub>(*R*)<sub>Pt</sub>-[PtCuCl(H-**2**)(5-Ph-dpp)](BF<sub>4</sub>). This unprecedented diastereoselectivity could be attributed to the low stability of the opposite (*R*)<sub>Cu</sub>(*R*)<sub>Pt</sub>/(*S*)<sub>Cu</sub>(*S*)<sub>Pt</sub>-isomers due to the steric hindrance between the bulky 5-phenyl group of the secondary ligand and the rigid macrocyclic framework.



**Figure 4.** The diastereoselective synthesis of chiral-at-bimetals heterodinuclear Pt<sup>II</sup>Cu<sup>I</sup> complexes: (a) Synthetic scheme of the chiral-at-bimetals heterodinuclear (*R*)<sub>Cu</sub>(*S*)<sub>Pt</sub>/(*S*)<sub>Cu</sub>(*R*)<sub>Pt</sub>-[PtCuCl(H-**2**)(5-Ph-dpp)](BF<sub>4</sub>) complexes; (b) <sup>1</sup>H NMR spectrum (500 MHz, 300 K, CDCl<sub>3</sub>/CD<sub>3</sub>CN = 9:1) for the racemic mixture of (*R*)<sub>Cu</sub>(*S*)<sub>Pt</sub>/(*S*)<sub>Cu</sub>(*R*)<sub>Pt</sub>-[PtCuCl(H-**2**)(5-Ph-dpp)](BF<sub>4</sub>).

#### 5. Conclusions and perspectives

In this study, anisotropic and asymmetric arrangement of metal ions with symmetric bisphenanthroline macrocycle was achieved in three ways: protonation-induced formation of metal-assembled nanofibers, sequential introduction of two different metal ions to synthesize macrocyclic heterodinuclear complexes, and the diastereoselective synthesis of chiral-at-bimetals a heterodinuclear Pt<sup>II</sup>Cu<sup>I</sup> complex. These findings would provide clues for developing unique anisotropic or asymmetric materials with macrocyclic building blocks such as electronical nanofibers, highly anisotropic metal clusters synthesis, and unprecedented asymmetric catalysts based on the heterometallic arrangement.

#### References

- [1] M. Shionoya *et al.*, *J. Am. Chem. Soc.* **2014**, *136*, 17946–17949.
- [2] M. Shionoya *et al.*, *Chem. Asian J.* **2013**, *8*, 1368–1371.
- [3] M. Shionoya *et al.*, *Inorg. Chem.* **2012**, *51*, 1508–1515.