

## 論文内容の要旨

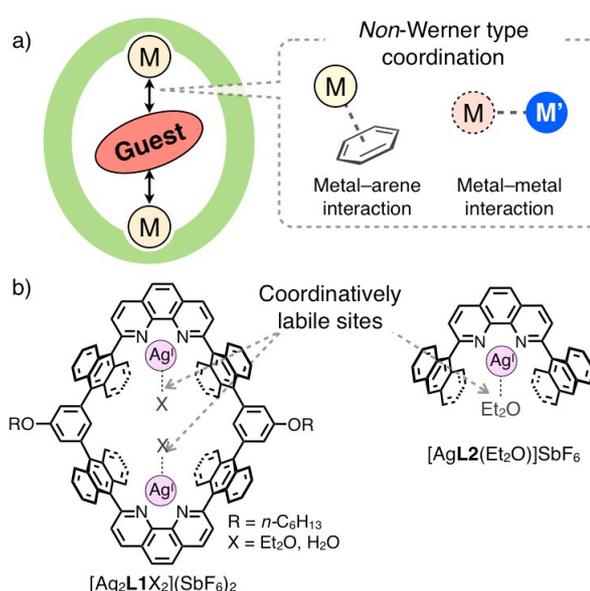
# Multipoint Molecular Recognition through *Non-Werner* Type Coordination Bonding by Ag(I)-Macrocycles

(Ag(I)大環状化合物による非ウェルナー型配位結合を用いた多点分子認識)

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### 1. Introduction

Macrocycles provide functional nano-spaces for molecular recognition and chemical reactions depending on their size, shape, and chemical properties of the inner surface. To construct functional nano-spaces, it is important to precisely arrange functional groups within the inner surfaces of their covalently-linked skeletons. In particular, metal ions have been widely used as function centers within nano-spaces taking advantage of their chemical and physical properties such as Lewis acidity, redox reactivity, and electrostatic natures etc. So far, a large number of excellent examples of metallo-macrocycles have been reported which utilize Werner type coordination as a driving force for guest binding or activation. However, metallo-macrocycles which utilize *non-Werner* type coordination for functions have not been extensively investigated so far (Figure 1a). *Non-Werner* type coordination, such as metal–arene and metal–metal interactions, is one of the most attractive coordination modes of metal ions, which exhibits coordination structures and reactivities quite distinct from conventional Werner type coordination. Herein, I report that molecular nano-spaces arranged with coordinatively labile sites of metal centers provide platforms for host-guest complexation aided by *non-Werner* type binding to exhibit unique structures, selectivity, and properties.



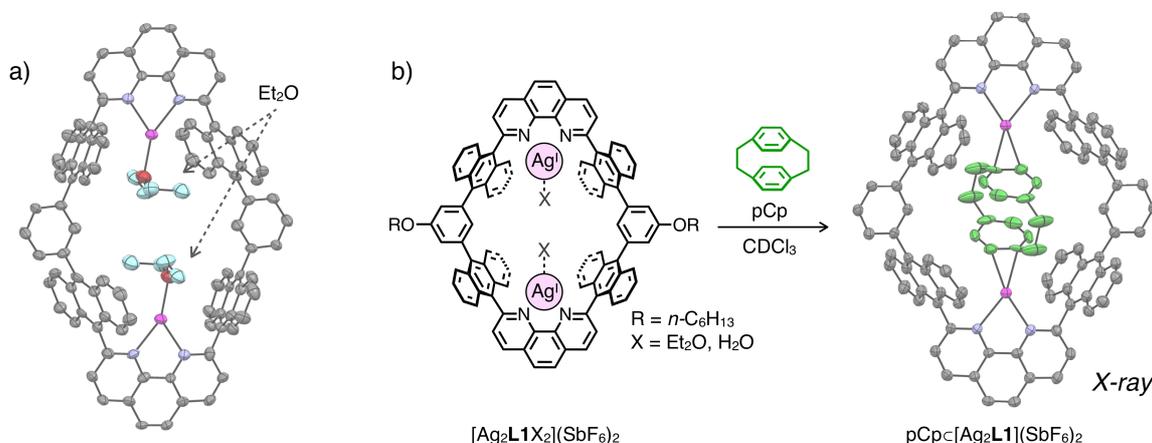
**Figure 1.** a) Metallo-macrocycle with *non-Werner* type coordination centers, b) molecular structures of metallo-hosts with Ag(I) ions.

With a view to developing host-guest systems based on *non*-Werner type coordination, I have prepared a dinuclear Ag(I)-macrocyclic  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  ( $\text{X} = \text{Et}_2\text{O}$  or  $\text{H}_2\text{O}$ ) and a mononuclear Ag(I)-half-macrocycle  $[\text{AgL2}(\text{Et}_2\text{O})]\text{SbF}_6$  as metallo-hosts (Figure 1b). These hosts possess anthracene-based nano-spaces arranged with coordinatively labile sites of one or two Ag(I) ions bound to the inner surfaces. These binding sites showed a high affinity toward aromatic  $\pi$ -planes and Lewis basic metal ions. In this study, I demonstrated host-guest chemistry using *non*-Werner type coordination specific to Ag(I) ion: Ag- $\pi$  and Ru-Ag bonding as the driving forces for guest binding.

## 2. Inclusion of aromatic molecules within a dinuclear Ag(I)-macrocyclic via multipoint Ag- $\pi$ interactions

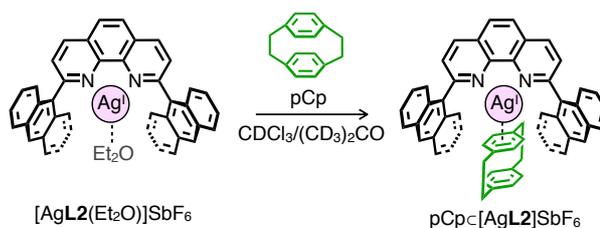
A dinuclear Ag(I)-macrocyclic was prepared and isolated as 1:1 co-crystals of  $[\text{Ag}_2\text{L1}(\text{Et}_2\text{O})_2](\text{SbF}_6)_2$  and  $[\text{Ag}_2\text{L1}(\text{H}_2\text{O})_2](\text{SbF}_6)_2$  by the complexation between **L1** and 4.0 eq of  $\text{AgSbF}_6$  in  $\text{CHCl}_3/(\text{CH}_3)_2\text{CO}$  followed by recrystallization by  $\text{Et}_2\text{O}$  vapor diffusion (Figure 2a). In the resulting crystal structure, two Ag(I) ions are bound within the inner surface of the macrocycle in about 9 Å apart from each other. Within the nano-space, each Ag(I) ion adapts trigonal planar coordination geometry with two phenanthroline nitrogens and oxygen of solvent ( $\text{Et}_2\text{O}$  or  $\text{H}_2\text{O}$ ) to provides a nano-space with a face-to-face arrangement of coordinatively labile sites of Ag(I) ions.

$[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  ( $\text{X} = \text{Et}_2\text{O}$  or  $\text{H}_2\text{O}$ ) shows significant affinity to [2.2]paracyclophane (pCp) which has a sandwich-shaped aromatic molecules to create a 1:1 host-guest complex  $\text{pCp}[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  in  $\text{CDCl}_3$  as revealed by NMR spectroscopy and ESI-TOF mass spectrometry ( $m/z = 918.80$  as  $\text{pCp}[\text{Ag}_2\text{L1}]^{2+}$ ) (Figure 2b). Notably, the binding constant  $K_a$  between  $[\text{Ag}_2\text{L1X}_2]^{2+}$  and pCp ( $K_a = [\text{guest}[\text{host}]/([\text{guest}][\text{host}]) \text{ M}^{-1}]$ ) was estimated to be as high as over  $10^9 \text{ M}^{-1}$  in  $\text{CDCl}_3$  at 300 K by  $^1\text{H}$  NMR titration experiment in the presence of competing guest molecule. The structure of the resulting complex revealed that pCp was bound to the Ag(I) centers within the nano-space via  $\eta^2$ -type Ag- $\pi$  multipoint interactions (Figure 2b right).



**Figure 2.** a) Crystal structure of  $[\text{Ag}_2\text{L1}(\text{Et}_2\text{O})_2](\text{SbF}_6)_2$  and b) host-guest interaction between  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  and pCp (the solvent molecules, side-alkyl chains, hydrogen atoms, and counter anions are omitted for clarity).

Based on this fact, the origin of such strong host-guest interaction between  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  and pCp was investigated to further develop a Ag- $\pi$  interaction-based host-guest system. Firstly, control experiments using dinuclear metal macrocycles with different metal centers  $[\text{M}_2\text{L1X}_n]^{m+}$  ( $\text{M} = \text{Hg}(\text{II}), \text{Cu}(\text{I}), \text{Zn}(\text{II}), \text{X} = \text{solvent or anion}$ ) or macrocyclic ligand **L1** itself as hosts were conducted to investigate the contribution of Ag- $\pi$  interactions to the strong binding



**Figure 3.** Host-guest interaction between pCp and  $[\text{AgL2}(\text{Et}_2\text{O})]\text{SbF}_6$ .

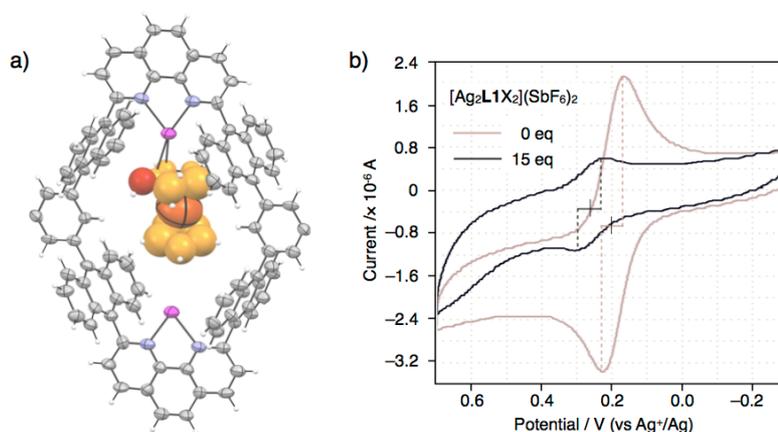
of pCp. As a result, neither **L1** nor  $[M_2L1X_n]^{m+}$  ( $M = \text{Hg(II)}, \text{Cu(I)}, \text{Zn(II)}$ ,  $X = \text{solvent or anion}$ ) exhibited any binding behaviors to pCp in  $\text{CDCl}_3/(\text{CD}_3)_2\text{CO}$  at 300 K, suggesting  $\text{Ag}-\pi$  interactions play as a central driving force for the pCp binding. Next, the effect of the confined cyclic cavity of  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  on the strong binding of pCp was evaluated by a control experiment using a mononuclear  $\text{Ag(I)}$ -half-macrocycle  $[\text{AgL2}(\text{Et}_2\text{O})]\text{SbF}_6$  as a host (Figure 3).  $^1\text{H}$  NMR titration experiment revealed that the 1:1 binding constant of  $[\text{AgL2}(\text{Et}_2\text{O})]\text{SbF}_6$  to pCp ( $K'_a = (1.9 \pm 0.5) \times 10^4 \text{ M}^{-1}$  in  $\text{CDCl}_3/(\text{CD}_3)_2\text{CO}$  at 300 K) was much smaller than that of  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  ( $K_a > 10^9 \text{ M}^{-1}$  in  $\text{CDCl}_3$  at 300 K). This suggests that the arrangement of  $\text{Ag(I)}$  ions within the macrocyclic cavity of  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  is in the right position to bind aromatic molecules via  $\text{Ag}-\pi$  interaction in a ditopic manner.

In summary, it was suggested that *non*-Werner type coordination centers arranged within the nano-space of  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  can work as useful structural motifs to recognize aromatic molecules which do not have hetero donor atoms in ditopic manners, taking advantage of the arrangement mode and unique coordination characters of the central  $\text{Ag(I)}$  ions.

### 3. Binding of redox reactive organometallic molecules

Guest molecules included in host molecules can often exhibit unique reactivities or physical properties due to the close interaction with the inner surfaces. Herein, I report that the dinuclear  $\text{Ag(I)}$ -macrocycle  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  ( $X = \text{Et}_2\text{O}$  or  $\text{H}_2\text{O}$ ) can also bind to a redox reactive organometallic molecule, ferrocene ( $\text{FeCp}_2$ ) and its derivatives, in a way similar to pCp. Notably, the host-guest interaction induced a significant change in the redox reactivity of  $\text{FeCp}_2$ .

The binding behavior of  $\text{FeCp}_2$  was investigated by NMR spectroscopy and ESI-TOF mass spectrometry ( $m/z = 907.08$  as  $\text{FeCp}_2\text{C}[\text{Ag}_2\text{L1}]^{2+}$ ). From  $^1\text{H}$  NMR titration experiments, the binding constant was estimated to be  $K_a = (6.2 \pm 0.9) \times 10^4 \text{ M}^{-1}$  at 300 K in  $\text{CDCl}_3$ . The crystal structure of the inclusion complex with a ferrocene derivative  $\text{FeCp}_2'\text{C}[\text{Ag}_2\text{L1}](\text{SbF}_6)_2$  ( $\text{FeCp}_2'$ : hydroxymethyl ferrocene) revealed the formation of a 1:1 host-guest complex, in which the  $\pi$ -planes of disordering Cp rings bound to  $\text{Ag(I)}$  centers via  $\text{Ag}-\pi$  interaction (Figure 4a). Then, the redox property of  $\text{FeCp}_2$  within  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  was investigated by cyclic voltammetry (Figure 4b). As the result, the redox potential of  $\text{FeCp}_2$  showed anodic shift (ca. +70 mV) upon mixing  $\text{FeCp}_2$  and 15 eq of  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$ . This indicates that the  $\text{FeCp}_2$  became difficult to be oxidized when it is included in the cavity and put between the two cationic  $\text{Ag(I)}$  centers. Thus,  $\text{Ag}-\pi$  interaction with well arranged  $\text{Ag(I)}$  ions has great potential to control the electrochemical property and reactivity of aromatic guest molecules which fit to the macrocyclic cavity.



**Figure 4.** a) Crystal structure of  $\text{FeCp}_2'\text{C}[\text{Ag}_2\text{L1}](\text{SbF}_6)_2$  (the solvent molecules, side-alkyl chains, and counter anions are omitted for clarity). b) Cyclic voltammograms of  $\text{FeCp}_2$  (200  $\mu\text{M}$ ) in the presence of 0–15 eq of  $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$  in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $\text{TBAPF}_6$  at 291 K.

### 4. Host-guest interaction via metal-to-metal dative bonding between mononuclear $\text{Ag(I)}$ -half-macrocycle and ruthenocene

Metal-to-metal dative bonding, formed between Lewis acidic and Lewis basic metal centers, can work as an effective driving force to construct supramolecular architectures, which would possibly exhibit structural and electronic properties specific to coupled hetero metal centers. In order to utilize metal-to-metal dative bonding to molecular recognition, host-guest complexation between a Lewis acidic mononuclear  $\text{Ag(I)}$ -half-macrocycle

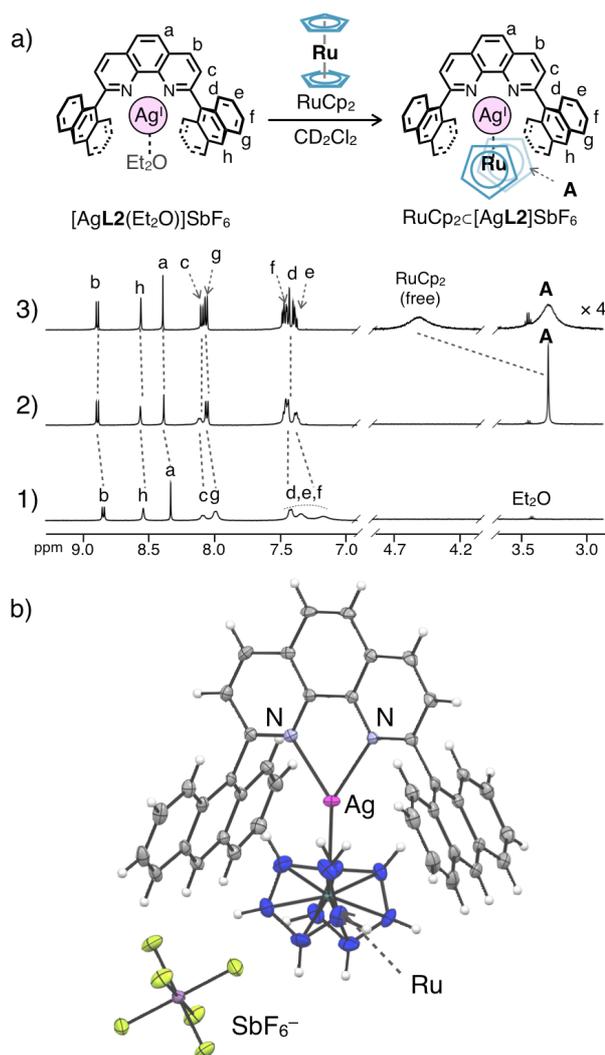
[AgL2(Et2O)]SbF6 and Lewis basic ruthenocene (RuCp2) which has a sterically accessible Ru(II) center was investigated.

Upon addition of RuCp2 as a guest molecule to a solution of [AgL2(Et2O)]SbF6 in CD2Cl2, 1H NMR signals were significantly shifted (Figure 5a). The binding of RuCp2 to the Ag(I) center was suggested by the significant up-field shift of the signals of RuCp2 (HA in Figure 4a) due to the strong shielding effect from the neighboring anthracene walls. From the integral ratio of the 1H NMR signals of the resulting complex at 210 K, the formation of a 1:1 host-guest complex RuCp2C[AgL2]SbF6 was suggested, as was supported by ESI-TOF mass spectrometry ( $m/z = 873.38$  as  $\text{RuCp}_2\text{C}[\text{AgL}_2]^+$ ). The molecular structure of  $\text{RuCp}_2\text{C}[\text{AgL}_2]^+$  was finally determined by single crystal X-ray analysis (Figure 5b). In the crystal structure, one molecule of RuCp2 binds to the Ag(I) center of [AgL2]+ via Ag–Ru type dative bonding (Ru–Ag: 2.782(0) Å) with a significant tilting of the two Cp rings. The binding constant for host-guest complexation ( $K_a = [\text{guest}\text{C}\text{host}]/([\text{guest}][\text{host}]) \text{ M}^{-1}$ ) was estimated to be over  $10^4 \text{ M}^{-1}$  in CD2Cl2 at 300 K, which is comparable to those reported for non-substituted metallocene binding to host molecules in non-polar solvents. Notably, neither ligand L2 itself nor metallo-hosts with some other metal centers [ML2Xn]m+ (M = Zn(II), Cu(I), X = anion or solvent) exhibited any binding behaviors to RuCp2, which suggests Ru–Ag type dative bonding works as an essential driving force for the guest binding.

These observations suggest a proper combination of Lewis acidic and basic metal centers would enable construction of host-guest complexes based on metal–metal interactions.

## 5. Conclusion

With a purpose of developing *non*-Werner type coordination as driving force for host-guest complexation, I prepared dinuclear Ag(I)-macrocycle [Ag2L1X2](SbF6)2 (X = Et2O or H2O) and mononuclear Ag(I)-half-macrocycle [AgL2(Et2O)]SbF6 which have anthracene-based nano-spaces arranged with Ag(I) ions. These metallo-hosts exhibit excellent binding abilities to aromatic molecules or a Lewis basic organometallic molecule via *non*-Werner type coordination: Ag– $\pi$  interaction or Ru–Ag dative bonding as driving forces. Furthermore, in the case of host-guest complex  $\text{FeCp}_2\text{C}[\text{Ag}_2\text{L}_1]^{2+}$ , the electrochemical behavior of FeCp2 was markedly modified due to the close interaction with the cationic Ag(I) centers. Thus, nano-spaces equipped with *non*-Werner type coordination centers provide novel binding motifs for host-guest complexation with unique structures and properties. Such nano-spaces are expected to provide a novel strategy to create guest activation sites taking advantage of specific reactivities of well-defined *non*-Werner type coordination centers.



**Figure 5.** a)  $^1\text{H}$  NMR spectra (500 MHz, 300 K in  $\text{CD}_2\text{Cl}_2$ ) of  $[\text{AgL}_2(\text{Et}_2\text{O})]\text{SbF}_6$  (1.1 mM) in the presence of 1) 0.0, 2) 1.0, and 3) 2.0 equiv. of  $\text{RuCp}_2$ . b) The crystal structure of  $\text{RuCp}_2\text{C}[\text{AgL}_2]\text{SbF}_6$  (the solvent molecules are omitted for clarity).