

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.

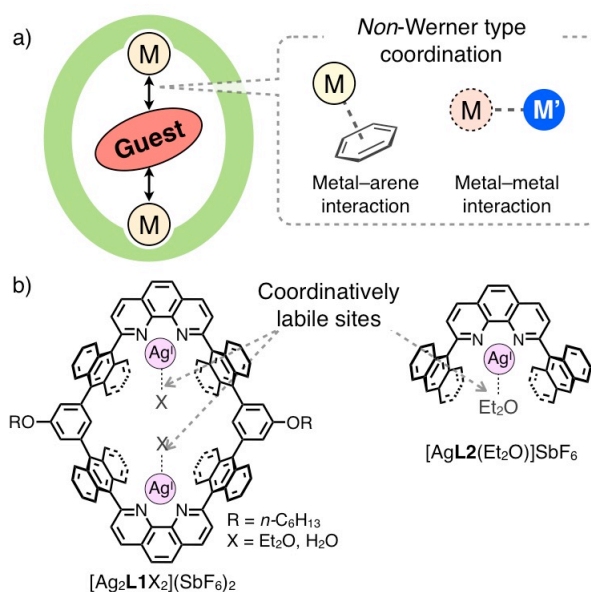


Figure 1. a) Metallo-macrocycle with *non-Werner type* coordination centers, b) molecular structures of metallo-hosts with Ag(I) ions.

With a view to developing host-guest systems based on *non*-Werner type coordination, I have prepared a dinuclear Ag(I)-macrocycle $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$ ($\text{X} = \text{Et}_2\text{O}$ or H_2O) 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 π -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- π and Ru-Ag bonding as the driving forces for guest binding.

2. Inclusion of aromatic molecules within a dinuclear Ag(I)-macrocycle via multipoint Ag- π interactions

A dinuclear Ag(I)-macrocycle 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 AgSbF_6 in $\text{CHCl}_3/(\text{CH}_3)_2\text{CO}$ followed by recrystallization by Et_2O 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 (Et_2O or H_2O) 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 H_2O) shows significant affinity to [2.2]paracyclophane (pCp) which has a sandwich-shaped aromatic molecules to create a 1:1 host-guest complex $\text{pCp} \subset [\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$ in CDCl_3 as revealed by NMR spectroscopy and ESI-TOF mass spectrometry ($m/z = 918.80$ as $\text{pCp} \subset [\text{Ag}_2\text{L1}]^{2+}$) (Figure 2b). Notably, the binding constant K_a between $[\text{Ag}_2\text{L1X}_2]^{2+}$ and pCp ($K_a = [\text{guest} \subset \text{host}] / ([\text{guest}][\text{host}]) \text{ M}^{-1}$) was estimated to be as high as over 10^9 M^{-1} in CDCl_3 at 300 K by ^1H 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 η^2 -type Ag- π multipoint interactions (Figure 2b right).

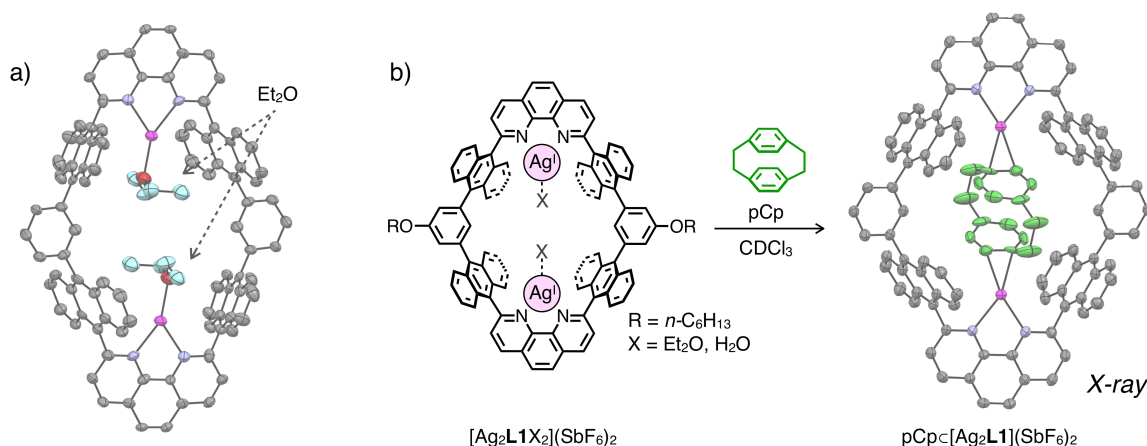


Figure 2. a) Crystal structure of $[\text{Ag}_2\text{L1}(\text{Et}_2\text{O})_2](\text{SbF}_6)_2$ and b) host-guest interaction between $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$ and pCp (the solvent molecules, side-alkyl chains, hydrogen atoms, and counter anions are omitted for clarity).

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- π 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- π interactions to the strong binding

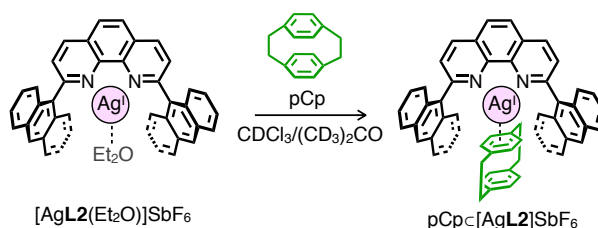


Figure 3. Host-guest interaction between pCp and $[\text{AgL2}(\text{Et}_2\text{O})]\text{SbF}_6$.

of pCp. As a result, neither **L1** nor $[M_2L_1X_n]^{m+}$ ($M = \text{Hg(II)}, \text{Cu(I)}, \text{Zn(II)}$, $X = \text{solvent or anion}$) 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 $[\text{Ag}_2L_1X_2](\text{SbF}_6)_2$ on the strong binding of pCp was evaluated by a control experiment using a mononuclear Ag(I)-half-macrocycle $[\text{Ag}L_2(\text{Et}_2\text{O})]\text{SbF}_6$ as a host (Figure 3). ^1H NMR titration experiment revealed that the 1:1 binding constant of $[\text{Ag}L_2(\text{Et}_2\text{O})]\text{SbF}_6$ 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 $[\text{Ag}_2L_1X_2](\text{SbF}_6)_2$ ($K_a > 10^9 \text{ M}^{-1}$ in CDCl_3 at 300 K). This suggests that the arrangement of Ag(I) ions within the macrocyclic cavity of $[\text{Ag}_2L_1X_2](\text{SbF}_6)_2$ 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 $[\text{Ag}_2L_1X_2](\text{SbF}_6)_2$ 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 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 Ag(I)-macrocycle $[\text{Ag}_2L_1X_2](\text{SbF}_6)_2$ ($X = \text{Et}_2\text{O}$ or H_2O) can also bind to a redox reactive organometallic molecule, ferrocene (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 FeCp_2 .

The binding behavior of FeCp_2 was investigated by NMR spectroscopy and ESI-TOF mass spectrometry ($m/z = 907.08$ as $\text{FeCp}_2\text{C}[\text{Ag}_2L_1]^{2+}$). From ^1H 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 CDCl_3 . The crystal structure of the inclusion complex with a ferrocene derivative $\text{FeCp}_2'\text{C}[\text{Ag}_2L_1](\text{SbF}_6)_2$ (FeCp_2' : hydroxymethyl ferrocene) revealed the formation of a 1:1 host-guest complex, in which the π -planes of disordering Cp rings bound to Ag(I) centers via $\text{Ag}-\pi$ interaction (Figure 4a). Then, the redox property of FeCp_2 within $[\text{Ag}_2L_1X_2](\text{SbF}_6)_2$ was investigated by cyclic voltammetry (Figure 4b). As the result, the redox potential of FeCp_2 showed anodic shift (ca. +70 mV) upon mixing FeCp_2 and 15 eq of $[\text{Ag}_2L_1X_2](\text{SbF}_6)_2$. This indicates that the FeCp_2 became difficult to be oxidized when it is included in the cavity and put between the two cationic Ag(I) centers. Thus, $\text{Ag}-\pi$ interaction with well arranged Ag(I) ions has great potential to control the electrochemical property and reactivity of aromatic guest molecules which fit to the macrocyclic cavity.

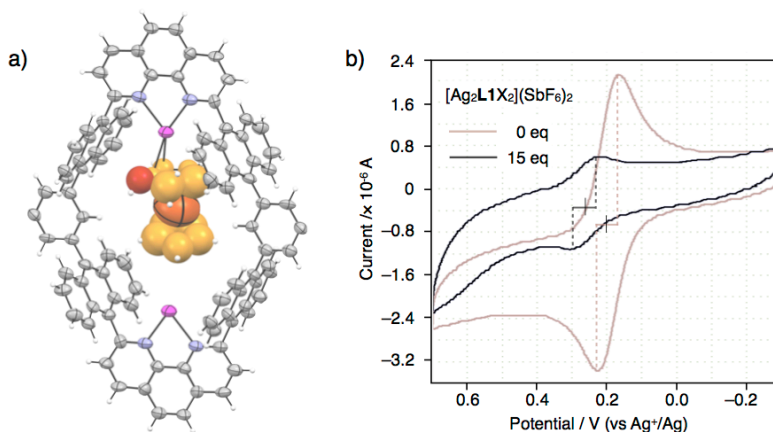


Figure 4. a) Crystal structure of $\text{FeCp}_2'\text{C}[\text{Ag}_2L_1](\text{SbF}_6)_2$ (the solvent molecules, side-alkyl chains, and counter anions are omitted for clarity). b) Cyclic voltammograms of FeCp_2 (200 μM) in the presence of 0–15 eq of $[\text{Ag}_2L_1X_2](\text{SbF}_6)_2$ in CH_2Cl_2 containing 0.1 M TBAPF₆ at 291 K.

4. Host-guest interaction via metal-to-metal dative bonding between mononuclear 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 Ag(I)-half-macrocycle

$[\text{AgL2}(\text{Et}_2\text{O})]\text{SbF}_6$ and Lewis basic ruthenocene (RuCp_2) which has a sterically accessible $\text{Ru}(\text{II})$ center was investigated.

Upon addition of RuCp_2 as a guest molecule to a solution of $[\text{AgL2}(\text{Et}_2\text{O})]\text{SbF}_6$ in CD_2Cl_2 , ^1H NMR signals were significantly shifted (Figure 5a). The binding of RuCp_2 to the $\text{Ag}(\text{I})$ center was suggested by the significant up-field shift of the signals of RuCp_2 (H_A 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 $\text{RuCp}_2\subset[\text{AgL2}]\text{SbF}_6$ was suggested, as was supported by ESI-TOF mass spectrometry ($m/z = 873.38$ as $\text{RuCp}_2\subset[\text{AgL2}]^+$). The molecular structure of $\text{RuCp}_2\subset[\text{AgL2}]^+$ was finally determined by single crystal X-ray analysis (Figure 5b). In the crystal structure, one molecule of RuCp_2 binds to the $\text{Ag}(\text{I})$ center of $[\text{AgL2}]^+$ 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 ($K_\text{a} = [\text{guest}\subset\text{host}]/([\text{guest}][\text{host}]) \text{ M}^{-1}$) was estimated to be over 10^4 M^{-1} in CD_2Cl_2 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 $[\text{ML2X}_n]^{m+}$ ($\text{M} = \text{Zn}(\text{II}), \text{Cu}(\text{I}), \text{X} = \text{anion or solvent}$) exhibited any binding behaviors to RuCp_2 , 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 $\text{Ag}(\text{I})$ -macrocycle $[\text{Ag}_2\text{L1X}_2](\text{SbF}_6)_2$ ($\text{X} = \text{Et}_2\text{O}$ or H_2O) and mononuclear $\text{Ag}(\text{I})$ -half-macrocycle $[\text{AgL2}(\text{Et}_2\text{O})]\text{SbF}_6$ which have anthracene-based nano-spaces arranged with $\text{Ag}(\text{I})$ ions. These metallo-hosts exhibit excellent binding abilities to aromatic molecules or a Lewis basic organometallic molecule via *non*-Werner type coordination: $\text{Ag}-\pi$ interaction or Ru-Ag dative bonding as driving forces. Furthermore, in the case of host-guest complex $\text{FeCp}_2\subset[\text{Ag}_2\text{L1}]^{2+}$, the electrochemical behavior of FeCp_2 was markedly modified due to the close interaction with the cationic $\text{Ag}(\text{I})$ 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.

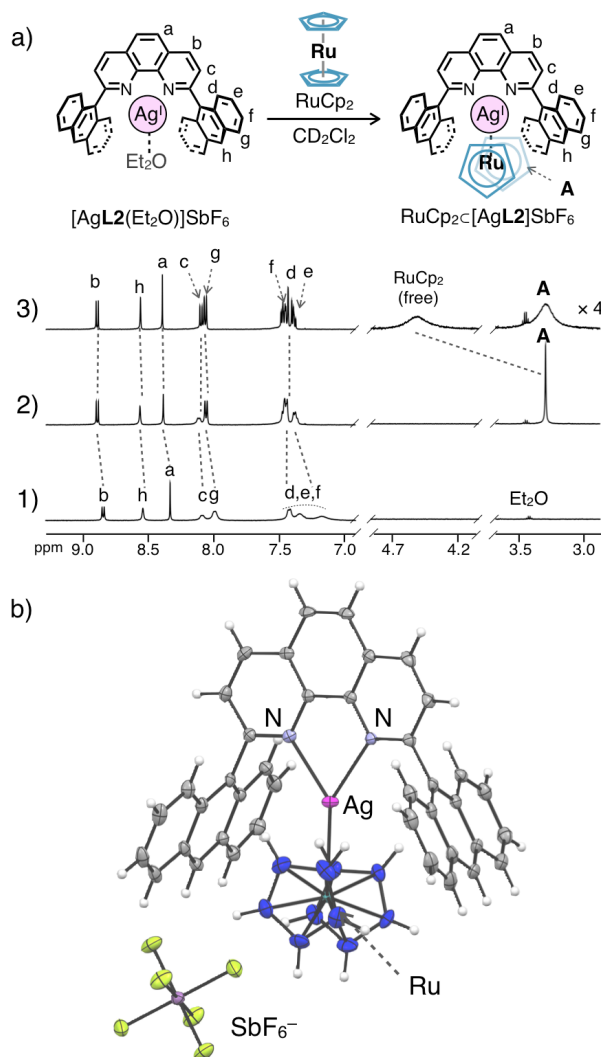


Figure 5. a) ^1H NMR spectra (500 MHz, 300 K in CD_2Cl_2) of $[\text{AgL2}(\text{Et}_2\text{O})]\text{SbF}_6$ (1.1 mM) in the presence of 1) 0.0, 2) 1.0, and 3) 2.0 equiv. of RuCp_2 . b) The crystal structure of $\text{RuCp}_2\subset[\text{AgL2}]\text{SbF}_6$ (the solvent molecules are omitted for clarity).