Multipoint Recognition of Ditopic Aromatic Guest Molecules via Ag−π Interactions within a Dimetal Macrocycle

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S *Supporting Information*

ABSTRACT: A macrocyclic host molecule possessing a nanocavity with two Ag^I centers for guest binding and four anthracene walls has been developed. This dimetal-macrocycle forms stable inclusion complexes with ditopic aromatic guest molecules, [2.2]paracyclophane, and ferrocene, in solution and/or in the solid state through Ag−π interactions within the nanocavity. The binding constants for the inclusion complexes were found to range roughly from 10^4 to 10^9 M^{-1}. Electrochemical measurement revealed that the oxidized form of the included cationic ferrocene was less stabilized due to the direct binding to the cationic two Ag^I centers.

Figure 1. Chemical structures of (a) a macrocyclic ligand **L1**, (b) a dinuclear Ag^I-macrocycle $[Ag_2L1X_2](SbF_6)_2$, and (c) schematic representation of binding modes of the inclusion complexes.

Transition metal centers of macrocyclic ligands have been widely used as a site for molecular recognition and activation.[1−9] So far, a large number of excellent examples of functional metal macrocycles have been reported taking advantage of chemical or physical properties of transition metals such as redox reactivity[1] or photoreactivity,[2] magnetism,[3] Lewis acidity,[4] and electrostatic properties.[5] In particular, metal macrocycles possessing a nanospace with a coordinatively labile site of the metal center[6] have great potential for molecular recognition,[7] array,[8] and activation[9] of guest molecules that directly bind to metal centers. In this regard, it is a challenge to arrange multiple metal centers within a macrocycle for metal-mediated multipoint recognition of guest molecules.

Metal binding with aromatic π-planes provides unique structural and electronic characteristics of the metal complexes which are distinct from those of Werner-type metal complexes.[10,11] We then envisioned a new coordination mode which can be used as a glue for host−guest binding in a confined space with high stability and modified chemical properties.[10] The Ag^I ion is well-known to bind to the periphery of many types of aromatic hydrocarbons through Ag−π interactions.[12] Moreover, the coordinatively labile nature of the Ag^I ion[7d,13] in host compounds possibly provides a platform for guest binding sites to construct thermodynamically stable assemblies. Herein we report a dinuclear Ag^I-macrocycle $[Ag_2L1X_2](SbF_6)_2$ (X = Et_2O or H_2O) with two Ag^I centers in the cavity which exhibits highly effective binding of ditopic aromatic guest molecules through multipoint Ag−π interactions (Figure 1).

Recently, we have reported that a diamond-shape macrocyclic ligand with two phenanthroline metal binding sites provides dinuclear metal complexes with Cu^I, Zn^{II}, or Pd^{II}.[14] Based on this macrocyclic skeleton, we newly synthesized a cyclophane-type macrocyclic ligand **L1** and its dinuclear Ag^I complex (Figure
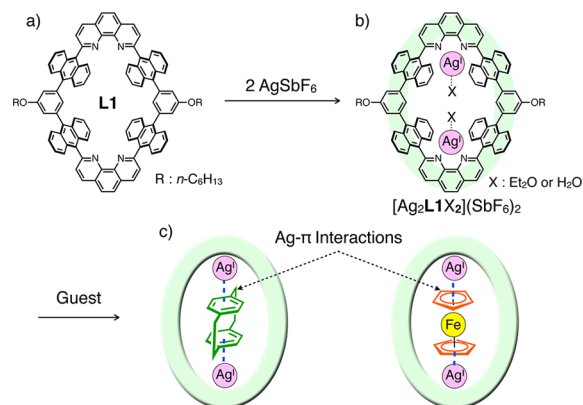
1a,b). Ligand **L1** possesses four anthracenes which are nearly orthogonal to the macrocyclic plane to provide a three-dimensional thick cavity for guest binding.[2c,15] The dinuclear Ag^I complex of **L1** forms a highly stable inclusion complex with a ditopic guest, [2.2]paracyclophane,[16] through multipoint Ag−π interactions in the cavity (Figure 1c). Ferrocene, a sandwich-shape metal complex, was also included into the cavity, and thereby its redox behavior was significantly influenced.[17]

Ligand **L1** was prepared by coupling phenanthrolines, anthracenes, and *m*-phenylene fragments sequentially by the Suzuki-Miyaura coupling method (see the Supporting Information (SI)). The final cyclization yield was 5%, and the resulting **L1** was characterized by NMR spectroscopy and high-resolution mass spectrum (Figures S4−S9). A dinuclear Ag^I-macrocycle was isolated in 63% yield as a 1:1 cocrystal consisting of $[Ag_2L1(Et_2O)_2](SbF_6)_2$ and $[Ag_2L1(H_2O)_2](SbF_6)_2$ by complexation of **L1** with 4.0 eq of $AgSbF_6$ in $CHCl_3$/acetone and subsequent recrystallization by ether vapor diffusion in the dark. In both components, the Ag^I ions adopt a trigonal planar geometry with two phenanthroline nitrogens and one oxygen of solvent (Et_2O or H_2O). The latter sites with Et_2O or H_2O are coordinatively labile on the two Ag^I centers, which are 9.43 or 9.18 Å apart from each other, respectively (Figure S17). Its ^1H NMR spectrum in $CDCl_3$ showed only one set of phenanthroline signals which were downfield shifted ($\Delta\delta$ = +0.2 ppm) from those of **L1** (Figure S19), and the spectral pattern showed the D_{2h}-symmetrical structure of Ag^I-macrocycle $[Ag_2L1X_2](SbF_6)_2$

(X = possibly Et_2O or H_2O) as observed in the crystal state. Notably, this complex was stable even in a highly diluted $CDCl_3$ solution (ca. 30 μM). Formation of $[Ag_2L1X_2](SbF_6)_2$ was also strongly supported by electrospray ionization-time-of-flight (ESI-TOF) mass spectrometry (m/z = 814.20 as $[Ag_2L1]^{2+}$, Figure S12).

The dinuclear Ag^I complex, $[Ag_2L1X_2]^{2+}$, was found to have high affinity for monocyclic aromatic hydrocarbons through Ag–π interactions. For instance, when a mixture of **L1** and 20 equiv of $AgCF_3SO_3$ in CH_2Cl_2/p-xylene was kept in the dark at rt for several days, yellow single crystals were obtained. Single-crystal X-ray analysis revealed that an inclusion complex, (p-xylene)$_2$⊂[Ag$_2$**L1**(CF$_3$SO$_3$)$_2$] in which two stacked p-xylene molecules bind simultaneously to the two Ag^I centers as η^1- to η^2-ligands in a disordering manner, was formed with an average bond distance of Ag–C = 2.53 Å (Figure S22). Although the interactions between p-xylene and $[Ag_2L1X_2]^{2+}$ in $CDCl_3$ were too weak to detect by ^{1}H NMR guest titration experiments in the range approximately 10^2 μM at 300 K (Figure S24), the stacked Ag–π–π–Ag structure with a π–π distance of ca. 3.5 Å in the crystal state suggested the capability of the macrocyclic host as an effective receptor of two aromatic rings close to each other.

Based on this finding, [2.2]paracyclophane (pCp) was then examined as a guest molecule. As pCp has a ditopic structure in which two benzene rings are linked with two ethylene groups and stacked intramolecularly with a π–π distance of ca. 3.1 Å, pCp was expected to form a stable inclusion complex through multiple Ag–π interactions with $[Ag_2L1X_2]^{2+}$.[18,19]

The interaction of pCp and $[Ag_2L1X_2](SbF_6)_2$ was studied by ^{1}H NMR titration. Upon addition of pCp to a solution of $[Ag_2L1X_2](SbF_6)_2$ in $CDCl_3$, the signal intensity of the original $[Ag_2L1X_2](SbF_6)_2$ gradually decreased and was finally replaced by a new set of signals in the aromatic region when 1.0 equiv of pCp was added (Figure 2a–c). This indicates that pCp⊂[Ag$_2$**L1**](SbF$_6$)$_2$ was formed as a 1:1 inclusion complex. The signals that newly appeared at 3.82 ppm (A_{in}) and 1.17 ppm (B_{in}) can be assigned as those of included pCp, which were highly upfield shifted due to the strong shielding effect of the anthracene moieties ($\Delta\delta$ = −2.6 and −1.9 ppm for A_{in} and B_{in}, respectively;
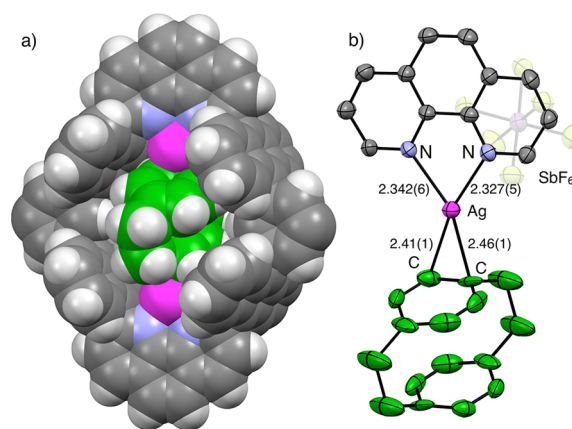
Figure 3. Crystal structure of pCp⊂[Ag$_2$**L1**](SbF$_6$)$_2$. One of two disordering patterns of pCp is shown; (a) a space filling and (b) 50% ORTEP views of a partial structure (solvents, side-alkyl chains, counteranions, and some H-atoms are omitted for clarity). Ag, magenta; C of **L1**, gray; C of pCp, green; F, yellow; H, white; N, blue; Sb, pink.

Figure 2c,d). This assignment was strongly supported by the distinct rotating frame Overhauser effect (ROE) correlation between A_{in} and the protons inside the cavity (H_i in Figure S29). The intermolecular guest exchange reaction was slower than the ^{1}H NMR time scale at 300 K, as the signals of $[Ag_2L1X_2](SbF_6)_2$ and pCp⊂[Ag$_2$**L1**](SbF$_6$)$_2$ were separate from each other in the presence of 0.5 equiv of pCp (Figure 2b). The formation of pCp⊂[Ag$_2$**L1**](SbF$_6$)$_2$ was also supported by ESI-TOF mass spectrometry (m/z = 918.80 as pCp⊂[Ag$_2$**L1**]$^{2+}$, Figure S26).

The molecular structure of pCp⊂[Ag$_2$**L1**](SbF$_6$)$_2$ was determined by single-crystal X-ray analysis. By diethyl ether vapor diffusion into a mixture of **L1**, 4.0 equiv of $AgSbF_6$, and 1.0 equiv of pCp in $CHCl_3$/acetone in the dark, pale yellow single crystals were obtained in 70% yield. In the resulting structure, one disordering pCp molecule was included in the cavity of $[Ag_2L1]^{2+}$ via η^2-type Ag–π bonding at the edge of the π-plane of pCp (Figure 3). The two crystallographically equivalent Ag^I centers were in a square-planar geometry with two N-atoms of phenanthroline and two C-atoms of pCp (Ag–N 2.327(5)– 2.342(6) Å; Ag–C 2.39(1)–2.56(1) Å; Figure S32). Although these Ag–π bonds are about 30° inclined from the vertical direction of the π-plane of pCp, the resulting Ag–π–π–Ag arrangement was quite similar to that of the aforementioned p-xylene inclusion complex. Multipoint CH–π interactions among aromatic rings of pCp and anthracene moieties appear to stabilize the complex as well in light of the fact that CH–π distances are in the range 2.55–2.81 Å. The ^{1}H NMR spectrum of the isolated crystal in $CDCl_3$ showed a signal pattern identical to that observed in the ^{1}H NMR titration (Figure 2c). This strongly indicates that the same inclusion complex is formed in the crystal and solution states. In the crystal structure, pCp in the cavity formed a C_i-symmetrical structure due to the η^2-type Ag–π bonding, whereas the proton signals of the included pCp showed two singlets only (A_{in} and B_{in} in Figure 2c) corresponding to a D_{2h}-symmetrical structure. This suggests fast and fluxional oscillation or a precession movement of pCp within the cavity via haptotropic shifts of Ag^I ions in solution at 300 K, whereas any rotational movements of pCp in the cavity appear to be sterically unlikely (Figure S38).[16a]

The binding affinity of $[Ag_2L1X_2](SbF_6)_2$ to pCp was evaluated by ^{1}H NMR titration experiments in $CDCl_3$ at 300 K. As above, dissociation of Ag^I ions from $[Ag_2L1X_2](SbF_6)_2$ is

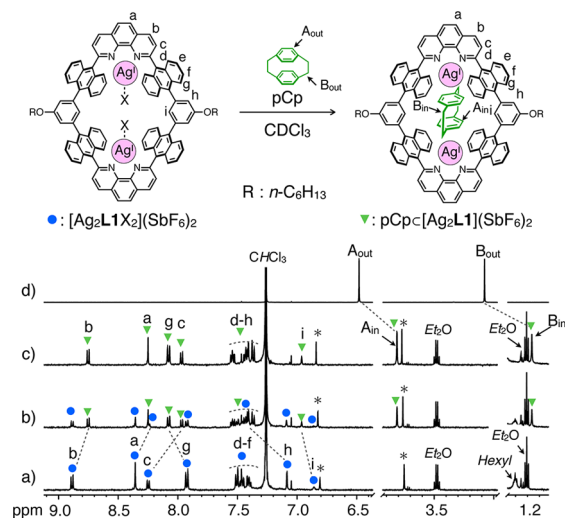**Figure 2.** ^{1}H NMR spectra (500 MHz, 300 K) of $[Ag_2L1X_2](SbF_6)_2$ in the presence of (a) 0.0, (b) 0.5, and (c) 1.0 equiv of pCp, and (d) pCp only in $CDCl_3$: $[[Ag_2L1X_2]^{2+}]$ = 107 μM. Asterisks show the signals of p-dimethoxybenzene used as an internal standard.

negligible in CDCl$_3$ when the concentration is over ca. 30 μM, and therefore the binding constant can be defined as K_a(guest) = [guest⊂Ag$_2$**L1**]/([guest][Ag$_2$**L1**]) M^{-1}. As the affinity of the [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$ to pCp is too high to determine directly from ^{1}H NMR titration, it was estimated by guest competition based on the binding constant for ferrocene (K_a(FeCp$_2$) = 6.2 ± 0.9 × 10^4 M^{-1} in CDCl$_3$ at 300 K, as described later). However, even when an excess (25 equiv) of ferrocene was added to a solution of pCp⊂[Ag$_2$**L1**](SbF$_6$)$_2$ in CDCl$_3$ (115 μM) at 300 K, no guest exchanges were observed by ^{1}H NMR spectroscopy, which suggests that K_a(pCp) is over 10^9 M^{-1} (Figure S52). The extremely high stability of the pCp inclusion complex can be attributed to multipoint Ag−π interactions in the cyclic framework as qualitatively evaluated by the following control ^{1}H NMR titration.

To estimate the contribution of Ag−π interactions to the stability of the inclusion complex, a control experiment was then performed using **L1** or dinuclear metal macrocycles with different metal ions [M$_2$**L1**X$_m$]$^{n+}$ (M = Hg^{II}, Zn^{II}, or Cu^I; X = solvent or anion) (Figure S38). Even when an excess amount of pCp was added to each solution of a host (68−124 μM) in CDCl$_3$/(CD$_3$)$_2$CO (= 75/1−75/0), the spectrum did not show any changes, suggesting very weak interactions between the host and guest. These results demonstrate that Ag−π interactions play a central role in the inclusion of pCp into [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$.

Next, to examine the effect of the cyclic structure of [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$ on the stability of the inclusion complex, a control experiment was performed using a noncyclic complex [Ag**L2**(Et$_2$O)]SbF$_6$ (**L2** = 2,9-bis(9-anthracenyl)-1,10-phenanthroline; see the SI) as a host molecule (Figures S39−S42).[20] As a result, significant interactions between [Ag**L2**(Et$_2$O)]SbF$_6$ and pCp were observed in CDCl$_3$/(CD$_3$)$_2$CO (= 80/1), and the binding constant for a 1:1 complex was determined to be K'_{a1}(pCp) = (1.9 ± 0.5) × 10^4 M^{-1} at 300 K by ^{1}H NMR titration experiment, which is much smaller than that of [Ag$_2$**L1**X$_2$]-(SbF$_6$)$_2$ (K_a(pCp) > 10^9 M^{-1}).[21] Such a remarkable contrast demonstrates that [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$ provides a well-defined cavity in which two Ag^I ions are in the right positions to capture ditopic aromatic molecules through multipoint Ag−π interactions. The high electron donation property of the π-planes of pCp, due to the distorted plane, may significantly contribute to the stabilization of the inclusion complex.[18]

Inspired by this result, sandwich-shape ferrocene (FeCp$_2$) was then examined as a redox reactive guest molecule with a π−π distance of 3.3 Å. Upon addition of FeCp$_2$ to a solution of [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$ in CDCl$_3$ (107 μM) at 300 K, the host's signals were sequentially shifted (Figure S45) due to host−guest interactions. ^{1}H NMR titration experiments at 220 K ([[Ag$_2$**L1**X$_2$]$^{2+}$] = 82 μM) demonstrated that a signal of included FeCp$_2$ at 1.8 ppm (A$_{in}$ in Figure 4c) showed a strong ROE correlation with protons inside the cavity (H$_i$ in Figure S47). Due to the strong shielding effect from anthracenes, this signal was highly upfield shifted ($\Delta\delta$ = −2.4 ppm). ESI-TOF mass measurement indicated formation of a 1:1 inclusion complex FeCp$_2$⊂[Ag$_2$**L1**](SbF$_6$)$_2$ in CDCl$_3$ (m/z = 907.08 as FeCp$_2$⊂[Ag$_2$**L1**]$^{2+}$, Figure S48). Despite numerous trials, no single crystals of FeCp$_2$⊂[Ag$_2$**L1**](SbF$_6$)$_2$ have yet been obtained. Molecular mechanics study based on the crystal structures of the aforementioned pCp⊂[Ag$_2$**L1**](SbF$_6$)$_2$ and previously reported complexes consisting of Ag^I and FeCp$_2$[22] suggests that FeCp$_2$ fits in the cavity of [Ag$_2$**L1**]$^{2+}$ to form a Ag−π−Fe−π−Ag arrangement (Figures S49−S50). Similarly to the case of pCp, the simple signal pattern of the included FeCp$_2$
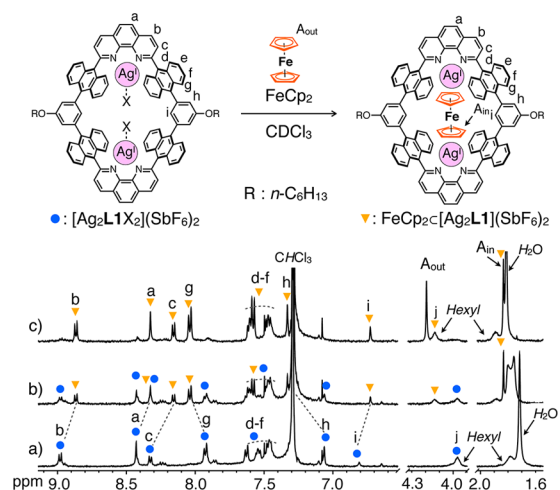

Figure 4. ^{1}H NMR spectra of [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$ (82 μM) with (a) 0.0, (b) 0.5, and (c) 1.5 equiv of FeCp$_2$ (CDCl$_3$, 500 MHz, 220 K).
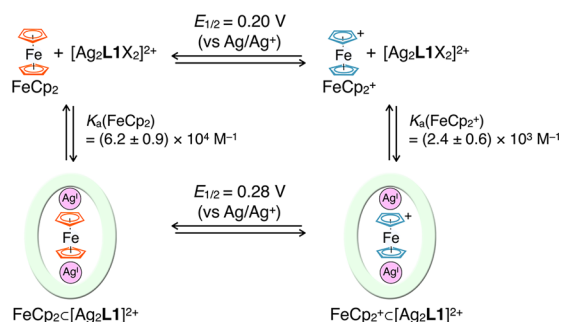

Figure 5. Coupled chemical and electrochemical equilibration for a mixture of [Ag$_2$**L1**](SbF$_6$)$_2$ and FeCp$_2$ in CDCl$_3$ at 300 K or 0.1 M TBAPF$_6$ in CH$_2$Cl$_2$ at 291 K, respectively.

(A$_{in}$) would suggest fast and fluxional oscillation or precession movement of FeCp$_2$ in the cavity with torsion of Cp−Fe−Cp bonds at 220 K. The binding constant between FeCp$_2$ and [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$ was determined to be as high as K_a(FeCp$_2$) = (6.2 ± 0.9) × 10^4 M^{-1} in CDCl$_3$ at 300 K by curve fitting of the ^{1}H NMR data of the titration experiment (Figure 5). In light of previously reported Ag^I complexes of FeCp$_2$, Ag−π interactions with the Cp ring of FeCp$_2$ seem to be weaker than those of ordinary aromatic hydrocarbons, which may give rise to the difference in K_a values for FeCp$_2$ and pCp.

Finally, the redox property of FeCp$_2$ within [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$ was investigated by cyclic voltammetry (Figure S53).[17b,c,e,f] When 15 equiv of the isolated crystals of [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$ were dissolved in a solution of FeCp$_2$ in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ at 291 K, a substantial decrease in the current intensity was observed. This indicates that a large part of FeCp$_2$ exists as a slowly diffusing inclusion complex in the solution. Moreover, the reversible current potential of FeCp$_2$ showed a significant anodic shift (ca. +80 mV). Based on this result, the binding constant, K_a(FeCp$_2^+$), between [Ag$_2$**L1**X$_2$]$^{2+}$ and the oxidized form of FeCp$_2$ (FeCp$_2^+$) was calculated to be (2.4 ± 0.6) × 10^3 M^{-1} at 300 K,[17b,c] which was roughly the same as that determined by ^{1}H NMR titration experiments (∼4 × 10^3 M^{-1}; see the SI). This suggests that the inclusion complex with FeCp$_2^+$ in the cavity is less stable compared with the neutral FeCp$_2$ due to the electrostatic repulsion between cationic Ag^I ions and FeCp$_2^+$.[17e,f]

In conclusion, a dinuclear Ag^I-macrocycle [Ag$_2$**L1**X$_2$](SbF$_6$)$_2$ possessing two Ag^I ions and anthracene linkers has been newly

synthesized. The nanocavity with two coordinatively labile Ag^I centers was used for encapsulation of ditopic aromatic guest molecules, pCp and $FeCp_2$, through multipoint $Ag-\pi$ interactions. Moreover, the electrochemical behavior of $FeCp_2$ was markedly changed when it is encapsulated in the cavity and put between the two Ag^I centers. Thus, $Ag-\pi$ bonding is a useful structural motif for host–guest chemistry and has great potential to control the electronic property and reactivity of guest molecules possibly leading to cooperative functions with photoreactive anthracene walls of the cavity.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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