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Molecular recognition of planar and non-planar aromatic hydrocarbons through multipoint Ag–π bonding in a dinuclear metallo-macrocycle

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Molecular recognition of planar and non-planar aromatic hydrocarbons through multipoint Ag–π bonding in a dinuclear metallo-macrocyle

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Exploration of a novel structural motif of host–guest interactions is one of the most fundamental topics to develop macrocycle-based host–guest/supramolecular systems. Herein, we present an unprecedented mode of inclusion of aromatic hydrocarbons into a macrocyclic cavity via multipoint Ag–π bonding as a driving force. A dinuclear AgI-macrocyle encapsulated one molecule of anthracene, a typical planar aromatic hydrocarbon, in solution and in the solid state. Single-crystal X-ray diffraction analysis of the host–guest inclusion complex revealed the binding of anthracene via multipoint Ag–π bonding to both AgI ions arranged within the open-ended nano-cavity of the dinuclear AgI-macrocyle. Notably, this binding motif based on Ag–π bonding was also applied to the inclusion of triptycene, a non-planar aromatic hydrocarbon with a sterically tripodal structure, to evaluate the rotational motion of the molecular paddle-wheel in the AgI-macrocyle.

Introduction

Since the discovery of crown ether by Pedersen, a great number of excellent examples of functional macrocycles have been reported which can bind guest molecules or ions within their inner spaces.1 Guest binding abilities of macrocycles play vital roles in providing various implications to advanced functions in host–guest/supramolecular systems, such as molecular recognition,2 activation,3 transportation4 and fabrication of specific supramolecular architectures (i.e. rotaxanes and catenanes).5 In general, a variety of non-covalent interactions including hydrogen bonding, coulombic interactions, van der Waals forces and solvophobic effects have been utilised as driving forces for guest uptake of macrocycles.6 Besides, metal coordination capable of forming stable, reversible and directional bonds is another binding mode between host and guest compounds, and therefore macrocycles with coordinatively labile metal centres in the cavity have received a lot of attention in recent years in the field of supramolecular chemistry.7

Aromatic hydrocarbons have been widely investigated as one of the most important classes of guest molecules for macrocycles owing to their ubiquitous structure and electronic properties related to π-conjugation.8 In the past few decades, a variety of macrocyclic receptors for aromatic molecules have been reported which can realise recognition,9 separation10 and regulation11 of their properties via host–guest interactions. However, in spite of the diversity of macrocyclic structures, molecular recognition of non-substituted, structurally simple aromatic hydrocarbons is still challenging because such hydrocarbons without polar functionalities are difficult to uptake by forming distinct chemical bonds (i.e. hydrogen bonds and coordination bonds) with a receptor, and alternatively vast-area contacts through a few weak interactions such as π–π, CH–π and van der Waals interactions are required to encapsulate a pristine aromatic hydrocarbon in a host framework (Fig. 1a). Such vast-area contacts generally need shape complementarity in the host–guest inclusion structure. Therefore, there are limitations in the diversity of host–guest structures, which make it difficult to rationally design a platform for the molecular recognition of non-planar aromatic hydrocarbons with a three-dimensional structure.

Herein, we present an unprecedented mode of inclusion of non-substituted aromatic hydrocarbons into a metallo-macrocyle utilising M–π bonding as a driving force. M–π bonding is a kind of non-Werner type coordination bonding mainly originating from the interactions among d orbitals of metals and π orbitals of aromatic hydrocarbons.9,10 In general, M–π bonding has higher directionality and site-specificity than the above-mentioned conventional intermolecular interactions, and the resulting M–π complexes have the potential to exhibit unique functions based on the chemical and physical properties of the metal centres. Therefore, metallo-macrocyces possessing a nano-space with multiple metal centres for M–π bonding are expected to provide a novel structural motif to recognise aromatic guest molecules, in which the inclusion structure and the guest selectivity can be affected by the type, number, and arrangement of the inner metal ions.12

Based on this concept, we have recently developed a dinuclear AgI-
Moreover, we found that this guest-binding motif based on Ag–π bonding does not require vast-area contacts between the host and guest, which achieved the binding of a non-planar aromatic hydrocarbon, triptycene, in a similar manner.

Results and discussion

The binding of anthracene (Ant) to a dinuclear Ag$^+$-macrocycle $\text{[Ag}_2\text{L}_1\text{X}_3\text{][SbF}_6]_2$ was first investigated by $^1$H NMR titration experiments at 220 or 300 K and mass spectrometry. Upon the addition of Ant to a solution of $\text{[Ag}_2\text{L}_1\text{X}_3\text{][SbF}_6]_2$ (0.07 mM) in CDCl$_3$, the $^1$H NMR signals of $\text{[Ag}_2\text{L}_1\text{X}_3\text{][SbF}_6]_2$ at 220 K were gradually replaced by a new set of signals with an increased area contacts (Fig. 1b). In this system, the Ag$^+$-macrocycle can accommodate a ditopic aromatic molecule such as cyclophanes and ferrocene utilising multiple Ag–π bonds as a main driving force.$^{20}$ Herein we report that the Ag$^+$-macrocycle effectively recognised an anthracene molecule, a planar aromatic hydrocarbon, in the open-ended cavity through multiple Ag–π bonds with both ends of anthracene (Fig. 1b). Moreover, we found that this guest-binding motif based on Ag–π bonding does not require vast-area contacts between the host and guest, which achieved the binding of a non-planar aromatic hydrocarbon, triptycene, in a similar manner.

![Diagram](image)

**Fig. 1** (a) Schematic representation of the binding mode of a non-substituted aromatic hydrocarbon within a macrocyclic host via vast-area contacts. (b) The chemical structure of a dinuclear Ag$^+$-macrocycle $\text{[Ag}_2\text{L}_1\text{X}_3\text{][SbF}_6]_2$ and the schematic representation of the binding modes of planar and non-planar aromatic hydrocarbons via multipoint Ag–π bonding.

Notably, at a temperature as high as 300 K, as the intermolecular exchange between bound and free Ant molecules is faster than the timescale of $^1$H NMR spectroscopy, $^1$H NMR titration experiments at 300 K resulted in the sequential shift of the signals of $\text{[Ag}_2\text{L}_1\text{X}_3\text{][SbF}_6]_2$ due to host–guest interactions (Fig. S1 and S2†). From the curve-fitting of the $^1$H NMR data at 300 K based on the formation of a 1 : 1 host–guest complex, the binding constant between Ant and the Ag$^+$-macrocycle ($K_\text{b}[\text{Ant}] = [\text{Ant}][\text{[Ag}_2\text{L}_1\text{X}_3\text{][SbF}_6]_2][\text{Ant}]]^{-1}$) M$^{-1}$ was determined to be $(3.0 \pm 0.4) \times 10^4$ M$^{-1}$ in CDCl$_3$ at 300 K (Fig. S3†), which is comparable to those of already reported examples of macrocyclic receptors for aromatic hydrocarbons.$^{9,11,14}$ The formation of a 1 : 1 host–guest complex was also supported by ESI-TOF mass measurements ($m/z = 903.72$ as Ant$^+[\text{Ag}_2\text{L}_1]^{2+}$, Fig. S6†).

The structure and binding mode of the resulting complex were finally determined by single-crystal X-ray analysis (Fig. 3). By slow n-pentane vapour diffusion into a mixture of L$_1$, AgSbF$_6$ (4.2 eq.) and Ant (10 eq.) in CH$_2$Cl$_2$ in the dark at room temperature, yellow block crystals suitable for single-crystal X-ray analysis were obtained. In the resulting crystal structure, one molecule of Ant was included in the cavity of $\text{[Ag}_2\text{L}_1]^{2+}$ via π-type Ag–π bonding at both terminal edges of the elongated π-surface in an anti-manner (Fig. 3a). These Ag$^+$ ions were in a distorted square pyramidal five-coordinate geometry with two N-atoms of phenanthroline, two C-atoms of the included Ant, and one Cl-atom of a coordinating solvent: CH$_2$Cl$_2$ (Ag–N1 2.280(6) Å; Ag–N2 2.356(5) Å; Ag–C55 2.454(8) Å; Ag–C56 2.449(8) Å; Ag–Cl3 2.984(2) Å, Fig. 3b). These observations

![Diagram](image)

**Fig. 2** Partial $^1$H NMR spectra of $\text{[Ag}_2\text{L}_1\text{X}_3\text{][SbF}_6]_2$ (0.07 mM) in the presence of (a) 0.0, (b) 0.5, (c) 1.0, (d) 1.5 and (e) 2.0 eq. of anthracene (Ant) (500 MHz, CDCl$_3$, 220 K). Ant$_{\text{in}}$ represents the signals of the included Ant.
suggest that multipoint Ag–π bonding between Ant and Ag† ions, which are precisely arranged on the inner surface of the nano-space, works as an effective driving force to bind Ant. Multipoint CH–π interactions between the H-atoms of the included Ant and the π-surface of anthracene-walls of the macrocycle may also contribute to stabilise the resulting complex as well. Notably, Ant⊂[Ag₂-L₁(CH₃Cl)₂]⁺ possesses a C₂-symmetrical structure in the crystal due to the inclination of the included Ant. On the other hand, the ¹H NMR spectrum of Ant⊂[Ag₂-L₁][SbF₆]₂ showed a simple set of ¹H NMR signals (Fig. 2b–e) suggesting a more symmetrical (D₂h) structure with successive fluxional movement of Ant in the nano-cavity via intramolecular Ag–π exchange.

Based on these results, the binding properties of [Ag₂-L₁X₂][SbF₆]₂ to other aromatic hydrocarbons of different sizes were examined. We previously reported that a smaller aromatic hydrocarbon, p-xylene, formed not a 1 : 1 but a 2 : 1 complex, (p-xylene)₂⊂[Ag₂-L₁]⁺, in the crystalline state.¹²m On the other hand, a ¹H NMR titration experiment using p-xylene showed negligible shift in the host signals (|Δδ| < 0.04 ppm) even after adding 4 eq. of p-xylene, suggesting a lower affinity to [Ag₂-L₁X₂][SbF₆]₂ or a different binding mode from that of Ant⊂ [Ag₂-L₁][SbF₆]₂ in solution (Fig. S22 and S24†). Similarly, naphthalene, which has an intermediate size between p-xylene and Ant, showed a smaller shift in the host signals (|Δδ| < 0.02 ppm) even after adding 4 eq. of naphthalene in the ¹H NMR titration experiment at 300 K (Fig. S23† and S24†). These results may reflect the insufficiency of the molecular size of p-xylene and naphthalene to simultaneously form Ag–π bonds at both Ag† centres arranged in the macrocyclic skeleton. These results suggest the importance of the arrangement mode of Ag† ions in the macrocycle in controlling the stability, selectivity and structure of the resulting host–guest complex.

In contrast, triptycene (Trip), which is a non-planar aromatic hydrocarbon with a steric tripodal structure, was found to be effectively included within the cavity of [Ag₂-L₁X₂][SbF₆]₂. The inclusion behavior of Trip was revealed by a ¹H NMR titration experiment in CDCl₃ at 220 K, in which the host signals were replaced by a new set of signals in the presence of more than 1.0 eq. of Trip to form an 1 : 1 host–guest complex Trip⊂[Ag₂-L₁][SbF₆]₂ (Fig. 4).¹¹ The signals of the included Trip (Bᵢₙ) showed a strong rotating frame Overhauser effect (ROE) correlation with the proton inside [Ag₂-L₁]⁺ (Hₗ), which suggests the existence of Trip within the nano-cavity of the macrocycle (Fig. S18†). The formation of Trip⊂[Ag₂-L₁][SbF₆]₂ was also supported by ESI-TOF mass analysis [m/z = 941.21 as Trip⊂[Ag₂-L₁]⁺, Fig. S20†].

Similar to the case of Ant, the rates of intermolecular exchange of bound and free Trip at a higher temperature (300 K) became faster than the timescale of ¹H NMR, which resulted in the observation of a dynamically averaged ¹H NMR spectrum (Fig. S9 and S10†). From the curve-fitting of the ¹H NMR data of the guest titration experiment at 300 K based on the formation of a 1 : 1 host–guest complex, the binding constant between Trip and the Ag⁺-macrocycle (K₅,[Ant] = [Trip⊂[Ag₂-L₁]⁺]) was determined to be (3.1 ± 0.2) × 10⁴ M⁻¹ in CDCl₃ at 300 K (Fig. S11†), which is comparable to that of Ant (K₅,[Ant] = (3.0 ± 0.4) × 10⁴ M⁻¹).¹⁴ This result suggests host–guest interactions between Trip and Ag⁺-macrocycle similar to that of Ant and Ag⁺-macrocycle, where multipoint Ag–π bonding simultaneously formed at both ends of the aromatic molecule works as a dominant driving force for guest binding. Molecular modeling of Trip⊂[Ag₂-L₁]⁺ based on the crystal structure of the aforementioned Ant⊂[Ag₂-L₁][SbF₆]₂ (Fig. 3) and that of a previously reported Ag⁺ complex of Trip supports the multipoint binding of Trip, where Ag⁺ ions coordinate to the π-planes of Trip in the anti or syn form (Fig. 5a and S21†).¹⁴d,e,k Such a binding motif of Trip suggests that the open-ended nano-cavity of [Ag₂-L₁X₂][SbF₆]₂ with two Ag⁺ ions would work...
as an effective receptor for not only planar but also non-planar aromatic molecules which allows multipoint Ag–π bonding.

Notably, the included Trip exhibits rotational motion at 220 K, which affects the symmetry of the resulting host–guest complex, $\text{Trip} \subset [\text{Ag}_2 \text{L1}] \subset [\text{SbF}_6]_2$, where Ag ions coordinate to the π-planes of Trip in an anti or a syn manner. (b–d) Plausible side cross-sectional views of the rotational motion of Trip, where Trip exhibits faster intramolecular rotational motion (b and c) and a slower intermolecular guest exchange (d) than the timescale of $^1\text{H}$ NMR observation.

**Conclusions**

In this study, host–guest interactions between a dinuclear Ag I macrocycle $[\text{Ag}_2 \text{L1X}_2] \subset [\text{SbF}_6]_2$ and aromatic hydrocarbons were investigated. $[\text{Ag}_2 \text{L1X}_2] \subset [\text{SbF}_6]_2$ has an ability to strongly include not only a planar (Anti) but also a non-planar (Trip) aromatic hydrocarbon which allows multipoint Ag–π bonding at both Ag centres simultaneously. Such a Ag I-based specific binding motif is quite distinct from those of conventional macrocyclic receptors for aromatic molecules which require close and vast-area contacts between the aromatic guest and the nano-cavity of the macrocycle. Such a unique binding motif utilising non-Werner type M–π coordination would provide us an important clue to the rational design of the structures, properties and metal-centred functions of the resulting host–guest complexes. This finding would help to develop a new dimension to macrocycle-based supramolecular chemistry and molecular machines based on the selectivity, reactivity and dynamics of M–π bonding within a confined space of metallo-macrocycles.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**


11 M–π bonding is considered to be different from cation–π interaction, which is originated from electrostatic interaction between a positively charged cation and an electron-rich π-system. (a) J. C. Ma and D. A. Dougherty, Chem. Rev., 1997, 97, 1303–1324; (b) A. S. Mahadevi and G. N. Sastry, Chem. Rev., 2013, 113, 2100–2138.


The integral ratios of the 1H NMR signals of the included guest molecules encapsulated in [Ag2L]2+ were evaluated to be smaller than those estimated from the structures of 1 : 1 complexes probably due to the fluxional dynamic movement of the included guest molecules within the nano-space, which caused broadening of the 1H NMR signals.

The stabilities of the host–guest complexes were temperature dependent. The binding constantKa estimated at 300 K seems to be smaller than that at 220 K, as revealed by the convergence of 1H NMR titration experiments.