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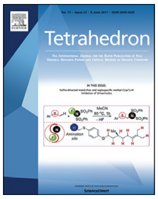

Expanded aromatic carboxylate anion induced molecular sandwich construction via a tetracationic imidazolium macrocycle conversion from molecular box to molecular tweezer

Zhen-Hua Ma [a], Huan-Rong Li [a, **], Han-Yuan Gong [b, *]

[a] Department of Chemistry, Renmin University of China, Beijing 100872, PR China
[b] College of Chemistry, Beijing Normal University, Beijing 100875, PR China

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The molecular box, namely cyclo[2](2,6-di(1H-imidazol-1-yl)pyridine)-[2](1,4-dimethylene benzene) ($\mathbf{1}^{4+}$; as PF_6^- salt), fold its conformation as molecular tweezer to clip the specific carboxylates with expanded aromatic plane. The binding modes between $\mathbf{1}^{4+}$ and carboxylate, namely pseudorotaxane, outside or clipping (i.e., sandwich like), also depend on the location of carboxylate on the large conjugated moiety. These finding develop the usability of $\mathbf{1}^{4+}$ and carboxylates as important building block pairs to create non-covalent self-assembly structures.

1. Introduction

Molecular tweezers are characterized via a rigid tether holding two flat pincers in a syn-conformation/configuration.[1–5] On the basis of non-covalent weak interactions (e.g., π-π donor-acceptor interaction), molecular tweezer half-open cavities tend to clip additional substrate for molecular recognition and functional self-assembly.[6–17] In past decades, macrocyclic moieties have been introduced as flat pincer part in molecular tweezer. Reported macrocyclic princer to accommodate guests involved crown ethers,[18] cyclotriveratrylenes (CTV),[19] calix[n]arenes and their derivatives,[20,21] dipyrene tweezer-like (DPT) molecules,[22–24] incorporating zinc porphyrins,[25] methylazacalix[4]pyridine (MACP-4),[26] and other macrocycles.[9,27–29] On the other hand, the strategy of molecular tweezer construction via macrocylic framework is under development. In this strategy, macrocycle tune its conformation as tweezer for additional guest clipping, and then achieve molecular recognition and supramolecular self-assembly formation. Recent examples of converting macrocyclic conformation as molecular tweezer included bis-tetrathiafulvalene-calix[2]pyrrole[2]thiophene,[29] tetra-tetrathiafulvalene-calix[4]pyrrole[30] and methyl-azacalix[4]- pyridine (MACP-4).[26]

Compared with the strategy using macrocyclic fragment as pincer, the example of the late approach is still lacking, which implied that the strategy to build molecular tweezer is still under development.

Herein, we demonstrated that a tetracationic imidazolium macrocyclic 'Texas-sized' molecular box, namely cyclo[2](2,6-di(1H-imidazol-1-yl)pyridine)[2](1,4-dimethylene benzene) ($\mathbf{1}^{4+}$; as PF_6^- salt), can change its conformation as boat, so that act as molecular tweezer to selectively clip carboxylate containing expanded conjugated plane. Furthermore, we summarized that three factors determined the different binding modes between $\mathbf{1}^{4+}$ and carboxylate precursor with aromatic ring: (1) the width of aromatic plane perpendicular to the linking carboxylate; (2) the species and site(s) of substitute group(s) on the aromatic ring of the carboxylate; (3) the location of carboxylate on the aromatic plane. This work shows a new mode and related strategy to construct functional self-assembly materials using cationic macrocyclic precursor and anionic species.

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* Corresponding author.
** Corresponding author.
E-mail addresses: hrli@ruc.edu.cn (H.-R. Li), hanyuangong@bnu.edu.cn (H.-Y. Gong).

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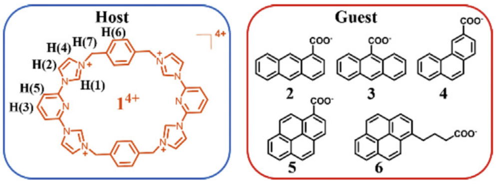
2. Results and discussion

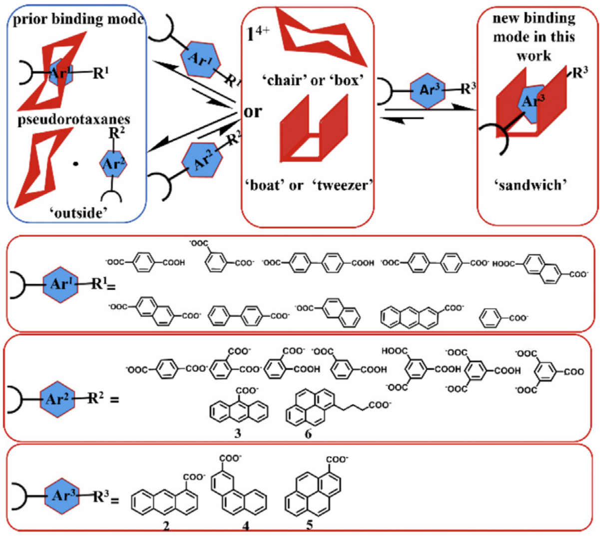
Our prior study presented that aromatic carboxylate (e.g., 2,6-naphthalene dicarboxylate dianion) or sulfonate anion (e.g., 2,6-naphthalene disulfonate dianion) species can easily thread the cavity of $\mathbf{1}^{4+}$ to form interpenetrated structures (i.e., pseudorotaxanes) and highly ordered interlocked complexes, including poly(pseudorotaxanes),[31–38] rotaxanated supramolecular frameworks (RSOFs)[39–43] and metal-organic rotaxane frameworks (MORFs).[44–47] These results also implied that the width of aromatic plane, which is perpendicular to the linking carboxylate or sulfonate, determine the complexation mode between $\mathbf{1}^{4+}$ and aromatic anionic precursor. When the width of aromatic ring on anion precursor is less than 5.8 Å,[50] $\mathbf{1}^{4+}$ may adopt the "chair" or "box" like conformation and formed pseudorotaxanes[48–50]; In contrast, while the width of conjugated plane on anion substrate larger than 5.8 Å, $\mathbf{1}^{4+}$ with "chair" or "box" framework would only can bind aromatic anion outside of its cavity.[49–51] But even the wide anion species (e.g. tri-1,3,5-benzenetricarboxylate anion) cannot thread through the core of $\mathbf{1}^{4+}$, it still have the possibility to combine with metal cation to construct mechanically interlocked molecules (MIMs) with environmental responsivity.[51]

To further explore usability of $\mathbf{1}^{4+}$ in the multi-component supramolecular self-assembly, our investigation turn to obtain deeper insights into the expanded aromatic plane effect on carboxylate anion precursor, namely how the big aromatic structure of the anion guests might influence the nature of the complex built up from $\mathbf{1}^{4+}$. Herein, we report the results of the interaction study between $\mathbf{1}^{4+}$ and a series of carboxylates containing large conjugated plane, including anthracene-1-carboxylate anion (**2**), anthracene-9-carboxylate anion (**3**), phenanthrene-3-carboxylate anion (**4**), pyrene-1-carboxylate anion (**5**) and pyrene-1-butyrate anion (**6**) (cf. Scheme 1). It is found that host $\mathbf{1}^{4+}$ bind anions **3** or **6** outside of its cavity both in solution and in solid state, since the width of guests larger than 5.8 Å, meanwhile $\mathbf{1}^{4+}$ adopt chair or box conformation. The result was consistent with the prior study.[49–51] Intriguingly, new sandwich-like binding mode between $\mathbf{1}^{4+}$ and aromatic carboxylate anion (e.g., guest **2**, **4** or **5**) is observed. In these cases, $\mathbf{1}^{4+}$ with "boat-like" framework clip anionic precusor both in solution and solid states (cf. Scheme 2). These new complexes continue to attract attention not only as the examples of using building blocks to create non-covalent organic frameworks or self-assembly materials, but also aggregate one dimensional supramolecular species which are stabilized by a combination of apparent electrostatic and donor-acceptor-donor (DAD) interactions.

Our initial investigation was to explore the binding between $\mathbf{1}^{4+}$ and anthracene-1-carboxylate anion (**2**) (studied as its tetramethylammonium (TMA^+) salt made in situ by mixing $H^+\cdot\mathbf{2}$ with 1 M equiv. of $TMA^+\cdot OH^-\cdot 5H_2O$) in DMSO-$d_6$ solution (for reasons of solubility, DMSO-d_6 was used as the solvent in all NMR studies unless noted otherwise). A direct ^1H NMR spectral titration of $\mathbf{1}^{4+}$ with **2** was carried out via maintaining the concentration of $\mathbf{1}^{4+}$ as 1 mM and changing the molar ratio of [**2**] to [$\mathbf{1}^{4+}$] from 0 to 4. It is observed that changes in the chemical shift of the peaks associated with the proton resonance on $\mathbf{1}^{4+}$ depend on the concentration of **2**, which are consistent with an interaction between $\mathbf{1}^{4+}$ and **2**. Further analysis (Job plot) was carried out. A [G]/([G] + [H]) ratio maximum at 0.6 suggested that the stoichiometry of 2:3 (H/G) best describes the interaction between $\mathbf{1}^{4+}$ and anion **2** in the solution, as had been seen in previous study of $\mathbf{1}^{4+}$.[52.] It was supposed that the 2:3 complex form from separate 1:1 (H:G) and 1:2 (H:G) complexes. More evidence of the assumption came from electrospray ionization mass spectrometry (ESI-MS) analysis, with revealed peaks at m/z values as 283.7856 and 536.2101 that correspond to the calculated mass for $[\mathbf{1}^{4+}\cdot\mathbf{2}]^{3+}$ and $[\mathbf{1}^{4+}\cdot\mathbf{2}_2]^{2+}$, respectively (cf. Supplementary data).



Scheme 1. Structures of macrocyclic host $\mathbf{1}^{4+}$ (as PF_6^- salt) and anionic guests shown in this work.



Scheme 2. Schematic summary of the binding modes between $\mathbf{1}^{4+}$ and carboxylates with aromatic plane moiety show in prior and this work.

From the ^1H NMR titration data, association constants of $\lg K_{a1} = 4.2(2)$, $\lg K_{a2} = 3.0(2)$ and $\lg K_{a3} = 3.7(4)$, corresponding to the formation of the initial 1:1 complex ($[\mathbf{1}^{4+}\cdot\mathbf{2}]^{3+}$), its subsequent conversion to 1:2 complex ($[\mathbf{1}^{4+}\cdot\mathbf{2}_2]^{2+}$), and the 2:3 complex $[(\mathbf{1}^{4+})_2\cdot\mathbf{2}_3]^{5+}$ constructed between ($[\mathbf{1}^{4+}\cdot\mathbf{2}_2]^{2+}$) and ($[\mathbf{1}^{4+}\cdot\mathbf{2}]^{3+}$), could be calculated. Association constants and the thermodynamic parameters (enthalpy and entropy changes ΔH^o and ΔS^o) corresponding to the interaction between $\mathbf{1}^{4+}$ and **2** were also calculated base on the isothermal titration calorimetry (ITC) data (cf. Table 1).[53] The association constants calculated via ITC investigation are well consistent with ^1H NMR titration results.

The width of **2** (7.3 Å) is larger than maximum cavity size of $\mathbf{1}^{4+}$ (5.8 Å),[50] such finding is consistent with the anionic guest **2** being bound to the outside of the central cavity of $\mathbf{1}^{4+}$, if $\mathbf{1}^{4+}$ prefer chair or box conformation in the complexation, rather than the formation of a pseudorotaxane or other MIM structure. Surprisingly, in the one-dimensional nuclear Overhauser enhancement spectroscopy (1D-NOE) of the mixture containing $\mathbf{1}^{4+}$ and 1 M equiv of **2**, the distinct correlations between protons on $\mathbf{1}^{4+}$ and guest **2** were observed (cf. Supplementary data). It implied that $\mathbf{1}^{4+}$ still include anionic guest **2** in its cavity. Herein, it is suggested that $\mathbf{1}^{4+}$ adopt 'boat-like' conformation as a molecular tweezer to clip guest **2**, so that a sandwich-like structure is finally formed (cf. Scheme 2), which is further supported via single crystal X-ray diffraction study (cf. Fig. 1).

Furthermore, diffusion ordered ^1H NMR spectroscopic (DOSY) analyses revealed that all proton signals, including those located on $\mathbf{1}^{4+}$ and **2**, were characterized by similar diffusion times in the 1:1