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Strong positive allosteric cooperativity in ternary complexes based on hydrogen-bonded aromatic amide macrocycles

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Three new hydrogen-bonded aromatic amide macrocycles with eight residues were synthesized. The first single crystal structure of this class of larger macrocycles was obtained, which reveals a saddle-like conformation. Interestingly, sharply contrasted to previous negative cooperativity in binding paraquat with cyclo[6]aramide, strong positive allosteric cooperativity in ternary complexes was observed. This may open an avenue to construction of mechanically interlocked molecules with these larger H-bonded macrocycles.

Cooperativity[1] is ubiquitous in biological systems arising from, e.g., the interplay of entities capable of assembling as a result of collective intermolecular non-covalent interactions. Understanding such cooperativity effect holds a significant position in molecular recognition and supramolecular self-assembly. Positive or negative cooperativity results when one non-covalent interaction favors or disfavors another[1a]. Positive cooperativity is advantageous in constructing multicomponent architectures in supramolecular chemistry by overcoming the entropy penalties. In effect, stabilization of biological assemblies is closely associated with such positive cooperativity.[2] Among the four types of cooperativities categorized so far,[1d] which include cooperative aggregation, allosteric cooperativity, chelate cooperativity, and interannular cooperativities, allosteric cooperativity is probably the most recognized and has found wide applications in artificial receptors-guest-based systems. Particularly, some of these systems involve the use of macrocycles such as calixarenes, [3] cyclodextrins,[4] crown ethers,[5] cucurbiturils[6] and other cyclic compounds.[7] However, few shape-persistent macrocycles exhibit a positive allosteric cooperativity.[8]

Hydrogen-bonded (H-bonded) aromatic amide macrocycles,[9] emerged in recent years as a class of shape-persistent[10] cyclic compounds featuring full amide linkages with pretty rigidified backbones due to the presence of intramolecular hydrogen bonds. They have exhibited a variety of intriguing properties as indicated by their uses in extraction,[11] separation technology,[12] transmembrane channels,[13] liquid crystal,[14] as well as catalysis.[15] Our previous studies demonstrated that hydrogen-bonded aromatic amide macrocycles with six residues,[16] namely, cyclo[6]aramides, are able to form a complex with paraquat in 2 : 1 stoichiometry .[17] Nevertheless, only negative cooperativity is observed. Herein we report a rare example of H-bonded aromatic amide macrocycles with eight residues **1** (cyclo[8]aramides for brevity) that show strong positive allosteric cooperativity towards binding bipyridinium **G1**-**G3** (Fig. 1 and Fig. S1-S6, ESI†). Also important to this work is the first successful growth

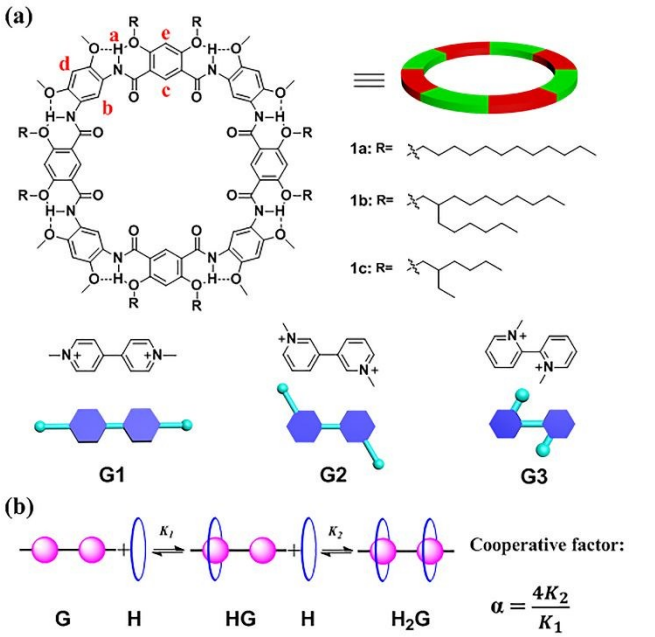

Fig. 1 (a) Chemical structures of cyclo[8]aramides (**1a**-**1c**) and bipyridinium salts **G1**-**G3**. (b) Intermolecular cooperative system and the definition of cooperative factor (α).

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of single crystals of cyclo[8]aramide for analysis of the molecular structure since the first report on their synthesis a decade ago.[18]

Compounds **1a-1c** bearing different alkyl groups as side chains were synthesized by coupling trimeric diamines with diacid chlorides. Reprecipitation from methylene chloride and acetone (or methanol) afforded cyclo[8]aramides with the isolate yields of ca. 30%. The macrocyclization proceeded under non-high dilution condition because of persistency of folded backbone in assisting the cyclization reaction.[9a] It is highly challenging to grow single crystals of cyclo[8]aramide because of the difficulty in balancing the solubility and selection of peripheral groups. This was finally accomplished by exploiting 4,4'-dibutylbipyridinium hexafluorophosphate to solubilize **1c** bearing 2-ethylhexyl in a mixed solvent of chloroform and methanol (9 : 1, v/v), followed by slow evaporation. The brownish yellow cubic plates of **1c** suitable for single-crystal X-ray structure determination was thus obtained (Fig. 2). The diameter of the cavity measures 11.6 Å (Fig. 2a, Fig. S7-S8 and Tab. S1-S3, ESI†), which is sufficiently large to engulf cationic guests such as **G1**-**G3**. Different from cyclo[6]aramide in a near-planar conformation, this macrocycle has a saddle-like conformation (Fig. 2b). Face-to-face π-π stacking between the macrocyclic aromatic backbones is observed with the curved backbone only partially overlapped (Fig. S9, ESI†). We attribute it to the presence of sterically hindered groups that preclude the rings from efficient intermolecular stacking.[19] Therefore, **1a** containing linear n-dodecyl groups was selected for the following cooperatively binding experiments to promote such intermolecular interaction, and **1b** having branched hexadecyl groups was used as a control.

Recently, we reported several host-guest systems based on rigid cyclo[6]aramide,[20] some of which exhibit 2 : 1 binding (H to G) and present negative cooperativity.[1717] We speculate that the steric hindrance from peripheral alkyl side chains may hamper the second macrocycle to approach, thus leading to negative cooperativity. To test this assumption, **1b** bearing branched alkyl groups was examined first for the binding of guest **G1**. The results from Job plot experiments indicated 1 : 1 stoichiometry for the inclusion complexes in $CHCl_3/CH_3CN$ (5 : 1) (Fig. S10, ESI†), which is corroborated by matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry (Fig. S13, ESI†). Therefore, indeed, the considerably strong repulsion between peripheral bulky groups prevents the second cycle from threading on **G1**, demonstrating anticooperative effect. The macrocycle **1b** also fail to display any cooperativity with **G2** and **G3**, all giving a 1 : 1 stoichiometry (Fig. S11-S12 and S14-S15, ESI†). In sharp contrast, **1a** offers a 2 : 1 stoichiometry with **G1** according to the Job plot (Fig. S16, ESI†) and MALDI-TOF results (Fig. S19, ESI†). Similar 2 : 1 binding modes were observed for guests **G2** and **G3** (Fig. S17-S18 and S20-S21, ESI†). ^{1}H NMR spectra of **G1-G3** binding by **1a** recorded in $CDCl_3/CD_3CN$ (1 : 1) show pronounced downfield shifts of guest protons in the complexes with respect to the free guests (Fig. S22-S24, ESI†). This is examplified by **G2**, which produces separated protons for the bound macrocycle upon addition of **1a** to the guest (Fig. 3). It should be noted that the low solubility of **1a** in the mixed solvent deters us from obtaining a NMR spectrum for comparison. Since the signal from the free guest is not observed even in the presence of excess **G1** (Fig. 3b), it indicates a fast chemical exchange on the NMR time scale. The response to the cationic guests, as reflected in the change of chemical shifts, suggests site-specific binding by the host.

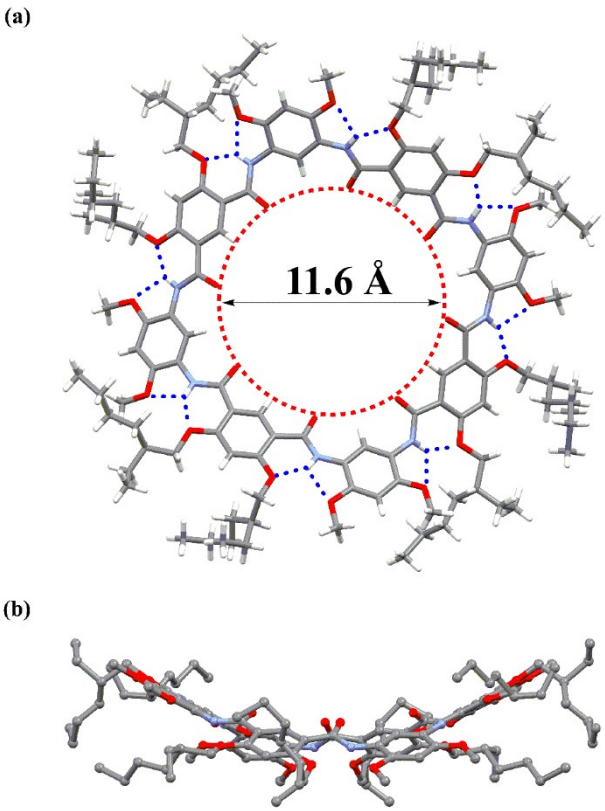

Fig. 2 X-ray crystal structure of cyclo[8]aramide **1c**. (a) Top view, (b) Side view in the CPK model, illustrating a saddle-like macrocyclic backbone. The dashed blue lines in (a) indicate hydrogen bonds.

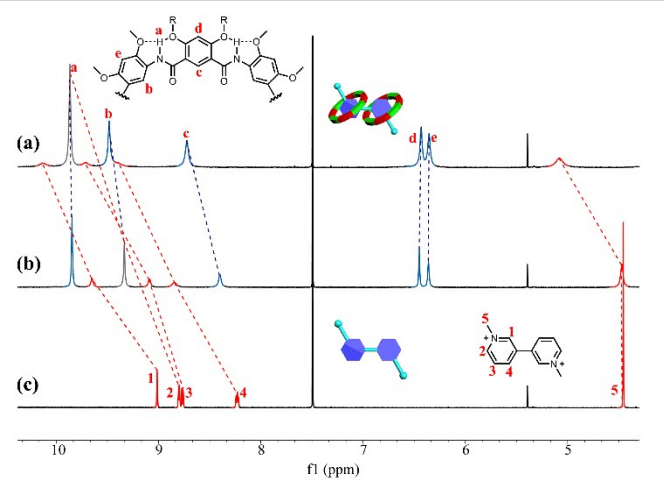

Fig. 3 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3/CD_3CN$ = 1 : 1, 298 K) of (a) 2 : 1 mixture of **1a** (4.0 mM) and **G2** (2.0 mM), (b) 1 : 1 mixture of **1a** and **G2** (each 2.0 mM) and (c) **G2** (2.0 mM). The spectrum of **1a** is not shown due to low solubility.

Threading of the guests through the cavity of a macrocycle is evidenced by the results from 2D nuclear overhauser effect spectroscopy (NOESY). NOESY experiments performed with a solution ($CDCl_3/CD_3CN$, 1 : 1) of **1a** and **G2** (or **G3**) reveal cross peaks between bipyridinium protons of **G2** (or **G3**) and the internal aromatic protons Hb and Hc of **1a** (Fig. S25-S26, ESI†). No through-space NOEs are observed with the mixture of **1a** and **G1** due to severely broadened signals caused by aggregation at high concentration (Fig. S83, ESI†). These ^{1}H NMR experiments with macrocycles of contrasted side chains (linear and branched) reveal that the steric barricade on the macrocyclic periphery plays a crucial role in effecting intermolecular interactions between cyclo[8]aramide molecules, which is manifested in two significantly different binding modes (2 : 1 and 1 : 1). As such, the follow-up discussions only involve the use of **1a** for cooperativity experiments.

A qualitative evaluation of the allosteric cooperativity in these systems was implemented by titration of guests into solutions of **1a**. The formation of complexes **1a⊃G1-G3** and **1a$_2$⊃G1-G3** and the presence of free **1a** were analyzed by fitting experimental data[21] from UV-vis spectroscopy (Fig. 4 and S27–S32, ESI†).

Positively cooperative systems are characteristic of the presence of only fully bound species (the final products) and fully unbound species (the starting host or guest) in the binding event.[1a] This is usually signalled by the persistence of a low concentration of intermediates throughout the titration process (Fig. S33-S35, ESI†). In the case of **G3**, the concentration profiles were obtained by fitting the entire series of spectra to the model shown in Fig. 1b. The mole fraction of the 1 : 1 complex (intermediate) only reaches 7% when titrating 1.0 equiv. of **G3** into the solution of **1a** in $CHCl_3/CH_3CN$ (1 : 1) and slowly rises to a maximum of 11% with 1.7 equiv. of **G3** (Fig. 4). Since less than 10% of **G3** was observed to exist in the form of the complex **1a⊃G1** with 1 equiv. of the guest in the titration process, it suggests that the intermediate is maintained at a very low concentration. At the same time, the 2 : 1 bound species **1a$_2$⊃G3** starts to predominate at 0.34 equiv. of **G3**. Taken all these results together, this demonstrates the presence of strong positive allosteric cooperativity in the complex **1a$_2$⊃G3**.

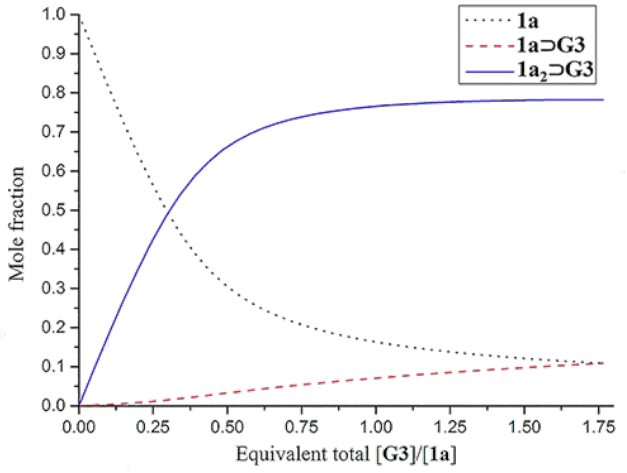

Fig. 4 Mole fraction evolution of existing species **1a$_2$⊃G3**, **1a⊃G3** and **1a** in the system when titrating **G3** into a solution of **1a** (50 μM, $CHCl_3/CH_3CN$ = 1 : 1) as monitored by UV-vis spectroscopy. Mole fraction is defined as the amount of a constituent (**1a$_2$⊃G3**, **1a⊃G3** or **1a**) divided by the total amount of all constituents in the mixture.

To quantitatively evaluate allosteric cooperativity, cooperative factor α was determined by UV-vis spectroscopy. The extent to which cooperativity works in a H-G system relies heavily upon types of guests and solvent polarity. [22] Thus, binding behaviours of three structurally isomerized bipyridinium cations and variation of solvent polarity were explored (Tab. S4-S5 and Fig. S36-82, ESI†). Partial data along with their ternary binding constants of **1a** with **G1**-**G4** are listed in Table 1. Isothermal titration calorimetry (ITC) experiments were also performed; however, the large error as a result of a very small change in heat prevented us from retrieving accurate binding constants. The ^{1}H NMR titration experiments also failed due to low solubility of **1a**.

Table 1. Association constants (K_a/M^{-1})[a] for complexation of various guests (**G1**, **G2**, **G3** and **G4**) by host **1a** at 298 K.

Guest	Solvent $CHCl_3/CH_3CN$	K_1 (×10^4)	K_2 (×10^4)	K_a/M^{-2} (×10^{10})	α^b
G1	1:1	59 ± 8.6	5.7 ± 0.4	3.4	0.39
G2	1:1	4.1 ± 1.0	42 ± 0.3	1.7	41
G3	1:1	1.6 ± 0.3	66 ± 6.6	1.1	165
G3	1.3:1	3.2 ± 0.5	32 ± 1.9	1.0	40.
G3	1.5:1	8.4 ± 1.7	28 ± 2.8	2.4	13
G3	1.7:1	24 ± 1.4	51 ± 5.5	12	8.5
G3	2:1	40 ± 9.0	70 ± 10	28	7
G4	1:1	2.9 ± 0.1	-	-	-

[a] The association constant K_a values were obtained by UV-vis titration spectroscopy†, the concentration of the host was fixed at 50 μM; [b] α represents the cooperativity factors defined as $\alpha = 4K_2/K_1$.

All cooperativity factors in Table 1 for the complexes between **1a** and **G1**-**G3** are larger than ca. 7 except for **G1**, indicative of a positive cooperativity. The binding affinity for the guest by the first macrocycle is comparable to that of the methylated pyridinium **G4** alone as indicated by a K_1 value of 2.91×10^4 M^{-1}. The increase of solvent polarity for **G3** brings about enhanced positive cooperativity. This holds true for **G2** (Tab. S4, ESI†), and **1a$_2$⊃G1** still exhibit negative cooperativity. Particularly noteworthy is the complex **1a$_2$⊃G3**, which gives a α value of 165. For allosteric cooperative systems associated with shape-persistent macrocycles, such high positive cooperativity is considered pretty large through weak interaction excluding ion-pair systems.

To gain a better understanding of the positive allosteric cooperativity, computational simulation based on the density function theory (DFT) method was performed with **1a$_2$⊃G3** as a representative example (Fig. S84-S86 and Tab. S6, ESI†). The result indicates that multiple π-π stacking interactions are presented, which is consistent with the π stacking observed in the crystal structure of **1c**. There are several C-H···O hydrogen bonds between two cyclo[8]aramides. Cation-dipole interaction between cyclo[8]aramide and bipyridinium salt also contributes to positive allosteric cooperativity.

Furthermore, the difference in the binding mode of macrocycles 1a and 1b (2:1 vs. 1:1) suggests that the van der Waals force constitute another factor to effect the cooperative action in forming the complexes. However, the essence of each specific interaction that is responsible for the collective cooperativity is still hardly understood.

In conclusion, we demonstrate strong positive allosteric cooperativity in solution of shape-persistent cyclo[8]aramide-based ternary complexes. A cooperativity factor of 165 is achieved with a bipyridinium salt as a result of combined weak interactions including π-π stacking, hydrogen bonding, cation-dipole interaction and van der Waals force. Increasing the polarity of solvent system tends to raise positive allosteric cooperativity. Also noteworthy in this work is the first single crystal structure of this series of H-bonded aromatic amide macrocycles of larger size. These findings offer opportunities for constructing mechanically interlocked molecules with H-bonded aromatic amide macrocycles of large lumen.

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