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RESEARCH ARTICLE

Recognition of anions by protonated methylazacalixpyridines

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Methylazacalixpyridines are a unique kind of macrocyclic molecules that are able to self-regulate their conformations to best fit the guests. They had shown good recognition to both neutral molecules such as diols and fullerenes and cations. After protonation, the conformation of methylazacalixpyridines became more flexible and could serve as receptors for anions. In the solution, the protonated methylazacalix[2]pyridine[2]arene formed complexes with halides yielding biding constants of 79 $(mol/L)^{-1}$ for chloride, 10 $(mol/L)^{-1}$ for bromide, and 79 $(mol/L)^{-1}$ for iodide, respectively. The crystal structures of the complexes between protonated methylazacalix[4]pyridine (MACP-4), methylazacalix[2]pyridine[2]arene (MACP-2-A-2), and iodide anion showed a multiple interaction mode including electrostatic attraction, hydrogen bonding, and anion-π interactions.

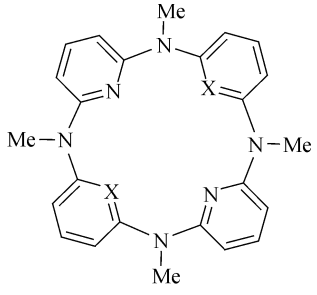
Keywords anion recognition, methylazacalixpyridine, protonation

1 Introduction

Anion recognition has attracted much attention because of its importance in biological and environmental sciences [1–6]. The design of anion receptors is particularly challenging because of the special properties of anions such as a lower charge to radius ratio, various geometries, and sensitivity to the environmental pH values. During the past years, a large number of synthetic host molecules has been designed aimed at anion recognition based on the principles of hydrogen bonding [7–13], electrostatic interaction [14–18], hydrophobic effect [19,20], and coordination to metal ions [21]. More recently, synthetic anion receptors on the basis of new anion-π interaction have also been reported [22–26].

Heteroatom-bridged calix(hetero)aromatic compounds [27–52] are an emerging generation of macrocyclic host molecules. Because of the different electronic nature of heteroatoms from carbon, the heteroatom-bridged calix (hetero)aromatic compounds exhibit intriguing and unique structural and molecular recognition properties with respect to t'he well-known calix[*n*]arenes [53–60] in which the (hetero) arene units are linked by methylene units. The introduction of heteroatoms, especially nitrogen atoms on the bridges result in the formation of different conformations and cavities owning to the fact that bridge nitrogen atoms can adopt sp^2 and/or sp^3 electronic configurations and can form various degrees of conjugations with the adjacent aromatic rings [43–48] More importantly, the heteroatom-bridged calix(hetero)aromatic compounds can self-regulate their conformations to best fit the guests when interacting with guest [44,46]. For example, azacalix[4]pyridine had shown a good recognition to both neutral molecules such as diols and fullerenes and metal cations [43–48]. We had also found that methylazacalixpyridines were easily protonated in the presence of acids. We therefore envisioned that methylazacalixpyridine macrocycles, powerful synthetic receptors for neutral guest molecules and cations, would act as anion receptors if they are protonated by acid. In addition, multiple interactions including electrostatic attraction and hydrogen bonding between the protonated methylazacalixpyridines and anion guest species would reinforce the host-guest interaction.

Herein, we report the halide recognitions by the fully protonated methylazacalix[4]pyridine (MACP-4) and methylazacalix[2]arene[2]pyridine (MACP-2-A-2) (Figure 1) under acidic conditions. In solution, the protonated MACP-2-A-2 was found to form complexes with all the halides tested. Interestingly, X-ray crystallography revealed a multiple interaction mode between the hosts and anions.



MACP-4 (X = 4)
MACP-2-A-2 (X = CH)

Figure 1 The structure of MACP-4 and MACP-2-A-2.

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2 Experimental

2.1 Preparation of methylazacalixpyridines

MACP-4 and MACP-2-A-2 was prepared according to our previous reports [43,44].

2.2 Spectral titrations

A stock solution of MACP-4 (2.531×10^{-6} mol/L) was prepared by dissolving MACP-4 in acetonitrile/methanol (1∶1, v∶v) containing 0.1 mol/L of $H_2SO_4\cdot50\%SO_3$. The pH value of the solution was -0.65. As reported previously, both MACP-4 and MACP-2-A-2 were fully protonated, and they formed $H_4(MACP\text{-}4)^{4+}$ and $H_2(MACP\text{-}2\text{-}A\text{-}2)^{2+}$, respectively [44]. The resulting host solution (2.531×10^{-6} mol/L, 2.5 mL) was added to the colorimetry cell, and spectral changes were recorded with an increments solution of tetrabutylammonium halides. UV-Vis and fluorescence titrations were carried out on a Shimadzu UV-2401PC and a Hitachi F-4500 spectrometer, respectively. For the fluorescence titrations, the excitation wavelength (λ_{ex}) was set to 345 nm for protonated MACP-4 and 350 nm for protonated MACP-2-A-2, respectively. The excitation and emission band widths were 10 nm and 20 nm, respectively. The titration data were fitted by a Hyperquad 2003 program in order to calculate the binding constants.

2.3 Single crystal preparations [61]

For the preparation of single crystal of $MACP\text{-}4\cdot2HI\cdot4I_2$ and $MACP\text{-}2\text{-}A\text{-}2\cdot2HI\cdot I_2\cdot CH_3OH$, MACP-4 (10 mg) and MACP-2-A-2 (10 mg) were dissolved in 20 mL methanol containing 40% HI solution (1∶1, v∶v), respectively. The solvent were evaporated slowly at 288 K. Prism purple red crystals with good quality were obtained, which were suitable for X-ray diffraction analysis.

3 Results and discussion

By means of spectral titration method, we first examined the interaction between protonated MACP-4, MACP-2-A-2 and halides in solution. As illustrated in Figure 2(a), the fluorescence intensity of the protonated MACP-4 showed an

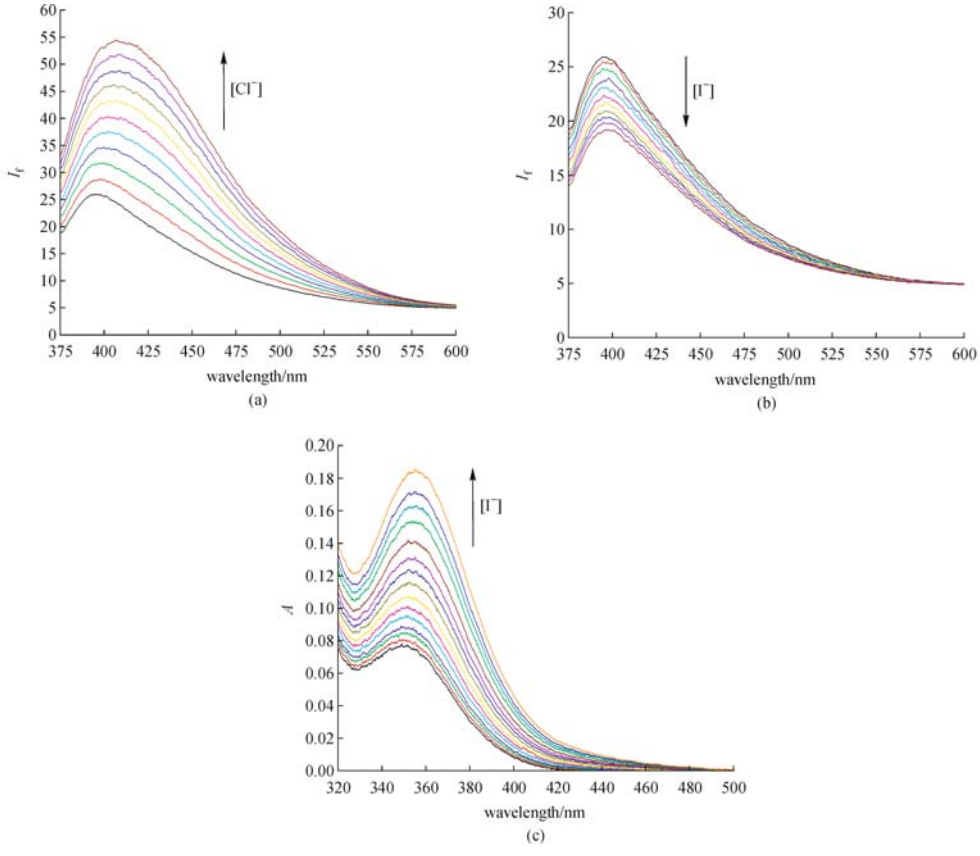

Figure 2 The fluorescence emission response of the protonated MACP-4 (2.531×10^{-6} mol/L) generated by the addition of (a) N(n-Bu)$_4$Cl (0–1.538×10^{-2} mol/L) and (b) N(n-Bu)$_4$I (0–8.988×10^{-3} mol/L). (c) The UV-Vis spectral change of the protonated MACP-4 with the addition of N(n-Bu)$_4$I (0–1.618×10^{-3} mol/L).

increase with the addition of Cl^-, while no UV-Vis spectral change was observed when it was titrated by Cl^-. The addition of Br^- did not lead to any obvious fluorescence or UV-Vis spectral response of protonated MACP-4. Iodide, on the other hand, resulted in a quench of the fluorescence (Figure 2(b)) and an increase in the absorbance (Figure 2(c)) when it interacted with the protonated MACP-4. Similar to that of the protonated MACP-4, the addition of Cl^- to the protonated MACP-2-A-2 also resulted in an increase of the fluorescence intensity (Figure 3(a)) but no UV-Vis spectral change. However, though the addition of Br^- did not affect the UV-Vis absorbance of the protonated MACP-2-A-2, it led to a quench of the fluorescence intensity (Figure 3(b)). When the protonated MACP-2-A-2 was titrated with I^-, fluorescence quench (Figure 3(c)) and absorbance increase (Figure 3(d)) were both observed.

The spectral data were fitted by the Hyperquad 2003 program in order to obtain the binding constants. When the stoichiometric ratio between the host and guest was 1∶1, the best fit was obtained, and hence, the binding constants were calculated. On the basis of the outcomes of fluorescence titrations, as listed in Table 1, binding

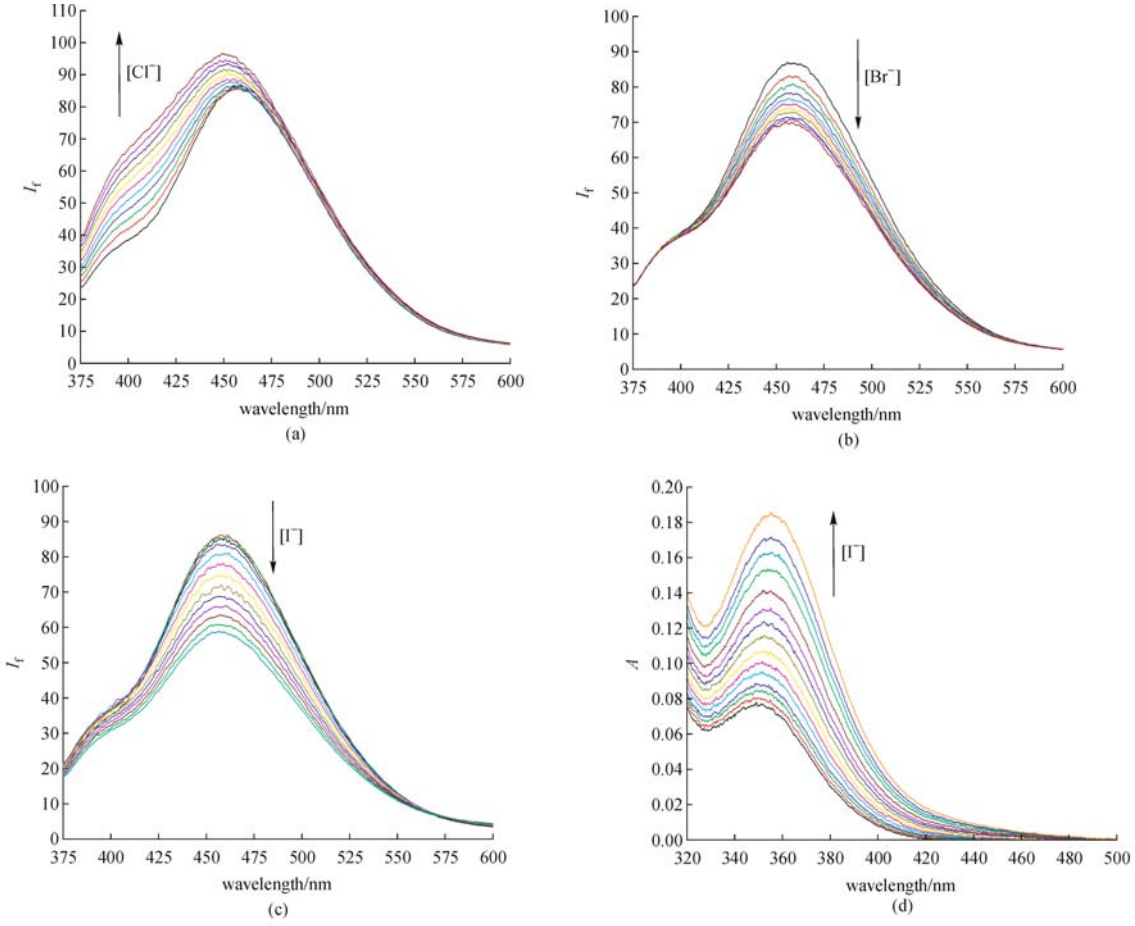

Figure 3 The fluorescence emission response of the protonated MACP-2-A-2 generated by the addition of (a) N(n-Bu)$_4$Cl (0–2.897×10^{-2} mol/L), (b) N(n-Bu)$_4$Br (0–1.538×10^{-2} mol/L), and (c) N(n-Bu)$_4$I (0–4.764×10^{-3} mol/L). (d) The UV-Vis spectral change of the protonated MACP-2-A-2 with the addition of N(n-Bu)$_4$I (0–2.022×10^{-3} mol/L).

Table 1 Calculated binding constants K_a ((mol/L)$^{-1}$) for the 1∶1 complex of protonated methylazacalixpyridines and halides[b]

host	method	Cl^-	Br^-	I^-
H_4(MACP-4)$^{4+}$	UV-Vis	–[a]	–[a]	20
	fluorescence	40	–[a]	25
H_2(MACP-2-A-2)$^{2+}$	UV-Vis	–[a]	–[a]	126
	fluorescence	79	10	79

a No spectral change was observed with the addition of anions.
b K_a was calculated by fitting the spectral data with the Hyperquad 2003 program.

constants of 40 $(mol/L)^{-1}$ and 25 $(mol/L)^{-1}$ were found for the complexes between protonated MACP-4 and chloride and iodide, respectively. On the other hand, the protonated MACP-2-A-2 formed complex with the three halides, giving biding constants of 79 $(mol/L)^{-1}$ for Cl^-, 10 $(mol/L)^{-1}$ for Br^-, and 79 $(mol/L)^{-1}$ for I^-, respectively.

To take a deep insight into the interaction between hosts and guests, single crystals of the complex were cultivated, and the X-ray molecular structures of the complexes between the protonated MACP-4, MACP-2-A-2, and iodide were obtained. As depicted in Figure 4(a) and (b), some interesting structural details are worth addressing. Taking the complex of MACP-4·2HI·4I_2 as an example, after forming a complex with iodide, the protonated MACP-4 adopted a saddle-like conformation with an S_4 symmetry, a conformation very different from its parent molecule MACP-4, which showed a 1,3-alternate conformation in the solid state [44]. This conformational change demonstrated that the protonated MACP-4 is flexible and would likely to adjust its conformation in order to form an efficient interaction with the guests [44]. Second, the four pyridine nitrogen atoms located on the same plane (Figure 4(a)) and the positive charges seemed to be delocalized into the whole molecule. Third, the saddle-like molecule formed two identical electron positive cavities and contained two guest anions in each cavity. The guest, on the other hand, was in a form of an interesting pentamer (I_5^-) in which the iodides combined each other through the halogen bond with the halogen bond distances ranging from 2.802 Å to

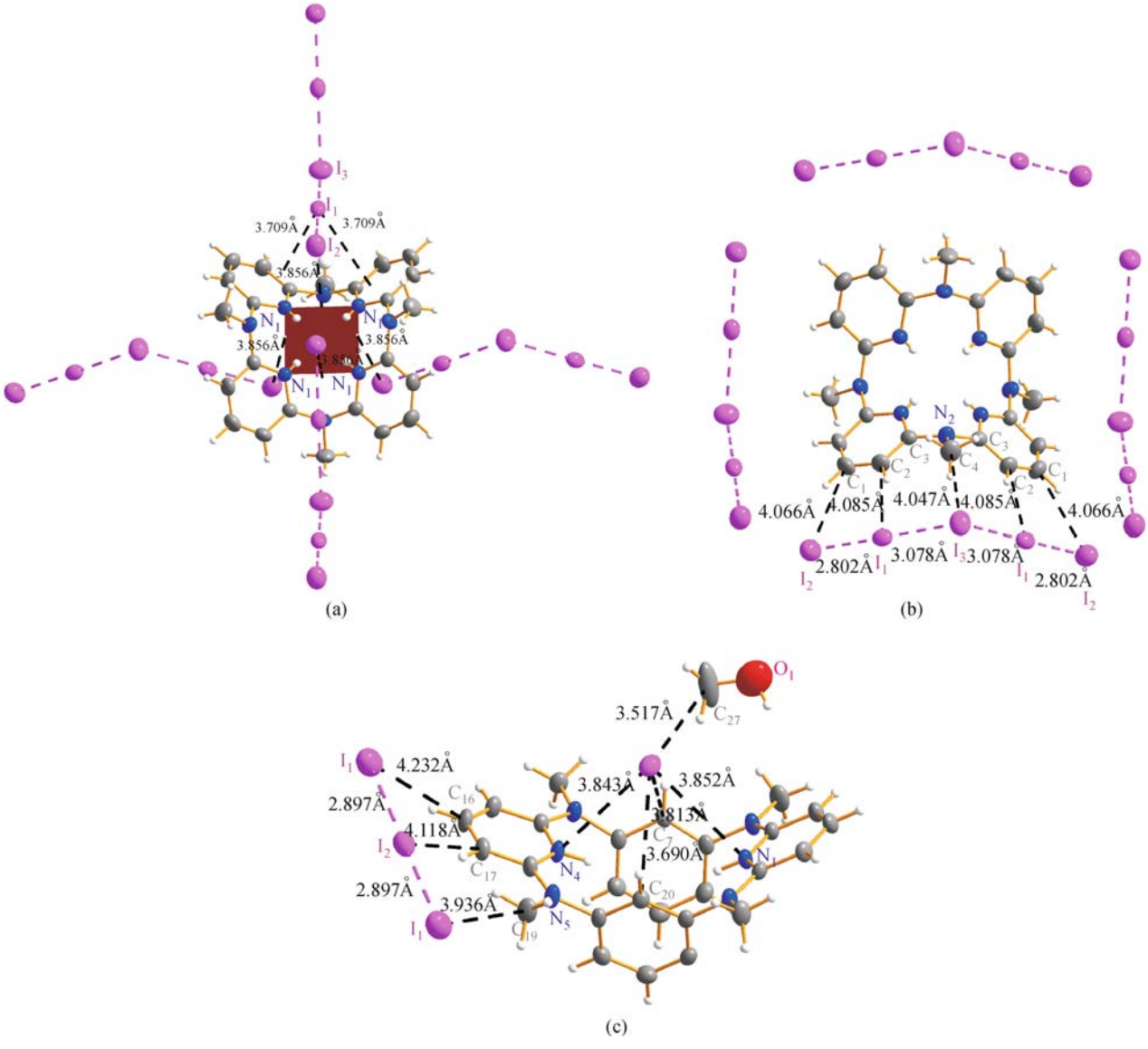

Figure 4 The X-ray structure of the complex (a) MACP-4, (b) MACP-4·2HI·4I_2, and (c) MACP-2-A-2·2HI·I_2·CH_3OH.

3.078 Å (Figure 4(b)). A multiple interaction mode was found between the protonated MACP-4 and I_5^-. First, electrostatic interactions between the host molecule and I_5^- anions were observed (Figure 4(a)), and the distance between I_5^- (d_{I_2}-plane) and the plane formed by the four pyridine nitrogen atoms was 3.856 Å. In addition, I_5^- anions interacted with the adjacent two pyridine rings through the anion-π interaction. This was proven by the almost same distances from the I_5^- anions (d_{I_1}-pyridine plane) to the plane and to the centroid of the pyridine ring, which were 3.709 Å and 3.792 Å, respectively, showing a typical anion-π interaction. Interestingly, the halogen bonds in I_5^- were directed by the shape of the host molecule (Figure 4(b)). For example, for the iodides aligned along the "saddle" edge of the molecule, the angle $\Leftrightarrow I_1$-I_3-I_1 was 107.93°, which was almost the same as that of the molecular "saddle" of 119.76° ($\Leftrightarrow C_3$-N_2-C_3).

The crystal structure of the protonated MACP-2-A-2 and iodide (MACP-2-A-2·2HI·I_2·CH_3OH) was shown in Figure 4(c). The macrocyclic ring of the protonated MACP-2-A-2 generated a 1,3-alternate conformation with an approximate C_{2v} symmetry. It is a conformation slightly different from its parent molecule MACP-2-A-2, which showed a distorted 1,3-alternate conformation. The symmetric conformation of the protonated MACP-2-A-2 in the complex indicated that the proton charges were delocalized into the whole molecule. The guest, both in I^- and I_3^- were found in the crystal. From the crystal structure of the complex, multiple interactions between the host and guest were also found. For example, the I^- anion was located in the cavity of the protonated MACP-2-A-2 through an electrostatic interaction. The distances between the iodide anion and pyridine nitrogen atoms were 3.852 Å (d_{I5}-N_1) and 3.843 Å (d_{I_5}-N_4), respectively. I^- also interacted with the two benzene rings through hydrogen bonding; the hydrogen bonding distances were 3.690 Å (d_{I_5}-C_{20}, $\Leftrightarrow I_5$-H-C_{20} 114.48°) and 3.813 Å (d_{I_5}-C_7, $\Leftrightarrow I_5$-H-C_7 118.96°), respectively. Furthermore, I^- interacted with a methanol thro-ugh the formation of a hydrogen bond I_3^- anion. However, it did not show any interaction with the host molecule.

4 Conclusion

In summary, we have shown that methylazacalixpyridines, the macrocyclic host molecules used for the recognition of metal cations and neutral molecules, were able to form protonated species to interact with halides under acid conditions. The 1∶1 binding constants with halides were up to 79 $(mol/L)^{-1}$. The solid state structure of the complex of protonated azacalix[4]pyridine and azacalix[2]arene[2]pyridine with iodide anion revealed multiple interactions, including electrostatic, hydrogen bond, and anion-π interactions between host and guest.

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