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Anion−π Interactions: Generality, Binding Strength, and Structure

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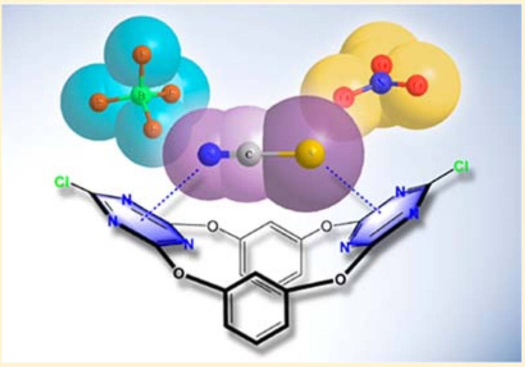
Supporting Information



ABSTRACT: Anion−π interactions have been systematically studied using tetraoxacalix[2]arene[2]triazine **1**, an electron-deficient and cavity self-tunable macrocyclic host, as an electron-neutral molecular probe. As revealed by electrospray ionization mass spectrometry (ESI-MS), fluorescence titration and X-ray crystallography, tetraoxacalix[2]arene[2]triazine has been found to form 1:1 complexes with four typical polyatomic anions of different geometries and shapes in the gaseous phase, in solution, and in the solid state. The association constants for the formation of anion−π complexes in acetonitrile are in the range of 239 to 16950 M^{-1}, following the order of $\mathbf{1}\cdot NO_3^-$ > $\mathbf{1}\cdot BF_4^-$ > $\mathbf{1}\cdot PF_6^-$ > $\mathbf{1}\cdot SCN^-$. X-ray molecular structures of the complexes showed that two opposing triazine rings of tetraoxacalix[2]arene[2]triazine act as a pair of tweezers to interact with the included anions through cooperative anion−π and lone-pair electron−π interactions. The generality of anion−π interactions and diverse anion−π interaction motifs can provide a new dimension in the study of molecular recognition and self-assembly. Moreover, this study potentiates the effect of anion−π interactions in chemical and biological systems, especially those involving anion and electron-deficient aromatic species.

INTRODUCTION

Exploration and comprehension of noncovalent bond interactions are one of the central tasks in chemistry as noncovalent bond interactions are ubiquitous in nature and play important roles in living systems.[1] Control of cooperative noncovalent bonding effects, on the other hand, is paramount in the fabrication of advanced functional materials and molecular devices.[1] In addition to well-known and classical noncovalent bond interactions ranging from hydrogen bonding to cation−π interaction and π−π stacking[2] etc., interactions between anions and aromatic rings have attracted growing interest in recent years.[3] Proposed by three research groups of theoreticians independently in 2002 based on their theoretical calculations,[4] anion−π interactions are defined as attractive interactions between negatively charged species and electron-deficient aromatic rings. There are two general types of anion−π interaction motifs. Typical anion−π interaction indicates the attraction of an anion species to the centroid of an aromatic ring while the weak σ-interaction describes special contacting modes in which an anion is located over the periphery of an aromatic ring.[3c,5]

In comparison to a plethora of theoretical calculations of anion−π interactions,[4−6] experimental studies on these intriguing noncovalent bond interactions are limited.[7] Most of the studies are based on molecular recognition models that combine anion−π interactions with other noncovalent bond interactions such as hydrogen bonding[7f,h,o] and halogen bonding.[7n] Indisputable evidence for the *pure and exclusive* anion−π attraction between anions and *electron-neutral* aromatics are still rare.[7a−e,k−m] Soon after the nearly simultaneous publication of the aforementioned seminal theoretical calculation works,[4] Kochi[7b] reported in 2004 the interactions of halides with electron-deficient arenes such as tetracyanobenzene and tetracyanopyrazine, showing weak σ-type anion−π interactions through a charge-transfer mechanism. Similar halide−π interactions were observed recently by Dunbar[7e] in the multisite interactions of 1,4,5,8,9,12-hexaazatriphenylene-hexacarbonitrile, an extended aromatic π-receptor, with halides both in the crystalline state and in THF solution. 1,4,5,8-Naphthalene diimides (NDIs) are also able to interact with anions.[7k−m,p] Very recent studies by Saha,[7k−m] for example, have indicated that the nature of anion−NDI interactions in solution varies from weak anion−π interactions to charge transfer and electron transfer depending on the Lewis basicity of anions and π-acidity of NDIs. However, the structures of anion-NDI complexes at molecular level are still lacking.

Heteracalixaromatics or heteroatom-bridged calix(hetero)arenes are a new generation of macrocyclic host molecules in supramolecular chemistry.[8] Being different from the methylene linkages between phenolic rings in conventional calixarenes, the

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bridging heteroatoms such as nitrogen in heteracalixaromatics can adopt different electronic configurations and, more remarkably, form varied degrees of conjugation with their neighboring aromatic rings. As a consequence, heteracalixaromatics are able to adopt self-regulated conformations and thus own fine-tuned cavities.[9] Moreover, the combination of various heteroatoms and aromatic rings and the interplay between aromatic components and linking elements engender diverse macrocycles of different electronic features and therefore unique binding properties toward electron-neutral[10] and charged guest species.[7c,d,i,j,11]

Tetraoxacalix[2]arene[2]triazine **1** (Figure 1), a member of heteracalixaromatics that is prepared readily by means of a fragment coupling approach from cheap and commercially available resorcinol and cyanuric chloride, exists as a 1,3-alternate conformer.[9a] While the two opposing benzene rings are face-to-face paralleled, the altering triazine rings tend to edge-to-edge positioned yielding an electron-deficient V-shaped cleft. It has been shown recently by us that this macrocycle can act as a receptor for halides in acetonitrile.[7c] The ternary complex of tetraoxacalix[2]arene[2]triazine with halide and water molecule revealed by X-ray crystallography indicated the formation of the typical anion−π and the lone-pair electron−π interactions between halide and triazine centroid and between oxygen of water and triazine centroid, respectively. Further careful scrutiny of the complex structures concluded that the fine and self-tunability of the cavity of tetraoxacalix[2]arene[2]triazine macrocycle is responsible for its recognition of anionic guest species. Encouraged by these preliminary results, we then envisioned that the unique structure of tetraoxacalix[2]arene[2]triazine featuring with a self-adjusting electron-deficient cavity would render a powerful anion receptor in probing the anion−π interactions. We report herein our systematic studies on the anion−π interactions of tetraoxacalix[2]arene[2]triazine with various anions of different geometry in solution and in the solid state by means of spectrometric titrations and X-ray crystallography, respectively. We discovered that all sorts of anions tested formed 1:1 complexes with tetraoxacalix[2]arene[2]triazine in acetonitrile giving association constants in the range of 239 to 16950 M^{-1}. Tetraoxacalix[2]arene[2]triazine was found indeed to act as a smart host to *chelate* differently shaped anions with its two triazine rings through the cooperative anion−π and lone-pair electron−π interactions.

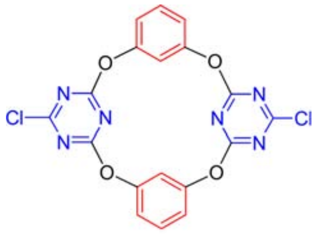

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Figure 1. Structure of tetraoxacalix[2]arene[2]triazine.

■ RESULTS AND DISCUSSION

In contrast to metal ions which are spherical, anions and, particularly, polyatomic anions possess abundant structural diversities. This has led to the studies of anion recognition being frustrating and intriguing. For selective recognition of anions of varied geometries and shapes, for instance, different synthetic receptors on the basis of principles of different noncovalent interactions and shape-match have to be synthesized.[1] Understanding and quantification of a specified noncovalent bonding between a single designed receptor or probe and diverse anions, on the other hand, becomes very difficult. Aimed at examination of the generality of anion−π interactions and also to understand the effect of the nature of anions on the anion−π interactions, we choose representative anions of varied geometry including linear thiocyanate (NCS^-), triangular nitrate (NO_3^-), tetrahedral tetrafluoroborate (BF_4^-), and octahedral hexafluorophosphate (PF_6^-) in the current study.

We first studied the interactions of tetraoxacalix[2]arene[2]triazine **1** with anions of tetrabutylammonium salts by means of spectrometric titrations. While the addition of all anions tested

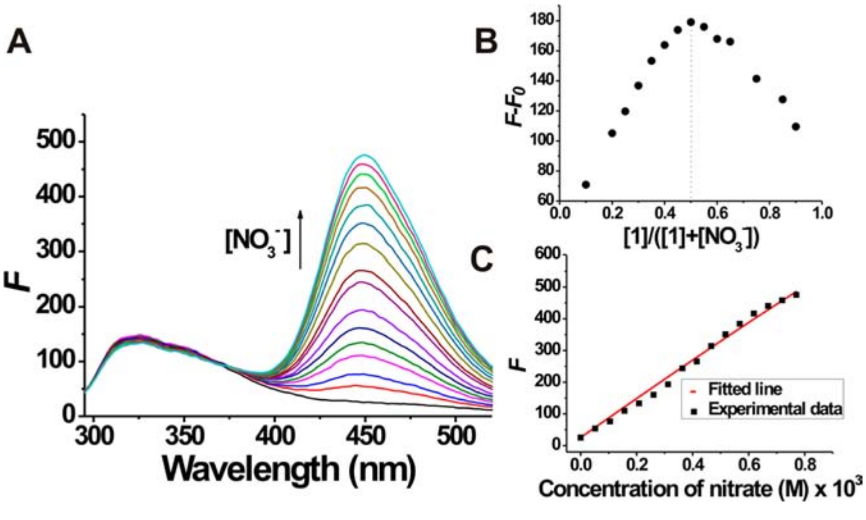

Figure 2. (A) Fluorescence titration of **1** (1.53×10^{-3} M in 2 mL of acetonitrile) upon the addition of tetrabutylammonium nitrate (0, 0.052, 0.10, 0.16, 0.21, 0.26, 0.31, 0.36, 0.41, 0.47, 0.52, 0.57, 0.62, 0.67, 0.72, 0.77 $\times 10^{-3}$ M), respectively. The excitation wavelength was 280 nm and the excitation and emission slits were set at 10 nm. (B) Job's plot of the complex of **1** and tetrabutylammonium nitrate with a total concentration being 1.53×10^{-3} M. (C) The least-squares nonlinear fitting (at 450 nm) with a Hyperquad2003 program.

Table 1. Association Constants for 1:1 Anion−π Complexes between Anions and Tetraoxacalix[2]arene[2]triazine 1 in CH_3CN at 298.15 K

	Cl^{-a}	NCS^-	NO_3^-	BF_4^-	PF_6^-
K_a (M^{-1})	4246 ± 83	239 ± 12	16950 ± 847	673 ± 34	291 ± 15
$\Delta G°$ (kJ·mol^{-1})^b	−20.7	−13.6	−24.1	−16.1	−14.1

[a] Data from ref 7c. [b] $T = 298.15$ K.

Table 2. Crystallographic Data for Anion−π Complexes

complex	Et_4N^+(**1**·SCN^-)	Et_4N^+(**1**·NO_3^-)	Et_4N^+(**1**·BF_4^-)	Et_4N^+(**1**·PF_6^-)
empirical formula	$C_{27}H_{28}Cl_2N_8O_4S$	$C_{26}H_{28}Cl_2N_8O_7$	$C_{26}H_{28}BCl_2F_4N_7O_4$	$C_{26}H_{28}Cl_2F_6N_7O_4P$
M_r	631.53	635.46	660.26	718.42
crystal size (mm^3)	0.45 × 0.26 × 0.15	0.50 × 0.43 × 0.30	0.31 × 0.30 × 0.29	0.20 × 0.17 × 0.09
crystal system	monoclinic	orthorhombic	triclinic	orthorhombic
space group	$P2(1)/c$	$Cmca$	$P\bar{1}$	$Cmma$
a (Å)	10.804(3)	36.529(7)	10.916(5)	15.947(2)
b (Å)	12.288(3)	17.756(4)	11.380(6)	16.119(2)
c (Å)	22.243(5)	17.766(4)	12.186(6)	12.028(2)
α (deg)	90.00	90.00	88.894(17)	90.00
β (deg)	90.85(3)	90.00	87.433(16)	90.00
γ (deg)	90.00	90.00	84.956(14)	90.00
V ($Å^3$)	2952.6(12)	11523(4)	1506.2(13)	3091.7(8)
d (g/cm^3)	1.421	1.465	1.456	1.543
Z	4	16	2	4
T (K)	173(2)	173(2)	173(2)	173(2)
R factor ($I > 2\sigma(I)$)	0.0728	0.0613	0.1467	0.0674
R factor (all data)	0.0798	0.0672	0.1546	0.0730
quality of fit	1.281	1.221	2.474	1.195
CCDC	907107	907105	907104	907106

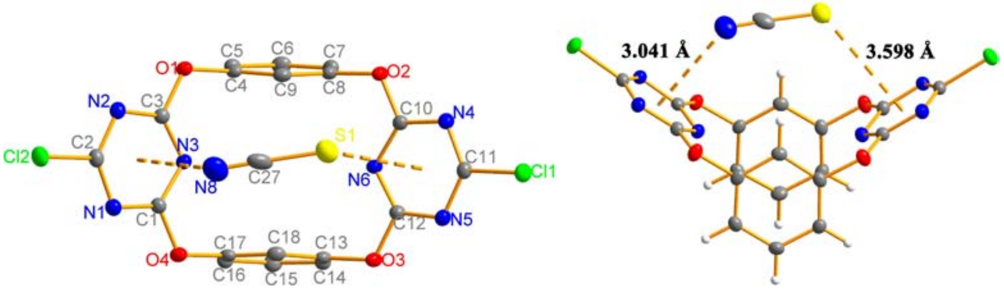

Figure 3. Molecular structure of Et_4N^+(**1**·SCN^-) with top (A) and side (B) views. Et_4N^+ ion was omitted for clarity. Selected distances (Å): 3.050 [N(8)···triazine(1) centroid], 3.041 [N(8)···triazine(1) plane], 3.643 [S(1)···triazine(2) centroid], 3.598 [S1···triazine(2) plane], 3.962 [C(27)···C(18)], 3.916 [C(27)···C(9)], 9.055 [C(2)···C(11)], 4.688 [N(3)···N(6)], 4.406 [C(9)···C(18)], 4.870 [C(6)···C(15)].

in the solution of host in acetonitrile did not cause any change of the electronic spectra, the variations of fluorescence emission of the macrocyclic host were found when anion species were titrated.

As illustrated in Figure 2 and Supporting Information, Figures S5−S7, the addition of anions including thiocyanate, nitrate, tetrafluoroborate, and hexafluorophosphate to the solution of **1** led to the emergence of a new emission band at 450 nm and the fluorescence intensity enhanced gradually upon the increase of anion concentration. The 1:1 stoichiometry between **1** and nitrate was obtained from Job's plot experiment (Figure 2B). All titration data were fitted very well with 1:1 complexation between host and anions (Figure 2C and Supporting Information, Figures S5−S7) and the association constants were calculated using a Hyperquad2003 program.[12] The outcomes along with that of **1**·halide interactions, which were summarized in Table 1, indicated that tetraoxacalix[2]arene[2]triazine **1** acted as an effective macrocyclic host to interact with anions of diverse geometry. The stability of the **1**·anion complexes followed the order of **1**·NO_3^- > **1**·Cl^- > **1**·BF_4^- > **1**·PF_6^- > **1**·SCN^-. It was remarkable that association constants varied dramatically based on anions, with a difference of 2 orders of magnitude being observed between $K_{(\mathbf{1}\cdot NO_3^-)}$ and $K_{(\mathbf{1}\cdot SCN^-)}$. It should also be noted that interactions of host **1** with all anions of tetrabutylammonium salts in CD_3CN did not affect ^1H and ^{13}C NMR spectra of the host (Supporting Information, Figures S8 and S9). This is in agreement with our previous observations for the anion−π interactions between halides and the host **1**.[7c] It also excluded other possible noncovalent arene C−H···anion interactions in solution (see Figure S13 in Supporting Information).

The formation of anion−π complexes between synthetic macrocyclic receptor **1** and anions was also evidenced in the gas phase. As shown clearly by the electrospray ionization mass

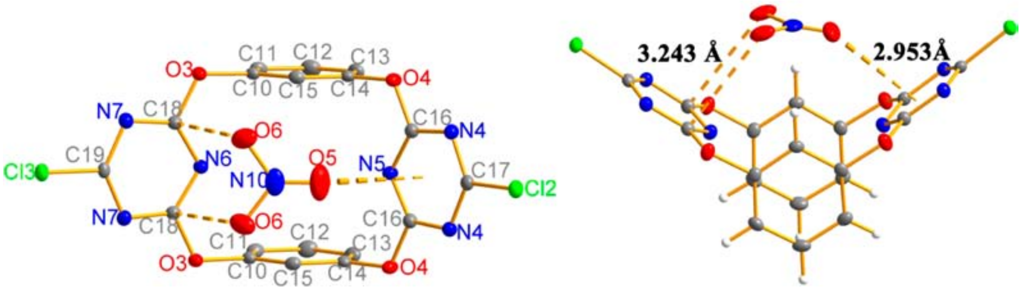

Figure 4. Molecular structure of $Et_4N^+(\mathbf{1}\cdot NO_3^-)$ top view (A) and side view (B). Et_4N^+ ion was omitted for clarity. Selected distances (Å): 3.084 [O(5)···triazine(1) centroid], 2.953 [O(5)···triazine(1) plane], 3.243 [O(6)···C(18)], 8.964 [C(17)···C(19)], 4.668 [N(5)···N(6)], 4.569 [C(15)···C(15)], 4.440 [C(12)···C(12)].

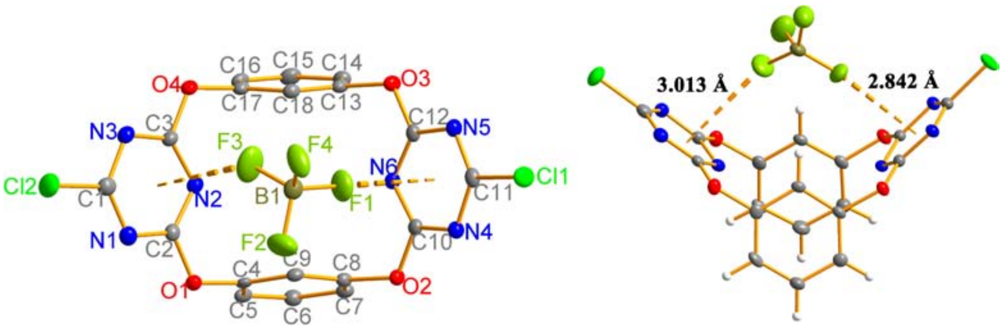

Figure 5. Molecular structure of $Et_4N^+(\mathbf{1}\cdot BF_4^-)$ top view (A) and side view (B). Et_4N^+ ion was omitted for clarity. Selected distances (Å): 2.855 [F(1)···triazine(1) centroid], 2.842 [F(1)···triazine(1) plane], 3.106 [F(3)···triazine (2) centroid], 3.013 [F(3)···triazine(2) plane], 8.613 [C(1)···C(11)], 4.648 [N(2)···N(6)], 4.320 [C(9)···C(18)], 5.206 [C(6)···C(15)], 3.581 [F(1)···C(9)], 3.447 [F(3)···C(18)].

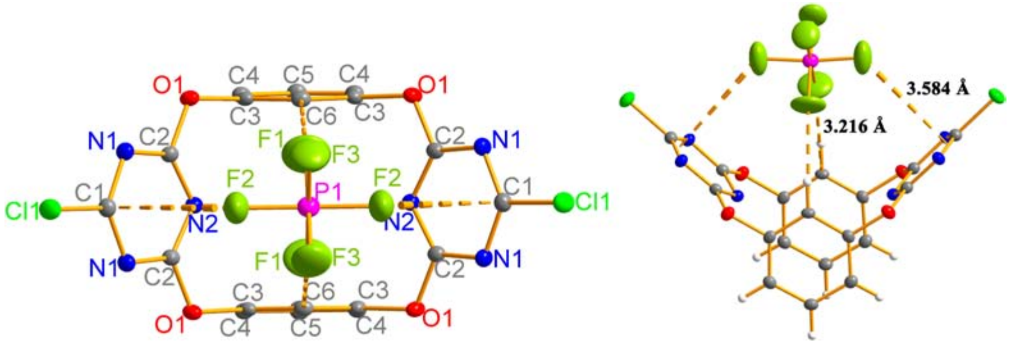

Figure 6. Molecular structure of $Et_4N^+(\mathbf{1}\cdot PF_6^-)$ top view (A) and side view (B). Et_4N^+ ion was omitted for clarity. Selected distances (Å): 3.703 [F(2)···triazine centroid], 3.584 [F(2)···triazine plane], 3.216 [F(1)···C(6)], 8.475 [C(1)···C(1)], 4.639 [N(2)···N(2)], 4.478 [C(6)···C(6)], 4.653 [C(5)···C(5)]. Selected angle (deg): <C6−H6A···F1 153.38.

spectrometry (ESIMS), all mixed samples of **1** with each anion gave the peak which corresponds with the mass of **1**·anion complex except for the mixture of **1** with tetrabutylammonium hexafluorophosphate (Figures S10−S12). No mass peaks other than the mass of **1**·anion were observed in all cases, reflecting the exclusive formation of 1:1 complexes between a π-electron-deficient cavity with an anion in the gaseous state.

To shed light on the anion−π interactions between tetraoxacalix[2]arene[2]triazine **1** and anions studied at molecular level, the single crystals of the complexes between tetraoxacalix[2]arene[2]triazine and the anions were cultivated through slow evaporation of solvent from the mixed dichloromethane/hexane, acetone/hexane, or dichloromethane/methanol solution of **1** and tetraethylammonium salts, or through diffusion of ethyl ether into the dichloromethane solution of **1** and tetraethylammonium salts at room temperature (see Supporting Information for the experimental details). High quality single crystals of the complexes between host **1** and Et_4NX ($X = SCN^-$, NO_3^-, BF_4^-, and PF_6^-) were obtained, and molecular structures of anion−π complexes were determined unambiguously by X-ray crystallography analysis (Table 2).

As depicted in Figures 3−6 and Supporting Information, Figures S1−S4, tetraoxacalix[2]arene[2]triazine **1** forms 1:1 complexes with all tetraethylammonium salts in the solid state. In all complexes, tetraoxacalix[2]arene[2]triazine behaves as an electron-neutral macrocyclic host to accommodate an anion in its π-electron-deficient V-shaped cleft that is composed of two triazine rings. Tetraethylammonium ion, on the other hand, does not contact with the macrocyclic receptor (Supporting Information, Figures S1−S4). Some interesting structural features are worth addressing. First of all, anion species such as thiocyanate, nitrate, and tetrafluoroborate, regardless of their geometrical or three-dimensional structures, form typical anion−π interaction with at least one of the triazine rings.

This has been evidenced clearly by the short distances of anions to the centroid or to the plane of triazine ring. For example, the distances of the nitrogen atom [N(8)] of the included thiocyanate to one triazine's centroid and plane in the tetraoxacalix[2]arene[2]triazine−thiocyanate complex are 3.050 Å and 3.041 Å, respectively (Figure 3), while in the case of the tetraoxacalix[2]arene[2]triazine−nitrate complex, one oxygen atom [O(5)] of nitrate is located above one of the triazine rings, giving its distance to the plane as 2.953 Å and to the centroid as 3.084 Å (Figure 4). As illustrated in Figure 5, one fluorine atom of BF_4^- [F(1)] has the shortest contact with one triazine ring with its respective distance to the centroid and the plane of triazine being 2.855 Å and 2.842 Å. Second, in addition to the typical anion−π interaction between one triazine ring and anions aforementioned, the other electron-deficient triazine moiety of the macrocyclic host also interacts with anions through the formation of either a typical anion−π interaction or a weak σ-interaction depending on the structure of anion guests. This has been exemplified by the observations of a typical anion−π binding of a triazine centroid with a sulfur atom of thiocyanate in the Et_4N^+(**1**·SCN^-) complex (Figure 3) and with one fluorine atom of tetrafluoroborate in the Et_4N^+(**1**·BF_4^-) complex (Figure 5). Noticeably, two oxygen atoms of nitrate in the Et_4N^+(**1**·NO_3^-) complex are positioned above the periphery of triazine ring with the distance between oxygen and the carbon of triazine being 3.243 Å (Figure 4), indicating weak σ-interactions between these two oxygen atoms and triazine ring. Additionally, long distances between arene C−H at the lower-rim positions and anions such as NCS^- and BF_4^- exclude the hydrogen bonding interaction between host and guest. Complexes Et_4N^+(**1**·SCN^-) and Et_4N^+(**1**·BF_4^-) represent therefore unprecedented examples of anion-neutral host complexes resulting solely from the typical anion−π interactions. It should also be noted that, in the X-ray molecular structure of Et_4N^+(**1**·NO_3^-) complex, the distances of oxygen atoms of nitrate to lower-rim carbons of benzene rings are in the range of 3.220 Å to 3.552 Å, suggesting the possible involvement of weak hydrogen bonding effect between arene C−H and nitrate. Furthermore, being different from the complexes of tetraoxacalix[2]arene[2]triazine with thiocyanate, nitrate or tetrafluoroborate in which multiple anion−π interactions are predominant, the anion−π interactions are very weak in Et_5N^+(**1**·PF_6^-) complex as the distances of fluorine atom of PF_6^- to the plane of triazine ring and to the upper-rim carbon of the triazine ring are 3.584 Å and 3.597 Å, respectively. A shorter distance between the fluorine atom of PF_6^- and the lower-rim carbon atom of the benzene ring (3.216 Å) suggests weak hydrogen bonding interactions between host and guest in the crystalline state (Figure 6). Last but not least, the cavity size of the macrocyclic host in each of the complexes, which is defined by the upper-rim distance between two triazine rings, decreased in comparison with that of the parent tetraoxacalix[2]arene[2]triazine. Depending on the anion guest accommodated in the cavity, the upper-rim distance between two triazine rings followed a decreasing order of 9.49 Å (free host **1**), 9.05 Å (**1**·SCN^-), 8.96 Å (**1**·NO_3^-), 8.61 Å (**1**·BF_4^-), and 8.48 Å (**1**·PF_6^-). Concomitantly, the dihedral angle of two triazine rings decreased from 133° (free host **1**) to 112° (**1**·SCN^-), 109° (**1**·NO_3^-), 98° (**1**·BF_4^-), and 94° (**1**·PF_6^-). The obvious variation of shape and size of the cleft formed by two opposing triazine rings in tetraoxacalix[2]arene[2]triazine substantiated the fine- and self-tunability of conformation and cavity of heteroatom-bridged calixaromatics. In other words, tetraoxacalix[2]arene[2]triazine **1** is able to self-regulate its cavity structure to achieve maximum and strongest interactions with the polyatomic anions of different geometries and three-dimensional shapes.

It is also important to address that as revealed by X-ray structures of the complexes such as **1**·SCN^- or **1**·NO_3^-, there are no π−π stacking interactions between a linear SCN^- anion or a planar NO_3^- anion and an electron-deficient triazine ring (see Figure S13(A) in Supporting Information), nor do the included anions position in such ways that hydrogen bonding interactions between anion and arene C−H moieties are preferentially achieved (see Figure S13(B) in Supporting Information) except for PF_6^- in the cavity of **1**. This has been best illustrated by the **1**·BF_4^- complex in which BF_4^- did not rotate 90° around its C_2 axis to allow the formation of two hydrogen bonds with two arene C−H moieties. Instead, orientations of polyatomic anions of linear SCN^-, plane triangular NO_3^-, and tetrahedral BF_4^- structures in the cavity all benefit the strongest cooperative anion−π and lone pair electron−π interactions between electron-rich guests and two triazine rings. The supramolecular motifs of the **1**·anion complexes can be roughly described as a half-sandwich in which anion is complexed by the surfaces of two triazine rings.

CONCLUSION

As a cavity self-tunable macrocyclic host molecule, tetraoxacalix[2]arene[2]triazine **1** was able to form inclusion complexes with polyatomic anions of varied structures in 1:1 stoichiometry in solution and gaseous phases and in the solid state. X-ray molecular structures of the **1**·anion complexes substantiated the formation of cooperative anion−π and lone-pair electron−π interactions between the included anions and two triazine rings of host. Although weak hydrogen bond interactions between anion and arene C−H moiety were reflected by the X-ray structure of **1**·PF_6^- complex, formation of hydrogen bonds between the macrocyclic host **1** and all anions tested was not evidenced at all in solution by ^1H NMR study. Measured by fluorescence titration, association constants for the formation of 1:1 anion−π complexes in acetonitrile increased following the order of **1**·SCN^- (239) < **1**·PF_6^- (291) < **1**·BF_4^- (673) < **1**·Cl^- (4246) < **1**·NO_3^- (16950). The outcomes of our study indicate that anion−π interactions occur generally between electron-rich species and electron-deficient aromatic rings. The anion−π interaction motifs can provide a new dimension in the study of molecular recognition and self-assembly. The effect of anion−π interactions, on the other hand, should not be overlooked in chemical and biological systems that involve anion and electron-deficient aromatic species.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, fluorescence titrations, X-ray structures of anion−π complexes (CIFs), NMR, and MS spectra. 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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