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The Mutual Interactions Based on Amphipathic Tetraoxacalix[2]arene[2]triazine: Recognition Cases of Anion and Cation Investigated by Computational Study

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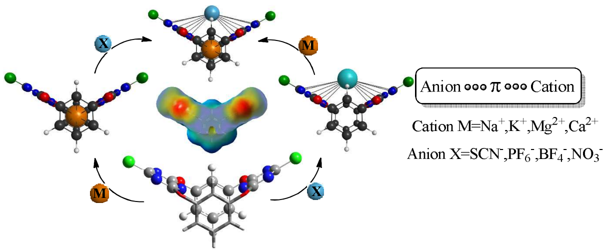

X
M
M
X
Anion ∘∘∘ π ∘∘∘ Cation
Cation M=Na$^+$,K$^+$,Mg^{2+},Ca^{2+}
Anion X=SCN$^-$,PF$_6^-$,BF$_4^-$,NO$_3^-$

ABSTRACT: The nature of anion···π (anion $X_{1\text{-}4}^-$ = SCN^-, PF_6^-, BF_4^- and NO_3^- respectively) interactions with electron-deficient and cavity self-tunable macrocyclic host tetraoxacalix[2]arene[2]triazine **1** as electron-acceptor (*J. Am. Chem. Soc.* **2013**, *135*, 892) have been theoretically investigated with the density functional theory (B3LYP, M06-2X, M06-L, M06, M05-2X, M05, DFT-D3) and the second-order Møller−Plesset perturbation theory (MP2) using a series of basis sets. The binding energies calculated are in good quantitative agreement with experiment. The LMO-EDA (local molecular orbital energy decomposition analysis) results show that the major contributors of anion···π are electrostatic. The alkali metal cations M^+ (Na^+, K^+) and alkaline earth metal cations M^{2+} (Mg^{2+}, Ca^{2+}) can also interact with **1** and the cation···π binding of M^{2+}···**1** is stronger than that of M^+···**1**, as well as their strength is gradually decreased along with the radius of $M^{+,2+}$ increasing. The investigation of interplay between the anion···π and the cation···π shows that the interactions among three-body, X^-, **1** and M^+ is varied with the different phase. The polar solvent can strongly reduces the strength of the interaction, and the more increased solvent polarity, the more reduced binding energy.

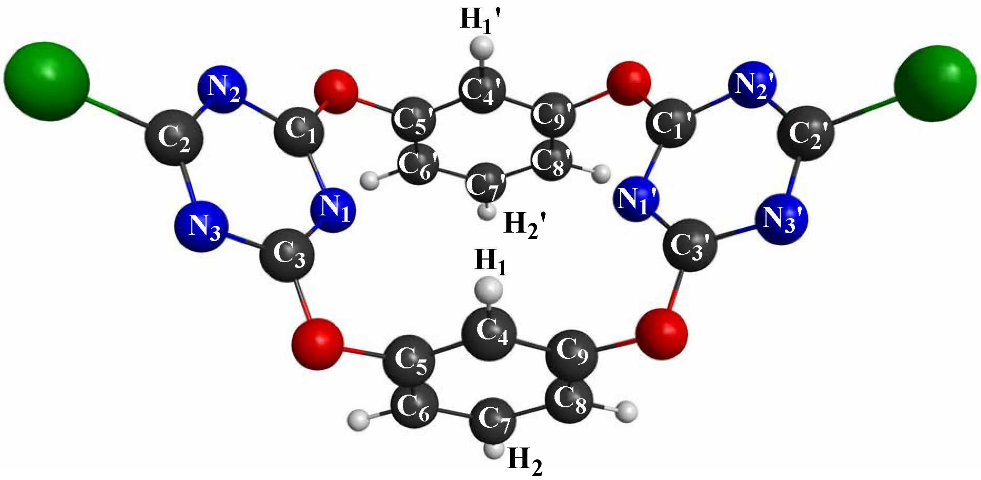
KEYWORDS: complexes · cooperative interaction · density functional theory · anion-π interaction · cation-π interaction

Introduction

The chemistry of noncovalent binding is the intelligent and, in most cases, elegant utilization of interactions between molecules.[1, 2] Nowadays, exploration and comprehension of noncovalent interactions are one of the central tasks in chemistry because noncovalent interactions are ubiquitous in nature and play important roles in controlling molecular recognition processes in biological and artificial systems and in the packing of molecules in crystals.[3, 4] As for well-known interactions ranging from hydrogen bonding to ionic interaction, metallophilic interaction,[5-8] hydrophobic interaction[2] and cation···π interaction[9-11] etc., have attracted growing interest in recent years. In close analogy to the widely studied cation···π interaction, although noncovalent forces between anions and electron-deficient aromatic rings, designated as "anion···π" interaction by three research groups[12-14] have been investigated for several years, systematically and deeply studies on them are still rare.[14-22] Two general types of anion···π interaction motifs were explored, one is typical anion···π interaction (attraction of an anion species to the centroid of an aromatic ring) and another is weak σ-interaction (an anion is located over the periphery of an aromatic ring).[3, 21] The anion···π noncovalent force, which is mainly dominated by the electrostatic interaction or the polarization,[12, 14, 23, 24] has been shown to be energetically favorable by theoretical[24-35] and experimental studies.[34-39] Comparing to numerous investigations of the anion···π interaction based on molecular recognition models that combine anion···π interactions with other noncovalent bond interactions (such as hydrogen bonding and halogen bonding), studies on interactions of combine anions, π and cations are limited.

Heteroatom-bridged heteroaromatic calixarenes are an emerging type of novel macrocyclic molecules.[40-43] They have recently been utilized as versatile host molecules in supramolecular chemistry.[44-48] As a typical example of heteroatom-bridged heteroaromatic calixarenes, electron-deficient tetraoxacalix[2]arene[2]triazine **1** has been recently reported to adopt a pre-organized 1,3-alternate conformation, yielding a cleft formed by two π-electron deficient triazine rings.[40, 49-51] This π-electron-deficient cavity has been envisioned that would act as a receptor to interact with anions through anion-π interactions.[3, 13, 16-24, 37] Recently, although Wang et al[3] reported experimental studies on the anion···π interactions of **1** with anions X$^-$ (SCN$^-$, PF$_6^-$, BF$_4^-$ and NO$_3^-$), in the gaseous phase, solution and the solid state, the influences of solvent on the interaction nature of anion···π interactions are still lacking. In Wang's investigations, the multitypes of noncovalent anion···π and lone pair (l.p.)···π interactions, and a formation of 1:1 complexes with target anions were observed.

In the present work, we report anions SCN$^-$, PF$_6^-$, BF$_4^-$ and NO$_3^-$, as well as alkaline metal cations M$^+$ (Na$^+$, K$^+$) and alkaline earth metal cations M^{2+} (Mg^{2+}, Ca^{2+}) recognized by tetraoxacalix[2]arene[2]triazine **1** (**Scheme 1**) host molecules, considerable interplay of cooperativity or anticooperativity between cation···π and anion···π interactions, how does the solvent influence the interaction nature. For an objective understanding of the actual driving



Scheme 1. Schematic structure of tetraoxacalix[2]arene[2]triazine **1**.

forces of the interaction, decomposition of the total energy into various components by LMO-EDA has been performed. We have focused this paper to understand the physical nature of the aforementioned interactions, which is benefit to choose the best aromatic molecule and the more appropriate ion to design a given system with a given function. This understanding also allows predicting how the strength of the interaction is going to be affected by the presence of other interactions.

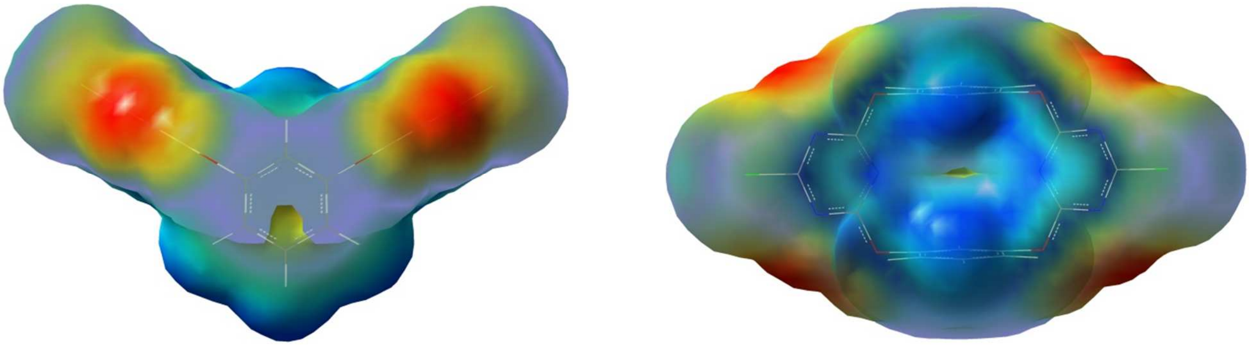
Computational Methods

We present here a combination of B3LYP,[52-54] M06-2X,[55] M06-L,[56] M06, M05-2X,[57] M05, MP2[58, 59] and B3LYP-D3[60, 61] methods with five basis sets [**BS1**: 6-31+G(d,p); **BS2**: 6-31++G(d,p); **BS3**: 6-311+G(d,p); **BS4**: 6-311++G(d,p); **BS5**: aug-cc-pVDZ] employed to obtain reliable geometries of complexes and the interaction energies with basis set superposition error (BSSE), ΔG^{CP}.[62] The different contributions to the interaction energies were obtained by using the LMO-EDA method developed by Su and Li[63] as implemented in GAMESS 2011.[64] The interaction energy has been decomposed into its electrostatic (E_{ES}), exchange (E_{EX}), repulsion (E_{REP}), polarization (E_{POL}) and the dispersion (E_{DISP}) contributions using the M05-2X method. The geometries of all the structures were fully optimized using the GAUSSIAN09 program suite.[65] The natural bond orbital (NBO) analysis was performed to evaluate the different electronic properties, the direction and magnitude of the charge-transfer (CT) interactions of the complexes[66-73] using the NBO 3.1, which is implemented in GAUSSIAN09 program suite. Electrostatic potential surfaces (ESP) of **1** were produced by mapping the electrostatic potential onto the electron density surface using Gaussview.

Results and Discussion

Structures of Complexes

Many functionals, such as M06-2X, M05-2X, B3LYP and DFT-D3 etc, have been previously reported to describe anion-π interactions.[32, 74-76] In order to seek the tractability of quantum chemical methods for complexes, we initially optimize one representative complex $SCN^-\cdots$**1** and the calculated parameters are listed in **Table 1S** (see **SI**). From **Table 1S**, the experimental and computational parameters are comparable at MP2/**BS1** level. As for M05-2X/**BS2**, although which is required more calculated time than M05-2X/**BS1**, it is more closed to the experimental by 0.003 Å.[77] The calculated parameters at other functionals are much deviated from experimental values. The cases indicate that M05-2X is a good predictor for studied complexes and considering accuracy versus economy in the following discussion, M05-2X/**BS2** is adopted to optimize the complexes. Also, the subsequent qualitative analyses are based on geometries at this level of theory.



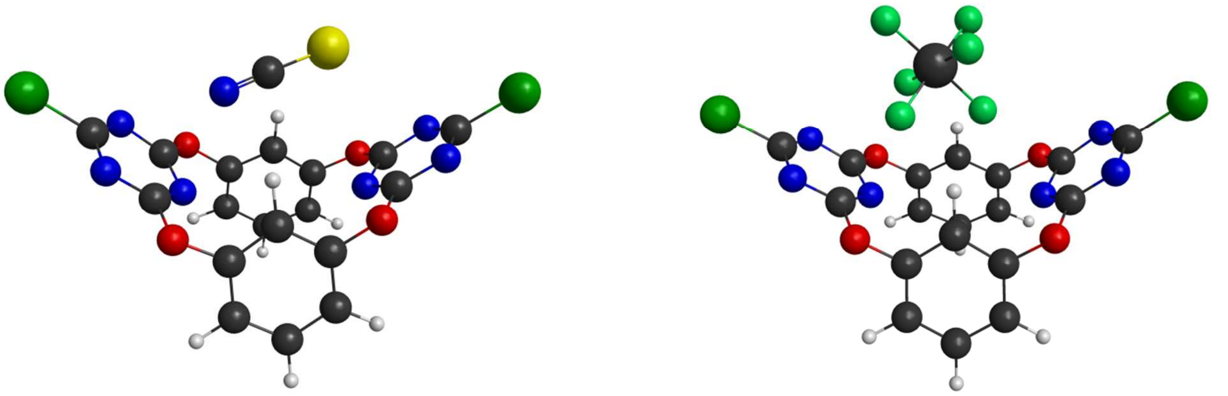
(a) **(b)**

Figure 1. Electrostatic potential surface of **1** (blue positive, red negative) side view (a) and face view (b).

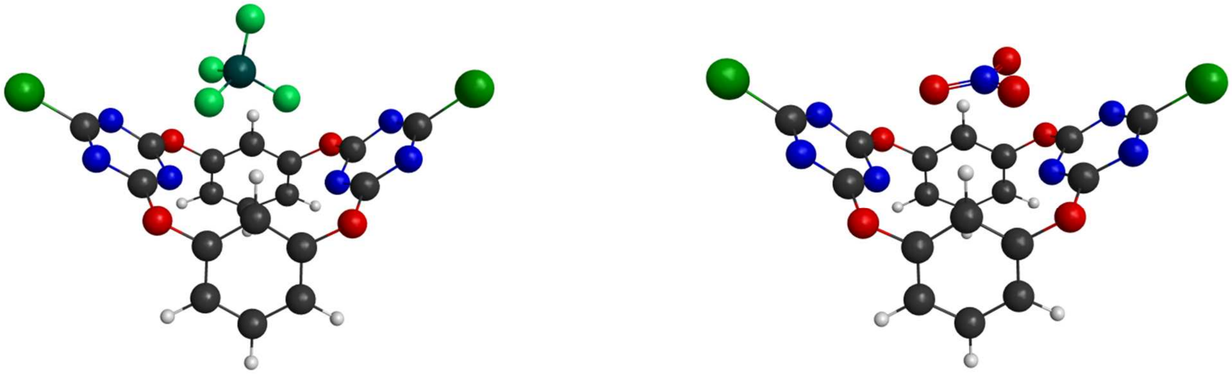
The ESP of **1** (**Figure 1**) shows that two triazine rings, H1 and H1′ atoms have localized areas of positive potential, which are required for anion interactions to occur. Instead, there is somewhat negative potential localized between two benzene rings, which show that the benzene rings can interact with the cations. Therefore, the **1** shows dual behavior which both favored the anion···π and the cation···π interactions.

Four geometry schemes of experiment anion···π complexes in calculation are displayed in **Figure 2**, the key parameters are listed in **Table 2S** (see **SI**).

For SCN^{-}···**1** complex, the N and the S atoms in SCN^{-} fragment attack the centroids of triazine(1) and triazine(2) with the interaction distances 2.891 and 3.426 Å respectively. The distance dCl-Cl of the two triazine rings decreases from 12.180 Å in the parent host molecule to 11.731 Å in SCN^{-}···**1** due to strong anion···π interactions, while the N1-N1′ distance



SCN^{-}···**1** PF_6^{-}···**1**



BF_4^{-}···**1** NO_3^{-}···**1**

Figure 2. The schemes of calculated anion···π complexes.

increases from 4.618 Å to 4.646 Å. The second-order perturbation stabilization energies ($E_{ij}^{(2)}$) are contributed by charge transfers LP(N)$\rightarrow\sigma^*$(N1-C1, N2-C2, N3-C3) ($E_{ij}^{(2)}$ =0.13, 0.09 and 0.69 kcal/mol) and LP(S)$\rightarrow\sigma^*$(N1′-C1′, N2′-C2′, N3′-C3′) ($E_{ij}^{(2)}$ = 1.25, 0.14, 0.30 kcal/mol), which supports the formation of a typical anion$\cdots\pi$ complex. The distance between interacting atoms is used as a simple criterion for deciding whether a weak bond, such as hydrogen bond and anion$\cdots\pi$ bond,[19, 78] is present or not. The sum of the covalent radii of N, S and H is 1.02, 1.33 Å, whilst the sum of their van der Waals radii is 2.75, 3.00 Å respectively. The distances of N$\cdots$H1 (2.408 Å) and S$\cdots$H1′ (2.758 Å) are both respectively in the range of the sum of the van der Waals radii of N and H, S and H, which indicates that both the N$\cdots$H and the S$\cdots$H hydrogen bond are formed in the complex $SCN^-\cdots$**1**. Also, this case is further supported by the orbital interaction σ(C-N)$\rightarrow\sigma^*$(C4-H1) and the LP(S)$\rightarrow\sigma^*$(C4′-H1′) ($E_{ij}^{(2)}$=2.24, 2.39 kcal/mol respectively). The similar results are also reported by the Russo's theoretical study[79] in that the combination of the H-bonding, anion-π and l.p.-π interactions.

For $PF_6^-\cdots$**1** complex, one F atom of PF_6^- attacks triazine(1)'s centroid. The interaction distance F···triazine(1) centroid is 3.125 Å. The dCl-Cl and dN1-N1′ decreases by 0.013 Å and 0.020 Å compared to those in the parent host, 12.180 Å and the 4.618 Å respectively. The orbital interactions LP(F)$\rightarrow\sigma^*$(C1-N2) ($E_{ij}^{(2)}$ = 0.15 kcal/mol) and LP(F)$\rightarrow\sigma^*$(N1-C3) ($E_{ij}^{(2)}$ = 0.06 kcal/mol) occurred between F atom and the triazine(1) ring whilst the electrons also can transfer from LP(F) to the orbital σ^*(C4-H1) and σ^*(C4′-H1′). The distances between two other F atoms closed to triazine(2) ring and the C3′, C1′ are 2.850 and 2.849 Å respectively, as well as the LP(F) orbits can interact with the σ^*(N1′-C3′) ($E_{ij}^{(2)}$ = 0.95 kcal/mol) and the σ^*(C1′-N2′) ($E_{ij}^{(2)}$ = 1.12 kcal/mol). Also, the two LP(F) orbits can interact with σ^*(C4-H1) and the σ^*(C4′-H1′) and the F···H bond is formed.

The structure of complex BF_4^-···**1** is similar to PF_6^-···**1**, one F atom is adjoined to triazine(1) ring (denotes as F1) and two F atoms are closed to triazine(2) ring (denotes as F2 and F3 respectively). These situations can prompt the electrons transferring from LP(F1) and LP(F2,3) to σ^*(C1-N2) ($E_{ij}^{(2)}$ = 0.27 kcal/mol), σ^*(N1-C3) ($E_{ij}^{(2)}$ = 0.10 kcal/mol) and σ^*(N1′-C3′) (1.19 kcal/mol), σ^*(C1′-N2′) ($E_{ij}^{(2)}$ = 1.30 kcal/mol) respectively and the anion-π interaction is formed. The orbit LP(F1) can interact with both σ^*(C4-H1) and σ^*(C4′-H1′). Two other LP(F2) and LP(F3) orbits can form stronger H-bonding with H1 and H1′ than F1, because the $E_{i,j}^{(2)}$ of LP(F2)→σ^*(C4-H1) and LP(F3)→σ^*(C4′-H1′) are both increased comparing those of the LP(F1)→σ^*(C4-H1, C4′-H1′).

In the case of the interaction between **1** and NO_3^-, the NO_3^-···**1** complex has C_s symmetry. One oxygen atom of nitrate (denotes as O1) is located above the triazine(1) ring, giving the distances to the plane as 2.886 Å and to the centroid as 3.051 Å, which are consistent with the experimental results 2.953 Å and 3.084 Å respectively. The other oxygen atoms, O2 and O3, give their distances to the plane of triazine(2) ring as 2.859 Å and the centroid of triazine(2) as 3.182 Å. The orbital interactions, LP(O1)→σ^*(N1-C1, N3-C3) ($E_{ij}^{(2)}$ = 0.27, 0.51 kcal/mol respectively), LP(O2)→σ^*(N3′-C3′) ($E_{ij}^{(2)}$ = 3.10 kcal/mol) and LP(O3)→σ^*(N1′-C1′) ($E_{ij}^{(2)}$ = 2.59 kcal/mol), urge the anion···π complex formation. Similar to complexes SCN^-···**1**, PF_6^-···**1** and BF_4^-···**1**, three oxygen atoms of NO_3^- fragment can all form the H-bonding with the H1 or H1′ atoms through the orbital interaction LP(O1)→σ^*(C4-H1, C4′-H1′), LP(O2)→σ^*(C4-H1) and LP(O3)→σ^*(C4′-H1′).

The chemistry community now recognizes the cation···π interaction as a major force for molecular recognition in determining macromolecular structure and drug-receptor interactions.

The alkaline metal cations (Na^+, K^+), alkaline earth metal cations (Mg^{2+}, Ca^{2+}) both act as the important roles in biology systems. Therefore, exploration the high efficient and stable host to recognize them is raised much interesting nowadays.[4, 9, 10, 29, 80, 81] In this section, Na^+ and K^+, as well as Mg^{2+} and Ca^{2+} are used to as the target guest molecules to study their interaction natures and recognition characters with the **1**. The geometries schemes of four cation···π complexes calculated are displayed in **Figure 1S** and the key parameters are listed in **Table 3S** (see **SI**).

Table 3S shows the geometry parameters of **1**···M^+ complexes. From **1**···Na^+ to **1**···K^+, the distances dN1-M^+ and the dN1′-M^+ are both elongated while the dCl-Cl and the ∠N1MN1′ are both decreased. As for **1**···M^{2+} complexes, the distances dCl-Cl, dN1-M^{2+} and dN1′-M^{2+} are all increased, whereas the angle ∠N1MN1′ is decreased. These cases indicate that the alkali metal and the alkaline earth metal cations show different interacted characters with the **1**. The two benzene rings of **1** can attack cations $M^{1+,2+}$ and forming the cation···π complexes, which is further reflected by the orbital interactions with considerable $E_{ij}^{(2)}$ as **Table 3S** listed. Additionally, the l.p.···cation interactions are also verified by the electrons transferring from LP(N1,1′) to LP^*(M).

In host monomer **1**, the triazine rings, H1 and H1′ atoms are electron-deficient whilst the benzene rings, N1, N1′ atoms are electron-rich, which leads **1** to form anion···π, anion···H, cation···π and l.p.···cation interactions with cations and anions simultaneously. The eight calculated geometries of anion···π···cation complexes are displayed in **Figure 2S** and the key parameters are listed in **Table 4S** (see **SI**).

The complexation of anion···π···cation trimer results in the geometries of subsystems changed substantially. As for X^-···**1**···M^+ complexes, the dCl-Cl for SCN^-···**1**···Na^+ is 12.106 Å, which is longer by 0.799 Å than that in dimer $SCN^{-}\cdots$**1**, whereas the dCl-Cl 11.307 Å for $SCN^{-}\cdots$**1**$\cdots K^{+}$ is decreased by 0.424 Å. Comparing to the free parent host molecule **1** (12.180 Å), the dCl-Cl of $X^{-}\cdots$**1**$\cdots M^{+}$ are decreased at least 0.074 Å while the dN1,1′-Na and -K are shorter than those in dimers **1**$\cdots Na^{+}$ and **1**$\cdots K^{+}$ respectively. The variations of geometry lead the interaction nature changed. An exact example is the interaction motif of anion$\cdots\pi$ for $SCN^{-}\cdots$**1** is typical anion-π interaction whereas for $SCN^{-}\cdots$**1**$\cdots$**M**$^{+}$ is σ-interaction, basing on their orbital interactions showing in **Table 2S** and **Table 4S**.

Interaction Energies

Researchers usually have no doubt about the existence of anion$\cdots\pi$ interactions in the gas phase and in the solid state, but few examples of attractive anion$\cdots\pi$ interactions in solution have been reported.[3, 77] The interaction energies ΔG^{CP} of dimers, $X^{-}\cdots$**1**, **1**$\cdots M^{+,2+}$ and trimers $X^{-}\cdots$**1**$\cdots M^{+,2+}$ at a series of calculated levels, including M05-2X/**BS2**//M05-2X/**BS2** and M05-2X/**BS2(PCM)**//M05-2X/**BS2** (when applicable) levels of theory were investigated.

Calculated and experimental interaction energies of four anion$\cdots\pi$ interactions are shown in **Table 5S**. From **Table 5S**, one can find that the the $\Delta G^{CP}{}_{gas}$ are substantially more negative than those obtained with other calculated operations, which suggests that the usage of gas phase will overestimate the binding strength of complexes. The $\Delta G^{CP}{}_{solvent(PCM,sp)}$ of complexes at M05-2X/**BS2**(PCM)//M05-2X/**BS2** and those of experiment are all in fairly close agreement respectively. For example, the BSSE-corrected interaction energies of $PF_6^{-}\cdots$**1** and $NO_3^{-}\cdots$**1** in CH_3CN are -3.5 kcal/mol and -5.8 kcal/mol, they are very consistent with their experiment results -3.4 and -5.8 kcal/mol. These cases further verified that the calculated level is reliable for the system and the M05-2X/**BS2(PCM)**/M05-2X/**BS2** method with BSSE correction used to calculate the interaction energies is fairly reliable.

The LMO-EDA results are reported in **Table 6S** (see **SI**). For the complexes, the contributors E_{ES}, E_{EX}, E_{DISP} and E_{POL} are attractive whereas the E_{REP} is repulsive. It is quite obvious that the total energy has a trend that very closely resembles that of the electrostatic energy. This leads to the inference that, in the investigated interactions, the E_{ES} term is the major contributor rather than E_{POL} in stabilizing the complex.

Table 1 lists the cation···π interaction energies in gas and solvent with BSSE correction. Along with the ion radius increased, the interaction energies ΔG^{CP} are decreased, either for **1**···M^{+} or **1**···M^{2+}, that is, the order $\Delta G^{\mathrm{CP}}{}_{\mathrm{Na}} > \Delta G^{\mathrm{CP}}{}_{\mathrm{K}}$ is consistent with the order $\Delta G^{\mathrm{CP}}{}_{\mathrm{Mg}} > \Delta G^{\mathrm{CP}}{}_{\mathrm{Ca}}$. It can be also seen that the binding energy reduces drastically in solution compared with that in the gas phase, and it decreases as the solvent polarity increases.

Table 1. The interaction energies ΔG^{CP} of binary complexes (kcal/mol).

	SCN^{-}···**1**	PF$_6^{-}$···**1**	BF$_4^{-}$···**1**	NO$_3^{-}$···**1**	**1**···M^{+}		**1**···M^{2+}	
					Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}
gas	-24.4	-19.2	-24.4	-29.0	-45.4	-29.0	-214.4	-143.8
CH$_3$CN	-5.5	-3.5	-4.4	-5.8	3.0	9.3	23.2	37.8
C$_6$H$_6$	-12.3	-9.1	-11.6	-14.4	-11.5	-8.5	-73.0	-30.1

From **Table 6S**, for cation···π complexes, **1**···Na^{+}, **1**···K^{+}, **1**···Mg^{2+} and **1**···Ca^{2+}, the contributors E_{ES}, E_{EX}, E_{DISP} and E_{POL} are attractive and the E_{REP} is repulsive, which is similar to those of anion-π complexes X^{-}···**1**, whereas the major contributors of them are the E_{POL}, which is different from those of the X^{-}···**1**.

Table 2. The interaction energies ΔG^{CP} of anion···π and cation···π in trimers (kcal/mol).

	X^{-}=SCN^{-}	X^{-}=PF$_6^{-}$	X^{-}=BF$_4^{-}$	X^{-}=NO$_3^{-}$

	M^+	$X^-\cdots\mathbf{1}\text{-}M^+$	$X^-\text{-}\mathbf{1}\cdots M^+$	$X^-\cdots\mathbf{1}\text{-}M^+$	$X^-\text{-}\mathbf{1}\cdots M^+$	$X^-\cdots\mathbf{1}\text{-}M^+$	$X^-\text{-}\mathbf{1}\cdots M^+$	$X^-\cdots\mathbf{1}\text{-}M^+$	$X^-\text{-}\mathbf{1}\cdots M^+$
Gas	Na^+	-94.2	-115.0	-86.2	-113.2	-93.8	-115.1	-101.4	-117.9
	K^+	-87.0	-91.7	-79.0	-89.0	-87.2	-91.9	-94.1	-94.2
CH_3CN	Na^+	-3.2	11.8	-2.0	10.0	-4.0	9.5	-6.4	8.6
	K^+	-6.1	2.2	-3.9	2.3	-5.7	1.5	-6.9	1.8
C_6H_6	Na^+	-42.9	-41.9	-38.0	-41.3	-42.8	-42.9	-47.4	-44.8
	K^+	-39.0	-35.4	-34.4	-34.0	-38.9	-36.0	-42.6	-37.0

Table 2 lists the ΔG^{CP} of anion···π ($X^-\cdots\mathbf{1}\text{-}M^+$) and cation···π ($X^-\text{-}\mathbf{1}\cdots M^+$) in trimers $X^-\cdots\mathbf{1}\cdots M^+$. By comparing the interaction energies in **Table 1** and **Table 2**, as for $X^-\cdots\mathbf{1}\text{-}M^+$ interactions, they are strengthened in C_6H_6, especially in gas phase because ΔG^{CP} of them are much negative comparing to those for dimers $X^-\cdots\mathbf{1}$. For example, the ΔG^{CP} of $SCN^-\cdots\mathbf{1}\text{-}Na^+$/$SCN^-\cdots\mathbf{1}\text{-}K^+$ is -42.9/-39.0 kcal/mol in C_6H_6 while in gas phase, it is -94.2/-87.0 kcal/mol. Also, not only in gas but also in C_6H_6, the ΔG^{CP} of $SCN^-\cdots\mathbf{1}\text{-}Na^+$/$SCN^-\cdots\mathbf{1}\text{-}K^+$ are four times to those of dimer $SCN^-\cdots\mathbf{1}$ in corresponding phase. Comparing, in CH_3CN phase, the ΔG^{CP} of $X^-\cdots\mathbf{1}\text{-}K^+$/$X^-\cdots\mathbf{1}\text{-}Na^+$ are much close/deviate to/from those of corresponding $X^-\cdots\mathbf{1}$. Similar to $X^-\cdots\mathbf{1}\text{-}M^+$, as for $X^-\text{-}\mathbf{1}\cdots M^+$ interaction, the formation of trimer can strengthen the cation-π interaction in gas/C_6H_6 phase and the ΔG^{CP} are four times to those of $\mathbf{1}\cdots M^+$. The ΔG^{CP} of $X^-\text{-}\mathbf{1}\cdots Na^+$/$X^-\text{-}\mathbf{1}\cdots K^+$ are close to those in $\mathbf{1}\cdots Na^+$/$\mathbf{1}\cdots K^+$ dimers and they are positive in CH_3CN, which indicates that the individual interaction $X^-\text{-}\mathbf{1}\cdots Na^+$/$X^-\text{-}\mathbf{1}\cdots K^+$ is unfavorable in this phase.

It can be seen from **Table 3** that the binding energy $\Delta G_{ternary}{}^{CP}$ of $X^-\cdots\mathbf{1}\cdots M^+$ reduces drastically in solution compared with that in the gas phase, and it decreases as the solvent polarity increases, which is same to that of the trend of the $\mathbf{1}\cdots M^{+,2+}$ and the $X^-\cdots\mathbf{1}$ complexes.

Also, from **Table 6S**, either $X^-\cdots\mathbf{1}\text{-}M^+$ or $X^-\text{-}\mathbf{1}\cdots M^+$ interaction, it is quite obvious that the total energy has a trend that very closely resembles that of the electrostatic energy. This leads to the inference that the E_{ES} term is the major contributor for the $X^-\cdots\mathbf{1}\text{-}M^+$ and $X^-\text{-}\mathbf{1}\cdots M^+$

interactions in gas phase.

Cooperativity or Anticooperativity? Interplay of Mutual Interactions

In this section, we pay attention to investigate the coexisting characters of the interactions and show that mutual influence between them leads to a cooperative or anticooperative effect. We separate the entire system into three subsystems, one is the anion···π bond subsystem consisting of **1** and an anion, one is the cation···π and l.p.···cation subsystem including **1** and a cation and the finally one includes a cation and an anion.

By means of the usual equations applicable in many-body analysis,[82-84] the influenced energy of three-body interaction ($\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$) can be calculated as well.[85] Depending on sign, $\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$ can give valuable information regarding the interplay between all the noncovalent interactions present in the ternary complexes and expresses the nonadditive term of the interactions in these three-body systems, also called cooperativity or anticooperativity.[86, 87] Helpful information regarding the interplay between all the non-covalent interactions in these complexes can be achieved from the calculated $\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$ in **Table 3**.[71, 79, 85, 88, 89] The $\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$ is defined as the energy difference between the three-body interaction energy ($\Delta G_{\mathrm{ternary}}^{\mathrm{CP}}$) and the sum of the two-body interaction energies, under the same geometry, and properly accounting for the BSSE terms. It can be seen from **Table 3**, in gas phase, the $\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$ is positive excepting the K^+ complexes SCN^-···**1**···K^+ and BF_4^-···**1**···K^+.

Table 3. The energies $\Delta G_{\mathrm{ternary}}^{\mathrm{CP}}$ and $\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$ of X^-···1···M^+ with BSSE correction ΔG^{CP} (kcal/mol)

		Gas		**CH_3CN**		**C_6H_6**	
		Na^+	K^+	Na^+	K^+	Na^+	K^+
SCN^-	$\Delta G_{\mathrm{ternary}}^{\mathrm{CP}}$	-139.3	-115.9	6.4	-3.0	-54.0	-47.5
	$\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$	22.0	-1.5	-11.8	-6.4	-3.2	-4.9
PF_6^-	$\Delta G_{\mathrm{ternary}}^{\mathrm{CP}}$	-142.7	-115.4	7.4	-0.8	-49.5	-42.8
	$\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$	148.7	105.1	-10.9	-7.3	-3.0	-5.8

BF_4^-	$\Delta G_{\mathrm{ternary}}^{\mathrm{CP}}$	-148.2	-122.0	5.6	-2.6	-54.1	-47.4
	$\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$	16.6	-7.0	-11.7	-9.3	-2.6	-6.5
NO_3^-	$\Delta G_{\mathrm{ternary}}^{\mathrm{CP}}$	-157.4	-130.7	3.1	-3.8	-58.8	-51.1
	$\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$	21.5	1.2	-10.5	-7.2	-1.7	-5.2

In CH_3CN and C_6H_6, although the $\Delta G_{\mathrm{thr}}^{\mathrm{CP}}$ values are all negative, the interaction in Na^+ complexes $X^-\cdots$**1**$\cdots Na^+$ are unfavor because of their positive $\Delta G_{\mathrm{ternary}}^{\mathrm{CP}}$. These cases show that the different types of noncovalent interactions including H-bonding, anion$\cdots\pi$, l.p.$\cdots$cation and cation$\cdots\pi$ interactions are in concurrent, leading to an/a anticooperative/cooperative effect in different phase. Interesting, the K^+ is more favored the cooperative trimers comparing to the Na^+ in gas, CH_3CN and C_6H_6 phases.

Conclusions

The characteristics of the interaction in dimer and trimer complexes formed by electron-deficient and cavity self-tunable macrocyclic host tetraoxacalix[2]arene[2]triazine **1**, anion X^- (SCN^-, PF_6^-, BF_4^- and NO_3^-), and cation $M^{+,2+}$ (Na^+, K^+, Mg^{2+}, Ca^{2+}) have been computationally studied. Test calculations show that the M05-2X/6-31++G(d,p) provide results in reasonable agreement with experiment. The tetraoxacalix[2]arene[2]triazine **1** is amphiphilic, which can act as an effective macrocyclic host not only to accept anions but also recognize the cations. For $X^-\cdots$**1** (anion$\cdots\pi$) interactions, the anions X^- interact with two triazine rings and their type is typical anion$\cdots\pi$ interaction while in $X^-\cdots$**1**-M^+, the interaction motif is σ-interaction. For **1**$\cdots M^{+,2+}$ (cation$\cdots\pi$) interactions, cations $M^{+,2+}$ interact with two benzene rings and possess sandwich structures. The solvent can strongly effect on the strength of the interaction. The cation$\cdots\pi$, anion$\cdots\pi$ and anion$\cdots\pi\cdots$cation complexes are favorable in gas phase whereas in solvent phase, especially in polar solvent, the stable of cation$\cdots\pi$ interaction is decreased. The modulating effect between anion$\cdots\pi$ and cation$\cdots\pi$ interaction was systematically studied. In trimers, the anion···π-cation and anion-π···cation are strongly strengthened comparing their dimers, anion···π and π···cation interactions respectively. LMO-EDA results indicate that the electrostatic term is the major component in anion···π and anion···π-cation interactions. The complexation of anion with π···cation complexes can modulate the interaction nature of π···cation from polarized to electrostatic. The three-body interaction X^-···**1**···Na^+ is anticooperative in gas and CH_3CN while the X^-···**1**···K^+ are cooperative both in polar CH_3CN and nopolar C_6H_6 phase. In addition, the PCM and SMD solvent models are tested and the results indicated that the PCM interaction energy values are more reasonable. The analysis applied in this work should be a promising tool for the investigation of the influence of cation over the anion···π interaction. The weak binding energies of X^-···**1**, **1**···$M^{+,2+}$ and X^-···**1**···M^+ in solution suggest that the anion···π and cation···π interactions can offer potential applications in anion, cation and catalysis transport and recognition using synthetic functional materials.

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Notes and References

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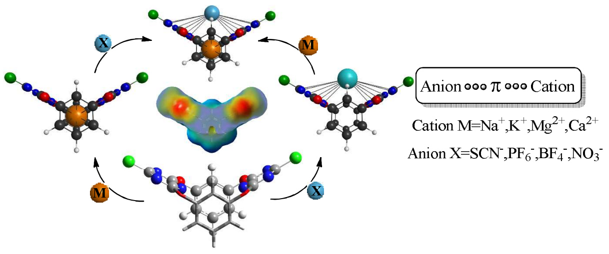

Calculations revealed that the tetraoxacalix[2]arene[2]triazine **1** is amphiphilic. In the present work, we report anions SCN$^-$, PF$_6^-$, BF$_4^-$ and NO$_3^-$, as well as alkaline metal cations Na$^+$, K$^+$ and alkaline earth metal cations Mg^{2+}, Ca^{2+} recognized by **1** host molecules, considerable interplay (cooperativity or anticooperativity) between cation···π and anion···π interactions, how does the solvent influence the interaction nature and how does the solvent effect on the strength of the interaction.