The mutual interactions based on amphipathic tetraoxacalix[2]arene[2]triazine: recognition cases of anion and cation investigated by a computational study†

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The nature of anion···π (anion X\textsubscript{1,4} = SCN\textsuperscript{−}, PF\textsubscript{6}\textsuperscript{−}, BF\textsubscript{4}\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−}, 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 the experiments. 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\textsuperscript{+} (Na\textsuperscript{+}, K\textsuperscript{+}) and alkaline earth metal cations M\textsuperscript{2+} (Mg\textsuperscript{2+}, Ca\textsuperscript{2+}) can also interact with 1 and, the cation···π binding of M\textsuperscript{2+}···1 is stronger than that of M\textsuperscript{+}···1, as well as their strength is gradually decreased along with an increase in the radius of M\textsuperscript{+}\textsuperscript{2+}. The investigation of interplay between the anion···π and the cation···π shows that the interactions among three-body, X\textsuperscript{−}, 1 and M\textsuperscript{+} is varied with different phases. The polar solvent can strongly reduce the strength of the interaction, and the more increased the solvent polarity, the more reduced is the binding energy.

Introduction

The chemistry of noncovalent binding is the intelligent and, in most cases, elegant utilization of interactions between molecules.\textsuperscript{1,2} Nowadays, the exploration and comprehension of noncovalent interactions is 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.\textsuperscript{3,4} Well-known interactions ranging from hydrogen bonding to ionic interaction, metallocophilic interaction,\textsuperscript{5,6} hydrophobic interaction\textsuperscript{7} and cation···π interaction\textsuperscript{8,9} 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,\textsuperscript{10–14} have been investigated for several years, systematic and deep studies on them are still rare.\textsuperscript{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).\textsuperscript{3,21}

The anion···π noncovalent force, which is mainly dominated by electrostatic interaction or polarization,\textsuperscript{12,14,23,24} has been shown to be energetically favorable by theoretical\textsuperscript{24–35} and experimental studies.\textsuperscript{34–39} Compared 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 the interactions of combining anions, π and cations are limited.

Heteroatom-bridged heteroaromatic calixarenes are an emerging type of novel macrocyclic molecules.\textsuperscript{40–43} They have recently been utilized as versatile host molecules in supramolecular chemistry.\textsuperscript{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.\textsuperscript{40,49–51} This π-electron deficient cavity has been envisioned to act as a receptor to interact with anions through anion···π interactions.\textsuperscript{3,13,16–24,37} Recently, although Wang et al.'s\textsuperscript{3} reported experimental studies on the anion···π interactions of 1 with anions X\textsuperscript{−} (SCN\textsuperscript{−}, PF\textsubscript{6}\textsuperscript{−}, BF\textsubscript{4}\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−}), in the gaseous phase, solution and the solid state,
knowledge of the influences of solvent on the interaction nature of anion···π interactions is 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, considering the interplay of cooperativity or anticooperativity between cation···π and anion···π interactions, and ask how does the solvent influence the nature of the interaction. For an objective understanding of the actual driving forces of the interaction, decomposition of the total energy into various components by LMO-EDA has been performed. We have focused this paper on understanding the physical nature of the aforementioned interactions, which is beneficial to choosing 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, MP258,59 and B3LYP-D360,61 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), \(\Delta G^\text{CP}\).62 The different contributions to the interaction energies were obtained by using the LMO-EDA method developed by Su and Li63 as implemented in GAMESS 2011.64 The interaction energy has been decomposed into its electrostatic (\(E_{\text{el}}\)), exchange (\(E_{\text{ex}}\)), repulsion (\(E_{\text{rep}}\)), polarization (\(E_{\text{pol}}\)) and dispersion (\(E_{\text{disp}}\)) 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 complexes66–73 using the NBO 3.1, which is implemented in the 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, 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 optimized one representative complex SCN\(^-\)···1, and the calculated parameters are listed in Table S1 (see ESI†). From Table S1 (ESI†), the experimental and computational parameters are comparable at the MP2/BS1 level. As for M05-2X/BS2, although it required more calculating time than M05-2X/BS1, it is closer to the experimental value by 0.003 Å.77 The calculated parameters at other functionals are significantly deviated from the 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. In addition, the subsequent qualitative analyses are based on geometries at this level of theory.

The ESP of 1 (Fig. 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 shows that the benzene rings can interact with the cations. Therefore, the 1 shows dual behavior, which favored both the anion···π and the cation···π interactions.

Four geometry schemes of experimental anion···π complexes in calculation are displayed in Fig. 2, and the key parameters are listed in Table S2 (see ESI†).
For SCN\(^{-}\)\(\cdot\)1 complex, the N and the S atoms in SCN\(^{-}\) fragment attack the centroids of triazine(1) and triazine(2) with 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\(^{-}\)\(\cdot\)1 due to strong anion\(\cdot\)π interactions, while the N1–N1’ distance 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\(^{-1}\)) and LP(S) \(\rightarrow\) \(\sigma^{*}(N1′–C1′, N2′–C2′, N3′–C3′)\) (\(E_{ij}^{(2)}\) = 1.25, 0.14, 0.30 kcal mol\(^{-1}\)), which supports the formation of a typical anion\(\cdot\)π complex. The distance between interacting atoms is used as a simple criterion for deciding whether a weak bond, such as hydrogen bond and anion\(\cdot\)π bond,\(^{19,78}\) is present or not. The sum of the covalent radii of N, S and H is 1.02 and 1.33 Å, whilst the sum of their van der Waals radii is 2.75 and 3.00 Å, respectively. The distances of N\(\cdot\)H1 (2.408 Å) and S\(\cdot\)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\(\cdot\)H and the S\(\cdot\)H hydrogen bonds are formed in the complex SCN\(^{-}\)\(\cdot\)1. In addition, this case is further supported by the orbital interaction \(\sigma(C–N) \rightarrow\) \(\sigma^{*}(C4′–H1′)\) and the LP(S) \(\rightarrow\) \(\sigma^{*}(C4′–H1′)\) (\(E_{ij}^{(2)}\) = 2.24, 2.39 kcal mol\(^{-1}\)) respectively. Similar results are also reported by the Russo’s theoretical study\(^{79}\) in the combination of the H-bonding, anion-π and l.p.-π interactions.

For PF\(_{6}\) \(\cdot\)1 complex, one F atom of PF\(_{6}\) attacks triazine(1)’s centroid. The interaction distance for F\(\cdot\) triazine(1) centroid is 3.125 Å. The dCl–Cl and dN1–N1’ decrease by 0.013 Å and 0.020 Å compared to those in the parent host, 12.180 Å and 4.618 Å respectively. The orbital interactions LP(F) \(\rightarrow\) \(\sigma^{*}(C1–N2)\) (\(E_{ij}^{(2)}\) = 0.15 kcal mol\(^{-1}\)) and LP(F) \(\rightarrow\) \(\sigma^{*}(N1–C3)\) (\(E_{ij}^{(2)}\) = 0.06 kcal mol\(^{-1}\)) occurred between F atom and the triazine(1) ring whilst the electrons also can transfer from LP(F) to the orbital \(\sigma^{*}(C4–H1)\) and \(\sigma^{*}(C4′–H1′)\). The distances between two other F atoms close to the triazine(2) ring and the C3’, C1’ are 2.850 and 2.849 Å respectively; as well the LP(F) orbits can interact with the \(\sigma^{*}(N1′–C3′)\) (\(E_{ij}^{(2)}\) = 0.95 kcal mol\(^{-1}\)) and the \(\sigma^{*}(C1′–N2′)\) (\(E_{ij}^{(2)}\) = 1.12 kcal mol\(^{-1}\)). In addition, the two LP(F) orbits can interact with \(\sigma^{*}(C4–H1)\) and \(\sigma^{*}(C4′–H1′)\) and the F\(\cdot\)H bond is formed.

The structure of complex BF\(_{4}\) \(\cdot\)1 is similar to PF\(_{6}\) \(\cdot\)1, one F atom is adjoined to the triazine(1) ring (denoted as F1) and two F atoms are close to the triazine(2) ring (denoted as F2 and F3 respectively). These situations can prompt the electrons transferring from LP(F1) and LP(F2,3) to \(\sigma^{*}(C1–N2)\) (\(E_{ij}^{(2)}\) = 0.27 kcal mol\(^{-1}\)), \(\sigma^{*}(N1–C3)\) (\(E_{ij}^{(2)}\) = 0.10 kcal mol\(^{-1}\)) and \(\sigma^{*}(N1′–C3′)\) (1.19 kcal mol\(^{-1}\)), \(\sigma^{*}(C1′–N2′)\) (\(E_{ij}^{(2)}\) = 1.30 kcal mol\(^{-1}\)) respectively, and the anion-π interaction is formed. The orbit LP(F1) can interact with both \(\sigma^{*}(C4–H1)\) and \(\sigma^{*}(C4′–H1′)\). Two other LP(F2) and LP(F3) orbits can form stronger H-bonding with H1 and H1’ than F1, because the \(E_{ij}^{(2)}\) of LP(F2) \(\rightarrow\) \(\sigma^{*}(C4–H1)\) and LP(F3) \(\rightarrow\) \(\sigma^{*}(C4′–H1′)\) are both increased compared to those of the LP(F1) \(\rightarrow\) \(\sigma^{*}(C4–H1, C4′–H1′)\).

In the case of the interaction between 1 and NO\(_{3}\)\(^{-}\), the NO\(_{3}\) \(\cdot\)1 complex has C\(_{3v}\) symmetry. One oxygen atom of nitrate (denoted 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 the 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_0 = 0.27, 0.51 kcal mol⁻¹ respectively), LP(O2) → σ*(N3’–C3’) (E_0 = 3.10 kcal mol⁻¹) and LP(O3) → σ*(N1’–C1’) (E_0 = 2.59 kcal mol⁻¹), urge the anion⋅⋅⋅π complex formation. Similar to complexes SCN⁻⋅⋅⋅1, PF₆⁻⋅⋅⋅1 and BF₄⁻⋅⋅⋅1, three oxygen atoms of NO₃⁻ 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⁺) and the alkaline earth metal cations (Mg²⁺, Ca²⁺) both play important roles in biology systems. Therefore, exploration of a highly efficient and stable host to recognize them is a raising considerable interest nowadays. In this section, Na⁺ and K+, as well as Mg²⁺ and Ca²⁺ are used as the target guest molecules to study their interaction natures and recognition characters with the 1. The geometry schemes of four cation⋅⋅⋅π complexes calculated are displayed in Fig. S1 (ESI†) and the key parameters are listed in Table S3 (see ESI†).

Table S3 (ESI†) 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 angle Ω N1MN1' are both decreased. As for 1⋅⋅⋅M⁺ complexes, the distances dCl–Cl, dN1–M⁺ and dN1’–M⁺ are all increased, whereas the angle Ω N1MN1’ is decreased. These cases indicate that the alkaline metal and the alkaline earth metal cations show different interacting characters with the 1. The two benzene rings of 1 can attack cations M⁺¹,²⁺ and form cation⋅⋅⋅π complexes, which is further reflected by the orbital interactions with considerable E_0 (as Table S3 (ESI†) listed. Additionally, the L.p.⋅⋅⋅cation interactions are also verified by the electrons transferring from LP(N1,1’C1) to LP(M).

In host monomer 1, the triazine rings, H1 and H1’ atoms are electron-deficient whilst the benzene rings, N1 and 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 Fig. S2 (ESI†) and the key parameters are listed in Table S4 (see ESI†).

The complexation of anion⋅⋅⋅π⋅⋅⋅cation trimer results in substantial changes in the geometries of subsystems. 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⁻⋅⋅⋅1, whereas the dCl–Cl of 11.307 Å for SCN⁻⋅⋅⋅1⋅⋅⋅K⁺ is decreased by 0.424 Å. Compared to the free parent host molecule 1 (12.180 Å), the dCl–Cl of X⋅⋅⋅1⋅⋅⋅M⁻ is decreased at least 0.074 Å while the dN1,1’–Na and –K are shorter than those in dimers 1⋅⋅⋅Na and 1⋅⋅⋅K respectively. The variations of geometry lead to changes in the nature of the interaction. An exact example is the interaction motif of anion⋅⋅⋅π for SCN⁻⋅⋅⋅1, which is a typical anion⋅⋅⋅π interaction, whereas SCN⁻⋅⋅⋅1⋅⋅⋅M⁺ is a σ-interaction based on their orbital interactions, as show in Tables 28 and 48 (ESI†).

### Interaction energies

Researchers usually have no doubt about the existence of anion⋅⋅⋅π interactions in the gas phase and in the solid state, but few examples of attractive anion⋅⋅⋅π interactions in solution have been reported. The interaction energies ΔGCP of dimers X⋅⋅⋅1, 1⋅⋅⋅M⁺²⁺ and trimers X⋅⋅⋅1⋅⋅⋅M⁺²⁺ at a series of calculated levels, including M05-2X/BS2/505-2X/BS2 and M05-2X/BS2(PCMV)/M05-2X/BS2 (when applicable) levels of theory, were investigated.

<table>
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<td>K⁺</td>
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<tr>
<td>Mg²⁺</td>
<td>Ca²⁺</td>
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### Table 1 The interaction energies ΔGCP of binary complexes (kcal mol⁻¹)

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<th>SCN⁻⋅⋅⋅1</th>
<th>PF₆⁻⋅⋅⋅1</th>
<th>BF₄⁻⋅⋅⋅1</th>
<th>NO₃⁻⋅⋅⋅1</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
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<td>−24.4</td>
<td>−29.0</td>
<td>−45.4</td>
<td>−29.0</td>
<td>−214.4</td>
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<tr>
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<td>−3.5</td>
<td>−4.4</td>
<td>−5.8</td>
<td>3.0</td>
<td>9.3</td>
<td>23.2</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>−12.3</td>
<td>−9.1</td>
<td>−11.6</td>
<td>−14.4</td>
<td>−11.5</td>
<td>−8.5</td>
<td>−73.0</td>
</tr>
</tbody>
</table>
From Table S6 (ESI†), forcation... 1 of gas phase. The... overlapping between... positive. In CH₃CN and CH₆, though... favorable in this phase.

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

Also, from Table S6 (ESI†), in either X - 1 - M' or X - 1 - M' interaction, it is quite obvious that the total energy has a trend that very closely resembles that of the electrostatic energy.

### Cooperativity or anticooperativity? Interplay of mutual interactions

In this section, we pay attention to investigate the coexisting character 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 final 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 ($\Delta G_{\text{thr}}$) can be calculated as well.85 Depending on sign, $\Delta G_{\text{thr}}$ 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 noncovalent interactions in these complexes can be achieved from the calculated $\Delta G_{\text{thr}}$ in Table 3.71,79,85,88,89 The $\Delta G_{\text{thr}}$ is defined as the energy difference between the three-body interaction energy ($\Delta G_{\text{ternary}}$) 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 $\Delta G_{\text{thr}}$ is positive except for the K' complexes SCN- - 1 - K' and BF4- - 1 - K'.

In CH₃CN and CH₆, although the $\Delta G_{\text{thr}}$ values are all negative, the interaction in Na+ complexes X - 1 - Na+ are unfavorable because of their positive $\Delta G_{\text{ternary}}$. These cases show that the different types of noncovalent interactions, including H-bonding, anion-π, l.p..cation and cation-π interactions are in concurrence, leading to an/a anticooperative/cooperative effect in different phase. Interestingly, the K' is more favored in the cooperative trimers compared to the Na+ in gas, CH₃CN and CH₆ phases.

### Conclusions

The characteristics of the interactions in dimer and trimer complexes formed by electron-deficient and cavity self-tunable macrocyclic host tetraacalix[2]aren[(2)B[3]irazine 1, anion X (SCN−, PF6−, BF4− and NO3−), and cation M2+ (Na+, K', Mg2+, Ca2+) have been computationally studied. Test calculations show...
that the M05-2X/6-31++G(d,p) provide results in reasonable agreement with the experiments. The tetraoxacalix[2]arene-triazine 1 is amphiphilic, which can act as an effective macrocyclic host not only to accept anions but also recognize the cations. For X−⋯1 (anion⋯π) interactions, the anions X− interact with two triazine rings and their type is typical anion⋯π interaction, while in X−⋯1−M+, the interaction motif is σ-interaction. For 1⋯M+⋯2− cation⋯π interactions, cations M+⋯2− interact with two benzene rings and possess sandwich structures. The solvent can strongly affect the strength of the interaction. The cation⋯π, anion⋯π and anion⋯π⋯cation complexes are favorable in gas phase, whereas in solvent phase, especially in polar solvent, the stability of cation⋯π interaction is decreased. The modulating effect between anion⋯π and cation⋯π interaction was systematically studied. In trimers, the anion⋯π⋯cation and anion⋯π⋯cation are strongly strengthened compared to 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 complexion 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 CH3CN, while the X−⋯1⋯K+ are cooperative both in polar CH3CN and nonpolar C6H6 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 a 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