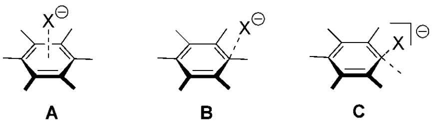
DOI: 10.1002/chem.201002307

Versatile Anion–π Interactions between Halides and a Conformationally Rigid Bis(tetraoxacalix[2]arene[2]triazine) Cage and Their Directing Effect on Molecular Assembly

De-Xian Wang,*[a] Qi-Qiang Wang,[a] Yuchun Han,[b] Yilin Wang,*[b]
Zhi-Tang Huang,[a] and Mei-Xiang Wang*[a, c]

Recent years have witnessed an increasing interest in anion–π interactions, that is, the interaction between an anion and an electron-deficient π-arene species.[1] A number of theoretical studies,[1,2] for example, have suggested noncovalent interactions of anions with aromatic compounds, such as perfluoro-, nitro- and cyano-substituted benzene, pyridine, pyrazine, and triazine derivatives. As proposed by Hay and his co-workers,[3] interaction of an anion with a aromatic π system leads to either a noncovalent anion–π complex **A**, a weak σ-complex **B**, or the Meisenheimer intermediate **C**.



A number of experimental studies[4] have demonstrated interactions between anions and π systems; however, experimental evidence to support "pure" anion–π interactions with charge-neutral arenes is very rare.[3,5] Indeed, a recent report indicated that the noncovalent anion–π interaction contributes less significantly to the formation of chloride–π-$C_6F_nH_{6-n}$ complex.[6]

Heteroatom-bridged calixaromatics are an emerging type of novel macrocyclic molecules and they exhibit unique and versatile structural and molecular recognition properties.[7] Very recently, we have discovered that tetraoxacalix[2]-arene[2]triazine, a conformationally flexible macrocyclic host molecule with two electron-deficient triazine rings, self-regulates its cavity structure to form ternary complexes with halides and water.[5b] Typical noncovalent anion–π interactions (type **A**) between chloride, bromide and triazine, and lone-pair-electrons–π (lpe–π) interactions between the included water molecule and triazine are observed in the solid state.

To obtain other types of halide–π interactions[3] and to explore the effect of anion–π interactions on the molecular assembly, we devised a conformationally rigid cage molecule that contains three electron-deficient V-shaped clefts. We envisioned that the electron-deficient triazine ring incorporated into a conformational rigid host might form various anion–π complexes. To our delight, different types of halide–π interactions with electron-deficient triazine rings were observed. Multiple anion–π interactions along with other noncovalent bond interactions, such as hydrogen bonding, halogen bonding, and lpe–π interactions, directed the formation of different molecular assemblies in the solid state. An isothermal titration calorimetry (ITC)[8] study revealed that, in acetonitrile, the cage molecule formed 1:1 complexes with fluoride, chloride, and bromide, with association constant being 361, 146, and 95 M^{-1}, respectively.

Scheme 1 illustrates the synthesis of cage molecule, bis(tetraoxacalix[2]arene[2]triazine) (**4**). The reaction of

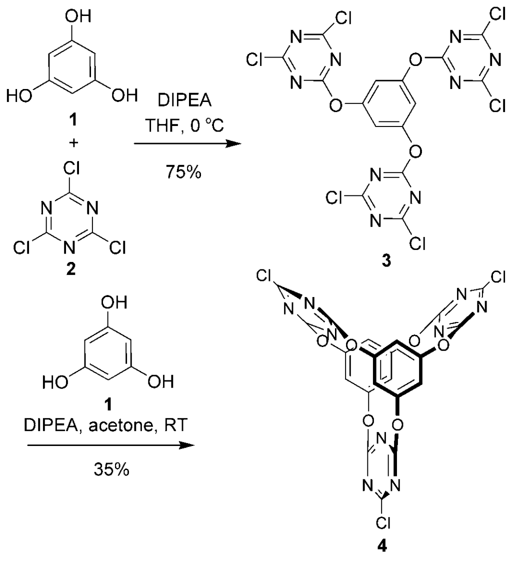
---

[a] Dr. D.-X. Wang, Q.-Q. Wang, Prof. Z.-T. Huang,
Prof. Dr. M.-X. Wang
Beijing National Laboratory for Molecular Sciences
CAS Key Laboratory of Molecular Recognition and Function
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100190 (P. R. China)
Fax: (+86) 10-62564723, (+86) 10-62565610
E-mail: wangmx@mail.tsinghua.edu.cn
dxwang@iccas.ac.cn

[b] Dr. Y. Han, Prof. Dr. Y. Wang
Beijing National Laboratory for Molecular Sciences
CAS Key Laboratory of Colloid and Interface Science
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100190 (P. R. China)
Fax: (+86) 10-82615802
E-mail: yilinwang@iccas.ac.cn

[c] Prof. Dr. M.-X. Wang
The Key Laboratory of Bioorganic Phosphorus Chemistry &
Chemical Biology (Ministry of Education)
Department of Chemistry, Tsinghua University
Beijing 100084 (P. R. China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002307.



Scheme 1. Synthesis of cage molecule **4**.

phloroglucinol **1** with an excess amount of cyanuric chloride **2** in the presence of diisopropylethylamine (DIPEA) at 0°C gave intermediate **3** in 75% yield. Further treatment of **3** with phloroglucinol **1** in acetone at room temperature afforded the desired product **4** in a moderate yield. As indicated by the NMR spectroscopic data and X-ray crystallography[9] (Figure 1), cage molecule **4** adopts a D_{3h} symmetric, all 1,3-alternate conformation with two benzene rings being eclipsed. Three highly electron-deficient triazine rings form three identical V-shaped clefts.

Single crystals of the complexes were cultivated by slow evaporation of the solvent from the solution of host **4** and tetraethylammonium halides in a mixture of dichloromethane and *n*-hexane at room temperature. As we expected, X-ray structures of the complexes $[\mathbf{4}\subset(\mathrm{Et_4NCl})_3\subset(\mathrm{H_2O})_3]$[10] and $[\mathbf{4}\subset(\mathrm{Et_4NBr})_2\subset\mathrm{H_2O}]$[11] showed intriguing interactions between host and guest species.

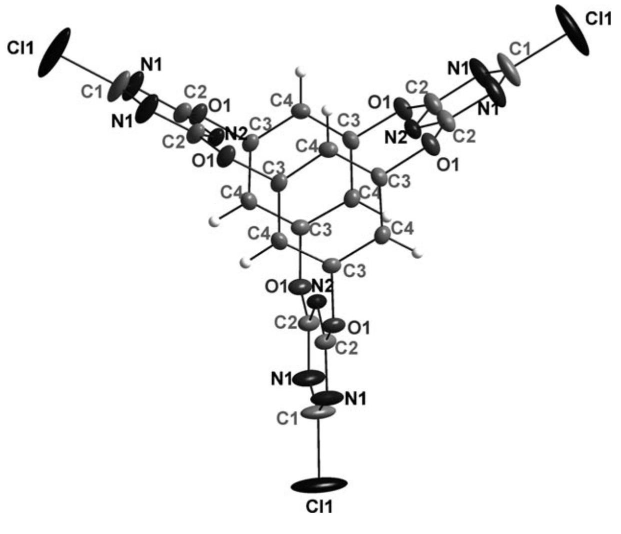


Figure 1. X-ray structure of cage molecule **4**. Selected distance: C1···C1 9.138 Å. Solvent is omitted for clarity.

As illustrated in Figure 2, the host of the complex $[\mathbf{4}\subset(\mathrm{Et_4NCl})_3\subset(\mathrm{H_2O})_3]$ remained almost the same symmetric cage conformation with two face-to-face paralleled benzene rings being very slightly twisted. Each V-shaped cleft accommodates one chloride anion and one $\mathrm{H_2O}$ molecule. Interestingly, all three chloride anions in different clefts are located in one plane, while the water molecules are in another. Being completely different from the previously reported type **A** anion–π interaction between tetraoxacalix[2]-arene[2]triazine and chloride,[5b] in **4** each triazine ring interacts with one chloride ion forming a weak σ complex (type **B** anion–π interaction); the chloride ion is situated just above the carbon atom of triazine ring with a chloride–carbon distance ($d_{\mathrm{Cl2-C2}}$) of 3.342 Å. In addition, the chloride ion also forms a hydrogen bond with the arene C−H of one benzene moiety, giving a $\mathrm{Cl^-}$···H−C distance of 3.541 Å. Moreover, the chloride ion also forms another hydrogen bond with the included water molecule ($d_{\mathrm{Cl2-O3}}=3.163$ Å);

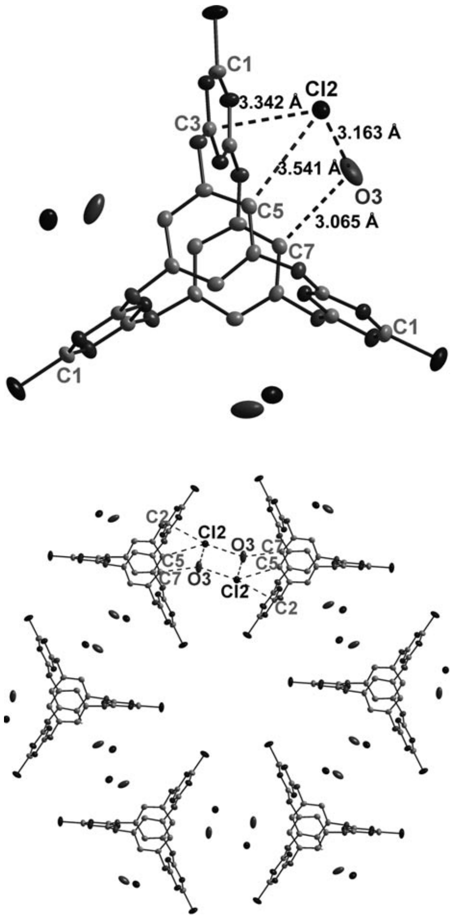


Figure 2. X-ray structure of complex of **4** with tetraethylammonium chloride and water (50% probability). Selected distances (in Å): C1···C1 9.152, C3···Cl2 3.342, C5···Cl2 3.541, Cl2···O3 3.163, C7···O3 3.065; selected hydrogen bond angles (in °): C5−H5···Cl2 150.5, O3-H3B-Cl2 175.5. Cations and hydrogen atoms are omitted for clarity.

in turn the water molecule interacts with an arene C−H of the other benzene ring through hydrogen bonding (d_{O3-C7} = 3.065 Å) (Figure 2, top). Finally, it is worth noting that through the formation of a hydrogen-bond network, the chloride ion and water molecule in each V-shaped cleft interact with other pairs of chloride ions and water molecules included in other hosts, yielding an infinite two-dimensional honeycomb-like assembly (Figure 2, bottom and Figure S1 in the Supporting Information). Layers of tetraethylammonium cations alternate with the layers of $[\{\mathbf{4}\subset(Cl{-}H_2O)_3\}_n]$ (Figure S2 in the Supporting Information).

In the case of complex $[\mathbf{4}\subset(Et_4NBr)_2\subset H_2O]$ (Figure 3), although the cage host still remained a trigonal conformation, the angles between triazine planes varied, producing three V-shaped clefts of different sizes ($d_{Cl1-Cl2}$ = 11.955, $d_{Cl1-Cl3}$ = 12.710, $d_{Cl2-Cl3}$ = 11.673 Å). In the smallest cleft, Br2 ion was in close contact with one of the triazine rings. The distance of Br2 to the plane and to the centroid of triazine ring is 3.429 Å (Figure 3, bottom) and 3.480 Å, respectively, indicating a strong π-bromide interaction. There was no other noncovalent interaction though host molecules A and B were face-to-face orientated (Figure 3, bottom).

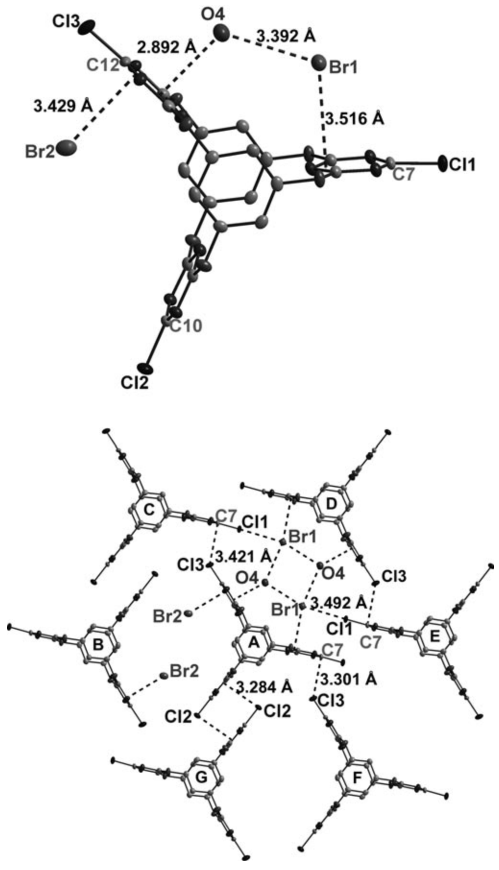


Figure 3. X-ray structure of complex of **4** with tetraethylammonium bromide and water (50% probability). Selected distances (in Å): O4⋯triazine plane 2.892, O4⋯Br1 3.392, Br1⋯triazine plane 3.516, Br2−triazine plane 3.429, O4⋯Br1 3.421, Br1⋯Cl1 3.492, Cl2⋯triazine plane 3.284, Cl3⋯C7 3.301, C12⋯C7 9.474, C7⋯C10 9.077, C10⋯C12 8.853. Cations and hydrogen atoms are omitted for clarity.

The multiple and various noncovalent binding modes among hosts and guests in the largest cleft are of note. First of all, the bromide ion and water molecule, which are hydrogen bonded to each other (d_{Br1-O4} = 3.392 Å), formed bromide–π and lpe–π interactions,[12] respectively, with two triazine rings. Both the bromide ion and the water molecule were located above the triazine planes, and the Br1–triazine-plane distance was 3.516 Å, while the distance between O4 and the plane of the other triazine was 2.892 Å (Figure 3, top). In addition, the bromide ion and water molecule interacted through a hydrogen-bond network with another bromide and water pair, accommodated by the neighboring host molecule D (Figure 3, bottom). Moreover, the bromide ions in the cavity formed halogen bonds[13] with the chloro substituents of host molecules C and E. This was evidenced by the short distance between the bromide and chlorine atom ($d_{Br1-Cl1}$ = 3.492 Å) and the linear orientation of bromide along the axis of Cl−C bond (Figure 3, bottom). Finally, there was also a short contact between a chlorine atom and triazine carbon (d_{Cl3-C7} = 3.301 Å), indicating a weak lpe–π interaction[11] between hosts A and C and between hosts A and E.

In the last cleft, apart from the weak lpe–π interaction between a chlorine atom of host A and the triazine of host F, there was a pair of strong lpe–π interactions between host A and host G. The distances between the chlorine atom and the centroid and the plane of triazine are 3.284 and 3.323 Å, respectively, and the chloro–centroid–plane angle is 80.92° (Figure 3, bottom).

The anion–π interaction between bromide and triazine and the lpe–π interaction between the oxygen of water and triazine are worth further addressing. Different from the ternary complex of tetraoxacalix[2]arene[2]triazine with bromide and water,[5b] in which bromide and water oxygen atom are just above the centroids of two triazine rings, the bromide and water moved toward the narrow rim of the cleft in the current case. For example, the d_{offset} values for Br1 and O4 are 0.915 and 0.341 Å, respectively. The π-complexed Br2 anion in the smallest cleft, however, shifted toward the wide-rim of the cleft with d_{offset} parameter of 0.594 Å (Figure 3, top). The offset positioning of bromide and oxygen atom might suggest η^3 anion–π and lpe–π complexing modes. It was very interesting to note that the electron-deficient triazine ring formed a complex with two electron-rich guests, bromide from one side and a lone pair electrons of oxygen from the other side (Figure 3, top). To the best of our knowledge, no such type of interaction has been previously reported. Multiple noncovalent interactions including bromide–π interactions between hosts and guests gave rise to a unique layered assembly (Figure 3, bottom and Figures S3 and S4 in the Supporting Information).

Host molecule **4** is capable of forming complexes with halide species in solution. The interaction pattern is, however, different from those observed in the solid state. Since cage molecule **4** gave no fluorescence emission under irradiation, and it did not show significant UV/Vis spectral changes upon titration of tetrabutylammonium chloride or bromide; the interaction of host molecule **4** with halides in solution was then studied by means of isothermal titration calorimetry (ITC).[8] Pleasingly, ITC provided a very powerful method for detecting the anion–π interaction in solution. As illustrated in Figure 4 (and Figures S5–S8 in the Supporting Information), the heat of interaction of cage molecule **4** with halides was observed after each injection. With the addition of the guest, the observed heat decreases gradually and finally tends to zero. The net heat effect of cage molecule **4** binding with halides was obtained by subtraction of the heat of the guest dilution, and the thermodynamic parameters (Table 1) were calculated on the basis of fitting the ITC curves. The thermodynamic results indicated that the cage molecule **4** formed approximately 1:1 complex with tetrabutylammonium halides. The binding constant was in the order of fluoride (361 M^{-1}), chloride (146 M^{-1}) and bromide (95 M^{-1}). Moreover, the values of enthalpy changes of the complexion were all exothermic. Especially for the complexion of cage molecule **4** with fluoride, the enthalpy change was significantly exothermic, while the entropy change had a large negative value, indicating the complexion of cage molecule **4** with fluoride is an enthalpy-driven process.

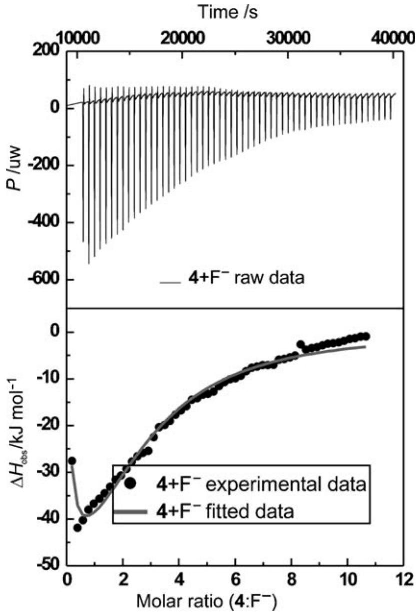


Figure 4. Microcalorimetric titration curve of host **4** with tetrabutylammonium fluoride in acetonitrile at 25 °C. Raw data for sequential injections of fluoride solution (6 μL, 96.7 mM) into host solution (5 mM; upper panel). Net heat effect of host **4** interacting with tetrabutylammonium fluoride obtained by subtracting the heat of dilution (dotted line) and the fitted heat effect (red line; lower panel).

Table 1. Binding constants (K_a) and standard Gibbs energy ($\Delta G°$) enthalpy change ($\Delta H°$) and entropy changes ($\Delta S°$) for the complex between **4** and halides in acetonitrile.

	Guest[a]	n[b]	K_a [M^{-1}]	$\Delta G°$ [kJ mol^{-1}][c]	$\Delta H°$ [kJ mol^{-1}]	$\Delta S°$ [J mol^{-1} K^{-1}]
1	F^-	1.3	361	−14.6	−207.2	−646.0
2	Cl^-	1.2	146	−12.3	−11.0	4.4
3	Br^-	1.2	95	−11.3	−6.6	15.8

[a] All as tetra-*n*-butylammonium salts. [b] Stoichiometry given by a fitting program. [c] $T=298.15$ K.

Although water molecules were found to participate in the formation of anion–π complexes in the solid state (supra vide), the presence of water in solution did not enhance the association of the host molecule with the halide guest. In comparison with the result listed in Table 1, for example, ITC study gave a slightly decreased association constant ($K_a = 101\,\text{M}^{-1}$) between **4** and tetrabutylammonium chloride when water was added (see Figure S7 in the Supporting Information). It indicated the different mechanisms of forming complexes in solution and in the solid state. Indeed, our further study, by means of diffusion ^{1}H NMR spectroscopy, revealed that the host cage molecule **4** and tetrabutylammonium chloride formed a complex in solution, while water was not involved at all (see Figure S9 in the Supporting Information). The variation of the association constant in the absence and in the presence of added water was probably due to the solvating effect of water on the tetrabutylammonium chloride guest.

It should be noted that the interaction between cage molecule **4** and various halide ions in solution does not originate from the hydrogen-bonding effect. We carefully measured the ^{1}H and ^{13}C NMR spectra of the host molecule upon titration of halides, but no shifts of proton and carbon signals were observed at all (see Supporting Information). The NMR titration studies showed convincingly that there is no Ar−H···X$^-$ hydrogen-bonding interaction between host and halide ions in solution. The interaction of host molecule **4** with chloride and bromide in solution was also evidenced by the observation of $[\mathbf{4}\subset Cl]^-$ and $[\mathbf{4}\subset Br]^-$ ion peaks in ESI mass spectra (see Figure S17 and S18 Supporting Information) when **4** was treated with tetrabutylammonium chloride and bromide, respectively. Additionally, ion peaks corresponding to $[\mathbf{4}\subset Bu_4NX\subset X]^-$ and $[\mathbf{4}\subset 2X]^-$ (X = Cl and Br) were also observed, indicating the formation of multiple component complexes between host and guest under mass spectrometry conditions.

In summary, we have shown that bis(tetraoxacalix[2]arene[2]triazine) **4**, a conformationally rigid cage molecule with three V-shaped electron-deficient clefts, was able to interact with halides. On the basis of ITC study, it formed 1:1 complex with fluoride, chloride, and bromide in acetonitrile, giving binding constants of 361, 146, and 95 M^{-1}, respectively. In the solid state, the triazine ring formed a weak σ complex with chloride, an η^3 complex with bromide, and π–lpe interactions with a water guest molecule. Different anion–π interactions along with hydrogen bonding, halogen bonding, and lpe–π interactions directed the formation of different molecular assemblies. The design of the host molecules for selective anion binding based on unique anion–π interactions are under further investigation in our laboratory.

Experimental Section

Preparation of 3: A mixture of phloroglucinol **1** (0.63 g, 5 mmol) and DIPEA (2.42 g, 18.8 mmol) in THF (30 mL) was added dropwise over a period of 20 min to an ice-cooled and well-stirred solution of cyanuric chloride **2** (4.15 g, 22.5 mmol) in THF (50 mL). The resulting mixture, which contained the precipitates formed from the reaction, was kept stirring for another 3 h at 0 °C. After filtration and concentration, the residue was subjected to chromatography on a silica gel (100–200 mesh) column eluting with a mixture of petroleum ether and acetone. Pure product **3** was obtained as a white solid (yield: 75 %). M.p. 240–142 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 7.17$ ppm (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 173.5$, 170.4, 151.7, 113.8 ppm; IR (KBr) $\tilde{\nu} = 1613$, 1530 cm^{-1}; MS (EI): m/z (%): 573 (4), 571 (8), 569 (10), 567 (5) $[M]^+$, 538 (17), 537 (10), 536 (57), 535 (12), 534 (100), 533 (10), 532 (57); elemental analysis calcd (%) for $C_{15}H_3N_9O_3Cl_6$: C 31.63, H 0.53, N 22.12; found: C 31.74, H 0.84, N 22.22.

Preparation of cage molecule 4: Solutions of **1** (0.126 g, 1 mmol) in acetone (50 mL) and **3** (0.57 g, 1 mmol) in acetone (50 mL) were added dropwise at the some rate to a solution of DIPEA (0.464 g, 3.6 mmol) in acetone (100 mL) over a period of 4 h at room temperature. After addition, the resulting mixture was kept stirring at room temperature for another 2.5 days. The solvent was removed and the residue was subjected to chromatography on a silica gel (100–200 mesh) column eluting with a mixture of petroleum ether and acetone. Pure cage molecule **4** was obtained as a white solid (yield: 35 %). M.p. >300 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 6.69$ ppm (s, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 175.1$, 172.7, 153.1 ppm; IR (KBr) $\tilde{\nu} = 1614$, 1550 cm^{-1}; MS (EI): m/z (%): 591 (4), 590 (28), 589 (28), 588 (19), 587 (96), 586 (22), 585 (100) $[M]^+$; HR-MS: m/z calcd for $C_{21}H_6N_9O_6Cl_3$: 584.9507; found: 584.0513.

Acknowledgements

We thank the National Natural Science Foundation of China (20875094, 20672115, 20532030), Ministry of Science and Technology (2007CB808005), Chinese Academy of Sciences for financial support. We also thank Dr. X. Hao and T.-L. Liang for X-ray structure determination and Dr. J.-F. Xiang for NMR measurements and discussions.

Keywords: anions · calixarenes · halides · host–guest systems · molecular assembly · pi interactions

---

[1] For reviews, see: a) P. Gamez, T. J. Mooibroek, S. J. Teat, J. Reedijk, *Acc. Chem. Res.* **2007**, *40*, 435; b) B. L. Schottel, H. T. Chifotides, K. R. Dunbar, *Chem. Soc. Rev.* **2007**, *36*, 68; c) B. P. Hay, V. S. Bryantsev, *Chem. Commun.* **2008**, 2417; d) P. Ballester in *Recognition of Anions* (Ed.: R. Vilar), Springer, Berlin, **2008**, p. 127.

[2] a) I. Alkorta, I. Rozas, J. Elguero, *J. Am. Chem. Soc.* **2002**, *124*, 8593; b) D. Quiñonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa, P. M. Deyà, *Angew. Chem.* **2002**, *114*, 3539; *Angew. Chem. Int. Ed.* **2002**, *41*, 3389; c) M. Mascal, A. Armstrong, M. D. Bartberger, *J. Am. Chem. Soc.* **2002**, *124*, 6274.

[3] O. B. Berryman, V. S. Bryantsev, D. P. Stay, D. W. Johnson, B. P. Hay, *J. Am. Chem. Soc.* **2007**, *129*, 48.

[4] For recent representative examples, see: a) S. Demeshko, S. Dechert, F. Meyer, *J. Am. Chem. Soc.* **2004**, *126*, 4508; b) V. Gorteau, G. Bollot, J. Mareda, A. Perez-Velasco, S. Matile, *J. Am. Chem. Soc.* **2006**, *128*, 14788; c) B. L. Schottel, H. T. Chifotides, M. Shatruk, A. Chouai, L. M. Pérez, J. Bacsa, K. R. Dunbar, *J. Am. Chem. Soc.* **2006**, *128*, 5895; d) G. Gil-Ramírez, E. C. Escudero-Adán, J. Benet-Buchholz, P. Ballester, *Angew. Chem.* **2008**, *120*, 4182; *Angew. Chem. Int. Ed.* **2008**, *47*, 4114; e) O. B. Berryman, A. C. Sather, B. P. Hay, J. S. Meisner, D. W. Johnson, *J. Am. Chem. Soc.* **2008**, *130*, 10895; f) M. Albrecht, C. Wessel, M. De Groot, K. Rissanen, A. Lüchow, *J. Am. Chem. Soc.* **2008**, *130*, 4600.

[5] a) Y. S. Rosokha, S. V. Lindeman, S. V. Rosokha, J. K. Kochi, *Angew. Chem.* **2004**, *116*, 4750; *Angew. Chem. Int. Ed.* **2004**, *43*, 4650; b) D.-X. Wang, Q.-Y. Zheng, Q.-Q. Wang, M.-X. Wang, *Angew. Chem.* **2008**, *120*, 7595; *Angew. Chem. Int. Ed.* **2008**, *47*, 7485.

[6] H. Schneider, K. M. Vogelhuber, F. Schinle, J. M. Weber, *J. Am. Chem. Soc.* **2007**, *129*, 13022.

[7] For recent reviews, see: a) M.-X. Wang, *Chem. Commun.* **2008**, 4541; b) W. Maes, W. Dehaen, *Chem. Soc. Rev.* **2008**, *37*, 2393; c) H. Tsue, K. Ishibashi, R. Tamura, *Top. Heterocycl. Chem.* **2008**, *17*, 73.

[8] F. P. Schmidtchen, *Isothermal Titration Calorimetry in Supramolecular Chemistry in Analytical Methods in Supramolecular Chemistry* (Ed.: C. Schalley), Wiley-VCH Weinheim, **2007**, pp. 55–78.

[9] Crystallographic data for **4** ($C_{21}H_6Cl_3N_9O_8$): $M_r = 618.70$, trigonal, space group $R\bar{3}c$, $a = 11.3135(16)$, $b = 11.3135(16)$, $c = 36.700(7)$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 120.00°$, $V = 4068.1(11)$ Å^3, $T = 293(2)$ K, full-matrix least-squares refinement on F^2 converged to $R_F = 0.0630$ $[I > 2\sigma(I)]$, 0.0750 (all data) and $Rw(F^2) = 0.1864$ $[I > 2\sigma(I)]$, 0.1962 (all data), goodness of fit 1.086. CCDC-734866 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] Crystallographic data for complex $[\mathbf{4} \subset (Et_4NCl)_3 \subset (H_2O)_3]$ ($C_{45}H_{72}Cl_6N_{12}O_9$): $M_r = 1137.85$, trigonal, space group $R\bar{3}$, $a = 20.5900(3)$, $b = 20.5900(3)$, $c = 24.9772(5)$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 120.00°$, $V = 9170.4(3)$ Å^3, $T = 173(2)$ K, full-matrix least-squares refinement on F^2 converged to $R_F = 0.0659$ $[I > 2\sigma(I)]$, 0.0712 (all data) and $Rw(F^2) = 0.1367$ $[I > 2\sigma(I)]$, 0.1392 (all data), goodness of fit 1.312. The diffuse electron density due to the disordered and unidentified moieties was treated with SQUEEZE routine within the PLATON software package (P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194). CCDC-734868 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] Crystallographic data for complex $[\mathbf{4} \subset (Et_4NBr)_2 \subset H_2O]$ ($C_{37}H_{48}Br_2Cl_3N_{11}O_7$): $M_r = 1025.03$, monoclinic, space group $C2m$, $a = 23.483(5)$, $b = 16.693(3)$, $c = 13.011(3)$ Å, $\alpha = 90.00$, $\beta = 117.10(3)$, $\gamma = 90.00°$, $V = 4540.4(20)$ Å^3, $T = 173(2)$ K, full-matrix least-squares refinement on F^2 converged to $R_F = 0.0546$ $[I > 2\sigma(I)]$, 0.0984 (all data) and $Rw(F^2) = 0.0853$ $[I > 2\sigma(I)]$, 0.0936 (all data), goodness of fit 1.081. The diffuse electron density due to the disordered and unidentified moieties was treated with SQUEEZE routine within the PLATON software package (see reference in [10]). CCDC-734867 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] For a review on lpe–π interaction, see: T. J. Mooibroek, P. Gamez, J. Reedijk, *CrystEngComm* **2008**, *10*, 1501.

[13] *Halogen Bonding* (Eds.: P. Metrangolo, G. Resnati), Springer, Berlin, **2008**.

Received: August 12, 2010