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Synthesis and Structure of Oxacalix[2]arene[2]triazines of an Expanded π-Electron-Deficient Cavity and Their Interactions with Anions

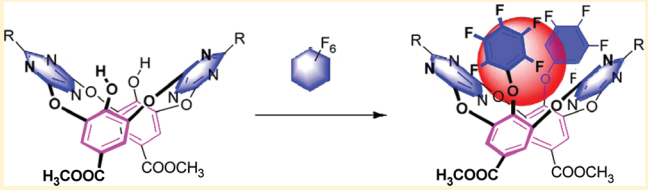
Sen Li,[†] Shi-Xin Fa,[†] Qi-Qiang Wang,[†] De-Xian Wang,*[,†] and Mei-Xiang Wang*[,†,‡]

[†]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[‡]The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China

Supporting Information

ABSTRACT: Novel macrocyclic anion receptors based on the principle of anion−π interactions were reported. By means of both post-macrocyclization modification protocol and the stepwise fragment coupling approach, functionalized oxacalix[2]arene[2]triazines bearing two other electron-deficient (hetero)aromatic rings on the lower rim were efficiently synthesized. The resulting oxacalix[2]arene[2]triazine macrocycles adopt 1,3-alternate conformation, yielding therefore an expanded electron-deficient cavity or space consisting of two triazine rings and two appending aromatic rings. Spectroscopic titration study showed the selective interaction of the pentafluorophenyl-substituted oxacalix[2]arene[2]triazine with azide and fluoride in solution with the binding constants ($K_{1:1}$) ranging from 1.33×10^3 to 3.52×10^3 M^{-1}.



INTRODUCTION

The design and synthesis of efficient receptors for anion recognition are challenging in supramolecular chemistry because anions, which differ from cations, have varied geometries, low charge density/radius ratios, and high free energies of solvation and a narrow pH window.[1] Among the anion receptors reported,[2] the binding between the host molecules and anions is dominated by the electrostatic interaction,[3] hydrogen bonding,[4] and Lewis acid−base interaction.[5] Recent years have witnessed a growing interest in intriguing anion−π interactions[6] since the theoretical studies which propose the noncovalent anion−π interactions between an anion and electron-deficient aromatics such as N-heterocycles and benzenes bearing perfluoro, nitro, and cyano substituents.[7] On the basis of DFT calculations, four different anion−π interaction motifs, viz. typical anion−π interaction, weak and strong σ interactions, and hydrogen bonding, have been suggested (Figure 1).[6d,7d] However, experimental evidence for unambiguous

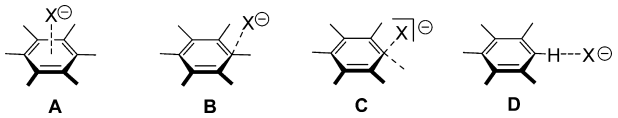


Figure 1. Different anion−π interaction motifs proposed by Hay and co-workers.

anion−π interactions between an anion and a *charge-neutral* electron-deficient arene is very rare. Moreover, only few examples of the anion−π interactions in solution have been reported.[8]

We have shown recently that oxacalix[2]arene[2]triazines, a type of conformation and cavity tunable macrocyclic host molecules, are able to strongly and selectively interact with halides in solution.[8c] Remarkably, using its electron-deficient V-shaped cleft of two triazine rings, oxacalix[2]arene[2]triazine forms ternary complexes with a halide and a water molecule in the solid state through simultaneous typical anion−π interaction between halide and one triazine ring and lone-pair electrons−π (lpe−π) interaction between the included water oxygen and the other triazine ring. Very recently, we have studied the interaction between halides and a conformationally rigid bis(oxacalix[2]arene[2]triazine) cage molecule.[8g] Astonishingly, a weak σ interaction motif between chloride and the triazine ring is observed in the host−guest complex in the crystalline state. As revealed by the powerful isothermal titration calorimetry (ITC) titration technique, there is anion−π interaction in the solution phase, albeit the binding appears very weak.

One of the salient structural features of heteroatom-bridged calix[2]arene[2]triazines is the formation of the shape-persistent 1,3-alternate conformation. A number of tetraoxacalix[2]arene[2]triazines, for example, give 1,3-alternate conformational structures in which two triazine rings form a V-shaped cleft, whereas two benzene rings are almost face-to-face paralleled.[9] The unique conformational structures render tetraoxacalix[2]arene[2]triazines the useful platforms for the fabrication of sophisticated molecular architectures.[10,11] On the basis of the V-shaped cleft of tetraoxacalix[2]arene[2]triazines, we envisioned therefore the construction of a π-electron-deficient cavity or space by introducing two extra electron-deficient aromatic rings on the lower rim positions of the benzene rings (Figure 2). The resulting

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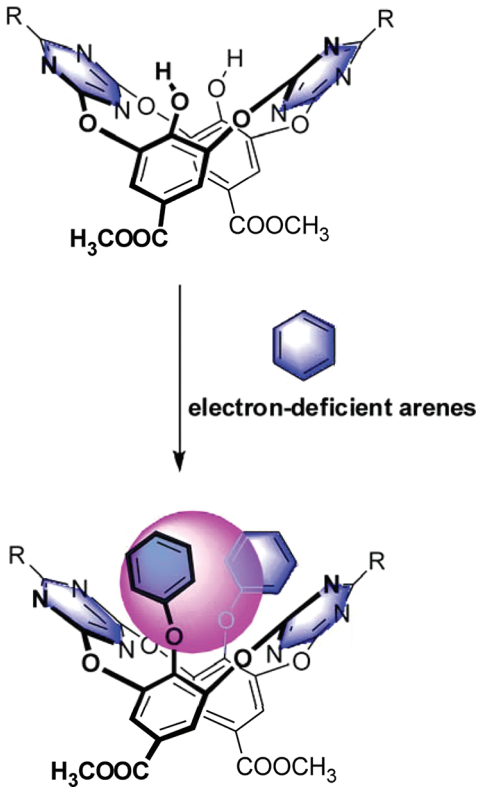


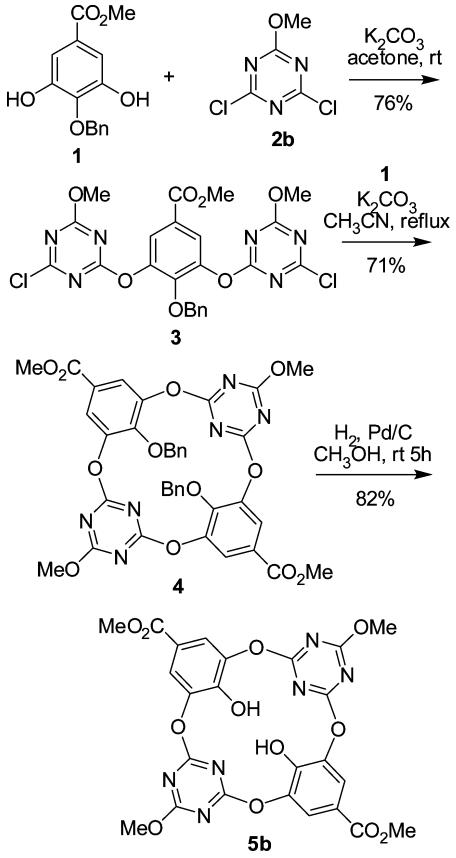
Figure 2. Construction of macrocyclic hosts of an expanded π-electron-deficient cavity.

cavity enabling multiple anion$-\pi$ interactions would provide the spacious microenvironment for anion species of larger sizes (Figure 2). We report herein the synthesis of electron-deficient aromatic ring-appending tetraoxacalix[2]arene[2]triazine host molecules by means of both fragment coupling approach and post-macrocyclization functionalization protocol. The functionalized macrocycles adopt 1,3-alternate conformation, giving indeed an expanded electron-deficient cavity on the lower rim position of benzene rings. The interaction of the synthetic host molecules with anions will also be discussed.

RESULTS AND DISCUSSION

Synthesis of Functionalized Tetraoxacalix[2]arene[2]-triazines. We initiated our study with the synthesis of target molecules based on the strategy of post-macrocyclization functionalization.[10] We have reported previously the facile synthesis of the lower rim dihydroxylated tetraoxacalix[2]arene[2]-triazine **5a** in which the triazine ring is arylated by a *p*-tolyl group.[10] To avoid the possible hydrogen bonding between arene C−H and the anion, a methoxy group was introduced instead of a *p*-tolyl group. Scheme 1 illustrates the preparation of tetraoxacalix[2]arene[2]triazine **5b** following our well-established fragment coupling approach.[10] The reaction between aromatic diol **1** and 2,4-dichloro-6-methoxytriazine **2b** in the presence of K_2CO_3 in acetone at ambient temperature proceeded smoothly to yield intermediate **3** in 76%. After optimization of the reaction conditions, varying bases, solvents, reaction temperature, and time (see Table S1 in Supporting Information), it was found that, under basic conditions, intermediate **3** underwent efficient macrocyclization reaction with **1** in hot acetonitrile to afford product **4** in good yield. Catalytic hydrogenolysis of **4** in methanol at room temperature led to the

Scheme 1. Preparation of Dihydroxylated Tetraoxacalix[2]arene[2]triazine 5b



removal of *O*-benzyl, producing dihydroxylated tetraoxacalix[2]-arene[2]triazine **5b** in 82% yield.

Macrocyclic compounds **5** provided a useful platform for the fabrication of sophisticated molecular architectures because of the versatile reactivity of two hydroxyl groups that append on the lower rim position. To construct a highly π-electron-deficient cavity, aromatic components such as triazinyl, 2,4-dinitrophenyl, and pentafluorophenyl were introduced. As depicted in Scheme 2, in the presence of K_2CO_3 as an acid scavenger, interaction of **5a** with 2,4-dichloro-6-methoxyltriazine **2b** at room temperature furnished the formation of **8a** in a yield of 53%. Similar reaction took place smoothly between macrocycle **5b** and **2b** in refluxing acetone, yielding the corresponding product **8b**, albeit in a slightly lower yield. To introduce the 2,4-dinitrophenyl group into the macrocycle, we first examined the reaction of **5** with 1-chloro-2,4-dinitrobenzene. The reaction outcomes were largely influenced by the conditions employed. Under various conditions screened (see Scheme S1 and Table S2 in Supporting Information), however, the highest yields of products **9a** and **9b** did not exceed 33 and 23%, respectively. When 1-iodo-2,4-dinitrobenzene **6** was applied, the aromatic nucleophilic substitution reaction proceeded effectively at 50−80 °C in *N*,*N*-dimethylformamide (DMF), and the chemical yields of **9a** and **9b** were improved to 48 and 37%, respectively. We then attempted synthesis of pentafluorophenyl-substituted tetraoxacalix[2]arene[2]triazines by means of nucleophilic substitution reaction of **5** with perfluorobenzene. Unfortunately, no desired reaction was observed under a wide variety of reaction conditions (see Table S3 in Supporting Information).

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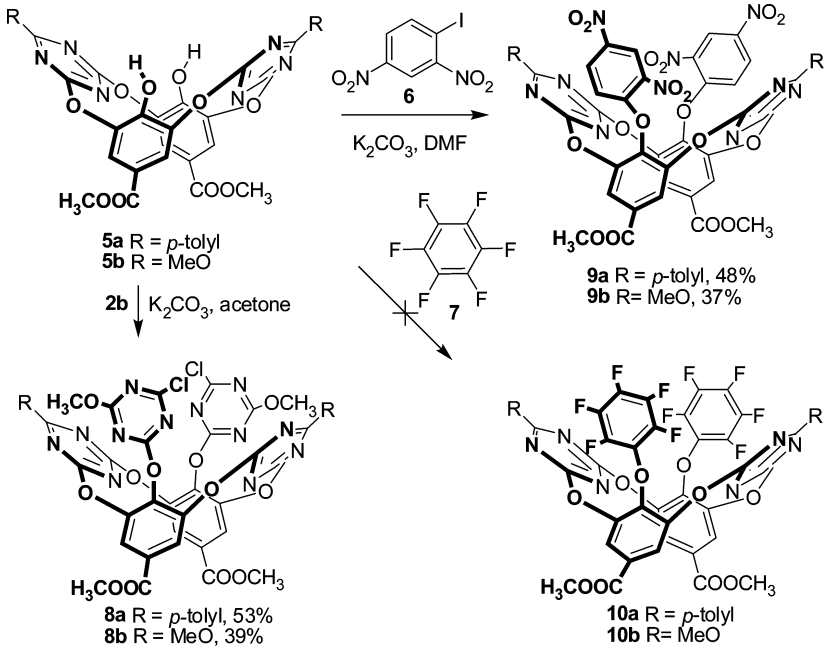
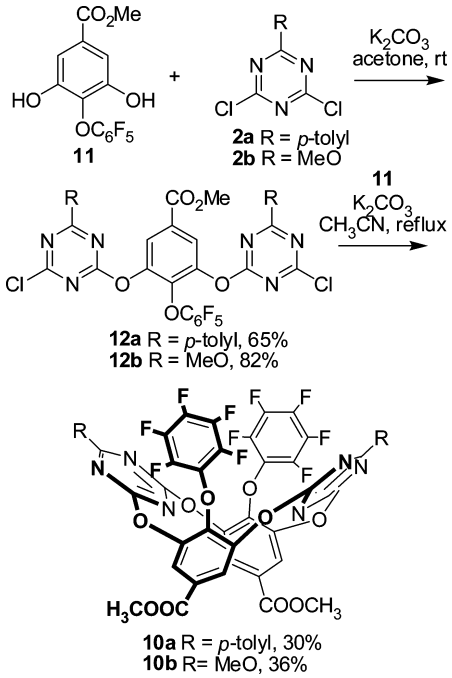
Scheme 2. Synthesis of Oxacalix[2]arene[2]triazine Products 8 and 9 by Means of Post-macrocyclization Functionalization Methods



In some cases, the reaction led to the decomposition of macrocyclic structure.

To obtain target molecules **10a** and **10b**, the fragment coupling synthetic method[9a] was then utilized (Scheme 3). The

Scheme 3. Fragment Coupling Approach to Functionalized Oxacalix[2]arene[2]triazine Products 10



two directional aromatic nucleophilic substitution reactions of methyl 3,5-dihydroxy-4-perfluorophenylbenzoate **11**, which was prepared in multiple steps starting from gallic acid methyl ester and perfluorobenzene (see Scheme S2 in Supporting Information), with 2,4-dichlorotriazine derivatives **2** under mild conditions generated efficiently fragments **12** in 65 to 82% yields. Further treatment of the intermediates **12** with **11** in refluxing acetonitrile with the aid of K_2CO_3 resulted in the macrocyclic products **10a** and **10b** in moderate yields (Scheme 3).

Structure of Functionalized Tetraoxacalix[2]arene[2]-triazines. The structure of all functionalized oxacalix[2]arene-[2]triazine compounds synthesized was established on the basis of spectroscopic data and microanalyses (see Supporting Information Figures S25−S54). To shed light on the conformational behaviors of the macrocycles, single crystals were cultivated and X-ray molecular structures of **8a**, **8b**, and **10b** were determined. As a comparison, oxacalix[2]arene[2]triazine **13** devoid of aryloxy groups on the lower rim position of the benzene rings was also synthesized (see Scheme S3 in Supporting Information) and its X-ray molecular structure was included. As shown in Figures 3−5 and Figures S1−S5 in Supporting Information, the O-aryloxylated oxacalix[2]arene-[2]triazines **8** and **10** and parent oxacalix[2]arene[2]triazine **13** appear very similar to other oxacalix[2]arene[2]triazine compounds documented in the literature,[9] adopting generally 1,3-alternate conformation in the solid state. Evidenced by the bond lengths and angles (captions in Figures 3−5 and Figures S1−S5), all bridging oxygen atoms form conjugation with the neighboring triazine rather than benzene ring. Careful scrutiny of the structures revealed that the introduction of two electron-deficient aromatic rings on the lower rim leads to the variation of cavity size. In comparison with the nonfunctionalized oxacalix[2]arene[2]triazine **13** in which the upper rim distance between two triazine rings is 10.22 Å, the V-cleft formed by two triazines becomes narrowed with the upper rim distance being 9.44 Å (**8a**), 8.98 Å (**8b**), and 8.87 Å (**10b**). Concomitantly, the lower rim distance between two benzene rings changes from 4.41 Å (**13**) to 4.53 Å (**8a**), 4.47 Å (**8b**), and 4.32 Å (**10b**). As we expected, the introduction of two electron-deficient aromatic rings on the hydroxy groups on the lower rim position of benzene rings tuned the V-cleft formed by two triazine rings of the macrocycle into an expanded cavity or space, although the

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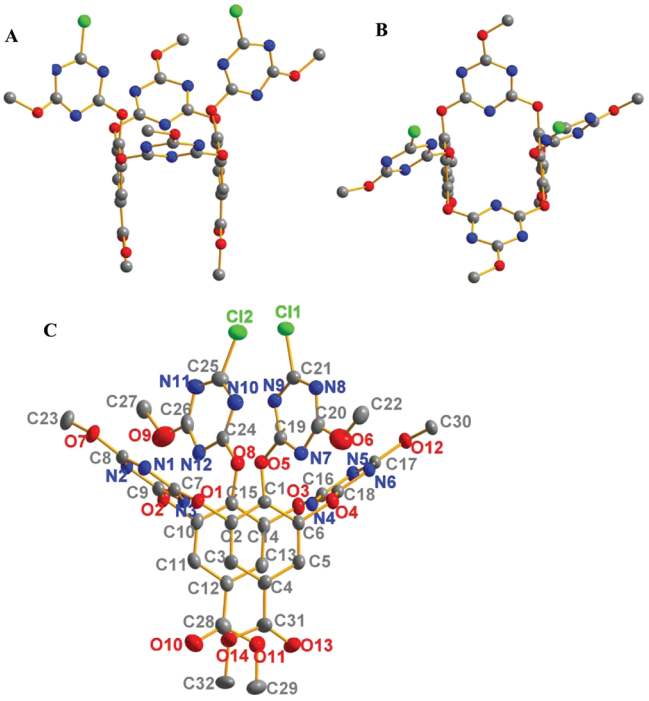

Figure 3. Molecular structure of **8b** with side view (A,C) and top view (B). Selected bond lengths [Å]: C2–O1 1.401, O1–C7 1.345, C9–O2 1.348, O2–C10 1.422, C14–O3 1.397, O3–C16 1.344, C18–O4 1.344, O4–C6 1.409. Selected angles: ∠C13–C14–O3 120.53°, ∠C14–O3–C16 116.26°, ∠O3–C16–N4 118.01°. The upper and lower rim distances [Å]: C8···C17 8.980, C4···C12 4.585, C1···C15 4.465, N3···N4 4.554, C21···C23 7.430. The probability is 25%. Hydrogen atoms were omitted for clarity.

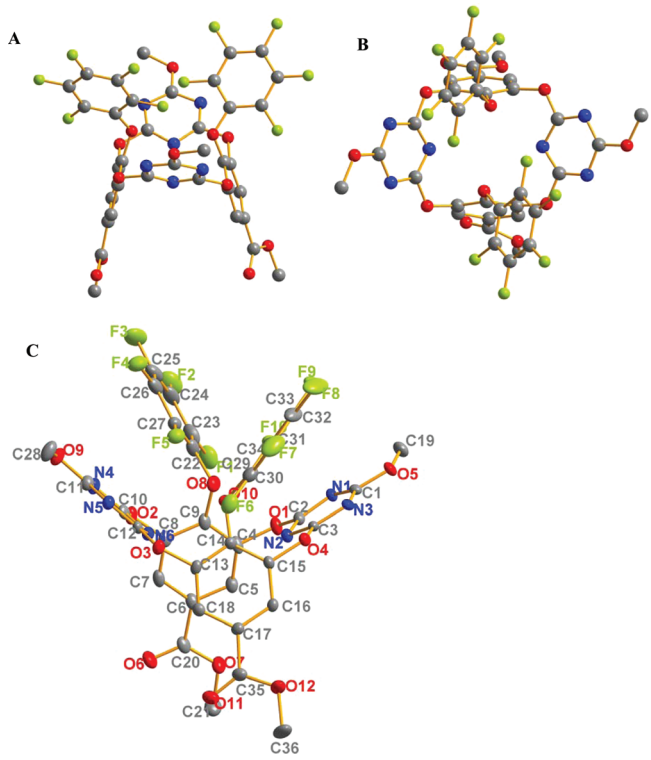

Figure 4. Molecular structure of **10b** with side view (A,C) and top view (B). Selected bond lengths [Å]: C4–O1 1.398, O1–C2 1.346, C8–O2 1.387, O2–C10 1.357, C12–O3 1.350, O3–C13 1.401, C15–O4 1.389, O4–C3 1.360. Selected angles: ∠C18–C13–O3 119.14°, ∠C13–O3–C12 118.84°, ∠O3–C12–N6 119.30°. The upper and lower rim distances [Å]: C1···C11 8.871, C6···C17 5.754, C9···C14 4.323, N2···N6 4.571. The probability is 25%. Hydrogen atoms were omitted for clarity.

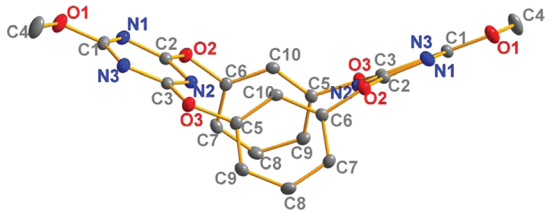

Figure 5. Molecular structure of **13**. Selected bond lengths [Å]: C5–O3 1.518, O3–C3 1.421, C2–O2 1.349, O2–C6 1.489, C5–O3 1.518, O3–C3 1.421, C2–O2 1.349, O2–C6 1.489. Selected angles: C9–C5–O3 117.82°, ∠C5–O3–C3 122.77°, ∠O3–C3–N3 117.87°. The upper and lower rim distances [Å]: C1···C1 10.217, N2···N2 4.963, C10···C10 4.410, C8···C8 5.728. The probability is 25%. Hydrogen atoms were omitted for clarity.

introduced two aromatic rings do not orientate in such a way to give an ideal cavity due to most probably packing effect in the crystalline state. In both the crystal structures of **8a** and **8b**, for example, each of the two introduced triazine rings tends to be perpendicular to the benzene ring with a dihedral angle of around 80 and 70°, respectively. Furthermore, these triazine rings orientate outward of the cavity, allowing therefore the favorable formation of intermolecular π–π stacking with the triazine rings of two neighboring molecules (Figure S1). In the case of pentafluorophenyl-substituted oxacalix[2]arene[2]triazine **10b**, two pentafluorophenyl moieties intrude into the cavity (Figure 4), and molecular packing therefore enables multiple intermolecular interactions (Figures S4 and S5).

It is important to address that all functionalized oxacalix[2]-arene[2]triazine products **8**–**10** showed a single set of signals in their NMR spectra at ambient temperature (see Supporting Information). Since the free rotation of individual aromatic rings within a macrocycle is prohibited because of the presence of bulky substituents, both ^{1}H and ^{13}C NMR spectroscopic data may indicate the shape-persistent symmetric 1,3-alternate conformational structure in solution. To shed light on the orientation of two introduced aromatic rings, such as being inward or outward of the V-cleft formed by two triazine rings, in solution phase, compound ethyl 4-(2,4-dinitrophenoxy)benzoate was prepared[12] and its ^{1}H NMR spectrum was compared with that of **9b**. Almost identical chemical shift values of aromatic protons were observed (see Figure S22 in Supporting Information), indicating that aromatic rings appending on the lower rim position do not experience shielding effect. In other words, these introduced aromatic rings are most likely not included in the cleft between two triazine rings of the macrocycle. It may also imply the generation of a π-electron-deficient cavity consisting of two triazine rings of macrocycle and two aromatic rings attached to the oxygen atoms on the lower rim position of benzene rings in solution.

Interactions between Functionalized Oxacalix[2]-arene[2]triazines and Anions. Having had the functionalized oxacalix[2]arene[2]triazines with an expanded π-electron-deficient cavity in hand, we then examined their interactions with anions by means of spectroscopic titrations. Pentafluorophenyl-substituted macrocyclic hosts **10a** and **10b** were chosen because they do not contain any aromatic C–H moiety and therefore exclude the possible hydrogen bonding interaction

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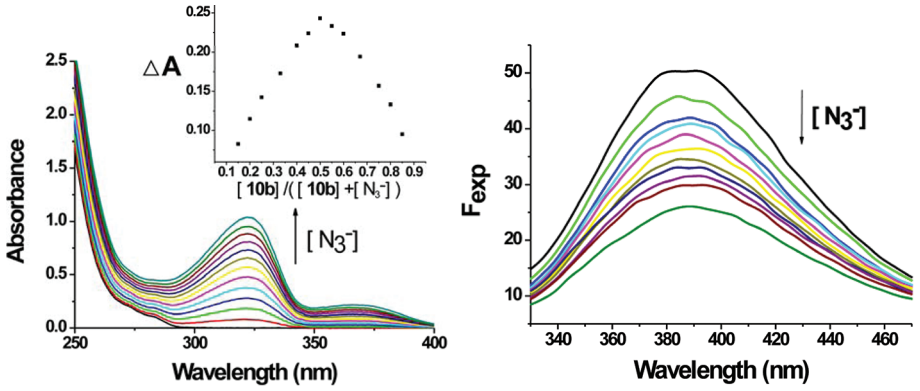
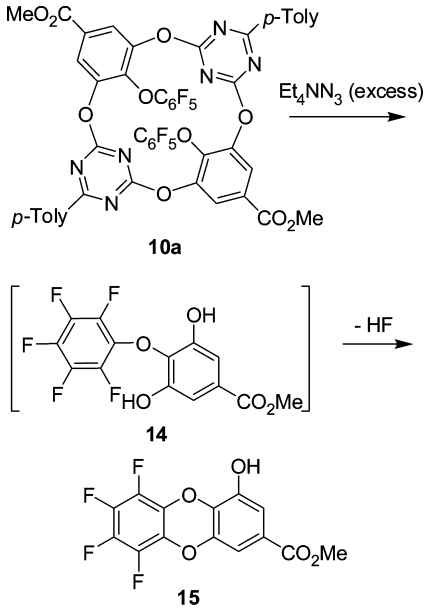


Figure 6. UV−vis spectroscopic titration (left) of **10b** (8.94×10^{-5} M in 1 mL of acetonitrile) upon the addition of $Bu_4N^+N_3^-$ (0, 4.60, 9.20, 13.7, 18.3, 22.9, 27.5, 32.1, 36.6, 41.2, 45.8, 50.4, 55.0 × 10^{-5} M), respectively. The inset is the Job's plot of **10b** and azide with a total concentration being 8×10^{-4} M. Fluorescence titration (right) of **10b** (0.80×10^{-4} M in 1 mL of acetonitrile) upon the addition of $Bu_4N^+N_3^-$ (0, 4.10, 5.13, 6.16, 7.18, 8.21, 9.23, 10.26, 11.29, 12.31, 14.36 × 10^{-4} M), respectively. The excitation wavelength was 253 nm, excitation and emission slits were all 10 nm, the scan speed was 240 nm/min, and voltage was 400 V.

between anions and C−H of the hosts. Unfortunately, no spectral changes were evidenced when both host molecules were titrated with most anion species including halides, thiocyanate, nitrate, and phosphate (Figures S7−S10). Interestingly, the interaction of both **10a** and **10b** with tetrabutylammonium azide led to the emerging of new absorption bands at 322 and 365 nm (Figure 6 and Figure S11). Job's plot experiments showed that hosts **10a** and **10b** formed a 1:1 complex with azide, and the association constants, which were calculated from the titration curves using a Hyperquad 2003 software,[13] are 1.47×10^3 M^{-1} for $[\mathbf{10a}{\cdot}N_3]^-$ and 1.33×10^3 M^{-1} for $[\mathbf{10b}{\cdot}N_3]^-$, respectively. The interaction of macrocyclic compounds with azide also resulted in the quenching of fluorescence emission of **10a** and **10b** at 385 and 335 nm, respectively (Figure 6 and Figure S12). The association constants calculated using fluorescence titration data are 2.15×10^3 M^{-1} ($[\mathbf{10a}{\cdot}N_3]^-$) and 3.52×10^3 M^{-1} ($[\mathbf{10b}{\cdot}N_3]^-$), respectively, which are comparable with that obtained from UV−vis titration measurement. It should be noted that, based on fluorescence titrations, hosts **10a** and **10b** also formed complexes with fluoride in solution, giving the association constants of 2.21×10^3 M^{-1} ($[\mathbf{10a}{\cdot}F]^-$) and 1.90×10^3 M^{-1} ($[\mathbf{10b}{\cdot}F]^-$), respectively. The formation of the complexes $[\mathbf{10a}{\cdot}N_3]^-$, $[\mathbf{10b}{\cdot}N_3]^-$, $[\mathbf{10a}{\cdot}F]^-$, and $[\mathbf{10b}{\cdot}F]^-$ was further supported by ESI mass spectrometry, which gave mass peaks corresponding to the complexes (Figures S14−S17). ^{1}H NMR spectroscopy was used to investigate the anion−π interactions. As illustrated in Figures S18−S21, no variation at all in the ^{1}H NMR spectra of **10a** and **10b** occurred upon the addition of anions, indicating the change of UV−vis absorbance and the quench of fluorescence emission of the macrocycles are the result of anion−π interaction, the results being in agreement with our previous reports.[8c,g]

To reveal the anion−π interaction between **10** and azide at molecular level, a single crystal of the complex was cultivated by slow evaporation of a solution of **10** and tetraethylammonium azide in a mixture of methanol and chloroform. Surprisingly, the single crystal obtained from the solution of **10a** and azide was not a host−guest complex as we expected. The X-ray diffraction analysis showed instead a fused ring structure **15** (Figure S6). Apparently, the interaction of perfluorophenyl-substituted oxacalix[2]arene[2]triazine **10a** with an excess amount of azide (1:5) during the process of crystallization caused cleavage of C−O bonds between the bridging oxygen and triazine, and the resulting intermediate **14** underwent intramolecular cyclization to furnish methyl 6,7,8,9-tetrafluoro-4-hydroxydibenzo[*b*,*e*][1,4]dioxine-2-carboxylate **15** (Scheme 4; for the synthesis of **15**, see Scheme S4).

Scheme 4. Formation of 15 from the Reaction of Tetrabutylammonium Azide with 10a



Concerning the possible reaction rather than noncovalent interaction between **10** and azide during spectroscopic titration which gave a new absorption band at 322 and 365 nm (supra vide), we examined the UV−vis spectra of compound **15** (Figure S13). The maximum absorption band of **15** was observed, however, at 298 nm, completely different from the UV−vis spectrum of host molecule **10**. In addition, the mixture of azide and **10** in acetonitrile, which was taken from spectroscopic titration experiments, was analyzed by means of HPLC analysis. No new peak corresponding to **15** was observed, and the retention time and integral peak area of **10** remained intact (Figures S23 and S24). These results excluded the possibility of reaction of host **10a** with azide guest and validated the formation of host−guest complex during titration. It is most

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likely that the presence of an excess amount of azide and high concentration under the crystallization conditions facilitated the reaction of azide toward oxacalix[2]arene[2]triazine. Although the molecular details of noncovalent anion−π interaction remain unclear at current stage, the outcomes of the reaction observed may imply the σ complexation of azide with the carbon of triazine.

CONCLUSION

In summary, we have synthesized a number of functionalized oxacalix[2]arene[2]triazine compounds using both the post-macrocyclization functionalization protocol and the fragment coupling approach. The introduction of an electron-deficient aromatic ring at the lower rim position of each benzene ring resulted in the macrocycles of an expanded π-electron-deficient cavity or space. The perfluorophenyl-appending oxacalix[2]-arene[2]triazine host molecules formed 1:1 noncovalent anion−π complexes with azide and fluoride in dilute acetonitrile solution, giving association constants in the range of 1.33×10^3 to 3.52×10^3 M^{-1}.

EXPERIMENTAL SECTION

Synthesis of 3. While keeping stirring at room temperature, a solution of methyl 4-(benzyloxy)-3,5-dihydroxybenzoate **1** (2.74 g, 10 mmol) in acetone (40 mL) was added dropwise to a mixture of 2,4-dichloro-6-methoxy-1,3,5-triazine **2b** (3.60 g, 20 mmol) and potassium carbonate (3.46 g, 25 mmol) in acetone (60 mL) during 3 h. The resulting mixture was stirred for another 5 min, until the reactants were consumed (TLC). After the solid was removed by filtration, the filtrate was concentrated and the residue was chromatographed on a silica gel column eluted with a mixture of petroleum ether, dichloromethane, and ethyl acetate (1:1:0.2, v/v/v) as the mobile phase to give pure product **3** (4.25 g, yield 76%) as a white solid: mp 133−134 °C; ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.83 (s, 2H), 7.25−7.23 (m, 3H), 7.15−7.12 (m, 2H), 5.07 (s, 2H), 3.96 (s, 6H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 173.2, 172.7, 171.7, 164.8, 146.8, 144.8, 135.6, 128.32, 128.30, 127.3, 126.0, 122.5, 75.8, 56.4, 52.6; IR (KBr) ν 1728, 1565, 1540, 1506, 804 cm^{-1}; MS (CI) m/z 560.1 [M^+] (100%), 561.1 [M + H]$^+$ (79), 562.1 [M + 2]$^+$ (86), 563.1 [M + H + 2]$^+$ (52), 564.1 [M + 4]$^+$ (22), 565.1 [M + H + 4]$^+$ (10). Anal. Calcd for $C_{23}H_{18}Cl_2N_6O_7$: C, 49.21; H, 3.23; N, 14.97. Found: C, 49.35; H, 3.28; N, 14.70.

Synthesis of 4. A solution of methyl 4-(benzyloxy)-3,5-dihydroxybenzoate **1** (960 mg, 3.5 mmol) and **3** (1.965 g, 3.5 mmol) in acetonitrile (200 mL) was added dropwise to a hot suspension of anhydrous potassium carbonate powder (605 mg, 4.375 mmol) in acetonitrile (200 mL) during 2 h. The resulting mixture was refluxed for another 20 min. After cooling down to room temperature and removal of solid by filtration, the filtrate was concentrated and the residue was chromatographed on a silica gel column eluted with a mixture of petroleum ether, dichloromethane, and ethyl acetate (5:5:0.1, v/v/v) as the mobile phase to give pure **4** (1.89 g, yield 71%) as a white solid: mp 189−190 °C ; ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.56 (s, 4H), 7.19−7.05 (m, 10H), 4.93 (s, 4H), 4.04 (s, 6H), 3.85 (s, 6H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 174.5, 172.8, 164.7, 146.9, 144.9, 135.8, 128.1, 128.0, 127.4, 125.5, 122.0, 75.4, 55.9, 52.3; IR (KBr) ν 1728, 1567, 1365, 1325 cm^{-1}; MS (MALDI-TOF) m/z 763.2 [M + H]$^+$ (100%), 785.1 [M + Na]$^+$ (97). Anal. Calcd for $C_{38}H_{30}N_6O_{12}$: C, 59.84; H, 3.96; N, 11.02. Found: C, 59.70; H, 3.99; N, 11.16.

Synthesis of 5b. Under hydrogen (balloon), a mixture of **4** (3.813 g, 5 mmol) and Pd/C (300 mg, 10%) in methanol (60 mL) was stirred at room temperature for 5 h. After removal of catalyst and solvent, recrystallization of residue in a mixture of ethyl acetate and methanol gave colorless crystalline product **5b** (2.401 g, 82%): mp 226−227 °C; ^{1}H NMR (acetone-d_6/300 MHz) 7.48 (s, 4H), 4.09 (s, 6H), 3.79 (s, 6H); ^{13}C NMR (acetone-d_6/75 MHz) δ 175.7, 174.0, 165.5, 147.3, 141.2, 122.6, 121.7, 56.2, 52.3; IR (KBr) ν 3479, 1722, 1569, 1361 cm^{-1}; MS (MALDI-TOF) m/z 583.2 [M + H]$^+$ (61), 605.2 [M + Na]$^+$ (100%), 621.2 [M + K]$^+$ (11). Anal. Calcd for $C_{24}H_{18}N_6O_{12}\cdot CH_3OH$: C, 48.87; H, 3.61; N, 13.68. Found: C, 48.56; H, 3.44; N, 13.79.

Synthesis of 8a. To a mixture **2b** (162 mg, 0.9 mmol) and anhydrous potassium carbonate powder (62 mg, 0.45 mmol) in acetone (20 mL) was added dropwise a solution of **5a**[10] (211 mg, 0.3 mmol) in acetone (100 mL) during 3 h. The resulting mixture was kept stirring at room temperature for another 12 h. After filtration, the filtrate was concentrated and the residue was chromatographed on a silica column eluted with a mixture of petroleum ether, dichloromethane, and ethyl acetate (1:1:0.2, v/v/v) as the mobile phase to give pure **8a** (157 mg, 53%) as a white solid: mp 271−272 °C; ^{1}H NMR ($CDCl_3$/300 MHz) δ 8.36 (d, J = 8.4 Hz, 4H), 7.75 (s, 4H), 7.30 (d, J = 8.4 Hz, 4H), 3.93 (s, 6H), 3.91 (s, 6H), 2.45 (s, 6H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 177.5, 173.4, 172.8, 172.1, 171.0, 164.4, 144.9, 144.5, 140.6, 131.2, 129.6, 129.5, 129.2, 122.7, 56.4, 52.7, 21.8; IR (KBr) ν 1732, 1574, 1526, 1371 cm^{-1}; MS (MALDI-TOF) m/z 989.3 [M + H]$^+$ (10), 991.4 [M + H + 2]$^+$ (6), 1011.3 [M + Na]$^+$ (100%), 1013.3 [M + Na + 2]$^+$ (80), 1015.3 [M + Na + 4]$^+$ (10), 1027.3 [M + K]$^+$ (44), 1029.3 [M + K + 2]$^+$ (38), 1031.3 [M + K + 4]$^+$ (5). Anal. Calcd for $C_{44}H_{30}Cl_2N_{12}O_{12}\cdot H_2O$: C, 52.44; H, 3.20; N, 16.68. Found: C, 52.24, H, 3.10, N, 16.25.

Synthesis of 8b. To a mixture of **2b** (720 mg, 4 mmol) and anhydrous potassium carbonate powder (415 mg, 3 mmol) in acetone (20 mL) was added dropwise a solution of **5b** (1.165 g, 2 mmol) in acetone (20 mL) during 1.5 h. The resulting mixture was kept stirring at room temperature for another 5 h. After filtration, the filtrate was concentrated and the residue was chromatographed on a silica gel column eluted with a mixture of petroleum ether, dichloromethane, and ethyl acetate (1:1:1, v/v/v) as the mobile phase to give pure **8b** (540 mg, 31%) as a white solid: mp 167−168 °C; ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.68 (s, 4H), 4.08 (s, 6H), 3.97 (s, 6H), 3.92 (s, 6H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 174.8, 173.4, 172.7, 172.6, 170.9, 164.3, 144.4, 140.2, 129.1, 122.7, 56.5, 56.3, 52.8; IR (KBr) ν 1733, 1571, 1356 cm^{-1}; MS (MALDI-TOF) m/z 907.1 [M + K]$^+$ (100%), 909.1 [M + K + 2]$^+$ (89), 911.1 [M + K + 4]$^+$ (5). Anal. Calcd for $C_{32}H_{22}Cl_2N_{12}O_{14}$: C, 44.20; H, 2.55; N, 19.33. Found: C, 44.12; H, 2.66; N, 19.22.

Synthesis of 9a. A mixture of **5a** (70 mg, 0.1 mmol), 1-iodo-2,4-dinitrobenzene **6** (118 mg, 0.4 mmol), and anhydrous potassium carbonate powder (28 mg, 0.2 mmol) in DMF (3 mL) was stirred at 80 °C for 3 h. After cooling to room temperature, hydrochloric acid (0.5 mL, 10%) and water (10 mL) were added, and the resulting mixture was extracted with ethyl acetate (5 × 50 mL). The combined organic phase was dried with anhydrous Na_2SO_4. After filtration, the filtrate was concentrated with a rotary evaporator to give crude product. After washing with ethyl acetate, pure **9a** (50 mg, yield 48%) was obtained as a pale yellow solid: mp 214−215 °C; ^{1}H NMR ($CDCl_3$/300 MHz) δ 8.75 (d, J = 2.7 Hz, 2H), 8.37 (dd, J = 9.2, 2.7 Hz, 2H), 8.25 (d, J = 8.1 Hz, 4H), 7.86 (s, 4H), 7.24 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 9 Hz, 2H), 3.95 (s, 6H), 2.41 (s, 6H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 177.4, 172.0, 164.2, 153.9, 144.9, 144.8, 142.5, 141.7, 137.8, 131.0, 129.9, 129.6, 129.5, 123.2, 123.0, 117.4, 53.0, 21.8; IR (KBr) ν 1732, 1576, 1530, 1370, 1337 cm^{-1}; MS (MALDI-TOF) m/z 1035.1 [M + H]$^+$ (21), 1057.0 [M + Na]$^+$ (100%). Anal. Calcd for $C_{48}H_{30}N_{10}O_{18}$: C, 55.71; H, 2.92; N, 13.54. Found: C, 55.89; H, 3.07; N, 13.60.

Synthesis of 9b. A mixture of **5b** (116 mg, 0.2 mmol), 1-iodo-2,4-dinitrobenzene **6** (236 mg, 0.8 mmol), and anhydrous potassium carbonate powder (55 mg, 0.4 mmol) in DMF (3 mL) was stirred at 50 °C for 29 h. After addition of water (15 mL), product precipitated from the solution. Filtration and washing with ethyl acetate gave pure **9b** (68 mg, yield 37%) as a pale yellow solid: mp 279−280 °C; ^{1}H NMR ($CDCl_3$/300 MHz) δ 8.86 (d, J = 2.7 Hz, 2H), 8.34 (dd, J = 9.3, 2.7 Hz, 2H), 7.82 (s, 4H), 6.93 (d, J = 9.3 Hz, 2H), 4.01 (s, 6H), 3.96 (s, 6H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 174.7, 172.5, 164.1, 153.8, 144.7, 142.5, 141.4, 137.8, 129.8, 129.5, 123.1, 117.3, 56.3, 53.0; IR (KBr) ν 1731,1608, 1560, 1340 cm^{-1}; MS (MALDI-TOF) m/z 937.3 [M + Na]$^+$ (100%). Anal. Calcd for $C_{36}H_{22}N_{10}O_{20}$: C, 47.28; H, 2.42; N, 15.31. Found: C, 47.24; H, 2.59; N, 15.39.

General Procedure for the Synthesis of 12a and 12b. To a mixture of **2a** or **2b** (4.4 mmol) and potassium carbonate (691 mg,

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5 mmol) in acetone (15 mL) was added dropwise a solution of **11** (700 mg, 2 mmol) in acetone (5 mL) during 1 h at room temperature while stirring. After stirring for another 15−30 min, the mixture was filtrated. The filtrate was concentrated to give a residue which was chromatographed on silica gel column eluted with a mixture of petroleum ether, chloroform, and acetone as the mobile phase to give pure product.

12a (65%) as a white solid: mp 120−121 °C; ^{1}H NMR ($CDCl_3$/300 MHz) δ 8.24 (d, J = 8.4 Hz, 4H), 8.02 (s, 2H), 7.22 (d, J = 8.1 Hz, 4H), 3.96 (s, 3H), 2.42 (s, 6H); ^{13}C NMR ($CDCl_3$/100 MHz) δ 175.8, 173.1, 170.6, 164.6, 145.6, 144.0, 143.0, 141.8 (dm), 139.5 (dm), 137.0 (dm), 130.9 (dm), 130.5, 129.8, 127.6, 123.4, 53.0, 21.9; IR (KBr) ν 1734, 1549, 1516, 1352 cm^{-1}; MS (MALDI-TOF) m/z 757.1 [M + H]$^+$ (80), 758.2 [M + 2]$^+$ (30), 759.2 [M + H + 2]$^+$ (69), 760.2 [M + 4]$^+$ (23), 761.2 [M + H + 4]$^+$ (12), 779.1 [M + Na]$^+$ (100%), 781.2 [M + Na + 2]$^+$ (74), 783.2 [M + Na + 4]$^+$ (8). Anal. Calcd for $C_{34}H_{19}Cl_2F_5N_6O_5$: C, 53.91; H, 2.53; N, 11.10. Found: C, 54.05; H, 2.72; N, 10.86.

12b (82%) as a white solid: mp 47−48 °C; ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.92 (s, 2H); 4.03 (s, 6H); 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$/100 MHz) δ 173.5, 172.8, 171.3, 164.2, 143.7, 141.7 (dm), 139.4 (dm), 136.9 (dm), 130.8 (dm), 127.7, 123.1, 56.6, 52.8; IR (KBr) ν 1731, 1566, 1538, 1347 cm^{-1}; MS (ESI) m/z 637.1 [M + H]$^+$ (100%), 638.1 [M + 2]$^+$ (24), 639.1 [M + H + 2]$^+$ (58), 640.1 [M + 4]$^+$ (14), 641.1 [M + H + 4]$^+$ (13), 659.1 [M + Na]$^+$ (73), 661.2 [M + Na + 2]$^+$ (63), 663.2 [M + Na + 4]$^+$ (17). Anal. Calcd for $C_{22}H_{11}Cl_2F_5N_6O_7$: C, 41.46; H, 1.74; N, 13.19. Found: C, 41.20; H, 1.90; N, 13.06.

Synthesis of 10a. A mixture of **12a** (222 mg, 0.3 mmol), **11** (105 mg, 0.3 mmol), and anhydrous potassium carbonate powder (52 mg, 0.375 mmol) in acetonitrile (60 mL) was refluxed for 6 h. After cooling down to room temperature, the mixture was filtrated and the filtration cake was collected. The filtrate was concentrated, and the resulting residue was mixed with acetonitrile (10 mL). After 15 min, the solution was filtered. The combined filtration cake was mixed with dichloromethane (15 mL) and washed with water (3 × 10 mL). The organic phase was dried with anhydrous Na_2SO_4. After removal of organic solvent, the residue was chromatographed on a silica gel column eluted with a mixture of petroleum ether, chloroform, and ethyl acetate (6:1:0.1, v/v/v) as the mobile phase to give the pure **10a** (170 mg, 55%) as a white solid: mp >300 °C; ^{1}H NMR ($CDCl_3$/400 MHz) δ 8.36 (d, J = 8 Hz, 4H), 7.74 (s, 4H), 7.33 (d, J = 7.6 Hz, 4H), 3.91 (s, 6H), 2.46 (s, 6H); ^{13}C NMR ($CDCl_3$/100 MHz) δ 177.6, 172.1, 164.4, 145.0, 144.7, 143.2, 141.8 (dm), 139.5 (dm), 137.0 (dm), 131.1, 129.6, 129.5, 127.7, 122.9, 52.7, 21.8; IR (KBr) ν 1734, 1576, 1520, 1372 cm^{-1}; MS (MALDI-TOF) m/z 1035.4 [M + H]$^+$ (100%), 1057.5 [M + Na]$^+$ (38). Anal. Calcd for $C_{48}H_{24}F_{10}N_6O_{10}$: C, 55.72; H, 2.34; N, 8.12. Found: C, 55.79; H, 2.51; N, 8.00.

Synthesis of 10b. A suspension of anhydrous potassium carbonate powder (173 mg, 1.25 mmol) in acetonitrile (20 mL) was heated to reflux. A mixture of **12b** (637 mg, 1 mmol) and **11** (350 mg, 1 mmol) in acetonitrile (80 mL) was then added dropwise during 1.5 h. The resulting mixture was refluxed for another 0.5 h. After cooling down to room temperature, the solid was removed by filtration. The filtrate was concentrated, and the residue was chromatographed on a silica gel column eluted with a mixture of petroleum ether, dichloromethane, and ethyl acetate (1:1:0.2, v/v/v) as the mobile phase to give pure **10b** (324 mg, 35%) as a white solid: mp 193−194 °C; ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.68 (s, 4H), 4.08 (s, 6H), 3.90 (s, 6H); ^{13}C NMR ($CDCl_3$/100 MHz) δ 175.2, 172.8, 163.9, 144.6, 143.4, 142.0 (dm), 139.6 (dm), 137.1 (dm), 131.3 (dm), 127.7, 122.9, 55.8, 52.2; IR (KBr) ν 1734, 1585, 1561, 1519, 1360, 1332 cm^{-1}; MS (MALDI-TOF) m/z 915.3 [M + H]$^+$ (100%), 937.3 [M + Na]$^+$ (32). Anal. Calcd for $C_{36}H_{16}F_{10}N_6O_{12}$: C, 47.28; H, 1.76; N, 9.19. Found: C, 47.52; H, 2.15; N, 8.84.

Synthesis of 6s. To a mixture of NaH (144 mg, 6 mmol) and DMF (10 mL) was added slowly methyl 3,5-bis(benzyloxy)-4-hydroxybenzoate (1.822 g, 5 mmol). After stirring at room temperature for 3 h, perfluorobenzene (1.395 g, 7.5 mmol) was added. The mixture was allowed to reflux for another 6 h. The resulting mixture was poured on ice slowly and extracted with ethyl acetate. The organic phase was dried with anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate (12:1, v/v) as the mobile phase to give pure **6s** (1.209 g, yield 46%) as a white solid: mp 111−112 °C; ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.41 (s, 2H), 7.36−7.26 (m, 10H), 5.08 (s, 4H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 166.2, 150.4, 142.2 (dm), 139.0 (dm), 138.8, 134.3 (dm, J = 260 Hz), 128.6, 128.4, 127.6, 126.6, 108.1, 71.3, 52.4; IR (KBr) ν 1710, 1516, 1108 cm^{-1}; MS (MALDI-TOF) m/z (%) 553.2 [M + Na]$^+$ (100%). Anal. Calcd for $C_{28}H_{19}F_5O_5$: C, 63.40; H, 3.61. Found: C, 63.35; H, 3.48.

Synthesis of 11. Under hydrogen (balloon), a mixture of **6s** (1.036 g, 1.95 mmol) and Pd/C (104 mg, 10%) in methanol (20 mL) was stirred at room temperature for 6 h. The resulting mixture was filtered, and the filtrate was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate (4:1, v/v) as the mobile phase to give pure **11** (600 mg, yield 88%) as a white solid: mp 192−193 °C; ^{1}H NMR (acetone-d_6/300 MHz) δ 9.12 (s, 2H); 7.18 (s, 2H); 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$/100 MHz) δ 166.5, 150.1, 143.3 (dm), 140.1 (dm), 137.1, 136.7 (dm), 128.2, 110.0, 52.4; IR (KBr) ν 3484, 3356, 1686, 1518, 996 cm^{-1}; MS (ESI) m/z (%) 329.0 [M − HF − H]$^-$ (100%), 349.1 [M − H]$^-$ (24). Anal. Calcd for $C_{14}H_7F_5O_5$: C, 48.02; H, 2.01. Found: C, 48.08; H, 2.12.

Synthesis of 13. A mixture of **2b** (360 mg, 2 mmol), resorcinol (220 mg, 2 mmol), and anhydrous potassium carbonate (345 mg, 2.5 mmol) in acetonitrile (20 mL) was allowed to reflux for 24 h. After filtration and removing the solvent of the filtrate, the residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate (2:1, v/v) as the mobile phase to give pure **13** (371 mg, yield 86%) as a white solid: mp 234−238 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (2H, t, J = 8.2 Hz), 6.85 (4H, dd, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.71 (2H, t, J = 2.2 Hz), 4.12 (6H, s); ^{13}C NMR (300 MHz, $CDCl_3$) δ 174.7, 173.4, 152.0, 130.1, 119.2, 116.6, 55.9; IR (KBr) ν 2956, 1586, 1483, 1427, 1371, 1267, 1201, 1146 cm^{-1}; MS (MALDI-TOF) m/z 435.1 (M + H$^+$) (100%), 457.1 (M + Na$^+$) (50), 473.1 (M + K$^+$) (10). Anal. Calcd for $C_{20}H_{14}N_6O_6$: C, 55.30; H, 3.25; N, 19.35. Found: C, 55.20; H, 3.27; N, 19.25.

Synthesis of 15. A mixture of anhydrous potassium carbonate (1.382 g, 10 mmol), methyl 3,4,5-trihydroxybenzoate (1.84 g, 10 mmol), and perfluorobenzene (1.86 g, 10 mmol) in DMF (25 mL) was stirred for 5 h at 100 °C. After cooling to room temperature, 10% HCl was used to neutralize the resulting mixture. The mixture was extracted with ethyl acetate, and the organic phase was dried with anhydrous Na_2SO_4 and filtered. The filtrate was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate (8:1, v/v) as the mobile phase to give pure **15** (607 mg, yield 18%) as a white solid: mp 253−254 °C; ^{1}H NMR (acetone-d_6/300 MHz) δ 7.35 (d, J = 1.8 Hz, 1H), 7.14 (d, J = 1.8 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (acetone-d_6/100 MHz) δ 164.8, 145.8, 140.6, 138.5 (dm), 136.0 (dm), 132.5, 128.7 (dm), 126.6, 114.5, 108.4, 51.8; IR (KBr) ν 3366, 1708, 1522 cm^{-1}; MS (CI) m/z (%) 331.0 [M + H]$^+$ (100%). Anal. Calcd for $C_{14}H_6F_4O_5$: C, 50.93; H, 1.83. Found: C, 50.68; H, 2.00.

Procedure of Spectroscopic Titrations. UV−vis and fluorescence titration experiments were performed with the concentration of **10a** and **10b** maintained constantly, and the spectral changes were recorded with the increase of the anion concentration. The spectroscopic titration data were fitted by a Hyperquad 2003 program to calculate the association constants.[13]

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterizations of products, ^{1}H and ^{13}C NMR spectra of products, UV−vis and fluorescence titration spectra, ^{1}H NMR spectra of **10a** and **10b** upon the addition of anions, ESI-MS spectra of **10a** and **10b** upon the addition of anions, cif documents of the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dxwang@iccas.ac.cn, wangmx@mail.tsinghua.edu.cn.

Notes

The authors declare no competing financial interest.

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