JOC*Article*

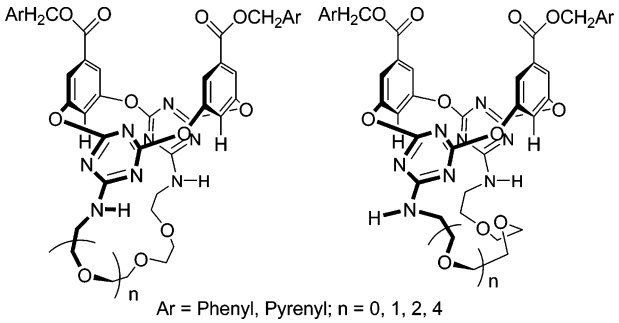
Synthesis and Structure of Upper-Rim 1,3-Alternate Tetraoxacalix[2]arene[2]triazine Azacrowns and Change of Cavity in Response to Fluoride Anion

Bao-Yong Hou, De-Xian Wang, Hai-Bo Yang, Qi-Yu Zheng, and Mei-Xiang Wang*

Beijing National Laboratory for Molecular Sciences, Laboratory of Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, China

mxwang@iccas.ac.cn

Received March 24, 2007



Ar = Phenyl, Pyrenyl; n = 0, 1, 2, 4

The upper-rim 1,3-alternate tetraoxacalix[2]arene[2]triazine azacrowns were constructed effectively by macrocyclic condensation reaction of diamines with dichlorinated tetraoxacalix[2]arene[2]triazine intermediates that were synthesized from the stepwise fragment coupling reactions of 3,5-dihydroxybenzoic acid esters with cyanuric chlorides. Because of the formation of conjugation of amino groups with triazine rings, tetraoxacalix[2]arene[2]triazine azacrowns existed in a mixture of syn- and anti-isomeric forms. Both fluorescence titration and ^{1}H NMR spectroscopic study showed that tetraoxacalix[2]arene[2]triazine azacrowns interacted with fluoride anion, leading to cavity changes of the host molecules.

Introduction

Calix[*n*]arenes are useful macrocyclic host molecules in supramolecular chemistry because of their easy availability, various conformational structures, and powerful binding ability toward different guest species.[1−3] Calix[*n*]arenes also act as the versatile platforms for the construction of elaborate host molecules with desired functions.[1−3] For example, incorporation of a crown ether into calix[*n*]arenes has led to the generation of calix[*n*]crowns, a new type of cavity molecules for selective cation recognition.[4,5] It is interesting to note that most of the calix[*n*]crowns reported contain a lower-rim crown ether moiety because of the advantageous reactivity of the phenol functionality of the calix[*n*]arenes.[4] The upper-rim calix[*n*]crowns,[5] however, have only been scatteringly investigated, most probably because of the synthetic difficulties. Although the study of calix[*n*]arenes and their analogous calixaromatics is still increasing, there is a growing interest in heteroatom-bridged calix(hetero)aromatics.[6−10] By comparison with calix[*n*]arenes and calixheteroarenes such as calixpyrroles,[11] calixpyridines,[12]

(1) (a) Gutsche, C. D. *Calixarenes*; The Royal Society of Chemistry: Cambridge, 1989. (b) Gutsche, C. D. *Calixarenes Revisited*; The Royal Society of Chemistry: Cambridge, 1998.

(2) (a) *Calixarenes in Action*; Mandolini, L., Ungaro, R., Eds.; Imperial College Press: London, 2000. (b) Lumetta, G. J.; Rogers, R. D.; Gopalan, A. S. *Calixarenes for Separation*; American Chemical Society: Washington, DC, 2000.

(3) *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Saadioui, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001.

(4) For a review, see: Casnati, A.; Ungaro, R.; Asfari, Z.; Vicens, J. Crown Ethers Derived from Calix[4]arenes. In *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Saadioui, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001; Chapter 20, pp 365−384 and references therein.

(5) (a) van Loon, J.-D.; Groenen, L. C.; Wijmenga, S. S.; Verboom, W.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 2378. (b) Paek, K.; Ihm, H. *Chem. Lett.* **1996**, 311. (c) Ihm, H.; Kim, H.; Paek, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1997. (d) Wasikiewicz, W.; Rokicki, G.; Roźniecka, E.; Kielkiewicz, J.; Brzózka, Z.; Böhmer, V. *Monatsh. Chem.* **1998**, *129*, 1169.

(6) For a useful overview of heteroatom-bridged calixarenes, see: König, B.; Fonseca, M. H. *Eur. J. Inorg. Chem.* **2000**, 2303.

(7) For a very recent review on thiacalixarenes, see: Morohashi, N.; Narumi, F.; Iki, N.; Hattori, T.; Miyano, S. *Chem. Rev.* **2006**, *106*, 5291.

10.1021/jo0706168 CCC: $37.00
Published on Web 06/05/2007

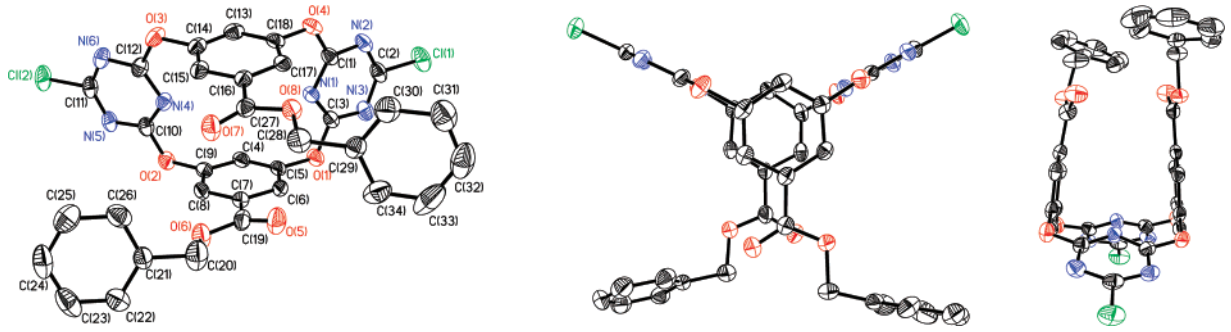


FIGURE 1. X-ray molecular structure of **11**: top (left) and side (middle and right) views. Selected interatomic distances (Å): N(1)···N(4) 4.591, C(2)···C(11) 9.240, Cl(1)···Cl(2) 12.313, C(4)···C(13) 4.579, C(7)···C(16) 4.145, N(4)···C(4), 3.284, C(4)···N(1) 3.209, N(1)···C(13) 3.274, C(13)···N(4) 3.200. Selected bond lengths (Å): C(10)···O(2) 1.334, O(2)···C(9) 1.413, C(5)···O(1) 1.411, O(1)···C(3) 1.345, C(1)···O(4) 1.337, O(4)···C(18) 1.404, C(14)···O(3) 1.410, O(3)···C(12) 1.333. Selected bond angles: C(10)−O(2)−C(9) 116.3°, C(5)−O(1)−C(3) 116.7°, C(1)−O(4)−C(18) 115.3°, C(14)−O(3)−C(12) 115.7°.

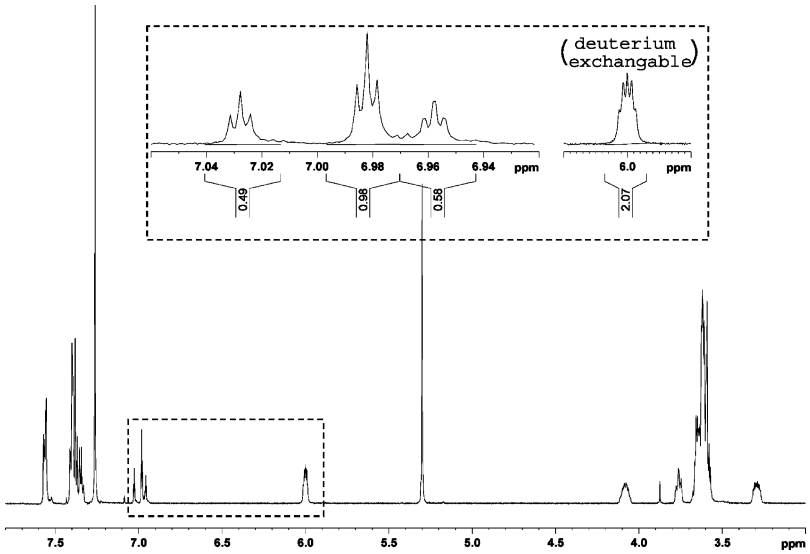
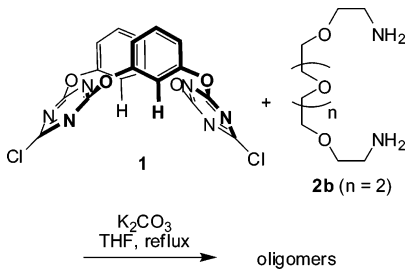
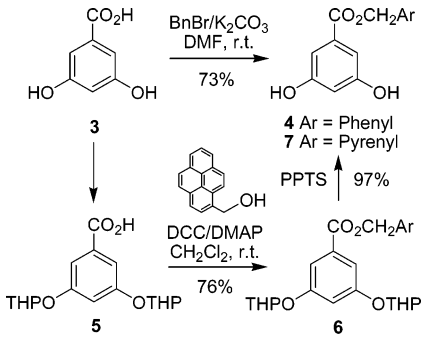


FIGURE 2. ^{1}H NMR spectrum of a mixture of **14a** and **14a′** in $CDCl_3$ at 298 K. Inset: partial expansion of the spectrum.

SCHEME 1. Reaction of Tetraoxacalix[2]arene[2]triazine 1 with Diamine 2b

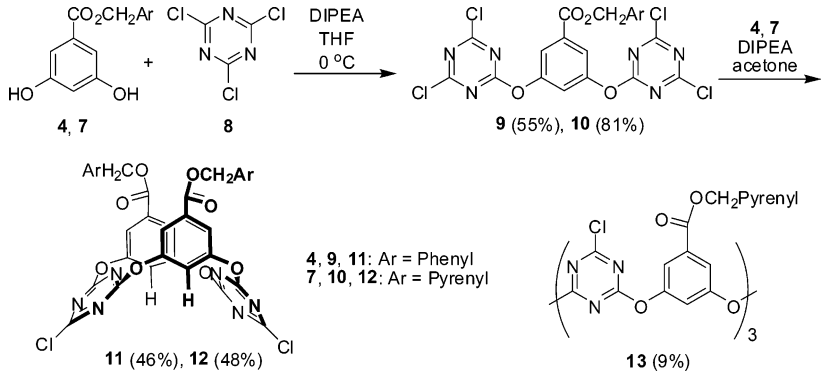


SCHEME 2. Synthesis of 3,5-Dihydroxybenzoic Acid Esters 4 and 7



and other calixaromatics[13] in which the (hetero)arene units are linked by methylenes, introduction of heteroatoms into the bridging positions has led to a wide variety of macrocyclic molecules. Because of the different electronic nature of heteroatoms from carbon, the heteroatom-bridged calix(hetero)-aromatics exhibit interesting structure and molecular recognition properties.[6−10] For example, we[9d−f] have shown that, because of the intrinsic nature of nitrogen that can adopt sp^2 and/or sp^3 electronic configurations to form or not to form conjugation with its adjacent aromatic rings, azacalix[*n*]pyridines and azacalix[*m*]arene[*n*]pyridines are able to pre-organize into different conformational and cavity structures to interact with metal ions,[9f] anions,[9e] fullerenes,[9d,e] and other small neutral molecules. Very recently, we[8a,k] reported an efficient and high-yielding synthesis of heteroatom-bridged calix[2]arene[2]-triazines based on a fragment coupling approach using cheap and readily available cyanuric chloride and different aromatic dinucleophilic agents. The cavity of the resulting heteroatom-bridged calix[2]arene[2]triazines can be tuned by the combination of bridging oxygen and nitrogen atoms and by the substituents on linking nitrogen atoms. Having considered the reactivity of the dichloro substituents on the triazine components in heteroatom-bridged calix[2]arene[2]triazines, we envisioned

SCHEME 3. Synthesis of Tetraoxacalix[2]arene[2]triazines 11 and 12



SCHEME 4. Synthesis of Upper-Rim Tetraoxacalix[2]arene[2]triazine Azacrowns

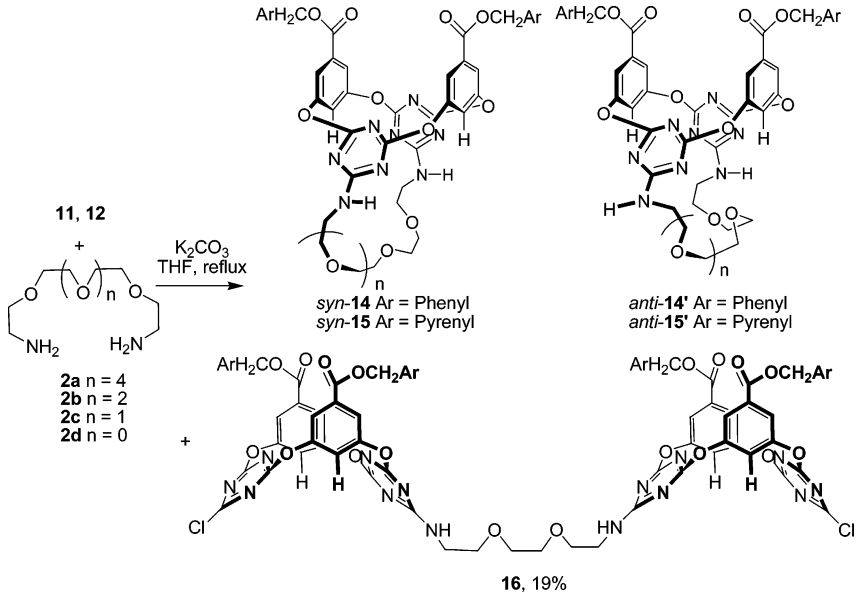


TABLE 1. Synthesis of Upper-Rim Tetraoxacalix[2]arene[2]triazine Azacrowns

entry	product	Ar	n	yield (%)[a]	syn/anti[b]	syn/anti[b,c]
1	**14a** + **14a′**	phenyl	4	79	1.1:1	1.1:1
2	**14b** + **14b′**	phenyl	2	79	0:1	0:1
3	**14c** + **14c′**	phenyl	1	56	1.5:1	1.6:1
4	**14d** + **14d′**	phenyl	0	29[d]	2:1	5:1
5	**15a** + **15a′**	1-pyrenyl	4	85	1:1	1:1
6	**15b** + **15b′**	1-pyrenyl	2	82	0:1	0:1
7	**15c** + **15c′**	1-pyrenyl	1	75	1.6:1	1.7:1
8	**15d** + **15d′**	1-pyrenyl	0	23	2.2:1	4.5:1

[a] Isolated yield. [b] Determined by ^{1}H NMR spectrum in $CDCl_3$ at 298 K. [c] After treatment with D_2O. [d] Product **16** was isolated in 19% yield.

that these novel heteroatom-bridged calixaromatics might provide a useful scaffold for the construction of upper-rim calixaromatic crowns. It was also expected that the interaction of the crown with the external stimulus would result in the molecular motion, namely, the change of conformational structure. Herein, we report the construction of upper-rim 1,3-alternate tetraoxacalix[2]arene[2]triazine azacrowns, their structures, and the change of cavity in response to the treatment of fluoride anion.

Results and Discussion

We began our investigation with the synthesis of tetraoxacalix[2]arene[2]triazine azacrowns. Dichlorinated tetraoxacalix[2]arene[2]triazine **1**, obtained readily from a two-step fragment coupling stretagy,[8a] underwent reaction rapidly with diamine **2b**. Unfortunately, no formation of crown product was observed. Instead, the reaction gave a mixture of unseparable oligomers (Scheme 1). The formation of oligomers rather than the desired crown was most probably because calix[2]arene[2]triazine **1** was very fluxional in solution.[8a,k] In other words, the rapid interconversion of the conformers of **1** did not favor its macrocyclic condensation with **2b**. To decrease the flexibility of tetraoxacalix[2]arene[2]triazine macrocycle and therefore to increase the chance of forming calixcrown structure, we then decided to introduce a bulky group such as benzoxycarbonyl on the benzene

(8) For recent examples of oxygen-bridged calixaromatics, see: (a) Wang, M.-X.; Yang, H.-B. *J. Am. Chem. Soc.* **2004**, *126*, 15412. (b) Katz, J. L.; Feldman, M. B.; Conry, R. R. *Org. Lett.* **2005**, *7*, 91. (c) Katz, J. L.; Selby, K. J.; Conry, R. R. *Org. Lett.* **2005**, *7*, 3505. (d) Katz, J. L.; Geller, B. J.; Conry, R. R. *Org. Lett.* **2006**, *8*, 2755. (e) Maes, W.; Van Rossom, W.; Van Hecke, K.; Van Meervelt, L.; Dehaen, W. *Org. Lett.* **2006**, *8*, 4161. (f) Hao, E.; Fronczek, F. R.; Vicente, M. G. H. *J. Org. Chem.* **2006**, *71*, 1233. (g) Chambers, R. D.; Hoskin, P. R.; Kenwright, A. R.; Khalil, A.; Richmond, P.; Sandford, G.; Yufit, D. S.; Howard, J. A. K. *Org. Biomol. Chem.* **2003**, 2137. (h) Chambers, R. D.; Hoskin, P. R.; Khalil, A.; Richmond, P.; Sandford, G.; Yufit, D. S.; Howard, J. A. K. *J. Fluorine Chem.* **2002**, *116*, 19. (i) Li, X. H.; Upton, T. G.; Gibb, C. L. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2003**, *125*, 650. (j) Yang, F.; Yan, L.-W.; Ma, K.-Y.; Yang, L.; Li, J.-H.; Chen, L.-J.; You, J.-S. *Eur. J. Org. Chem.* **2006**, 1109. (k) Konishi, H.; Tanaka, K.; Teshima, Y.; Mita, T.; Morikawa, O.; Kobayashi, K. *Tetrahedron Lett.* **2006**, *47*, 4041. (l) Konishi, H.; Mita, T.; Morikawa, O.; Kobayashi, K. *Tetrahedron Lett.* **2007**, *48*, 3029.

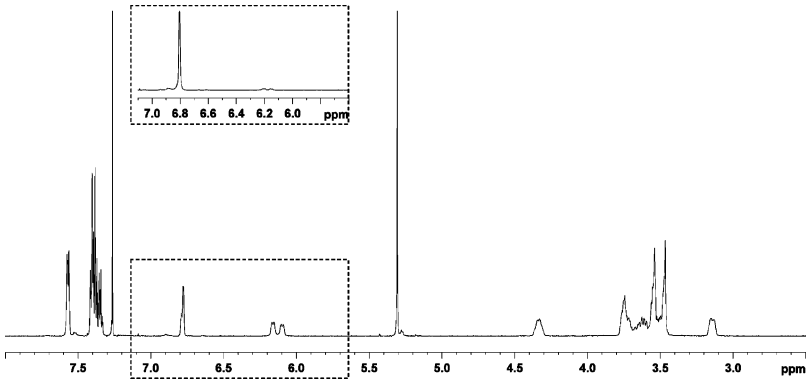


FIGURE 3. ^{1}H NMR spectrum of product **14b′**. Inset: partial spectrum after D_2O exchange.

ring. Benzyl 3,5-dihydroxybenzoate **4**, obtained directly from the reaction of 3,5-dihydroxybenzoic acid **3** with benzyl bromide with the aid of K_2CO_3 in DMF at ambient temperature (Scheme 2), reacted smoothly with 2 equiv of cyanuric chloride **8** at 0 °C in the presence of diisopropyl(ethyl)amine (DIPEA) to give intermediate **9** in 55% yield. Macrocyclic coupling reaction of **9** with **4** proceeded effectively at room temperature to afford tetraoxacalix[2]arene[2]triazine derivative **11** in 46% yield (Scheme 3). To have fluorescent labeling groups on the macrocyclic ring, pyren-1-ylmethyl 1,3-dihydroxybenzoate **7** was prepared following the route depicted in Scheme 2. Similar to the synthesis of **11**, the reaction of pyrenyl 1,3-dihydroxybenzoate **7** with **8** gave 81% yield of the intermediate **10**, which underwent macrocyclic condensation reaction with another pyren-1-ylmethyl 1,3-dihydroxybenzoate **7** to furnish pyrenyl-containing tetraoxacalix[2]arene[2]triazine derivative **12** in 48%. The reaction also gave the ring an expanded homologue, oxygen-bridged calix[3]arene[3]triazine **13**, in 9% yield (Scheme 3).

The structures of the oxygen-bridged calixaromatics were established on the basis of their spectroscopic data, microanalyses, and X-ray single-crystal diffraction analysis. The X-ray molecular structure of **11** (Figure 1) shows that the macrocyclic skeleton of the product adopts almost a 1,3-alternate conformation with an approximate C_{2v} symmetry. Two benzene rings are nearly face-to-face parallel with the distance ranging from 4.145 to 4.579 Å, while two triazine rings tend toward edge-to-edge orientation. Both the bond lengths and bond angles (see caption of Figure 1) of the bridging oxygen atoms indicate the conjugation of all bridging oxygen atoms with their adjacent triazines rather than benzene rings.

Bearing two benzyloxycarbonyl substituents on the benzene rings on the upper-rim, the 1,3-alternate tetraoxacalix[2]arene[2]triazine **11** reacted efficiently with diamine **2b** in the presence of K_2CO_3 to afford the desired upper-rim calix[2]arene[2]triazine azacrown **14b′** in 79% yield. Compound **11** then proved to be a very good scaffold for the construction of crown architectures. Larger and smaller azacrowns **14a** and **14a′** and **14c** and **14c′** were readily synthesized, respectively, from macrocyclic condensation reaction of **11** with diamines having a longer (**2a**) or a shorter (**2c**) chain. The reaction of pyrenyl-substituted tetraoxacalix[2]arene[2]triazine **12** with diamines **2a**−**c** proceeded equally well, and the corresponding azacrown products **15a**−**c** and **15a**−**c′** were produced in the yield of 75−85%. Even with a diamine **2d** derived from triglycol, condensation reaction of **11** or **12** afforded azacrown **14d** and **14d′** or **15d** and **15d′**, albeit in a lower chemical yield (Table 1). From the reaction of **11** with **2d**, a bis(tetraoxacalix[2]arene[2]triazine) product **16** was also isolated in 19% yield (Scheme 4).

The structures of upper-rim tetraoxacalix[2]arene[2]triazine azacrown products are worth addressing. Unlike both lower-rim and upper-rim calix[*n*]crowns[4,5] which give no stereoisomers of the crown subunits, most of the upper-rim tetraoxacalix[2]arene[2]triazine azacrowns synthesized existed in a pair of syn- and anti-stereoisomers because of the formation of conjugation of amino groups with triazines which resulted in two different orientations of the azacrown chain in solution (Scheme 4). This has been shown clearly by their ^{1}H and ^{13}C NMR spectra, which show two sets of the signals corresponding to syn- and anti-isomers (see Supporting information). For example, the ^{1}H NMR spectrum of a mixture of **14a** and **14a′** (Figure 2) gave three triplet signals (J = 2.1 Hz) centered at 7.03, 6.98, and 6.96 ppm, in which two (at 7.03 and 6.96 ppm) were of the same intensity, corresponding to the aromatic protons at 2-position of the resorcinol rings. The ratio of syn-isomer to anti-isomer, which was listed in Table 1, was roughly estimated by means of integrating the intensity of these signals. Tetraoxacalix[2]arene[2]triazine azacrown products **14b′** and **15b′** derived from 3,6,9,12-tetraoxatetradecane-1,14-diamine **2b** gave one set of proton signals in their ^{1}H NMR spectra (Figure 3 and Supporting information), and observation of only one peak at 6.78 or 6.72

(9) For recent examples of nitrogen-bridged calixaromatics, see: (a) Ito, A.; Ono, Y.; Tanaka, K. *New J. Chem.* **1998**, 779. (b) Ito, A.; Ono, Y.; Tanaka, K. *J. Org. Chem.* **1999**, *64*, 8236. (c) Miyazaki, Y.; Kanbara, T.; Yamamoto, T. *Tetrahedron Lett.* **2002**, *43*, 7945. (d) Wang, M.-X.; Zhang, X.-H.; Zheng, Q.-Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 838. (e) Gong, H.-Y.; Zhang, X.-H.; Wang, D.-X.; Ma, H.-W.; Zheng, Q.-Y.; Wang, M.-X. *Chem.*−*Eur. J.* **2006**, *12*, 9262. (f) Gong, H.-Y.; Zheng, Q.-Y.; Zhang, X.-H.; Wang, D.-X.; Wang, M.-X. *Org. Lett.* **2006**, *8*, 4895. (g) Tsue, H.; Ishibashi, K.; Takahashi, H.; Tamura, R. *Org. Lett*. **2005**, *7*, 11. (h) Fukushima, W.; Kanbara, T.; Yamamoto, T. *Synlett* **2005**, *19*, 2931. (i) Selby, T. D.; Blackstock, S. C. *Org. Lett.* **1999**, *1*, 2053. (j) Suzuki, Y.; Yanagi, T.; Kanbara, T.; Yamamoto, T. *Synlett* **2005**, *2*, 263. (k) Ishibashi, K.; Tsue, H.; Tokita, S.; Matsui, K.; Takahashi, H.; Tamura, R. *Org. Lett.* **2006**, *8*, 5991. (l) Wang, Q.-Q.; Wang, D.-X.; Ma, H.-W.; Wang, M.-X. *Org. Lett.* **2006**, *8*, 5967.

(10) For examples of other heteroatom-bridged calixaromatics, see: (a) König, B.; Rödel, M.; Bubenitschek, P.; Jones, P. G.; Thondorf, I. *J. Org. Chem.* **1995**, *60*, 7406. (b) König, B.; Rödel, M.; Bubenitschek, P.; Jones, P. G. *Angew. Chem., Int. Ed.* **1995**, *34*, 661. (c) Yoshida, M.; Goto, M.; Nakanishi, F. *Organometallics* **1999**, *18*, 1465. (d) Avarvari, N.; Mezailles, N.; Ricard, L.; Le Floch, P.; Mathey, F. *Science* **1998**, *280*, 1587. (e) Avarvari, N.; Maigrot, N.; Ricard, L.; Mathey, F.; Le Floch, P. *Chem.*−*Eur. J.* **1999**, *5*, 2109.

(11) For a review of calixpyrroles, see: Gale, P. A.; Anzenbacher, P.; Sessler, J. L. *Coord. Chem. Rev.* **2001**, *222*, 57.

(12) Sessler, J. L.; Cho, W.-S.; Lynch, V.; Král, V. *Chem.*−*Eur. J.* **2002**, *8*, 1134 and references therein.

(13) For more examples, see a recent review: Kumar, S.; Paul, D.; Singh, H. *Adv. Heterocycl. Chem.* **2005**, *89*, 65.

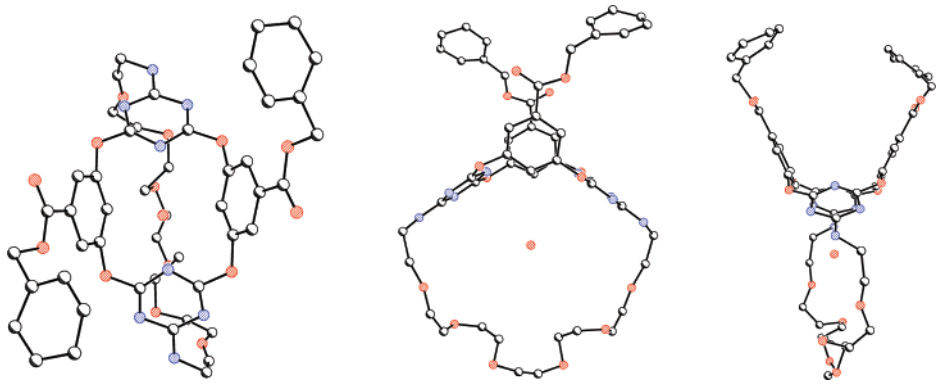


FIGURE 4. X-ray molecular structure of **14a′**: top (left) and side (middle and right) views.

TABLE 2. Association Constants (log K_a) for the 1:1 Interaction of 14 and 15d (15d′) with R_4NF in a Mixture of CH_3CN and $CHCl_3$ (95:5) at 25 °C

	14a (14a′)	14b (14b′)	14c (14c′)	14d (14d′)	15d (15d′)
^{n}Bu$_4$NF	1.61 ± 0.01	1.94 ± 0.01	1.80 ± 0.00	2.49 ± 0.00	2.12 ± 0.00
Et$_4$NF	1.88 ± 0.00	1.88 ± 0.00	1.91 ± 0.00	2.69 ± 0.00	

ppm corresponding to two aromatic protons at 2-position of each resorcinol ring suggested the anti-form of the products. As indicated by the results in Table 1, the ratio of syn-isomer over anti-isomer is dependent upon the length of the azacrown chain. When the chain length is shorter than 13 non-hydrogen atoms such as in the cases of **14c**,**d** and **15c**,**d**, the syn-isomer formed preferably (entries 3, 4, 7, and 8). Only the anti-isomers **14b′** and **15b′** were observed when a diamine **2b** derived from 3,6,9,-12-tetraoxatetradecane-1,14-diol was incorporated into the molecules (entries 2 and 6). Still longer aliphatic diamine **2a** led to the formation of an almost equal amount of syn- and anti-isomers (entries 1 and 5). The dependence of the ratio of syn-isomer over anti-isomer upon the length of the diamine most probably reflects the steric effect of the upper-rim tetraoxacalix-[2]arene[2]triazine azacrown products. Apparently, the calix-azacrowns bearing a shorter azacrown moiety would tend to adopt syn-configuration to reduce the steric strains in the anti-form. The preference for syn-isomer in the cases of the short azacrown chain-containing calixazacrowns was confirmed by the observation of the further movement of the syn−anti equilibrium to the syn-side after treatment with D_2O (entries 4 and 8 in Table 1). To identify calix[2]arene[2]triazine azacrown structure beyond doubt, X-ray diffraction analysis was attempted. From slow evaporation of the solvent, a single crystal of **14a′** was yielded and its X-ray diffraction data were collected at 298 K. Most probably because of the disorder of the atoms of the crown and benzyl moieties at room temperature, a less satisfactory refinement [$R_F = 0.2236$ ($I > 2\sigma(I)$)] was obtained. Nevertheless, Figure 4 showed that the molecule **14a′** adopted an anti-isomeric 1,3-alternate calix[2]arene[2]triazine azacrown conformation in the solid state. All bridging oxygen atoms and amino substituents are coplanar with their adjacent triazine rings.

To explore the molecular recognition property of the upper-rim tetraoxacalix[2]arene[2]triazine azacrowns synthesized, we initially examined the interaction of **14** with cations. Surprisingly, no interaction at all was observed between all calixazacrown molecules with metal ions ranging from all alkali and alkaline earth metal ions to Mn^{2+}, Co^{2+}, Ag^{+}, Hg^{2+}, and Pb^{2+} by means of spectrophotometric titration. By testing the interaction with ammonium salts, we accidentally found that fluoride anion can induce the changes of electronic absorption and fluorescence emission of the host molecules **14** in acetonitrile (see Supporting Information). For example, upon the titration of fluoride, the intensity of fluorescence of **14d** (**14d′**) at 335 nm was quenched with concomitance of the emerging of a new and weak emission at 425 nm (Figure 5). The Job plot (inset in Figure 5) indicated a 1:1 interaction model between **14** and *n*-Bu$_4$NF. On the basis of the fluorescence titration data, we calculated the association constants for the 1:1 complexs of the tetraoxacalix[2]arene[2]triazine azacrowns with *n*-Bu$_4$NF or Et$_4$-NF using a Hyperquad2003 program. The results summarized in Table 2 showed modest interactions of the hosts with fluoride, and the strongest interaction was between fluoride and calix-azacrown **14d** (**14d′**), which derived from the shortest aliphatic diamine **2d**. It is worth noting that careful examination of the UV−vis and fluorescence titrations with *n*-Bu$_4$NX salts revealed no interaction of all calixazacrowns **14** (**14**) with other anions, including X = Cl^-, Br^-, I^-, CH_3COO^-, ClO_4^-, and PF_6^-.

The quench of fluorescence of tetraoxacalix[2]arene[2]triazine azacrowns **14** (**14′**) by fluoride anion was most probably due to the interaction of fluoride anion with the amino (NH) groups of the azacrown subunit. As a hydrogen bond acceptor, for example, fluoride might be able to form intermolecular hydrogen bonds with both amino groups to form a N−H···F$^-$···H−N complex (Figure 6A). The other possible interaction model might treat fluoride as a base to deprotonate one proton from two amino groups, resulting in the formation of an intramolecular hydrogen bond between amino and deprotonated amino groups (N−H···N$^-$ ↔ N$^-$···H−N) (Figure 6B). Both interaction mechanisms would pull two triazine rings in close proximity and rigidify their motions. Concomitantly, the other two alternate benzene rings in tetraoxacalix[2]arene[2]triazine azacrowns would sit apart from each other and enjoy their motions more freely, which would cause the decrease of fluorescence intensity. To elucidate the interaction models, the fluorescence titration of **14d** (**14d′**) with *n*-Bu$_4$NOH was conducted.[14] As illustrated in Figure S31, interaction of *n*-Bu$_4$NOH with **14d** (**14d′**) led to almost identical spectral changes as observed from the interaction between *n*-Bu$_4$NF and **14d** (**14d′**) (Figure 5). The outcome

(14) We thank one of the reviewers for the helpful suggestion.

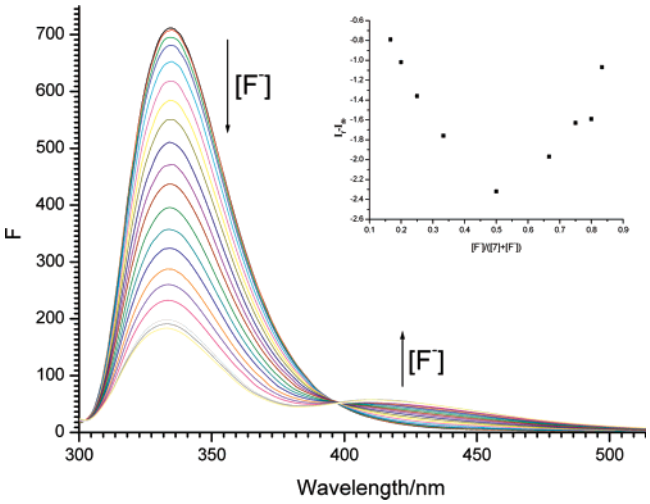


FIGURE 5. Fluorescence emission response of **14d** (**14d′**) (1.118×10^{-4} M) with *n*-Bu_4NF in acetonitrile solution with increasing [F^-] at 25 °C. The concentrations of F^- for curves from top to bottom are 0, 0.57, 1.70, 2.83, 5.09, 7.36, 9.62, 11.89, 14.15, 16.41, 18.68, 20.94, 23.21, 25.47, 27.73, 30.00, 32.26, 34.53, 36.79, 39.05, and 41.32×10^{-4} M. $\lambda_{ex} = 289$ nm, and the excitation and emission band widths are 10 nm. Inset: Job plot for **14d** (**14d′**)−F^- complex in a mixture of acetonitrile and chloroform (v/v = 9/1) solution ([**14d** (**14d′**)] + [F^-] = 4.983×10^{-4} M). $\lambda_{ex} = 289$ nm, and the excitation and emission band widths are 5 nm.

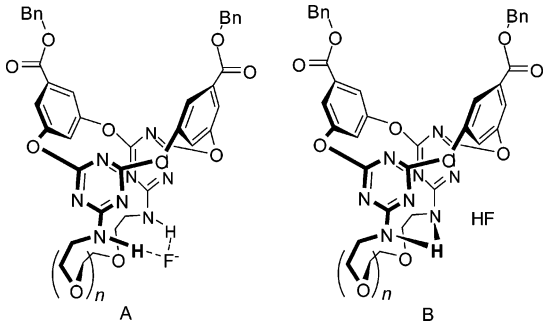


FIGURE 6. Two proposed models for the interaction of calixazacrowns **14** (**14′**) with fluoride anion.

suggested therefore a deprotonation mechanism that was depicted in Figure 6B.

The interaction of calixazacrowns with fluoride or a base implied that the cavity or the cleft of tetraoxacalix[2]arene[2]-triazines, namely the distance between two parallel benzene rings, might be regulated by an external stimulus. To manifest the change of the cavity in response to an external stimulus, emission spectra of pyrene-labeled tetraoxacalix [2]arene[2]-triazine azacrown **15d** (**15d′**) were studied upon its interaction with *n*-Bu_4NF and *n*-Bu_4NOH. In the absence of any guest species, the fluorescence spectrum of **15d** (**15d′**) in a mixture of acetonitrile and chloroform (v/v = 95/5) gave mainly the emission band of pyrene excimer at 477 nm in addition to very weak and structured emission bands of the pyrene monomer at 378−396 nm. With the increase of *n*-Bu_4NF (Figure 7) and *n*-Bu_4NOH (Figure S32), the emission at 477 nm decreased and eventually disappeared, while the emission bands in the region of 378−396 nm increased. The changes of emission spectra shown in Figure 7 demonstrated convincingly that a pair of face-to-face parallel benzene rings moved separately when the pendent azacrown interacted with 1 equiv of fluoride anion. In

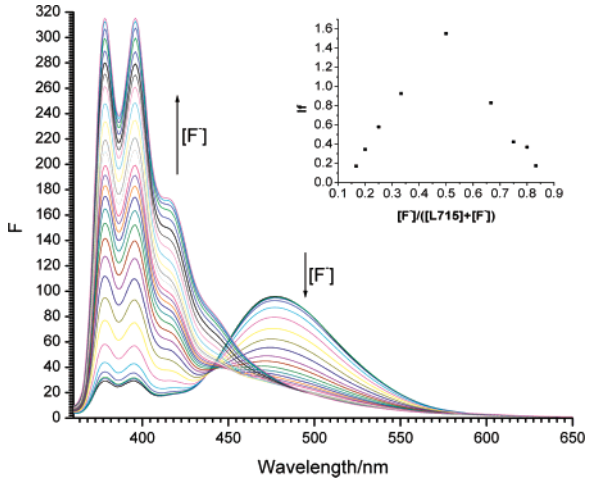


FIGURE 7. Fluorescence emission response of **15d** (**15d′**) (5.41×10^{-6} M) with *n*-Bu_4NF in acetonitrile chloroform (v/v = 95/5) solution with increasing [F^-] at 25 °C. The concentrations of F^- for curves from top to bottom (excimer) are 0, 0.1, 0.31, 0.72, 1.13, 1.54, 1.95, 2.36, 2.76, 3.17, 3.58, 3.99, 4.4, 4.81, 5.22, 5.63, 6.04, 6.45, 6.86, 7.88, 9.93, 13, 18.12, 23.24, 28.36, 33.48, 38.6, 43.72, 48.84, and 53.96×10^{-3} M. $\lambda_{ex} = 343$ nm, and the excitation and emission band widths are 10 nm. Inset: Job plot for **15d** (**15d′**)−F^- complex in a mixture of acetonitrile and chloroform (v/v = 9/1) ([**15d** (**15d′**)] + [F^-] = 3.28 $\times 10^{-5}$ M). $\lambda_{ex} = 343$ nm, and the excitation and emission band widths are 5 nm.

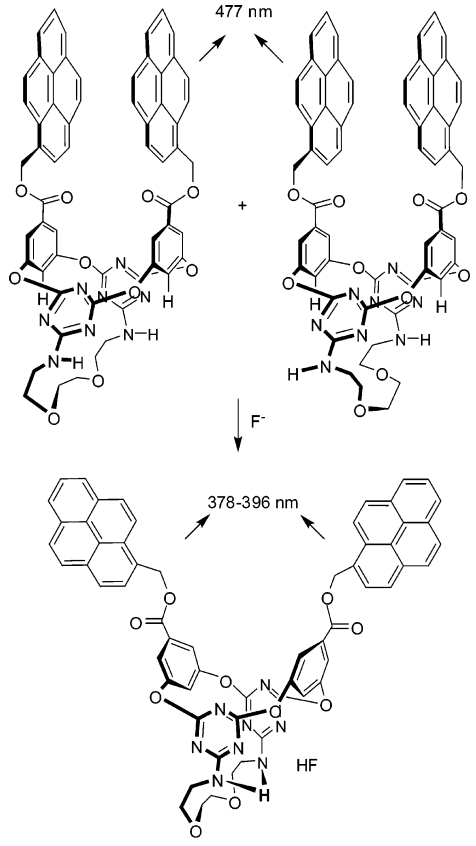


FIGURE 8. Schematic presentation of tuning of the cavity of tetraoxacalix[2]arene[2]triazine azacrown **15d** (**15d′**) by an external fluoride anion stimulant.

other words, the upper-rim tetraoxacalix[2]arene[2]triazine azacrowns behaved like a molecular clip, and the cavity or the cleft formed by two face-to-face aligned benzene rings expanded

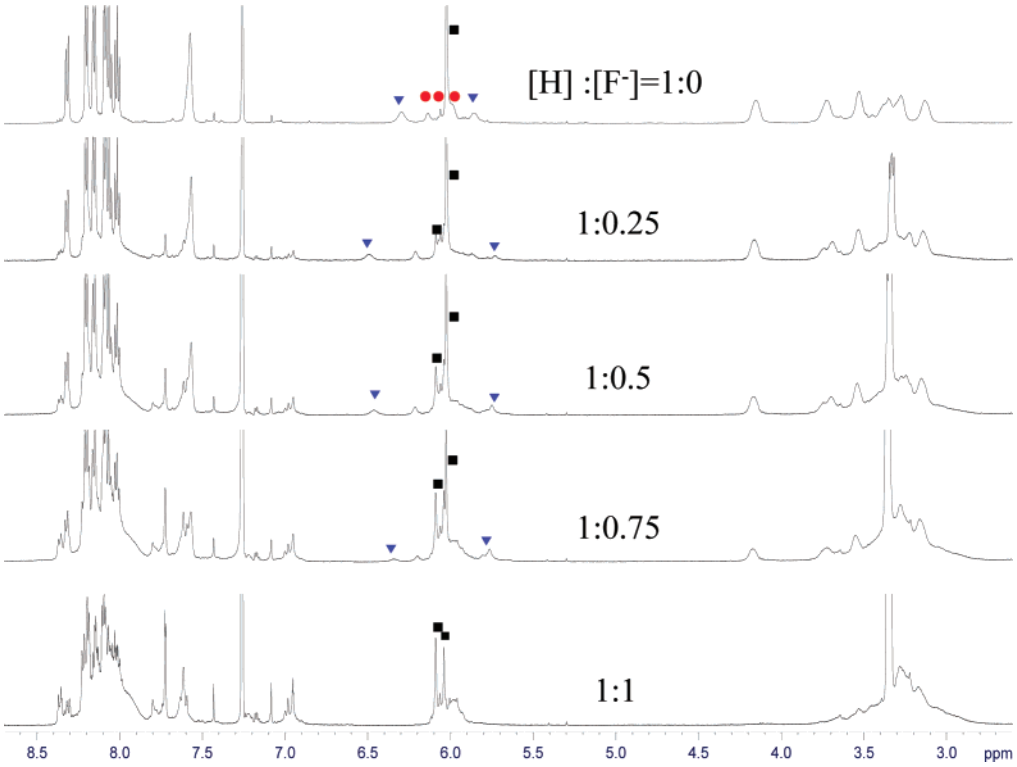


FIGURE 9. ^{1}H NMR titration of **15d** (**15d′**) with *n*-Bu_4NF in $CDCl_3$ at 298 K (blue ▼: two NH proton signals; red ●: the aromatic protons at the 2-position of two resorcinol rings; black ■: signals of two CH_2 protons).

when two triazine rings embedded in azacrown contracted in response to an external fluoride anion stimulant (Figure 8).

To shed further light on the change of the cavity of tetraoxacalix[2]arene[2]triazine azacrown **15d** (**15d′**) upon the treatment of fluoride anion, ^{1}H NMR spectra of a mixture of **15d** (**15d′**) and fluoride anion in different ratios were determined (Figure 9). With the increase of the concentration of fluoride, the amino proton signals of the azacrown shifted and broadened. When the ratio reached 1:1, the amino proton signals were not observed. More noticeably, increasing the fluoride concentration also led to the proton signals of pyrenylmethyl and azacrown moieties become more complicated. This indicated the destruction of parent 1,3-alternate conformational structure, which is in agreement with the results of fluorescence titration. It should be noted that tetraoxacalix[2]arene[2]triazine azacrown **15d** (**15d′**) was much more stable than tetranitro-substituted tetraoxacalix[4]arene.[8k,l] As indicated by the thin layer chromatography analysis, the macrocyclic structure of **15d** (**15d′**) remained intact after interacting with fluoride anion.

Conclusion

In summary, we have shown an efficient method for the construction of the upper-rim 1,3-alternate tetraoxacalix[2]arene[2]triazine azacrowns starting from the fragment coupling preparation of dichlorinated tetraoxacalix[2]arene[2]triazine intermediates followed by macrocyclic condensation reaction with diamines. Because of the formation of conjugation of amino groups with triazines, tetraoxacalix[2]arene[2]triazine azacrowns existed in a mixture of syn- and anti-isomeric forms in solution. We have also demonstrated by means of fluorescence titration and ^{1}H NMR spectroscopic study that the resulting calixazacrown host molecules can interact with fluoride anion. Such interaction led to the change of the cavity of calixazacrown host molecules. The convenient and efficient construction of tetraoxacalix[2]arene[2]triazine azacrowns and their conformational mobility in response to an external stimulant would render host molecules in supramolecular assemblies and in the design of molecular devices.

Experimental Section

Synthesis of 9 and 10. To an ice-bath cooled solution of cyanuric chloride **8** (9.23 g, 50 mmol) in THF (100 mL) was added dropwise a mixture of **4** (6.1 g, 25 mmol) and diisopropyl(ethyl)amine (8.06 g, 62.5 mmol) in THF (50 mL) during 1 h. The resulting mixture was stirred for another 2 h. After removal of diisopropyl(ethyl)-amine hydrochloride salt through filtration, the filtrate was concentrated and chromatographed on a silica gel column (100−200 mesh) with a mixture of petroleum ether and acetone as the mobile phase to give pure **9** (7.43 g, 55%) as white solid: mp 165−166 °C; IR (KBr) ν 1729, 1528 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (2H, d, J = 2.2 Hz, CH), 7.38−7.45 (5H, m, CH), 7.30 (1H, t, J = 2.2 Hz, CH), 5.38 (2H, s, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 170.6, 163.9, 151.4, 135.1, 133.6, 128.7, 128.6, 128.4, 121.2, 119.5, 67.7; MS (EI) *m*/*z* (%) 542 (3), 540 (5), 538 (M^+, 4), 433 (100), 431 (72), 406 (35), 404 (26), 91 (54). Anal. Calcd for $C_{20}H_{10}Cl_4N_6O_8$: C, 44.47; H, 1.87; N, 15.56. Found: C, 44.44; H, 2.06; N, 15.33. Following the same procedure, pure **10** (81%) was obtained as pale yellow solid: mp 212−213 °C; IR (KBr) ν 1726, 1535 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (1H, d, J = 9.2 Hz, CH), 8.24−8.02 (8H, m, CH), 7.86 (2H, d, J = 2.2 Hz, CH), 7.24 (1H, t, J = 2.2 Hz, CH), 6.10 (2H, s, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 170.5, 164.0, 151.3, 133.6, 132.1, 131.2, 130.6, 129.8, 128.6, 128.1, 128.08, 127.9, 127.3, 126.3, 125.8, 125.6, 124.9, 124.6, 122.6, 121.2, 119.5, 66.4; MS (MALDI-TOF) *m*/*z* (%) 661.9 ($M + H^+$, 71), 664.9 (35), 665.9 (87), 666.9 (32), 667.9 (21), 669.9 (4). Anal. Calcd for $C_{30}H_{14}N_6O_4Cl_4$: C, 54.24; H, 2.12; N, 12.65. Found: C, 53.88; H, 2.35; N, 12.84.

Synthesis of 11. At room temperature, both solutions of monomer **4** (4 mmol) in acetone (200 mL) and the trimer **9** (4 mmol) in acetone (200 mL) were added dropwise at the same rate to a solution of diisopropyl(ethyl)amine (1.24 g, 9.6 mmol) in acetone (1400 mL). After addition of two reactants, which took about 12 h, the resulting mixture was stirred at room temperature for another 24 h. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column (200−300 mesh) with a mixture of petroleum ether and acetone as the mobile phase to give pure **11** (1.309 g, 46%) as white solid: mp 216−217 °C; IR (KBr) ν 1725, 1551 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (4H, d, J = 2.2 Hz, CH), 7.36−7.40 (10H, m, CH), 6.92 (2H, t, J = 2.2 Hz, CH), 5.30 (4H, s, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.0, 172.1, 163.8, 151.4, 135.0, 133.6, 128.7, 128.6, 128.4, 121.0, 120.4, 67.7; MS (MALDI-TOF) *m*/*z* (%) 710.9 (M + H$^+$, 100), 711.9 (42), 712.9 (70), 713.9 (26), 714.9 (16), 715.9 (6). Anal. Calcd for $C_{34}H_{20}N_6O_8Cl_2$: C, 57.40; H, 2.83; N, 11.81. Found: C, 57.33; H, 3.12; N, 11.75. X-ray quality single crystals were obtained from slow evaporation of solution of **11** in a mixture of petroleum ether and ethyl acetate.

Synthesis of 12. To an ice-bath cooled solution of **7** (0.368 g, 1 mmol) and **10** (0.664 g, 1 mmol) in acetone (500 mL) was added diisopropyl(ethyl)amine (0.323 g, 2.5 mmol). The resulting mixture was stirred in an ice bath for 2 h. After addition of ice water (200 mL), hydrochloric acid (1 N) was added to the suspension until the pH value of the mixture was around 7. After removal of acetone under vacuum, the residue was extracted with CH_2Cl_2 (3 × 250 mL). The combined organic phases were then washed with water (200 mL) and brine (200 mL). The organic phase was dried over with anhydrous Na_2SO_4, filtered, and concentrated. The residue was chromatographed on a silica gel column (200−300 mesh) with a mixture of petroleum ether and acetone as the mobile phase to give pure **12** (0.462 g, 48%) and **13** (90 mg, 9%). **12**: pale yellow solid; mp 215−216 °C; IR (KBr) ν 1727, 1550 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24−7.97 (18H, m, CH), 7.52 (4H, d, J = 2.2 Hz, CH), 6.60 (2H, t, J = 2.2 Hz, CH), 5.96 (4H, s, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 172.0, 163.9, 151.3, 133.5, 132.0, 131.1, 130.5, 129.7, 128.5, 128.1, 128.0, 127.8, 127.2, 126.2, 125.7, 125.6, 124.8, 124.6, 124.5, 122.5, 121.0, 120.3, 66.1; MS (MALDI-TOF) *m*/*z* (%) 958.0 (M + H$^+$, 100), 959.0 (62), 969.9 (39), 961.9 (19), 962.9 (8). Anal. Calcd for $C_{54}H_{28}N_6O_8Cl_2$: C, 67.58; H, 2.94; N, 8.76. Found: C, 67.38; H, 3.04; N, 8.70. **13:** Pale yellow solid; mp 222−223 °C; IR (KBr) ν 1727, 1550 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23−7.97 (27H, m, CH), 7.64 (6H, d, J = 2.0 Hz, CH), 7.04 (3H, s, br, CH), 5.98 (6H, s, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 171.8, 163.9, 151.0, 133.4, 131.9, 131.1, 130.6, 129.6, 128.5, 128.0, 127.9, 127.8, 127.2, 126.2, 125.7, 125.6, 124.8, 124.6, 124.5, 122.5, 120.6, 120.3, 66.0; MS (MALDI-TOF) *m*/*z* (%) 1436.9 (67), 1437.9 (66), 1438.9 (M + H$^+$, 100), 1440.9 (53), 1441.9 (29), 1442.9 (14), 1443.9 (7), 1444.9 (4), 1460.6 (M + Na$^+$), 1477.9 (M + K$^+$). Anal. Calcd for $C_{81}H_{42}N_9O_{12}Cl_3$: C, 67.58; H, 2.94; N, 8.76. Found: C, 67.53; H, 3.28; N, 8.74.

General Procedure for the Synthesis of the Upper-Rim 1,3-Alternate Tetraoxacalix[2]arene[2]triazine Azacrowns 14a−d (14a−d′) and 15a−c (15a−c′). Both solutions of a diamine **2** (0.5 mmol) in THF (100 mL) and a dichlorinated tetraoxacalix[2]arene-[2]triazine **11** or **12** (0.5 mmol) in THF (100 mL) were added dropwise at the same rate to a refluxing suspension of K_2CO_3 (0.212 g, 1.5 mmol) in THF (240 mL). After addition of the reactants, which took about 10 h, the resulting mixture was refluxed for another 12 h. Filtration removed the solids, and the filtrate was concentrated under vacuum. The residue was then chromatographed on a silica gel column (200−300 mesh) with a mixture of petroleum ether and acetone as the mobile phase to give pure products **14a−d** (**14a−d′**) as white solids or **15a−c** (**15a−c′**) as pale yellow solids. In the case of synthesis of **14d** (**14d′**), product **16** was also obtained.

14a (14a′): mp 244−245 °C; IR (KBr) ν 3277, 3151, 1728, 1583 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57−7.55 (4H, m, CH), 7.41−7.33 (10H, m, CH), 7.03 (0.52H, t, J = 2.1 Hz, CH), 6.98 (0.96H, t, J = 2.1 Hz, CH), 6.96 (0.52H, t, J = 2.1 Hz, CH), 6.01−5.99 (2H, m, NH), 5.30 (4H, s, CH_2), 4.10−4.06 (2H, m, CH_2), 3.76−3.75 (2H, m, CH_2), 3.66−3.57 (22H, m, CH_2), 3.31−3.29 (2H, m, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 172.0, 171.4, 169.0, 164.6, 152.04, 152.0, 151.9, 135.4, 132.4, 128.6, 128.4, 128.3, 128.2, 121.5, 120.2, 70.7, 70.6, 70.5, 70.4, 70.3, 70.2, 69.4, 69.3, 67.2, 41.2, 41.1; MS (MALDI-TOF) *m*/*z* 963.1 (M + H$^+$), 985.1 (M + Na$^+$), 1001.0 (M + K$^+$). Anal. Calcd for $C_{48}H_{50}N_8O_{14}$: C, 59.87; H, 5.23; N, 11.64. Found: C, 59.48; H, 5.28; N, 11.78. Evaporation of the solvent from the sample solution in a mixture of dichloromethane and ethanol gave single crystals.

14b (14b′): mp 274−275 °C; IR (KBr) ν 3276, 3146, 1727, 1585 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58−7.56 (4H, m, CH), 7.42−7.33 (10H, m, CH), 6.79−6.78 (2H, m, CH), 6.17−6.15 (1H, m, NH), 6.10−6.09 (1H, m, NH), 5.31 (4H, s, CH_2), 4.34−4.33 (2H, m, CH_2), 3.74−3.47 (16H, m, CH_2), 3.15−3.13 (2H, m, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) 172.1, 172.0, 171.5, 170.0, 164.6, 152.3, 152.1, 135.4, 132.6, 128.6, 128.4, 128.3, 120.8, 120.6, 120.1, 119.9, 71.1, 70.8, 70.5, 70.1, 70.0, 69.9, 69.7, 67.3, 40.7; MS (MALDI-TOF) *m*/*z* 875.3 (M + H$^+$), 897.3 (M + Na$^+$), 913.3 (M + K$^+$). Anal. Calcd for $C_{44}H_{42}N_8O_{12}$: C, 60.41; H, 4.84; N, 12.81. Found: C, 60.52; H, 4.93; N, 12.79.

14c (14c′): mp 248−249 °C; IR (KBr) ν 3274, 3144, 1729, 1589 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62−7.59 (4H, m, CH), 7.43−7.33 (10H, m, CH), 6.64 (0.6H, s, br, CH), 6.54 (0.6H, s, br, CH), 6.47 (0.8H, s, br, CH), 5.88 (1H, s, br, NH), 5.82 (1H, s, br, NH), 5.32 (4H, s, CH_2), 4.42−4.34 (2H, m, CH_2), 3.72−3.70 (2H, m, CH_2), 3.64−3.52 (6H, m, CH_2), 3.43 (1H, s, br, CH_2), 3.31−3.29 (2H, m, CH_2), 3.14−3.08 (3H, m, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 171.9, 171.5, 170.7, 164.6, 153.1, 152.8, 152.7, 152.2, 135.4, 132.9, 128.7, 128.5, 128.4, 128.3, 119.4, 119.1, 118.8, 71.2, 70.3, 69.2, 68.6, 67.3, 40.7, 40.4, 30.9; MS (MALDI-TOF) *m*/*z* 831.3 (M + H$^+$); Anal. Calcd for $C_{42}H_{38}N_8O_{11}$: C, 60.72; H, 4.61; N, 13.49. Found: C, 60.73; H, 4.62; N, 13.64.

14d (14d′): mp > 300 °C; IR (KBr) ν 3278, 3182, 3141, 1734, 1587 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (4H, s, CH), 7.42−7.34 (10H, m, CH), 6.92 (1H, s, br, NH), 6.36 (0.66H, s, CH), 6.16 (0.66H, s, CH), 6.08 (0.68H, s, CH), 5.94 (1H, s, br, NH), 5.32 (4H, s, CH_2), 4.23 (2H, s, br, CH_2), 3.81 (1H, s, br, CH_2), 3.73 (1H, s, br, CH_2), 3.59 (2H, s, br, CH_2), 3.47 (1H, s, br, CH_2), 3.38 (2H, s, br, CH_2), 3.22 (3H, s, br, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 172.8, 172.5, 172.0, 170.9, 164.6, 155.4, 155.0, 153.9, 135.4, 133.3, 129.2, 128.6, 128.4, 117.2, 117.0, 115.4, 114.4, 70.9, 69.7, 67.3, 41.7; MS (MALDI-TOF) *m*/*z* 787.2 (M + H$^+$). Anal. Calcd for $C_{40}H_{34}N_8O_{10}$: C, 61.07; H, 4.36; N, 14.24. Found: C, 60.68; H, 4.72; N, 14.06.

16: mp 139−140 °C; IR (KBr) ν 3413, 3280, 1728, 1592 cm^{-1}; ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.43 (2H, s, br, NH), 7.50−7.34 (32H, m, CH), 5.26 (8H, s, CH_2), 3.59−3.52 (12H, m, CH_2); ^{13}C NMR (75 MHz, d_6-DMSO) δ 127.6, 171.6, 171.5, 171.3, 171.25, 171.2, 171.0, 170.6, 168.5, 168.0, 167.6, 164.8, 164.0, 163.7, 163.6, 161.4, 161.3, 158.7, 158.5, 152.64, 152.61, 152.3, 152.27, 152.2, 152.1, 152.05, 152.0, 151.3, 151.2, 151.0, 150.8, 149.9, 135.9, 135.67, 135.6, 135.5, 131.8, 131.7, 131.6, 131.5, 131.3, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 121.9, 121.6, 121.1, 121.0, 120.7, 120.2, 120.1, 120.0, 119.9, 119.2, 114.2, 114.0, 113.4, 113.3, 113.1, 69.6, 69.2, 68.5, 68.0, 66.8, 66.4, 30.9, 22.0, 13.9; MS (MALDI-TOF) *m*/*z* (%) 1497.0 (M + H$^+$, 89), 1498.0 (84), 1499.0 (100), 1500.0 (66), 1501.0 (39), 1502.0 (19), 1503.0 (9), 1504.0 (4). Anal. Calcd for $C_{74}H_{54}N_{14}O_{18}Cl_2$: C, 59.32; H, 3.63; N, 13.09. Found: C, 59.59; H, 3.85; N, 12.80.

15a (15a′): mp 176−177 °C; IR (KBr) ν 3281, 1725, 1585 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (2H, d, J = 9.1 Hz, CH), 8.17 (4H, d, J = 7.6 Hz, CH), 8.12−8.10 (4H, m, CH), 8.06−8.04 (4H, m, CH), 8.02−7.98 (4H, m, CH), 7.55−7.53 (4H, m, CH), 6.98 (0.5H, t, J = 2.2 Hz, CH), 6.93 (1.0H, t, J = 2.2 Hz, CH), 6.90 (0.5H, t, J = 2.2 Hz, CH), 5.98 (4H, s, CH_2), 5.94−5.93 (2H, m, NH), 4.04−4.01 (2H, m, CH_2), 3.72−3.70 (2H, m, CH_2), 3.63−3.54 (22H, m, CH_2), 3.25−3.23 (2H, m, CH_2); ^{13}C NMR (75 MHz,

d_6-DMSO) δ 171.1, 170.5, 170.4, 168.5, 163.9, 152.3, 152.2, 152.1, 131.6, 131.0, 130.6, 130.0, 128.8, 128.6, 128.0, 127.9, 127.6, 127.1, 126.5, 126.4, 126.2, 125.5, 125.4, 124.6, 123.8, 123.6, 122.8, 121.5, 118.7, 69.8, 69.78, 69.7, 69.6, 68.4, 65.1, 62.8, 40.4; MS (MALDI-TOF) *m*/*z* 1212.3 (M + H^+), 1234.3 (M + Na^+), 1250.3 (M + K^+). Anal. Calcd for $C_{68}H_{58}N_8O_{14}$: C, 67.43; H, 4.83; N, 9.25. Found: C, 67.06; H, 4.81; N, 9.03.

15b (15b′): mp 206−207 °C; IR (KBr) ν 3276, 1725, 1587 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (2H, d, J = 9.3 Hz, CH), 8.18 (4H, d, J = 8.9 Hz, CH), 8.12−8.11 (4H, m, CH), 8.08−8.04 (4H, m, CH), 7.99−7.94 (4H, m, CH), 7.55−7.54 (4H, m, CH), 6.72 (2H, s, br, CH), 5.99 (4H, s, CH_2), 5.78−5.72 (2H, m, NH), 4.29−4.27 (2H, m, CH_2), 3.72−3.67 (4H, m, CH_2), 3.61−3.42 (12H, m, CH_2), 3.11−3.08 (2H, m, CH_2); ^{13}C NMR (75 MHz, d_6-DMSO) δ 171.3, 171.1, 170.7, 170.6, 169.1, 163.9, 153.0, 152.9, 152.8, 152.7, 131.9, 131.1, 130.6, 130.1, 128.8, 128.6, 128.1, 127.6, 127.2, 126.3, 125.5, 125.4, 124.6, 123.9, 123.7, 122.9, 117.8, 79.1, 70.1, 70.0, 69.8, 69.7, 69.6, 69.2, 68.9, 65.2; MS (MALDI-TOF) *m*/*z* 1123.6 (M + H^+), 1145.6 (M + Na^+), 1161.5 (M + K^+); Anal. Calcd for $C_{64}H_{50}N_8O_{12}$: C, 68.44; H, 4.49; N, 9.98. Found: C, 68.24; H, 4.85; N, 9.96.

15c (15c′): mp 200−201 °C; IR (KBr) ν 3276, 1725, 1589 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (2H, d, J = 9.0 Hz, CH), 8.18 (4H, d, J = 7.6 Hz, CH), 8.14−8.12 (4H, m, CH), 8.06 (4H, d, J = 9.0 Hz, CH), 8.04−7.99 (4H, m, CH), 7.57 (4H, t, J = 19.4 Hz, CH), 6.58 (0.62H, s, br, CH), 6.48 (0.62H, s, br, CH), 6.42 (0.76H, s, br, CH), 6.00 (4H, s, CH_2), 5.75 (1.28H, s, br, NH), 5.71−5.70 (0.72H, m, NH), 4.37−4.30 (2H, m, CH_2), 3.68−3.48 (8H, m, CH_2), 3.39 (1H, s, br, CH_2), 3.25 (2H, s, br, CH_2), 3.09−3.03 (3H, m, CH_2); ^{13}C NMR (75 MHz, d_6-DMSO) δ 170.9, 169.8, 164.0, 163.9, 153.4, 153.2, 132.2, 131.9, 131.1, 130.6, 130.1, 128.8, 128.7, 128.1, 127.7, 127.6, 127.2, 126.3, 125.5, 125.4, 124.6, 123.9, 123.7, 122.9, 119.8, 117.8, 117.0, 70.4, 69.6, 69.1, 68.5, 68.1, 67.9, 65.2; MS (MALDI-TOF) *m*/*z* 1080.2 (M + H^+), 1102.2 (M + Na^+), 1118.2 (M + K^+). Anal. Calcd for $C_{62}H_{46}N_8O_{11}$: C, 69.01; H, 4.30; N, 10.38. Found: C, 68.71; H, 4.45; N, 10.38.

Preparation of the Upper-Rim 1,3-Alternate Tetraoxacalix[2]arene[2]triazine Azacrown 15d (15d′). A suspension of **12** (600 mg, 0.625 mmol), diamine **2d** (92.5 mg, 0.625 mmol), and K_2CO_3 (1.725 g, 12.5 mmol) in dry THF (1800 mL) was refluxed with stirring for 1 h. After removal of the solvent under vacuum, the resulting residue was dissolved in CH_2Cl_2 (400 mL) and then washed three times with water. The organic phase was dried over with anhydrous Na_2SO_4. The solvent was removed under vacuum to give a residue that was chromatographed on a silica gel column (200−300 mesh) with a mixture of petroleum ether and acetone as the mobile phase to afford pure **15d** (**15d′**) (0.146 g, 23%) as pale yellow solid: mp 202−203 °C; IR (KBr) ν 3277, 1725, 1591 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (2H, d, J = 9.2 Hz, CH), 8.20 (4H, d, J = 7.6 Hz, CH), 8.16 (4H, d, J = 8.8 Hz, CH), 8.10−8.08 (4H, m, CH), 8.06 (2H, d, J = 8.8 Hz, CH), 8.00 (2H, t, J = 7.6 Hz, CH), 7.57 (4H, s, br, CH), 6.30 (1H, s, br, NH), 6.13 (0.6H, s, br, CH), 6.06 (0.6H, s, br, CH), 6.02 (4H, s, CH_2), 6.00 (0.8H, s, br, CH), 5.86 (1H, s, br, NH), 4.15 (2H, s, br, CH_2), 3.73 (2H, s, br, CH_2), 3.53 (2H, s, br, CH_2), 3.35 (2H, s, br, CH_2), 3.27 (2H, s, br, CH_2), 3.13 (2H, s, br, CH_2); ^{13}C NMR (75 MHz, d_6-DMSO) δ 172.5, 171.6, 171.3, 170.5, 170.3, 170.2, 163.7, 155.4, 154.6, 153.6, 152.0, 133.1, 131.1, 130.6, 130.1, 128.9, 128.6, 128.1, 127.7, 127.2, 126.3, 125.5, 125.4, 124.6, 123.9, 123.7, 123.0, 119.1, 115.9, 115.5, 112.5, 70.2, 70.1, 69.1, 65.4, 41.0; MS (MALDI-TOF) *m*/*z* 1035.4 (M + H^+), 1057.4 (M + Na^+), 1073.4 (M + K^+). Anal. Calcd for $C_{60}H_{42}N_8O_{10}\cdot H_2O$: C, 68.43; H, 4.21; N, 10.64. Found: C, 68.28; H, 4.13; N, 10.46.

Acknowledgment. We thank the National Natural Science Foundation of China, Ministry of Science and Technology, and Chinese Academy of Sciences for financial support.

Supporting Information Available: Preparation of starting materials, ^{1}H and ^{13}C NMR spectra of all products, fluorescence spectra upon titration with fluoride anion, and X-ray structures of **11** and **14a′** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0706168