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Synthesis, structure, and conformation of *ortho*-linked oxacalix[*n*]arene[*n*]hetarenes

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ABSTRACT

ortho-Linked oxacalix[*n*]arene[*n*]hetarenes (*n*=2, 3) were prepared by one-step cyclooligomerization of catechol and *meta*-dichlorinated nitrogen containing heterocycles or via a two-step reaction process. Solid state structure of the *ortho*-linked oxacalix[*n*]arene[*n*]hetarenes (*n*=2, 3) has been determined by X-ray crystallography. 1,3-Alternate and 1,3,5-alternate conformations were found for *ortho*-linked oxacalix[2]arene[2]pyrazine (**1**) and oxacalix[3]arene[3]pyrazine (**2**), respectively. However, a core conformation with C_3 symmetry was found for *ortho*-linked oxacalix[3]arene[3]pyrimidine (**4**), which is completely different from that of its isomer, compound **2**.

1. Introduction

Calixarenes[1] are macrocyclic compounds with interesting conformational and cavity structures. They have been widely used in studying host–guest chemistry,[2] molecular encapsulation,[3] as scaffolds for the synthesis of multivalent ligands.[4] Heteroatom-bridged calixaromatics, structural isomers of calixarenes, have recently attracted considerable attention in the area of supramolecular chemistry.[5] Extensive work have been done on the synthesis and applications of tetrathiacalix[4]arene.[6] Much of the work on the construction of oxa- and aza-calixarene derivatives have been done by Katz and co-workers,[7] Wang and co-workers,[8] and others.[9] Due to the electron donating nature of the heteroatoms, the heteroatom-bridged calixaromatics could offer unique coordinating and recognition properties,[10,11] which would ultimately bring to their practical applications, for example, ionic sensors.[12,13] As far as we aware all the above-mentioned heteroatom-bridged calixaromatics are composed of *meta*-linked phenyls or heterocycles. *ortho*-Linked heteroatom-bridged calixaromatics are rare. Only one report appeared very recently on the synthesis and structure of *ortho*-linked oxacyclophane generated from 2,7-dichloro-1,8-naphthyridine and naphthalene-2,3-diol. Due to the large arene space of naphthyridine, the two naphthalene units are separated by 7.0 Å and defined a tweezer cavity, which could incorporate a CH_3CN molecule in the solid state. This compound was also found to selectively bind *ortho*-salicylic acid.[7d]

Recently, we became interested in the synthesis of heteroatom-bridged calixaromatics with novel macrocyclic backbones and their applications in supramolecular chemistry. We envisioned that if catechol is employed in the construction of oxacalix[*n*]arene-[*n*]hetarenes instead of resorcinol, the close proximity of the two oxygen atoms in catechol would result in oxacalix[*n*]arene-[*n*]hetarenes with less molecular flexibilities and smaller cavities than those known oxacalix[*n*]arene[*n*]hetarenes formed from resorcinol. Consequently, the new macrocyclic compounds generated from the condensation of catechol and *meta*-dihalogenated azaheterocyclic aromatics might offer unique scaffolds for special guest recognition and metal coordination. Herein we describe the first synthesis, structure, and conformation of *ortho*-linked oxacalix[2]arene[2]hetarenes and oxacalix[3]arene[3]hetarenes generated from the cyclooligomerization of catechol with *meta*-dichlorinated nitrogen containing heterocycles (pyridine, pyrazine, and pyrimidine).

2. Results and discussion

Previous work done by Katz and co-workers has shown that cyclocondensation of resorcinols with electrophilic *meta*-dihalogenated azaheterocyclic aromatics (2,6-dichloropyrazine, 2,6-dichloropyridine, and 4,6-dichloropyrimidine) resulted in the formation of oxacalix[2]arene[2]hetarenes in high yields.[7c] We surmise that *ortho*-linked oxacalix[2]arene[2]hetarenes could be formed by condensing those same azaheterocyclic electrophiles employed in Katz's work with catechol. By slightly modifying Katz's reaction condition, catechol reacted with 2,6-dichloropyrazine in the presence of Cs_2CO_3 in DMSO at room temperature for 8 h and then at 120 °C for 16 h resulted in the formation of expected

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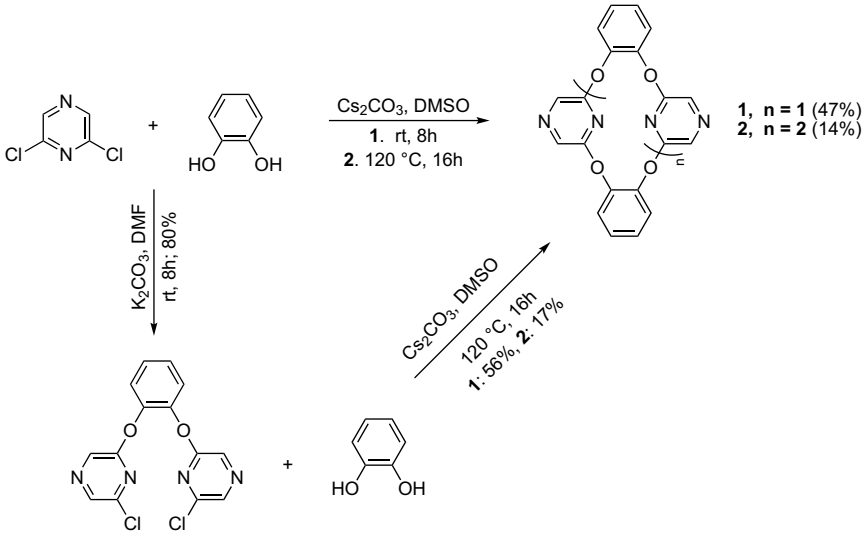
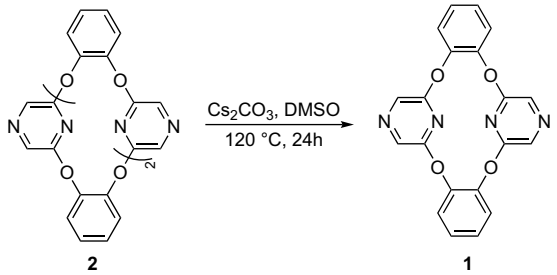
ortho-linked oxacalix[2]arene[2]pyrazine (**1**) and oxacalix[3]-arene[3]pyrazine (**2**) in the yields of 47% and 14%, respectively (Scheme 1). Byproducts, possibly larger cyclooligomers and polymeric species, were also formed, but were difficult to separate from the reaction mixture. In order to improve the yield of compound **1**, a fragment coupling strategy was examined (in Scheme 1). To our surprise, compound **1** was formed in an overall yield of only 45% and compound **2**, unexpectedly in a 17% yield. The formation of compound **2** was a result of the C–O bond breaking and reformation in the reaction process. This was also evidenced in the following experiment shown in Scheme 2, in which compound **2** could be converted to **1** at 120 °C in the presence of Cs_2CO_3, while the reverse process was not found to take place under this condition. This result demonstrates that compound **1** was thermodynamically more stable than compound **2**. During the investigation of *ortho*-linked oxacalix[2]arene[2]pyrazine (**1**) synthesis, other bases (Na_2CO_3, K_2CO_3, NaH, di(isopropyl)ethylamine (DIPEA), and pyridine) and solvents (DMF, THF, and CH_3CN) with different combination were screened for better reaction system in the synthesis of compound **1**, however, the results showed that the Cs_2CO_3/DMSO system was superior to other combinations.

the reaction mixture. However, the coupling reaction of 4,6-dichloropyrimidine with catechol in the presence of Cs_2CO_3 in DMSO, both at room temperature and at 120 °C, provided only *ortho*-linked oxacalix[3]arene[3]pyrimidine (**4**), with no expected *ortho*-linked oxacalix[2]arene[2]pyrimidine. In order to synthesize *ortho*-linked oxacalix[2]arene[2]pyrimidine, we also tried the two-step reaction sequence similar as in Scheme 1, by replacing 2,6-dichloropyrazine with 4,6-dichloropyrimidine, and found compound **4** was the sole isolated product in both room temperature and 120 °C in this two-step reaction. The results demonstrated that compound **4** is both kinetically and thermodynamically favored product in this reaction.

Calix[4]arenes can adopt cone, partial cone, 1,2-alternate, and 1,3-alternate conformations.[1] Oxacalix[4]arenes reported so far all adopt 1,3-alternate conformation.[8a,9h,9k] In order to analyze the structures and conformations of the synthesized compounds, single crystals of **1**, **2**, and **4** with X-ray diffraction quality were grown by slow evaporation from ethyl acetate. As expected, the crystal structure of **1** adopts a 1,3-alternate conformation (Fig. 1).[14] The four bridging oxygen atoms are located nearly in the same plane with a deviation of less than 0.18 Å. The pair of the opposite



Scheme 1. Synthesis of *ortho*-linked oxacalix[*n*]arene[*n*]pyrazines (*n*=2, 3).



Scheme 2. Conversion of compound **2** to compound **1** under heating.

Similarly, *ortho*-linked oxacalix[2]arene[2]pyridine (**3**) has been obtained in 38% yield by the reaction of 2,6-dichloropyridine and catechol in the presence of Cs_2CO_3 in DMSO at room temperature for 8 h and then at 120 °C for 16 h. Other products including *ortho*-linked oxacalix[3]arene[3]pyridine have not been separated from

pyrazine rings are arranged eclipsing, with a dihedral angle of 27.2°, creating transannular N···N distances of 4.199 Å between the two upper rim nitrogen atoms and 2.865 Å of the two lower rim nitrogen atoms, respectively. The two phenyl rings are placed in a face-to-face orientation with a dihedral angle of 28.6°, and a centroid–centroid distance of 5.371 Å. Due to the narrow space created by this conformation, no guest molecules (solvent molecules) were found to be included in the solid states (Fig. 1). There are two bridge oxygen atoms were found to conjugate with pyrazine rings (average C–O length 1.35 Å), while the other two bridge atoms are partially conjugated to the pyrazine rings (average C–O length 1.37 Å), and no conjugation existing between the bridging oxygen atoms and the phenyl rings (average C–O length 1.39 Å). Oxacalix[*n*]arenes (*n*>4) appeared to be more difficult to synthesize,[9b,h–j] and the structural information of this class of compounds remains unavailable. Fortunately, *ortho*-linked oxacalix[3]arene[3]pyrazine (**2**) was also isolated in this reaction. The crystal structure of **2** revealed that it adopts a 1,3,5-alternate conformation

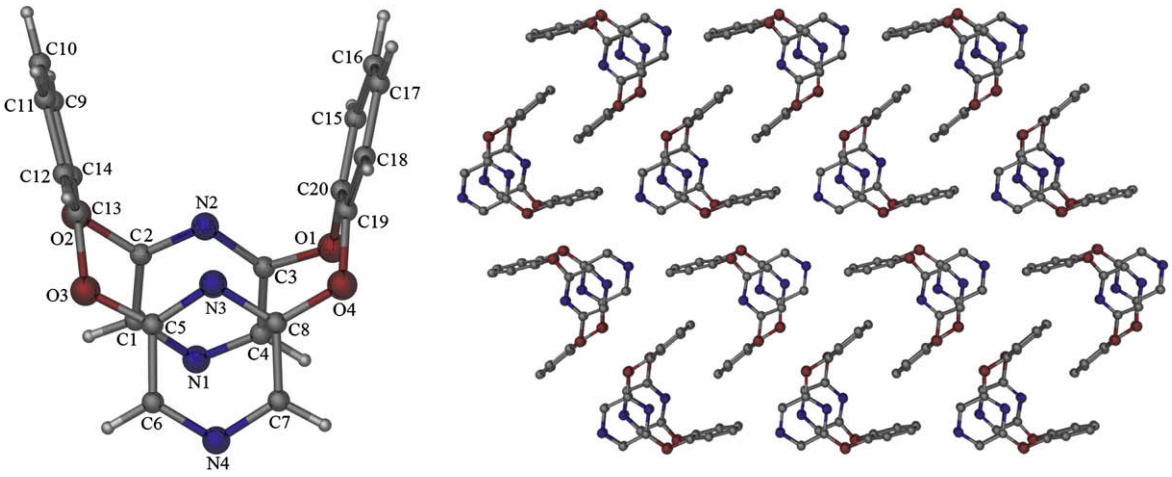


Figure 1. X-ray single crystal structure and molecular packing of compound **1**.

in the solid state (Fig. 2).[15] The structure shows that a pair of pyrazine rings (two out of three) is arranged eclipsing with a dihedral angle of 29.2° and a centroid–centroid distance of 3.949 Å. Two phenyl rings (two out of three) are positioned almost parallel with a dihedral angle of only 9.6° and a centroid–centroid distance of 4.310 Å. The remaining pyrazine ring and the phenyl ring are pointed in an opposite direction with a dihedral angle of 21.7°. The molecule revealed an unsymmetrical rectangular geometry and

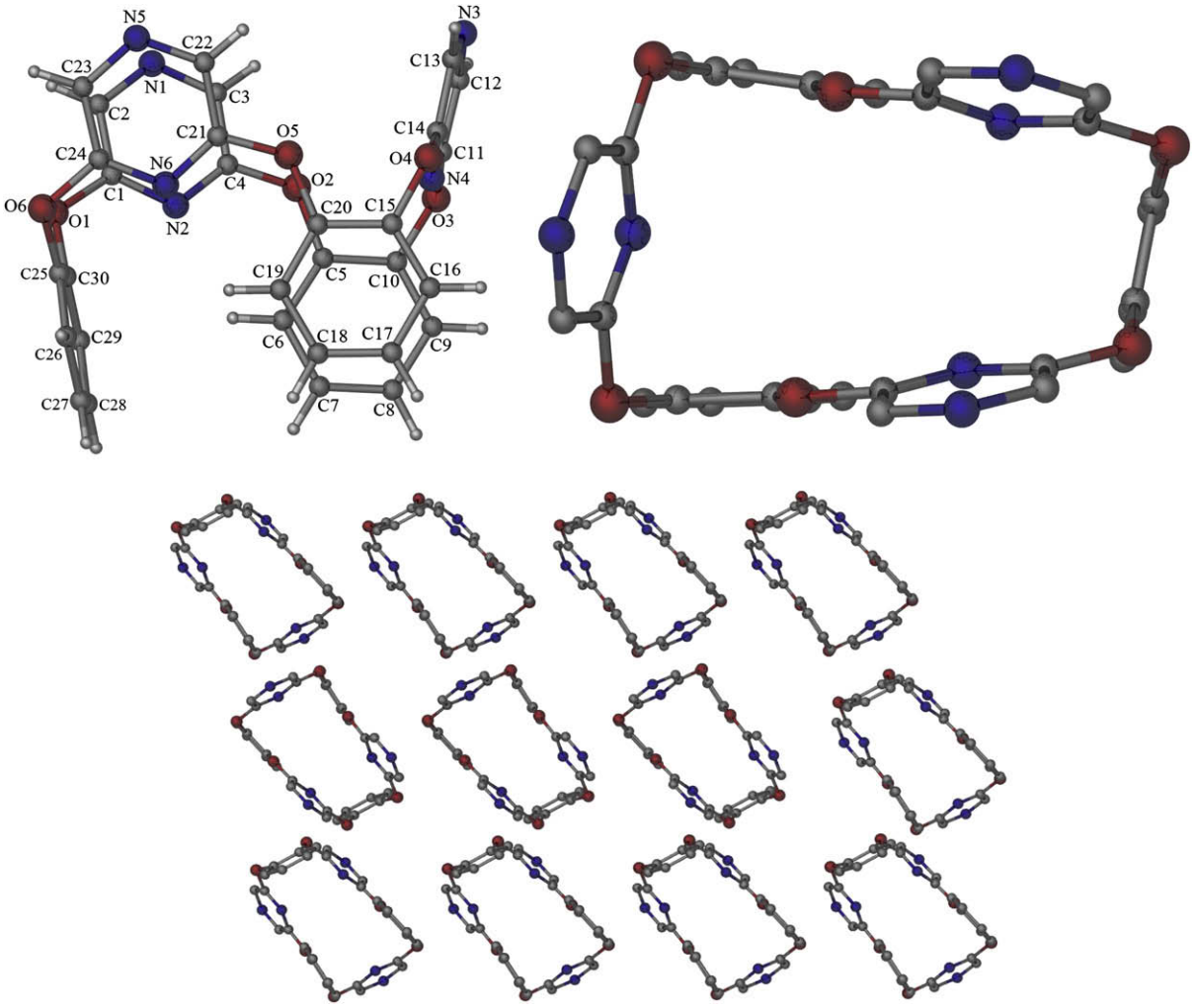


Figure 2. X-ray single crystal structure of compound **2**, side view (top left), top view (top right), and molecular packing (bottom).

thus generated a narrow space, which is hardly hosting any guest molecules (such as solvent molecules, Fig. 2).

The crystal structure of *ortho*-linked oxacalix[3]arene[3]pyrimidine (**4**),[16] however, adopts a complete different conformation from its isomer, compound **2**. Compound **4** revealed a core conformation with C_3 symmetry in the solid state (Fig. 3). The position of the nitrogen atoms in the heterocyclic rings is believed to be responsible for this difference, yet the mechanistic details remain to be known. In this structure, the six rings are arranged in a triangular shape, in which the three phenyl segments are located at the angle positions of the triangle and the three pyrimidine rings are placed at the line segments of the triangle. The three pyrimidine rings are oriented almost perpendicular to the triangular plane with a slight bent toward the triangular core while the three phenyl rings are bent away from the triangular core. This conformation thus created no cavity space for taking up guest molecules (Fig. 3).

3. Conclusions

In summary, new types of *ortho*-linked oxacalix[2]arene[2]hetarenes and oxacalix[3]arene[3]hetarenes have been prepared by condensation of catechol and *meta*-dichlorinated nitrogen containing heterocycles. Crystal structure analyses revealed 1,3-alternate and 1,3,5-alternate conformations for *ortho*-linked oxacalix[2]arene[2]pyrazine (**1**) and *ortho*-linked oxacalix[3]arene-[3]pyrazine (**2**), respectively. *ortho*-Linked oxacalix[3]arene[3]pyrimidine (**4**), an isomer of **2**, however, was found to adopt a core conformation with C_3 symmetry. No cavity spaces were formed under those conformations adopted, and consequently no guest species were found being taken up by these molecules in the solid state.

4. Experimental

4.1. General

All chemicals were used as received without further purification. Chemical reactions were performed in oven-dried glassware under an atmosphere of nitrogen. Classic column chromatography was performed using Merck 60 (70–230 mesh) silica gel. ^{1}H and ^{13}C NMR spectra were recorded at Bruker Avance 500 spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million versus tetramethylsilane. Mass spectra were recorded on a Bruker micrOTOF-Q spectrometer (LC/MS). Single crystal X-ray diffraction data were collected on a Bruker SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube (λ=0.71073 Å).

4.2. Synthesis of *ortho*-linked oxacalix[2]arene[2]pyrazine (1) and *ortho*-linked oxacalix[3]arene[3]pyrazine (2)

Cesium carbonate (7.16 g, 22 mmol) was dissolved in 250 mL DMSO, catechol (1.1 g, 10 mmol), and 2,6-dichloropyrazine (1.49 g, 10 mmol) were added to the DMSO solution. The reaction mixture was stirred at room temperature for 8 h, then heated at 120 °C for additional 16 h. The reaction mixture was poured into 500 mL water and extracted with ethyl acetate for three times. The combined organic layer was washed with water and brine, dried over Na_2SO_4. The solvent was evaporated and the crude products **1** and **2** were purified by FC (PE/AcOEt 8:1).

*4.2.1. ortho-Linked oxacalix[2]arene[2]pyrazine (**1**)*

Yield: 0.87 g (47%). White powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 4H), 7.05–7.02 (m, 4H), 6.96–6.94 (m, 4H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 157.04, 145.16, 126.24, 125.97, 124.12; HRMS: $C_{20}H_{13}N_4O_4^+$ *m*/*z* calcd 373.0931, found 373.0939.

*4.2.2. ortho-Linked oxacalix[3]arene[3]pyrazine (**2**)*

Yield: 0.26 g (14%). White powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 6H), 7.24–7.19 (m, 12H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 156.88, 144.40, 126.66, 125.15, 123.13; HRMS: $C_{30}H_{19}N_6O_6^+$ *m*/*z* calcd 559.1366, found 559.1353.

4.3. Synthesis of *ortho*-linked oxacalix[2]arene[2]pyrazine (1) and *ortho*-linked oxacalix[3]arene[3]pyrazine (2) by the two-step reaction protocol

2,6-dichloropyrazine (4.47 g, 60 mmol) and potassium carbonate (6.10 g, 44 mmol) were dissolved in 50 mL DMF and stirred for 15 min. Catechol (2.0 g, 20 mmol) in 100 mL DMF was added dropwise to the above reaction mixture. The reaction was monitored by TLC. After the reaction was complete, the reaction mixture was poured to 500 mL ice-water and extracted with ethyl acetate for three times. The combined organic layer was washed with water and brine, dried over Na_2SO_4. The solvent was evaporated and the crude product 1,2-bis(6-chloropyrazin-2-ybxy)benzene was purified by FC (PE/AcOEt 9:1).

4.3.1. 1,2-bis(6-chloropyrazin-2-yloxy)benzene

Yield: 5.38 g (80%). White powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 2H), 8.20 (s, 2H), 7.35–7.40 (m, 4H); ^{13}C NMR (500 MHz,

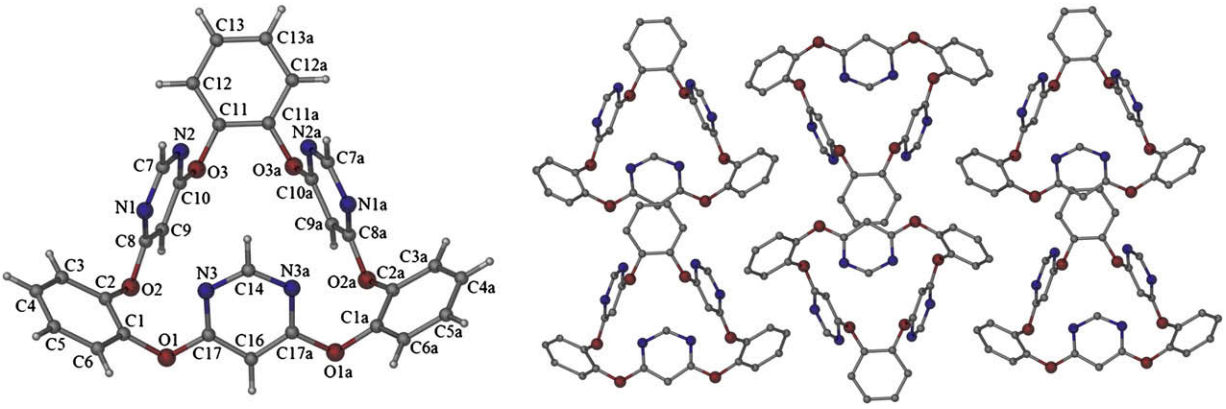


Figure 3. X-ray single crystal structure and molecular packing of compound **4**.

$CDCl_3$): δ 157.90, 145.71, 144.06, 137.98, 132.13, 126.95, 123.47; HRMS: $C_{14}H_9Cl_2N_4O_2^+$ m/z calcd 335.0097, found 335.0098.

Cesium carbonate (3.10 g, 9.2 mmol) was dissolved in 100 mL DMSO and slowly heated to 120 °C. Under vigorous stirring, catechol (0.46 g, 4.2 mmol) in 100 mL DMSO and 1,2-Bis(6-chloropyrazin-2-ybxy)benzene (1.41 g, 4.2 mmol) in 100 mL DMSO were slowly added to the reaction mixture dropwise in a same rate. After complete addition, the reaction mixture was maintained at this temperature until the completion of the reaction (based on TLC). The work-up was the same as that in Section 4.2. Compound **1** (0.87 g) was obtained in 56% yield (overall 45%) and compound **2** (0.40 g) was obtained in 17% yield. The analytical data for **1** and **2** were seen in Section 4.2.

4.4. Conversion of *ortho*-linked oxacalix[3]arene[3]pyrazine (2) to *ortho*-linked oxacalix[2]arene[2]pyrazine (1)

ortho-Linked oxacalix[3]arene[3]pyrazine (**2**) (5.6 mg 0.01 mmol) and cesium carbonate (6.5 mg, 0.02 mmol) were dissolved in 5 mL DMSO and heated at 120 °C, the reaction process was monitored by TLC. After 24 h, over 95% of compound **2** were transformed to *ortho*-linked oxacalix[2]arene[2]pyrazine (**1**) (based on TLC).

4.5. Synthesis of *ortho*-linked oxacalix[2]arene[2]pyridine (3)

Cesium carbonate (7.16 g, 22 mmol) was dissolved in 250 mL DMSO, catechol (1.1 g, 10 mmol) and 2,6-dicholoropyridine (1.48 g, 10 mmol) were added to the DMSO solution. The following procedure was the same as that of the synthesis of *ortho*-linked oxacalix[2]arene[2]pyrazine (**1**).

4.5.1. ortho-Linked oxacalix[2]arene[2]pyridine (3)

Yield: 0.71 g (38.3%). White powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (t, 2H, J=8), 6.99–6.94 (m, 8H), 6.43 (d, 4H, J=8); ^{13}C NMR (500 MHz, $CDCl_3$): δ 161.11, 146.07, 141.66, 124.94, 124.27, 102.75; HRMS: $C_{22}H_{15}N_4O_4^+$ m/z calcd 371.1032, found 371.1012.

4.6. Synthesis of *ortho*-linked oxacalix[3]arene[3]-pyrimidine (4)

(a) Cesium carbonate (7.16 g, 22 mmol) was dissolved in 250 mL DMSO, catechol (1.1 g, 10 mmol) and 4,6-dichloropyrimidine (1.48 g, 10 mmol) were added to the DMSO solution and reaction mixture was stirred at room temperature for 48 h. The work-up was the same as that of compound **1**. *ortho*-Linked oxacalix[3]arene[3]pyrimidine (**4**, 0.65 g) was obtained in 35% yield.

(b) Cesium carbonate (7.16 g, 22 mmol) was dissolved in 250 mL DMSO, catechol (1.1 g, 10 mmol) and 4,6-dichloropyrimidine (1.48 g, 10 mmol) were added to the DMSO solution and reaction mixture was stirred at room temperature for 8 h, then heated at 120 °C for 16 h. After the work-up, *ortho*-linked oxacalix[3]arene[3]pyrimidine (**4**, 0.76 g) was obtained in 41% yield.

4.6.1. ortho-Linked oxacalix[3]arene[3]pyrimidine (4)

White powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 3H), 7.37–7.35 (m, 6H), 7.29–7.20 (m, 6H), 6.28 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 170.59, 157.66, 144.29, 126.90, 123.70, 91.68; HRMS: $C_{30}H_{19}N_6O_6^+$ m/z calcd 559.1366, found 559.1371.

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References and notes

1. Gutsche, C. D. *Calixarenes Revisited*; Royal Society of Chemistry: Cambridge, 2000.
2. (a) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713; (b) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713; (c) Rebek, J., Jr. *Acc. Chem. Res.* **1999**, *32*, 278; (d) Rebek, J., Jr. *Angew. Chem., Int. Ed.* **2002**, *41*, 1488.
3. (a) Cram, D. J.; Cram, J. M. *Container Molecules and their Guests*; Royal Society of Chemistry: Cambridge, 1994; (b) Hof, F.; Trembleau, L.; Ullrich, E. C.; Rebek, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3150; (c) Biros, S. M.; Ullrich, E. C.; Hof, F.; Trembleau, L.; Rebek, J. *J. Am. Chem. Soc.* **2004**, *126*, 2870; (d) Hooley, R. J.; Van Anda, H. J.; Rebek, J. *J. Am. Chem. Soc.* **2007**, *129*, 13464.
4. Baldini, L.; Casnati, A.; Sansone, F.; Ungaro, R. *Chem. Soc. Rev.* **2007**, *36*, 254.
5. König, B.; Fonseca, M. H. *Eur. J. Inorg. Chem.* **2000**, 2303.
6. Lhotak, P. *Eur. J. Org. Chem.* **2004**, 1675.
7. (a) Katz, J. L.; Feldman, M. N.; Conry, R. R. *Org. Lett.* **2005**, *7*, 91; (b) Katz, J. L.; Selby, K. J.; Conry, R. R. *Org. Lett.* **2005**, *7*, 3505; (c) Katz, J. L.; Feldman, M. N.; Conry, R. R. *Org. Lett.* **2006**, *8*, 2755; (d) Katz, J. L.; Geller, B. J.; Foster, P. D. *Chem. Commun.* **2007**, 1026.
8. (a) Wang, M.-X.; Yang, H.-B. *J. Am. Chem. Soc.* **2004**, *126*, 15412; (b) Wang, M.-X.; Zhang, X.-H.; Zhang, Q.-Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 838; (c) Wang, Q.-Q.; Wang, D.-X.; Ma, H.-W.; Wang, M.-X. *Org. Lett.* **2006**, *8*, 5967; (d) Liu, S.-Q.; Wang, D.-X.; Zheng, Q.-Y.; Wang, M.-X. *Chem. Commun.* **2007**, 3856; (e) Yang, H.-B.; Wang, D.-X.; Wang, Q.-Q.; Wang, M.-X. *J. Org. Chem.* **2007**, *72*, 3757; (f) Wang, Q.-Q.; Wang, D.-X.; Zhang, Q.-Y.; Wang, M.-X. *Org. Lett.* **2007**, *9*, 2847.
9. (a) Ito, A.; Ono, Y.; Tanaka, K. *J. Org. Chem.* **1999**, *64*, 8236; (b) Li, X.-H.; Upton, T. G.; Gibb, C. L. R.; Gibb, B. C. *J. Am. Chem. Soc.* **2003**, *125*, 650; (c) Konishi, H.; Mita, T.; Moritawa, O.; Kobayashi, K. *Tetrahedron Lett.* **2007**, *48*, 3029; (d) 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; (e) Miyazaki, Y.; Kanbara, T.; Yamamoto, T. *Tetrahedron Lett.* **2002**, *43*, 7945; (f) Selby, T. D.; Blackstock, S. C. *Org. Lett.* **1999**, *1*, 2053; (g) Maes, W.; Rossom, W. V.; Hecke, K. V.; Meervelt, L. V.; Debaen, W. *Org. Lett.* **2006**, *8*, 4161; (h) Hao, E.; Fronczek, F. R.; Vicente, M.; Graca, H. *J. Org. Chem.* **2006**, *71*, 1233; (i) Yang, F.; Yan, L.; Ma, K.; Yang, L.; Li, J.; Chen, L.; You, J. *Eur. J. Org. Chem.* **2006**, 1109; (j) Konishi, H.; Tanaka, K.; Teshima, Y.; Mita, T.; Morikawa, O.; Kobayashi, K. *Tetrahedron Lett.* **2006**, *47*, 4041; (k) Rossom, W. V.; Maes, W.; Kishore, L.; Ovaere, M.; Meervelt, L. V.; Debaen, W. *Org. Lett.* **2008**, *10*, 585.
10. Gong, H.-Y.; Wang, D.-X.; Xiang, J.-F.; Zheng, Q.-Y.; Wang, M.-X. *Chem.—Eur. J.* **2007**, *13*, 7791.
11. Gong, H.-Y.; Zhang, X.-H.; Wang, D.-X.; Ma, H.-W.; Zheng, Q.-Y.; Wang, M.-X. *Chem.—Eur. J.* **2006**, *12*, 9262.
12. Gong, H.-Y.; Zhang, Q.-Y.; Zhang, X.-H.; Wang, D.-X.; Wang, M.-X. *Org. Lett.* **2006**, *8*, 4895.
13. Hou, B.-Y.; Wang, D.-X.; Yang, H.-B.; Zhang, Q.-Y.; Wang, M.-X. *J. Org. Chem.* **2007**, *72*, 5218.
14. Crystallographic data for *ortho*-linked oxacalix[2]arene[2]pyrazine (**1**): $[C_{20}H_{12}N_4O_4]$; M_r=372.34; triclinic; space group $P\bar{1}$; a=7.15620(10); b=10.0339(2); c=12.7082(2) Å; α=97.4090(10); β=94.1430(10); γ=109.3420(10)°; V=847.352 Å^3; ρ_{calcd}=1.459 g cm^{-3}; T=296(2) K; 11,617 independent measured reflections; F^2 refinement; R_1=0.0540; wR_2=0.1355.
15. Crystallographic data for *ortho*-linked oxacalix[3]arene[3]pyrazine (**2**): $[C_{30}H_{18}N_6O_6]$; M_r=558.50; triclinic; space group $P\bar{1}$; a=8.730(3); b=9.001(3); c=17.867(6) Å; α=77.598(5); β=87.461(6); γ=72.300(6)°; V=1305.9(7) Å^3; ρ_{calcd}=1.420 g cm^{-3}; T=293(2) K; 6775 independent measured reflections; F^2 refinement; R_1=0.0828; wR_2=0.2148.
16. Crystallographic data for *ortho*-linked oxacalix[3]arene[3]pyrimidine (**4**): $[C_{15}H_9N_3O_3]$; M_r=279.25; orthorhombic; space group *pnma*; a=17.3767(6); b=21.4937(7); c=6.8235(2) Å; V=2548.51(14) Å^3; ρ_{calcd}=1.456 g cm^{-1}; T=296(2) K; 27,886 independent measured reflections; F^2 refinement; R_1=0.0299; wR_2=0.0753.