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Tetraphenylethylene-Based Expanded Oxacalixarene: Synthesis, Structure, and Its Supramolecular Grid Assemblies Directed by Guests in the Solid State

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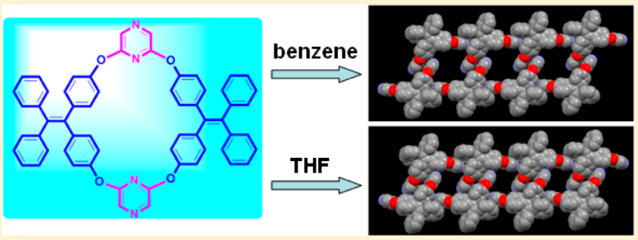
S Supporting Information

ABSTRACT: A novel TPE-based expanded oxacalixarene with typical aggregation-induced emission properties was synthesized by the S_NAr reaction of dihydroxytetraphenylethylene with 2,6-dichloropyrazine. The conformation of the oxacalixarene is adjusted by the encapsulated guests (benzene or THF), which results in different supramolecular grid structures in the solid state.



Oxacalixarenes,[1,2] in which the carbon linkages between the aromatic units are replaced by oxygen atoms, have attracted increased interest in recent years because of their availability, tunable cavities and potential applications in supramolecular chemistry. Consequently, different methods for the synthesis of oxacalixarenes, including the fragment coupling approach (FCA)[3] and one-pot macrocyclic condensation reactions,[4] have been developed to tune the size and electronic properties of the cavity and therefore to improve their assembly and recognition abilities. For example, enlarged oxacalix[*n*]arenes ($n > 4$) have been synthesized successfully by different protocols in recent years.[5] The other strategy to enlarge the cavity of oxacalixarenes is to employ large-sized building blocks. For instance, Katz and co-workers reported a new class of naphthyridine-based or naphthalene-based oxacalixarenes in which the two naphthalene units separated by 7.0 Å could form a defined tweezerlike cavity for selective binding of salicylic acid in solution and the incorporation of a CH_3CN molecule in the solid state.[6] Chen and co-workers introduced triptycene units into the oxacalix[4]arene system, which resulted in several new oxacalix[4]arenes with enlarged cavities and fixed conformations, and they found that this class of oxacalix[4]arene compounds could assemble into tubular structures in the solid state and encapsulate some interesting guests such as fullerene.[7] Recently, Wang[2h] and Wen[2f] constructed *m*-terphenylene-based oxacalixarenes with enlarged cavities. The introduction of novel building blocks into oxacalixarene scaffolds has been recognized as one of the most important driving forces to promote advances in oxacalixarene chemistry.

Tetraphenylethylene derivatives (TPEs)[8,9] are a class of interesting compounds that exhibit propeller-like and nonplanar conformations and have a well-known aggregation-induced emission (AIE) effect. With the unique structure, TPE-based porous materials have been constructed, including conjugated microporous polymers[10] and TPE-bridged metal—organic frameworks.[11] Taking advantage of the AIE feature enables the construction of various TPE-based chemo/biosensors.[12] Although TPEs have attracted more and more attention because of their AIE feature, construction of calixarene scaffolds utilizing TPE as the skeleton building blocks has been unexplored.[13] Herein we report the efficient synthesis, structure, and the AIE properties of TPE-based expanded oxacalixarenes. Moreover, the conformation of the TPE-based expanded oxacalixarenes was efficiently adjusted by the encapsulated guests, resulting in different supramolecular grid structures in the solid state.[14]

The synthesis of the expanded oxacalixarene is depicted in Scheme 1. Dihydroxytetraphenylethylene **2** was prepared according to the literature method.[13] The one-pot coupling reaction of **2** with 2,6-dichloropyrazine (**3**) in the presence of Cs_2CO_3 in DMSO at 120 °C for 10 h resulted in the formation of the expected TPE-based oxacalixarene **1** in a yield of 42.2%. The chemical structure of oxacalixarene **1** was characterized by ^1H and ^{13}C NMR spectroscopy, MALDI-TOF MS, and elemental analysis.[15]

The ^1H NMR spectrum of macrocycle **1** in $CDCl_3$ shows only one singlet at 8.07 ppm for the proton H_a of the pyrazine

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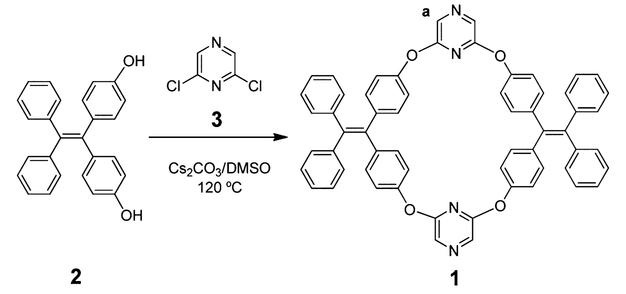
Scheme 1. Synthesis of TPE-Based Oxacalixarene 1



moiety, while its ^{13}C NMR spectrum showed only 12 signals for the carbons. The presence of only one set of proton and carbon signals in the corresponding ^{1}H and ^{13}C NMR spectra indicates that the conformation of the macrocycle **1** is fixed. Moreover, no significant spectral changes were observed in variable-temperature ^{1}H NMR experiments on oxacalixarene **1** (Figure S3 in the Supporting Information), which furthermore confirmed the fixed conformation of **1** in solution.

Oxacalixarene **1** shows typical AIE properties. The fluorescence spectra of **1** in solution were measured. As expected, the compound is almost nonfluorescent in solution (Figure 1), in accordance with previous studies.[9,12] However, the fluorescence of **1** "turns on" upon aggregation. Figure 1 shows the fluorescence spectra of **1** in THF after the addition of different amounts of water. It was found that the fluorescence intensity of **1** is significantly enhanced when the water/THF volume ratio is larger than 3/1. Such fluorescence enhancement can be detected by the naked eye, as shown in Figure S5 in the Supporting Information, which presents photographs of compound **1** in solutions with different water/THF ratios under UV irradiation. The fluorescence enhancement for **1** is due to the formation of aggregates because the compound is not water-soluble, and thus, the addition of water to its solution in THF induces its aggregation. As shown in Figure S6 in the Supporting Information, the results of transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) analysis indicated that oxacalixarene **1** aggregated into amorphous nanoparticles with a size distribution of 50−150 nm when the water/THF ratio was 10/1.

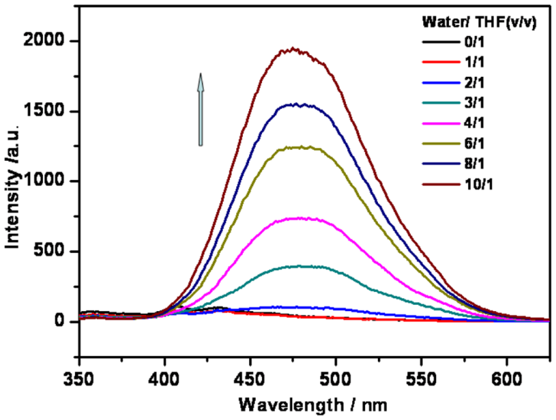


Figure 1. Fluorescence spectra of oxacalixarene **1** in THF after the addition of various amounts of water (excitation wavelength: 350 nm).

To investigate the solid-state structure of oxacalixarene **1** and to examine the guest-induced conformational changes in the structure, single crystals of **1** were cultivated in different solvent systems. Single crystals of **1**·C_6H_6 and **1**·0.5C_4H_8O were obtained by slow evaporation of the benzene/CH_3CN and THF solutions, respectively.[15] As shown in Figure 2, **1** is in a 1,3-alternate conformation in the solid state, which is similar to the conformational structures of most literature-documented oxacalixarenes.[2] In the crystal structure of **1**·C_6H_6 and **1**·0.5C_4H_8O, the four bridging oxygen atoms are located in one plane. Because of the encapsulation of different guests, oxacalixarene **1** displayed different conformations in the solid state. As shown in Figure 2, the two pyrazine rings are eclipsed with dihedral angles of 62.67° and 76.09° in the crystals of **1**·C_6H_6 and **1**·0.5C_4H_8O, respectively. The transannular N···N distances for the lower and upper rims are 9.270 and 13.999 Å for **1**·C_6H_6 and 9.405 and 13.748 Å for **1**·0.5C_4H_8O, respectively.

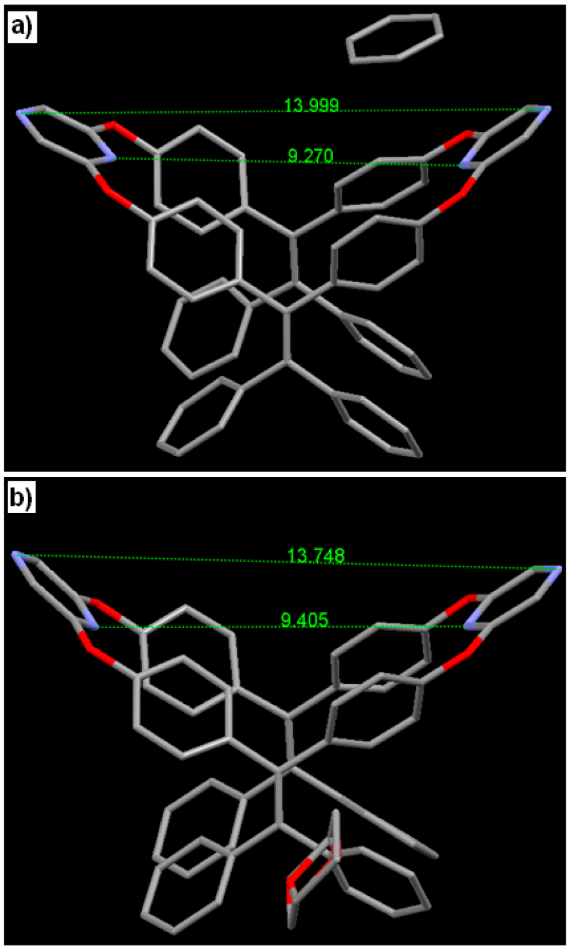


Figure 2. Crystal structures of (a) **1**·C_6H_6 and (b) **1**·0.5C_4H_8O. Hydrogen atoms have been omitted for clarity.

Moreover, oxacalixarene **1** assembled into different supramolecular assemblies introduced by the different guests. In **1**·C_6H_6, two molecules of **1** with different directions form a dimer structure by a couple of C−H···N interactions between the aromatic protons of the TPE moiety and the nitrogen atom of the pyrazine ($d_{\text{H}\cdots\text{N}}$ = 2.477 Å, $\theta_{\text{C}-\text{H}\cdots\text{N}}$ = 146.69°) and a $\pi-\pi$ stacking interaction between the pyrazine moieties of the adjacent oxacalixarenes ($d_{\pi-\pi}$ = 3.435 Å) (Figure 3a and Figure S7 in the Supporting Information). By another a couple of C−H···N interactions ($d_{\text{H}\cdots\text{N}}$ = 2.499 Å, $\theta_{\text{C}-\text{H}\cdots\text{N}}$ = 136.59°) and a

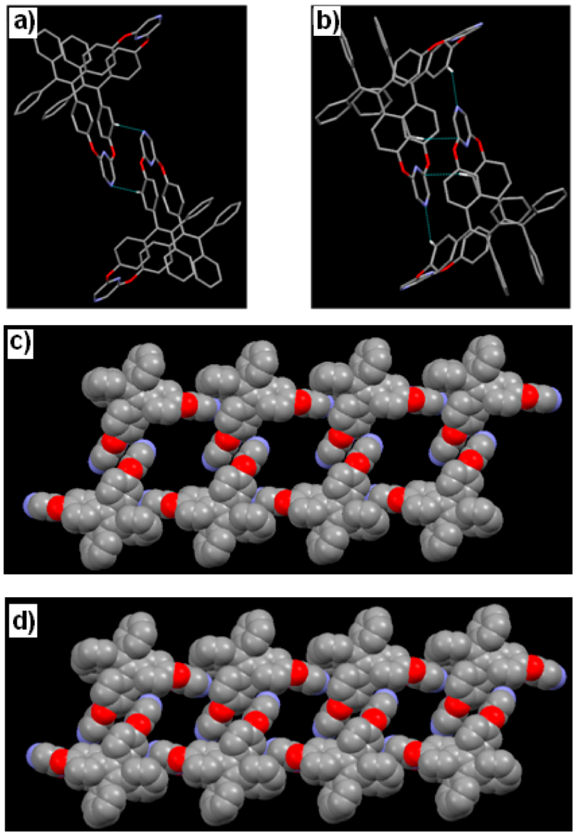


Figure 3. The dimer structures of oxacalixarene **1** in (a) **1**·C_6H_6 and (b) **1**·$0.5C_4H_8O$ and the grid structures assembled in (c) **1**·C_6H_6 and (d) **1**·$0.5C_4H_8O$. Solvent molecules and hydrogen atoms have been omitted for clarity.

couple of $\pi-\pi$ stacking interactions ($d_{\pi-\pi}$ = 3.248 Å) between adjacent dimers, oxacalixarene **1** assembles into a grid structure with dimensions of 16.302 Å × 14.169 Å. In each grid, two benzene molecules are located by a $\pi-\pi$ stacking interaction ($d_{\pi-\pi}$ = 3.270 Å) (Figure 3c and Figure S8 in the Supporting Information). In **1**·$0.5C_4H_8O$, two molecules of **1** with different directions also form a dimer structure by a couple of C–H···N interactions ($d_{H\cdots N}$ = 2.547 Å, $\theta_{C-H\cdots N}$ = 125.99°) and a couple of C–H···π interactions ($d_{H\cdots\pi}$ = 2.768 Å) (Figure 3b and Figure S9 in the Supporting Information). By virtue of a couple of C–H···N interactions ($d_{H\cdots N}$ = 2.364 Å, $\theta_{C-H\cdots N}$ = 155.91°), adjacent dimers also assemble into a grid structure with dimensions of 11.866 Å × 10.482 Å, which can contain only one molecule of THF (Figure 3d and Figure S10 in the Supporting Information). The difference in the oxacalixarene assembly in **1**·C_6H_6 and **1**·$0.5C_4H_8O$ might have resulted from the different template effects of the guests (benzene and THF).

In conclusion, we have synthesized the novel TPE-based expanded oxacalixarene **1** by the S_NAr reaction of dihydroxytetraphenylethylene with 2,6-dichloropyrazine. Oxacalixarene **1** shows typical AIE properties. Moreover, the conformation of **1** is efficiently adjusted by the encapsulated guests, resulting in different supramolecular grid structures in the solid state. The AIE properties of the novel TPE-based oxacalixarene would render it an interesting host for the recognition of some guests.

■ EXPERIMENTAL SECTION

General Methods. Materials obtained commercially were used without further purification. The NMR experiments were performed on a 400 MHz NMR spectrometer. MALDI mass determination was performed on a MALDI-TOF mass spectrometer with CCA.

Synthesis of 1. Under a dry argon atmosphere, a mixture of TPE **2** (100 mg, 0.28 mmol), 2,6-dichloropyrazine (**3**) (41 mg, 0.28 mmol), and anhydrous Cs_2CO_3 (182 mg, 0.56 mmol) in anhydrous DMSO (5 mL) was stirred vigorously at 120 °C for 10 h and then cooled to rt. The reaction mixture was partitioned between EtOAc (50 mL) and H_2O (40 mL) and then separated, and the aqueous layer was extracted twice with EtOAc (20 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (eluent: 1/5 CH_2Cl_2/petroleum ether) to give **1** as a white solid (51 mg, 42.2%). Mp: >300 °C. IR (KBr): 1640.54, 1582.37, 1538.86, 1501.44, 1450.85, 1405.09, 1315.37, 1260.27, 1205.76, 1172.57, 1103.35 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.83 (d, J = 8.0 Hz, 8H), 6.99 (d, J = 8.0 Hz, 8H), 7.07 (m, 8H), 7.10 (m, 12H), 8.07 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 121.0, 126.7, 127.3, 127.9, 131.4, 132.2, 132.6, 139.3, 140.3, 141.7, 143.9, 151.0. MALDI-TOF-MS: m/z 880.8 (M^+). Anal. Calcd for $C_{60}H_{40}N_4O_4$: C, 81.80; H, 4.58; N, 6.36. Found: C, 82.03; H, 4.41; N, 6.50. Crystallographic data for **1**·C_6H_6 ($C_{66}H_{46}N_4O_4$): M_r = 959.07; triclinic, space group $P\bar{1}$; a = 12.024(3) Å, b = 12.744(3) Å, c = 18.613(5) Å, α = 97.529(4)°, β = 98.367(4)°, γ = 115.203(3)°, V = 2493.1(11) $Å^3$; Z = 2; ρ_{calcd} = 1.278 g/cm^3; μ = 0.080 mm^{-1}; reflections collected 20886; data/restraints/parameters 9747/0/667; GOF on F^2 0.971; final R_1 = 0.0554, wR_2 = 0.1236; R indices (all data) R_1 = 0.1294, wR_2 = 0.1611; largest diffraction peak and hole 0.274 and −0.297 e/$Å^3$, respectively; CCDC-975767. Crystallographic data for **1**·$0.5C_4H_8O$ ($C_{62}H_{44}N_4O_{4.5}$): M_r = 959.07; triclinic, space group $P\bar{1}$; a = 12.237(4) Å, b = 12.745(4) Å, c = 17.157(6) Å, α = 79.464(6)°, β = 89.857(6)°, γ = 65.497(5)°, V = 2385.7(14) $Å^3$; Z = 2; ρ_{calcd} = 1.277 g/cm^3; μ = 0.081 mm^{-1}; reflections collected 17716; data/restraints/parameters 8355/30/649; GOF on F^2 0.951; final R_1 = 0.0615, wR_2 = 0.1291; R indices (all data) R_1 = 0.1588, wR_2 = 0.1738; largest diffraction peak and hole 0.776 and −0.312 e/$Å^3$, respectively; CCDC-975768.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR, IR, and MS spectra of **1**; TEM image of **1**; and X-ray crystallographic data and refinement parameters (including CIF files) for **1**·C_6H_6 and **1**·$0.5C_4H_8O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For recent reviews, see: (a) Wang, M.-X. *Chem. Commun.* **2008**, 4541. (b) Maes, W.; Dehaen, W. *Chem. Soc. Rev.* **2008**, *37*, 2393. (c) Wang, M.-X. *Acc. Chem. Res.* **2012**, *45*, 182.

(2) For recent examples of oxacalixarenes, see: (a) Xie, T.; Hu, S.-Z.; Chen, C.-F. *J. Org. Chem.* **2013**, *78*, 981. (b) Yang, C.; Chen, Y.; Wang, D.-X.; Zhao, L.; Wang, M.-X. *Org. Lett.* **2013**, *15*, 4414. (c) Wang, D.-X.; Wang, M.-X. *J. Am. Chem. Soc.* **2013**, *135*, 892. (d) Visitaev, Y.; Goldberg, I.; Vigalok, A. *Inorg. Chem.* **2013**, *52*, 6779. (e) Li, S.; Fa, S.-X.; Wang, Q.-Q.; Wang, D.-X.; Wang, M.-X. *J. Org. Chem.* **2012**, *77*, 1860. (f) Hu, W.-J.; Zhao, X.-L.; Ma, M.-L.; Guo, F.; Mi, X.-Q.; Jiang, B.; Wen, K. *Eur. J. Org. Chem.* **2012**, 1448. (g) Bizier, N. P.; Vernamonti, J. P.; Katz, J. L. *Eur. J. Org. Chem.* **2012**, 2303. (h) Naseer, M. M.; Wang, D.-X.; Wang, M.-X. *Heterocycles* **2012**, *84*, 1375. (i) Wang, D.-X.; Fa, S.-X.; Liu, Y.; Hou, B.-Y.; Wang, M.-X. *Chem. Commun.* **2012**, *48*, 11458. (j) Van Rossom, W.; Caers, J.; Robeyns, K.; Van Meervelt, L.; Maes, W.; Dehaen, W. *J. Org. Chem.* **2012**, *77*, 2791. (k) Zhu, Y.; Yuan, J.; Li, Y.; Gao, M.; Cao, L.; Ding, J.; Wu, A. *Synlett* **2011**, 52. (l) Chen, Y.; Wang, D.-X.; Huang, Z. T.; Wang, M.-X. *Chem. Commun.* **2011**, *47*, 8112. (m) Van Rossom, W.; Kundrat, O.; Ngo, T. H.; Lhotak, P.; Dehaen, W.; Maes, W. *Tetrahedron Lett.* **2010**, *51*, 2423. (n) Van Rossom, W.; Kishore, L.; Robeyns, K.; Van Meervelt, L.; Dehaen, W.; Maes, W. *Eur. J. Org. Chem.* **2010**, 4122. (o) Alberto, M. E.; Mazzone, G.; Russo, N.; Sicilia, E. *Chem. Commun.* **2010**, *46*, 5894. (p) Li, X.-Y.; Liu, L.-Q.; Ma, M.-L.; Zhao, X.-L.; Wen, K. *Dalton Trans.* **2010**, *39*, 8646. (q) Wang, D.-X.; Wang, Q.-Q.; Han, Y.; Wang, Y.; Huang, Z.-T.; Wang, M.-X. *Chem.—Eur. J.* **2010**, *16*, 13053. (r) Ma, M.-L.; Li, X.-Y.; Wen, K. *J. Am. Chem. Soc.* **2009**, *131*, 8338. (s) Van Rossom, W.; Maes, W.; Kishore, L.; Ovaere, M.; Van Meervelt, L.; Dehaen, W. *Org. Lett.* **2008**, *10*, 585. (t) Wang, D.-X.; Zheng, Q.-Y.; Wang, Q.-Q.; Wang, M.-X. *Angew. Chem., Int. Ed.* **2008**, *47*, 7485.

(3) Wang, M.-X.; Yang, H.-B. *J. Am. Chem. Soc.* **2004**, *126*, 15412.

(4) (a) Katz, J. L.; Feldman, M. B.; 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.; Geller, B. J.; Conry, R. R. *Org. Lett.* **2006**, *8*, 2755.

(5) (a) Li, X.; Upton, T. G.; Gibb, C. L. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2003**, *125*, 650. (b) Maes, W.; Rossom, W. V.; Hecke, K. V.; Van Meervelt, L.; Dehaen, W. *Org. Lett.* **2006**, *8*, 4161. (c) Hao, E.; Fronczek, F. R.; Vicente, M. G. H. *J. Org. Chem.* **2006**, *71*, 1233. (d) Van Rossom, W.; Robeyns, K.; Ovaere, M.; Van Meervelt, L.; Dehaen, W.; Maes, W. *Org. Lett.* **2011**, *13*, 126. (e) Van Rossom, W.; Ovaere, M.; Van Meervelt, L.; Dehaen, W.; Maes, W. *Org. Lett.* **2009**, *11*, 1681. (f) Wackerly, J. W.; Meyer, J. M.; Crannell, W. C.; King, S. B.; Katz, J. L. *Macromolecules* **2009**, *42*, 8181.

(6) Katz, J. L.; Geller, B. J.; Foster, P. D. *Chem. Commun.* **2007**, 1026.

(7) (a) Chen, C.-F. *Chem. Commun.* **2011**, *47*, 1674. (b) Hu, S.-Z.; Chen, C.-F. *Chem. Commun.* **2010**, *46*, 4199. (c) Hu, S.-Z.; Chen, C.-F. *Org. Biomol. Chem.* **2011**, *9*, 5838. (d) Zhang, C.; Chen, C.-F. *J. Org. Chem.* **2007**, *72*, 3880.

(8) For a recent review, see: Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40*, 5361.

(9) For recent examples of TPE, see: (a) Chen, Q.; Zhang, D. Q.; Zhang, G. X.; Yang, X. Y.; Feng, Y.; Fan, Q. H.; Zhu, D. B. *Adv. Funct. Mater.* **2010**, *20*, 3244. (b) Chan, C. Y. K.; Zhao, Z. J.; Lam, J. W. Y.; Liu, J. Z.; Chen, S. M.; Lu, P.; Mahtab, F.; Chen, X. J.; Sung, H. H. Y.; Kwok, H. S.; Ma, Y. G.; Williams, I. D.; Wong, K. S.; Tang, B. Z. *Adv. Funct. Mater.* **2012**, *22*, 378. (c) Leung, C. W. T.; Hong, Y.; Chen, S.; Zhao, E.; Lam, J. W. Y.; Tang, B. Z. *J. Am. Chem. Soc.* **2013**, *135*, 62. (d) Wang, Z.; Chen, S.; Lam, J. W. Y.; Qin, W.; Kwok, R. T. K.; Xie, N.; Hu, Q.; Tang, B. Z. *J. Am. Chem. Soc.* **2013**, *135*, 8238. (e) Huang, G.; Ma, B.; Chen, J.; Peng, Q.; Zhang, G. X.; Fan, Q.; Zhang, D. Q. *Chem.—Eur. J.* **2012**, *18*, 3886. (f) Srinivasan, S.; Babu, P. A.; Mahesh, S.; Ajayaghosh, A. *J. Am. Chem. Soc.* **2009**, *131*, 15122. (g) Babu, S. S.; Mahesh, S.; Kartha, K. K.; Ajayaghosh, A. *Chem.—Asian J.* **2009**, *4*, 824. (h) Gu, X. G.; Yao, J. J.; Zhang, G. X.; Zhang, C.; Yan, Y. L.; Zhao, Y. S.; Zhang, D. Q. *Chem.—Asian J.* **2013**, *8*, 2362.

(10) (a) Xu, Y.; Chen, L.; Guo, Z.; Nagai, A.; Jiang, D. *J. Am. Chem. Soc.* **2011**, *133*, 17622. (b) Chen, Q.; Wang, J.-X.; Yang, F.; Zhou, D.; Bian, N.; Zhang, X.-J.; Yan, C.-G.; Han, B.-H. *J. Mater. Chem.* **2011**, *21*, 13554.

(11) (a) Shustova, N. B.; McCarthy, B. D.; Dincă, M. *J. Am. Chem. Soc.* **2011**, *133*, 20126. (b) Shustova, N. B.; Ong, T.-C.; Cozzolino, A. F.; Michaelis, V. K.; Griffin, R. G.; Dincă, M. *J. Am. Chem. Soc.* **2012**, *134*, 15061.

(12) (a) Wang, M.; Zhang, G. X.; Zhang, D. Q.; Zhu, D. B.; Tang, B. Z. *J. Mater. Chem.* **2010**, *20*, 1858. (b) Liu, Y.; Deng, C. M.; Tang, L.; Qin, A. J.; Hu, R. R.; Sun, J. Z.; Tang, B. Z. *J. Am. Chem. Soc.* **2011**, *133*, 660. (c) Wang, M.; Gu, X. G.; Zhang, G. X.; Zhang, D. Q.; Zhu, D. B. *Anal. Chem.* **2009**, *81*, 4444. (d) Gu, X. G.; Zhang, G. X.; Zhang, D. Q. *Analyst* **2012**, *137*, 365. (e) Gu, X. G.; Zhang, G. X.; Wang, Z.; Liu, W. W.; Xiao, L.; Zhang, D. Q. *Analyst* **2013**, *138*, 2427. (f) Sanji, T.; Shiraishi, K.; Nakamura, M.; Tanaka, M. *Chem.—Asian J.* **2010**, *5*, 817. (g) Hu, X. M.; Chen, Q.; Wang, J. X.; Cheng, Q. Y.; Yan, C. G.; Cao, J.; He, Y. J.; Han, B. H. *Chem.—Asian J.* **2011**, *6*, 2376. (h) Liu, N.-N.; Song, S.; Li, D.-M.; Zheng, Y.-S. *Chem. Commun.* **2012**, *48*, 4908.

(13) For the first TPE-based macrocycle, see: Song, S.; Zheng, Y.-S. *Org. Lett.* **2013**, *15*, 820.

(14) For a recent example of guest-induced conformational change of a host, see: Han, Y.; Cao, J.; Li, P.-F.; Zong, Q.-S.; Zhao, J.-M.; Guo, J.-B.; Xiang, J.-F.; Chen, C.-F. *J. Org. Chem.* **2013**, *78*, 3235.

(15) See the Supporting Information.