JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Triptycene-Derived Homooxacalixarene Analogues: Synthesis, Structures, and Complexation with Fullerenes C_{60} and C_{70}

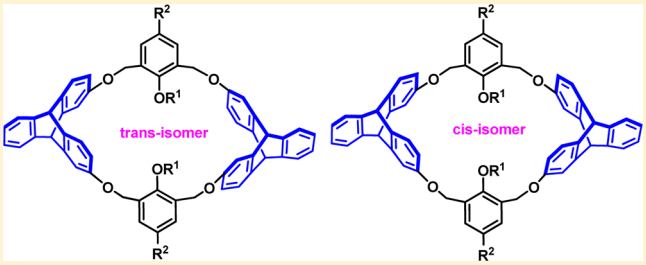
Tao Xie,[†,‡] Shu-Zhen Hu,[†] and Chuan-Feng Chen*[,†]

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

[‡]University of Chinese Academy of Sciences, Beijing 100049, China

Supporting Information

ABSTRACT: A series of triptycene-derived homooxacalixarene analogues were conveniently synthesized by a one-pot approach starting from 2,7-dihydroxytriptycene and 1,3-bisbromomethylbenzene derivatives under mild reaction conditions. Similarly, two pairs of "basket-like" triptycene-derived homooxacalixarene analogues were also designed and synthesized. Structures of these macrocyclic molecules in both solution and solid state were studied by NMR experiments and X-ray crystallography. Because of the rigid triptycene units, the homooxacalixarene analogues showed large cavities and fixed conformations even up to 380 K. It was also found that these novel macrocycles could be served as efficient host molecules for complexation with fullerenes C_{60} and C_{70}.



INTRODUCTION

The design and synthesis of novel macrocyclic host molecules are undoubtedly one of the most important research topics in host–guest chemistry and also supramolecular chemistry.[1] Among various types of known synthetic macrocyclic hosts, calixarenes have attracted much attention for their ready availabilities, unique conformations and cavities, and powerful recognition properties.[2] Along with the development of calixarene chemistry, recent years have witnessed a fast growing interest in heterocalixarenes,[3−6] in which the methylene groups of calixarenes were replaced by heteroatoms such as oxygen, nitrogen, and sulfur. Because of the different electronic nature of heteroatoms, the heterocalixarenes exhibited interesting conformations, cavity structures, and molecular recognition properties. Compared with heterocalixarenes, homoheterocalixarenes, a class of heterocalixarene analogues in which the heteroatoms were partly or completely replaced by CH_2XCH_2 (X = O, NR, et al.) groups, showed the increased cavity sizes, which could also result in their different conformations and recognition properties with those of heterocalixarenes as well as calixarenes.[7]

During the past several years, we have proven that triptycene with a unique 3D rigid structure could be used as a useful building block for the design and synthesis of novel macrocyclic hosts with specific structures and properties.[8,9] Thus, several different kinds of macrocycles including triptycene-derived calixarenes[9h,i] and heterocalixarenes[9e,g,j] with enlarged cavities and fixed conformations have been constructed. Our continuous interest in exploring new kind of macrocyclic hosts has led us to design and synthesize homooxacalixarene analogues by the insertion of methylene units into the bridging positions of triptycene-derived oxacalixarenes. Herein, we report the synthesis of a series of novel triptycene-derived homooxacalixarene analogues. Their structures and self-assemblies in the solid state were also investigated. Moreover, it was found that the homooxacalixarene analogues show efficient complexation properties toward fullerenes C_{60} and C_{70}.[10]

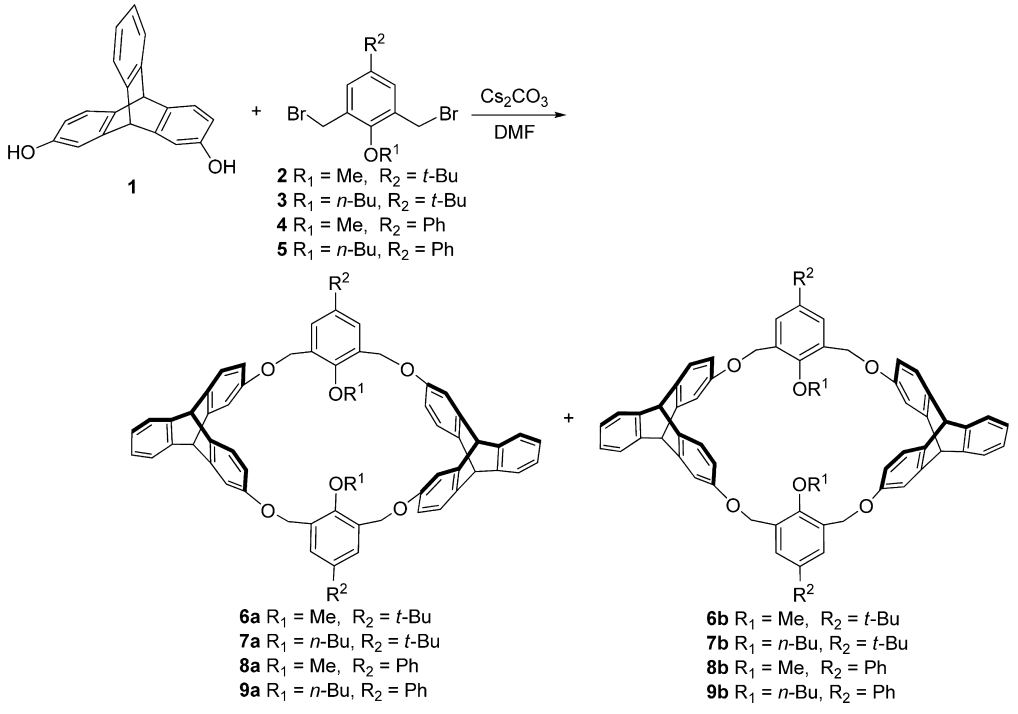
RESULTS AND DISCUSSION

Synthesis of Triptycene-Derived Homooxacalixarene Analogues. Synthesis of the macrocyclic molecules **6**−**9** through a one-pot approach is depicted in Scheme 1. According to the procedure described previously, 2,7-dihydroxytriptycene **1** was first prepared.[9e] Owing to the 3D rigid structure of triptycene, there exist two possible linking modes of **1** for the cyclization reaction, and two different macrocyclic products as a pair of diastereomers could be obtained. Consequently, by the one-pot coupling reaction of 1 and 1,3-bis(bromomethyl)-5-*tert*-butyl-2-methoxybenzene **2**[7a] in DMF for 48 h in the presence of Cs_2CO_3, the macrocycles **6a** and **6b** were obtained in 18 and 22% yield, respectively. Under the same reaction conditions, the target macrocyclic molecules **7a**−**9a** and **7b**−**9b** were conveniently prepared by the one-pot reaction of 2,7-dihydroxytriptycene **1** with compounds **3**−**5**, respectively. All new compounds were characterized by the ^{1}H NMR, ^{13}C NMR, MALDI-TOF mass spectra, and elemental analysis.

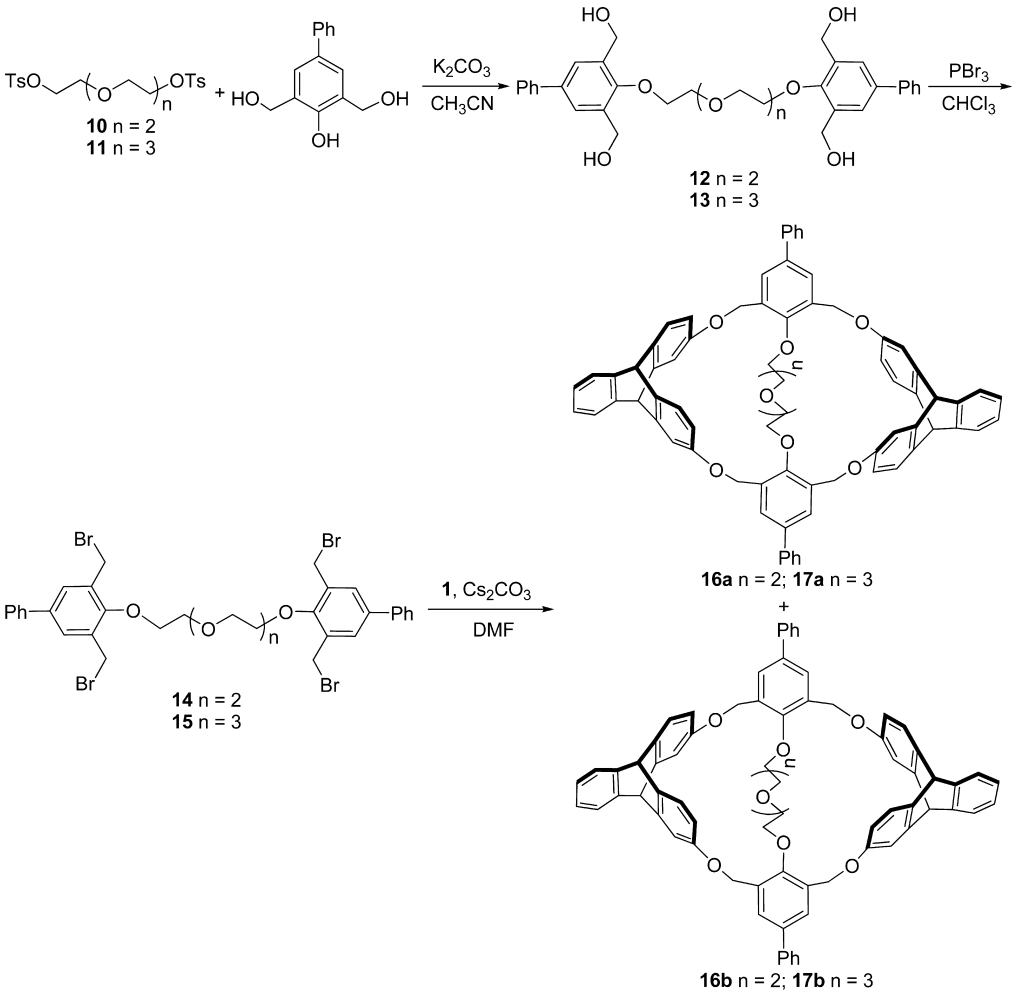
Similarly, two pairs of "basket-like" triptycene-derived homooxacalixarene analogues **16a,b** and **17a,b** in which the

Received: November 9, 2012
Published: December 27, 2012

Scheme 1. Synthesis of the Triptycene-Derived Homooxacalixarene Analogues 6–9



Scheme 2. Synthesis of the Triptycene-Derived Homooxacalixarene analogues 16 and 17



dx.doi.org/10.1021/jo302459m | J. Org. Chem. 2013, 78, 981–987

two *p*-phenyl-substituted benzene rings were linked together by crown ether chains were also designed, and their synthetic route is depicted in Scheme 2. First, reaction of 2,5-dihydroxymethyl-4-phenylphenol with bistosylate **10** in CH_3CN gave compound **12** in 76% yield, which was then treated with PBr_3 in $CHCl_3$ to afford compound **14** in 85% yield. Finally, the target molecules **16a** and **16b** were obtained in 8 and 37% yield, respectively, by the reaction of **14** with 2,7-dihydroxytriptycene **1** in DMF under high dilution conditions in the presence of Cs_2CO_3. Following the same procedure, the homooxacalixarene analogues **17a** and **17b** were prepared in 21 and 23%, respectively.

Structures of the Macrocyclic Molecules in Solution. The structural characterization of the macrocyclic molecules in solution was studied by the ^{1}H NMR experiments. Because of the different orientation of the triptycene moieties in the two diastereomers, diverse shielding or deshielding effects of the benzene ring to the triptycene bridgehead protons would lead to different chemical shifts of the bridgehead protons, which are important information for the discrimination of the two diastereomers in solution.[9e] As a result, it was found that the ^{1}H NMR spectrum of **8b** in $CDCl_3$ exhibited two singlets at 5.29 and 5.23 ppm ($\Delta\delta$ = 0.06 ppm) for the bridgehead protons in triptycenes (Figure 1); meanwhile, the bridgehead

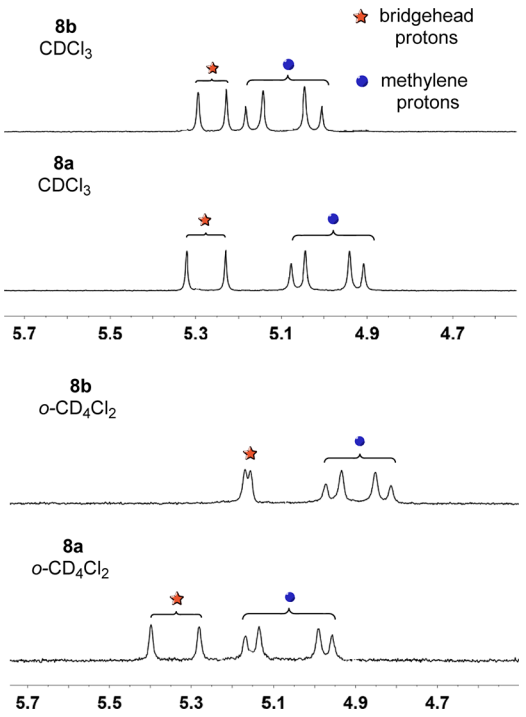


Figure 1. Partial ^{1}H NMR spectra of **8a** and **8b** in $CDCl_3$ and *o*-$C_6D_4Cl_2$ at 298 K.

proton signals of **8a** at 5.32 ppm and 5.23 ppm with $\Delta\delta$ of 0.09 ppm were observed. The similar $\Delta\delta$ values of the bridgehead proton signals, as well as similar split peaks in the aromatic region of the two macrocycles, made it difficult to discriminate between them. However, when the ^{1}H NMR experiments were carried out in *o*-$C_6D_4Cl_2$, the bridgehead protons of **8b** showed two singlets at 5.17 and 5.16 ppm with only $\Delta\delta$ = 0.01 ppm, which implied that it was a *cis*-isomer with a high symmetric structure.[9e] Meanwhile, macrocycle **8a** exhibited two singlets (5.40 and 5.28 ppm) with $\Delta\delta$ of 0.12 ppm, which indicated it could be a *trans*-isomer. For other pairs of the triptycene-derived homooxocalixarene analogues, the similar spectral properties of the diastereomers were also found, which proved their structures in solution.

As shown in Figure 1, the methylene protons of both of the isomers appeared as a pair of well-defined doublet signals, which indicated that these macrocycles might have fixed conformations at room temperature due to the presence of rigid triptycene moieties.[9h] In order to further investigate the conformational mobility, variable-temperature ^{1}H NMR experiments of **8a** and **8b** in *o*-$C_6D_4Cl_2$ were carried out. As shown in Figure 2, the two sets of doublet signals of methylene group in

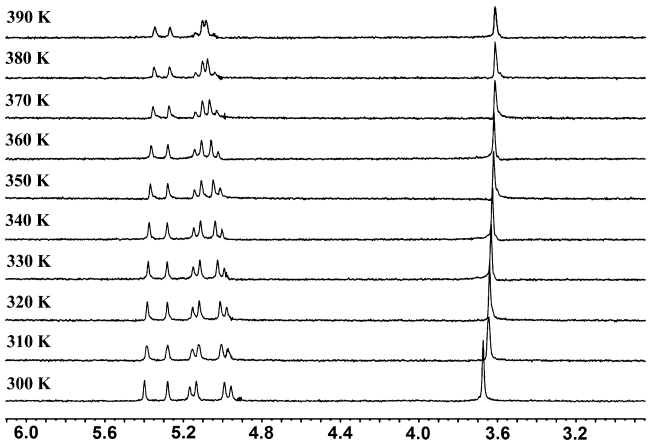


Figure 2. Partial ^{1}H NMR spectra of **8a** (*o*-$C_6D_4Cl_2$, 300 MHz) at various temperatures.

the *trans*-isomer **8a** were gradually changed to one set of doublet signals above 370 K, which meant that the rigid conformation of **8a** was no longer existed at very high temperature. But in the case of *cis*-isomer **8b**, no obvious changes in the methylene proton signals were observed with increasing the temperature up to 380 K (Figure 3). These results indicated that the structure of the *cis*-isomer is more rigid than that of the *trans*-isomer. For the macrocycles **17a** and **17b**, because the two *p*-phenyl-substituted benzene rings were linked together by crown ether chains and could not rotate freely; consequently, their conformations kept fixation up to 380 K (see the Supporting Information).

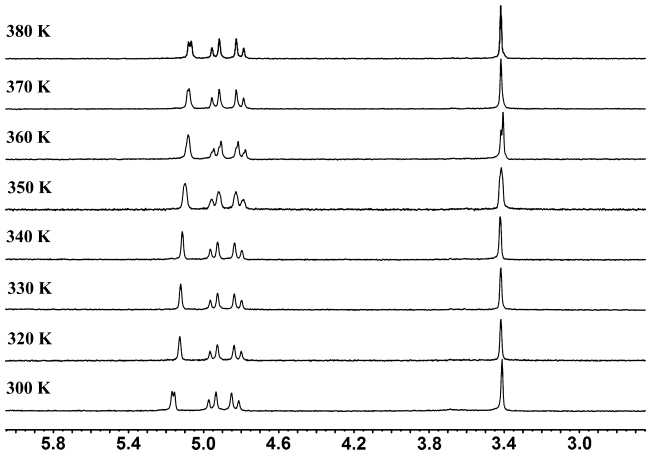


Figure 3. Partial ^{1}H NMR spectra of **8b** (*o*-$C_6D_4Cl_2$, 300 MHz) at various temperatures.

dx.doi.org/10.1021/jo302459m | J. Org. Chem. 2013, 78, 981−987

Structures of the Macrocyclic Molecules in the Solid State. To investigate the structures of the macrocyclic isomers in the solid state, we obtained single crystals of **7a** and **7b** suitable for X-ray diffraction analysis. The crystal structures clearly showed that compounds **7a** and **7b** are a pair of diastereomers, in which **7a** is a *trans* isomer with chairlike conformation while **7b** is a *cis* isomer with a boatlike conformation (Figure 4). These results are consistent with those in solution. For *trans*-isomer **7a**, it was found that the two *tert*-butylphenol rings are nearly parallel each other and the alkoxyl groups point to the center of the cavity. The centroid distances between two pairs of face-to-face paralleled benzene rings of the triptycene subunits are 11.55 and 10.18 Å, respectively. For *cis*-isomer **7b**, the dihedral angle between the two *tert*-butylphenol rings is 136.03° and the alkoxyl groups also point to the center of the cavity, while the dihedral angles between two pairs of face-to-face benzene rings of the triptycene subunits are 38.27° and 58.40°, respectively, and the macrocycle has a boatlike conformation with a cavity cross-section from 10.07 × 12.83 Å (narrower rim) to 10.48 × 15.00 Å (wider rim).

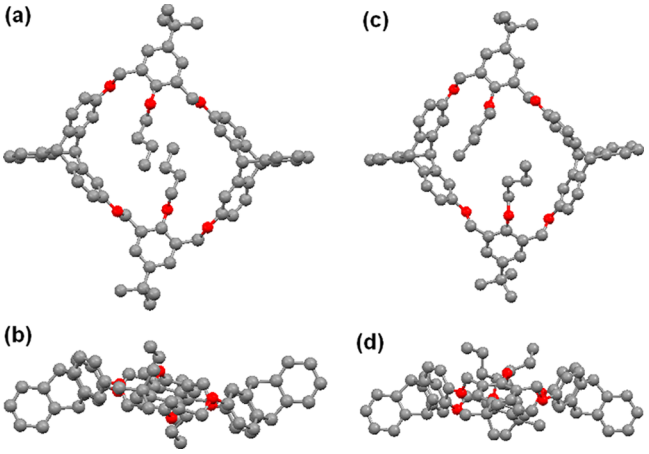


Figure 4. Crystal structures: (a) top view and (b) side view of **7a**; (c) top view and (d) side view of **7b**. Solvent molecules and hydrogen atoms are omitted for clarity.

We also obtained a single crystal of macrocycle **9a** suitable for X-ray diffraction analysis by vapor diffusion of diisopropyl ether into a solution of **9a** in $CHCl_3$. The crystal structure showed that the macrocycle is a *trans*-isomer with a chairlike conformation (Figure 5a), which is also consistent with the result in solution. Moreover, we further studied the self-assembly of homooxacalixarene analogue **9a** in the solid state. As shown in Figure 5, macrocyclic molecule **9a** could form a tubular assembly[9e,11] with the aromatic rings as the wall (Figure 5b), and further 3D microporous architecture (Figure 5c) viewed along the *a*-axis by a pair of intermolecular complementary C−H···π ($d_{C-H\cdots\pi}$ = 2.86 and 2.89 Å) interactions between the aromatic proton of the triptycene moiety of one molecule and the aromatic ring of the triptycene moiety of its adjacent molecule, and another C−H···π interactions ($d_{C-H\cdots\pi}$ = 2.86 Å) between the proton of the bridging methylene and the aromatic ring of the *p*-phenyl moiety of its adjacent molecule.

Complexation with Fullerenes C_{60} and C_{70}. After the triptycene-derived homooxacalixarene analogues with fixed conformations and large electron-rich cavities were established, we further investigated their complexation properties toward fullerenes C_{60} and C_{70}. Consequently, the complexation properties of macrocycle **9b** toward fullerenes C_{60} and C_{70}

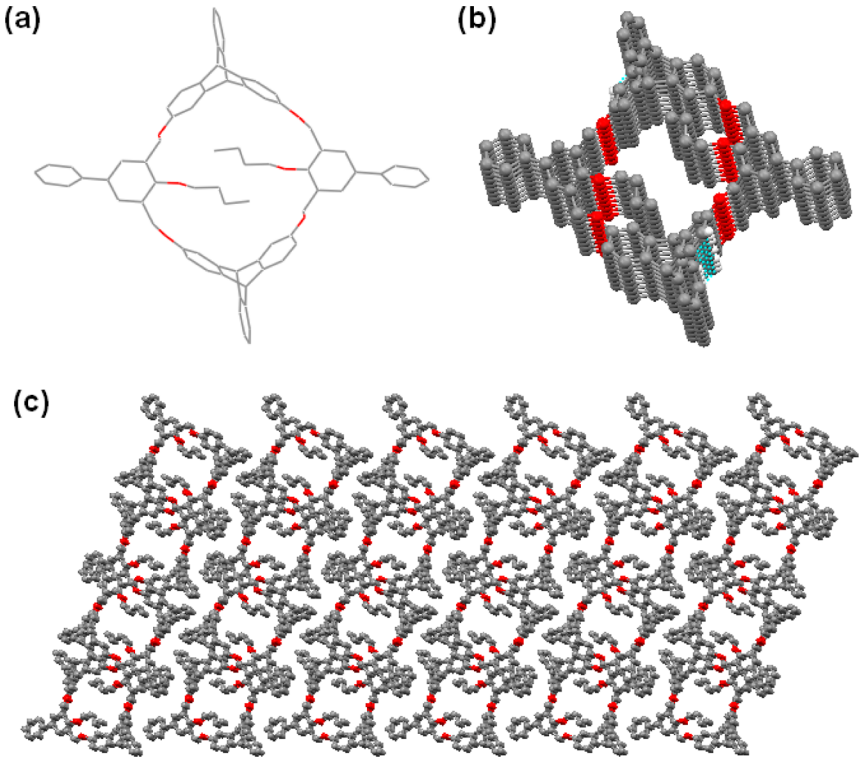


Figure 5. (a) Crystal structure of **9a**. (b) Tubular assembly and (c) the 3D microporous architecture of **9a** viewed along the *a*-axis. Solvent molecules and hydrogen atoms are omitted for clarity.

dx.doi.org/10.1021/jo302459m | *J. Org. Chem.* 2013, 78, 981−987

were first tested by fluorescence methods. As shown in Figure 6a, the fluorescence of **9b** in toluene decreased constantly with

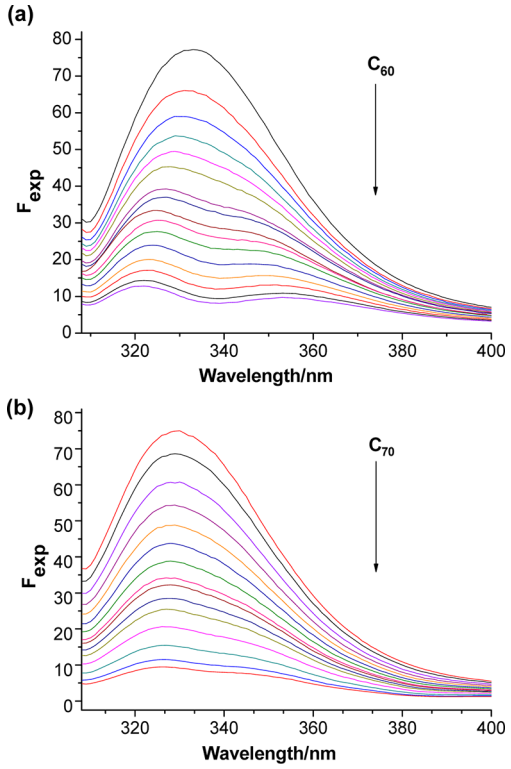


Figure 6. (a) Emission spectra (λ_{ex} = 293 nm) of **9b** (1×10^{-5} mol dm^{-3}) in the presence of C_{60} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 equiv) at 298 K in toluene. (b) Emission spectra (λ_{ex} = 293 nm) of **9b** (1×10^{-5} mol dm^{-3}) in the presence of C_{70} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 equiv) at 298 K in toluene.

increasing amount of C_{60}. A Job plot and fluorescence titration experiments showed that a 1:1 complex between **9b** and C_{60} was formed, and the association constant K_a of complex **9b**·C_{60} was calculated from a plot of F_0/F_{cal} vs C_{60} concentration to be $(1.50 \pm 0.09) \times 10^5$ M^{-1}. Similar to the case of C_{60}, macrocycle **9b** formed a 1:1 host/guest complex with C_{70} as well, and the association constant of $(1.44 \pm 0.09) \times 10^5$ M^{-1} for complex **9b**·C_{70} was obtained (Figure 6b). Similarly, it was found that the homooxacalixarene analogues **9a**, **6a** and **6b**, **7a** and **7b**, and **8a** and **8b** could all show strong affinities toward both C_{60} and C_{70}, and they could all form 1:1 complexes with the fullerenes.[5a,9j] As shown in Table 1, the different substituents of the macrocycles seemed to have no obvious influence on the affinity and selectivity toward fullerenes, which implied that the fluorescence changes mainly resulted from the interaction between the macrocyclic skeleton and the fullerenes. Moreover, it was also found that in most cases, the *cis*-isomers showed a little larger affinity toward C_{60} while the *trans*-isomers have larger affinity toward C_{70}, which might be due to the relative symmetrical cavities of the *cis*-isomers to fit well with the sphere C_{60} and the relative flat cavities of the *trans*-isomers to fit well with the oval C_{70}.

Table 1. Association Constants for the 1:1 Complexation between the Host Molecules and Fullerenes C_{60} and C_{70}

	K_a (1:1 complex with C_{60})	K_a (1:1 complex with C_{70})
6a	$(1.01 \pm 0.02) \times 10^5$	$(1.05 \pm 0.04) \times 10^5$
6b	$(1.18 \pm 0.05) \times 10^5$	$(1.10 \pm 0.04) \times 10^5$
7a	$(0.96 \pm 0.03) \times 10^5$	$(1.25 \pm 0.06) \times 10^5$
7b	$(1.15 \pm 0.03) \times 10^5$	$(1.06 \pm 0.03) \times 10^5$
8a	$(1.04 \pm 0.05) \times 10^5$	$(1.11 \pm 0.04) \times 10^5$
8b	$(1.13 \pm 0.04) \times 10^5$	$(1.14 \pm 0.04) \times 10^5$
9a	$(1.28 \pm 0.04) \times 10^5$	$(1.48 \pm 0.07) \times 10^5$
9b	$(1.50 \pm 0.09) \times 10^5$	$(1.44 \pm 0.09) \times 10^5$

CONCLUSION

In summary, four pairs of novel triptycene-derived homooxacalixarene analogues have been conveniently synthesized by a one-pot approach. Similarly, two pairs of "basket-like" triptycene-derived homooxacalixarene analogues in which the two *p*-phenyl-substituted benzene rings were linked together by crown ether chains were designed and synthesized as well. The structural studies revealed that the macrocyclic molecules have well-defined structures in both solution and solid state. Moreover, the macrocycles showed fixed conformations even at high temperatures by the variable-temperature ^{1}H NMR experiments owing to the introduction of the triptycene moiety with a rigid 3D structure. We also found that macrocyclic molecule **9a** could form a tubular assembly with the aromatic rings as the wall, and further 3D microporous architecture in the solid state. Furthermore, it was found that macrocycles **6**–**9** showed efficient complexation abilities toward fullerenes C_{60} and C_{70}. We believe that these novel triptycene-derived homooxacalixarene analogues could find more applications in molecular recognition and molecular assembly, which are underway in our laboratory.

EXPERIMENTAL SECTION

Compounds 6a and 6b. Under an argon atmosphere, a mixture of 2,7-dihydroxytriptycene (286 mg, 1 mmol), **2** (350 mg, 1 mmol), and Cs_2CO_3 (1.30 g, 4 mmol) in dry DMF (100 mL) was stirred at 60 °C for 48 h. The mixture was cooled to room temperature, and the solvent was removed. The crude residue was dissolved in a mixture of CH_2Cl_2 and water. The organic layer was separated, washed with water and then brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel with CH_2Cl_2/petroleum ether as eluent to give the products **6a** (85 mg, 18%) and **6b** (104 mg, 22%) as white solids. **6a**. Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (s, 18H), 3.55 (s, 6H), 4.83 (d, J = 9.6 Hz, 4H), 4.98 (d, J = 9.7 Hz, 4H), 5.20 (s, 2H), 5.30 (s, 2H), 6.57 (dd, J = 2.1, 8.0 Hz, 4H), 6.99–7.01 (m, 8H), 7.23–7.26 (m, 4H), 7.35–7.41 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.4, 34.4, 52.4, 54.3, 63.8, 66.5, 108.7, 112.6, 123.2, 123.7, 125.0, 125.3, 129.1, 129.7, 138.2, 144.7, 145.9, 146.7, 147.0, 156.5, 156.8. MALDI-TOF MS: m/z 971.6 $[M + Na]^+$. Anal. Calcd for $C_{66}H_{60}O_6 \cdot H_2O$: C, 81.96; H, 6.46. Found: C, 81.91; H, 6.50. **6b**. Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 18H), 3.67 (s, 6H), 4.94 (d, J = 11.5 Hz, 4H), 5.09 (d, J = 11.5 Hz, 4H), 5.20 (s, 2H), 5.29 (s, 2H), 6.59 (d, J = 7.2 Hz, 4H), 6.99–7.01 (m, 8H), 7.21–7.25 (m, 4H), 7.34–7.38 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.3, 34.3, 52.4, 54.4, 63.1, 66.3, 111.0, 112.0, 123.1, 123.6, 123.8, 124.9, 125.2, 127.8, 129.6, 138.4, 144.8, 145.9, 146.7, 146.9, 155.1, 156.3. MALDI-TOF MS: m/z 971.6 $[M + Na]^+$. Anal. Calcd for $C_{66}H_{60}O_6 \cdot 2H_2O$: C, 80.46; H, 6.55. Found: C, 80.23; H, 6.51.

Compounds 7a and 7b. Starting from **1** (286 mg, 1 mmol) and **3** (392 mg, 1 mmol), following the same procedure for the synthesis of **6**, compounds **7a** (103 mg, 20%) and **7b** (119 mg, 23%) were obtained. **7a**. Mp: 174–176 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, J = 7.7 Hz, 6H), 1.22 (s, 18H), 1.34–1.42 (m, 4H), 1.59–1.66 (m, 4H), 3.71 (t, J = 6.2 Hz, 4H), 4.96 (d, J = 11.9 Hz, 4H), 5.07 (d, J = 11.9 Hz, 4H), 5.16 (s, 2H), 5.27 (s, 2H), 6.58 (dd, J = 2.0, 7.9 Hz,

dx.doi.org/10.1021/jo302459m | J. Org. Chem. 2013, 78, 981–987

4H), 6.95−7.01 (m, 8H), 7.20−7.23 (m, 4H), 7.30−7.36 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 19.3, 31.3, 32.3, 34.3, 52.4, 54.5, 66.0, 75.4, 111.2, 112.1, 123.1, 123.5, 123.7, 124.9, 125.2, 127.2, 129.7, 138.3, 144.9, 146.0, 146.6, 146.7, 153.3, 156.3. MALDI-TOF MS: m/z 1055.7 $[M + Na]^+$. Anal. Calcd for $C_{72}H_{72}O_6{\cdot}H_2O$: C, 82.25; H, 7.09. Found: C, 82.11; H, 7.32. **7b**. Mp: 282−283 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.39 (t, J = 7.3 Hz, 6H), 0.80−0.87 (m, 4H), 1.22−1.25 (m, 4H), 1.25 (s, 18H), 3.65 (t, J = 6.8 Hz, 4H), 4.87 (d, J = 10.4 Hz, 4H), 5.02 (d, J = 10.4 Hz, 4H), 5.20 (s, 2H), 5.28 (s, 2H), 6.57 (dd, J = 2.2, 8.0 Hz, 4H), 6.99 (br, s, 8H), 7.20−7.23 (m, 4H), 7.35−7.38 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 18.8, 31.4, 32.1, 34.4, 52.4, 54.5, 66.1, 76.1, 109.6, 112.1, 123.1, 123.7, 124.9, 125.3, 128.5, 129.6, 138.2, 144.8, 146.0, 146.7, 146.8, 154.7, 156.5. MALDI-TOF MS: m/z 1055.7 $[M + Na]^+$. Anal. Calcd for $C_{72}H_{72}O_6$: C, 83.69; H, 7.02. Found: C, 83.53; H, 7.20.

Compounds 8a and 8b. Starting from **1** (286 mg, 1 mmol) and **4** (370 mg, 1 mmol), following the same procedure for the synthesis of **6**, compounds **8a** (79 mg, 16%) and **8b** (99 mg, 20%) were obtained. **8a**. Mp: 222−224 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.64 (s, 6H), 4.92 (d, J = 10.0 Hz, 4H), 5.06 (d, J = 10.0 Hz, 4H), 5.23 (s, 2H), 5.32 (s, 2H), 6.60 (dd, J = 2.4, 8.0 Hz, 4H), 7.00−7.02 (m, 8H), 7.25−7.28 (m, 4H), 7.31−7.33 (m, 2H), 7.37−7.42 (m, 8H), 7.53−7.56 (m, 4H), 7.64 (br, s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.4, 54.3, 63.9, 65.9, 108.9, 112.4, 123.2, 123.7, 123.8, 125.0, 125.3, 127.0, 127.2, 128.7, 130.4, 130.8, 137.4, 138.2, 140.1, 144.6, 145.8, 146.7, 156.3, 158.0. MALDI-TOF MS: m/z 1011.5 $[M + Na]^+$. Anal. Calcd for $C_{70}H_{52}O_6{\cdot}0.5H_2O$: C, 84.23; H, 5.35. Found: C, 83.98; H, 5.57. **8b**. Mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 6H), 5.03 (d, J = 11.9 Hz, 4H), 5.16 (d, J = 11.9 Hz, 4H), 5.23 (s, 2H), 5.29 (s, 2H), 6.61 (dd, J = 2.4, 8.0 Hz, 4H), 6.96−7.03 (m, 8H), 7.22−7.24 (m, 4H), 7.30−7.40 (m, 10H), 7.47−7.50 (m, 4H), 7.60 (br, s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.4, 54.3, 64.0, 65.9, 108.9, 112.4, 123.2, 123.7, 123.8, 125.0, 125.3, 127.1, 127.2, 128.7, 130.4, 130.8, 137.4, 138.3, 140.1, 144.6, 145.9, 146.7. MALDI-TOF MS: m/z 1011.5 $[M + Na]^+$. Anal. Calcd for $C_{70}H_{52}O_6{\cdot}0.5H_2O$: C, 84.23; H, 5.35. Found: C, 84.11; H, 5.38.

Compounds 9a and 9b. Starting from **1** (286 mg, 1 mmol) and **5** (412 mg, 1 mmol), following the same procedure for the synthesis of **6**, compounds **9a** (101 mg, 19%) and **9b** (123 mg, 23%) were obtained. **9a**. Mp: 105−107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, J = 7.3 Hz, 6H), 1.26−1.41 (m, 4H), 1.60−1.67 (m, 4H), 3.74 (t, J = 6.5 Hz, 4H), 5.04 (d, J = 12.4 Hz, 4H), 5.14 (d, J = 12.4 Hz, 4H), 5.19 (s, 2H), 5.28 (s, 2H), 6.60 (dd, J = 2.2, 8.0 Hz, 4H), 6.96−7.01 (m, 8H), 7.21−7.37 (m, 14H), 7.43−7.46 (m, 4H), 7.58 (br, s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 19.2, 32.3, 52.5, 54.5, 65.7, 75.5, 111.3, 111.9, 123.2, 123.5, 123.8, 124.9, 125.3, 127.0, 127.1, 128.5, 128.7, 131.0, 137.2, 138.5, 140.4, 144.9, 146.0, 146.7, 154.8, 156.3. MALDI-TOF MS: m/z 1095.3 $[M + Na]^+$. Anal. Calcd for $C_{76}H_{64}O_6{\cdot}0.5H_2O$: C, 84.34; H, 6.05. Found: C, 84.48; H, 6.08. **9b**. Mp: 205−206 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.54 (t, J = 7.3 Hz, 6H), 0.97−1.09 (m, 4H), 1.35−1.45 (m, 4H), 3.73 (t, J = 6.6 Hz, 4H), 4.97 (d, J = 11.3 Hz, 4H), 5.10 (d, J = 11.2 Hz, 4H), 5.22 (s, 2H), 5.29 (s, 2H), 6.58 (dd, J = 2.0, 8.0 Hz, 4H), 6.95−6.99 (m, 8H), 7.20−7.35 (m, 14H), 7.45−7.47 (m, 4H), 7.58 (br, s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 18.9, 32.1, 52.4, 54.4, 65.2, 76.2, 109.7, 111.9, 123.1, 123.6, 123.7, 124.9, 125.3, 127.0, 127.1, 128.6, 129.3, 130.8, 137.4, 138.2, 140.1, 144.8, 146.0, 146.6, 155.7, 156.2. MALDI-TOF MS: m/z 1095.3 $[M + Na]^+$. Anal. Calcd for $C_{76}H_{64}O_6$: C, 85.05; H, 6.01. Found: C, 84.79; H, 6.23.

Compound 12. A mixture of 2,5-dihydroxymethyl-4-phenylphenol (1.15 g, 5 mmol), the bistosylate **10** (1.145 g, 2.5 mmol), and K_2CO_3 (2.76 g, 20 mmol) in CH_3CN (100 mL) was refluxed for 12 h. The resulting mixture was cooled to room temperature and the solvent was removed under vacuum, and the residue was chromatographed on a silica gel column with a mixture of CH_2Cl_2 and ethyl acetate as the mobile phase to give pure **12** (1.09 g, 76%) as a white solid. Mp: 139−140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.51 (br, s, 4H) 3.81 (br, s, 4H), 3.87−3.90 (m, 4H), 4.21−4.23 (m, 4H), 4.74 (s, 8H), 7.28−7.33 (m, 2H), 7.37−7.42 (m, 4H), 7.50−7.55 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 61.1, 70.5, 70.7, 73.7, 126.9, 127.2, 128.2, 128.7, 134.5, 137.4, 140.3, 155.0. MALDI-TOF MS: m/z 597.3 $[M + Na]^+$. Anal. Calcd for $C_{34}H_{38}O_8$: C, 71.06; H, 6.67. Found: C, 70.75; H, 6.69.

Compound 13. Following the same procedure for the synthesis of **12**, compound **13** (73%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.48 (br, s, 4H), 3.66 (br, s, 8H) 3.70−3.73 (m, 4H), 4.00−4.02 (m, 4H), 4.65 (s, 8H), 7.27−7.29 (m, 2H), 7.33−7.37 (m, 4H), 7.46−7.51 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 60.8, 70.4, 70.5, 70.6, 73.6, 126.9, 127.1, 127.8, 128.7, 134.6, 137.2, 140.3, 154.8. MALDI-TOF MS: m/z 641.3 $[M + Na]^+$. Anal. Calcd for $C_{36}H_{42}O_9$ ·0.6CH_2Cl_2: C, 65.64; H, 6.50. Found: C, 65.70; H, 6.54.

Compound 14. At room temperature, PBr_3 (5.0 mmol) in $CHCl_3$ (20 mL) were added dropwise to a solution of compound **12** (2.30 g, 4 mmol) in $CHCl_3$ (150 mL) in 0.5h. The resulting mixture was stirred at room temperature for another 3h. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a mixture of petroleum ether and CH_2Cl_2 as the mobile phase to give pure **14** (2.81 g, 85%) as a white solid. Mp: 117−119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90 (br, s, 4H), 3.98−4.01 (m, 4H), 4.35−4.38 (m, 4H), 4.71 (s, 8H), 7.33−7.38 (m, 2H), 7.41−7.46 (m, 4H), 7.54−7.59 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.0, 70.6, 71.2, 74.2, 127.0, 127.6, 128.9, 130.9, 132.4, 138.2, 139.5, 154.6. MALDI-TOF MS: m/z 848.9 $[M + Na]^+$. Anal. Calcd for $C_{34}H_{34}Br_4O_4$: C, 49.42; H, 4.15. Found: C, 49.73; H, 4.23.

Compound 15. Following the same procedure for the synthesis of **14**, compound **15** (85%) was obtained as a white solid. Mp: 79−81 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83−3.84 (m, 8H) 3.94−3.97 (m, 4H), 4.33−4.35 (m, 4H), 4.69 (s, 8H), 7.32−7.37 (m, 2H), 7.40−7.45 (m, 4H), 7.53−7.58 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.9, 70.3, 70.8, 70.9, 74.0, 126.8, 127.5, 128.7, 130.7, 132.3, 138.0, 139.3, 154.4. MALDI-TOF MS: m/z 893.0 $[M + Na]^+$, 908.9 $[M + K]^+$. Anal. Calcd for $C_{36}H_{38}Br_4O_5{\cdot}0.6CH_2Cl_2$: C, 47.72; H, 4.29. Found: C, 47.53; H, 4.20.

Compounds 16a and 16b. Under an argon atmosphere, a mixture of 2,7-dihydroxytriptycene **1** (286 mg, 1 mmol), compound **14** (413 mg, 0.5 mmol), and Cs_2CO_3 (1.30 g, 4 mmol) in dry DMF (100 mL) was stirred at 60 °C for 48 h. The mixture was cooled down to room temperature, and the solvent was removed. The crude residue was dissolved in CH_2Cl_2 and water. The organic layer was separated, washed with water and brine, dried over Na_2SO_4, and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel with CH_2Cl_2/petroleum ether as eluent to give the products **16a** (43 mg, 8%) and **16b** (199 mg, 37%) as white solids. **16a**. Mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (m, 2H), 2.30 (m, 2H), 3.03 (m, 4H), 3.84 (m, 4H), 4.80 (d, J = 9.3 Hz, 4H), 5.14 (d, J = 9.4 Hz, 4H), 5.19 (s, 2H), 5.31 (s, 2H), 6.58 (dd, J = 2.1, 7.9 Hz, 4H), 6.95−7.01 (m, 8H), 7.25−7.45 (m, 14H), 7.59−7.61 (m, 4H), 7.67 (br,s, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 30.1, 52.7, 67.3, 70.4, 70.8, 75.8, 111.4, 112.4, 123.5, 124.0, 124.2, 125.3, 125.7, 127.3, 127.7, 129.2, 130.4, 131.5, 137.5, 139.0, 140.4, 145.1, 146.3, 147.3, 156.8, 157.1. MALDI-TOF MS: m/z 1097.7 $[M + Na]^+$. Anal. Calcd for $C_{74}H_{58}O_8{\cdot}0.1CH_2Cl_2$: C, 82.12; H, 5.41. Found: C, 82.00; H, 5.48. **16b**. Mp: >300 °C . ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.80−2.82 (m, 2H), 3.11−3.24 (m, 6H), 3.89−3.93 (m, 4H), 5.01 (d, J = 10.7 Hz, 4H), 5.14 (d, J = 10.7 Hz, 4H), 5.23 (s, 2H), 5.30 (s, 2H), 6.60 (dd, J = 2.3, 8.0 Hz, 4H), 6.94−7.03 (m, 8H), 7.23−7.25 (m, 4H), 7.28−7.42 (m, 10H), 7.53−7.56 (m, 4H), 7.65 (br, s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.4, 54. 5, 66.8, 70.1, 70.5, 75.4, 110.9, 112.0, 123.2, 123.7, 123.8, 125.0, 125.4, 127.1, 127.3, 128.8, 130.3, 131.0, 137.4, 138.6, 140.2, 144.6, 145.7, 146.9, 156.4, 156.6. MALDI-TOF MS: m/z 1097.7 $[M + Na]^+$. Anal. Calcd for $C_{74}H_{58}O_8$: C, 82.66; H, 5.44. Found: C, 82.31; H, 5.63.

Compounds 17a and 17b. From starting materials **1** (286 mg,1 mmol) and **15** (435 mg, 0.5 mmol), following the same procedure for the synthesis of **16**, compounds **17a** (117 mg, 21%) and **17b** (128 mg, 23%) were obtained as white solids. **17a**. Mp: 269−271 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.99−3.00 (m, 4H), 3.09 (brs, 8H), 3.84 (m, 4H), 4.82 (d, J = 9.7 Hz, 4H), 5.21 (d, J = 8.3 Hz, 4H), 5.22 (s, 2H), 5.30 (s, 2H), 6.58 (dd, J = 2.0, 8.0 Hz, 4H), 6.98−7.00 (m, 8H), 7.23−7.26 (m, 4H), 7.29−7.44 (m, 10H), 7.57−7.60 (m, 4H), 7.66 (brs, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.3, 54.3, 65.8, 69.5, 70.0, 70.5,

dx.doi.org/10.1021/jo302459m | J. Org. Chem. 2013, 78, 981−987

75.2, 108.4, 112.6, 123.1, 123.6, 123.6, 124.9, 125.3, 127.0, 127.2, 128.7, 130.8, 137.4, 138.2, 140.0, 144.5, 145.8, 146.7, 156.4, 157.0. MALDI-TOF MS: m/z 1141.6 $[M + Na]^+$. Anal. Calcd for $C_{76}H_{62}O_9 \cdot 0.1CH_2Cl_2$: C, 81.04; H, 5.56. Found: C, 81.11; H, 5.71. **17b**. Mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.20−3.26 (m, 6H), 3.35−3.47 (m, 4H), 3.56−3.62 (m, 2H), 3.70−3.84 (m, 4H), 5.06 (d, J = 11.5 Hz, 4H), 5.13 (d, J = 11.5 Hz, 4H), 5.23 (s, 2H), 5.29 (s, 2H), 6.64 (dd, J = 2.4, 8.0 Hz, 4H), 6.94−7.03 (m, 8H), 7.23−7.25 (m, 4H), 7.28−7.42 (m, 10H), 7.53−7.56 (m, 4H), 7.65 (br, s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.4, 54.3, 66.3, 69. 9, 70.5, 70.6, 74.6, 111.1, 112.4, 123.2, 123.6, 123.8, 125.0, 125.3, 127.0, 127.2, 128.7, 129.3, 131.0, 137.4, 138.7, 140.3, 144.6, 145.7, 146.8, 155.2, 156.5. MALDI-TOF MS: m/z 1141.6 $[M + Na]^+$. Anal. Calcd for $C_{76}H_{62}O_9 \cdot 0.6CH_2Cl_2$: C, 78.62; H, 5.44. Found: C, 78.50; H, 5.67.

Crystal Data for 7a. $C_{72}H_{72}O_6$, M_w = 1033.30, trigonal, space group R-3, a = 38.388(1) Å, b = 38.388 (1) Å, c = 12.218(2) Å, α = 90.00(1)°, β = 90.00(1)°, γ = 120.00(15)°, V = 15593(3) Å^3, Z = 9, D = 0.99 Mg m^{-3}, T = 173(2) K, 46470 reflections measured, 7907 unique (R_{int} = 0.0935), final R indices [$I > 2\sigma(I)$]: R_1 = 0.1550, wR_2 = 0.3120, R indices (all data): R_1 = 0.1742, wR_2 = 0.3246.

Crystal Data for 7b. $C_{72}H_{72}O_6$, M_w = 1033.30, triclinic, space group P-1, a = 12.299(3) Å, b = 16.054(3) Å, c = 17.763(4) Å, α = 81.15(3)°, β = 88.58(3)°, γ = 74.64(3)°, V = 3341.2(12) Å^3, Z = 2, D = 1.027 Mg m^{-3}, T = 173(2) K, 43959 reflections measured, 15246 unique (R_{int} = 0.0563), final R indices [$I > 2\sigma(I)$]: R_1 = 0.0840, wR_2 = 0.2302, R indices (all data): R_1 = 0.1092, wR_2 = 0.2483.

Crystal Data for 9a. $C_{78}H_{66}Cl_6O_6$, M_w = 1312.01, triclinic, space group P-1, a = 8.884(2) Å, b = 17.286(5) Å, c = 23.428(6) Å, α = 109.558(3)°, β = 90.173(5)°, γ = 100.381(6)°, V = 3326.7(16) Å^3, Z = 2, D = 1.310 Mg m^{-3}, T = 173(2) K, 36598 reflections measured, 11725 unique (R_{int} = 0.0675), final R indices [$I > 2\sigma(I)$]: R_1 = 0.1084, wR_2 = 0.2376, R indices (all data): R_1 = 0.1367, wR_2 = 0.2545.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of new compounds. Variable-temperature ^{1}H NMR spectra of **17a** and **17b**. Fluorescence titrations of **6**−**9** with C_{60} and C_{70}. X-ray crystallographic files (CIF) for compounds **7a**, **7b**, and **9a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cchen@iccas.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (20972162, 91127009) and the National Basic Research Program (2011CB932501) for financial support.

■ REFERENCES

(1) (a) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, D., MacNicol, D. D., Vögtle, F., Lehn, J.-M., Eds.; Elsevier: Amsterdam, 1996. (b) Pedersen, C. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1021. (c) Cram, D. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1009. (d) Lehn, J.-M. *Angew. Chem., Int. Ed.* **1988**, *27*, 89.

(2) (a) Gutsche, C. D. *Calixarenes Revisited*; The Royal Society of Chemistry: Cambridge, 1998. (b) *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Saadioui, M., Eds.; Kluwer Academic Publishers: Amsterdam, 2001.

(3) For reviews of heterocalixarenes, see: (a) König, B.; Fonseca, M. H. *Eur. J. Inorg. Chem.* **2000**, 2303. (b) Wang, M. X. *Chem. Commun.* **2008**, 4541. (c) Maes, W.; Dehaen, W. *Chem. Soc. Rev.* **2008**, *37*, 2393. (d) Wang, M. X. *Acc. Chem. Res.* **2012**, *45*, 182.

(4) For some recent examples on oxacalixarenes, 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) Li, X. H.; Upton, T. G.; Gibb, C. L. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2003**, *125*, 650. (g) 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. (h) Zhu, Y. P.; Yuan, J. J.; Li, Y. T.; Gao, M.; Cao, L. P.; Ding, J. Y.; Wu, A. X. *Synlett* **2011**, *1*, 52. (i) Ma, M. L.; Wang, H. X.; Li, X. Y.; Liu, L. Q.; Jin, H. S.; Wen, K. *Tetrahedron* **2009**, *65*, 300. (j) Ma, M. L.; Li, X.-Y.; Wen, K. *J. Am. Chem. Soc.* **2009**, *131*, 8338−8339. (k) Li, S.; Fa, S. X.; Wang, Q. Q.; Wang, D. X.; Wang, M. X. *J. Org. Chem.* **2012**, *77*, 1860.

(5) Some examples on azacalixarenes: (a) Wang, M. X.; Zhang, X. H.; Zheng, Q. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 838. (b) Gong, H. Y.; Zhang, X. H.; Wang, D. X.; Zheng, Q. Y.; Wang, M. X. *Chem.—Eur. J.* **2006**, *12*, 9262. (c) Gong, H. Y.; Zheng, Q. Y.; Wang, D. X.; Wang, M. X. *Org. Lett.* **2006**, *8*, 4895. (d) Tsue, H.; Ishibashi, K.; Takahashi, H.; Tamura, R. *Org. Lett.* **2005**, *7*, 11. (e) Ishibashi, K.; Tsue, H.; Tokita, S.; Matsui, K.; Takahashi, H.; Tamura, R. *Org. Lett.* **2006**, *8*, 5991. (f) Wang, L. X.; Wang, D. X.; Huang, Z. T.; Wang, M. X. *J. Org. Chem.* **2010**, *75*, 741.

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

(7) (a) Masci, B.; Finelli, M.; Varrone, M. *Chem.—Eur. J.* **1998**, 2018. (b) Ibach, S.; Prautzsch, V.; Vögtle, F. *Acc. Chem. Res.* **1999**, *32*, 729. (c) Thomas, J.; Van Hecke, K.; Robeyns, K.; Van Rossom, W.; Van Meervelt, L.; Smet, M.; Maes, W.; Dehaen, W. *Chem.—Eur. J.* **2011**, *17*, 10339. (d) Chen, Y.; Wang, D, X.; Wang, M. X. *J. Org. Chem.* **2010**, *75*, 3786.

(8) (a) Chen, C.-F. *Chem. Commun.* **2011**, *47*, 1674. (b) Jiang, Y.; Chen, C.-F. *Eur. J. Org. Chem.* **2011**, *32*, 6377. (c) Chen, C.-F.; Han, T.; Jiang, Y. *Chin. Sci. Bull.* **2007**, *52*, 1349.

(9) (a) Zhu, X.-Z.; Chen, C.-F. *J. Am. Chem. Soc.* **2005**, *127*, 13158. (b) Zong, Q.-S.; Chen, C.-F. *Org. Lett.* **2006**, *8*, 211. (c) Zhu, X.-Z.; Chen, C.-F. *Chem.—Eur. J.* **2006**, *12*, 5603. (d) Peng, X.-X.; Lu, H.-Y.; Han, T.; Chen, C.-F. *Org. Lett.* **2007**, *9*, 895. (e) Zhang, C.; Chen, C.-F. *J. Org. Chem.* **2007**, *72*, 3880. (f) Xue, M.; Chen, C.-F. *Chem. Commun.* **2008**, 6128. (g) Xue, M.; Chen, C.-F. *Org. Lett.* **2009**, *11*, 5294. (h) Tian, X.-H.; Chen, C.-F. *Chem.—Eur. J.* **2010**, *16*, 8072. (i) Tian, X.-H.; Hao, X.; Chen, C.-F. *Org. Lett.* **2010**, *12*, 524. (j) Hu, S.-Z.; Chen, C.-F. *Chem. Commun.* **2010**, *46*, 4199.

(10) (a) Tsubaki, K.; Tanaka, K.; Kinoshita, T.; Fuji, K. *Chem. Commun.* **1998**, 895. (b) Ikeda, A.; Hatano, T.; Kawaguchi, M. *Chem. Commun.* **1999**, 1403. (c) Ikeda, A.; Yoshimura, M.; Udzu, H. *J. Am. Chem. Soc.* **1999**, *121*, 4296. (d) Ikeda, A.; Udzu, H.; Yoshimura, M. *Tetrahedron* **2000**, *56*, 1825. (e) Hirsh, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2326. (f) Kawase, T.; Kurata, H. *Chem. Rev.* **2006**, *106*, 5250. (g) Perez, E. M.; Martin, N. *Chem. Soc. Rev.* **2008**, *37*, 1512.

(11) (a) Semetey, V.; Didierjean, C.; Briand, J.-P.; Aubry, A.; Guichard, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1895. (b) Amorin, M.; Castedo, L.; Granja, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 2844. (c) Horne, W. S.; Stout, C. D.; Ghadiri, M. R. *J. Am. Chem. Soc.* **2003**, *125*, 9372.