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Triptycene-Derived Calix[6]arenes: Synthesis, Structures, and Their Complexation with Fullerenes C_{60} and C_{70}

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Abstract: Two pairs of novel triptycene-derived calix[6]arenes **4a**,**b** and **5a**,**b** have been efficiently synthesized through both one-pot and two-step fragment-coupling strategies starting from 2,7-bis(hydroxymethyl)-1,8-dimethoxytriptycene **1**. Subsequent demethylation of **4a**,**b** and **5a**,**b** with BBr_3 in dry dichloromethane gave the macrocyclic compounds **6a**,**b** and **7a**,**b**. Treatment of either **4a** or **6a** with $AlCl_3$ resulted in the same debutylated product **8**, while **9** was similarly obtained from either **5a** or **7a**. Structural studies revealed that all of the macrocycles have well-defined structures with fixed conformations both in solution and in the solid state owing to the introduction of the triptycene moiety with a rigid three-dimensional (3D) structure, making them very different from their classical calix[6]arene counterparts. As a consequence, it was found that all of these the triptycene-derived calix[6]arenes could encapsulate small neutral molecules in their cavities in the solid state. Moreover, it was also found that the macrocycles **4b** and **5b** showed highly efficient complexation abilities toward fullerenes C_{60} and C_{70}, forming 1:1 complexes with association constants ranging from $(5.22\pm0.20)\times10^4$ to $(8.68\pm0.30)\times10^4\,M^{-1}$.

Keywords: calixarenes · fullerenes · host–guest systems · synthesis design · triptycene

Introduction

The design and synthesis of new classes of hollow host compounds with inner cavities large enough to encapsulate organic guests is always an interesting and exciting research topic in supramolecular chemistry.[1] Among the various known types of macrocyclic molecules, calixarenes,[1,2] a class of well-defined phenol-derived cyclic oligomers bridged by methylene groups, have been the focus of considerable attention in the last two decades. However, it was noted that the cavities of calix[4]arenes are too small to complex common organic guests except some small solvent molecules, while calix[6]arenes and larger calixarenes have so many conformations that their cavities are also difficult to utilize.[3] Indeed, only through appropriate functionalization on both the lower and upper rims to fix the conformation were Arduini et al. able to show that triphenylureidocalix[6]arene derivatives could be used as "wheels" for the synthesis of pseudorotaxanes and rotaxanes.[4] Recently, Reinaud and co-workers reported a class of calix[6]arene-based ligands that could act as biomimetic molecular receptors.[5] However, experimental and theoretical studies have shown that calix[6]arenes display extreme conformational flexibility due to facile ring inversion of their aromatic units, which must be restricted in order to obtain suitably pre-organized subunits. For this reason, several research groups[6] have developed various strategies for the conformational restriction of calix[6]arenes, which have proven to be more difficult to implement for the larger cyclic oligomers.

Recently, we showed that triptycene derivatives with a rigid three-dimensional (3D) structure could be used as useful building blocks for the synthesis of different kinds of novel macrocyclic compounds with specific structures and properties.[7] We further envisaged that if one or more phenol group(s) in the classical calix[4]arene were to be replaced by appropriate triptycene moieties, a new class of triptycene-derived calixarenes with larger cavities and fixed conformations would be obtained. Consequently, we synthe-

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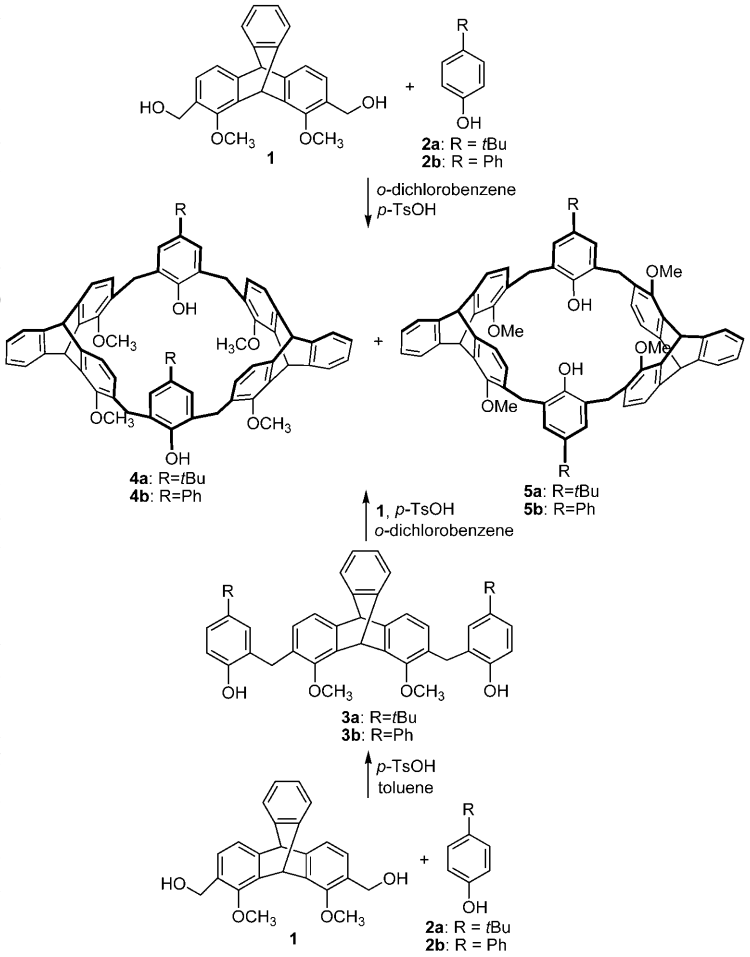
sized some novel triptycene-derived calix[6]arenes with fixed conformations and found that they formed tubular assemblies in the solid state.[8a] More recently, we also reported a series of triptycene-derived calix[5]arene derivatives with fixed cone conformations in solution and in the solid state.[8b] In this paper, we report: 1) the synthesis of a series of triptycene-derived calix[6]arene derivatives, 2) their well-defined structures with fixed conformations, 3) their encapsulation of small neutral molecules in the solid state, and 4) their highly efficient complexation abilities toward C_{60} and C_{70}.

Results and Discussion

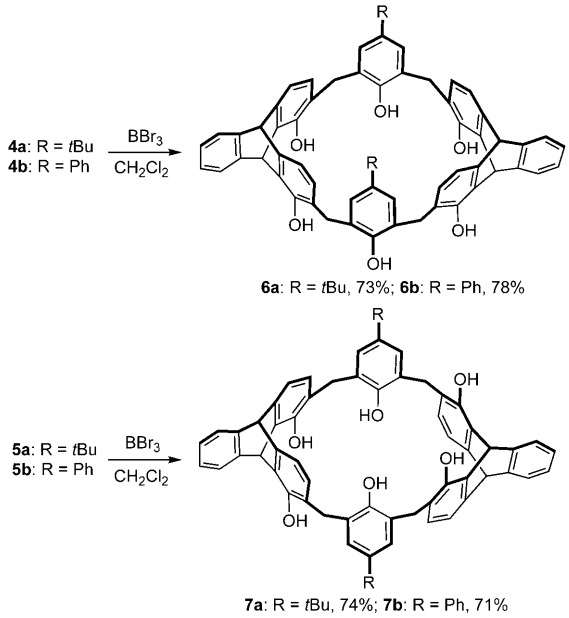
Synthesis of triptycene-derived calix[6]arenes: The synthesis of the triptycene-derived calix[6]arenes **4** and **5** is depicted in Scheme 1. We previously reported that the diastereomeric triptycene-derived calix[6]arenes **4a** and **5a** could be conveniently synthesized by one-pot reaction of the triptycene derivative **1** and *p-tert*-butylphenol in *o*-dichlorobenzene in the presence of 4-methylbenzenesulfonic acid.[8a] Following the same approach, the calix[6]arenes **4b** and **5b** were synthesized in 17 and 11% yield, respectively, by the one-pot reaction of **1** and *p*-phenylphenol. The macrocycles **4** and **5** could also be synthesized by a two-step fragment-coupling approach. As shown in Scheme 1, reaction of the triptycene derivative **1** with an excess of *p*-substituted phenol **2a** or **2b** in refluxing toluene in the presence of *p*-toluenesulfonic acid gave the trimers **3a** and **3b** in yields of 89 and 83%, respectively.[8b] The macrocycles **4** and **5** were then obtained in 17–25% yield by the reaction of **1** and **3** in *o*-dichlorobenzene in the presence of *p*-toluenesulfonic acid. Compared with the one-pot reaction, the ready accessibility of the [1+2] product **3** and the subsequent higher yields of the cyclization reactions, showed that the fragment-coupling method may be more practical for the preparation of the desired macrocycles.

Moreover, we found that treatment of **4a**,**b** and **5a**,**b** with BBr_3 in dry dichloromethane further afforded the demethylated compounds **6a**,**b** and **7a**,**b**, respectively, in high yields (Scheme 2). Treatment of **6a** and **7a** with $AlCl_3$ in toluene at room temperature resulted in the debutylated products **8** and **9** in yields of 61 and 54%, respectively. Under the same conditions, we also found that the macrocycles **4a** and **5a** could not only be debutylated, but also demethylated to yield **8** and **9** in moderate yields (Scheme 3). The new compounds were all characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

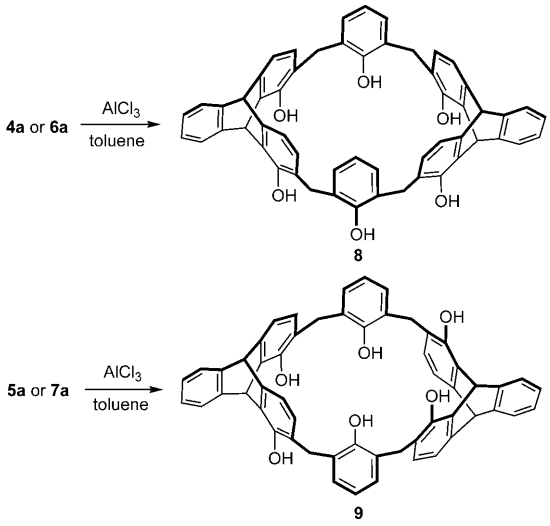
Structures of the triptycene-derived calix[6]arenes in solution: We have previously proved that the macrocycles **4a** and **5a** are a pair of diastereomers, with **4a** being a *cis* isomer with cone conformation and **5a** being a *trans isomer* with a chair conformation.[8a] Similarly, macrocycles **4b** and **5b** are also a pair of diastereomers, and their ^1H NMR spectra were seen to be very different. As shown in Figure 1, the



Scheme 1. Synthesis of triptycene-derived calix[6]arenes.



Scheme 2. Demethylation of triptycene-derived calix[6]arenes.



Scheme 3. Debutylation of triptycene-derived calix[6]arenes.

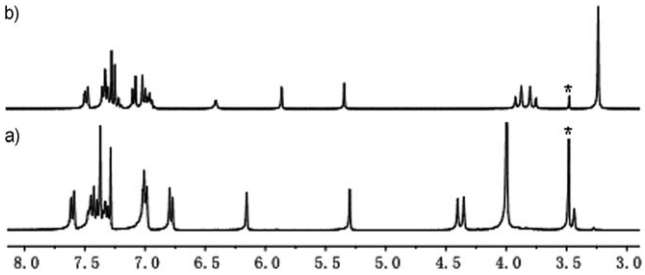


Figure 1. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of a) **4b** and b) **5b**; * denotes the peak of CH_3OH.

^{1}H NMR spectra of both **4b** and **5b** showed two singlets due to the bridgehead protons of the triptycene moiety and one singlet due to the methoxy protons, but their corresponding chemical shifts are very different. In particular, it was noted that **4b** showed a pair of doublet signals at $\delta = 3.42$ and 4.34 ppm ($\Delta\delta = 0.92$) due to the methylene protons, while a pair of doublets at $\delta = 3.78$ and 3.90 ppm ($\Delta\delta = 0.12$) was observed in the spectrum of **5b**. The results indicated that **4b** has a *syn* orientation of the two triptycene moieties, while in **5b** they are in an *anti* orientation.[9] Moreover, we also found that only four signals due to the aliphatic carbons were observed in the ^{13}C NMR spectra of **4b** and **5b**. These observations are all consistent with their highly symmetrical structures and fixed conformations in solution.

As in the case of their precursors **4** and **5**, the demethylated products **6a** and **6b** are also a pair of diastereomers, as are **7a** and **7b**. Their ^{1}H NMR spectra all showed a pair of doublet signals due to the protons of the methylene bridges and two singlets due to the bridgehead protons of the triptycene moiety. Meanwhile, five signals due to the aliphatic carbons were observed in the ^{13}C NMR spectra of **6a** and **7a**, and three signals due to the aliphatic carbons were observed in the ^{13}C NMR spectra of **6b** and **7b**. These results indicated that the macrocycles **6** and **7** each had symmetrical structures and fixed conformations in solution, similar to those of their respective precursors. The ^{1}H and ^{13}C NMR spectral features of the debutylated macrocycles **8** and **9** corresponding to their methylene bridges are also quite similar to those of their precursors **4a–7a**, indicating that **8** and **9** adopt the same fixed conformations as those of their precursors.

In order to further investigate the conformational mobility, variable-temperature ^{1}H NMR experiments on **5a** in [D_6]DMSO were also carried out. As shown in Figure 2, no obvious changes in the methylene proton signals of **5a** were observed upon increasing the temperature, which is in accord with its fixed conformation. In addition, the upfield

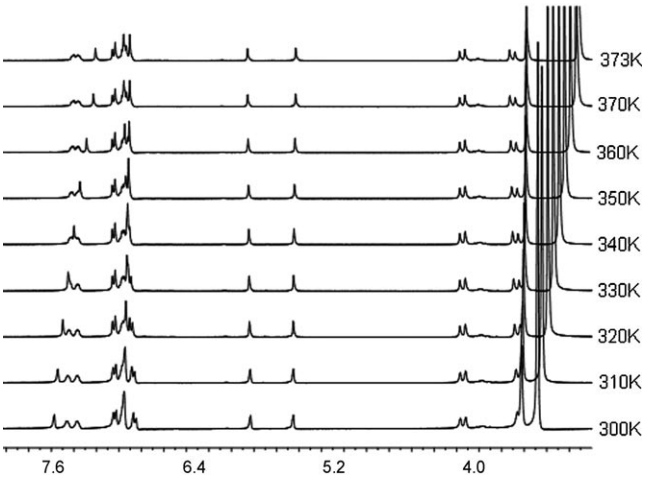


Figure 2. Variable-temperature ^{1}H NMR spectra of **5a** in [D_6]DMSO at 300 MHz.

shift of the methoxy proton signal and the slight downfield shift of the triptycene proton signals indicate that the triptycene moieties are continuously stretching out and the four methoxy groups present on the narrow rim of the calix[6]arene are oriented inwards toward the cavity with increasing temperature. Moreover, it was also found that variable-temperature ^{1}H NMR experiments on **4a** and **6a** gave similar results to those obtained for **5a**. Therefore, it could be concluded that although these triptycene-derived calix[6]arenes have the cavities of classical calix[6]arenes, they show fixed conformations similar to those of classical calix[4]arenes, and the most significant factor responsible for determining the conformational mobility of these novel calix[6]arenes is not the bulky *tert*-butyl groups at the *para* position of the phenol groups, but mainly the introduction of the triptycene moiety with its rigid 3D structure.

X-ray crystal structures of the triptycene-derived calix[6]arenes: The X-ray crystal structures of the macrocyclic compounds **4a**,[8a] **5a**,[8a] **5b**, **6a**, and **8** were determined, and their crystallographic data are summarized in Table 1. Owing to the rigid 3D structure of the triptycene moieties, the macrocycles **4a**, **5a**, **5b**, **6a**, and **8** all have highly symmetrical structures and specific fixed conformations in the

Table 1. X-ray crystallographic data of **4a**, **5a**, **5b**, **6a**, and **8**.

Compound	**4a**·2 CH_3OH	**5a**·4 CH_2Cl_2·2 CH_3OH	**5b**·3 CH_2Cl_2	**6a**·2 $CHCl_3$·2 H_2O	**8**·H_2O
formula	$C_{70}H_{72}O_8$	$C_{74}H_{80}Cl_8O_8$	$C_{75}H_{62}Cl_6O_6$	$C_{66}H_{58}Cl_6O_8$	$C_{56}H_{42}O_7$
M_r	1041.28	1380.98	1271.95	1189.81	826.9
crystal size [mm]	0.59×0.57×0.06	0.25×0.20×0.18	0.25×0.23×0.18	0.20×0.20×0.16	0.25×0.22×0.11
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P\bar{1}$	*P*21/*n*	*C*2*m*	*P*21/*c*
a [Å]	14.953(3)	7.4028(15)	16.4382(15)	22.281(4)	12.055(7)
b [Å]	13.561(3)	15.554(3)	18.8836(16)	16.835(3)	11.236(6)
c [Å]	29.634(6)	16.174(3)	20.9472(19)	19.708(4)	38.750(2)
α [°]	–	78.87(3)	–	–	–
β [°]	104.15(3)	81.79(3)	103.707(6)	99.98(3)	95.588(6)
γ [°]	–	82.09(3)	–	–	–
V [Å^3]	5827(2)	1797.0(6)	6317.1(10)	7086(2)	5224(4)
Z	4	1	4	4	4
ρ_{calcd} [g cm^{-3}]	1.187	1.276	1.337	1.115	1.051
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)
GOF on F^2	1.273	1.809	1.059	1.064	1.588
R_1 [$I>2\sigma(I)$]	0.0769	0.1194	0.0913	0.1029	0.1088
ωR_2 (all data)	0.1607	0.3979	0.2846	0.3068	0.2928

solid state, which are in agreement with the results obtained in solution.

Similar to **5a**,[8a] the macrocycle **5b** is also a *trans* isomer, in which the face-to-face benzene rings of the triptycene moieties are each parallel to one another, and the centroid distances between the face-to-face benzene rings are 8.205 and 8.649 Å, respectively (Figure 3). Interestingly, it was found that the two *p*-phenylphenol rings are opposite and coplanar, with the distance between the two phenolic oxygen atoms being 6.051 Å. Moreover, we also found that by virtue of a pair of C–H···O hydrogen bonds ($d_{C-H\cdots O}$= 2.552 and 2.684 Å) between the aromatic protons of the phenol ring in one macrocycle and the phenolic oxygen of its adjacent macrocycle and a π–π interaction ($d_{\pi-\pi}$= 3.358 Å) between the phenyl rings of adjacent triptycene moieties, the molecule **5b** could self-assemble into a 1D supramolecular structure (Figure 3c), which could further assemble into a microporous architecture (Figure 3d).

In the case of **6a**, the crystal structure exhibited a typical cone conformation with a highly symmetrical C_{2v} space group (Figure 4a, b). There exist two pairs of O–H···O hydrogen bonds ($d_{O\cdots O}$=2.757 and 2.829 Å, respectively) between the phenolic hydroxyl groups and the adjacent phenolic hydroxyl groups of the triptycene moieties. Consequently, two face-to-face *p-tert*-butylphenol rings are almost parallel to one another, and the dihedral angle between them is reduced to 7.44° compared with 138.23° in the precursor **4a**,[7a] mainly because of the enhanced intraannular hydrogen bonds after demethylation. Moreover, it was found that the cavity cross-section of **6a** ranges from 9.56× 12.09 Å (upper rim) to 7.91×8.84 Å (lower rim). The macrocycle **8** showed similar structural features to those of **6a** (Figure 4c, d). The structure also features two pairs of O–H···O hydrogen-bonding interactions ($d_{O\cdots O}$=2.752 and 2.830 Å, respectively) between the adjacent phenolic hydroxyl groups. The dihedral angle between the face-to-face phenolic rings is 6.95°, which is smaller than that in **6a**. Moreover, the cavity cross-section of **8** ranges from 9.22×

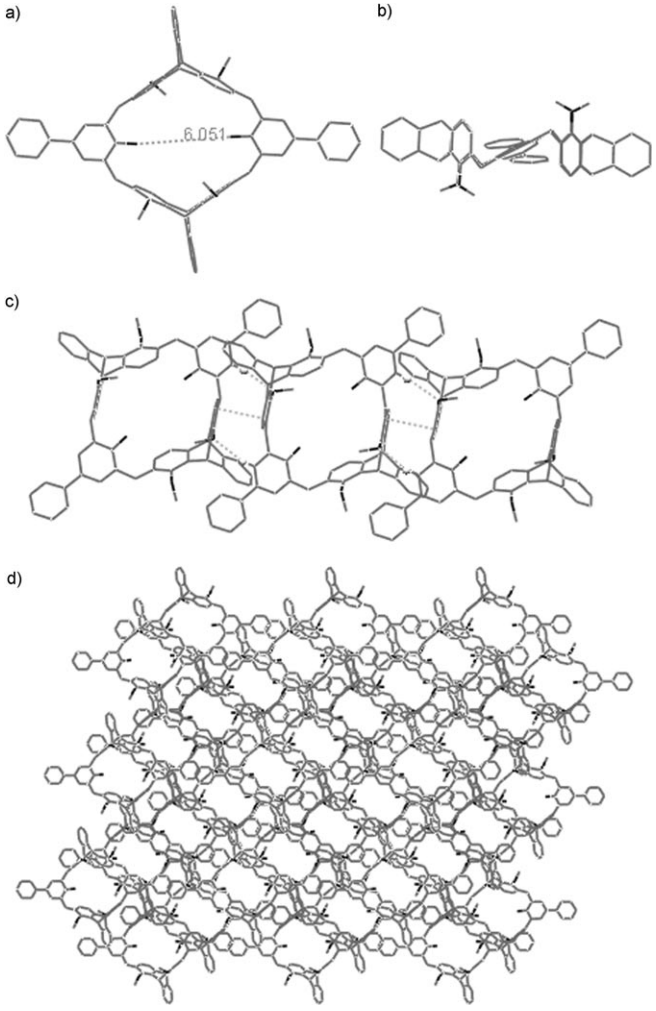


Figure 3. a) Top view and b) side view of **5b**. c) The noncovalent interactions between the adjacent molecules, and d) a microporous structure viewed along the *b* axis. Solvents and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

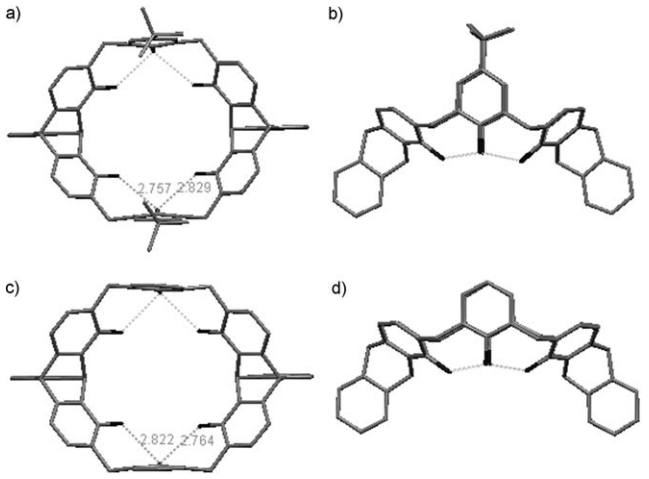


Figure 4. a) Top view and b) side view of **6a**. c) Top view and d) side view of **8**. Dashed lines show the hydrogen bonds. Hydrogen atoms and solvents are omitted for clarity.

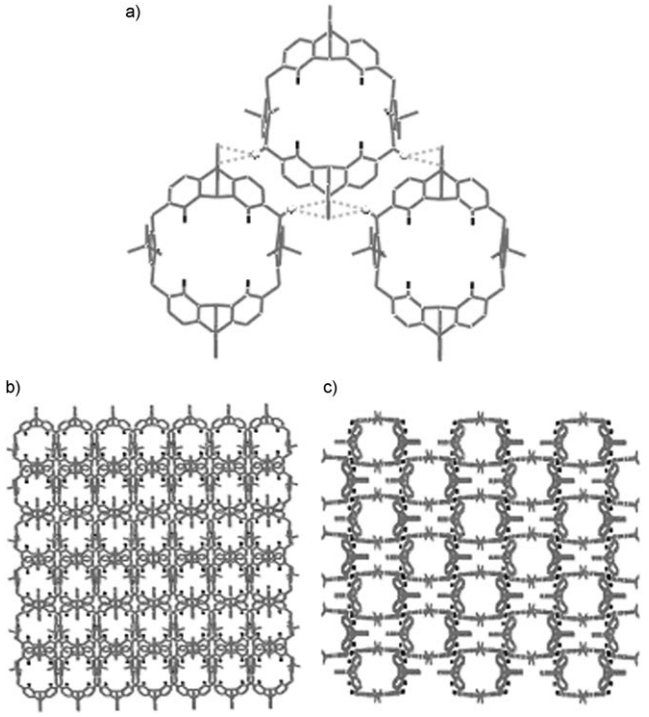


Figure 5. Crystal packing of **6a**. The noncovalent interactions between the adjacent macrocycles in one layer (a); the 3D microporous structure viewed along the b) *a* axis and c) *c* axis. Solvents and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

11.91 Å (upper rim) to 7.63×8.87 Å (lower rim), and the centroid distances between the face-to-face benzene rings in the triptycene moieties were found to be 9.70 and 9.686 Å, respectively.

It was further found that macrocycle **6a** could arrange alternately to form a 2D layer structure through two pairs of C–H···π interactions ($d_{C-H\cdots\pi}$=2.814 Å) between the methylene protons of one molecule and the phenyl rings of the triptycene moieties of the adjacent molecules (Figure 5a).

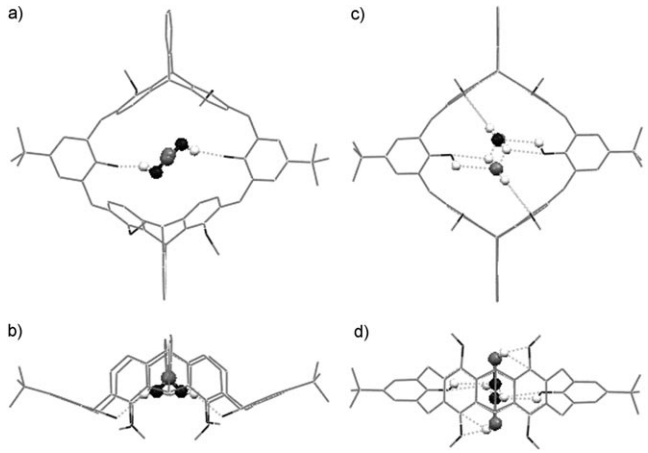


Figure 6. a) Top view and b) side view of the crystal structure of 2 CH_3OH@**4a**. c) Top view and d) side view of the crystal structure of 2 CH_3OH@**5a**. Dashed lines show the hydrogen-bonding interactions. Hydrogen atoms are omitted for clarity.

These layers could then further stack into two sets of perpendicular channels, as illustrated when viewed along the *a* axis (Figure 5b) and the *c* axis (Figure 5c), in which $CHCl_3$ molecules reside.[10]

Encapsulation of small neutral molecules in the solid state: As expected, the triptycene-derived calix[6]arenes not only have large enough cavities to serve as hosts, but also have specific fixed conformations. By virtue of these structural features, they can easily encapsulate small neutral guest molecules within their cavities in the solid state. Consequently, it was found that **4a** could encapsulate two CH_3OH molecules in its cavity, mainly due to its conformational rigidification, which is impossible for its corresponding classical calix[6]arene counterpart. It was found that in the host–guest complex 2 CH_3OH@**4a** there exist a pair of O–H···O hydrogen bonds ($d_{O-H\cdots O}$=2.115 Å) between the phenolic oxygen atom and the hydroxyl proton of CH_3OH (Figure 6a, b). As in the case of **4a**, it was found that **5a** could also accommodate two CH_3OH molecules in its cavity (Figure 6(c, d)), anchored by three pairs of O–H···O hydrogen-bonding interactions ($d_{O-H\cdots O}$=2.363 and 2.573 Å, respectively) between the hydroxyl group of CH_3OH and the phenolic hydroxyl group, a pair of C–H···O hydrogen bonds ($d_{C-H\cdots O}$= 2.556 Å) between the methyl protons of CH_3OH and the phenolic oxygen atom, and a pair of C–H···π interactions ($d_{C-H\cdots\pi}$=2.845 Å) between the methyl protons of CH_3OH and the phenyl ring of the triptycene moiety in **5a**. Moreover, in 2 CH_3OH@**5a**, a pair of O–H···O hydrogen-bonding interactions between the hydroxyl groups of the two methanol molecules with distances of 1.548 Å are also observed. These multiple noncovalent interactions play an important role in the formation of the complex.

In the case of **5b**, a CH_2Cl_2 molecule is encapsulated in its cavity (Figure 7a, b), anchored by one pair of O–H···Cl hydrogen-bonding interactions ($d_{O-H\cdots Cl}$=2.60 and 2.654 Å, re-

spectively) between the chlorine atoms of CH_2Cl_2 and the phenolic protons in **5b**, one pair of C–H···O hydrogen-bonding interactions ($d_{C-H\cdots O}$ = 2.603 and 2.690 Å, respectively) between the methylene protons of CH_2Cl_2 and the phenolic oxygen atoms, and one C–H···π interaction ($d_{C-H\cdots\pi}$ = 2.802 Å) between a proton of CH_2Cl_2 and the phenyl ring of the triptycene moiety in **5b**. For **6a**, it was found that a $CHCl_3$ molecule is accommodated in its cavity (Figure 7c, d) by virtue of a pair of C–H···π ($d_{C-H\cdots\pi}$ = 2.841 Å) interactions between the proton of $CHCl_3$ and the phenyl rings of the triptycene moiety. Similarly, we also found that one water molecule could be encapsulated within the cavity of macrocycle **8** (Figure 7e, f) by one C–H···O hydrogen-bonding interaction ($d_{C-H\cdots O}$ = 2.484 Å) between the bridgehead proton of the triptycene moiety and the oxygen atom of water, and a pair of O–H···O hydrogen-bonding interactions ($d_{O-H\cdots O}$ = 1.829 and 1.965 Å, respectively) between the phenolic protons of the triptycene moiety and the oxygen atom of water. Thus, the present triptycene-derived calix[6]arenes with fixed conformation could all encapsulate small neutral molecules in their cavities in the solid state, in contrast to their classical calix[6]arene analogues.[11]

Complexation of the triptycene-derived calix[6]arenes with fullerenes C_{60} and C_{70}: During the past two decades, fullerenes and their derivatives have been extensively investigated owing to their wide potential applications, for example in enzyme imitation[12] and material sciences.[13] Constructing new classes of supramolecular containers for fullerenes is also of great interest in relation to the development of fullerene-based functional materials. For this purpose, various macrocyclic hosts for complexation with fullerenes have hitherto been reported,[14] and among them calixarenes have received considerable attention since the pioneering work of Atwood's group in purifying fullerenes C_{60} and C_{70} by selective complexation with calix[8]arene.[15]

Having established that the present triptycene-derived calix[6]arenes exhibited well-defined fixed conformations and sufficiently large electron-rich cavities, we reasoned that they could also serve as efficient hosts for complexation with fullerenes. Consequently, we investigated the complexation properties of macrocycles **4b** and **5b** with fullerenes C_{60} and C_{70} by a fluorescence method. As shown in Figure 8, the fluorescence of **4b** at 334 nm was significantly quenched upon the addition of C_{60} to a solution of this macrocycle in toluene. A Job plot and fluorescence titration experiments showed that a 1:1 complex was formed between **4b** and C_{60}. Accordingly, the association constant K_a of the complex **4b**·C_{60} was calculated from a plot of F_0/F_{cal} (F_{cal}: the calibrated fluorescence intensity[16]) versus C_{60} concentration to be $68970 \pm 1706\ M^{-1}$. Under the same conditions, it was found that addition of C_{70} also led to a significant quenching of the fluorescence of **4b**. The fluorescence titration and the Job plot revealed that **4b** formed a 1:1 complex with C_{70} with an association constant K_a of $52214 \pm 2039\ M^{-1}$.[10] As in the case of **4b**, we further found that **5b** could also form 1:1 complexes with both C_{60} and C_{70}, and the corresponding association constants K_a were calculated to be $86787 \pm 2984\ M^{-1}$ and $59007 \pm 3798\ M^{-1}$, respectively.[10]

It is known that classical calix[6]arene and *p-tert*-butyl calix[6]arene analogues in the double-cone conformation can form 1:2 complexes with C_{60} and C_{70} through torsion along the CAr–CH_2–CAr bonds prior to complexation.[17] In contrast, macrocycles **4b** and **5b** can only form 1:1 complexes

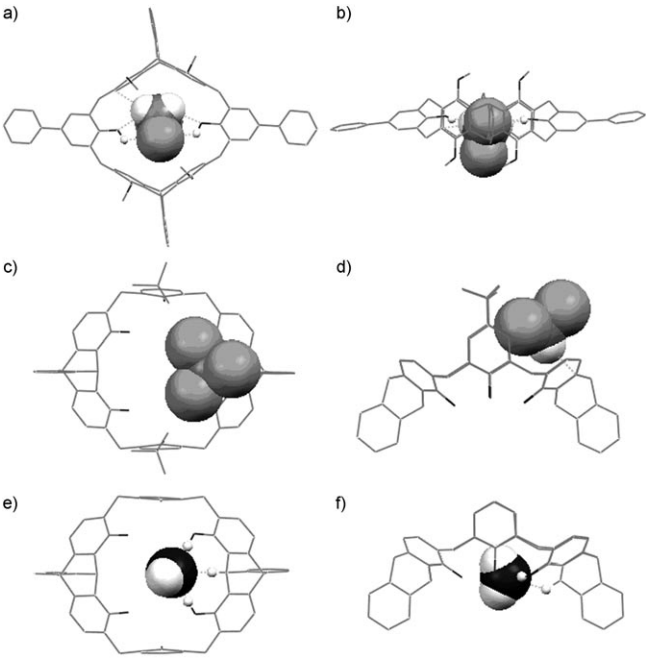


Figure 7. a) Top view and b) side view of the crystal structure of CH_2Cl_2@**5b**. c) Top view and d) side view of the crystal structure of $CHCl_3$@**6a**. e) Top view and f) side view of the crystal structure of H_2O@**8**. Dashed lines show the hydrogen-bonding interactions. Hydrogen atoms are omitted for clarity.

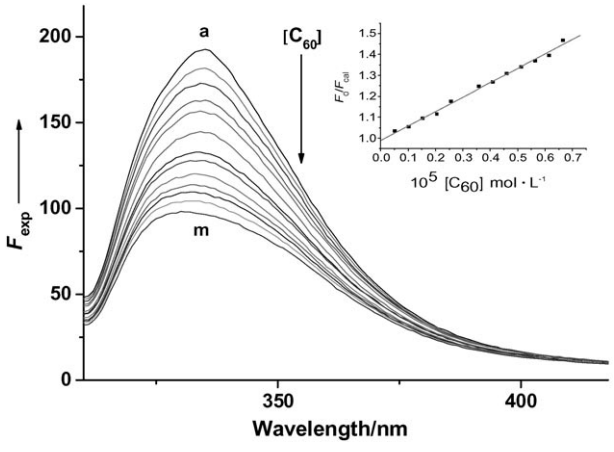


Figure 8. Emission spectra (λ_{ex} = 296 nm) of **4b** (3.2×10^{-6} mol dm^{-3}) in the presence of C_{60} in toluene at 25 °C. The concentrations of C_{60} for curves a–m (from top to bottom) were 0, 0.0512, 0.1024, 0.1536, 0.2048, 0.256, 0.3584, 0.4096, 0.4608, 0.512, 0.5632, 0.6144, and 0.6656 ($\times 10^{-5}$ mol dm^{-3}). Inset: The variation of fluorescence intensity F_0/F_{cal} of **4b** with increasing C_{60} concentration.

with C_{60} and C_{70}, which may be mainly attributed to the fact that introduction of the triptycene moiety confines them to a rigid conformation. Moreover, compared with the complexation of fullerene C_{60} by the classical calix[5]arene and calix[6]arene derivatives ($K_a = 9$–$1300\ M^{-1}$),[18] **4b** and **5b** exhibited much higher affinities toward C_{60} and C_{70}, indicating that the advantage of introducing a triptycene framework into these novel calix[6]arenes is not only that it fixes their conformations, but also that it increases the electron density of the aromatic rings, and therefore might further contribute to enhancing the interaction of the concave cavities of the macrocyclic hosts with the electron-deficient convex surface of the fullerenes.

Conclusion

In conclusion, we have synthesized two pairs of novel triptycene-derived calix[6]arenes **4a**,**b** and **5a**,**b** through both one-pot and two-step fragment-coupling strategies starting from 1,8-dimethoxy-2,7-dihydroxymethyltriptycene. Subsequent demethylation of **4a**,**b** and **5a**,**b** with BBr_3 in dry dichloromethane gave the macrocyclic compounds **6a**,**b** and **7a**,**b**. Treatment of either **4a** or **6a** with $AlCl_3$ resulted in the same debutylated product **8**, while under the same conditions the debutylated compound **9** could be obtained from either **5a** or **7a**. Structural studies have revealed that all of the macrocycles have well-defined structures with fixed conformations both in solution and in the solid state owing to the introduction of the triptycene moiety with a rigid 3D structure, which are very different from those of their classical calix[6]arene counterparts. As a consequence, it was found that all of these triptycene-derived calix[6]arenes could encapsulate small neutral molecules in their cavities in the solid state. Moreover, it was also found that macrocycles **4b** and **5b** showed highly efficient complexation abilities toward fullerenes C_{60} and C_{70}. We believe that these novel triptycene-derived calix[6]arenes will find wide applications in molecular recognition and molecular assembly, areas that are actively being pursued in our laboratory.

Experimental Section

General: Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^1H and ^{13}C NMR spectra were measured on a Bruker DMX300 NMR spectrometer. MALDI-TOF mass spectra were obtained on a Bruker BIFLEXIII mass spectrometer. Elemental analyses were performed at the Analytical Laboratory of the Institute of Chemistry, Chinese Academy of Sciences.

General procedure for the preparation of 4 and 5

Method A: A solution of **1** (1 mmol) and **2a** (1 mmol) in *o*-dichlorobenzene (120 mL) was slowly added to a solution of a catalytic amount of *p*-TsOH in *o*-dichlorobenzene (60 mL) under an argon atmosphere at 100 °C. After 24 h, an additional portion of **2a** (1 mmol) was added, and the mixture was heated for a further 24 h. The dark solution was then concentrated in vacuo, and the residue was separated by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:10). Recrystallization of the appropriate fractions from CH_3OH/CH_2Cl_2 afforded the products **4a** and **5a** in yields of 19 and 13%, respectively. Similarly, **4b** and **5b** were obtained in yields of 17 and 11%, respectively, by the reaction of **1** and **2b**.

Method B: Under the same conditions as described in Method A, reaction of **1** and **3a** afforded **4a** and **5a** in yields of 25 and 19%, respectively. Analogously, **4b** (20%) and **5b** (17%) could be obtained by the reaction of **1** and **3b**.

4b: White solid. M.p. >300 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.42$ (d, $J = 15.3$ Hz, 4H), 3.96 (s, 12H), 4.34 (d, $J = 15.3$ Hz, 4H), 5.26 (s, 2H), 6.12 (s, 2H), 6.74 (d, $J = 7.5$ Hz, 4H), 6.95–6.98 (m, 8H), 7.29–7.55 (m, 16H), 7.58 ppm (d, $J = 7.5$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.4$, 42.6, 53.7, 62.5, 120.0, 123.4, 123.6, 125.2, 125.3, 126.5, 126.6, 126.6, 128.7, 128.8, 129.6, 132.3, 136.7, 140.8, 144.8, 145.9, 146.5, 152.0, 152.4 ppm; MALDI-TOF MS: *m/z*: 1016 $[M]^+$, 1039 $[M+Na]^+$, 1055 $[M+K]^+$; elemental analysis calcd (%) for $C_{72}H_{56}O_6 \cdot 1.5\,CH_3OH \cdot 0.5\,H_2O$: C 82.17, H 5.91; found: C 82.34, H 5.99.

5b: White solid. M.p. >300 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.24$ (s, 12H), 3.78 (d, $J = 14.5$ Hz, 4H), 3.90 (d, $J = 14.5$ Hz, 4H), 5.35 (s, 2H), 5.87 (s, 2H), 6.41 (s, 2H), 6.96–6.98 (m, 4H), 7.01 (d, $J = 7.5$ Hz, 4H), 7.09 (d, $J = 6.8$ Hz, 4H), 7.22–7.36 (m, 13H), 7.49–7.52 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.3$, 42.6, 53.8, 61.9, 119.5, 123.4, 123.6, 125.2, 125.3, 126.4, 126.6, 127.7, 128.0, 128.3, 128.5, 130.5, 133.1, 136.8, 140.8, 144.3, 146.3, 146.5, 152.4, 153.2 ppm; MALDI-TOF MS: *m/z*: 1016 $[M]^+$, 1039 $[M+Na]^+$, 1055 $[M+K]^+$; elemental analysis calcd (%) for $C_{72}H_{56}O_6 \cdot 1.5\,CH_3OH$: C 82.87, H 5.87; found: C 82.96, H 5.79.

General procedure for the preparation of 6 and 7: A solution of boron tribromide (0.6 g, 2.4 mmol) in dry dichloromethane was added dropwise to a solution of **4** or **5** (0.10 mmol) in dry dichloromethane (20 mL). The mixture was stirred at room temperature for 10 h. Dilute hydrochloric acid was then added to quench the reaction. The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was submitted to column chromatography (petroleum ether/EtOAc 6:1) and then recrystallized from CH_3OH/CH_2Cl_2 to give the product.

6a: Yield 73%. White solid. M.p. >300 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.06$ (s, 18H), 3.42 (d, $J = 14.4$ Hz, 4H), 4.05 (d, $J = 14.4$ Hz, 4H), 5.34 (s, 2H), 6.10 (s, 2H), 6.94–7.03 (m, 18H), 7.27–7.36 (m, 6H), 7.43–7.46 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.3$, 32.1, 33.9, 40.8, 54.2, 116.7, 123.4, 123.5, 125.1, 125.2, 125.3, 125.9, 127.8, 130.2, 144.2, 145.1, 146.2, 146.5, 147.0, 148.1 ppm; MALDI-TOF MS: *m/z*: 943 $[M+Na]^+$, 959 $[M+K]^+$; elemental analysis calcd (%) for $C_{64}H_{56}O_6 \cdot CH_3OH$: C 81.91, H 6.34; found: C 82.07, H 6.30.

6b: Yield 78%. White solid. M.p. >300 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.49$ (d, $J = 14.6$ Hz, 4H), 4.12 (d, $J = 14.5$ Hz, 4H), 5.33 (s, 2H), 6.12 (s, 2H), 6.92–7.07 (m, 13H), 7.14–7.23 (m, 6H), 7.20–7.25 (m, 7H), 7.30–7.38 (m, 2H), 7.45 (d, $J = 6.3$ Hz, 2H), 8.48 ppm (br s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.8$, 54.2, 76.6, 77.0, 77.4, 116.8, 123.5, 124.9, 125.1, 125.2, 126.6, 126.7, 127.0, 127.7, 128.4, 130.2, 134.9, 140.6, 145.0, 146.4, 146.5, 148.0, 148.9 ppm; MALDI-TOF MS: *m/z*: 983 $[M+Na]^+$, 999 $[M+K]^+$; elemental analysis calcd (%) for $C_{68}H_{48}O_6 \cdot 1.3\,CH_3OH$: C 83.01, H 5.35; found: C 83.17, H 5.30.

7a: Yield 74%. White solid. M.p. >300 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.19$ (s, 18H), 3.61 (d, $J = 14.7$ Hz, 4H), 3.90 (d, $J = 14.7$ Hz, 4H), 5.34 (s, 2H), 6.05 (s, 2H), 6.83–7.22 (m, 18H), 7.26–7.77 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.4$, 33.3, 34.0, 40.3, 54.1, 116.7, 116.9, 123.3, 123.6, 125.0, 125.2, 125.4, 126.1, 126.4, 126.8, 131.5, 144.9, 145.4, 146.6, 146.7, 149.8 ppm; MALDI-TOF MS: *m/z*: 943 $[M+Na]^+$, 957 $[M+K]^+$; elemental analysis calcd (%) for $C_{64}H_{56}O_6 \cdot CH_3OH \cdot 0.5\,H_2O$: C 81.14, H 6.39; found: C 81.32, H 6.36.

7b: Yield 71%. White solid. M.p. >300 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.71$ (d, $J = 14.7$ Hz, 4H), 3.96 (d, $J = 14.7$ Hz, 4H), 5.34 (s, 2H), 5.97 (s, 2H), 6.45 (s, 4H), 6.58 (s, 2H), 6.89–6.97 (m, 4H), 7.00 (s, 8H), 7.29–7.40 ppm (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.8$, 40.5, 54.2, 116.7, 123.4, 123.7, 124.0, 125.0, 125.1, 126.8, 127.0, 127.1, 128.0, 131.3, 134.9, 140.4, 145.0, 146.4, 146.6, 149.1, 151.6 ppm; MALDI-TOF MS: *m/z*: 983 $[M+Na]^+$, 999 $[M+K]^+$; elemental analysis calcd (%) for $C_{68}H_{48}O_6 \cdot 1.5\,CH_3OH$: C 82.72, H 5.39; found: C 82.54, H 5.48.

General procedure for the preparation of 8 and 9: Anhydrous aluminum chloride (0.09 g, 0.67 mmol) was added to a solution of **4a** or **5a** (0.13 mmol) and phenol (0.06 g, 0.62 mmol) in toluene (20 mL) under argon. The mixture was stirred at room temperature for 3 h and then quenched with dilute hydrochloric acid. The organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was submitted to column chromatography (petroleum ether/EtOAc) and then further recrystallized from CH_3OH/CH_2Cl_2 to give **8** and **9** in yields of 61 and 54%, respectively. Following the same procedure as described above, macrocycles **8** and **9** could also be obtained from **6a** and **7a** in yields of 57 and 46%, respectively.

8: White solid. M.p. >300°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.45 (d, J=14.5 Hz, 4H), 4.10 (d, J=14.5 Hz, 4H), 5.35 (s, 2H), 6.10 (s, 2H), 6.70 (t, J=7.5 Hz, 2H), 6.95–7.00 (m, 16H), 7.32–7.41 (m, 2H), 7.40–7.46 (m, 2H), 8.07 (brs, 4H), 8.62 ppm (brs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.7, 40.7, 54.1, 116.8, 121.7, 123.5, 124.9, 125.5, 126.7, 127.7, 128.9, 130.2, 144.9, 146.3, 148.0, 149.3 ppm; MALDI-TOF MS: *m/z*: 831 $[M+Na]^+$, 847 $[M+K]^+$; elemental analysis calcd (%) for $C_{56}H_{40}O_6{\cdot}CH_3OH$: C 81.41, H 5.27; found: C 81.22, H 5.34.

9: White solid. M.p. >300°C; ^{1}H NMR (300 MHz, CD_3CN): δ=3.77 (d, J=14.2 Hz, 4H), 4.06 (d, J=14.3 Hz, 4H), 5.55 (s, 2H), 6.10 (s, 2H), 6.61 (s, 3H), 6.79 (t, J=7.5 Hz, 3H), 6.95 (s, 2H), 7.07–7.31 (m, 16H), 7.51–7.52 ppm (m, 4H); ^{13}C NMR (75 MHz, CD_3CN): δ=31.5, 41.1, 54.3, 117.1, 121.6, 124.26, 124.31, 125.7, 125.8, 127.0, 128.5, 128.8, 129.6, 132.2, 145.8, 146.9, 147.4, 149.4, 152.1 ppm; MALDI-TOF MS: *m/z*: 831 $[M+Na]^+$, 847 $[M+K]^+$; elemental analysis calcd (%) for $C_{56}H_{40}O_6{\cdot}0.5\,CH_3OH$: C 82.26, H 5.13; found: C 82.37, H 5.19.

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