Synthesis and Supramolecular Assemblies of Tripodal 1,3,5-Tris(phenoxymethyl)-2,4,6-triethylbenzene Analogues

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Tripodal 1,3,5-tris(phenoxymethyl)-2,4,6-triethylbenzene analogues have been synthesized and structurally characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy and HRMS, and additionally, the single crystal structures of compounds bearing *ortho*- (**7**), *meta*- (**9**) and *para*-hydroxymethyl (**11**) functions have been determined by X-ray diffraction analysis. The structural study revealed that compounds **7**, **9**, and **11** do not adopt the expected 1,3,5-alternate conformation in the solid state. The packing diagrams of compounds **7**, **9**, and **11** revealed that six hydrophilic hydroxymethyl groups from six individual molecules (**7**, **9** and **11**) were arranged in close contact via intermolecular hydrogen-bond interactions. For compounds **7** and **9**, the six hydroxyl groups formed a distorted hexagonal ring; however, formation of such a hexagonal ring was not clear in the case of compound **11**. Compounds **9** and **11** were found to form hydrophobic cavities via intermolecular hydrogen-bond interactions in the solid state, and the cavities were occupied by two ethyl groups from the two cavity-forming molecules.

Keywords 1,3,5-tris(phenoxymethyl)-2,4,6-triethylbenzene, conformation analysis, hydrogen bond, crystal structure

Introduction

The principle in designing supramolecular assemblies is to align functional groups of a respective molecular motif via specific interactions to achieve a targeted structure.[1] Molecules possess special topologies are particular attractive in this prospective, such as cyclodextron,[2] calixarenes,[3] and fused (aromatic) rings.[4] Due to the steric gearing, the three functional substituents of 1,3,5-functinonalized triethylbenzene, prepared from 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene,[5] are often disposed on the same side of the central phenyl plane, while the three ethyl groups are positioned on the opposite side of the central benzene ring, thus forming an alternating *up-down* geometrical pattern. This structural motif provides an ideal molecular platform in studying supramolecular systems,[6] and it has been exploited by many researchers in achieving conformational control via its preorganized geometry. Examples include the creation of a catechol-containing tripodal ligand for Fe^{3+} chelation as the mimic of the natural ligand (enderobaction),[7] scaffolds for assembling supramolecular structures via their coordination with Pd^{2+}, Co^{2+}, Cu^{2+}, and Cd^{2+},[8-10] and molecular hosts for cations,[11] anions[9b,12] and neutral[13] guests. However, in some case, the 1,3,5-functionalized triethylbenzenes do not possess the expected *up-down* alternate arrangement, only two functional arms of the scaffold lie on one side of the central benzene ring, while the third functional group together with the three ethyl groups locate on the opposite side of the central benzene plane.[14] 1,3,5-Tris-(phenoxymethyl)-2,4,6-triethylbenzene derivatives, have not been structurally characterized previously, and the conformation of these class of molecules remains unclear. Herein, we wish to report our results on the synthesis, conformation analysis of several new 1,3,5-tris-(phenoxymethyl)-2,4,6-triethylbenzene derivatives. Single crystal structure studies revealed that compounds with hydroxymethyl functions in *ortho*- (**7**), *meta*- (**9**), and *para*- (**11**) positions of the 1,3,5-phenolic substituents do not adopt the expected *up-down* alternate conformation, but with their two functional arms residing on one side of the central benzene plane, and the third functional arm, together with the three ethyl groups, residing on the opposite side of the central benzene ring.

Results and discussion

Synthesis

The tripodal tris(phenoxymethyl)-2,4,6-triethylbenzene species were synthesized by the reaction of 1,3,5-tris-

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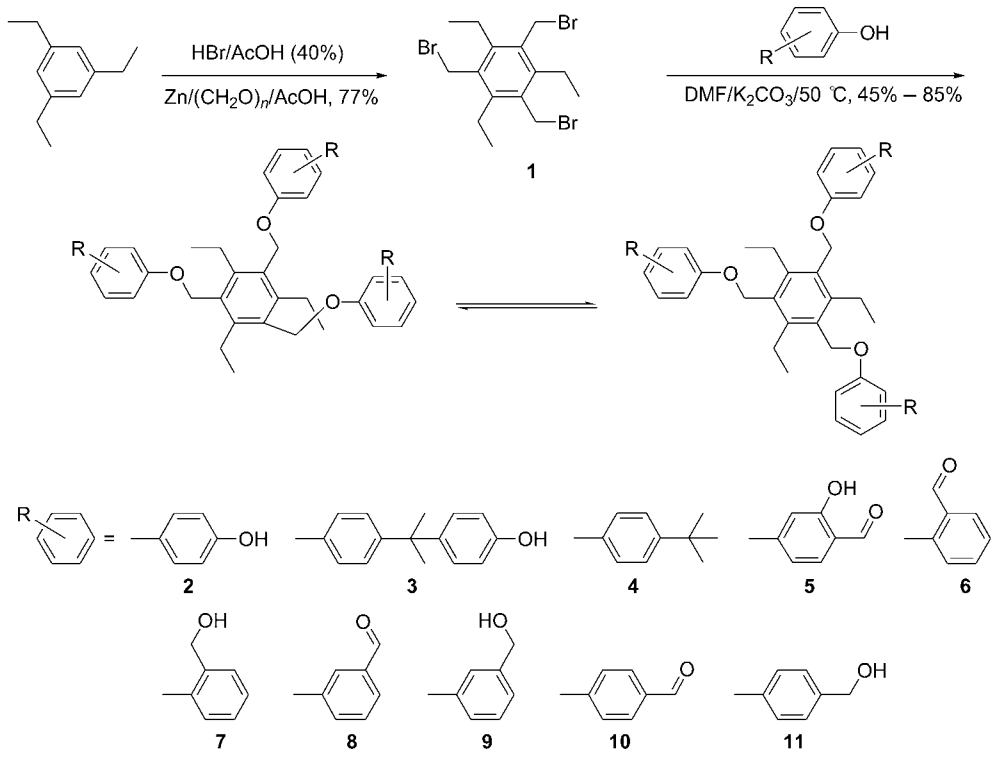
(bromomethyl)-2,4,6-triethylbenzene **1** (obtained from triethylbenzene according to literature procedure)[5] with appropriate phenols in DMF under basic condition, as shown in Scheme 1. Compounds (**2** and **3**) with free phenols on the phenolic substituents were synthesized by employing large access of the corresponding di-phenols, and compounds **2** and **3** were obtained in the yields of 44.7% and 74.3%, respectively (see experimental section). Compounds **4**, **5**, **6**, **8** and **10** were obtained with the yields ranging from 60.2% to 84.6%. Compounds **7**, **9**, and **11** bearing hydroxymethyl functions on the phenolic substituents were obtained in high yields (>88%) via $NaBH_4$ reduction of the corresponding aldehyde groups of compounds **6**, **8** and **10**. Single crystals of **7**, **9**, and **11** suitable for X-ray diffraction studies were grown in EtOAc and *n*-hexane. Two step reaction sequences were employed in the synthesis of compound **13** (with each phenolic substituent bearing two hydroxyl groups). Compound **12** was first generated by the reaction of compound **1** and 5-hydroxy-1,3-phenylene diacetate,[15] followed by direct hydrolysis, compound **13** was obtained in a combined yield of 31.7% (Scheme 2). Attempts to grow single crystals of compound **13** failed. All compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR and HRMS. The ^{1}H and ^{13}C NMR spectra of these molecules are in accord with the presence of high levels of symmetry (see experimental section).

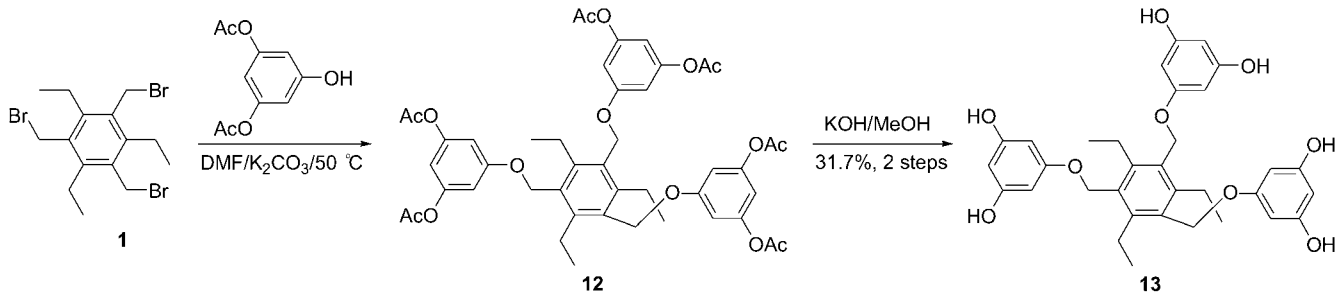
Solid state structure analysis

As shown in Figure 1, the crystal structure of compound **7** reveals that it does not adopt the expected 1,3,5-alternate conformation in the solid state. Instead, compound **7** adopts a highly unsymmetrical conformation with two out of its three *o*-phenolic substituents residing on one side of the central benzene ring, and the third *o*-phenolic substituent, together with the three ethyl groups, locating on the opposite side of the central benzene plane. Thus, no molecular pocket is formed by the

Scheme 1 General synthesis of tripodal 1,3,5-tris(phenoxymethyl)-2,4,6-triethyl-benzene analogues



Scheme 2 Synthesis of compound **13**



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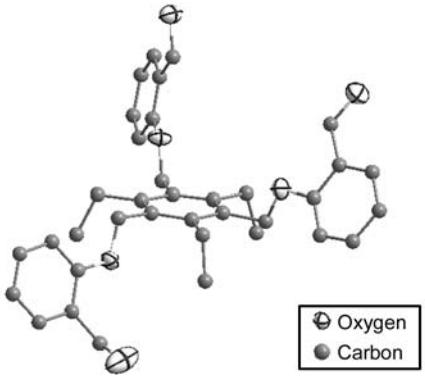

Figure 1 Molecular structure of compound **7**.

three *o*-phenolic substituents through intramolecular hydrogen-bond interactions between the three hydroxymethyl groups (Figure 1). As shown in Figure 2a, two molecules of **7** stacked together via intermolecular hydrogen-bond interactions between two pairs of hydroxyl groups ($d_{O\cdots O}$=2.788 Å, $d_{OH\cdots OH}$=1.970 Å, $\theta_{O-H\cdots OH}$= 175.6°) and offset face-to-face π-π stack interactions between the two central benzene rings (3.470 Å). The three ethyl groups in each molecule (**7**) are directed away from the center of the molecular stack. As shown in Figure 2b, six hydroxymethyl groups from six individual molecules are in close contacts via intermolecular hydrogen bonds ($d_{O\cdots O}$ ranged from 2.709 Å to 2.788 Å,

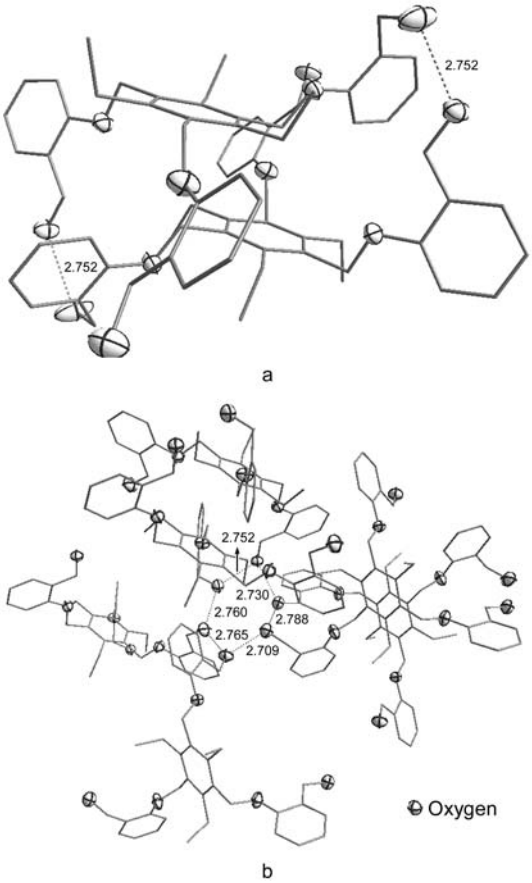

Figure 2 Molecular stacks (a) and hydrophilic hexagonal ring (b) formed by compound **7**.

$d_{OH\cdots OH}$ from 1.902 Å to 2.021 Å, and $\theta_{O-H\cdots OH}$ angles varied from 150.6° to 175.6°), resulting in the formation of a distorted hexagonal ring. No solvent molecules were found trapped in the crystal lattice.

As shown in Figure 3, compounds **9** and **11** adopt a similar conformation to that of **7** with two out of the three phenolic substituents (*meta*-hydroxymethyl substituted for **9** and *para*-hydroxymethyl substituted for **11**) residing on one side of the central benzene rings, and the third phenolic substituent, together with the three ethyl groups, residing on the opposite side of the benzene plane. No intramolecular hydrogen-bond interactions exist between the hydroxyl groups in both compounds **9** and **11**, and no expected molecular cavities were formed by the three phenolic substituents in the solid state. As shown in Figure 4a, a cavity-like supramolecular structure was formed by two molecules of **9** via intermolecular hydrogen-bond interactions between two pairs of hydroxymethyl groups ($d_{O\cdots O}$=2.690 Å, $d_{OH\cdots OH}$=1.888 Å, $\theta_{O-H\cdots OH}$=165.4°). The cavity is filled by two ethyl groups from the two cavity-forming molecules. The third hydroxymethyl group in **9** is directed away from the center of this cavity. For the two cavity-forming molecules (**9**), the two central benzene rings are arranged in parallel, while two pairs of *m*-hydroxymethyl substituted phenolic rings are arranged in a face-to-face manner. Similar to compound **7**, six hydroxyl groups from six individual molecules (**9**) are in close contact via the interaction of intermolecular hydrogen bonds ($d_{O\cdots O}$ ranged from 2.690 Å to 2.738 Å, $d_{OH\cdots OH}$ from 1.888 Å to 1.923 Å, and $\theta_{O-H\cdots OH}$ angles varied from 165.4° to 172.8°), resulting in the formation of a distorted hexagonal ring (Figure 4b). No solvent molecules were found trapped in the crystal lattice.

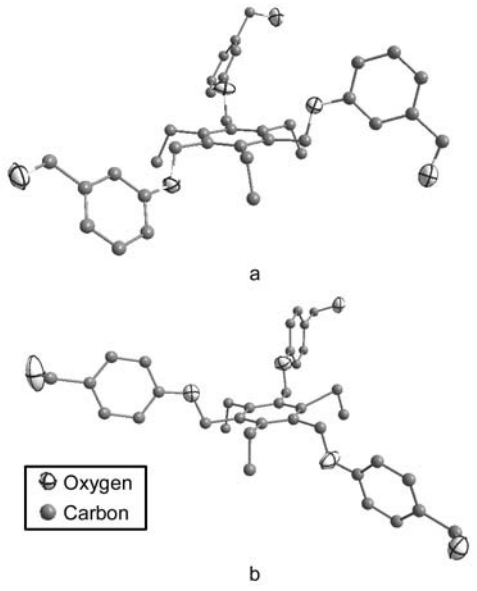

Figure 3 Molecular structures of **9** (a) and **11** (b).

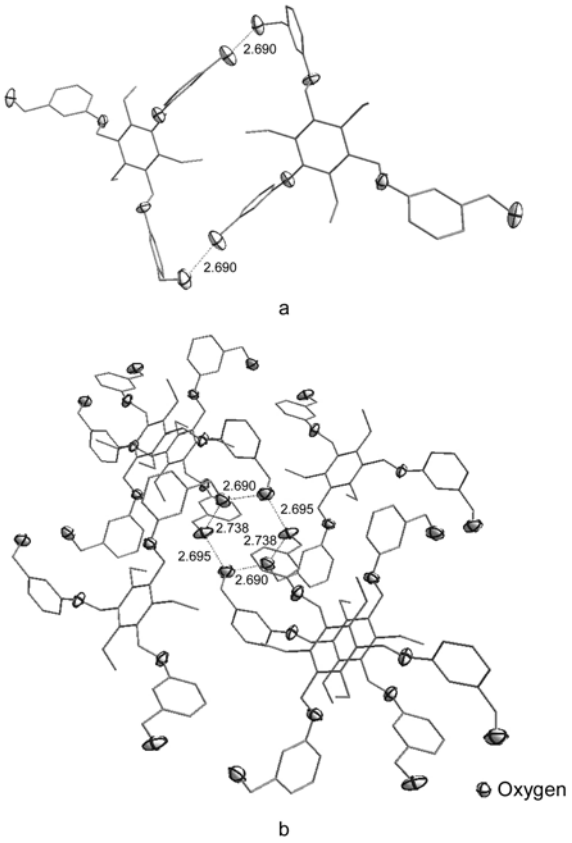

Figure 4 Hydrophobic cage (a) and hydrophilic hexagonal ring (b) formed by compound **9** in the solid state.

Figure 5a shows the formation of a one-dimensional supramolecular polymer by compound **11** in the solid state via intermolecular hydrogen-bond interactions between hydroxyl groups ($d_{O\cdots O}$ = 2.844 and 2.868 Å, $d_{OH\cdots OH}$ = 1.819 and 2.148 Å, $\theta_{O-H\cdots OH}$ = 124.5° and 146.4°). In the supramolecular polymer, two different types of ring structures were formed and lined alternately along the polymeric chain, and both rings are filled by two ethyl groups from the two cavity-forming molecules of **11**. The packing diagram shows that six hydroxymethyl functions from six individual molecules of **11** are grouped together via intermolecular hydrogen bond interactions ($d_{O\cdots O}$ ranged from 2.669 Å to 2.868 Å, $d_{OH\cdots OH}$ from 1.997 Å to 2.000 Å, and $\theta_{O-H\cdots OH}$ angles varied from 158.4° to 179.1°), however, there is no clear hexagonal ring formed as of those found for compounds **7** and **9** (Figure 5b). No solvent molecules were found trapped in the crystal lattice.

Conclusions

Twelve tripodal 1,3,5-tris(phenoxymethyl)-2,4,6-triethylbenzene derivatives have been synthesized and structurally characterized. ^{1}H and ^{13}C NMR spectra of these molecules are in accord with the presence of high levels of symmetry. Single crystal X-ray diffraction studies of 1,3,5-tris(phenoxymethyl)-2,4,6-triethylbenzene derivatives bearing hydroxymethyl functions on *ortho*- (**7**), *meta*- (**9**), and *para*- (**11**) positions of the phenolic substituents revealed that they all do not adopt the expected *up-down* alternating conformation in the solid state, but a conformation with two out of the three phenolic substituents residing on one side of the central benzene ring and the third phenolic substituent, together with the three ethyl groups, residing on the opposite side of the central benzene plane. The packing diagrams revealed the formation of supramolecular assemblies by these compounds via intermolecular hydrogen-bond interactions, as well as π-π stacking interaction (**7**). Compounds **9** and **11** were found to form cavity-like supramolecular structures in the solid state, and such cavities, in the case of compound **11**, could form a one-dimensional supramolecular polymer via the linkage of individual cavities by hydrogen bonds, and these cavities were found filled by two ethyl groups from the two cavity-forming molecules.

Experimental

General methods

DMF was dried before use, other solvents and reagents for synthesis were commercially available and used as received. Chemical reactions were performed in oven-dried glassware under an atmosphere of nitrogen. Classic column chromatography was performed using Merck 60 (70—230 mesh) silica gel. ^{1}H and ^{13}C NMR spectra were recorded at Bruker Avance 500 spectrometer in DMSO-d_6 or $CDCl_3$. Chemical shifts are versus tetramethylsilane. Mass spectra were recorded on a Bruker micrOTOF-Q spectrometer (LC/MS). Single crystal X-ray diffraction data were collected on a Bruker SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube (λ = 0.71073 Å).

General procedure for synthesis of compounds 2 and 3

Potassium carbonate (37.3 g, 270 mmol) and diphenol (210.0 mmol) were dissolved in DMF (150 mL) and the mixture was slowly heated to 50 ℃. A solution of compound **1** (6.0 g, 14.0 mmol) in DMF (50 mL) was then added dropwise in 1 h, and the reaction was monitored by TLC until completion. The reaction mixture was poured into ice water (400 mL) and extracted by EtOAc (200 mL × 3). The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude products were purified by re-crystallization in PE/EA to afford the pure products.

1,3,5-Tri[(4-hydroxyphenoxy)methyl]-2,4,6-triethylbenzene (2) White solid, yield 44.7%. m.p. 186.3—187.4 ℃; ^{1}H NMR (DMSO-d_6) δ: 8.92 (s, 3H), 6.89 (d, J = 9.0 Hz, 6H), 6.70 (d, J = 7.5 Hz, 6H), 4.94 (s, 6H), 2.70—2.75 (m, 6H), 1.13—1.18 (m, 9H); ^{13}C NMR (DMSO-d_6) δ: 151.58, 151.45, 145.13, 131.07, 115.80, 115.34, 64.53, 22.37, 16.27; IR (KBr) v: 3421, 3373,

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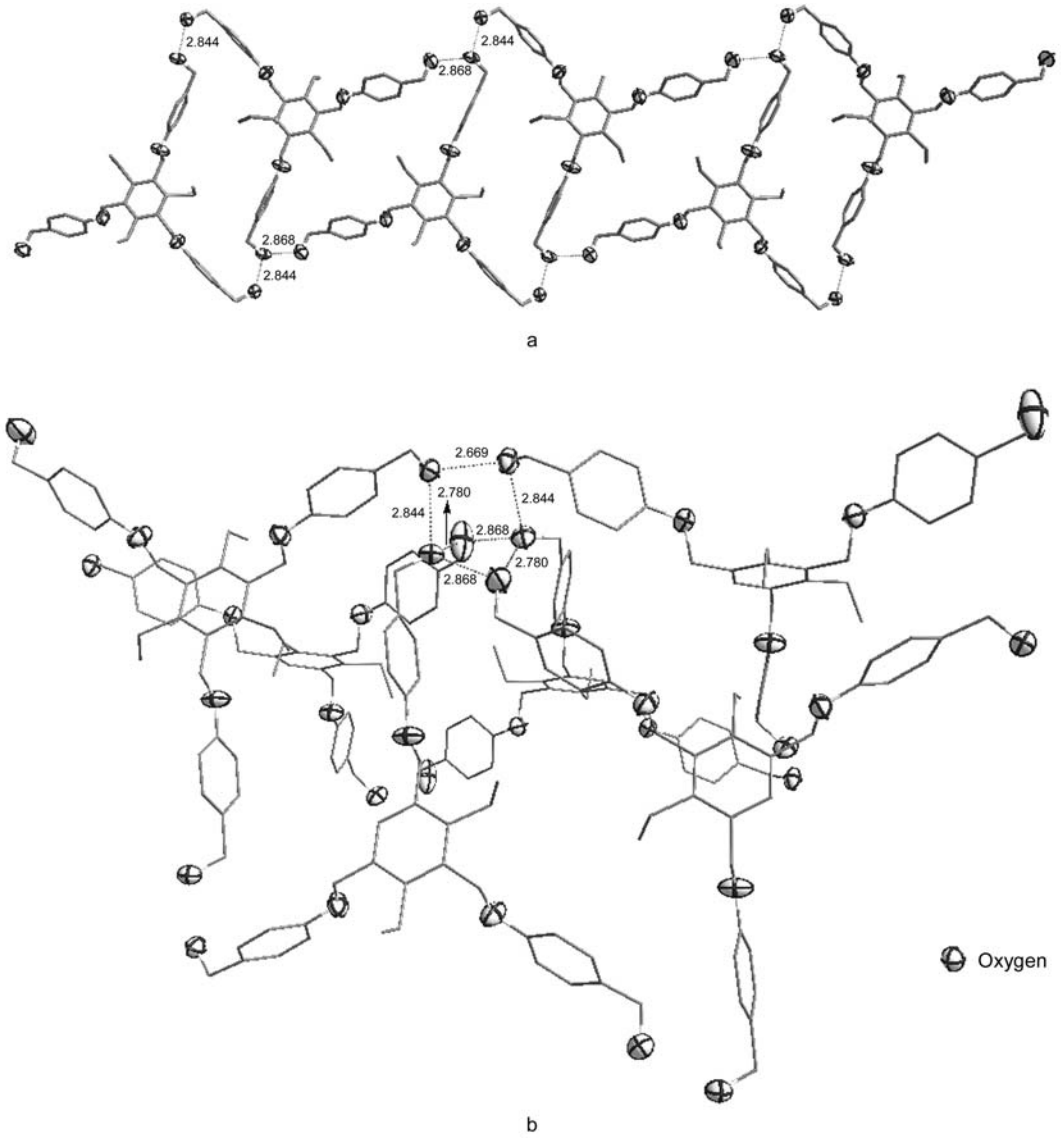

Figure 5 Hydrophobic cages (a) and clustered six hydrophilic hydroxymethyls (b) formed by compound **11** in the solid state.

3031, 2964, 1705, 1632, 1605, 1571, 1508, 1455, 1371, 1295, 1219, 1103, 1048, 996, 828, 793, 761, 614 cm^{-1}. HRMS calcd for $C_{33}H_{36}O_6Na^+$ [M＋Na^+] 551.2404, found 551.2392.

1,3,5-Tri((4-(2-(4hydroxyphenyl)propan-2-yl)phenoxy)methyl)-2,4,6-triethylbenzene (3) White solid, yield 74.3%. m.p. 90.1—90.4 ℃; ^{1}H NMR ($CDCl_3$) δ: 7.17 (d, J=8.7 Hz, 6H), 7.13 (d, J=8.6 Hz, 6H), 6.92 (d, J=8.7 Hz, 6H), 6.74 (d, J=8.6 Hz, 6H), 5.04 (s, 6H), 4.66 (s, 3H), 2.80—2.84 (m, 6H), 1.65 (s, 18H), 1.21—1.28 (m, 9H); ^{13}C NMR (DMSO-d_6) δ: 156.27, 154.98, 145.39, 143.17, 140.69, 130.84, 127.49, 127.31, 114.62, 113.69, 63.86, 41.06, 30.80, 22.40, 16.28; IR (KBr) v: 3502, 3430, 3030, 2967, 2874, 2364, 1879, 1723, 1608, 1509, 1458, 1368, 1294, 1230, 1180, 1106, 1047, 1010, 831, 561 cm^{-1}. HRMS calcd for $C_{60}H_{66}O_6Na^+$ [M＋Na^+] 905.4752, found 905.4734.

General procedure for synthesis of 4, 5, 6, 8 and 10

Potassium carbonate (18.6 g, 134.4 mmol) and substituted phenol (49.6 mmol) were dissolved in DMF (150 mL) and the mixture was slowly heated to 50 ℃. A solution of compound **1** (6.0 g, 14.0 mmol) in DMF (50 mL) was then added dropwise and the reaction was monitored by TLC until completion. The reaction mixture was poured into ice water (400 mL) and extracted by EtOAc (200 mL × 3). The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to provide a white solid, and the crude products were purified by recrystallization in petroleum ether/ethyl acetate to afford the pure products.

1,3,5-Tri((4-*tert*-butylphenoxy)methyl)-2,4,6-triethylbenzene (4) White solid, yield 67.7%. m.p. 207.2—209.5 ℃; ^{1}H NMR ($CDCl_3$) δ: 7.35 (dd, J=2.0, 9.0 Hz, 6H), 6.98 (dd, J=2.0, 9.0 Hz, 6H), 5.06 (s, 6H), 2.81—2.84 (m, 6H), 1.32 (s, 27H), 1.22—1.26 (m, 9H); ^{13}C NMR ($CDCl_3$) δ: 156.68, 146.12, 143.54, 131.16, 126.27, 113.94, 63.97, 34.09, 31.53, 22.93, 16.51; IR (KBr) v: 3047, 2960, 2903, 2870, 2363, 1874, 1743,

1608, 1579, 1510, 1476, 1366, 1294, 1236, 1182, 1118, 1048, 1014, 999, 863, 826, 770, 677, 552 cm^{-1}. HRMS calcd for $C_{45}H_{60}O_3Na^+$ [M + Na^+] 671.4434, found 671.4415.

1,3,5-Tri((3-formyl-4-hydroxyphenoxy)methyl)-2,4,6-triethylbenzene (5) White solid, yield 60.2%. m.p. 186.4—188.5 ℃; ^{1}H NMR ($CDCl_3$) δ: 11.54 (s, 3H), 9.76 (s, 3H), 7.48 (d, J = 10.0 Hz, 3H), 6.61—6.63 (m, 6H), 5.14 (s, 6H), 2.78—2.80 (m, 6H), 1.22—1.27 (m, 9H); ^{13}C NMR ($CDCl_3$) δ: 194.40, 165.79, 164.54, 146.76, 135.34, 130.21, 115.40, 108.85, 101.11, 64.61, 23.05, 16.34; IR (KBr) v: 2964, 2837, 2361, 1644, 1576, 1502, 1368, 1330, 1291, 1224, 1184, 1166, 1117, 1042, 990, 835, 806, 745, 707, 641, 551 cm^{-1}. HRMS calcd for $C_{36}H_{37}O_9^+$ [M + H^+] 613.2432, found 613.2452.

1,3,5-Tri((2-formylphenoxy)methyl)-2,4,6-triethylbenzene (6) White solid, yield 68.2%. m.p. 178.7—180.5 ℃; ^{1}H NMR ($CDCl_3$) δ: 10.42 (s, 3H), 7.88—7.90 (m, 3H), 7.63—7.66 (m, 3H), 7.25 (d, J = 8.0 Hz, 3H), 7.09—7.12 (m, 3H), 5.23 (s, 6H), 2.85—2.89 (m, 6H), 1.23—1.26 (m, 9H); ^{13}C NMR ($CDCl_3$) δ: 189.50, 161.08, 146.82, 136.03, 130.26, 128.41, 125.09, 121.14, 112.37, 64.74, 23.04, 16.56; IR (KBr) v: 3427, 2969, 2871, 2760, 2362, 1686, 1598, 1482, 1456, 1396, 1373, 1286, 1229, 1191, 1162, 1101, 1044, 985, 855, 831, 759, 653, 530 cm^{-1}. HRMS calcd for $C_{36}H_{36}O_6Na^+$ [M + Na^+] 587.2404, found 587.2415.

1,3,5-Tri((3-formylphenoxy)methyl)-2,4,6-triethylbenzene (8) White solid, yield 84.6%. m.p. 161.7—162.9 ℃; ^{1}H NMR ($CDCl_3$) δ: 10.04 (s, 3H), 7.60 (s, 3H), 7.51—7.56 (m, 6H), 7.32 (t, J = 5.0 Hz, 3H), 5.20 (s, 6H), 2.88 (q, J = 5.0 Hz, 6H), 1.29 (t, J = 5.0 Hz, 9H); ^{13}C NMR ($CDCl_3$) δ: 192.05, 159.36, 146.42, 137.87, 130.67, 130.18, 124.10, 122.26, 112.08, 64.39, 22.99, 16.40; IR (KBr) v: 3381, 2970, 2906, 2871, 2831, 2724, 2363, 1698, 1594, 1486, 1448, 1387, 1321, 1289, 1256, 1168, 1147, 1079, 1047, 1010, 985, 839, 798, 680, 650, 574 cm^{-1}. HRMS calcd for $C_{36}H_{36}O_6Na^+$ [M + Na^+] 587.2404, found 587.2393.

1,3,5-Tri((4-formylphenoxy)methyl)-2,4,6-triethylbenzene (10) White solid, yield 68.4%. m.p. 147.5—150.2 ℃; ^{1}H NMR ($CDCl_3$) δ: 9.92 (s, 3H), 7.91 (d, J = 8.6 Hz, 6H), 7.15 (d, J = 8.6 Hz, 6H), 5.20 (s, 6H), 2.81—2.86 (m, 6H), 1.24—1.27 (m, 9H): ^{13}C NMR ($CDCl_3$) δ: 190.68, 163.68, 146.65, 132.10, 130.47, 130.30, 114.82, 64.49, 23.06, 16.38; IR (KBr) v: 3237, 3031, 2968, 2874, 2740, 2365, 1691, 1600, 1576, 1507, 1455, 1371, 1307, 1246, 1161, 1106, 1045, 987, 864, 830, 793, 766, 679, 573 cm^{-1}. HRMS calcd for $C_{36}H_{37}O_6^+$ [M + H^+] 565.2585, found 565.2606.

General procedure for synthesis of compounds 7, 9 and 11

$NaBH_4$ (250.0 mg, 6.32 mmol, 96%) was added to methanol in an ice bathed flask potion-wise to generate a clear solution. Compound **6** (**8** or **10**) was then added to the reacion mixture. The mixture was stirred at 5 ℃ for 30 min and warmed to room temperature. The reaction mixture was then heated at 50 ℃ for an additional 30 min. After the completion of the reaction (monitored by TLC), MeOH was removed under reduced pressure. The residue was extracted by EtOAc (200 mL × 3) and the combined organic layer was washed with water, dried over $MgSO_4$. The organic layer was filtered and concentrated under reduced pressure. The crude products were purified by silica gel chromatography eluted with PE : EtOAc = 9 : 1 (Volune ratio) to afford the pure product **7** (**9** or **11**). Single crystals of compound **7** (**9** or **11**) were obtained by dissolving compound **7** (**9** or **11**, 10 mg) in EtOAc (3 mL), and *n*-hexane (5 mL) was then added slowly on top of EtOAc solution to form a clear interface. The setup was kept at room temperature in dark environment in two weeks, and single crystals suitable for X-ray analysis were grown.

1,3,5-Tri((2-(hydroxymethyl)phenoxy)methyl)-2,4,6-triethylbenzene (7) White solid, yield 90.1%. m.p. 161.9—162.9 ℃; ^{1}H NMR (DMSO-d_6) δ: 7.41 (d, J = 7.5 Hz, 3H), 7.26—7.30 (m, 6H), 6.98—7.00 (m, 3H), 5.10 (s, 6H), 4.43 (s, 6H), 2.75—2.80 (m, 6H), 1.16 (t, J = 7.5 Hz, 9H); ^{13}C NMR (DMSO-d_6) δ: 155.4, 145.9, 130.9, 130.5, 127.7, 126.9, 120.4, 111.1, 64.2, 57.9, 22.3, 16.3; IR (KBr) v: 3294, 3066, 2965, 2873, 2286, 1685, 1599, 1490, 1454, 1371, 1287, 1227, 1112, 1043, 1001, 755, 704, 680, 575 cm^{-1}. HRMS calcd for $C_{36}H_{43}O_6^+$ [M + H^+] 571.3054, found 571.3059.

Crystallographic data for 7 [$C_{72}H_{84}O_{12}$]; M_r = 1141.39; triclinic; space group $P\bar{1}$; a = 12.9868(4) Å; b = 13.3224(4) Å; c = 21.4200(6) Å; α = 74.4870(10)°; β = 76.2150(10)°; γ = 61.7020(10)°; V = 3116.96(16) $Å^3$; ρ_{calcd} = 1.216 g•cm^{-3}; T = 296(2) K; 36912 independent measured reflections; F^2 refinement; R_1 = 0.0446; wR_2 = 0.1076. These data were deposited in the Cambridge Crystallographic data centre, CCDC 752636.

1,3,5-Tri((3-(hydroxymethyl)phenoxy)methyl)-2,4,6-triethylbenzene (9) White solid, yield 89.9%. m.p. 179.9—180.7 ℃; ^{1}H NMR (DMSO-d_6) δ: 7.29—7.26 (m, 3H), 7.06 (s, 3H), 6.93—6.96 (m, 6H), 5.08 (s, 6H), 4.51 (s, 6H), 2.75 (q, J = 7.0 Hz, 6H), 1.19 (t, J = 7.0 Hz, 9H); ^{13}C NMR (DMSO-d_6) δ: 158.65, 145.42, 144.45, 130.92, 129.26, 118.89, 112.77, 112.21, 63.93, 62.85, 22.46, 16.28; IR (KBr) v: 3237, 2961, 2906, 2872, 1700, 1595, 1489, 1447, 1372, 1255, 1156, 1010, 986, 952, 922, 882, 779, 688, 574 cm^{-1}. HRMS calcd for $C_{36}H_{43}O_6^+$ [M + H^+] 571.3054, found 571.3066.

Crystallographic data for 9 [$C_{36}H_{42}O_6$]; M_r = 570.70; Triclinic; space group $P\bar{1}$; a = 9.6330(2) Å; b = 12.1626(2) Å; c = 14.1905(3) Å; α = 88.8440(10)°; β = 78.7670(10)°; γ = 73.5960(10)°; V = 1563.29(5) $Å^3$; ρ_{calcd} = 1.212 g•cm^{-3}; T = 296(2) K; 18521 independent measured reflections; F^2 refinement; R_1 = 0.0482; wR_2 = 0.1278. These data were deposited in the Cambridge Crystallographic data centre, CCDC 752637.

1,3,5-Tri((4-(hydroxymethyl)phenoxy)methyl)-2,4,6-triethylbenzene (11) White solid, yield 88.5%. m.p. 166.2—167.1 ℃; ^{1}H NMR ($CDCl_3$) δ: 7.28 (d, J =

8.0 Hz, 6H), 6.97 (d, J=8.5 Hz, 6H), 5.03 (s, 6H), 4.57 (s, 6H), 2.75—2.80 (m, 6H), 1.73 (s, 3H), 1.16—1.19 (m, 9H); ^{13}C NMR (DMSO-d_6) δ: 157.6, 145.3, 134.9, 130.9, 128.0, 114.0, 64.1, 62.6, 22.4, 16.2; IR (KBr) v: 3239, 2963, 2929, 2873, 2363, 1611, 1584, 1511, 1455, 1372, 1301, 1236, 1175, 1110, 1045, 999, 861, 835, 767, 679, 573 cm^{-1}. HRMS calcd for $C_{36}H_{42}O_6Na^+$ [M+Na^+] 593.2874, found 593.2859.

Crystallographic data for 11 [$C_{36}H_{42}O_6$]; M_r=570.70; monoclinic; space group $C2/c$; a=36.0607(12) Å; b=9.5663(3) Å; c=25.2886(8) Å; α=90°; β=131.8380(10)°; γ=90°; V=6499.5(4) Å^3; ρ_{calcd}=1.166 g•cm^{-3}; T=296(2) K; 37189 independent measured reflections; F^2 refinement; R_1=0.0727; wR_2=0.1825. These data were deposited in the Cambridge Crystallographic data centre, CCDC 752638.

The synthesis 1,3,5-tri((3,5-dihydroxyphenoxy)-methyl)-2,4,6-triethylbenzene (13) To a mixture of compound **1** (2.1 g, 4.8 mmol) and potassium carbonate (4.0 g, 28.8 mmol) in DMF (200 mL), 5-hydroxy-1,3-phenylene diacetate[15] (3.3 g, 15.7 mmol) was added and the reaction was monitored by TLC until completion. The reaction mixture was poured into ice water (400 mL) and acidified with 1 mol/L hydrochloride acid to pH of 5—6. The mixture was extracted by CH_2Cl_2 (300 mL×3) and the combined organic layer was washed with brine, dried over $MgSO_4$. The crude product **12** obtained after filtration and solvent removing was used directly in next step. The residue **12** was dissolved in 1 mol/L potassium hydroxide methanol solution (100 mL) and stirred at room temperature overnight. MeOH was removed under reduced pressure and the residue was extracted by CH_2Cl_2 (300 mL×3). The combined organic layer was washed with brine and dried over $MgSO_4$. After filtration and solvent removing, the crude product was purified by silica gel chromatography to afford compound **13** (0.88 g, 31.7%) as a white solid. m.p. 191.3—193.3 ℃; ^{1}H NMR (DMSO-d_6) δ: 9.26 (s, 6H), 5.93 (s, 6H), 5.88 (s, 3H), 4.93 (s, 6H), 2.69—2.71 (m, 6H), 1.14—1.17 (m, 9H); ^{13}C NMR (DMSO-d_6) δ: 160.47, 159.09, 145.22, 130.89, 95.78, 93.18, 63.71, 22.32, 16.14; IR (KBr) v: 3382, 2970, 2362, 1607, 1496, 1372, 1349, 1261, 1150, 1035, 1009, 950, 825, 781, 680, 572 cm^{-1}. HRMS calcd for $C_{33}H_{37}O_9^+$ [M+H^+] 577.2432, found 577.2415.

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