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Trigonal Rigid Triphenols: Self-Assembly and Multicomponent Lattice Inclusion

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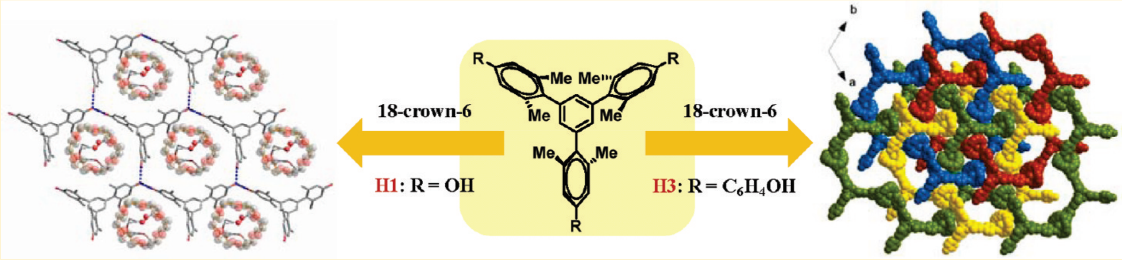
Supporting Information

ABSTRACT:



The sterics introduced via methyl groups impart rigidity and inclusion behavior to trigonal C_3-symmetric triphenol hosts **H1**−**H4**. Triphenol **H1** is found to mimic the O−H···O hydrogen-bonded self-assembly of trimesic acid to yield porous honeycomb nets. It is found that 18-crown-6⊂**H1** in turn binds guest molecules in the hexagonal voids to yield guest⊂guest⊂host multicomponent molecular crystals. The triphenol **H2** and the homologous derivatives **H3** and **H4** are also found to crystallize with 18-crown-6 and other guests to yield multicomponent crystals, but in these cases the 18-crown-6 is found to serve as a spacer. While the structure of **H2** is determined in its guest-free form, some of the inclusion compounds of triphenols lend themselves to crystal packings that are deciphered based on network topologies. The networks observed for **H1**−**Tol** and **H3**−**C**−**B**−**Et** are unique; in the latter, the crystal packing analysis reveals organization of molecules into a pattern that is reminiscent of borromean rings.

INTRODUCTION

The ability to organize molecules in a desirable manner is pertinent to the development of materials with predefined properties.[1] Although crystal structures, which represent an extreme of periodic organization of molecules in three dimension, cannot yet be predicted a priori, it is increasingly becoming possible to control the molecular order to some degree based on directed hydrogen bonding and metal-assisted self-assembly.[2] One aspect of self-assembly that has been advantageously exploited is in the construction of porous materials.[1,3] Indeed, development of porous metal−organic materials/frameworks (MOMs/MOFs) for the binding of gases is an intensely pursued topic of research at present.[4] Insofar as hydrogen-bonded self-assembly is concerned, a prototype example that yields a predictable honeycomb porous network constitutes the case of trimesic acid.[5] It has been found to exhibit dimorphism with hexagonal channels of diameter ca. 14 Å, which are interpenetrated. The interpenetration has been shown to be destroyed by crystallization of trimesic acid in the presence of guest molecules such as coronene, [18]annulene, hexahelicene, and pyrene.[6]

Recently, we envisaged that the C_3-symmetric triphenols **H1** and **H2** (Chart 1) should be unique in undergoing hydrogen-bonded self-assembly into porous networks for guest inclusion.[7] It was shown that both **H1** and **H2** do indeed exhibit strong propensity to self-assemble into porous networks in which the guest molecules could be included to construct multicomponent molecular crystals. A feature that is inherent to these host systems is that the sterics enforced via methyl groups ensure that the hydroxyphenyl/aryl rings lie orthogonally to the central aromatic core. A result of this is higher thickness of the interior cavities thus generated via self-assembly; we have shown that host **H1** undergoes hydrogen-bonded self-assembly into honeycomb networks with hexagonal voids that include 18-crown-6 and other neutral as well as ionic guest molecules to afford guest⊂guest⊂host multicomponent crystals in a manner akin to Russian dolls.[8] Further, in these systems, the self-assembly via phenolic hydroxy groups over carboxyl functionalities was deemed advantageous from the point of view of flexibility in the adoption of supramolecular synthons.[9] The phenolic hydroxy groups hydrogen bond in a variety of modes/synthons[10] as compared to the

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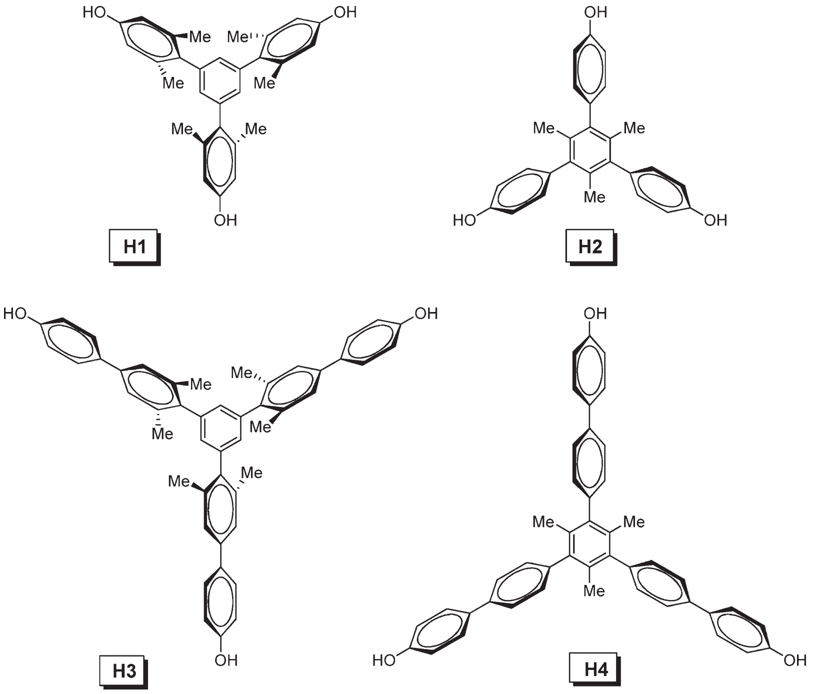
Chart 1. Molecular Structures of Hosts H1 and H2, and their Phenyl-Extended Homologues H3 and H4, respectively



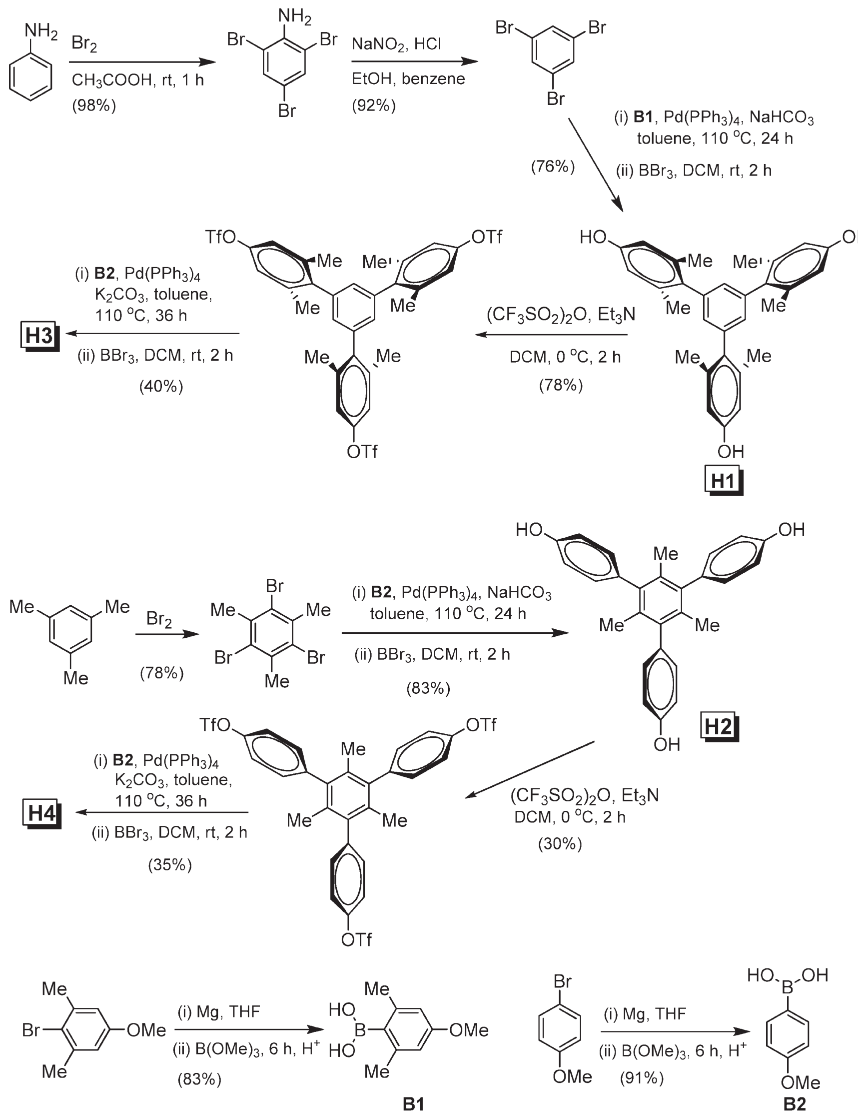
carboxylic acids, which predominantly exhibit dimeric and catemeric motifs.[11] The flexibility in synthon adoption, although detrimental to predictable organization of molecules, may confer the hosts with the liberty to explore packing modes that are suitable to a given guest system. In other words, the synthon flexibility may render the hosts to be *responsive* systems to include any guest molecule type. In the present investigation, we have expanded our initial findings with hosts **H1** and **H2** and designed homologous systems **H3** and **H4** for guest inclusion. Given that the phenyl rings are almost coplanar in the crystal structures of simple biaryls,[12] it was surmised that the self-assembly of homologous hosts **H3** and **H4** may lead to networks with considerably larger cavities.[13] We have found that the solvent of crystallization is crucial to obtain the inclusion compounds, which alludes to the importance of solvent on synthon adoption. Herein, we report the formation of novel multicomponent inclusion compounds with hosts **H1**, **H3**, and **H4**. The crystal structure of host **H2** in its guest-free form is also described.

RESULTS AND DISCUSSION

Synthesis of Triphenols H1−H4. The synthesis and characterization of triphenol hosts **H1** and **H2** have already been published by us elsewhere.[7] The hosts **H3** and **H4** were readily synthesized starting from **H1** and **H2**; the latter were converted to their triflates and subjected to Suzuki coupling with 4-methoxyphenyl boronic acid under Pd(0)-catalyzed conditions. The resultant methoxy derivatives were demethylated using BBr_3 to afford extended triphenol hosts **H3** and **H4** (Scheme 1).

Inclusion Behavior of the Triphenols H1−H4. In our numerous crystallization experiments with hosts **H1** and **H2**, we found that they invariably form inclusion crystals in neat DMSO and EtOAc solvents, respectively.[7] In the absence of these solvents, both **H1** and **H2** failed to crystallize. To examine the extent to which the choice of solvent influences crystallization of **H1** and **H2** in the absence and presence of guests, crystallization in several combinations of solvents containing either DMSO or EtOAc as a partner was explored. We were successful in obtaining the crystals of both **H1** and **H2** in DMSO-$CHCl_3$-toluene and EtOAc-CH_2Cl_2-pet. ether, respectively. The crystals obtained in these solvents were found to be indeed different from those obtained in neat solvent systems, cf. Table 1. The solvent/guest-dependent molecular assembly of hosts **H1** and **H2** prompted us to explore further such a property in the presence of 18-crown-6 guest, which was shown to be readily included in the crystal lattices of both **H1** and **H2** in our previous investigation.[7] Thus, crystallization of **H1** with 18-crown-6 and DME-H_2O led to multicomponent molecular crystals containing the solvent and water. Indeed, the crystals were found to be isostructural with those containing methanol−water and methanol-nitromethane,[7] cf. Table 1. Likewise, multicomponent crystals were also obtained when ammonium acetate was employed in conjunction with 18-crown-6. The host **H2** was found to crystallize in its guest-free form, while our attempts to obtain the crystals of **H2** in our previous investigations were unsuccessful. This shows that slight variation in solvent/s of crystallization influences the host−guest phenomenon. The crystallization of hosts **H3** and **H4** was explored in various solvents and in several combinations of solvents with and without macrocyclic 18-crown-6 guest. The host **H3** yielded crystals in an ethanol−acetonitrile−benzene mixture containing 18-crown-6, while **H4** afforded crystals in toluene−EtOAc with and without inclusion of 18-crown-6. All the host−guest inclusion compounds were characterized by X-ray studies as well as by ^1H NMR analysis of the crystals. The details of inclusion compounds, space groups, and abbreviations adopted for the inclusion compounds are given in Table 1, and the crystal data are collected in Table 2. The metrics for important hydrogen bonds that are responsible for the self-assembly are collated in Table 3. In the following are described the modes of self-assembly and

Scheme 1. Synthetic Routes for the Inclusion Hosts H1−H4



the ways in which the guest species are bound in the crystal lattices.

H1-Tol. Good quality crystals of triphenol host **H1** were obtained from a DMSO−$CHCl_3$−toluene mixture by slow evaporation. The crystals were found to be monoclinic ($C2/c$) with one molecule of **H1** and two molecules of toluene in the asymmetric unit cell; the host−guest stoichiometry was also confirmed by TGA analysis, cf. Supporting Information. The dimethylhydroxyphenyl rings of **H1** in its structure are found to be roughly orthogonal to the plane of the central benzene ring with the angles between the benzene plane and the orthogonal aryl rings being ca. 87−88°. The crystal packing reveals that the phenolic OH groups are bonded via O−H···O hydrogen bonds in a zigzag manner down the *b*-axis to lead to a three-dimensional (3D) assembly (Figure 1). One observes channels down the *b*-axis in which the guest toluene molecules are found to be located. The guests seemingly enjoy translational motion to account for the observed disorder.

The topology of the hydrogen-bonded assembly was examined by TOPOS program.[14] The Schläfli notation that is determined for the H-bonded molecular assembly is $4^4 \cdot 6^{11}$. To the best of our knowledge, the network of this vertex symbol is heretofore unknown.

H1-C-DME. As mentioned already, crystallization of triphenols **H1** and **H2** in the presence of 18-crown-6 yielded multicomponent molecular crystals in which the crown is filled with solvents, that is, $CH_3OH/CH_3NO_2/H_2O$.[7] Host **H1** readily yielded the crystals with dimethoxyethane in the presence of 18-crown-6. The X-ray crystal structure determination revealed that the crystals belong to monoclinic lattice system (space group: $C2/c$) with one molecule each of **H1**, 18-crown-6 and half molecule of dimethoxyethane and 1.5 water molecules in the asymmetric unit. As shown in Figure 2, the hydrogen-bonded self-assembly of triphenol **H1** leads to infinite 2D chicken-wire networks with hexagonal voids along the *ab*-plane down the *c*-axis. The guest 18-crown-6 molecules nicely fit into the hexagonal enclosures resulting from the assembly of three **H1** building blocks. The vacant space in the crown is found to be filled by two disordered water molecules. The chicken-wire layers in the *ab*-plane are marginally shifted relative to each other with the solvent dimethoxyethane

Table 1. Details of Crystallization of Hosts H1−H4 with and without Guests and their Codes

host	guest and/or solvent/s used for crystallization	host-guest composition	space group	code
H1	DMSO	**H1**•DMSO•H_2O (1:2:1)[7]	$P2_12_12_1$	**H1-DMSO**
H1	DMSO, $CHCl_3$, toluene	**H1**•toluene (1:1.5)	*C2/c*	**H1-Tol**
H1	MeOH, EtOH, 18-crown-6	**H1**•18-crown-6•MeOH•H_2O (1:1:1:1)[7]	*C2/c*	**H1-C-MeW**
H1	MeOH, NO_2Me, 18-crown-6	**H1**•18-crown-6•MeOH•H_2O (1:1:1:1)[7]	*C2/c*	**H1-C-MeW**
H1	DMSO, 18-crown-6, DME	**H1**•18-crown-6•DME •H_2O (1:1:0.5:1.5)	*C2/c*	**H1-C-DME**
H1	DMSO, 18-crown-6, CH_3COONH_4	**H1**•18-crown-6• CH_3COONH_4•H_2O (1:1:1:1)	$P2_1/n$	**H1-C-Aac**
H2	EtOAc	**H2**•EtOAc (1:1)[7]	*P2/n*	**H2-EA**
H2	EtOAc, CH_2Cl_2, pet. ether	**H2**	*I4cm*	**H2**
H2	EtOAc, dioxane, 18-crown-6	**H2**•18-crown-6•H_2O (1:1:2)	*P–1*	**H2-C-W**
H3	ethanol, CH_3CN, benzene, 18-crown-6	**H3**•18-crown-6•benzene• CH_3CN•H_2O (1:1:0.167:0.5:4)	*R–3*	**H3-C-B-Et**
H4	EtOAc, toluene	**H4**•toluene (1:1)	*I–4*	**H4-Tol**
H4	EtOAc, toluene, 18-crown-6	**H4**•18-crown-6•toluene•H_2O (1:1:4:3)	$P2_12_12_1$	**H4-C-Tol**

molecules occupying the interlayer voids (Figure 2). All the guest molecules, that is, 18-crown-6, water and dimethoxyethane, are found to be severely disordered. While each of the **H1** molecules self-assembles with its three hydroxyphenyl rings via O−H···O hydrogen bonds, a closer analysis shows that one of the water molecules that is bonded to the crown forms a strong O−H···O hydrogen bond with one of the hydroxy group of **H1** in the adjacent layer approximately down the *c*-axis, cf. Figure 2b.

H1-C-Aac. As mentioned already, host **H1** forms honeycomb networks in all crystals containing 18-crown-6 as one of the guests. Recently, Nangia and co-workers have demonstrated the crucial role of cation in the self-assembly of *cis*,*cis*-1,3,5-cyclohexanetricarboxylic acid.[15] With the latter, they have shown that one obtains networks of β-arsenic topology with $Na^+ \subset$18-crown-6 and black phosphorus network with $NH_4^+ \subset$18-crown-6. We wished to explore if the presence of a cation such as NH_4^+ can make any difference. The crystallization of host **H1** in the presence of 18-crown-6 and CH_3COONH_4 yielded crystals, whose structure determination revealed the presence of one host molecule **H1**, one 18-crown-6, one CH_3COONH_4, and an adventitious water molecule in the asymmetric unit cell, that is, **H1**·18-crown-6·CH_3COONH_4·H_2O. The crystal packing reveals the absence of anticipated honeycomb network. One observes that the host triphenol molecules are interconnected by water as well as the acetate counteranion to lead to a two-dimensional (2D) layered structure along the *ac* plane as shown in Figure 3. The layers in the *ac* plane are offset with respect to each other to make up the crystal. The guest crown molecules are found to be located in the voids thus formed. Of course, the ammonium cation is found to be trapped by the crown via N−H···O hydrogen bonds with the disordered oxygens, which is also supported by cation−dipole interactions.

H2. The crystals of host **H2** in its guest-free form were not realized from several crystallization experiments.[7] As mentioned earlier, the crystallization of **H2** in a EtOAc−CH_2Cl_2−pet. ether solvent mixture led to needle-shaped crystals. The crystal structure determination revealed that the crystals belong to the tetragonal lattice system with *I4cm* space group. The asymmetric unit cell was found to contain only half of the host **H2** with the molecule lying on the mirror plane. One of the hydroxyphenyl rings is found to be disordered. The crystal packing analysis shows that the molecules that are related by 4-fold rotational symmetry are O−H···O hydrogen-bonded down the *c*-axis. The typical crystal packing diagram is shown in Figure 4. The tetrameric association between the molecules that are related by C_4-rotational symmetry is one of the common modes of the assembly of hydroxy compounds.[10] We note that the triphenol **H2** does not readily crystallize in its guest-free form unless crystallized under the conditions described above. A perspective view of the crystal packing down the *c*-axis shows that the hydrogen-bonding motifs in the close packed layers reminisce the "piedfort" motif.[16]

H2-C-W. We noted earlier that the methyl groups of the central mesitylene ring in **H2** may fill the voids partially to account for the absence of honeycomb organization for inclusion of 18-crown-6.[7] The guest crown molecules were found to mediate the assembly by functioning as spacers. It was shown that crystallization of **H2** in EtOAc containing ethanol and benzene leads to multicomponent crystals in which the ethanol guests expand the dimensions of hexagonal voids to allow inclusion of 18-crown-6 that also binds two water molecules.[7] The crystallization in dioxane and EtOAc mixture containing 18-crown-6 with exclusion of ethanol led to rhombus-shaped crystals, whose structure determination revealed the presence of 18-crown-6 and adventitious water in the lattice. The crystals were found to belong to triclinic (space group: $P\bar{1}$) with one molecule each of **H2** and 18-crown-6 and two molecules of water in the asymmetric unit cell. The typical crystal packing of **H2-C-W** is shown in Figure 5. As can be seen, both **H2** and 18-crown-6 are found to form columns that alternate along the *c*-axis. The crown is found to serve as a guest as well as a spacer in the hydrogen-bonded assembly of triphenols into distorted honeycomb networks (Figure 5).

H3-C-B-Et. The phenyl extended triphenol **H3** is expected to exhibit the self-assembly and guest inclusion behavior similar to its simple analogue **H1** with more porosity. The crystallization of **H3** was tried out with and without the addition of 18-crown-6.

Table 2. The Crystal Data for Multicomponent Molecular Compounds of Hosts H1−H4 with Various Guests

	H1-Tol	H1-C-DME	H1-C-Aac	H2
molecular formula	$C_{81}H_{84}O_6$	$C_{88}H_{124}O_{23}$	$C_{44}H_{63}NO_{12}$	$C_{27}H_{24}O_3$
formula weight	1153.48	1549.87	797.95	396.46
crystal system	monoclinic	monoclinic	monoclinic	tetragonal
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$I4cm$ (No. 108)
a (Å)	23.376(7)	23.562(5)	13.932(3)	23.059(2)
b (Å)	13.341(3)	13.960(5)	11.104(2)	23.059(2)
c (Å)	23.042(5)	28.168(7)	28.633(6)	7.478(3)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	105.77(7)	113.15(9)	100.75(6)	90.00
γ (deg)	90.00	90.00	90.00	90.00
volume (Å^3)	6916.0(3)	8519.0(4)	4351.9(5)	3975.8(6)
Z	4	4	4	8
calculated density (mg/m^3)	1.108	1.208	1.218	1.325
absorption coefficient (mm^{-1})	0.068	0.086	0.088	0.085
$F(000)$	2472	3344	1720	1680
goodness-of-fit on F^2	1.050	1.086	1.034	1.046
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0852$, $wR_2 = 0.1936$	$R_1 = 0.1033$, $wR_2 = 0.2736$	$R_1 = 0.0656$, $wR_2 = 0.1221$	$R_1 = 0.0401$, $wR_2 = 0.0996$
R indices (all data)	$R_1 = 0.1621$, $wR_2 = 0.2261$	$R_1 = 0.1695$, $wR_2 = 0.3162$	$R_1 = 0.1278$, $wR_2 = 0.1398$	$R_1 = 0.0447$, $wR_2 = 0.1027$

	H2-C-W	H3-C-B-Et	H4-Tol	H4-C-Tol
molecular formula	$C_{39}H_{48}O_{11}$	$C_{138}H_{164}N_1O_{36}$	$C_{52}H_{44}O_3$	$C_{85}H_{91}O_{12}$
formula weight	692.77	2419.23	716.87	1304.58
crystal system	triclinic	trigonal	tetragonal	orthorhombic
space group	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)	$I\bar{4}$ (No. 82)	$P2_12_12_1$ (No. 19)
a (Å)	10.446(5)	21.037(3)	34.693(5)	9.393(1)
b (Å)	13.758(7)	21.037(3)	34.693(5)	22.498(1)
c (Å)	16.201(8)	53.661(1)	7.198(3)	37.809(9)
α (deg)	108.82(8)	90.00	90.00	90.00
β (deg)	93.86(1)	90.00	90.00	90.00
γ (deg)	108.65(1)	120.00	90.00	90.00
volume (Å^3)	2050.1(8)	20566.0(3)	8664.0(4)	7990.0(2)
Z	2	3	8	4
calculated density (mg/m^3)	1.122	1.184	1.099	1.090
absorption coefficient (mm^{-1})	0.082	0.085	0.067	0.071
$F(000)$	740	7784	3040	2812
goodness-of-fit on F^2	1.092	1.134	1.062	1.061
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.1315$, $wR_2 = 0.3219$	$R_1 = 0.1180$, $wR_2 = 0.3001$	$R_1 = 0.0934$, $wR_2 = 0.2188$	$R_1 = 0.1046$, $wR_2 = 0.2318$
R indices (all data)	$R_1 = 0.1735$, $wR_2 = 0.3736$	$R_1 = 0.1981$, $wR_2 = 0.3498$	$R_1 = 0.1527$, $wR_2 = 0.2513$	$R_1 = 0.1927$, $wR_2 = 0.2699$

Good quality crystals of host **H3** were readily obtained when the crystallization was performed in the presence of 18-crown-6 using an EtOH−CH_3CN−C_6H_6 solvent mixture. The crystals were found to belong to the trigonal lattice system with $R\bar{3}$ space group. The asymmetric unit cell was found to contain two host **H3** molecules sitting on the special position with one-third of occupancy along with one 18-crown-6, half CH_3CN, one-sixth of benzene, and four water molecules. The crystal packing down the *b*-axis reveals two independent host molecules in the asymmetric unit cell, that is, A and B, which self-assemble into layers that are connected by crowns as bridges (Figure 6). Each of the layers in the *ab*-plane shows that the hydroxyphenyl rings of the triphenol are found to be interconnected through O−H···O hydrogen bonds with one water molecule, which is in turn O−H···O hydrogen-bonded to one of the oxygen atoms of 18-crown-6. In other words, the host **H3** self-assembles by the mediation of water molecules that are accommodated as guests in 18-crown-6. The open network structure thus formed is found to be 4-fold interpenetrated as shown in Figure 6. Thus, the voids still left after interpenetration are found to be filled by benzene, acetonitrile, and ethanol as guest molecules. A further inspection of the crystal packing shows that the oxygen atom of one hydroxyphenyl ring of each triphenol molecule involves in a C−H···O hydrogen-bond ($d_{H\cdots O}$ = 2.49 Å, $D_{C\cdots O}$ = 3.42 Å, and $\theta_{C-H\cdots O}$ = 166.0°) to yield a cyclic array of hydroxyphenyl rings in a chair geometry that is overall reminiscent of a rosette at the center of which lies benzene guest, cf. Figure 6. A comparison of the crystal packing of **H3** with **H1** is quite instructive: while **H1** assembles into a 2D honeycomb network in the presence of crowns, the expanded host **H3** assembles into a hexagonal (6,3) net that is bridged by crowns functioning as spacers. The (6,3) net is 4-fold interpenetrated. The point to note here is that the observed molecular assembly is exactly similar to that of the **H1-DMSO**, which is 8-fold interpenetrated.[7] These two structures illustrate the crucial dependence of the host size (in terms of the lengths of the aryl groups) on the self-assembly to afford voids that encapsulate crowns. It is also relevant to point out the fact that the 4-fold penetration closely resembles 3-fold interpenetrated Borromean networks that are based on hydrogen-bonded self-assembly reported recently.[17]

Table 3. The Geometrical Parameters for Important O−H···O Hydrogen Bonds Observed in the Inclusion Compounds of H1−H4

compound	atoms[a]	H···O (Å)	O···O (Å)	∠O−H···O (deg)
H1-Tol[b]	O1−H1···O3		2.72(1)	
	O2−H2···O1		2.72(1)	
	O2−H2···O2		2.76(1)	
H1-C-DME	O1−H1···O3	1.93(1)	2.76(1)	178.7(2)
	O2−H2···O(W)	1.81(1)	2.63(1)	165.1(3)
	O3−H3···O2	1.82(1)	2.65(1)	170.9(2)
H1-C-Aac	O3−H3···O2	1.85(1)	2.68(1)	169.7(1)
	O1−H1···O(ac)	1.82(1)	2.63(1)	161.0(2)
	O2−H2···O(W2)	1.74(1)	2.56(1)	165.1(1)
	O(W1)−H···O3	1.81(1)	2.79(1)	156.4(1)
	O(W3)−H···O(ac)	1.59(1)	2.60(1)	173.7 (1)
H2	O1−H1···O1	1.95(1)	2.75(1)	158.9(1)
H2-C-W	O1−H1···O3	1.90(1)	2.69(1)	160.9(3)
	O(W1)−H···O2		2.75(1)	
	O3−H3···O(W2)	1.77(1)	2.56(1)	163.4(1)
H3-C-B-Et	O1−H1···O(W1)	1.85(1)	2.64(1)	156.0(3)
	O2−H2···O(W2)	1.81(1)	2.65(1)	174.5(3)
H4-Tol	O1−H1···O1	1.90(1)	2.65(1)	148.4(3)
	O2−H2···O2	1.91(1)	2.67(1)	149.3(3)
H4-C-Tol	O3−H3···O1	2.22(1)	3.02(1)	159.0(5)
	O1−H1···O(W1)	1.83(1)	2.67(2)	173.0(7)
	O2−H2···O(W2)	1.86(1)	2.69(1)	170.8(3)

[a] “W” and “ac” refer to water molecules and acetate anion. [b] Hydrogen atoms are disordered.

H4-Tol. Although the host **H4** was found to include a variety of guest molecules and yield crystals that were seemingly good, their isolation from the mother liquor for structural determinations proved very difficult; the crystals developed cracks upon removal from the mother liquor to preclude structure determinations successfully. Similar to the guest-free self-assembly of **H2**, the phenyl-extended homologue **H4** also exhibited tetragonal crystal packing with the space group $I\bar{4}$. The asymmetric unit cell was found to contain one host and one guest toluene molecule. One of the hydroxyphenyl rings and the toluene guest molecule were found to be disordered. One observes that the O−H···O hydrogen-bonded molecules are related by C_4-rotational symmetry down the *c*-axis. The adjacent layers are offset in a manner that one observes again a “piedfort” motif[16] for the hydrogen-bonded motif down the *c*-axis (Figure 7).

H4-C-Tol. The crystallization of host **H4** with 18-crown-6 using equimolar mixture of EtOAc and toluene furnished thick needle-shaped crystals, which were found to belong to orthorhombic lattice system with the space group $P2_12_12_1$. The asymmetric unit cell was found to contain one molecule each of host **H4** and 18-crown-6 along with four toluene and three water molecules. As in **H2-C-W** and **H3-C-B-Et**, the crown guest molecules are found to function as spacers in linking up triphenol **H4** molecules. The two water molecules bonded to the crown oxygens are also found to form O−H···O hydrogen bonds with the hydroxyphenyl rings of **H4**. In the process, each triphenol engages two hydroxyphenyl rings. The resultant 2D hydrogen-bonded assembly propagates to develop a pseudohoneycomb structure as shown in Figure 8. In other words, each triphenol unit is found to self-assemble with the aid of 18-crown-6 guest molecules into a pseudo-honeycomb structure to furnish corrugated 2D sheets.[10] Two such adjacent sheets interpenetrate to make up the crystal. As the host **H4** is an extended version of **H2**,

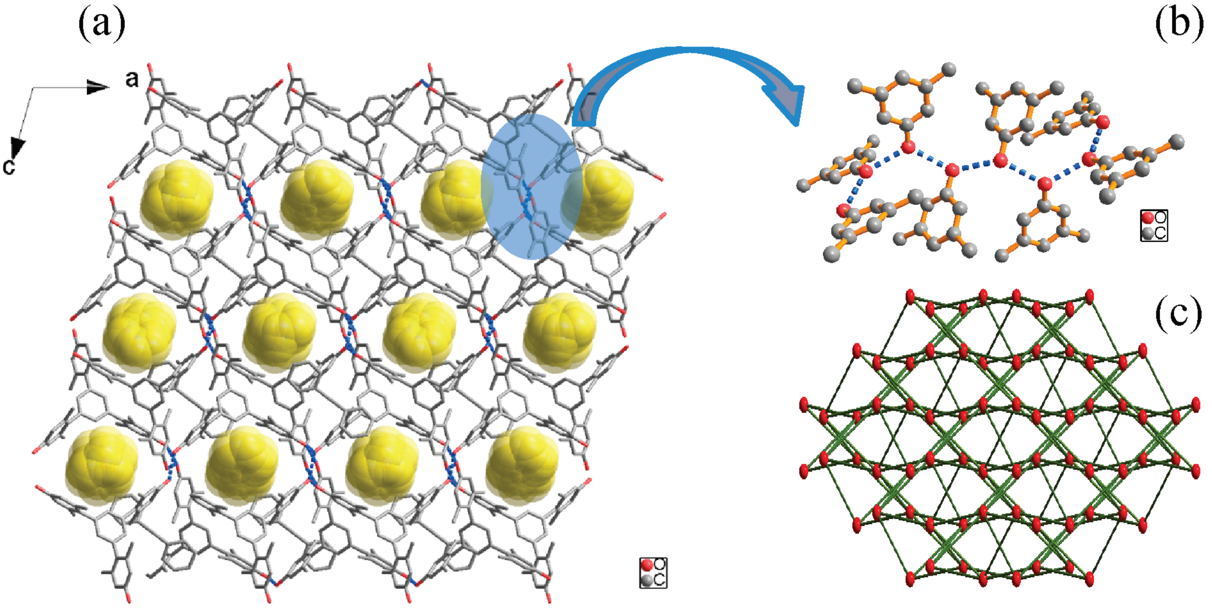


Figure 1. The crystal packing of **H1-Tol** inclusion compound (a), and the pattern of O−H···O hydrogen-bonded assembly (b). Schematic representation of the host assembly upon reduction of the host structure into a 3-connecting module (c).

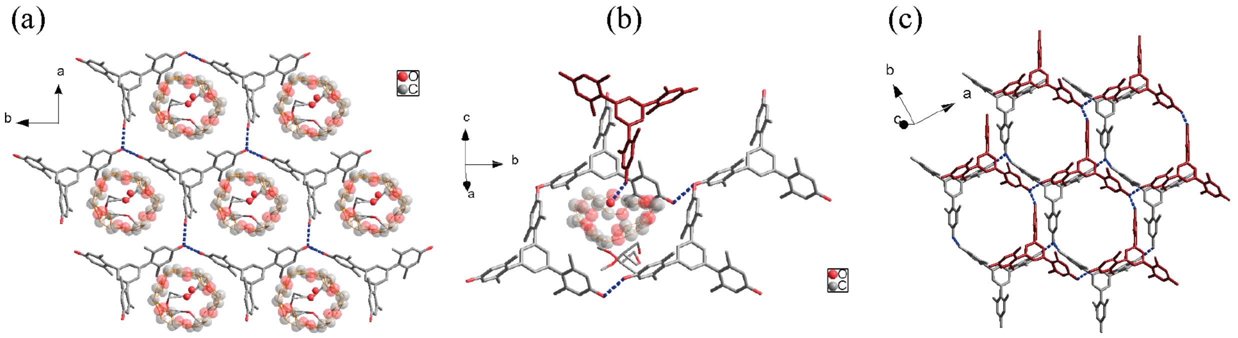


Figure 2. (a) The O−H···O hydrogen bond-mediated self-assembly of **H1** into honeycomb layers. The water included in the crown hydrogen bonds with hydroxyl oxygen of another **H1** in the adjacent layer (b). The crystal packing down *c*-axis without the guests is shown at far right (c).

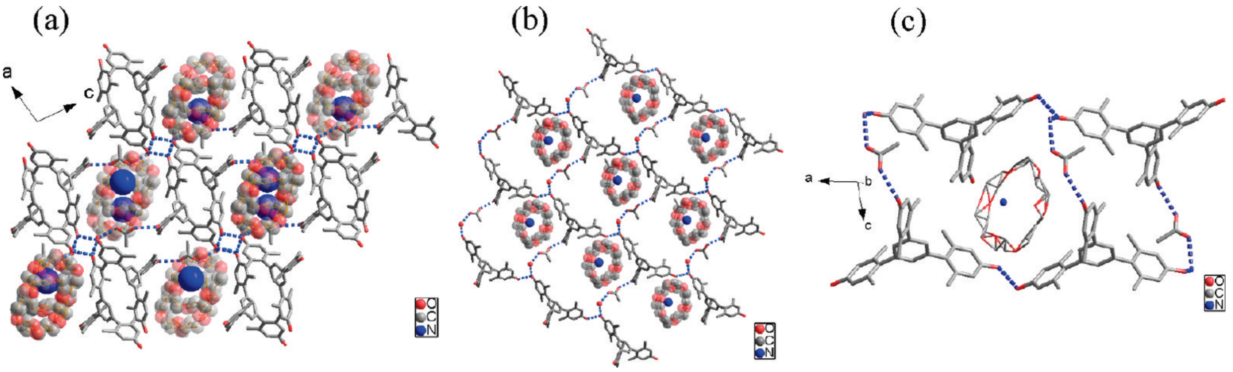


Figure 3. The crystal packing of **H1-C-Aac** (a) and the molecular organization in one of the layers to exemplify the self-assembly that leads to voids for guest inclusion (b). A segment of hydrogen-bonded assembly involving acetate anion is also shown (c).

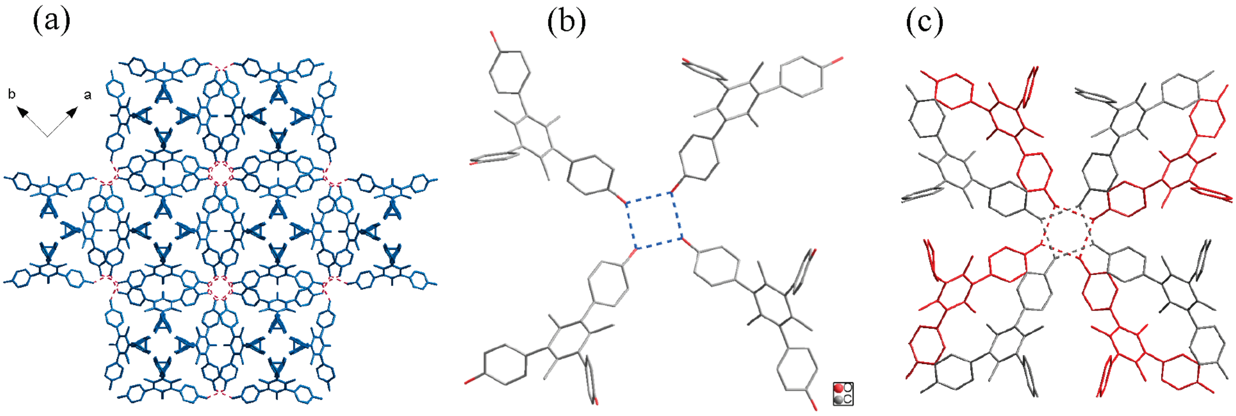


Figure 4. The crystal packing of **H2** (a). The O−H···O hydrogen bond-mediated tetrameric association down the *c*-axis is shown separately (b). Notice that the hydrogen-bonding motif down the *c*-axis appears like a piedfort motif (c). The hydrogen atoms have been removed for clarity.

larger cavities of the former are filled by interpenetration, and the guest toluene molecules are found to be accommodated in the void spaces.

Generalizations Concerning Hydrogen-Bonded Self-Assembly of H1−H4 and Formation of Multicomponent Molecular Crystals. Phenols are acidic and hence can involve in hydrogen bonding by functioning both as strong hydrogen bond donors and acceptors.[9] Indeed, one may observe a range of synthons for the association of phenols, which include dimers, trimers, linear chains, helices, etc.[10] Thus, the self-assembly based on phenols as applied to rational development of porous organic materials in general and inclusion host compounds in particular should be appealing from the point of synthon flexibility;[1,3,9] the latter may facilitate guest-dependent crystal packing or adoption of synthons. A cursory perusal of the literature reveals a variety of hosts that are based on phenolic functionality. These include hydroquinone,[18] Dianin's compound,[18] hexa-host,[19] anthracene bisresorcinols,[20] bifluorene-tetraphenols,[13a,b,21] bimesityl-based tetraphenols reported from our laboratory,[22] binaphthols,[23] H-shaped tetraphenols,[24] T-shaped bisphenols,[25] calixarenes,[26] resorcinarenes,[26] etc.[27] In the backdrop of this noted propensity of phenols to assemble via O−H···O hydrogen bonds, we were

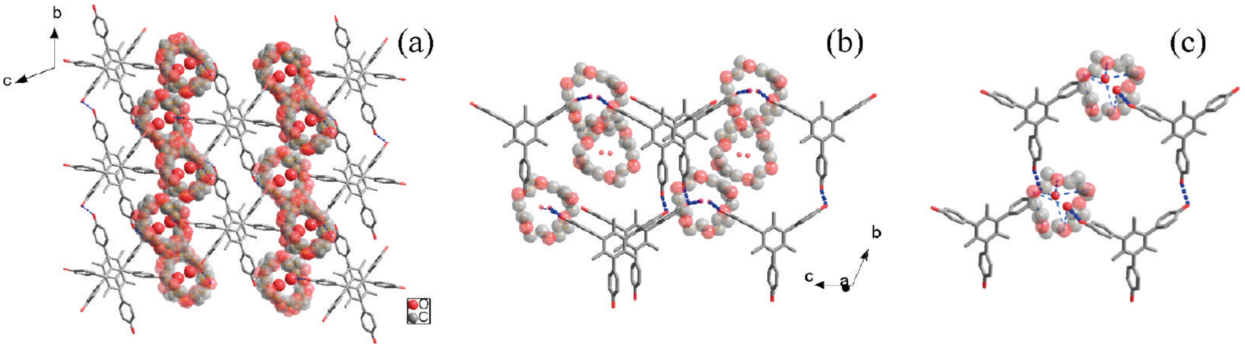


Figure 5. The molecular packing in the crystals of **H2-C-W** (a). The guest crown molecules mediate the assembly with the aid of water molecules that are in turn bound via O−H···O hydrogen bonds (b). Notice that the crystal packing is akin to **H1-C-DME**, except that the trimeric assembly down the *a*-axis is mediated by crown guest molecules (c).

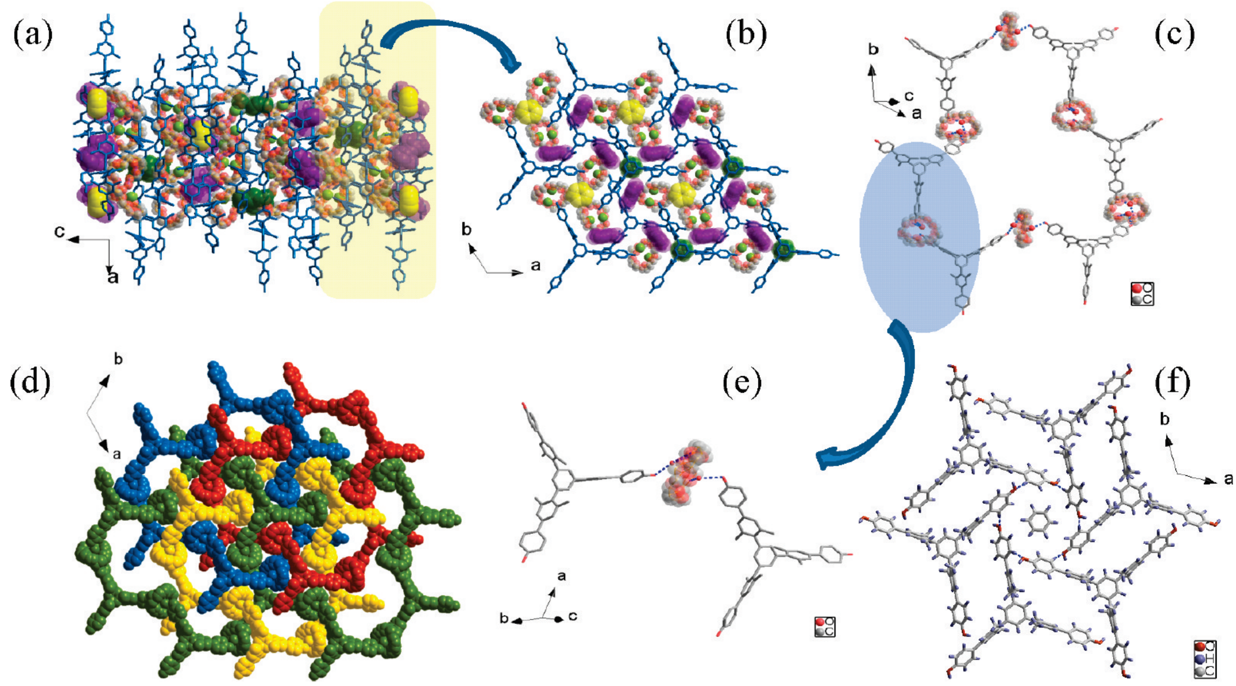


Figure 6. The crystal packing of **H3-C-B-Et** down the *b*-axis (a); each of the layers in the *ab*-plane is shown separately on the right (b). The basic motif of the (6,3) net (c), which undergoes 4-fold interpenetration (d). The water embedded in crown-mediated linkage of the triphenols is shown (e) along with the C−H···O hydrogen-bonded motif that augments the self-assembly of the host **H3** in the *ab*-plane (f).

intrigued by the reported observation that the trigonal 1,3,5-tris(4-hydroxyphenyl)benzene does not undergo self-assembly into an expected (6,3) honeycomb porous 2D net.[28] We envisaged that rigidification of the hydroxyphenyl rings by exploiting sterics introduced through methyl groups as in **H1** and **H2** might allow porous honeycomb networks to be observed in the presence of suitable guests.[7] The motivation for rigidification was indeed derived from remarkable inclusion behavior uncovered for tetraarylpyrenes characterized by perpendicular planes that are devoid of functional groups that exhibit strong intermolecular hydrogen bonding.[29]

Although inclusion compounds were obtained with **H1** and **H2** previously, the change in crystallization solvents evidently leads to new inclusion compounds with **H1** and **H2**. Indeed, **H2** is found to crystallize in the guest-free form under the changed solvent conditions. While the host **H1** is found to undergo self-assembly either into a highly interpenetrated 2D network (in **H1-DMSO**) or a 3D unique net (in **H1-Tol**),[7] one observes the formation of expected porous 2D honeycomb networks with 18-crown-6 as a guest; indeed the crowns fit into the hexagonal voids and in turn include solvent water molecules. It should be noted that the multicomponent inclusion compounds with 18-crown-6, DME, and water is isostructural with **H1-C-MeW** and **H1-C-MeNM** (Table 1) reported earlier. This suggests the fact that the self-assembly remains unaltered with subtle variation of solvents and is robust to replacement of one kind of solvent with another. In the case of **H1-C-Aac**, water, and acetate anions are found to expand the hydrogen-bonded assembly to yield corrugated layers with pseudohexagonal voids in which $NH_4^+\subset$crown complexes are bound. From the present as well as our previous investigations, host **H2** is found not to yield such hydrogen-bonded 2D honeycomb networks with hexagonal voids in the presence of

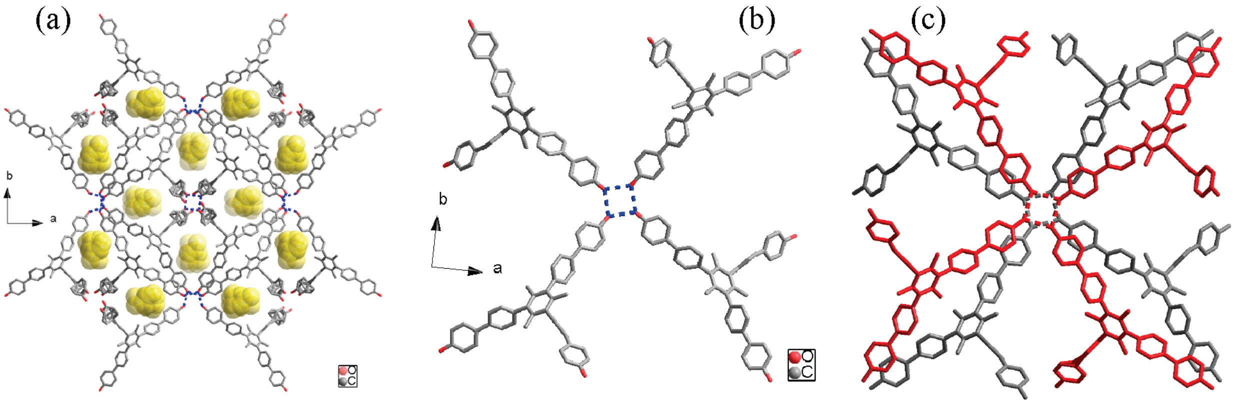


Figure 7. The crystal packing of **H3-Tol** (a); notice that one of the hydroxyphenyl rings is disordered. The O−H···O hydrogen bonded tetrameric assembly (b). Notice that the layers down the *c*-axis are offset such that the hydrogen-bonded motif appears like a piedfort (c).

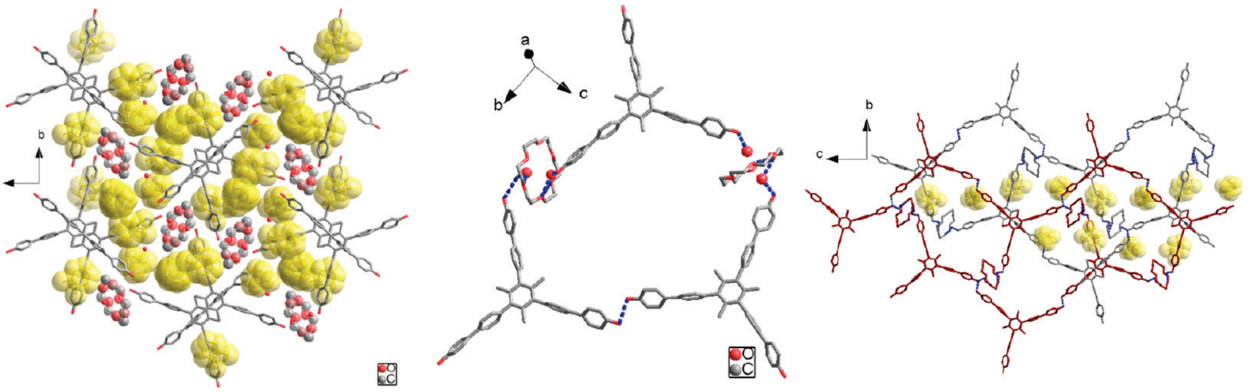


Figure 8. The crystal packing of **H4-C-Tol** (a). Water molecules bound in the crowns are found to expand the hydrogen-bonded assembly of **H4** (b). Notice the 2-fold interpenetration of corrugated 2D nets constructed by the mediation of crown-water complexes (c).

18-crown-6, which underscores the importance of (i) thickness of the interior pores that result and (ii) location of methyl groups that protrude into the hexagonal voids, if the self-assembly analogous to **H1** were to occur. Otherwise, it should be noted that **H2** does crystallize with inclusion of 18-crown-6 in the lattice. In the crystal structure of **H2-C-W**, water and the crown that bind the former are found to mediate the overall self-assembly as shown in Figure 5. In other words, the crown is found to function as a spacer in all of the inclusions compounds of **H2**. Presumably, the assembly of the triphenol does not lead to pores with sufficient thickness to include 18-crown-6. The extended triphenol **H3** is found to crystallize in the presence of 18-crown-6 to yield multicomponent molecular crystals by including benzene and acetonitrile also as guest species. The crystal packing reveals the absence of a honeycomb structure. A careful analysis shows that the crowns act as spacers to yield a hexameric assembly that is highly porous to undergo self-interpenetration. In fact, the packing akin to **H1**-**DMSO** in which the (6,3) net undergoes 8-fold interpenetration.[7] In this instance, the crown-mediated hexameric honeycomb network is found to be 4-fold interpenetrated (Figure 6). In the crystal structure, the hydroxyphenyl ring and the dimethyl phenyl ring are found to be almost coplanar with the angles between the planes to be ca. 32°; in fact, this is approximately the magnitude that is found in a majority of the crystal structures of biphenyls deposited in CSD.[30] This means that the biphenyl ring can be considered to be rigid enough to permit assembly of the host into the basic trimeric motif with large hexagonal pores. The fact that one does not observe honeycomb network could also be a consequence of the dimensions of the employed guest crown being too small compared to the void dimensions that would otherwise be created. There is no reason to believe that the porous 2D network cannot be observed with a suitable guest. Insofar as 18-crown-6 as the guest is concerned, **H4** self-assembles with the former as a spacer to afford pseudohexagonal (6,3) net that is self-interpenetrated. A scenario that is similar to **H2** is observed in the crystals of **H4-C-Tol**; the crown is found to serve as a spacer to yield a pseudohoneycomb assembly that is doubly interpenetrated.

■ CONCLUSIONS

All the triphenol hosts **H1**−**H4** exhibit notable guest inclusion, which attests to the importance of orthogonal aromatic planes—a feature ensured via sterics. In other words, the results illustrate the fact that the desired crystal packing with porosity for guest inclusion can be engineered via rational molecular design that exploits sterics.[29,31] The host **H1** reliably yields perfect honeycomb structure with hexagonal voids in which the 18-crown-6 nicely fits; of course, the latter further binds guests such as methanol,[7] nitromethane,[7] ammonium cation, water, etc. to furnish guest⊂guest⊂host multicomponent inclusion compounds.[8] That the length of the rigid aryl moiety is crucial for such an assembly is demonstrated by the crystal structure of **H3-C-B-Et**, which yields crown-spaced assembly. The host triphenols **H2** and **H4** do assemble with inclusion of crown, but the latter serves as a spacer. In the absence of crown, the triphenols include solvent molecules and self-assemble into nets that are 2- and 3D (for **H1-Tol** and **H4-Tol**). The host **H2** is found to crystallize in guest-free form via O−H···O hydrogen-bonded tetrameric assembly that propagates.

A variety of C_3-symmetric inclusion compounds are reported in the literature. This symmetry is so much apparent in several important host systems such as tri-*ortho*-thymotide (TOT),[32] perhydrotriphenylene,[32] triphenyl methane,[32] tris(*o*-phenylenedioxy)cyclotriphosphazene,[4e,f,33] etc.[34] The prototype example of a C_3-symmetric host that undergoes hydrogen-bonded self-assembly into a porous hexagonal network constitutes 1,3,5-benzenetricarboxylic acid (trimesic acid).[5,6] The results with **H1** show that honeycomb networks with hexagonal voids can likewise be constructed with triphenol **H1**. Given the synthon flexibility that is inherent to phenols, we believe that the rigid triphenols **H1**−**H4** reported herein should be an invaluable addition to the class of C_3-symmetric inclusion hosts.

■ EXPERIMENTAL SECTION

Anhydrous tetrahydrofuran (THF) was freshly distilled over sodium prior to use. All other solvents were distilled prior to use. The progress of reactions was monitored by analytical thin layer chromatography (TLC) using aluminum sheets precoated with silica gel. Column chromatography was conducted with silica gel (60−120 mesh). ^{1}H and ^{13}C NMR spectra were recorded on 400 and 500 MHz spectrometers using deuterated solvents. The TGA and DSC measurements were carried out on a TGA-DSC1 with a heating rate of 10 °C/min under N_2 atmosphere. Commercial chemicals were used as received.

Synthesis of Triphenol Hosts H1−H4. A general procedure for the synthesis of triphenols **H1**−**H4** involved 3-fold Suzuki coupling of tribromobenzenes/triaryl triflates with suitably functionalized boronic acids using $Pd(PPh_3)_4$ as a catalyst (Scheme 1). The preparation of triphenol hosts **H1** and **H2**, that is, 1,3,5-tris(2,6-dimethyl-4-hydroxyphenyl)benzene and 1,3,5-tris(4-hydroxyphenyl)mesitylene, has previously been published by us.[7]

General Procedure for the Esterification of Phenols with Triflic Anhydride. To a solution of triphenol (1.0 mmol) in anhydrous CH_2Cl_2 (30 mL) were added Et_3N (4.5 mmol) and triflic anhydride (3.1 mmol). The reaction mixture was stirred at 0−5 °C for 2 h. At the end of this period, the reaction mixture was quenched by pouring the contents into 50 mL of ice-cold water. The organic material was extracted with DCM, washed with water, dried over anhyd Na_2SO_4, and concentrated in vacuo. Filtration over a short-pad of silica gel gave the pure triaryl triflate as a colorless solid.

1,3,5-Tris(2,6-dimethyl-4-trifluoromethylsufonylphenyl)benzene. Yield 78%. Colorless powder; mp 164−168 °C; IR (KBr) cm^{-1} 2962 (m), 1602 (s), 1427 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (18H, s), 6.94 (6H, s), 7.03 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 118.8 (q, J = 38.75 Hz), 119.9, 128.4, 138.6, 140.8, 141.2, 148.4; ESI-MS$^+$ m/z Calcd for $C_{33}H_{27}O_9F_9S_3$ 834.75 [M + Cl]$^-$, found 869.0362.

1,3,5-Tris(4-trifluoromethylsulfonylphenyl)mesitylene. Yield 30%; mp 128−132 °C; IR (KBr) cm^{-1} 2930 (m), 1914 (w), 1504 (s), 1432 (s), 1219 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (9H, s), 7.21 (6H, d, J = 8.20 Hz), 7.30 (6H, d, J = 8.20 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 118.7 (q, J = 39.0 Hz), 121.6, 131.1, 133.6, 138.3, 141.9, 148.4; ESI-MS$^+$ m/z Calcd for $C_{30}H_{21}O_9F_9S_3$ 792.67 [M + Cl], found 826.9898.

General Procedure for the Suzuki Coupling with Aryl Triflates. Triflate (1.0 mmol), arylboronic acid (4.5 mmol), $Pd(PPh_3)_4$ (10 mol %, with respect to the triflate), and K_2CO_3 (10 mmol) were introduced into an initially oven-dried and cooled (under N_2) pressure tube. To this mixture, dry toluene (15 mL) was added. The reaction mixture was heated slowly at 70−100 °C and maintained at this temperature for 36 h with constant stirring. After this period, the reaction mixture was cooled to 20 °C, and a saturated aqueous solution of NH_4Cl was added. The organic matter was extracted with $CHCl_3$ and the combined extract was dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo to yield a crude product, which was subjected to column chromatography to isolate the methyl aryl ether as a colorless solid material.

1,3,5-Tris(2,6-dimethyl-4-(*p*-anisyl)phenyl)benzene. Yield 57%. Colorless powder; mp 136−140 °C; IR (KBr) cm^{-1} 2924 (s), 2854 (m), 1607 (s), 1512 (s), 1467 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (18H, s), 3.85 (9H, s), 6.97 (6H, d, J = 8.20 Hz), 7.00 (3H, s), 7.31 (6H, s), 7.56 (6H, d, J = 8.20 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 55.3, 114.1, 125.7, 128.1, 128.4, 133.6, 136.3, 139.4, 140.2, 141.2, 159.0; ESI-MS$^+$ m/z Calcd for $C_{51}H_{48}O_3$ 708.93 [M + H], found 709.3680.

1,3,5-Tris(4-(*p*-anisyl)phenyl)mesitylene. Yield 48%. Colorless powder; mp 160−164 °C; IR (KBr) cm^{-1} 2924 (m), 2836 (m), 1607 (s), 1495 (s), 1458 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (9H, s), 3.78 (9H, s), 6.91 (6H, d, J = 8.80 Hz), 7.22 (6H, d, J = 8.20 Hz), 7.53 (6H, d, J = 8.80 Hz), 7.56 (6H, d, J = 8.20 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 55.3, 114.2, 126.7, 128.0, 129.8, 133.4, 133.5, 138.7, 139.6, 140.4, 159.0; ESI-MS$^+$ m/z Calcd for $C_{48}H_{42}O_3$ 666.85 [M + NH_4], found 684.3474.

Synthesis of Extended Triphenols H3 and H4

General Procedure for Demethylation of Methyl Aryl Ethers. To a solution of methyl aryl ether (0.5 mmol) in 15 mL of dry CH_2Cl_2 at 0 °C was added dropwise BBr_3 solution (0.6 mmol) under a N_2 gas atmosphere. The reaction mixture was allowed to stir overnight. Subsequently, it was quenched with 10% HCl, extracted with ethyl acetate, dried over Na_2SO_4, treated with charcoal, filtered, and concentrated. The pure product was obtained as a colorless solid after filtration over a short pad of silica gel using a mixture of ethyl acetate and pet. ether (50:50), followed by recrystallization from ethyl acetate and pet. ether.

1,3,5-Tris(2,6-dimethyl-4-(*p*-hydroxyphenyl)phenyl)benzene (H3). Yield 72%. mp 188−192 °C colorless powder; IR (KBr) cm^{-1} 3404 (s, br), 1608 (m), 1514 (m), 1466 (m); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.15 (18H, s), 6.82 (6H, d, J = 8.6 Hz), 6.90 (3H, s), 7.33 (6H, s), 7.49 (6H, d, J = 8.6 Hz), 9.47 (3H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.6, 115.6, 124.9, 127.5, 135.6, 139.4, 177.8; ESI-MS$^+$ m/z Calcd for $C_{48}H_{42}O_3$ 666.85 [M + Cl]$^-$, found 701.2825.

1,3,5-Tris(4-(*p*-hydroxyphenyl)phenyl)mesitylene (H4). Yield 73%. mp 182−186 °C Colorless powder; IR (KBr) cm^{-1} 3369 (s, br), 2926 (s), 1609 (m), 1498 (s), 1448 (m), 1258 (s); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.45 (9H, s), 6.84 (6H, d, J = 8.65 Hz), 7.40 (6H, d, J = 8.25 Hz), 7.54 (6H, d, J = 8.65 Hz), 7.65 (6H, d, J = 8.25 Hz), 9.56 (3H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.3, 115.7, 126.0, 127.6, 129.6, 130.5, 132.5, 138.3, 139.0, 139.5, 157.0; ESI-MS$^+$ m/z Calcd for $C_{45}H_{36}O_3$ 624.77 [M + Cl]$^-$, found 659.2356.

Crystallization of Triphenol Hosts H1−H4 with and without Guest Molecules. *Crystallization of **H1-Tol** and **H2**.* A 1:1 mixture of $CHCl_3$ and toluene was layered over a solution of host **H1** (50.0 mg, 0.114 mmol) in DMSO (2.0 mL). Slow evaporation of the resultant clear solution over a period of a week led to square-shaped crystals in a quantitative yield. The crystals were characterized by ^{1}H NMR, TGA, and X-ray crystallography. A similar procedure was used for the crystallization of **H2**. In this instance, a CH_2Cl_2−pet. ether mixture was layered over **H2** in ethyl acetate solution. The crystals thus obtained were found to be devoid of any guest inclusion.

*Crystallization of **H1-C-DME** and **H1-C-Aac**.* **H1** (50.0 mg, 0.114 mmol) and 18-crown-6 (45.0 mg, 0.171 mmol) were dissolved in dimethoxyethane (5.0 mL). Slow evaporation of the resultant clear solution over a period of 4−5 days led to rectangular-shaped crystals. Filtration followed by washing with a $CHCl_3$−pet. ether (50:50) mixture led to isolation of the compound in 70−75% yield based on host **H1**. The crystals were characterized by TGA, DSC, and X-ray crystallography.

A similar procedure was used for the synthesis of **H1-C-Aac**. In this case, ammonium acetate in water was employed; yield of the inclusion compound was 80−85% based on host **H1**.

Preparation of H2-C-W, H3-C-B-Et, and H4-C-Tol. 18-Crown-6 (45.0 mg, 0.171 mmol) dissolved in EtOAc (2.0 mL) was slowly added to a solution of **H2** (50.0 mg, 0.114 mmol) in dioxane (3.0 mL). Slow evaporation of the resultant clear solution over a period of 5−7 days led to square-shaped crystals in a quantitative yield.

A similar procedure was used for the preparation of **H3-C-B-Et** and **H4-C-Tol**. In all cases, the appropriate guest and the solvent were used for crystallization.

X-ray Crystal Structure Determinations. A good quality crystal in each case was mounted in a glass capillary and cooled to 100 K, and the intensity data were collected on a Bruker Nonius SMART APEX CCD detector system with Mo-sealed Siemens ceramic diffraction tube ($\lambda = 0.71073$) and a highly oriented graphite monochromator operating at 50 kV and 30 mA. The data were collected on a hemisphere mode and processed with Bruker SAINTPLUS. Empirical absorption correction was made using Bruker SADABS. The structure was solved in each case by Direct Methods using SHELXTL package and refined by full matrix least-squares method based on F^2 using SHELX97 program. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in their ideal positions with fixed isotropic U values and were allowed to ride with their respective non-hydrogen atoms. The experimental details of crystal data, intensity measurements, structure solution, and refinement are presented in Table 2.

■ ASSOCIATED CONTENT

S Supporting Information. X-ray crystallographic information files (CIF), details of refinement, ^{1}H NMR spectral reproductions and TGA profiles for the multicomponent crystals are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

This paper is dedicated to Prof. K. Venkatesan on the occasion of his 80th birthday.

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