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Guest⊂Guest⊂Host Multicomponent Molecular Crystals: Entrapment of Guest⊂Guest in Honeycomb Networks Formed by Self-Assembly of 1,3,5-Tri(4-hydroxyaryl)benzenes

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Abstract: Sterically-engineered rigid trigonal molecular modules based on 1,3,5-tri(4-hydroxyphenyl)benzenes **H1** and **H2** undergo O-H···O hydrogen-bonded self-assembly into eight-fold catenated hexagonal (6,3) and two-fold interpenetrated undulated square (4,4) networks, respectively. In the presence of [18]crown-6 as a guest, the triphenol **H1** is found to self-assemble into a honeycomb network with hexagonal voids created between three triphenol building blocks. The guest [18]crown-6 molecules are found to be nicely nested in hexagonal enclosures. The empty spaces within the crowns can be further filled with neutral (MeOH/water, MeOH/$MeNO_2$) or ionic guest species such as KI/KAcAc to furnish novel multicomponent assemblies, that is, guest⊂guest⊂host, that typify Russian dolls. In contrast, triphenol **H2** is found to yield analogous multicomponent molecular crystals in which the guest crown–K^+ acts as a spacers in the hydrogen-bonded self-assembly that leads to distorted chicken wire networks.

Keywords: clathrates · crystal engineering · host–guest systems · inclusion compounds · self-assembly

Introduction

Formation of solids with open framework structures based on metal–ligand coordination bonds is a topical and frontier research.[1] In contrast to a number of porous metal-organic frameworks (MOFs) with diverse topologies reported to date, the networks sustained by rather less stronger, yet directional N/O-H···N/O hydrogen bonds are limited.[2] The early examples of organic solids with open framework structures based on self-assembly of rationally programmed molecular modules constitute trigonal trimesic acid and tetrahedral adamantane tetracarboxylic acid, which lead to honeycomb and diamondoid networks, respectively.[3] The debilitating problem of catenation aside, it is becoming increasingly evident that crystal structures of organic compounds can indeed be analyzed, in analogy to MOFs, by treating the constituent molecules as spacers and the interactions that stitch them together as nodes.[2,4] In other words, the desired target crystal structures can be approached by astute design of molecular modules programmed with functional groups that predictably manifest in the intended supramolecular synthons.[5] In continuation of our studies focusing on exploitation of sterically-hindered molecular systems for development of functional organic materials,[6] we wondered if rigidification of the aryl rings of 1,3,5-triarylbenzenes orthogonally via steric hindrance would lead to expanded honeycomb networks with increased thickness of the interior pores; incidentally, the self-assembly of 1,3,5-tri(*p*-carboxyphenyl)benzene and its triphenol analogue is not known to lead to honeycomb networks.[7] Based on our analysis that i) the organization of host systems made up of rigid phenolic moieties is somewhat well-defined and predictable, and ii) the consideration that phenols with one hydrogen bond may exhibit flexibility in their self-assembly as compared to carboxylic acids that form a linear and rigid hydrogen-bonded dimer motifs,[3,5] we targeted the self-assembly of two distinct C_3-symmetric sterically-hindered 1,3,5-triarylphenols, that is, **H1** and **H2** (Table 1). Herein, we report on the novel self-assembly of **H1** and **H2** into catenated hexagonal (6,3) and undulated square (4,4) networks, respectively. Further, we show that eight-fold catenation of **H1** can be destroyed in the presence of [18]crown-6 leading to hydrogen-bonded honeycomb networks with hexagonal voids of increased thickness, which permit realization of both neutral as well as ionic guest⊂guest⊂host multicomponent molecu-

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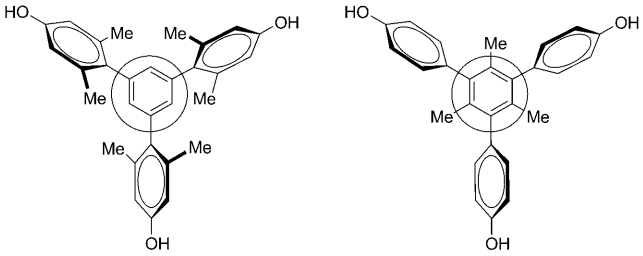
Table 1. Structures of triphenol hosts **H1** and **H2** and their inclusion/multicomponent molecular crystals.



Host	Guests	Inclusion/multicomponent crystals and host–guest ratio	Code
H1	DMSO, H_2O	**H1**·DMSO·H_2O (1:2:1)	**H1**-DMSO
H1	[18]crown-6, MeOH, H_2O	**H1**·[18]crown-6·MeOH·H_2O (1:1:1:1)	**H1**-C-MeW
H1	[18]crown-6, MeOH, $MeNO_2$	**H1**·[18]crown-6·MeOH·$MeNO_2$ (1:1:1:1)	**H1**-C-MeNM
H1	[18]crown-6, KI	{K^+⊂[18]crown-6⊂**H1**} I^- (1:1:1)	**H1**-C-KI
H1	[18]crown-6, K^+AcAc^-, MeOH, EtOH	{K^+⊂[18]crown-6⊂**H1**}·$AcAc^-$·EtOH·MeOH (1:1:1:1:0.5)	**H1**-C-KAcAc
H2	ethyl acetate	**H2**·ethyl acetate (1:1)	**H2**-EA
H2	[18]crown-6, EtOH, H_2O, benzene	**H2**·[18]crown-6·EtOH·benzene·H_2O (1:1:1:1:1)	**H2**-C-Et
H2	KBr, *p*-xylene	**H2**·[18]crown-6·K^+Br^-·xylene (1:1:1:0.5)	**H2**-C-KBr
H2	KI, *p*-xylene	**H2**·[18]crown-6·K^+I^-·xylene (1:1:1:0.5)	**H2**-C-KI
H2	KOAc, EtOH	**H2**·[18]crown-6·K^+OAc^-·EtOH (1:1:1:0.5)	**H2**-C-KOAc

lar inclusion compounds similar to molecular Russian dolls.[8]

Results and Discussion

The triphenol hosts **H1** and **H2** were readily synthesized starting from 1,3,5-tribromobenzene and 1,3,5-tribromomesitylene via Suzuki coupling with 2,6-dimethyl-4-methoxyphenylboronic acid and 4-methoxyphenylboronic acid, respectively, under Pd^0-catalyzed conditions. Demethylation of the resulting products using BBr_3 led to triphenol hosts **H1** and **H2**, respectively (cf. Supporting Information). Recrystallization of both **H1** and **H2** in the presence of diverse guest molecules such as cycloalkanes, benzene, substituted benzenes, naphthalene, pyrene, C60, invariably led to crystals of **H1** and **H2** containing DMSO and ethyl acetate (EA), respectively; in the absence of the latter solvents, the triphenols hosts failed to crystallize. However, both **H1** and **H2** readily crystallized with added [18]crown-6. Inspired by this observation, we investigated the possibility of binding the complexes of crown with alkali metal ions. Indeed, the multicomponent molecular crystals of **H1** and **H2** with crown and neutral guest molecules as well as KX, where X = Br^-/I^-/OAc^-/$AcAc^-$and $AcAc^-$ = acetyl acetonate, were readily isolated by crystallization in the presence of [18]crown-6 and other guest species[9] (cf. Table 1 and Supporting Information).

In Figures 1 and 2 are shown the structures of **H1**-DMSO and **H2**-EA, which were found to belong to $P2_12_12_1$ and *P2/n* space groups, respectively. The asymmetric unit of **H1**-DMSO was found to contain two independent host molecules, four DMSO and two H_2O molecules, while that in **H2-**EA was found to contain one triphenol and one ethyl

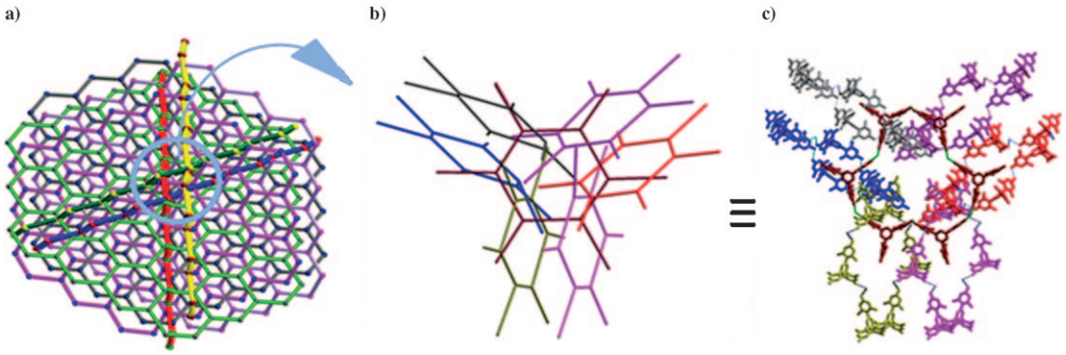


Figure 1. a) and b) Node and spacer representation of the O-H···O hydrogen-bonded self-assembly observed for **H1**-DMSO. c) The partial crystal packing with eight-fold interpenetration of hexagonal (6,3) nets with each one depicted in a different color; the guest DMSO molecules occupying the vacant spaces are not shown.

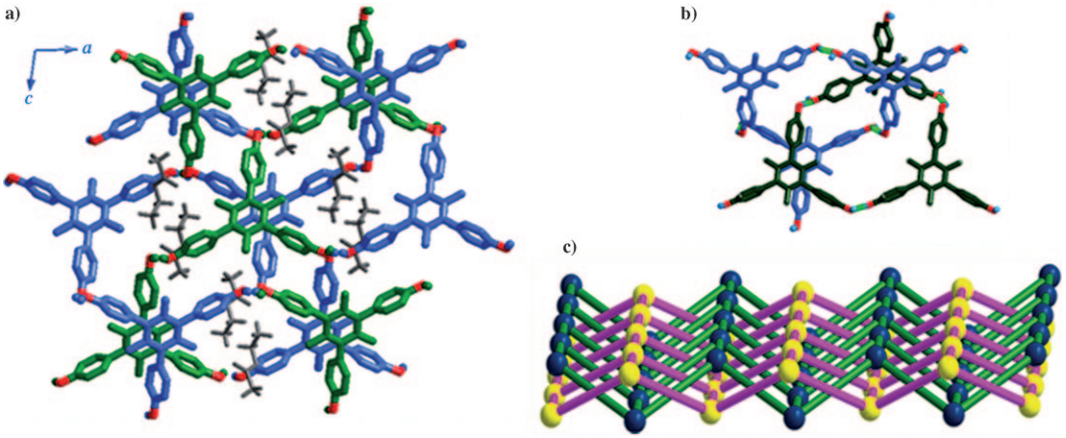


Figure 2. a) Self-assembly of triphenol **H2** into a doubly interpenetrated square (4,4) net with guest EA molecules; the layers are shown with different colors. b) Typical interpenetration of the molecular assembly. c) Schematic representation of the doubly interpenetrated undulated square networks.

acetate. As can be seen in Figure 1, one observes O-H···O hydrogen-bonded assembly of **H1** into a hexagonal (6,3) net sustained by two water molecules.[10] The internal void space is destroyed by interlacing of seven other such nets as shown in Figure 1; the solvent DMSO molecules are found to fill the vacant spaces that still remain. In contrast, the triphenol **H2** is found to self-assemble via O-H···O hydrogen bonds into an undulated square (4,4) net,[10] which is doubly interpenetrated, (cf. Figure 2). The empty space in the doubly interpenetrated network is found to be filled by ethyl acetate molecules.

The self-interpenetration of metal-organic as well as organic open framework structures is very common.[2,11] Insofar as organic structures are concerned, trimesic acid constitutes a prototype example of interpenetrated two-dimensional network sustained by O-H···O hydrogen bonds of carboxyl groups.[3a] The interpenetration can indeed be destroyed in the presence of appropriate guest molecules that fill the voids.[12] Crystallization of triphenols **H1** and **H2** in the presence of [18]crown-6 yielded crystals in which such interpenetration is absent. Both **H1** and **H2** were found to crystallize with the crown included in their crystal lattices. Crystallization of **H1** in methanol with added [18]crown-6 led to thick rectangular crystals (**H1**-C-MeW, Table 1); its structure determination revealed the presence of one crown, one methanol and one adventitious water molecule. The crystals were found to belong to *C2/c* space group. In a similar manner, crystallization in nitromethane/methanol led to crystals (**H1**-C-MeNM), which were found to be isostructural to those containing methanol/water, with the only difference that water is replaced by nitromethane. In contrast, the crystals of **H2** with [18]crown-6 appeared only in a particular solvent combination, that is, ethanol/benzene containing a trace amount of water (**H2**-C-Et, Table 1). The ^{1}H NMR analyses and/or X-ray structure determinations revealed the presence of one molecule each of crown, ethanol, benzene and water. The crystals were found to belong to *C2/c*.

In Figure 3, crystal packing diagrams for **H1**-C-MeW and **H2**-C-Et are shown. The packing in **H1**-C-MeNM is identical with that in **H1**-C-MeW. In both of these cases, hydrogen-bonded self-assembly of the triphenols leads to infinite two-dimensional chicken-wire networks with hexagonal voids, which derive from the assembly of three triphenol building blocks (Figure 3a). As shown in Figure 3, the guest [18]crown-6 molecules nicely fit into the hexagonal enclosures. The vacant space that still remains is evidently filled by solvent molecules, that is, methanol/water and methanol/nitromethane. The chicken-wire layers in the *ab* plane are marginally shifted relative to each other to make up the crystal. In contrast, the hexagonal enclosures in the case of **H2** are apparently not large enough to permit [18]crown-6 guest molecules. Two solvent ethanol molecules thus expand the dimensions of hexagonal voids to allow inclusion of [18]crown-6, which also binds two water molecules. Benzene serves to fill the remaining vacant space in the ethanol-expanded hexagonal enclosures (cf. Figure 3b). Otherwise, the hydrogen-bonded self-assembly of both **H1** and **H2** that leads to voids for inclusion of primary guest such as [18]crown-6, which in turn binds neutral secondary solvent guest molecules to furnish ternary/quaternary multicomponent molecular crystals (cf. Figure 3), is reminiscent of molecular Russian dolls.[8]

To logically replace the solvent guest molecules bound to the crown, crystallization of triphenols was attempted in the presence of [18]crown-6 and KX (X = Br/I/OAc/AcAc). Remarkably, the triphenol **H1** in the presence of [18]crown-6 with KI yielded the crystals of $\{K^+\subset$[18]crown-6$\subset$**H1**$\}I^-$(**H1**-C-KI, Table 1). Further addition of acetylacetone as a guest led to anion exchange to afford multicomponent molecular crystals of **H1** with [18]crown-6, KAcAc and solvent ethanol and methanol $\{K^+\subset$[18]crown-6$\subset$**H1**$\}AcAc^-$, EtOH, MeOH (**H1**-C-KAcAc).[13] While the crystals of the former corresponded to C_2 space group, those of the latter were found to belong to $P\bar{1}$ space group. The crystal packing analyses show close similarities in terms of the host organization

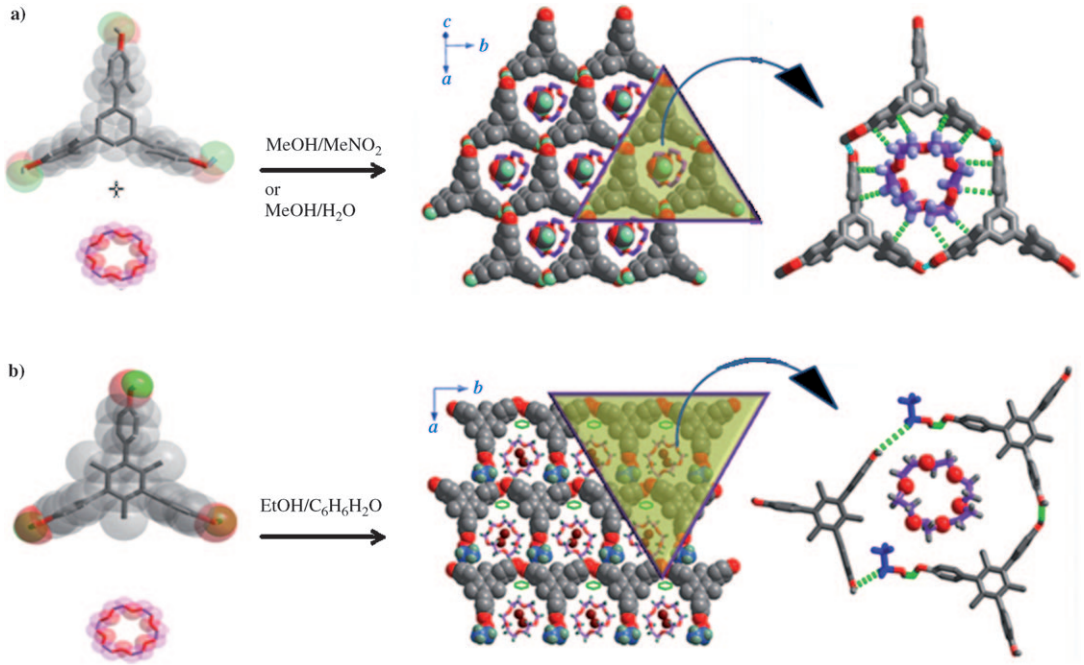


Figure 3. a) Structures of multicomponent molecular crystals of **H1** with [18]crown-6 and guest solvent molecules. The C-H protons of the crown are found to be involved in C-H···π interactions with the orthogonal aryl rings of **H1**. b) The distorted chicken-wire networks of **H2** with guest [18]crown-6 and solvent molecules.

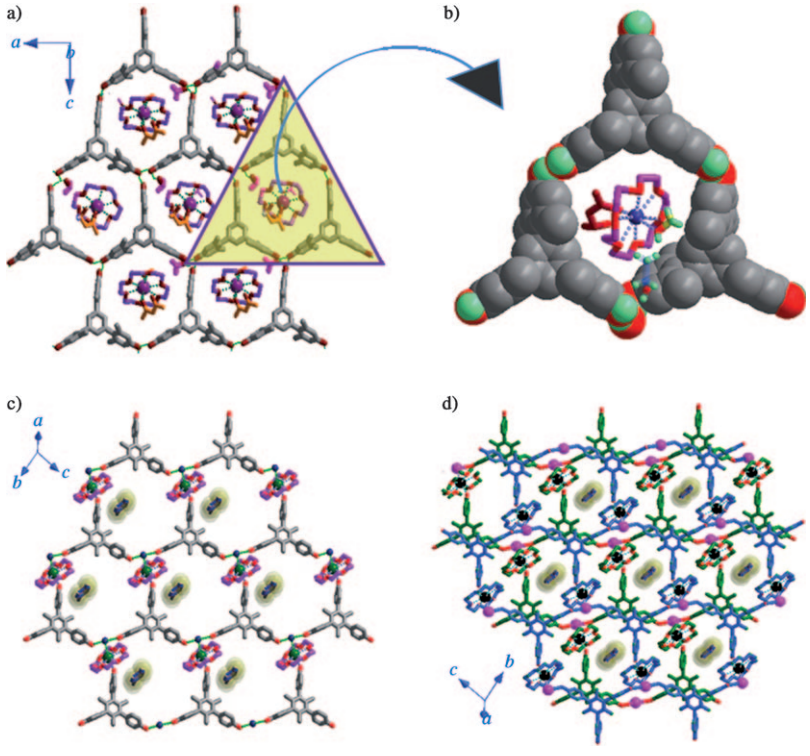


Figure 4. a) Honeycomb pattern arising from hydrogen-bonded self-assembly of **H1**-C-KAcAc. b) The partial structure showing how the hydrogen-bonded assembly of three triphenol building blocks leads to a hexagonal void in which [18]crown-6 and other guests are included. c) The self-assembly of triphenol **H2** with crown-KI/KBr/KOAc acting as a spacer. Notice that I^-as well as K^+ ions are involved in the overall association leading to the honeycomb pattern. d) Offset of two layers that leads to reduction in the void volume of one layer by partial occupation of the crown guest molecules of the second layer.

and location of the included guest, that is, K^+–[18]crown-6. In Figure 4 is shown a typical hydrogen-bonded assembly of the host into an infinite two-dimensional honeycomb network that contains [18]crown-6 guest molecules in the hexagonal voids. The latter in turn bind KI/AcAc at the center in both multicomponent crystals; the remaining space in the case of **H1**-C-KAcAc is filled by solvent guest molecules, namely, ethanol and methanol. In a similar manner, the host **H2** crystallized readily with [18]crown-6 and KBr/KI/KOAc to yield **H2**·[18]crown-6 K^+X^-(X^-=Br^-/I^-/OAc^-), *p*-xylene/EtOH (**H2**-C-KI, **H2**-C-KBr and **H2**-C-KOAc, Table 1). The crystals in all cases were found to be isostructural with the space group $P\bar{1}$. In contrast to the scenario with the triphenol **H1**, the crown complexes of K^+ were found to be altogether different in that in all these cases the crown–K^+ was found to serve

as a spacer in the hydrogen-bonded assembly of the triphenol into honeycomb networks (cf. Figure 4c); it is noteworthy that [18]crown-6 has similarly been found to function as a spacer in the expansion of the networks derived from trimesic acid and 1,3,5-cyclohexanetricarboxylic acid.[14] Indeed, the counter anions, that is, $I^-/Br^-/OAc^-$, are also found to mediate the formation of chicken-wire honeycomb networks as shown in Figure 4c. The channels are filled by adjacent layers that are offset (cf. Figure 4d). Of course, *p*-xylene/ethanol fills the remaining void spaces.

In a nutshell, the triphenol **H1** is found to self-assemble in DMSO into a hydrogen-bonded hexagonal (6,3) net. However, in all of its neutral as well as ionic multicomponent molecular crystals containing [18]crown-6, that is, **H1**-C-MeW, **H1**-C-MeNM, **H1**-C-KI and **H1**-C-KAcAc, hydrogen-bonded self-assembly into honeycomb networks with hexagonal enclosures is found to occur. The thick enclosures generated by the orthogonally-oriented dimethyl-substituted phenols in **H1** are evidently able to nestle [18]crown-6 nicely as suggested by the ready crystallization of the triphenol **H1** in different solvents as well as in the presence of cations that bind the crown. Further, inclusion of neutral or ionic guests by **H1**-crown complexes to furnish multicomponent molecular crystals (cf. Table 1) is in analogy to Russian dolls.[8] A similar honeycomb network in which the hexagonal enclosures are expanded by mediation of either solvent (EtOH in **H2**-C-Et) or crown–K^+ is observed in all the multicomponent molecular crystals of **H2**.

A feature that is common to both hosts **H1** and **H2** is that the aryl rings are almost orthogonal (the angle between the central ring and the hydroxyphenyl rings is found to be about 69.1–89.7°, cf. Supporting Information) in both cases due to the methyl groups at 2,6-positions of the hydroxyphenyl rings in **H1** and at the 1,3,5-positions of the central benzene ring in **H2**. While the methyl groups attached to the central ring in **H2** are expected to reduce the void space of the hexagonal enclosure, those of the 2,6-dimethyl-4-hydroxyphenyl rings in **H1** contribute to increasing the depth of the void volume. Evidently, the sterics introduced via methyl groups to cause the hydroxyphenyl rings orthogonal to the central ring manifest differently leading to eight-fold interpenetrated (6,3) net in the case of **H1**-DMSO and two-fold interpenetrated (4,4) net in the case of **H2**-EA. Insofar as the crown conformation is concerned,[15] a careful analysis reveals that the geometry adopted is dictated by effective exploitation of C-H···π interactions. As shown in the Figure 3, the C–H protons of the crown are found to be involved in C-H···π interactions with the orthogonal aryl rings of the host triphenol **H1**.

The formation of binary solids is a fairly advanced field of research. A variety of binary crystals can be obtained from a number of ways that include host–guest chemistry involving both unimolecular as well as multimolecular inclusion host systems, acid–base pairing, charge transfer, hydrogen-bonded assembly.[8] Indeed, the applications of binary solid materials are widespread in pharmaceutical co-crystals, nonlinear optical materials, conductivity, etc.[16,17] On the contrary, the construction of ternary and higher-order multicomponent crystals is conceptually challenging.[18] Consequently, the utility of organic multicomponent molecular materials still remains scantly explored in contrast to wide ranging applications of hybrid materials comprising organic and inorganic components.[19] As demonstrated herein, the construction of multicomponent molecular materials based on a combination of molecular self-assembly and host–guest chemistry may pave the way for new hybrid materials.

Conclusion

We have shown that sterically-hindered and rigid C_3-symmetric molecular modules based on 1,3,5-tri(4-hydroxyphenyl)benzenes **H1** and **H2** undergo O-H···O hydrogen-bonded self-assembly into eight-fold interpenetrated hexagonal (6,3) and two-fold interpenetrated undulated square (4,4) networks, respectively. The interpenetration in both cases can be destroyed in the presence of [18]crown-6 as a guest. The triphenol **H1** is found to self-assemble into a chicken-wire network with hexagonal voids. The guest [18]crown-6 molecules are found to be nicely nestled in the hexagonal enclosures. The empty space within the crown can be further filled with neutral (MeOH/water, MeOH/$MeNO_2$) or ionic guest species such as KI/KAcAc to furnish novel multicomponent assemblies, that is, guest⊂guest⊂host, in a manner akin to Russian dolls. In contrast, the triphenol **H2** is found to yield analogous multicomponent molecular crystals in which crown–K^+ acts as a spacer in the hydrogen-bonded self-assembly leading to distorted chicken wire networks.

Experimental Section

Anhydrous tetrahydrofuran (THF) was freshly distilled over sodium prior to use. All other solvents were distilled prior to use. The reaction in each case was monitored by analytical thin-layer chromatography (TLC) using aluminum sheets pre-coated with silica gel (Merck). Column chromatography was conducted with silica gel (Acme, Mumbai, 60–120 mesh). ^1H and ^{13}C NMR spectra were recorded on JEOL-Lambda (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^{-1} under nitrogen gas atmosphere. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrophotometer. The melting points were determined with a Perfit Melting point apparatus (India). Commercial chemicals were used as received.

Synthesis of triarylbenzenes H1 and H2: The general procedure for the synthesis of triarylbenzenes **H1** and **H2** involved three-fold Suzuki coupling of tribromobenzenes with suitably functionalized boronic acids using $[Pd(PPh_3)_4]$ as a catalyst. The Suzuki coupling reaction between 1,3,5-tribromobenzene with 4-methoxy-2,6-dimethylphenylboronic acid furnished **H1**; the required boronic acid was prepared starting from 4-methoxy-2,6-dimethylbromobenzene, which was reacted with Mg followed by treatment of the resultant Grignard with trimethyl borate.[20] The triphenol host **H2** was similarly prepared by Suzuki coupling of tribromomesitylene[21] with 4-methoxyphenylboronic acid under Pd^0-catalyzed conditions.

Typical procedure for the Suzuki coupling: A 100 mL two-necked round bottom flask, removed hot from oven, was cooled under N_2 atmosphere

and charged with 1,3,5-tribromobenzene (2.0 g, 6.35 mmol), 4-methoxy-2,6-dimethylphenylboronic acid (4.6 g, 25.4 mmol), $[Pd(PPh_3)_4]$ (0.37 g, 0.32 mmol), toluene (40 mL) and $NaHCO_3$ (2 M solution, 10 mL). The resultant reaction mixture was heated at 110 °C. The pale-yellow turbid solution turned clear yellow over a period of 2 h. Subsequently, the heating was continued for 22 h, after which time the color of the reaction mixture turned dark brown. At this stage, the reaction mixture was cooled and extracted with $CHCl_3$. The combined extracts were washed with water, dried over Na_2SO_4 and concentrated. The pure product was isolated by silica-gel column chromatography using petroleum ether (60–80 °C) as an eluent, to afford triarylphenol **H1** in the form of a white solid (2.63 g, 86%). ^{1}H NMR (500 MHz, [D$_6$]DMSO, TMS): $\delta = 1.92$ (s, 18H), 6.46 (s, 6H), 6.63 (s, 3H), 9.11 ppm (s, 3H); ^{13}C NMR (125 MHz, [D$_6$]DMSO, TMS): $\delta = 25.84$, 119.28, 134.14, 137.63, 141.49, 146.03, 161.17 ppm; IR (KBr): $\tilde{\nu} = 2920$, 3394 cm^{-1}; ESI-MS$^-$: *m/z*: calcd for $C_{30}H_{30}O_3$: 437.56 $[M-H]^-$; found 437.55; elemental analysis calcd (%) for $C_{30}H_{30}O_3$: C 82.16, H 6.89; found: C 81.74, H 6.88.

A similar procedure using 1,3,5-tribromomesitylene[21] and 4-anisylboronic acid led to the host **H2** in the form of a white solid in 81% isolated yield. ^{1}H NMR (500 MHz, [D$_6$]DMSO, TMS): $\delta = 1.59$ (s, 9H), 6.76 (d, $J = 8.4$ Hz, 6H), 6.89 (d, $J = 8.4$ Hz, 6H), 9.32 ppm (s, 3H); ^{13}C NMR (125 MHz, [D$_6$]DMSO, TMS): $\delta = 19.87$, 115.81, 130.56, 132.81, 132.23, 139.65, 156.30 ppm; IR (KBr): $\tilde{\nu} = 3341$ cm^{-1}; ESI-MS$^+$: *m/z*: calcd for $C_{27}H_{24}O_3$: 397.17 $[M+H]^+$; found 397.18; elemental analysis calcd (%) for $C_{27}H_{24}O_3$: C 81.79, H 6.10; found C 81.54, H 5.86.

X-ray crystal structure determinations: A good quality crystal in each case was mounted in a glass capillary, 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.[22] 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 S1 (cf. Supporting Information).

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