

Synthesis and Solid-State Self-Assembly of Polyphenols

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ABSTRACT: A simple synthetic strategy for polyphenols (**1–3**) is outlined, and their crystallographic investigations are described. Interesting self-assembled structures were observed in the crystal lattice owing to the 3D structure and hydrogen-bonding interactions between the hydroxyl groups. In the crystal lattice of trisphenol **1**, each hydroxyl group participates in forming monohelical chains of hydrogen bonds along the *a*-axis. Each molecule of trisphenol **1** is linked to six adjacent molecules through O–H···O hydrogen bonds. In the crystal lattice of trisphenol **2**, each molecule is linked to six symmetrically oriented trisphenol neighbors through a total of six hydrogen bonds, thereby creating a distorted ladder-type hydrogen bonded chains. Pentaphenol **3** crystallizes as tetrahydrate and water molecules are incorporated into the crystal lattice through the formation of cyclic water hexamer with a chair conformation. In all the above structures, both the number and the position of the hydroxyl groups on the triphenylmethane core play an important role in the formation of supramolecular architectures.

Introduction

Understanding the solid state self-assembly of molecular building blocks is an interesting topic owing to its potential towards developing novel functional materials.¹ Selectivity and directionality of the hydrogen bonds make it an indispensable tool for the construction and stabilization of large non-covalently bonded molecular and supramolecular structures.² Many interesting supramolecular architectures with O–H···O were observed in the solid lattice from simple molecular building blocks incorporated with more than one hydroxyl group.^{3–6} Desiraju et al.^{3d} have reported the formation of organic ladders from compounds with multiple -O–H groups. Crystallographic studies on phenols and their aza complexes have been reported by Nangia et al.^{3a–c} Molecular tectonic approach has been used to generate fascinating architectures in the crystal lattice of tetraphenols.⁷

The recent years have been intensively active in experimental^{8a–c} and theoretical^{8d–k} research focusing on the intricate characterization of water clusters. Water clusters play an important role in the stabilization of supramolecular systems both in solution and in the solid state. A myriad of studies directed towards investigating the changes in structural and spectral properties of small water clusters with increasing cluster size have been reported.⁹ Many discrete water clusters such as trimers,¹⁰ tetramers,¹¹ pentamers,¹² and hexamers¹⁶ have been observed in the crystal lattice of organic host molecules. Of these, the water hexamer signifying the simplest supramolecular analogue of cyclohexane has gained considerable attention. The study of the three-dimensional hexamer of water clusters has been promising because it is known to be the tiniest possible unit illustrating some of the bulk properties of water.^{13–15} Custeclean et al.^{16a} have reported the formation of a one-dimensional chain of water hexamer molecules occupying the channels of an organic

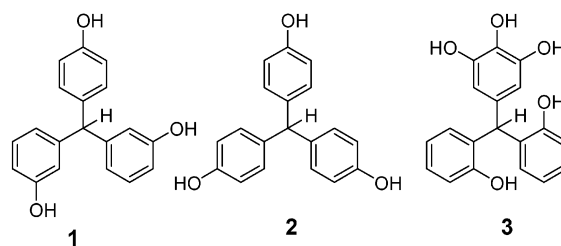


Figure 1. Molecular structure of the target phenols (**1–3**).

host. Planar cyclic form of water hexamer trapped in an organic complex has been observed by Moorthy and co-workers.^{16b} An excellent review of water clusters has been reported by Infantes and Motherwell.¹⁷

Our interest is focused on the design and characterization of supramolecular architectures through the self-assembly of molecular building blocks. Recently, we have reported the self-assembly of symmetric diamide and diacid molecules in the crystal lattice.¹⁸ Here we discuss the synthesis and characterization of supramolecular structures from functionalized triphenylmethane building blocks (Figure 1). It can be expected that a combination of the effect of the number and orientation of the hydroxyl groups coupled with a bulky triphenylmethane core greatly influences the self-assembly process in the crystal lattice.

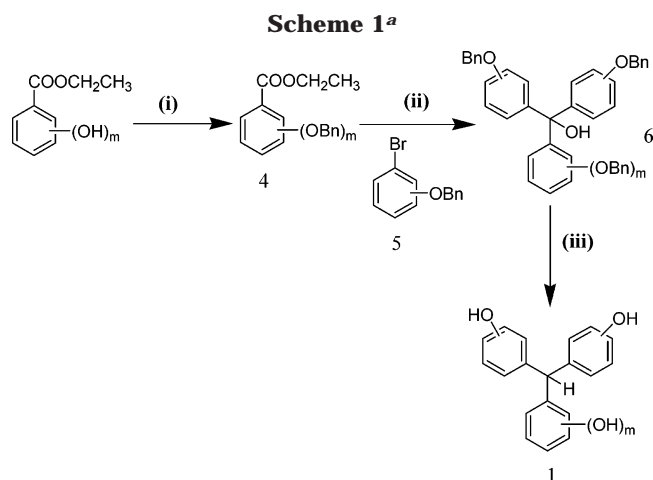
Experimental Section

All reagents were used as received without further purification unless stated. Tetrahydrofuran (THF) was freshly distilled over sodium under N₂ atmosphere. Bromophenols (ortho, meta, para), benzyl bromide, anhydrous potassium carbonate, 1-bromododecane, sodium hydride (NaH), methyl iodide, methyl-3,4,5-trihydroxybenzoate and ethyl-4-hydroxybenzoate were bought from Aldrich. Merck silica gel 60 F₂₅₄ plastic backed plates (20 × 20 cm) were used for thin-layer chromatography (TLC). Column chromatography was carried out with Merck silica gel (230–400 mesh). The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-300 spectrophotometer with trimethylsilane (TMS) as the internal standard (NMR solvents CDCl₃, CD₃COCD₃, DMSO-*d*₆ from Aldrich). Mass spectra (EI)

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were collected on a Finnigan MAT LCQ or Finnigan TSQ 7000 mass spectrometer at an ion spray voltage of 4.5 kV, and a capillary temperature of 270 or 350 °C. All melting points were determined with a Reichert-Jung Thermo Galen Hot Stage microscope and uncorrected. The elemental analyses were performed at the Department of Chemistry, National University of Singapore. X-ray diffraction data on single crystals were collected on a Bruker AXS SMART CCD 3-circle diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) at 23 °C. The software SMART¹⁹ was used for collecting frames of data, indexing reflections, and determining lattice parameters; SAINT¹⁹ for integration of intensity of reflections and scaling; SADABS²⁰ for absorption corrections; and SHELXTL²¹ for space group determination, structure solution, and least-squares refinements on F^2 . All the hydrogen atoms have been located. However, all the C-H hydrogen atoms were fixed at ideal positions and were not refined. The isotropic parameters and the positional parameters of all the O-H hydrogen atoms were refined in the final structural models.

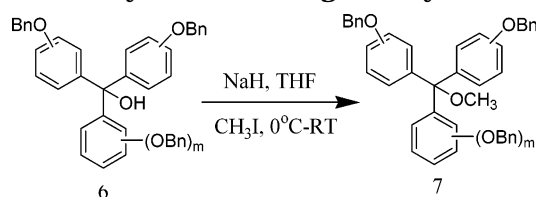
Synthesis. To obtain a series of easily accessible phenolic building blocks, a simple synthetic approach using methyl-3,4,5-trihydroxybenzoate or ethyl-4-hydroxybenzoates as the starting material was selected (Scheme 1).



^a Reagents: (i) BnBr, K₂CO₃, MEK, 80 °C; (ii) Mg, I₂, 5, 0 °C-RT; (iii) Pd(OH)₂/C, H₂, 2–3 mbar, CH₃OH/THF/H₂O (1:1:0.1); $m = 1$ or 3.

Polyphenols (**1–3**) were successfully synthesized using Grignard chemistry. A modified literature procedure was adopted for the *O*-alkylation of methyl-3,4,5-trihydroxybenzoate, ethyl-4-hydroxybenzoate, and 2-hydroxybromobenzene.^{22,23} The appropriate Grignard reagents were synthesized from the *O*-Bn derivative of the bromophenol (**5**, ortho, meta, and para). Two equivalents of the magnesium salt of the bromophenols were reacted with the methyl or ethyl benzoate (**4**) to give the crude tertiary alcohol (**6**). The formation of the tertiary -OH group was confirmed via methylation of the alcoholic group using methyl iodide to get the methoxy derivative (Scheme 2).²⁴

Scheme 2. Characterization of the Formation of Tertiary Alcohol through Methylation



Hydrogenolysis of the benzylated derivative (**6**) using H₂ gas over Pd(OH)₂ as a catalyst gave deprotected polyphenols (**1–**

3). During the debenzylation, the tertiary hydroxyl group was replaced by a hydrogen atom at the tertiary carbon atom.

Methyl-3,4,5-tribenzyloxybenzoate (4).²³ A modified literature procedure was used in which a mixture of 20 g (0.10 mol) of ethyl-3, 4, 5-trihydroxybenzoate, 80 g of anhydrous potassium carbonate, and 90 mL (0.5 mol) of benzyl bromide in 500 mL of MEK was refluxed for 24 h. Excess solvent was removed under vacuum. The residue was dissolved in dichloromethane and washed with water (2 × 150 mL) followed by dilute sodium hydroxide solution and water. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash chromatography using hexane followed by dichloromethane as eluents. The ester was obtained as a white solid, yield 80%, mp 98 °C. ¹H NMR (300 MHz, CDCl₃, δ ppm): 3.87 (-CH₃, s, 3H), 5.10 (Ar-OCH₂, s, 2H), 5.12 (Ar-OCH₂, s, 4H), 7.20–7.50 (Ar-H, m, 17H). ¹³C NMR (75.4 MHz, CDCl₃, δ ppm): 52.6 (-CH₃), 71.6 (Ar-OCH₂), 75.5 (Ar-OCH₂), 109.4, 125.6, 127.9, 128.3, 128.4, 128.5, 128.9, 137.0, 137.8, 142.8, 152.9 (ArC), 167.0 (C=O). Cal. C: 76.90, H: 6.02; Found C: 77.02, H: 6.18.

Ethyl-4-benzyloxybenzoate (4). Same procedure as above, colorless oil, yield 85%, ¹H NMR (300 MHz, CDCl₃, δ ppm): 1.35 (-CH₃, t, 3H), 4.25 (-CH₂-, q, 2H), 5.08 (Ar-OCH₂, s, 2H), 6.95 (Ar-H, d, 2H, $J = 7.2$ Hz), 7.23–7.42 (Ar-H, m, 5H), 7.98 (Ar-H, d, 2H, $J = 7.2$ Hz). ¹³C NMR (75.4 MHz, CDCl₃, δ ppm): 14.6 (-CH₃), 60.9 (-CH₂), 70.3 (Ar-OCH₂), 114.7, 123.5, 127.7, 128.4, 128.9, 131.8, 136.6, 162.7 (ArC), 166.5 (C=O). Cal. C: 74.98, H: 6.29; Found C: 75.02, H: 6.38.

2-Benzyloxybromobenzene (5_a). A mixture of 25 g (0.14 mol) of 2-bromophenol, 40 g (0.28 mol) of anhydrous potassium carbonate, and 37 mL (0.22 mol) of benzyl bromide in 250 mL of MEK was refluxed for 24 h. Excess solvent and benzyl bromide were removed under high vacuum. The residue was refluxed in methanol/water (3:1) mixture for overnight in the presence of 3 equiv of sodium hydroxide pellets. The organic layer was separated from the aqueous layer using a separating funnel, mixed with dichloromethane, and washed with dilute hydrochloric acid followed by water. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated. The product obtained after removing the solvent was purified using flash chromatography with hexane and followed by dichloromethane as eluent, colorless oil, yield 90%, ¹H NMR (300 MHz, CDCl₃, δ ppm): 5.07 (Ar-OCH₂, s, 2H), 6.78 (Ar-H, t, 1H, $J = 7.2$ Hz), 6.87 (Ar-H, d, 1H, $J = 7.6$ Hz), 7.15 (Ar-H, t, 1H, $J = 7.2$ Hz), 7.2–7.4 (Ar-H, m, 3H), 7.43 (Ar-H, d, 2H, $J = 7.6$ Hz), 7.52 (Ar-H, d, 1H, $J = 7.6$ Hz). ¹³C NMR (75.4 MHz, CDCl₃, δ ppm): 71.0 (Ar-OCH₂), 112.8, 114.2, 122.5, 127.3, 127.9, 128.0, 128.2, 128.7, 128.9, 133.7 (ArC). Cal. C: 59.34, H: 4.21, Br: 30.37; Found C: 59.38, H: 4.30, Br: 30.46.

3-Benzyloxybromobenzene (5_b). The same procedure was used as given above, white powder, yield 90%, mp 61 °C. ¹H NMR (300 MHz, CDCl₃, δ ppm): 5.02 (Ar-OCH₂, s, 2H), 6.88 (Ar-H, d, 1H, $J = 7.5$ Hz), 7.05–7.13 (Ar-H, m, 4H), 7.30–7.41 (Ar-H, m, 4H). ¹³C NMR (75.4 MHz, CDCl₃, δ ppm): 70.7 (Ar-OCH₂), 114.3, 118.7, 123.3, 124.5, 127.9, 128.6, 129.1, 131.0, 136.9, 160.0 (ArC). Cal. C: 59.34, H: 4.21, Br: 30.37; Found C: 59.40, H: 4.24, Br: 30.37.

4-Benzyloxybromobenzene (5_c). Same procedure was used as given for **5_a**, white solid, yield 90%, mp 64 °C. ¹H NMR (300 MHz, CDCl₃, δ ppm): 4.98 (Ar-OCH₂, s, 2H), 6.86 (Ar-H, d, 2H, $J = 7.6$ Hz), 7.3–7.5 (Ar-H, m, 7H). ¹³C NMR (75.4 MHz, CDCl₃, δ ppm): 70.6 (Ar-OCH₂), 113.5, 117.1, 127.8, 128.5, 129.1, 132.7, 137.0, 158.3 (ArC). Cal. C: 59.34, H: 4.21, Br: 30.37; Found C: 59.48, H: 4.34; Br: 30.40.

Typical Procedure for Grignard Synthesis. Magnesium turnings (1.2 equiv wrt bromocompound) were placed in a flame dried three-neck round-bottom flask and was flushed with argon while heating and cooling. A catalytic amount of iodine and a few milliliters of dry THF was added to cover the magnesium turnings at 0 °C. One milliliter of the bromocompound (1 equiv) was added to it, and the mixture was warmed until the disappearance of iodine color or the appearance of cloudiness. The remaining amount of the bromocompound was added, and the solution was warmed until all the magnesium

Table 1. Crystallographic Data and Refinement Details of Polyphenols (1–3)

	compound 1	compound 2	compound 3
emp form	C ₁₉ H ₁₆ O ₃	C ₁₉ H ₁₆ O ₃	C ₁₉ H ₂₄ O ₉
form wt	292.32	292.32	396.38
temp (K)	223(2)	223(2)	223(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁	<i>C</i> <i>c</i>	<i>P</i> 1
unit cell dimen	<i>a</i> = 5.1773(7) Å <i>b</i> = 15.729(2) Å <i>c</i> = 9.0925(12) Å α = 90° β = 101.548(3)° γ = 90°	<i>a</i> = 12.428(2) Å <i>b</i> = 18.546(3) Å <i>c</i> = 7.5612(12) Å α = 90° β = 115.000(3)° γ = 90°	8.3808(7) Å 10.8134(9) Å 11.1500(9) Å α = 75.083(2)° β = 88.217(2)° γ = 87.818(2)°
volume	725.45(17) Å ³	1579.5(4) Å ³	975.47(14) Å ³
<i>Z</i>	2	4	2
density (calcd)	1.338 g/cm ³	1.229 g/cm ³	1.350 g/cm ³
absorption coefficient	0.090 mm ⁻¹	0.083 mm ⁻¹	0.108 mm ⁻¹
<i>F</i> (000)	308	616	420
cryst size (mm ³)	0.14 × 0.12 × 0.08	0.4 × 0.35 × 0.20	0.4 × 0.2 × 0.1
θ range for data collection	2.29 to 29.99°	2.12 to 30.01°	1.89 to 30.01°
index ranges	−7 ≤ <i>h</i> ≤ 7 −20 ≤ <i>k</i> ≤ 21 −12 ≤ <i>l</i> ≤ 6	−11 ≤ <i>h</i> ≤ 17 −19 ≤ <i>k</i> ≤ 26 −10 ≤ <i>l</i> ≤ 10	−11 ≤ <i>h</i> ≤ 11 −15 ≤ <i>k</i> ≤ 15 −15 ≤ <i>l</i> ≤ 15
reflns collected	5693	6298	15063
independent reflns	3813	3608	5639
<i>R</i> (int)	0.0626	0.0886	0.0556
completeness to θ = 26.37° (%)	96.2	99.5	99.1
max/min transmission	0.8170/0.6611	0.8585/0.6430	0.9828/0.6663
data/restraints/parameters	3813/1/223	3608/2/224	5639/0/319
goodness-of-fit on <i>F</i> ²	1.060	1.010	1.046
final indices <i>I</i> > 2 σ (<i>I</i>)	<i>R</i> 1 = 0.0596 <i>wR</i> 2 = 0.1224	<i>R</i> 1 = 0.0529 <i>wR</i> 2 = 0.0774	<i>R</i> 1 = 0.0521 <i>wR</i> 2 = 0.1167
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1146 <i>wR</i> 2 = 0.1751	<i>R</i> 1 = 0.0983 <i>wR</i> 2 = 0.0867	<i>R</i> 1 = 0.0692 <i>wR</i> 2 = 0.1227
largest diff. peak/hole (e Å ⁻³)	0.254/−0.214	0.184/−0.167	0.340/−0.276

turnings were consumed. The mixture was cooled to 0 °C using an ice bath and the ester (0.1 equiv) dissolved in dry THF was added dropwise and refluxed on a water bath for 6 h. The solution was cooled, and saturated solution of ammonium chloride and crushed ice were added. The solution was extracted with diethyl ether; the combined organic layer was washed with brine and water. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated. The product obtained was purified using flash chromatography with hexane, followed by dichloromethane as eluents.

(6a). [16 mL (0.05 mol) of *O*-Bn protected compound (**5a**), 1.44 g (0.06 mol) of Mg turnings, 5 g (0.01 mol) of ester (**4**)] yielded (50%) white powder. mp 131 °C. ¹H NMR (300 MHz, CDCl₃, δ ppm): 4.68 (Ar–OCH₂, m, 4H), 4.82 (Ar–OCH₂, s, 4H), 5.05 (Ar–OCH₂, s, 2H), 5.28 (s, 1H, C–OH), 6.66 (Ar–H, s, 2H), 6.8–7.0 (Ar–H, m, 10H), 7.10–7.3 (Ar–H, m, 21H), 7.48 (Ar–H, m, 2H). ¹³C NMR (75.4 MHz, CDCl₃, δ ppm): 70.6 (Ar–OCH₂), 71.1 (Ar–OCH₂), 75.6 (Ar–OCH₂), 81.6 (C–OH), 108.4, 113.6, 121.0, 127.6, 127.9, 128.03, 128.08, 128.5, 128.7, 128.8, 128.9, 129.1, 130.1, 134.7, 137.1, 137.7, 138.6, 142.6, 152.1, 156.9 (ArC).

(6b). [20.57 g (0.08 mol) of *O*-Bn protected compound (**5b**), 2.4 g (0.1 mol) of Mg turnings, 5 g (0.02 mol) of ester (**4**)] yield 65% light yellow oil. ¹H NMR (300 MHz, CDCl₃, δ ppm): 4.82 (Ar–OCH₂, s, 4H), 5.02 (Ar–OCH₂, s, 2H), 5.28 (s, 1H, C–OH), 6.81–6.95 (Ar–H, m, 10H), 7.06–7.43 (Ar–H, m, 17H). ¹³C NMR (75.4 MHz, CDCl₃, δ ppm): 70.5 (Ar–OCH₂), 70.6 (Ar–OCH₂), 81.2 (C–OH), 113.3, 114.1, 121.0, 127.6, 127.9, 128.0, 128.3, 128.6, 129.0, 129.8, 130.1, 135.2, 137.1, 137.7, 156.8, 158.1 (ArC).

(6c). Procedure as above. [20.57 g (0.08 mol) of *O*-Bn protected compound (**5c**), 2.4 g (0.1 mol) of Mg turnings, 5 g (0.02 mol) of ester (**4**)] yield 75% red oil. ¹H NMR (300 MHz, CDCl₃, δ ppm): 4.9 (Ar–OCH₂, s, 4H), 5.03 (Ar–OCH₂, s, 2H), 5.25 (s, 1H, C–OH), 6.8–6.9 (Ar–H, m, 8H), 7.1–7.4 (Ar–H, m, 19H). ¹³C NMR (75.4 MHz, CDCl₃, δ ppm): 70.4 (Ar–OCH₂), 70.5 (Ar–OCH₂), 82.0 (C–OH), 114.0, 114.6, 115.2,

121.1, 127.9, 128.0, 128.3, 128.4, 128.9, 129.0, 129.3, 129.6, 137.3, 137.4, 139.6, 149.0, 158.4, 158.8 (ArC).

General Procedure for Debenzylation.²³ To a solution of 2 g of compound (**6**) in 10 mL of THF were added 10 mL of methanol, 1 mL of water, and 20 wt % of Pd(OH)₂/C (containing up to 50% of H₂O). The mixture was stirred under 2.5–3.0 mbar H₂ for 4–6 h and filtered over Celite or cotton pad. The residue was washed with methanol, and the combined filtrate was evaporated to give crude polyols. The pure compound was obtained after flash chromatography (hexane/acetone = 8:2).

Target Compounds (1). Pale yellow solid, yield 86%, mp 207 °C. ¹H NMR (300 MHz, DMSO-*d*₆, δ ppm): 5.4 (s, 1H, C–H), 6.62–6.73 (Ar–H, m, 6H), 6.83 (Ar–H, d, 2H, *J* = 8.2 Hz), 7.03 (Ar–H, d, 2H, *J* = 8.2 Hz), 7.2 (Ar–H, m, 2H), 9.3 (–OH, s, 3H); ¹³C NMR (75.4 MHz, DMSO-*d*₆, δ ppm): 55.0 (C–H), 113.0, 114.9, 116.0, 119.8, 129.0, 129.9, 134.0, 145.9, 155.6, 157.1 (ArC). Calc. C: 78.06, H: 5.52 Found C: 78.20, H: 5.59; **(2).** Red solid, yield 84%, mp 240 °C. ¹H NMR (300 MHz, DMSO-*d*₆, δ ppm): 5.37 (s, 1H, C–H), 6.8 (Ar–H, d, 6H, *J* = 8.0 Hz), 6.98 (Ar–H, d, 6H, *J* = 8.1 Hz), 9.3 (–OH, s, 3H). ¹³C NMR (75.4 MHz, DMSO-*d*₆, δ ppm): 53.6 (C–H), 114.8, 129.7, 135.2, 155.3 (ArC). Calc. C: 78.06, H: 5.52 Found C: 78.16, H: 5.47; **(3).** Red solid, yield 88%, mp 189 °C. ¹H NMR (300 MHz, DMSO-*d*₆, δ ppm): 6.25 (s, 1H, C–H), 6.38 (Ar–H, s, 2H), 7.10–7.22 (Ar–H, m, 6H), 7.42 (Ar–H, m, 2H), 8.20 (–OH, s, 1H), 8.99 (–OH, s, 2H), 9.5 (–OH, s, 2H). ¹³C NMR (75.4 MHz, DMSO-*d*₆, δ ppm): 42.9 (C–H), 109.2, 115.8, 119.2, 127.6, 130.7, 131.9, 135.3, 146.5, 155.7 (ArC). Calc. C: 70.36, H: 4.97 Found C: 70.45, H: 5.02.

Results and Discussion

Solid State Self-Assembly of Unsymmetrical Trisphenol 1. Good quality crystals of trisphenol **1** were obtained from methanol by slow evaporation and

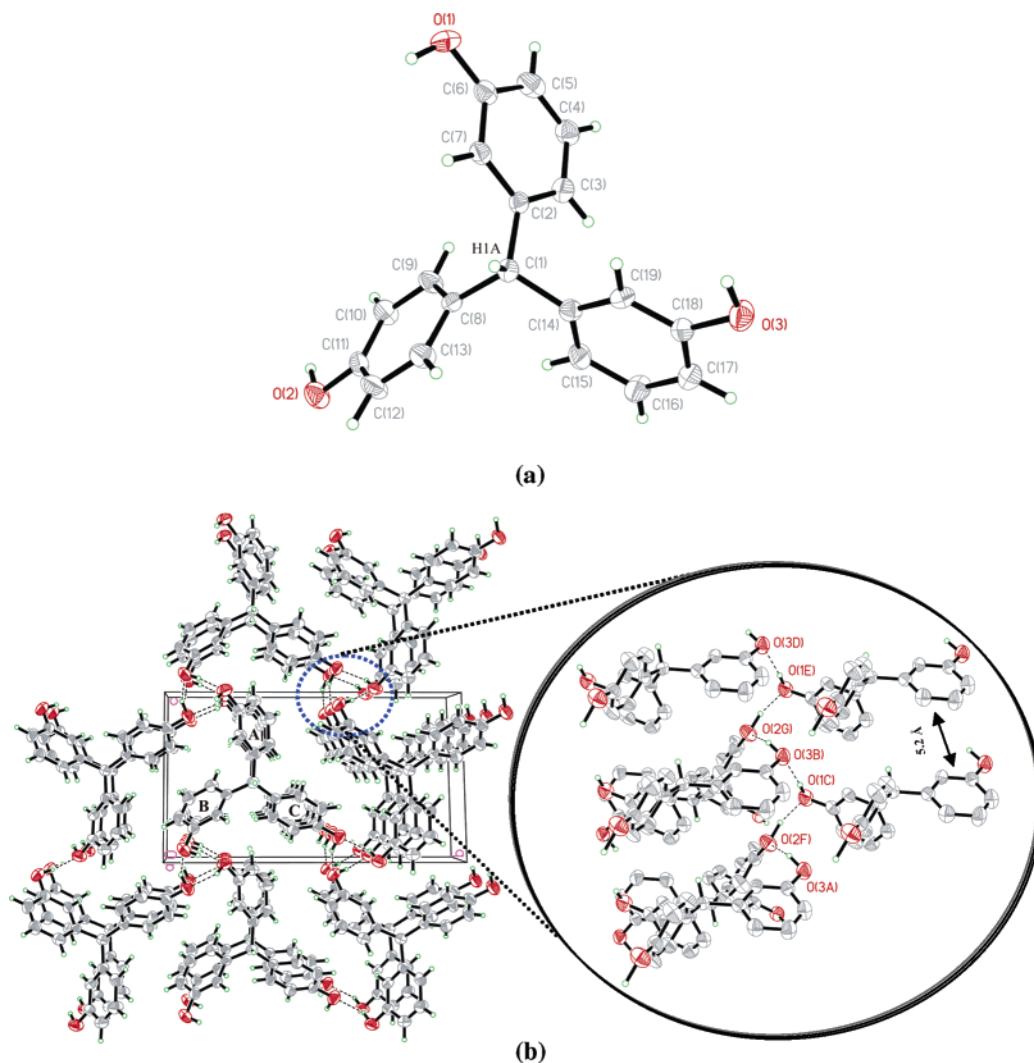


Figure 2. (a) The ORTEP representation of the compound **1** with atom-labeling scheme. The displacement ellipsoids are drawn at the 50% probability level for non-hydrogen atoms; (b) molecular packing in the crystal lattice of **1** and one of the hydrogen-bonded monohelices is highlighted. Hydrogen atoms attached to carbon atoms are omitted for clarity, and hydrogen bonds are indicated by dashed lines. Color code: O, red; C, gray; H, light green.

Table 2. Selected Torsion Angles (°) for 1

H1A–C1–C2–C3	148.0	H1A–C1–C8–C9	136.0
H1A–C1–C14–C15	138.0		

found to have a monoclinic crystal lattice with the $P2_1$ space group. The ORTEP representation and atom-labeling of the trisphenol **1** is shown in Figure 2a.

Figure 2b reveals the packing of trisphenol **1** as viewed along the a -axis. The triol crystallizes with a series of hydrogen-bonded monohelical chains surrounded by parallel channels. The hydroxyl group on the ring **A** forms intermolecular hydrogen bonds with the adjacent hydroxyl groups on the ring **B** or **C**. This allows each hydroxyl group to hydrogen bond with two neighboring hydroxyl groups to form monohelices in the lattice. The triphenylmethane molecules are eclipsed along a column axis and are staggered among the adjacent columns (Figure 2b). The phenolic rings are parallel along the column axis with an intermolecular distance of ca. 5.2 Å (Figure 2b).

Owing to the 3D structure of triphenol derivatives, each hydrogen bonded monohelix creates three isolated channels with dimensions of ca. 15×6 Å (Figure 2b) around it, and there are three distinct O–H \cdots O bonds

Table 3. Hydrogen-Bonding Geometry (Å, °) for Trisphenol 1^a

D–H \cdots A	d (D–H)	d (H \cdots A)	\angle D \cdots A	d (D–H \cdots A)
O1–H1 \cdots O3 ⁱ	0.92 (4)	1.90 (4)	2.813 (5)	173.0 (4)
O2–H2 \cdots O1 ⁱⁱ	1.18 (4)	1.64 (4)	2.746 (4)	153.0 (3)
O3–H3 \cdots O2 ⁱⁱⁱ	1.00 (5)	1.89 (5)	2.785 (5)	148.0 (3)

^a Symmetry codes: (i) $[x, y, z - 1]$; (ii) $[-x, y + 1/2, -z]$; (iii) $[-x + 1, y - 1/2, -z + 1]$.

along the helix (Table 3). Since all the O–H groups are hydrogen bonded to two other hydroxyl groups, the channels are hydrophobic in nature with no additional functional groups to stabilize the solvents inside the cavity.

Solid State Self-Assembly of Symmetrical Trisphenol 2. Good quality crystals of trisphenol **2** were obtained from a mixture of methanol and THF solvent (1:1) by slow evaporation. Single crystals of **2** were found to have monoclinic crystal lattices with space group of Cc . The structure solution and refinement parameters are given in Table 1. Figure 3a shows the ORTEP representation of **2**, giving the atom-labeling scheme.

In the crystal lattice of **2**, the molecules are linked via hydrogen bonds with a ladder-type motif. Unlike the

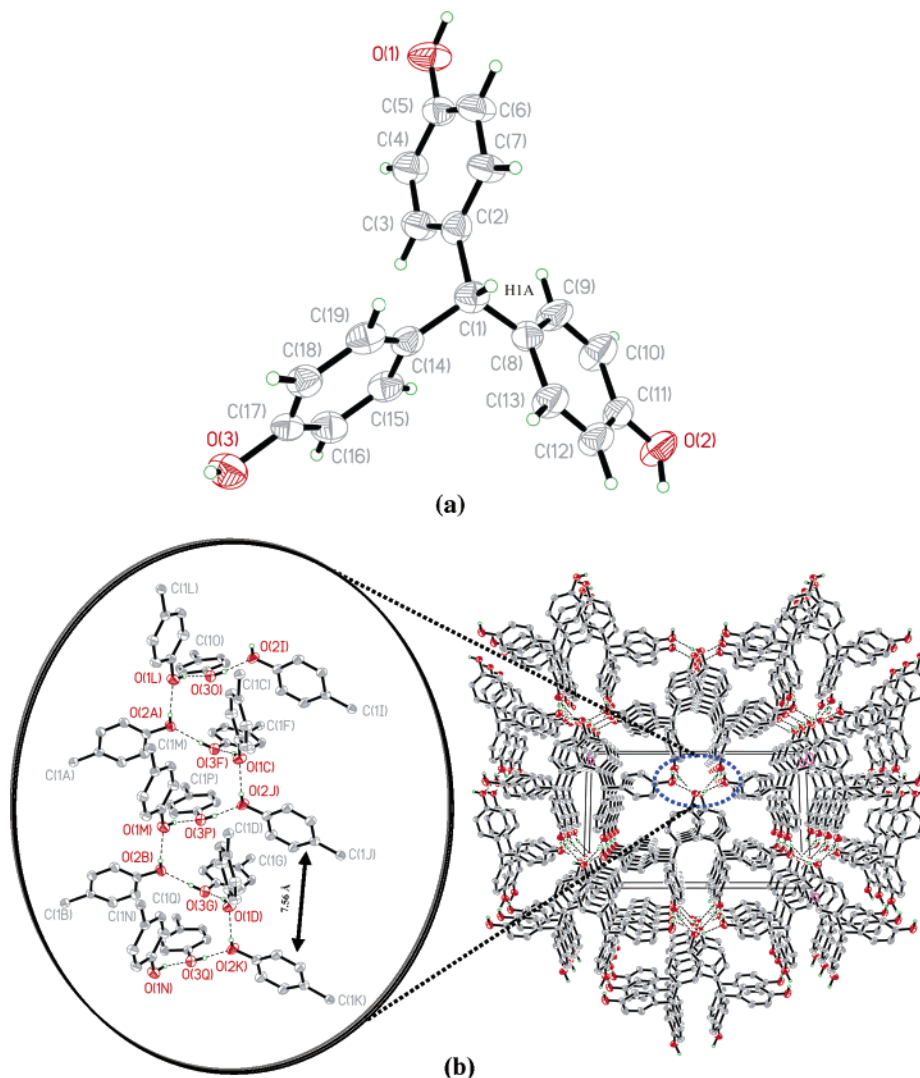


Figure 3. (a) ORTEP representation of the trisphenol **2** with atom numbering scheme. (b) Packing of molecules with O—H \cdots O hydrogen bonds as viewed along *c*-axis. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and benzene rings are truncated for clarity in the enlarged portion. Hydrogen bonds are represented by dashed lines. Color codes: O, red; C, gray; H, light green.

Table 4. Selected Torsion Angles (°) for 2

H1A—C1—C2—C7	19.0	H1A—C1—C8—C13	61.0
H1A—C1—C14—C19	26.0		

staircase ladder structures reported by Bishop et al.,^{6a-c} the formation of a distorted ladder in symmetrically oriented trisphenol **2** could be attributed to the involvement of hydroxyl group from the neighboring columns.

Figure 3b shows that the molecular packing with each hydroxyl group on the trisphenol unit is hydrogen-bonded with the neighboring hydroxyl groups located above and below the molecular plane. Each molecule inside the lattice is hydrogen bonded to six adjacent molecules through strong hydrogen bonds. There are three distinct hydrogen-bond distances and angles as given in the Table 5. The distance of the repeat unit of the phenolic moiety in the eclipsed direction of the hydrogen bonded chain is approximately 7.56 Å (Figure 3b).

In trisphenol **2**, the molecular aggregates are held together via edge-to-face aromatic C—H \cdots π interactions. The angle (taken to the centroid of the phenyl ring) is 151.0° with C—H \cdots π distances of 3.376 Å [C(4)—H(4) \cdots π (C8—C13) at (*x*, *y*, 1 + *z*)].

Table 5. Hydrogen-Bonding Geometry (Å, °) for Trisphenol 2^a

D—H \cdots A	<i>d</i> (D—H)	<i>d</i> (H \cdots A)	\angle D \cdots A	<i>d</i> (D—H \cdots A)
O1—H1 \cdots O3 ⁱ	0.93 (3)	1.77 (3)	2.670 (3)	162.0 (3)
O2—H2 \cdots O1 ⁱⁱ	0.82 (4)	1.94 (4)	2.670 (3)	147.0 (4)
O3—H3 \cdots O2 ⁱⁱⁱ	0.70 (3)	1.99 (4)	2.680 (4)	164.0 (5)

^a Symmetry codes: (i) [*x* + 1, *y*, *z* + 1]; (ii) [*x* − 1/2, −*y* + 1/2, *z* − 3/2]; (iii) [*x* − 1/2, *y* − 1/2, *z*].

Hydrogen-Bonded Supramolecular Architecture from Pentaphenol 3. Crystallization of pentaphenol **3** was achieved by slow evaporation from methanol. Single crystals of pentaphenol **3** were found to have a triclinic crystal system associated with four moles of water as revealed by X-ray crystallography. The ORTEP representation of molecule **3**, showing the atom-labeling scheme (Figure 4a), is given.

The five hydroxyl groups in pentaphenol **3** are organized in different orientations. Of the five hydroxyl groups, two ortho hydroxyl groups (O5/O4) on the phenyl rings (**i** and **ii**) are hydrogen bonded to the adjacent molecule in an inverse fashion that leads to the formation of channel **A** with a bond distance of

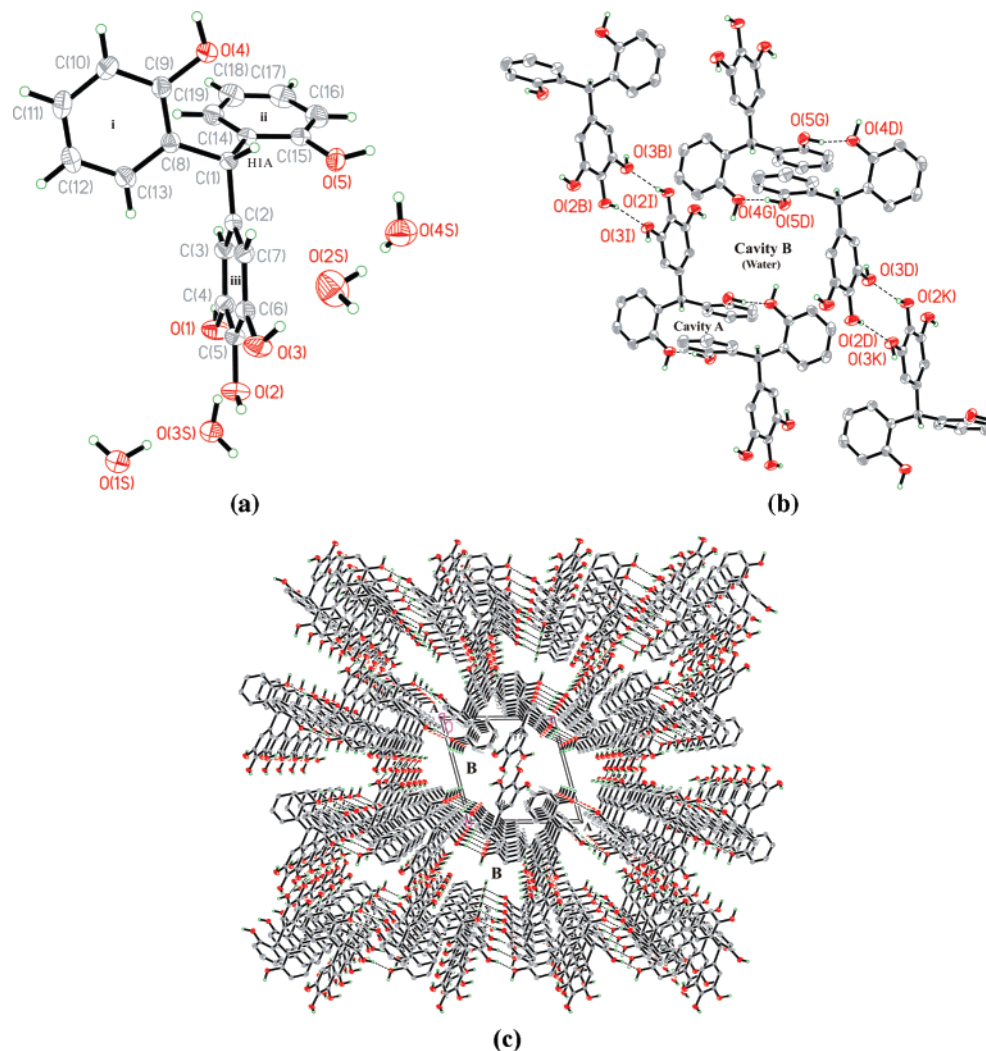


Figure 4. (a) ORTEP diagram with atom numbering scheme for pentaphenol **3**·4H₂O; (b) the hydrogen bonds between the organic skeleton that stabilizes the water cluster: [°]: O2–H2···O3: $d(\text{O}–\text{H})$ 0.88(2), $d(\text{O}···\text{O})$ 2.806(1), $d(\text{H}···\text{O})$ 2.03(2), $\angle\text{O}–\text{H}···\text{O}$ 147.0(2)° [$-x+2, -y+1, -z+1$]; O5–H5···O4: $d(\text{O}–\text{H})$ 0.91(2), $d(\text{O}···\text{O})$ 2.762(1), $d(\text{H}···\text{O})$ 1.89(2), $\angle\text{O}–\text{H}···\text{O}$ 160.0(2)° [$-x+1, -y, -z+2$]; (c) perspective view of the packing viewed along the *a*-axis. The water molecules in the lattice are omitted for clarity. The hydrogen bonds are denoted by dashed lines. The thermal ellipsoids are drawn at the 50% probability level. Color codes: O, red; C, gray; H, light green.

$d(\text{H}···\text{O}) = 0.91(2)$ Å and bond angle ($\angle\text{O}–\text{H}···\text{O}$) of 160.0(2)° at ($-x+1, -y, -z+2$), Figure 4b. Solvated water molecules were observed in the crystal lattice which are formed by hydrogen bonds between phenolic hydroxyl groups (Figure 5a,c). The hydroxy atom O4 act as a hydrogen bond donor to atom O1S at [$x, y-1, z+1$] and acceptor for O5 at [$-x+1, -y, -z+2$], thus stabilizing the water cluster in the lattice. The channel A approximately 8.3×3.2 Å wide is formed by strong hydrogen bonds between the hydroxyl groups cited at the ortho position on the phenyl rings. Two out of three hydroxyl groups (O3/O2) on the phenyl ring (iii) are hydrogen bonded to adjacent molecules as viewed along the *a*-axis (Figure 4b) with bond distance $d(\text{H}···\text{O}) = 0.88(2)$ Å and bond angle $\angle\text{O}–\text{H}···\text{O}$ of 147.0(2)° [Figure 4b, ($-x+2, -y+1, -z+1$)]. However, additional hydrogen-bond donor sites (O3/O4) and acceptor sites (O5) are available to interact with the water molecules. The hydroxy atom O3S acts as an anchor and donates both its hydrogen atoms to O5 at [$-x+1, -y+1, -z+1$] and O1 with $d(\text{O}···\text{O})$ 2.909(2) and 2.778(2) Å, respectively, which suggests a strong hydrogen bond in-

teraction (Figure 5c). Because of interesting O–H···O hydrogen bonds, unique O(1)H_p··· π (arene) interactions are formed inside the crystal lattice (Figure 5a). The π electron rich aromatic ring (C8–C13) serves as the acceptor and the hydroxyl groups on the ring (iii) behaves as the donor. The O–H_p··· π bonds closer to ring carbon atoms are from C8 to C13 with the angle $\angle\text{O1}–\text{H1}···(\text{Cg}1)$ being 152° and the $d(\text{O}–\text{H}_p···\pi)$ distances 2.660 Å at ($1-x, -y, 1-z$), respectively. Thus, the O–H_p··· π interactions, by bringing the hydrogen atom of the phenyl ring in close proximity with one or more other ring carbons directs it to the π face that further propagates the interaction.

The void space marked as channel B, Figure 4b in the crystal lattice of **3** is of the dimension ca. 11×7 Å and is occupied by water molecules. The water molecules in the channel forms a chair-type hexameric unit and are stabilized by strong O–H···O hydrogen bonds with the hydroxyl groups forming the channel walls (Figure 5a,c).

The water molecules are stabilized by organic skeletons and organized to form water hexamers that

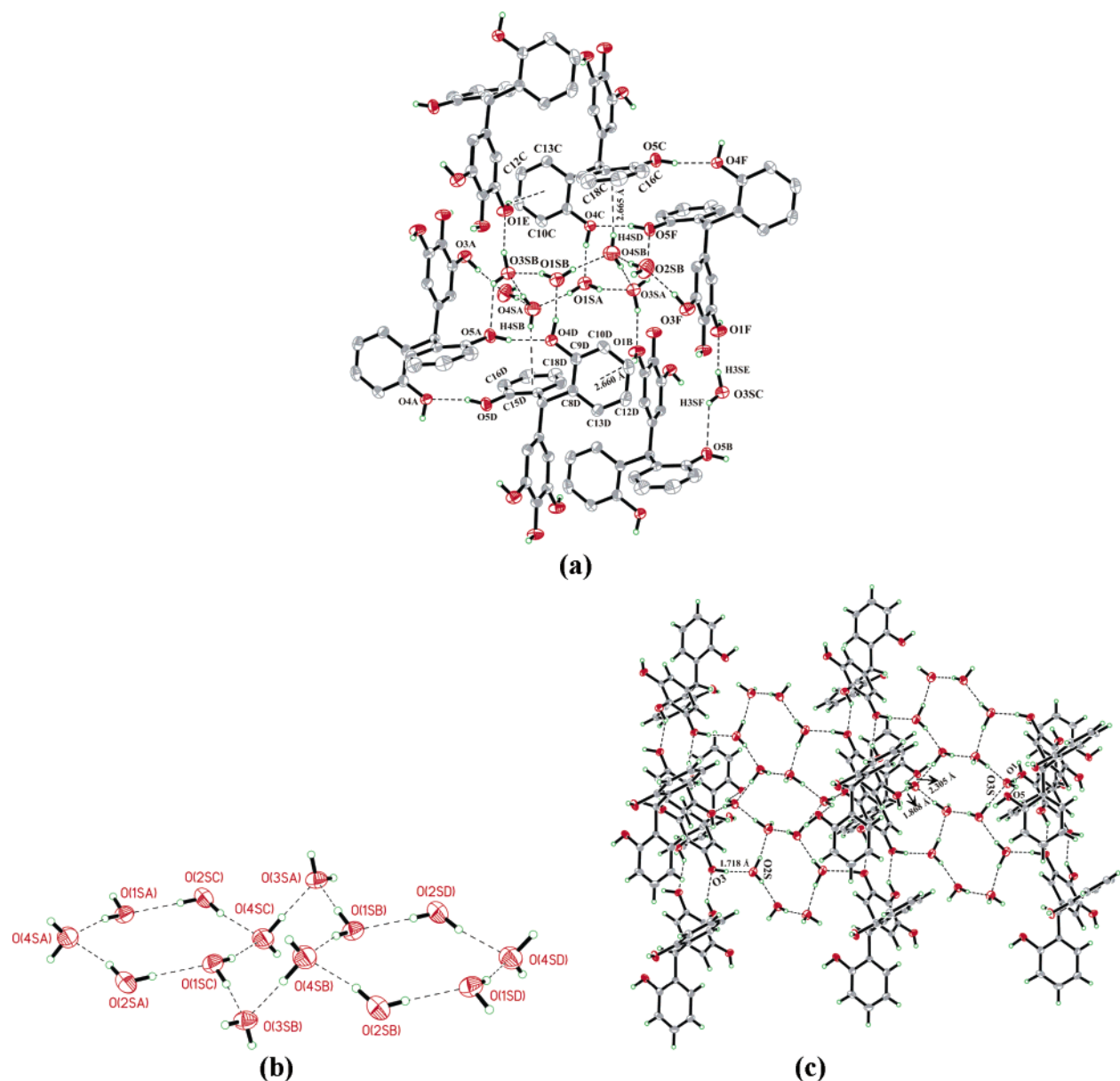


Figure 5. Hydrogen-bonded hexameric water clusters in **3**, (a) showing O–H_w(water)··· π (arene), and O–H_p (aryl)··· π (arene) interactions. (b) Hydrogen bonds among the water clusters (c) representation of the packing of the extended array of water molecules in the crystal lattice (one-dimensional tapes). Hydrogen bond lengths [Å] and the angles [°]: O3–H3···O2S: d(O···O) 2.619(2), d(H···O) 1.72(2), \angle O–H···O 171.0(2)°; O4–H4···O1S: d(O···O) 2.659(1), d(H···O) 1.77(2), \angle O–H···O 169.0(2)° [x , y – 1, z + 1]; O2S–H2SH···O4S: d(O–H) 0.94(3), d(O···O) 2.797(2), d(H···O) 1.87(3), \angle O–H···O 167.0(2)°; O2S–H2SC···O1S: d(O–H) 0.85(3), d(O···O) 2.772(2), d(H···O) 1.94(3), \angle O–H···O 166.0(2)° [$-x$ + 2, $-y$ + 1, $-z$ + 1]; O3S–H3SB···O5S: d(O–H) 0.83(3), d(O···O) 2.909(2), d(H···O) 2.31(2), \angle O–H···O 129.0(3)° [$-x$ + 1, $-y$ + 1, $-z$ + 1]. The non H-atoms and benzene molecules are truncated for clarity. The hydrogen-bonds are denoted by dashed lines and thermal ellipsoids are drawn at 50% probability level. Color codes: O, red; C, gray; H, light green.

extends into one-dimensional tapes in the crystal lattice as shown in the Figure 4b. The tape is very unique in that, the central water hexamer which has the chair like conformation is sandwiched between planar water hexamer, which is known to be a high-energy cyclic form (Figure 5b).^{8k,16b} The tapes are stabilized by the hydroxyl groups from the channel walls through strong hydrogen bonding. The hydrogen-bond distances of O1S–H1SB···O3S and O4S–H4SA···O3S [$-x$ + 1, $-y$ + 1, $-z$ + 1] are 1.85(3) and 1.78(3) Å, respectively, and these bonds serve as a connector of two water hexameric units for the extension of the hydrogen-bonded water clusters inside the channel. One of the hydrogen atoms of the water molecule (O4S) does not have hydrogen-

bond acceptor and shows an unusual O4S–H4S··· π (arene) interactions (Figure 5a). The other hydrogen atom and its own oxygen atom is simultaneously hydrogen bonded to another molecule of water, to complete the ring Figure 5a–c. The O–H_w··· π bonds closer to ring carbon atoms are from C14 to C19 with the angle \angle O4S–H4S···(Cg2) being 156.0° and the d(O–H_w··· π) distances 2.665 Å at (x , 1 + y , -1 + z).

On the basis of literature, the nearest neighboring O···O distance in ice I_h at atmospheric pressure calculated by Lonsdale from diffraction data is 2.759 Å at -90 °C.^{14a,b} The geometric parameters of the water hexamer (Figure 5a) are summarized in Table 7. In pentaphenol **3**, the average O···O separation is 2.745

Table 6. Selected Torsion Angles (°) for 3

H1A–C1–C2–C3	–151.0	H1A–C1–C8–C13	–133.0
H1A–C1–C14–C15	45.0		

Table 7. Geometric Parameters for the Cyclic Water Hexamers in Pentaphenol 3·4H₂O^a

group	dimensions			
	d(O–H)	d(O···O)	d(H···O)	∠O–H···O
O1S–H1SA···O4S (Å) ⁱ	0.87 (2)	2.742 (2)	1.89 (2)	169.0 (2)
O1S–H1SB···O3S (Å)	0.91 (2)	2.730 (2)	1.85 (3)	163.0 (2)
O2S–H2SA···O1S (Å) ⁱⁱ	0.85 (3)	2.772 (2)	1.94 (3)	166.0 (2)
O2S–H2SB···O4S (Å)	0.94 (3)	2.797 (2)	1.87 (3)	167.0 (2)
O4S–H4S···O3S (Å) ⁱⁱⁱ	0.99 (3)	2.765 (2)	1.78 (3)	176.0 (2)
$\angle \text{O} \cdots \text{O} \cdots \text{O}$				
O4S···O3S···O1S (°)	94.0 (2)			
O4S···O1S···O2S (°)	137.0 (2)			
O3S···O4S···O2S (°)	106.0 (2)			
O1S···O2S···O4S (°)	121.0 (2)			

^a Symmetry operators: (i) $[x, y, z - 1]$; (ii) $[-x + 2, -y + 1, -z + 1]$; (iii) $[-x + 1, -y + 1, -z + 1]$.

Å, which is similar to that observed in natural ice. From the observed lattice, it appears that the water molecules in the lattice experience a molecular surrounding similar to the one in ice or water.^{14a,b} The water molecules in the one-dimensional supramolecular tapes are in different planes and give an appearance of connected “butterfly wings” (Figure 5b).

Comparison of the Motifs. The hydrogen bonding between the hydroxyl groups results in the formation of a three-dimensional network with parallel channels whose contours and dimensions vary considerably with the structure of the molecules. The unsymmetrical trisphenol **1** with three hydroxyl groups facilitated the formation of hydrogen bonded open monohelical strands in the crystal lattice. Each of the three hydroxyl groups on the symmetrical trisphenol **2** showed a distorted ladder-type hydrogen-bonded chain in the crystal lattice. In the case of pentaphenol **3**, O–H··· π (arene) interactions were observed in the lattice. Each hydroxyl group of the pentaphenol participates in the hydrogen bonding to stabilize the organic framework and water clusters are present in the lattice. The observed differences in the self-assembly of polyphenols could be attributed to the 3D architecture of the molecules, number and orientation of the hydroxyl groups on the phenyl rings. Further studies reflecting on the encapsulation of water in the crystal lattice of other organic molecules are currently under investigation.

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Supporting Information Available: Crystallographic information files are available free of charge via the Internet at <http://pubs.acs.org>.

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