Electronic Supplementary Information

Synthesis: An aqueous solution of $KBrO_3$ (550 mg, 3.3 mmol) and KBr (800 mg, 6.7 mmol) in 20 ml water was added slowly to phloroglucinol (1.26 g, 10.0 mmol) dissolved in 20 ml water and 0.85 ml of conc. HCl at 0 ºC. The reaction mixture was stirred over-night at room temperature, extracted with Et_2O, and the product was purified by column chromatography.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.42 (s, 1H), 5.77 (s, 1H), 5.51 (s, 2H, OH).
IR (KBr): 3454, 1595, 1495, 1449, 1385, 1269 cm^{-1}.

X-ray Crystallography: Crystal data was collected on Bruker SMART APEX CCD with Mo-Kα radiation (λ = 0.71073 Å). **DBPG•4H_2O**: C_6 H_{12} Br_2 O_7, *Mr* = 355.98, monoclinic, *C*2/*c*, *a* = 16.0309(12), *b* = 10.6848(8), *c* = 7.3246(5) Å, *β* = 111.4500(10), *V* = 1167.71(15) Å^3, *Z* = 4, *R*1 = 0.0198, *wR*2 = 0.0502, *T* = 100 K. **DBPG•4H_2O**: C_6 H_{12} Br_2 O_7, *Mr* = 355.98, monoclinic, *C*2/*c*, *a* = 16.135(4), *b* = 10.740(2), *c* = 7.4390(17) Å, *β* = 111.354(3), *V* = 1200.5(5) Å^3, *Z* = 4, *R*1 = 0.0253, *wR*2 = 0.0667, *T* = 298 K. **DBPG**: C_6 H_4 Br_2 O_3, *Mr* = 283.91, orthorhombic, *Pbcn*, *a* = 5.4011(5), *b* = 12.8974(13), *c* = 10.9478(11) Å, *V* = 762.63(13) Å^3, *Z* = 4, *R*1 = 0.0298, *wR*2 = 0.0794, *T* = 298 K. All non-hydrogen atoms were refined anisotropically and H atoms connected to oxygens were located from difference electron density maps. In DBPG•4H_2O structure at 298 K, seven restraints are due to fixing O–H distances at 0.82 Å and four restraints are due to fixing H–O–H angles at 105º. All O–H hydrogens were experimentally located in the 100 K data structure. In both tetrahydrate structures one phenolic hydrogen H1 is disordered over two positions due to symmetry and one water hydrogen is disordered over two positions, H4b and H4c with 0.5 occupancy each. In anhydrous DBPG three restraints are due to fixing O–H distances at 0.82 Å. Each phenolic hydrogen is disordered over two positions with 0.5 occupancy. H atoms connected to carbons were located in calculated positions. Intensities were corrected for absorption effects using the multi-scan technique (SADABS). Structure solution and refinement were carried out with Bruker SHELXTL.

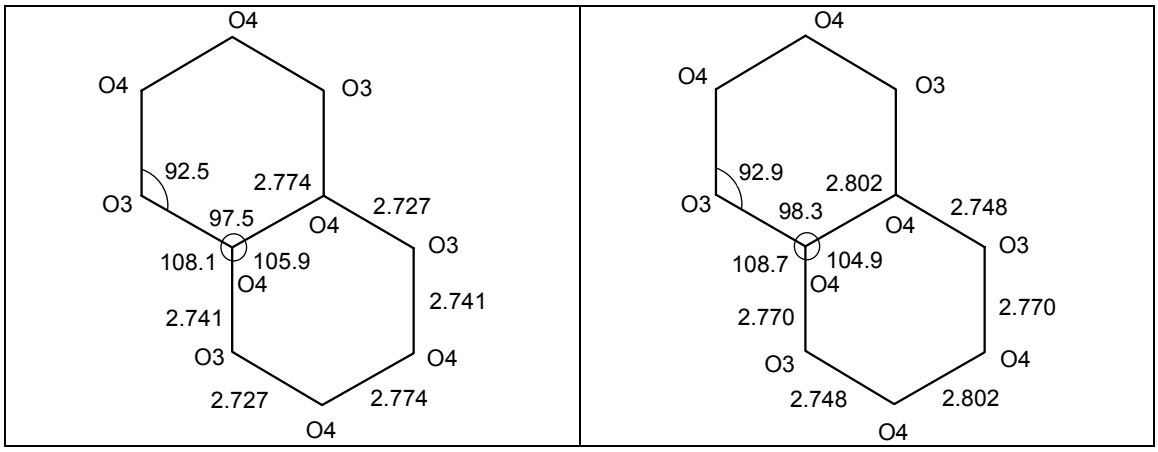

Figure S1 Comparison of H bond distances/ angles in DBPG•4H_2O at 100 K (left) and 298 K (right).

Table S1 Hydrogen bonds and interaction (neutron-normalized geometry).

Interactions	Symmetry	d, Å	D, Å	θ, º
	DBPG•$4H_2O$ (100K)			
O–H(1)···O(4)	x, 1-y, 1/2+z	1.84	2.770(3)	157.2
O–H(2)···O(3)	x, y, z	1.69	2.669(2)	172.4
O–H(3a)···O(2)	1/2-x, 3/2-y, 2-z	1.85	2.806(3)	164.4
O–H(3b)···O(4)	x, 2-y, 1/2+z	1.76	2.727(3)	167.6
O–H(4a)···O(3)	x, y, z	1.78	2.741(3)	164.3
O–H(4b)···O(4)	-x, 2-y, 1-z	1.81	2.774(3)	167.4
O–H(4c)···O(1)	-x, 1-y, 1-z	1.85	2.770(3)	154.9
Br···Br	1/2-x, 1/2-y, 2-z		3.452(4)	140.5, 140.5
	DBPG•$4H_2O$ (298 K)			
O–H(1)···O(4)	x, 1-y, 1/2+z	1.95	2.802(3)	142.8
O–H(2) ···O(3)	x, y, z	1.72	2.684(3)	167.0
O–H(3a)···O(2)	1/2-x, 3/2-y, 2-z	1.90	2.828(4)	156.9
O–H(3b)···O(4)	x, 2-y, 1/2+z	1.81	2.748(4)	159.3
O–H(4a)···O(3)	x, y, z	1.85	2.770(4)	155.2
O–H(4b)···O(4)	-x, 2-y, 1-z	1.82	2.801(4)	178.1
O–H(4c)···O(1)	-x, 1-y, 1-z	2.05	2.802(3)	131.5
Br···Br	1/2-x, 1/2-y, 2-z		3.477(1)	142.6, 142.6
	DBPG (anhydrous form)			
O–H(1)···O(2)	1/2-x, 1/2+y, z	2.11	2.916(5)	138.0
O–H(2a)···O(2)	-x, -y, 1-z	2.21	3.123(6)	153.4
O–H(2b)···O(1)	-1/2+x, -1/2+y, 3/2-z	2.07	2.916(5)	142.7
Br···Br	-1/2+x, 1/2-y, 1-z		3.491(1)	170.0, 87.5