Electronic Supplementary Information

Synthesis of 2,4,6-tris(2-chloro-3-pyridinoxy)-1,3,5-triazine 2: 2-Chloro-3-pyridinol and KOH (4.0 equiv each) were dissolved in acetone and stirred for 30 minutes. Cyanuric chloride (1.0 equiv) was added to the reaction mixture at 0 ºC and stirred for 1 h. The reaction mixture was allowed to stir for 1 d at room temperature, poured into crushed ice, the resulting white precipitate was suction filtered and then washed with methanol. The product was purified by column chromatography and crystallized from the appropriate solvent.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, J = 4 Hz, 3 H), 7.53 (d, J = 8 Hz, 3 H), 7.28 (dd, J = 8, 4 Hz 3 H).
IR (KBr): 3047, 1581, 1419, 1367, 1267, 1246, 1211 cm^{-1}.

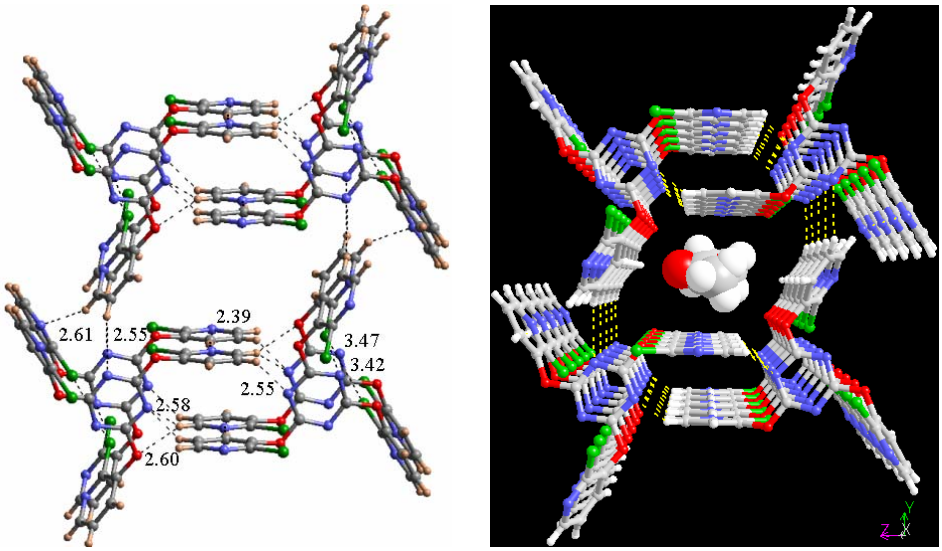
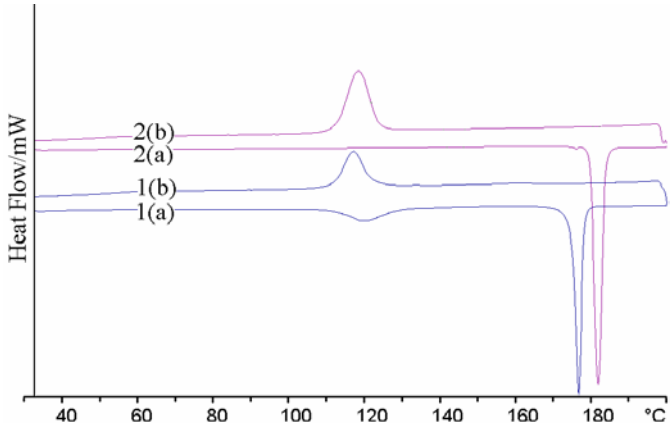
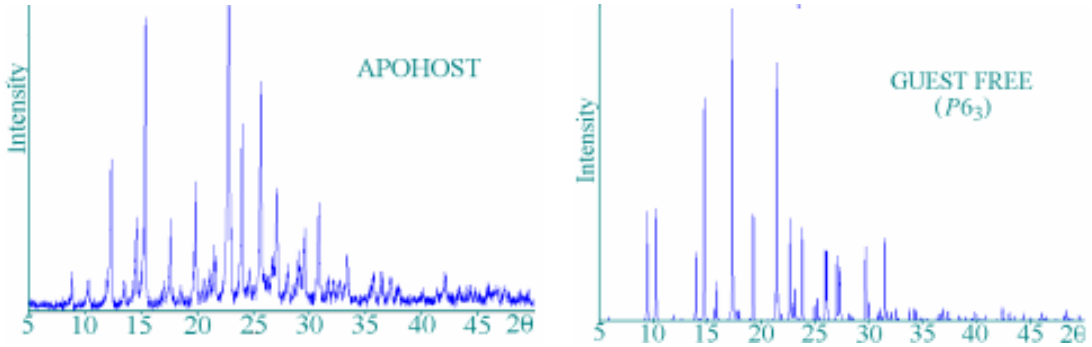


Fig. S1 Packing in **2.**EtOAc crystal structure (shown above) is isostructural to **2.**MeCOEt (see Figs. 2 and 3) even though these structures have slightly different triclinic unit cell parameters.



(a)



(b)

Fig. S2 (a) DSC heat–cool–heat cycles: curve 1 is **2.**acetone and curve 2 is guest-free $P6_3$ crystals. T_{onset} of apohost = 177 ºC and T_{onset} of guest-free solid = 182 ºC. The exotherm on cooling is due to solidification. (b) Powder XRD of apohost and simulated peaks of guest-free crystal structure. The guest-free structure (Fig. 6) is different from the apohost solid based on DSC and PXRD.

Table S1 Intermolecular interactions in **2.**MeCOEt and **2.**EtOAc.

Interaction	d, Å	D, Å	θ, deg
	2.MeCOEt		
C(5)-H(5)···N(4)	2.55	3.553(3)	153.4
C(6)-H(6)···N(6)	2.56	3.583(3)	157.5
C(10)-H(10)···N(5)	2.38	3.464(3)	175.9
C(11)-H(11)···N(2)	2.54	3.481(3)	144.0
C(12)-H(12)···O(3)	2.62	3.617(3)	153.0
C(12)-H(12)···N(2)	2.62	3.543(3)	142.2
C(15)-H(15)···Cl(3)	2.92	3.627(3)	122.8
C(16)-H(16)···N(1)	2.52	3.434(4)	141.7
C(17)-H(17)···N(4)	2.51	3.471(4)	147.3
Cl(1)···Cl(3)		3.488(1)	140.1(1), 120.0(1)
Cl(3)···N(2)		3.439(2)	149.4(1)

		2.EtOAc	
C(5)-H(5)···N(4)	2.56	3.557(4)	152.5
C(6)-H(6)···N(6)	2.54	3.566(5)	158.0
C(10)-H(10)···N(5)	2.39	3.466(4)	174.5
C(11)-H(11)···N(2)	2.55	3.497(5)	145.3
C(12)-H(12)···O(3)	2.60	3.599(4)	152.8
C(12)-H(12)···N(2)	2.58	3.503(5)	142.9
C(15)-H(15)···Cl(3)	2.90	3.623(4)	124.0
C(16)-H(16)···N(1)	2.55	3.392(4)	133.8
C(17)-H(17)···N(4)	2.61	3.561(5)	145.8
Cl(1)···Cl(3)		3.475(2)	139.7(1), 120.0(1)
Cl(3)···N(2)		3.416(3)	148.4(1)