Electronic Supplementary Information (ESI)

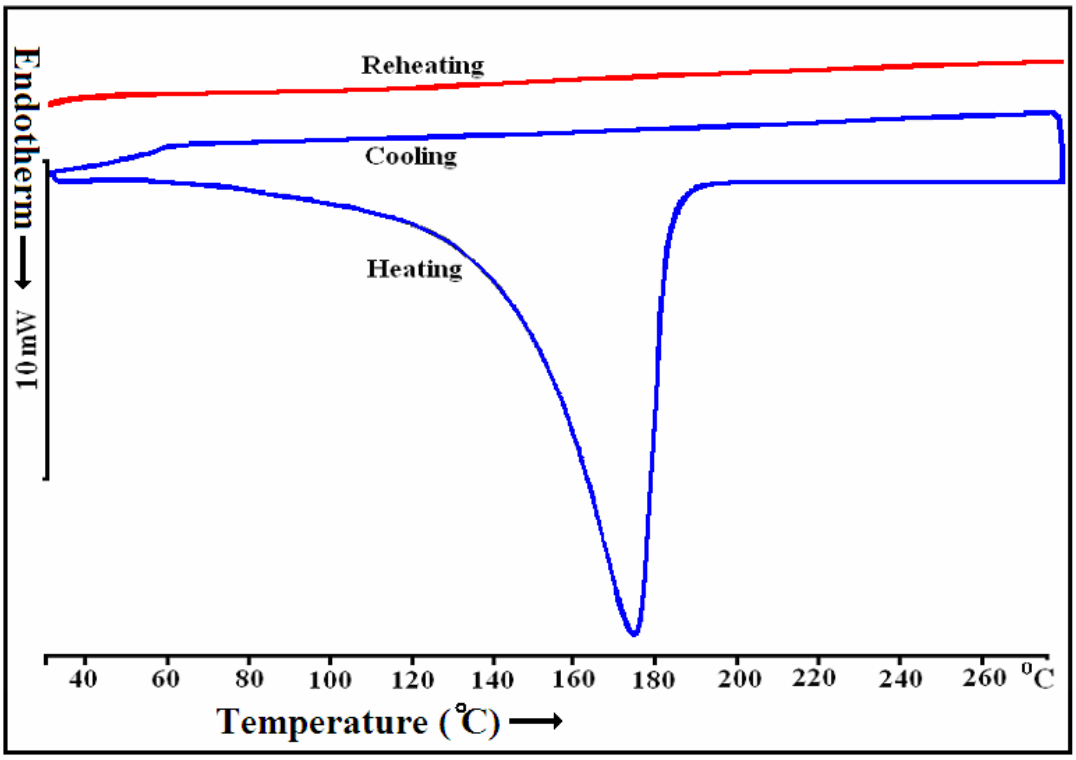

Figure S1 Differential scanning calorimetry. A heat–cool–heat cycle of TPM-$SO_3H \cdot (H_2O)_{12}$ (sample dried at 150 °C/ 0.5 Torr) shows complete loss of water below 200 ºC and no weight loss in the second heating cycle.

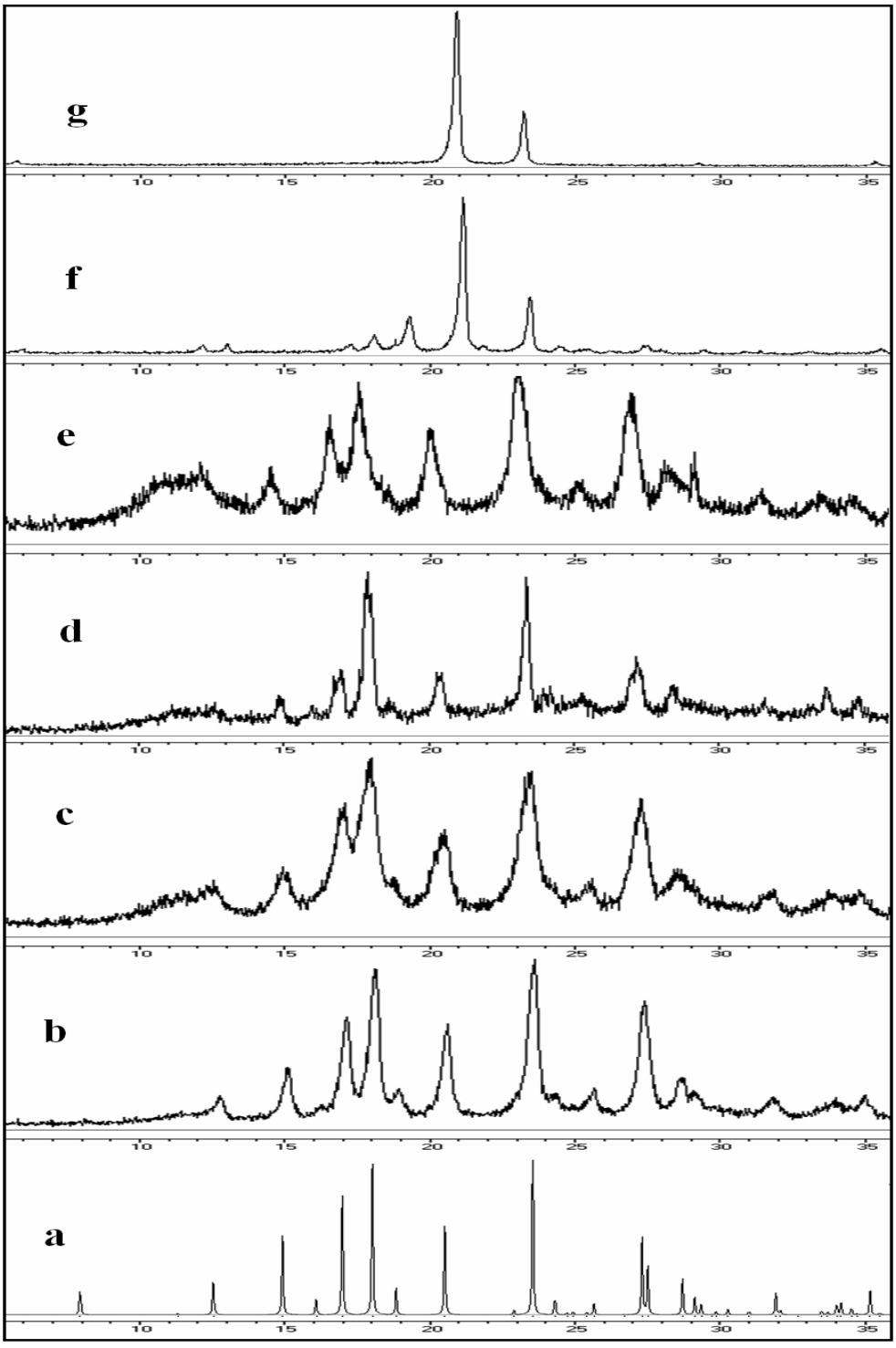

Figure S2: Powder X-ray diffraction pattern of TPM-$SO_3H \cdot (H_2O)_{12}$ under different dehydration conditions. (a) TPM-$SO_3H \cdot (H_2O)_{12}$.Simulated from the X-ray crystal structure. (b) Dodecahydrate host material. (c-e) Dried sample at 100, 200, 250 °C/ 0.5 Torr. There is little change in the powder lines due to immediate re-absorption of water

by the apohost during sample handling and data collection. The amorphous content varies after heat–cool cycles. (f) The solid was immediately coated with wax after heating at 200 °C/ 0.5 Torr. (g) Reference wax. The powder diffraction lines in profiles (b-e) are similar. The new crystalline phase in (f) is possibly the anhydrous form.

Table S1: O···O and O···H distances in H bonds calculated using PLATON.

Interaction	Distance /Å	
	< ΣvdW = 3.0 Å	3.0-4.0 Å
O1A···O5	2.810(12)	
O1A···H6	2.48(4)	
O1B···O5		3.842(8)
O1B···O6B	2.39(3)	
O1B···O2		3.838(8)
O1B···O5		3.306(9)
O1B···O6B		3.40(3)
O1B···H6		3.39(4)
O1B···O6A	2.60(2)	
O1B···O6B	2.89(2)	
O2···O5		3.468(6)
O2···H6	2.60(4)	
O2···O4	2.716(6)	
O3···O4	2.697(6)	
O3···O5	2.729(6)	
O3···O6A		3.66(2)
O3···O6B		3.81(3)
O3···H3	2.67(4)	
O6A···O5	2.71(2)	
O6A···H6		3.37(5)
O6A···O6B	2.74(4)	
O6B···O2		3.74(2)
O6B···O5	2.58(2)	
O6B···O6A	2.74(4)	
O6B···O6A		3.34(4)
O6B···H6		3.11(5)

C–H···O distances (neutron-normalized C–H = 1.083 Å).

Interaction	H···O/Å	C···O/ Å	∠C–H···O/º
C3–H3···O3	2.50	3.467(6)	147
C5–H 5···O5	2.70	3.460(6)	126
C5–H5···O4	2.94	3.669(6)	124
C6–H6···O2	2.54	3.342(6)	129

Electronic Supplementary Material for CrystEngComm

The Cambridge Structural Database (version 5.27, ConQuest 1.9, Jan 2007 update) was searched to obtain results reported in Table S2 and S3. Crystal structures were visualized in Mercury 1.4.1.

Table S2: Free volume in the host molecule (from tetrahedral moiety) for solvent inclusion and solvent occupied volume in the crystal structure were calculated in PLATON. Organic crystal structures having no disorder, no errors, not polymeric, and 3D coordinates determined were retrieved. Refcodes are arranged in decreasing order of free volume for solvent inclusion. TPM-SO_3H is highlighted in bold.

Refcode	Free vol. for solvent inclusion	Solvent occupied volume	Refcode	Free vol. for solvent inclusion	Solvent occupied volume
XUVBEV	65.94	-	DEKTOC	43.26	14.66
XUVBAR	63.75	-	QOWDIP	42.35	13.74
VOJFEF	61.88	29.71	UJOFEE	41.43	15.34
QOWDAH	57.49	27.17	XOGJEI	40.91	12.18
LASVEH	55.96	24.46	KAPGAK	40.88	9.20
EVEMOH	54.61	27.17	NUJKIM	40.06	10.38
EGILAH	53.17	11.54	OGENUJ	39.81	11.21
OMADOV	51.67	23.52	XECWOS	39.06	4.32
LOJRAD	49.90	18.44	DAHHAW	38.48	3.58
XOVLID	48.98	22.20	LOJQUW	37.98	9.54
ZADROL	48.87	-	QOVZUW	37.78	10.38
BONBEL	48.50	22.50	NAWSOU	37.06	10.43
TAHHAL	47.75	20.16	DEKTUI	36.97	4.91
XOVLAV	47.61	19.90	RARRIM	36.88	9.51
NUJKEI	47.38	17.04	QOLMOT	36.78	6.04
XEBTIH	47.23	17.31	EVEBAI	36.62	8.51
EVEMUN	46.90	13.14	QOWBAF	36.19	7.93
TPMSO3H	**46.50**	**19.10**	LONDUT	35.77	4.94
BEQFIN	46.30	12.30	ABUCUV	35.40	7.97
XOGJAE	46.05	13.72	QOWBEJ	34.22	10.43
HEXXAJ	45.69	17.48	FEWDOB	33.49	10.08
WANGAU	45.14	18.01	QOWCOU	32.22	4.22
FOMKUO	44.89	15.14	QOWCIO	31.04	4.24
BAGBAM	43.50	14.01			

Table S3: List of CSD refcodes of dodecahydrate crystal structures (32 hits). There are 16 ordered structures and remaining 16 structures are disordered. There are 6 structures with all hydrogen atoms (including those of water) located. Organic crystal structures with the 'All Text phrase' 'dodecahydrate' and having *R*-factor < 0.10, no disorder, no error, not polymeric, and 3D coordinate determined were retrieved. The lower *R*-factor structure was retained for duplicate refcodes.

Refcode	Space Group	Temperature / K	Ordered structure (Yes/No)	Water Hs located (Yes/No)
ACTDGU10	$P2_12_12_1$	295	No	No
AGAZOX	$P1$	298	No	No
ARACEB	$P1$	150	No	No
BCDEXD10	$P2_1$	295	No	No
EDOJOW	$P2_1/c$	100	No	No
GOSQOU	$C2$	295	No	No
HIFKEM	$P2_1$	295	Yes	Yes
IJOLUO	$C2$	293	No	No
IQOZIX	$P2_12_12_1$	150	No	No
JOSTOA	P-1	295	Yes	Yes
KAFPEN	$P1$	123	Yes	No
KUTKOZ	$P2_1$	295	No	No
LEDRUH	$P2_12_12_1$	295	No	No
LOZMUI	$C2/c$	90	Yes	One H located
LOZNAP	$C2/c$	153	Yes	One H located
LOZNET	$C2/c$	90	Yes	One H located
LOZNIX	$C2/c$	93	Yes	Yes
LOZNOD	$C2/c$	86	Yes	One H located
LOZNUJ	$C2/c$	93	Yes	One H located
MORSAN	P-1	100	Yes	Yes
NOJPAD	$P2_12_12_1$	295	No	No
NUKFII	$Aba2$	295	No	No
OGIZIN	$P2_12_12_1$	293	No	No
PAANTD01	$P2_12_12$	295	No	No
PEZNAJ	$P2_12_12_1$	193	Yes	Yes
POXKIW	P-1	295	Yes	No
REGRIE	$P2_1/n$	123	No	No
SAFJEO10	P-1	295	Yes	No
XIVWAA	$P2_1$	173	Yes	No
XUSBOC	$P2/c$	123	Yes	Yes
ZUWQEN	$P2_1$	295	Yes	No
QENTIN	$P2_1$	200	No	No