Electronic Supplementary Material (ESI) for CrystEngComm.

SUPPORTING INFORMATION

Single-crystal-to-single-crystal transformation of the desolvation of a cyclotriveratrylene-acetonitrile inclusion complex via a gating mechanism with subsequent polymorphism

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Table S1 Hydrogen bonding parameters as obtained from PLATON[1]

Hydrogen bonding atoms	D-H / Å	H···A / Å	D···A / Å	D-H···A / °	Symmetry operators
1a					
C16B-H16D···O1A	0.98	2.49	3.209(2)	130	x,y,-1+z
C2S-H2SC···O5A	0.98	2.57	3.546(2)	172	x,y,z
C25A-H25A···N1S	0.98	2.53	3.458(2)	158	-x,1-y,2-z
C25B-H25E···O5A	0.98	2.54	3.390(2)	145	-x, ½+y,3/2-z
C26A-H26A···N1S	0.98	2.56	3.313(2)	134	x,y,z
C2S-H2SA···Cg1[a]		2.97		110	
C2S-H2SB···Cg2[b]		2.71		140	
2a					
C7B-H7BB···O6A	0.98	2.47	3.104(2)	122	x, ½-y,- ½+z
C8A-H8AB···O5A	0.98	2.49	3.452(3)	167	-x,-y,3-z

[a]Cg1 (C1A/C2A/C3A/C4A/C5A/C6A), [b] Cg2 (C10A/C11A/C12A/C13A/C14A/C15A)

Data collection	**Time elapsed / hrs**	**SQUEEZE analysis of electrons per unit cell**	**Number of acetonitrile molecules per asymmetric unit***	**Site occupancy factor for C26A**
1	2	92	1.05	1.00
2	4	84	0.95	1.00
3	6	54	0.61	0.37
4	8	47	0.53	0.43
5	10	43	0.49	0.66
6	12	34	0.39	0.65
7	14	31	0.35	0.74
8	16	27	0.31	0.67
9	18	25	0.28	0.80
10	20	22	0.25	0.69
11	22	18	0.20	0.69
12	24	18	0.20	0.60

Table S2 SQUEEZE analysis of 12 consecutive data collections (2 hours each) on a crystal of 1a at 50°C

*Based on 22 electrons per acetonitrile molecule

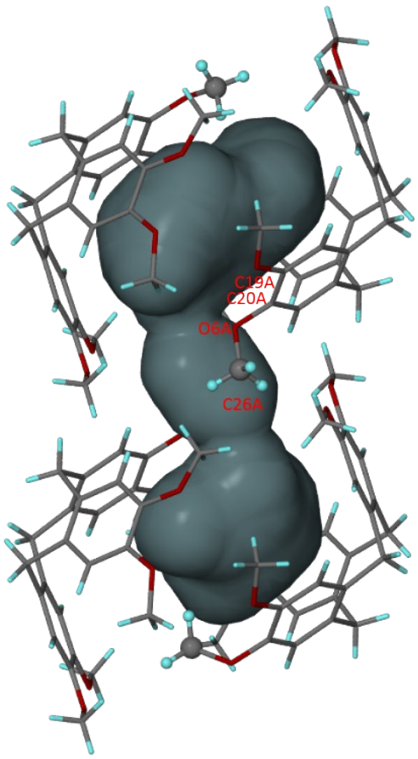
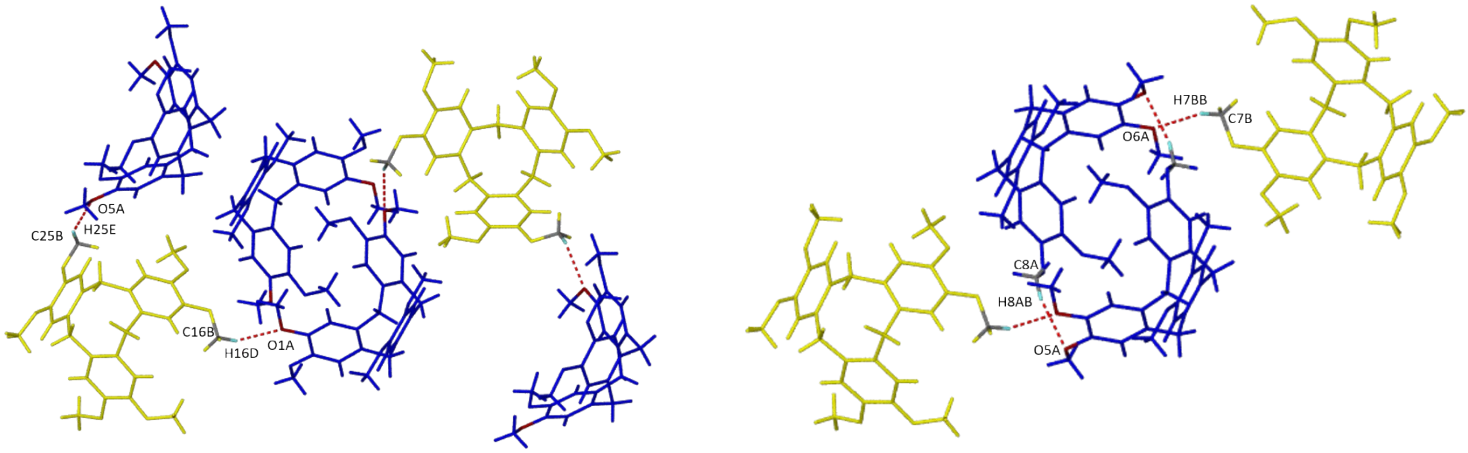


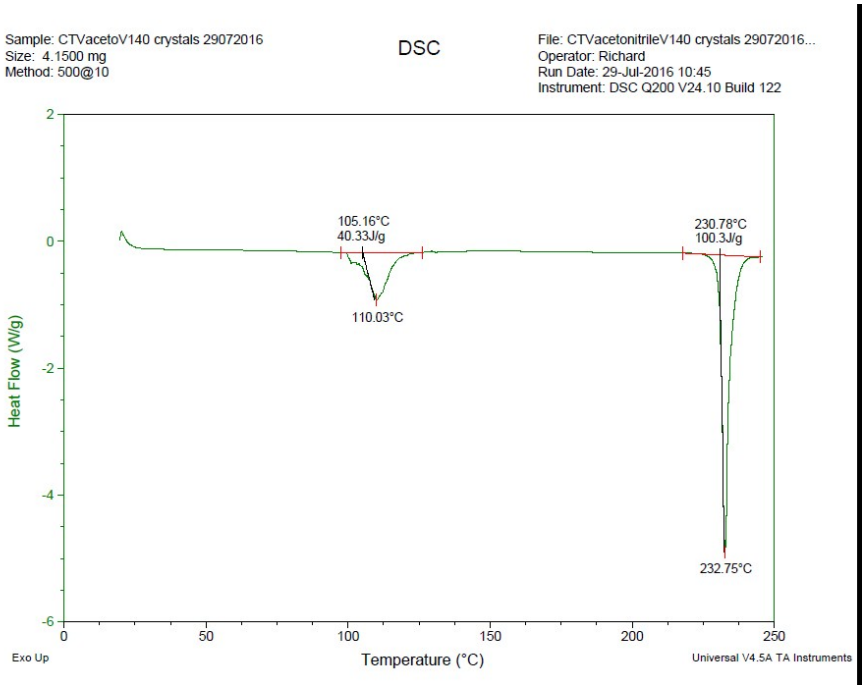
Figure S1 Two adjacent dimers in the **1a** structure along the ~10 Å axis. Artificial rotation by 75° of the O6 methyl group (labelled atoms in ball and stick representation) around the C20A-O6A bond away from the dimer cavity results in two neighbouring voids connecting. A probe radius of 1.5 Å was used in the program MSROLL.[2] Only the labelled methyl group was rotated as MSROLL requires a closed cavity.



(a) (b)

Figure S2 'Stack' CTV molecules (in yellow) in (a) **1a** are connected on two sides to different dimer molecules (in blue), whilst in (b) **2a** they are connected only on one side to a dimer forming isolated hydrogen-bonded tetramers. Atoms involved in hydrogen bonding are shown with CPK colours and the unique atoms labelled.

(a)



(b)

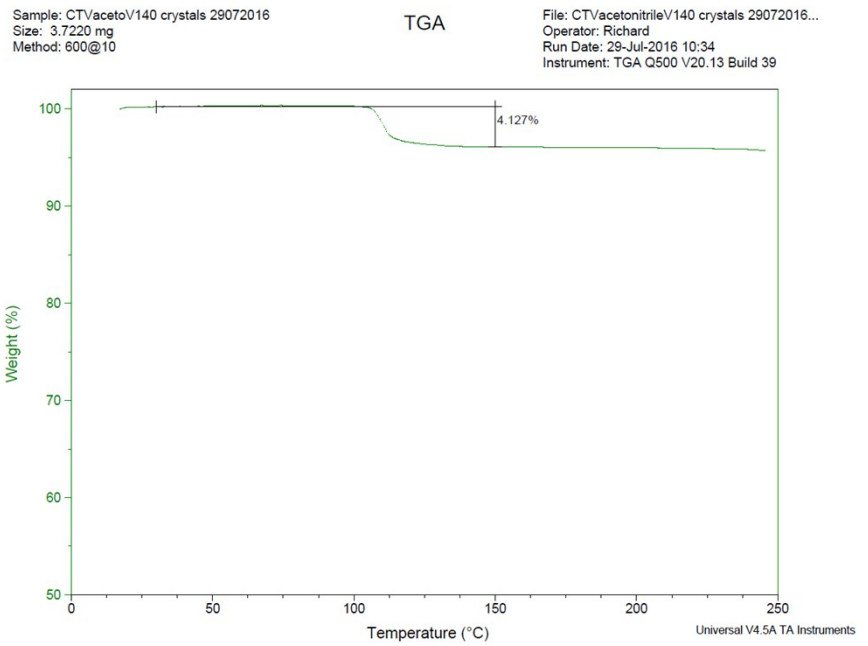


Figure S3 DSC and TGA thermograms of **1a**

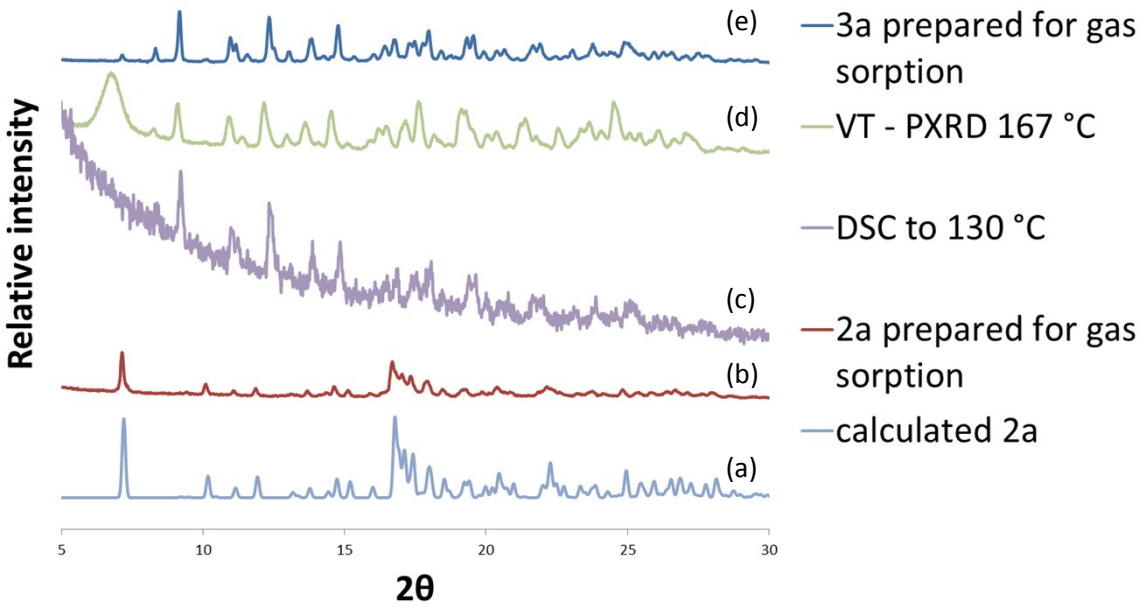


Figure S4 PXRD patterns of (a) calculated **2a** (b) **2a** prepared for gas sorption (**1a** heated to 85°C in an oven) (c) **1a** heated to 130°C on the DSC equipment (d) **3a** at 167°C on VT-PXRD (e) **3a** prepared for gas sorption calculated (**1a** heated to 165°C in an oven)

Supporting information references

1 A. L. Spek, *Acta Crystallographica Section D-Biological Crystallography,* 2009, **65**, 148-155 (DOI:10.1107/S090744490804362X).

2 M. L. Connolly, *J. Mol. Graph.,* 1993, **11**, 139 141 (DOI:10.1016/0263-7855(93)87010-3).