Supporting information

Determination of host:guest ratios:

In the present study the host:guest ratio was obtained by refining the guest occupancies and then summing over the various overlapped sites. This has been shown to be a reliable method of obtaining remarkably accurate host:guest ratios *as long as the guest disorder model is correct* (we therefore first identified the symmetry-related and distinct sites that are overlapped from the 100% occupied crystals). When bulk samples are available we routinely correlate the single-crystal diffraction occupancies with those determined using Thermal Gravimetric Analysis (TGA) and quantitative high resolution NMR spectroscopy. Unfortunately, since pure-phase bulk samples were only available for the 100% occupied crystals we had to rely solely on the single-crystal analysis for the majority of the study.

ESI. Table I: Unit cell and conformational parameters as a function of guest occupancy for TATM/acetone and TATM/DCE.

Crystal	% Guest	τ_1(º)	τ_2(º)	τ_3(º)	$\angle_1$(º)	$\angle_2$(º)	$\angle_3$(º)	Orientation of C=O wrt S
				TATM/acetone				
1	100	2.73	109.92	163.25	87.96(6)	25.79(9)	73.45(7)	*SSS*
1a	84	3.80	109.37	162.85	87.39(8)	25.49(12)	73.21(9)	*SSS*
1b	80	4.32	109.25	162.43	86.78(7)	25.46(11)	72.91(9)	*SSS*
1c	60	5.57	109.84	161.89	85.82(12)	25.93(19)	72.27(15)	*SSS*
1d	40	7.34	109.46	161.25	84.58(15)	26.06(24)	71.71(18)	*SSS*
1e	24	7.47	111.11	160.94	84.09(14)	26.61(22)	71.11(17)	*SSS*
				TATM/DCE				
2	100	6.60	104.76	160.49	85.56(5)	22.16(08)	70.76(6)	*SSS*
2a	26	8.39	108.23	160.51	83.58(21)	24.98(34)	70.47(25)	*SSS*
2b	24	8.28	109.05	160.23	83.74(18)	25.46(28)	70.43(21)	*SSS*
2c	24	7.98	108.99	160.30	83.46(13)	25.23(20)	70.41(15)	*SSS*
2d	21	7.46	109.19	160.26	83.83(18)	25.55(29)	70.29(22)	*SSS*
2e	6	7.73	110.41	159.88	83.29(10)	26.55(15)	70.51(11)	*SSS*

ESI. Table II: Crystal data, data collection and final refinement parameters for **1aA**, **1bB** and **3**. All data sets are collected at 125K and analyzed in space group P-1.

Crystal	**1aA**	**1bB**	**3**
Empirical formula	$2(C_{19}H_{16}O_3S_3)$ 1(acetone)	$2(C_{19}H_{16}O_3S_3)$ 0.96(acetone)	$2(C_{19}H_{16}O_3S_3)$ 0.39(DCE)0.50(acetone)
Formula wt (g/mol)	835.07	832.75	844.63
a (Å)	8.1018(6)	8.1349(6)	8.036(3)
b (Å)	10.5888(8)	10.5100(8)	10.800(4)
c (Å)	12.3159(9)	12.3775(9)	12.235(5)
α (º)	94.999(1)	94.624(1)	96.582(5)
β (º)	107.765(1)	108.274(1)	106.786(5)
γ (º)	95.960(1)	95.778(1)	96.366(5)
V ($Å^3$)	992.84(13)	992.70(13)	998.3(7)
Crystal dimensions	0.32 × 0.32 × 0.16	0.32 × 0.32 × 0.10	0.32 × 0.20 × 0.10
Reflections measured	12331	12349	10706
Unique reflections	5473	5497	4055
R (int)	0.0246	0.0159	0.0471
Final R indices (>2σ) (all data)	R_1 = 0.0403 wR_2 = 0.1214	R_1 = 0.0325 wR_2 = 0.0937	R_1 = 0.0877 wR_2 = 0.2103

ESI. Table III: Crystal data, collection and refinement parameters for the TATM/DCE/acetone mixed guest system. All data sets are collected at 100K and analyzed in space group P-1.

DCE:acetone	**100:0**	**76:24**	**64:36**	**40:60**	**0:100**
Empirical formula	$2(C_{19}H_{16}O_3S_3)$ 1(DCE)	$2(C_{19}H_{16}O_3S_3)$ 0.76(DCE)0.24(acetone)	$2(C_{19}H_{16}O_3S_3)$ 0.64(DCE)0.36(acetone)	$2(C_{19}H_{16}O_3S_3)$ 0.40(DCE)0.60(acetone)	$2(C_{19}H_{16}O_3S_3)$ 1(acetone)
Formula wt (g/mol)	875.95	866.14	861.23	851.42	835.07
a (Å)	7.9495(7)	7.9555(3)	7.9656(6)	7.9717(6)	8.1164(16)
b (Å)	10.9743(10)	10.9385(5)	10.9124(8)	10.8775(7)	10.570(2)
c (Å)	12.1800(12)	12.1457(5)	12.1583(9)	12.1307(9)	12.351(3)
α (º)	97.623(5)	97.452(2)	97.297(3)	97.149(4)	95.006(7)
β (º)	105.816(4)	105.862(2)	105.982(4)	106.072(4)	107.786(6)
γ (º)	96.665(4)	96.676(2)	96.641(4)	96.567(4)	95.944(6)
V ($Å^3$)	1000.33(16)	995.27(7)	995.12(13)	990.62(12)	995.6(3)
Crystal dimensions	0.35 × 0.35 × 0.20	0.35 × 0.20 × 0.12	0.56 × 0.32 × 0.28	0.20 × 0.28 × 0.32	0.16 × 0.15 × 0.15
Reflections measured	35685	43763	21863	13226	13911
Unique reflections	11389	14668	9393	5736	4005
R (int)	0.0238	0.0246	0.0296	0.0325	0.0534
Final R indices (>2σ) (all data)	$R_1 = 0.0335$ $wR_2 = 0.0949$	$R_1 = 0.0368$ $wR_2 = 0.1095$	$R_1 = 0.0444$ $wR_2 = 0.1277$	$R_1 = 0.0478$ $wR_2 = 0.1314$	$R_1 = 0.0597$ $wR_2 = 0.1612$