Electronic Supporting Information

Solid-state structural studies of oxacalix[2]arene[2]naphthalene as a molecular tweezer

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A. Simulated Powder Diffractograms

X-ray powder diffractograms were calculated using the Lazy Pulverix[1] programme suite *via* the X-Seed interface. In each case, the model after final refinement of single-crystal intensity data was used as input.

B. Guest Disorder

For phases **1b-1d**, the guest molecule was modeled as disordered over two sites in each case (see Fig. S1).
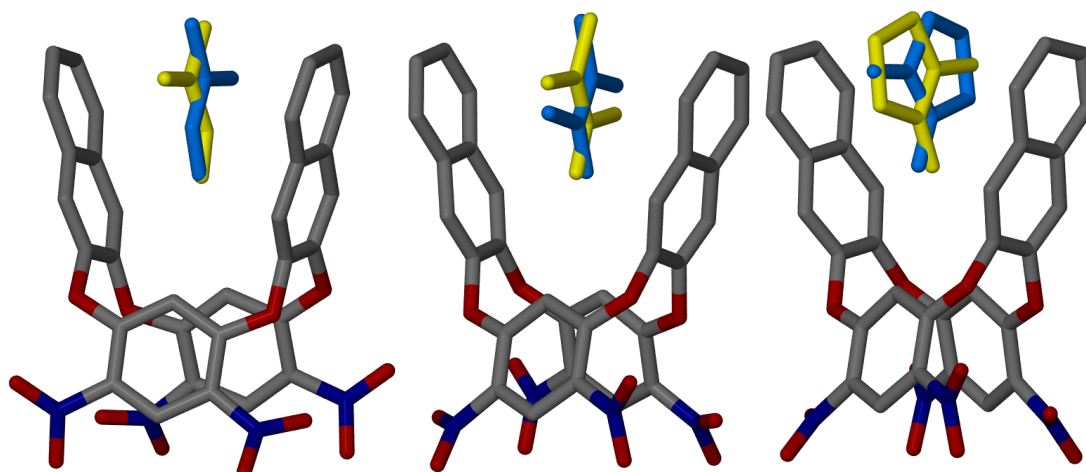

Fig. S1.   Perspective views of the isoskeletal solvates **1b-1d** (from left to right) showing the twofold disorder of the respective guest molecules (situated between the pincer arms). In each case the more favorable position of the guest is shown in yellow in and the less favorable orientation in blue. All non-hydrogen atoms are shown in capped-stick representation and all hydrogen atoms are omitted for clarity.

C. Variable Temperature PXRD

The variable temperature powder diffractograms (Fig. S2) were collected on an PANalytical X'Pert PRO MPD equipped with an Anton Paar TTK450 variable temperature stage. Height adjustment of the sample during the diffraction experiment was achieved using the Anton Paar *Stage Mover* software.
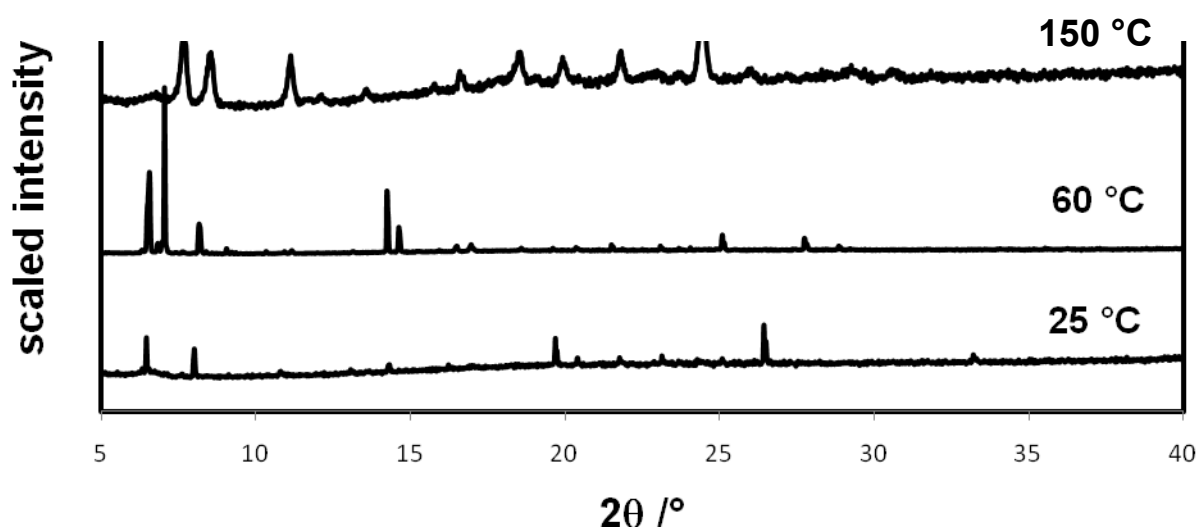

Fig. S2. Variable PXRD diffractograms showing the as-yet unknown guest-free phase (i.e. the phase at 60 °C), apohost phase **1a** (i.e. the phase at 150 °C) and the NBZ solvate **1e** (i.e. the phase at 25 °C). Desolvation of both crystallographically unique NBZ guests yielded the unknown guest-free phase. Heating the unknown guest-free phase results in apohost phase **1a**.
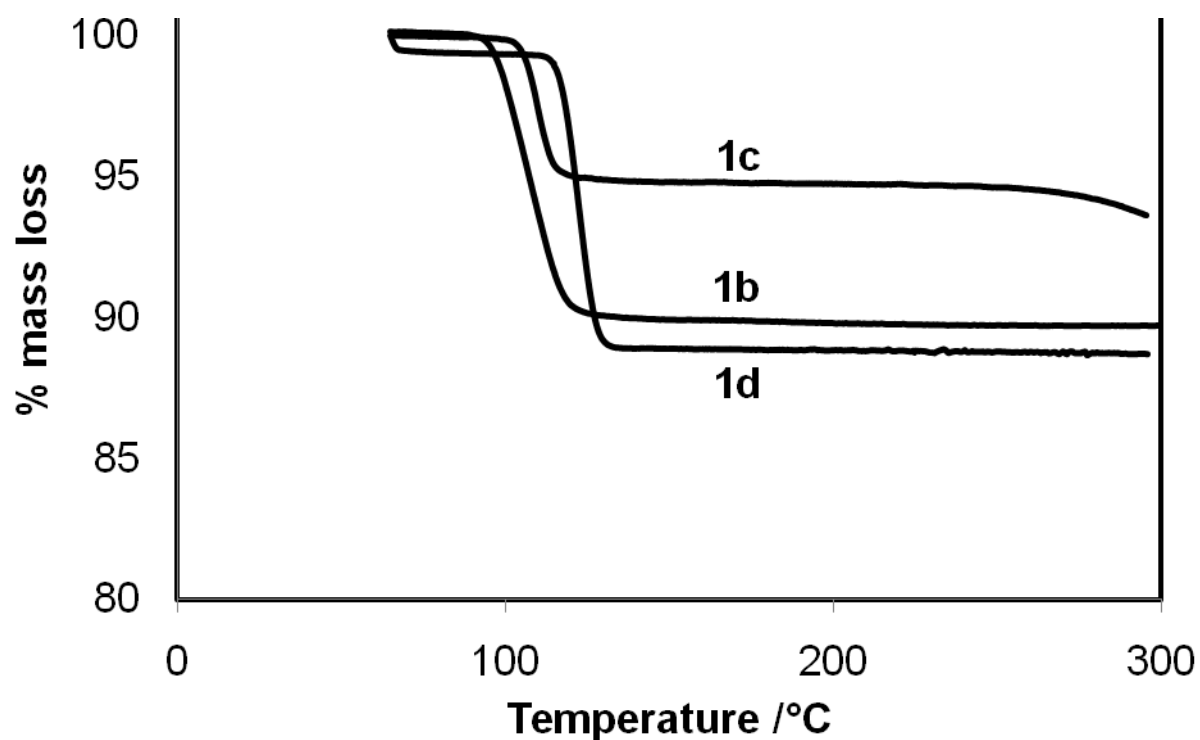
D. Thermal Analysis

Fig. S3. TGA thermograms of the isoskeletal solvates **1b-1d**. Desolvation results in the formation of phase **1a** in each case. Mass loss percentages are listed in Table 3 of the main text. Decomposition of phase **1a** is not shown since the abscissa terminates at 300 °C.
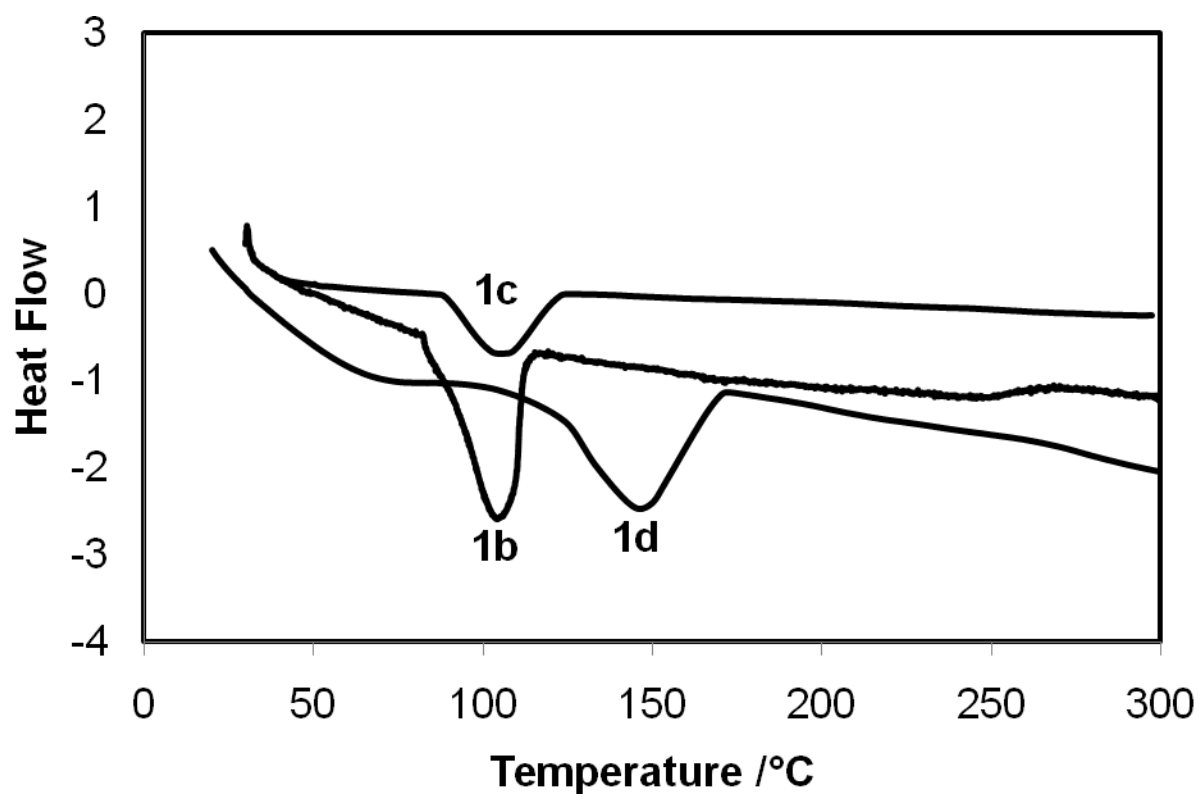
Fig. S4. DSC thermograms of the isoskeletal solvates **1b-1d**. Desolvation results in the formation of phase **1a** in each case (as confirmed by PXRD). The abscissa is once again only shown to 300 °C. Onset temperatures for the endothermic peaks are listed in Table 3 of the main text.
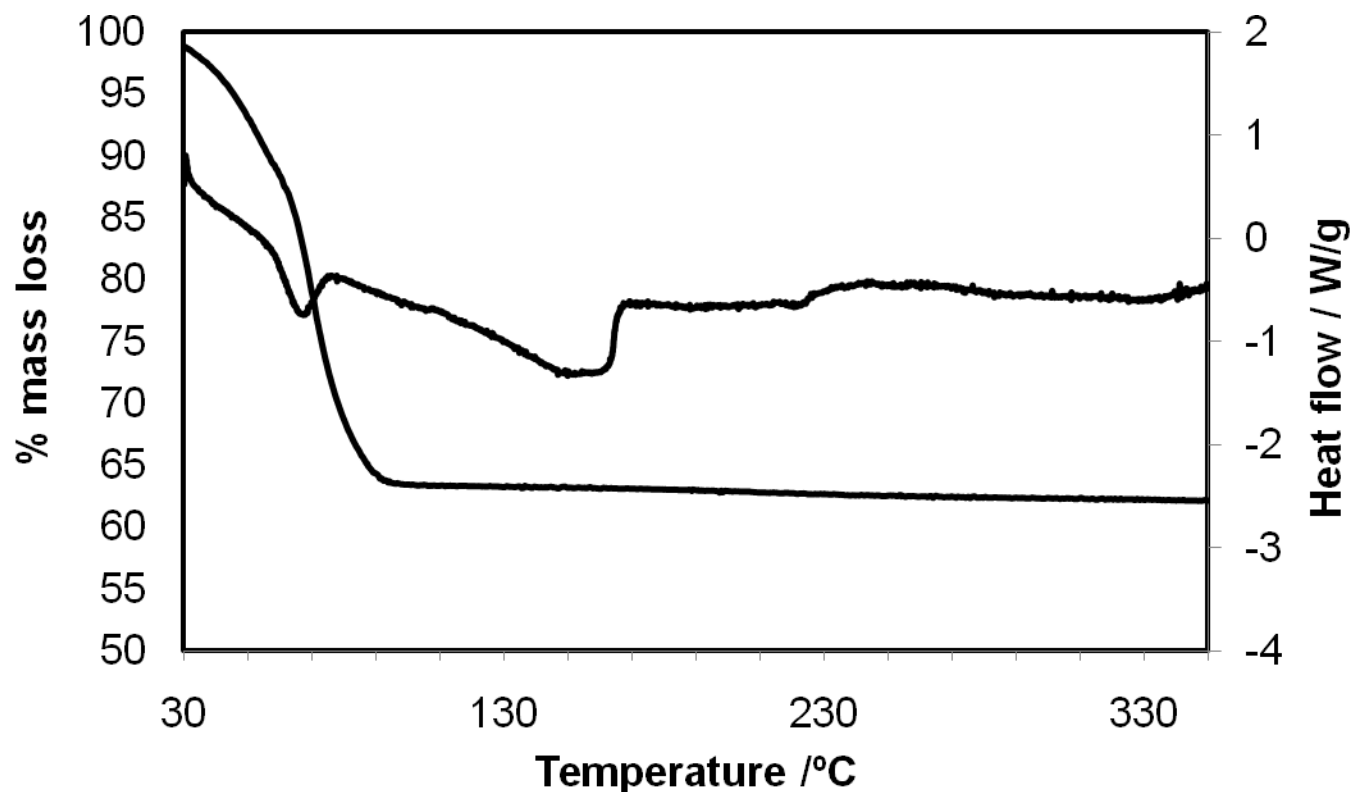

Fig. S5. TGA and DSC of the NBZ solvate **1e**. The 36.9% weight loss between ambient temperature and 90 °C is consistent with the loss of two nitrobenzene molecules per host and corresponds to peak A of the DSC trace. According to variable-temperature PXRD an as-yet unknown guest free phase is formed upon loss of nitrobenzene, and this phase undergoes a polymorphic phase transition to 1a upon further heating (peak B). We note that the sample heating conditions were not identical for the two experiments: TGA was carried out with the sample purged with nitrogen gas while DSC was carried out with the sample in a sealed pan.

E. Characterization

M.p.: >350 ºC (dec.); IR (ATR, cm⁻¹): v_{max} 3063 (sp^2 aromatic stretch), 1594 and 1352 (C-NO$_2$), 1288 (C-O stretch), 837 (sp^2 aromatic out of plane stretch); ^{1}H-NMR (DMSO-D$_6$, 400MHz): δ 6.03 (2H, s, ArH), 7.48-7.51 (4H, dd, J = Hz, ArH), 7.79-7.81 (4H, dd, J = Hz, ArH), 8.08 (4H, s, ArH), 8.76 (2H, s, ArH); ^{13}C-NMR (DMSO-D$_6$, 400 MHz): δ 153.5, 141.29, 132.17, 131.12, 127.62, 127.35, 125.72, 123.22, 106.3; MS (ES⁻): m/z 648, M$^+$, 666, M$^+$ + H$_2$O, 665 (100%, M$^+$ + OH⁻).

D. Hydrogen Bonding

Table S1 Hydrogen bonding parameters

D-H···A	D···A/♦

1b		
	C18-H31⋯O8A	3.340(4)
	C18-H31⋯O8B	3.358(12)
	C36-H36⋯O8A	3.315(4)
	C36-H36⋯O8B	3.221(12)

1c		
	C18-H18⋯O5A	3.369(6)
	C18-H18⋯O5B	3.568(8)
	C36-H36⋯O5A	3.347(6)
	C36-H36⋯O5B	3.207(8)

1d		
	C18-H18⋯O1A	3.357(4)
	C18-H18⋯O1B	3.572(16)
	C36-H36⋯O1A	3.325(4)
	C36-H36⋯O1B	3.192(14)

1e		
	C18-H18⋯O1A	3.328(15)
	C36-H36⋯O1A	3.467(15)

References

1. K. Yvon, W Jeitschko and E. Parthe, *J. Appl. Cryst.,*1977, **10**, 73