Electronic Supplementary Material (ESI) for CrystEngComm.

Comparison of inclusion properties between *p-tert*-butylcalix[4]arene and *p-tert*-butylthiacalix[4]arene towards primary alcohols in crystals

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Supporting Information

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I. Powder X-ray diffraction (PXRD) studies

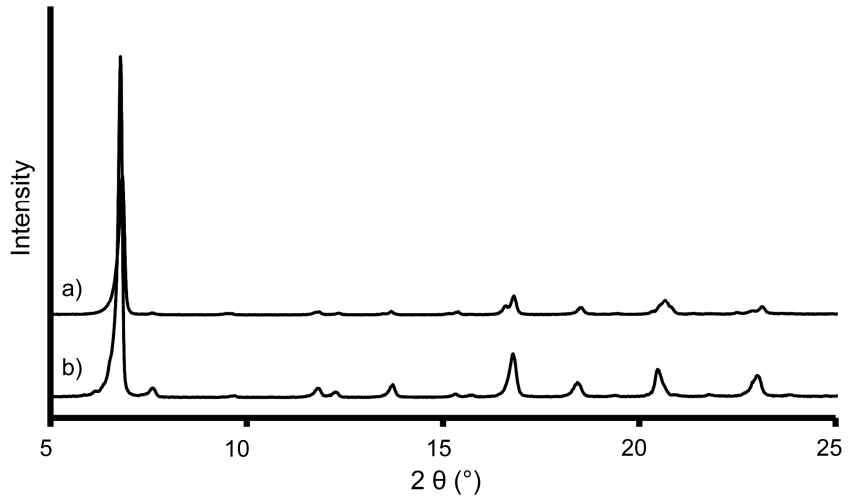

Figure S1. PXRD patterns of the inclusion crystals of compound **1** with PentOH (a) and HexOH (b) obtained by crystallization.

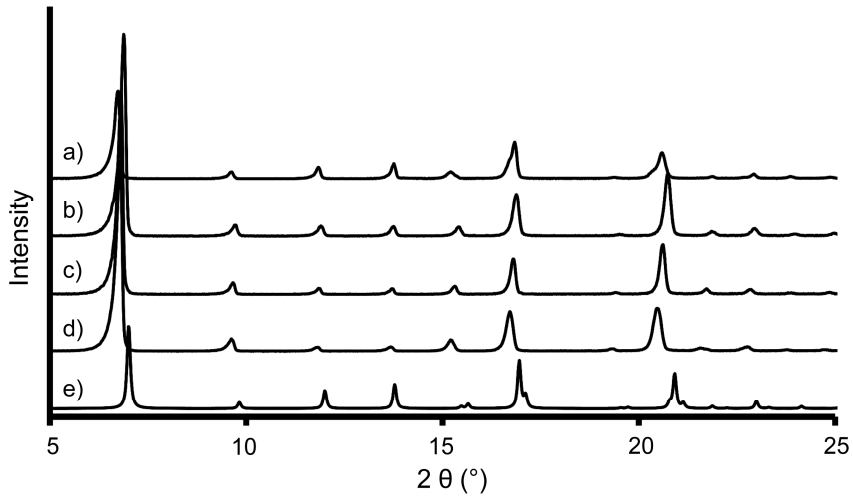

Figure S2. PXRD patterns of the inclusion crystals of compound **1** with MeOH (a), EtOH (b), PrOH (c) and BuOH (d) obtained by the suspension method, and a simulation from XRD data of **1**·EtOH measured at 100 K (e).

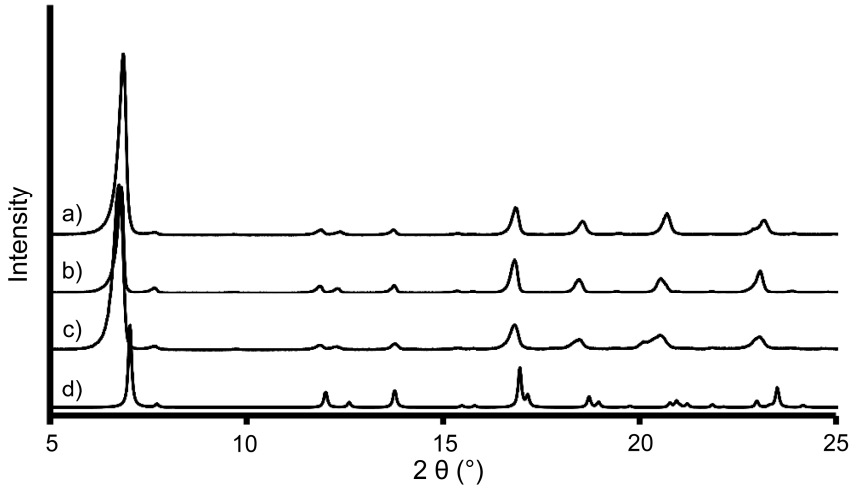

Figure S3. PXRD patterns of the inclusion crystals of compound **1** with PentOH (a), HexOH (b) and HeptOH (c) obtained by the suspension method, and a simulation from XRD data of $\mathbf{1}_2$·PentOH measured at 100 K (d).

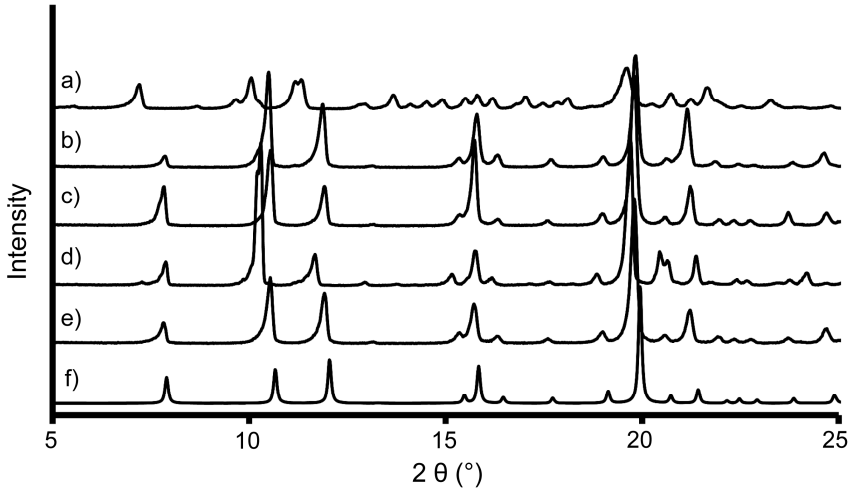

Figure S4. PXRD patterns of a crystalline powder of compound **2** (a) and its inclusion crystals with MeOH (b), EtOH (c) and PrOH (d) obtained by crystallization and with EtOH obtained by the suspension method (e), and a simulation from XRD data of **2**·EtOH measured at 223 K (f).

II. Single crystal X-ray diffraction (XRD) studies for inclusion crystals of compound 1

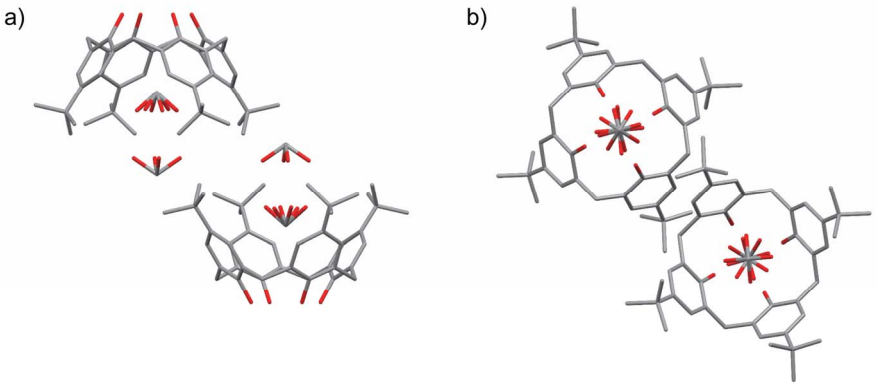

Figure S5. X-ray structure of **1**·MeOH: Side view (a) and top view (b). Hydrogen atoms are omitted for clarity.

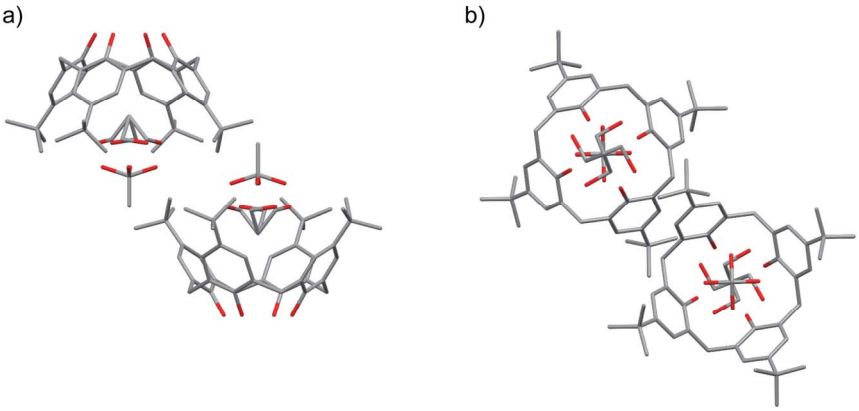

Figure S6. X-ray structure of **1**·EtOH: Side view (a) and top view (b). Hydrogen atoms are omitted for clarity.

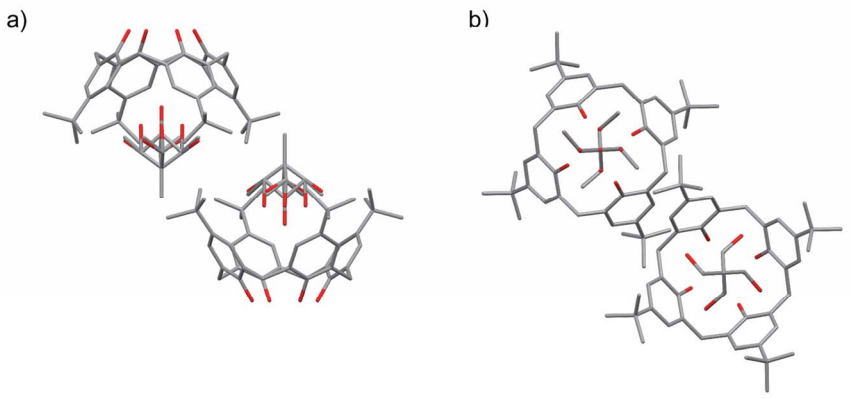

Figure S7. X-ray structure of **1**·PrOH: Side view (a) and top view (b). Hydrogen atoms are omitted for clarity.

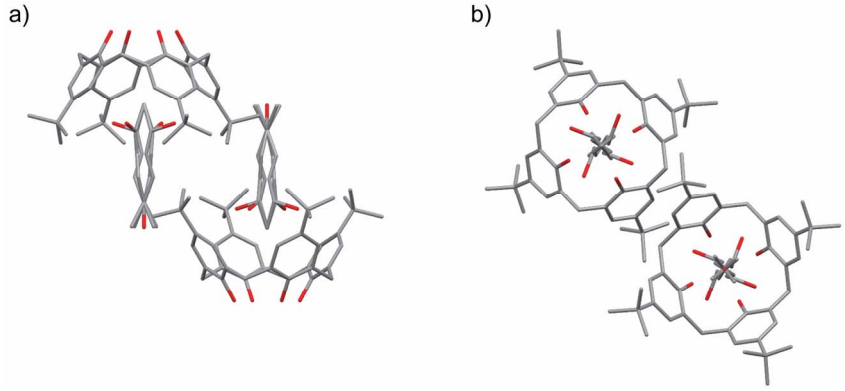

Figure S8. X-ray structure of **1**·PentOH: Side view (a) and top view (b). Hydrogen atoms are omitted for clarity.

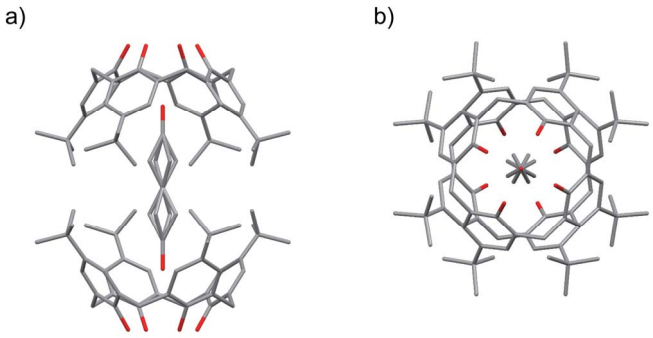

Figure S9. X-ray structure of $\mathbf{1}_2$·PentOH: Side view (a) and top view (b). Hydrogen atoms are omitted for clarity.

III. Single crystal X-ray diffraction (XRD) studies for inclusion crystals of compound 2

The structures of inclusion crystals **2**·MeOH, **2**·EtOH and **2**·PrOH reported in a preliminary communication[1] were reanalyzed under the restraint of disordered *tert*-butyl groups and guest molecules. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 1050720–1050722.

Data for 2·MeOH. $C_{41}H_{52}O_5S_4$, fw = 753.07, tetragonal, *P*4/nmm, a = 15.7827(7) Å, b = 15.7827(7) Å, c = 8.2365(7) Å, V = 2051.7(2) Å^3, Z = 2, T = 223(2) K, 11188 reflections measured, 1332 independent reflections, 1190 reflections were observed ($I > 2\sigma(I)$), R_1 = 0.0955, wR_2 = 0.2366 (observed), R_1 = 0.1011, wR_2 = 0.2559 (all data).

Data for 2·EtOH. $C_{42}H_{54}O_5S_4$, fw = 767.09, tetragonal, *P*4/nmm, a = 15.8115(11) Å, b = 15.8115(11) Å, c = 8.2875(12) Å, V = 2071.9(4) Å^3, Z = 2, T = 223(2) K, 11205 reflections measured, 1341 independent reflections, 1107 reflections were observed ($I > 2\sigma(I)$), R_1 = 0.0864, wR_2 = 0.2301 (observed), R_1 = 0.0962, wR_2 = 0.2557 (all data).

Data for 2·PrOH. $C_{43}H_{56}O_5S_4$, fw = 781.12, tetragonal, *P*4/nmm, a = 15.7986(9) Å, b = 15.7986(9) Å, c = 8.5474(10) Å, V = 2133.4(3) Å^3, Z = 2, T = 223(2) K, 11373 reflections measured, 1378 independent reflections, 1174 reflections were observed ($I > 2\sigma(I)$), R_1 = 0.0980, wR_2 = 0.2420 (observed), R_1 = 0.1063, wR_2 = 0.2630 (all data).

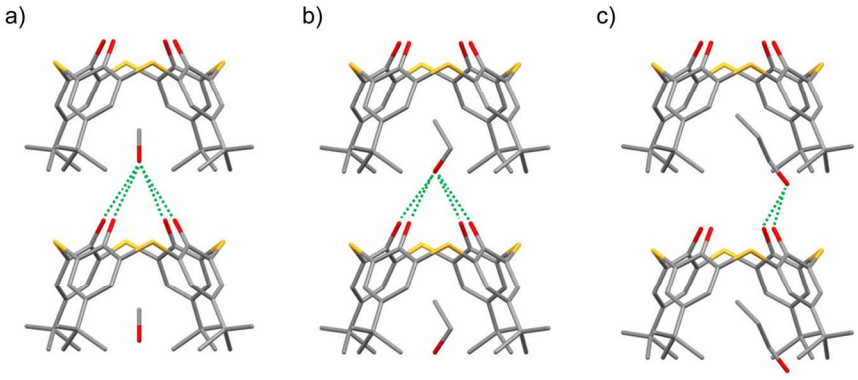

Figure S10. X-ray structures of **2**·MeOH (a), **2**·EtOH (b) and **2**·PrOH (c), showing partial packing structures along the *c*-axis. Hydrogen atoms and disordered atoms are omitted for clarity. Green dotted lines represent intermolecular hydrogen bonds; the O···O distances are 3.480 Å (a), 3.122 Å (b) and 2.688 Å (c), respectively. A CH–π interaction is observed between the terminal methyl group of an alcohol molecule and the benzene rings of the host molecule including the alcohol molecule in its cavity; the C···Ar distances are 3.842 Å (a), 3.685 Å (b) and 3.651 Å (c), respectively.

IV. Reference

[1] N. Morohashi, S. Noji, H. Nakayama, Y. Kudo, S. Tanaka, C. Kabuto and T. Hattori, *Org*. *Lett*., 2011, **13**, 3292.