**Unique inclusion properties of crystalline powder *p-tert*-butylthiacalix[4]arene toward alcohols and carboxylic acids**

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**Supporting Information**

Contents:



## I. Materials

Alcohols (MeOH, EtOH and PrOH) and $HCO_2H$ as guest were distilled before use. $MeCO_2H$ and $EtCO_2H$ were used as purchased. Other solvents were distilled before use. *p-tert*-Butylthiacalix[4]arene (**2**) was synthesized as reported previously [1].

## II. Powder X-ray Diffraction (PXRD) Studies

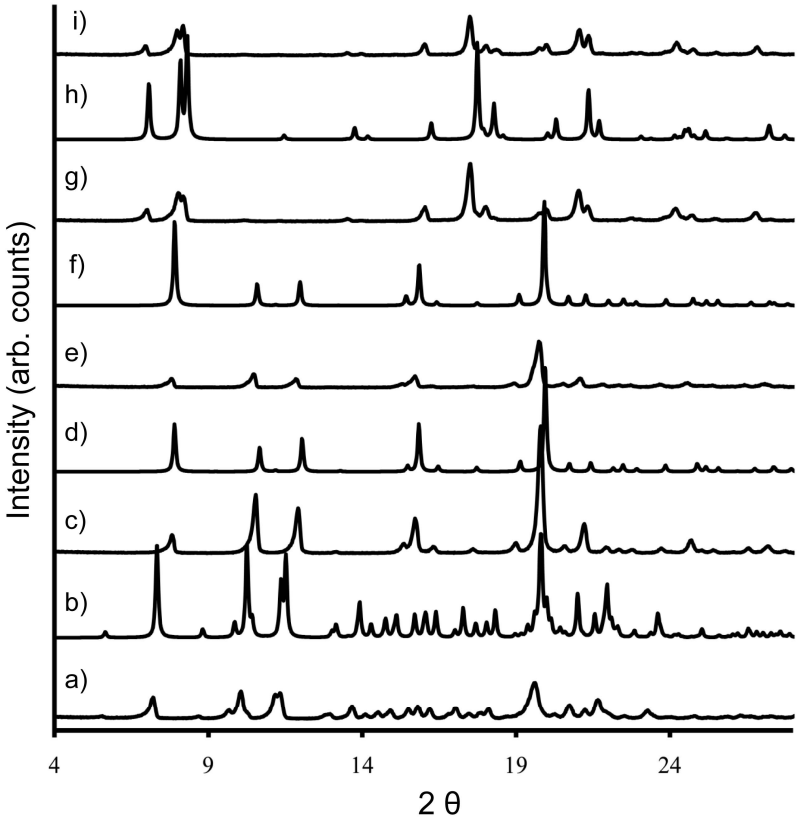


**Figure S1.** PXRD patterns of a crystalline powder of compound **2** and its inclusion crystals with alcohols and acids: (a) experimental chart for **2**, (b) simulation from XRD data of **2** [2], (c) experimental chart for inclusion crystals taken from EtOH, (d) simulation from XRD data of **2**·EtOH, (e) experimental chart for inclusion crystals taken from $MeCO_2H$, (f) simulation from XRD data of **2**·$MeCO_2H$, (g) experimental chart for inclusion crystals taken from $EtCO_2H$, (h) simulation from XRD data of **2**·$[EtCO_2H]_3$, (i) experimental chart for inclusion crystals taken from an equimolar mixture of $MeCO_2H$ and $EtCO_2H$.

## III. Thermogravimetric Analysis (TGA)

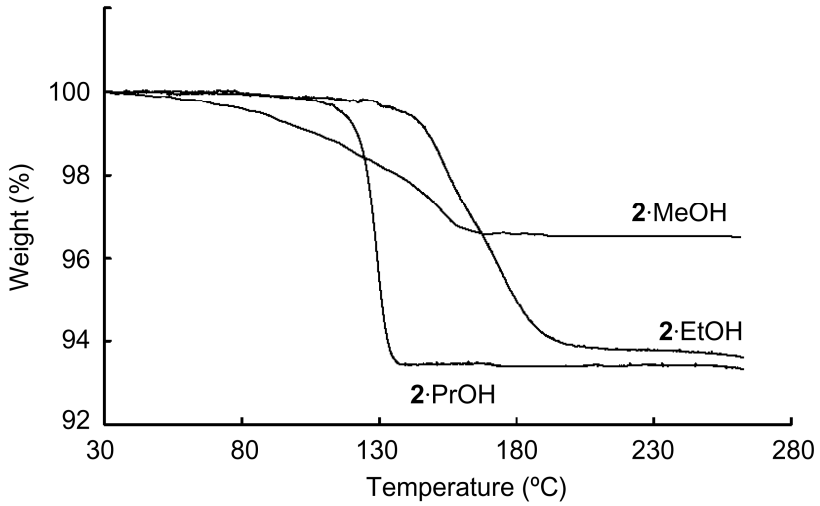


**Figure S2.** TGA desorption curves for **2**·MeOH, **2**·EtOH and **2**·PrOH.

## IV. Single crystal X-ray diffraction (XRD) studies

Single-crystal X-ray diffraction data were collected with a Bruker APEX II CCD diffractometer using Mo-*K*α radiation (λ = 0.71073 Å) employing a "Bruker Helios multilayered confocal mirror" as monochromator and a "Bruker TXS fine-focus rotating anode" as radiation source. Data integration and reduction were performed with the SAINT and XPREP software and the absorption correction was performed by the semi-empirical method with SADABS [3]. The structure was solved by the direct method using SHELXS-97 [4] and refined by using least-squares methods on $F^2$ with SHELXL-97 [4]. X-ray analysis was undertaken using the free GUI software of Yadokari-XG 2009 [5].

**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 ($I > 2\sigma(I)$), $R_1$ = 0.1021, $wR_2$ = 0.2658 (observed), $R_1$ = 0.1072, $wR_2$ = 0.2874 (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 ($I > 2\sigma(I)$), $R_1$ = 0.0975, $wR_2$ = 0.2933 (observed), $R_1$ = 0.1078, $wR_2$ = 0.3189 (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 ($I > 2\sigma(I)$), $R_1$ = 0.1216, $wR_2$ = 0.3761 (observed), $R_1$ = 0.1298, $wR_2$ = 0.4127 (all data).

**Data for 2·MeCO$_2$H.** $C_{42}H_{52}O_6S_4$, fw = 781.08, tetragonal, *P*4/nmm, $a$ = 15.8002(7) Å, $b$ = 15.8002(7) Å, $c$ = 8.3491(7) Å, $V$ = 2084.3(2) Å$^3$, $Z$ = 2, $T$ = 223(2) K, 11175 reflections measured, 1346 independent reflections, 1140 reflections were observed ($I > 2\sigma(I)$), $R_1$ = 0.1050, $wR_2$ = 0.3192 (observed), $R_1$ = 0.1124, $wR_2$ = 0.3539 (all data).

**Data for 2·[EtCO$_2$H]$_3$.** $C_{49}H_{66}O_{10}S_4$, fw = 943.26, tetragonal, *I*4/mmm, $a$ = 15.401(8) Å, $b$ = 15.401(8) Å, $c$ = 21.204(10) Å, $V$ = 5029(4) Å$^3$, $Z$ = 4, $T$ = 100(2) K, 13823 reflections measured, 1665 independent reflections, 1591 reflections were observed ($I > 2\sigma(I)$), $R_1$ = 0.1094, $wR_2$ = 0.2935 (observed), $R_1$ = 0.1152, $wR_2$ = 0.2993 (all data).

## V. References


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