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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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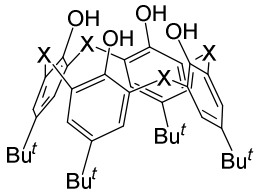
Powdery crystals of *p-tert*-butylcalix[4]arene (**1**), when suspended in primary alcohols with C1–C7 carbon chains, absorb the alcohols to form 1:2, 1:1 and 2:1 (host : guest) inclusion crystals with the C1, C2–C4 and C5–C7 alcohols, respectively, whereas powdery crystals of compound **2** absorbs only ethanol by the same treatment. In competitive experiments, the crystals of compound **1** preferentially absorb propanol and hexanol among the alcohols that form 1:1 and 2:1 inclusion crystals, respectively, but the selectivities are inferior to the selectivity of compound **2** towards ethanol. These differences in inclusion properties between compounds **1** and **2** are attributed to the difference in crystal packing of the inclusion crystals. X-ray analysis reveals that compound **1** constructs a bilayer structure with the aid of a network of the intermolecular CH–π interaction between a methylene group of a host molecule and a benzene ring of an adjacent host molecule. The bilayers are laminated in two difference manners depending on the size of the guest compounds. A small alcohol is included into the cavity of a host molecule to form 1:1 inclusion crystals, whereas a large alcohol is included into a molecular capsule constructed by two host molecules gathered in a head-to-head manner to form 2:1 inclusion crystals. The inclusion crystals with the same packing structure have almost the same spaces to accommodate guest molecules, regardless of the guest size, which produces the good receptivity of compound **1** towards alcohols. On the other hand, compound **2**, which lacks methylene bridges, forms a CH–π interaction with the terminal methyl group of an alcohol molecule included into its cavity, and the alcohol molecule forms hydrogen bonds with the hydroxy groups of an adjacent host molecule to construct a columnar structure. The difference in stability of the columnar structure among the alcohols causes the high inclusion selectivity of compound **2** towards ethanol.

Introduction

The separation of similar organic molecules using distillation or crystallization requires a costly and energy-intensive process. Nanoporous materials with molecular-scale pores are of great importance in molecular and gas separation, as are relatively less costly and are easily manipulated. Recently, the research for nanoporous materials has greatly advanced through the development of metal–organic frameworks (MOFs)[1] and covalent organic frameworks (COFs).[2] Nanoporous molecular crystals are another kind of nanoporous materials. They do not have extended network structures through coordination or covalent bonding as observed in MOFs and COFs, respectively, but are composed of discrete organic molecules, among which only weak noncovalent interactions operate.[3] Inclusion crystals having a potential for constructing nanoporous molecular crystals after the desorption of included molecules have also been reported.[4] The selective absorption and separation of organic molecules using nanoporous molecular crystals have been studied.[5]

In this decade, calixarenes (e.g., **1** and **2**)[6,7] have become representative host molecules and have been shown to construct nanoporous molecular crystals with no interconnected pore channels.[3,8] Atwood *et al.*[9] and Ripmeester *et al.*[10] have rigorously and intensively investigated guest adsorption with the crystal of *p-tert*-butylcalix[4]arene (**1**). For example, Atwood *et al.* reported that a single crystal of compound **1** absorbed small molecules from a gaseous or liquid phase into its molecular cavity and underwent phase transition into a

single crystal of an inclusion complex with a crystal lattice different from that of the original.[9a,b,f] Ripmeester *et al.* followed the absorption of CO_2 into a single crystal of compound **1** by ^{13}C NMR and XRD.[10c] They also reported that powdery crystals of *p*-octanoylcalix[4]arene absorbed hydrocarbons, xenon and CO_2 well.[10d] Gorbatchuk *et al.* reported the inclusion of vaporized guests into powdery crystals of compound **1** and *p-tert*-butylthiacalix[4]arene (**2**).[11] However, there is only a few report on the selective capture of small molecules using calixarene crystals under competitive conditions, although the selective crystallization of inclusion complexes with xylene[12] and fullerene[13] has been reported. Very recently, Tsue *et al.* reported that powdery crystals of azacalix[n]arenes selectively adsorbed CO_2 from air.[14] We have also been engaged in the development of a method to collect or separate organic compounds by using calixarene crystals.[15] In a preliminary communication, we reported that powdery crystals of compound **2** selectively absorbed ethanol from 1:1 methanol–ethanol and ethanol–propanol mixtures.[15a] To the best of our knowledge, this is the first successful example of the selective inclusion of a small organic compound into calixarene crystals under competitive conditions. This finding prompted us to examine the discrimination capability of methylene-bridged calix[4]arene **1** towards alcohols. In this paper, we compare inclusion properties between compounds **1** and **2** towards primary alcohols in crystals.



1: X = CH_2
2: X = S

Experimental section

General

^1H NMR spectra were measured on a Bruker AV-400 spectrometer using tetramethylsilane as an internal standard. Compound **1**[16] and **2**[17] were prepared according to the literature procedure. Methanol and toluene were distilled before use and other solvents were used as purchased.

Typical procedure for the inclusion of alcohols by crystallization

A boiling guest solvent (4.0–6.0 mL) was nearly saturated with compound **1** (10.0 mg) and the solution was allowed to cool to room temperature to precipitate inclusion crystals, which were collected by filtration, washed with hexane (5 mL × 3), dried *in vacuo* (0.5–1.0 kPa) for 2 h and analysed by ^1H NMR spectroscopy to determine the $\overline{n}$ value. For the inclusion of methanol, ethanol and propanol with compound **1**, mixtures of each alcohol (0.12 mol) and *tert*-butylbenzene (1 mL) were used as solvents. For the inclusion experiment of these alcohols with compound **2**, the *tert*-butylbenzene was replaced with toluene (1 mL).

Inclusion experiment by the suspension method

Compounds **1** and **2** were crystallized from xylene–acetone, and under reduced pressure (0.5–1.0 kPa), the crystals were heated at 200 °C for 24 h for **1** and at 140 °C for 4 h for **2** to give guest-free crystals of compounds **1** and **2** as powders, the PXRD patterns of which were in reasonable agreement with those of self-included crystals reported in the literature.[18,19] The powdery crystals (5.0 mg) were placed in a screw cap vial equipped with a stir bar and suspended by the addition of an alcohol (1.5 mL) or an equimolar mixture of two kinds of alcohols (1.5 mL). The suspension was stirred at a fixed temperature until equilibrium was reached (1–8 d), and the resulting powder was collected by filtration, washed with hexane (5 mL × 3), dried *in vacuo* (0.5–1.0kPa) at room temperature for 2 h and analysed by ^1H NMR spectroscopy to determine the $\overline{n}$ value. The inclusion crystals with methanol were washed with water (5 mL × 3) instead of hexane. In the competition experiment between two of the C3–C7 alcohols, the $\overline{n}$ value was determined by GC analysis using a Shimadzu GC-18A apparatus equipped with a flame ionization detector and a TC-WAX column (GL Science Inc., 0.32 mm i.d. × 30 m, DF = 0.50 μm).

Powder X-ray diffraction (PXRD) analysis

Powder X-ray diffraction data were collected on a Rigaku RINT-2200VHF powder X-ray diffractometer using CuKα radiation. Data were collected at increments of 0.02° and an exposure time of 1.2 s/step in the angular range 2-60° (2θ) at room temperature.

Differential scanning calorimetric (DSC) analysis

DSC analysis was carried out using a Seiko Instrument DSC6100 calorimeter. Inclusion crystals (25−29 mg) were placed on an aluminium pan and heated at a rate of 1 °C min^{-1} under nitrogen atmosphere. An empty aluminium pan was used as a reference.

X-ray crystallographic analysis

Single-crystal X-ray diffraction data were collected with a Bruker APEX II CCD diffractometer equipped with a Helios multi-layered confocal mirror and a TXS fine-focus rotating anode, using Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by the direct method and refined by using least-squares methods on F^2 with SHELXL-97.[20] X-ray analysis was undertaken using the free GUI software of Yadokari-XG 2009.[21] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 1050715–1050719.

Data for 1·(MeOH)$_2$. $C_{46}H_{64}O_6$, fw = 712.97, tetragonal, *P*4/n, *a* = 12.7797(12) Å, *b* = 12.7797 (12) Å, *c* = 12.7967(17) Å, *V* = 2090.0(4) Å^3, *Z* = 2, *T* = 100(2) K, 11455 reflections measured, 2403 independent reflections, 2012 reflections were observed (*I*

$> 2\sigma(I)$), $R_1 = 0.0454$, $wR_2 = 0.1216$ (observed), $R_1 = 0.0548$, $wR_2 = 0.1316$ (all data).

Data for 1·EtOH. $C_{46}H_{62}O_5$, fw = 694.96, tetragonal, $P4/n$, a = 12.8388(18) Å, b = 12.8388 (18) Å, c = 12.6024(17) Å, V = 2077.3(5) Å^3, $Z = 2$, T = 100(2) K, 11283 reflections measured, 2381 independent reflections, 1998 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0617$, $wR_2 = 0.1896$ (observed), $R_1 = 0.0712$, $wR_2 = 0.1998$ (all data).

Data for 1·PrOH. $C_{47}H_{64}O_5$, fw = 708.98, tetragonal, $P4/n$, a = 12.8486(18) Å, b = 12.8486 (18) Å, c = 12.6773(18) Å, V = 2092.9(5) Å^3, $Z = 2$, T = 100(2) K, 11283 reflections measured, 2381 independent reflections, 1998 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0660$, $wR_2 = 0.1881$ (observed), $R_1 = 0.0907$, $wR_2 = 0.2109$ (all data).

Data for 1·PentOH. $C_{49}H_{68}O_5$, fw = 737.03, tetragonal, $P4/n$, a = 12.977(2) Å, b = 12.977(2) Å, c = 12.563(2) Å, V = 2115.9(7) Å^3, $Z = 2$, T = 100(2) K, 11850 reflections measured, 2439 independent reflections, 2078 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0706$, $wR_2 = 0.2095$ (observed), $R_1 = 0.0789$, $wR_2 = 0.2205$ (all data).

Data for 1_2·PentOH. $C_{46.5}H_{62}O_{4.5}$, fw = 692.96, tetragonal, $P4/nnc$, a = 12.8494(13) Å, b = 12.8494(13) Å, c = 25.110(3) Å, V = 4145.8(7) Å^3, $Z = 4$, T = 100(2) K, 21539 reflections measured, 2402 independent reflections, 2000 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0579$, $wR_2 = 0.1849$ (observed), $R_1 = 0.0693$, $wR_2 = 0.1948$ (all data).

Results and discussions

Inclusion of alcohols with compounds 1 and 2

First, the inclusion capabilities of compounds **1** and **2** towards primary alcohols with C1–C7 carbon chains were investigated by crystallization.[8a,13,22] A host compound was added portionwise to boiling alcohol until the solution was nearly saturated, and the solution was subsequently allowed to cool to room temperature to induce crystallization. The crystals were collected by filtration, dried *in vacuo*, and analysed by ^{1}H NMR spectroscopy to determine the average number of guest molecules per host molecule ($\overline{n}$) in the crystals (Table 1). In inclusion experiments for the C1–C3 alcohols with compound **1** and those for the C1–C7 alcohols with compound **2**, *tert*-butylbenzene and toluene were added as co-solvents, respectively, because the host compounds were insufficiently soluble in these alcohols; the molar ratio was adjusted to 20:1 (alcohol : co-solvent). It has been reported that compound **1** forms inclusion crystals with a stoichiometry of either 1:1 or 2:1 (host : guest) with various organic compounds.[10,22,23] The observed $\overline{n}$ values (*ca.* 1) for the inclusion of the C1–C6 alcohols with compound **1** suggested that compound **1** formed 1:1 inclusion complexes with these alcohols. X-ray crystallographic analysis supported this suggestion for the C2–C4 alcohols but revealed the formation of 1:2 inclusion crystals for methanol with a packing structure similar to that for the 1:1 inclusion crystals of the C2–C4 alcohols (*vide infra*). PXRD analysis of the inclusion crystals of the C5 and C6 alcohols showed a diffraction peak characteristic of 2:1 inclusion crystals at 2θ = 18.5° (Fig. S1†). This combined with the observed $\overline{n}$ values indicates the predominant formation of 1:1 inclusion crystals together with a small amount of 2:1 inclusion crystals. On the other hand, the $\overline{n}$ value (0.54) for heptanol suggested the formation of 2:1 inclusion crystals.[23] Unlike compound **1**, compound **2** formed inclusion crystals only with the C1–C3 alcohols and as reported in our preliminary communication,[15a] they are 1:1 inclusion crystals. The low $\overline{n}$ values for the methanol inclusion crystals with compound **1** (0.83) and compound **2** (0.61) were attributed to methanol being easily released from these inclusion crystals, even at room temperature. The inclusion ratio was uncertain for the inclusion of the C4–C7 alcohols with compound **2** because of low $\overline{n}$ values (< 0.3) and no change in the powder X-ray diffraction (PXRD) patterns before and after crystallization.

Table 1 Inclusion ratio ($\overline{n}$) for the inclusion of primary alcohols with compounds **1** and **2** using the crystallization and suspension methods.[a]

	1		**2**	
alcohol	crystallization	suspension	crystallization	suspension
MeOH	0.83	0.66	0.61	–[c]
EtOH	0.76	0.88	0.92	0.92
PrOH	0.87	1.08	0.90	–[c]
BuOH	0.99	0.94	–[b]	–[c]
PentOH	0.88	0.55	–[b]	–[c]
HexOH	0.85	0.58	–[b]	–[c]
HeptOH	0.54	0.47	–[b]	–[c]

[a] Average value of measurements repeated more than three times. [b] Inclusion ratio could not be determined. [c] Inclusion was not observed.

Next, we investigated the inclusion of the C1–C7 alcohols with crystals of compounds **1** and **2**. Thus, powdery crystals of a host compound were suspended in an alcohol and the suspension was stirred at room temperature until the inclusion reached equilibrium (24 h). The resulting powder was collected by filtration, dried *in vacuo* and submitted to ^{1}H NMR or GC analysis to determine the $\overline{n}$ value. This procedure is denoted hereafter as the suspension method. The host crystals employed were those with a well-defined packing structure, in which a pair of calixarenes with a cone conformation include each other's *tert*-butyl groups into their cavities to form a self-inclusion complex.[18,19] Table 1 summarizes the inclusion ratios obtained by the suspension method. The comparison between the $\overline{n}$ values obtained by the two methods indicates that compound **1** shifted the boundary of the selective formation of 1:1 inclusion crystals over 2:1 inclusion crystals, from between hexanol and heptanol to between butanol and pentanol, by changing the method from crystallization to suspension. On the other hand, compound **2** included only ethanol by the suspension method. These differences seem to originate from the difference in the inclusion mechanism between the two

methods; for example, the absorption of guest molecules into the host crystals composed of self-inclusion complexes requires a phase transition, while the crystallization of inclusion complexes does not.

Competition experiments were carried out using the suspension method between two alcohols, which are different in length by one methylene unit (Table 2). The crystals of compound **2** selectively absorbed ethanol over methanol and propanol. However, the selectivity was not perfect in spite of the fact that the crystals absorbed only ethanol from the neat alcohols (*vide supra*). This may indicate that some of ethanol molecules in the inclusion crystals were replaced with the molecules of another alcohol. Another possibility is that during the formation of ethanol inclusion crystals, some molecules of another alcohol directly got into the crystal lattice. Complete selectivity towards ethanol over methanol was kinetically achieved in a run conducted at −40 °C for 8 h. On the other hand, the crystals of compound **1** preferentially absorbed propanol and hexanol among the alcohols that form 1:1 and 2:1 inclusion crystals, respectively. The recognition abilities of compound **1** towards these alcohols were inferior to the recognition ability of compound **2** towards ethanol, judging from the comparison of the excess percentage (ex %) values obtained for the relevant alcohols between compound **1** and compound **2**. Interestingly, both alcohols were absorbed into the crystals of compound **1** from a mixture of butanol and pentanol with the sum of $\bar{n}$ values ca. 1. It should be recalled that compound **1** formed 1:1 and 2:1 inclusion crystals with butanol and pentanol, respectively, from neat alcohols by the suspension method. Therefore, this observation suggests that butanol, which was absorbed into the host crystals in preference to pentanol, determined the crystal lattice.

Table 2 Inclusion ratio ($\bar{n}$) and selectivity (ex %) for competitive inclusion from an equimolar mixture of two alcohols using the suspension method.[a]

alcohols	**1**		**2**	
	$\bar{n}$	ex %[b]	$\bar{n}$	ex %[b]
MeOH / EtOH	0.04/0.71	89 (EtOH)	0.07/0.78	84 (EtOH)
			–[c]/0.71[d]	100 (EtOH)
EtOH / PrOH	0.39/0.54	16 (PrOH)	0.90/0.11	78 (EtOH)
PrOH / BuOH	0.85/0.13	73 (PrOH)	–[e]	
BuOH / PentOH	0.53/0.43	10 (BuOH)	–[e]	
PentOH / HexOH	0.17/0.43	43 (HexOH)	–[e]	
HexOH / HeptOH	0.46/0.14	53 (HexOH)	–[e]	

[a] Average value of measurements repeated more than three times. [b] Calculated as a difference between the abundance percentages of alcohols included into the crystals. The major alcohol is indicated in parentheses. [c] Not detected. [d] Stirred at –40 °C for 8 h. [e] Not examined.

X-ray analysis of inclusion crystals

As mentioned so far, compounds **1** and **2** exhibited a distinct difference in primary alcohol inclusion properties. In order to gain insight into its origin, X-ray analysis was carried out. Figure 1 shows the PXRD patterns of compound **1** and its inclusion crystals with the C1–C7 alcohols obtained by the suspension method. The inclusion crystals of the C1–C4 alcohols exhibit similar PXRD patterns (Fig. 1b–e). PXRD patterns for the inclusion crystals of the C5–C7 alcohols are also similar (Fig. 1f–h), but different from those of the C1–C4 alcohols (Fig. 1b–e). In addition, the PXRD patterns of the C1–C4 alcohols and the C5–C7 alcohols are in reasonable agreement with those simulated from the XRD data of single crystals formulated as **1**·EtOH and $\mathbf{1}_2$·PentOH, respectively (*vide infra*) (Figs. S2 and S3†). These observations clearly indicate that the C1–C4 alcohols and the C5–C7 alcohols formed 1:1 and 2:1 inclusion crystals with crystal packings similar to those of **1**·EtOH and $\mathbf{1}_2$·PentOH, respectively. Furthermore, the crystals of compound **2** formed inclusion crystals with ethanol with the same crystal packing to that of a single crystal formulated as **2**·EtOH prepared by crystallization, as evidenced by the comparison of the PXRD pattern of the former with the simulated PXRD pattern of the latter (Fig. S4†).

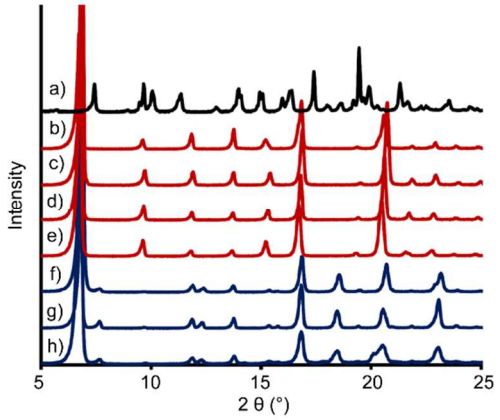


Fig. 1 PXRD patterns of a crystalline powder of compound **1** (a) and its inclusion crystals of MeOH (b), EtOH (c), PrOH (d), BuOH (e), PentOH (f), HexOH (g) and HeptOH (h), obtained using the suspension method.

We succeeded in preparing single crystals of inclusion complexes of compound **1** with several alcohols as follows: crystallization of compound **1** from mixed solvents, methanol–*tert*-butylbenzene, ethanol–toluene and propanol–toluene, gave single crystals formulated as **1**·$(MeOH)_2$, **1**·EtOH and **1**·PrOH, respectively. Two kinds of single crystals formulated as **1**·PentOH and $\mathbf{1}_2$·PentOH simultaneously precipitated from a pentanol solution of compound **1** at room temperature; crystallization at a higher temperature (70 °C) gave only $\mathbf{1}_2$·PentOH, suggesting that $\mathbf{1}_2$·PentOH is more stable than **1**·PentOH. The inclusion crystals **1**·$(MeOH)_2$, **1**·EtOH, **1**·PrOH and **1**·PentOH belong to the tetragonal system with the *P*4/n space group, commonly seen in 1:1 inclusion crystals of compound **1**.[8-10,22] In each crystal, compound **1** adopts a cone conformation with C_4 symmetry and one or two alcohol molecules are included into the cavity of compound **1** and/or in the vicinity of the *tert*-butyl groups (Figs. 2, 3a and 3b). Although all the alcohol molecules in the crystals are disordered with C_4 symmetry around the central axis of the calixarene, we will describe only one disordered structure for each independent alcohol molecule; refer to the supporting information for detailed disordered structures of the alcohol

molecules (Figs. S5–9†). Positions of hydrogen atoms in the alcohol molecules could not be determined due to the disorder.

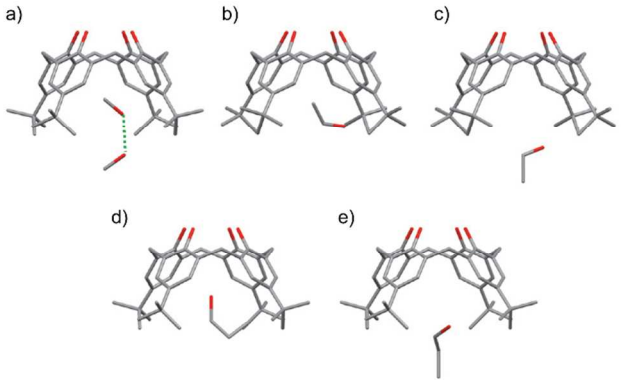


Fig. 2 X-ray structures of **1**·$(MeOH)_2$ (a), **1**·EtOH (b, c) and **1**·PrOH (d, e). A disordered structure is shown. Hydrogen atoms are omitted for clarity. The green dotted line represents an intermolecular hydrogen bond.

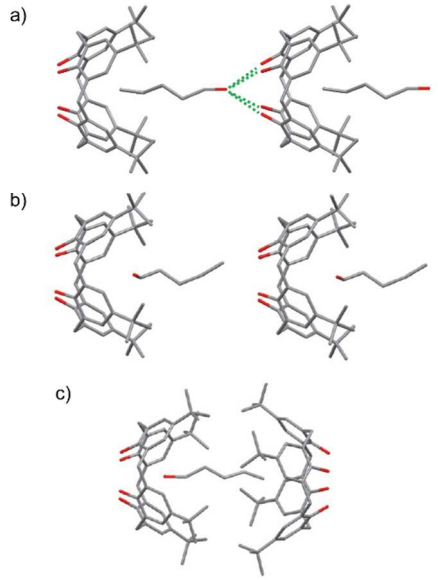


Fig. 3 X-ray structures of **1**·PentOH (a, b) and $\mathbf{1}_2$·PentOH (c). A disordered structure is shown for each independent alcohol molecule. Hydrogen atoms are omitted for clarity. Green dotted lines represent hydrogen bonds.

In the crystal of **1**·$(MeOH)_2$, one methanol molecule is deeply embedded in the cavity of compound **1**, while the other one resides in the vicinity of the *tert*-butyl groups (Fig. 2a). An intermolecular hydrogen bond is observed between the alcohol molecules; the average O···O distance is 2.435 Å. Interestingly, CH–π and OH–π interactions are observed between the alcohol molecule inside the cavity and the four aromatic rings of compound **1** and between the same alcohol molecule and the nearest aromatic ring of the host molecule, respectively; the distances from the C and O atoms of the alcohol molecule to the centroid of each and the nearest benzene ring of compound **1** are 3.697 Å and av. 3.408 Å, respectively.[24] The distance between the oxygen atom of the alcohol molecule placed near the *tert*-butyl groups and the closest hydrogen atom of a *tert*-butyl group indicates the presence of a weak CH–O interaction between them; the H···O distance is 2.590 Å (Fig. 4). Another CH–O interaction is observed between the same oxygen atom and the closest *tert*-butyl hydrogen of an adjacent host molecule, which is in an adjacent bilayer (*vide infra*) directing the *tert*-butyl groups towards the alcohol molecule (Fig. 4); the H···O distance is 2.633 Å.

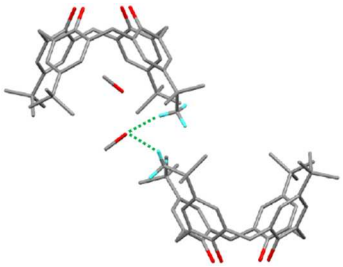


Fig. 4 The CH–O interactions between the oxygen atom of the methanol molecule placed near the *tert*-butyl groups and the closest *tert*-butyl hydrogens of two host molecules for **1**·$(MeOH)_2$. Hydrogen atoms are omitted for clarity except those of the *tert*-butyl groups participating in the CH–O interactions.

In the crystals of **1**·EtOH and **1**·PrOH, the ethanol and propanol molecules are disordered in two independent positions; one is embedded in the calix cavity (Fig. 2b and 2d) and the other resides in the vicinity of the *tert*-butyl groups (Fig. 2c and 2e). Although the carbon and oxygen atoms of these alcohol molecules were assigned based on thermal parameters and bond lengths, the terminal carbon and oxygen atoms of each alcohol molecule may change positions with each other. The distance between the centroid of each benzene ring of compound **1** and the terminal heavy atom (X) of the alcohol molecule included into the cavity indicates the presence of an XH–π interaction between them; the average X···Ar distances are 3.813 Å for **1**·EtOH and 3.854 Å for **1**·PrOH.[24] As observed in **1**·$(MeOH)_2$, the oxygen atom of the alcohol molecule placed near the *tert*-butyl groups exhibits CH–O interactions with both the closest *tert*-butyl hydrogen of the host molecule including the alcohol and that of an adjacent host molecule, if the hydroxy group of the alcohol is oriented towards the *tert*-butyl groups as shown in Figure 2c and 2e; the X···H distances are 2.466 and 2.466 Å for **1**·EtOH and av. 2.537 and 2.455 Å for **1**·PrOH. On the other hand, the shortest distances between the terminal heavy atom of the alcohol molecule placed near the *tert*-butyl groups and the hydroxyl groups of a host molecule disposed adjacently along the *c*-axis (Fig. 5a) are 4.472 and 4.434 Å for **1**·EtOH and **1**·PrOH, respectively. This indicates the absence of intermolecular hydrogen bonds between these molecules, even if the hydroxy group of the alcohol oriented towards the adjacent host molecule.

In the crystal of **1**·PentOH, a pentanol molecule is included into the cavity of a calixarene, directing the methyl (Fig. 3a) or hydroxy group inside (Fig. 3b). The calixarene aromatic rings display a CH–π interaction with the methyl group of the former pentanol molecule and an OH–π interaction with the hydroxyl group of the later; the C···Ar and O···Ar distances are 3.697 and 3.268 Å, respectively. In addition, intermolecular hydrogen bonds are observed between the hydroxy group of the former

pentanol molecule and the four phenolic hydroxy groups of a host molecule disposed adjacently along the *c*-axis (Fig. 3a); the O···O distance is 2.953 Å.

Contrary to the aforementioned four inclusion crystals, $\mathbf{1}_2$·PentOH belongs to the tetragonal system with the *P*4/nnc space group, as same as the crystal structure of $\mathbf{1}_2$·HeptOH reported previously.[23] In the crystal, the two host molecules adopt a cone conformation with C_4 symmetry and approach each other in a head-to-head manner to form a capsule, in which a pentanol molecule is included (Fig. 3c); the two host molecules are twisted by 45° around the symmetry axis and engaged with each other so as to avoid steric repulsion among the *tert*-butyl groups. The pentanol molecule is disordered over two positions so that the hydroxy groups point in opposite directions. Although the carbon and oxygen atoms of the alcohol molecule were assigned based on thermal parameters and bond lengths, the terminal carbon and oxygen atoms may change positions with each other. One of the terminal heavy atoms (X) of the pentanol molecule forms an XH–π interaction with the capsule; the X···Ar is 3.493 Å.

The above-mentioned 1:1 inclusion crystals adopt essentially the same bilayer structure, as representatively shown for **1**·EtOH in Figure 5a and 5b. In these figures, a host molecule (coloured in red) is correlated with a neighboring host molecule (coloured in blue) by the n-glide operation and, therefore, a space to accommodate guest molecule(s) spreads between two host molecules disposed adjacently along the *c*-axis. The volume of this space (V_0) was calculated by PLATON[25] as a solvent accessible void to be 165 Å^3 for **1**·EtOH after removing the guest molecule from the X-ray structure. It should be noted that the V_0 values are almost the same for **1**·$(ROH)_2$ and **1**·ROH, regardless of the size of the alcohol molecules to be included; the V_0 values are 170, 165 and 181 Å^3 for **1**·$(MeOH)_2$, **1**·PrOH and **1**·PentOH, respectively. The V_0 value for **1**·BuOH (202 Å^3) calculated from its reported X-ray structure[23] is in reasonable agreement with these values, taking it into account that the diffraction data were collected at a higher temperature (293 K) than that of our study (100 K).

Compound **1** also constructed a bilayer structure in $\mathbf{1}_2$·PentOH (Fig. 5c and 5d). Each bilayer is laminated along the *c*-axis so as to form molecular capsules with adjacent bilayers. The volume of the inner space (V_0) was calculated to be 253 Å^3, indicating that a large cavity occurs in the capsule. The reported X-ray structure of $\mathbf{1}_2$·HeptOH[23] has a somewhat larger V_0 value (308 Å^3) at 293 K.

The bilayer structure is seen in most 1:1 and 2:1 inclusion crystals of compound **1**.[8-10,22] In addition, it is reported that compound **1** can form guest-free crystals with a bilayer structure.[9a] To the best of our knowledge, however, there is no report on the origin of the bilayer formation. Figure 6 shows CH–π interactions among host molecules in **1**·EtOH. A pair of complementary CH–π interactions is observed between a methylene group of a host molecule and a benzene ring of an adjacent host molecule and *vice versa* (Fig. 6a); the average CH···Ar distance is 2.963 Å. Since each host molecule is surrounded by four host molecules in a bilayer, four pairs of such complementary CH–π interactions operate per molecule (Fig. 6b). Similar observations were made for $\mathbf{1}_2$·PentOH, as well as the other 1:2 and 1:1 inclusion crystals; the average CH···Ar distance is 3.007 Å for $\mathbf{1}_2$·PentOH. Therefore, it is concluded that compound **1** constructs a bilayer structure in the crystals with the aid of a network of the intermolecular CH–π interactions among the host molecules.

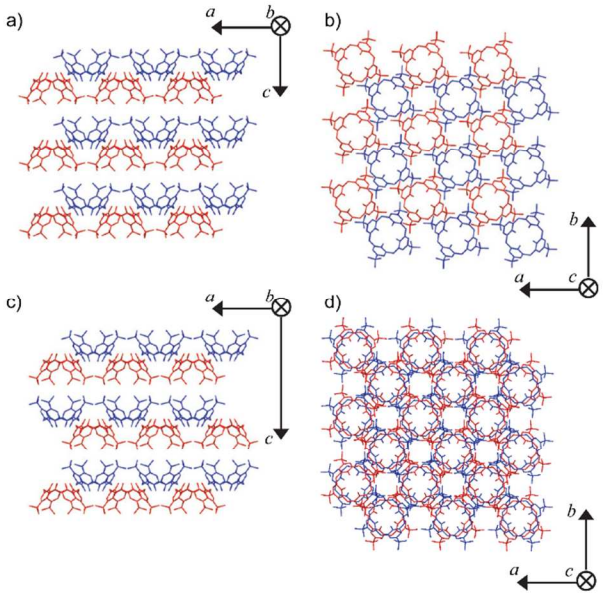


Fig. 5 Crystal packings of **1**·EtOH (a, b) and $\mathbf{1}_2$·PentOH (c, d). Views looked from the directions of the *b*-axis (a, c) and the *c*-axis (b, d). Hydrogen atoms, disordered atoms and all guest molecules are omitted for clarity. Molecules are colour-coded to clarify the packing structure.

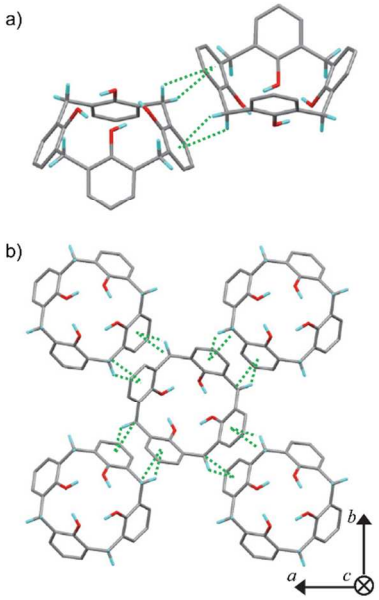


Fig. 6 CH-π interactions of a host molecule with a neighboring host molecule (a) and four neighboring host molecules (b) in **1**·EtOH. Selected hydrogen atoms, *tert*-butyl groups, disordered atoms and guest molecules are omitted for clarity. Green dotted lines represent intermolecular CH-π interactions.

In a preliminary communication,[15a] we reported the X-ray structures of **2**·MeOH, **2**·EtOH and **2**·PrOH. The structures were reanalysed under the restraint of disordered *tert*-butyl groups and guest molecules and are shown in Figure S10†.[26] In the crystals, compound **2** adopts a cone conformation and an alcohol molecule is included in its cavity, directing the alkyl group inside, which is similar to the crystal structure of **1**·PentOH shown in Figure 3a. A CH–π interaction is observed between the terminal carbon atom of the alcohol molecule and the four benzene rings of the host molecule, and intermolecular hydrogen bonds are observed between the hydroxy group of the guest molecule and two adjacent (**2**·PrOH) or all the four hydroxy groups of a host molecule disposed adjacently along the *c*-axis (**2**·MeOH and **2**·EtOH). Through the CH–π interaction and the hydrogen bonds, an alcohol molecule joins two neighboring host molecules in a head-to-tail manner to construct an infinite columnar structure, as representatively shown for **2**·EtOH in Figure 7. Among host molecules, any interaction which should be specially mentioned was not observed. Therefore, it is presumed that this packing structure was constructed by gathering of inclusion complexes as dense as possible.

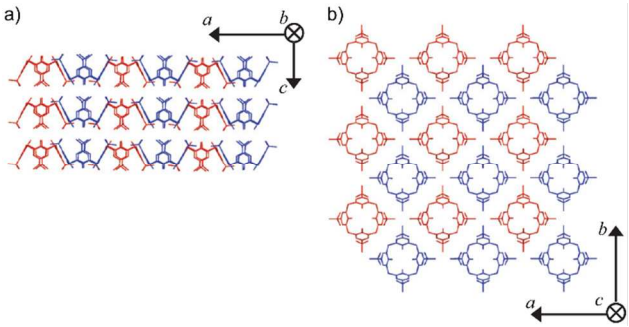


Fig. 7 Crystal packing of **2**·EtOH. Views looked from the direction of the *b*-axis (a) and the *c*-axis (b). Hydrogen atoms, disordered atoms and guest molecules are omitted for clarity. Molecules are colour-coded to clarify the packing structure.

Consideration of inclusion properties of compounds 1 and 2

As mentioned above, factors determining the crystal packing are different between the inclusion crystals of compounds **1** and **2**. In the case of compound **1**, a network of intermolecular CH–π interactions among the host molecules constructs a bilayer, which piles up in two different manners, depending on the size of guest compounds, to form either a 1:1 (1:2) or 2:1 inclusion crystal. In the case of compound **2**, which lacks methylene bridges necessary for the intermolecular CH–π interactions among the host molecules, CH–π interactions and H-bonds with a guest compound construct a columnar structure. These packing structures exhibited different selectivities towards guest compounds.

The crystals of compound **2** exhibited high recognition ability towards ethanol over methanol and propanol in the competitive experiments (Table 2). As discussed in a preliminary communication,[15a] the X-ray structures of **2**·MeOH, **2**·EtOH and **2**·PrOH suggested that compound **2** accommodates ethanol in its cavity most stably among the three alcohols. This was supported by thermogravimetric analysis (TGA); ethanol required a higher temperature range to be released from **2**·ROH than methanol and propanol.[15a] We then carried out differential scanning calorimetry (DSC) (Fig. 8). The DSC profile of **2**·MeOH exhibited a broad endothermic peak between 30 and 120 °C, followed by an exothermic peak with a maximum at 133 °C; this profile is in reasonable agreement with that reported by Gorbatchuk *et al.*[11c] The former and latter peaks are reportedly attributed to the release of methanol and the phase transition of the resulting metastable phase to the self-inclusion crystals of compound **2**, *i.e.* the starting crystals of compound **2**, respectively. On the other hand, the DSC profiles of **2**·EtOH and **2**·PrOH only showed endothermic peaks with peak bottom temperatures of 156 and 123 °C, respectively. This suggests that the transformation of **2**·EtOH and **2**·PrOH into the self-inclusion crystals of compound **2** does not pass through a metastable phase because of the high temperatures required to release the guest molecules. The DSC analysis allowed us to calculate the enthalpy changes for the formation of **2**·EtOH and **2**·PrOH from the self-inclusion crystals of compound **2** and gaseous alcohols to be −40 ± 1 and −30 ± 3 kJ·mol^{-1} for **2**·EtOH and **2**·PrOH, respectively; the enthalpy change for the formation of **2**·MeOH could not be calculated because of low reproducibility of the DSC profile. These observations further confirm that ethanol is included into the inclusion crystals most stably among the three alcohols. Therefore, it is concluded that the high recognition ability of compound **2** towards ethanol originates from the stability of the **2**·EtOH inclusion crystal.

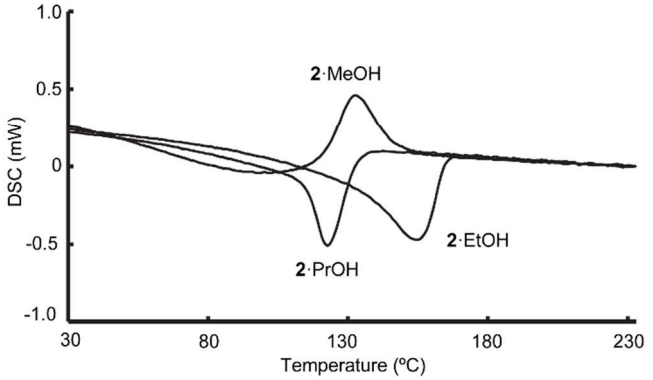


Fig. 8 DSC profiles of **2**·MeOH, **2**·EtOH and **2**·PrOH prepared by crystallization. Each data set was corrected using 233 °C as 0.0 mW for easy comparison.

Compound **2** did not form inclusion crystals with alcohols bearing alkyl groups of more than three carbon atoms (Table 1). In the X-ray structures of the inclusion crystals (Fig. S10†), the intervals between two host molecules, which were calculated from the distance between the mean planes defined by the four sulfur atoms of compound **2**, are 8.236 Å (**2**·MeOH), 8.287 Å (**2**·EtOH) and 8.547 Å (**2**·PrOH). The X-ray structure of **2**·PrOH reveals that the interplanar distance is too short for a propanol molecule to form hydrogen bonds simultaneously with four hydroxyl groups of an adjacent host molecule (Fig. S10c†). This indicates that the interplanar distance for **2**·PrOH

is maintained partly at the expense of the stabilizing effects that should be obtained by forming four simultaneous intermolecular hydrogen bonds, in other words, it is no more impossible to form tight packing with a longer interplanar distance. Therefore, it may be concluded that primary alcohols with more than three carbon atoms are too long to be included into the space between two adjacent host molecules in the columnar structure of **2**·ROH.

In contrast to compound **2**, which exhibited high recognition ability towards a specific alcohol, *i.e.* ethanol, compound **1** included a number of alcohols with different lengths by forming 1:2, 1:1 or 2:1 inclusion crystals (Table 2). As mentioned above, the 1:2 and 1:1 inclusion crystals have cavities of similar sizes (*ca.* 170 Å^3 at 100 K) but they are smaller than the inner space of a capsule in the 2:1 inclusion crystals by *ca.* 80 Å^3. The volumes of void spaces left after inclusion (V_1) were calculated, without taking hydrogen atoms of alcohol molecules into account, to be 27, 67, 42 and 25 Å^3 for **1**·$(MeOH)_2$, **1**·EtOH, **1**·PrOH and **1**·BuOH (293 K),[23] respectively. This suggests that the cavity of a 2:1 inclusion crystal is too large to form stable inclusion crystals with these alcohols. On the other hand, the V_1 values were calculated to be 58 and 68 Å^3 for $\mathbf{1}_2$·PentOH and $\mathbf{1}_2$·HeptOH (293 K).[23] The volume of a heptanol molecule occupying in the capsule was roughly estimated by the difference between the V_0 and V_1 values for $\mathbf{1}_2$·HeptOH to be 240 Å^3, which is apparently larger than the cavity of a 1:1 inclusion crystal. Thus, the sole formation of 1:1, 1:2 and 2:1 inclusion crystals with these alcohols regardless of the inclusion methods can be explained in terms of the size complementarity between the cavities and guest compounds. However, in the 1:2 and 1:1 inclusion crystals, any of the C1–C4 alcohols seem not to fit in with the cavities, judging from the severe disorder of the alcohol molecules included, in addition to the V_1 values. The same is true of the 2:1 inclusion crystals with the C5–C7 alcohols. As a result, compound **1** seems to have exhibited good receptivity towards alcohols at the expense of selectivity.

Conclusion

Compounds **1** and **2** exhibited distinct differences in inclusion properties towards primary alcohols, which originated from the difference in crystal packing of the inclusion crystals. Further studies to broaden the applicability and selectivity of the suspension method and to switch its selectivity are underway.

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† Electronic Supplementary Information (ESI) available: X-Ray structures, PXRD patterns and TGA of inclusion crystals. CCDC 1050715–1050722. For ESI and crystallographic data in CIF, see DOI: 10.1039/b000000x/

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Crystals of *p*-*tert*-butylcalix[4]arene (**1**) and *p*-*tert*-butylthiacalix[4]arene (**2**) exhibit distinct differences in inclusion properties toward primary alcohols, which originates form the difference in crystal packing of the inclusion crystals.