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Synthesis of *p*-*tert*-Butylthiacalix[4]arene and its Inclusion Property[1]

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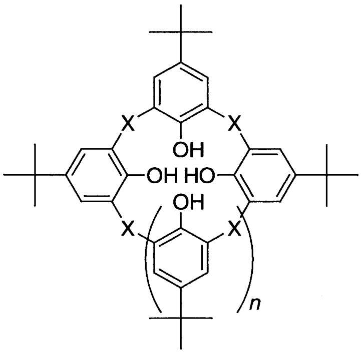
Abstract—A practical method for the synthesis of *p*-*tert*-butylthiacalix[4]arene (TC4A), in which the methylene bridges of *p*-*tert*-butylcalix[4]arene (C4A) are replaced by epithio groups, is presented by heating a mixture of *p*-*tert*-butylphenol, elemental sulfur S_8, and NaOH as a base catalyst in tetraethylene glycol dimethyl ether. The inclusion behavior of TC4A for a wide range of solvent molecules is examined by recrystallization, showing preference for the guests depending upon the size and/or the substituent of the guests. The X-ray structure of a 1:2 host–guest complex of TC4A with 1,2-dichloroethane reveals that one guest molecule is included in the cavity of TC4A, while the other is included in the crystal lattice to form a clathrate-type complex. It is shown that the inclusion in the cavity is attained by a cooperative deformation of both the host and the guest.

Introduction

Calixarenes are often called 'the third host molecules'[2] or 'macrocycles with (almost) unlimited possibilities,'[3] because of their attractive features such as ready availability by base-catalyzed condensation of *p*-alkylphenols and ease in the functionalization via modification of their lower rims (phenolic OH groups) and/or upper rims (the *p*-position),[4–6] which are not attainable by the conventional hosts such as crown ethers and cyclodextrins. By use of these synthetic advantages, quite a number of calixarene-based receptors have been synthesized and their functions have been utilized in various manners such as sensory, chromatography, separation chemistry and so on.[6] On the other hand, there has been very little initiative to develop functions of calixarenes via direct replacement of the bridging methylene groups by heteroatoms such as O, N, and S. As one of such endeavors, Sone et al. first synthesized *p*-*tert*-butylthiacalix[4]arene (TC4A, Scheme 1), in which bridging CH_2 groups of *p*-*tert*-butylcalix[4]arene (C4A) are replaced by S, by acid catalyzed cyclization of an acyclic tetramer (4% yield),[7] and they reported the results of ^1H NMR study.[8] König et al. synthesized *p*-*tert*-butylsilacalix[4]arenetetramethyl ether, in which the linking units (X) are $Si(CH_3)_2$, by stepwise reaction of *p*-*tert*-butylmethoxybenzene and dichlorodimethylsilane followed by cyclization (13% yield).[9] However, these works were seemingly only limited to the synthesis and study of the physicochemical properties of hetero-calixarenes themselves, as the synthetic difficulty prevented investigation and development of the functions of such hetero-calixarenes as high-performance materials.



Calix[*n*]arenes	X	*n*
C4A	CH_2	4
C5A	CH_2	5
C6A	CH_2	6
TC4A	S	4
TC5A	S	5
TC6A	S	6

Scheme 1. The structure and abbreviations of *p*-*tert*-butylcalix[*n*]arene (C*n*A) and *p*-*tert*-butylthiacalix[*n*]arene (TC*n*A).

Keywords: thiacalixarenes; calixarenes; sulfurization; inclusion complex.

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In a previous communication,[1] we first reported the simple one-step synthesis of TC4A in satisfactory yield (54%), which has enabled us to engage in a project to develop the functions of thiacalix[4]arenes as high-performance materials. As one of the successful outcomes, TC4A was found to bind transition metal ions very well without introduction of supplementary ligating groups at the lower or upper rims as required for conventional calixarenes,[10] owing to the coordination of the bridging sulfur to metal ions.[11] Chemical modifications have expanded the functions of TC4A in the following manner: (1) Oxidation of the bridging sulfur afforded sulfinyl- and sulfonylcalix[4]-arenes, which showed intrinsic metal ion selectivity determined by the hardness and softness of the ion.[12] (2) Conformation selective tetra-*O*-alkylation at the lower rim of TC4A by use of ethyl bromoacetate was accomplished to afford three kinds of conformers (i.e. cone, partial cone, and 1,3-alternate) of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis[(ethoxycarbonyl)methoxy]-2,8,14,20-tetrathiacalix[4]arene, which exhibited conformation-dependent selectivity toward alkali metal ions.[13,14] (3) Subsequent hydrolysis of the ester moiety of the tetra-*O*-alkylation products followed by amidation with chiral amines afforded optically active TC4As, which have been used as chiral stationary phases for gas chromatography.[15,16] (4) Sulfonation of the upper rim of TC4A gave thiacalix[4]-arenetetrasulfonate, which could bind small halogenated organic compounds in water, providing a hopeful resort to remove this class of environmentally hazardous materials.[17,18]

Considering the increasing interest in the chemistry of TC4As,[19] herein we report in detail the practical synthesis of TC4A and its inclusion properties for various solvent molecules examined by recrystallization.

Results and Discussion

Synthesis and properties of *p-tert*-butylthiacalix[4]arene

Our method for the synthesis of TC4A consists of heating a mixture of *p-tert*-butylphenol with elemental sulfur in tetraethylene glycol dimethyl ether (tetraglyme) in the presence of NaOH at 230°C to afford the desired product in a satisfactory yield (54%, Scheme 2).[1,20] Also isolated from the reaction mixture were *p-tert*-butylthiacalix[5]arene (TC5A) and *p-tert*-butylthiacalix[6]arene (TC6A), though only in small amounts (see Experimental).

Although NMR patterns for TC*n*A (n=4–6) were essentially the same, the mass spectra provided the unambiguous proof of the formation of cyclic oligomers; the *m*/*z* values for TC*n*As were simply 180×n (for n=4–6). The rather simple NMR pattern of TC*n*As should be the result of the averaged signals between the stable conformers interconverting rapidly in solution similar to those of C*n*As.[21] Table 1 lists the spectral data for OH groups of TC*n*As and C*n*As[21] (for n=4–6) obtained by ^{1}H NMR in $CDCl_3$ solution and by IR in solid matrix (KBr). Comparison of the data for TC*n*As with those of C*n*As suggests several important features of TC*n*As as follows: (1) It may be said that the hydrogen bondings comprising a cyclic array of the phenolic OH groups do exist in TC*n*As. (2) However, they are weaker than the ones in the corresponding C*n*As due to the enlarged skeleton of TC*n*As caused by replacement of the bridging CH_2 by S as suggested by the X-ray structures of TC4A[22] (vide infra) and the tetraether derivative.[13] (3) The hydrogen bonding of TC6A seems to be stronger than that of TC4A as in the case of C*n*A family. The ^{1}H NMR signal for OH proton of TC5A was not observed, the reason for which is not clear at present; it is interesting to note that C5A also shows some irregularity as compared to C4A and C6A.

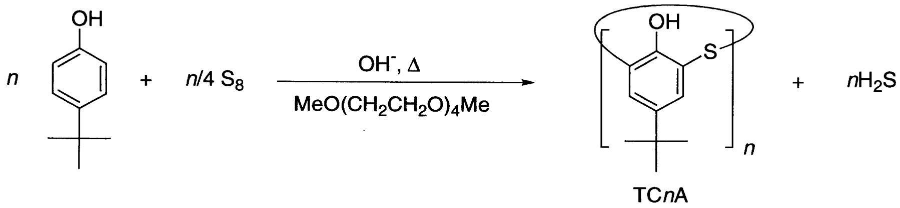
Table 1. Spectroscopic data of calix[*n*]arenes (the data for C*n*A are cited from Ref. 21)

Calix[*n*]arenes	ν_{OH} (cm^{-1})	δ_{OH} (ppm)
C4A	3164	10.2
C5A	3303	8.0
C6A	3127	10.5
TC4A	3324	9.10
TC5A	N.d.[a]	Not obsd
TC6A	3279	9.18

[a] For TC5A, ν_{OH} was not determined because of the scarcity of the sample.

As for the base catalyst in the direct sulfurization of *p-tert*-butylphenol with elemental sulfur, replacement of NaOH by LiOH caused a significant reduction in the yield of TC4A (28%). The reaction using KOH or CsOH gave a complex mixture containing many condensation products from the phenol, while mass and HPLC scrutiny of the reaction mixture did not indicate the formation of TC4A in appreciable amounts. Thus, NaOH should be the base of choice for the synthesis of TC4A; a template effect of Na^+ ion or thermal stability of TC4A in the presence of NaOH may explain the preferential formation of it among other sulfurized products.

Besides *p-tert*-butylphenol, *p*-(1,2,3,3-tetramethylbutyl)-phenol could be converted to the corresponding thiacalix[4]arene in low but synthetically useful yield by reaction with elemental sulfur under similar conditions (see Experimental), indicating the potential of the sulfurization



Scheme 2.

protocol for the synthesis of a series of *p*-substituted thiacalix[4]arene derivatives.

Inclusion properties

Inclusion of several guests by host TC4A upon recrystallization from solvents has been investigated by Sone et al.[8] They claimed that benzene, dichloromethane, and 1,2-dichloroethane were included in a 2:1 (=host/guest) manner and 1,4-dioxane in a 1:1 manner, whereas toluene, *o*-xylene, acetone, and methanol were not included in the crystal of TC4A.

Now having had substantial amounts of TC4A in hand, we examined the inclusion behavior of TC4A for a wider range of guest species, which revealed rather different results for acetone, benzene, and 1,2-dichloroethane from the ones reported by Sone et al. Although the reason for the discrepancy is not clear at present, differences in the recrystallization conditions and/or procedures may be responsible.

Table 2 summarizes the contents of solvent molecules in the crystals, host versus guest ratio, and also shown are the shapes of the crystals obtained by recrystallization of host TC4A from various solvents. As listed, TC4A readily formed crystals having defined shapes, representative micrographs of which are shown in Fig. 1. Among them, the crystals obtained from triethylene glycol dimethyl ether (triglyme) were unexpectedly large. Concerning the content of solvents in the crystals, TC4A formed 1:1 complexes in many cases, which did not lose the guests at ambient temperature under vacuum (2–4 mmHg) for more than 2 h; examples of such guests are trichloromethane, tetrachloromethane, benzene, methylcyclohexane, cyclohexane, decalin, triglyme and 1,4-dioxane (Table 2). For the crystals of stoichiometry other than 1:1 host versus guest ratios were also found. For instance, 1,2-dichloroethane formed a 1:2 complex, which agreed well with the results of X-ray crystallography as discussed in the next section. Interestingly, the inclusion behavior was sensitive to the substituent on a benzene ring; benzene was included as a 1:1 (=host/guest) complex and toluene as a 2:1 complex, whereas chlorobenzene and ethylbenzene were not included to show that the solid TC4A could differentiate the substitution pattern of benzene derivatives.

Table 2. The content of solvent and the **H**/**G** ratio in the inclusion complex formed with TC4A

Solvent	Content of solv. (mol%)[a]	**H**/**G**[b]	Shape of crystal[c]	Duration under vacuum at RT (h)
Acetone[d]	41	3:2		2
Trichloromethane	50[e]	1:1	Cubic	2
Tetrachloromethane	50[e]	1:1	Cubic	2
Benzene	53	1:1	Cubic	1
1,2-Dichloroethane	63.5	1:2		2
Methylcyclohexane[d]	49	1:1		2
Toluene	34	2:1	Cubic	1
Chlorobenzene	0	−	Cubic	2
Ethylbenzene	0	−	Cubic	1
Cyclooctane	5.2	+		4
Cyclohexane[d]	45	1:1	Cubic	2
Aniline	22	+		2
1,4-Dioxane[d]	51	1:1	Cubic	2
Triglyme[d]	49	1:1	Prismatic	4
n-Octane[d]	7.2	+		2
m-Xylene	6.8	+		2
o-Xylene	6.5	+		2
p-Xylene	6	+	Cubic	1
Decalin	48	1:1		4

[a] Estimated by ^{1}H NMR (400 MHz).
[b] −: Inclusion complex does not form. +: host to guest ratio is not clear.
[c] Sufficiently large crystals having defined shape could not be obtained for the solvents indicated by blank.
[d] Optical micrographs are available in Fig. 1.
[e] Estimated by elemental analysis.

The ability of the inclusion complex to hold guest molecules was examined for selected crystals by heating at 100°C for 2 h in vacuo (2–4 mmHg). As a result, the contents of guests were substantially reduced to the level of 0, 2.7 and 1.2% for cyclohexane, 1,4-dioxane and *o*-xylene, respectively, indicating that the inclusion complexes rapidly released the included solvents at elevated temperature in vacuo.

It is interesting to know whether the TC4A–guest complexes are inclusion types or clathrates. Recently, Hosseini et al. reported the X-ray crystal structures of 1:1 inclusion complexes of TC4A with dichloromethane, trichloromethane, and methanol, which revealed the C_4 symmetric structure of TC4A holding the guest molecules in the cavity.[22] On the other hand, 1,2-dichloroethane is revealed to present an example of the clathrate-type complexes as discussed below.

X-Ray structure of a clathrate of TC4A

The discrepancy in the composition of TC4A complex with 1,2-dichloroethane obtained by us and that reported by Sone et al.[8] prompted us to study the X-ray structure of the complex. The single crystal of the inclusion complex of TC4A with 1,2-dichloroethane was only moderately stable under atmospheric conditions, so that the intensity data were collected at low temperature (150 K) by coating with an epoxy-resin. Figs. 2 and 3 show the molecular structure and crystal packing of TC4A complex to clearly indicate that TC4A adopts cone conformation and 1,2-dichloroethane molecules were included in the cavity and the host lattice to form a 1:2 (=host/guest) complex, which coincides well with the results of ^{1}H NMR analysis of the complex (see Table 2). Therefore, the 1,2-dichloroethane complex should be regarded as a clathrate-type complex rather than a simple inclusion complex.

A reduced symmetry of TC4A is another structural feature of the 1,2-dichloroethane complex different from the 1:1 inclusion complexes with dichloromethane, trichloromethane and methanol.[22] The conformation of calix[4]arenes has been characterized by the dihedral angle (θ) of the phenyl ring with respect to the mean plane defined by the bridging groups.[23] Thus, TC4A in the 1,2-dichloroethane complex has θ=125.9, 118.7, 136.5, 124.1° for **A**–**D** rings, respectively, meaning that the molecular structure is slightly distorted from regular C_4 symmetry. The distortion is clearly caused by including 1,2-dichloroethane (marked **E**) to localize it in the vicinity of **A** and **B** rings in the cavity (Fig. 3). Therefore the skeleton of TC4A should be flexible

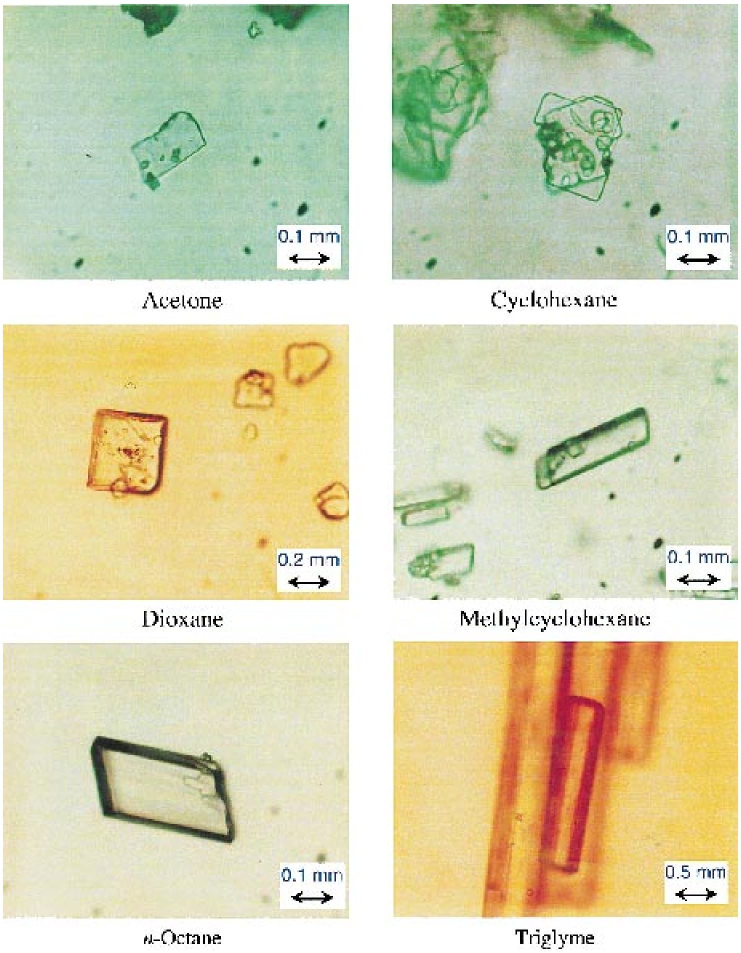


Figure 1. Optical micrographs for selected TC4A crystals obtained by recrystallization from various solvents. Note that TC4A crystals are colorless. The color of the images originated from the light source.

enough to deform and include guest molecules, representing a typical case of the so-called 'induced fit.'[24]

Concerning the guest-induced distortion of host TC4A, it is interesting to note the conformations of the guests in the crystal; the dihedral angle for $Cl–CH_2–CH_2–Cl$ of **E** was 70.0° whereas the one of **F** was 178.6°. Those clearly indicate that the TC4A cavity forced 1,2-dichloroethane **E** to change its conformation from *anti* to *gauche* to accommodate it in the cavity, while crystal lattice did not perturb the most stable conformation of 1,2-dichloroethane **F**. The former case could be said as 'host-induced guest-deformation' as opposed to the usual case of 'guest-induced host-deformation.' This suggests an interesting aspect for assembling the host–guest inclusion complex by the mutual trade-off of conformational stability of both host and guest.

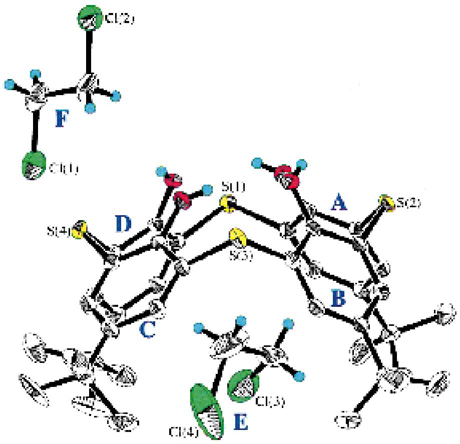


Figure 2. The ORTEP drawing $TC4A{\cdot}2(C_2H_4Cl_2)$ with thermal ellipsoids drawn at 30% probability. Hydrogen atoms for aromatic and *tert*-butyl groups and the disordered carbon atoms of methyl groups in *tert*-butyl groups at **A** and **C** rings are not shown for clarity.

In spite of the structural deviation from C_4 symmetry as induced by the guest, TC4A still maintains its cone conformation, as is demonstrated by the presence of cyclic array of hydrogen bondings by four phenolic hydroxy groups; $O\cdots O$=av. 2.784(4), O–H=av. 0.8, $O\cdots H$=av. 2.1 Å, $O–H\cdots O$=av. 146°. The distances are slightly longer than those of C4A ($O\cdots O$=2.67 Å),[25] which coincides with the results of IR measurement very well. Other noticeable structural features of the TC4A moiety are as follows: (1) The longer C–X bond (av. 1.777 Å) in TC4A (X=S) than that of calix[4]arene (1.516–1.581 Å, $X=CH_2$)[23] indicates the enlarged skeleton of TC4A compared to C4A, which agrees well with the previously reported results.[13,22] (2) The dihedral angles between the opposite phenyl rings (α) are 82.5° for rings **A** vs. **C** and 62.7° for rings **B** vs. **D**, forming a rectangular cavity. (3) The bridging S atoms deviate

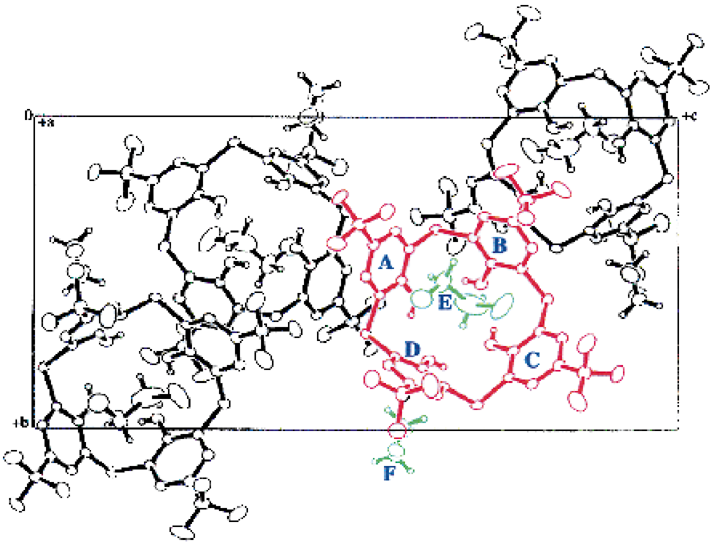


Figure 3. Molecular packing of TC4A·2($C_2H_4Cl_2$) along the *a* axis.

0.0182–0.185 Å from the planes of the phenyl rings outside from the center cavity, implying that the C–S bonds are bent by max. 6.0° outward from the mean plane of phenyl rings. (4) The possibility of weak O–H···S hydrogen bondings as suggested by the distances S···O=av. 3.023(3), S···H=av. 2.59 Å, O–H···S=av. 115.2°.

Conclusion

Being provided a practical method for the synthesis in substantial quantities, *p-tert*-butylthiacalix[4]arene (TC4A) will add a series of hopeful novel host compounds in the field of calixarene chemistry. Although it has been reported that TC4A crystallizes from various solvents to give 2:1 or 1:1 (host/guest) inclusion complexes, it was shown that the complexes of other compositions were also formed. Also shown was the possibility that TC4A could form not only inclusion complexes but also clathrate-type complexes as exemplified by X-ray crystallography of a 1:2 complex of 1,2-dichloroethane. The X-ray structure of the complex revealed mutual conformational change of the guest and the host to form the stable crystal, the TC4A still retaining a cone conformation by the cyclic array of hydrogen bondings comprising four OH groups.

Experimental

General methods

Melting points were taken using a Yamato MP-21 apparatus and are uncorrected. Microanalyses were carried out in Cosmo Research Institute. Merck silica gel $60GF_{254}$ was used for TLC. ^1H NMR was measured on a Bruker DPX-400 spectrometer operated at 400 MHz. IR spectra were obtained with a Shimadzu IR-460. Mass spectra were recorded with a JEOL JMS-SX 102A spectrometer.

The reaction of *p-tert*-butylphenol with sulfur

A mixture of *p-tert*-butylphenol (64.5 g, 0.43 mol), elemental sulfur S_8 (27.5 g, 0.86 mol), and NaOH (8.86 g, 0.215 mol) in tetraethylene glycol dimethyl ether (19 cm^3)[20] was stirred under nitrogen. The stirred mixture was heated gradually to 230°C over a period of 4 h and kept at this temperature for further 3 h with concomitant removal of the evolving hydrogen sulfide with a slow stream of nitrogen. The resulting dark red product was cooled to ambient temperature and diluted with toluene (35 cm^3) and 4 M aq. sulfuric acid solution (140 cm^3), followed by addition of diethyl ether (140 cm^3) with stirring to give a suspension. The precipitate was collected by filtration, recrystallized from chloroform and dried in vacuo (100°C, 4 h) to give an essentially pure sample of TC4A (37.9 g, 49% based on the *p-tert*-butylphenol) as confirmed by elemental analysis and spectral data. The mother liquor of the recrystallization was concentrated in vacuo, and chromatography of the residue on silica gel (hexane/$CHCl_3$=4:6) afforded additional TC4A (3.9 g, 5.0%), the combined yield of TC4A amounting to 54%.

***p-tert*-Butylthiacalix[4]arene (TC4A).** Colorless prisms (from $CHCl_3$), mp 320–322°C. FD MS *m/z* 720 (M^+); IR (KBr) 3324; 2962 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ=1.22 (36H, s, $C(CH_3)_3$), 7.64 (8H, s, Ar-H), and 9.60 (4H, s, OH). ^{13}C NMR (400 MHz, $CDCl_3$, TMS) δ=31.3 ($C(\mathit{C}H_3)_3$), 34.2 ($\mathit{C}(CH_3)_3$) and 120.5, 136.4, 144.7, and 155.6 (Ar). Found: C, 66.37; H, 6.57; S, 17.50%. Calcd for $C_{40}H_{48}O_4S_4$: C, 66.62; H, 6.71; S, 17.79%.

The organic phase from the filtration of the above suspension was chromatographed (silica-gel, hexane/$CHCl_3$=4:6). Close scrutiny of the effluent fractions by HPLC and FD MS suggested the existence of TC*n*A where $n\geq5$, among which samples of TC5A (trace) and TC6A (10 mg) were obtainable by MPLC and confirmed by spectral data.

***p-tert*-Butylthiacalix[5]arene (TC5A).** FD MS *m/z* 900

(M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ=1.21 (54H, s, $C(CH_3)_3$) 7.47 (12H, s, Ar-H). The OH resonance (5H, s) was not observed. ^{13}C NMR (400 MHz, $CDCl_3$, TMS) δ=31.3 ($C(\mathit{C}H_3)_3$), 34.2 ($\mathit{C}(CH_3)_3$), and 119.6, 133.6, 144.1 and 154.3 (Ar). Found: C, 66.34; H, 6.71; S, 17.79%. Calcd for $C_{50}H_{60}O_5S_5$: C, 66.62; H, 6.71; S, 17.79%. IR data were not available due to the consumption of the sample.

***p-tert*-Butylthiacalix[6]arene (TC6A).** Mp 295°C (decomp.). Mp 289–291°C. FD MS *m/z* 1080 (M^+). IR (KBr) 3279 (OH), 2960 (CH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ=1.23 (54H, s, $C(CH_3)_3$) 7.59 (12H, s, Ar-H), 9.18 (6H, s, OH). ^{13}C NMR (400 MHz, $CDCl_3$, TMS) δ=31.3 ($C(\mathit{C}H_3)_3$), 34.2 ($\mathit{C}(CH_3)_3$), and 120.4, 135.4, 144.4 and 155.3 (Ar). Found: C, 66.61; H, 6.65; S, 17.55%. Calcd for $C_{60}H_{72}O_6S_6$: C, 66.62; H, 6.71; S, 17.79%.

The reaction of *p*-(1,1,3,3-tetramethylbutyl)phenol with sulfur

A mixture of *p*-(1,1,3,3-tetramethylbutyl)phenol (50.0 g, 0.22 mol), elemental sulfur S_8 (14.72 g, 0.46 mol), and NaOH (8.8 g, 0.22 mol) in tetraethylene glycol dimethyl ether (15 cm^3) was treated by the same procedure as mentioned for the preparation of TC4A except that it was heated up to 250°C. The resulting dark red product was cooled to ambient temperature and diluted with toluene (70 cm^3), and then 2 M sulfuric acid (120 cm^3) was added with stirring. After phase separation, methanol was added to the toluene phase to precipitate the crude product, which was then collected by filtration. The crude product was recrystallized from chloroform and then from benzene, and dried in vacuo (100°C, 4 h) to give an essentially pure sample of *p*-(1,1,3,3-tetramethylbutyl)thiacalix[4]arene (7.2 g, 14% based on *p*-(1,1,3,3-tetramethylbutyl)phenol) as confirmed by elemental analysis and spectral data.

***p*-(1,1,3,3-tetramethylbutyl)thiacalix[4]arene.** Mp 260–261°C. FAB MS *m/z* 944 (M^+). IR (KBr) 3300 (OH), 2955 (CH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ=0.56 (36H, s, $-C(CH_3)_2CH_2C(C\mathit{H}_3)_3$), 1.24 (24H, s, $-C(C\mathit{H}_3)_2CH_2C(CH_3)_3$), 1.59 (8H, s, $-C(CH_3)_2C\mathit{H}_2C(CH_3)_3$), 7.57 (8H, s, Ar-H), 9.20 (4H, s, OH). ^{13}C NMR (400 MHz, $CDCl_3$, TMS) δ=31.2, 31.7, 32.3, 38.0, 57.0 ($-C(CH_3)_2CH_2C(CH_3)_3$) and 120.4, 136.6 143.4 and 155.1 (C_{Ar}). Found: C, 71.14; H, 8.58; S, 13.53%. Calcd for $C_{56}H_{80}O_4S_4$: C, 71.13; H, 8.53; S, 13.57%.

Preparation of inclusion complexes

Host TC4A was added to the solvent being heated at the boiling point until it was saturated. The solution was then allowed to cool to RT to recrystallize. The precipitated crystals were filtered off, dried in vacuo (2–4 mmHg) at RT for 1–4 h, and then subjected to ^{1}H NMR or elemental analysis to determine the content of the guest molecules in the crystal. The stability of several inclusion complexes was investigated by drying in vacuo (2–4 mmHg) at 100°C for 2 h followed by ^{1}H NMR measurement.

X-Ray crystallography

Single crystal of TC4A was obtained by slow evaporation of the solvent from the 1,2-dichloroethane solution. Crystal data for TC4A: $C_{40}H_{48}O_4S_4 \cdot 2(C_2H_4Cl_2)$, FW=918.99, monoclinic, $P2_1/c$ (#14), Crystal size=0.2×0.4×0.6 mm, temperature=150 K, Cu-Kα radiation, a=13.481(7), b=13.24(1), c=26.940(8) Å, β=95.48(4)°, V=4785(4) $Å^3$, Z=4, D_c=1.276 g/cm^3, Full-matrix least-squares, R=0.072 and R_w=0.071 for observed 6382 reflections [$I_0 > 3\sigma(I_0)$]. Two *tert*-butyl carbons at the **A** and **C** rings are disordered in the occupancies of 0.75 and 0.25. The *D*-map allowed location of H(O) atoms in reasonable geometry of hydrogen bondings. Further details of the X-ray analysis of TC4A are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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