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ORIGINAL ARTICLE

Recovery of host crystals from inclusion crystals of *p-tert*-butylcalix[4]arene and *p-tert*-butylthiacalix[4]arene by the treatment with a solvent and/or supercritical CO_2

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Abstract

Upon stirring inclusion crystals of *p*-*tert*-butylthiacalix[4]arene (**2**) in solvents with heating, guest compounds were efficiently desorbed to yield guest-free crystals. More specifically, upon treatment with methanol, the exchange of guest compounds with methanol in the crystals, followed by the desorption of the methanol afforded metastable host crystals **2β**, whereas, upon treatment with heptane, the dissolution of the inclusion crystals and simultaneous crystallization of compound **2** afforded stable host crystals **2α**. Further, a host crystal of *p*-*tert*-butylcalix[4]arene (**1**) was recovered by the treatment of 2:1 (host/guest) inclusion crystals of compound **1** with supercritical carbon dioxide (scCO_2), and through the combination of the guest exchange of 1:1 inclusion crystals of compound **1** with hexane and scCO_2 treatment of the resulting 2:1 inclusion crystals $\mathbf{1}_2$·hexane. Although the recovered host crystal of compound **1** contained a small amount of CO_2, it could be reused for the inclusion of organic compounds.

Keywords *p*-tert-Butylcalix[4]arene · *p*-tert-Butylthiacalix[4]arene · Inclusion crystal · Guest desorption

Introduction

Recently, the collection and separation of inorganic gases and organic compounds using nanoporous materials, such as zeolites [1–3], metal–organic frameworks (MOFs) [4–7], covalent organic network polymers (COFs) [8–10], and nanoporous molecular crystals (NMCs) [11–13], have received significant attention in the context of establishing green and low-cost storage and purification methods. Calixarenes such as *p*-*tert*-butylcalix[4]arene (**1**) are representative examples of host compounds employed in the construction of NMCs and their inclusion properties in the crystal form have been intensively investigated by the Atwood's [14–20], Ripmeester's [21–26], and Gorbatchuk's groups [27–31]. Several studies on the selective inclusion of inorganic gases or organic compounds by crystals of calixarene analogs have also been reported, including the selective absorption of CO_2 by crystals of azacalix[n]arenes [32–36] and the selective inclusion of alkanes [37] and aromatic compounds [38] by crystals of pillar[n]arenes. Although crystals of calix[4]arenes (e.g., **1** and **2**) do not possess empty channels unlike other nanoporous materials, they can include inorganic gases and organic compounds, accompanied by a structural change; after this structural feature, they are classified as NMCs with "porosity without pores"[39]. As such, a tiny difference in the structures of guest compounds can influence the stabilities of the resulting inclusion crystals, as well as the activation energies required for the inclusion to take place, and thereby selective inclusion is achievable. Actually, we succeeded in the selective inclusion of alcohols [40, 41], carboxylic acids [40, 42], methylamines [43], and disubstituted benzenes [44] by using crystals of *p*-*tert*-butylcalix[4]arene (**1**) and *p*-*tert*-butylthiacalix[4]arene (**2**). We also succeeded in switching the guest selectivity in the competitive inclusion of methylamines [43] and carboxylic

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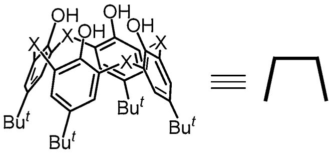
acids [42] under kinetic and thermodynamic control. Important properties for the nanoporous materials used for the storage and purification of inorganic gases and organic compounds are not only high collection efficiencies, high selectivities, and wide applicability, but also facile guest desorption and material reuse. Despite such promising properties of the crystals of calix[4]arenes as separation materials, few studies currently exist on the guest desorption from their inclusion crystals [45–47], as is the case with other NMCs [48, 49]. The desorption of guest molecules from inclusion crystals is usually evaluated by thermogravimetric analysis (TGA) and/or differential scanning calorimetry (DSC) [50], and such thermal desorption requires, in general, high temperatures. For example, the inclusion crystal of compound **2** with dichloromethane (**2**·CH_2Cl_2), requires heating at 140 °C for 3 days under a reduced pressure (0.5–1.0 kPa) to recover the host crystal [45]. In this study, we investigated the recovery of host crystals from inclusion crystals of compounds **1** and **2** by guest desorption through treatment with organic solvents and supercritical carbon dioxide ($scCO_2$).



1: X = CH_2
2: X = S

Experimental

General

^{1}H NMR spectra were measured on a Bruker Avance-400 MHz spectrometer using $CDCl_3$ and tetramethylsilane as a solvent and internal standard, respectively. Guest free crystals of compounds **1** (**1α**) [51] and **2** (**2α**) [52] were prepared, according to the literature procedure [41]. Guest compounds and solvents were used as purchased.

Preparation of inclusion crystals of compounds 1 and 2

Inclusion crystals were prepared by suspending powdery crystals of compounds **1** (**1α**) or **2** (**2α**) in a neat guest at room temperature for 24 h [40–45]. In the preparation of **2**·$Me_2NH·H_2O$ and **2**·Me_3N, aqueous solutions of respective amines were used instead of neat amines [43]. A portion of the resulting crystals were dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy to determine the inclusion ratio of the guest compound $\bar{n}_g$, which is defined as the mean number of guest molecules in the crystals per host molecule.

Treatment of inclusion crystals of compound 2 with organic solvents

Inclusion crystals of compound **2** (20 mg) were placed in a screw cap vial equipped with a stir bar and suspended by the addition of an organic solvent (1.5 mL). The suspension was stirred at a fixed temperature for 24 h, and the resulting crystals were collected by filtration, washed with hexane or methanol (5 mL × 3), dried in vacuo (0.5–1.0 kPa) at room temperature for 2 h, weighted, and analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ to determine the inclusion ratios for the guest compound remaining in the crystals ($\bar{n}'_g$) and the solvent ($\bar{n}_s$).

Treatment of inclusion crystals of compound 1 with $scCO_2$

Inclusion crystals of compound **1** (50 mg) were placed in a 50 mL autoclave and the apparatus was charged with liquefied CO_2 by using a solvent delivery pump (JASCO PU-2080-CO_2) to reach 10 MPa at a fixed temperature. After standing for a predetermined time, the autoclave was depressurized and the resulting crystals were analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ to determine the $\bar{n}'_g$ value.

Results and discussions

First, we examined the desorption of guest molecules from inclusion crystals of compound **2** upon treatment with organic solvents. For this purpose, methanol, heptanol, and heptane were employed as solvents, because they are not only poor solvents for host crystals **2α** and **2β** to be formed (vide infra) but also not included in the host crystals in a stable form. Inclusion crystals of compound **2** with an inclusion ratio of $\bar{n}_g$ were suspended in an organic solvent (1.5 mL), and the suspension was stirred at a fixed temperature for 24 h. The resulting crystals were collected by filtration, dried in vacuo, weighted, and analyzed by ^{1}H NMR spectroscopy to determine the inclusion ratio of the guest compound remaining in the crystals ($\bar{n}'_g$). When the solvent was included in the crystals, its inclusion ratio ($\bar{n}_s$) was also determined. The recovery of compound **2** (*R*%) was then estimated from the weight of obtained crystals and inclusion ratios $\bar{n}'_g$ and $\bar{n}_s$. Table 1 shows the results for the inclusion crystal of compound **2** with dimethylamine (**2**·$Me_2NH·H_2O$) [43]; The content of water molecules was not considered for the estimation of $\bar{n}$ and *R*%. Although only a slight desorption of the amine, accompanied by a partial incorporation of a solvent, was observed with every solvent at room temperature (entries 1, 3, and 6), the amine was completely

Table 1 Desorption of dimethylamine from $\mathbf{2}\cdot Me_2NH\cdot H_2O$ by the treatment with organic solvents

Entry	Solvent	Temp. (°C)	$\bar{n}_g$	$\bar{n}'_g$	$\bar{n}_s$	R%[a]
1	Methanol	r.t.	0.98	0.80	0.12	81
2	Methanol	60	0.87	–[b]	–[b]	83 (**2β**)
3	Hexanol	r.t.	0.97	0.87	0.30	64
4	Hexanol	60	0.98	0.44	–[b]	63
5	Hexanol	80	0.88	–[b]	–[b]	76 (**2α**)
6	Heptane	r.t.	0.94	0.87	0.32	64
7	Heptane	60	0.89	0.04	–[b]	68
8	Heptane	80	0.92	–[b]	–[b]	85 (**2α**)

Conditions: $\mathbf{2}\cdot Me_2NH\cdot H_2O$ (20 mg), solvent (1.5 mL), 24 h

[a] Crystal phase is shown in parentheses

[b] Inclusion was not detected

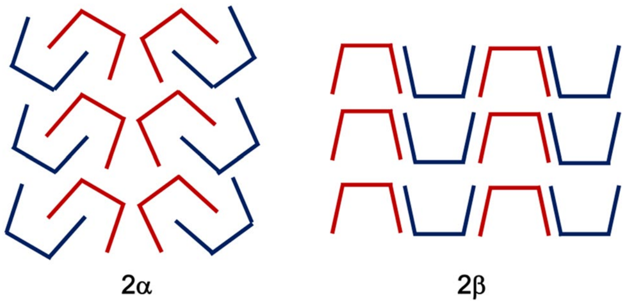


Fig. 1 Schematic views of packing structures of **2α** and **2β**

desorbed from the inclusion crystals by heating at 60 °C in methanol and 80 °C in either hexanol or heptane, thereby resulting in the formation of empty host crystals in yields of 76–85% (entries 2, 5, and 8). Comparison of the PXRD patterns of the resulting crystals with those of authentic samples revealed that the starting crystal **2α** was recovered from hexanol and heptane, whereas methanol gave metastable crystal **2β** (Figs. 1 and S1).

We then tested the applicability of this guest-desorption method to other inclusion crystals, using methanol and pentane as solvents. Inclusion crystals of compound **2** with ethanol, trimethylamine, acetic acid, and propionic acid (i.e., $\mathbf{2}\cdot EtOH$ [40], $\mathbf{2}\cdot Me_3N$ [43], $\mathbf{2}\cdot MeCO_2H$ [40], $\mathbf{2}\cdot[EtCO_2H]_3$ [40]) were treated with methanol at 60 °C and with heptane at 80 °C for 24 h (Table 2). In all cases, the guest compounds were completely desorbed, giving **2β** from methanol and **2α** from heptane in high recovery yields. On the other hand, the recovery of guest-free crystals resulted in failure from inclusion crystals of compound **1** by the treatment with hexane or hexanol; instead, inclusion crystals of these solvents were obtained (Table S1).

To gain insight into the mechanism for the desorption of dimethylamine from $\mathbf{2}\cdot Me_2NH\cdot H_2O$, the time course of the changes in $\bar{n}'_g$ and R% was analyzed for the treatment with methanol and heptane at 60 °C. Upon immersing $\mathbf{2}\cdot Me_2NH\cdot H_2O$ in methanol, the $\bar{n}'_g$ value decreased immediately and reached to zero after ~18 h (Fig. 2). The inclusion of methanol ($\bar{n}_s$ = ~0.3) was observed initially, but the $\bar{n}_s$ value decreased with time and reached to zero after 24 h. The R% value was kept high (~80%) throughout the experiment. It is known that the crystallization of compound **2** from methanol/toluene affords $\mathbf{2}\cdot MeOH$. However, we recently found that when this inclusion crystal was left

Table 2 Guest desorption from inclusion crystals of compound **2** by the treatment with methanol or heptane

Entry	Inclusion crystal	Solvent	Temp. (°C)	$\bar{n}_g$	$\bar{n}'_g$	$\bar{n}_s$	R%[a]
1	$\mathbf{2}\cdot EtOH$	Methanol	60	0.92	–[b]	–[b]	92 (**2β**)
2	$\mathbf{2}\cdot EtOH$	Heptane	80	0.92	–[b]	–[b]	80 (**2α**)
3	$\mathbf{2}\cdot Me_3N$	Methanol	60	1.00	–[b]	–[b]	94 (**2β**)
4	$\mathbf{2}\cdot Me_3N$	Heptane	80	1.00	–[b]	–[b]	92 (**2α**)
5	$\mathbf{2}\cdot MeCO_2H$	Methanol	60	0.90	–[b]	–[b]	83 (**2β**)
6	$\mathbf{2}\cdot MeCO_2H$	Heptane	80	0.90	–[b]	–[b]	82 (**2α**)
7	$\mathbf{2}\cdot[EtCO_2H]_3$	Methanol	60	2.61	–[b]	–[b]	87 (**2β**)
8	$\mathbf{2}\cdot[EtCO_2H]_3$	Heptane	80	2.75	–[b]	–[b]	70 (**2α**)

Conditions: inclusion crystal (20 mg), solvent (1.5 mL), 24 h

[a] Crystal phase is shown in parentheses

[b] Inclusion was not detected

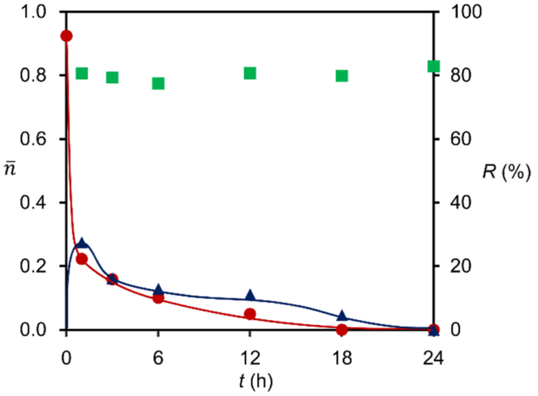


Fig. 2 Time course of the changes in the inclusion ratios ($\bar{n}$) of dimethyl amine (filled circle) and methanol (filled triangle) and the recovery yield of compound **2** (filled square) in the desorption of dimethylamine from **2**·Me_2NH·H_2O in methanol at 60 °C

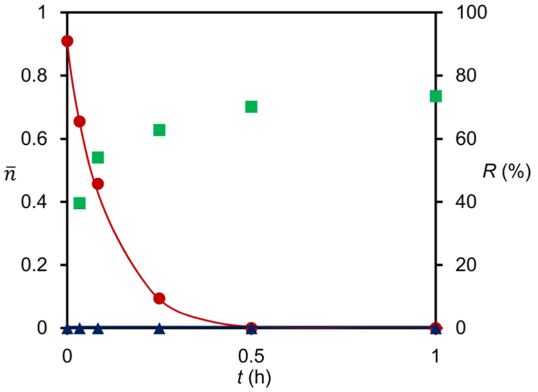


Fig. 3 Time course of the changes in the inclusion ratios ($\bar{n}$) of dimethyl amine (filled circle) and heptane (filled triangle) and the recovery yield (*R*%) of compound **2** (filled square) in the desorption of dimethylamine from **2**·Me_2NH·H_2O in heptane at 60 °C

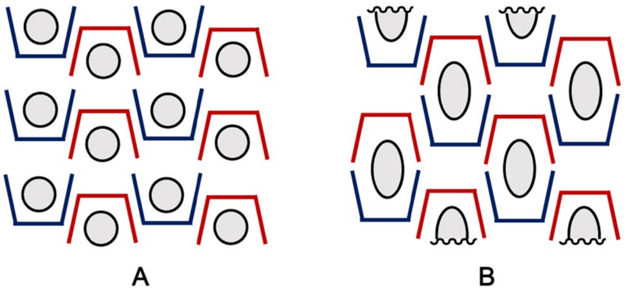


Fig. 4 Schematic views of packing structures (**A**) and (**B**) generally seen in inclusion crystals of compound **1**

Table 3 Guest desorption from inclusion crystals of compound **1** by the treatment with $scCO_2$

Entry	Inclusion crystal	Temp. (°C)	Time	$\bar{n}_g$	$\bar{n}'_g$
1	$\mathbf{1}_2$·Hexane	80	1	0.48	–[a]
2	$\mathbf{1}_2$·Hexane	60	3	0.48	–[a]
3	$\mathbf{1}_2$·Hexanol	80	3	0.57	–[a]
4	$\mathbf{1}_2$·Hexanol	60	6	0.57	–[a]
5	**1**·*m*-Dichlorobenzene	80	3	0.76	0.20
6	**1**·*p*-Chlorotoluene	80	3	0.84	0.15
7	**1**·CH_2Cl_2	80	3	0.92	0.89
8	**1**·CH_2Cl_2	100	24	0.92	0.73

Conditions: inclusion crystal (50 mg), CO_2 (10 MPa)

[a] Inclusion was not detected

in the mixed solvent at room temperature with stirring, the methanol in the crystal was spontaneously desorbed to afford guest-free **2β** [42]. On the basis of this finding, the observed time dependence of $\bar{n}'_g$ and $\bar{n}_s$ can be interpreted as that the desorption of dimethylamine from the inclusion crystal proceeded through the guest exchange with methanol, followed by the desorption of the methanol. The constantly high *R*% values support this mechanism.

In heptane, the desorption of dimethylamine was faster than in methanol; the $\bar{n}'_g$ value reached to zero only after 30 min (Fig. 3). In this case, the *R*% value was ~40% at the beginning but it increased with time, reaching 73% after 1 h and 85% after 24 h. This observation suggests that **2α** was precipitated simultaneously with the dissolution of **2**·Me_2NH·H_2O in heptane.

Next, we examined the extraction of guest compounds from inclusion crystals of compound **1** using $scCO_2$ (60–100 °C, 10 MPa). It is known that compound **1** forms 1:1 and 2:1 (host/guest) inclusion crystals with packing structures **A** and **B** (Fig. 4), respectively. This is originated from a tendency of compound **1** to form a bilayer structure with the conical cavities of the calixarene molecules appearing on both the surfaces; this bilayer structure is stabilized by a network of intermolecular CH–π interaction between a methylene group of a host molecule and a benzene ring of an adjacent host molecule [41]. The bilayers are laminated in two different manners to construct packing structures **A** and **B** [14, 21, 41]. Larger guest compounds tend to adopt packing structure **B**, because each void space capable of accommodating guest molecule(s) is larger in **B** than **A**. Inclusion crystals with packing structures **A** and **B** showed different behaviors toward $scCO_2$ as follows.

Guest compounds were readily desorbed from 1:2 inclusion crystals with packing structure **B**. Thus, the treatment of $\mathbf{1}_2$·hexane [53] with $scCO_2$ at 80 °C for 1 h or at 60 °C for 3 h in an autoclave resulted in complete desorption of the hexane molecules (entries 1 and 2 in Table 3). A similar treatment of $\mathbf{1}_2$·hexanol [41] with $scCO_2$ at 60 or 80 °C also released hexanol, although a longer treatment time was required to complete the desorption (entries 3 and 4). The crystal obtained from $\mathbf{1}_2$·hexanol by the

Table 4 Guest exchange of inclusion crystals of compound **1** with hexane

Entry	Inclusion crystal	Temp. (°C)	Time (h)	$\bar{n}_g$	$\bar{n}'_g$	$\bar{n}_s$	Yield (%)[a]
1	**1**·*m*-Dichlorobenzene	r.t.	1	0.84	–[b]	0.57	96
2	**1**·*p*-Chlorotoluene	r.t.	1	0.84	0.42	0.50	–[c]
3	**1**·*p*-Chlorotoluene	r.t.	3	0.84	0.31	0.60	–[c]
4	**1**·*p*-Chlorotoluene	60	1	0.84	–[b]	0.44	93
5	**1**·CH_2Cl_2	r.t.	1	0.90	0.05	0.55	–[c]
6	**1**·CH_2Cl_2	r.t.	3	0.88	–[b]	0.61	85

Conditions: inclusion crystal (20 mg), solvent (1.5 mL)

[a] Yield of $\mathbf{1}_2$·hexane

[b] Inclusion was not detected

[c] Yield was not calculated

$scCO_2$ treatment at 80 °C showed a similar PXRD pattern to that of **1**·EtOH (Fig. S2) [41], indicating that the crystal packing of $\mathbf{1}_2$·hexanol (**B**) was changed to **A** by releasing the guest molecules. In thermogravimetric analysis, this crystal lost weight by ~ 1.5% at a temperature range of 25–175 °C (Fig. S3), suggesting that it included a small quantity of CO_2 ($\bar{n}_s$ = ~ 0.2). These observations, combined with the fact that **1α** upon treatment with high-pressure CO_2 affords **1**·$(CO_2)_2$ with crystal packing **A** [24], allowed us to conclude that the treatment of $\mathbf{1}_2$·hexanol with $scCO_2$ afforded **1**·$(CO_2)_2$ by guest exchange, which was followed by the desorption of the majority of CO_2 molecules upon depressurization of the system.

In contrast to the 2:1 inclusion crystals, 1:1 inclusion crystals with crystal packing **A**, **1**·*m*-dichlorobenzene [44] and **1**·*p*-chlorotoluene [44], upon treatment with $scCO_2$ at 80 °C for 3 h, left ~ 20% of the guest molecules in the crystals (entries 5 and 6). Further, almost no release of guest molecules was observed for **1**·CH_2Cl_2 [45] under these conditions, and the majority of guest molecules remained even by treating the crystal at 100 °C for 24 h (entries 7 and 8). We then devised an alternative method for the 1:1 inclusion crystals, taking advantage of the finding that in hexane and hexanol, inclusion crystals of compound **1** exchanged guest compounds with solvents (vide supra). The conditions for the guest exchange were optimized for hexane (Table 4). When 1:1 inclusion crystals were suspended in hexane at either room temperature or 60 °C for 1–3 h, $\mathbf{1}_2$·hexane was obtained in good yields. Since $\mathbf{1}_2$·hexane readily released the hexane molecules by the treatment with $scCO_2$ (entries 1 and 2 in Table 3), the recovery of the host crystal of compound **1** was achieved from the 1:1 inclusion crystals. Although the resulting crystal contained a small amount of CO_2 (vide supra), it could be reused for the inclusion of organic compounds (Table S2); the performance was comparable to that of **1α**. Further, the crystal could be converted into **1α** by heating at 200 °C for 2 h under a reduced pressure (0.5–1.0 kPa).

Conclusion

We demonstrated that inclusion crystals of *p*-*tert*-butylthiacalix[4]arene (**2**) desorbed guest compounds by heating in an organic solvent to recover the guest-free host crystal **2α** or **2β**, depending on the solvent. Similarly, a crystal of *p*-*tert*-butylcalix[4]arene (**1**), which is reusable for the inclusion of organic compounds, was obtained by the treatment of 2:1 inclusion crystals of compound **1** with $scCO_2$, and the guest exchange of 1:1 inclusion crystals of compound **1** with hexane and subsequent treatment with $scCO_2$. As one of the few examples of studies on the desorption of guest compounds from inclusion crystals by practical methods other than simple heating, we believe that our report is a significant contribution to the literature and will lead to the development of novel materials and methods for the green and low-cost separation and/or collection of organic molecules.

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