Photoresponsive self-assembled hexameric capsules based on calix[4]resorcinarenes bearing azobenzene dendron conjugates as side chains

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We synthesized calix[4]resorcinarenes bearing various azobenzene dendron conjugates as side chains, wherein the azobenzene moiety is a photoresponsive unit and the dendron moiety is a capsule-destabilizing unit, and then studied the photoresponsive properties of their self-assembled hexameric capsules in conjunction with guest encapsulation in H_2O-saturated $CDCl_3$. It was found that correlation between the *trans*-to-*cis* photoisomerization of the azobenzene dendron side chains of hosts and the consequent capsule destabilization leading to guest release largely depends on the nature of the dendron moieties, such as their steric bulkiness or hydrophilicity.

Introduction

One attractive goal of supramolecular chemistry is to control molecular self-assembly by an external stimulus. The use of light for this purpose has attracted much attention because light is a clean stimulus and available whenever needed without the requirement for the addition of external chemicals to the system.[1] Photoresponsive capsules have attracted considerable attention, particularly in the field of drug delivery systems. Covalently bound hemicarcerands with a photochemically irreversible or reversible gated function have been reported.[2] Azobenzene is a well-known building block for photoresponsive host–guest systems and supramolecular architectures, in which the *trans*-to-*cis* photoisomerization of the azobenzene unit causes reversible structural changes.[1a,3-5] Capsules and deep cavitands with azobenzene unit(s) have also been reported, wherein the azobenzene unit controls the size and environment of the inner cavity space by *trans*-to-*cis* photoisomerization.[6] However, controlling the assembly–disassembly–reassembly process of self-assembled capsules in conjunction with guest encapsulation–release–re-encapsulation by light stimulus remains a challenge.

Calix[4]resorcinarene **1** (R = $C_{11}H_{23}$) is a valuable host molecule for molecular recognition of polar guest molecules.[7] It is known that host **1** in H_2O-saturated $CDCl_3$ forms a self-assembled hexameric capsule $[(\mathbf{1})_6\bullet(H_2O)_8]$ via hydrogen bonding of six molecules of **1** as a face with eight molecules of H_2O as a vertex, which encapsulates a variety of guest molecules (Fig. 1a).[8,9] We have designed calix[4]resorcinarenes (*trans*-**2**–**5**) bearing various azobenzene dendron conjugates as four side chains R,[10,11] wherein the azobenzene moiety is a photoresponsive unit and the dendron moiety is a capsule-destabilizing unit (Fig. 1b).[12] We anticipated that a calix[4]resorcinarene with *trans*-azobenzene dendron side chains self-assembles into a hexameric capsule with guest encapsulation, whereas the *trans*-to-*cis* photoisomerization of the azobenzene units causes steric repulsion of dendron units between host molecules, inducing destabilization or disassembly of a hexameric capsule (Fig. 1c and Fig. 2). We now report the synthesis of host molecules *trans*-**2**–**5** and the photoresponsive properties of their self-assembled hexameric capsules in conjunction with guest encapsulation, wherein the photoinduced capsule destabilization leading to guest release largely depends on the nature of the dendron moieties, such as their steric bulkiness or hydrophilicity.

Results and discussion

Synthesis and characteristics of *trans*-2–5

Host molecules *trans*-**2**–**5** were synthesized following a five-step procedure (Scheme 1 and ESI†). The phenolic hydroxy groups of a calix[4]resorcinarene derivative (**8**, R = $(CH_2)_4$-O-CH_2Ph)[13] were protected with MOM-Cl to give **9**, and then the debenzylation of **9** with H_2/Pd-C gave **10** (R = $(CH_2)_4$-OH). The mesylation of the hydroxy groups of the side chains R of **10** afforded **11** (R = $(CH_2)_4$-O-SO_2CH_3) as a synthetic key intermediate. The reaction of **11** with hydroxyazobenzene dendron conjugates **12**, **13**, **14**, and **15**† in the presence of K_2CO_3 followed by the deprotection of the MOM groups gave *trans*-**2**, *trans*-**3**, *trans*-**4**, and *trans*-**5**, respectively.

Characteristics of azobenzene dendron conjugates as side chains R in *trans*-**2**–**5** are as follows (Fig. 1b). Host *trans*-**2** possesses the dichotomous branching of two triethylene glycol monomethyl ether (TEG) chains[14a] at the *para* position of the

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Electronic Supplementary Information (ESI) available: Synthetic procedures of *trans*-**2**–**5** and additional data. See DOI: 10.1039/x0xx00000x

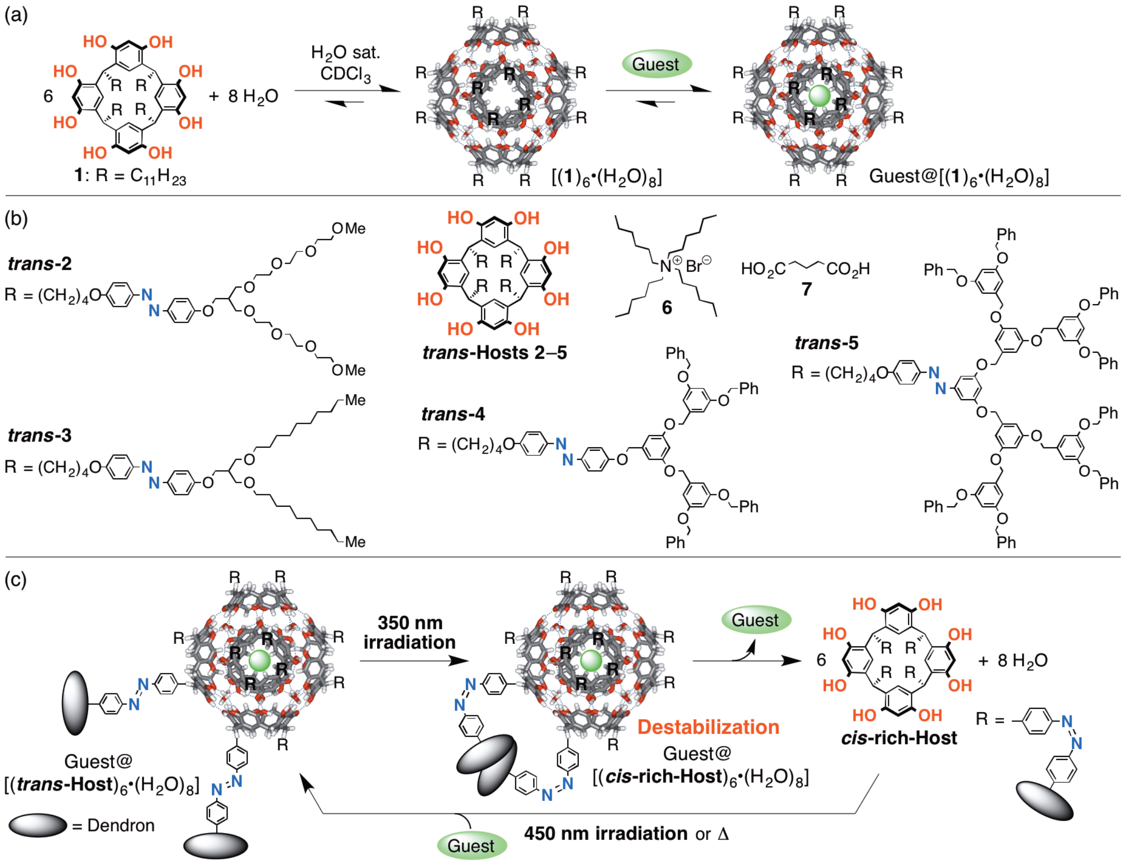
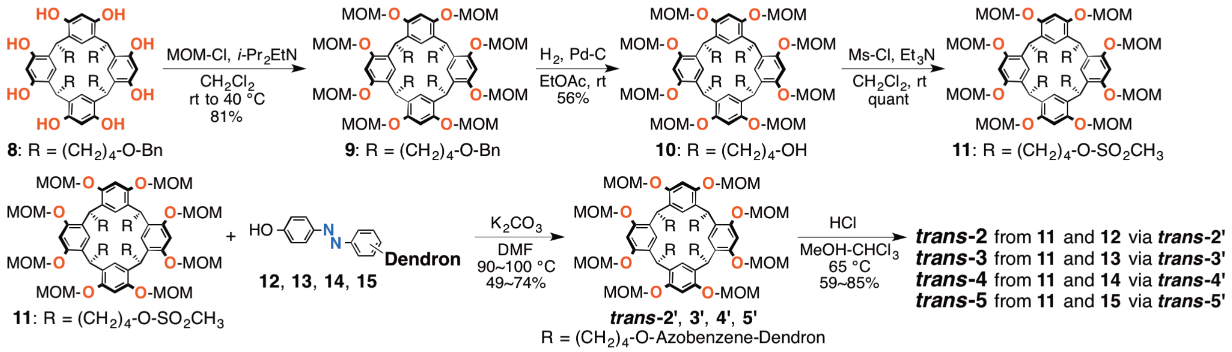


Fig. 1 (a) Self-assembly of **1** and H_2O into a hexameric capsule [(**1**)$_6$•(H_2O)$_8$] and guest encapsulation.[8,9] (b) Structures of hosts *trans*-**2**–**5** and guests **6** and **7**. (c) Schematic representation of assembly–disassembly–reassembly process of self-assembled hexameric capsules [(**2**–**5**)$_6$•(H_2O)$_8$] in conjunction with guest encapsulation–release–re-encapsulation by light stimuli.



Scheme 1 Synthesis of hosts *trans*-**2**–**5**.

azobenzene unit (Fig. 2a), affording a highly hydrophilic R. Host *trans*-**3** is a hydrophobic analogue of *trans*-**2** with alkyl chains in place of TEG chains. Host *trans*-**4** has a Frechét-type 2nd-generation benzyl dendron[14b] at the *para* position of the azobenzene unit, which would be a more sterically hindered but less hydrophilic R than that of *trans*-**2**. Host *trans*-**5** possesses two 2nd-generation benzyl dendrons at the *meta*

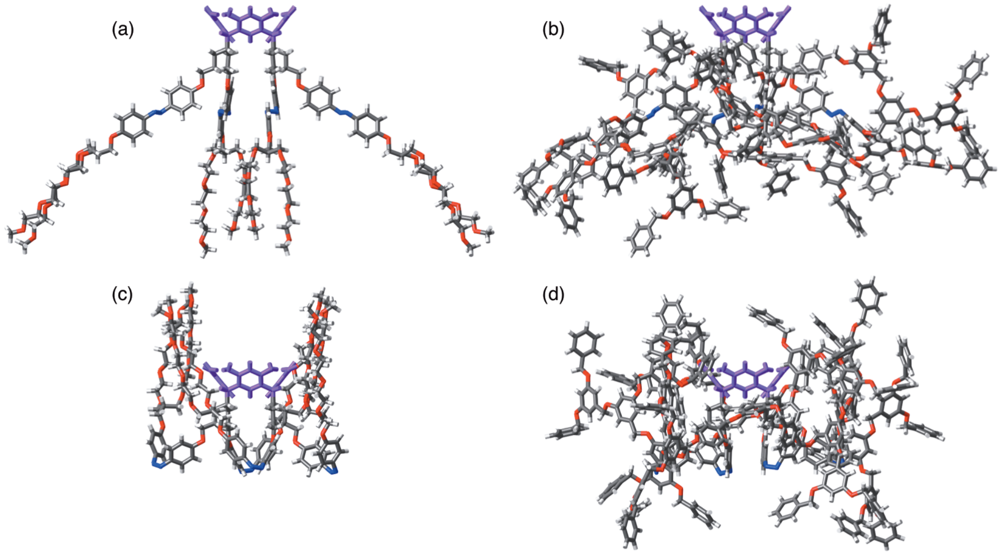


Fig. 2 Molecular models of (a) *trans*-**2**, (b) *trans*-**5**, (c) *cis*-**2**, and (d) *cis*-**5**, calculated at the MMFF level, wherein the calix[4]resorcinarene moiety is shown in purple color.

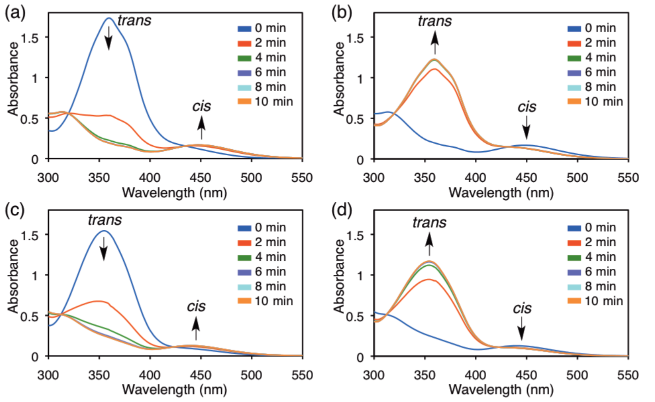


Fig. 3 UV–vis absorption spectral changes of (a) and (b) *trans*-**2** and (c) and (d) *trans*-**5** in CH_2Cl_2 (0.015 mM each), upon irradiation (a) and (c) at 350 nm for 0–10 min and then (b) and (d) at 450 nm for 0–10 min.[15]

positions of the azobenzene unit, which is a more sterically hindered R than that of *trans*-**4** (Fig. 2b).

Hosts **2**–**5** showed similar photoresponsive behavior (Fig. S2†). Fig. 3 shows the UV–vis spectral changes of *trans*-**2** and *trans*-**5** as representative hosts in CH_2Cl_2 ([host] = 0.015 mM) upon light irradiation. Irradiation of these solutions with 350 nm light[15] resulted in the photoisomerization to *cis*-rich **2** and **5** as average forms of four side chains R, as evidenced by a decrease in the absorbance at 350 nm and an increase in the absorbance at 450 nm (Fig. 3a and 3c).[12] In both cases, the photostationary states were reached within 6 min. Irradiation of the solutions with 450 nm light[15] resulted in the reversion to *trans*-rich **2** and **5** as average forms (Fig. 3b and 3d), wherein the photostationary states were also reached within 6 min.

Capsule formation with guest encapsulation

It is known that the encapsulation of $(n\text{-}C_6H_{13})_4NBr$ (**6**) in a calix[4]resorcinarene derivative is evidence for the formation of self-assembled hexameric capsule.[8,9] The *trans*:*cis* ratio as an average form of four side chains R at each photostationary state and the assembly–disassembly–reassembly process of self-assembled hexameric capsules in conjunction with guest encapsulation–release–re-encapsulation by light stimulus were monitored and determined by ^1H NMR analysis under the conditions of [host] = 6 mM and [**6**] = 3 mM or 9 mM as guest in H_2O-saturated $CDCl_3$ at 298 K.[8b,9b] The results are summarized in Table 1. In the same manner as for **1**,[8b,9b] hosts *trans*-**2**–**5** self-assembled into hexameric capsules with guest encapsulation to form **6**@[(*trans*-host)$_6$•$(H_2O)_8$]. The ^1H NMR signals of the terminal methyl protons of the encapsulated **6** were shifted upfield by 2.12~2.21 ppm relative to that of free **6**, owing to the ring-current effect of the aromatic cavities of the calix[4]resorcinarene subunits, as shown in Fig. 4a and 4f (see also Figs. S3, S9, S13, and S15†). When it is assumed that the host completely self-assembles into the hexameric capsule, namely $[\text{capsule}]_{\text{initial}}$ = 1 mM, the ratio of the **6**-encapsulating capsule concentration to the initial capsule concentration (encapsulation ratio) can be estimated. The encapsulation ratio decreased in the order **1** (86%) > *trans*-**3** (79%) > *trans*-**4**

(69%) > *trans*-**5** (58%) > *trans*-**2** (43%), indicating that the thermodynamic stability of [(*trans*-host)$_6$•(H_2O)$_8$] depends on the nature of the dendron moieties.

In contrast to **1**, which forms ($CHCl_3$)$_6$@[(**1**)$_6$•(H_2O)$_8$] in H_2O-saturated $CHCl_3$ in the absence of **6**,[9a,c] the encapsulation of $CHCl_3$ molecules was not observed for *trans*-**2** (Fig. S4†). In a manner similar to the behavior of **1**, the ^{1}H NMR signals of the phenolic hydroxy protons of *trans*-**3**, *trans*-**4**, and *trans*-**5** appeared at 9~10 ppm in H_2O-saturated $CDCl_3$ (Figs. S9, S13, and S15†), which are characteristics of the formation of self-assembled hexameric capsule.[8] However, the corresponding signals were not observed for *trans*-**2** (Fig. S3†). These results indicate that *trans*-**2** exists as a monomer in H_2O-saturated $CDCl_3$ in the absence of **6**, i.e., the formation of **6**@[(*trans*-**2**)$_6$•(H_2O)$_8$] is the guest-induced assembly by **6**.

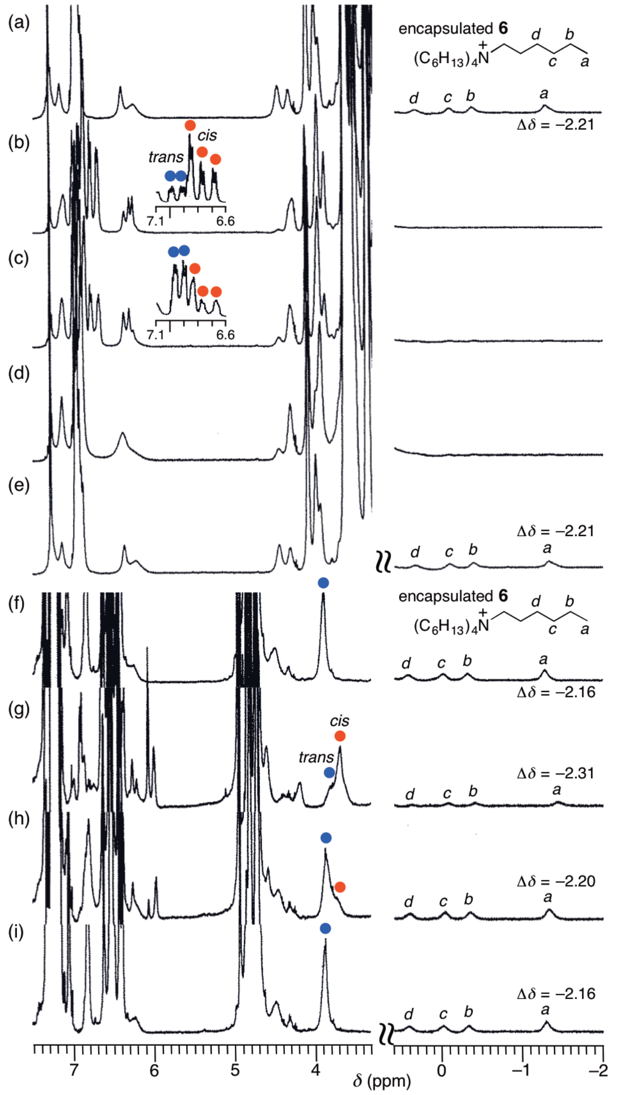


Fig. 4 ^{1}H NMR spectral changes (400 MHz, H_2O-saturated $CDCl_3$, 600 μL, 25 °C): [*trans*-**2**] = 6 mM and [**6**] = 9 mM, (a) before irradiation, (b) after irradiation at 350 nm for 5.5 h, (c) after irradiation at 450 nm for 3 h, (d) after heating at 50 °C for 3 h, and (e) upon addition of 50 μL of H_2O-saturated $CDCl_3$; [*trans*-**5**] = 6 mM and [**6**] = 3 mM, (f) before irradiation, (g) after irradiation at 350 nm for 7 h, (h) after irradiation at 450 nm for 3 h, and (i) after heating at 50 °C for 3 h. Blue and red circles are representative signals of *trans*- and *cis*-hosts, respectively. $\Delta\delta = \delta$(encapsulated **6**-Me) − δ(free **6**-Me).

Photoresponsive properties of guest@capsule

Irradiation of the solutions of **6**@[(*trans*-host)$_6$•(H_2O)$_8$] with 350 nm light resulted in the photoisomerization to *cis*-rich **2**–**5** as average forms. The results are summarized in Table 1 and Fig. 5. In contrast to the UV–vis spectral changes mentioned above, the photoisomerizations in the NMR studies were very slow because of the high concentrations of sample solutions; it took 330~420 min to reach the photostationary states of *cis*-rich **2**–**5**. Irradiation of **6**@[(*trans*-**2**)$_6$•(H_2O)$_8$] with 350 nm light showed a *trans*:*cis* ratio of 23:77 at the photostationary state (330 min) and the encapsulation ratio decreased from 43% to 0% (Fig. 4a vs 4b and Fig. 5a).† The photoisomerization to *cis*-rich **2** caused complete disassembly of the capsule and guest release. Upon irradiation for 30 min, 60 min, 90 min, 120 min, and 150 min, the encapsulation ratios (and average *trans*:*cis* ratios) changed dramatically to 32% (81:19), 20% (65:35), 7% (54:46), 3% (47:53), and 0% (40:60), respectively. Irradiation of the *cis*-rich **2** with 450 nm light resulted in the reversion to *trans*-rich **2** (*trans*:*cis* = 58:42 at the photostationary state (180 min)), but the encapsulation ratio remained at 0% (Fig. 4c). Heating this solution at 50 °C for 60 min completely restored all the *trans* form and the encapsulation ratio recovered to 32%.† Surprisingly, upon additional heating of this solution for 120 min, the encapsulation ratio again dropped to nearly 0%, despite the all *trans* form of **2** (Fig. 4d). Amazingly, upon addition of 50 μL of H_2O-saturated $CDCl_3$ to this solution (600 μL) at room temperature, the encapsulation ratio immediately recovered to 43%, as in the initial state (Fig. 4e). Host *trans*-**2** also formed a complex with glutaric acid (**7**) in a similar way to **1** (Fig. S20†).[7b,9d] This complex showed similar photo- and thermally-responsive behaviors to **6**@[(*trans*-**2**)$_6$•(H_2O)$_8$].[16]†

The results for **2** arise from the hydration ability of the highly hydrophilic TEG chains of **2**.[17] A possible mechanism is as follows. The TEG chains of *cis*-rich-**2** would expropriate H_2O molecules from [(*cis*-rich-**2**)$_6$•(H_2O)$_8$], leading to complete disassembly of the capsule. In a molecular model of *cis*-**2** (Fig. 2c), the TEG chains can be located adjacent to the calix[4]resorcinarene moiety. The photoinduced reversion to *trans*-rich **2** does not assist the reassembly of *trans*-rich **2** and H_2O molecules into the capsule, probably because of the strong hydration ability of the TEG chains. Heating the sample solution induces not only the thermal reversion to complete *trans*-**2** but also dehydration from TEG chains.[17] This restores [(*trans*-**2**)$_6$•(H_2O)$_8$] to some extent, with a 32% encapsulation ratio. However, prolonged heating of this solution would promote hydration of the TEG chains under thermodynamic control to expropriate H_2O molecules from [(*trans*-**2**)$_6$•(H_2O)$_8$], which consequently leads to complete disassembly of the capsule and guest release again. Finally, the addition of H_2O-saturated $CDCl_3$ to this solution restored [(*trans*-**2**)$_6$•(H_2O)$_8$] and the encapsulation ratio was recovered to 43%, as in the initial state.

This hypothesis would be supported by host **3** as the hydrophobic alkyl chain analogue of **2**, because the photo- and thermally-responsive behaviors of **6**@[(*trans*-**3**)$_6$•(H_2O)$_8$] are significantly different from those of **6**@[(*trans*-**2**)$_6$•(H_2O)$_8$] (Fig.

Table 1 Guest encapsulation and photoresponsive properties of hosts **2–5** in H_2O-saturated $CDCl_3$ at 298 K[a]

trans-host	**2**	**3**	**4**	**5**	**1**[b]
before irradiation					
encapsulation ratio (%)[c]	43	79	69	58	86
$\Delta\delta$ (ppm)[d]	−2.21	−2.13	−2.12	−2.16	−2.10
irradiation at 350 nm					
photostationary state (min)	330	420	420	420	
average *trans*:*cis* ratio	23:77	29:71	41:59	27:73	
encapsulation ratio (%)[c]	0[e]	79	68	34	
$\Delta\delta$ (ppm)[d]	na[f]	−2.25	−2.22	−2.31	
irradiation at 450 nm					
photostationary state (min)	180	180	180	180	
average *trans*:*cis* ratio	58:42	73:27	75:25	75:25	
encapsulation ratio (%)[c]	0	79	69	58	
$\Delta\delta$ (ppm)[d]	na	−2.18	−2.12	−2.20	
heating at 50 °C					
time (min)	60 (180)[g]	180	180	180	
average *trans*:*cis* ratio	100:0	100:0	100:0	100:0	
encapsulation ratio (%)[c]	32 (0)[g] (43)[h]	79	69	58	
$\Delta\delta$ (ppm)[d]	−2.21	−2.13	−2.12	−2.16	

[a] [**3**~**5**] = 6.0 mM and [$(n\text{-}C_6H_{13})_4NBr$ (**6**)] = 3.0 mM, and [**2**] = 6.0 mM and [**6**]= 9.0 mM. Photoirradiation was conducted with a 300 W Xe lamp through a color filter for 350 nm or 450 nm light. [b] See ref. 9b. [c] Ratio of the **6**-encapsulating capsule concentration to the initial capsule concentration, wherein it is assumed that the host completely self-assembles into the hexameric capsule: $[\text{capsule}]_{\text{initial}}$ = 1.0 mM. Errors are within 10%. [d] $\Delta\delta = \delta$(encapsulated **6**) – δ(free **6**) for methyl protons. [e] Irradiation time = 150 min: average *trans*:*cis* ratio = 40:60 and encapsulation ratio = 0%. [f] Irradiation time = 120 min: average *trans*:*cis* ratio = 47:53, encapsulation ratio = 3%, and $\Delta\delta$ = –2.25 ppm. [g] When heated at 50 °C for 180 min, the encapsulation ratio = 0%. [h] Upon addition of 50 μL of H_2O-saturated $CDCl_3$, the encapsulation ratio = 43% immediately.

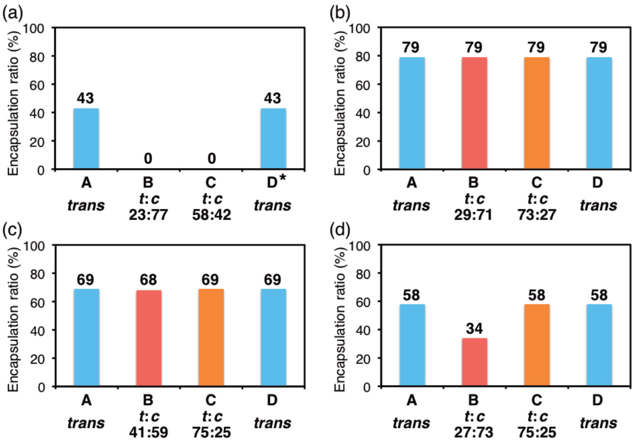


Fig. 5 Correlation between guest encapsulation ratio and average *trans*:*cis* ratio of (a) **2**, (b) **3**, (c) **4**, and (d) **5** in H_2O-saturated $CDCl_3$ under the conditions of **A**: before irradiation, **B**: after 350 nm irradiation, **C**: after 450 nm irradiation, and **D**: after heating at 50 °C. The details are shown in Table 1. *For state **D** of **2**, addition of 50 μL of H_2O-saturated $CDCl_3$ was required for the capsule reformation after heating.

5b vs 5a).† Irradiation of **6**@[(*trans*-**3**)$_6$•$(H_2O)_8$] with 350 nm light showed a *trans*:*cis* ratio of 29:71 at the photostationary state (420 min), but, in contrast to *cis*-rich **2**, the encapsulation ratio remained unchanged before and after irradiation (79%). After irradiation of the solution with 450 nm light and then heating at 50 °C for 180 min, the encapsulation ratio remained the same as for the initial state.

Next, benzyl dendron hosts **4** and **5**, which have more sterically hindered but less hydrophilic R than that of **2**, were investigated (Table 1 and Fig. 5c,d). Upon irradiation of **6**@[(*trans*-**4**)$_6$•$(H_2O)_8$] with 350 nm light, the *trans*:*cis* ratio changed to 41:59 at the photostationary state (420 min), but the encapsulation ratio remained virtually unchanged before and after irradiation (69% vs 68%) (Fig. 5c),† indicating inadequacy of the steric bulkiness of R in **4**. On the other hand, irradiation of **6**@[(*trans*-**5**)$_6$•$(H_2O)_8$] with 350 nm light showed a *trans*:*cis* ratio of 27:73 at the photostationary state (420 min) and the encapsulation ratio decreased from 58% to 34% (Fig. 4f vs 4g and Fig. 5d),† indicating a certain level of adequacy of the steric bulkiness of R in **5**. A molecular model of *cis*-**5** indicates that the benzyl dendrons overhang the calix[4]resorcinarene moiety (Fig. 2d). Coupled with the capsule destabilization upon *cis* photoisomerization, the ^{1}H NMR signal of the terminal methyl protons of encapsulated **6** was shifted further upfield by 0.15 ppm (Fig. 4g), suggesting a somewhat constrictive or distorted inner space of **6**@[(*cis*-rich-**5**)$_6$•(H$_2$O)$_8$] ($\Delta\delta$ = –2.31 ppm), compared with **6**@[(*trans*-**5**)$_6$•(H$_2$O)$_8$] ($\Delta\delta$ = –2.16 ppm). Irradiation of the *cis*-rich **5** solution with 450 nm light resulted in the reversion to *trans*-rich **5** (*trans*:*cis* = 75:25 at the photostationary state (180 min)), and the encapsulation ratio was restored to 58%, as in the initial state (Fig. 4h). Heating this solution at 50 °C for 180 min completely restored **6**@[(*trans*-**5**)$_6$•(H$_2$O)$_8$] to the initial state, and the 58% encapsulation ratio was maintained (Fig. 4i), in contrast to *trans*-**2**. Thus, in the benzyl dendron hosts **4** and **5**, correlation between the *cis* photoisomerization of the azobenzene dendron side chains R of the hosts and the consequent capsule destabilization leading to guest release largely depends on the steric bulkiness of the dendron moieties.

Conclusions

In summary, we have demonstrated that in the hydrogen-bonded self-assembled cubic capsules constructed from calix[4]resorcinarenes bearing various azobenzene dendron conjugates as side chains and H$_2$O molecules, the assembly–disassembly–reassembly process of the cubic capsule in conjunction with guest encapsulation–release–re-encapsulation can be controlled by light stimulus. Correlation between the *trans*-to-*cis* photoisomerization of the azobenzene dendron side chains of hosts and the resulting capsule destabilization leading to guest release largely depends on the steric bulkiness or hydrophilicity of the dendron moieties. Studies on the improvement of hosts' ability to provide a quick photoresponse are underway in our laboratory.

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