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Stabilization and Controlled Release of Reactive Molecules by Solid-State van der Waals Capsules

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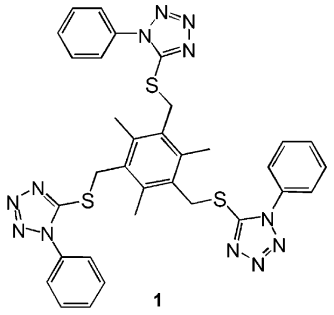
In nature, reactive molecules are physically isolated from the environment by biological hosts until they are required for a particular reaction.[1] To mimic the functionality of natural hosts, numerous molecular containers have been constructed[2–6] by means of hydrogen,[3] metal–ligand,[4] or covalent bonding[5,6] and some have been used to stabilize reactive and short-lived species within their internal cavities.[6,7] However, these materials can only be practically applied under conditions in which 1) the molecular container is rigid enough for guest storage at ambient temperature, 2) the release process is sufficiently sensitive to external stimuli, such as heat or chemical agents, 3) after releasing guests, the host molecules are easily separated from the system and can be recycled multiple times, and 4) the preparation of the host is relatively simple and low-cost. Therefore, the design and synthesis of new recyclable host matrices for both storage and controlled release of the reactive species, like natural hosts, remain a great challenge for supramolecular chemists.

Recently, solid or crystalline materials that exhibit the properties of molecular encapsulation have received considerable attention.[8] Among these materials, molecular capsules that are assembled by van der Waals (vdW) forces only have received particular attention.[9–12] It is evident that such vdW assemblies are not sufficiently stable in solution because solvation effects are usually stronger than the vdW forces holding the molecular capsules together. However, such solid-state capsules are known to bind neutral guest molecules within their interior cavities and, more importantly, the weak nature of vdW interactions can give these systems the flexibility necessary to allow guest capture and release under controlled conditions.[9] For instance, Ripmeester and co-workers reported that the controlled release of some gases by thermal programming can be accomplished in a *para-tert*-butylcalix[4]arene vdW capsule.[9e] Ananchenko and co-workers also showed that a vdW nanocapsule based on *para*-hexanoylcalix[4]arene can undergo efficient guest exchange in a single crystal at the proper temperature.[9f] In addition, the vdW hosts usually have the advantage of low cost and simple preparation in large quantities compared with solution-stable molecular containers.[3–7] These characteristics have encouraged us to explore the use of solid-state vdW capsules as host matrices for taming reactive guest species by molecular encapsulation and controlled release.

Another key issue concerning the storage function of vdW capsules is that the vdW structure must have a sufficient robustness to ensure effective isolation of the reactive species from each other. Therefore, we selected a tripodal host molecule, **1**, because it adopts an all-*syn* conformation



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and forms a thermodynamically favored cavity.[11a] In the crystal structure, two identical tripodal molecules can be arranged face-to-face with their pendant groups mutually interdigitated, and thus create a capsule-shaped dimer that accommodates the guest molecule. To the best of our knowledge, this construction mode, which is based on the complementary shape of two identical tripodal molecules, has rarely been adopted for the formation of vdW capsules,[11] although some examples involving hydrogen bonding or electrostatic interactions have been reported.[12] Such an interdigitated structure should certainly be capable of providing steric hindrance great enough to effectively prevent the escape of the guest molecule and is thus expected to endow the capsule with the necessary rigidity to stabilize reactive molecules under ordinary conditions.

Herein, we show that the dimeric capsule $(\mathbf{1})_2$, assembled from a pair of tripodal host **1** molecules by vdW forces, can be used to stabilize a series of reactive appropriately sized molecules in the crystalline state (Scheme 1). Within the

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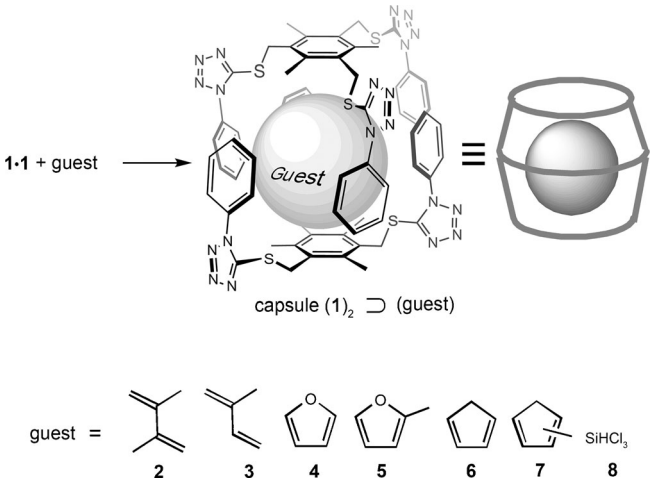

Scheme 1. Synthesis of capsule compound $(\mathbf{1})_2\supset$guest with various reactive guests.

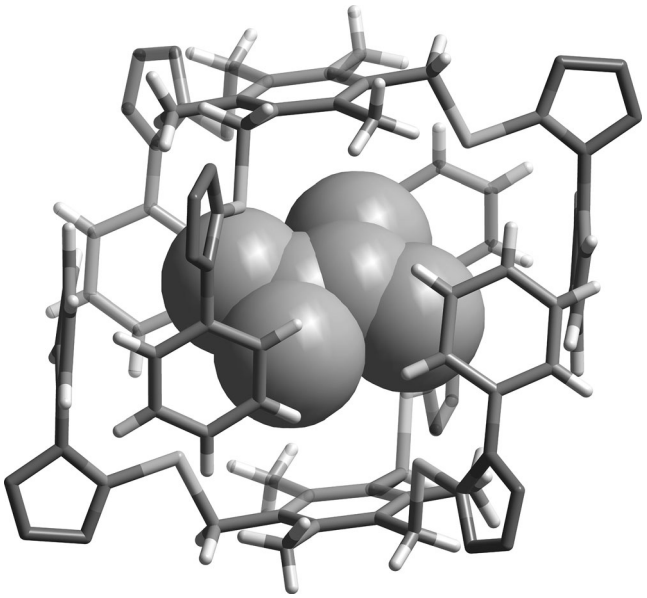

Figure 1. View of the dimeric capsule $(\mathbf{1})_2\supset\mathbf{2}$. Encapsulated **2** is shown as a space-filling model and its hydrogen atoms are not represented for clarity.

solid-state capsule, the homodimerization of cyclopentadiene and the hydrolysis of trichlorosilane were suppressed, even under relatively harsh conditions. More importantly, these guest molecules can be controllably released for further chemical reaction into liquid media by thermal programming and the insoluble host molecules are easily separated and reused.

The host molecule, **1**, was readily synthesized according to the literature in high yield.[11a] The dimeric capsule, $(\mathbf{1})_2\supset\mathbf{2}$, was prepared by adding 2,3-dimethyl-1,3-butadiene (**2**) to a solution of **1** in dichloromethane and was isolated as colorless block crystals by slow evaporation of the solvent at room temperature. Single-crystal X-ray analysis shows a dimeric capsule structure in the unit cell.[13] As shown in Figure 1, guest **2** is disordered between methyl and vinyl, and is sealed in the cavity of the capsule by its hydrophobic walls without any obvious interaction between the host and guest. ^{1}H NMR spectroscopic measurement of the single-crystal samples dissolved in $CDCl_3$ shows that the ratio of the host to the guest is 2:1. Alternatively, this inclusion compound can also be readily prepared by directly mixing concentrated solutions of **1** with excess **2** in dichloromethane. The resultant white precipitate is a nonstoichiometric compound in which approximately 64% of the capsules contain the guest molecule.[14] Despite the different host–guest ratios, both the single-crystal and the nonstoichiometric compounds are denoted identically by $(\mathbf{1})_2\supset\mathbf{2}$ to emphasize the encapsulation behavior of the molecular capsule.

Similarly to the procedure for the synthesis of $(\mathbf{1})_2\supset\mathbf{2}$, nearly identical capsule compounds were synthesized in high yields when isoprene (**3**), furan (**4**), and 2-methylfuran (**5**) were employed as guests instead of **2**. These molecules were selected because of their moderate size, which is well matched to that of the cavity in the capsule.[11a] Single-crystal X-ray analysis[13] and X-ray powder diffraction (XRPD) confirmed that the compounds obtained have similar structures, all of which consist of dimeric capsules as was observed for $(\mathbf{1})_2\supset\mathbf{2}$ (see the Supporting Information). Although **2**–**5** can be handled in air at ambient temperature, they are all potentially reactive, forming polymeric peroxides, in particular on exposure to light.[15] Interestingly, the compounds obtained show exceptional stability toward heat, atmospheric oxidation, and light when crystallized with host molecule **1** to form the inclusion compounds $(\mathbf{1})_2\supset\mathbf{G}$ (in which $\mathbf{G}=\mathbf{2}$, **3**, **4**, or **5**). At room temperature, these compounds were stable in air without release of the guest molecules for a period of several weeks. For compounds with volatile guests, **2**–**5**, a slight weight loss occurred at temperatures was above 40°C, but this process was quite slow, unless the temperature exceeded 100°C. For instance, compounds $(\mathbf{1})_2\supset\mathbf{2}$ and $(\mathbf{1})_2\supset\mathbf{4}$ retain approximately 90% of the guest molecules even after 12 h at 60°C. When exposed to sunlight in air for several days, the corresponding inclusion compounds did not show any changes in terms of their color or ^{1}H NMR spectra (see the Supporting Information).

The effects of molecular encapsulation were unambiguously demonstrated by the stabilization of the more reactive cyclopentadiene (**6**), which rapidly homodimerize under ordinary conditions
.[16] After adding a concentrated solution of **1** in dichloromethane to freshly prepared **6**, the crystalline precipitate formed was filtered off and dried immediately to obtain the corresponding compound, $(\mathbf{1})_2\supset\mathbf{6}$, the crystal form of which was confirmed by its XRPD pattern (Figure 2a). ^{1}H NMR spectroscopic measurements demonstrated that the guest occupancy in the capsule was 72% (Figure 2b). However, attempts to grow single crystals of $(\mathbf{1})_2\supset\mathbf{6}$ failed because dicyclopentadiene (**9**), produced by the dimerization of **6**, led to a different type of crystal packing.[11a] Similarly to $(\mathbf{1})_2\supset\mathbf{2}$, the molecules of **6** in the capsule possessed exceptional stability at elevated temperature, with approximately 92, 77,

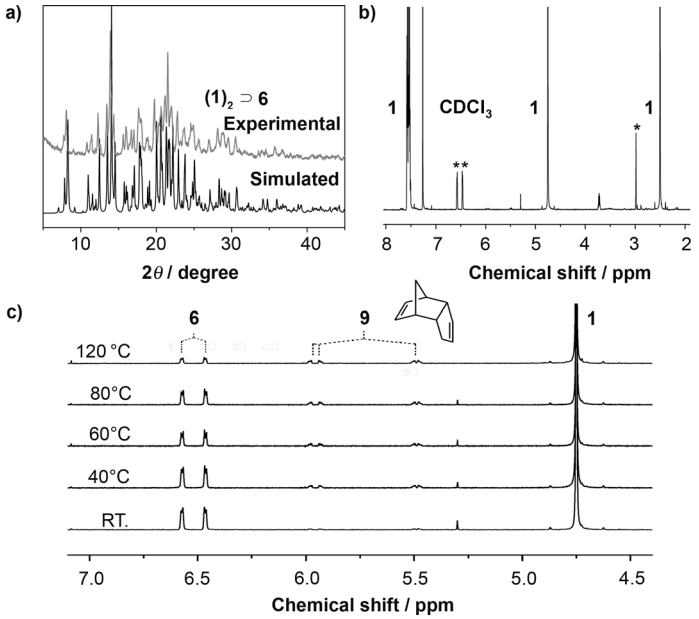

Figure 2. a) XRPD patterns for $(\mathbf{1})_2\supset\mathbf{6}$. Simulated data are generated from single-crystal X-ray diffraction data of $(\mathbf{1})_2\supset\mathbf{5}$. b) ^{1}H NMR spectrum of $(\mathbf{1})_2\supset\mathbf{6}$ dissolved in $CDCl_3$. The signals of **6** are marked with *. c) Partial ^{1}H NMR spectra of $(\mathbf{1})_2\supset\mathbf{6}$, which was treated at different temperatures for 12 h under vacuum.

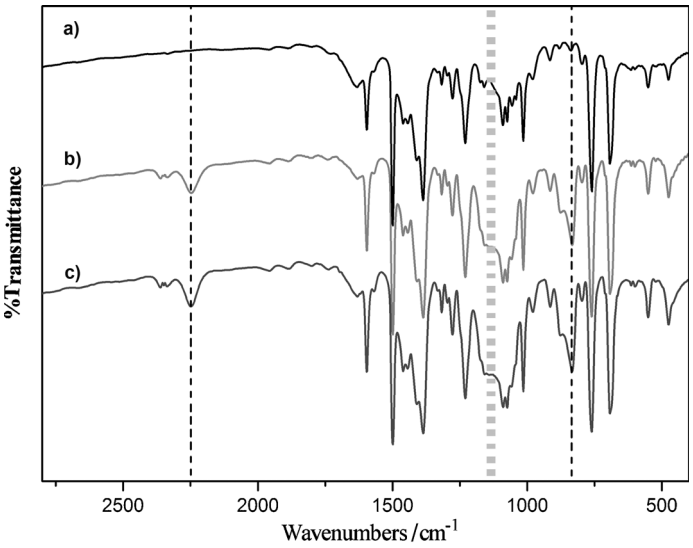

Figure 3. IR spectra of a) $(\mathbf{1})_2\supset CHCl_3$,[17] b) $(\mathbf{1})_2\supset\mathbf{8}$, and c) the solid $(\mathbf{1})_2\supset\mathbf{8}$ in water at 70 °C for 48 h.

and 73 % of the guest molecule retained after treatment under vacuum for 12 h at 40, 60, and 80 °C, respectively (Figure 2c). Taking the high reactivity and low boiling point of **6** (approximately 40 °C) into account, it is amazing that approximately 30 % of guest **6** was still contained within the crystalline capsule compound after treatment at 120 °C for 12 h (Figure S7 in the Supporting Information). Moreover, the observation that the amount of **9** present failed to increase even with the elevation of the temperature implies the effective isolation of **6** by the capsule (Figure 2c). As an analogue of **6**, the freshly prepared methylcyclopentadiene (**7**), an equimolar mixture of 1-methyl and 2-methylcyclopentadiene, was also successfully included in the dimeric capsule, thus suggesting the versatility of this encapsulation process (Figure S13 in the Supporting Information).

More importantly, the reactive molecules encapsulated can be controllably released into the proper liquid medium by thermal programming. Firstly, because of the highly hydrophobic nature of **1**, the entrapped guest can be efficiently protected from surrounding water molecules by the capsule. Compound $(\mathbf{1})_2\supset$trichlorosilane (**8**) represents an example of this effect. The hydrolysis of **8** is completely inhibited even when $(\mathbf{1})_2\supset\mathbf{8}$ was exposed to hot water for days, as confirmed by the characteristic IR signals of **8** at $\tilde{\nu}=2248$, 1060, and 833 cm^{-1} (Figure 3). By contrast, when immersed in methanol, the capsule compounds can release the guest molecules through the transformation of its crystal form into another undefined form (Figure S6 in the Supporting Information). Although slightly soluble in pure methanol, host **1** was insoluble in a methanol/water mixed system, even when the volumetric proportion of methanol was 80 % (Figure S14 in the Supporting Information). Consequently, the CH_3OH/H_2O system is an ideal liquid medium, in which the capsule compound is expected to release the guest molecules in a heterogeneous manner at a given temperature by adjusting the composition of the CH_3OH/H_2O system. As shown in Figure 4, the percentage of guest **6** released from $(\mathbf{1})_2\supset\mathbf{6}$ differed greatly with temperature and composition of the CH_3OH/H_2O medium. For example, $(\mathbf{1})_2\supset\mathbf{6}$ remained intact at room temperature but completely released its guest molecules at 60 °C within 5 h in CH_3OH/H_2O (v/v = 7:3). These results suggest a convenient way to control the release of guest molecules for further reaction.

To investigate the temperature-controlled initiation of the reaction of **6** in the liquid medium, excess dimethyl fumarate was added to a 6:4 mixture of CD_3OD and D_2O. At room temperature, no perceptible NMR signals attributable

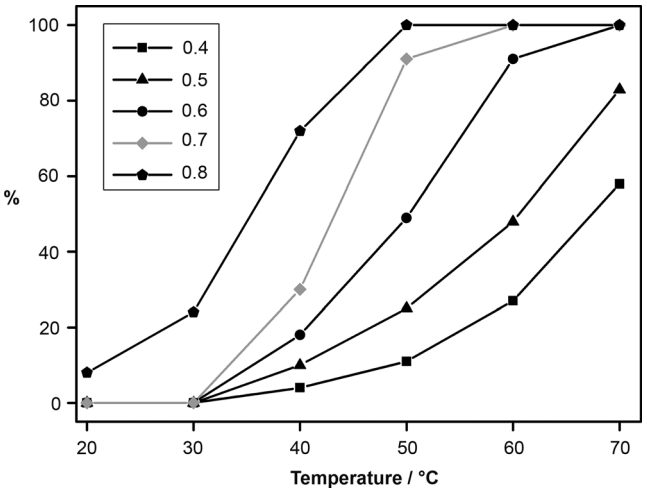

Figure 4. Percentage of **6** released from solid $(\mathbf{1})_2\supset\mathbf{6}$ at different temperatures after 5 h. The lines correspond to CH_3OH/H_2O media with different volume ratios varying from 0.4 to 0.8.

to guest **6** were found, whereas the formation of the Diels–Alder adduct of **6** and dimethyl fumarate, dimethyl bicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylate (**10**), was observed upon heating the system to 50 °C (Figure 5). The appearance of

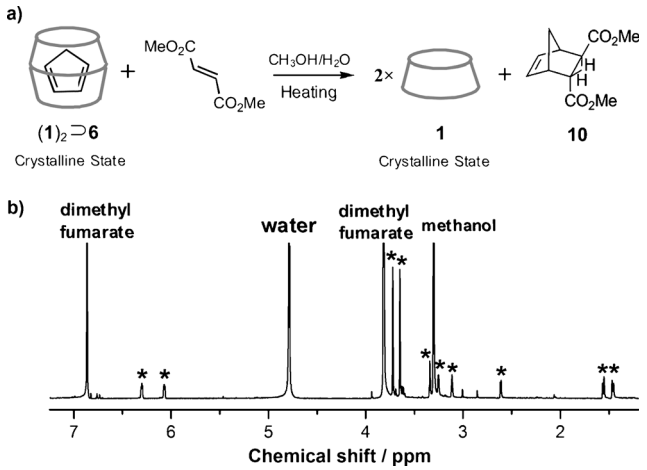

Figure 5. a) Reaction between the crystalline capsule compound $(\mathbf{1})_2\supset\mathbf{6}$ and dimethyl fumarate in CH_3OH/H_2O mixed medium at elevated temperature. b) ^1H NMR spectrum of the reaction mixture in the presence of excess dimethyl fumarate in CD_3OD/D_2O (v/v = 5:5) at 50 °C after 12 h. The signals of Diels–Alder product **10** are marked with *.

ten resonances in the ^1H NMR spectrum was in good agreement with the expected product **10**.[18] Meanwhile, no NMR signals attributable to **1** were found after the reaction (Figure 5b), which implies that **1** is insoluble in this solution system and does not influence the purity of the reaction product. The solid obtained after filtration and drying was proven to be pure **1** and can be reused as is.

In summary, we have shown that the isolated environment provided by a solid-state van der Waals capsule with an interdigitated structure can efficiently stabilize a series of reactive molecules, such as cyclopentadiene and trichlorosilane, in the crystalline state, even under relatively harsh conditions. More importantly, in CH_3OH/H_2O liquid medium, the capsule compound can be stimulated to conveniently release its guest molecules by adjusting the temperature of the system, and the host molecules are easily separated and reused because of their insolubility in CH_3OH/H_2O solution. As a representative application, the capsule can stabilize molecules of cyclopentadiene at ambient temperature and then controllably release it upon heating for further reaction to produce a Diels–Alder adduct. This work demonstrates that stabilization and extraordinary control over reactive molecules can be achieved by solid-state vdW assemblies which are facilely prepared and recycled. Furthermore, the approach could be generalized to a wide variety of different reactive molecules through rational tailoring of the supramolecular hosts.

Experimental Section

Single-crystal X-ray diffraction data were collected on a Bruker Smart APEX II CCD-based diffractometer by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). X-ray power diffraction (XRPD) patterns were collected in a sealed glass capillary on a Rigaku DMAX 2500 powder diffractometer with ultra 18 kW Cu radiation. ^1H NMR data were collected by using Bruker AVANCE III 600 spectrometers. See the Supporting Information for more experimental details.

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Keywords: host–guest systems · inclusion compounds · solid-state structures · supramolecular chemistry · X-ray diffraction

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