

A two-dimensional hydrogen bonded organic framework self-assembled from a three-fold symmetric carbamate†

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A flexible organic sheet spontaneously assembled under mild conditions from a tri-carbamate. By introducing cyclohexyl side chains as 'pillars' between the sheets, a hydrogen bonded organic framework was formed which displayed a capacity for accommodating and releasing guest molecules. The guest size/shape selectivity of the lamellar framework was demonstrated by testing with various guests.

Hydrogen bonded organic frameworks (HOFs) have attracted significant attention due to their promising applications in gas storage¹ and separation.² Compared to widely used coordination interactions in the study of host frameworks,³ hydrogen bonds are weaker and conformationally more flexible. They are therefore more difficult to control. However, Nature chooses to use hydrogen bonds to achieve sophisticated functions and complex tasks such as enzymatic catalysis and receptor activation demonstrating the power of these flexible systems.

Using hydrogen bonds, our research group has recently discovered and studied a series of chiral organic sheets that were constructed from achiral molecules with stereogenic axes (*supramolecular atropisomer*).⁴ Similar to the β -sheets of polypeptides, the hydrogen bonded backbone of the chiral sheet does not involve side chains. Side chains typically allow introduction of different functional groups with suitable sizes onto the flexible sheet platform. Thus, the sheet can achieve a desired function by tuning the properties with these functional groups.

Herein, we report a flexible organic lamellar framework with the capacity of accommodating guest molecules by introducing cyclohexyl side chains as "pillars" between the sheets. There are only a few lamellar organic host systems reported in the literature, for example, the GS sheet (guanidinium ion and sulfonate network)⁵

and organic laminate (ammonium ion and carboxylate network).^{6,7} Featured with an exceptional structural flexibility and a high surface area, soft layered materials have shown applications in host-guest chemistry, clay mimics, chiral resolution and photopolymerization reactions.^{5–10}

A facile and reliable way to obtain the crystalline sheets starts with injecting an organic solution of benzene-1,3,5-triyl tris-(cyclohexylcarbamate) **1** into water with stirring. This process was then accomplished by evaporating the solvent mixture under ambient conditions. TEM images showed that the size of the organic sheets obtained by this method was up to several square micrometers (see ESI†). A small amount of nanoscale crystals of tri-carbamate **1** were also observed by TEM at the same time. As illustrated by the synthetic method, this layered crystalline material is water stable. Even when the lamellar material was boiled in water for 12 h, the structure remained intact. The water stability is an important property required for many applications such as gas storage.

High quality crystals of tri-carbamate **1**·(THF) with guest molecules were obtained by slowly evaporating a THF tri-carbamate solution. The ¹H NMR spectrum showed that the ratio of the tri-carbamate host to THF guest molecules in the crystals is 1:1 (see ESI†). The lamellar crystal structure was confirmed by X-ray crystallography as shown in Fig. 1. The structure consists of hydrogen bonded sheets extended in the crystallographic *ab* plane through a fully saturated hydrogen bonded network. Within the sheet, each tri-carbamate molecule is connected to four neighbors through six intermolecular hydrogen bonds (Fig. 1b, each cyclohexyl side chain is replaced with a carbon atom for simplicity). The hydrogen bonding connection is different from the three reported sister sheet structures, in which each molecule is connected to five^{4b} or six^{4a} neighbors. The average length of the six hydrogen bonds between N–H and C=O groups of the three carbamates in **1**·(THF) is 2.86 Å. This length falls between those found in the sister hydrogen bonded lamellar structures of *N,N',N''*-tris(*n*-octyl)-benzene-1,3,5-tricarboxamide (2.83 Å)^{4a} and benzene-1,3,5-triyl tris(propylcarbamate) (2.90 Å).^{4b} The small difference in length reveals that the sheet backbone hydrogen bonds are as strong as

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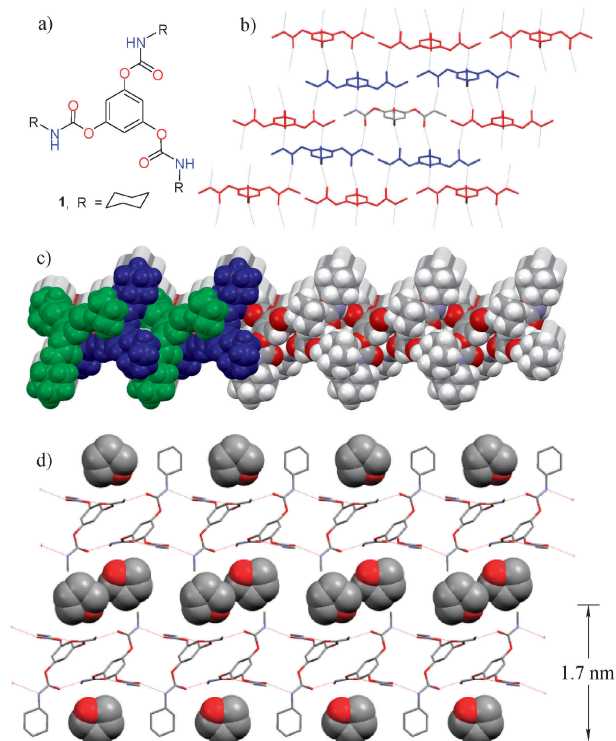


Fig. 1 Structural formula: (a) benzene-1,3,5-triyl tris(cyclohexyl-carbamate), **1**. Crystal structure of **1**·(THF); (b) a top view of the chiral sheet backbone (colors are introduced to illustrate the hydrogen bonding networks); (c) a side view of the space-filling model of the sheet showing the surfaces and edges. Only 100 (10 × 10) molecules are shown for simplicity. Four tri-carbamate molecules are in green or blue color to show the orientation of the molecules and their cyclohexyl side chains; (d) a side view of the capped sticks model showing two layers of the sheet with the THF guests in the space-filling model. (Hydrogen atoms are omitted, and the chains inlaid in the sheets and between the two layers are replaced with carbon atoms for simplicity.)

those two reported. In the sheet structure, two nearest neighboring molecules formed complementary conformations such that three cyclic alkyl arms of one molecule is “up-up-down” and the other is “down-down-up”, with regard to the hydrogen bonded sheet planes (Fig. 1c). Noticeably, the two cyclohexyl groups of each tri-carbamate on the same side of the sheet are partially inlaid within the surfaces of the sheet to fill the gaps within the hydrogen bonded network. The third cyclohexyl group stands up from the surface of the sheet and becomes a pillar between the sheets. The interlayer spaces between these cyclohexyl pillars are occupied by the disordered guest THF molecules (Fig. 1d).

The crystals **1**·(THF) were also readily obtained from 1:1 mixtures of THF with diethyl ether, pentane, ethyl acetate, acetonitrile, or toluene, respectively. The preference of THF as a guest is presumable mainly because the size and shape of the THF molecule fits well with the interlayer spaces created by the cyclohexyl pillars. Furthermore, although there is no hydrogen bonding between the host and guest, the oxygen atoms of nearest neighboring THF guests point towards the polar hydrogen bonded networks in the opposite direction. Thus, the dipole-dipole interactions between the host and guest probably offer additional stability for the encapsulation of

Table 1 Guest selectivity experiments of the lamellar material

Entry	Solvent (ratio)	Crystal
1	THF ^a	1 ·(THF)
2	C ₆ H ₆ –CH ₃ CN (1:2)	1 ·(C ₆ H ₆)
3	C ₆ H ₁₂ –acetone (1:2)	1 ·(C ₆ H ₁₂)
4	C ₅ H ₁₀ –EA–CH ₃ CN (1:2:2)	1 ·(C ₅ H ₁₀)
5	THF–C ₆ H ₆ –C ₆ H ₁₂ –C ₅ H ₁₀ (1:1:1:1)	1 ·(0.92THF·0.03C ₆ H ₆ · 0.02C ₆ H ₁₂ ·0.03C ₅ H ₁₀) ^b
6	THF–C ₆ H ₆ (1:1)	1 ·(0.76THF·0.24C ₆ H ₆) ^c

^a Wet THF contains 5% water. ^b The guest ratio was determined by ¹H NMR. ^c The guest ratio was determined by ¹H NMR, and it is an average of three experiments: THF ratio 0.76 = (74.4% + 76.7% + 78.3%)/3.

THF between the polar hydrogen bonded networks and non-polar cyclohexyl groups.

Table 1 presents more guest selectivity experiments. When benzene, which is also close to the cyclohexyl pillars in size and shape, was used in the 1:2 solvent mixture of CH₃CN or acetone, new crystals of **1**·(C₆H₆) with benzene as guests formed. Crystals of **1**·(C₆H₁₂) with cyclohexane guests were obtained from a mixture of cyclohexane and acetone (1:2), and **1**·(C₅H₁₀) with cyclopentane guests were successfully obtained from a solvent mixture of cyclopentane, ethyl acetate and CH₃CN (1:2:2). Moreover, when the above four guests were used in the same ratio as the solvent mixture to let them compete with each other, the crystals of tri-carbamate **1** accommodating all four guests were obtained with a high preference for THF (Table 1, entry 5). When a 1:1 mixture of THF and benzene was used, crystals of **1**·(0.76THF·0.24C₆H₆) were obtained. THF was the most favorite guest, which was consistent with our above hypothesis about the size/shape selectivity and polarity match.

Although the sizes and shapes of all the four guests (THF, C₆H₆, C₆H₁₂, and C₅H₁₀) are close to the cyclohexyl pillars, none of them are the same. The flexibility of the hydrogen bonded sheet plays a key role in accommodating these guest molecules. Without changing the sheet backbone, the cell parameters of the crystal vary up to about 12% (Table S1 in ESI†).

The crystals of **1**·(THF) can slowly release the THF guest molecules under ambient conditions. The powder XRD spectra show the appearance of a new set of peaks after one week of exposure of **1**·(THF) to the atmosphere together with the original peaks (Fig. 2). The thermal properties of the crystals of **1**·(THF) were then examined by DSC. As shown in the ESI†, an endothermic peak was found at around 130 °C, which corresponded to the volatilization of THF molecules from the crystals. Thus, the fresh crystals of **1**·(THF) were heated at 140 °C for 2 h. It was verified by ¹H NMR that all the guest molecules were completely removed. The powder XRD spectra showed the appearance of the new set of peaks with complete disappearance of the original peaks after heating. The characteristic 2 theta peak of **1**·(THF) at 6.5° shifted to 7.7° showing that the interlayer distance between the hydrogen bonded sheets was reduced to about 2 Å due to the loss of guests. All the peaks in the new powder pattern matched well with those of the ground fresh crystals grown in acetonitrile showing an excellent retention of crystallinity. Pictures of two planar crystals of **1**·(THF) and **1** are included in the ESI†. Furthermore, the tri-carbamate solid that was obtained directly from synthesis has the same powder pattern as that of the guest-free crystals grown in acetonitrile.

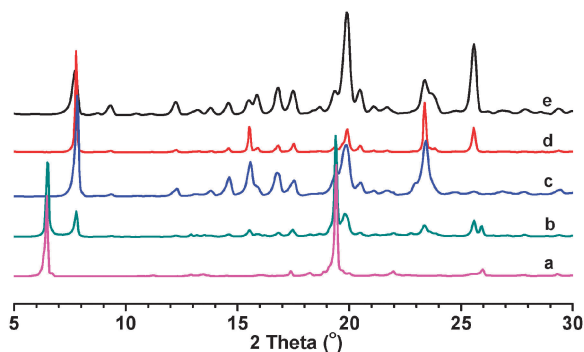


Fig. 2 Powder XRD: (a) fresh crystals of **1**·(THF) obtained by the slow evaporation of the wet THF solution; (b) crystals of **1**·(THF) after 1 week under ambient conditions showing the presence of crystals **1**; (c) crystals of **1**·(THF) with THF guests completely removed by heating at 140 °C for 2 h; (d) single crystals of **1** grown in a CH₃CN solution; (e) the powder obtained directly from the synthesis without further processing.

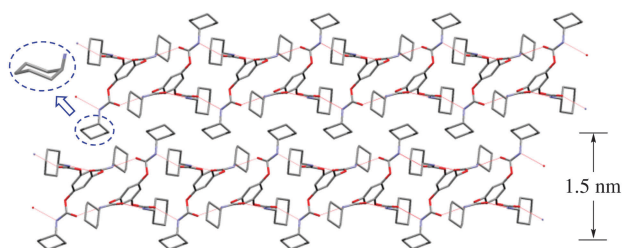


Fig. 3 A side view showing two layers of the sheets in crystal **1** for comparison with Fig. 1d. The two blue circles on the upper left corner show the cyclohexyl group with about 90° difference in view angle.

The single crystal X-ray data of guest-free tri-carbamate **1** from acetonitrile solution were collected for comparison. The crystal **1** and the crystals with guests all have the same hydrogen bond network (see ESI†). As shown in Fig. 3 and 1d, the basic framework **1** exhibits the same sheet package pattern as that of the crystal **1**·(THF). While the cyclohexyl pillars are connected to the sheet by equatorial bonds to support the interlayer space for accommodating guests in **1**·(THF), those cyclohexyl rings in crystals of **1** are linked to the sheet with axial bonds to occupy all the interlayer space. To achieve close packing, the neighboring sheets of guest-free crystals of **1** are packed like meshing gears. Consequently, the sheets in **1** are separated from each other by about 1.5 nm, approximately 2 Å less than that in **1**·(THF). The volume of the unit cell of **1**·(THF) is about 15% larger than that of the crystal **1** without guest molecules. The average hydrogen bond in **1**·(THF), whose data were collected at 220 K, is even 0.01 Å shorter than that of guest-free **1** collected at 100 K revealing that the sheet backbone hydrogen bonds of **1**·(THF) are slightly stronger.

Upon immersing freshly grown guest-free crystals of **1** or desolvated crystals from **1**·(guest) in a nearly saturated THF solution of **1**, they were able to absorb the solvent to form **1**·(THF). The crystals of **1** absorbed nearly 100% of the THF guest (**1**–THF ratio, 1:1) in two days and about 80% in two hours (see ESI†). The absorption and desorption processes were repeated four times without an obvious loss in efficiency.

In conclusion, continuing our previous work on the self-assembly of molecules with a threefold rotational symmetry^{4,11,12} into organic

sheets, we reveal that the hydrogen bonded organic sheet can be further extended to the three-armed carbamates with cyclohexyl side chains. The sheet structure remains unaltered with substantial variation in the connection pattern showing the generality of the two-dimensional hydrogen bonded network. More importantly, this water stable clay-like material has created a cavity environment and displayed guest size/shape selectivity and dynamic host–guest responses.^{8a} The lamellar material was able to be transferred to a new crystalline state by absorbing the guest molecules, and then desolvated and returned to its guest-free crystalline form. The facile synthesis, water stability, and properties of selectively accommodating guests demonstrate potential applications of the reusable organic clay in molecular storage, separation, and materials science.

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