



Cite this: *Chem. Commun.*, 2016, 52, 9781

Received 24th May 2016,
Accepted 6th July 2016

DOI: 10.1039/c6cc04310k

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We demonstrate, for the first time, that a hydrogen-bonded low-density organic framework can be applied as a platform to achieve periodic alignment of paired molecules of C_{60} , which is the smallest example of a finite-numbered cluster of C_{60} . The framework is a layered assembly of a hydrogen-bonded 2D hexagonal network (LA-H-HexNet) composed of dodecadihydrotribenzo[18]annulene derivatives.

Dimensionally-controlled assemblies of functional π -conjugated molecules are of substantial interest from optical and electronic viewpoints. In particular, those of fullerene (C_{60}) derivatives have been intensively studied because of their specific optoelectronic properties such as a significant electron accepting ability originating in the spherical π -system.^{1,2}

Crystalline lattices are a potential platform to achieve controlled arrangements of C_{60} molecules. To date, molecularly-isolated arrangements (Fig. 1a)³ and one-dimensionally (1-D) (Fig. 1b)^{2d,4} or two-dimensionally (2-D) (Fig. 1c)⁵ aligned infinite structures of C_{60} have been reported in various crystalline frameworks. On the other hand, isolated arrangements of finite-numbered clusters of C_{60} molecules are still challenging to construct due to the lack of a general methodology, although seven examples have been reported for an isolated-dimer structure of C_{60} (Fig. 1d), which is the smallest example of a finite-numbered cluster.^{6,7}

In this study, we propose that a hydrogen-bonded low density framework can be applied as a platform to construct an isolated arrangement of finite-numbered clusters of C_{60} molecules. Previously, we have reported that C_3 -symmetric cyclic planar π -conjugated molecules with three 4,4'-dicarboxy-*o*-terphenyl moieties can form hydrogen-bonded 2D hexagonal network (H-HexNet) structures with multiple voids and that the H-HexNet sheets

Alignment of paired molecules of C_{60} within a hexagonal platform networked through hydrogen-bonds†

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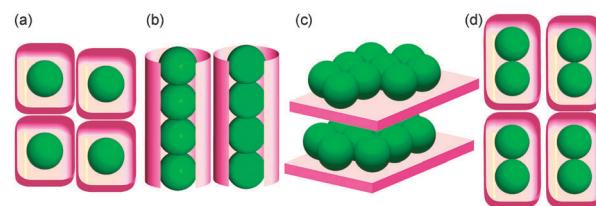


Fig. 1 Schematic representation of dimensionally-controlled alignments of C_{60} . (a) Molecularly-isolated, (b) one-dimensional, (c) two-dimensional, and (d) finite-number-isolated arrangements.

are stacked without interpenetration to give low-density layered assemblies of H-HexNets (LA-H-HexNets).⁸ In particular, a H-HexNet of dodecadihydrotribenzo[18]annulene derivative **T18** (Fig. 2)^{8a,c} can provide a space suitable for aligning C_{60} molecules.

T18 was synthesised using our reported method^{8a} and was initially crystallized *via* slow evaporation of a mixed solution of *o*-dichlorobenzene (*o*DCB) and *N,N*-dimethylformamide (DMF) at 50 °C to yield *P1* crystal **T18**-*o*DCB as shown in Fig. 3a–c.‡

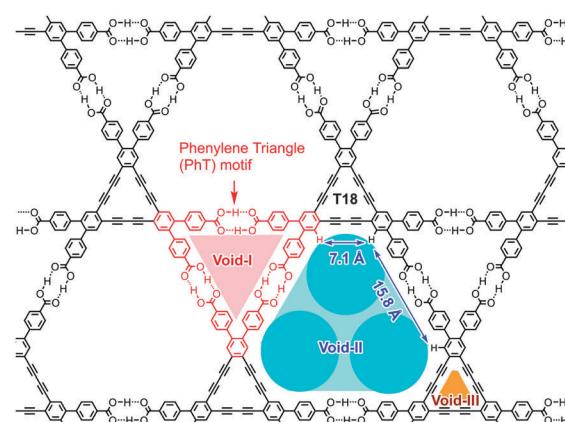


Fig. 2 Multi-porous, hydrogen-bonded hexagonal network (H-HexNet) sheet composed of **T18**. The sheet contains void-I, which is surrounded by the phenylene triangle (PhT) motif, void-II with the largest non-regular hexagonal space, and void-III intrinsically-generated in molecule **T18**. Void-II has a space large enough to accommodate three C_{60} molecules.

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† Electronic supplementary information (ESI) available: Experimental details, CSD searches. CCDC 1481305, 1481306 and 1487277. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc04310k



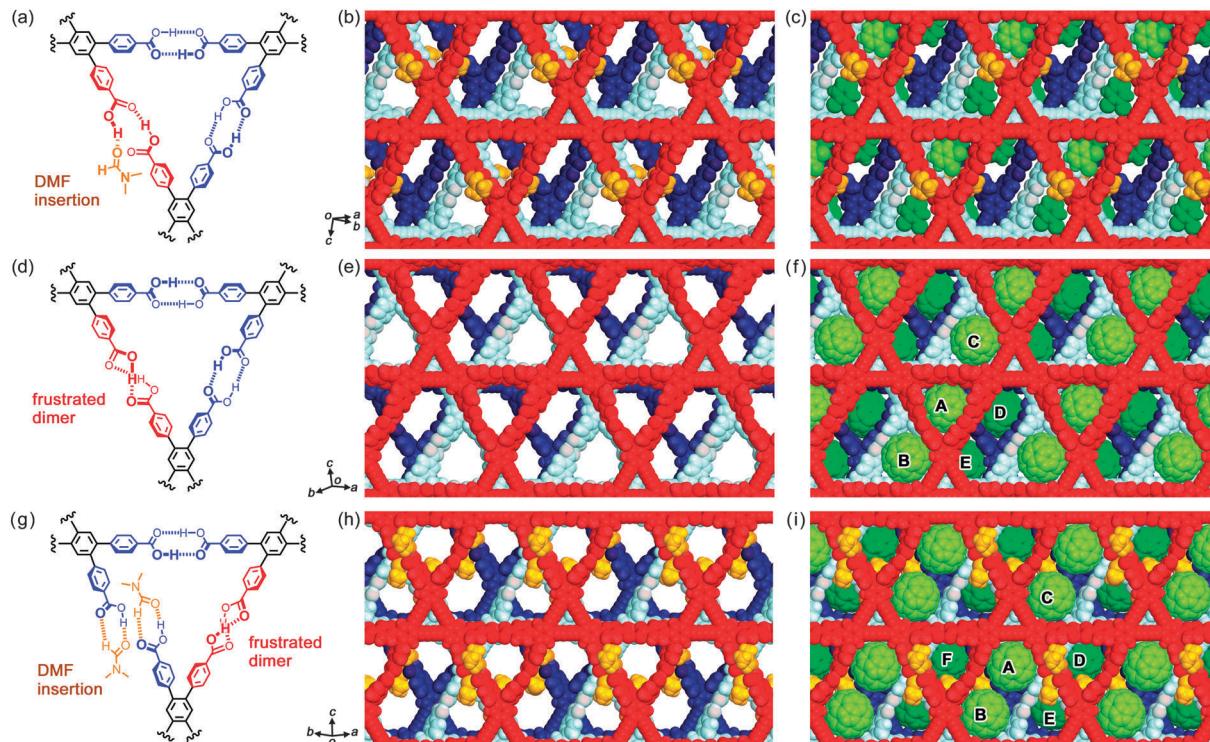


Fig. 3 Crystal structures of LA-H-HexNets (a–c) **T18-oDCB**, (d–f) **T18-C₆₀-1** and (g–i) **T18-C₆₀-2**. (a, d and g) Hydrogen-bonded phenylene triangle motifs. (b, e and h) Stacking manners of three layers of H-HexNet frameworks. (c, f and i) Arrangements of oDCB or C₆₀ molecules within the LA-H-HexNets. oDCB molecules filling the void spaces in (f) and (i) are omitted for clarity. Colours: red, light cyan, and blue (**T18**); orange (DMF); light green (C₆₀ or oDCB in an upper layer); green (C₆₀ or oDCB in a lower layer).

T18-oDCB assembles into a H-HexNet framework by forming a so-called phenylene triangle (PhT) motif, in which one pair of carboxy dimers is truncated by DMF. The HexNet sheets are stacked in a XX' manner without interpenetration, where the adjacent layers X and X' are related by an inversion center, affording a LA-H-HexNet structure. In the center of triangular void-I, oDCB molecules are located, indicating that oDCB may act as a template to stabilize the PhT motif.

Subsequently, crystallization of **T18** was performed under the above mentioned conditions in the presence of C₆₀, yielding two types of LA-H-HexNet crystals including C₆₀ molecules (**T18-C₆₀-1** and **T18-C₆₀-2**), as shown in Fig. 3d–i.‡ These are formed concomitantly and a condition for the selective preparation of either of the two forms has not been established yet in spite of our great efforts. The final convergence factors of these crystals, such as relatively high *R* values, are mostly predetermined by the nature of the crystals showing large triclinic cells and extensive disorder involving chlorine atoms.

*P*1 crystal **T18-C₆₀-1** consists of **T18**, DMF, C₆₀, and oDCB in a ratio of 1:2:1:4. **T18** molecules assemble into a H-HexNet framework by forming a PhT motif with three hydrogen-bonded dimers of carboxyphenyl groups, one of which exhibits geometrical frustration⁸ (Fig. 3d), and the H-HexNet sheet is stacked to give a LA-H-HexNet structure (Fig. 3e). Within the H-HexNet layer, C₆₀ molecules are located in two positions: one molecule labelled A (C₆₀A) is in contact with the rim of a PhT (void-I); the others (C₆₀B or C₆₀C) are at the corners of non-regular

hexagonal spaces (void-II) (Fig. 3f). In both cases, interactions between the H-HexNet framework and C₆₀ molecules are van der Waals forces such as $\pi \cdots \pi$ and $\text{CH} \cdots \pi$ contacts. In Table 1, intermolecular distances between the centres of adjacent C₆₀ molecules (*L*) are listed. In crystal **T18-C₆₀-1**, C₆₀ molecules are molecularly isolated. For example, the distances *L* for C₆₀A–C₆₀B and C₆₀A–C₆₀C are 13.2 Å and 14.9 Å, respectively.

*P*1 crystal **T18-C₆₀-2** consists of **T18**, DMF, C₆₀, and oDCB in a ratio of 1:2:1:4. The crystal density of **T18-C₆₀-2** is slightly higher (1.518 vs. 1.481 g⁻¹ cm⁻³) and C₆₀ is rotationally less disordered than in **T18-C₆₀-1**. One of the hydrogen-bonded dimers in the PhT motif of **T18-C₆₀-2** is completely dissociated, and each of the carboxy groups forms a heterodimer with a DMF molecule (Fig. 3g), although the H-HexNet framework

Table 1 Intermolecular distances between C₆₀ molecules (*L*)^a

Crystal	C ₆₀ pair	<i>L</i> /Å	Type	Symmetry code
T18-C₆₀-1	A–B	13.17	Intra-layer	B: $(-x, 1 - y, -z)$
	A–C	14.92	Intra-layer	C: $(1 - x, -y, 1 - z)$
	A–D	13.82	Inter-layer	D: $(1 + x, y, z)$
	A–E	13.16	Inter-layer	E: $(1 - x, 1 - y, -z)$
T18-C₆₀-2	A–B	11.15	Intra-layer	B: $(-x, 1 - y, 2 - z)$
	A–C	16.36	Intra-layer	C: $(1 - x, 1 - y, 3 - z)$
	A–D	16.28	Intra-layer	D: $(1 + x, y, z)$
	A–E	15.12	Intra-layer	E: $(1 - x, 1 - y, 2 - z)$
	A–F	16.30	Intra-layer	F: $(x, 1 + y, z)$

^a *L* denotes the distance between the centroids of two C₆₀ molecules.

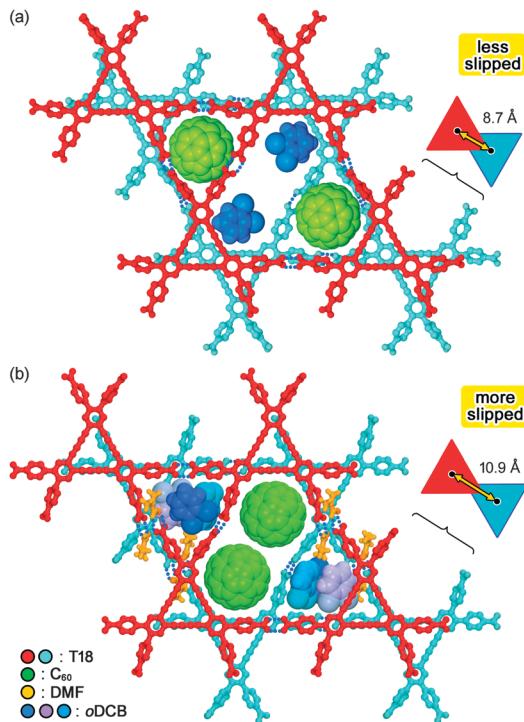


Fig. 4 Bi-layered rhombic frames of (a) **T18-C₆₀-1** and (b) **T18-C₆₀-2** with C₆₀ and oDCB molecules. (inset) Schematic representations of two overlapped **T18** cores, in which black dots and yellow arrows indicate centroids of the **T18** core and the slipping distances of the core, respectively.

itself is retained owing to the other two homodimers. The H-HexNet sheets are again stacked in a XX' manner, affording a LA-H-HexNet framework as in the case of the former two (Fig. 3h). Interestingly, void-II in **T18-C₆₀-2** accommodates two C₆₀ molecules (C₆₀A and C₆₀B) at its corners and the resulting dimeric array of C₆₀ is isolated from the adjacent dimers by the H-HexNet framework (Fig. 3i). The distance (L_1) between the nearest two molecules (C₆₀A and C₆₀B) is 11.2 Å and that (L_2) for the second nearest two molecules (C₆₀A and C₆₀E) is 15.12 Å. This is regarded as the smallest system of an infinite-number-isolated array of C₆₀.

To conduct a more detailed comparison of these two structures, we next focused on the bi-layer of the rhombic framework,

which is a motif of the H-HexNet sheet (Fig. 4). The two adjacent rhombic frameworks are stacked in an inverted manner, giving three partitioned voids: one central space and two side spaces. In **T18-C₆₀-1**, each of the side spaces is occupied by one C₆₀ molecule and the central one accommodates oDCB molecules (Fig. 4a), although they are disordered within it. In **T18-C₆₀-2**, on the other hand, each of the side spaces is filled with three oDCB molecules and the central one is filled with two C₆₀ molecules (Fig. 4b). It is not trivial that the width of the central space of **T18-C₆₀-2** is expanded by slipping the rhombic frameworks by 2.2 Å compared with those of **T18-C₆₀-1** to accommodate bulky C₆₀ molecules (inset in Fig. 4). In addition, the existence of hydrogen-bonded DMF molecules contributes to subtle structural tuning to achieve the present molecular arrangements.

The isolated C₆₀ pair observed in the present system is a unique type of C₆₀ array. Indeed, a survey of the Cambridge Structural Database (CSD) revealed that, among the structure-available 200 registries of C₆₀ containing crystals, seven crystal structures contained an isolated dimer of a neutral parent C₆₀ molecule as summarised in Table 2. Crystals referred to by the Ref Codes BIBVUE,^{6b} LIZSIX,^{6c} and VAJYIP^{6a} have crystalline lattices composed of porphyrin arrays connected through van der Waals interactions. Notably, in the case of BIBVUE, a C₆₀ dimer with intermolecular distance $L_1 = 9.95$ Å is well isolated from the adjacent dimers ($L_2 = 14.23$ Å, $L_{12} = 4.29$ Å). In DAYXAE,^{6e} FUMBIZ,^{6d} NIFXUV,^{6f} and NIFYAC,^{6f} C₆₀ molecules form 1:1 host-guest complexes with a bowl-shaped or tripodal receptor, and the complexes are arranged through van der Waals contacts. Although the present C₆₀ pairs have relatively long intermolecular distances (i.e., $L_1 = 11.2$ Å), the pairs are well separated from adjacent pairs ($L_2 = 15.1$ Å and $L_{12} = 4.0$ Å). It should be noted that it is almost impossible to predict and design an arrangement of C₆₀ molecules in a crystalline lattice constructed by non-directional van der Waals interactions, although a sophisticated C₆₀-isolated pair has been achieved. The present system is the first example of an isolated C₆₀ dimeric pair within a well-defined, hydrogen-bonded, low density framework.

In conclusion, we adopted a low-density layered assembly of a hydrogen-bonded hexagonal network (LA-H-HexNets) of dodecadelhydrotribenzo[18]annulene derivatives **T18** to align

Table 2 Structural features of crystals with isolated C₆₀ dimers

Crystal/RefCode ^a	Host compound	L_1 ^b /Å	L_2 ^c /Å	dL_{12} ^d /Å	Type of framework	Ref.
T18-C₆₀-2	T18	11.15	15.12	3.97	HB 2D lattice ^e	This work
BIBVUE	Porphyrin array	9.94	14.23	4.29	vdW lattice ^f	6b
LIZSIX	Porphyrin array	10.21	12.51	2.30	vdW lattice ^f	6c
VAJYIP	Zn porphyrin dimer	9.93	13.37	3.43	vdW lattice ^f	6a
DAYXAE	Bowl shaped π-system	9.94	13.07	3.13	H/G complex ^g	6e
FUMBIZ	Tripodal anthracene system	9.76	11.70	1.94	H/G complex ^g	6d
NIFXUV	Calix[5]arene derivative	10.18	11.08	0.90	H/G complex ^g	6f
NIFYAC	Calix[5]arene derivative	10.17	11.20	1.03	H/G complex ^g	6f

^a Crystals denoted by RefCodes were extracted by a CSD search. ^b L_1 denotes the intermolecular distance between the centroids of the nearest two C₆₀ molecules. ^c L_2 denotes the intermolecular distance between the centroids of the second nearest two C₆₀ molecules. ^d L_{12} denotes differences between L_1 and L_2 . ^e HB 2D lattice denotes a 2D lattice connected by a hydrogen bonded network. ^f vdW lattice denotes a lattice constructed through van der Waals contacts. ^g H/G complex denotes that C₆₀ and a host compound form a 1:1 complex, which subsequently constructs crystals through van der Waals contacts.

C₆₀, yielding two types of C₆₀ included crystals: **T18-C₆₀-1** and **T18-C₆₀-2**. In the latter, an alignment of an isolated molecular pair of C₆₀ partitioned by 2D hexagonal frameworks was achieved. This arrangement is the smallest example of a finite-numbered cluster of C₆₀. These results imply that the present LA-H-HexNet can be applied as a platform to align functional molecules, aimed at developing for example, artificial photosynthetic systems.⁹ Selective preparation of **T18-C₆₀-1** and **T18-C₆₀-2** and the subsequent investigation of their optical and electronic properties are currently underway.

This work was supported by a Grant-in-Aid for Scientific Research (C) (JPT15K04591) and for Scientific Research on Innovative Areas: π -System Configuration (JP15H00998) from MEXT Japan. We would like to thank Prof. Hidehiro Sakurai, Osaka University, for NMR measurements and Prof. Mikiji Miyata, Osaka University, for fruitful discussions. Finally, we would like to thank the referrers for their important and constructive comments, which led to the improvement of the manuscript. Crystallographic data were partly collected using synchrotron radiation at the BL38B1 and BL02B2 in the SPring-8 with the approval of JASRI (Proposal No. 2014B1976, 2015B1397, and 2015B1685).

Notes and references

‡ Crystal data for **T18-oDCB**: (C₇₂H₃₆O₁₂)·3(C₆H₄Cl₂)·(C₃H₇N), $F_w = 1607.08$, $a = 12.0893(3)$ Å, $b = 17.1939(4)$ Å, $c = 24.6711(6)$ Å, $\alpha = 104.880(2)^\circ$, $\beta = 90.0510(19)^\circ$, $\gamma = 98.3470(19)^\circ$, $V = 4899.8(2)$ Å³, $T = 213$ K, triclinic, space group $\bar{P}\bar{1}$, $Z = 2$, 30849 collected, 15945 unique ($R_{int} = 0.052$) reflections, the final $R1$ and $wR2$ values 0.1254 ($I > 2.0\sigma(I)$) and 0.4149 (all data), respectively. Crystal data for **T18-C₆₀-1**: (C₇₂H₃₆O₁₂)·(C₆₀)·4(C₆H₄Cl₂), $F_w = 2400.74$, $a = 13.8208(4)$ Å, $b = 17.4812(6)$ Å, $c = 24.2884(9)$ Å, $\alpha = 76.082(3)^\circ$, $\beta = 87.204(3)^\circ$, $\gamma = 70.991(3)^\circ$, $V = 5382.5(3)$ Å³, $T = 100$ K, triclinic, space group $\bar{P}\bar{1}$, $Z = 2$, 90205 collected, 28131 unique ($R_{int} = 0.102$) reflections, the final $R1$ and $wR2$ values 0.1497 ($I > 2.0\sigma(I)$) and 0.4352 (all data), respectively. Crystal data for **T18-C₆₀-2**: (C₇₂H₃₆O₁₂)·(C₆₀)·2(C₃H₇NO)·4(C₆H₄Cl₂), $F_w = 2547.93$, $a = 16.2768(7)$ Å, $b = 16.3003(7)$ Å, $c = 23.6077(8)$ Å, $\alpha = 94.242(3)^\circ$, $\beta = 5.588(3)^\circ$, $\gamma = 115.579(4)^\circ$, $V = 5575.6(4)$ Å³, $T = 100$ K, triclinic, space group $\bar{P}\bar{1}$, $Z = 2$, 77 670 collected, 20 249 unique ($R_{int} = 0.0984$) reflections, the final $R1$ and $wR2$ values 0.1414 ($I > 2.0\sigma(I)$) and 0.4453 (all data), respectively. CCDC numbers: **T18-oDCB** (CCDC 1487277), **T18-C₆₀-1** (CCDC 1481306) and **T18-C₆₀-2** (CCDC 1481305).

§ Distances between the centroids and the molecular planes of the two overlapped T18 cores are 7.9 Å and 3.7 Å, respectively, for **T18-C₆₀-1** and 10.1 Å and 4.0 Å, respectively, for **T18-C₆₀-2**. Based on these distances, the slipping distances of the two overlapped T18 cores A and B can be estimated as 8.7 Å for **T18-C₆₀-1** and 10.9 Å for **T18-C₆₀-2**.

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