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

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

Dimensionally-controlled assemblies of functional  $\pi$ -conjugated molecules are of substantial interest from optical and electronic viewpoints. In particular, those of fullerene (C<sub>60</sub>) derivatives have been intensively studied because of their specific optoelectronic properties such as a significant electron accepting ability originating in the spherical  $\pi$ -system.<sup>1,2</sup>

Crystalline lattices are a potential platform to achieve controlled arrangements of C<sub>60</sub> molecules. To date, molecularly-isolated arrangements (Fig. 1a)<sup>3</sup> and one-dimensionally (1-D) (Fig. 1b)<sup>2d,4</sup> or two-dimensionally (2-D) (Fig. 1c)<sup>5</sup> aligned infinite structures of C<sub>60</sub> have been reported in various crystalline frameworks. On the other hand, isolated arrangements of finite-numbered clusters of C60 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<sub>60</sub> (Fig. 1d), which is the smallest example of a finite-numbered cluster.<sup>6,7</sup>

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<sub>60</sub> molecules. Previously, we have reported that  $C_3$ -symmetric cyclic planar  $\pi$ -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

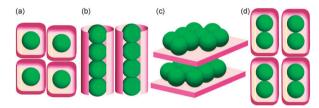


Fig. 1 Schematic representation of dimensionally-controlled alignments of C<sub>60</sub>. (a) Molecularly-isolated, (b) one-dimensional, (c) two-dimensional, and (d) finite-number-isolated arrangements.

are stacked without interpenetration to give low-density layered assemblies of H-HexNets (LA-H-HexNets).8 In particular, a H-HexNet of dodecadehydrotribenzo[18]annulene derivative **T18** (Fig. 2)<sup>8a,c</sup> can provide a space suitable for aligning C60 molecules.

T18 was synthesised using our reported method8a and was initially crystallized via slow evaporation of a mixed solution of o-dichlorobenzene (oDCB) and N,N-dimethylformamide (DMF) at 50 °C to yield P1 crystal T18-oDCB as shown in Fig. 3a-c.‡

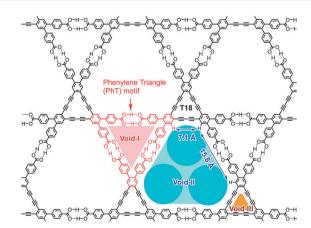


Fig. 2 Multi-porous, hydrogen-bonded hexagonal network (H-HexNet) sheet composed of T18. The sheet contains void-I, which is surrounded by the phenylene triangle (PhT) motif, void-II with the largest non-regular hexagonal space, and void-III intrinsically-generated in molecule T18 Void-II has a space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

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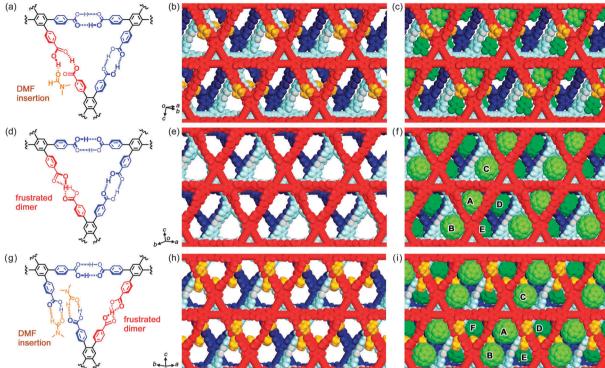


Fig. 3 Crystal structures of LA-H-HexNets (a-c) **T18-oDCB**, (d-f) **T18-C<sub>60</sub>-1** and (g-i) **T18-C<sub>60</sub>-2**. (a, d and g) Hydrogen-bonded phenylene triangle motifs. (b, e and h) Stacking manners of three layers of H-HexNet frameworks. (c, f and i) Arrangements of oDCB or  $C_{60}$  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 ( $C_{60}$  or oDCB in an upper layer); green ( $C_{60}$  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  $C_{60}$ , yielding two types of LA-H-HexNet crystals including  $C_{60}$  molecules (**T18-C<sub>60</sub>-1** and **T18-C<sub>60</sub>-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.

 $P\bar{1}$  crystal **T18-C<sub>60</sub>-1** consists of **T18**, C<sub>60</sub>, and oDCB in a ratio of 1:1:4. **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 frustration<sup>8</sup> (Fig. 3d), and the H-HexNet sheet is stacked to give a LA-H-HexNet structure (Fig. 3e). Within the H-HexNet layer, C<sub>60</sub> molecules are located in two positions: one molecule labelled A (C<sub>60</sub>A) is in contact with the rim of a PhT (void-I); the others (C<sub>60</sub>B or C<sub>60</sub>C) are at the corners of non-regular

hexagonal spaces (void-II) (Fig. 3f). In both cases, interactions between the H-HexNet framework and  $C_{60}$  molecules are van der Waals forces such as  $\pi \cdots \pi$  and  $CH \cdots \pi$  contacts. In Table 1, intermolecular distances between the centres of adjacent  $C_{60}$  molecules (L) are listed. In crystal **T18-C<sub>60</sub>-1**,  $C_{60}$  molecules are molecularly isolated. For example, the distances L for  $C_{60}A-C_{60}B$  and  $C_{60}A-C_{60}C$  are 13.2 Å and 14.9 Å, respectively.

 $P\bar{1}$  crystal T18-C<sub>60</sub>-2 consists of T18, DMF, C<sub>60</sub>, and oDCB in a ratio of 1:2:1:4. The crystal density of T18-C<sub>60</sub>-2 is slightly higher (1.518 vs. 1.481 g<sup>-1</sup> cm<sup>-3</sup>) and C<sub>60</sub> is rotationally less disordered than in T18-C<sub>60</sub>-1. One of the hydrogen-bonded dimers in the PhT motif of T18-C<sub>60</sub>-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 C<sub>60</sub> molecules (L)<sup>a</sup>

Crystal	C <sub>60</sub> pair	$L/{ m \AA}$	Туре	Symmetry code
T18-C <sub>60</sub> -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-C <sub>60</sub> -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: $(x, 1+y, z)$

 $<sup>^</sup>a$  L denotes the distance between the centroids of two  $C_{60}$  molecules.

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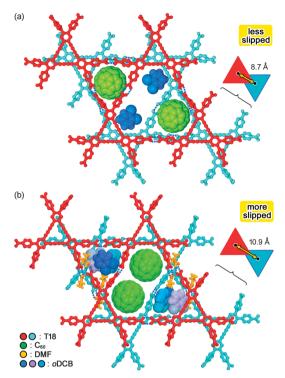


Fig. 4 Bi-layered rhombic frames of (a)  $T18-C_{60}-1$  and (b)  $T18-C_{60}-2$  with  $C_{60}$  and oDCB molecules. (inset) Schematic representations of two overlapped T18 cores, in which black dots and yellow arrows indicate centroids of the T18 core and the slipping distances of the core, respectively.

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-C<sub>60</sub>-2** accommodates two C<sub>60</sub> molecules (C<sub>60</sub>A and C<sub>60</sub>B) at its corners and the resulting dimeric array of C<sub>60</sub> is isolated from the adjacent dimers by the H-HexNet framework (Fig. 3i). The distance ( $L_1$ ) between the nearest two molecules (C<sub>60</sub>A and C<sub>60</sub>B) is 11.2 Å and that ( $L_2$ ) for the second nearest two molecules (C<sub>60</sub>A and C<sub>60</sub>E) is 15.12 Å. This is regarded as the smallest system of an infinite-numberisolated array of C<sub>60</sub>.

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-C<sub>60</sub>-1, each of the side spaces is occupied by one C<sub>60</sub> molecule and the central one accommodates oDCB molecules (Fig. 4a), although they are disordered within it. In T18-C<sub>60</sub>-2, on the other hand, each of the side spaces is filled with three oDCB molecules and the central one is filled with two C<sub>60</sub> molecules (Fig. 4b). It is not trivial that the width of the central space of T18-C<sub>60</sub>-2 is expanded by slipping the rhombic frameworks by 2.2 ŧ compared with those of T18-C<sub>60</sub>-1 to accommodate bulky C<sub>60</sub> 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 C<sub>60</sub> pair observed in the present system is a unique type of C<sub>60</sub> array. Indeed, a survey of the Cambridge Structural Database (CSD) revealed that, among the structureavailable 200 registries of C<sub>60</sub> 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 VAJYIP6a 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 C<sub>60</sub> 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 C<sub>60</sub> pairs have relatively long intermolecular distances (i.e.,  $L_1 = 11.2 \text{ Å}$ ), the pairs are well separated from adjacent pairs ( $L_2 = 15.1 \text{ Å}$  and  $L_{12} = 4.0 \text{ Å}$ ). 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 C<sub>60</sub>-isolated pair has been achieved. The present system is the first example of an isolated C<sub>60</sub> 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 dodecadehydrotribenzo[18]annulene derivatives T18 to align

Table 2 Structural features of crystals with isolated C<sub>60</sub> dimers

Crystal/RefCode <sup>a</sup>	Host compound	${L_1}^b/{ m \AA}$	${L_2}^c/{ m \AA}$	$\mathrm{d}{L_{12}}^d/\mathrm{\mathring{A}}$	Type of framework	Ref.
T18-C <sub>60</sub> -2	T18	11.15	15.12	3.97	HB 2D lattice <sup>e</sup>	This work
BIBVUE	Porphyrin array	9.94	14.23	4.29	vdW lattice $^f$	6 <i>b</i>
LIZSIX	Porphyrin array	10.21	12.51	2.30	vdW lattice <sup>f</sup>	6 <i>c</i>
VAJYIP	Zn porphyrin dimer	9.93	13.37	3.43	vdW lattice $^f$	6 <i>a</i>
DAYXAE	Bowl shaped π-system	9.94	13.07	3.13	H/G complex <sup>g</sup>	6 <i>e</i>
FUMBIZ	Tripodal anthracene system	9.76	11.70	1.94	H/G complex <sup>g</sup>	6d
NIFXUV	Calix[5]arene derivative	10.18	11.08	0.90	H/G complex <sup>g</sup>	6 <i>f</i>
NIFYAC	Calix[5]arene derivative	10.17	11.20	1.03	H/G complex <sup>g</sup>	6f

<sup>&</sup>lt;sup>a</sup> Crystals denoted by RefCodes were extracted by a CSD search. <sup>b</sup>  $L_1$  denotes the intermolecular distance between the centroids of the nearest two  $C_{60}$  molecules. <sup>c</sup>  $L_2$  denotes the intermolecular distance between the centroids of the second nearest two  $C_{60}$  molecules. <sup>d</sup>  $L_{12}$  denotes differences between  $L_1$  and  $L_2$ . <sup>e</sup> HB 2D lattice denotes a 2D lattice connected by a hydrogen bonded network. <sup>f</sup> vdW lattice denotes a lattice constructed through van der Waals contacts. <sup>g</sup> H/G complex denotes that  $C_{60}$  and a host compound form a 1:1 complex, which subsequently constructs crystals through van der Waals contacts.

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 $C_{60}$ , yielding two types of  $C_{60}$  included crystals: **T18-C<sub>60</sub>-1** and **T18-C<sub>60</sub>-2**. In the latter, an alignment of an isolated molecular pair of  $C_{60}$  partitioned by 2D hexagonal frameworks was achieved. This arrangement is the smallest example of a finite-numbered cluster of  $C_{60}$ . 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. Selective preparation of **T18-C<sub>60</sub>-1** and **T18-C<sub>60</sub>-2** and the subsequent investigation of their optical and electronic properties are currently underway.

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## Notes and references

‡ Crystal data for **T18-oDCB**:  $(C_{72}H_{36}O_{12})\cdot 3(C_6H_4Cl_2)\cdot (C_3H_7N)$ ,  $F_w =$ 1607.08, a = 12.0893(3) Å, b = 17.1939(4) Å, c = 24.6711(6) Å,  $\alpha = 12.0893(3)$  $104.880(2)^{\circ}$ ,  $\beta = 90.0510(19)^{\circ}$ ,  $\gamma = 98.3470(19)^{\circ}$ ,  $V = 4899.8(2) \text{ Å}^3$ , T=213 K, triclinic, space group  $P\overline{1}$ , Z=2, 30849 collected, 15945 unique ( $R_{\text{int}} = 0.052$ ) reflections, the final R1 and wR<sub>2</sub> values 0.1254  $(I > 2.0\sigma(I))$  and 0.4149 (all data), respectively. Crystal data for **T18-C<sub>60</sub>-1**:  $(C_{72}H_{36}O_{12})\cdot(C_{60})\cdot4(C_{6}H_{4}Cl_{2}), F_{w}=2400.74, a=13.8208(4) Å, b=17.4812(6) Å, c=24.2884(9) Å, <math>\alpha=76.082(3)^{\circ}, \beta=87.204(3)^{\circ}, \gamma=12.4812(6)$  $70.991(3)^{\circ}$ , V = 5382.5(3) Å<sup>3</sup>, T = 100 K, triclinic, space group  $P\overline{1}$ , Z = 2, 90205 collected, 28131 unique ( $R_{int} = 0.102$ ) reflections, the final R1 and  $wR_2$  values 0.1497 ( $I > 2.0\sigma(I)$ ) and 0.4352 (all data), respectively. Crystal data for **T18-C**<sub>60</sub>-2:  $(C_{72}H_{36}G_{12})\cdot(C_{60})\cdot2(C_{3}H_{7}NO)\cdot4(C_{6}H_{4}Cl_{2}), F_{w}=2547.93,$  a=16.2768(7) Å, b=16.3003(7) Å, c=23.6077(8) Å,  $\alpha=94.242(3)^{\circ}, \beta=16.2003(7)$  $5.588(3)^{\circ}$ ,  $\gamma = 115.579(4)^{\circ}$ ,  $V = 5575.6(4) \text{ Å}^3$ , T = 100 K, triclinic, space group  $P\overline{1}$ , Z = 2, 77 670 collected, 20 249 unique ( $R_{\text{int}} = 0.0984$ ) reflections, thes final R1 and wR<sub>2</sub> values 0.1414 ( $I > 2.0\sigma(I)$ ) and 0.4453 (all data), respectively. CCDC numbers: T18-oDCB (CCDC 1487277), T18-C<sub>60</sub>-1 (CCDC 1481306) and **T18-C<sub>60</sub>-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-C<sub>60</sub>-1 and 10.1 Å and 4.0 Å, respectively, for T18-C<sub>60</sub>-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-C<sub>60</sub>-1 and 10.9 Å for T18-C<sub>60</sub>-2.

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