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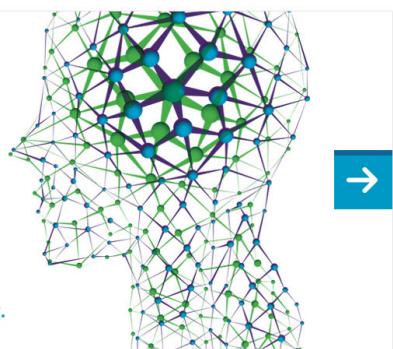
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Construction of single-crystalline supramolecular networks of perchlorinated hexa-peri-hexabenzocoronene on Au(111)

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The self-assembly of the perchlorinated hexa-*peri*-hexabenzocoronene (PCHBC) molecules on Au(111) has been studied by a low temperature scanning tunneling microscopy (STM) combining with density functional theory based first principle calculations. Highly ordered supramolecular networks with single domains limited by the terraces are formed on Au(111) substrate. High resolution images of the PCHBC molecules, confirmed by first principle simulations, are obtained. It reveals the close-packed arrangement of the PCHBC molecules on Au(111). The calculated charge distribution of PCHBC molecules shows the existence of attractive halogen–halogen interaction between neighboring molecules. Compared with the disordered adsorption of hexa-*peri*-hexabenzocoronene on Au(111), we conclude that the formation of attractive Cl••Cl interactions between neighbors is the key factor to form the highly ordered, close-packed networks. Due to the steric hindrance resulted from the peripheral chlorine atoms, the PCHBC molecule is contorted and forms the doubly concave conformation, which is different from the hexa-*peri*-hexabenzocoronene with a planar structure. By using this supramolecular network as a template, we deposited C₆₀ molecules on it at room temperature with low coverage. The STM images taken at low temperature show that the C₆₀ molecules are mono-dispersed on the networks and adsorb on top of the PCHBC molecules, forming a typical concave-convex host-guest system. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4907369>]

INTRODUCTION

Supramolecular architectures have attracted great interest because of their potential applications in organic electronics.^{1–5} One approach to fabricate them is based on the organic molecular self-assembly which is dominated by the non-covalent bonds.^{6–9} A great variety of self-assembled structures with different intermolecular interactions, such as van der Waals forces¹⁰ and hydrogen bonds,^{6,11–14} have been reported. As a kind of non-covalent interactions, halogen bonding is supposed to have the fitness for constructing two-dimensional supramolecular networks.¹⁵ The anisotropic charge distribution and electrostatic potential of the halogen atoms in organic halides make halogen bonds much more sensitive to the steric hindrance and show specific orientation as compared to hydrogen bonds.¹⁶ To date, however, most of the supramolecular structures assembled by halogen bonds are made of brominated^{15,17,18} or iodinated¹⁹ molecules. The self-assembly of chlorinated molecules has rarely been

investigated, especially by scanning tunneling microscopy (STM).

In this paper, we present the first case of the STM study on the self-assembly of a fully chlorinated large polycyclic aromatic molecule, namely, perchlorinated hexa-*peri*-hexabenzocoronene (PCHBC), on Au(111) surface. STM experiments show that PCHBC molecules spontaneously form single-crystalline networks. High resolution STM images of PCHBC molecules have been obtained. The density functional theory (DFT) based first principle simulations confirm that the contorted molecules arrange in a close-packed way. We find that the attractive and directional Cl••Cl interaction between molecules is important to constructing single crystalline PCHBC networks. We further demonstrate that the double concave conformation of PCHBC makes it suitable to capture C₆₀ and forms the concave-convex host-guest system.

EXPERIMENTAL AND CALCULATION DETAILS

The experiments were conducted using a commercial Omicron ultrahigh vacuum (UHV) low temperature STM (LT-STM) with a base pressure better than 1×10^{-10} millibars. The atomically clean Au(111) surface was obtained by cycles

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of argon-ion sputtering and annealing to 470 °C. The PCHBC molecules were thermally deposited onto Au(111) by a Knudsen cell. The substrate was kept at room temperature during the deposition, and the sample was directly transferred to the low temperature chamber for STM characterization after the deposition process. All the STM images were obtained at 5 K in constant-current mode, using an electrochemically etched tungsten tip. The bias of the STM was applied to the sample. The Nanotec Electronica WSxM software²⁰ was used to process the STM images shown here.

DFT based first principle calculations were performed with the help of Vienna *ab initio* simulation packages (VASP) and the STM simulation image was obtained within the Tersoff-Hamann approximation.^{21–23} The charge density difference, which was used to study the intermolecular halogen–halogen interaction, is defined as $\Delta\rho = \rho_{\text{tot}} - (\rho_C + \rho_{\text{Cl}})$, where ρ_{tot} is the electron density of the PCHBC molecule, and ρ_C and ρ_{Cl} are the unperturbed electron densities of the carbon skeleton and isolated Cl atoms in PCHBC molecule, respectively.

RESULTS AND DISCUSSION

The chemical structure of PCHBC, a perchlorinated polycyclic aromatic hydrocarbon, is shown in Figure 1. PCHBC molecule comprises of 42 carbon and 18 chlorine atoms and is contorted due to the steric hindrance induced by the congested chlorine atoms on its periphery. More specifically, every other chlorinated benzene ring is up-warped with respect to the carbon backbone, while its neighbor counterparts are warped in the opposite direction. As a result, PCHBC exhibits a three-fold rather than a six-fold symmetry (Figure 1(a)). The side-view shown in Figure 1(b) demonstrates the distinct spatial configuration of PCHBC. The vertical height and the lateral length of a free PCHBC molecule are evaluated to be 0.44 nm and 1.18 nm, respectively.

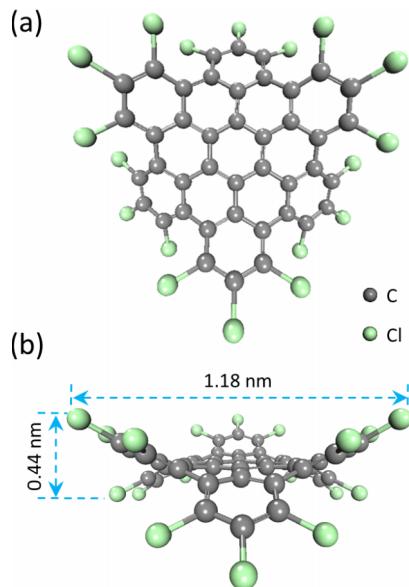


FIG. 1. Chemical structures of PCHBC molecules. (a) Top-view. (b) Side-view.

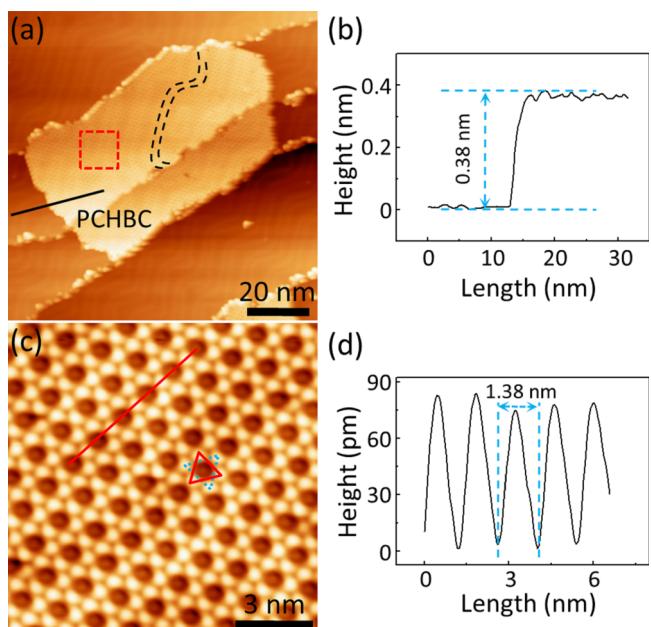


FIG. 2. (a) Large area STM image of PCHBC adsorbed on Au(111). The PCHBC molecules prefer to form islands on Au(111) without destroying the herringbone reconstruction underneath (outlined by black dashed curves). (b) Line profile along the black line in (a) shows the height of the island is ~0.38 nm. (c) Zoom-in STM image obtained from the area marked by a red dashed square in (a). The molecules self-assemble into highly ordered supramolecular networks. The triangles indicate the probable structural units of the network. (d) Line profile along the red line in (c) shows the period of the network is 1.38 nm. Scanning parameters: $U = -3$ V and $I_t = 50$ pA for (a) and $U = -2$ V and $I_t = 50$ pA for (c).

Figure 2(a) shows the STM image of PCHBC islands after deposition of sub-monolayer molecules on Au(111) surface at room temperature. A herringbone-like structure stemming from the typical reconstruction of Au(111) surface is apparently visible on the islands, as outlined by two black dashed curves. It implies that the adsorption of PCHBC does not destroy the reconstruction of Au(111) as chlorine atoms do.²⁴ A line profile analysis along the black solid line in Figure 2(a) reveals that the apparent height of the island is about 0.38 nm (Figure 2(b)). This value is very close to the vertical height of a free PCHBC. Therefore, we are convinced that each island contains only one layer of PCHBC. To find out the exact arrangement of the PCHBC molecules, we got the zoom-in STM image (Figure 2(c)) from the area marked by a red dashed square in Figure 2(a). It clearly shows that the PCHBC molecules self-assemble into highly ordered networks. The most fascinating feature of the networks is the bright protrusions which seem to form the regular Kagome lattice. The distance between two nearest protrusions is about 0.70 nm, and it is much smaller than the lateral length (1.18 nm) of a PCHBC molecule. Thus, we can rule out the possibility that a protrusion or every three nearest protrusions is an individual PCHBC molecule. Another fascinating feature is the “holes” surrounded by the protrusions. The line profile along the red line reveals a 1.38 nm periodicity of the “holes” (Figure 2(d)), which is slightly larger than the theoretical lateral size of the free PCHBC molecule. For a PCHBC lying on the Au(111) surface, its carbon backbone should be lower than the up-warped chlorine

atoms. Hence, it is reasonable to assume that the “holes” are the carbon backbones of the PCHBC molecules, and the bright protrusions are from the electronic states of chlorine atoms. Considering the three-fold symmetry of the PCHBC molecules, we can divide the six protrusions around a hole into two groups. Each group contains three protrusions and possesses three-fold symmetry, as marked by a blue dashed and a red regular triangle in Figure 2(c). The side lengths of these two regular triangles are measured to be 1.22 nm, which are very close to the lateral length of the PCHBC molecules as shown in Figure 1(b). We thus infer that one of the two groups of protrusions, as well as the “hole” surrounded by them, must stem from the same molecule, while the remaining three protrusions belong to different molecules.

Figure 3(a) is a high-resolution STM image of the networks. Interestingly, the bright protrusions shown in Figure 2(c) appear as lune here. Careful observation reveals that each lune is comprised of three spots, as represented by three solid light green circles in the image, with the middle one being brighter than the other two. What is more, the carbon backbones of PCHBC are faintly visible in this image. Much higher resolution STM images can be obtained by pushing the tip closer to the sample, as shown in Figure 3(b). Every molecule can be easily identified, and the correspondence between the lunes and the chlorine atoms becomes evident. For comparison, we carried out the DFT simulations on a single free PCHBC molecule, as shown in Figure 3(c) (in which the lune profiles of PCHBC observed in Figure 3(a) have been outlined by blue dashed lunes). We superimpose

the simulation into Figure 3(a), revealing that the STM images agree fairly well with the simulation result. We also carried out the DFT simulation on the close-packed PCHBC lattice as shown in Figure 3(d), which is partially blended into the STM image in (b) to indicate the good agreement between them. The blue dashed lunes are superimposed in Figures 3(b) and 3(d) to guide the eyes.

It is worth pointing out that no domain boundaries were observed within each island. Even when we increased the coverage of PCHBC to a monolayer, there was still only one domain within the same terrace of Au(111) surface. This means that the PCHBC molecules can form large area single-crystalline domains which are only limited by the terraces of Au(111) surface. What is more, the networks remained unchanged after we annealed the sample to 200 °C, which indicates a good thermal stability of the PCHBC networks.

It has been reported that the hexa-*peri*-hexabenzocoronene (HBC) molecules exhibit disordered adsorption without forming the molecular lattice on Au(111) at low coverage due to the repulsive intermolecular force. The molecular lattice only formed at relatively high coverage and the intermolecular distances decrease with the increase of coverage.²⁵ In our case, however, the PCHBC molecules form highly ordered single crystalline networks with unique lattice constant both at low coverage and high coverage. To understand these different behaviors, we investigated the role of chlorine atoms in the self-assembly of PCHBC. Since the PCHBC molecules are close-packed, the intermolecular interaction induced by the chlorine atoms cannot be ignored. For organic halides, the charge distribution around the halogen atoms is anisotropic: The pole along the C–X (X = Br, Cl, and I) bond axis is positively polarized while the equator around the halogen atom is negatively polarized. The attractive intermolecular halogen–halogen interactions are supposed to form due to this anisotropic charge distribution.^{16,18,26} To verify the existence of C–Cl•••Cl–C interactions in our supramolecular networks, we calculated the charge density difference of the PCHBC as shown in the upper half of Figure 4(a). A ball-stick structural model of PCHBC is exhibited in the lower half of Figure 4(a) as a reference to indicate the positions of the chlorine atoms. In the charge density difference image, the red and blue parts represent the positively charged and negatively charged regions, respectively. It clearly shows that, as expected, the charge distribution around the chlorine atom is non-spherical. The polar regions along the C–Cl bonds are electron-deficient sites and the equatorial regions are electron-rich sites. According to this charge distribution model, attractive intermolecular Cl•••Cl interactions are expected, and we sketched out the possible halogen bonds (for the convenience of discussion, we simply call the halogen–halogen interactions as the halogen bonds, despite that they are indeed intermolecular interactions rather than chemical bonds) among three PCHBC molecules of the self-assembled networks by dashed lines in Figure 4(b). Based on their positions, all the chlorine atoms in PCHBC can be simply divided into two groups marked as Cl1 and Cl2 as shown in Figure 4(b). It can be clearly found out that there are four halogen bonds between any two neighboring PCHBC molecules: two Cl1•••Cl1 bonds (blue dashed lines) and two

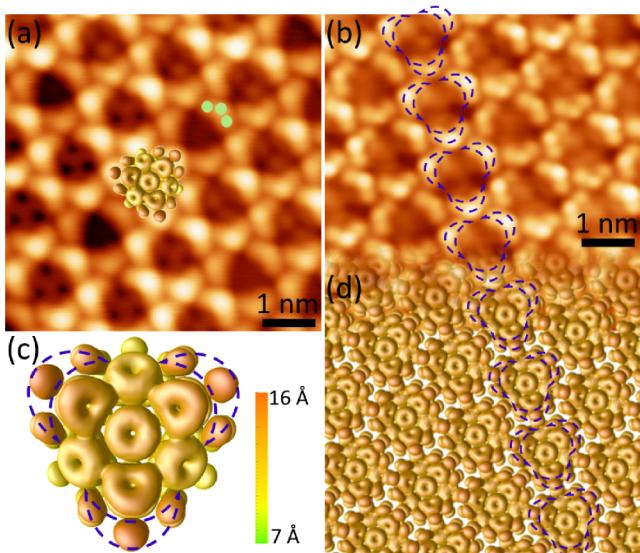


FIG. 3. (a) High-resolution STM image of the networks. Every bright protrusion of the network shown in Fig. 2(c) is found to be comprised of three spots. Three solid light green circles are superimposed to indicate the arrangement of the spots. A DFT simulation model is superimposed to identify the PCHBC. (b) STM image obtained in the same area of (a) with higher resolution. The backbones of the PCHBC molecules can be clearly identified. (c) DFT simulation of the PCHBC molecule. The lune profiles observed in (a) are outlined by blue dashed lines. (d) The DFT simulation of the close-packed PCHBC lattice which is partially blended into the STM image in (b) to guarantee the agreement between them. The blue dashed lunes are superimposed to guide the eyes. Scanning parameters: $U = -0.5$ V and $I = 50$ pA for (a) and $U = -0.3$ V and $I = 50$ pA for (b).

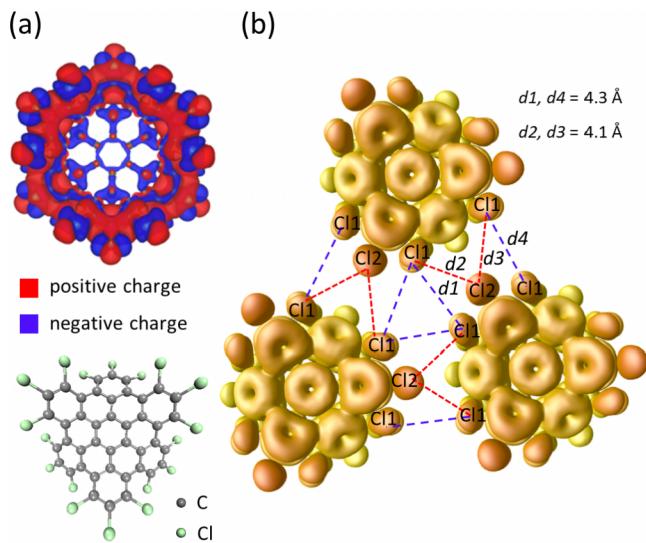


FIG. 4. Halogen bonds in the supramolecular networks. (a) Calculated charge density difference of the PCHBC molecule. The chlorine atoms show charge depletion in the polar region and charge excess in the equatorial region. Red and blue indicate the distribution of positive charge and negative charge, respectively. The ball-stick model of PCHBC is exhibited below the calculated model as a reference. (b) Halogen bonds in the close packed networks. The lattice distance has been magnified for clarity. The red and blue dashed lines indicate the possible $\text{Cl}\cdots\text{Cl}$ bonds. The chlorine atoms in PCHBC can be divided into two groups: Cl1 and Cl2, according to their sites as indicated in the figure. There are four halogen bonds between any two PCHBC molecules: two $\text{Cl1}\cdots\text{Cl2}$ bonds (red dashed lines) and two $\text{Cl1}\cdots\text{Cl1}$ bonds (blue dashed lines). The experimentally measured halogen bond distances are 4.1 Å and 4.3 Å for $\text{Cl1}\cdots\text{Cl2}$ bond (d2 and d3) and $\text{Cl1}\cdots\text{Cl1}$ bond (d1 and d4), respectively.

$\text{Cl1}\cdots\text{Cl2}$ bonds (red dashed lines). We also measured the distance of the chlorine atoms between which the halogen bonds formed and the distances are very close: 4.1 Å for the $\text{Cl1}\cdots\text{Cl2}$ bonds and 4.3 Å for the $\text{Cl1}\cdots\text{Cl1}$ bonds. These attractive directional halogen bonds are responsible and fatal for the formation of single crystalline supramolecular networks, and this can also interpret the different adsorption behavior of PCHBC and HBC molecules on Au(111).

The double concave conformation of PCHBC molecules on Au(111) renders the highly ordered molecular networks to be a perfect host for guest molecules.^{27,28} Considering the size and shape of PCHBC, we chose C_{60} as the guest molecule. We thermally deposited low coverage C_{60} onto the sample after deposition of one monolayer PCHBC on Au(111) at room temperature. Figure 5(a) shows the STM image of C_{60} adsorbed on the networks formed by the self-assembled PCHBC molecules. The network host remains uniform after the deposition of C_{60} guests which appear as spherical bright protrusions. The line profile analysis reveals the apparent height of C_{60} with respect to the network layer is about 0.61 nm (Figure 5(b)). This value is slightly smaller than the theoretical value for a free C_{60} . In order to confirm that the C_{60} guests are adsorbed on the PCHBC rather than on the Au(111) surface, we also deposited C_{60} directly on clean Au(111) surface. The apparent height of C_{60} on bare Au(111) is measured to be 0.60 nm, which is also smaller than the theoretical one. This difference is reasonable since the apparent height is, in fact, a relative height with respect to the reference layer

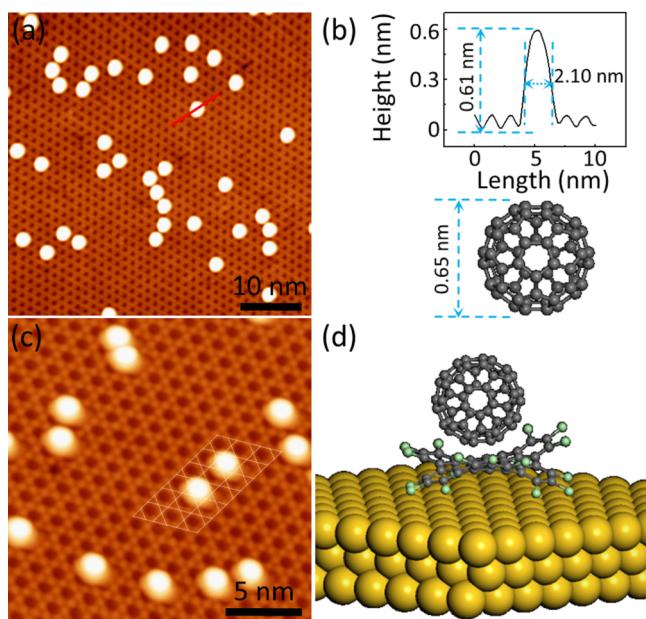


FIG. 5. (a) STM image of C_{60} molecules adsorbed on the networks formed by the self-assembled PCHBC molecules. The bright protrusions have the same size and shape. (b) Line profile along the red line in (a) and the theoretical size of the C_{60} molecule. The FWHM of the protrusion is about 2.10 nm and the apparent height is about 0.61 nm. The natural size of a free C_{60} molecule is calculated to be 0.65 nm. The height difference between the experimental and theoretical values may arise from the relative strong density of states of the reference layer underneath the C_{60} . (c) Zoom-in STM image of the networks and the C_{60} molecules. A lattice grid of the network is superimposed to determine the adsorption site of the C_{60} molecules. (d) Schematic representation of the PCHBC- C_{60} host-guest system on Au(111) surface. Scanning parameters: $U = -3$ V and $I_t = 50$ pA for both (a) and (c).

(in our case shown here, the reference layer is gold surface or PCHBC layer) underneath the C_{60} and is related to the electronic density of states (DOS); hence, it may arise from the relative strong DOS of the reference layer. As we have shown in Figure 2(b), the apparent height of the PCHBC layer on Au(111) is about 0.38 nm. Considering that the warp of PCHBC happens in two directions, the height of the backbone of PCHBC should at least be 0.19 nm. Supposing that the C_{60} molecules shown in Figure 5(a) are adsorbed directly on the bare Au(111) surface, the apparent height of C_{60} with respect to the networks layer is expected to be about 0.41 nm, which is much smaller than the corresponding value shown in Figure 5(b). It is therefore convinced that the C_{60} molecules are located above the PCHBC. Figure 5(b) also shows that the full width at half maximum (FWHM) of a single protrusion is about 2.10 nm, much larger than the theoretical size of a free C_{60} . It is a common phenomenon in STM imaging that a single C_{60} exhibits larger FWHM due to the dispersion of the electronic states. The FWHM of a single C_{60} larger than or close to 2 nm has already been reported before.^{27,29} We thus conclude that each bright protrusion in Figure 5(a) is indeed a single C_{60} .

To verify that the C_{60} guests are indeed located on top of the “holes” of the networks rather than the chlorine lune, we got the zoom-in STM image as shown in Figure 5(c). Due to the large FWHM of C_{60} , the PCHBC hosts underneath the C_{60} guests are totally invisible. We hence superimpose grid

lines onto the ordered networks to determine the position of the buried PCHBC. It clearly shows that C₆₀ molecules are all located on the centers of the hexagonal lattices, which represent the “holes” of the networks. Based on the analysis above, we come to a conclusion that C₆₀ molecules are mono-dispersed on the networks, forming the concave-convex host-guest systems, as demonstrated in Figure 5(d).

CONCLUSIONS

We have studied the self-assembly of PCHBC molecules on Au(111) surface by LT-STM. The formation of 2D supramolecular single-crystalline networks has been observed. High resolution STM images indicate that the PCHBC molecules arrange in a close-packed way with uniform orientation. The topography images of the PCHBC molecules are well reproduced by our DFT based first principle simulations. The charge density difference of the PCHBC confirms the existence of halogen bonds in the supramolecular networks, which result in the highly ordered self-assembly behavior. We further demonstrate that the doubly concave PCHBC molecules could serve as a host for the C₆₀ to form the PCHBC-C₆₀ host-guest system, where the C₆₀ molecules are mono-dispersed and located on the top of the PCHBC molecules.

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