

Directing two-dimensional molecular crystallization using guest templates

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The use of a coronene guest template directs the formation of a 2D Kagomé network in preference to alternative close packed and parallel hydrogen-bonded structures of tetracarboxylic acid tectons self-assembled from solution on a graphite surface.

The exploitation of supramolecular chemistry for the controlled assembly of molecules has reached a level of maturity where the products of specific self-assembly processes can be predicted to a high level of accuracy in many cases.^{1,2} In comparison to solution-phase self-assembly,¹ and to a lesser extent solid-state crystal engineering,² surface-based supramolecular chemistry is less well understood and has been receiving a great deal of attention over recent years.³ Amongst the intermolecular interactions that have been used to facilitate controlled self-assembly processes on surfaces are hydrogen-bonding interactions.⁴ Hydrogen-bonds represent versatile intermolecular interactions that can be designed into molecular building-blocks, or tectons, allowing the targeted design of specific self-assembled structures.

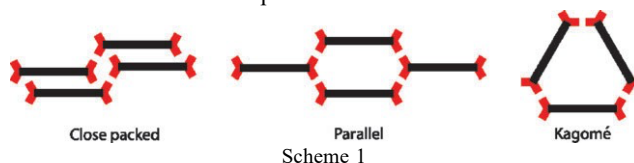
A recent study by Wuest and co-workers⁵ elegantly illustrated the self-assembly of tetracarboxylic acid molecules on a highly oriented pyrolytic graphite (HOPG) surface following crystallization from heptanoic acid solutions. Imaging of the resultant structures by scanning tunneling microscopy (STM) reveals hydrogen-bonded framework structures that utilize inter-carboxylic acid hydrogen-bonding interactions. Two framework motifs are anticipated and observed, a so-called parallel network and a Kagomé network⁶ (Scheme 1). The balance between the two polymorphic structural arrangements leads to frustrated 2D molecular crystallization.⁷ Independently and in parallel to the studies by Wuest we have been investigating the assembly of related tetracarboxylic acid tectons. In this study we demonstrate an approach to overcome the crystallization frustration by the use of a guest templating molecule that significantly enhances the stability of the Kagomé network polymorph. The use of guest molecules to influence and to transform the structures of two-dimensional surface networks has recently been demonstrated in networks that utilise alkyl-chain interdigitation for network formation.⁸ However, our study illustrates that by judicious

choice of guest molecule stronger intermolecular, network forming, interactions, in this instance hydrogen-bonds, can be controlled to direct two-dimensional network structures.

The tetracarboxylic acids 1 and 2 (Fig. 1(a) and (b), respectively) were prepared either by reported procedures (1)⁹ or in the case of 2 *via* the Suzuki coupling of 2,6-dibromonaphthalene with diethyl isophthalate 5-boronic acid and subsequent hydrolysis (see ESI[†]). Both 1 and 2 form hydrogen-bonded arrays on the HOPG surface following deposition from a nonanoic or heptanoic acid solution. It can be seen that the structures formed by 1 (Fig. 1(c)) and 2 (Fig. 1(d)) differ in their hydrogen bonding arrangements and in forming two-dimensional sheet structures. The molecular arrangements for 1 and 2 vary in their respective hydrogen-bonding arrangements and can be interpreted in terms of the models illustrated in Fig. 2. Thus, 1 adopts the parallel structure observed previously for related tetracarboxylate molecules⁵ with all four carboxylic acid groups of each molecule of 1 participating in double hydrogen-bonds. In contrast, 2 adopts a more close-packed structure (Scheme 1 and Fig. 2(b)), in which two carboxylic acid groups per molecule participate in intermolecular RCOOH...HOOCR double hydrogen-bonding interactions (R^2 (8) graph set notation¹⁰), with the remaining carboxylic acid groups believed to adopt weaker OH...O or C-H...O interactions.

We have confirmed, using DFT calculations, that the proposed arrangements are stable and have lattice constants which are in excellent agreement with the values measured from our images (see ESI[†]).

In contrast to the study of Wuest and co-workers⁵ our studies of 1 and 2 do not exhibit frustrated crystallization with no evidence for the formation of a Kagomé network. We were interested to investigate whether we could enhance the formation of the Kagomé network structure *via* the use of a guest species to act as a template for this structure. Thus, coronene was chosen as a guest molecule that was anticipated to act as a suitable template to favour the formation of the



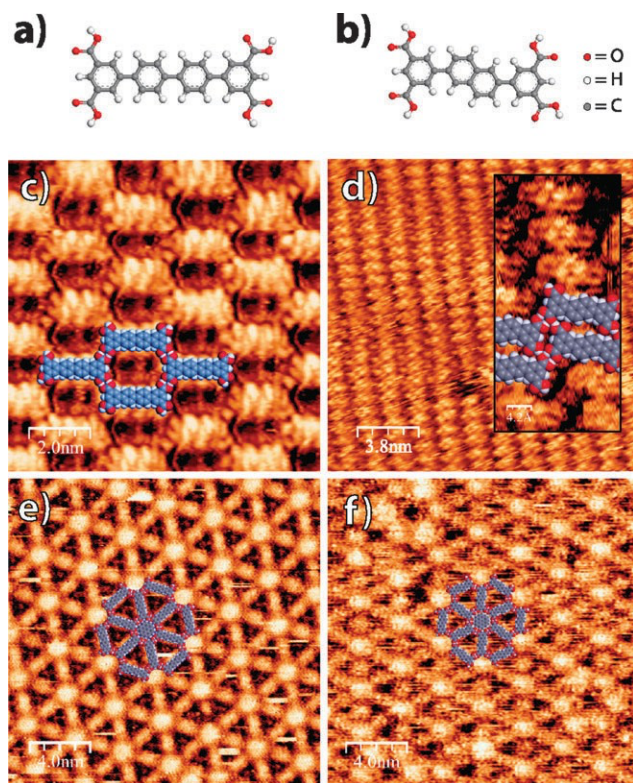
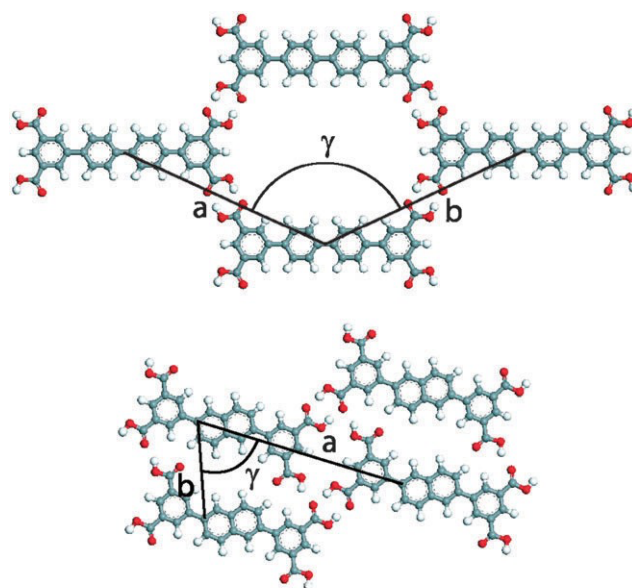


Fig. 1 Tetracarboxylic acid tectons (a) 1 and (b) 2. STM images of (c) 1 adsorbed on HOPG showing the parallel network structure and (d) 2 adopting a close-packed arrangement. Both molecules adopt a Kagome' network structure when co-adsorbed with coronene, (e) tecton 1, (f) tecton 2. Image dimensions and operation parameters: (c) $100 \times 100 \text{ \AA}$, +1.2 V, 100 pA; (d) $190 \times 190 \text{ \AA}$, -1.0 V, 200 pA (inset $20 \times 40 \text{ \AA}$; -1.5 V, 300 pA); (e) $200 \times 200 \text{ \AA}$, +1.3 V, 5 pA; (f) $200 \times 200 \text{ \AA}$, +1.3 V, 5 pA. Schematic representations of compounds 1 or 2 overlaid to illustrate tecton arrangement.

Kagome' network (Scheme 1). The choice of coronene is based upon previous studies that have demonstrated that coronene is of a suitable size and shape to fit within the circular pores that can be formed by isophthalate moieties, such as those formed by trimesic acid,¹¹ extended isophthalate functionalised molecules¹² and related molecules.¹³ Thus the addition of coronene as a template molecule was anticipated to favour the formation of the Kagome' network in the case of 1 and 2.

Coronene was added to nonanoic acid solutions of 1 or 2 prior to surface deposition on a HOPG surface. STM images of the resulting structures confirm the formation of the Kagome' network structure for both 1 (Fig. 1(e)) and 2 (Fig. 1(f)) with coronene sitting in the circular hexa-isophthalate node of each framework. The networks have measured periods of $3.2 \pm 0.2 \text{ nm}$ (1) and $2.9 \pm 0.2 \text{ nm}$ (2). Following addition of coronene to the deposition solutions there is no evidence for the formation of the parallel or close-packed networks. Indeed only the Kagome' network, with co-adsorbed coronene, is observed on the surface. These images clearly demonstrate the successful use of a guest template in pre-determining the formation of a network arrangement that is less stable in the absence of the guest molecule.⁸

In the case of molecule 2 two enantiomorphic arrangements can be adopted by the molecule upon surface adsorption.



Unit cell parameters	Molecule 1 : parallel		Molecule 2: close packed	
	STM	DFT	STM	DFT
a	$2.0 \pm 0.1 \text{ nm}$	$1.97 \pm 0.01 \text{ nm}$	$2.0 \pm 0.1 \text{ nm}$	$1.95 \pm 0.1 \text{ nm}$
b	$2.0 \pm 0.1 \text{ nm}$	$1.97 \pm 0.01 \text{ nm}$	$0.9 \pm 0.1 \text{ nm}$	$0.90 \pm 0.1 \text{ nm}$
γ	$130^\circ \pm 1^\circ$	$130.1^\circ \pm 0.1^\circ$	$70^\circ \pm 1^\circ$	$68.9^\circ \pm 1^\circ$

Fig. 2 Schematic representations of the supramolecular arrangement observed for tecton 1 parallel network (above) and tecton 2 close-packed arrangement (below) with both measured and calculated unit cell parameters.

Although we cannot resolve the enantiomorphs from the STM images, simple geometric requirements mean that within a given Kagome' network all of the molecules of 2 must adopt the same enantiomorph. It is reasonable to conclude that both enantiomorphs are present on the surface in different chiral domains.

A model for the experimentally observed stabilisation of coronene within the Kagome' network is shown in Fig. 3(a), (b). The stabilisation of the hexa-isophthalate node by the inclusion of a guest coronene molecule is supported by DFT calculations. Modeling of the Kagome' network hexa-isophthalate node using trimesic acid as a representative molecule to form this node, Fig. 3(c), gives an energy gain of -0.17 or -0.20 eV per coronene molecule depending on molecular orientation (Fig. 3(d), (e), see ESI[†]) and a theoretical estimate for the period of the network shown in Fig. 3(a), (b) of $3.1 \pm 0.01 \text{ nm}$ ($3.0 \pm 0.01 \text{ nm}$ for network formed from 2) which is in excellent agreement with measured values. The stabilisation of the hexa-isophthalate node by coronene is clearly important in favouring the formation of the Kagome' network instead of other network arrangements. The calculation reported here does not assess the overall stabilisation of the whole Kagome' network as other factors, including surface/adsorbate and van der Waals interactions as well as solvent effects, are not taken into account. However, agreement between the reported calculations and the experimental results clearly confirm the value of this simple theoretical approach.

In summary we have demonstrated the successful application of a templating approach to surface-based crystallization by the use of a suitably designed guest molecule, coronene,

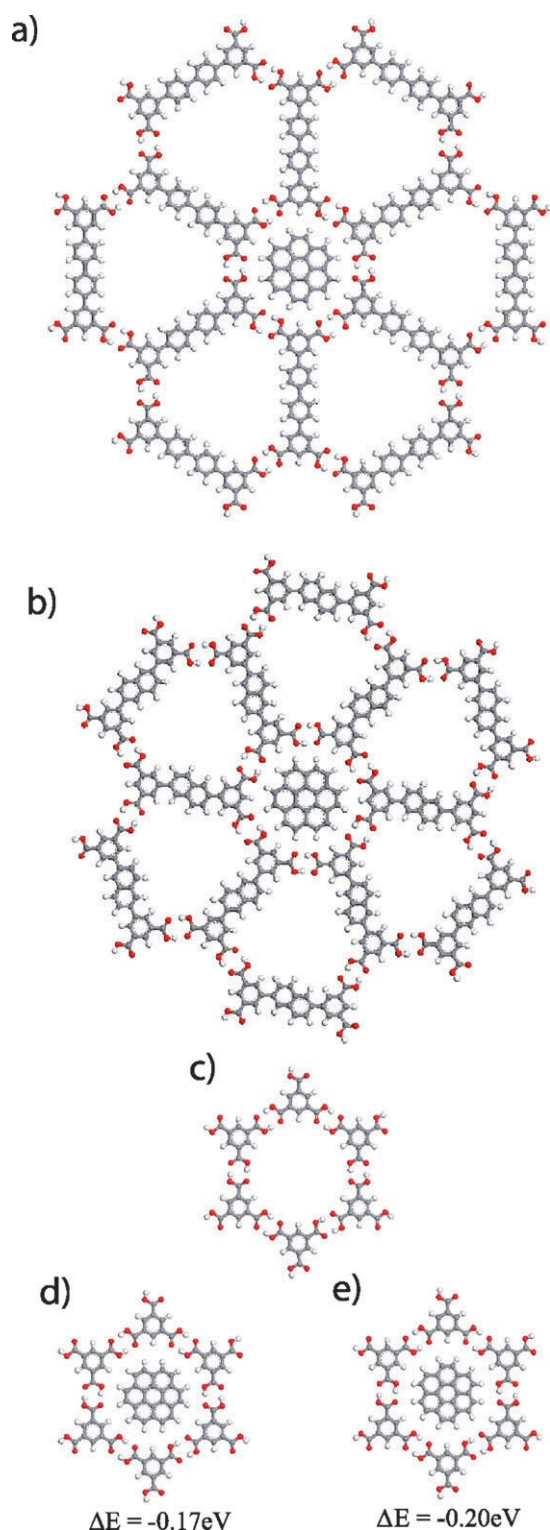


Fig. 3 Schematic representations of the Kagome' network supramolecular arrangements observed with coronene positioned in the circular hexa-isophthalate sub-unit: (a) tecton 1; (b) tecton 2; (c) the circular hexa-isophthalate sub-unit observed with trimesic acid used in DFT calculations; (d), (e) the two orientations of coronene positioned within the circular hexa-isophthalate sub-unit observed with trimesic acid, similarly used in DFT calculations.

which significantly enhances the stability of one network arrangement, the Kagome' network, over another, the parallel network. We are currently developing these studies to other network types and guest species to further elaborate the tecton-based supramolecular approach to surface-based self-assembly.

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SUPPLEMENTARY INFORMATION

Directing Two-Dimensional Molecular Crystallization by using Guest Templates.

Matthew Blunt, Xiang Lin, Maria del Carmen Gimenez-Lopez, Martin Schröder, Neil R.

Champness* and Peter H. Beton*

Synthesis.

Compound **1** was prepared according to a previously reported method.¹

Synthesis of 2, Naphthylene 2,6-bis(3,5-benzenedicarboxylic acid).

2,6-Dibromonaphthalene (0.286 g, 1 mmol), diethyl isophthalate 5-boronic acid (0.64 g, 2.4 mmol) and K₃PO₄ (2.10 g, 10 mmol) were mixed in 1,4-dioxane (30 ml), and the mixture was de-aerated using N₂. Pd(PPh₃)₄ (0.05 g, 0.043 mmol) was added to the reaction mixture with stirring and the mixture was heated to 80°C for 3 days under a N₂ atmosphere. The resultant mixture was evaporated to dryness and extracted into CHCl₃, which was in turn dried over MgSO₄. The solution was evaporated to dryness and the residue was briefly washed with EtOH (10ml). The resulting crude product (mainly tetra-ethyl esters of the target ligand) was hydrolysed by refluxing the crude product in 2M aqueous NaOH, followed by acidification with 37% HCl affording **2**. Yield: 0.28 g, 65%. ¹H NMR (DMSO-*d*⁶, 300MHz), **2**: 8.56(d, 2H, *J*=3.2Hz), 8.50(dd, 1H, *J'*=13.92Hz, *J*²=3.0), 8.42(s, 1H), 8.24 (d, 1H, *J*=6.1Hz), 7.96 (d, 1H, *J*=12.7Hz). Elemental analysis (% calc/found) for **2** (C₂₆O₈H₁₆): C 68.42/68.03, H 3.53/3.79.

STM images

All images were obtained using mechanically cut PtIr (90:10) wire, and were taken in solution at the liquid/solid interface. Images c), e), and f) were obtained on a *Molecular Imaging PicoSPM* and image d) was obtained on a *Veeco Multimode Microscope* using a *Nanoscope IIIa* controller. The detailed experimental details for each image and expanded versions of the images from the main text are as follows:

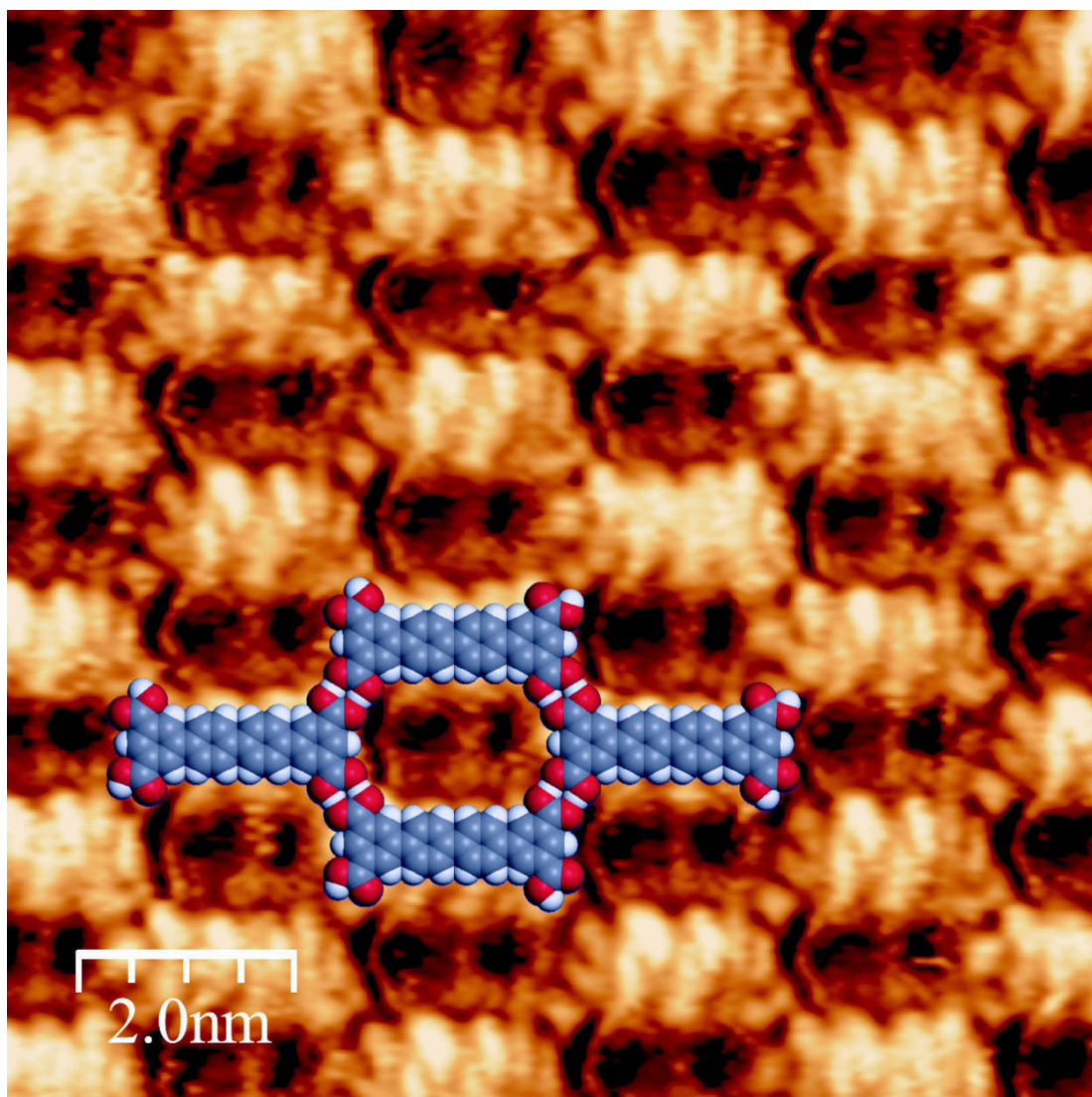


Figure 1(c) 30 μL of a saturated nonanoic acid solution of **1** was placed onto a freshly cleaved HOPG sample and imaged immediately. Image parameters: image size: 10nm x 10nm; tunnel current: 100pA; sample bias: +1.2V.

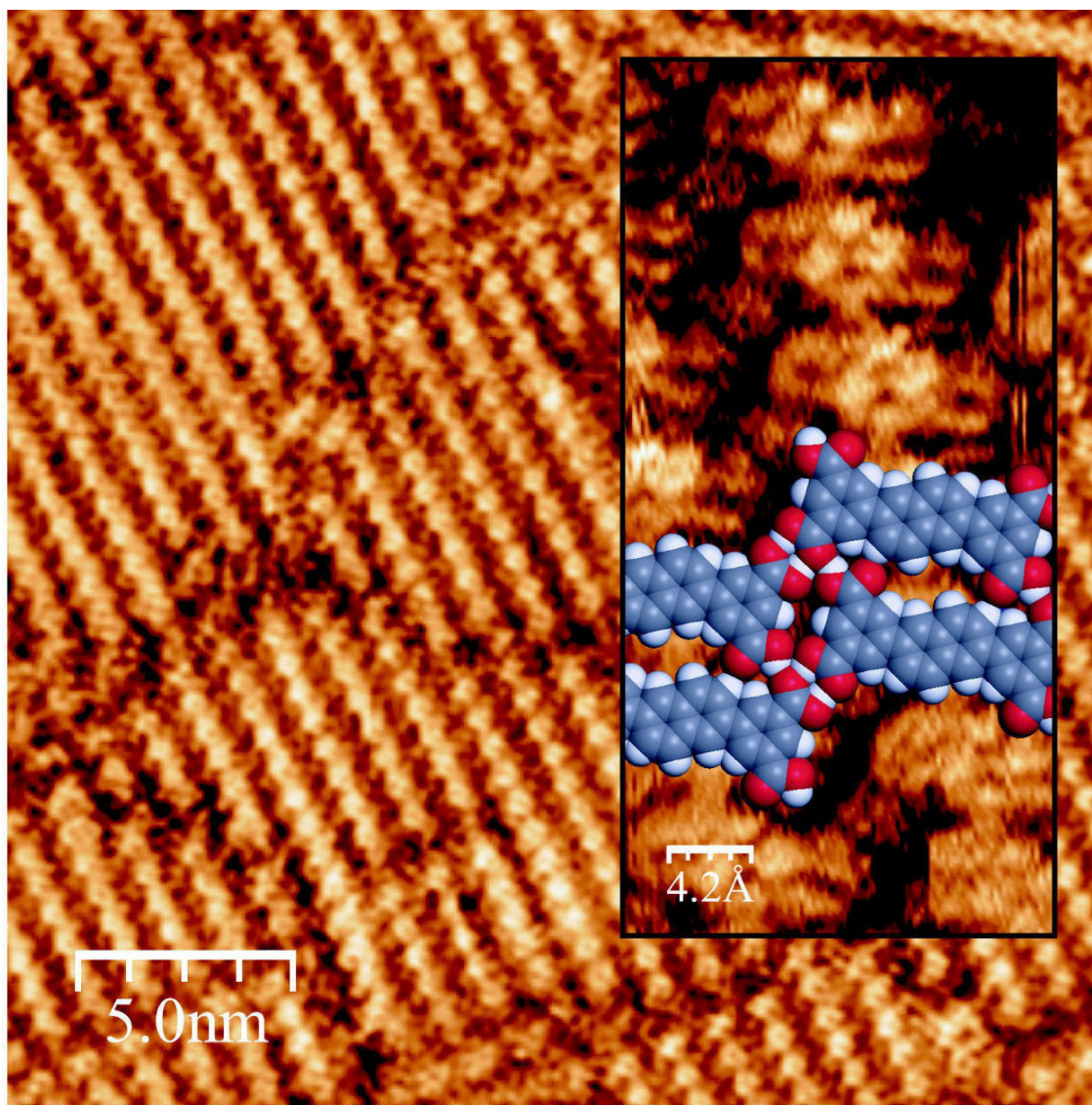


Figure 1(d) 30 μL of a saturated heptanoic acid solution of **2** was placed onto a freshly cleaved HOPG sample and imaged immediately. The same molecular arrangement is observed when saturated nonanoic acid solutions are used. Images parameters (main image): image size: 25nm by 25nm; tunnel current: 200pA; sample bias: -1.0V. Inset, image parameters: image size: 2nm x 4nm; tunnel current: 300pA; sample bias: -1.5V

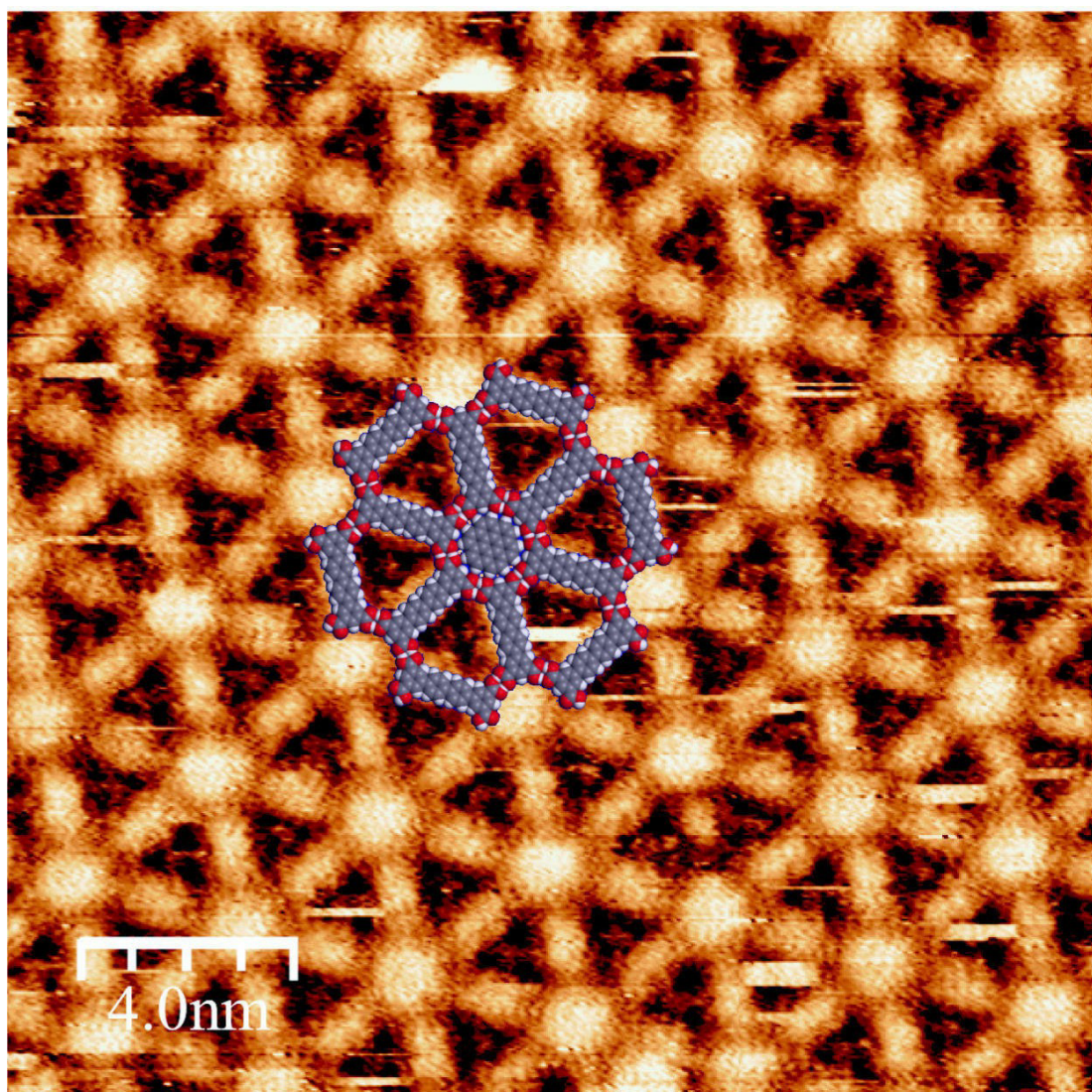


Figure 1(e) 30 μL of a one to one mixture of saturated nonanoic acid solution of **1**, and 0.03mg/mL coronene in nonanoic acid, was placed onto a freshly cleaved HOPG sample and imaged immediately. Images parameters: image size: 20nm x 20nm; tunnel current: 5pA; sample bias: 1.3V.

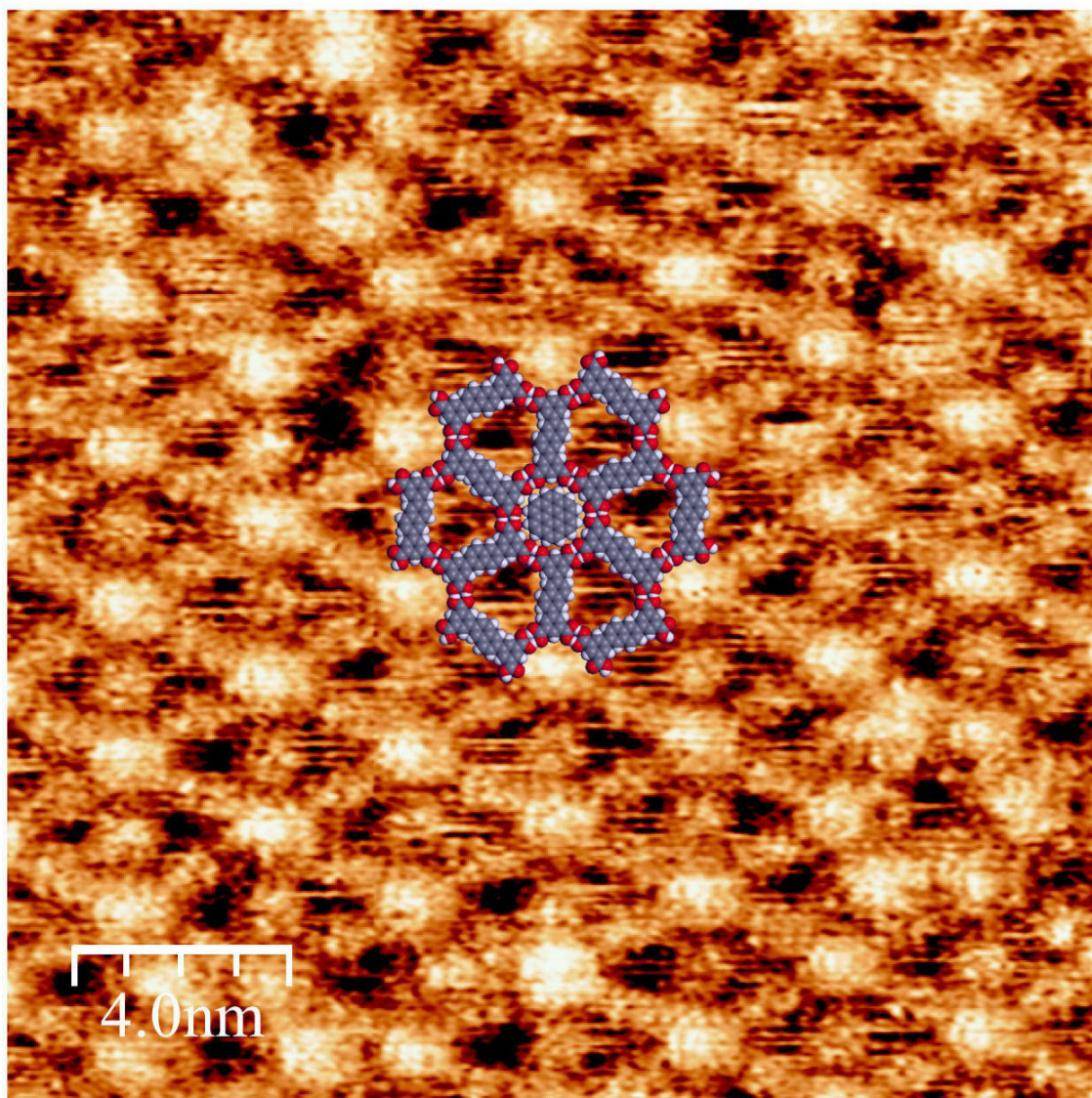


Figure 1(f) 30 μL of a one to one mixture of saturated nonanoic acid solution of **2**, and 0.03mg/mL coronene in nonanoic acid, was placed onto a freshly cleaved HOPG sample and imaged immediately. Images parameters: image size: 20nm x 20nm; tunnel current: 5pA; sample bias: 1.3V.

Accurate unit cell dimensions were determined by obtaining images with both molecular resolution of the network, and atomic resolution of the underlying graphite. These images were then drift-corrected using the graphite lattice for calibration. For compound **1** *Fig S1* shows a drift corrected image collected from the deposition of a 30 μ L of saturated **1** in heptanoic acid solution placed on to HOPG and imaged immediately. Tunnel parameters: tunnel current = 300pA (network), 1000pA (graphite); sample bias = 1.2V (network), 0.05V (graphite). After drift correction unit cell parameters of $\mathbf{a} = \mathbf{b} = 2.0 \pm 0.1\text{nm}$, $\gamma = 130^\circ \pm 1^\circ$ were obtained.

For compound **2** *Fig S2* shows a drift corrected image collected from the deposition of a 30 μ L of saturated **2** in heptanoic acid solution placed on to HOPG and imaged immediately. Tunnel parameters: tunnel current = 300pA (network), 1000pA (graphite); sample bias = -1.2V (network), 0.10V (graphite). After drift correction unit cell parameters of $\mathbf{a} = 2.0 \pm 0.1\text{nm}$, $\mathbf{b} = 0.9 \pm 0.1\text{nm}$, $\gamma = 70^\circ \pm 1^\circ$ were obtained.

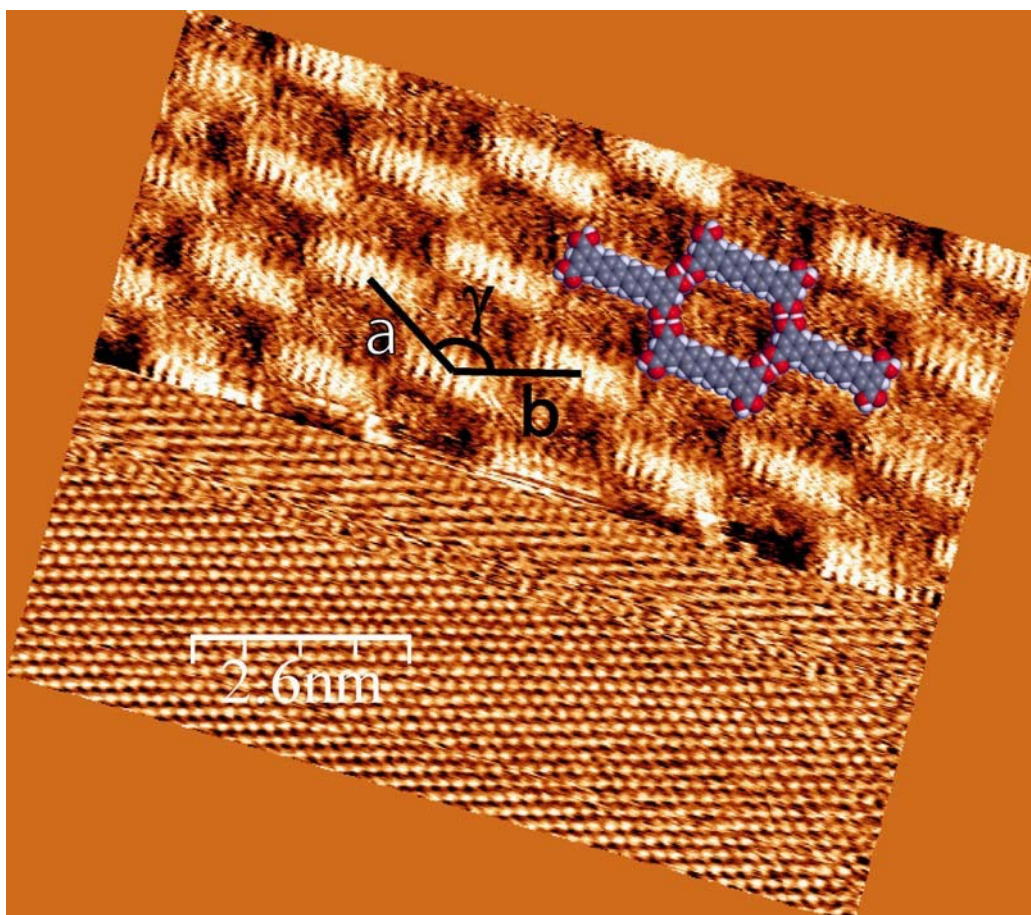


Figure S1.

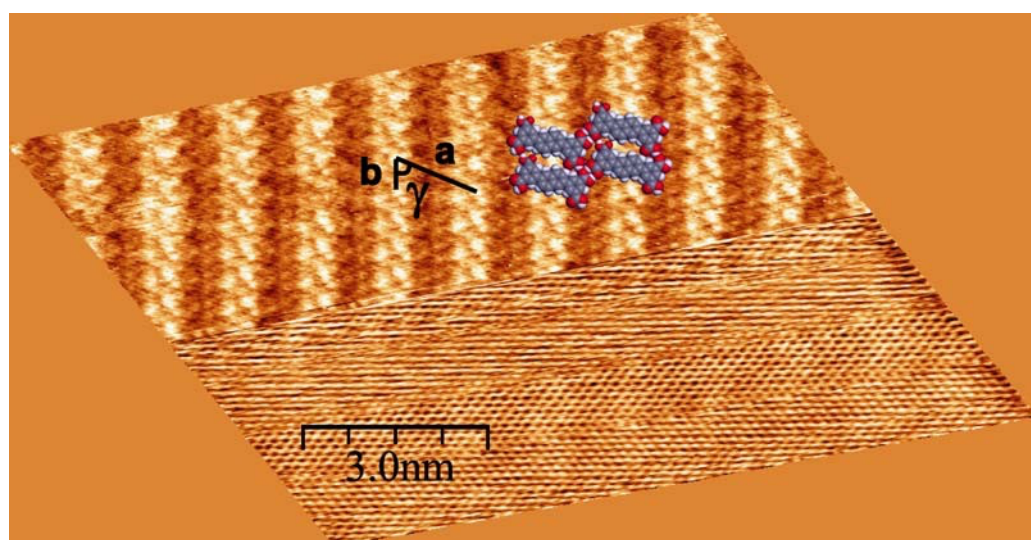


Figure S2.

Theoretical Simulations:

All density functional theory (DFT) calculations were carried out using the DMol³ package in Materials Studio. The generalised gradient approximation functional of Perdew-Burke-Enzerhof was implemented². Core electrons were represented by effective core potentials constructed according to the method of Bergner *et. al.*³, while double numerical basis sets with polarization functions were used for the valence electrons. The radius within which the atomic orbitals are strictly localized was set to 3.7 angstroms. For geometry optimisations the structure was considered to have converged when the force on the atoms was $< 0.1 \text{ eV } \text{\AA}^{-1}$. A default convergence tolerance of 10^{-5} eV was employed for the self-consistent field cycle at each stage of the optimization process.

The optimised geometries of molecules **1**, **2**, and coronene were found to be planar in the gas phase without the need to introduce constraints. Simulations were then performed for the proposed network structures of molecules **1**, and **2** which are shown on Figs S1 and S2, (examples of the simulated structures are shown in Fig S3). In these simulations the central components of the molecules were constrained to be planar, however the carboxylic acid groups were left unconstrained to allow rotation.

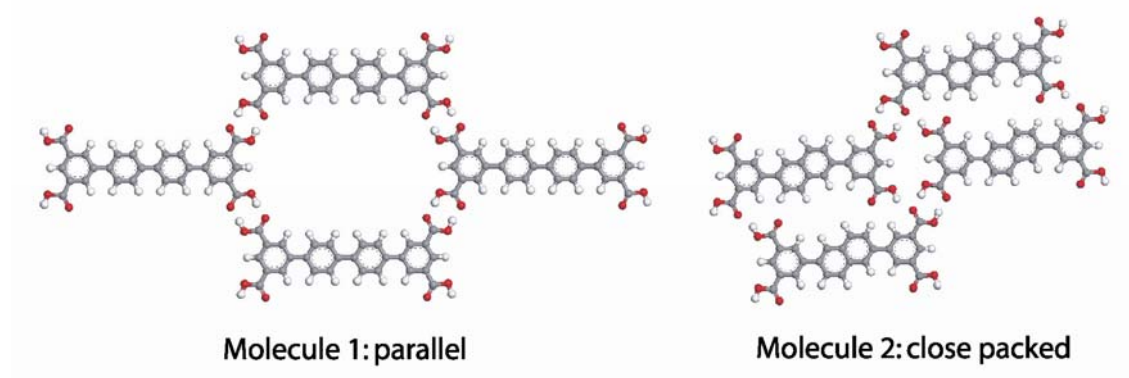


Figure S3.

Accurate values for the simulated unit cell dimensions (see Fig S4) of both network structures were collected and compared to the equivalent values from the experimental images. Excellent agreement was obtained between the experimentally derived measurements and their simulated counterparts (see table S1).

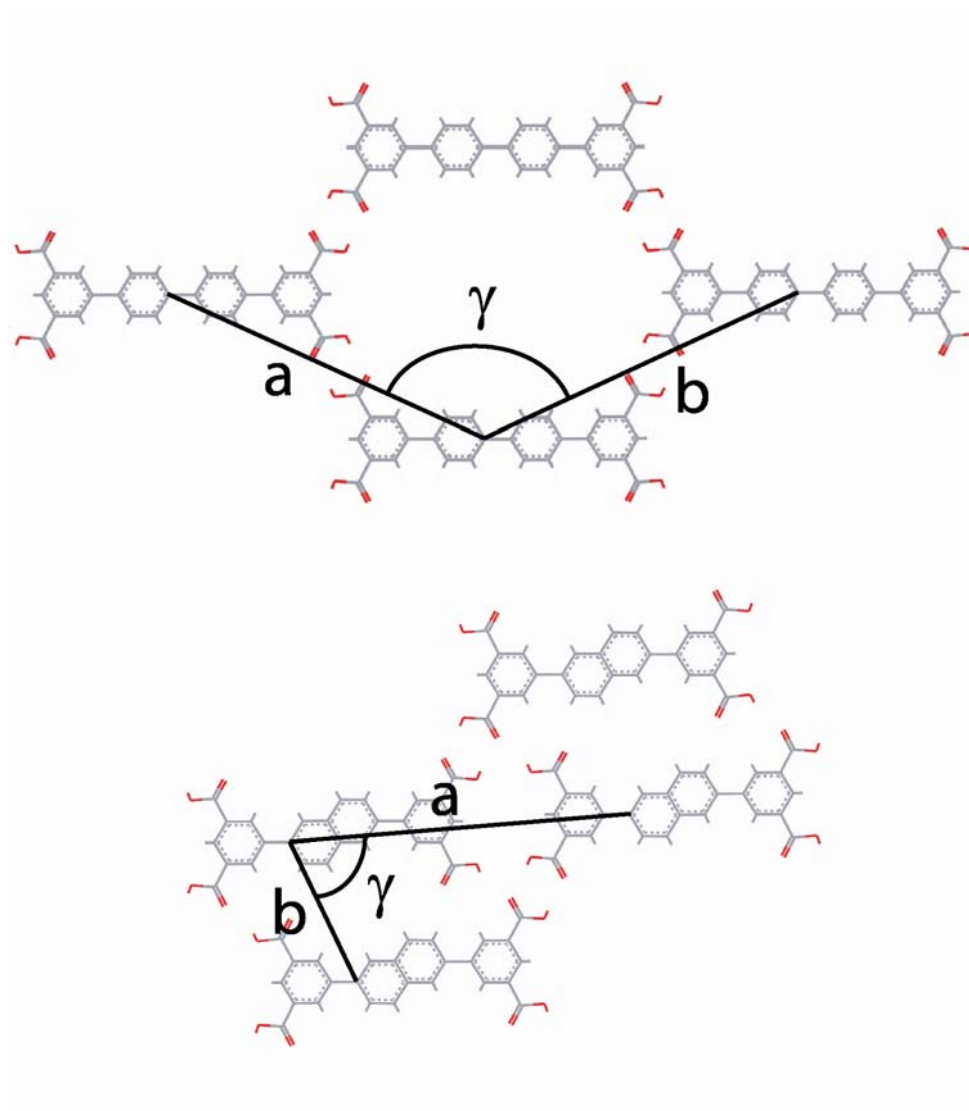


Figure S4.

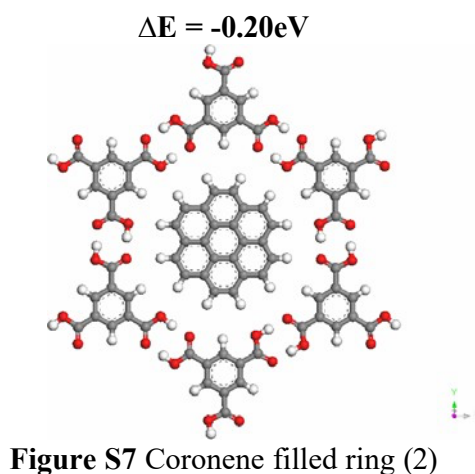
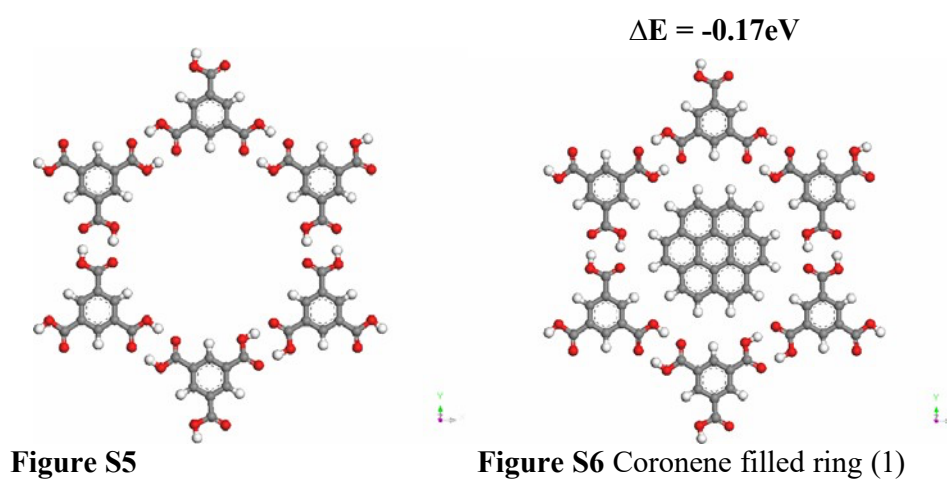
Unit cell parameters	Molecule 1 : parallel		Molecule 2: close packed	
	<i>STM</i>	<i>DFT</i>	<i>STM</i>	<i>DFT</i>
a	2.0 + 0.1 nm	1.97 + 0.01 nm	2.0 + 0.1 nm	1.95 + 0.01 nm
b	2.0 + 0.1 nm	1.97 + 0.01 nm	0.9 + 0.1 nm	0.90 + 0.01 nm
γ	$130^\circ \pm 1^\circ$	$130.1^\circ \pm 0.1^\circ$	$70^\circ \pm 1^\circ$	$68.9^\circ \pm 1^\circ$

Table S1.

Using the energies calculated for the individual molecules the energy gain per molecule due to hydrogen bonding was calculated for the parallel ordering of molecule 1

and the close packed ordering of molecule **2**. Values of -1.57eV per molecule, for molecule **1** in the parallel arrangement, and -1.42eV per molecule, for molecule **2** in the close packed arrangement were obtained.

To estimate the energy change induced by placing a coronene molecule in the hexa-isophthalate wheel of a trimesic acid network, mimicking the Kagomé network, three calculations were carried out. Firstly, a set of six trimesic acid molecules were simulated in the appropriate arrangement (Fig S5). Two further calculations were performed with a coronene molecule present at the hexa-isophthalate vertex in different orientations, (Figs S6 & S7).



The energy change due to the presence of coronene in the hexa-isophthalate vertex was calculated by summing the energies of the trimesic acid ring and the energy of a single coronene molecule, and comparing this value with the energies of the trimesic

acid ring and coronene combinations. The energy change due to hydrogen bonding between the empty trimesic acid ring and the filled trimesic acid ring (1), Fig S6, was calculated as -0.17 eV. The energy change due to hydrogen bonding between the empty trimesic acid ring and the filled trimesic acid ring (2), Fig S7, was calculated to be -0.20 eV.

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