SUPPLEMENTARY INFORMATION

Directing Two-Dimensional Molecular Crystallization by using Guest Templates.
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Synthesis.
Compound 1 was prepared according to a previously reported method.1

Synthesis of 2, Napthylene 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 tetraethyl 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-d6, 300MHz), 2: 8.56(d, 2H, J = 3.2Hz), 8.50(dd, 1H, J1 = 13.92Hz, J2 = 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 µL 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 $a = b = 2.0 \pm 0.1$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 µL 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 $a = 2.0 \pm 0.1$nm, $b = 0.9 \pm 0.1$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 eV Å⁻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.

![Molecule 1: parallel and Molecule 2: close packed](image)

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).
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).

\[ \Delta E = -0.17 \text{eV} \]

Figure S5 Figure S6 Coronene filled ring (1)

\[ \Delta E = -0.20 \text{eV} \]

Figure S7 Coronene filled ring (2)

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.

