Supporting Online Material for

**Random Tiling and Topological Defects in a Two-Dimensional Molecular Network**

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Random Tiling and Topological Defects in a Two-Dimensional Molecular Network

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Molecular Synthesis

1 was prepared from the oxidation of the methyl groups of 3,5,3’,5’-tetramethyl-p-terphenyl, 2, see Scheme 1.

Scheme 1: Suzuki coupling reaction of 2,6-Dibromobenzene with 3,5-dimethylphenylboronic acid follow by oxidation of the methyl groups.

Synthesis of 3,5,3’,5’-tetramethyl-p-terphenyl (2)

2,6-Dibromobenzene (378 mg, 1.6 mmol), an excess of 3,5-dimethylphenylboronic acid (600 mg, 4 mmol) and Cs₂CO₃ (1.4 g, 4 mmol) were mixed in ethanol (10 ml), and the mixture was de-aerated using N₂. Pd(PPh₃)₄ (18.5 mg, 1% of 1.6 mmol) was
added to the reaction mixture with stirring and the mixture was refluxed to 80°C for 3
days under a N₂ atmosphere. The resultant mixture was evaporated to dryness,
extracted into CHCl₃ and washed with water. The organic layer was dried over
MgSO₄ and the solvent was removed under reduced pressure to provide a crude
product which was purified by silica gel chromatography using hexane as eluent. The
product was obtained as a colourless crystalline solid. Yield: 328 mg, 75%. ¹H NMR
(acetone-δ6, 270MHz): 7.73 (s, 4H), 7.33(s, 4H), 7.03(s, 2H), 2.38 (s, 12H). ¹³C NMR
(acetone-δ6, 270MHz): δ 140.87, 140.24, 138.37, 129.01, 127.48, 125.05, 21.523. EI-
MS (m/z) found: 287.1807 ([M+H]+, 100%). Elemental analysis (% calc/found) for
C₂₃H₂₂: C 92.26/92.33, H 7.74/7.73.

Synthesis of p-terphenyl-3,5,3’,5’-Tetracarboxylic acid (TPTC) (I)

3,5,3’,5’-Tetramethyl-p-terphenyl (171 mg, 0.6 mmol) and NaOH (381 mg, 9.5
mmol) were dissolved in t-BuOH:water (16 mL, 1:0.6). The reaction was heated to
55°C and an excess of KMnO₄ (1.12 g, 7.1 mmol) was added in portions over 2 days.
The reaction was kept at this temperature whilst being stirred for two weeks until the
oxidation process was completed. A few drops of ethanol were added to the mixture
to destroy excess KMnO₄. Afterwards, the mixture was heated to 90°C before vacuum
filtration to remove MnO₂. The filtrate was concentrated in vacuo and concentrated
HCl was added dropwise with stirring until no more white precipitated formed
(pH=2). The product was collected by centrifugation and washed with water to
eliminate excess acid, further washed with acetone and dried in vacuo. Yield: 100
mg, 41 %. ¹H NMR (DMSO-δ6, 270MHz): 8.48 (t, 2H, J=1.53 Hz), 8.45 (d, 4H,
J=1.53 Hz), 7.92 (s, 4H). ¹³C NMR (acetone-δ6, 270MHz): δ 167.07, 140.82, 138.73,
132.86, 131.72, 129.58, 128.32. EI-MS (m/z) found: 405.0609 ([M+H]+, 100%),
361.0752 ([M-H-(COOH)]⁺, 82.6%). Elemental analysis (% calc/found) for C₂₂H₁₄O₈:
C 65.03/64.95, H 3.47/3.43.
Experimental details

Saturated solutions of TPTC were prepared by mixing approximately 10mg of TPTC with 5ml of nonanoic acid and sonicating for ten minutes. The resulting fine suspension was allowed to settle and the clear solution was decanted from the top. All images were collected using a Molecular Imaging PicoSPM using mechanically cut PtIr (90:10) wire, and were taken in solution at the liquid/solid interface. In all the experiments highly orientated pyrolytic graphite substrates (HOPG) were used. The HOPG samples were sonicated in methanol, dried and then mechanically cleaved prior to each experiment. A PTFE liquid cell was used to both hold down the samples during imaging, and to stop the solution escaping.

Image analysis and processing:

In order to eliminate the effects of drift from measurements of the network dimensions the underlying HOPG substrate was used as a calibration. Images were acquired in which parameters were switched from those normally used to image the molecular network to those used for imaging HOPG. The resultant images (see Figure S1) show both the network structure, and the underlying HOPG. By assuming that the rate of drift remains unchanged between the two halves of the image we can use the known lattice constant of graphite to determine the dimensions of the network structure. The pore-to-pore separation for the network structure shown in Figure S1 is 1.66nm ± 0.08nm, and the hexagonal network of pores is rotated by 6° ± 1° with respect to the underlying HOPG lattice. The value of the pore-to-pore separation is the same, within error, to that reported for a hexagonal network of trimesic acid molecules ~1.7nm [1].
Figure S1: Composite image showing the network structure in the upper section of the image (topography data collected during the forward trace) and the underlying HOPG in the lower section (Current data collected during the forward trace). Imaging parameters, tunnel current: 5pA (top), 1nA (bottom); tip bias: +1.2V (top), +0.1V (bottom).

Figure S2: Schematic diagram Showing a random section of TPTC network (a = b = 1.66nm ± 0.08nm, γ = 60° ± 1°). An overlay displaying a small section of the rhombus tiling for this network is also shown.

In order to create the rhombus tilings of STM images drift correction (based on the calibration described above) is performed followed by a conversion to a binary image, and finally the replacement of molecules by tiles to form a tiling (see Figure S2 for a schematic diagram of the tiling process). The tilings produced for the two STM images used in the calculation of the correlation function shown in Figure 4, are displayed in Figure S3.
Calculation of Binding Energies and Geometries

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 implemented [2]. 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 3.7Å. For geometry optimisations the structure was considered to have converged when the force on the atoms was < 0.1eV 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 stabilization energy associated with a single parallel (E_p) or arrowhead (E_T) carboxylic-carboxylic hydrogen bond was calculated by dividing the total stabilization energies by the number of such bonds giving E_p = -0.80eV and E_T = -0.80eV. The optimized geometry for a single TPTC molecule was found to be planar.
without the need to apply any constraints. Following this, the optimized geometries for two different (parallel and arrowhead) arrangements of TPTC molecules were calculated (see Figure S4 a & b). 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. Using the energies calculated for the individual molecules the energy gains per molecule due to hydrogen bonding were calculated for the parallel and arrowhead arrangements (see Figure S4a and b).

**Tiling Statistics.**

The following section details the distribution of tile orientations, number of defects, and defect density for the tilings of the 80nm and 100nm STM images used to generate Figure 4E. The tiling of the 80nm STM image has 2775 tiles in total with 914, 938, and 903 in the three different orientations (33.2%, 34.1%, and 32.8%). The tiling of the 100nm STM image has 4138 tiles in total with 1376, 1383, and 1379 in the three different orientations (33.3%, 33.4%, and 33.3%). The tiling of the 80nm STM image has six defects in total (four of one charge, two of the other) giving a defect density of $2.2 \times 10^{-3}$, and an average defect separation of ~20 lattice spacings. The tiling of the 100nm STM image has twelve defects in total (six of one charge, six
of the other) giving a defect density of $2.9 \times 10^{-3}$, and an average defect separation of 
$\sim 17$ lattice spacings.

References:

