

Supplementary Information

Packing of Isophthalate Tetracarboxylic Acids on Au(111): Rows and Disordered Herringbone Structures

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1. Synthesis

BPTC, TPTC and QPTC molecules were synthesised as reported previously¹.

2. Calculations

Density functional theory (DFT) calculations were carried out using the DMol3 package in Materials Studio. The generalised gradient approximation functional of Perdew-Burke-Ernzerhof² was implemented. 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 Å. 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 BPTC, TPTC and QPTC were found to be planar in the gas phase without the need to introduce constraints.

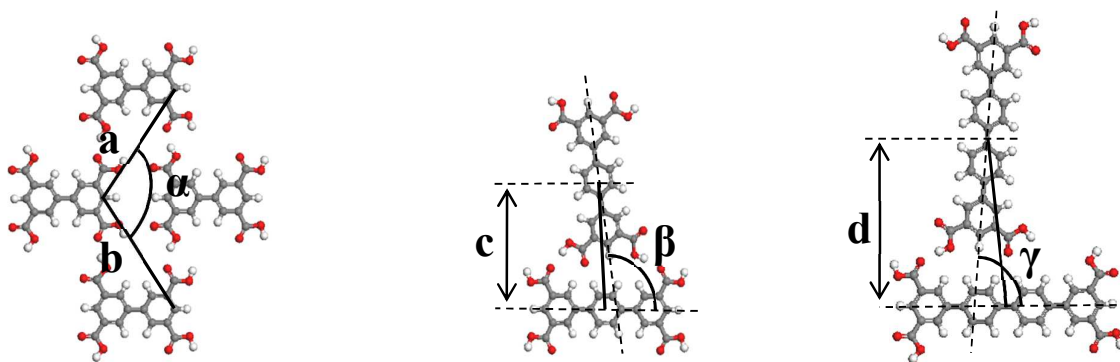


Figure S1. Schematic representation of a) unit cell formed by BPTC molecules; b) hydrogen bonds forming junction of two TPTC molecules and c) two QPTC molecules.

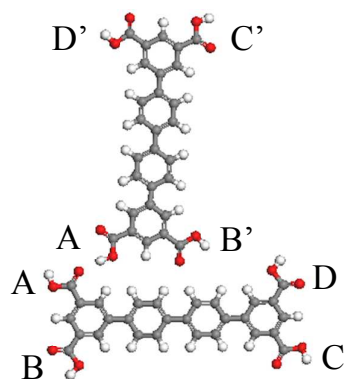


Figure S2. Hydrogen bonding in carboxylate moieties of QPTC

Table S1. DFT analysis for packing of BPTC

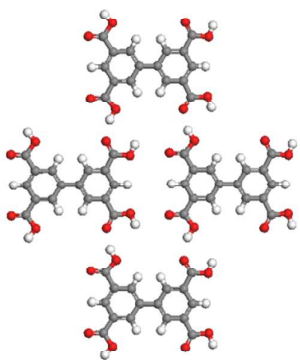
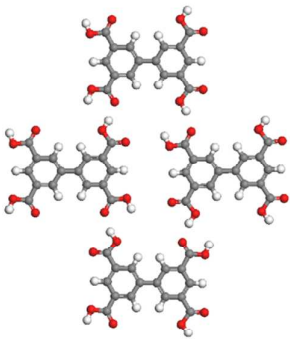
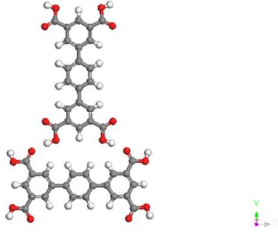
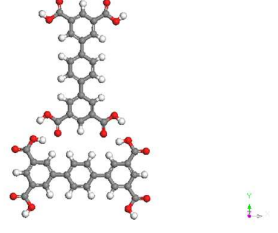
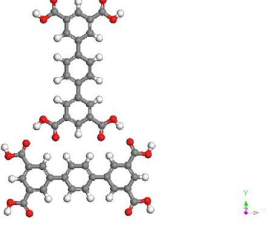
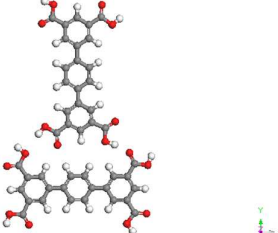
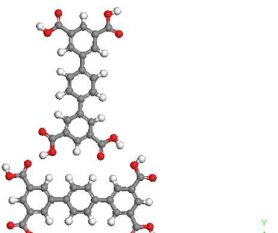
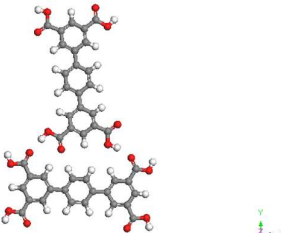
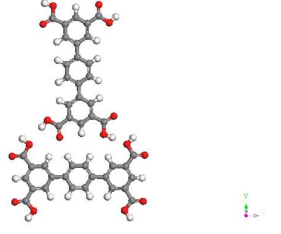
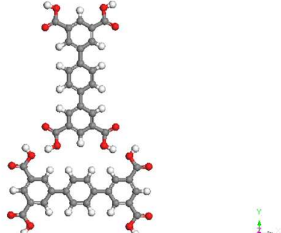
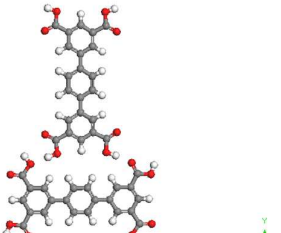
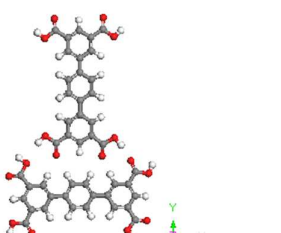
Model 1	Model 2
	
$\Delta E = -1.23 \text{ eV}$	$\Delta E = -1.20 \text{ eV}$
$a = b = 1.18 \text{ nm} \pm 0.01 \text{ nm}$	$a = b = 1.18 \text{ nm} \pm 0.01 \text{ nm}$
$\alpha = 108.9 \pm 0.1^\circ$	$\alpha = 109.9 \pm 0.1^\circ$

Table S2. DFT analysis for packing of TPTC

TPTC-1-TPTC-1 $\Delta E = -0.53 \text{ eV}$ $c = 1.19 \text{ nm}$ $\beta = 88.2^\circ$	
TPTC-2-TPTC-2 $\Delta E = -0.31 \text{ eV}$ $c = 1.14 \text{ nm}$ $\beta = 88.3^\circ$	
TPTC-1-TPTC-2 $\Delta E = -0.44 \text{ eV}$ $c = 1.13 \text{ nm}$ $\beta = 88.9^\circ$	
TPTC-3-TPTC-3 $\Delta E = -0.37 \text{ eV}$ $c = 1.17 \text{ nm}$ $\beta = 92.4^\circ$	
TPTC-4-TPTC-4 $\Delta E = -0.38 \text{ eV}$ $c = 1.17 \text{ nm}$ $\beta = 88.1^\circ$	

<p>TPTC-1-TPTC-3</p> <p>$\Delta E = -0.62 \text{ eV}$</p> <p>$c = 1.15 \text{ nm}$</p> <p>$\beta = 97.2^\circ$</p>	
<p>TPTC-2-TPTC-3</p> <p>$\Delta E = -0.29 \text{ eV}$</p> <p>$c = 1.16 \text{ nm}$</p> <p>$\beta = 93.7^\circ$</p>	
<p>TPTC-2-TPTC-1</p> <p>$\Delta E = -0.44 \text{ eV}$</p> <p>$c = 1.17$</p> <p>$\beta = 90.1^\circ$</p>	
<p>TPTC-3-TPTC-1</p> <p>$\Delta E = -0.49 \text{ eV}$</p> <p>$c = 1.17 \text{ nm}$</p> <p>$\beta = 89.1^\circ$</p>	
<p>TPTC-3-TPTC-2</p> <p>$\Delta E = -0.25 \text{ eV}$</p> <p>$c = 1.14 \text{ nm}$</p> <p>$\beta = 88.8^\circ$</p>	

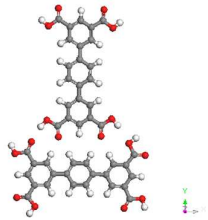
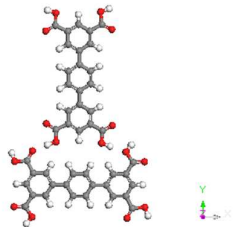
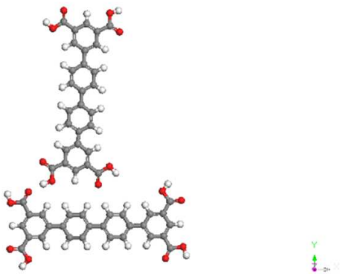
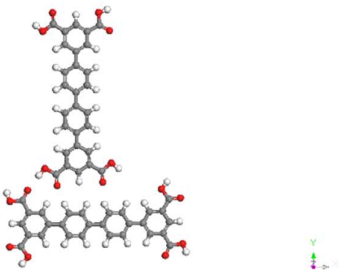
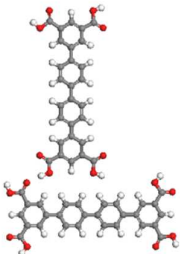

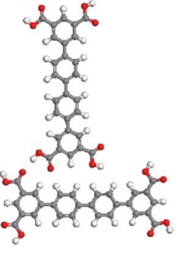

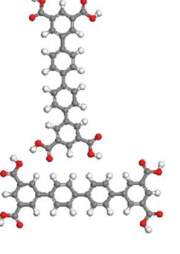

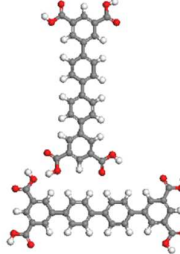

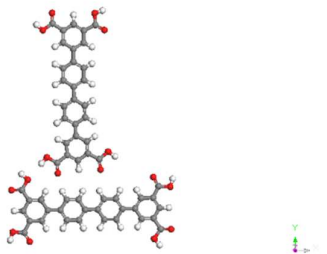
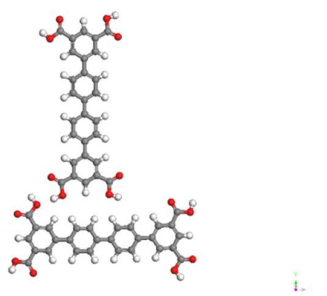
TPTC-4-TPTC-2 $\Delta E = -0.25 \text{ eV}$ $c = 1.16 \text{ nm}$ $\beta = 90.7^\circ$	
TPTC-4-TPTC-1 $\Delta E = -0.48 \text{ eV}$ $c = 1.14 \text{ nm}$ $\beta = 91.3^\circ$	

Table S3. DFT analysis for packing of QPTC

The nomenclature ‘O H O’ etc. indicates whether an O/H atom is directed towards the neighbouring molecule in the positions A, A’ and B’ defined above.

QPTC_1- QPTC_1 O H O $\Delta E: -0.39 \text{ eV}$ $d = 1.39 \text{ nm}$ $\gamma = 85.5^\circ$	
QPTC_1- QPTC_2 O O O $\Delta E: -0.37 \text{ eV}$ $d = 1.37 \text{ nm}$ $\gamma = 89.9^\circ$	

<p>QPTC_1- QPTC_3</p> <p>O H H</p> <p>ΔE: -0.28 eV</p> <p>d=1.41 nm</p> <p>$\gamma= 89.3^\circ$</p>	 
<p>QPTC_1- QPTC_4</p> <p>O O H</p> <p>ΔE: -0.30 eV</p> <p>d=1.37 nm</p> <p>$\gamma=90.6^\circ$</p>	 
<p>QPTC_5- QPTC_5</p> <p>H O H</p> <p>ΔE: -0.11 eV</p> <p>d=1.38 nm</p> <p>$\gamma=92.8^\circ$</p>	 
<p>QPTC_5- QPTC_1</p> <p>H H O</p> <p>ΔE: -0.33 eV</p> <p>d=1.38 nm</p> <p>$\gamma= 86.7^\circ$</p>	 

QPTC_5- QPTC_2 H O O ΔE : -0.21 eV $d=1.38$ nm $\gamma= 90.2^\circ$	
QPTC_5- QPTC_3 H H H ΔE : -0.20 eV $d=1.40$ nm $\gamma= 89.2^\circ$	

3. X-ray photoelectron spectroscopy (XPS) measurements

A Kratos AXIS ULTRA DLD instrument with a mono-chromated Al K_α X-ray source (1486.6 eV) was used and operated at 10 mA emission current and 12 kV anode potential. The lens mode used was hybrid-slot and pass energies 80 eV and 20 eV were used for the wide and high resolution scans respectively. Spectra were acquired at room temperature.

XPS spectra in Figure S3 provide information about the chemical state of adsorbed species. For TPTC deposited from water on gold (Figure S3c) the main C1s peak (~ 284.0 eV) is assigned to carbon atoms in aromatic rings. Two peaks at ~ 285.0 eV and ~ 286.4 eV can be attributed to possible minor contaminations since similar features are found in C1s spectra for a control gold sample which had been immersed in water for several minutes (Figure S3e). The peak at ~ 288.0 eV is attributed to carbon atoms in COOH groups. For the same molecule in the O1s region broad peak can be decomposed into two contributions from carbonyl (~ 531.3 eV) and hydroxy (~ 532.9 eV) groups respectively (Figure S3d). XPS spectra of TPTC can be compared to those obtained for a powder sample (Figure S3a,b). These

measurements confirm that the carboxylic acid groups of TPTC molecule remain protonated upon adsorption on the Au(111) surface under the conditions employed in this study.

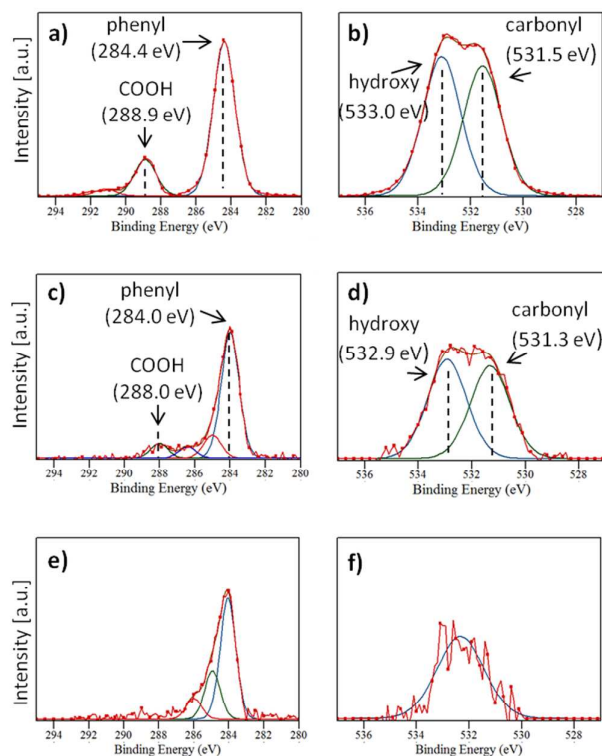


Figure S3. XPS Spectra of C1s and O1s for: a), b) TPTC powder sample; c), d) TPTC adsorbed from water on Au(111) and e), f) bare gold sample immersed in water.

Table S4. Binding energies fitted from C1s and O1s spectra of following samples: TPTC-powder sample, TPTC deposited from water on Au(111) and bare Au(111) immersed in water.

Bulk/powder	TPTC-H2O	Au-H2O	C1s
284.40	284.00	284.05	C-C
-	285.01	284.94	C
-	286.43	286.01	C
288.90	288.03	-	COOH
291.17	-	-	shake-up

Bulk/powder	TPTC-H2O	Au-H2O	O1s
531.55	531.32	-	C=O
533.09	532.93	-	COH

4. STM Images

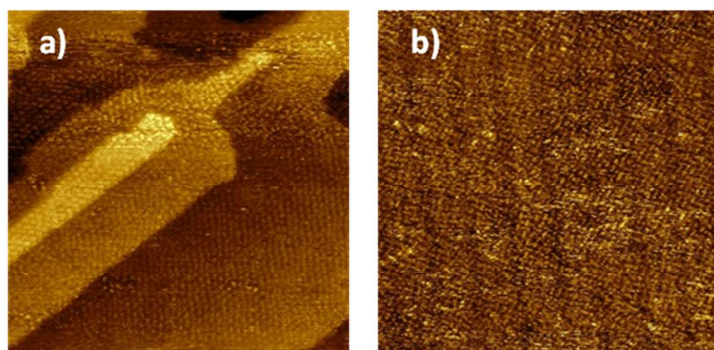


Figure S4. Additional STM images (50 nm × 50 nm): a) BPTC and b) TPTC molecules respectively on Au(111) surface.

1. Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schröder, M., High H₂ Adsorption by Coordination-Framework Materials. *Angewandte Chemie International Edition* **2006**, 45 (44), 7358-7364.
2. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys Rev Lett* **1997**, 78 (7), 1396-1396.