

Supporting Information

Balancing noncovalent interactions in self-assembly of nonplanar aromatic carboxylic acid MOF linkers at the solution/solid interface: HOPG vs. Au(111)

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Synthesis of ethene based MOF linkers.

Materials. Tetraphenylethene, bromine, CuCN, 4-methoxycarbonylphenylboronic acid, cesium fluoride, tetrakis(triphenylphosphine)palladium and all organic solvents were purchased from VWR and were used after drying without further purification. Tetra(4-bromophenyl)ethylene was synthesized according to previous reported procedure.¹

(1) 4,4',4''-(ethene-1,1,2,2-tetrayl)tetrabenzoic acid (**ETC**) synthesis was carried out following a previously reported procedure.^{2,3}

Tetrakis(4-bromophenyl)ethene. Tetraphenylethene (10 g, 0.03 mol) was ground into a fine powder and then transferred evenly between two evaporating dishes. The dishes were placed in a desiccator on top of a vial containing bromine (15 mL, 0.3 mol). The powder reacted with the bromine vapor for two weeks at room temperature. The resulting orange powder was recrystallized in methanol and dichloromethane, yielding a white crystalline product. ¹H NMR (400 MHz, CD₂Cl₂) δ 6.87 (d, 8H), 7.27 (d, 8H).

Tetra(4-cyanophenyl)ethene. Dried N-N'-dimethylformamide (DMF, 20 mL) was transferred via cannula to a 100 mL flask under nitrogen containing tetra(4-bromophenyl)ethene (1.5 g, 2.31 mmol) and CuCN (1.143 g, 12.7 mmol). After refluxing for 24 h the reaction was cooled to room temperature. Water (50 mL) was added to the reaction flask and the mixture was filtered leaving a grey and yellow product. The solid was dried then suspended in water (100 mL). To the suspension, ethylenediamine (4.50 g, 75 mmol) was added producing a vibrant violet color. The suspension was stirred for 2 h at 25 °C. The suspension was then filtered to give a pale-yellow product. The solid was dried and then dissolved in dichloromethane and passed over a short pad of silica. The dichloromethane was then removed, and the remaining residue was recrystallized in a mixture of methanol and dichloromethane. Pale yellow crystals were collected and dried under vacuum. ¹H NMR (400 MHz, CDCl₃) δ 7.07 (d, 4H), 7.48 (d, 4H).

Tetrakis(4-carboxyphenyl)ethene (ETC). Tetrakis(4-cyanophenyl)ethene (0.16 g, 0.37 mmol) was added to a flask containing potassium hydroxide (0.26 g, 4.64 mmol) and ethylene glycol (12 mL). After refluxing for 3 days at 200 °C the reaction solution was cooled to room temperature and water (10 mL) was added to the flask. The resulting water/ethylene glycol mixture was washed with dichloromethane (3 x 50 mL). The water/ethylene glycol solution was then acidified using HCl (6 M) yielding a yellow precipitate. The solid was filtered and washed with excess water. The solid was then dried under vacuum to yield the product. ¹H NMR (400 MHz, DMSO) δ 7.11 (d, 4H), 7.74 (d, 4H), 12.95 (s, 2H).

(2) (E)-4',4''-(1,2-diphenylethene-1,2-diyl)bis([1,1'-biphenyl]-4-carboxylic acid) (**BPDC**) was synthesized by the modification of previously reported procedure.¹

1,2-bis(4-bromophenyl)-1,2-diphenylethene. This compound was synthesized following a previously reported procedure. ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.20 (m, 4H), 7.15-7.09 (m, 6H), 7.01-6.96 (m, 4H), 6.90-6.86 (t, 4H).

Dimethyl 4',4''-(1,2-diphenylethene-1,2-diyl)bis([1,1'-biphenyl]-4-carboxylate). 1,2-bis(4-bromophenyl)-1,2-diphenylethene (1.009 g, 2.06 mmol) and 4-methoxycarbonylphenylboronic acid (1.025 g, 5.70 mmol), cesium fluoride (2.116 g, 13.9 mmol), and tetrakis(triphenylphosphine)palladium (0.170 g, 0.147 mmol) were added together under nitrogen to a 250 mL flask. Degassed dimethoxyethane (DME, 100 mL) was transferred via

cannula to the reaction flask. The reaction was heated at 80 °C for 30 h then cooled to room temperature. DME was then removed using a vacuum. The remaining residue was suspended in water (150 mL) which was then extracted with dichloromethane (3 x 50 mL) using a separatory funnel. The organic layer was then dried using anhydrous magnesium sulfate, filtered, and the dichloromethane was removed using heating and vacuum. The remaining residue was further purified through a silica column using an 8:2 hexanes: dichloromethane solvent system. The resulting bands were recrystallized in methanol and dichloromethane. (62%) ¹H NMR (400 MHz, CD₂Cl₂) δ 3.90 (s, 6H), 7.14 (m, 14H), 7.43 (d, 4H), 7.65 (d, 4H), 8.05 (d, 4H).

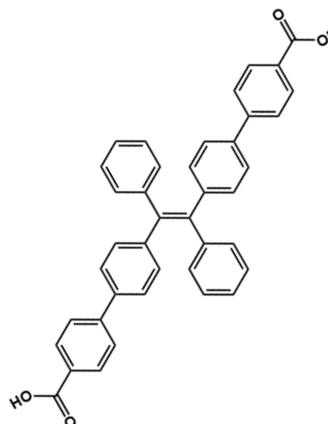
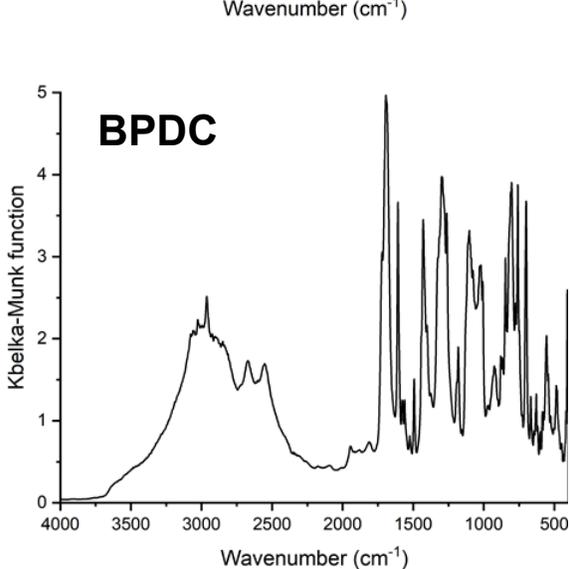
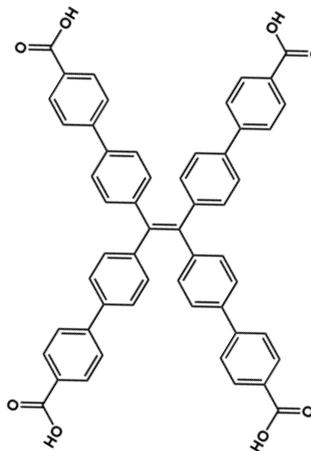
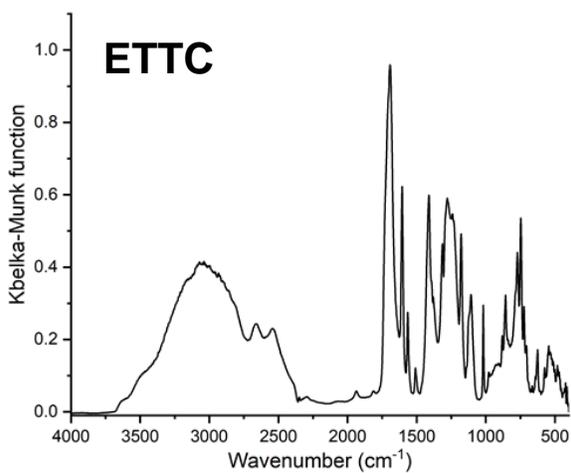
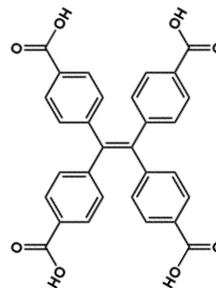
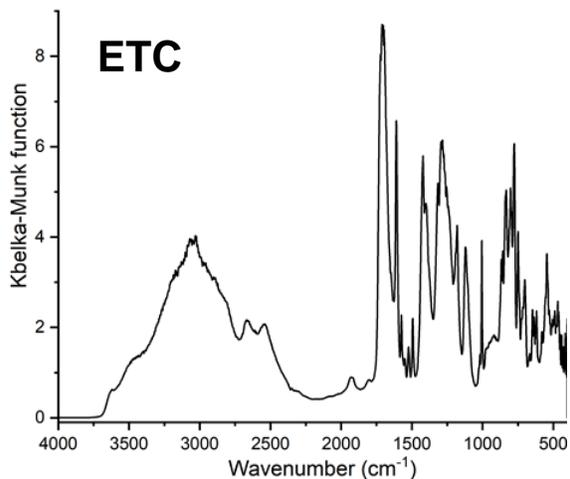
4',4'''-(1,2-diphenylethene-1,2-diyl)bis([1,1'-biphenyl]-4-carboxylic acid). Dimethyl 4',4'''-(1,2-diphenylethene-1,2-diyl)bis([1,1'-biphenyl]-4-carboxylate (0.187 g, 0.3 mmol) and potassium hydroxide (0.609 g, 10.8 mmol) were added to a flask containing 120 mL of a solution of methanol, THF, and water in a 1:1:1 ratio. The reaction was refluxed overnight. Once at room temperature, the organic solvents were removed via heating and vacuum. The remaining aqueous solution was acidified using HCl (6 M). The resulting yellow precipitate was filtered and washed with water. (0.118 g, 66%) ¹H NMR (400 MHz, DMSO) δ 7.00 (m, 2H), 7.06 (d, 4H), 7.12 (m, 8H), 7.53 (d, 4H), 7.72 (d, 4H), 7.95 (d, 4H).

(3) 4',4''',4''''',4''''''-(ethene-1,1,2,2-tetrayl)tetrakis((1,1'-biphenyl)-4-carboxylic acid) (**ETTC**) was synthesized following previously reported procedure.⁴

Me₄ETTC (Tetramethyl 4',4''',4''''',4''''''-(ethene-1,1,2,2-tetrayl)tetrakis([1,1'-biphenyl]-4-carboxylate)). Degassed DME (250 mL) was transferred via cannula to a 500 mL three necked flask under N₂ containing tetrakis(4-bromophenyl)ethylene (1.056 g, 1.63 mmol), 4-methoxycarbonylphenylboronic acid (1.447 g, 8.04 mmol), cesium fluoride (6.0 g, 39.5 mmol), and tetrakis(triphenylphosphine)palladium (0.4 g, 0.3 mmol). The solution was heated at 80 °C for 48 hours. After cooling the reaction mixture to room temperature, the DME was removed under vacuum. The remaining brown solid was dissolved in dichloromethane and washed 3 times with water using a separatory funnel. The washed dichloromethane was dried with anhydrous magnesium sulfate and filtered. The dichloromethane was removed using vacuum and heating. The solid was recrystallized using a mixture of dichloromethane and methanol to yield a light-yellow product. ¹H NMR (400 MHz, CDCl₃) δ 3.93 (s, 12H), 7.21 (d, 8H), 7.47 (q, 12H), 7.77 (d, 4H), 7.98 (d, 4H), 8.26 (s, 4H).

H₄ETTC (4',4''',4''''',4''''''-(ethene-1,1,2,2-tetrayl)tetrakis([1,1'-biphenyl]-4-carboxylic acid)). A solution of Me₄ETTC (1.6 g, 1.8 mmol) dissolved in 100 mL of THF was added to a 500 mL flask. Potassium hydroxide (1.7 g, 30 mmol) dissolved in 100 mL water and 100 mL of methanol were added to the flask. The solution was refluxed overnight. The organic solvents were removed using heating and vacuum. The aqueous phase was then acidified with concentrated HCl to yield a bright yellow precipitate. The solid was filtered, washed with water and acetone, and dried under vacuum to yield a yellow solid. ¹H NMR (400 MHz, DMSO) δ 7.19 (d, 8H), 1.62 (d, 8H), 7.77 (d, 8H), 7.97 (d, 8H), 12.99 (s, 2H).

Diffuse reflectance infrared fourier transform spectra (DRIFTS) of the solid linker samples acquired using ThermoScientific Nicolet iS10 FTIR outfitted with a with Praying Mantis attachment from Harrick Scientific Products. The spectra of ETC and BPDC are those of neat samples; the ETC sample was diluted in KBr (1:4).



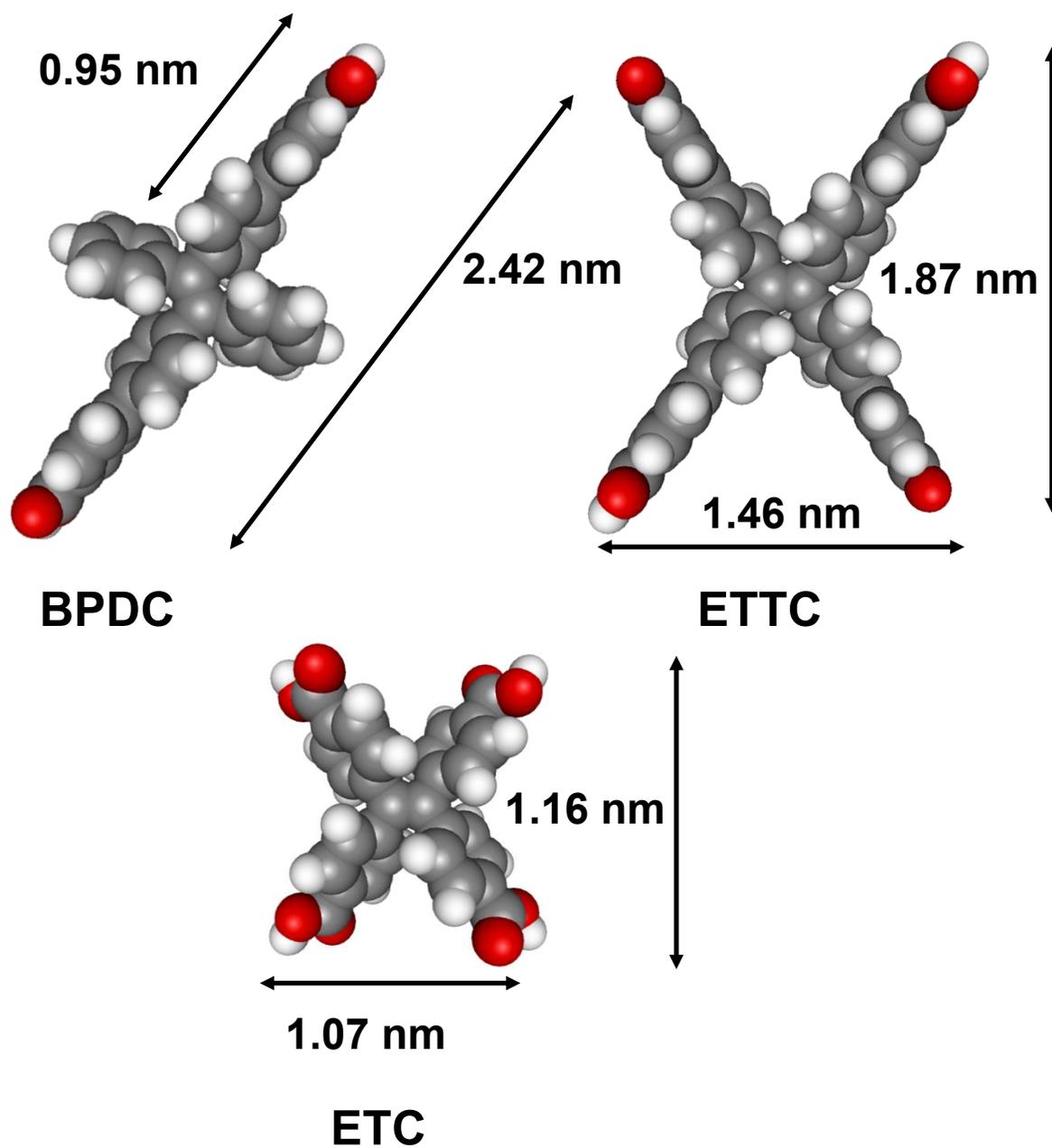


Figure S1. Molecular structures and corresponding DFT optimized structures (shown as CPKs) of MOF linkers with dimensions: tetraphenyl ethene tetracarboxylic acid (ETC), tetraphenyl ethene tetrakis-phenyl carboxylic acid (ETTC), and tetraphenyl ethene bisphenyl carboxylic acid (BPDC). The thickness of the linkers is ~ 0.40 nm

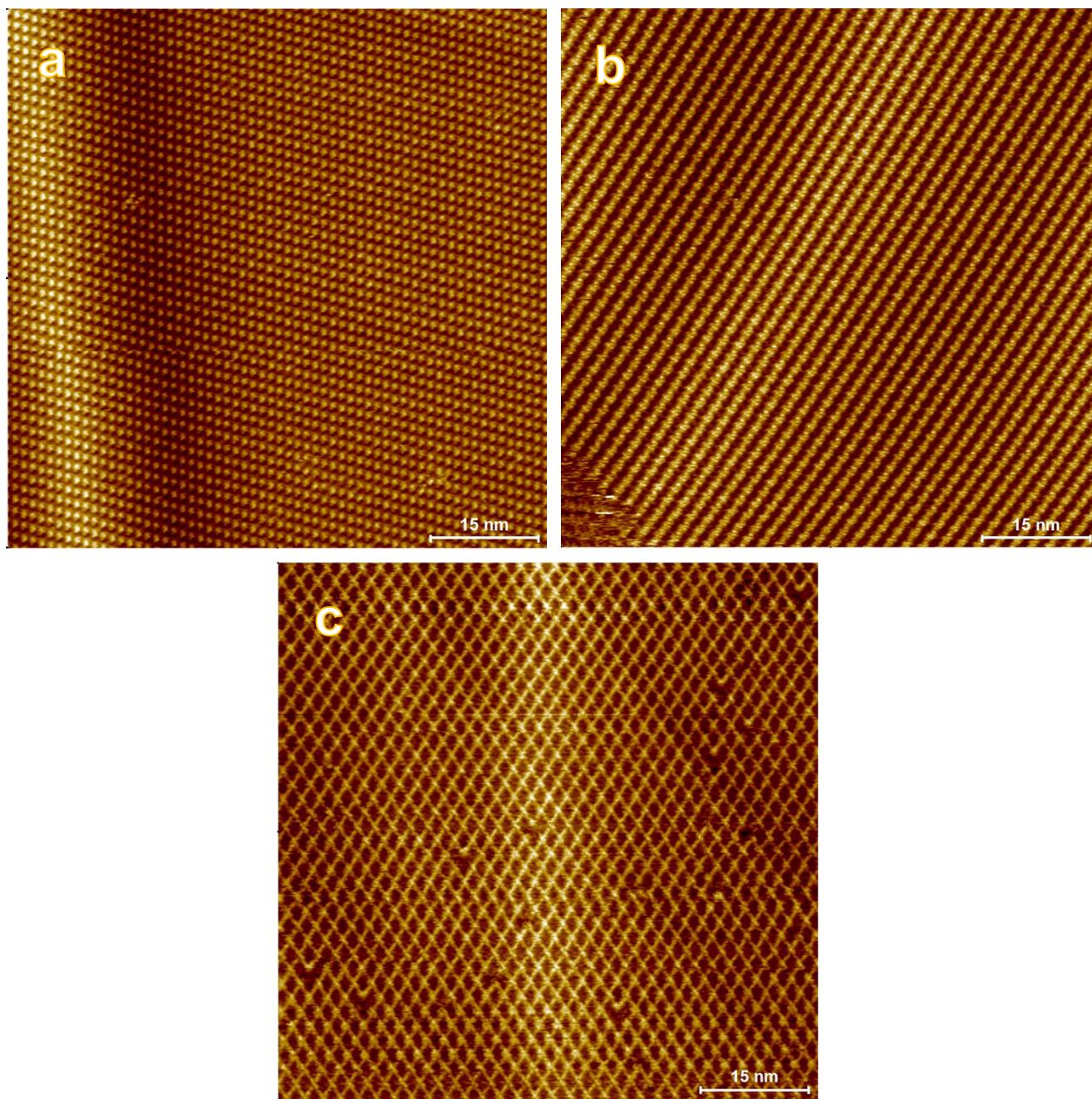


Figure S2. Large area images of ETC (a), BPDC (b), and ETTC (c) 1×10^{-4} M solutions in heptanoic acid deposited on HOPG. Vacancies in the monolayer (c) are due to compound impurities where some of the TTC molecules are missing one or more of their phenyl substituents. The images were collected under ambient conditions with -0.6 V bias voltage and between 20 and 30 pA tunneling current.

Unit cells of MOF linkers on HOPG.

Surface unit cells for ETC, BPDC and ETCC adsorbates in heptanoic acid at 25 °C were obtained by averaging the results of 5 to 10 drift corrected images per molecular system. The values for lengths and interior angle are given in Table 2 of the manuscript.

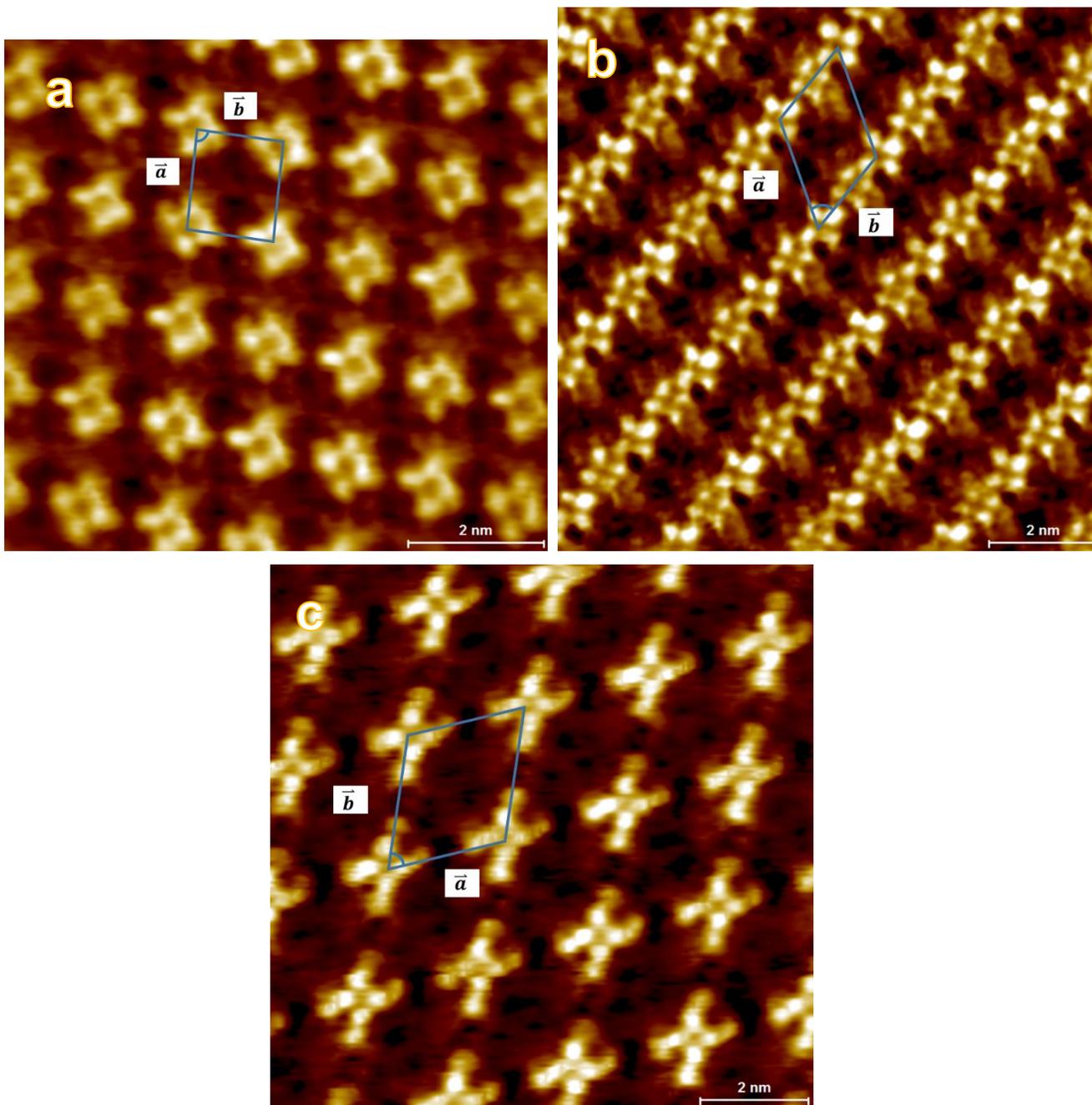
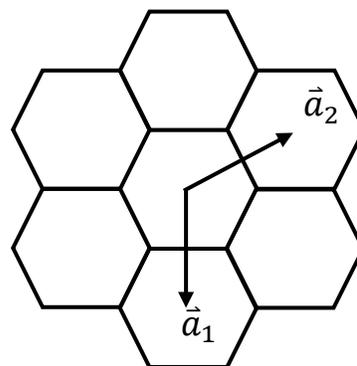


Figure S3. Unit cells for ETC (a), BPDC(b), and ETTC (c) when 1×10^{-4} M solutions in heptanoic acid are in equilibrium with the HOPG surface.

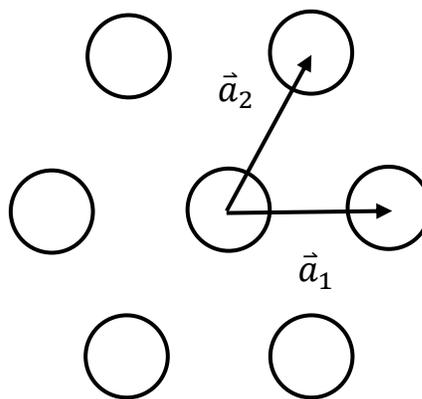
Epitaxial structure of MOF linkers on HOPG and Au(111). These structures best match the observed lattice vectors and orientation of the lattices with the underlying HOPG or Au structure. The HOPG \mathbf{a}_1 direction is [1, 1, -2, 0] and it is 0.246 nm long. The \mathbf{a}_1 direction on gold is the [1, -1, 0] direction, is 0.288 nm long, and is perpendicular to the surface reconstruction lines.

Molecule	Table S1: Epitaxial structure on HOPG substrate		
	unit cell parameters		
	a (nm)	b (nm)	α (°)
ETC	1.37	1.28	81.0
	$-6\mathbf{a}_1 - 3\mathbf{a}_2$	$-\mathbf{a}_1 + 5\mathbf{a}_2$	
BPDC	1.92	2.35	60.6
	$-5\mathbf{a}_1 + 4\mathbf{a}_2$	$5\mathbf{a}_1 - 11\mathbf{a}_2$	
ETTC	2.50	2.46	59.8
	$-9\mathbf{a}_1 + 2\mathbf{a}_2$	$2\mathbf{a}_1 + 11\mathbf{a}_2$	



HOPG lattice unit vectors used.

Molecule	Table S2: Epitaxial structure on Au(111) substrate		
	unit cell parameters		
	a (nm)	b (nm)	α (°)
ETC	2.08	0.58	72.9
	$-2\mathbf{a}_1 + 8\mathbf{a}_2$	$2\mathbf{a}_1$	
BPDC	2.29	0.58	78.9
	$-3\mathbf{a}_1 + 9\mathbf{a}_2$	$2\mathbf{a}_1$	
ETTC	2.36	0.58	72.2
	$-2\mathbf{a}_1 + 9\mathbf{a}_2$	$2\mathbf{a}_1$	



Au (111) unit vectors used.

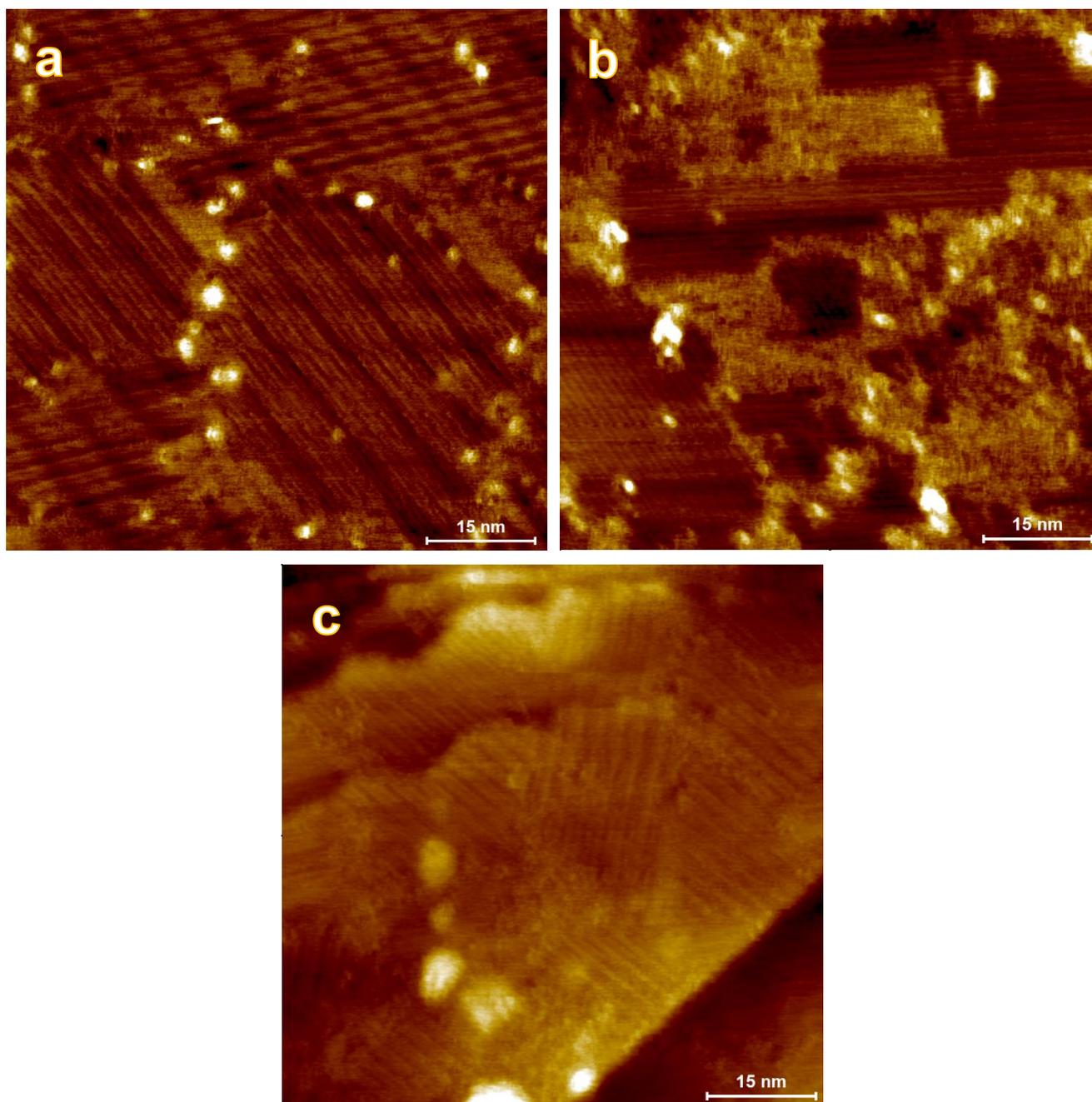


Figure S4. Large area images of ETC (a), BPDC (b), and ETTC (c) 5×10^{-5} M solutions in heptanoic acid deposited on Au(111). The images were collected under ambient conditions with -0.6V bias voltage and 50 pA tunneling current.

Unit cells for MOF linkers on Au(111).

Surface unit cells for ETC, BPDC and ETTC adsorbed on Au(111) from heptanoic acid at 25 °C were obtained by averaging the results of 5 to 10 drift corrected images per molecular system. The values for lengths and interior angle are given in Table 2 of the manuscript.

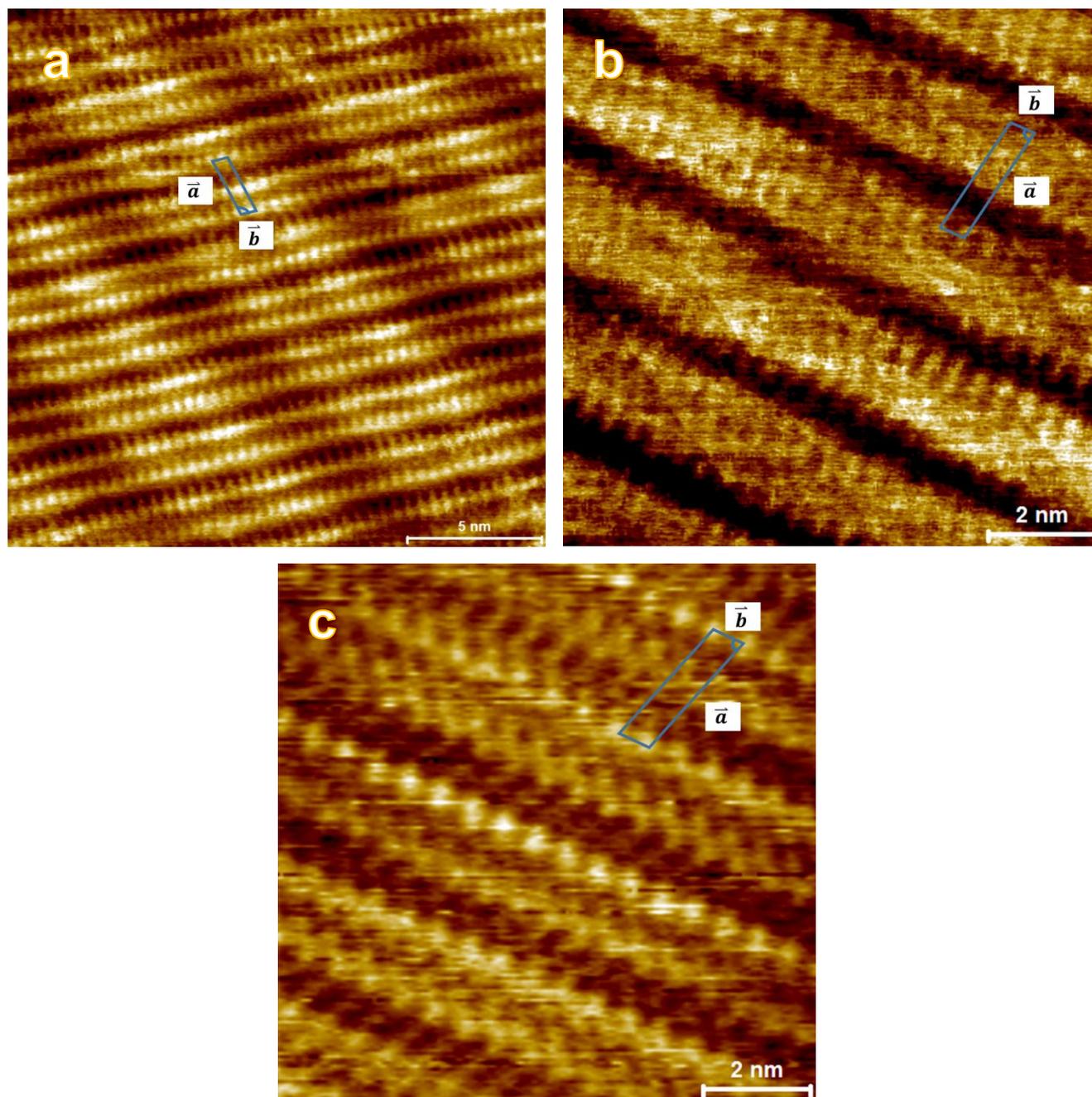


Figure S5. Unit cells for ETC (a), BPDC (b), and ETTC (c) when 5×10^{-5} M solutions in heptanoic acid are in equilibrium with the Au(111) surface at 25°C.

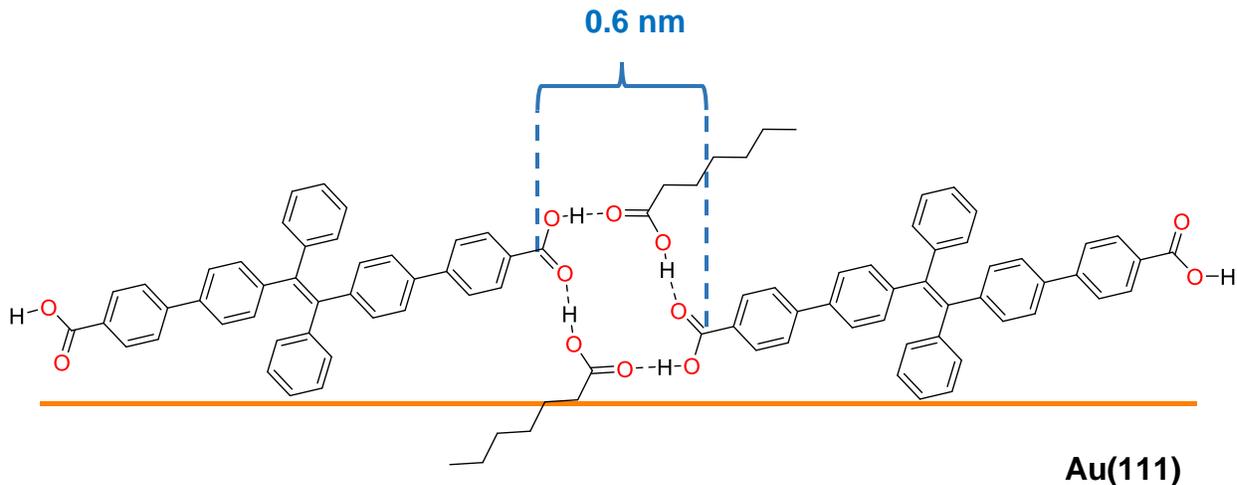


Figure S6. A proposed model structure with two solvent molecules bridging two BPDC synthons adsorbed on Au(111) from 5×10^{-5} M heptanoic acid solution. See Figure S5b for reference. The orange line identifies the gold surface. The calculated separation between the two BPDC molecules is 0.6 nm.

References

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- 2 Bhunia, A.; Vasylyeva, V.; Janiak, C. From a Supramolecular Tetranitrile to a Porous Covalent Triazine-based Framework with High Gas Uptake Capacities. *Chem. Commun.* **2013**, *49*, 3961-3963.
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