SUPPORTING INFORMATION

Hydrogen bonding vs molecule-surface interactions in 2D self-assembly of [C60]fullerenecarboxylic acids

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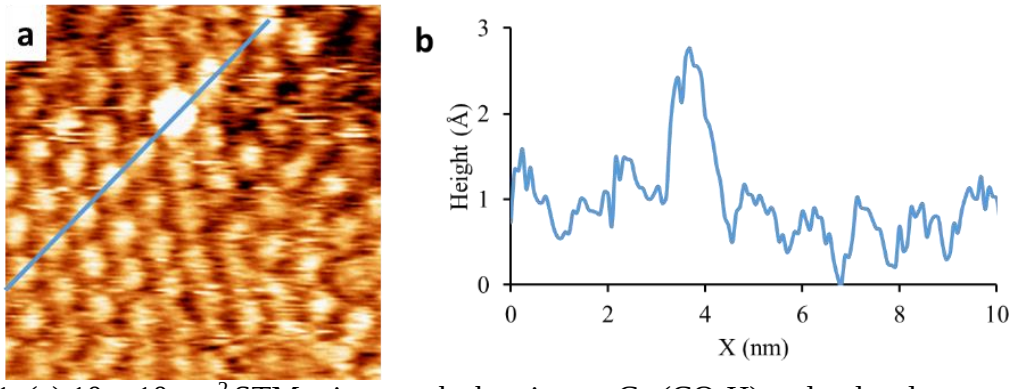

Figure S1. (a) 10 × 10 nm^2 STM micrograph showing an $C_{61}(CO_2H)_2$ admolecule on top of $C_{61}(CO_2H)_2$ monolayer at phenyloctane/Au (111) interface. (b) cross section profile along the blue line in (a) V_b = 600 mV, I_t = 0.2 nA

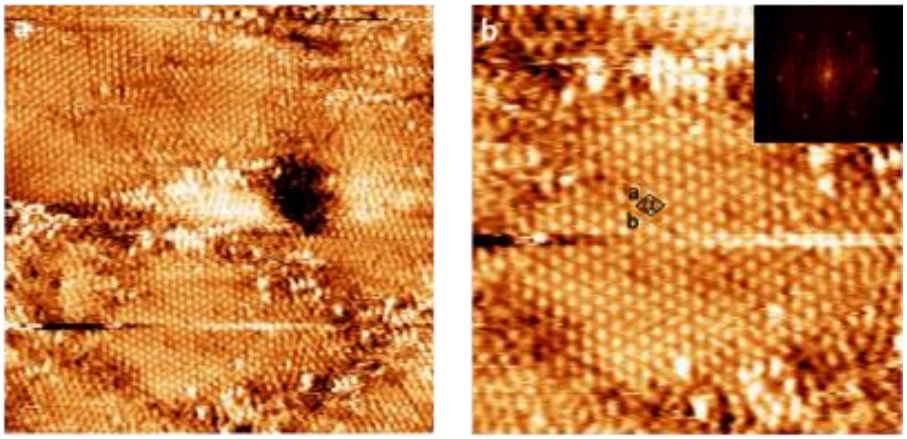

Figure S2. STM image showing the formation hexagonal close network of C_{60} on top of bare Au(111). (a) 60×60 nm^2, (a) 31×31 nm^2. The unit cell is: a=b=1.07± 0.1nm; α=63 ± 4°. V_b = 700 mV, I_t = 0.3 nA.

Table S1. Calculated binding energies for $C_{61}(CO_2H)_2$ dimers and trimer, using M06-2X and dispersion-corrected (GD3BJ) B3LYP functionals, with 6-31G(d) basis set.

	Total Binding energy,[a] E_{tot} (kcal/mol)		**VdW energy,[b] E_{vdW} (kcal/mol)**		**H bonding energy per molecule,[c] $E_{H\text{-}b}$ (kcal/mol)**	
	M06-2X	B3LYP	M06-2X	B3LYP	M06-2X	B3LYP
Dimer I	–12.4	–16.1	–1.5	–4.3	–10.8	–11.7
Dimer II	–11.0	–12.3	-	-	–11.0	–12.3
Dimer III	–9.8	–11.4	-	-	–9.8	–11.4
Trimer	–14.8	–21.4	–4.3	–9.5	–10.6	–11.9

a) $E_{tot} = E(\text{cluster}) - nE(\text{monomer})$, where n is the number of monomers in a cluster. b) This was estimated as a total binding energy of corresponding (dimer/trimer) clusters of unsubstituted C_{60} fullerene. c) $E_{H\text{-}b} = (E_{tot} - E_{vdW})/n$, where E_{vdW} was calculated from the analogues clusters lacking COOH groups.

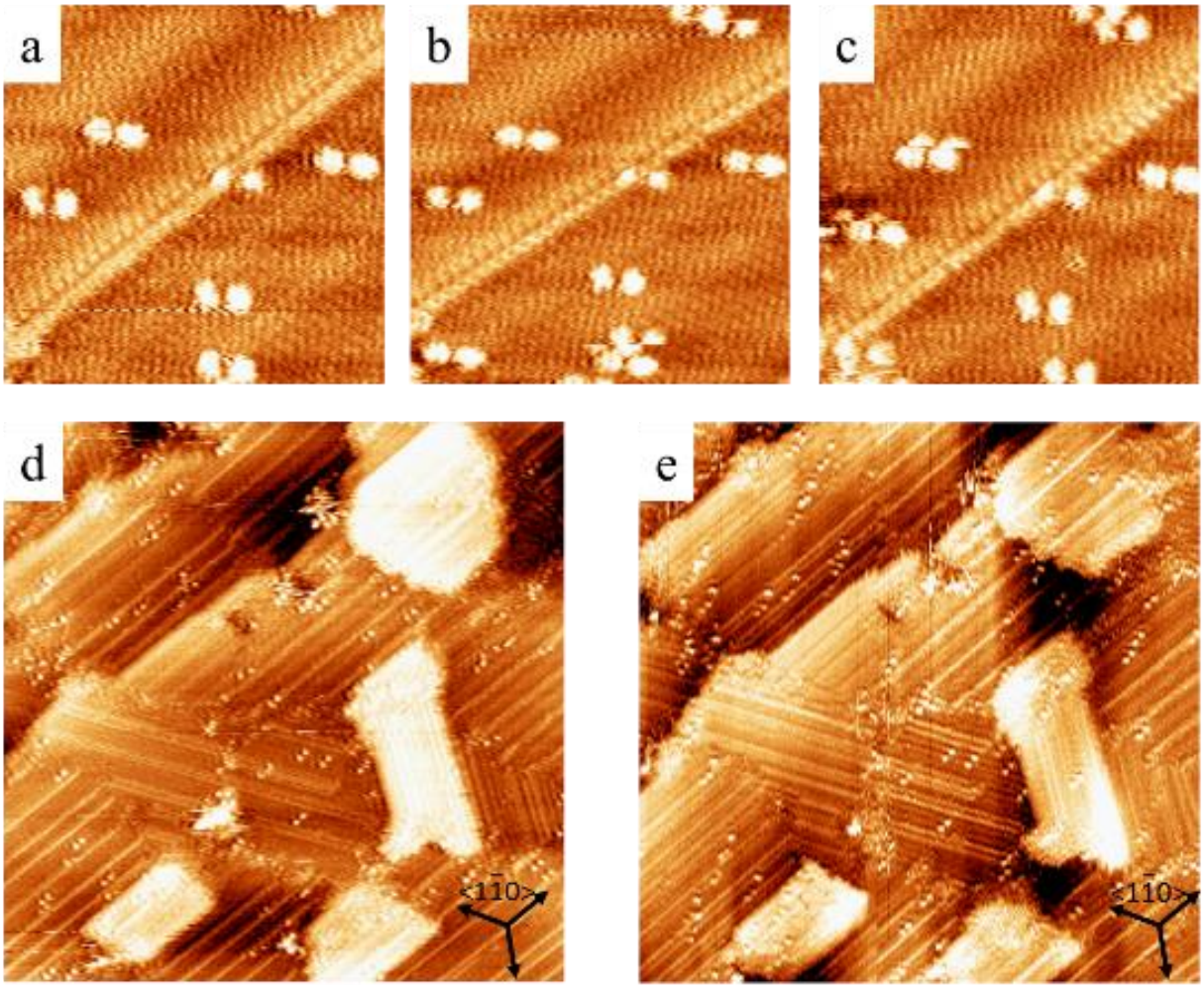

Figure S3. (a), (b), and (c) Consecutive STM images showing the stability of C_{61}-$(CO_2H)_2$ dimers. (13.8 × 13.8 nm^2). (d) and (e) a representative 81 × 81 nm STM image of C_{61}-$(CO_2H)_2$ dimers on PFBT/Au at 0° and 90° scanning angle respectively. V_b = 800 mV, I_t = 0.15 nA.

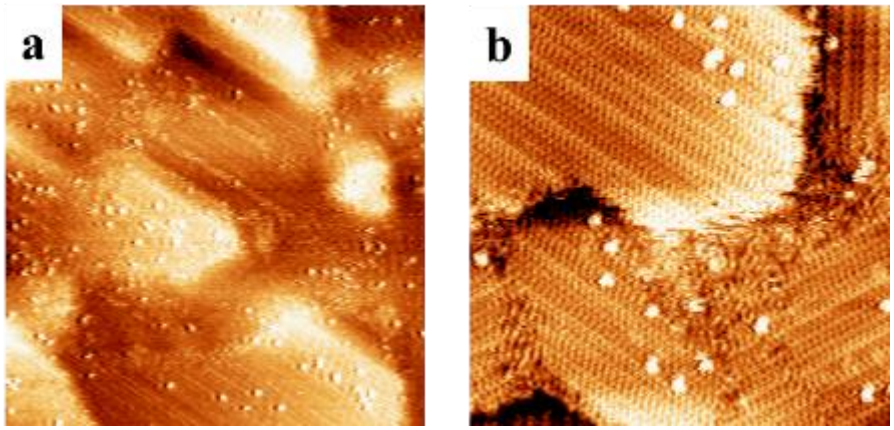

Figure S4. (a) Representative 70 × 70 nm^2 STM images of C_{61}-$(CO_2Et)_2$ on PFBT/Au. (b) High resolution STM image showing isolated C_{61}-$(CO_2Et)_2$ molecules. 31 × 31 nm^2. V_b = 700 mV, I_t = 0.15 nA

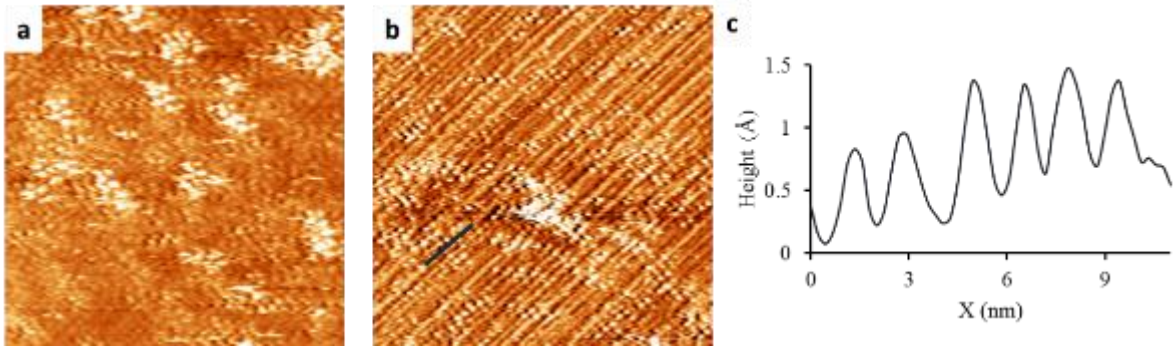

Figure S5. (a) STM images showing domains of a C_{66}-$(CO_2H)_{12}$ monolayer on PFBT/Au (111). (b) STM image showing one domain of C_{66}-$(CO_2H)_{12}$ .60 × 60 nm^2. (c) Cross sectional profile along the blue line in (b). V_b = 800 mV, I_t = 0.2 nA.

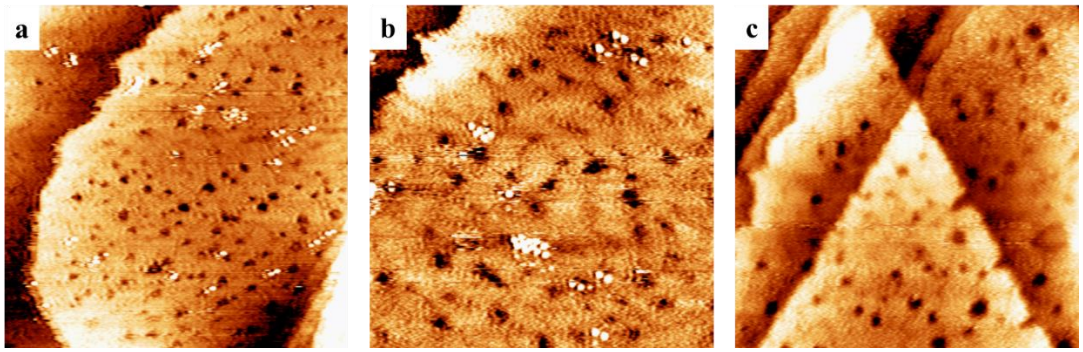

Figure S6. (a) and (b) STM images of phenyloctane/ BT@Au(111) in the presence of $C_{61}(CO_2H)_2$ (a few scatterd clusters are visible). 98 × 98 nm^2 and 60 × 60 nm^2. (c) STM image of phenyloctane/ BT@Au(111) in the presence of C_{61}-$(CO_2Et)_2$ (no adsorption). 64 × 64 nm^2. V_b = 800 mV, I_t = 0.15 nA.

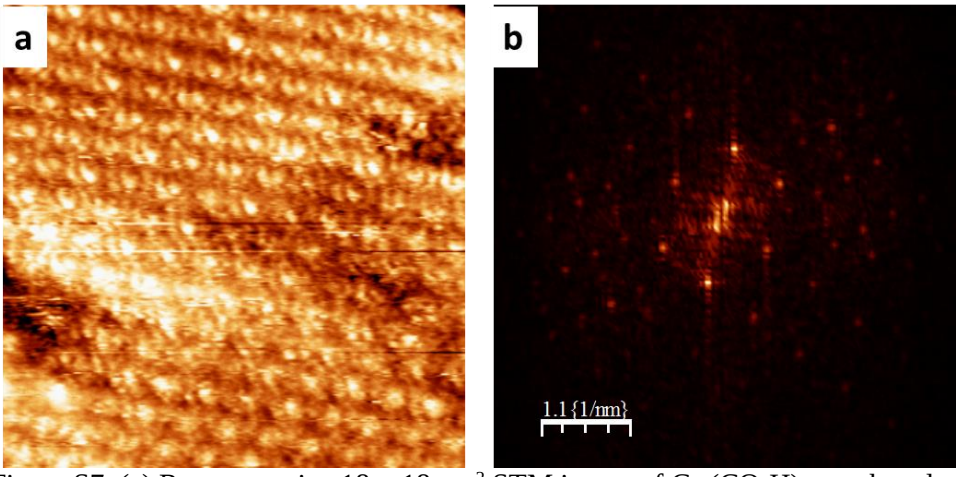

Figure S7**.** (a) Representative 18 × 18 nm^2 STM image of $C_{66}(CO_2H)_{12}$ at phenyloctane/Au (111) interface. (b) Fourier transform (FFT) image of the STM micrograph.