Supporting information

Self-Assembled Monolayers of Oligophenylenecarboxylic Acids on Silver Formed at the Liquid-Solid Interface

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1. Additional STM images

a) Ph-$(COOH)_2$

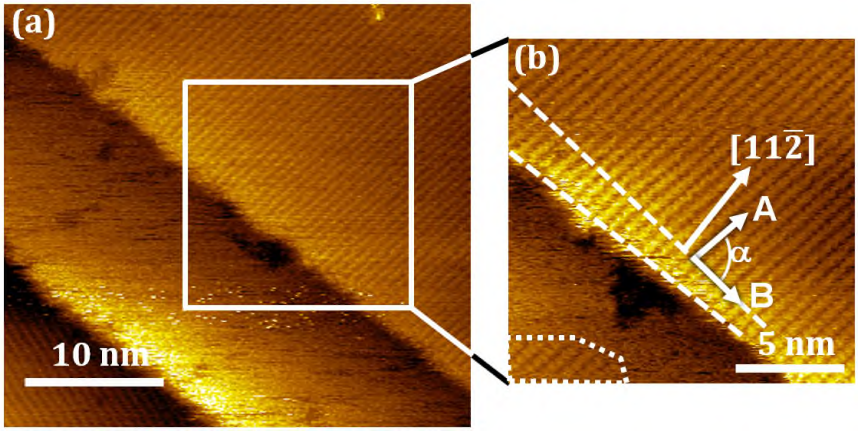

Figure S1. STM images of Ph-$(COOH)_2$ on UPD-Ag/Au/mica. Two consecutive scans of the same area with image (b) recorded after (a).

Area framed by dotted line in image (b) marks a domain not resolved in image (a) recorded in a preceding scan, thus, illustrating resolution can be temporarily lost despite the SAM being highly crystalline.

Fig. S1b demonstrates that the unit cell vectors of the terephthalic acid SAM is not aligned with the symmetry axes of the substrate. They are 10° (A) and 5° (B) off the $< 11\bar{2} >$ and $< 1\bar{1}0 >$, respectively, which yields an angle of $\alpha = 85°$.

b) Ph_2-$(COOH)_2$

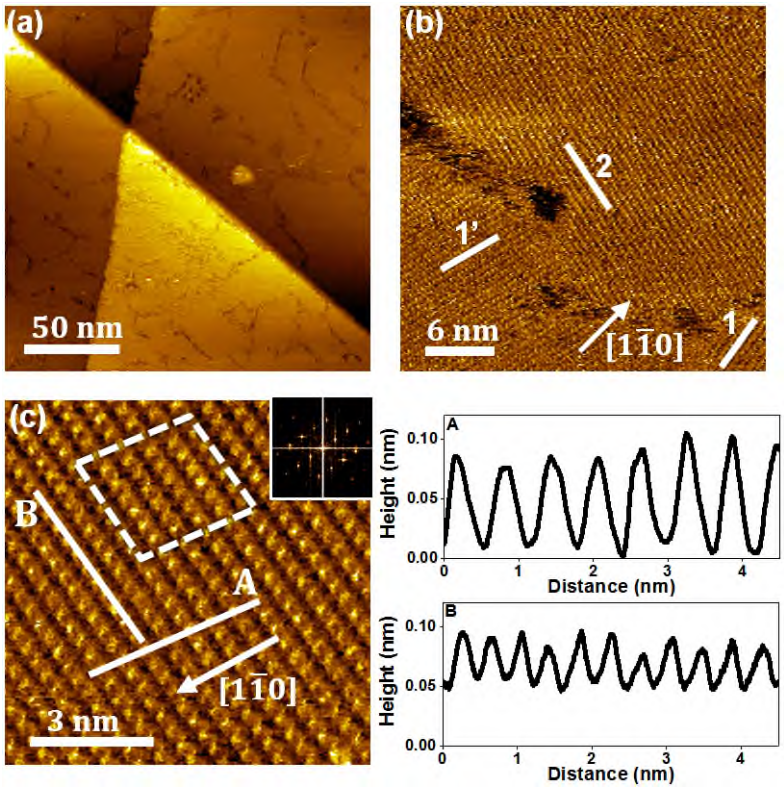

Figure S2. STM images of the Ph_2-$(COOH)_2$ SAM on UPD-Ag/Au/mica. (a) A large scale image with domain boundaries visible as lines. (b) High resolution image illustrating the presence of rotational and mirror domains. (c) Molecular resolution image of the monolayer with the Fourier transform in the insert and lines marking the height profiles shown. Dashed parallelogram shows unit cell presented in Fig. 6 of article.

2. XPS data

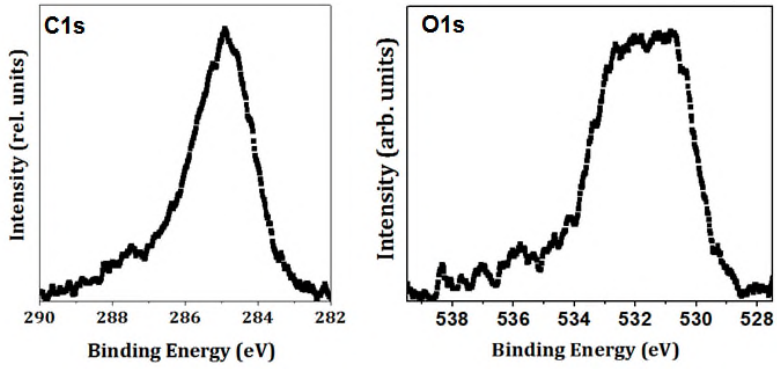

Figure S3. C1s and O1s spectra of a UPD-Ag/Au/mica substrate acquired with a non-monochromatic Al K_α source.[1]

The intensity of the C1s signal whose peak is shifted by about 1eV compared to the SAM spectra shown in Fig. 7 of article is equivalent to the amount of carbon of a Ph-COOH layer.

The O1s spectrum reveals the presence of different oxygen containing adsorbate species such as H_2O or OH, which originate from electrochemical deposition of the Ag UPD layer.

	C_{COOH}/C_{COO-}		$C_{ring}/(C_{COOH} + C_{COO-})$	
	350 eV	580 eV	350 eV	580 eV
Ph-COOH	-	-	11.1	7.1
Ph_2-COOH	-	-	30.9	18.4
Ph_2-COOH	-	-	54.4	26.4
Ph-$(COOH)_2$	1.4	0.9	10.6	4.3
Ph_2-$(COOH)_2$	2.0	1.4	13.1	8.0

Table S1. Intensity ratios for the C 1s XP spectra for the peaks related to carboxylic acids, carboxylate groups and aromatic carbons for each monolayer at photon energies of 350 eV and 580 eV.

Table S1 compiles the ratio of the intensities of C_{COOH}/C_{COO-} and $C_{ring}/(C_{COOH} + C_{COO}^-)$ signals calculated from the peak fitting of the C 1s spectra. The error margin is about 25% which is determined by the accuracy of the fits of the low intensity COOH and COO^- peaks and defined by the uncertainty in the background subtraction. For all SAMs, there is a decrease in the ratio of $C_{ring}/(C_{COOH} + C_{COO}^-)$ recorded at 580 eV compared to 350 eV since the contribution from the COO^- carbon atoms is larger at higher photon energies. For the dicarboxylic acids, the intensity ratio of C_{COOH}/C_{COO}^- have also been compiled. Again, at higher photon energies, the increased escape depth means the larger signal for COO^- carbon atoms results in a decrease in these ratios.

The ratios of signal intensities deviate significantly from the stoichiometry of the molecules as illustrated by the monocarboxylic acids. The intensity ratios of C_{ring}/C_{COO-} should be 6, 12 and 18 for Ph-COOH, Ph_2-COOH and Ph_3-COOH respectively. However, due to the strong attenuation of the signals, especially the COO^- signal, what is actually measured is 11, 31 and 54 at 350 eV.

3. Calculation of tilt and twist angles from models:

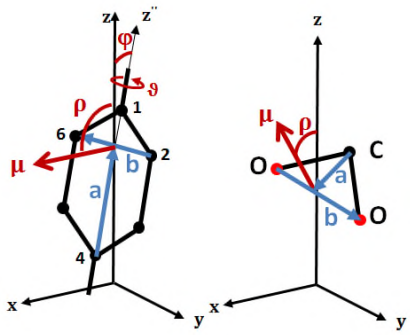

Figure S4. Definition of vectors to calculate angles ρ, φ and ϑ. Surface is in the x,y-plane.

Orientation of benzene rings:

i) *Tilt angle of the biphenyl moiety* is given by the angle between its 4,4′-axis of and the z-axis. If a vector $\vec{c}$ is defined by the coordinates of the C4 and C4' atoms of the biphenyl unit, its tilt angle is given by: $\varphi = \tan^{-1}\left(\frac{c_z}{|c|}\right)$

ii) Orientation of individual benzene rings and the correlation between ρ, φ and ϑ as defined in Fig. S4.

The direction of the transition dipole moment μ of a benzene ring is given by the cross product

$$\vec{\mu} = \vec{a} \times \vec{b}$$

with $\vec{a}$ defined by the coordinates of atoms C_4 and the midpoint between atoms C_2 and C_6. $\vec{b}$ is given by C_2 and C_6.

Relationship between ρ, φ and ϑ is

$$\rho = \cos^{-1}(\cos\vartheta \sin\varphi)$$

with ϑ = 0 if μ is in the z,z″-plane.

$$\varphi = \tan^{-1}\left(\frac{a_z}{|a|}\right)$$

$$\rho = \tan^{-1}\left(\frac{\mu_z}{|\mu|}\right)$$

Rotation around z-axis

$$\alpha = \tan^{-1}\left(\frac{a_x}{a_y}\right) \qquad T_1 = \begin{pmatrix} \cos(\alpha) & \sin(\alpha) & 0 \\ -\sin(\alpha) & \cos(\alpha) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

aligns $\vec{a}$ with (x′,z′)-plane (z′||z):

$$\vec{a}' = T_1 \vec{a}$$

Rotation around y′-axis

$$\beta = \tan^{-1}\left(\frac{a_z'}{a_x'}\right) \qquad T_2 = \begin{pmatrix} \cos(\beta) & 0 & \sin(\beta) \\ 0 & 1 & 0 \\ -\sin(\alpha) & 0 & \cos(\beta) \end{pmatrix}$$

aligns $\vec{a}$ with x″-axis of (x″, y″, z″) coordinate system

$$\vec{a}'' = T_2 \vec{a}'$$

$\vec{b}$ yields then the twist angle through

$$\vartheta = \sin^{-1}\left(\frac{b_z''}{|b|}\right)$$

iii) *Orientation of transition dipole moment of COO-/COOH groups*

From Fig. S4 it is seen that orientation of μ is cross product of

$$\vec{\mu} = \vec{a} \times \vec{b}$$

where $\vec{a}$ is defined by coordinates of C-atom and midpoint of vector $\vec{b}$ (defined by O-atoms)

As above tilt angle of is μ given by

$$\rho = \tan^{-1}\left(\frac{\mu_z}{|\mu|}\right)$$

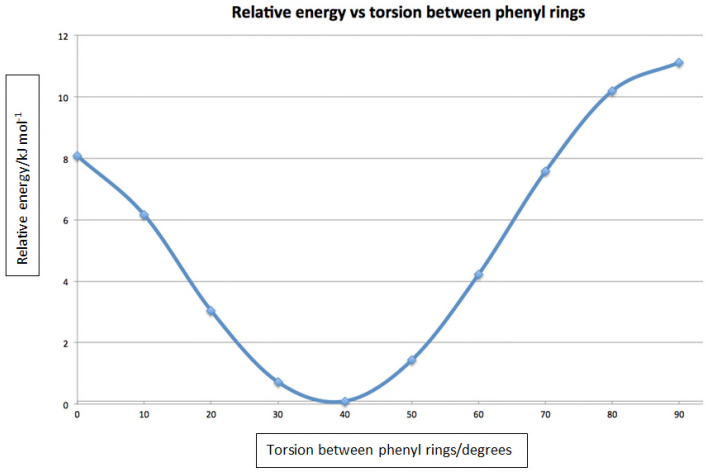

Figure S5. Plot of relative energy versus torsion angle between phenyl rings of Ph_2-COOH using PBE/6-31+G*.

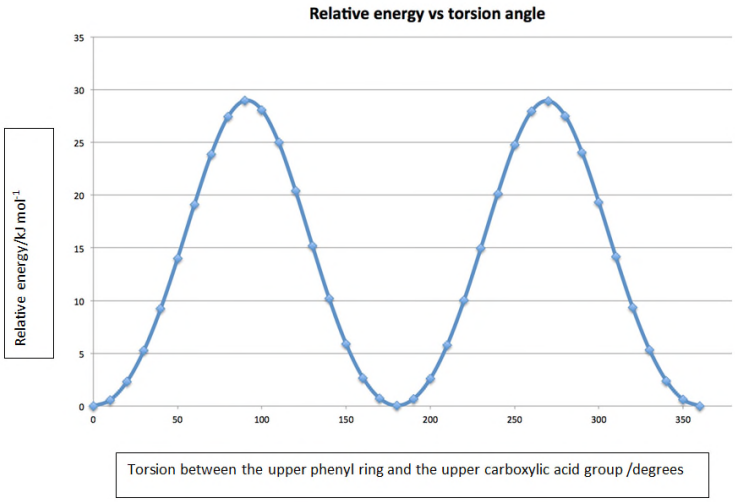

Figure S6. Plot of relative energy versus torsion angle between the phenyl ring and the adjacent carboxylic acid group Ph_2-$(COOH)_2$ in using PBE/6-31+G*.

[1]Preparation and XPS measurement by R. Ortiz de la Morena, S. Francis, and F. Grillo are gratefully acknowledged.