**Supporting Information**

# Deducing 2D Crystal Structure at the Liquid/Solid Interface with Atomic Resolution: a Combined STM and SFG Study

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**Materials:** $K_2CO_3$, anhydrous $MgSO_4$, and all solvents were purchased from Fisher Scientific. 1-bromoheptadecane was purchased from TCI and isophthalic acid-2,4,5,6-$d_4$ was purchased from Icon Isotopes. All reagents were used as received.

**Synthesis:** Diheptadecyl isophthalate (**17-*m*-diester**) was synthesized as previously reported.[1] Preparation of diheptadecyl isophthalate-2,4,5,6-$d_4$ (**17-*m*-diester-$d_4$**): To a mixture of isophthalic acid-2,4,5,6-d4 (2.41 mmol) and 1-bromoheptadecane (4.82 mmol) in N,N-dimethylformamide (10 mL) was added $K_2CO_3$ (4.82 mmol). The mixture was heated at 80 °C for 5 hr. $CH_2Cl_2$ (20 mL) was added to the mixture and the organic layer was washed with brine three times. The organic layer was dried over anhydrous $MgSO_4$ and solvent was removed under vacuum. After dissolving the residue in $CH_2Cl_2$ (10 mL), methanol (5 mL) was slowly added. The white precipitated solid was collected and then dried under vacuum.

Yield: 80.2%. mp: 48.9-49.4 °C. IR: IR: 2955 (s), 2918 (vs), 2848 (s), 1718 (s), 1470 (s), 1233 (m), 719 (m) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 0.86 (t, $J$ = 6.8 Hz, 6H), 1.26-1.53 (m, 56H), 1.76 (quint, $J$ = 7.1 Hz, 4H), 4.32 (t, $J$ = 6.8 Hz, 4H). $^{13}C$ NMR (100 MHz, $CDCl_3$, δ): 14.33, 22.91, 26.23, 28.91, 29.51, 29.58, 29.76 (broad), 32.15, 65.71, 128.21 (t, $J_{C\text{-}D}$ = 25.0 Hz), 130.58 (t, $J_{C\text{-}D}$ = 24.5 Hz), 131.00, 133.46 (t, $J_{C\text{-}D}$ = 25.5 Hz), 166.10. Anal. Calcd for $C_{42}H_{70}D_4O_4$: C 77.96 H 12.15; Found: C 78.16, H 12.14. MS (EI+): m/z 646.7 [M+].

(1) Plass, K. E.; Kim, K.; Matzger, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 9042-9053.

**Scanning tunneling microscopy:** A Nanoscope E STM (Digital Instruments) was used to obtain all the images. Highly oriented pyrolytic graphite (HOPG) (SPI-1 grade, Structure Probe Inc.) was used as a substrate for monolayer formation. A 1-phenyloctane solution of the desired molecule was made and 1 μL placed on freshly cleaved HOPG to obtain a self-assembled monolayer. The tips were made from Pt/Ir wire (20% Ir, 0.010 inch diameter, California Fine Wire) by mechanical cutting. STM imaging

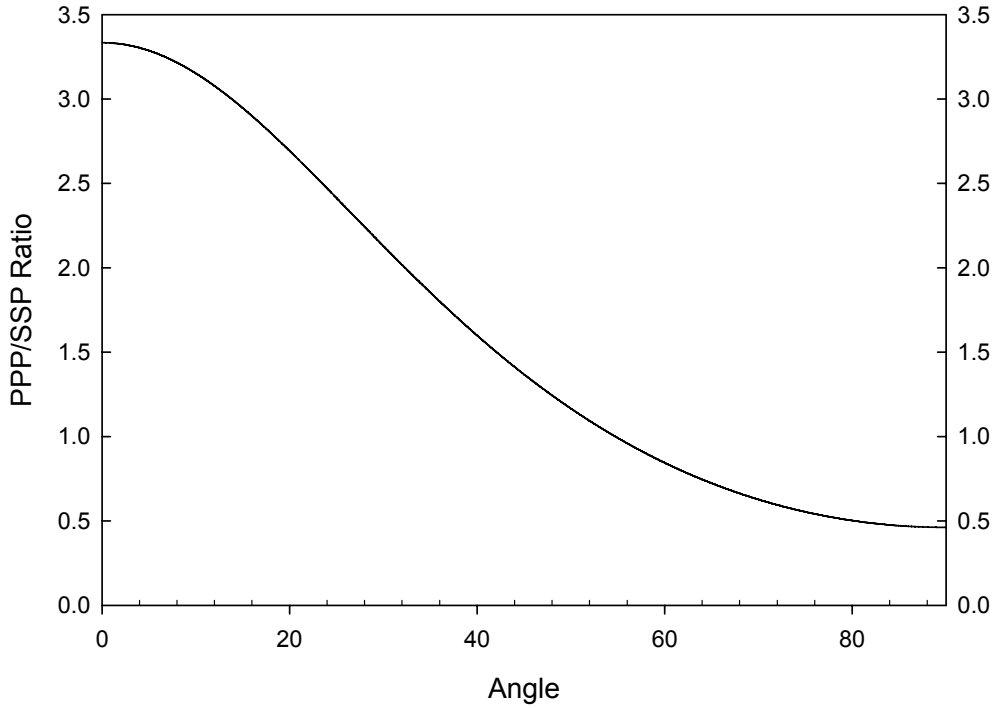
were performed using a quasi-constant height mode under ambient conditions and typical STM settings include 300 pA of current and 700-900 mV of bias voltage (sample positive). All images are unfiltered.

**Computational modeling:** The packing structures apparent from the metrics and symmetry of the STM images were modeled using Cerius[2] version 4.2 (Accelrys Inc.). Energy minimization was performed using a COMPASS force field. This method has been shown to yield reasonable energies for the relative stabilization of three dimensional polymorphic packing in molecular crystals (Mitchell-Koch, K; Matzger, A. J. *J. Pharm. Sci.* **2008**, *97*, 2121-2129.). Non-periodic assemblies from these models were overlaid on a fixed graphite slab and energy minimized to get the optimized packing structure on HOPG.

**Table S1.** Unit Cell Parameters in Monolayer of **17-*m*-diester-d$_4$**.

| | computed | | | experimental | | | |
|---|---|---|---|---|---|---|---|
| molecule | *a* (Å) | *b* (Å) | *α* (deg) | *a* (Å) | *b* (Å) | *α* (deg) | plane group |
| 17-*m*-diester-d$_4$ | 60.0 | 8.9 | 90 | 61.5±1.5 | 9.0±0.2 | 90±3 | *cm* |

**SFG Orientation Analysis:**




The hyperpolarizability of the C=O stretching mode can be deduced by the IR transition moment and Raman polarizability of the mode. Since C=O group has a $C_{\infty v}$ group, it is feasible to deduce the relation between the SFG susceptibility and hyperpolarizability, which was done in the literature (Tyrode, E.; Johnson, C. M.; Baldelli, S.; Leygraf, C.; Rutland, M. W. *J. Phys. Chem. B* **2005**, *109*, 329-341.) For the $C_{\infty v}$ group we have three nonzero hyperpolarizabilities as shown in Eq. 1 and written in the molecular coordinates where c is along the C=O axis and the ab plane is perpendicular to the C=O axis.

$$\beta_{aac} = \beta_{bbc}; \beta_{ccc} \qquad \textbf{Eq. 1}$$

To determine orientation of the C=O bond, we need to know the relative values of the nonzero $\beta^{(2)}$'s which can be estimated directly from the Raman depolarization ratio since in this case there are only two independent hyperpolarizabilities and they have equal transition dipole moments $\mu_c$. It follows then that

$$r = \frac{\beta_{aac}}{\beta_{ccc}} = \frac{\alpha_{aa}}{\alpha_{cc}} \qquad \textbf{Eq. 2}$$

The parameter r is related to the Raman depolarization ratio ρ as follows

$$\rho = \frac{3}{4}\left[1 + \frac{5}{4}\left(\frac{2r+1}{r-1}\right)^2\right]^{-1} \qquad \textbf{Eq. 3}$$

The Raman depolarization ratio ρ is reported as 0.1 in the literature (Yokoyama, I.; Miwa, Y.; Machida, K. *J. Phys. Chem.* **1991**, *95*, 9740-9746., Yokoyama, I.; Miwa, Y.; Machida, K. *J. Am. Chem. Soc.* **1991**, *113*, 6458-6464.) Two values of r satisfy equation 3, r = 0.3 and r = 12. The r = 12 is unreasonable as the change in polarizability along the C=O bond should be higher than the change in polarizability across the C=O bond. The expressions for the relevant $\chi^{(2)}$ components are as follows:

$$\begin{aligned} \chi_{zzz} &= \frac{N}{\varepsilon_0} < \beta_{zzz} > = \frac{N}{\varepsilon_0}\beta_{ccc}\left[r < Cos\theta > + (1-r) < Cos^3\theta >\right] \\ \chi_{yyz} &= \frac{N}{\varepsilon_0} < \beta_{yyz} > = \frac{1}{2}\frac{N}{\varepsilon_0}\beta_{ccc}[(r+1) < Cos\theta > + (r-1) < Cos^3\theta >] \end{aligned} \qquad \textbf{Eq. 4}$$

where N is the number of oscillators, θ is the angle between the C=O axis and the surface normal. In the prism sample geometry, the PPP polarization combination is dominated by the $\chi_{zzz}$ component. The $\chi_{zzz}$ component is an order of magnitude greater than any other χ component. The $\chi_{yyz}$ component contributes to the signal in the SSP polarization combination.

If we assume that all the C=O group adopt the same orientation, we can use a delta distribution to describe such an orientation. In that case, the relation between the SFG susceptibility and hyperpolarizability was calculated. The relation for the ratio between PPP and SSP versus the orientation angle (the angle between the C=O group and the surface normal) is displayed.

The SFG signal is given by equation 5 (Wang, J.; Paszti, Z.; Even, M. A.; Chen, Z. *J. Am. Chem. Soc.* **2002**, *124*, 7016-7023):

$$\begin{aligned} S(\omega) &= \frac{8\pi^3\omega^2 \sec^2\beta}{c^3 n_1(\omega) n_1(\omega_2) n_1(\omega_3)} |\chi_{eff}^{(2)}|^2 I_1(\omega_1) I_2(\omega_2) AT \\ \chi_{ijk}^{(2)} &= \chi_{NR}^{(2)} + \sum_q \frac{A_{ijk,q}}{\omega_2 - \omega_q + i\Gamma_q} \end{aligned} \qquad \textbf{Eq. 5}$$

Since we are taking a ratio between two polarization combinations, everything except the oscillator strength will be a constant that will drop out in the ratio. Therefore, the spectra were fit to

$$S(\omega) = Offset + |NR + \frac{A}{\omega - \omega_0 + i\Gamma}|^2 \qquad \textbf{Eq. 6}$$

The orientation of the C=O group from the fitted PPP/SSP signal strength ratio was measured to be 64 degrees from the surface normal for all concentrations.