Hydrogen-bonded order in mercury-supported monolayers of end-functionalized alkanes: *Supporting Information*

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Abstract

This document contains a description of the experimental methods, and additional information on the period doubling transition in 16-mercapto-1-hexadecanoic acid (o2-s).

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1. Experimental methods

The experimental methods used are essentially the same as those of our previous studies of mercurysupported LFs, ^{1–6} and thus will be described here only briefly. The surface-normal and surfaceparallel structure were studied by X-ray reflectivity (XR), grazing incidence diffraction (GID) and Bragg rod (BR) measurements, employing a synchrotron-based liquid surface diffractometer.^{7,8} A purpose-built Langmuir trough, allowing simultaneous x-ray and surface tension measurements was employed. We now discuss briefly the relevant experimental details.

1.1 Surface Thermodynamics: Isotherms

1.1.1 The Langmuir trough:

The trough, machined from KelF, had an area of $6.5 \times 17.5 \text{ cm}^2$, and required 55 ml of mercury to fill slightly about the rim. The 0.3 mm thick bottom of the trough provides a good thermal contact to the brass baseplate supporting the trough, which is temperature-controlled to $\pm 0.1^{\circ}$ C by a commercial water circulator. The trough and baseplate are mounted on a spill-catching teflon tray, residing inside a hermetically sealed aluminum enclosure. To reduce possible mercury surface oxidation and contamination a slow gas flow of helium (for x-ray measurements) or nitrogen (for surface tension measurements) was maintained inside the enclosure throughout the experiment.

1.1.2 Pressure-Area Isotherms:

The surface coverage by the LF was monitored by pressure-area $\pi - A$ isotherm measurements. The surface pressure, $\pi = \sigma_0 - \sigma_c$, is the difference in surface tension (σ) between the bare ($\sigma_0 = 490 \text{ mN/m}$) and the film covered (σ_c) surface. *A* is the nominal area per molecule as calculated from the number of molecules deposited and the mercury's surface area. The surface tension was measured by the Wilhelmy plate method, ⁹using a mercury-amalgamated platinum plate and a balance based on an linear variable differential transformer (LVDT).²

1.1.3 Materials and procedures:

Mercury (Merck Co., triple distilled, 99.999% pure, or Bethlehem Apparatus Co., quadruple distilled, 99.9995% pure), was used as received. Standard spreading solutions were prepared with molarities in the range of $(3-8) \times 10^{-4}$ using HPLC grade, 99.9% pure chloroform (Aldrich). It was ascertained that pure chloroform evaporates rapidly without leaving any traces on the mercury subphase or changing σ_0 .

Each experiment started by opening the enclosure and cleaning the trough with isopropanol and chloroform. The enclosure was then sealed and purged for 30 minutes with a gas flow to remove solvent vapour. The trough was next filled with mercury from a reservoir, mounted on top of the sealed enclosure, through a capillary, and the surface tension of the bare mercury measured to ensure surface purity.

The LF was formed by depositing the stock solution on the mercury surface in steps of 4-8 μ l through a sealable opening in the enclosure's top, waiting for the surface tension to relax after each step. This stepwise deposition method for increasing the surface coverage was adopted because a well-sealing movable barrier is very difficult to construct for a mercury subphase.¹⁰ The surface tension was monitored throughout the process, and the deposition stopped upon reaching the desired surface pressure.

1.2 Surface Structure: X-ray Measurements.

The deposited LF's structure was studied by surface-specific X-ray techniques using the Harvard/BNL liquid surface diffractometer at beamline X22B, NSLS, Brookhaven National Laboratory, U.S.A. and x-rays of a wavelength $\lambda = 1.507 \pm 0.001$. The trough enclosure was mounted on an active vibration isolation unit residing on the diffractometer's sample sage. This arrangement effectively eliminated pickup of vibrations from the environment, which plagued early X-ray surface studies of the mercury surface and of LFs on mercury.^{11,12}

1.2.1 Surface-normal structure:

The surface-normal electron density profile $\rho(z)$ of the LF-covered mercury surface is determined by x-ray reflectivity (XR) measurements.^{13,14} The XR curve, $R(q_z)$, is the fraction of the incident beam's intensity specularly reflected from the surface at an angle β equal to the incidence angle, α . The surface-normal wavevector transfer q_z is given by $q_z = (4\pi/\lambda) \sin \alpha$. $\rho(z)$ is related to $R(q_z)$ by:^{14,15}

$$R(q_z)/R_F(q_z) = \left| \rho_b^{-1} \int (\mathrm{d} \langle \rho(z) \rangle / \mathrm{d} z) \exp(-iq_z z) \mathrm{d} z \right|^2, \tag{1}$$

where $R_F(q_z)$ is the reflectivity from an ideally smooth and abrupt surface, and $\rho_b = 3.25 \text{ e/Å}^3$ is the bulk electron density of mercury. The surface-normal density profile is obtained from $R(q_z)$ by constructing a physically motivated model for $\rho(z)$, calculating $R(q_z)/R_F(q_z)$ for this model from Eq. (1), and fitting it to the measured $R(q_z)/R_F(q_z)$ to obtain the values of the profile-defining parameters of the model.^{2,14–16}

1.2.2 Surface Parallel Structure:

Grazing incidence diffraction (GID) was used to determine the LF's surface-parallel order. GID is measured by setting $\alpha < \alpha_c \approx 0.4^\circ$ (where α_c is the critical angle for total external reflection ^{13,14}) and scanning the detector out of the reflection plane by an angle $2\theta_d$. The scattering vector in this case is almost surface-parallel, $q_{\parallel} = (2\pi/\lambda)(\cos^2 \alpha + \cos^2 \beta - 2\cos \alpha \cos \beta \cos \theta_d)^{1/2} \approx$ $(4\pi/\lambda)\sin(2\theta_d/2)$, and thus explores the surface-parallel structure at the interface. The scattered intensity $I(q_{\parallel})$ is measured with a 10-cm-long, linear position sensitive detector aligned in the surface normal *z* direction. This arrangement allows the measurement of the intensity distribution in the surface-normal direction over a broad range of angles β at each $2\theta_d$ position. When occurring at the $2\theta_d$ position of GID peaks, this distribution is called called a Bragg rod (BR), and provides information on the molecular length, and the molecular tilt and its azimuthal direction, in the LF's laterally ordered part.^{2,14–17}

Our x-ray measurements were carried out over a temperature range of $5^{\circ}C \le T \le 25^{\circ}C$. The

XR measurements covered the q_z -range of $0 \text{ Å}^{-1} \le q_z \le 1.7 \text{ Å}^{-1}$. The GID and BR measurements covered the ranges of 0.14 $\text{ Å}^{-1} \le q_{\parallel} \le 1.7 \text{ Å}^{-1}$ and $0 \text{ Å}^{-1} \le q_z \le 1.25 \text{ Å}^{-1}$.

2. The period doubling transition in o2-s

Figure 1(b) exhibits the GID pattern measured at high coverage, $A \leq 50 \text{ Å}^2$ /molecules, where the LF is a trilayer of lying-down o2-s molecules. For comparison, the GID patterns obtained for the monolayer, Figure 6 in the paper, is also shown in Figure 1(a). For the trilayer phase, the observed peak at $q_{\parallel} = 0.39 \text{ Å}^{-1}$ indicates the existence of a dimeric stripe phase. However, the much stronger peaks at $q_{\parallel} = 0.26$ and 0.52 Å^{-1} indicate that the dimeric stripe phase coexists with a much more extensive monomeric stripe phase, in spite of the low temperature, and the long time that has elapsed since deposition. The inhibition of a full transition from the monomeric stripe phase to the dimeric stripe phase in the trilayer LF sharply contrasts with the abrupt and full transition to such phase observed in the monolayer LF. The difference may stem from the stronger intermolecular van der Waals interaction, and consequently lower translational freedom, in the trilayer as compared with the monolayer.

References

- (1) Kraack, H.; Ocko, B. M.; Pershan, P. S.; Deutsch, M. Science 2002, 298, 1404.
- (2) Kraack, H.; Ocko, B. M.; Pershan, P. S.; Sloutskin, E.; Deutsch, M. J. Chem. Phys. 2003, 119, 10339–10349.
- (3) Tamam, L.; Kraack, H.; Sloutskin, E.; Ocko, B. M.; Pershan, P. S.; Ulman, A.; Deutsch, M. J. Phys. Chem. B 2005, 109, 12534.
- (4) Kraack, H.; Tamam, L.; Sloutskin, E.; Pershan, P. S.; Deutsch, M.; Ocko, B. M. *Langmuir* 2007, 23, 7571–7582.
- (5) L. Tamam et al., Soft Matt. 2010, 6, 526.



Figure 1: (a) Measured and background subtracted (symbols) GID patterns of the lying down monolayer phases of o2-s at the listed temperatures and times after deposition. The lines are fits to a single Gaussian for each peak. (b) Same as (a) but for a trilayer phase. The weak peak at $q_{\parallel} \approx 0.39 \text{ Å}^{-1}$, coexisting with the strong peaks at $q_{\parallel} = 0.20$ and 0.52 Å^{-1} , indicate the persistence of an extensive monomeric phase (shown in Figure 5(d) in the paper) in coexistence with a less-extensive dimeric phase (shown in Figure 5(b) in the paper) in this trilayer.

- (6) Tamam, L.; Ocko, B. M.; Reichert, H.; Deutsch, M. Phys. Rev. Lett. 2011, 106, 197801.
- (7) Sanyal, M. K.; Sinha, S. K.; Huang, K. G.; Ocko, B. M. Phys. Rev. Lett. 1991, 66, 628.
- (8) Braslau, A.; Pershan, P. S.; Swislow, G.; Ocko, B. M.; Als-Nielsen, J. *Phys. Rev. A* 1988, *38*, 2457.
- (9) Gaines, G. L. Insoluble Monolayers at Liqid Gas Interface; Wiley: New York, 1966.
- (10) Smith, T. Adv. Coll. Interf. Sci. 1972, 3, 161.
- (11) S.W. Barton et al., *Nature* **1986**, *321*, 685.
- (12) Bosio, L.; Cortes, R.; Folcher, G.; Froment, M. J. Eelectrochem. Soc. 1992, 139, 2110.
- (13) M. Deutsch and B.M. Ocko, *Encyclopedia of Applied Physics*; VCH: New York, USA, 1998; Vol. 23.
- (14) Als-Nielsen, J.; McMorrow, D. *Elements of Modern X-ray Physics*; Wiely: New York, USA, 2001.
- (15) B.M. Ocko et al., Phys. Rev. E 1997, 55, 3164.
- (16) Als-Nielsen, J.; Jacquemain, D.; Kjaer, K.; Leveiller, F.; Lahav, M.; Leiserowitz, L. *Phys. Rep.* **1994**, 246, 252.
- (17) Kaganer, V. M.; Möhwald, H.; Dutta, P. Rev. Mod. Phys. 1999, 71, 779.