Supporting Information for

Molecular Orientation of Organic Thin Films on Dielectric Solid Substrates: A Phase-sensitive Vibrational SFG Study

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1. Synthesis of Partially deuterated octadecyltrichlorosilane (CD$_3$(CD$_2$)$_{16}$(CH$_2$)SiCl$_3$)
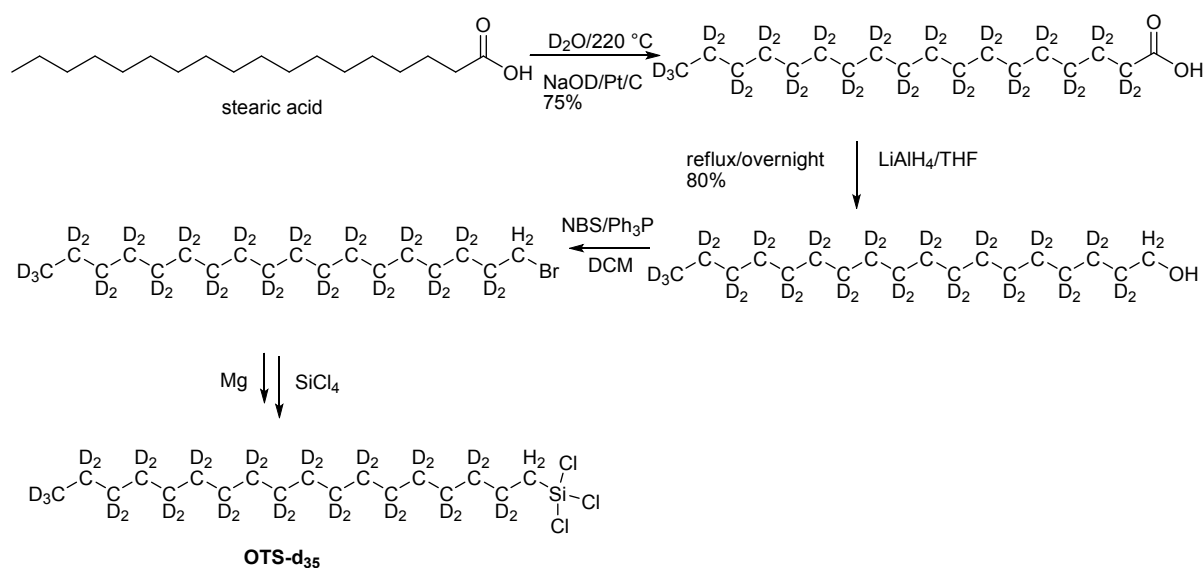
Scheme S1. Synthesis scheme for partially deuterated d_{35}-OTS.

Stearic acid was deuterated using hydrothermal H/D exchange procedure[1] according to Scheme S1. The stearic acid-d_{35} was then reduced to stearol-d_{35} using LiAlH$_4$ which placed a CH$_2$ methylene unit at the end of the chain next to the hydroxyl group. The alcohol was converted to the corresponding bromide according to Scheme S1 which was then used to produce d_{35}-OTS according to the procedure below.

To a warm (50 °C) solution of stearylbromide-d_{35} (5.0 g, 11.8 mmol) in dry diethyl ether (25 mL) was added Mg turnings (0.85 g, 35.44 mmol) under argon atmosphere. After refluxing for 2 h the reaction mixture brought to RT. Tetrachlorosilane (10 mL) was then added at once. The reaction continued to stir at RT for overnight under argon atmosphere. Solvent and tetrachlorosilane were removed under reduced pressure and the residue was subjected to Kugelrohr distillation at 280 °C and 0.05 mm pressure to give d_{35}-OTS as a colourless viscous liquid in 50% yield. The NMR data is in an excellent agreement with that of protonated OTS from commercial sources.

¹H NMR (CDCl$_3$) residual protons δ 0.84 (m, 0.5H), 1.23 (m, 3.3 H), 1.40 (s, 2H, (CH$_2$)), 1.47 (m, 0.4H), 1.55 (m, 0.2H)

²H NMR (CDCl$_3$) δ 0.81 (s, 3D), 0.91-1.30 (m, 27.44D), 1.34 (m, 2.47D), 1.51 (m, 1.76D).

¹³C NMR (CDCl$_3$) δ 13.3 (m), 21.4 (m), 24.4 (s, CH$_2$), 28.4 (m), 29.5 (m), 30.6 (m).

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2. Phase Correction Procedure

According to the description in the main text, the phase-sensitive SFG spectra before phase correction can be expressed as:

$$I_{PS\text{-}SFG} = \frac{E_{sample} r_{sample}^{*} E_{LO}^{*} e^{-i\omega\Delta t}}{E_{ref} r_{ref}^{*} E_{LO}^{*} e^{-i\omega\Delta t}} = E_{sample}\frac{r_{sample}^{*}}{E_{ref} r_{ref}^{*}} = |k|e^{i\phi}\chi_{sample}^{(2)}$$

(Eq. 3 in main text)

Since the self-assembly monolayer of OTS on the fused quartz surface is a well-known system where terminal CH$_3$ group are pointed away from the substrate and the absolute orientation has been elucidated,[2, 3] that we performed the phase correction for the obtained complex spectra of OTS SAM to obtain the imaginary spectrum and value of ϕ. The imaginary spectrum was chosen to do phase correction because it shows a symmetric spectral shape at resonance which is easier to be analysed than the real spectrum with dispersive features.
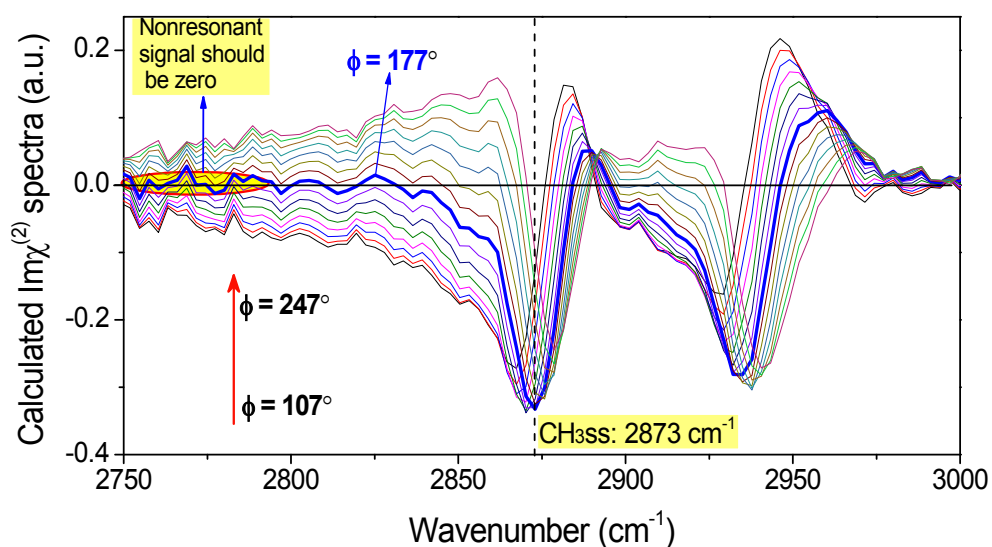
Figure S1. Illustration for phase correction of $\text{Im}\chi^{(2)}$ spectrum of OTS SAM to obtain the value of ϕ.

In Figure S1, different values of ϕ are used to calculate the imaginary $\chi^{(2)}$ spectra of an OTS SAM (in the figure, only the results between $\phi = 107°$ and $\phi = 247°$ are shown). It can be seen that the spectral shape of calculated $\text{Im}\chi^{(2)}$ spectra depends on the value of ϕ. The peak position of CH_3ss mode for OTS SAM is known to be 2873 cm^{-1}.[2] Moreover, the nonresonant signal from the fused quartz substrate is believed to be real and does not contribute to the imaginary $\chi^{(2)}$ spectrum.[3] Therefore, the $\text{Im}\chi^{(2)}$ intensity should be zero in the region (2750~2800 cm^{-1}) far from the C-H stretching region. On the basis of such knowledge, it can be seen that for the spectrum with $\phi = 177°$ should be the most likely $\text{Im}\chi^{(2)}$ spectrum for OTS SAM (blue bold line in Figure S1). (The CH_3ss peak was chosen as negative-going to be consistent with recent phase-sensitive SFG spectra of surfactant monolayers with methyl groups pointing toward air reported by other groups[3-5])

Since the value of ϕ has been obtained, the $\chi^{(2)}_{sample}$ spectra for other samples can be obtained by dividing the factor of $e^{i\phi}$:

$$I^{corrected}_{PS\text{-}SFG} = {I_{PS\text{-}SFG}}\Big/{e^{i\phi}} = |k|\chi^{(2)}_{sample} \propto \chi^{(2)}_{sample}$$
(Eq. 4 in the main text)

In this case, it is important to ensure that the heights of the OTS SAM and other samples are same, because even small height difference will significantly result in phase shift for ϕ. In the present work, the above phase correction procedure has been used for the solid/air interface. However, we found the same procedure cannot be readily applied for the CaF_2 prism/liquid interface due to the lack of reference sample and difficulty of height measurement at the buried prism/liquid interface, so we only present the frequency-domain interferograms of the water molecules at charged solid/water interfaces. We propose that use of a CaF_2 plate coated with a thin layer of SiO_2 may overcome these problems, because the OTS SAM can be formed on the SiO_2 surface as a reference sample and the height of the upper surface of CaF_2 plate can be accurately controlled.

References:

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