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Molecular Interactions of Organic Molecules at the Air/Water Interface Investigated by Sum Frequency Generation Vibrational Spectroscopy

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1. Spectral fitting of SFG-VS Signal

The intensity of the sum-frequency radiation is proportional to the square of the effective second-order susceptibility, which has been introduced in plenty of studies.[1-3]

$$I(\omega_{SFG}) \propto \left|\chi_{eff}^{(2)}\right|^2 I_1(\omega_{Vis}) I_2(\omega_{IR}) \quad \text{(S1)}$$

$\chi_{eff}^{(2)}$ can be expressed as the sum of resonant and nonresonant components, $\chi_R^{(2)}$ and $\chi_{NR}^{(2)}$. And the frequency dependence of $\chi_{eff}^{(2)}$ is described by eq. (S2).

$$\chi_{eff}^{(2)}(\omega) = \chi_{NR}^{(2)} + \sum_{\upsilon} \frac{A_\upsilon}{\omega - \omega_\upsilon + i\Gamma_\upsilon} \quad \text{(S2)}$$

A_υ, ω_υ, and Γ_υ are the amplitude of the SFG transition moment, frequency, and the line width of the transition, respectively. A_υ could be either positive or negative depending on the phase of the vibrational mode. A_υ, ω_υ, and Γ_υ can be extracted by fitting the spectrum.

2. The ssp and ppp spectra of four dibutyl ester molecules at the air/water interface at SP=5 and 10 mN/m

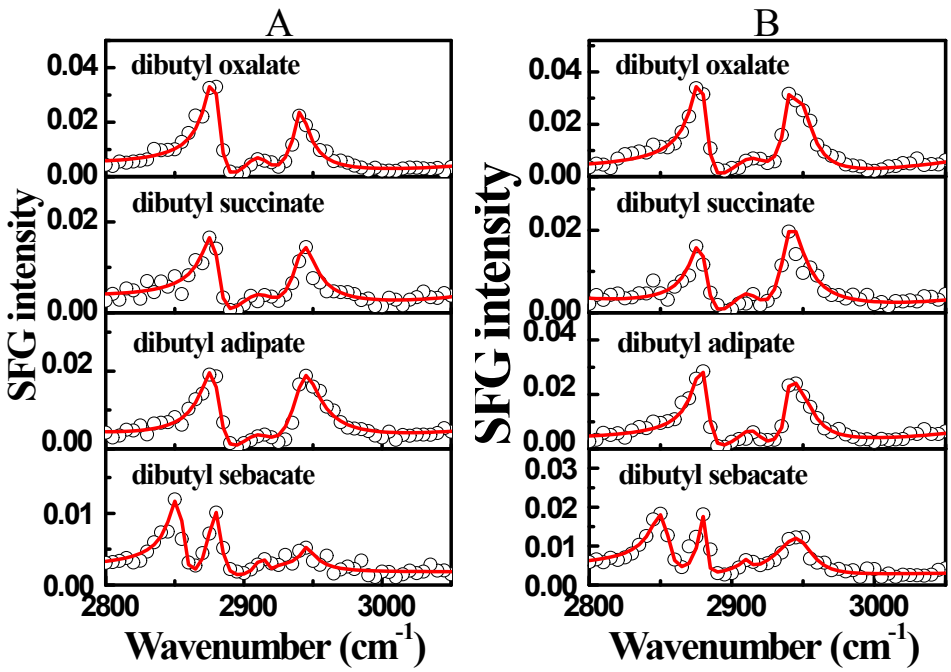

Figure S1. The ssp spectra of four dibutyl ester molecules at the air/water interface. A) at SP=5 mN/m, B) at SP=10 mN/m

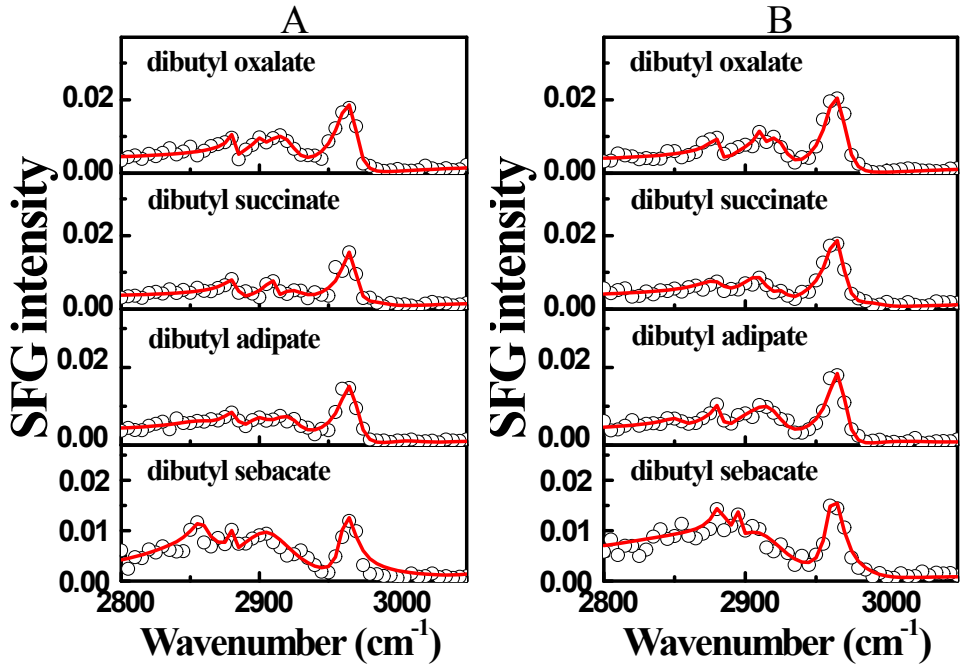

Figure S2. The ppp spectra of four dibutyl ester molecules at the air/water interface. A) at SP=5 mN/m, B) at SP=10 mN/m.

3. The calculated intensity ratio of $\chi^{(2)}_{ppp}(CH_3, as)/\chi^{(2)}_{ssp}(CH_3, ss)$ as a function of the tilt angle.

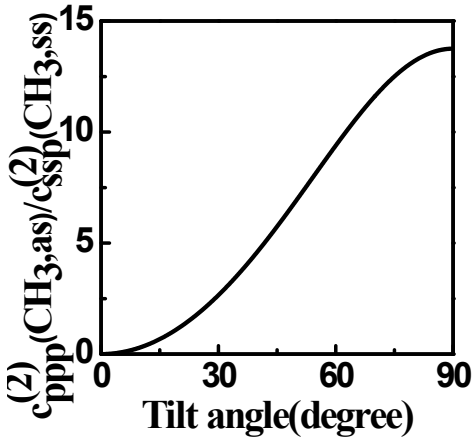

Figure S3. The calculated intensity ratio of $\chi^{(2)}_{ppp}(CH_3,as)/\chi^{(2)}_{ssp}(CH_3,ss)$ as a function of the tilt angle.

4. The 45°76°P spectra of four dibutyl ester molecules at the air/water interface at SP=5 & 10 mN/m

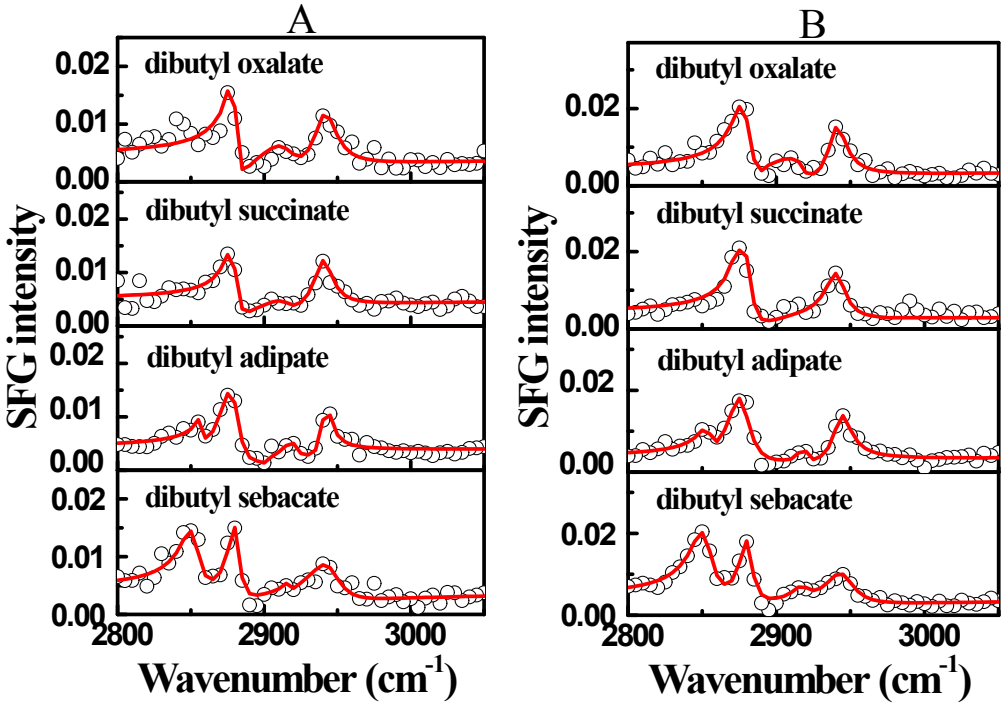

Figure S4. 45°76°P spectra of four dibutyl ester molecules at the air/water interface. A) at SP=5 mN/m; B) at SP=10 mN/m

4. SFG ssp spectra of DBP/PVC (a) and DEP/PVC (b) samples taken from reference 4.

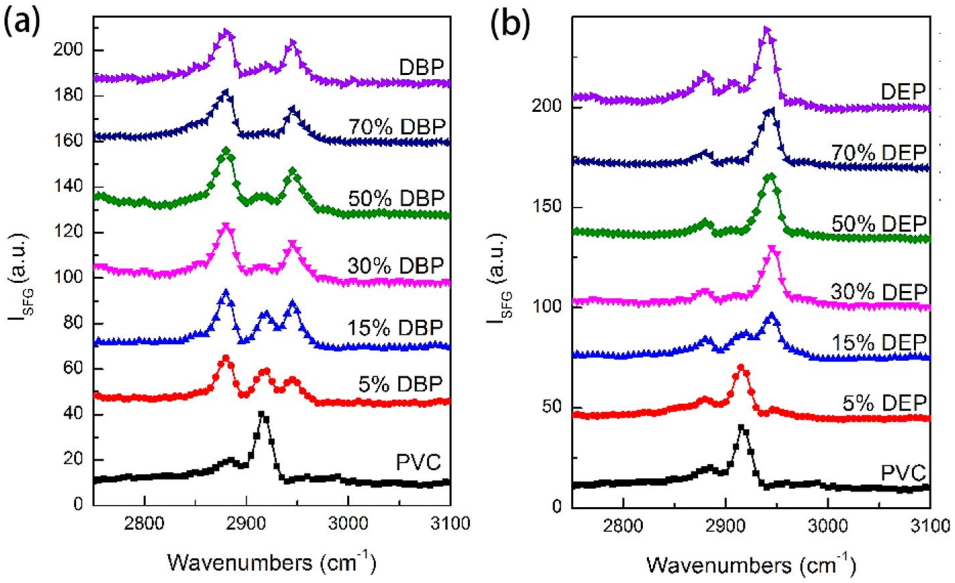

Figure S5. SFG ssp spectra of DBP/PVC (a) and DEP/PVC (b) samples with different phthalate bulk concentrations. (Figure S5 reproduced with permission from *Langmuir,* 2013,29 (12), 4008-4018, Copyright 2013, Am. Chem. Soc.)

5. SFG ssp spectra of pure PVC, TBAC, and PVC-TBAC hybrid films with various bulk TBAC concentrations taken from reference 5.

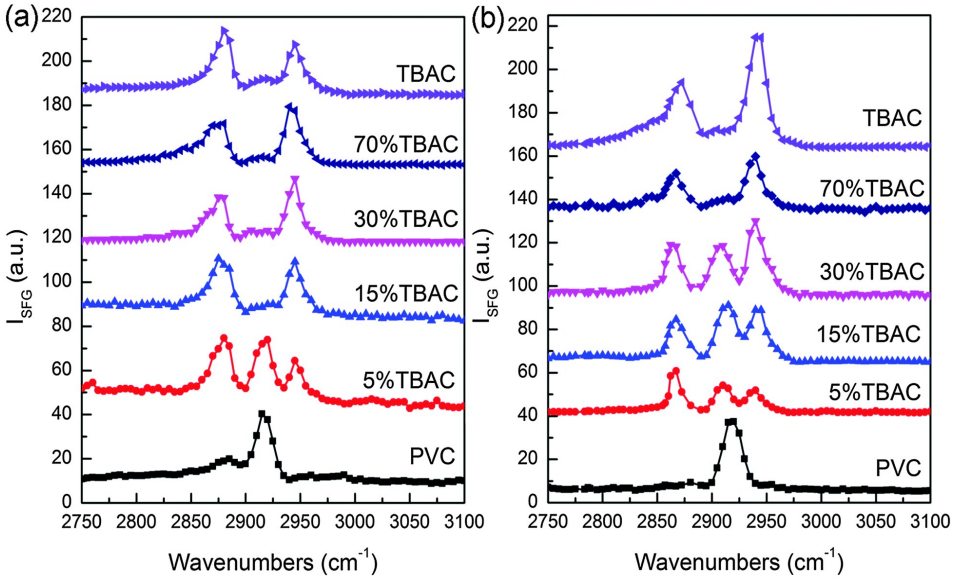

Figure S6. SFG ssp spectra of pure PVC, TBAC, and PVC-TBAC hybrid films with various bulk TBAC concentrations before (a) and after (b) water contact. (Figure S6 reproduced with permission from *Phys. Chem. Chem. Phys.*, 2015, 17(6), 4472-4482, Copyright 2015, Roy. Soc. Chem.)

References

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