Supporting Information for: Fabrication of Supramolecular Chirality from Achiral Molecules at the Liquid/Liquid Interface Studied by Second Harmonic Generation

Lu Lin,[†,‡] Zhen Zhang,[‡] Yuan Guo,[*,‡,¶] and Minghua Liu[*,‡]

†*National Center for Nanoscience and Technology, Beijing 100190, P. R. China*

‡*Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China*

¶*University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

E-mail: guoyuan@iccas.ac.cn; liumh@iccas.ac.cn

Fresnel Coefficients

In eq 1, a_i $(i = 1 - 7)$ denote the Fresnel coefficients, which can be expressed as:

$$\begin{aligned}
a_1 &= L_{yy}\left(2\omega\right) L_{zz}\left(\omega\right) L_{yy}\left(\omega\right) \sin\beta \\
a_2 &= -2L_{xx}\left(2\omega\right) L_{zz}\left(\omega\right) L_{xx}\left(\omega\right) \cos^2\beta \sin\beta \\
a_3 &= L_{zz}\left(2\omega\right) L_{xx}\left(\omega\right) L_{xx}\left(\omega\right) \cos^2\beta \sin\beta \\
a_4 &= L_{zz}\left(2\omega\right) L_{zz}\left(\omega\right) L_{zz}\left(\omega\right) \sin^3\beta \\
a_5 &= L_{zz}\left(2\omega\right) L_{yy}\left(\omega\right) L_{yy}\left(\omega\right) \sin\beta \\
a_6 &= 2L_{xx}\left(2\omega\right) L_{zz}\left(\omega\right) L_{yy}\left(\omega\right) \cos\beta \sin\beta \\
a_7 &= 2L_{yy}\left(2\omega\right) L_{zz}\left(\omega\right) L_{xx}\left(\omega\right) \cos\beta \sin\beta
\end{aligned} \tag{1}$$

with

$$\begin{aligned}
L_{xx}\left(\omega_i\right) &= \frac{2n_1\left(\omega_i\right)\cos\gamma}{n_1\left(\omega_i\right)\cos\gamma + n_2\left(\omega_i\right)\cos\beta} \\
L_{yy}\left(\omega_i\right) &= \frac{2n_1\left(\omega_i\right)\cos\beta}{n_1\left(\omega_i\right)\cos\beta + n_2\left(\omega_i\right)\cos\gamma} \\
L_{zz}\left(\omega_i\right) &= \frac{2n_2\left(\omega_i\right)\cos\beta}{n_1\left(\omega_i\right)\cos\gamma + n_2\left(\omega_i\right)\cos\beta}\left(\frac{n_1\left(\omega_i\right)}{n'\left(\omega_i\right)}\right)^2
\end{aligned} \tag{2}$$

In the above equations, n_1 and n_2 are the refractive indices of water and organic phase, n' is the refractive index of the interfacial layer, β is the incident angle, and γ is the refracted angle. Here we choose $n_1\left(\omega\right) = 1.329$, $n_1\left(2\omega\right) = 1.339$ and $n_2\left(\omega\right) = n_2\left(2\omega\right) = 1.445$. According to Zhuang *et al.* (Phys. Rev. B 1999, 59, 12632), $n' = n_1\sqrt{\frac{n_2^2\left(n_2^2+5\right)}{4n_2^2+2}}$.

Calculation of the Orientational Angle

The tensor elements χ_{zzz}, χ_{zxx}, χ_{xxz} and χ_{yxz} can be obtained by fitting the SHG curves. The fitting results are listed in Table S1.

We use χ_{zzz}, χ_{zxx} and χ_{xxz} to calculate the orientational angle. By assuming $\beta_{caa} = 0$,

Table 1: Fitting results of the tensor elements.

Concentration (mM)	χ_{zzz}	χ_{zxx}	χ_{xxz}	χ_{yxz}
0.005	123.84	25.05	24.84	0.01
0.010	140.11	31.74	31.45	0.09
0.025	243.33	61.98	57.85	0.91
0.035	312.64	87.68	81.42	2.88
0.060	369.98	91.36	83.90	2.56
0.075	565.86	109.30	102.86	1.88
0.100	682.75	122.00	113.74	1.03
0.150	721.19	126.58	116.89	0.37
0.300	782.09	130.60	126.99	0.32

χ_{zxx} should be equal to χ_{xxz}. As shown in Table S1, the values of χ_{zxx} are close to that of χ_{xxz}. Therefore, it is reasonable to neglect β_{caa} for calculating the orientational angle. To minimize the error, we suppose:

$$\frac{\chi_{zzz}}{\chi_{zzz}+\chi_{zxx}+\chi_{xxz}} \approx \frac{\langle\cos^3\theta\rangle}{\langle\cos^3\theta\rangle+\left\langle\sin^2\theta\cos\theta\right\rangle} \tag{3}$$

Assuming θ has a very narrow distribution, we have:

$$\theta = \arccos\left(\sqrt{\frac{\chi_{zzz}}{\chi_{zzz}+\chi_{zxx}+\chi_{xxz}}}\right) \tag{4}$$

We shall assess the error of the calculation. By assuming a narrow distribution of θ, we have:

$$\frac{\chi_{zzz}}{\chi_{zzz}+\chi_{zxx}+\chi_{xxz}} = \frac{\cos^2\theta+\frac{\beta_{caa}}{\beta_{ccc}}\sin^2\theta\,\langle\cos^2\psi\rangle}{1+\frac{\beta_{caa}}{2\beta_{ccc}}} \tag{5}$$

The ratio of β_{caa} and β_{ccc} can be estimated as:

$$\frac{\beta_{caa}}{\beta_{ccc}} \approx \frac{\chi_{zxx}-\chi_{xxz}}{(\chi_{zxx}+\chi_{xxz})\sin^2\theta} \leq 0.15 \tag{6}$$

At lower concentrations, ψ is randomly distributed. With increasing concentration, ψ approaches zero. It is thus reasonable to suggest $\frac{1}{2} \leq \langle\cos^2\psi\rangle \leq 1$. Let $\theta = 33°$, then the calculated value for θ lies between 33.4° and 34.7°. Therefore, the error of the calculated orientation is less than 2°.

Langmuir Fitting of Adsorption

According to the Langmuir adsorption model, we have

$$\frac{\chi_{zzz}}{\cos^3\theta} \approx N_s \beta_{ccc} = A \frac{Kc}{1+Kc} \tag{7}$$

where c is the bulk concentration, A and K are constants. The values of A and K can be obtained by fitting. Then the coverage can be calculated as $\frac{\chi_{zzz}}{A\cos^3\theta}$.