

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/275558842>

# Significant Chiral Signal Amplification of Langmuir Monolayers Probed by Second Harmonic Generation

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · APRIL 2015

Impact Factor: 7.46 · DOI: 10.1021/acs.jpcllett.5b00472

CITATION

1

READS

32

## 7 AUTHORS, INCLUDING:



**Lu Lin**

Chinese Academy of Sciences

4 PUBLICATIONS 12 CITATIONS

SEE PROFILE



**Li Zhang**

Mississippi State University

104 PUBLICATIONS 997 CITATIONS

SEE PROFILE



**Yuan Guo**

Chinese Academy of Sciences

37 PUBLICATIONS 590 CITATIONS

SEE PROFILE



**Minghua Liu**

Chinese Academy of Sciences

246 PUBLICATIONS 5,272 CITATIONS

SEE PROFILE

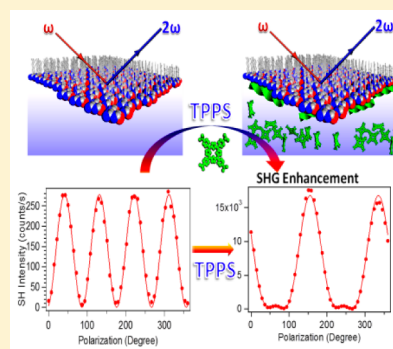
# Significant Chiral Signal Amplification of Langmuir Monolayers Probed by Second Harmonic Generation

Kai Lv, Lu Lin, Xiaoyu Wang, Li Zhang, Yuan Guo,\* Zhou Lu, and Minghua Liu\*

Beijing National Laboratory of Molecular Sciences, CAS Key Laboratory of Colloid, Interface and Thermodynamics, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

## Supporting Information

**ABSTRACT:** With the development of the nonlinear optical technique such as SHG (second harmonic generation), the in situ measurements of the chirality in the monolayers at the air/water interface have become possible. However, when performing the SHG measurement of the chirality in a monolayer, it is still a great challenge to obtain the chiral signals with a good S/N (signal-to-noise) ratio. In this Letter, interfacial assemblies with induced supramolecular chirality were used to amplify the weak chiral SHG signals from the monolayers at the air/water interface. Tetrakis(4-sulfonatophenyl) porphyrin (TPPS) J aggregates were used as the subphase, and when chiral amphiphilic molecules were spread on it, chiral domains of the amphiphile/TPPS J aggregates were formed and then significantly amplified chiral signals that otherwise could not be detected. Moreover, the sign of the DCE (degree of chiral excess) changed with the chirality of the amphiphilic molecules, thus providing a possible way to obtain the absolute chiral information in situ in the monolayers.



Chiral monolayers at the air/water interface have become immensely important because of its similarity to highly organized biomembranes where chirality controls a great number of recognition and enzymatic processes.<sup>1–6</sup> Previous studies have proved that both achiral and chiral molecules are possible to form the chiral domains or chiral nanostructures.<sup>7–10</sup> However, there still remains the challenge to detect this chirality in situ in the monolayers. Although the grazing incidence X-ray diffraction (GIXD) could be used to detect the chirality in the monolayers, the crystallization is necessary.<sup>11,12</sup> In addition, a strong beam source such as synchrotron radiation is required. Brewster angle microscopy has also proved to be able to detect the large chiral domains in the monolayers,<sup>13,14</sup> but it could not detect the interactions between different molecules. Other methods such as circular dichroism (CD) and optical rotatory dispersion (ORD) techniques are widely used to characterize the chiral systems; they are generally not applicable for the in situ monolayer detection. SEM and STM images are only performed after the Langmuir films are transferred onto solid substrates as these instrumentations do not allow the signals to be directly measured at the air/water interface. Thus, a sensitive technique for in situ detection of interfacial chirality in monolayers is urgently needed.

Second harmonic generation (SHG) is well suited for the detection of interfacial molecular behaviors as it can only be observed when inversion symmetry is broken and thus is prohibited in the bulk of centrosymmetric materials.<sup>15,16</sup> Second harmonic generation linear dichroism (SHG-LD) has been proven to be not only interface-selective but also chiral-sensitive, especially for the weak interfacial chirality.<sup>17–19</sup> The nonlinear chiroptical method has undergone many developments since some pioneering studies have demonstrated that

SHG is an ideal in situ technique to probe the supramolecular chirality of the Langmuir monolayer at the air/water interface.<sup>20–29</sup> Even with this merit, SHG is usually not sensitive to intramolecular chirality under nonresonant conditions because the chiral terms of the molecular hyperpolarizability are in general negligible compared with the achiral terms.<sup>17,30</sup> As a result, it is difficult for Langmuir monolayers composed of chiral enantiopure molecules, such as amino acid derivatives, to generate detectable chiral SHG signals if the molecules form domains or aggregates with laterally symmetric patterns. This flaw impedes further applications of the SHG chiral measurements on monolayers. Therefore, exploring the possibilities to amplify interfacial chiral signals is an important task in studying supramolecular chirality and is a necessary first step in realizing, for example, chiral SH images.

Persoons and co-workers have detected the strong enhancement of nonlinear optical properties in the Langmuir–Blodgett film of chiral helicene supramolecular assemblies.<sup>31,32</sup> Simpson and co-workers also reported the chiral-specific SHG signals with the DCE (degree of chiral excess) value of 44% from dyes interacting with chiral-templated solid/liquid surfaces.<sup>33</sup> On the basis of these works, we provide a general strategy to amplify the chiral SHG signals in situ at the air/water interface. It is clearly demonstrated in this work that the enhanced SHG chiral signals with the DCE as large as about 200% from the supramolecular assemblies are correlated with the absolute molecular chiral configurations of the template amphiphiles and

Received: March 6, 2015

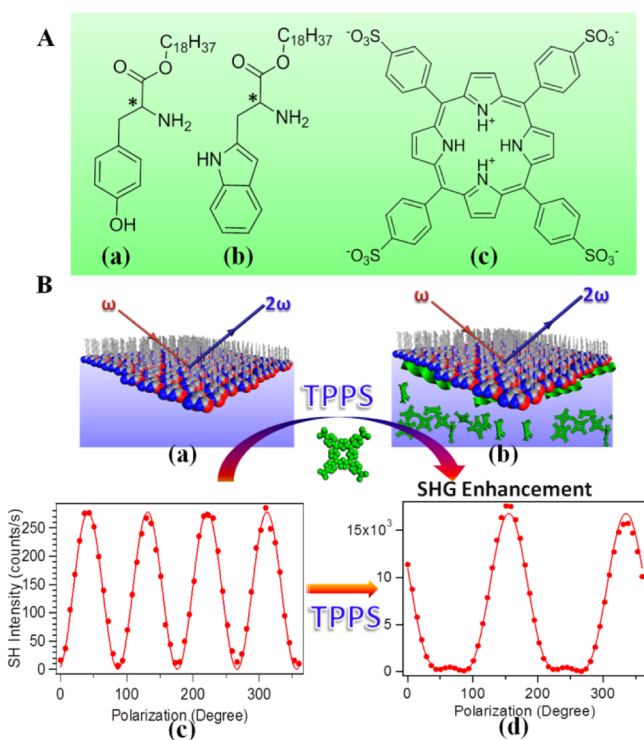
Accepted: April 21, 2015

Published: April 21, 2015



thus can significantly improve the signal-to-noise ratio in the chiral SHG measurement and provide an efficient method to directly differentiate the enantiomers within a monolayer.

The SHG-LD experimental setup was similar to that previously reported (see the Supporting Information).<sup>22,27,28</sup> The idea is based on the following. When chiral amphiphiles interact with selected assembly aggregations, the SH intensity could be amplified as well as the chiral signals. Tetrakis(4-sulfonatophenyl) porphyrin (TPPS) is well-known to form J aggregates when existing as the zwitterionic species. Previously, we have found that the J aggregation of TPPS can be promoted by the cationic amphiphiles at the air/water interface.<sup>10,34</sup> Herein, the chiral amphiphiles-tyrosine derivative (D-TyrC18 or L-TyrC18, Figure 1A, a) was spread on the TPPS solution



**Figure 1.** (A) Chemical structures of TyrC18 (a), TrpC18 (b), and TPPS (c). (B) The illustration of SHG of TyrC18 monolayers on the water subphase (a) and the pH = 2.5 TPPS solution subphase (b) and the corresponding SHG signal (c,d).

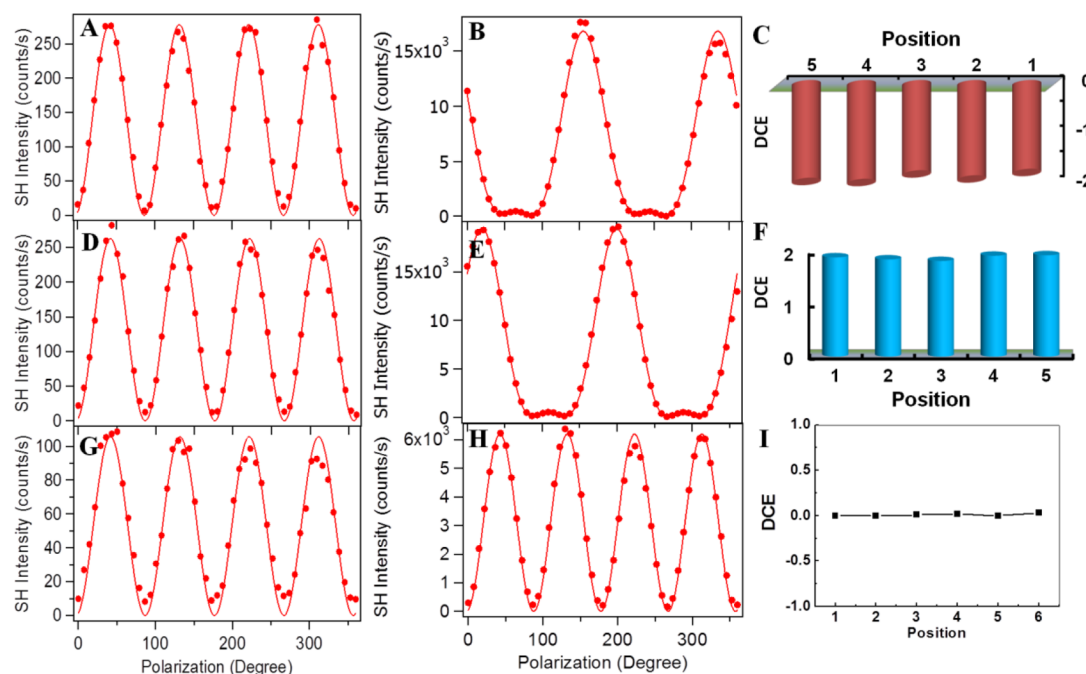
subphase (Figure 1A, c). As described in detail in the next paragraph, the chiral amphiphilic monolayer (Figure 1B, a) on pure water generates no detectable SHG-LD signals (Figure 1B, c), indicating that no chiral architecture could be formed by the amphiphiles themselves. However, an obvious enhancement of the chiral SHG signal (Figure 1B, d) by the TPPS J aggregates assembled with the amphiphilic monolayer (Figure 1B, b) was observed, although the TPPS is an achiral molecule. This experiment provides a novel method to help characterize the weak interfacial chirality using a nonlinear optical method, which was a great challenge in the past.

The polarization-dependent SH intensities from the TyrC18 Langmuir monolayer on the pure water and TPPS subphase are shown in Figure 2. Figure 2A and D shows the SHG polarization dependence curves of TyrC18 monolayers on the water subphase. The SHG signals at the incident polarization angle of  $45^\circ$  are equal to the signals at  $135^\circ$  ( $I_{45^\circ} = I_{135^\circ}$ , DCE =

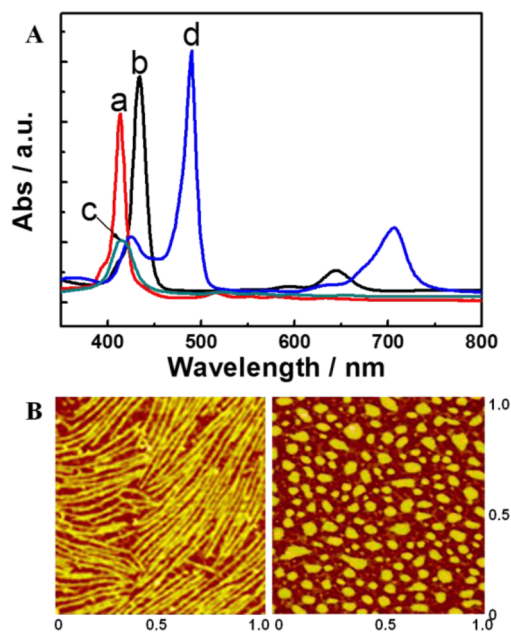
0) (see eq 2), indicating that no chiral signal was detected for the plain TyrC18 monolayer despite their intrinsic molecular chirality. It implied that the chiral signatures in the TyrC18 monolayer itself are too weak to be detected by SHG-LD technique. However, when the TyrC18 amphiphiles interacted with TPPS (pH = 2.5) to induce the J aggregation of TPPS at the air/water interface, the SHG signals at  $45^\circ$  were not equal to the signal at  $135^\circ$  ( $I_{45^\circ} \neq I_{135^\circ}$ ) (Figure 2B and E), indicating that the supramolecular chirality originated from the complex of the amphiphiles and TPPS J aggregates can be detected at the interface. If we define the SHG intensity at  $45^\circ$  to be larger than that of  $135^\circ$  as positive chirality, a positive chirality is obtained for the D-TyrC18 amphiphile, and a negative one is found for L-TyrC18, implying that the induced supramolecular chirality followed the chirality of the interfacial amphiphiles. In order to confirm the reliability of our experiment, we carried out the SHG-LD measurements at several different locations for the same monolayer and also performed several sets of experiments on the different monolayers. Figure 2C and F show the quantitative comparison of the chirality at various positions of the monolayer calculated by the DCE values, indicating that the monolayer of L-TyrC18/TPPS (pH = 2.5) or D-TyrC18/TPPS (pH = 2.5) formed the homochiral domains under the same experimental conditions. Also, we obtained the surprisingly large average DCE value for the L-TyrC18/TPPS monolayer of  $-1.83 \pm 0.04$ , and that for D-TyrC18/TPPS monolayer was  $1.88 \pm 0.04$ . The DCE value can provide a quantitative and straightforward criterion for the sign and degree of the interface chirality. To our best knowledge, it is rare to observe the large DCE values such as  $\sim 200\%$  as we reported here.<sup>33</sup> Therefore, the TPPS J aggregates can be potentially used in SHG imaging to study the chiral heterogeneity at the liquid interface.

In order to further understand the interaction between TyrC18 and TPPS molecules at the air/water interface, we investigated the rac-TyrC18 on the water subphase and TPPS subphase (pH = 2.5). Figure 2G and H show the resulting SHG intensity dependence curve. The SHG intensities are almost equal when the incident polarization angle is  $45^\circ$  and  $135^\circ$ , which means that no chiral signal was detected for rac-TyrC18 monolayers, although the rac-TyrC18 can enhance the overall achiral SHG intensity (Figure 2H) as well, owing to the near-resonant SHG wavelength ( $\lambda_{\text{SHG}} = 400 \text{ nm}$ ). As shown in Figure 2I, the value of DCE is zero for most positions that we have detected on the Langmuir monolayer of rac-TyrC18/TPPS. This result further proved that the interfacial chiral supramolecular assemblies can be controlled by the chiral amphiphile at the air/water interface.

As we know, TPPS exists as a zwitterionic monomer at pH = 2.5 and can be characterized by the Soret band at 434 nm and Q band at 644 nm in the UV-vis adsorption spectra shown in Figure 3A, b. The amphiphiles could also be protonated in this situation to be cationic. The TPPS molecule in this pH still carries overall negative charges. When the anionic TPPS molecules are adsorbed onto cationic amphiphilic monolayers of TyrC18, it can form the J aggregate in the LB films (Figure 3A, d), indicated by a large red shift of the intense Soret band at 490 nm and Q band at 709 nm. Meanwhile, another weak adsorption band at 422 nm was observed, which was also ascribed to the formation of J aggregates.<sup>35</sup> However, when the pH of the TPPS solution was adjusted to 5.4, the TPPS existed as a free base species, and the adsorption spectrum consisted of an intense Soret band (B band) at 413 nm and four very weak



**Figure 2.** SHG intensities versus the incident polarization angles for L-TyrC18 (A), D-TyrC18 (D), and rac-TyrC18 (G) monolayers on the neat water subphase and L-TyrC18 (B), D-TyrC18 (E), and rac-TyrC18 (H) monolayers on the pH = 2.5 TPPS solution subphase fitted using eq 1. The circles indicate experimental values, and the solid curves represent the fitting results. The laser power used for measurements on the pH = 2.5 TPPS solution subphase was 150 mW, and it was 600 mW for measurements on the water subphase. Panels C, F, and I show the DCE of different positions in the Langmuir monolayers of L-TyrC18 (C), D-TyrC18 (F), and rac-TyrC18 on the pH = 2.5 TPPS solution subphase. (The monolayers formed in this work were seen as laterally isotropic interfaces, ruling out the possibility of false chirality. The detailed discussion of ruling out the false chirality can be found in the Supporting Information.)



**Figure 3.** (A) (a) UV-vis adsorption spectra of the TPPS solution (pH = 5.4), (b) TPPS solution (pH = 2.5), (c) 30-layer films of L-TyrC18 with TPPS (pH = 5.4, transferred at 20 mN/m), and (d) 30-layer films of L-TyrC18 with TPPS (pH = 2.5, transferred at 20 mN/m). (B) AFM images of a one-layer complex LB film of L-TyrC18 and TPPS (left: pH = 2.5, right: pH = 5.4) transferred at 20 mN/m (scale bars: μm).

Q bands at 648, 580, 552, and 515 nm. These adsorption band did not change when TPPS complexed with amphiphile,

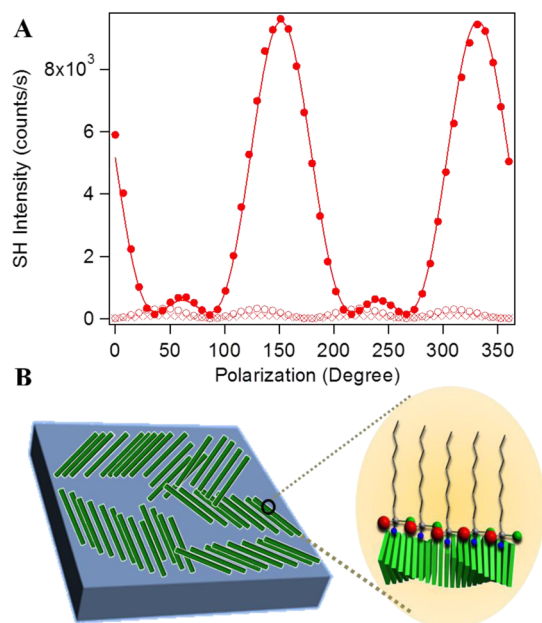
implying that no J aggregation formed at pH = 5.4. This can be used to explain that the weak SHG signals from the TyrC18 monolayer on the TPPS subphase with pH = 5.4 (see Figure 1S, Supporting Information). To compare the results obtained from TyrC18 monolayers on different pH TPPS subphases, we transferred the monolayers onto mica surfaces and measured the morphologies of the samples by atomic force microscopy (AFM). The morphology of the complexed film further confirmed the J aggregation at pH = 2.5 (Figure 3B, left), and long threadlike structures could be observed, while only some amorphous domains (Figure 3B, right) were detected for TyrC18/TPPS LB film transferred at pH 5.4.

Therefore, at pH = 2.5, the TPPS molecules exist in the form of J aggregates, which could be responsible for the observed chiral signal amplifications. We speculate that macrocyclic molecules like TPPS carry two crossed transition dipole moments, which thus leads to two axes of transition dipole moments of the porphyrin aggregate.<sup>36</sup> Thus, it is possible that the J aggregates may interact with the coexisting chiral amphiphile in an asymmetric fashion and exhibit a specific chiral nonlinear optical property, as seen from Figure 2. In addition, the enhancement of the SHG signal of TPPS J aggregates in this work cannot be simply assigned to the increase of the interfacial concentration but to the remarkable increase of the hyperpolarizability at the near-resonant SHG wavelength condition. Thus, both the enlargement of hyperpolarizability and an asymmetric molecular alignment of the J aggregates induced by the chiral amphiphiles may help improve the signal-to-noise ratio in the chiral SHG measurement. As a result, the J aggregation of TPPS as a second-order photo-material has a good potential utility in studying the chiral structure at the air/water interface. The more thorough study



on the exact mechanism of the chiral SHG signal is anticipated in future work.

We also chose another amphiphilic molecule (TrpC18, see Figure 1A, b) to investigate the interaction between amphiphiles and TPPS molecules at the air/water interface, and a similar result was obtained. Figure 4A shows the



**Figure 4.** (A) Dependence curves of the SHG intensity versus the incident polarization angle for L-TrpC18 monolayers on the pH = 2.5 TPPS solution subphase (●), on the pH = 5.4 TPPS solution subphase (○), and on the water subphase (×). The laser power for the pH = 2.5 TPPS solution subphase was 150 mW, and it was 600 mW for the pH = 5.4 TPPS solution subphase and the water subphase. (B) Illustration of possible stacking of TPPS with the amphiphilic molecules at the air/water interface. TPPS formed helical aggregates under the induction of the chiral amphiphiles and then formed nanofiber structures further.

polarization-dependent SHG intensities for L-TrpC18 on the TPPS subphase. It indicated that the L-TrpC18/TPPS (pH = 2.5) film formed obvious chiral structures as well (DCE =  $-1.76 \pm 0.04$ ), and the chirality of TPPS aggregates also followed the absolute chirality of the amphiphiles at the air/water interface. The intensity of the SHG signal again showed about 1000 times enhancement compared to the L-TrpC18 monolayer on the water subphase or the TPPS subphase with pH = 5.4, which is similar to what was observed when using the TyrC18 amphiphiles as described above.

Figure 4B shows the possible stacking of TPPS with the amphiphilic molecules at the air/water interface.<sup>10</sup> The interface chiral molecules can induce the achiral TPPS in the subphase to form chiral aggregates, and the chiral SHG signal can be enhanced remarkably. Also, the chirality of these chiral aggregates can be changed by the molecular chirality of the amphiphile. On the contrary, the amphiphile cannot form chiral aggregates on the plain water subphase, which can be supported by the undetectable chiral SHG signal. Similar observations were made for either TyrC18 or TrpC18, which suggests that this method can be commonly used to detect the weak chirality at the interfaces.

In summary, our findings clearly demonstrate that the TyrC18 and TPPS molecules can form supramolecular chiral structures at the air/water interface. The SH intensity and DCE

of the complex film were significantly amplified when aggregates were formed. Furthermore, the sign of DCE value followed the chirality of the amphiphile at the interface. Therefore, the present investigation sheds new light on the fundamental issue of chirality propagation in supramolecular assemblies, provides a base for the future chiral SHG imaging technique, and affords an efficient way for the in situ detection of the weak chirality at the interfaces.

**SHG-LD Measurement.** In SHG-LD, the incident light is linearly polarized. The SHG intensity is proportional to the square of the mode of the effective second-order susceptibility of the interface and is governed by the second-order nonlinear susceptibility  $\chi_{ijk}$ , which is a third-rank tensor with 27 elements. For isotropic chiral interfaces, there are four nonzero independent tensor elements,  $\chi_{zzz}$ ,  $\chi_{zxx} = \chi_{zyy}$ ,  $\chi_{xzx} = \chi_{xxz} = \chi_{yyz} = \chi_{yzy}$ , and  $\chi_{xyx} = \chi_{xzy} = -\chi_{yzx} = -\chi_{yxz}$ . Of the four elements, only the  $\chi_{xyz}$  is related to the interfacial chirality, named  $\chi_{\text{chiral}}$ , and the other tensor elements are achiral. For s-detection, the output polarization angle is  $\pi/2$ , and the SHG intensity can be expressed as<sup>15,22,25,37</sup>

$$I_s \propto |\chi_{\text{eff},45s} \sin 2\alpha + \chi_{\text{eff},\text{chiral}} \cos^2 \alpha|^2 \quad (1)$$

where  $\alpha$  is the incident polarization angle and  $\chi_{\text{eff}}$  is related to  $\chi_{ijk}$ . From eq 1, it can be deduced that the SH intensities are different at incident polarization angles of 45 and 135° if the interface is chiral. To quantitatively characterize the interfacial chirality, the DCE has been introduced. It is defined as<sup>27,38</sup>

$$\frac{\Delta I}{I} = \frac{2(I_{45^\circ} - I_{135^\circ})}{(I_{45^\circ} + I_{135^\circ})} \quad (2)$$

where  $I_{135^\circ}$  and  $I_{45^\circ}$  are the SHG intensity with incident laser polarization of 135 and 45°, respectively. The chiral and achiral Langmuir monolayers at the air/liquid interface are usually considered rotationally isotropic with respect to the interface normal. For the achiral Langmuir interface,  $I_{135^\circ} = I_{45^\circ}$ , and consequently,  $\Delta I/I = 0$ , while for the chiral Langmuir interface,  $I_{135^\circ} \neq I_{45^\circ}$ , and consequently,  $\Delta I/I \neq 0$ .

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental setup, chemicals, false chirality discussion, and SHG-LD curves of the TyrC18 monolayer on the TPPS (pH = 5.4) subphase. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00472.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: liumh@iccas.ac.cn (M.L.).

\*E-mail: guoyuan@iccas.ac.cn (Y.G.).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21227802, 21321063, and 91427302) and the Basic Research Development Program (2013CB834504).

## ■ REFERENCES

(1) Michinobu, T.; Shinoda, S.; Nakanishi, T.; Hill, J. P.; Fujii, K.; Player, T. N.; Tsukube, H.; Ariga, K. Mechanical Control of

- Enantioselectivity of Amino Acid Recognition by Cholesterol-Armed Cyclen Monolayer at the Air–Water Interface. *J. Am. Chem. Soc.* **2006**, *128*, 14478–14779.
- (2) Jiménez-Millán, E.; Giner-Casares, J. J.; Martín-Romero, M. T.; Brezesinski, G.; Camacho, L. Chiral Textures inside 2D Achiral Domains. *J. Am. Chem. Soc.* **2011**, *133*, 19028–19031.
- (3) Vysotsky, Y. B.; Fomina, E. S.; Belyaeva, E. A.; Aksenenko, E. V.; Fainerman, V. B.; Vollhardt, D.; Miller, R. Quantum-Chemical Analysis of Thermodynamics of Two-Dimensional Cluster Formation of Racemic  $\alpha$ -Amino Acids at the Air/Water Interface. *J. Phys. Chem. B* **2011**, *115*, 2264–2281.
- (4) Ariga, K.; Ji, Q.; Mori, T.; Naito, M.; Yamauchi, Y.; Abe, H.; Hill, J. P. Enzyme Nanoarchitectonics: Organization and Device Application. *Chem. Soc. Rev.* **2013**, *42*, 6322–6345.
- (5) Barry, D. E.; Kitchen, J. A.; Albrecht, M.; Faulkner, S.; Gunnlaugsson, T. Near Infrared (NIR) Lanthanide Emissive Langmuir–Blodgett Monolayers Formed Using Nd(III) Directed Self-Assembly Synthesis of Chiral Amphiphilic Ligands. *Langmuir* **2013**, *29*, 11506–11515.
- (6) Ma, S.; Li, H.; Tian, K.; Ye, S.; Luo, Y. In Situ and Real-Time SFG Measurements Revealing Organization and Transport of Cholesterol Analogue 6-Ketocholesterol in a Cell Membrane. *J. Phys. Chem. Lett.* **2014**, *5*, 419–424.
- (7) Yuan, J.; Liu, M. H. Chiral Molecular Assemblies from a Novel Achiral Amphiphilic 2-(Heptadecyl) Naphtha[2,3]imidazole through Interfacial Coordination Chiral Molecular Assemblies from a Novel Achiral Amphiphilic 2-(Heptadecyl) Naphtha[2,3]imidazole through Interfacial Coordination. *J. Am. Chem. Soc.* **2003**, *125*, 5051–5056.
- (8) Huang, X.; Li, C.; Jiang, S. G.; Wang, X. S.; Zhang, B. W.; Liu, M. H. Self-Assembled Spiral Nanoarchitecture and Supramolecular Chirality in Langmuir–Blodgett Films of an Achiral Amphiphilic Barbituric Acid. *J. Am. Chem. Soc.* **2004**, *126*, 1322–1323.
- (9) Zhang, L.; Yuan, J.; Liu, M. H. Supramolecular Chirality of Achiral TPPS Complexed with Chiral Molecular Films. *J. Phys. Chem. B* **2003**, *107*, 12768–12773.
- (10) Zhang, L.; Lu, Q.; Liu, M. H. Fabrication of Chiral Langmuir–Schaefer Films from Achiral TPPS and Amphiphiles through the Adsorption at the Air/Water Interface. *J. Phys. Chem. B* **2003**, *107*, 2565–2569.
- (11) Mannsfeld, S. C. B.; Virkar, A.; Reese, C.; Toney, M. F.; Bao, Z. Precise Structure of Pentacene Monolayers on Amorphous Silicon Oxide and Relation to Charge Transport. *Adv. Mater.* **2009**, *21*, 2294–2298.
- (12) Viani, L.; Risko, C.; Toney, M. F.; Breiby, D. W.; Brédas, J.-L. Substrate-Induced Variations of Molecular Packing, Dynamics, and Intermolecular Electronic Couplings in Pentacene Monolayers on the Amorphous Silica Dielectric. *ACS Nano* **2014**, *8*, 690–700.
- (13) Jiménez-Millán, E.; Giner-Casares, J. J.; Martín-Romero, M. T.; Brezesinski, G.; Camacho, L. Tuning of the Hydrophobic and Hydrophilic Interactions in 2D Chiral Domains Tuning of the Hydrophobic and Hydrophilic Interactions in 2D Chiral Domains. *J. Phys. Chem. C* **2012**, *116*, 19925–19933.
- (14) Rubia-Payá, C.; Jimenez-Millán, E.; Giner-Casares, J. J.; Brezesinski, G.; Martín-Romero, M. T.; Caamacho, L. From Two-Dimensional to Three-Dimensional at the Air/Water Interface: The Self-Aggregation of the Acridine Dye in Mixed Monolayers. *Langmuir* **2013**, *29*, 4796–4805.
- (15) Shen, Y. R. Optical Second Harmonic Generation at Interfaces. *Annu. Rev. Phys. Chem.* **1989**, *40*, 327–350.
- (16) Shen, Y. R. Surface Properties Probed by Second-Harmonic and Sum-Frequency Generation. *Nature* **1989**, *337*, 519–525.
- (17) Fischer, P.; Hache, F. Nonlinear Optical Spectroscopy of Chiral Molecules. *Chirality* **2005**, *17*, 421–437.
- (18) Simpson, G. J. Molecular Origins of the Remarkable Chiral Sensitivity of Second-Order Nonlinear Optics. *ChemPhysChem* **2004**, *5*, 1301–1310.
- (19) Balkin, M. A.; Shen, Y. R. Non-Linear Optical Spectroscopy as a Novel Probe for Molecular Chirality. *Int. Rev. Phys. Chem.* **2005**, *24*, 257–299.
- (20) Fu, L.; Liu, J.; Yan, E. C. Y. Chiral Sum Frequency Generation Spectroscopy for Characterizing Protein Secondary Structures at Interfaces. *J. Am. Chem. Soc.* **2011**, *133*, 8094–8097.
- (21) Reeve, J. E.; Corbett, A. D.; Boczarow, I.; Kaluza, W.; Barford, W.; Bayley, H.; Wilson, T.; Anderson, H. L. Porphyrins for Probing Electrical Potential Across Lipid Bilayer Membranes by Second Harmonic Generation. *Angew. Chem., Int. Ed.* **2013**, *52*, 9044–9048.
- (22) Lin, L.; Liu, A.; Guo, Y. Heterochiral Domain Formation in Homochiral  $\alpha$ -Dipalmitoylphosphatidylcholine (DPPC) Langmuir Monolayers at the Air/Water Interface. *J. Phys. Chem. C* **2012**, *116*, 14863–14872.
- (23) Kriech, M. A.; Conboy, J. C. Imaging Chirality with Surface Second Harmonic Generation Microscopy. *J. Am. Chem. Soc.* **2005**, *127*, 2834–2835.
- (24) Benichou, E.; Derouet, A.; Russier-Antoine, I.; Jonin, C.; Lascoux, N.; Liu, M. H.; Brevet, P. Supramolecular Chirality at the Air/Water Interface. *Opt. Mater. Express* **2011**, *1*, 17–26.
- (25) Kauranen, M.; Verbiest, T.; Maki, J. J.; Persoons, A. Second-Harmonic Generation from Chiral Surfaces. *J. Chem. Phys.* **1994**, *101*, 8193–8199.
- (26) Petralli-Mallow, T.; Wong, T. M.; Byers, J. D.; Yee, H. I.; Hicks, J. M. Circular Dichroism Spectroscopy at Interfaces: A Surface Second Harmonic Generation Study. *J. Phys. Chem.* **1993**, *97*, 1383–1388.
- (27) Xu, Y. Y.; Rao, Y.; Zheng, D. S.; Guo, Y.; Liu, M. H.; Wang, H. F. Inhomogeneous and Spontaneous Formation of Chirality in the Langmuir Monolayer of Achiral Molecules at the Air/Water Interface Probed by In Situ Surface Second Harmonic Generation Linear Dichroism. *J. Phys. Chem. C* **2009**, *113*, 4088–4098.
- (28) Lin, L.; Wang, T. Y.; Lu, Z.; Liu, M. H.; Guo, Y. In Situ Measurement of the Supramolecular Chirality in the Langmuir Monolayers of Achiral Porphyrins at the Air/Aqueous Interface by Second Harmonic Generation Linear Dichroism. *J. Phys. Chem. C* **2014**, *118*, 6726–6733.
- (29) Hauptert, L. M.; Simpson, G. J. Chirality in Nonlinear Optics. *Annu. Rev. Phys. Chem.* **2009**, *60*, 345–365.
- (30) Ji, N.; Shen, Y. R. A Novel Spectroscopic Probe for Molecular Chirality. *Chirality* **2006**, *18*, 146–158.
- (31) Verbiest, T.; Elshoche, S. V.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. Strong Enhancement of Nonlinear Optical Properties Through Supramolecular Chirality. *Science* **1998**, *282*, 913–915.
- (32) Verbiest, T.; Kauranen, M.; Persoons, A. Second-Order Nonlinear Optical Properties of Chiral Thin Films. *J. Mater. Chem.* **1999**, *9*, 2005–2012.
- (33) Burke, B. J.; Moad, A. J.; Polizzi, M. A.; Simpson, G. J. Experimental Confirmation of the Importance of Orientation in the Anomalous Chiral Sensitivity of Second Harmonic Generation. *J. Am. Chem. Soc.* **2003**, *125*, 9111–9115.
- (34) El-Hachemi, Z.; Mancini, G.; Ribó, J. M.; Sorrenti, A. Role of the Hydrophobic Effect in the Transfer of Chirality from Molecules to Complex Systems: From Chiral Surfactants to Porphyrin/Surfactant Aggregates. *J. Am. Chem. Soc.* **2008**, *130*, 15176–15184.
- (35) Castriciano, M. A.; Romeo, A.; Luca, G. D.; Villari, V.; Scolaro, L. M.; Micali, N. Scaling the Chirality in Porphyrin J-Nanoaggregates. *J. Am. Chem. Soc.* **2011**, *133*, 765–767.
- (36) Fujiwara, K.; Wada, S.; Monjushiro, H.; Watarai, H. Ion-Association Aggregation of an Anionic Porphyrin at the Liquid/Liquid Interface Studied by Second Harmonic Generation Spectroscopy. *Langmuir* **2006**, *22*, 2482–2486.
- (37) Byers, J. D.; Yee, H. I.; Petralli-Mallow, T.; Hicks, J. M. Second-Harmonic Generation Circular-Dichroism Spectroscopy from Chiral Monolayers. *Phys. Rev. B* **1994**, *49*, 14643–14647.
- (38) Verbiest, T.; Kauranen, M.; Maki, J. J.; Teerenstra, M. N.; Schouten, A. J.; Nolte, R. J. M.; Persoons, A. Linearly Polarized Probes of Surface Chirality. *J. Chem. Phys.* **1995**, *103*, 8296–8298.