Supporting Information: C-H Stretch for Probing Kinetics of Self-Assembly into Macromolecular Chiral Structures at Interfaces by Chiral Sum Frequency Generation Spectroscopy

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(I) The SFG setup and experiments

The broad-bandwidth SFG spectrometer used in the study was described in detail in *Ma et al*.[1] It contains a 6-W regenerative amplifier seeded by a 120-fs 1.9-W Ti:sapphire oscillator (Mai Tai, Spectra-Physics) and is pumped by two Nd:YLF pump lasers (16 W, Empower, Spectra-Physics). One half of the amplifier output (3 W) pumped an OPA (TOPAS, Spectra-Physics) to generate a 120-fs pulsed IR beam in the range of 3800–900 cm^{-1}. The other half (3W) of the amplifier 800-nm output entered a pulse shaper to yield ~2 ps pulses to a narrow bandwidth of ~7 cm^{-1}. The pulse shaper consisted of a grating, a planoconvex cylindrical lens, and a homemade slit. The reflected SFG signal was filtered, focused onto the slit of the monochromator (SP-2558, Princeton Instruments), and detected by a CCD (Spec-10:400BR/LN, Princeton Instruments). The 800 nm beam has an incident angle of 56° and the IR beam has an incident angle of 69°. The spot size of

the 800-nm beam is ~60 μm and that of the IR beam is ~70 μm in diameter. To prevent heating effects from laser irradiation, as is discussed by Backus *et al*.,[2] we use a spectrometer with a relatively long pulse duration (120 fs) and high repetition rate (5 kHz), and thus relatively low IR pulse energy and power (~4 μJ, 20 mW, C-H). Besides, the IR and visible beams are focused slightly below the interface. To maintain the constancy of the surface level when acquiring the SFG spectra, we used a reference point provided by the reflection of the 800-nm visible beam. After addition of the HCl or NaOH solution, we adjusted the height of the sample stage to bring the reflection of the 800-nm beam to the same reference point, which allowed us to ensure that the surface level is constant.

To determine the IR profile, we used the method specified in Ma *et al*.[1] Briefly, we placed a nonlinear GaAs crystal on the sample stage and took a nonresonant SFG spectrum from the surface of GaAs. The spectrum of GaAs provided the energy profile of the IR beam, which was used to normalize the SFG spectra.

(II) Supplementary Data

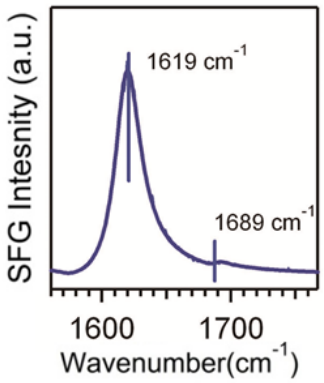

Figure S1. cSFG spectrum in the amide I region of $LK_7\beta$ at the air-water interface at pH ~7.4.

Table S1. Peak assignments and fitting parameters of the spectra of the initial (Figure 1B) and Refolded (Figure 1C) states of $LK_7\beta$.

Assignments	Parameters	Initial	Refolded
Nonresonance	$\chi_{NR}^{(2)}$	0.00047±0.00572	0.00084±0.00298
CH_2 SS	A_1 (a.u.)	0.79±2.07	0.90±0.63
	ω_1 (cm^{-1})	2854.5±13.8	2851.1±2.5
	Γ_1 (a.u.)	19.3±18.0	19.5±4.7
CH_3 SS	A_2 (a.u.)	0.82±1.98	0.80±0.96
	ω_2 (cm^{-1})	2872.3±8.6	2868.0±0.0
	Γ_2 (a.u.)	17.2±16.0	22.8±14.9
CH_2 FR	A_3 (a.u.)	0.39±0.96	0.27±0.37
	ω_3 (cm^{-1})	2900.7±5.7	2893.0±0.0
	Γ_3 (a.u.)	9.6±9.5	10.1±6.9
CH_2 AS	A_4 (a.u.)	0.30±1.04	0.70±0.19
	ω_4 (cm^{-1})	2911.1±5.9	2909.0±0.0
	Γ_4 (a.u.)	9.2±13.2	10.3±1.8
CH_3 FR	A_5 (a.u.)	-1.20±0.07	-0.63±0.05
	ω_5 (cm^{-1})	2932.6±0.5	2934.5±0.7
	Γ_5 (a.u.)	6.8±0.5	5.1±0.6
CH_3 AS	A_6 (a.u.)	1.89±0.03	1.42±0.04
	ω_6 (cm^{-1})	2958.1±0.2	2959.0±0.2
	Γ_6 (a.u.)	7.5±0.1	7.0±0.1
C_α-H Stretch	A_7 (a.u.)	0.79±0.07	0.93±0.07
	ω_7(cm^{-1})	2988.0±0.0	2984.3±0.3
	Γ_7 (a.u.)	9.6±0.8	10.4±0.6

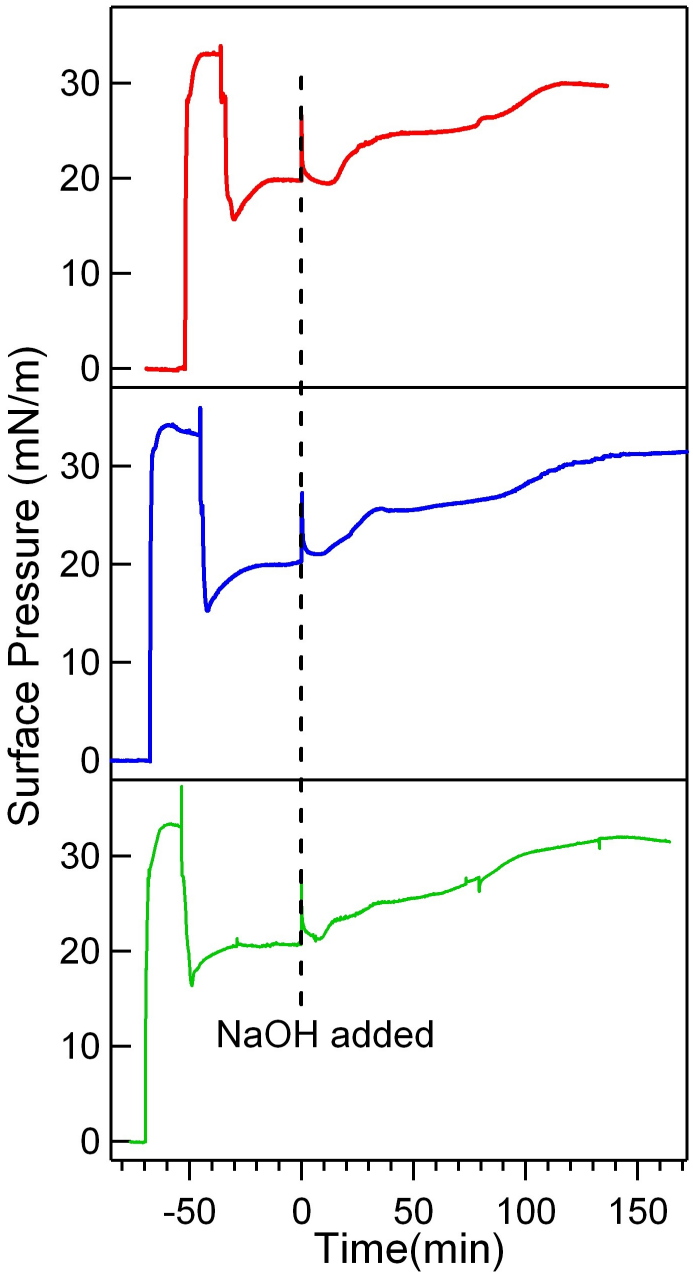

Figure S2. Three independent experiments of surface pressure measurements: the dashed line indicates addition of NaOH at $t = 0$, i.e., the beginning of the refolding process.

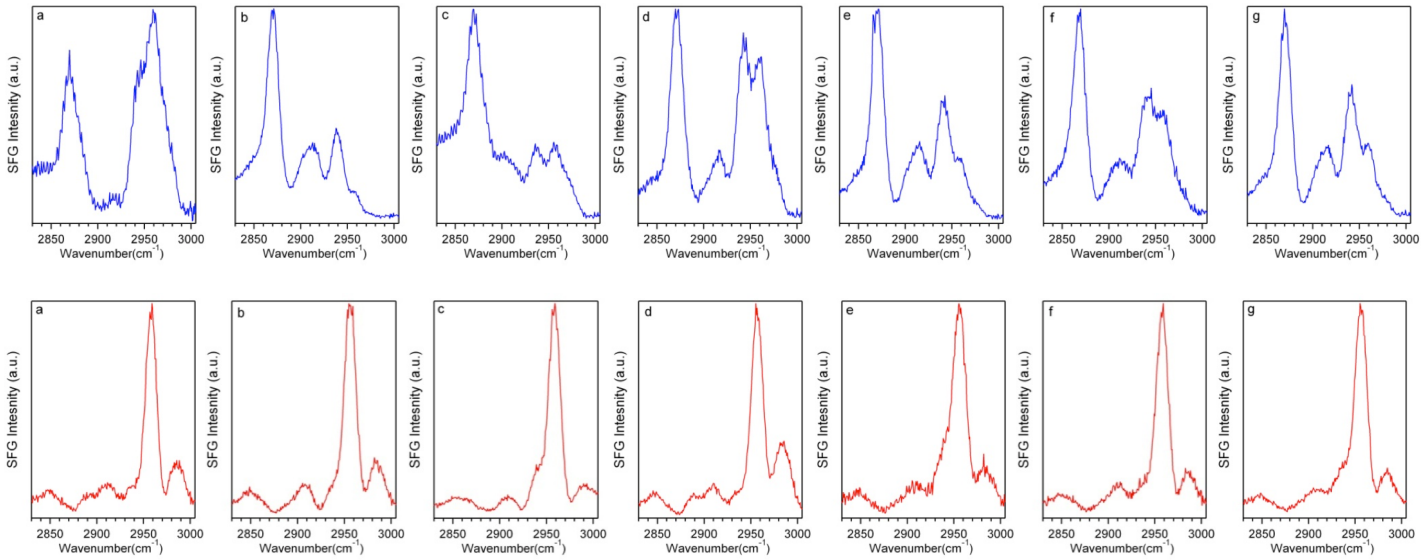

Figure S3. The achiral (ssp, blue) versus chiral (psp, red) SFG spectra for the folded state of $LK_7\beta$. The notations (a) to (g) represent various positions at the air-water interface; the same letter in the achiral and chiral spectra represents the same position. Data in (a) to (c) are presented in the main text.

References

1. Ma, G.; Liu, J.; Fu, L.; Yan, E. C. Y., Probing Water and Biomolecules at the Air-Water Interface with a Broad Bandwidth Vibrational Sum Frequency Generation Spectrometer from 3800 to 900 cm(-1). *Applied Spectroscopy* **2009,** *63* (5), 528-537.
2. Backus, E. H. G.; Bonn, D.; Cantin, S.; Roke, S.; Bonn, M., Laser-Heating-Induced Displacement of Surfactants on the Water Surface. *J Phys Chem B* **2012,** *116* (9), 2703-2712.