Supplementary Information
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Infrared Free Electron Laser or Polarized Ultraviolet Photolysis of Hierarchical and Chiral Components of Interleukin-6, Alanyl-Alanine and Alanine

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Table S1. Summary of ^{1}H-NMR data for Ala-ala after LP (linear polarized) IR-FEL irradiation (6.49 μm, 3.0 Hz, 3.3 mJ/pulse). Hereafter, in tables of NMR results, dq, d, and m denote double-doublet, doublet, and multiplet splitting, respectively.

Time (min)	*L*-ala-*L*-ala/D_2O (7.8×10^{-3} M)					*D*-ala-*D*-ala/D_2O (7.8×10^{-3} M)				
	Chemical shift	J-coupling	J (Hz)	proton	integrated value	Chemical shift	J-coupling	J (Hz)	proton	integrated value
5	3.91	dq	24.4, 7.2	2H	2.00	3.91	dq	25.2, 7.2	2H	2.00
	1.36	d	6.9	3H	3.01	1.36	d	7.2	3H	3.03
	1.17	d	7.2	3H	3.07	1.17	d	7.6	3H	3.02
10	3.91	dq	24.9, 7.2	2H	2.00	3.91	dq	25.7, 7.2	2H	2.00
	1.36	d	7.2	3H	3.00	1.36	d	7.2	3H	3.01
	1.17	d	7.2	3H	3.06	1.17	d	7.2	3H	3.01
20	3.91	dq	24.7, 7.2	2H	2.00	3.91	dq	25.5, 7.2	2H	2.00
	1.36	d	7.2	3H	3.01	1.36	d	6.9	3H	3.01
	1.17	d	7.2	3H	3.00	1.17	d	7.2	3H	3.00
30	3.91	dq	24.3, 7.2	2H	2.00	3.91	dq	26.0, 7.2	2H	2.00
	1.36	d	6.9	3H	3.01	1.36	d	7.2	3H	3.04
	1.17	d	7.2	3H	2.99	1.17	d	8.6	3H	3.01

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Table S2. Summary of ^{1}H-NMR data for Ala-ala after LCP (left circular polarized) IR-FEL irradiation (6.49 μm, 3.0 Hz, 3.3 mJ/pulse).

Time (min)	*L*-ala-*L*-ala/D_2O (7.8×10^{-3} M)					*D*-ala-*D*-ala/D_2O (7.8×10^{-3} M)				
	Chemical shift	J-coupling	J (Hz)	proton	integrated value	Chemical shift	J-coupling	J (Hz)	proton	integrated value
5	3.90	dq	25.4, 7.3	2H	2.00	3.91	dq	25.0, 7.2	2H	2.00
	1.35	d	7.2	3H	3.07	1.36	d	6.9	3H	3.01
	1.16	d	7.2	3H	3.03	1.17	d	7.2	3H	3.00
10	3.84-3.99	d	-	2H	2.00	3.91	dq	24.8, 7.2	2H	2.00
	1.36	d	6.9	3H	3.01	1.36	d	7.2	3H	3.06
	1.17	d	7.6	3H	3.04	1.17	d	7.2	3H	3.03
20	3.91	dq	24.2, 7.3	2H	2.00	3.91	dq	24.9, 7.2	2H	2.00
	1.36	d	7.2	3H	3.05	1.36	d	6.9	3H	3.01
	1.17	d	7.2	3H	3.04	1.17	d	7.2	3H	3.06
30	3.91	dq	23.7, 7.2	2H	2.00	3.91	dq	25.2, 7.2	2H	2.00
	1.36	d	6.9	3H	2.95	1.36	d	7.2	3H	3.00
	1.17	d	7.2	3H	2.95	1.17	d	7.2	3H	3.00

Table S3. Summary of ^{1}H-NMR data for Ala-ala after LP (linear polarized) UV irradiation.

Time (min)	*L*-ala-*L*-ala/D_2O (7.8×10^{-3} M)					*D*-ala-*D*-ala/D_2O (7.8×10^{-3} M)				
	Chemical shift	J-coupling	J (Hz)	proton	integrated value	Chemical shift	J-coupling	J (Hz)	proton	integrated value
5	3.91	dq	24.4, 7.2	2H	2.00	3.91	dq	25.2, 7.2	2H	2.00
	1.36	d	6.9	3H	3.01	1.36	d	7.2	3H	3.03
	1.17	d	7.2	3H	3.07	1.17	d	7.6	3H	3.02
10	3.91	dq	24.9, 7.2	2H	2.00	3.91	dq	25.7, 7.2	2H	2.00
	1.36	d	7.2	3H	3.00	1.36	d	7.2	3H	3.01
	1.17	d	7.2	3H	3.06	1.17	d	7.2	3H	3.01
20	3.91	dq	24.7, 7.2	2H	2.00	3.91	dq	25.5, 7.2	2H	2.00
	1.36	d	7.2	3H	3.01	1.36	d	6.9	3H	3.01
	1.17	d	7.2	3H	3.00	1.17	d	7.2	3H	3.00
30	3.91	dq	24.3, 7.2	2H	2.00	3.91	dq	26.0, 7.2	2H	2.00
	1.36	d	6.9	3H	3.01	1.36	d	7.2	3H	3.04
	1.17	d	7.2	3H	2.99	1.17	d	8.6	3H	3.01

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Table S4. Summary of ^{1}H-NMR data for Ala-ala after LCP (left circular polarized) UV irradiation.

time (min)	Chemical shift	J-coupling	J (Hz)	proton	integrated value	Chemical shift	J-coupling	J (Hz)	proton	integrated value
	L-ala/D_2O (5.0×10^{-4} M)					*D*-ala/D_2O (5.0×10^{-4} M)				
5	3.61	q	7.2	1H	1.00	3.60	q	7.3	1H	1.00
	1.31	d	7.2	3H	3.00	1.30	d	7.2	3H	3.01
10	3.61	q	7.2	1H	1.00	3.61	q	7.2	1H	1.00
	1.31	d	7.2	3H	2.94	1.31	d	7.2	3H	3.02
20	3.60	q	7.2	1H	1.00	3.60	q	7.2	1H	1.00
	1.30	d	7.2	3H	3.08	1.30	d	7.2	3H	3.01
30	3.61	q	7.2	1H	1.00	3.61	q	7.2	1H	1.00
	1.31	d	7.2	3H	3.03	1.31	d	7.2	3H	3.00

Table S5. Summary of ^{1}H-NMR data for Ala in the solid state after LP (linear polarized) IR-FEL irradiation (6.49 μm, 3.0 Hz, 3.3 mJ/pulse).

time (min)	*L*-ala, IR-FEL LP					*D*-ala, IR-FEL LP				
	chemical shift	J-coupling	J (Hz)	proton	integrated value	chemical shift	J-coupling	J (Hz)	proton	integrated value
0	3.64	q	7.2	1H	1.00	3.64	q	7.2	1H	1.00
	1.34	d	7.2	3H	3.09	1.34	d	7.2	3H	3.00
30	3.65	q	7.1	1H	1.00	3.65	q	7.3	1H	1.00
	1.35	d	7.2	3H	2.98	1.34	d	7.2	3H	3.10

Table S6. Summary of ^{1}H-NMR data for Ala in the solid state after LP (lienar polarized), LCP (left circular polarized), and RCP (right circular polarized) UV irradiation (6.49 μm, 3.0 Hz, 3.3 mJ/pulse).

time (min)	Chemical shift	J-coupling	J (Hz)	proton	integrated value	Chemical shift	J-coupling	J (Hz)	proton	integrated value
	L-ala/D_2O (5.0×10^{-4} M), UV LP					*D*-ala/D_2O (5.0×10^{-4} M), UV LP				
15	3.63	q	7.2	1H	1.00	3.62	q	7.2	1H	1.00
	1.32	d	7.2	3H	3.01	1.32	d	7.2	3H	3.00
30	3.62	q	7.3	1H	1.00	3.62	q	7.2	3H	1.00
	1.32	d	7.2	3H	3.05	1.32	d	7.2	3H	3.09
60	3.61	q	7.2	1H	1.00	3.61	q	7.2	1H	1.00
	1.31	d	7.2	3H	3.04	1.31	d	7.2	3H	3.00
	L-ala/D_2O (5.0×10^{-4} M), UV LCP					*D*-ala/D_2O (5.0×10^{-4} M), UV LCP				
30	3.62	q	7.2	1H	1.00	3.62	q	7.2	1H	1.00
	1.32	d	7.2	3H	3.02	1.32	d	7.2	3H	3.08
	L-ala/D_2O (5.0×10^{-4} M), UV RCP					D-ala/D_2O (5.0×10^{-4} M), UV RCP				
30	3.62	q	7.2	1H	1.00	3.62	q	7.2	1H	1.00
	1.32	d	7.2	3H	3.02	1.32	d	7.2	3H	3.01

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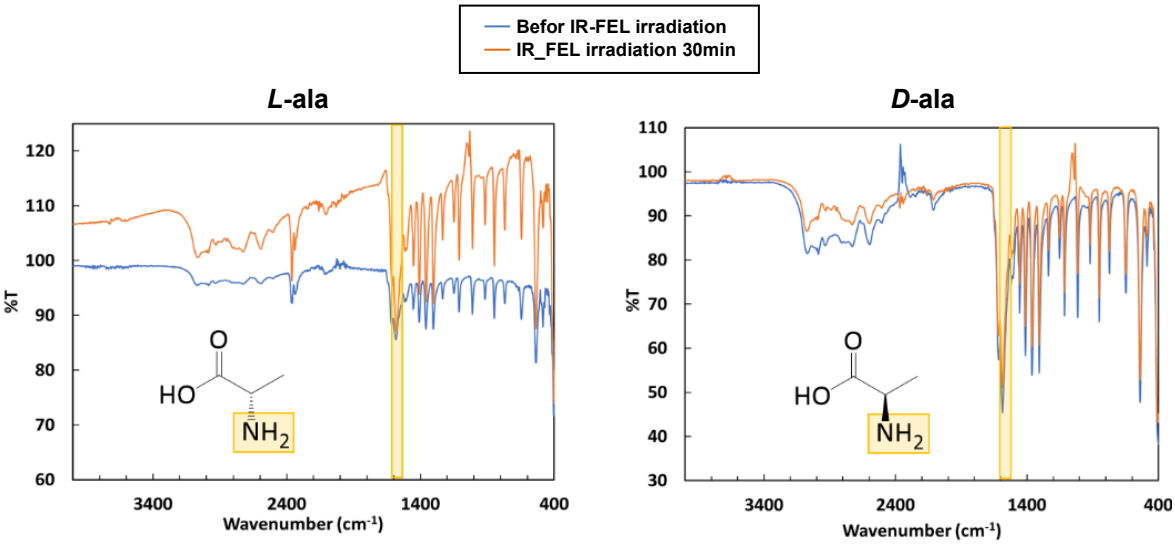

Figure S1. FT-IR of spectra of Ala in the solid state before and after IR-FEL irradiation.

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