Supporting Information

Flowing microenvironments regulate the helical pitch of a semi-artificial polymer

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General: UV–Vis spectra were recorded using a JASCO V-670 apparatus equipped with a thermo controller. CD spectra were recorded using a JASCO J-720 spectrometer. DLS data were obtained using a Malvern Zetasizer Nano-ZS. AFM images were acquired in air using a Shimadzu SPM 9600 instrument (tapping mode); samples were cast on mica and dried for 6 h under reduced pressure prior to observation. Optical microscopy images of the microflow system were acquired using a Keyence VW-6000 microscope. Microfluidic devices were purchased from IMT as custom-made products. All reagents and solvents were purchased from Wako Pure Chemical Industries, Tokyo Chemical Industry, Nacalai Tesque, and Aldrich.

Flow design: The focusing hydrodynamic flow featured a cross-point having depth and width of 45 and 100 μm, respectively. The channel length from the inlet to the cross-point was 18 mm. The total channel length was 98 mm.

Sample preparation: An aqueous solution [DMSO/water, 1:9 (v/v)] of CUR-Chl (0.5 mg/mL, 0.32 mM/repeating unit) was injected into the central leg at 20 μL/min and squeezed by lateral THF solutions (0.16 mM) containing bipyridyl ligands injected at 10 μL/min. The flow rate ratio (central flow/side flow) was fixed at 1.0:0.5, giving a total flow rate of 40 μL/min. The eluted solution (200 μL) was diluted with water (200 μL). The final solvent composition was DMSO/THF/water at 1:10:29 (v/v/v).

In the case of PyPhe-PBI ligand, DMF was used instead of THF, due to poor solubility. An aqueous solution [DMSO/water, 1/9 (v/v)] of CUR-Chl (1.0 mg/mL, [0.64 mM/repeating unit]) and a DMF solution of PyPhe-PBI (0.32 mM) were injected from the central and side legs, respectively. An aqueous solution containing CUR-Chl was injected from the central leg at 40 μL/min and squeezed by lateral DMF solutions (0.16 mM) containing PyPhe-PBI injected at 20 μL/min. The flow rate ratio (central flow/side flow) was fixed at 1.0:0.5, giving a total flow rate of 80 μL/min. To avoid precipitation of the resulting complex, the eluted solution (200 μL) was poured into mixed solvent [DMF/water, 1:9 (v/v); 200 μL] instead of water. The final solvent composition was DMSO/DMF/water at 1:12:27 (v/v/v).

The final concentration of the CUR-Chl/PyPhe-PBI complex was double that of the CUR-Chl/Py-PBI complex. When the standard concentration of DMF solution (0.16 mM) containing PyPhe-PBI was used, no UV–Vis and CD spectral changes were observed. This result suggests that the binding ability of CUR-Chl depends on the applied flow rate, which influences the orientation of the adjacent chlorophyll units. Under higher flow rates, elongation of the helix decreased its binding ability toward PyPhe-PBI.

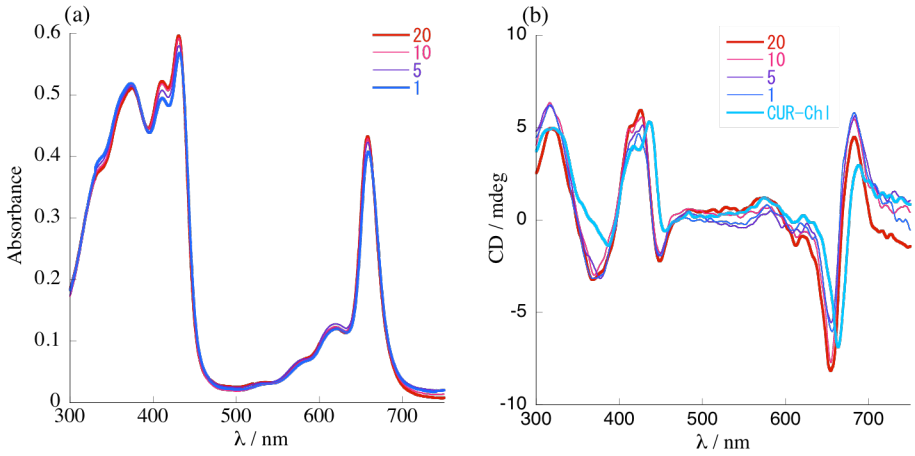

Figure S1. (a) UV–Vis (3-mm cell, r.t.) and (b) CD (10-mm cell, r.t.) spectra of CUR-Chl/PVP complexes created in a microflow. Insets: Applied flow rates (μL/min). The [PVP]/[chlorophyll unit] ratio was fixed at 0.5.

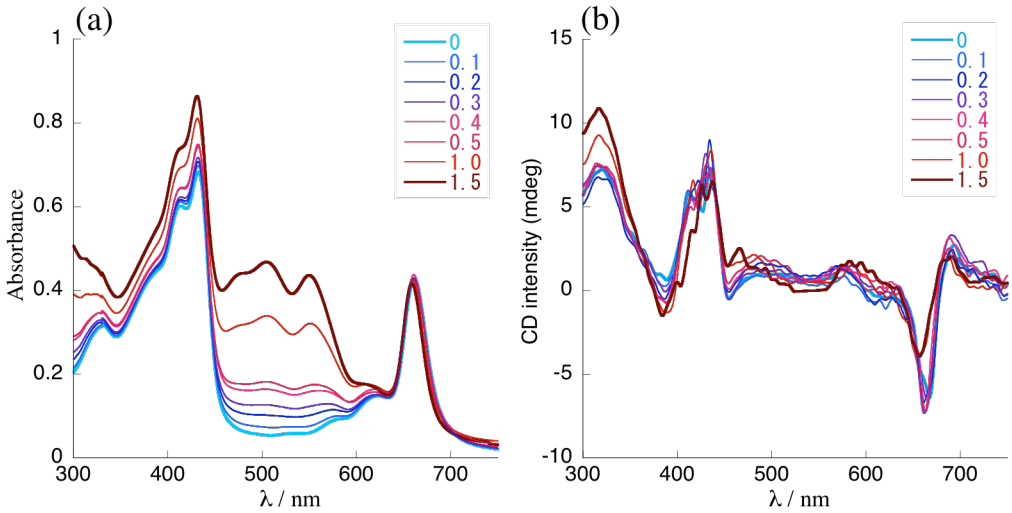

Figure S2. (a) UV–Vis (3-mm cell, r.t.) and (b) CD (10-mm cell, r.t.) spectra of solutions of CUR-Chl and Py-PBI [DMSO/THF/water, 1:10:29 (v/v/v)]. These solutions were prepared in a vial through conventional mixing. Insets: [Py-PBI]/[CUR-Chl] ratios. Final concentration of CUR-Chl: 0.12 mg/mL.

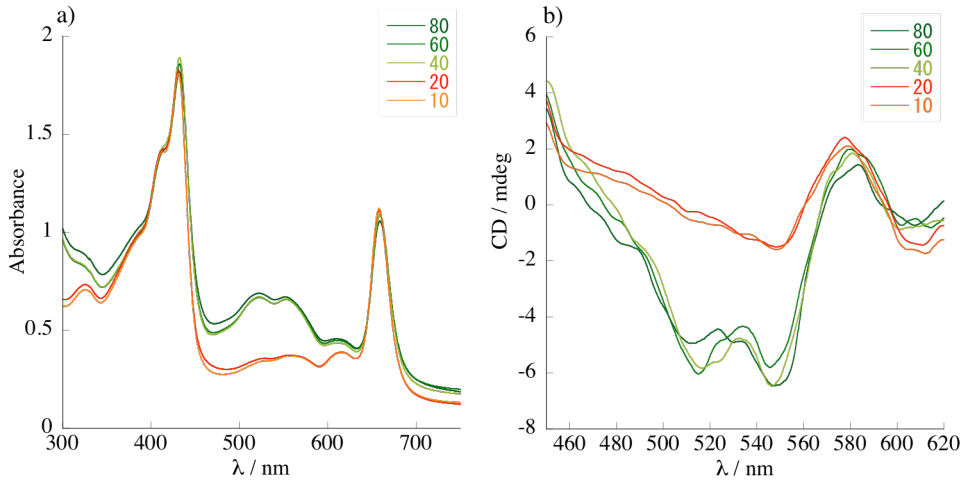

Figure S3. (a) UV–Vis (3-mm cell, r.t.) and (b) CD (10-mm cell, r.t.) spectra of CUR-Chl/PyPhe-PBI complexes formed at various flow rates [DMSO/DMF/water, 1:12:27 (v/v/v)]. Inset: Applied flow rates (μL/min). [PyPhe-PBI]/[chlorophyll unit] ratio: 0.5. Final concentration of CUR-Chl: 0.24 mg/mL.

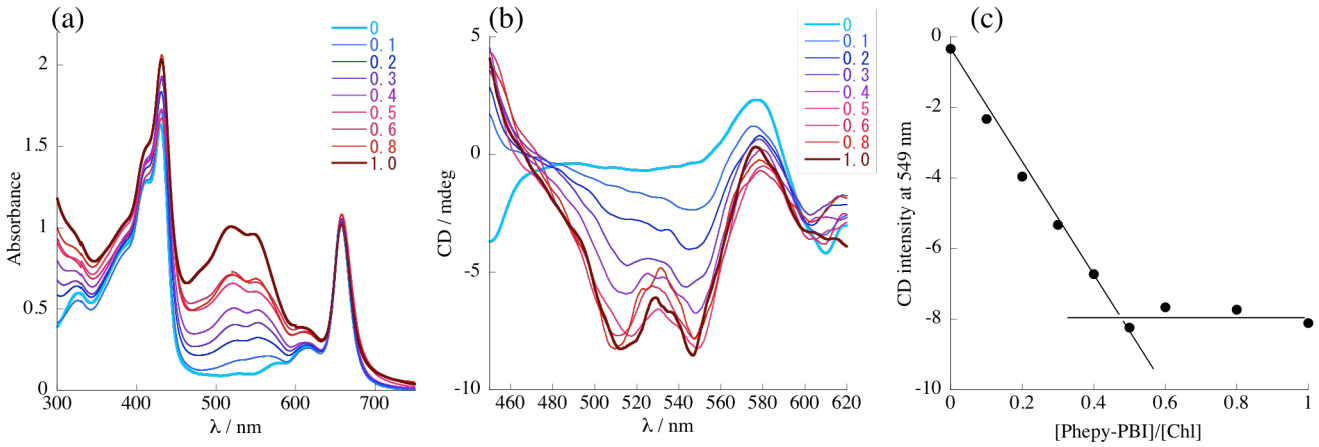

Figure S4. (a) UV–Vis (3-mm cell, r.t.) and (b) CD (10-mm cell, r.t.) spectra of CUR-Chl/PyPhe-PBI complexes [DMSO/DMF/water, 1:12:27 (v/v/v)] obtained upon changing the [PyPhe-PBI]/[Chlorophyll unit] ratio; inset: [PyPhe-PBI]/[CUR-Chl] ratio. (c) Plot of CD intensity at 549 nm with respect to [PyPhe-PBI]/[chlorophyll unit] ratio. Final concentration of CUR-Chl: 0.24 mg/mL.

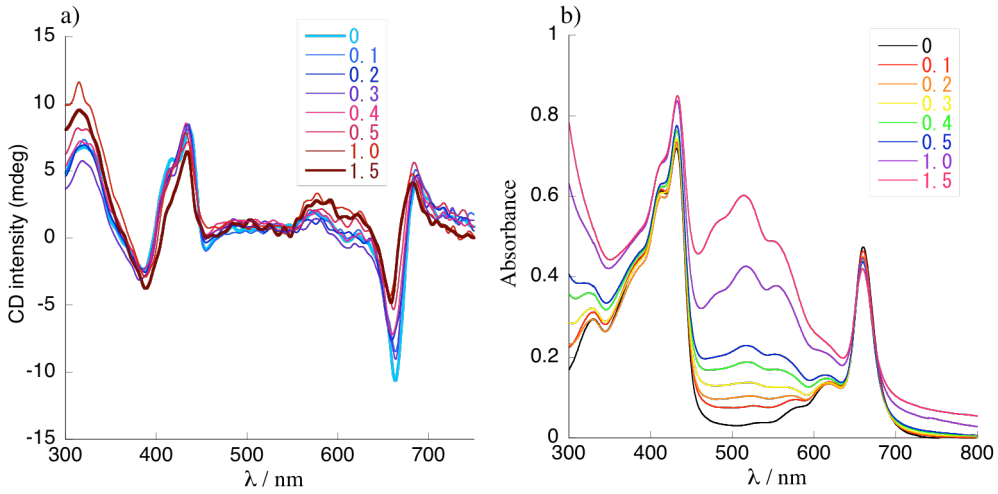

Figure S5. (a) UV–Vis (3-mm cell, r.t.) and (b) CD (10-mm cell, r.t.) spectra of solutions containing CUR-Chl and PyPhe-PBI [DMSO/DMF/water, 1:12:27 (v/v/v)]. The solutions were prepared in a vial through conventional mixing. Insets: [PyPhe-PBI]/[Chlorophyll units] ratio. Final concentration of CUR-Chl: 0.12 mg/mL.

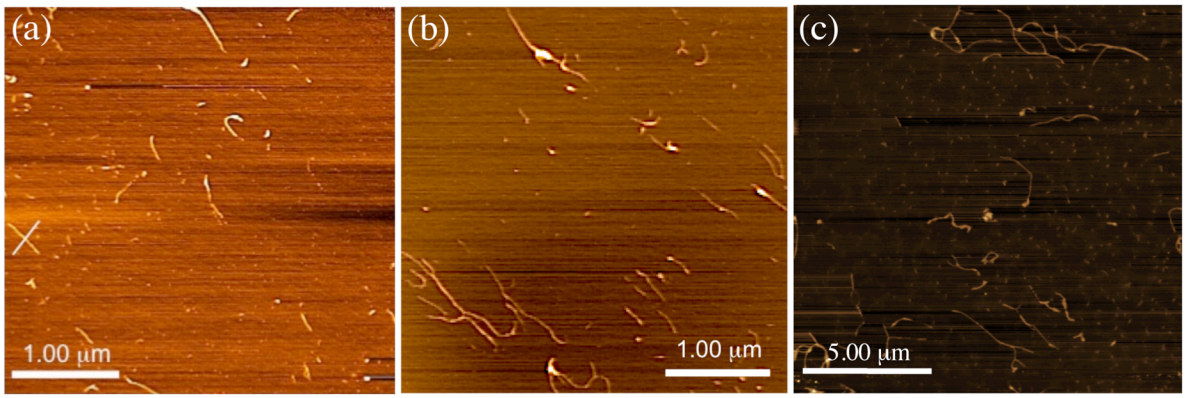

Figure S6. AFM images of (a) the Py-PBI/CUR-Chl complex formed at a flow rate of 40 µL/min and (b, c) the PyPhe-PBI/CUR-Chl complex formed at a flow rate of 80 µL/min. [Ligand]/[Chlorophyll units] ratio: 0.5; mica substrate.

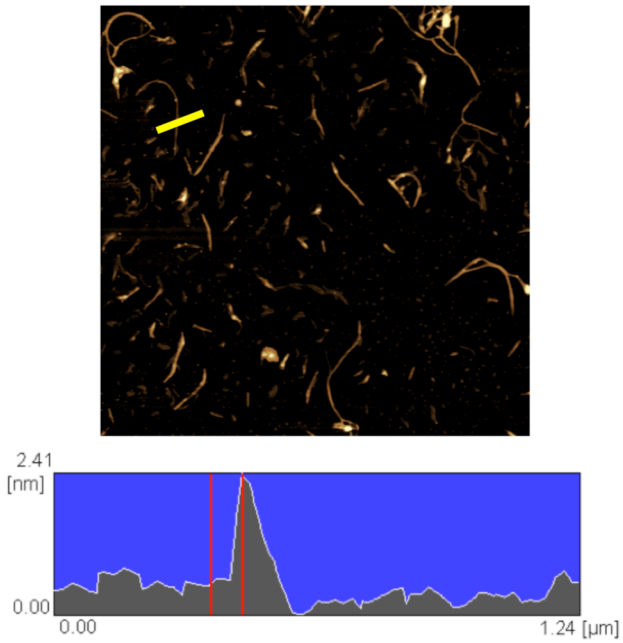

Figure S7. AFM height profile (along the yellow line) of the PyPhe-PBI/CUR-Chl complex formed at a flow rate of 80 µL/min.