

Supplementary Information for

Cross-Linked Conjugated Polymer Assemblies at Air-Water Interface through Supramolecular Bundling

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Experimental

Materials.

All starting materials and solvents were purchased from Tokyo Kasei Chemicals or Wako Chemicals and used as received. **CP** ($M_w = 48$ kDa, average number of repeating units $n = 73$) and compound **1** were synthesized with the reported procedure.¹ **CP-1** complex was formed by adding a chloroform solution of **1** ($7.3 \mu\text{M}$) to a chloroform solution of **CP** ($75.1 \mu\text{M}$ /repeating unit). Water used for the subphase was distilled and deionized using an ELGA PURELAB Life Science (resistivity $> 18.0 \text{ M}\Omega\cdot\text{cm}$). Spectroscopic grade chloroform was used as the spreading solvent.

Other measurements.

Pressure-area (π -A) isotherms were measured at $20.0 \text{ }^\circ\text{C}$ using an USI system FSD-300 Langmuir trough equipped with a Wilhelmy type surface pressure sensor. Compression was commenced at a rate of 0.2 mm/s 10 min after spreading chloroform solutions of samples. Temperature of the sub-phase was controlled within $20.0 \pm 0.2 \text{ }^\circ\text{C}$. *In situ* UV-Vis spectra were measured with an Otsuka intensified multichannel photodetector MCPD-7000 equipped with an optical fiber. LB films were prepared using a vertical dipping method with up-stroke and down-stroke motions of 10 mm/min on a quartz substrate or a silicon wafer. AFM measurements of transferred films on silicon wafers were conducted with SII SPA-400 (tapping mode) using SII SF-D20 (16 N/m , 137 kHz).

Molecular models of adjacent polymer packing of CPs.

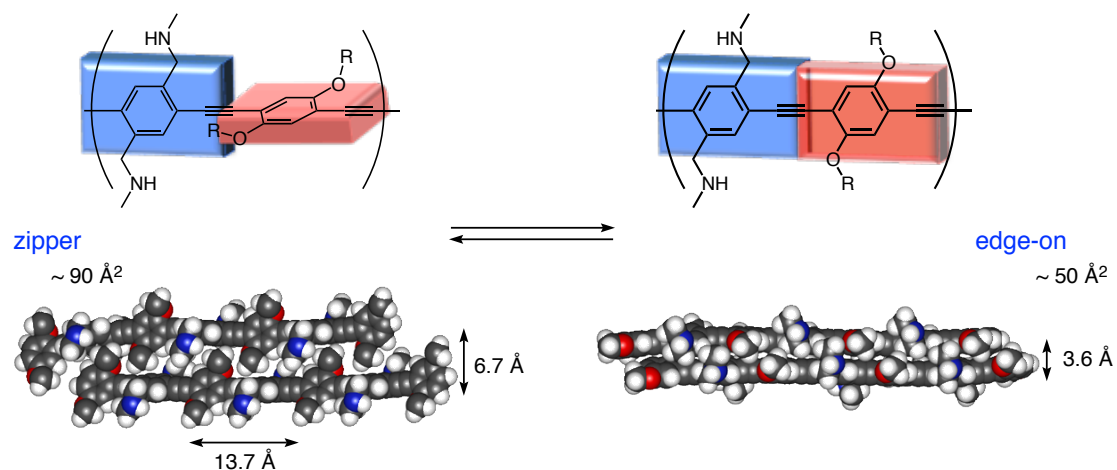


Fig. S1 Molecular models of adjacent polymer packing of CP.

In situ UV-Vis. spectra of CP and CP-1 under compression.

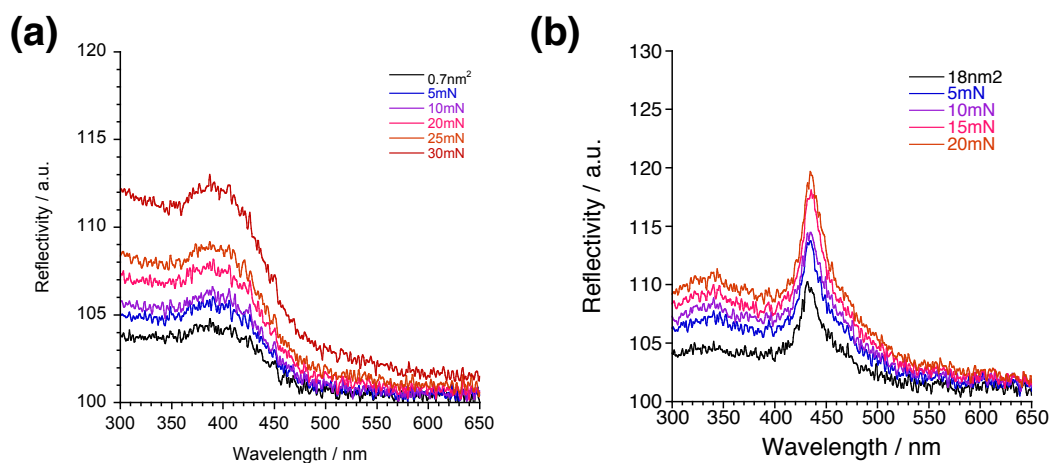


Fig. S2 In situ UV-Vis. spectra of (a) CP and (b) CP-1 under compression.

Pressure–area isotherms of **1**.

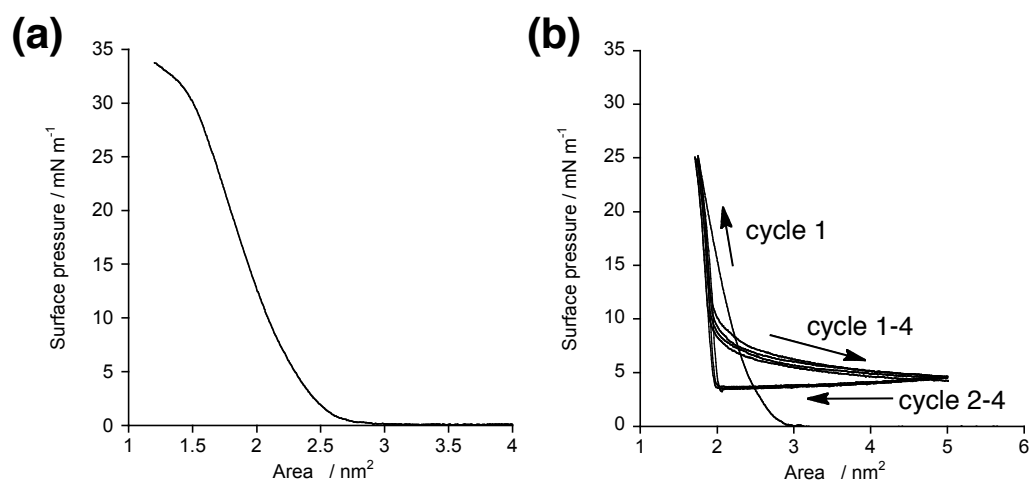


Fig. S3 Pressure–area isotherms of **1** (left: first compression, right: cyclic measurements).

Comparison of UV-Vis. spectra of CP-1 at air-water interface and in a chloroform solution.

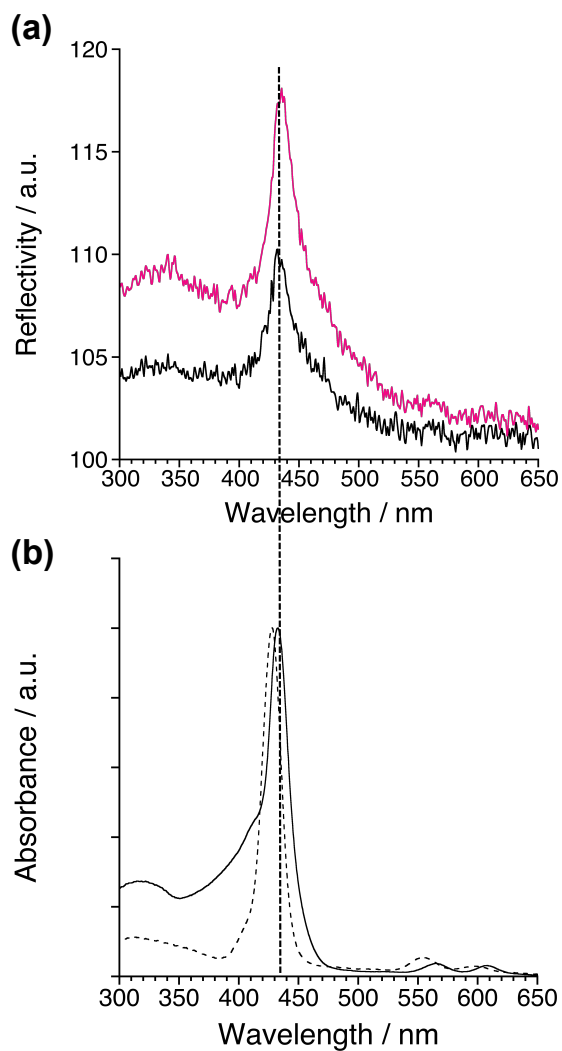


Fig. S4 (a) *in situ* UV-Vis. spectra of **CP-1** before (black) and after (pink) compression and (b) UV-Vis. spectra of **1** (dashed) and **CP-1** (solid) in chloroform. The absorption maximum wavelengths are 435 nm (a), 433 nm (b, solid) and 428 nm (b, dashed).

Polarized UV-Vis spectra of CP and CP-1.

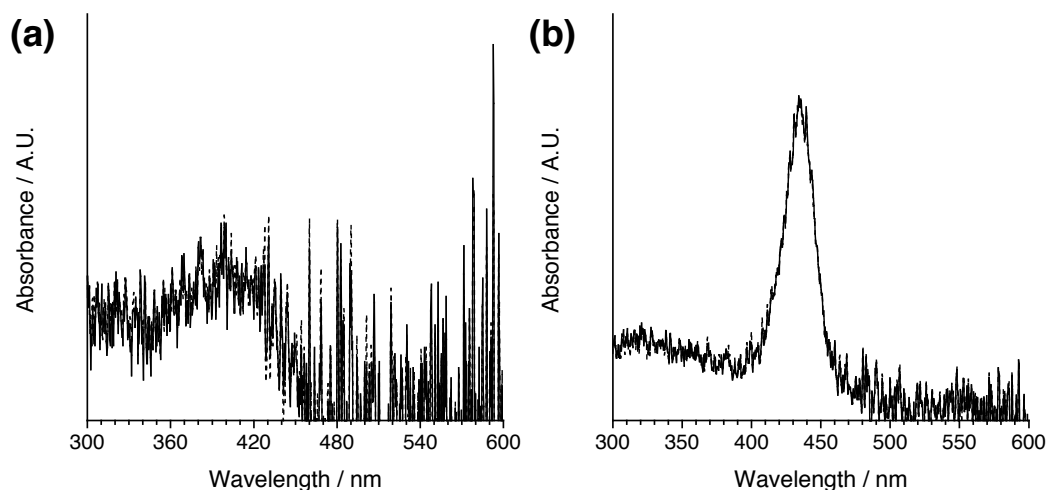


Fig. S5. Polarized UV-Vis spectra of (a) **CP** and (b) **CP-1** (dashed; perpendicular, solid; parallel to the dipped direction).

Fluorescence spectra of CP and CP-1.

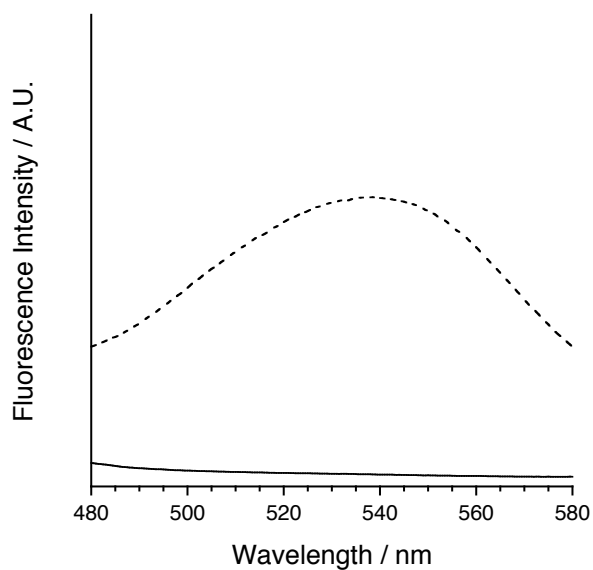


Figure S6. Fluorescent spectra on a quartz cell of **CP** (dashed) and **CP-1** (solid).

References.

- 1) Kubo, Y.; Kitada, Y.; Wakabayashi, R.; Kishida, T.; Ayabe, M.; Kenji, K.; Takeuchi, M.; Shinkai, S. *Angew. Chem. Int. Ed.* **2005**, *45*, 1548–1553.