ESI for

Pressure-dependent guest binding and release on a supramolecular polymer

1. General methods

Absorption spectra in solution were studied with a JASCO V-670 spectrophotometer. Fluorescence spectra were measured with a spectrofluorometer (JASCO FP-8500). TEM measurements were performed by JEOL JEM-2200. Unstained specimens were prepared by dropping the sample solutions onto carbon-coated copper grids. All spectroscopic measurements under high pressure were performed using a custom-built high-pressure vessel.[S1] The apparatus was designed and manufactured by Syn-Corporation (Kyoto, Japan). A quartz inner cell (4 mm × 4 mm) is connected to a Kalrez® tube, which is filled with a sample solution. The compression of this tube part adjusts the volume change of sample solution under pressurization. The inner cell with the Kalrez® tube was put inside the high pressure cell, in which water was filled to apply the hydrostatic pressure. The pressure inside the high pressure cell was adjusted by a hand pump unit. Measurement and excitation were conducted through Sapphire windows.

2. Supplemental spectra

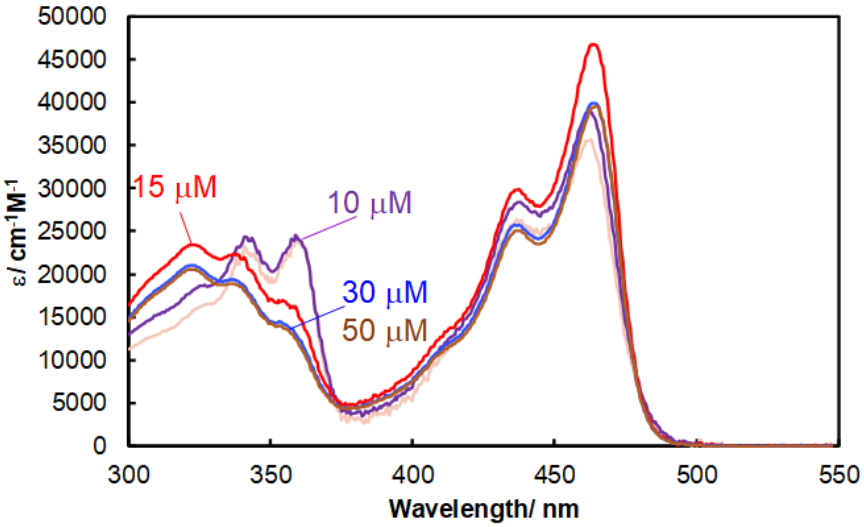

Fig. S1 Absorption spectra of (*R*)-**1** in an MCH/chloroform (9:1) mixture at various concentrations.

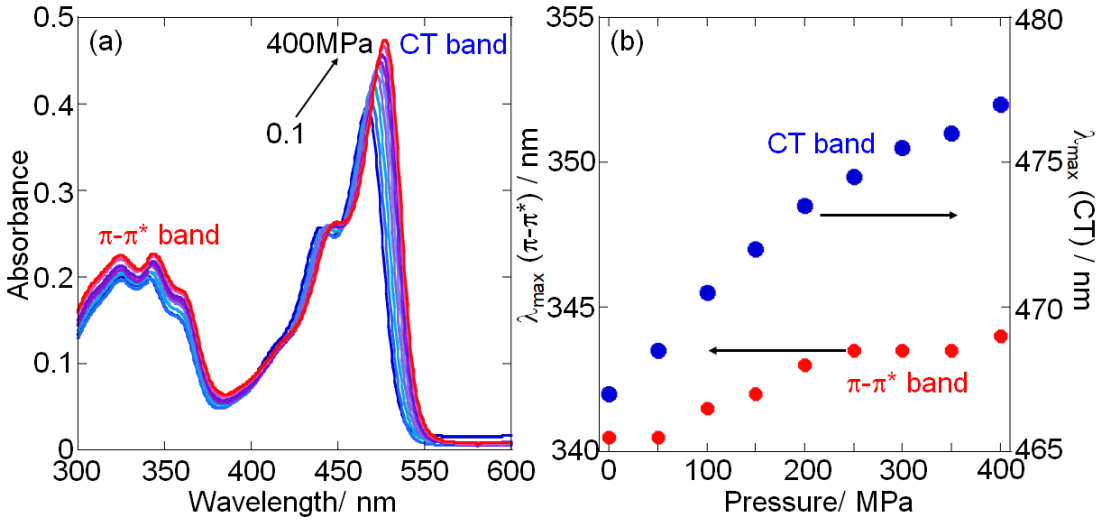

Fig. S2 (a) Absorption spectral change of (*R*)-**1** in an MCH/chloroform (9:1) mixture upon pressurization ([**1**] = 3.0×10^{-5} M). (b) Plots of absorbance maxima of π-π* and charge transfer bands.

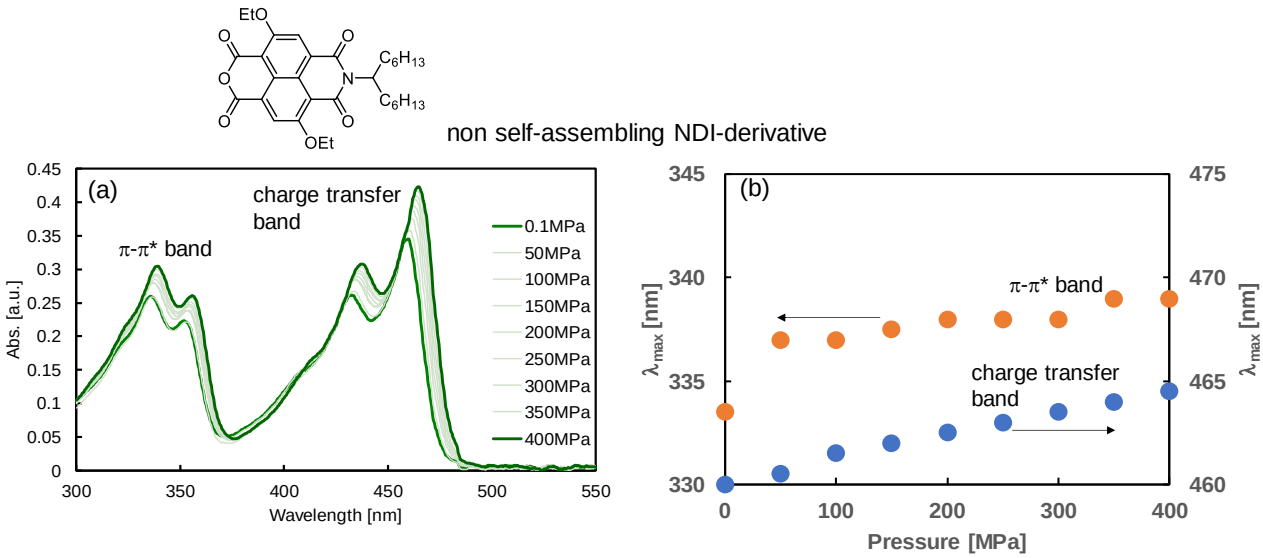

Fig. S3 (a) Absorption spectral change of an NDI-derivative in a MCH/chloroform (9:1) mixture upon pressurization. Concentration: 6.0×10^{-5} M. (b) Plots of absorbance maxima of π-π* and charge transfer bands.

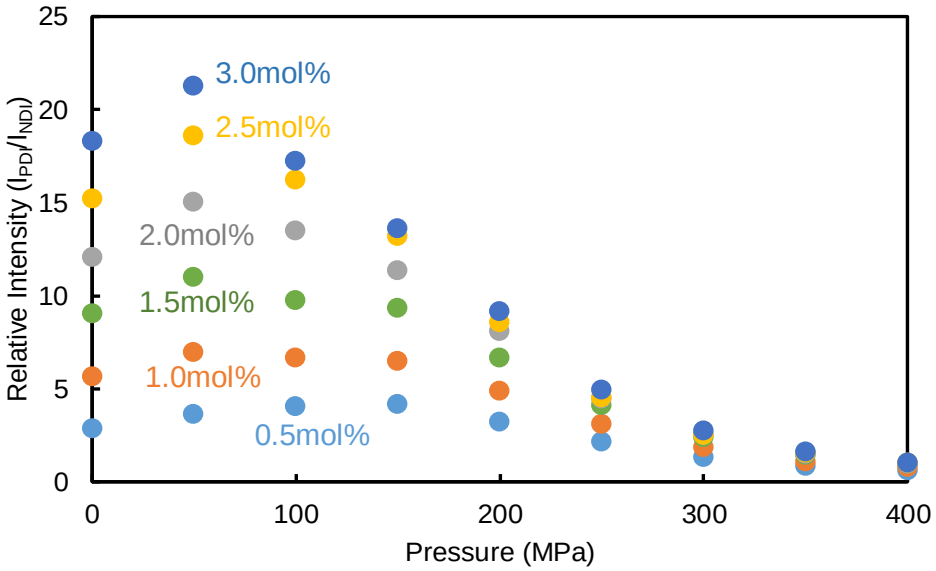

Fig. S4 Plots of the relative emission intensity (I_{PDI}/I_{NDI}) as a function of pressure at various contents of guest (*S*)-**3**. [**1**] = 3.0×10^{-5} M.

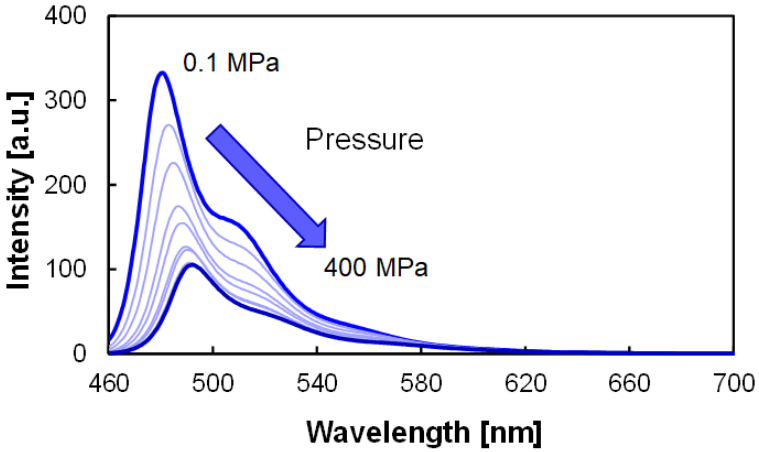

Fig. S5 Fluorescence spectral change of (*R*)-**1** in an MCH/chloroform (9:1) mixture upon pressurization. [**1**] = 3.0×10^{-5} M.

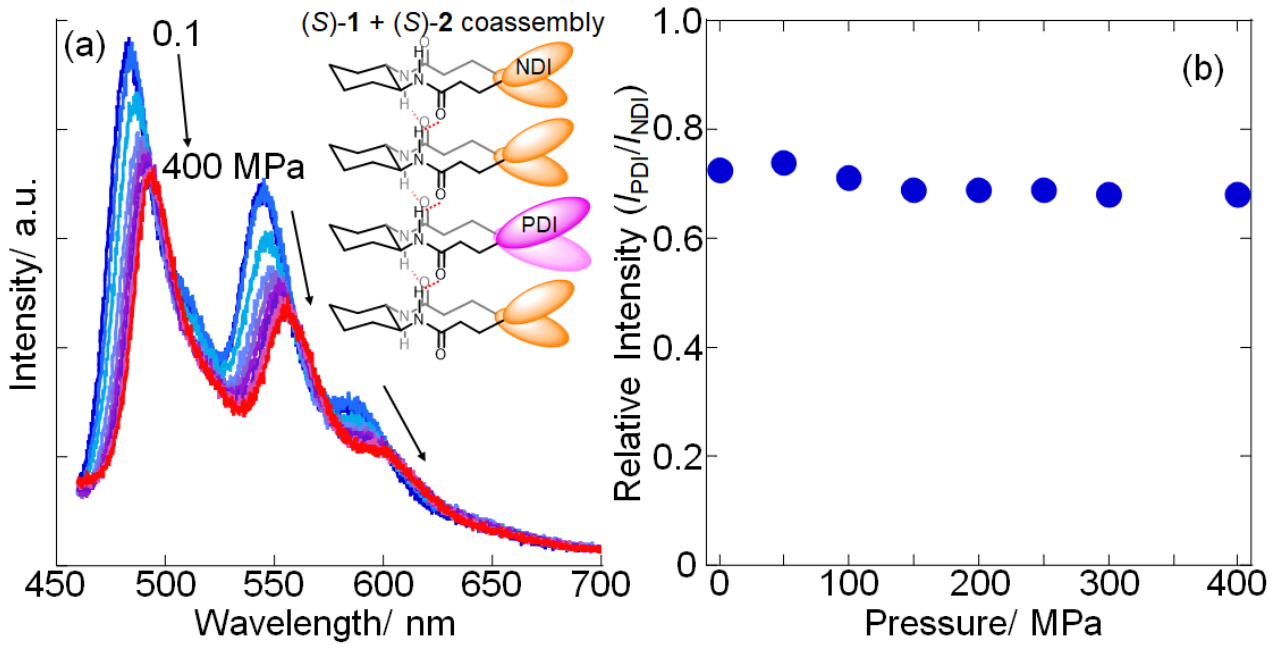

Fig. S6 (a) Fluorescence spectral change of (*S*)-**1** in an MCH/chloroform (14:1) mixture in the presence of 2.5 mol% of (*S*)-**2** upon pressurization. [**1**] = 3.0×10^{-5}, [**2**] = 7.5×10^{-7} M, λ_{ex} = 410 nm. Inset: schematic illustration of (*S*)-**1**–(*S*)-**2** coassembly. b) The relative emission intensity (I_{PDI}/I_{NDI}) as a function of pressure.

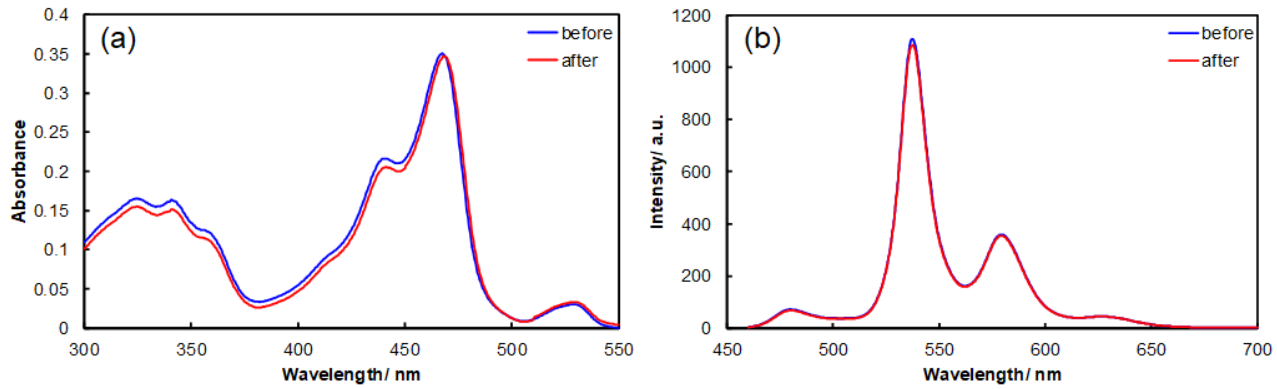

Fig. S7 (a) Absorption and (b) fluorescence spectral changes of (*R*)-**1**/(*S*)-**3** (100:2.5) an MCH/chloroform (9:1) mixture at ambient pressure before and after the pressurization (400 MPa). [**1**] = 3.0×10^{-5} M, [**3**] = 7.5×10^{-7} M.

3. TEM measurement

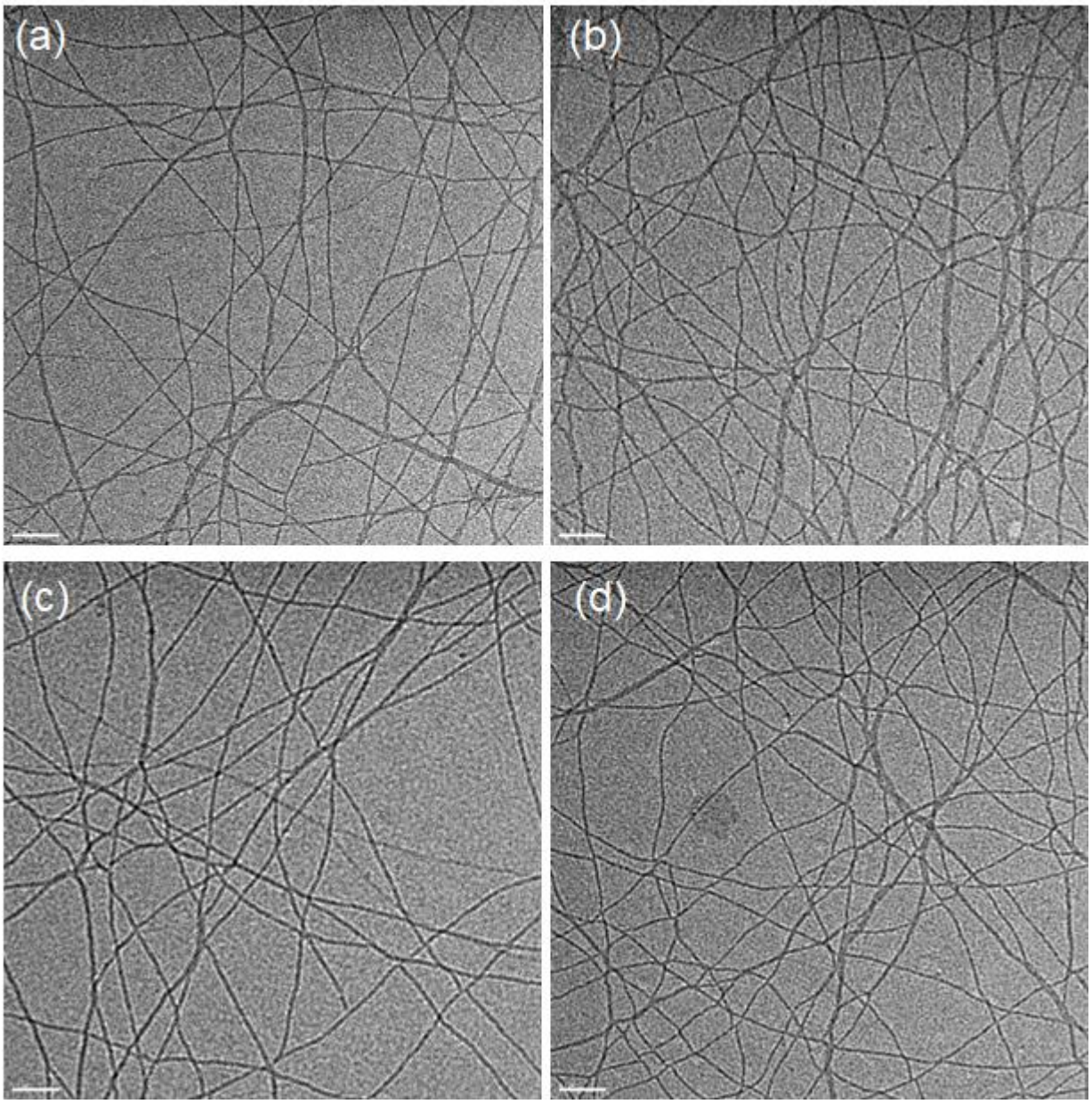

Fig. S8 TEM images of (a,b) (*R*)-**1** and (c,d) (*R*)-**1**/(*S*)-**3** (100:2.5) assembly (a,c) before pressurization and (b,d) after pressurization-depressurization procedure (Scale bar: 100 nm).

4. Fluorescence anisotropy[S2]

For the evaluation of biding affinity of guest molecules towards the host-nanofibers **1**, polarized fluorescence emissions at the peak positions with polarized excitations at 530 nm were analyzed for anisotropy. Four parameters based on the emission intensity (I_{VV}, I_{VH}, I_{HV}, and I_{HH}) were measured, where $I_{N,M}$ corresponds to fluorescence intensity and N and M correspond to the angle (*V*: vertical, *H*: horizontal) of polarization for excitation and emission, respectively, and anisotropy (g) was obtained by the following equations.

$$G = \frac{I_{HV}}{I_{HH}} \quad (1)$$

$$\gamma = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad (2)$$

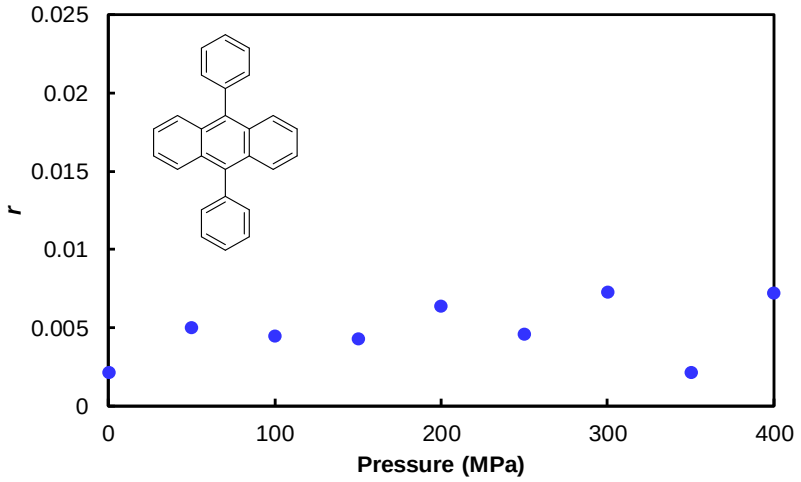

Fig. S9 Fluorescence anisotropy (*r*) change of a standard dye (9,10-diphenylanthracene) in an MCH/chloroform (9:1) mixture upon pressurization. Concentration: 7.5×10^{-5} M

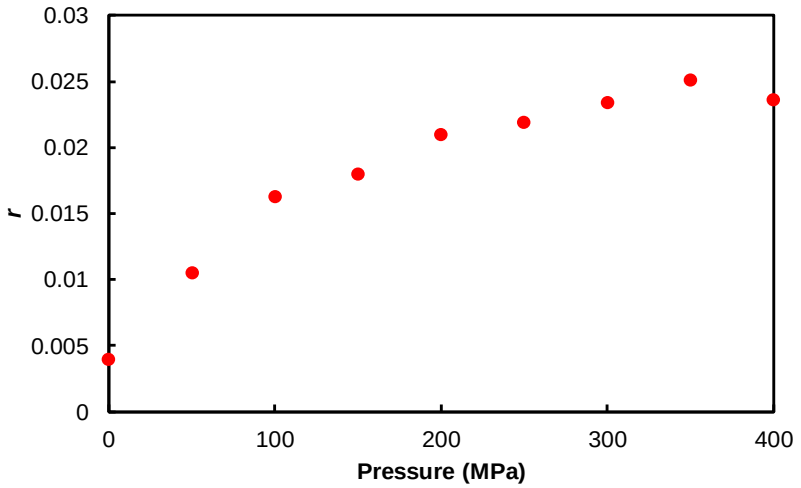

Fig. S10 Fluorescence anisotropy (*r*) change of (*R*)-**3** in an MCH/chloroform (9:1) mixture upon pressurization. Concentration: 7.5×10^{-7} M

5. Temperature dependent behavior

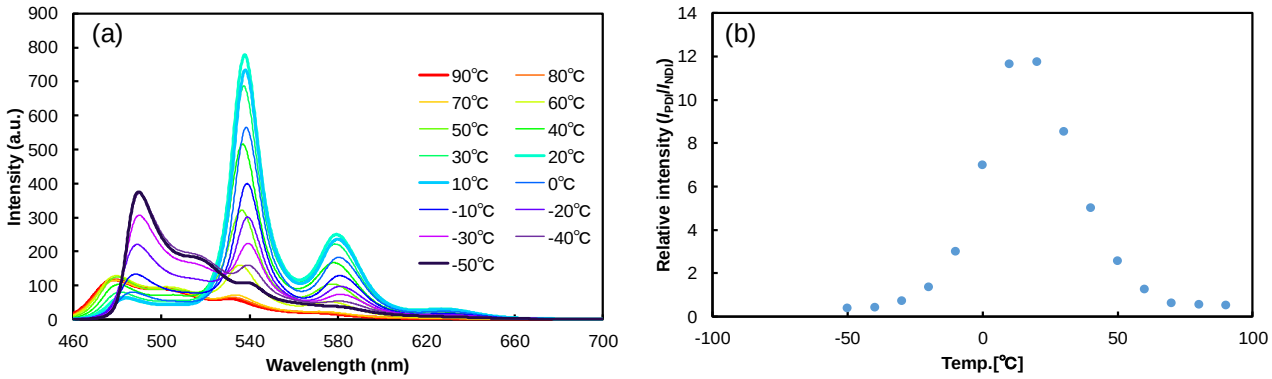

Fig. S11 (a) Fluorescence spectral change of (*R*)-**1** in an MCH/chloroform (9:1) mixture in the presence of 2.5 mol% of (*S*)-**3** with changing temperature. [**1**] = 3.0×10^{-5}, [**3**] = 7.5×10^{-7} M. (b) The relative emission intensity (I_{PDI}/I_{NDI}) as a function of temperature.

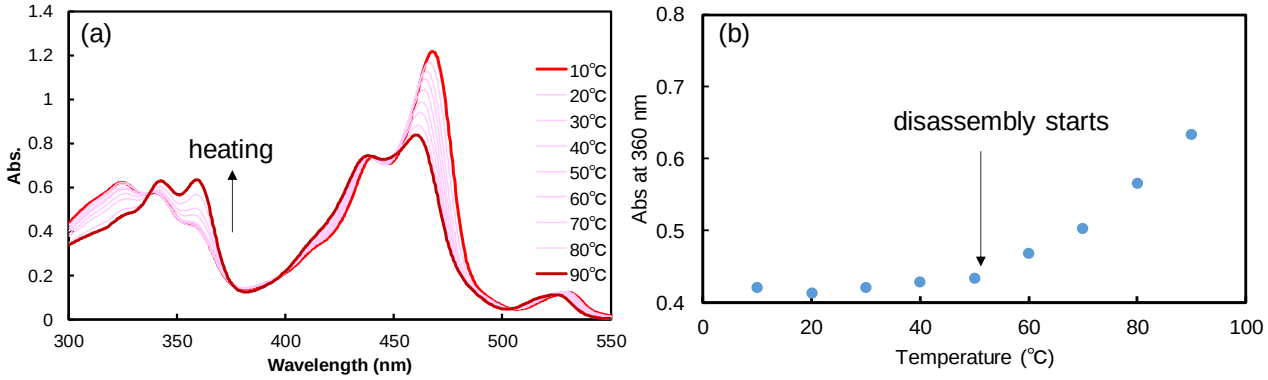

Fig. S12 (a) Absorption spectral change of (*R*)-**1** in an MCH/chloroform (9:1) mixture in the presence of 2.5 mol% of (*S*)-**3** with changing temperature. [**1**] = 3.0×10^{-5}, [**3**] = 7.5×10^{-7} M. (b) Plot of absorbance at 360 nm as a function of temperature.

The temperature decrease from 20 °C led to the decrease of sensitized emission of (*S*)-**3** along with the recovery of fluorescence in (*R*)-**1** (Fig. S11). The cooling of solution should result in the reinforcement of self-association of **1**, releasing the guest **3**. Meanwhile, the decrease of sensitized emission of (*S*)-**3** was also observed upon heating above 30 °C, at which self-assembling structure of (*R*)-**1** is maintained (Fig. S12). This result suggests that the host-guest cross-species association interactions are weaker than the same-species homo self-association assembly of (*R*)-**1** as suggested by the pressure-dependent study.

References

S1. A. J.-L. Ayitou, G. Fukuhara, E. Kumarasamy, Y. Inoue and J. Sivaguru, *Chem. Eur. J.*, 2013, **19**, 4327-4334.

S2. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy, 2nd ed.*, Kluwer Academic, New York, 1999.