Electronic Supplementary Information

Experimental Procedures

Synthesis of PT-1 and preparation of its aggregates

PT-1 with a number-averaged molar mass of 12.7 kg/mol was synthesized using previously described methods.[12] **Aggregate A** of PT-1 was formed without evaporation, by adding methanol (MeOH, a poor solvent) to a solution of PT-1 in chloroform ($CHCl_3$, a good solvent) , where the mixture ratio of MeOH to $CHCl_3$ was 7 to 3. **Aggregate B** of PT-1 was prepared as follows. At first, 3 mL of MeOH were added to 7 mL of $CHCl_3$ solution of PT-1. This solution containing non-aggregated PT-1 (4×10^{-5} M) was evaporated by a rotary evaporator, and then **aggregate B** of PT-1 was formed. The evaporation was carried out in a rotary evaporator at 180 rpm with a water bath at 40 °C, and stopped when the color of the solution changed from yellow to dark purple. The final concentration of PT-1 was 2×10^{-4} M for both *P*-type **aggregate B** and *M*-type **aggregate B**.

Instrumental Techniques

Electronic absorption and ECD spectra were measured using a JASCO V-570 spectrometer and a JASCO J-725 spectrodichrometer, respectively, using an optical quartz cuvette with 1 cm path length. The diffuse transmittance spectra were measured in the absorbance mode, with regular reflection using JASCO V-570 by employing an integral sphere accessory. Fluorescence spectra were measured using a monochromator (JASCO CT-25CP) equipped with a photomultiplier (Hamamatsu Photonics R5509-42) cooled at 193 K. For fluorescence measurements, a continuous wave Xe lamp

(Hamamatsu Photonics C2577) equipped with a monochromator (JASCO CT-10) was employed as the excitation light source.

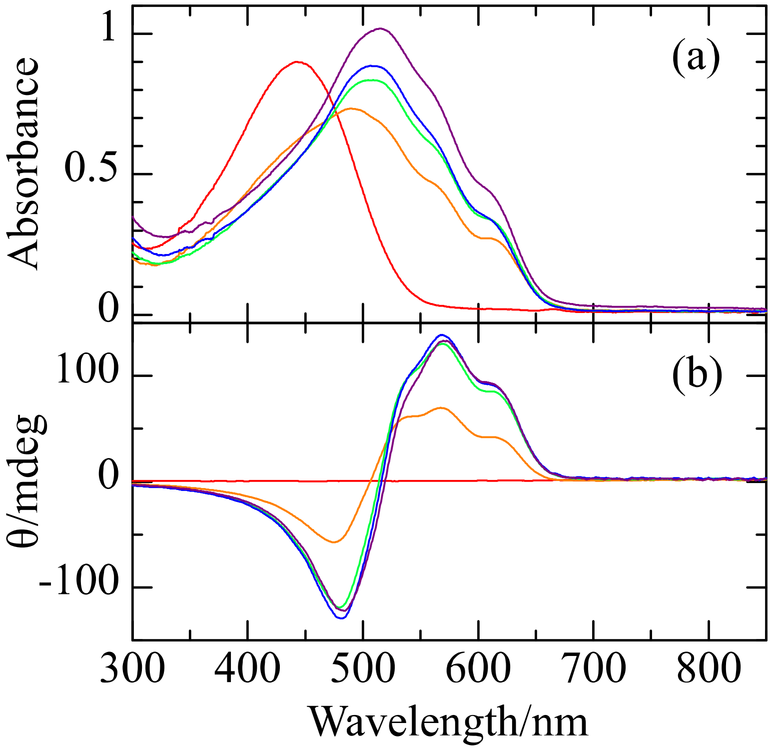

Fig. S1 Electronic absorption and ECD spectra of **aggregate A** at different ratios of MeOH and $CHCl_3$ (red: MeOH/$CHCl_3$ = 3/7, orange: MeOH/$CHCl_3$ = 4/6, green: MeOH/$CHCl_3$ = 5/5, blue: MeOH/$CHCl_3$ = 6/4, purple: MeOH/$CHCl_3$ = 7/3). When the percentage of $CHCl_3$ was more than 80 %, **aggregate B** was not formed under the fast or slow evaporation condition. On the other hand, the percentage of $CHCl_3$ was less than 60 %, **aggregate A** was formed before the evaporation. Thus, a 7:3 mixture of $CHCl_3$ and MeOH was appropriate for preparation of **aggregate B** by the evaporation.

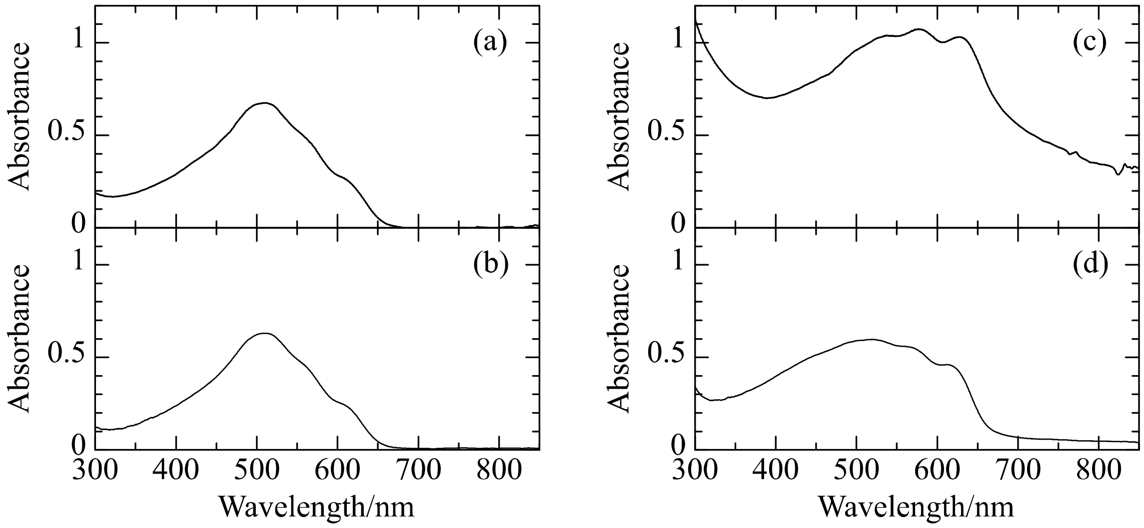

Fig. S2 Simple transmission (a, c) and diffuse transmission spectra (b, d) of **aggregate A** (a, b) and **aggregate B** (c, d). Here, in diffuse transmission spectra, the scattered light could be detected by an integral sphere accessory, while the scattered light could not be detected in simple transmission spectra. In the case of **aggregate A**, the optical density at 850 nm was negligible, which indicates that **aggregate A** is the solution state. On the other hand, in the case of **aggregate B**, the optical density at 850 nm was significant in its simple transmission spectrum, while it was negligibly small in its diffuse transmission spectrum. Thus, although the solutions of both **aggregates A** and **B** seem transparent, the existence of the scattered light indicates that the solution of **aggregate B** suspended to some extent.

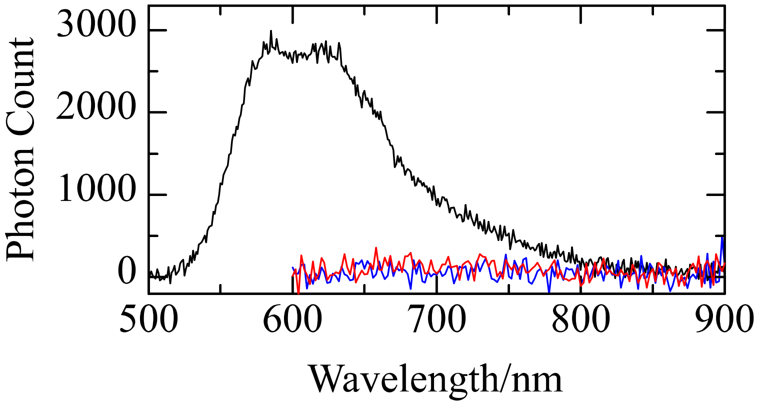

Fig. S3 Fluorescence spectra of non-aggregated PT-1 (black, Ex. 445 nm), **aggregate A** (blue, Ex. 510 nm) and **aggregate B** (red, Ex. 520 nm). While non-aggregated PT-1 showed relatively intense fluorescence, fluorescence attributable to **aggregate A** or **aggregate B** could not be observed even by increasing accumulation times. This suggests that both **aggregates A** and **B** are H-aggregates.

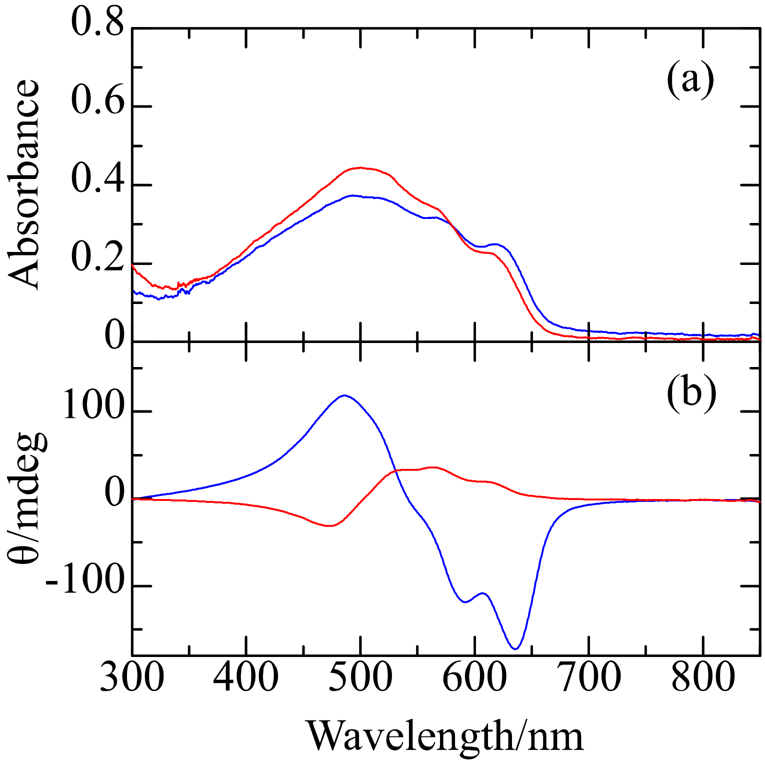

Fig. S4 Electronic absorption (a) and ECD spectra (b) of aggregates prepared by the evaporation at 30 °C (red solid lines: prepared by fast evaporation, blue solid lines: prepared by slow evaporation). Even at 30 °C, the fast evaporation (150 hPa, 3.5 min) affords negative/positive spectral pattern due to *P*-type aggregates, while the slow evaporation (350 hPa, 21 min) provides the opposite positive/negative spectral pattern owing to *M*-type aggregates.

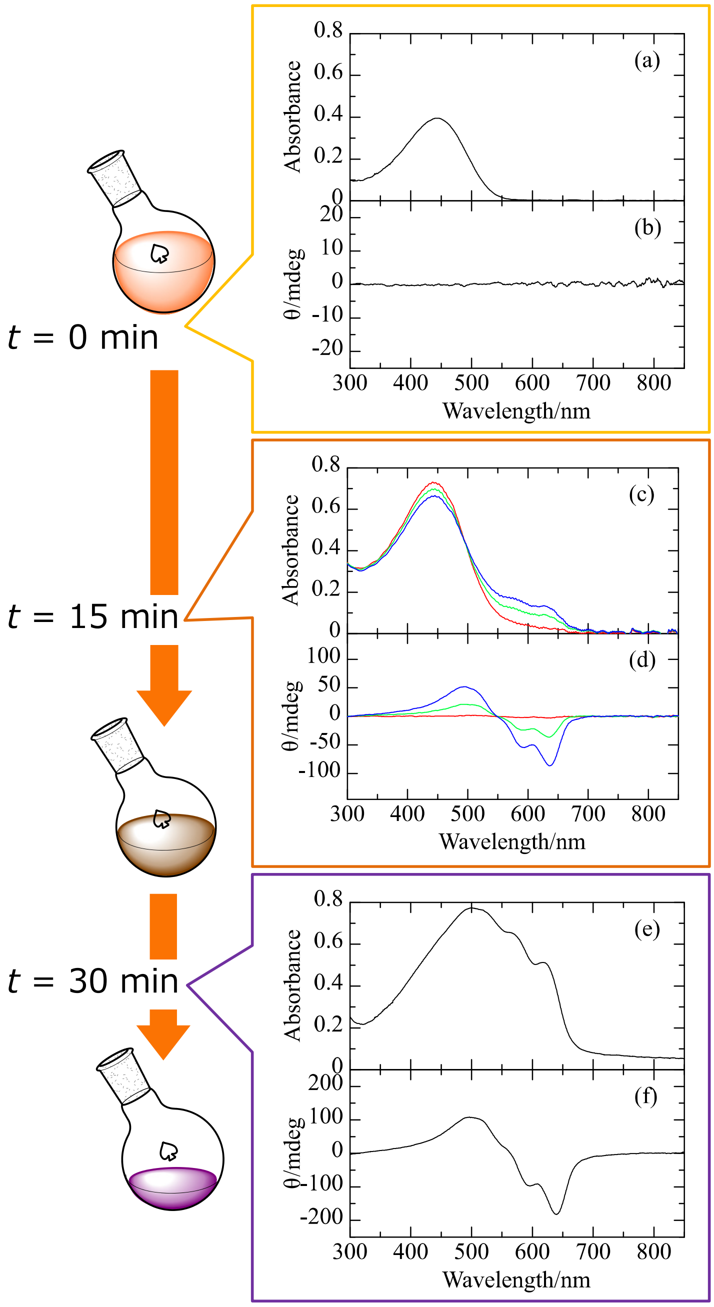

Fig. S5 Electronic absorption (a, c, e) and ECD (b, d, f) spectra before the evaporation (a, b: *t* = 0 min), after the evaporation for 15 min (c, d: *t* = 15 min), and after completing the evaporation (e, f: *t* = 30 min) under the slow evaporation condition (520 hPa, 40 °C). Since 15 min correspond to the time just before the initial state of aggregation, the absorption band and the positive/negative ECD spectral pattern due to the aggregates grew even after stopping the evaporation (c, d).

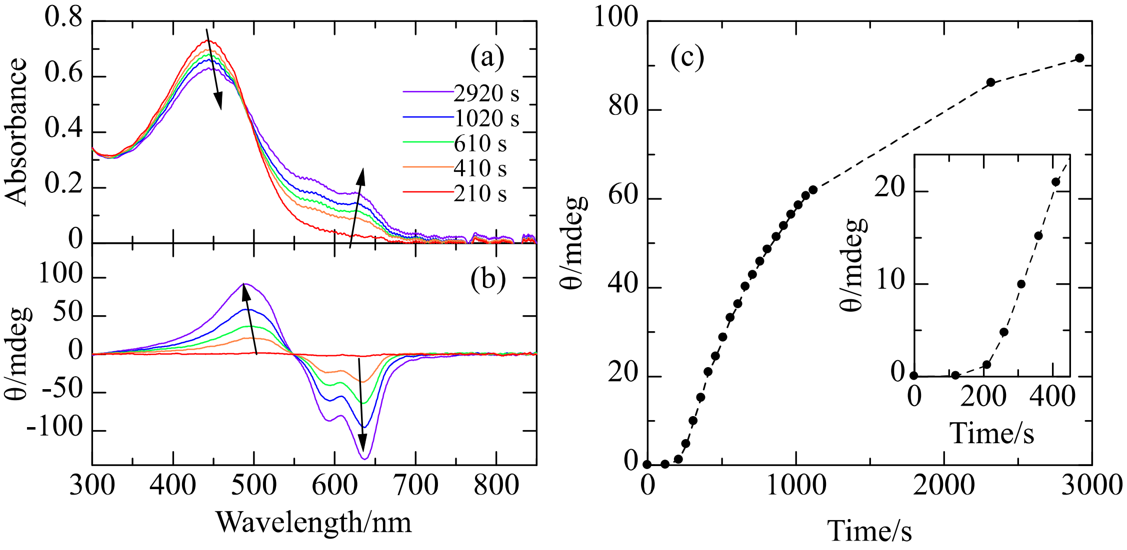

Fig. S6 Time-dependences of electronic absorption (a) and ECD spectra (b) after stopping evaporation of the solution containing non-aggregated PT-1, as well as a time profile of the positive ECD signal at 490 nm (c). The solution of non-aggregated PT-1 was evaporated for 15 min under the slow evaporation condition (520 hPa, 40 °C). Since 15 min correspond to the time just before the initial state of aggregation, a positive/negative ECD spectral pattern grew with increasing the absorbance due to aggregates. The time-profile shows an induction time without ECD signals followed by a sudden increase in the ECD signal, which suggested that the ECD signal increased in the elongation process after nucleation. Thus, the present aggregation process is attributed to cooperative.