Supplementary Material (ESI) for Chemical Science

Memory of Chirality in J-Type Aggregates of Achiral Perylene Dianhydride Dye Created in a Chiral Asymmetric Catalytic Synthesis

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Electronic Supporting Information

Table of contents

1. Materials, Measurements and Experimental Procedures

Materials Reagents and solvents were used as received from commercial sources without further purification. L-(+)-tartaric acid (>99%), D-(-)-tartaric acid (>99%), and perylene-3,4,9,10-tetracarboxylic dianhydride (PDA, > 98%) were purchased from Acros Oganics. Other chemicals (AR) including octadecyltrimthylammonium bromide (OcTAB), cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), decyltrimethylammonium bromide (DTAB), and HCl and KOH were purchased from Guoyao (Shanghai, China).

Potassium perylene tetracarboxylate (PTK) was obtained from hydrolysis of PDA.[1] Solution of 1.96 g (5 mmol) PDA and 1.12 g (20 mmol) KOH in 20 mL water was heated at 50 °C for 5 hours, during which the dark red PDA powder gradually dissolved to lead to a dark red solution. After filtration, ethanol was added to the filtrate to precipitate PTK that was then collected through filtration and dried under vacuum, affording 2.73 g yellow PTK powder with a yield of 93%.

Measurements Absorption and CD spectra were recorded on Varian Cary-300 UV/Vis spectrophotometer and JASCO J-810 spectropolarimeter, respectively. Fluorescence spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) was performed on Bruker ESQUIRE-3000 plus mass spectrometer by injection of DMF solution of the sample. ^{1}H NMR and ^{13}C NMR spectra in D_2O were recorded on Bruker AV400 spectrometer. X-ray diffraction (XRD) was performed on Panalytical X'pert PRO diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). Zeta potential data were obtained on ZetaPALS Zeta potential analyzer. These measurements were carried out at 25 °C.

For CD spectral measurements, the sample solution in a cell was stirred before the measurement. Then the sample was azimuthally rotated 90^{o} around the light axis for consecutive measurements and thus obtained CD spectra were found to be the same. Therefore the CD signals originated exclusively from the molecular phenomena but not from optical artifacts such as the interference of linear dichroism.[2]

Experimental Procedures 8 mL PTK (62.5 μM) in CTAB (5 mM) solution and 2 mL L- or D-tartaric acid (2.5 mM, 10 equiv) in CTAB (5 mM) solution were mixed in 10 mL flask at 17 °C. The flask was sealed and held at 17 °C for 36 hours. The final transparent solution was in magenta

color and was hardly luminescent. The final concentration of PDA in CTAB solution was 50 μM. Formation of PDA was confirmed by ESI-MS (Figure S1).

Purification of the synthesized chiral PDA J-aggregates was performed using precipitation method. Increasing ionic strength, *e.g.* by addition of saturated KBr solution, resulted in brown precipitate. After filtration and washing with cold saturated KBr solution for 3 times, the precipitate was carefully washed with cold water by avoiding heavy stirring and dried under vacuum below 15 °C. The obtained dark red precipitate can be re-dissolved in pure water under stirring to form transparent magenta solution.

Concentration of the purified PDA J-aggregates re-dissolved in water was measured by absorption spectrophotometry.[3] 200 μL PDA J-aggregates solution was injected into 1.8 mL aqueous solution of KOH (1 mM) and CTAB (5 mM), hydrolysis of PDA to PTK occurred immediately and the solution color turned to bright green. The concentration of perylene derivatives was calculated by the absorbance at 472 nm in comparison with the standard working curve of the absorbance at 472 nm against PTK concentration, independently prepared from absorption spectral measurements on standard PTK solutions.

2. ESI-MS of PDA aggregates dissociated in DMF

ESI-MS characterization was performed in the negative ion mode. Sample solution was prepared by quick injection of 40 μL PDA (50 μM) CTAB solution into 2 mL DMF.

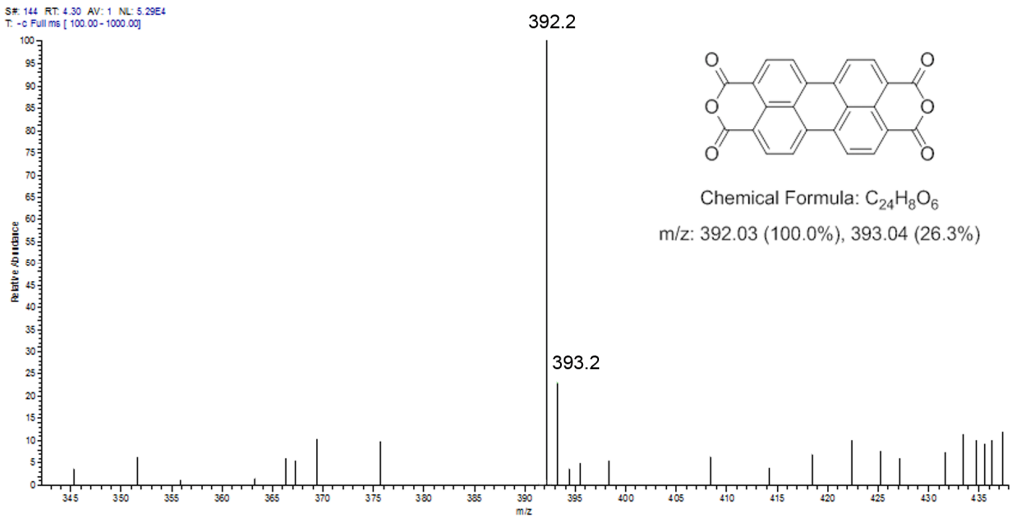

Fig. S1 ESI-MS of PDA monomer in DMF

3. Absorption and fluorescence spectra of PDA monomer in DMF

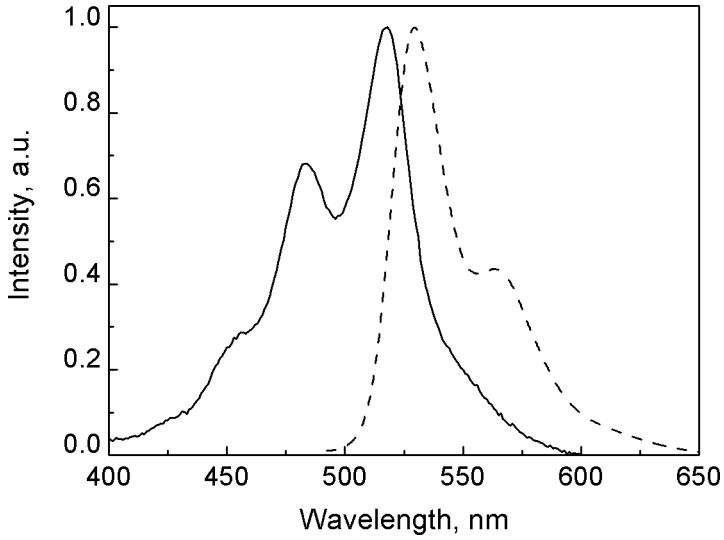

Fig. S2 Normalized absorption (solid trace) and fluorescence (dash trace, λ_{ex} = 480 nm) spectra of PDA (2.5 μM) in DMF.

4. Absorption and CD spectra of PDA J-aggregates mediated by L-lactic acid

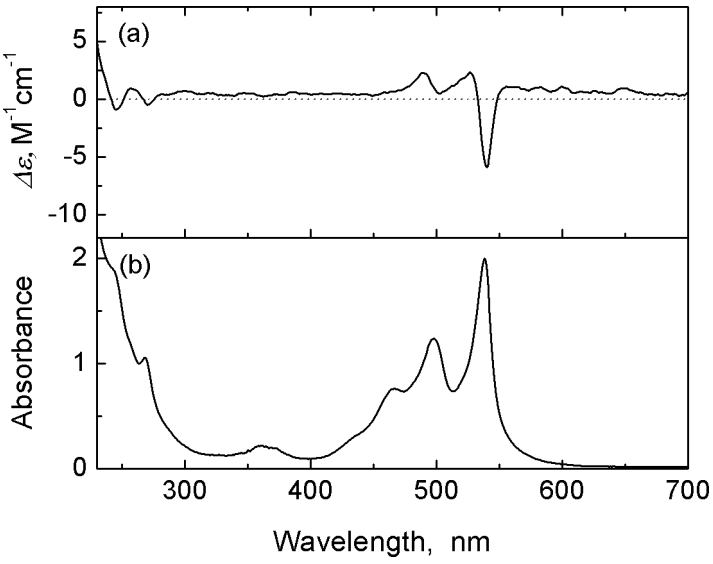

Fig. S3 (a) CD and (b) absorption spectra of PDA (50 μM) J-aggregates mediated by L-lactic acid in aqueous CTAB (5 mM) solution.

5. CD spectra of PDA J-aggregates mediated by L-tartaric acid without and with later addition of excess D-tartaric acid

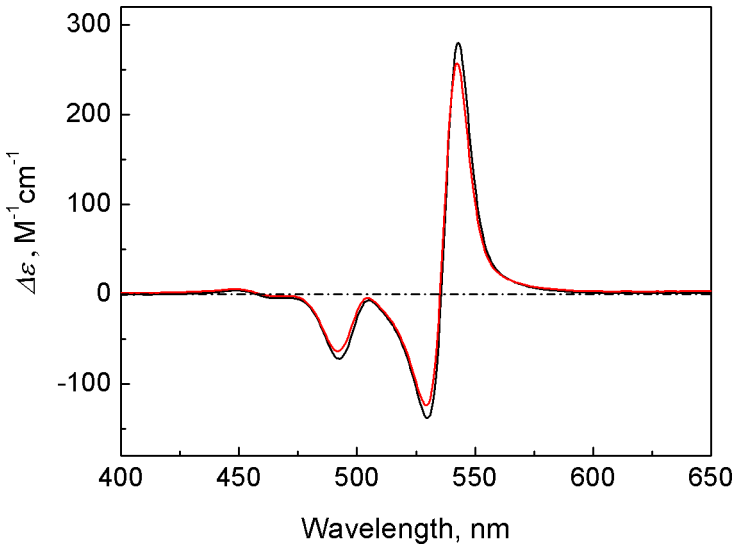

Fig. S4 CD spectrum of the PDA (10 μM) J-aggregates in the presence of L-tartaric acid (0.1 mM) (black) and that over one week after later addition of 10-fold excess of D-tartaric acid (1 mM) at 10-15 °C (red) in aqueous CTAB solutions.

6. ^{1}H NMR spectra of PDA J-aggregates and of PTK and CTAB

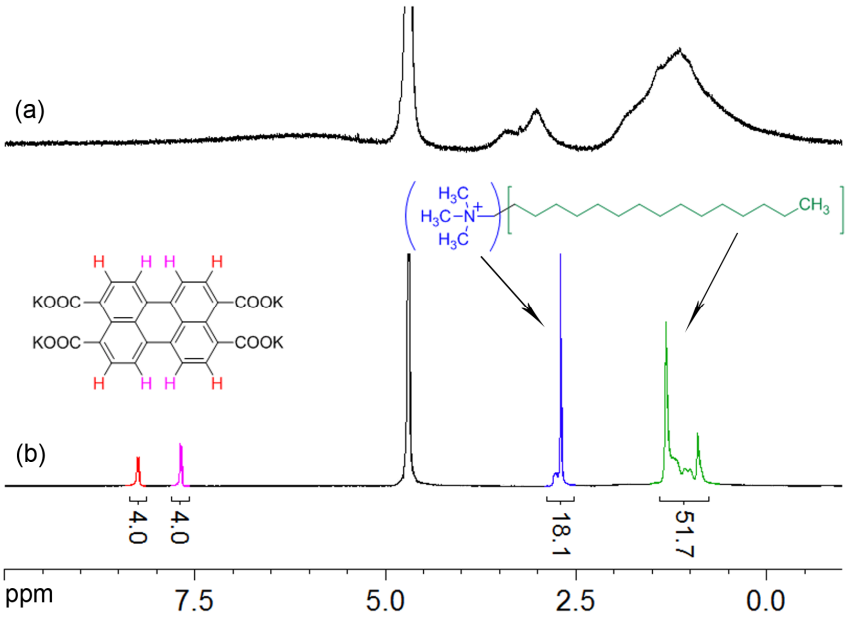

Fig. S5 ^{1}H NMR spectra of (a) purified PDA J-aggregates in D_2O and (b) after dissociation of the aggregates by adding excess solid KOH in the same D_2O solution. Signals of protons in both PTK and CTAB are distinct, whereas no C*–H signal of tartrate at 4.23 ppm (Fig. S6) was observed. The amount of possibly remaining tartaric acid in the purified PDA J-aggregates was therefore estimated to be much less than 0.5% of PDA (Fig. S7).

7. ^{1}H NMR spectrum of potassium L-tartrate in D_2O

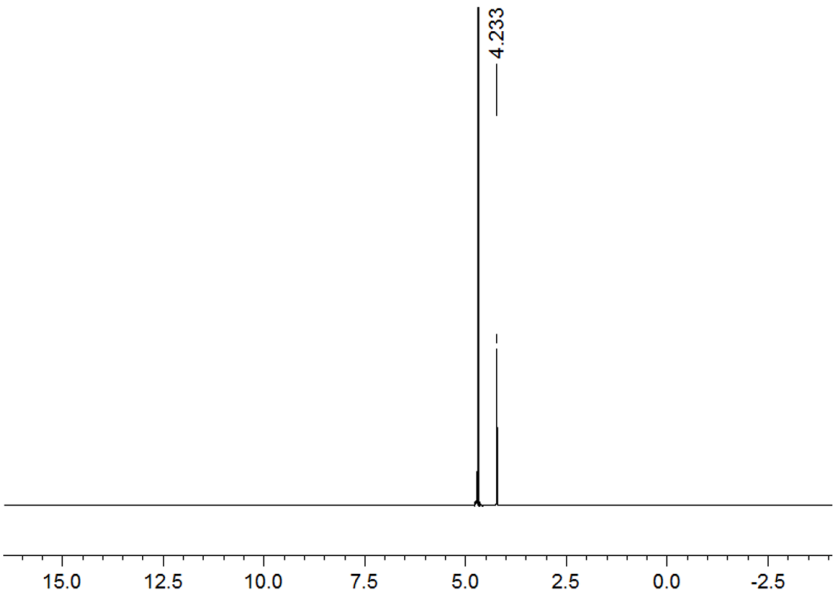

Fig S6 ^{1}H NMR spectrum of potassium tartrate (20 mM) in D_2O.

8. ^{1}H NMR spectra of potassium tartrate in D_2O

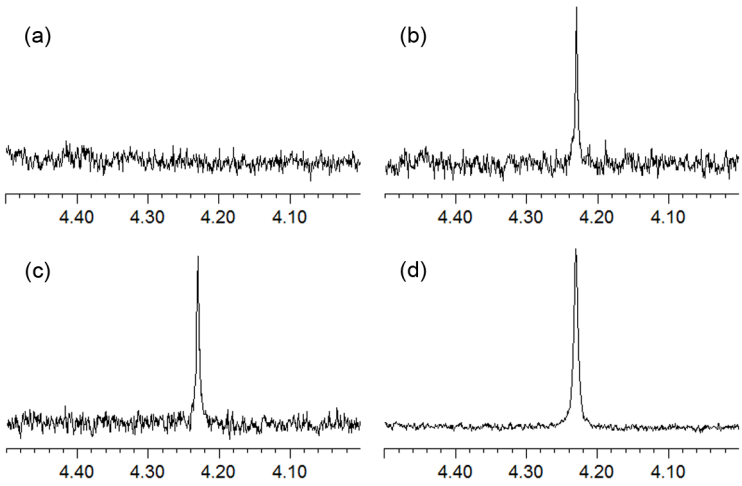

Fig. S7 ^{1}H NMR spectra of (a) purified PDA aggregates dissociated by KOH (portion of Fig. S5b, concentration of the formed PTK was *ca.* 20 mM) and potassium tartarate at concentration of (b) 0.1 mM (0.5% of PTK), (c) 0.2 mM (1% of PTK) and (d) 1 mM (5% of PTK) in the presence of PTK (20 mM) in D_2O.

9. CD and absorption spectra of PDA J-aggregates before and after purification

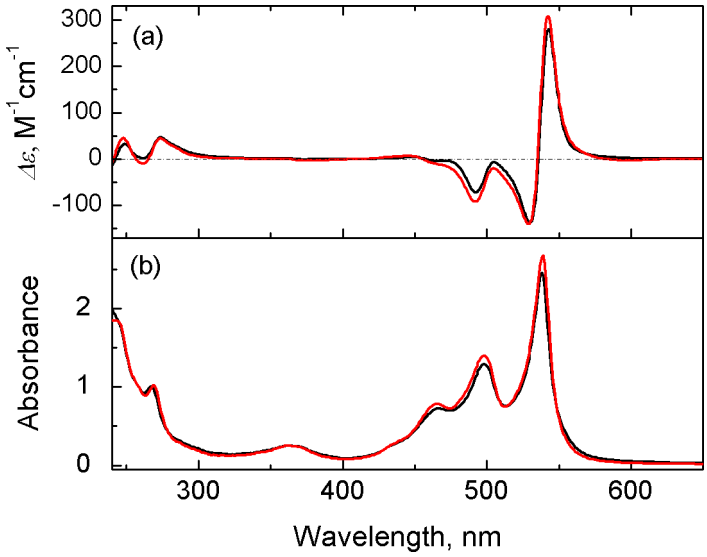

Fig. S8 (a) CD and (b) absorption spectra of the PDA (50 μM) J-aggregates mediated by L-tartaric acid before (black trace, in aqueous CTAB solution) and after (red trace, in water) purification.

10. CD spectra of purified PDA J-aggregates mediated by L-tartaric acid without and with later addition of D-tartaric acid

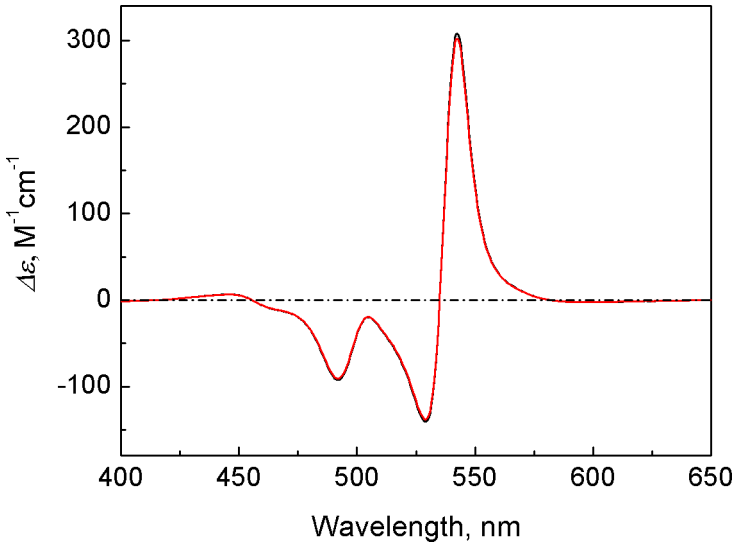

Fig. S9 CD spectra of purified PDA J-aggregates (10 μM, black trace, in water) mediated by L-tartaric acid and the PDA J-aggregates (10 μM) after later addition of D-tartaric acid (1 mM, red trace, in water). The two traces are almost the same.

11. XRD of purified PDA J- and H-aggregates

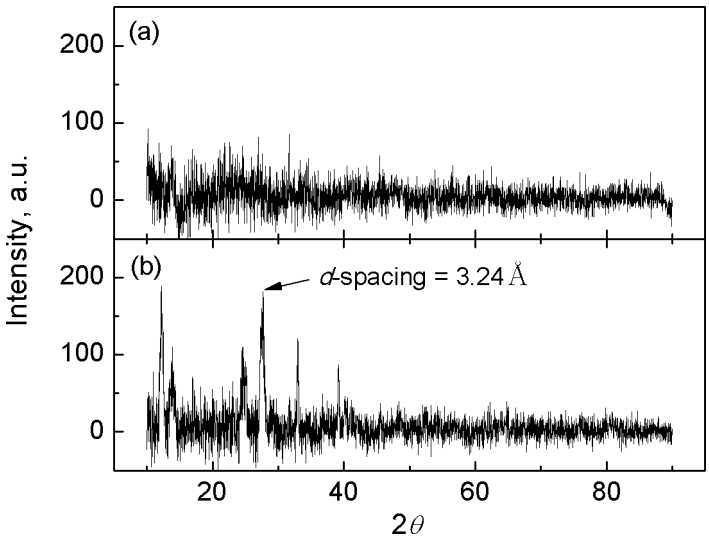

Fig. S10 Powder XRD patterns of the purified PDA (a) J- and (b) H-aggregates. The H-aggregates derived from J- to H-aggregates transition in water at 30 °C.

12. CD and absorption spectra of PDA in L-tartaric acid/TTAB solutions

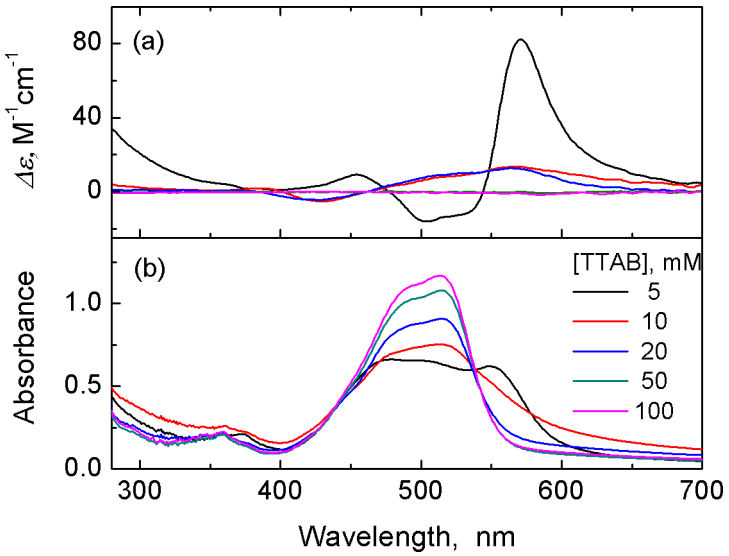

Fig. S11 (a) CD and (b) absorption spectra of PDA (50 μM) in TTAB solution of varying concentration in the presence of 0.5 mM *L*-tartaric acid.

13. References

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