Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information for

Excimer-origin CPL *vs* monomer-origin magnetic CPL in photoexcited chiral binaphthyl-ester-pyrenes: Critical role of ester direction

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1. Materials

(*R*)- and (*S*)-1,1′-dihydroxy-2,2′-binaphthyl and poly(methyl methacrylate) (PMMA) were purchased from Wako Pure Chemical Corp. 1-Pyrenecarboxylic acid and 1-pyrenol were purchased from Tokyo Chemical Industry (TCI). (*R*)- and (*S*)-1,1′-dicarboxy-2,2′-binaphthyl were provided by Mitsubishi Tanabe Pharma Co., Ltd. $CHCl_3$ for solution-state measurements was purchased from FUJIFILM Wako Pure Chemical Corp. (*R*)- and (*S*)-**1** and 4-(*N*,*N*-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) were prepared by previously reported methods.[S1]

2. Experimental

2.1. Absolute PL quantum yields

The absolute PL quantum yield in $CHCl_3$ solution and the PMMA film state were measured using an Absolute PL Quantum Yield Measurement System (C9920-02, Hamamatsu Photonics) in air at room temperature. The excitation wavelength for **1** and **2** was 330 nm in both $CHCl_3$ solution (path length = 10 mm) and the PMMA film state. The PMMA films were prepared using a Mikasa Opticoat MS-A100 spin coater (3000 rpm).

2.2. PL and CPL spectra

The PL and CPL spectra were recorded using a JASCO CPL-300 spectrofluoropolarimeter at room temperature. A scattering angle of 0° was used for the unpolarised monochromatic incident light with an excitation bandwidth of 10 nm and an emission bandwidth of 10 nm. The scanning speed was 50 nm min^{-1} and the PMT time constant was 8 s. The excitation wavelength for **1** and **2** was 330 nm in both $CHCl_3$ solution (path length = 1 or 10 mm) and the PMMA film state. The PMMA films were prepared using a Mikasa Opticoat MS-A100 spin coater (3000 rpm).

2.3. CD and UV-Vis absorption spectra

The CD and UV-Vis absorption spectra in $CHCl_3$ solution (path length = 1 mm) and in the PMMA film state were recorded using a JASCO J-820 spectropolarimeter at room temperature. The PMMA films were prepared using a Mikasa Opticoat MS-A100 spin coater (3000 rpm).

2.4. NMR spectra

^{1}H- and ^{13}C-NMR spectra were recorded using a JEOL ECA 600 spectrometer. Tetramethylsilane (Me_4Si) was used as an internal reference.

2.5. Mass spectra

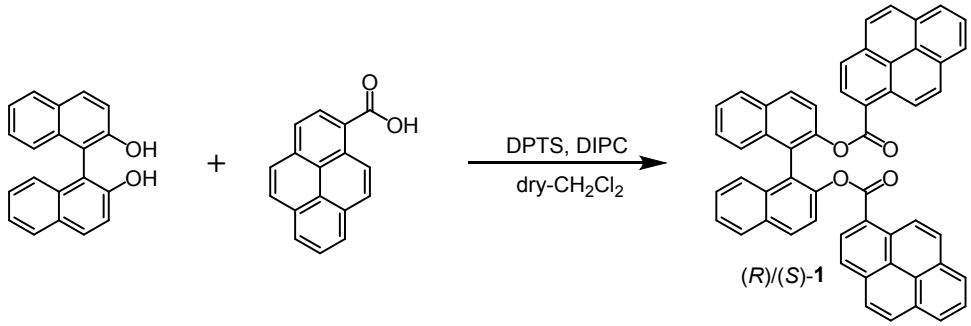
Mass spectra were recorded using an AXIMA Confidence mass spectrometer (Shimazdu Co.) under the following conditions: ionisation method, laser desorption ionisation method; matrix, none; mass range, *m/z* 1–3000; mode, reflection (negative); laser power, 65–95. Calibration was performed using C_{60} (*m/z* 720.0005 for $[M]^-$), angiotensin II (*m/z* 1044.5272 for $[M - H]^-$), and α-cyano-4-hydroxycinnamic acid (*m/z* 189.0431 for $[M - H]^-$) as external standards.

Reference

S1. P. Rajakumar and K. Visalakshi. *Synth. Commun.* 2013, **43**, 2226.

3. Synthesis of (*R*)/(*S*)-1 and (*R*)/(*S*)-2

3.1. Synthesis of (*R*)/(*S*)-1



(*R*)-1,1′-Dihydroxy-2,2′-binaphthyl (172 mg, 0.6 mmol) and 1-pyrenecarboxylic acid (300 mg, 1.3 mmol) were dissolved in dry CH_2Cl_2 under N_2. DPTS (383 mg, 1.3 mmol) was added to the solution mixture at room temperature. After 15 min, diisopropylcarbodiimide (DIPC) (0.3 mL, 1.8 mmol) was added dropwise, and the mixture was stirred for 21 h. The mixture was extracted with dichloromethane and washed with water. The combined organic layer was dried over $MgSO_4$, concentrated, and purified by silica gel column chromatography using chloroform/hexane (1:2, v/v) as the eluent to obtain (*R*)-**1** (172 mg, 38% yield) as a yellow solid. (*S*)-**1** was prepared in an identical manner from (*S*)-1,1′-dihydroxy-2,2′-binaphthyl to give the desired product in 32% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.86 (d, *J* = 9.0 Hz, 2H), 8.18 (dd, *J* = 6.0 Hz, 4H), 8.10 (dd, *J* = 6.0 Hz, 4H), 8.06 (dd, *J* = 7.8 Hz, 2H), 8.02–7.96 (m, 8H), 8.40 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.76 (d *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 6.6 Hz, 2H), 7.42 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 165.9, 147.5, 134.5, 133.7, 131.8, 131.4, 130.9, 130.2, 129.7, 129.3, 128.7, 128.1, 127.1, 127.0, 126.4, 126.3, 126.2, 125.9, 124.7, 124.6, 124.2, 124.0, 122.3, 122.2; MS: found *m/z* 742.2141, Calcd. *m/z* 742.2150 for $[M]^-$ (M: $C_{54}H_{30}O_4$).

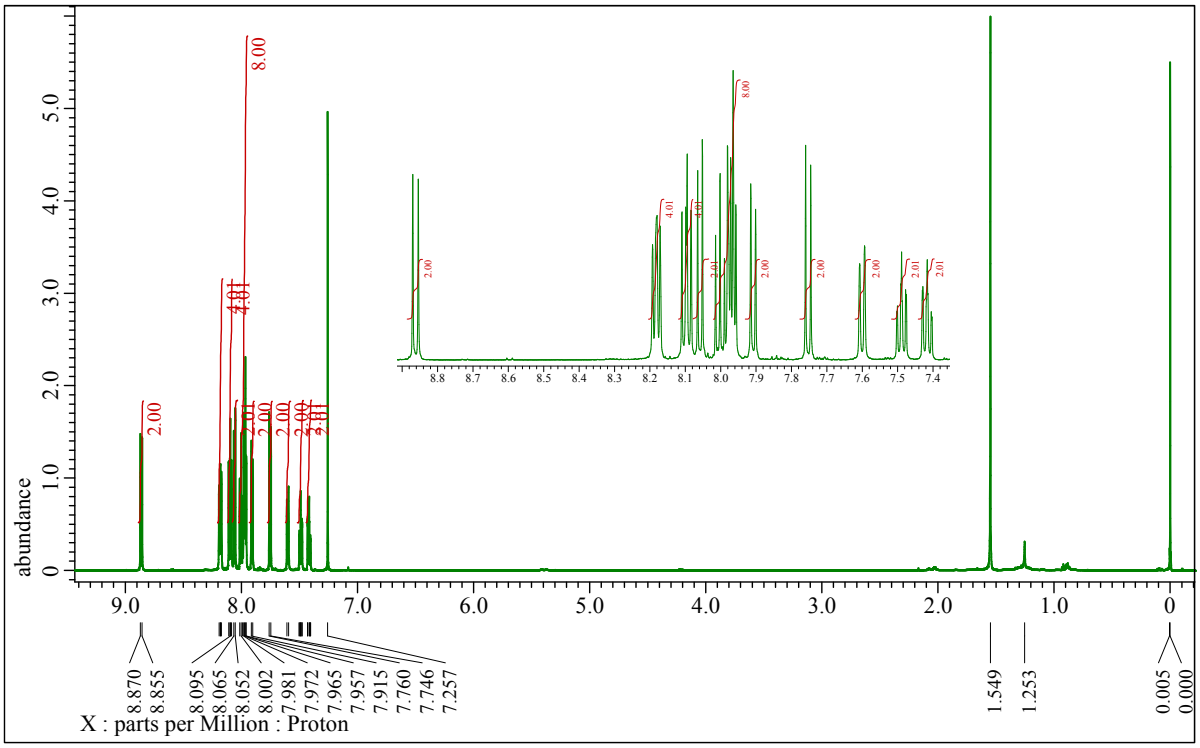


Fig. S1. ^{1}H-NMR spectrum of (*R*)-**1** (600 MHz, $CDCl_3$, 298 K, Me_4Si).

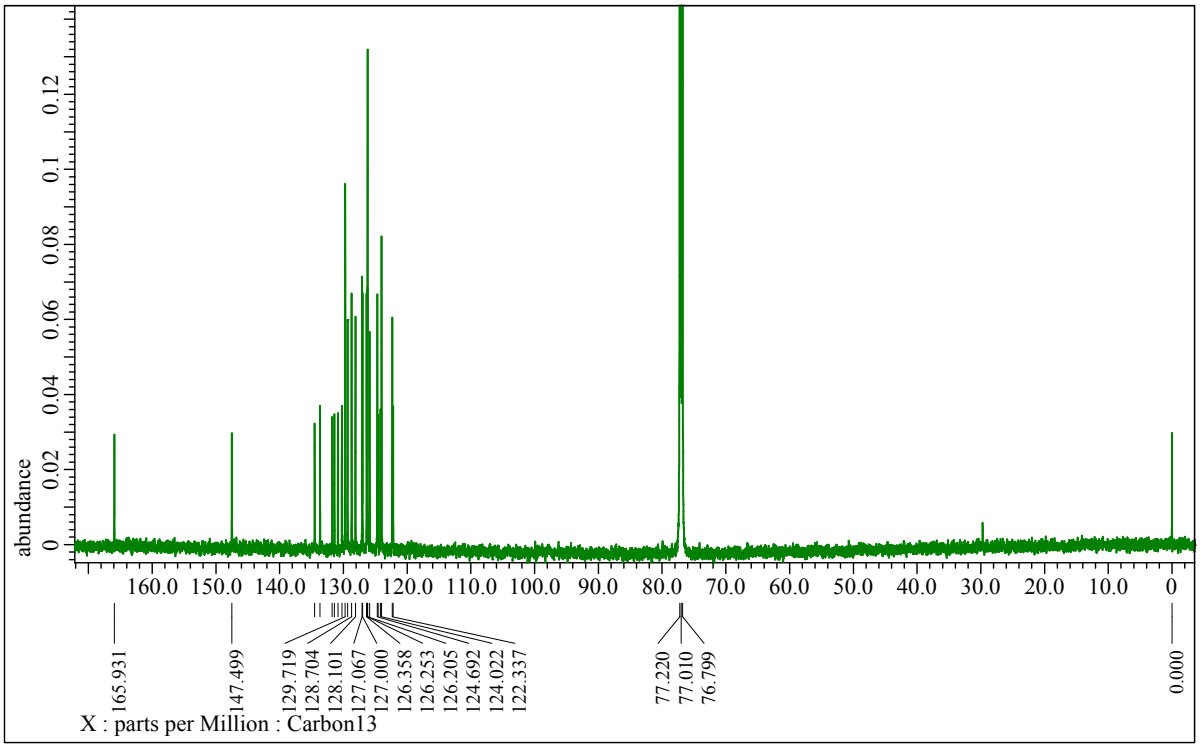


Fig. S2. ^{13}C-NMR spectrum of (*R*)-**1** (150 MHz, $CDCl_3$, 298 K, Me_4Si).

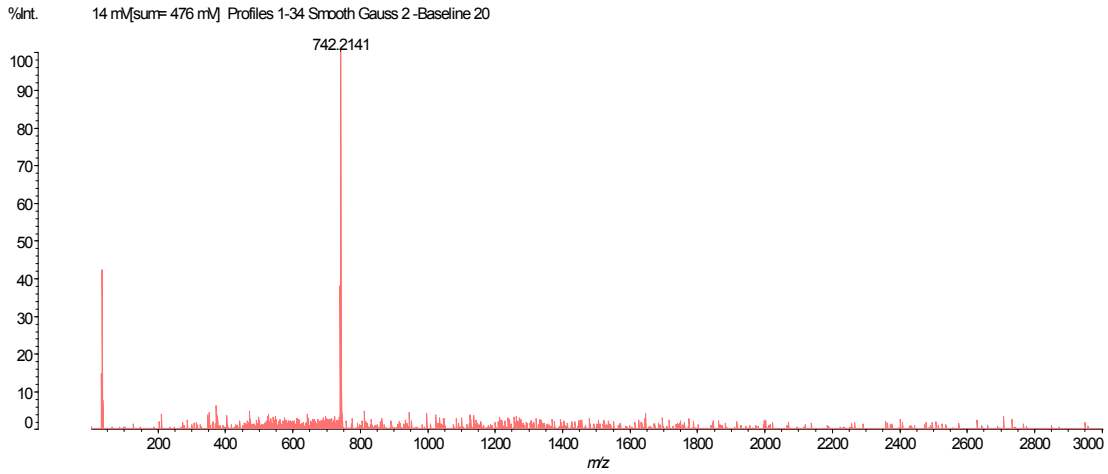
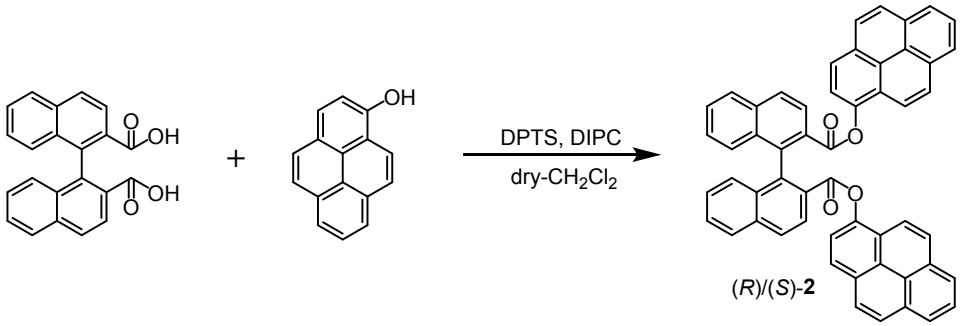


Fig. S3. Mass spectrum of (*R*)-**1**.

3.2. Synthesis of (*R*)/(*S*)-2



(*R*)-1,1′-Dicarboxy-2,2′-binaphthyl (103 mg, 0.30 mmol) and 1-pyrenol (141 mg, 0.65 mmol) were dissolved in dry CH_2Cl_2 under N_2. Then, DPTS (164 mg, 0.65 mmol) was added to the solution mixture at room temperature. After 15 min, DIPC (0.15 mL, 0.9 mmol) was added dropwise, and the mixture was stirred for 48 h. The mixture was extracted with dichloromethane and washed with water. The combined organic layer was dried over $MgSO_4$, concentrated, and purified by silica gel column chromatography using chloroform/hexane (1:2, v/v) as the eluent to obtain (*R*)-**2** (170 mg, 76.3% yield) as a yellow solid. (*S*)-**2** was prepared in an identical manner from (*S*)-1,1′-dicarboxy-2,2′-binaphthyl to give the desired product in 76% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.80 (d, *J* = 7.2 Hz, 2H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.92 (t, *J* = 7.2 Hz, 2H), 7.88 (dd, *J* = 7.2 Hz, 6.0 Hz, 4H), 7.77 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 9.0 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.58 (q, *J* = 9.0 Hz, 4H), 7.51 (dd, *J* = 9.6 Hz, 7.8 Hz, 4H), 7.16–7.13 (m, 2H), 7.00–6.99 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 154.1, 134.2, 131.1, 130.9, 130.5, 130.3, 129.5, 129.3, 128.6, 127.6, 127.2, 127.1, 127.0, 126.1, 125.7, 125.4, 125.0, 124.9, 124.4, 124.3, 124.1, 123.6, 122.7, 121.5, 116.7, 70.3; MS: found *m/z* 742.2153, Calcd. *m/z* 742.2150 for $[M]^-$ (M: $C_{54}H_{30}O_4$).

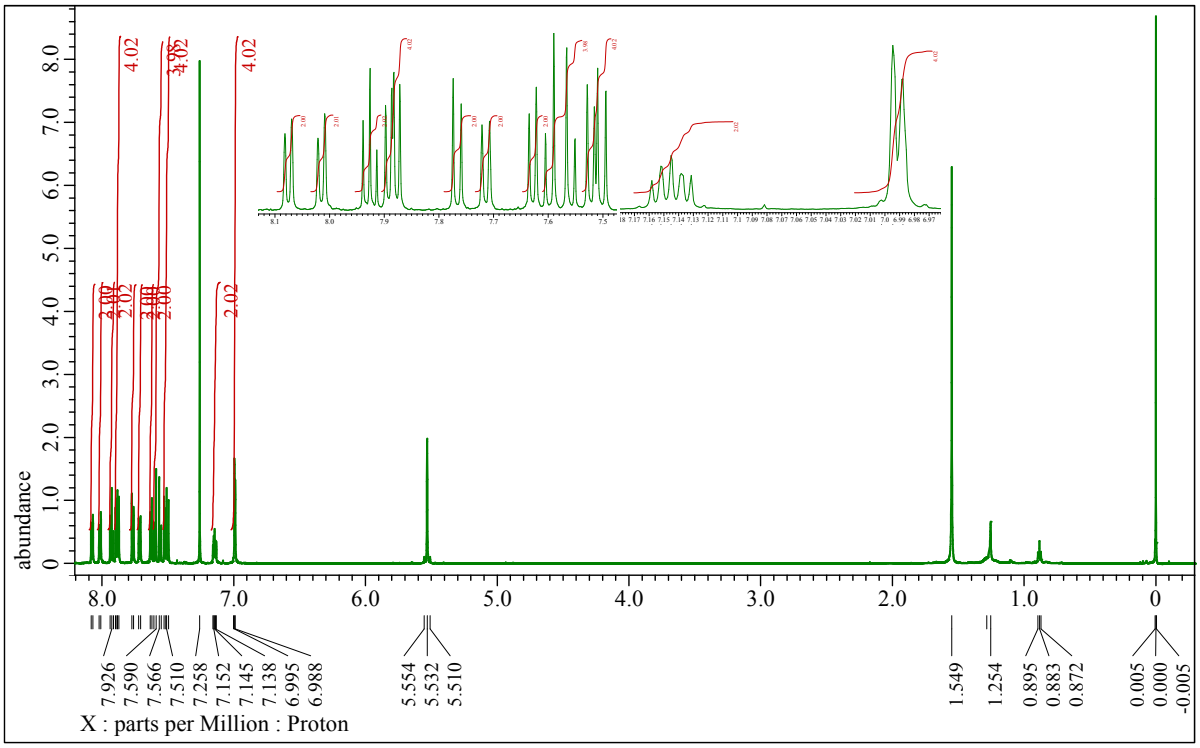


Fig. S4. ^{1}H-NMR spectrum of (*R*)-**2** (600 MHz, $CDCl_3$, 298 K, Me_4Si).

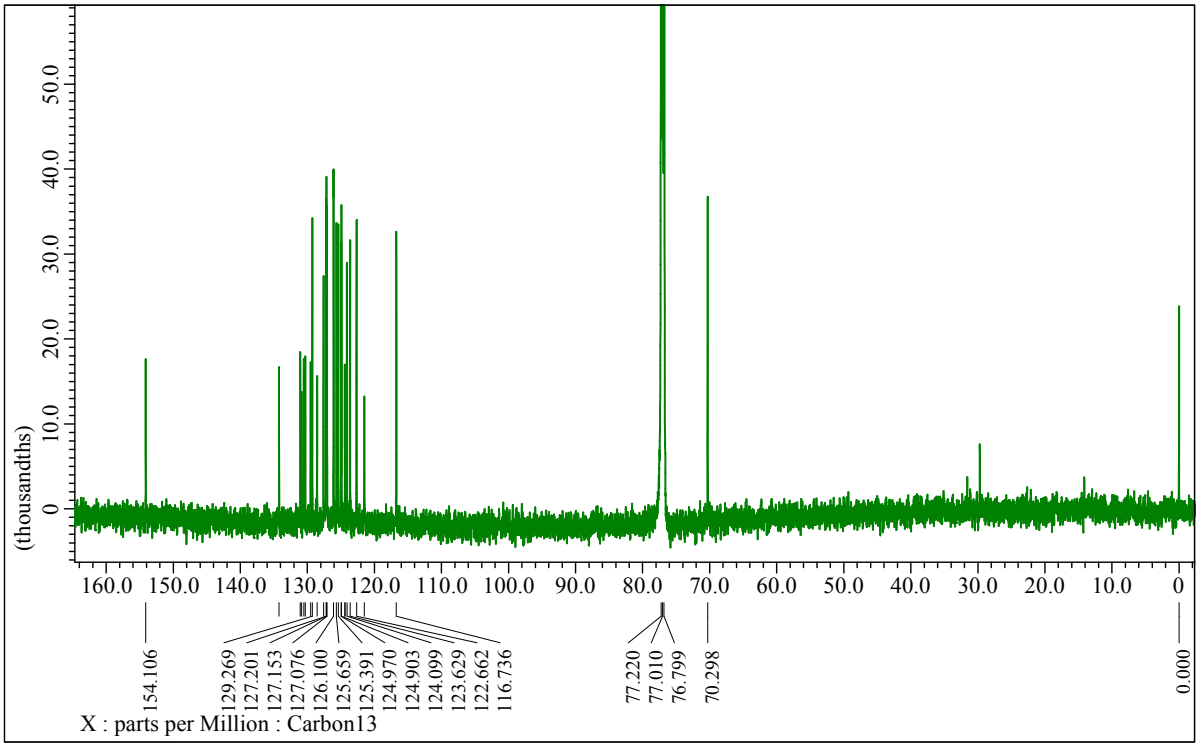


Fig. S5. ^{13}C-NMR spectrum of (*R*)-**2** (150 MHz, $CDCl_3$, 298 K, Me_4Si).

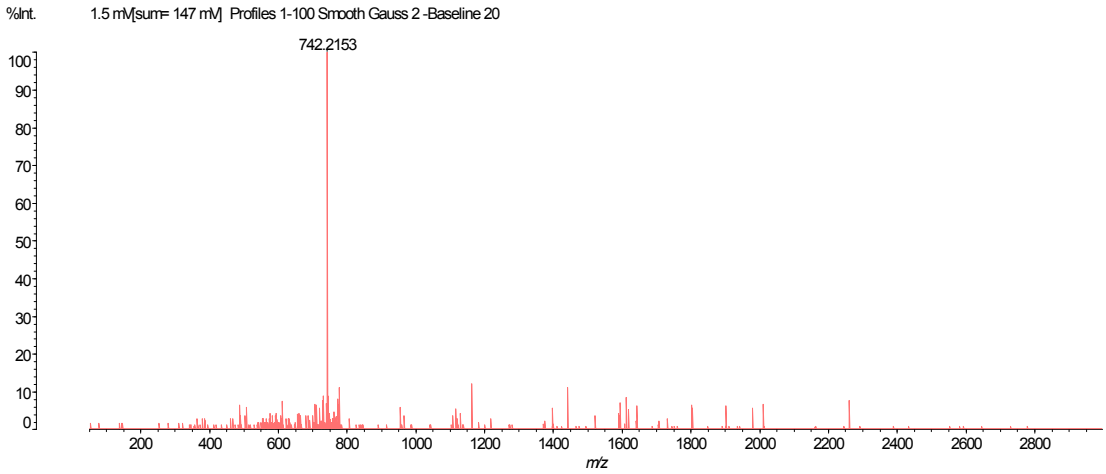


Fig. S6. Mass spectrum of (*R*)-**2**.

4. CPL and PL spectra of (*R*)/(*S*)-1 in $CHCl_3$ solution

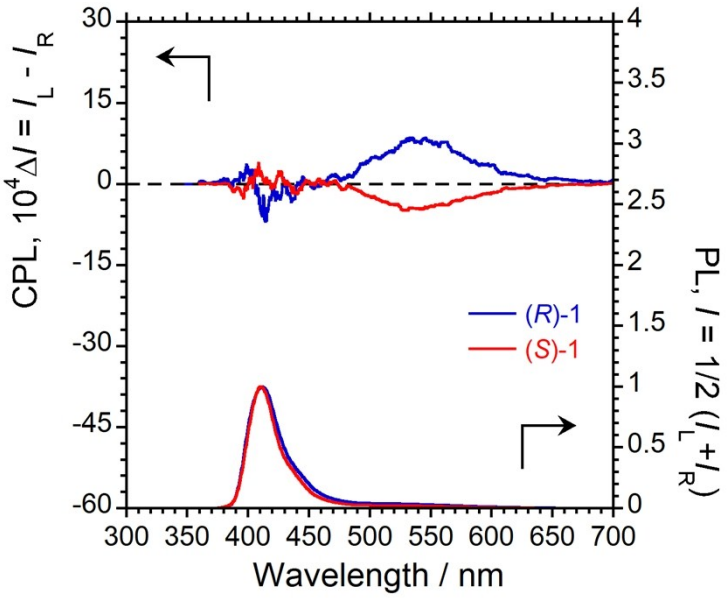


Fig. S7. CPL (upper) and PL (lower) spectra of **1** in $CHCl_3$ solution (1.0×10^{-3} M, path length = 1 mm, 25 °C).

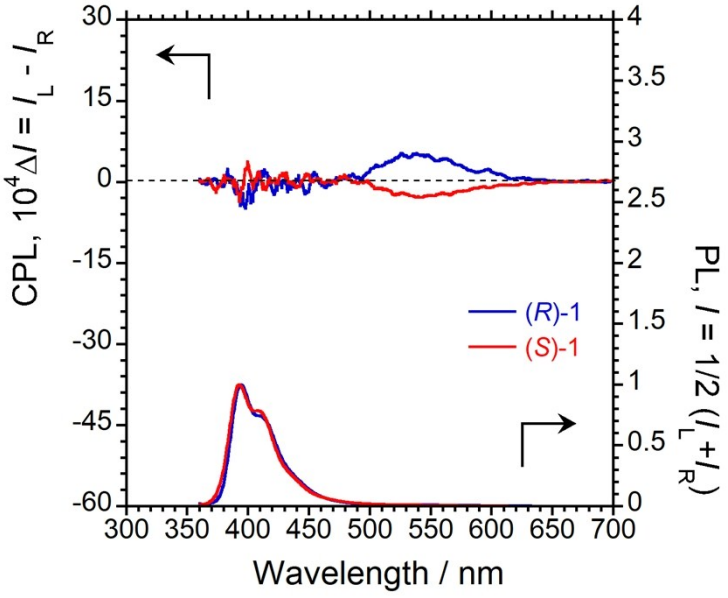


Fig. S8. CPL (upper) and PL (lower) spectra of **1** in $CHCl_3$ solution (1.0×10^{-5} M, path length = 10 mm, 25 °C).

5. CPL and PL spectra of (*R*)/(*S*)-1 in powder form

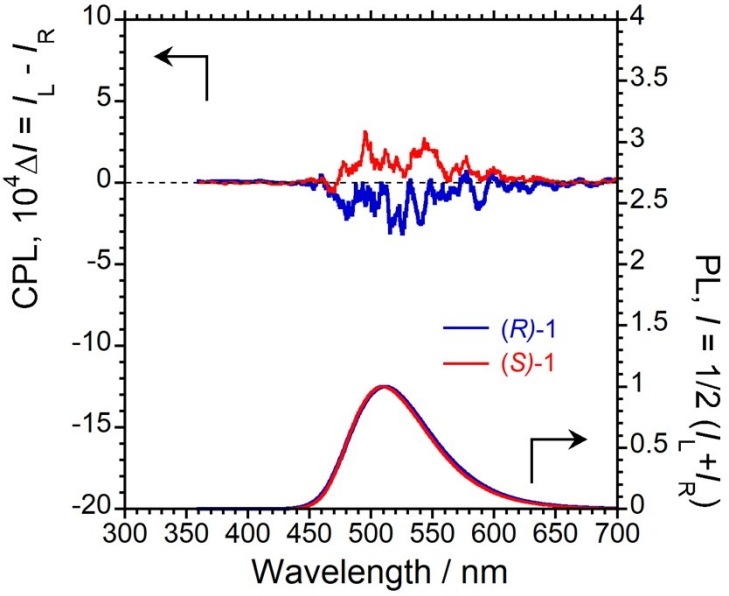


Fig. S9. CPL (upper) and PL (lower) spectra of **1** in powder form (25 °C).

6. CD, UV-Vis absorption, CPL and PL spectra of (*R*)/(*S*)-1 in PMMA-film

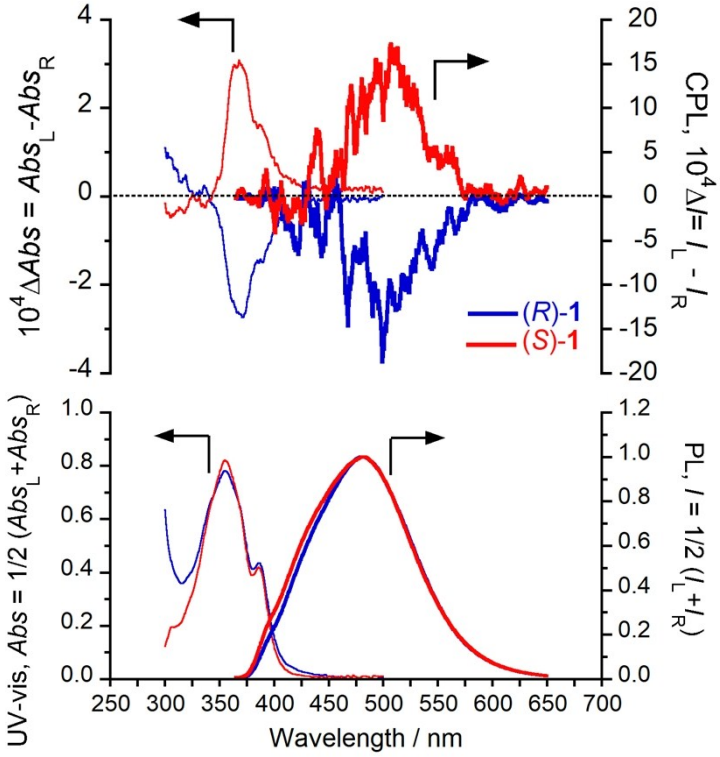


Fig. S10. CD (upper), UV-vis absorption (lower), CPL (upper) and PL (lower) spectra of **1** in PMMA-film state (25 °C).

7. CD, UV-Vis absorption, CPL and PL spectra of (*R*)/(*S*)-2 in PMMA-film

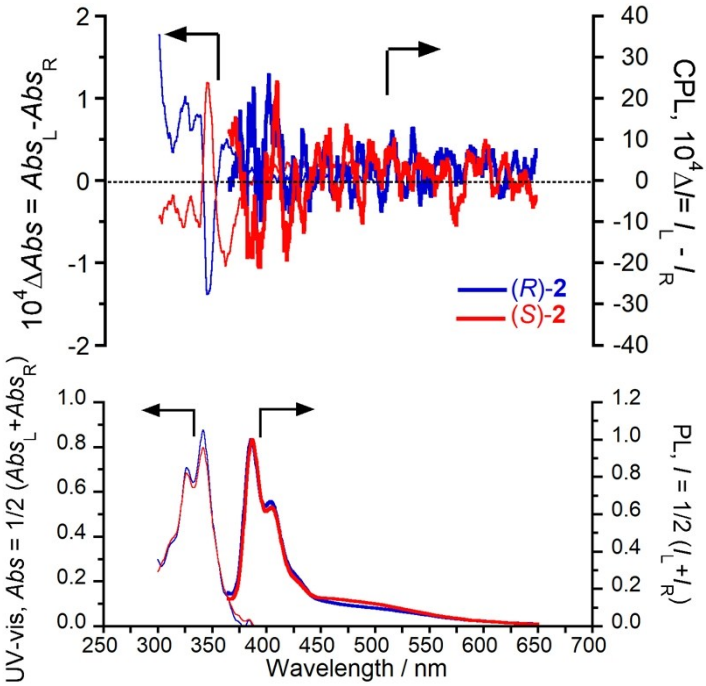


Fig. S11. CD (upper), UV-vis absorption (lower), CPL (upper) and PL (lower) spectra of **2** in PMMA-film state (25 °C).

8. MCPL and PL spectra of (*R*)/(*S*)-1 in $CHCl_3$ solution

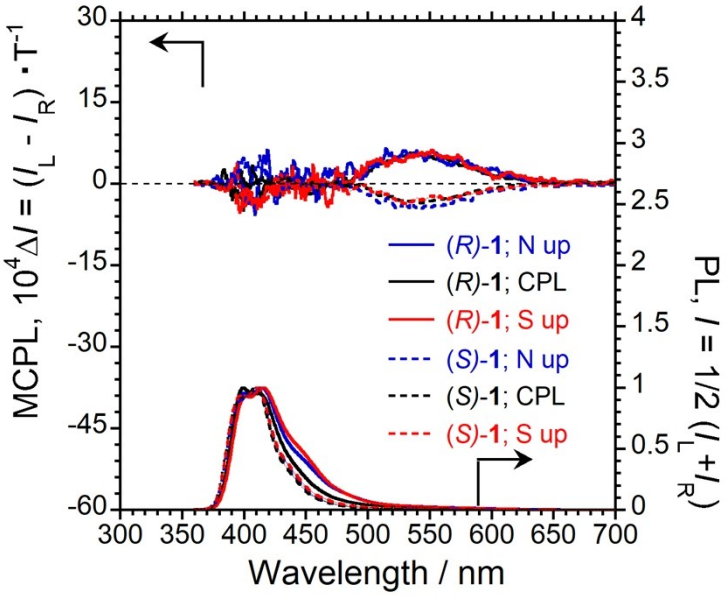


Fig. S12. MCPL (upper) and PL (lower) spectra of (*R*)/(*S*)-**1** in $CHCl_3$ solution state under application of a 1.6 T magnetic field (1.0×10^{-4} M, path length = 5 mm, 25 °C).

9. MCPL and PL spectra of (*R*)/(*S*)-2 in $CHCl_3$

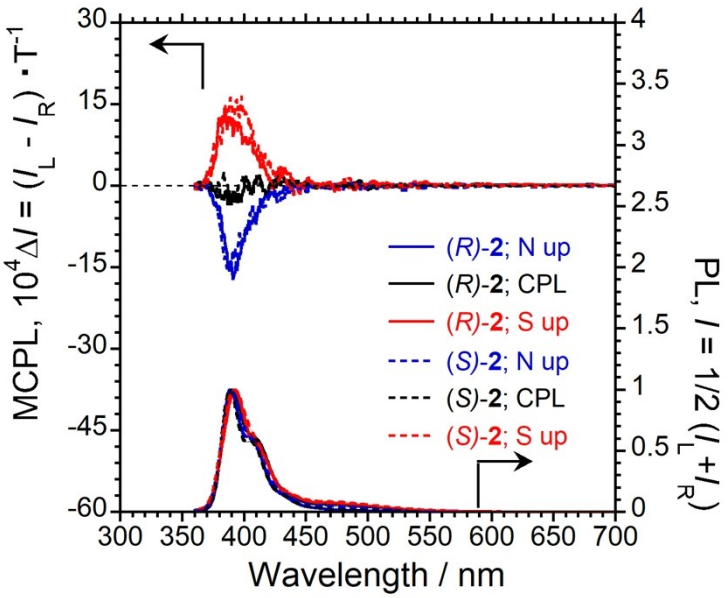


Fig. S13. MCPL (upper) and PL (lower) spectra of (*R*)/(*S*)-**2** in $CHCl_3$ solution state under application of a 1.6 T magnetic field (1.0×10^{-4} M, path length = 5 mm, 25 °C).

10. MCPL and PL spectra of (*R*)/(*S*)-1 in PMMA-film

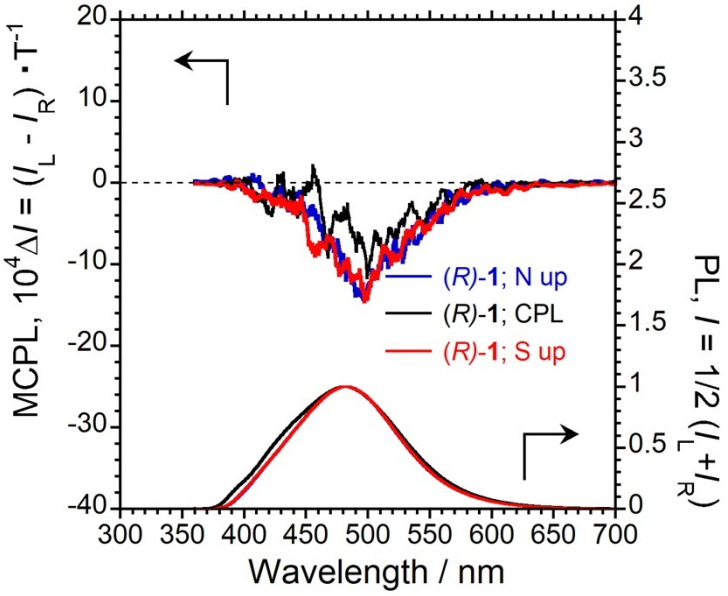


Fig. S14. MCPL (upper) and PL (lower) spectra of (*R*)/(*S*)-**1** in PMMA-film state under application of a 1.6 T magnetic field (25 °C).

11. MCPL and PL spectra of (*R*)/(*S*)-2 in PMMA-film

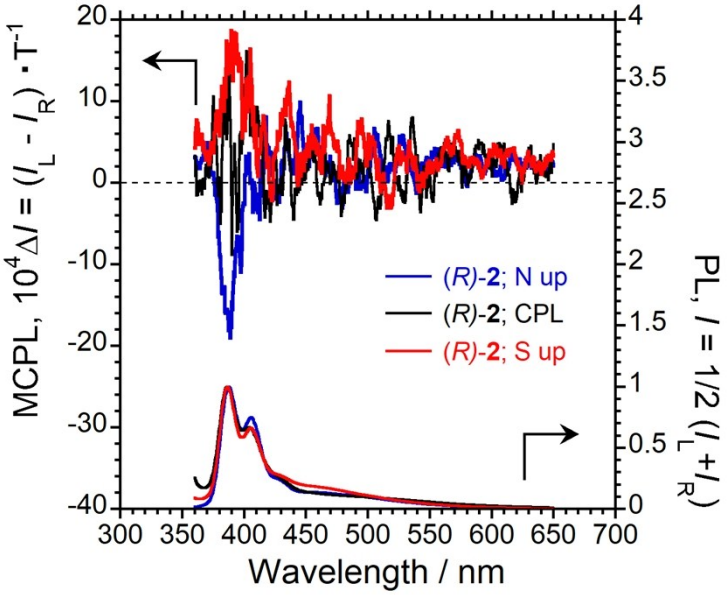


Fig. S15. MCPL (upper) and PL (lower) spectra of (*R*)/(*S*)-**2** in PMMA-film state under application of a 1.6 T magnetic field (25 °C).