

Electronic Supporting Information for

Pyrene Magic: Chiroptical Enciphering and Deciphering 1,3-Dioxolane Bearing Two Wirepullings to Drive Two Remote Pyrenes

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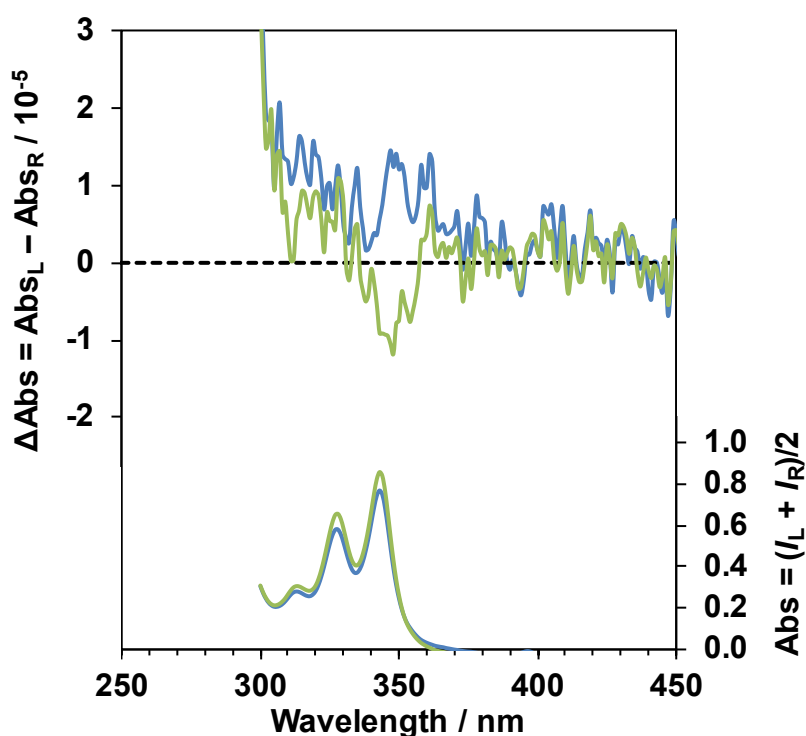


Fig. S1. CD (top) and UV-Vis (bottom) absorption spectra of (R,R)-1 (blue lines) and (S,S)-1 (green lines) in galssy PMMA films.

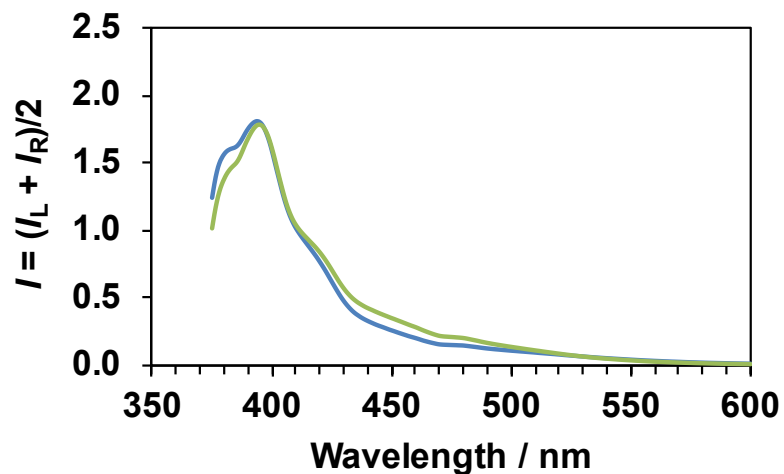


Fig. S2. The PL spectra of (*R,R*)-**1** (blue line) and (*S,S*)-**1** (green line) dispersed in PMMA film. $\lambda_{\text{ex}} = 345$ nm. The sign and magnitudes of CPL signals were not reproducible.

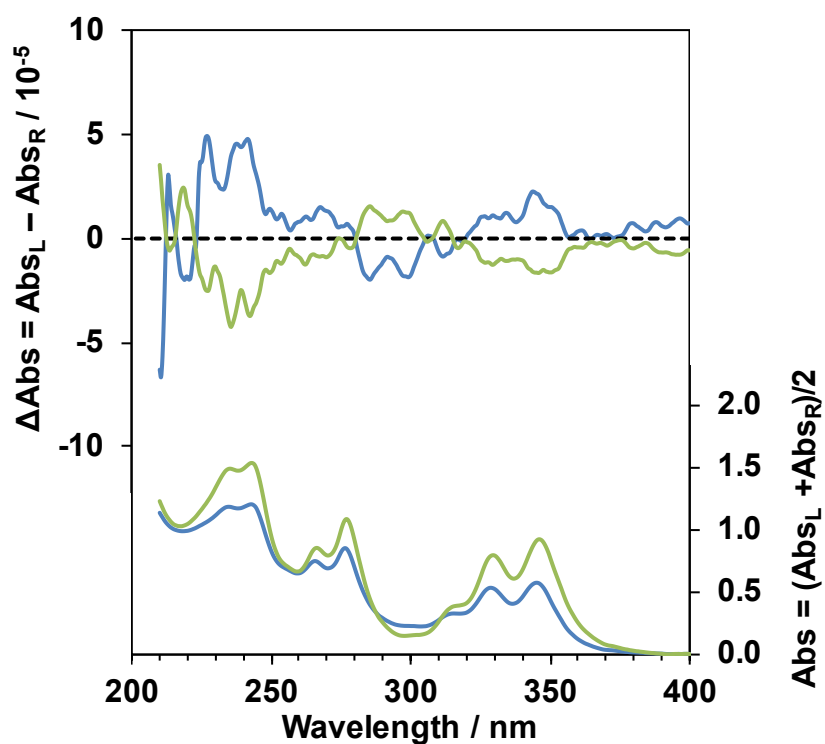
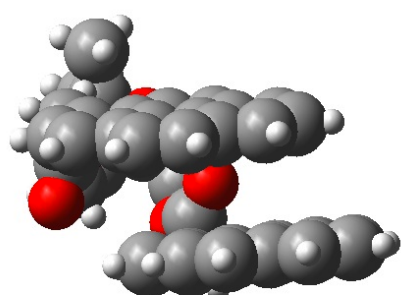
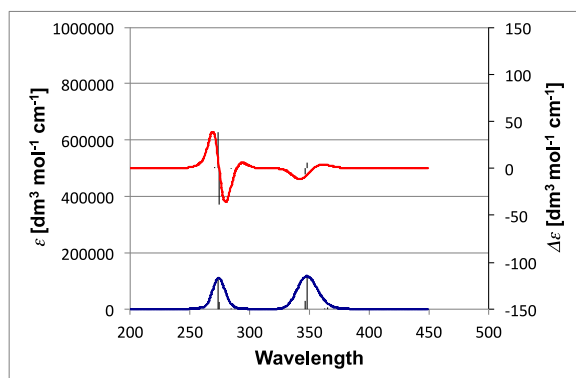
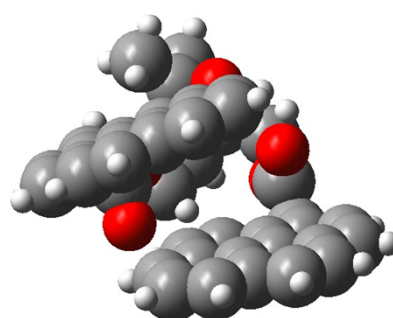
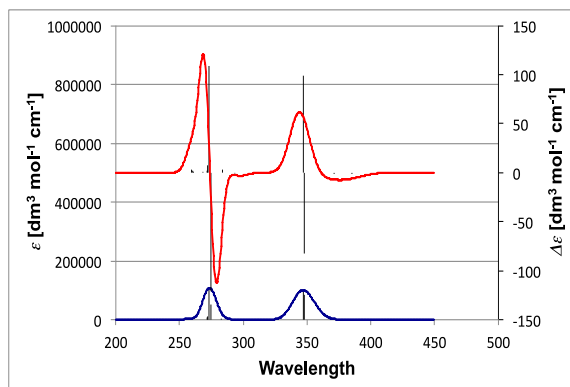


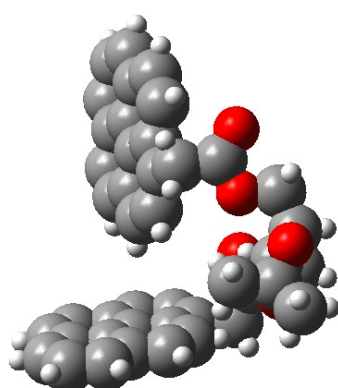
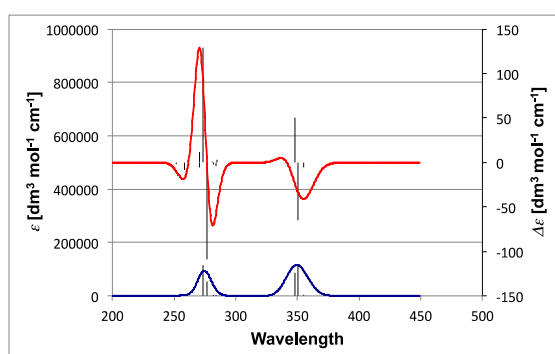
Fig. S3. CD (top) and UV-Vis (bottom) absorption spectra of (*R,R*)-**1** (blue lines) and (*S,S*)-**1** (green lines) dispersed in the KBr pellet.



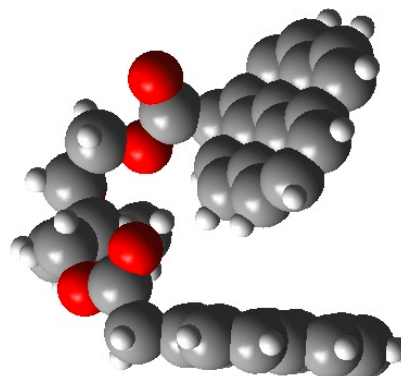
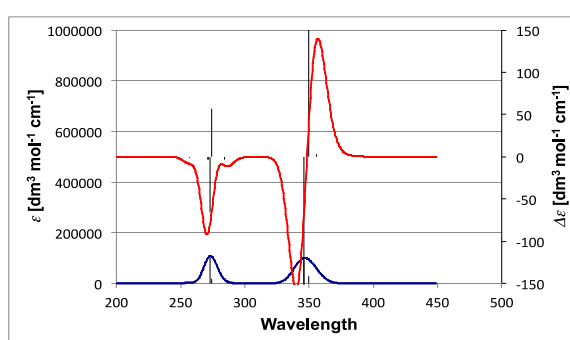
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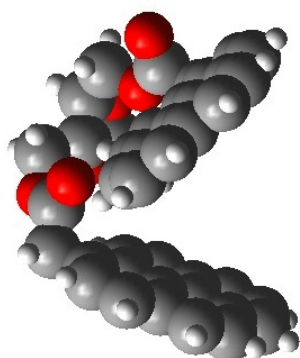
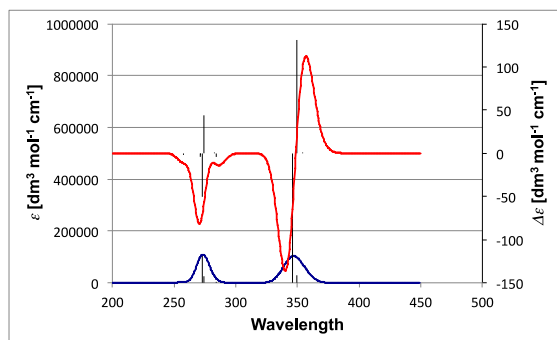
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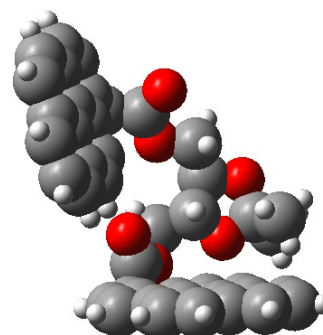
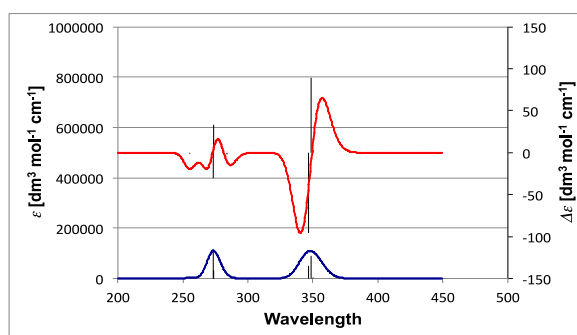
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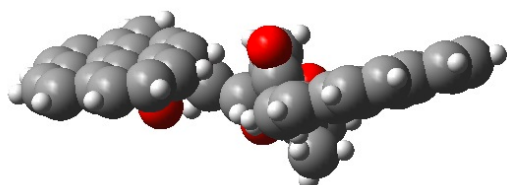
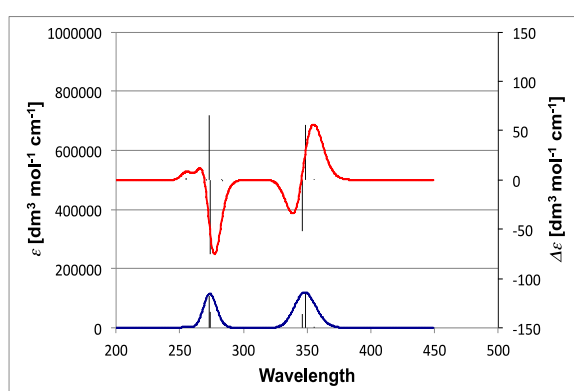
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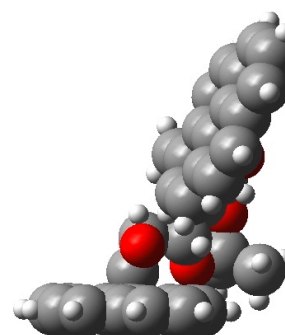
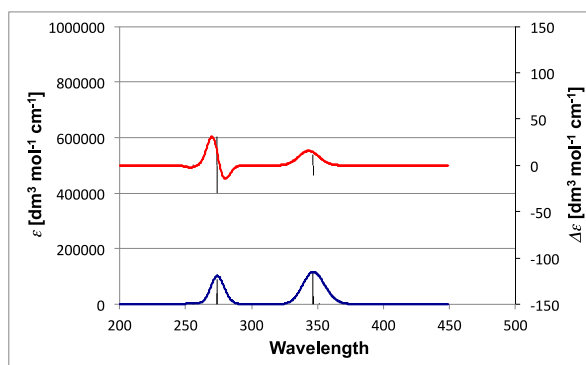
ID179_6.9% (the 4th probability)



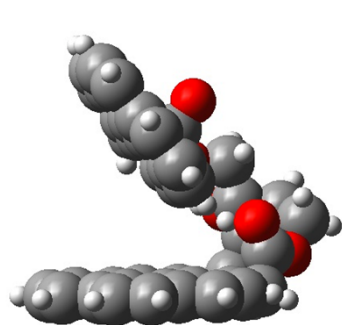
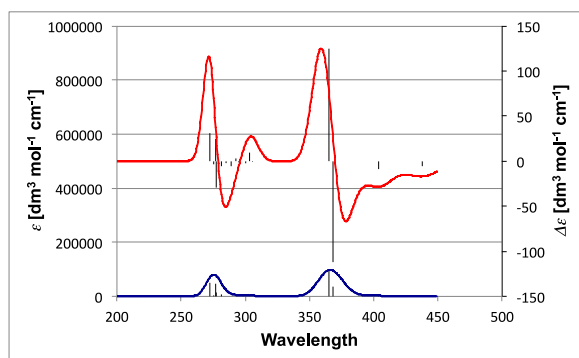
ID221_7.2% (the 3rd probability)



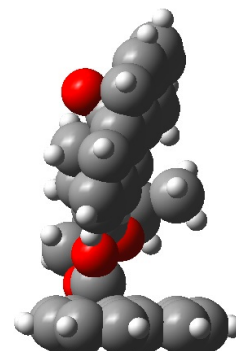
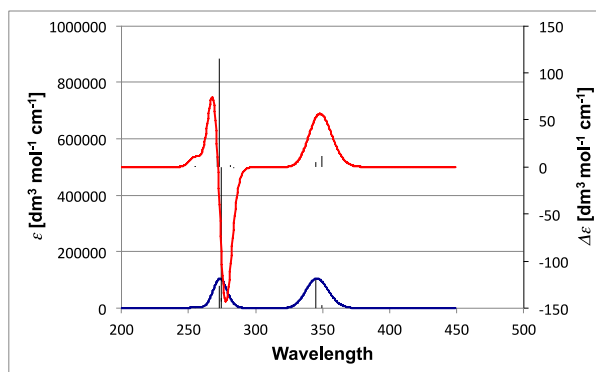
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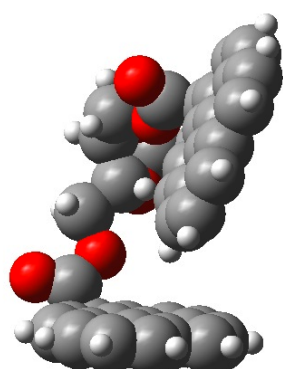
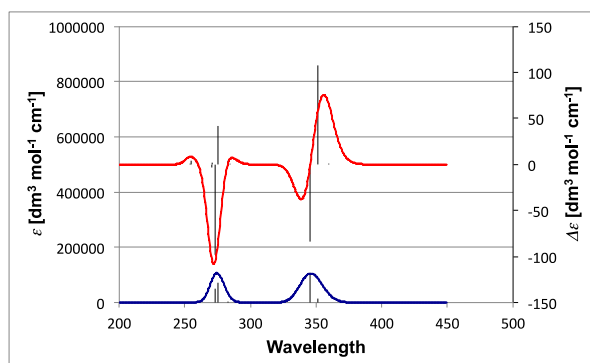
ID175_52.8% (the 1st probability)



ID177_0.4%



ID184_5.2%



ID187_21.1% (the 2nd probability)

Fig. S4. Calculated CD and UV-Vis spectra of eleven conformers of (*R,R*)-**1** and their Boltzmann distribution.

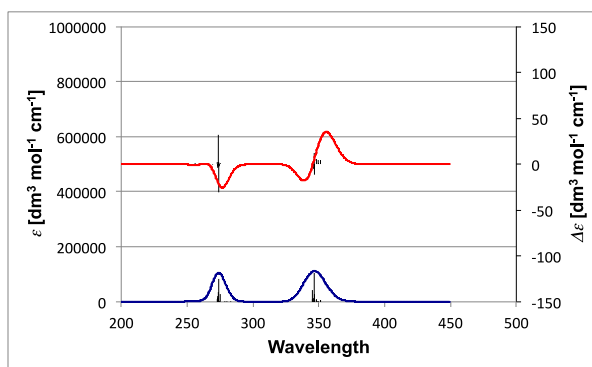


Fig. S5. Averaged CD and UV-Vis spectra of eleven conformers by weighted by their Boltzmann distribution.

Experimental method

General methods

Chloroform (CHCl₃), PMMA, KBr and chloroform-*d*, purchased from Wako Pure Chemical (Osaka, Japan), were used for the measurements. All (–)-2,3-*O*-isopropylidene-*D*-threitol, (+)-2,3-*O*-isopropylidene-*L*-threitol, 1-pyreneacetic acid, *N,N'*-dicyclohexylcarboimide, 4-*N,N*-dimethylaminopyridine and dichloromethane (CH₂Cl₂) were purchased from Tokyo Chemical Industry (Tokyo, Japan) and used as received.

Syntheses of [(4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bismethanoyl bis-1-pyrene [(*R,R*)-1] and [(4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bismethanoyl bis-1-pyrene [(*S,S*)-1]

(–)-2,3-*O*-Isopropylidene-*D*-threitol (119 mg, 0.734 mmol) was added to a mixture of 1-pyreneacetic acid (400 mg, 1.54 mmol), *N,N'*-dicyclohexylcarboimide (633 mg, 3.07 mmol), and 4-*N,N*-dimethylaminopyridine (67.8 mg, 0.555 mmol) in dry CH₂Cl₂ (10 mL). The reaction mixture was stirred for 72 h under an argon atmosphere at room temperature. Then, CH₂Cl₂ was added to the reaction mixture and washed with saturated aqueous sodium bicarbonate (NaHCO₃) and brine. The organic layer was dried over anhydrous MgSO₄ and concentrated under vacuum. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate/hexane = 1/2 (v/v)). (*R,R*)-1 was obtained as a pale yellow solid [23 mg (yield: 5 %)]. (*S,S*)-1 was also prepared by the same procedure in 5% yield, from (+)-2,3-*O*-isopropylidene-*L*-threitol. ¹H NMR (chloroform-*d*, 400 MHz): δ 8.17-8.13 (m, 6H), 8.07-8.05 (d, *J* = 8.8 Hz, 4H), 8.01-7.97 (m, 6H), 7.84-7.82 (d, *J* = 8.0 Hz, 2H), 4.25 (s, 4H), 4.13-4.03 (m, 4H), 3.81 (brs, 2H), 1.16 (s, 6H). ¹³C NMR (chloroform-*d*, 100 MHz): δ 171.0, 131.3, 130.9, 130.7, 129.4, 128.3, 128.0, 127.6, 127.4, 126.0, 125.3, 125.2, 125.0, 124.9, 124.7, 123.1, 110.0, 77.20, 75.53, 63.90, 39.12, 26.58. HRMS(MALDI-TOF): *m/z*: calcd for C₄₃H₃₄O₆: 646.2355; found: 646.2350.

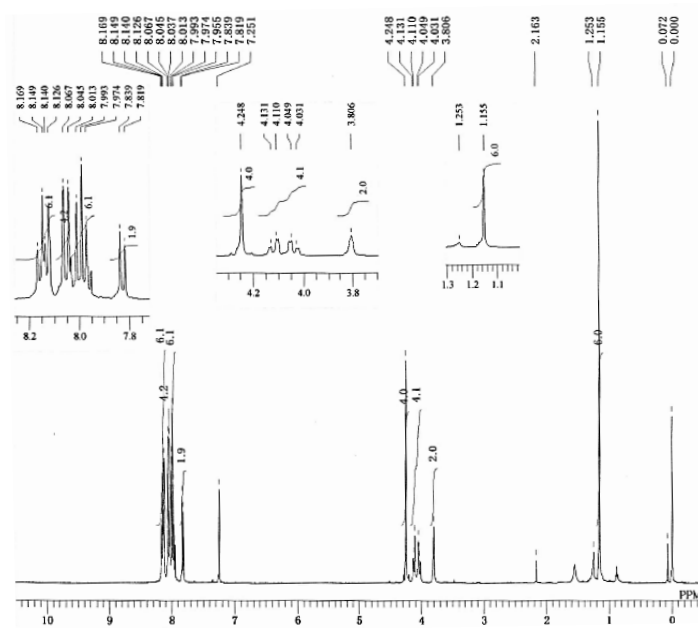


Fig. S6. ^1H NMR spectrum of (*R,R*)-**1** (chloroform-*d*, 400 MHz). δ 8.17-8.13 (m, 6H), 8.07-8.05 (d, $J = 8.8$ Hz, 4H), 8.01-7.97 (m, 6H), 7.84-7.82 (d, $J = 8.0$ Hz, 2H), 4.25 (s, 4H), 4.13-4.03 (m, 4H), 3.81 (brs, 2H), 1.16 (s, 6H).

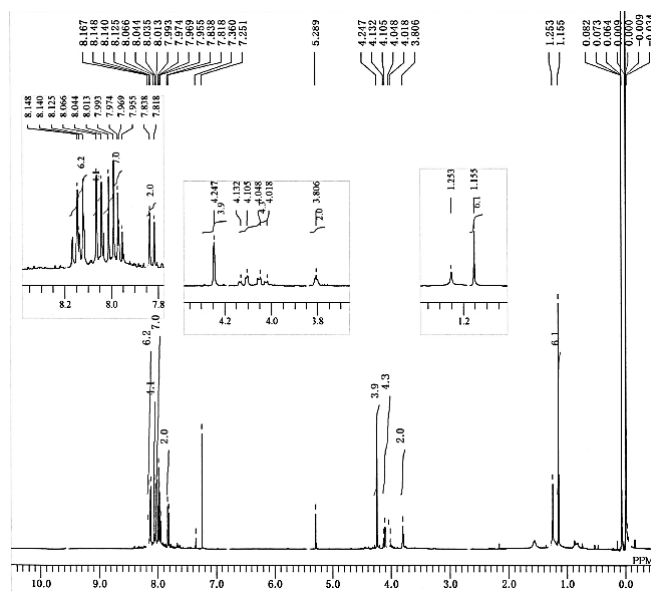


Fig. S7. ^1H NMR spectrum of (*S,S*)-**1** (chloroform-*d*, 400 MHz). δ 8.17-8.13 (m, 6H), 8.07-8.04 (d, $J = 8.8$ Hz, 4H), 8.01-7.97 (m, 6H), 7.84-7.82 (d, $J = 8.0$ Hz, 2H), 4.25 (s, 4H), 4.13-4.02 (m, 4H), 3.81 (brs, 2H), 1.16 (s, 6H).

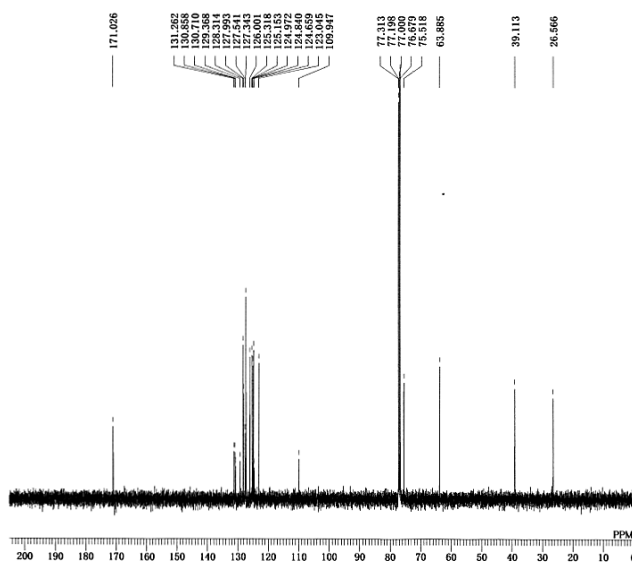


Fig. S8. ^{13}C NMR spectrum of (*R,R*)-**1** (chloroform-*d*, 100 MHz): δ 171.0, 131.3, 130.9, 130.7, 129.4, 128.3, 128.0, 127.5, 127.3, 126.0, 125.3, 125.2, 125.0, 124.8, 124.7, 123.0, 110.0, 77.20, 75.52, 63.89, 39.11, 26.57.

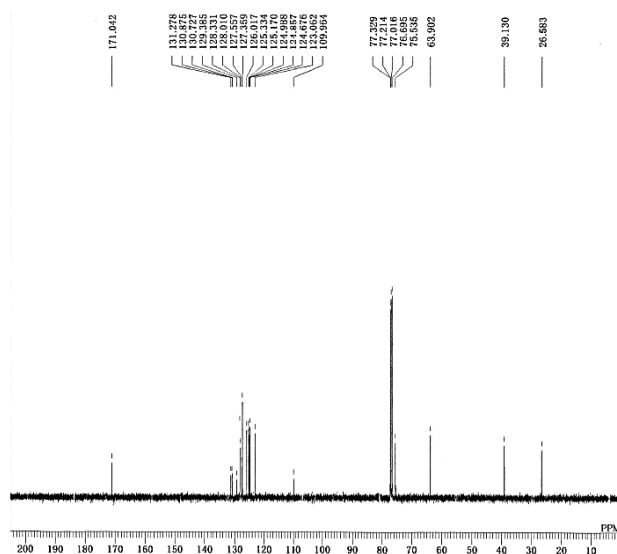


Fig. S9. ^{13}C NMR spectrum of (*S,S*)-**1** (chloroform-*d*, 100 MHz). δ 171.0, 131.3, 130.9, 130.7, 129.4, 128.3, 128.0, 127.6, 127.4, 126.0, 125.3, 125.2, 125.0, 124.9, 124.7, 123.1, 110.0, 77.20, 75.54, 63.90, 39.13, 26.58.

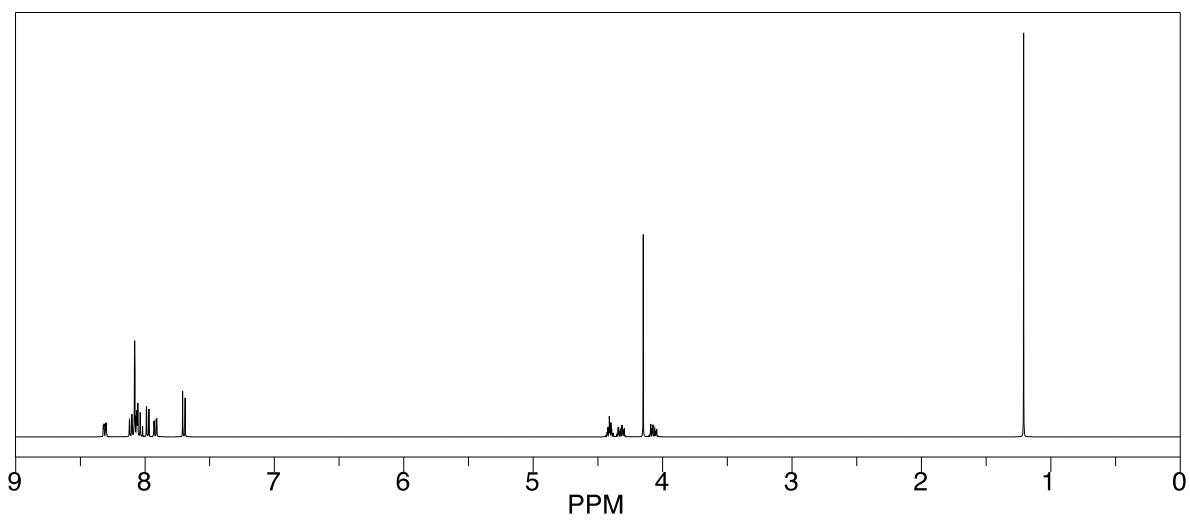
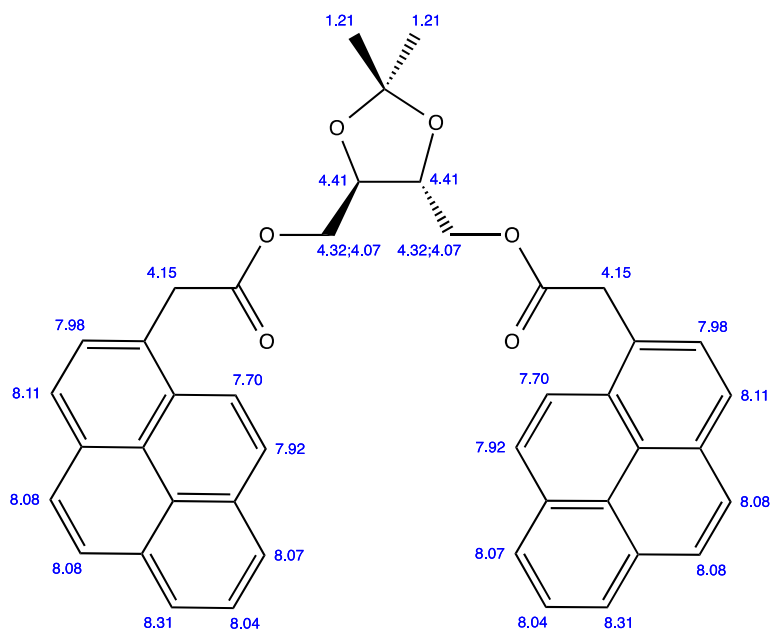


Fig. S10. ¹H NMR spectrum of (*R,R*)-**1** simulated with ChemBioDraw (ver. 13.02.3020, mac).

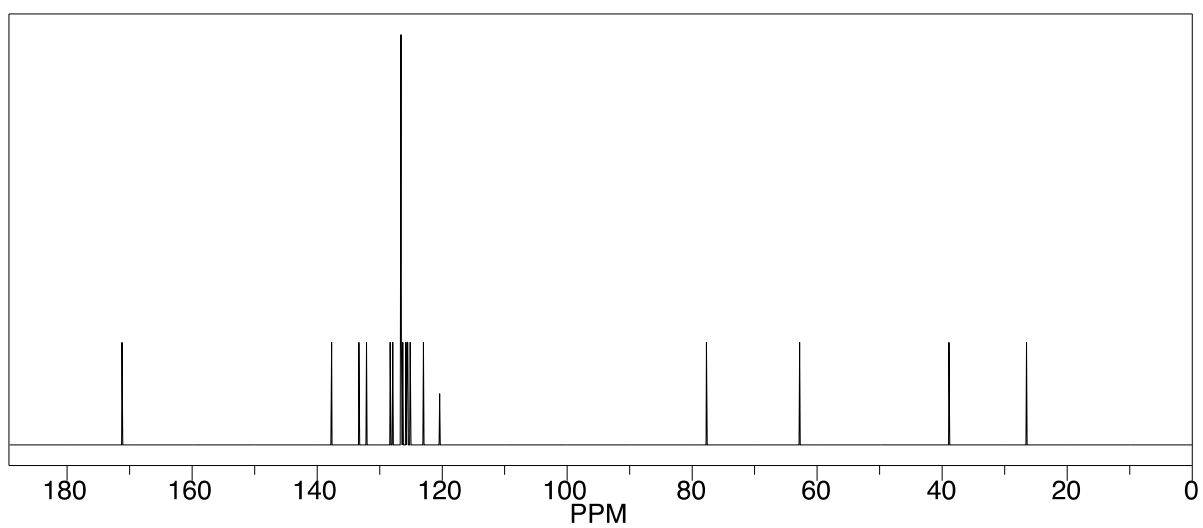
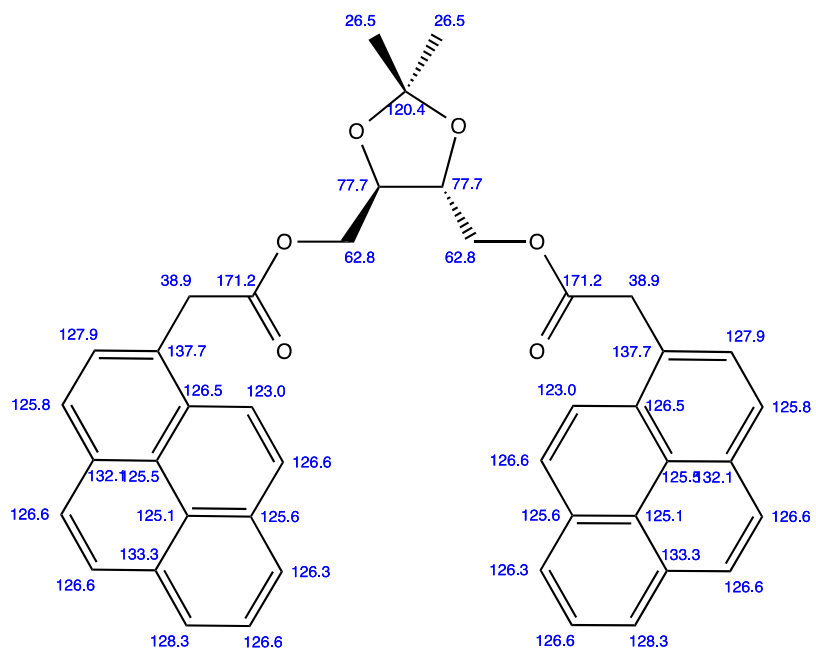


Fig. S11. ^{13}C NMR spectrum of (*R,R*)-**1** simulated with ChemBioDraw (ver. 13.02.3020, mac).

1.3. Measurement of the fluorescence spectra

Fluorescence spectra and absolute photoluminescence quantum yields in CHCl_3 solution, poly(methyl methacrylate) (PMMA) film, KBr pellet, and direct powder state were measured using an absolute unpolarised photoluminescence (PL) quantum yield measurement system (Hamamatsu Photonics C9920-02, Hamamatsu, Japan) under an air atmosphere at room temperature. PMMA film doped with chiral **1** was prepared using a spin coater at 3000 rpm (Opticoat MS-A100, Mikasa, Tokyo, Japan). The chiral **1**-doped PMMA film was prepared by drop-casting tetrahydrofuran (THF) solutions, in which the PMMA concentration was fixed at 0.1 g/mL, onto a quartz plate. Chiral **1** was added to the PMMA/THF solutions at a concentration of 0.01 mol/L. The cast films were dried at room temperature. The KBr pellet samples were prepared according to the standard procedure for obtaining glassy KBr matrices.¹ Chiral **1** was excited at 345 nm in all the three states.

The circularly polarized luminescence (CPL) spectra in the CHCl_3 solution and PMMA film were measured using a JASCO CPL-200 spectrofluoropolarimeter (Tokyo, Japan) at room temperature. The instrument used a scattering angle of 0° from the excitation of unpolarised, monochromated incident light with a bandwidth of 10 nm. The CPL spectra were approximated using the simple moving average (SMA) method.

1.4. Measurement of the circular dichroism (CD) and UV-Vis absorption spectra

CD and UV absorption spectra for all the compounds when dissolved in CHCl_3 or dispersed in the PMMA film were measured using a JASCO J-820 spectropolarimeter, at room temperature. CD and UV absorption spectra for all the compounds, when dispersed in the KBr pellet, were measured using a universal chiroptical spectrophotometer equipped with a Stokes-Mueller matrix analysis system.² The CD spectra were approximated using the SMA method.

References

1. R. Kuroda and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 433.
2. R. Kuroda, T. Harada, and Y. Shindo, *Rev. Sci. Instrum.*, 2001, **72**, 3802.