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.

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Fig. S2. The PL spectra of (R,R)-1 (blue line) and (S,S)-1 (green line) dispersed in PMMA film. $\lambda_{ex} = 345$ 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.
ID179_6.9% (the 4th probability)

ID221_7.2% (the 3rd probability)

ID080_1.0%

ID175_52.8% (the 1st 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 [(4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bismethanolyl bis-1-pyrene [(R,R)-1] and [(4S,5S)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bismethanolyl 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. $^1$H NMR spectrum of (R,R)-1 (chloroform-$d$, 400 MHz). $\delta$ 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. $^1$H NMR spectrum of (S,S)-1 (chloroform-$d$, 400 MHz). $\delta$ 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): $\delta$ 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). $\delta$ 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. $^1$H 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. 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. The CD spectra were approximated using the SMA method.
References
