Supporting Information For:

Supramolecular Chiral Sensing by Supramolecular Helical Polymers

Takehiro Hirao[1,†], Sei Kishino[1,†], and Takeharu Haino[1,2,*]

[1]Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University, 1–3–1 Kagamiyama, Higashi-Hiroshima, Hiroshima, 739-8526, JAPAN.

[2]International Institute for Sustainability with Knotted Chiral Meta Matter (SKCM^2), Hiroshima University, 1–3–1 Kagamiyama, Higashi-Hiroshima, Hiroshima, 739-8526, JAPAN.

To whom correspondence should be addressed: *E-mail: haino@hiroshima-u.ac.jp

[†]These two authors contributed equally.

Contents

General

All solvents were commercial reagent grade and were used without further purification except where noted. Dry 1,2-dichloroethane and dry NEt_3 was obtained by distillation over CaH_2 and KOH, respectively. ^{1}H,^{13}C, and 2D NMR (DQF-COSY, NOESY, and HSQC) spectra were recorded on a JEOL ECA-600 spectrometer, and chemical shifts were reported on the delta scale in ppm relative to residual pyridine ($\delta = 8.74$ and 150.4 for ^{1}H and ^{13}C, respectively). Diffusion-ordered ^{1}H NMR spectroscopic (DOSY) measurement was carried out on a JEOL ECA-500 spectrometer. Melting points (M.p.) were measured with a Yanagimoto micro melting point apparatus. Infrared (IR) spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZeSe ATR accessory. Preparative separations were performed by silica gel gravity column chromatography (Silica Gel 60 N (spherical, neutral)). Preparative medium pressure liquid chromatography (MPLC) separations were carried out with a YAMAZEN smart flash EPCLC AL-580S using a preparative Bio-Beads (S-X1) column. Recycling preparative GPC-HPLC separations were carried out on JAI LaboACE LC-5060 using preparative JAIGEL-2.5HH, 2HH columns in series. UV/vis absorption spectra were recorded on a JASCO V-760 spectrometer. Circular dichroism (CD) spectra were recorded on a JASCO J-1500 spectrometer. Morphological evaluation of the samples was performed using atomic force microscopy (AFM) using a Bruker Multimode 8HR under ambient conditions with a Bruker cantilever model NCHV in the tapping mode. NanoScope Analysis 2.0 was used for the AFM image analysis. **1**[1] and 2-octyldecanol[2] were synthesized according to reported methods.

Method

Determination of an affinity constant (K_a) corresponding to the intermolecular interactions between bis(porphyrin) moieties of ***2***.[3]

A hyperbolic curve was obtained by plotting the concentrations of **2** against the extinction coefficients (ε) (λ = 435 nm). Curve fitting analysis was performed using Igor pro program based on an isodesmic model. The fitting functions are given by eq. S1,

$$\varepsilon(C) = \frac{2K_aC + 1 - \sqrt{4K_aC + 1}}{2{K_a}^2C^2}(\varepsilon 1 - \varepsilon a) + \varepsilon a \qquad (S1)$$

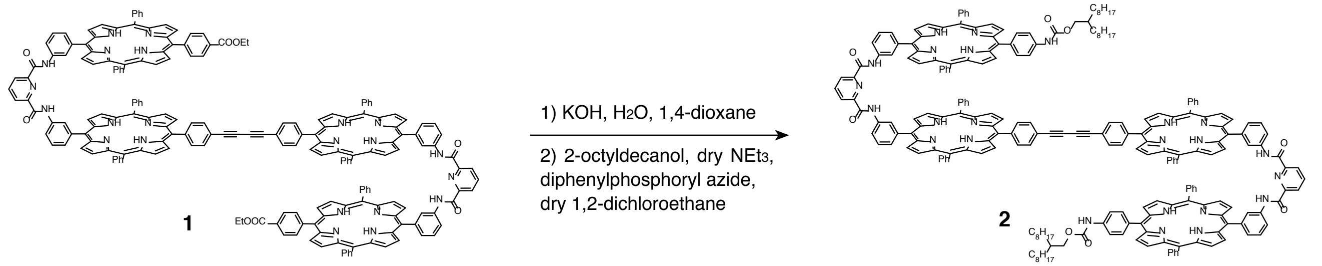
where C, K_a, ε_1, and ε_a denote the total concentration of **2**, the affinity constant, the ε of the monomer, and the ε of the aggregate species, respectively.

Determination of diffusion coefficient (D) of the molecular species in the solution of ***2***.[4]

Chloroform-*d* solutions of **2** were placed in an NMR sample tube (3 mmΦ). The pulse-field gradient diffusion NMR spectra were recorded using a bipolar pulse pair stimulated echo pulse sequence on a JEOL JNM-ECA500 spectrometer with a three mm inverse H3X/FG probe at 24 °C. The resulting DOSY data were analyzed using a MestReNova program to obtain the diffusion coefficient values (D) shown in Fig. 2b. The signal decay of the selected protons was fit to fitting functions given by eq. S2 (Fig. S5), where I and I_0 denote the NMR signal intensities in the presence and absence of gradient pulses, respectively. D is the diffusion coefficient value.

$$I = I_0 e^{-xD} \qquad (S2)$$

The x denotes $[-\gamma^2 g^2 \delta^2(\Delta - \delta/3)]$, where γ, g, δ, and Δ indicate the gyromagnetic ratio, gradient strength, its duration, and separation between the edges of the gradient pulses, respectively.



Scheme S1. Synthesis of **2**.

bis(porphyrin) dimer 2: To a solution of **1** (61.2 mg, 20.6 μmol) in 1,4-dioxane (9.8 mL) and water (0.82mL) was added potassium hydroxide (23.0 mg, 410 μmol). The mixture was stirred for 2 h at 100 °C under a nitrogen atmosphere. The reaction mixture was acidified with 1M hydrochloric acid to pH 4. After concentrating the organic layer to 1/2 of its original volume, the resulting precipitate was filtered off, washed with water and MeOH, and dried over under the reduced pressure. The resulting solid was dissolved in dry 1,2-dichloroethane (2.7 mL) in a pressure tube, and dry triethylamine (50 μL), diphenylphosphoryl azide (11.5 mg, 41.8 μmol), and 2-octyldecanol (159 mg, 588 μmol) were added at room temperature. The mixture was stirred for 20 h at 90 °C under a nitrogen atmosphere and diluted with $CHCl_3$. The organic layer was washed with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated under the reduced pressure. MPLC (chloroform, eluent), subsequent silica-gel column chromatography (4% MeCN in toluene, eluent), and GPC gave the desired product **2** (25.0 mg, 35%, for 2 steps) as a purple solid.

M.p.: > 300 °C. ^{1}H NMR (pyridine-*d*$_5$, 600 MHz): δ 11.39 (s, 2H), 11.27 (s, 4H), 9.25 (d, 4H, *J* = 5.0 Hz), 9.13 (d, 4H, *J* = 4.8 Hz), 9.11 (d, 4H, *J* = 4.8 Hz), 9.08 (d, 4H, *J* = 5.0 Hz), 8.98 (m, 8H), 8.87 (m, 8H), 8.52 (*overlapped*, 4H), 8.49 (*overlapped*, 8H), 8.43 (*overlapped*, 4H), 8.32 (*overlapped*, 10H), 8.16 (*overlapped*, 12H), 8.03 (m, 4H), 7.69–7.81 (*overlapped*, 16H), 7.63 (m, 4H), 7.55 (m, 8H), 4.52 (d, 4H, *J* = 6.3 Hz), 1.90 (m, 2H), 1.22–1.57 (m, 56H), 0.90 (t, 12H, *J* = 6.5 Hz), –2.51 (s, 4H), –2.55 (s, 4H). ^{13}C{^{1}H} NMR (chloroform-*d*$_1$, 100 MHz): δ 163.3, 163.2, 155.8, 144.5, 143.3, 143.2, 142.9, 142.8, 141.3, 139.5, 137.9, 137.8, 136.9, 135.4, 135.3, 132.1, 131.7, 128.7, 128.7, 128.3, 127.9, 127.7, 126.1, 122.1, 121.7, 121.5, 121.4, 121.1, 121.0, 120.5, 120.0, 118.0, 83.6, 76.6, 68.3, 38.8, 32.7, 32.2, 30.9, 30.4, 30.1, 27.7, 23.5, 14.8. HRMS (ESI$^+$) calcd. for $C_{232}H_{201}O_8N_{24}$ *m/z* 1150.2014 [M+3H]$^{3+}$, found *m/z* 1150.2024.

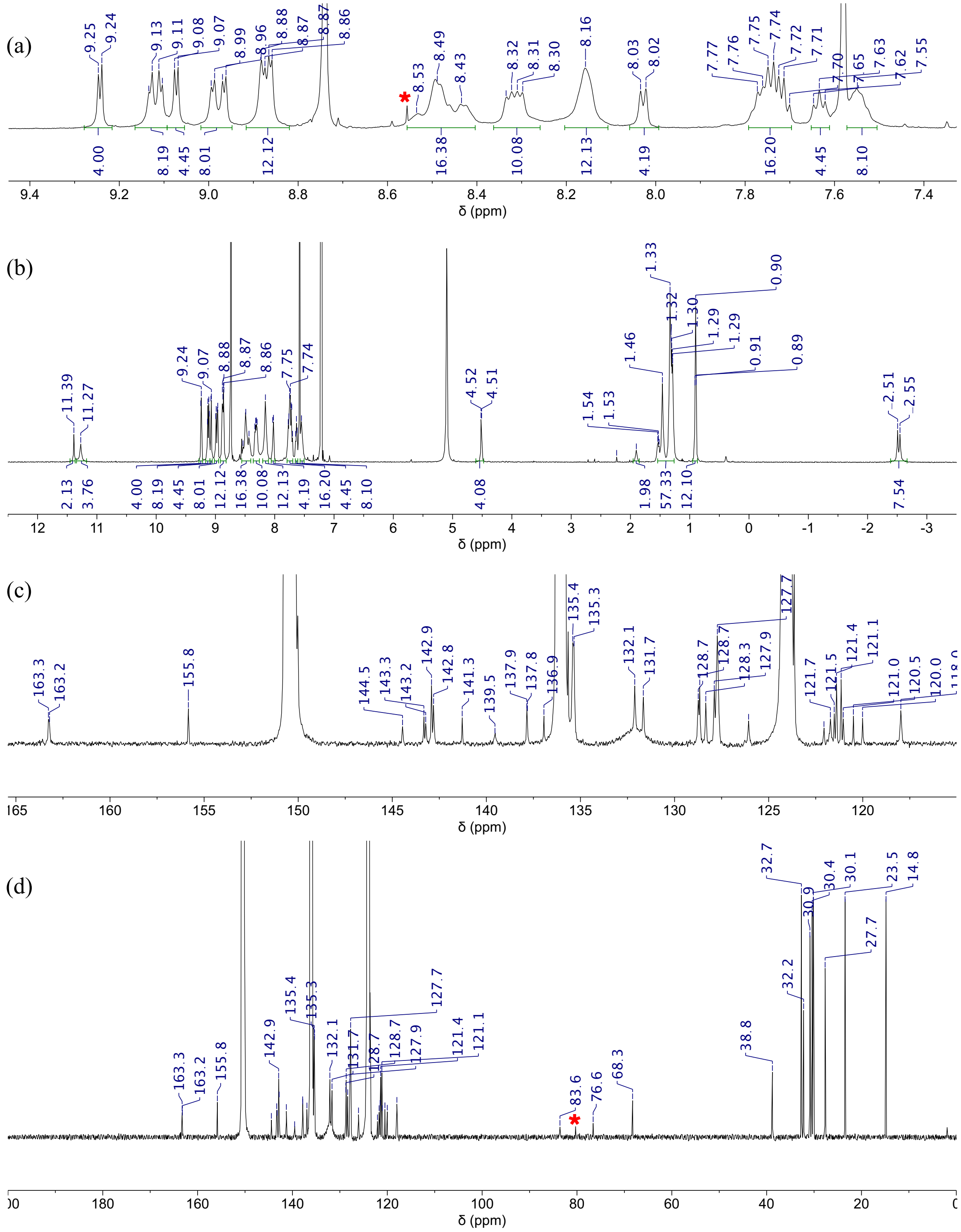


Figure S1. ^{1}H (600 MHz) and ^{13}C{^{1}H} (150 MHz) spectra of **2** in pyridine-d_5. The expanded views of the spectra and the full spectra are shown in panels (a), (c) and (b), (d), respectively. Asterisk (*) denotes residual chlorofom.

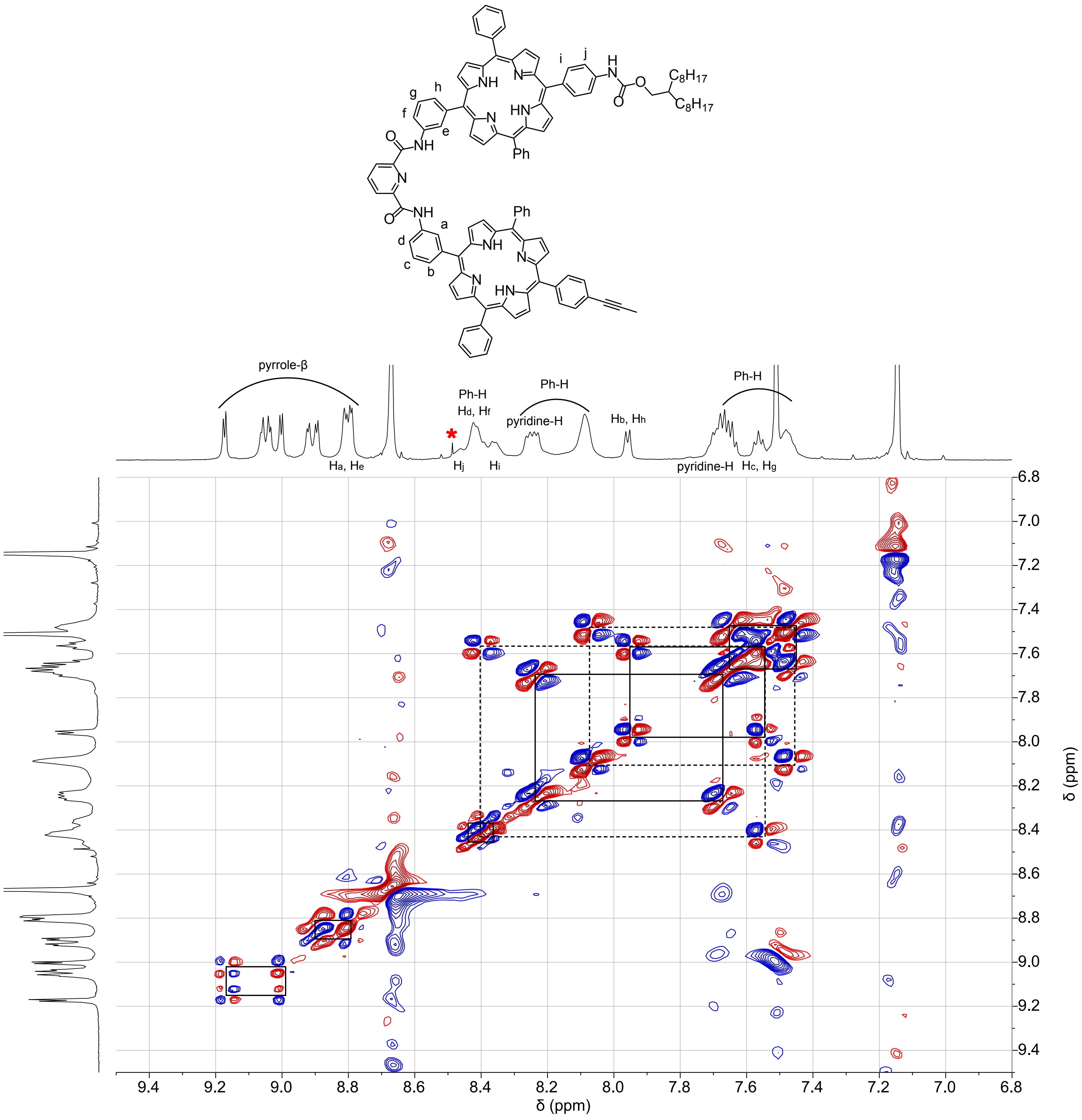


Figure S2. DQF-COSY spectrum of **2** in pyridine-*d*$_5$. Asterisk (*) denotes residual chlorofom.

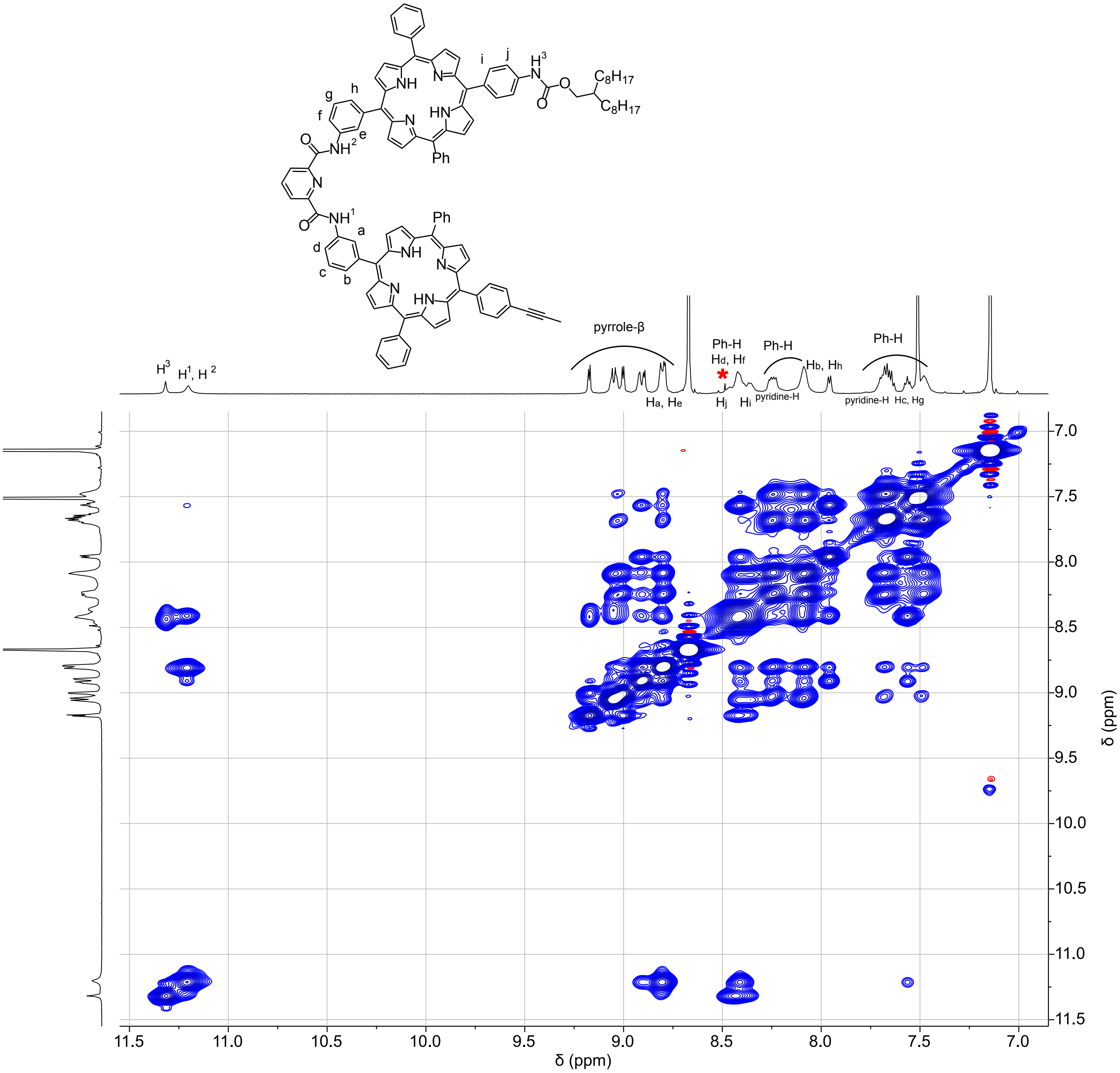


Figure S3. NOESY spectrum of **2** in pyridine-*d_5*. Asterisk (*) denotes residual chlorofom.

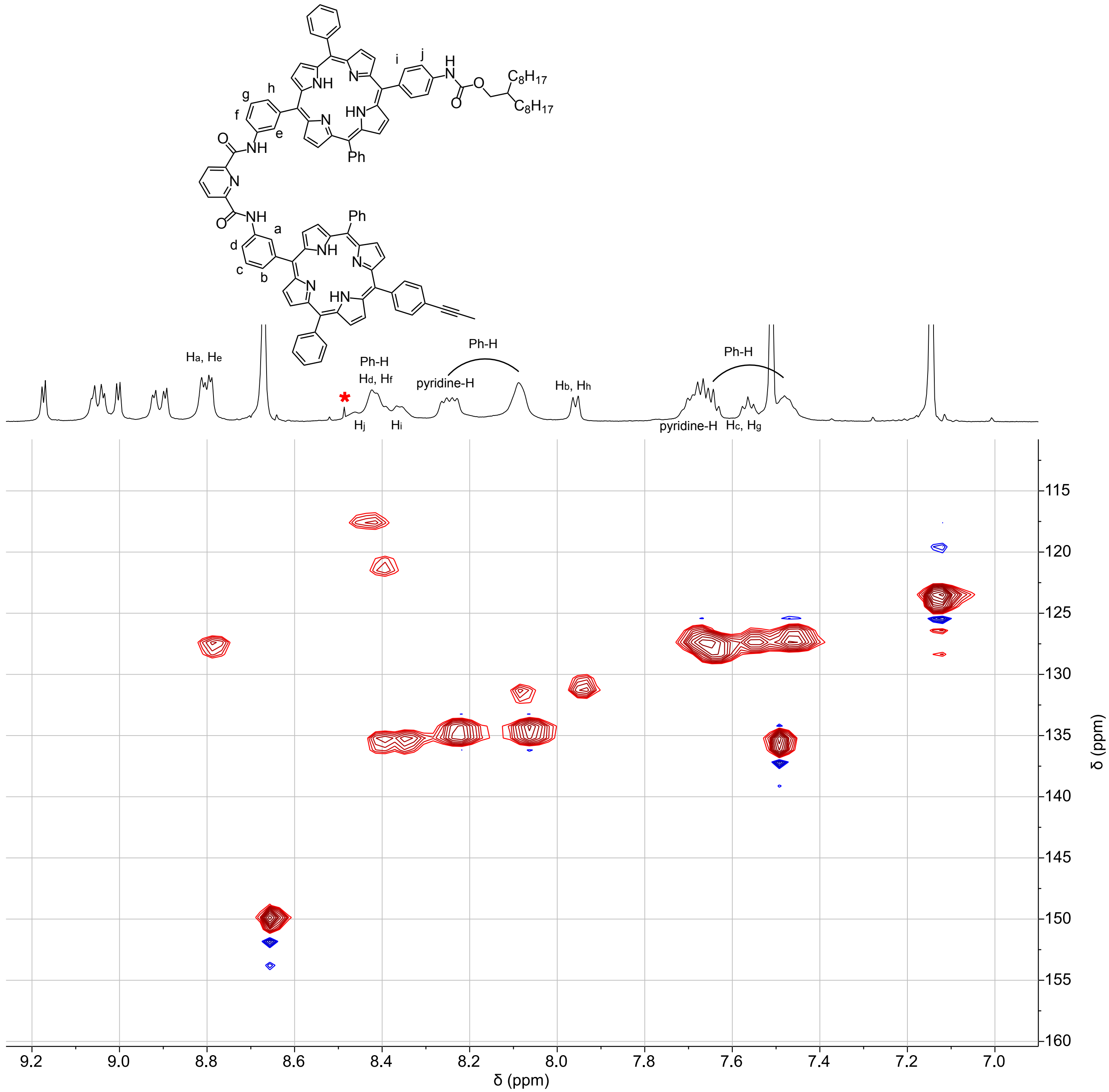


Figure S4. HSQC spectrum of **2** in pyridine-d_5. CH_3 and CH carbons are phased up (red), and CH_2 carbons are phased down (blue). Asterisk (*) denotes residual chlorofom.

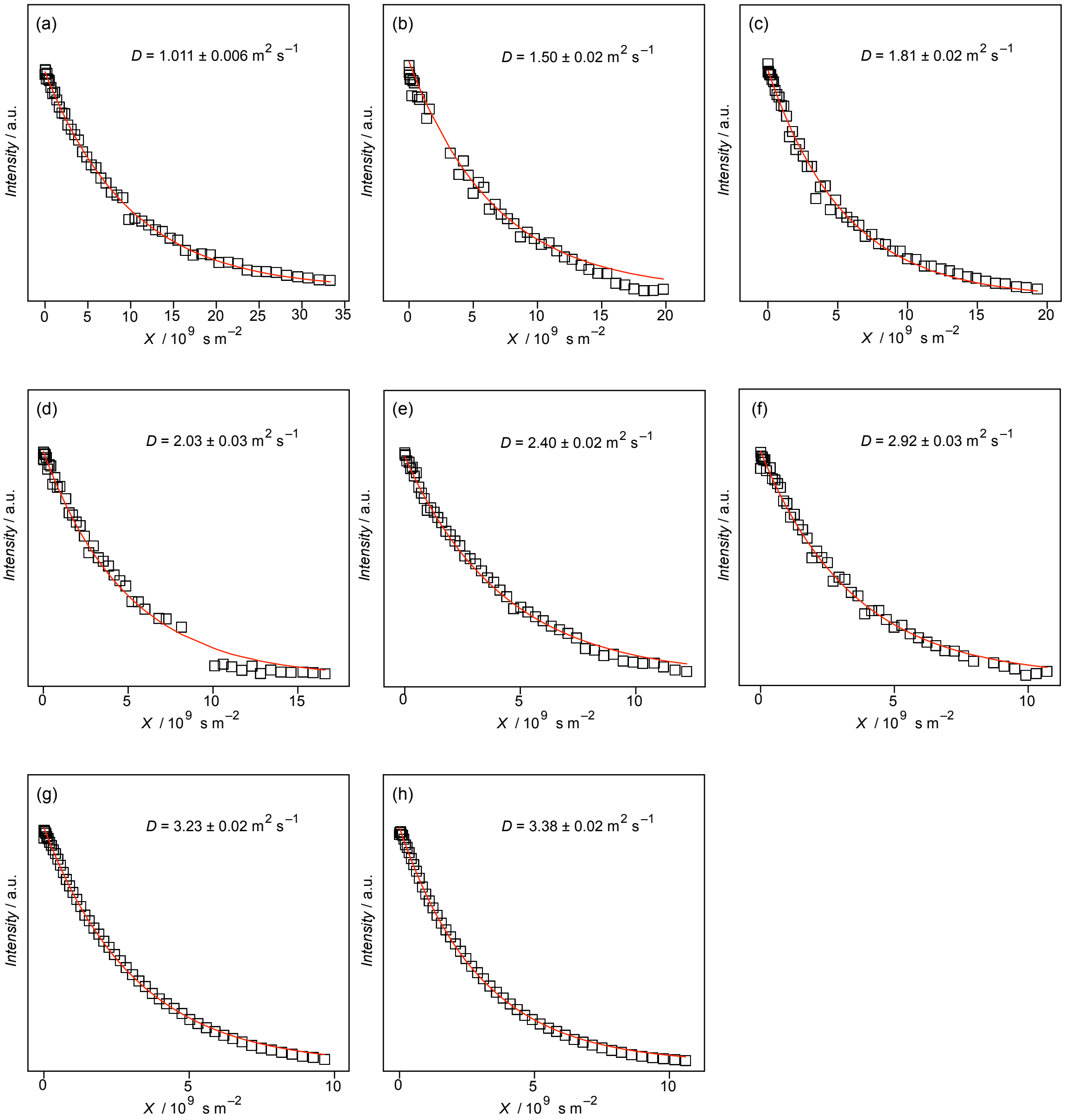


Figure S5. Plot of ^{1}H NMR signal intensities obtained from the diffusion experiments for **2** in chloroform-*d* at the concentrations of (a) 30, (b) 20, (c) 15, (d) 10, (e)8.0, (f) 5.0, (g) 2.0, and (h) 1.0 mmol L^{-1} and their fitting curves (red lines).

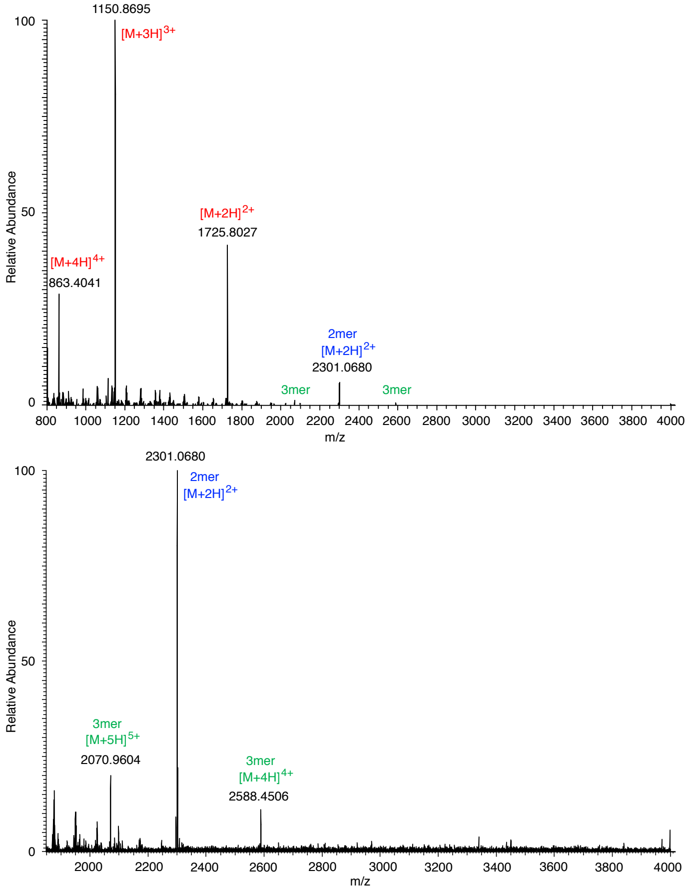


Figure S6. HRMS (ESI$^+$) spectrum of **2** (top panel) and its expanded view (bottom panel).

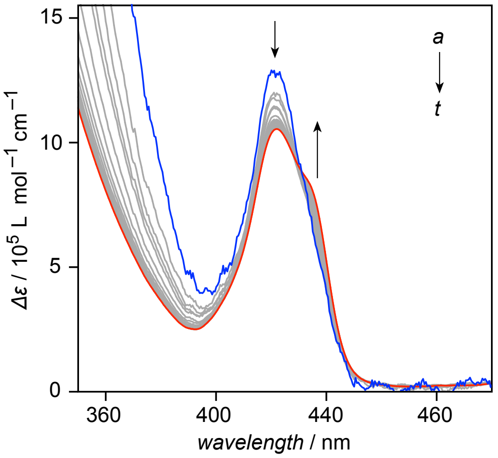


Figure S7. UV/vis spectral absorption changes seen for **2** in (+)-limonene at 90 °C. The concentrations are (a-t) 0.51, 1.0, 1.5, 2.0, 2.5, 3.5, 4.4, 5.3, 6.3, 7.2, 8.0, 8.9, 9.7, 10.6, 11.4, 12.2, 13.0, 14.0, 15.0, 15.8 × 10^{-8} mol L^{-1}. The blue and red lines indicate spectra of **2** at the concentrations of 0.51 × 10^{-8} mol L^{-1} and 15.8 × 10^{-8} mol L^{-1}, respectively.

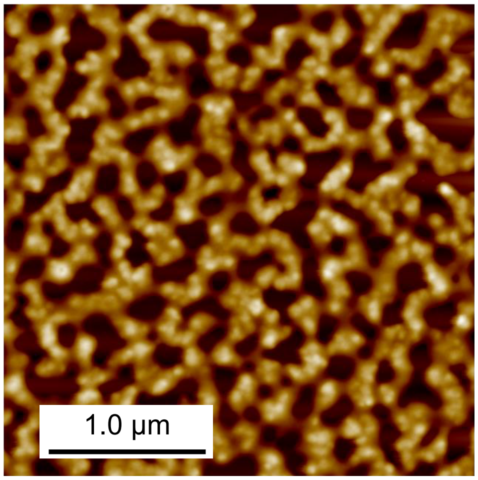


Figure S8. AFM image of the cast films of **2** on mica prepared from its (+)-limonene solution.

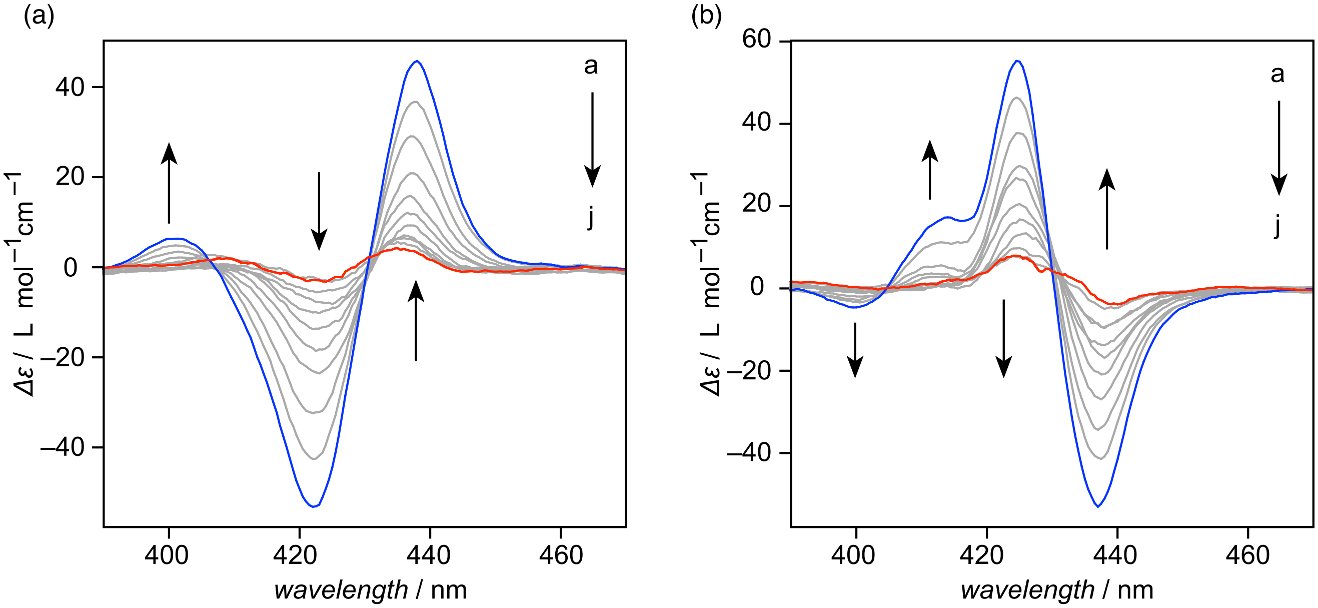


Figure S9. Valuable temperature ECD spectra of **2** (2.5×10^{-5} mol L^{-1}) in (a) (–)-α-pinene and (b) (–)-β-pinene. The temperatures are (a-j) 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0 °C. The red and blue lines denote the spectra observed at 100 °C and 0 °C, respectively.

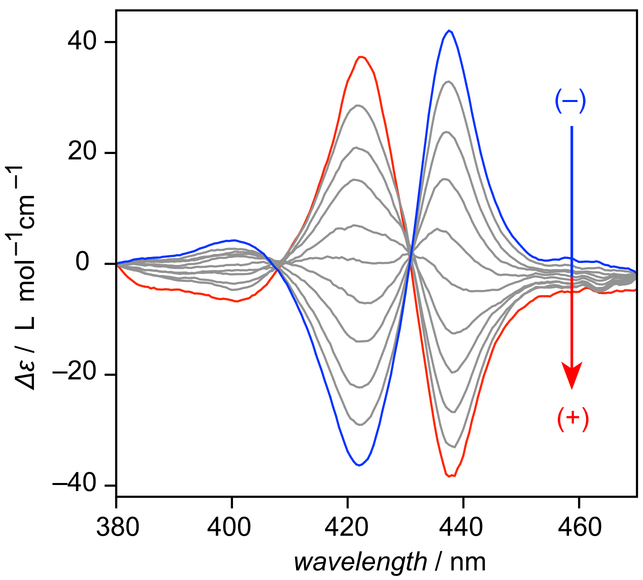
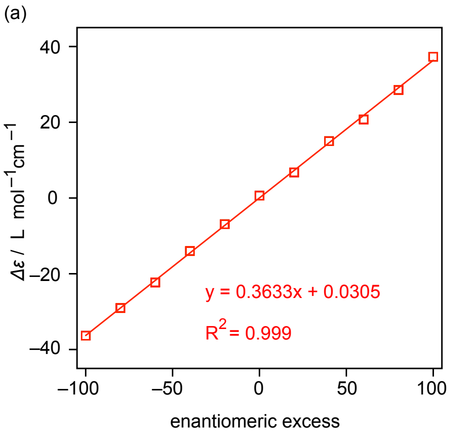
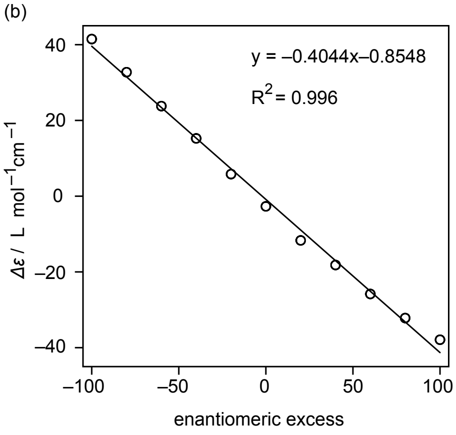


Figure S10. ECD spectra of **2** (2.5×10^{-5} mol L^{-1}) in the mixture of (+)- and (–)-α-pinene with various ee values. The ee values are 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0, –10, –20, –30, –40, –50, –60, –70, –80, –90, –100%, where ee = ([(+)-α-pinene] – [(–)-α-pinene]) / ([(+)-α-pinene] + [(–)-α-pinene])}.



422nm	
ee	Δ ε
100	37.2927433
80	28.5187582
60	20.7358768
40	15.0092076
20	6.76389828
0	0.62267451
-20	-6.9165056
-40	-14.000052
-60	-22.297289
-80	-29.040231
-100	-36.354081



437nm	
ee	Δ ε
100	-37.903137
80	-32.181483
60	-25.824892
40	-18.178104
20	-11.68455
0	-2.6949081
-20	5.81970634
-40	15.2501915
-60	23.7771043
-80	32.7335909
-100	41.4838001

Figure S11. Δ*ε* values of **2** (2.5×10^{-5} mol L^{-1}) in the mixture of (+)- and (–)-α-pinene with various ee values and the linear regression lines for the ee vs Δ*ε* values observed at (a) 422 nm and (b) 437 nm. The x and y indicate ee and Δ*ε* values, respectively. Enantiomeric excess (ee) = {([(+)-α-pinene] – [(–)-α-pinene]) / ([(+)-α-pinene] + [(–)-α-pinene])}.

References

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