Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Materials

Induced Preference for Axial Chirality in a Triarylmethylium *o,o*-Dimer upon Complexation with Natural γ-Cyclodextrin: Strong ECD Signaling and Fixation of Supramolecular Chirality to Molecular Chirality

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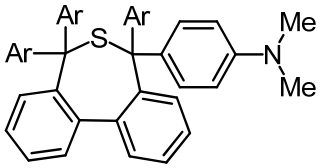
Experimental Details:

・Preparation of *rac*-5,7-dihydro-5,5,7,7-tetrakis(dimethylaminophenyl)dibenzo[*c*,*e*]thiepin **2**



To an aqueous solution of **1a**$^{2+}$·$(BF_4^-)_2$ (20.3 mg, 24.4 μmol) (10 mL) was added an aqueous solution of $Na_2S·9H_2O$ (290 mg, 1.21 mmol) (2 mL), and the mixture was stirred for 30 min. The resulting suspension was extracted with AcOEt (10 mL × 3), and the combined organic layer was washed with water (10 mL × 3) and brine. After drying over Na_2SO_4, the solvent was removed to give pure **2** (16.9 mg) as a white solid in quantitative yield.

decomp. 228-235 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.30-7.05 (br, 4H), 7.00 (dd, *J* = 7.7, 1.4 Hz, 2H), 6.88 (dt, *J* = 7.7, 1.7 Hz, 2H), 6.81 (dt, *J* = 7.3, 1.7 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 4H), 6.46 (d, *J* = 8.8 Hz, 2H), 6.39 (dd, *J* = 7.3, 1.4 Hz, 2H), 6.35 (s, 4H), 2.90 (s, 12H), 2.83 (s, 12H) ppm; IR (KBr) ν 3037, 2880, 2794, 1608, 1559, 1513, 1474, 1439, 1352, 1208, 1183, 1160, 1142, 1058, 1004, 948, 895, 811, 776, 749, 714, 578, 567, 535 cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε / M^{-1}cm^{-1}) 274 (60200), (MeCN) : 272 (64000); LR-MS (FD) m/z = 690 (20), 689 (55), 688 (M^+, bp), 656 (11), 537 (16), 536 (36), 329 (6), 328 (M^{2+}, 11); Anal. Calcd. for $C_{46}H_{48}N_4S$·0.5AcOEt: C 78.65, H 7.15, N 7.64. Found: C 78.67, H 7.85, N 7.50.

・Optical resolution of **2** by HPLC

A solution of *rac*-**2** in $CHCl_3$ (0.05 mL) was diluted with a solvent mixture (0.95 mL, hexane/AcOEt = 10). The whole mixture was charged on a column (Chiralpak IA) and eluted with hexane/AcOEt = 10. After 3 cycles, the enantiomers appeared as two peaks, and (*P*)-**2** was collected as the first fraction: ECD (MeCN) λ_{ext} / nm ($\Delta\varepsilon$/ $M^{-1}cm^{-1}$) 255 (–37), 275 (+11), and 309 (–9.1). The stereochemical assignment was carried out based on the DFT calculation.

・Preparation of optically active 5,7-dihydro-5,5,7,7-tetrakis(dimethylaminophenyl) dibenzo[*c*,*e*]thiepin (*M*)-**2** through treatment of $\mathbf{1a}^{2+}$ with Na_2S in the presence of γ-CyD

To a solution of $\mathbf{1a}^{2+}\cdot(BF_4^-)_2$ (20.4 mg, 24.6 μmol) in H_2O (4 mL) was added γ-CyD (64.7 mg, 49.9 μmol) at 24 °C, and the mixture was stirred for 75 min. Then the mixture was cooled down to 0 °C, and further stirred for 30 min. To the solution was added $Na_2S\cdot 9H_2O$ (110 mg, 459 μmol) at 0 °C, and the mixture was stirred for 3.5 h. The resulting suspension was allowed to warm up to 25 °C, and stirred for 16 h. After addition of 5 mL of saturated $NaHCO_3$ aq., the solution was cooled to 0 °C. The mixture was extracted with precooled AcOEt, and the organic layer was washed with precooled water and brine. The organic layer was cooled to −78 °C. To precooled MeCN in a cuvette were added a few drops of the above prepared solution of **2**, and the mixture was subjected to the measurement. The concentration was determined on the basis of UV-Vis spectrometry. According to the ECD spectrum [λ_{ext} / nm ($\Delta\varepsilon$/ $M^{-1}cm^{-1}$) 255 (+9.3)], optical purity of the sample was determined to be 25%ee.

Supplementary Figures:

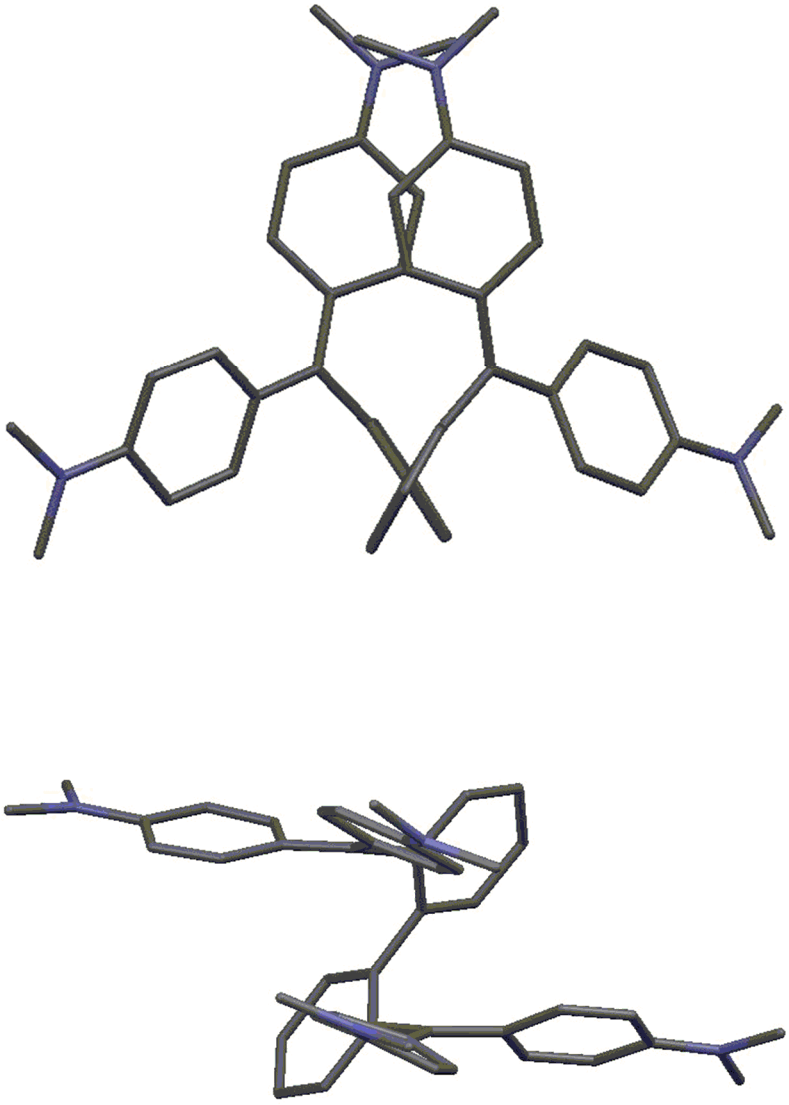


Fig. S1 Two views of molecular geometry determined by X-ray analysis on *rac*-**1a**$^{2+}$·($SbCl_6^-$)$_2$ (ref. 6a). The counter anions are omitted for clarity. The dication has a rough dimension of W 15 × D 7 × H 10 Å.

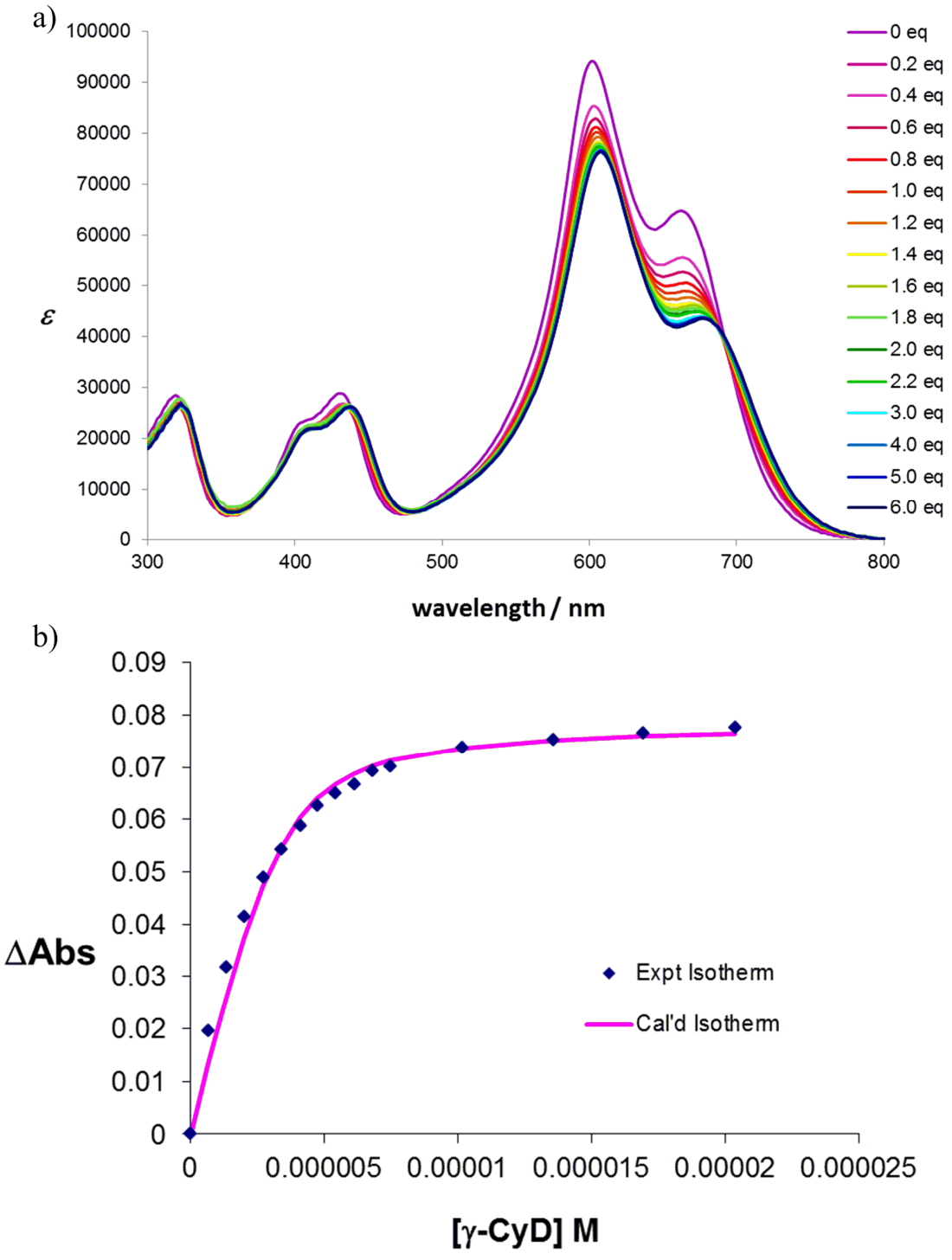


Fig. S2 (a) Changes in the UV-Vis spectrum of $\mathbf{1a}^{2+}\cdot(BF_4^-)_2$ (3.4×10^{-6} M) in H_2O upon addition of γ-CyD (0.2 - 6.0 equiv.) at 25 ºC. (b) The isotherm plot of ΔAbs at 662 nm.

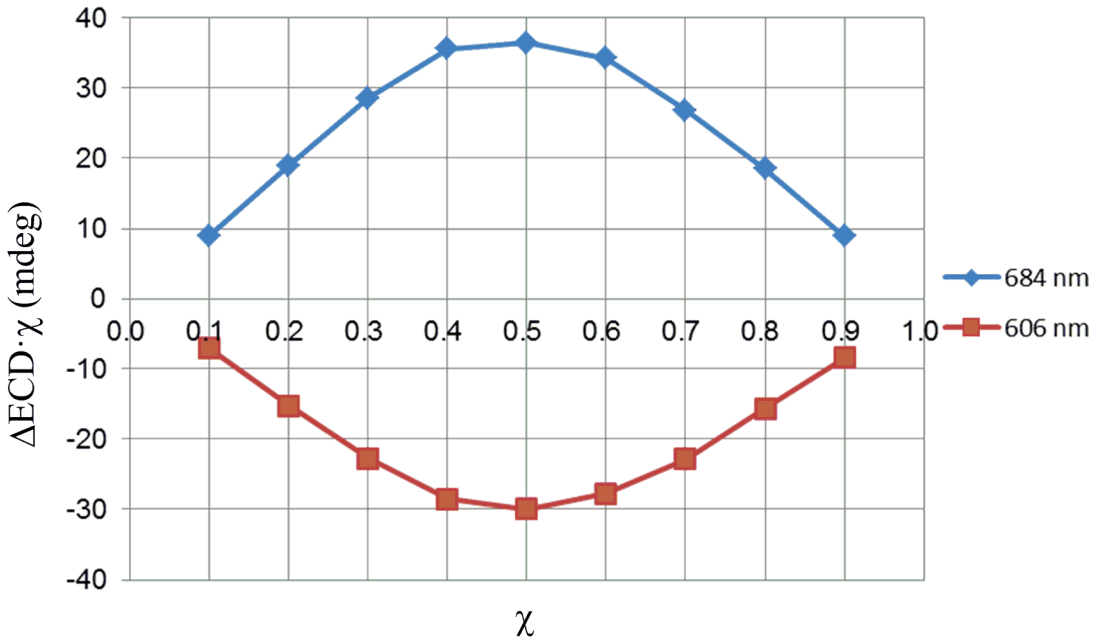


Fig. S3 Job plot for complexation between **1a**$^{2+}$·$(BF_4^-)_2$ and γ-CyD in H_2O monitored by ECD. χ = mol fraction of **1a**$^{2+}$·$(BF_4^-)_2$, [**1a**$^{2+}$·$(BF_4^-)_2$] / [**1a**$^{2+}$·$(BF_4^-)_2$]+[γ-CyD].

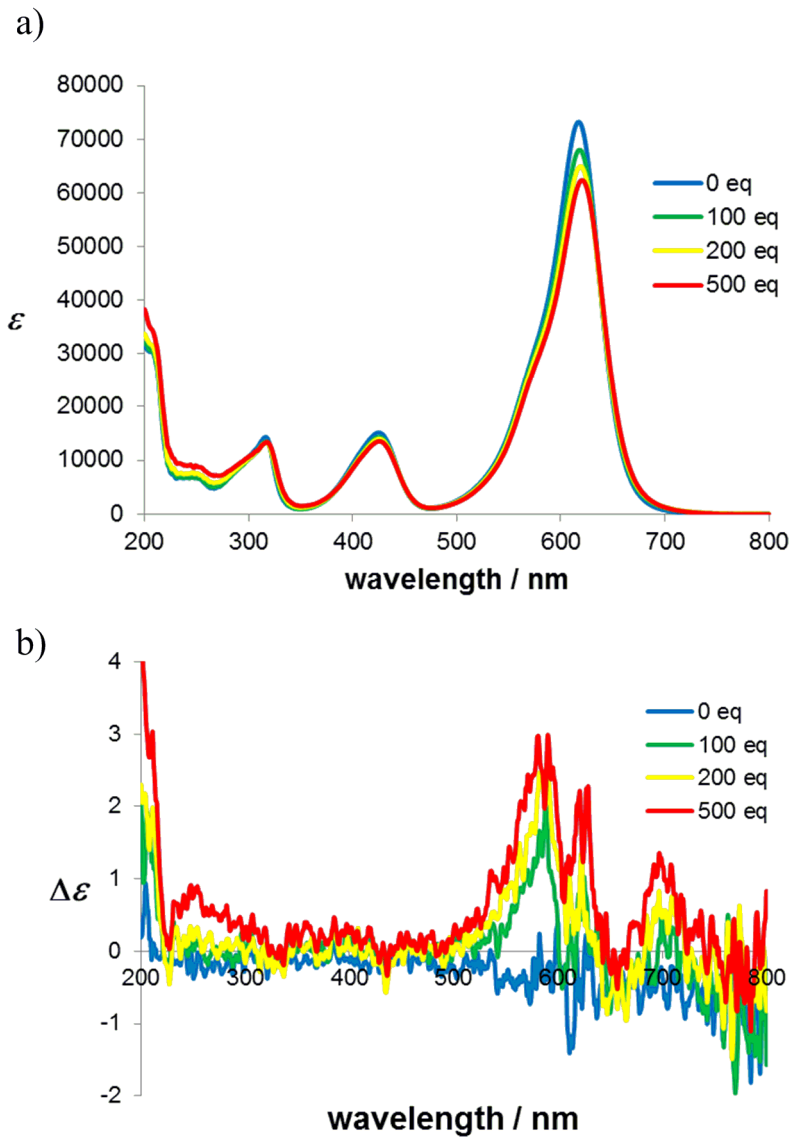
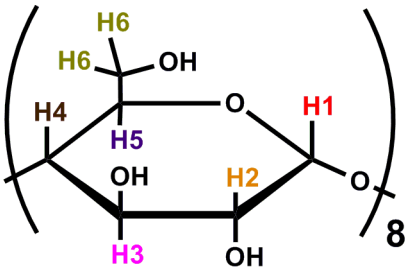


Fig. S4 Changes in the (a) UV-Vis and (b) ECD spectra of MG salt **3**·(BF_4^-) (1.9×10^{-5} M) in H_2O upon addition of γ-CyD (100 - 500 equiv.) at 25 ºC.



γ-CyD

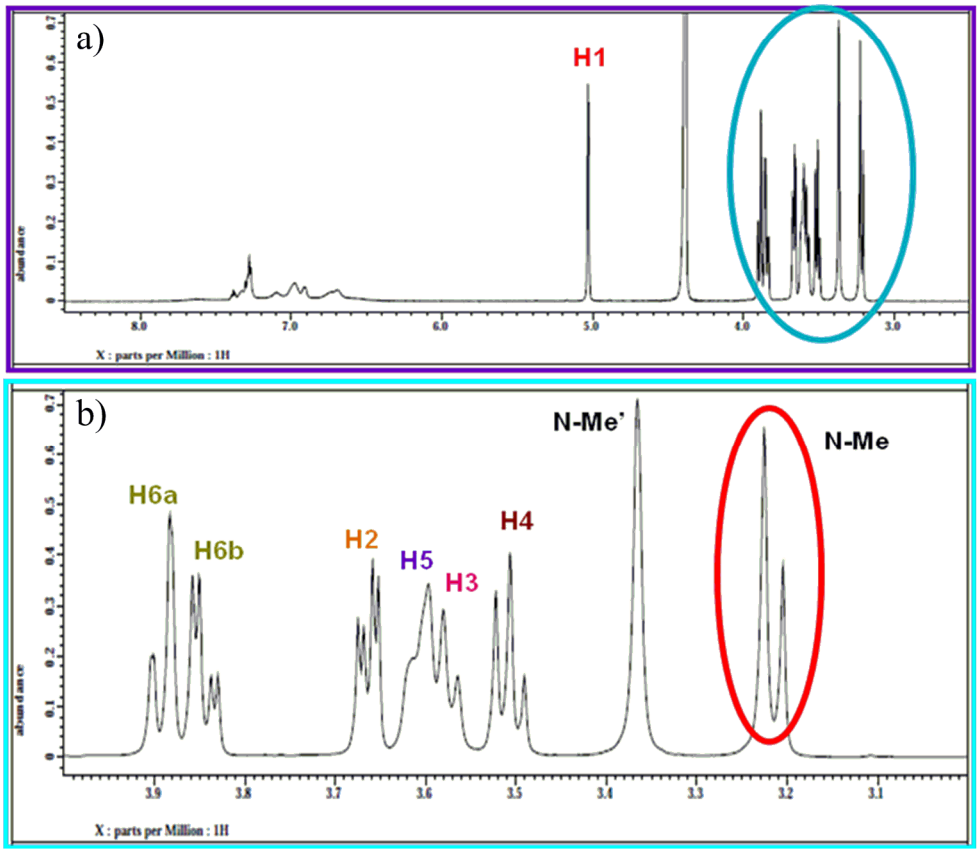


Fig. S5 (a) ^{1}H NMR spectrum (600 MHz) of **1a**$^{2+}$·$(BF_4^-)_2$ (1.0×10^{-3} M) in the presence of γ-CyD (1.0×10^{-3} M), and (b) its partial region, measured in D_2O at 65 ºC.

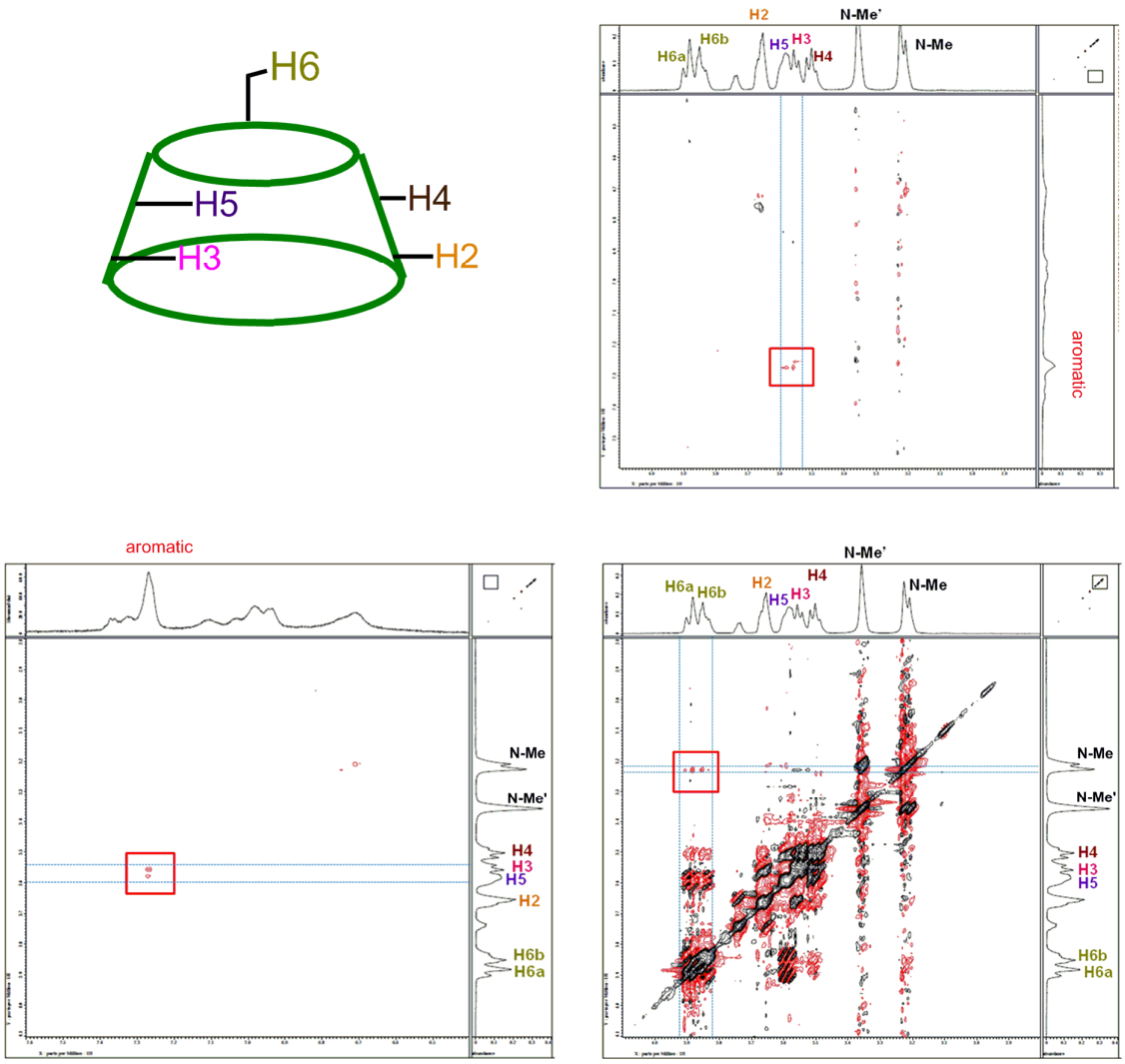


Fig. S6 Three partial regions of the ROESY spectrum (600 MHz) of **1a**$^{2+}$·(BF_4^-)$_2$ (3.3×10^{-4} M) in the presence of γ-CyD (3.3×10^{-4} M), measured in D_2O at 65 ºC.

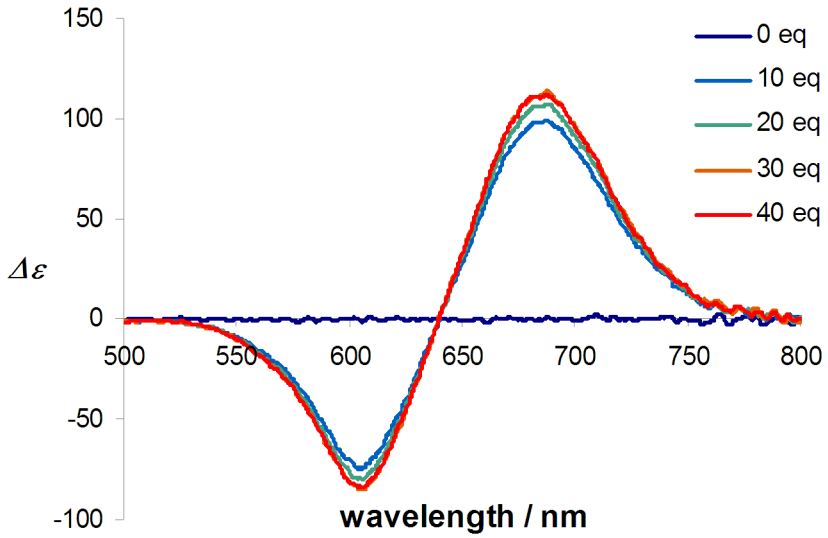


Fig. S7 Changes in the ECD spectrum of $\mathbf{1a}^{2+}\cdot(BF_4^-)_2$ (1.0×10^{-5} M) upon addition of γ-CyD (10 - 40 equiv.), measured in H_2O at 65 ºC. The orange (30 equiv.) and red (40 equiv.) lines are overlapped to indicate that γ-CyD (4.0×10^{-4} M) was enough to completely bias the equilibrium between free $\mathbf{1a}^{2+}$ and $\mathbf{1a}^{2+}$@γ-CyD in favor of the complexed state.

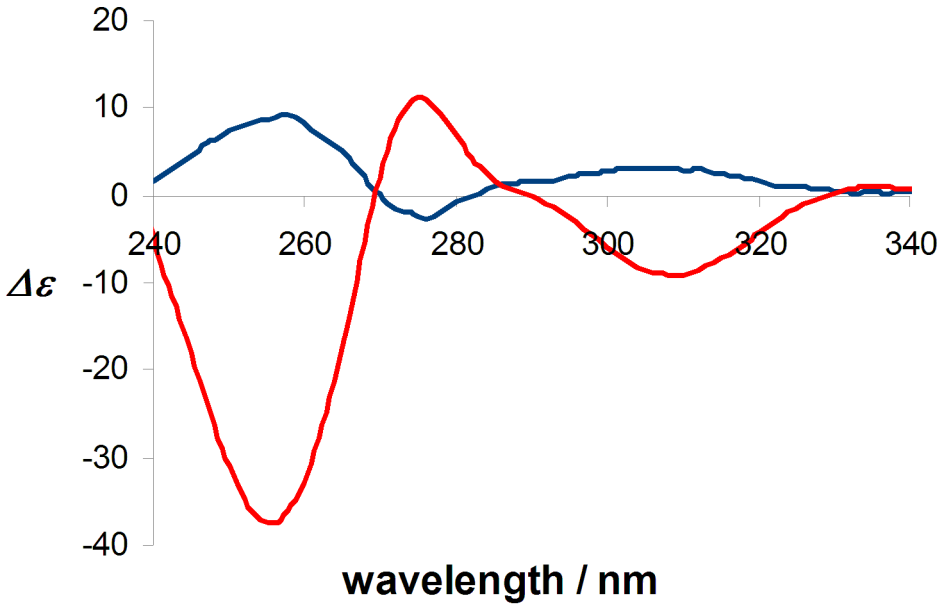


Fig. S8 ECD spectra of optically resolved **2** (1st fraction, *P*-helicity) (red line) and as-prepared **2** from $\mathbf{1a}^{2+}$ and Na_2S in the presence of γ-CyD (25%ee, *M*-helicity) (blue line), measured in MeCN.

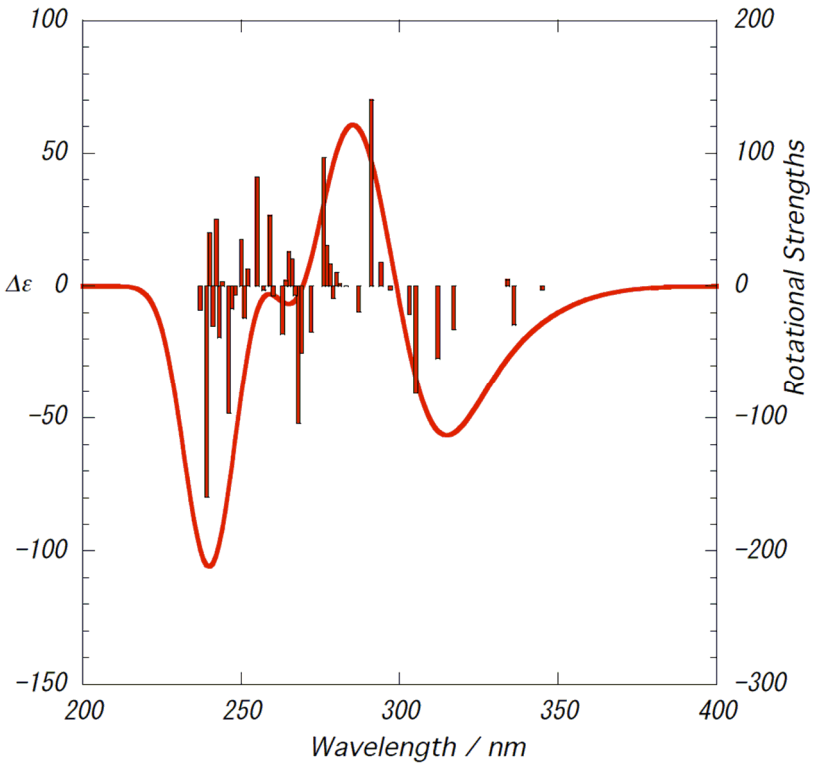


Fig. S9 Calculated CD spectrum of (*P*)-**2** by TD-DFT method (B3LYP/cc-pVDZ) including a PCM solvent effect. The molecular geometry was obtained after optimization by the DFT method (B3LYP/6-31G(d)) with a PCM solvent effect. The resultant rotational strengths were converted into a single CD curve by using a sum of Gaussian functions with a σ value of 1800 cm^{-1}.