Electronic Supplementary Information (ESI)

Achiral Guest-Induced Chiroptical Changes of Planar-Chiral Pillar[5]arene Containing One π-Conjugated Unit

Tomoki Ogoshi, Daiki Yamafuji, Tomohiro Akutsu, Masahiro Naito and Tada-aki Yamagishi*

Table of Contents

Experimental section

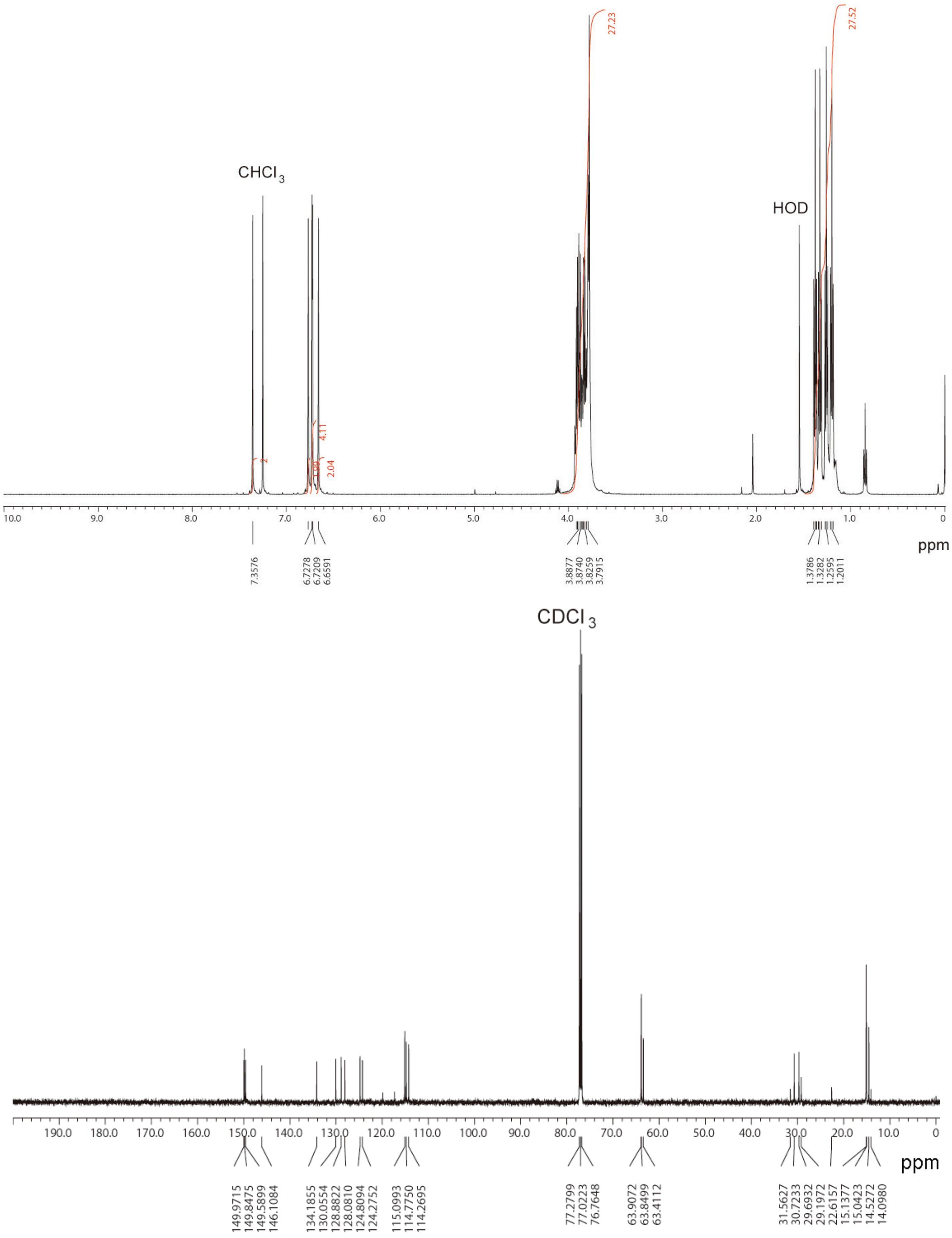
Materials. All solvents and reagents were used as supplied.

Measurements. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. Absorption spectra were recorded with a JASCO V-670. Fluorescence spectra were recorded on a Hitachi F-2500 fluorescence spectrometer at room temperature. For absorption and fluorescence measurements, one centimeter quartz cuvets were used. Chiral analytical HPLC was performed with a Chiral Pak IA column (0.46 × 25 cm) purchased from Daicel Chemical Industries, LTD. Separation was achieved using co-solvent (hexane:ethanol = 99:1) at a flow rate of 1 mL/min.

H3. Under a nitrogen atmosphere **H2**[S1] (834 mg, 1.00 mmol) was dissolved in dichloromethane (10 mL). Pyridine (480 mg, 6.00 mmol) and trifluoromethanesulfonic anhydride (0.500 mL, 3.00 mmol) were added and the reaction mixture was stirred. Then, propargyl bromide (0.25 mL, 3.00 mmol) was added at 0 °C and the reaction mixture was stirred at 25 °C for 24h. After removal of the solvent, the resulting solid was dissolved in dichloromethane and water. The organic layer was dried over anhydrous Na_2SO_4. After filtration, solvents were evaporated to give a solid. Silica column chromatography afforded a white solid (**H3**, 999 mg, 0.910 mmol, Yield: 91%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.36, 6.77, 6.73, 6.72, 6.66 (s, 10H), 3.36-4.00 (m, 26H, methylene), 1.20-1.45 (m, 24H, methyl). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 150.0, 149.8, 149.6, 146.1, 134.2, 130.1, 128.9, 128.1, 124.8, 124.3, 115.1, 114.8, 114.3, 63.9, 63.8, 63.4, 31.6, 30.7, 29.7, 29.2, 15.1, 15.0, 14.5. HRFABMS: m/z Calcd for C53H60F6O14S2 $[M]^+$: 1098.3329, found 1098.3294.

H4. To a solution of **H3** (527 mg, 0.480 mmol) in a mixture of THF (5 mL) and water (2 mL), 2,2'-bithiophene-5-boronic acid[S2] (403 mg, 1.92 mmol), Na_2CO_3 (20. Mg, 1.92 mmol) and $Pd(PPh_3)_4$ (110 mg, 0.0960 mmol) were added. The reaction mixture was refluxed for 24h. After removal of the solvent, the resulting solid was dissolved in dichloromethane and water. The organic layer was dried over anhydrous Na_2SO_4. After filtration, solvents were evaporated to give a solid. Silica column chromatography afforded a yellow solid (**H4**, 454 mg, 0.401 mmol, Yield: 84%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.25 (br, 2H), 7.21-7.24 (br, 2H), 7.12-7.14 (br, 2H), 7.03-7.07 (m, 4H), 6.72, 6.69, 6.64, 6.58, 6.08 (s, 10H), 3.52-4.14 (m, 26H), 1.30 (t, J = 6.9 Hz, 6H), 1.16 (t, J = 6.9 Hz, 6H), 1.02 (t, J = 6.9 Hz, 6H), 0.97 (t, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 150.1, 149.9, 149.7, 149.6, 142.3, 137.7, 137.5, 136.9, 133.6, 132.8, 129.0, 128.7, 127.8, 127.4, 127.2, 124.2, 123.7, 123.3, 115.4, 115.2, 114.9, 114.3, 64.1, 63.5, 33.3, 30.2, 29.4, 15.2, 15.0, 14.6. HRESIMS: *m*/*z* Calcd for C67H70Na1O8S4 $[M+Na]^+$: 1153.3851, found 1153.3848.

^{1}H and ^{13}C NMR spectra of H3



×

Fig. S1 ^{1}H and ^{13}C NMR spectra of **H3** in $CDCl_3$ at 25 °C.

^{1}H and ^{13}C NMR spectra of H4

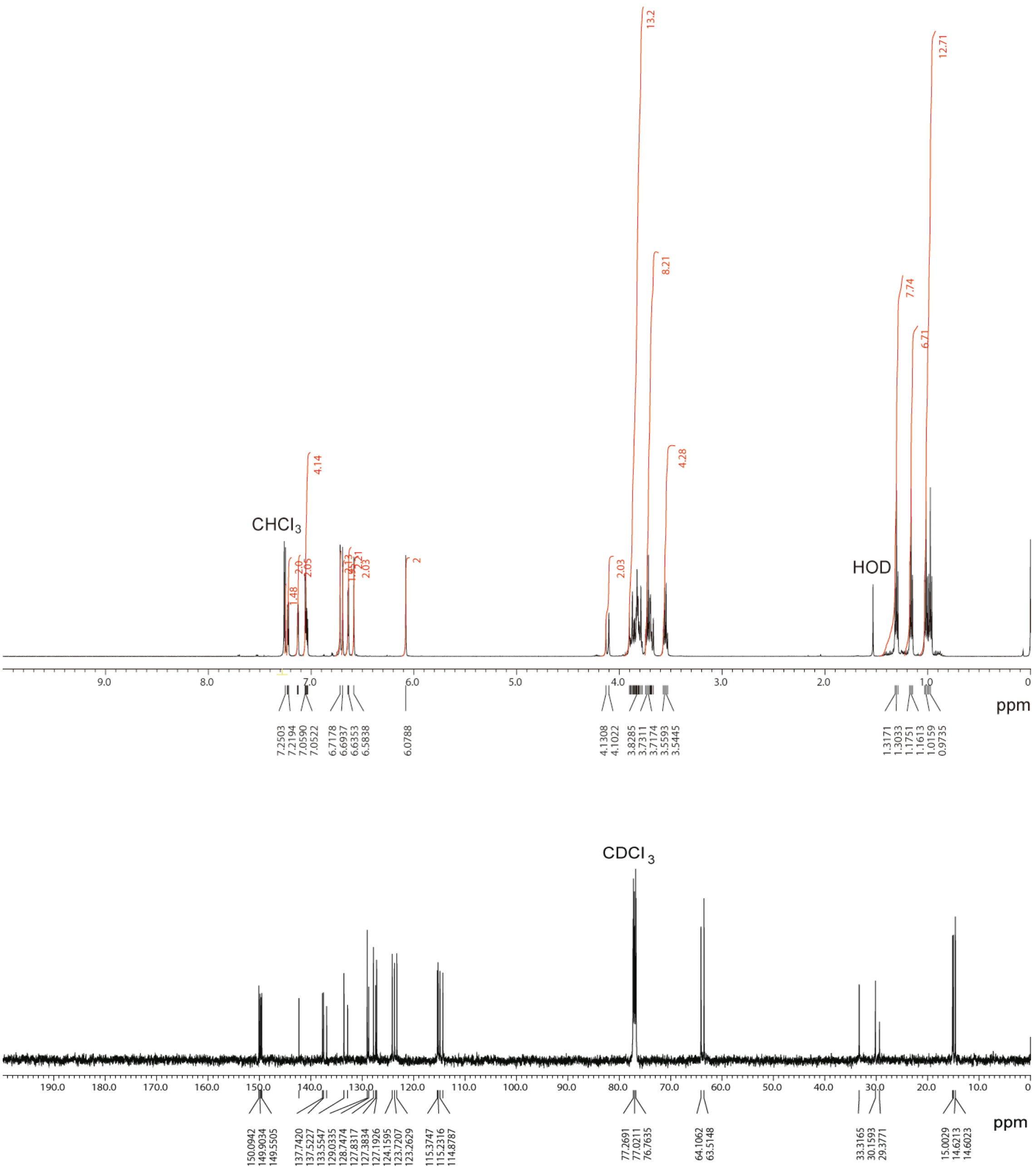


Fig. S2 ^{1}H and ^{13}C NMR spectra of **H4** in $CDCl_3$ at 25 °C.

Chiral HPLC trace of H4

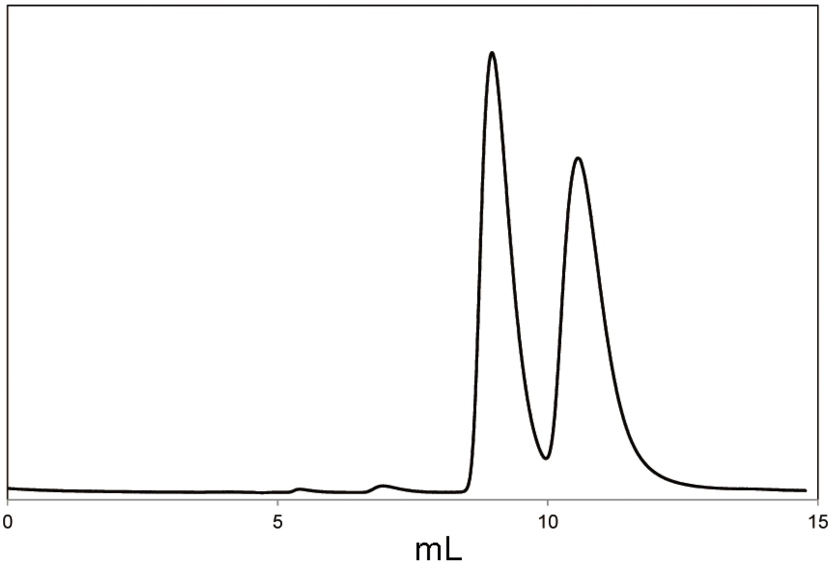


Fig. S3 Chiral HPLC trace of **H4**. Hexene/EtOH = 99/1 (vol %) was used as eluent.

CD spectra of planar-chiral [2]rotaxane consisting of pillar[5]arene wheel connecting two pyrene groups by etherification

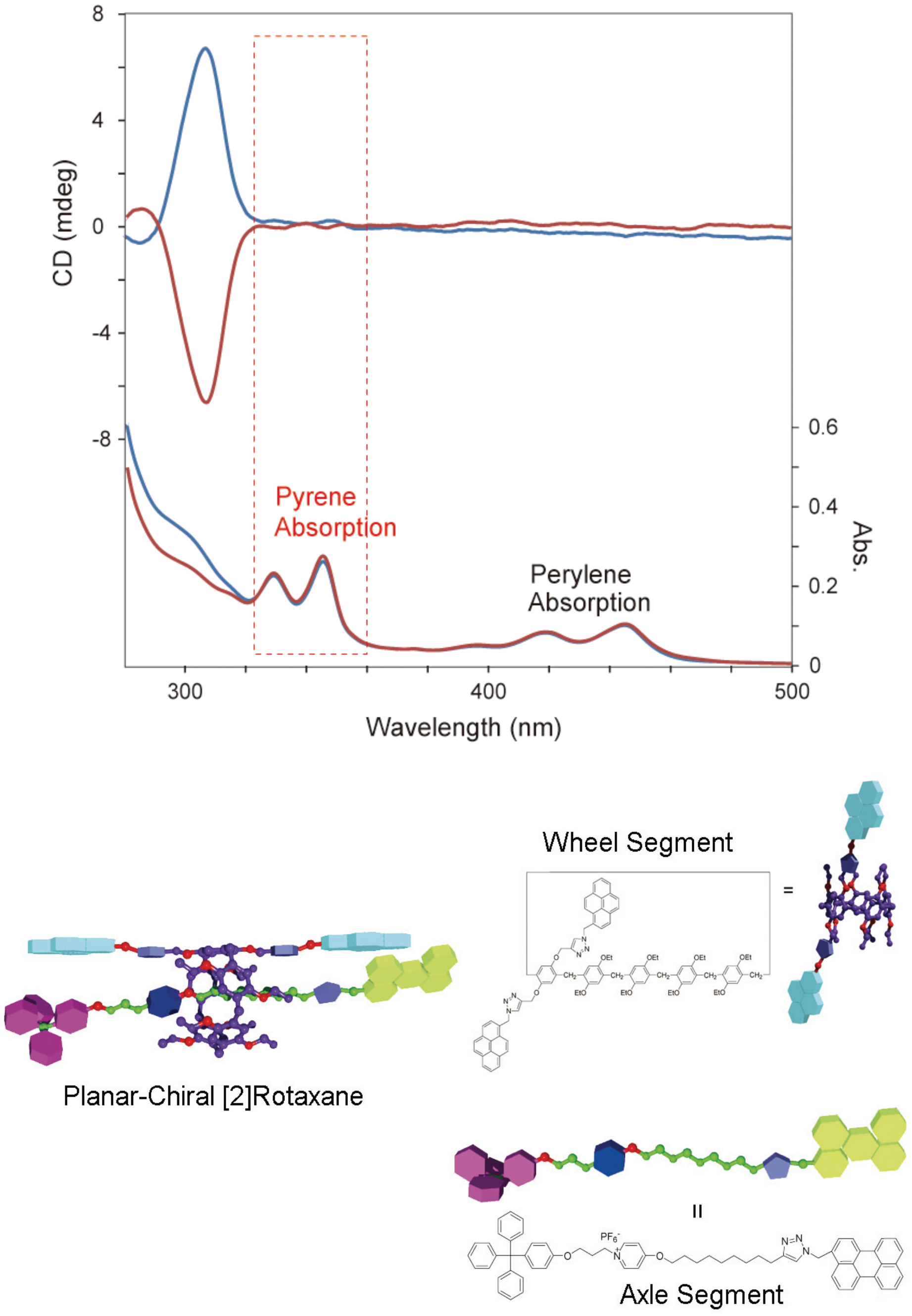


Fig. S4 UV and CD spectra of the planar-chiral [2]rotaxane consisting of *pR* or *pS* form wheel.[S3]

CPL spectra of *pR*-H4

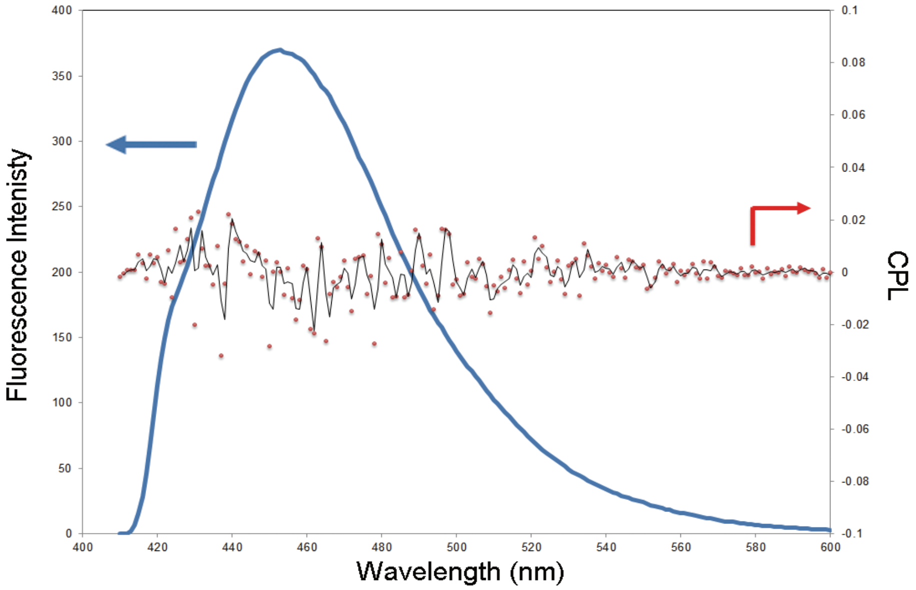


Fig. S5 Fluorescence (blue line) and CPL (red dots) spectra of *pR*-**H4** (40 µM) with 1,4-dicyanobutane (30 equiv. to *pR*-**H4**) in chloroform at 25 ^{o}C (excited at 340 nm).

CD spectral changes of *pS*-H4 with 1,4-dicyanobutane

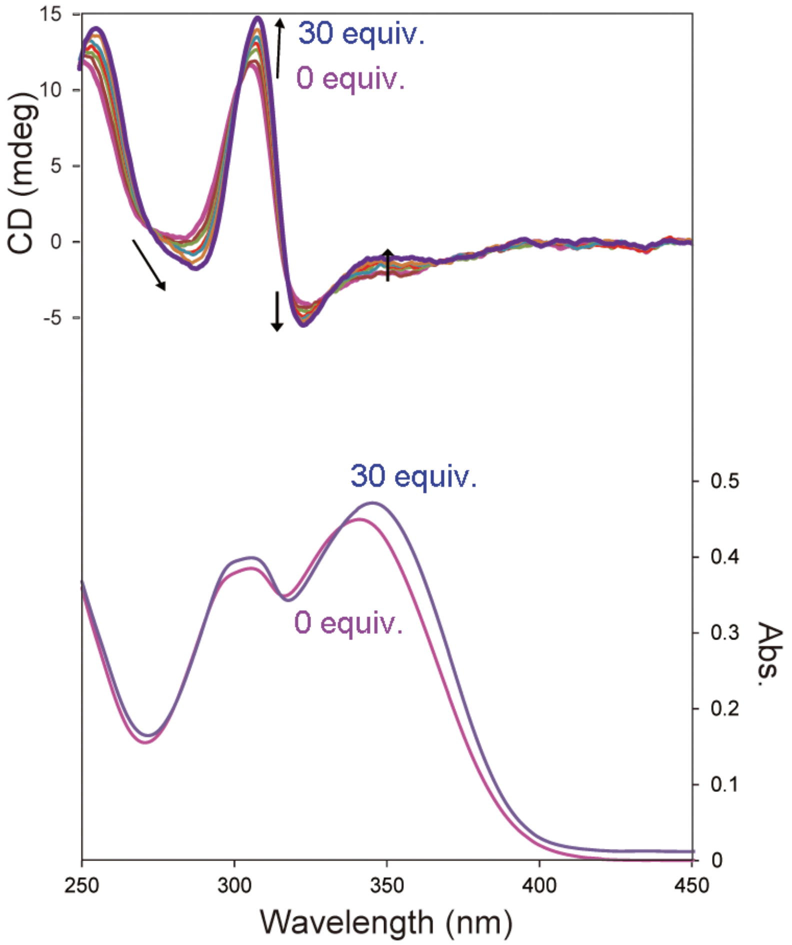


Fig. S6 CD spectral changes (40 μM, $CHCl_3$, 25 °C) of *pS*-**H4** upon addition of 1,4-dicyanobutane (0−30 equiv. to *pS*-**H4**).

CD titration of *pR*-H4 with 1,4-dicyanobutane

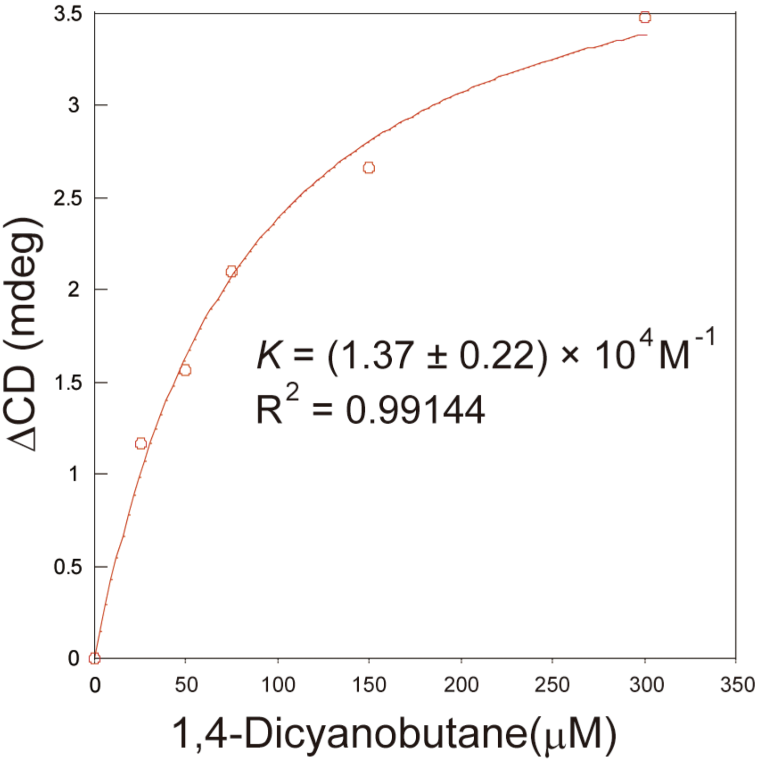


Fig. S7 CD titration of *pR*-**H4** with 1,4-dicyanobutane in $CHCl_3$ at 25 °C.

References

(S1) T. Ogoshi, D. Yamafuji, D. Kotera, T. Aoki, S. Fujinami and T. Yamagishi, *J. Org. Chem.*, 2012, **77**, 11146.
(S2) D. S. Kim and K. H. Kim, *J. Org. Chem.*, 2008, **73**, 6831.
(S3) T. Ogoshi, D. Yamafuji, T. Yamagishi and A. M. Brouwer, *Chem. Commun.*, 2013, **78**, 5468.