Supporting Information

Asymmetric Induction of Supramolecular Helicity in Calix[4]arene-based Triple-Stranded Helicate

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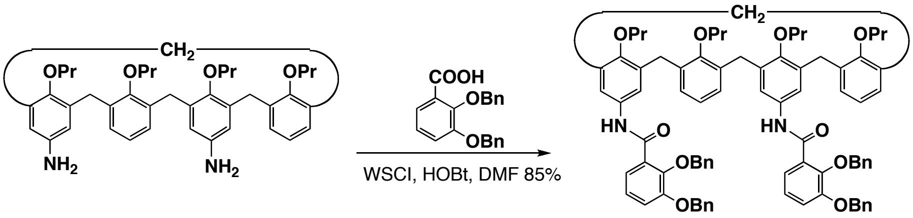
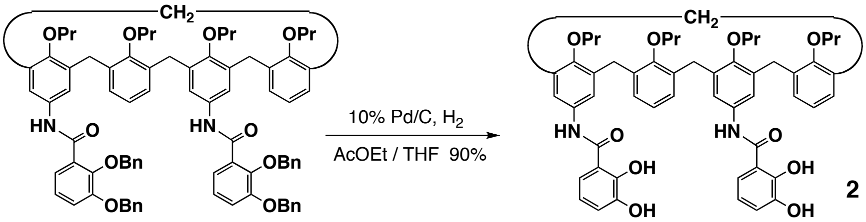
Synthetic procedures.



To a solution of the benzoic acid (540 mg, 1.6 mmol), and HOBt (220 mg, 1.6 mmol) in DMF (30 ml) was added WSCI•HCl (310 mg, 1.6 mmol), and the diaminocalix[4]arene (500 mg, 0.8 mmol). After stirred at room temperature for 4 h, the reaction mixture was poured into 1N hydrochloric acid and extracted with EtOAc. The organic layer was washed with aqueous sodium bicarbonate, dried over sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2) to give the desired calixarene as a white solid (850 mg, 85%). M.p. 259–261 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 2H), 7.88 (d, 2H, *J* = 6.0 Hz), 7.53–7.20 (m, 24H), 7.05 (s, 4H), 6.10–6.30 (m, 6H), 5.20 (s, 8H), 4.36 (d, 4H, *J* = 13.2 Hz), 3.95 (t, 4H, *J* = 7.8 Hz), 3.67(t, 4H, *J* = 7.8 Hz), 3.00 (d, 4H, *J* = 13.2 Hz), 1.88 (sext, 8H, *J* = 7.2 Hz), 1.10 (t, 6H, *J* = 7.2 Hz), 0.87 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ 162.4, 155.1, 154.3, 151.7, 146.5, 136.9, 136.4, 136.0, 133.0, 132.0, 129.2, 128.9, 128.8, 128.7, 128.3, 127.7, 127.5, 124.6, 123.6, 122.0, 120.5, 117.3, 77.2, 76.9, 76.5, 71.4, 30.9, 23.5, 22.9, 10.8, 9.9; IR (KBr) 3341, 1668, 1541 cm^{-1}; HR MS (FAB$^+$) *m/z*, calcd for $C_{82}H_{83}N_2O_{10}$ $[M+H]^+$ 1255.6047, found 1255.6031; Anal. Calcd for $C_{82}H_{82}N_2O_{10}$•$0.5H_2O$: C 77.88, H 6.62, N 2.22. Found: C 77.86, H 6.54, N 2.21.



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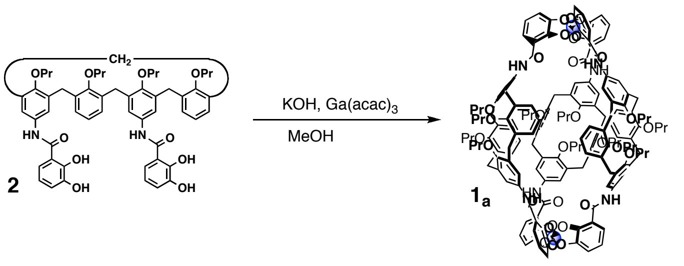
The above calix[4]arene derivative (300 mg, 0.24 mmol) were dissolved in EtOAc (10 ml) and THF (30 ml) in the presence of Pd/C (30 mg). After being stirred overnight under H_2 atmosphere at 45 ºC, the reaction mixture was filtered over celite column. The filtrate was concentrated in vacuo. The residue was purified by recrystallized from methanol to give white solid **2** (190 mg, 90%). M.p. 282–285 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.41 (s, 2H), 7.50 (s, 2H), 6.93 (d, 4H, *J* = 7.5 Hz), 6.92 (d, 2H, *J* = 7.8 Hz), 6.82 (t, 2H, *J* = 7.5 Hz), 6.68 (d, 2H, *J* = 7.8 Hz), 6.60 (s, 4H), 6.46 (t, 2H, *J* = 7.8 Hz), 5.68 (s, 2H), 4.48 (d, 4H, *J* = 13.0 Hz), 3.97 (t, 2H, *J* = 7.5 Hz), 3.76 (t, 2H, *J* = 7.5 Hz), 3.20 (d, 4H, *J* = 13.0 Hz), 2.10–1.86 (m, 8H), 1.05 (t, 6H, *J* = 7.5 Hz), 0.95 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ 168.1, 157.1, 153.9, 148.9, 145.8, 135.6, 135.1, 130.1, 128.7, 122.4, 121.3, 118.6, 118.2, 115.7, 114.1, 77.3, 76.7, 37.0, 23.3, 23.0, 10.5, 10.1; IR (KBr) 3382, 1644, 1462 cm^{-1}; HR MS (FAB$^+$) *m/z*, calcd for $C_{54}H_{58}N_2O_{10}$ $[M]^+$ 894.4091, found 894.4120; Anal. Calcd for $C_{54}H_{58}N_2O_{10}$: C 72.46, H 6.53, N 3.13. Found: C 72.06, H 6.38, N 3.11.



A 0.42 M solution of KOH (30 µl, 0.0125 mmol) in CH_3OH, and $Ga(acac)_3$ (1.48 mg, 0.004 mmol) was added to a solution of **2** (5.1 mg, 0.0057 mmol) in CH_3OH. The reaction mixture was stirred for 1h, and the solvent was removed in vacuo. The crude compound was washed with acetone to give desired compound $\mathbf{1_a}$ (5.6 mg, 90%). M.p. >300 ºC; ^{1}H NMR (300 MHz, CD_3OD) δ 7.18 (d, 12H, J = 7.5 Hz), 7.05 (dd, 6H, J = 8.1, 1.5 Hz), 6.93 (t, 6H, J = 7.5 Hz), 6.74 (dd, 6H, J = 7.5, 1.5 Hz), 6.39 (dd, 6H, J = 8.1, 7.5 Hz), 6.37 (s, 12H), 4.56 (d, 12H, J = 12.9 Hz), 4.21(m, 12H), 3.75 (t, 12H, J = 6.6 Hz), 3.25 (d, 12H, J = 12.9 Hz), 2.22–1.90 (m, 24H), 1.19 (t, 18H, J = 7.5 Hz), 0.98 (t, 18H, J = 7.2 Hz).

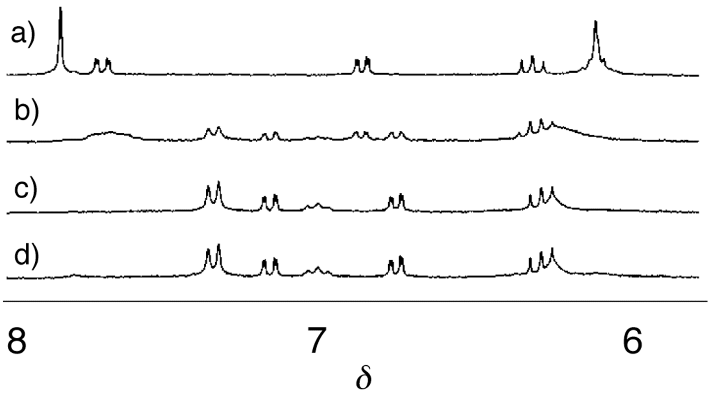


Figure S1. ^{1}H NMR spectra of $\mathbf{1_a}$ (3.7×10^{-3} M) in the presence of $Ga(acac)_3$ in CD_3OD at 298K. The concentrations of $Ga(acac)_3$ are (a) 0.0, (b) 1.1×10^{-3}, (c) 2.5×10^{-3}, (d) 3.7×10^{-3} mol L^{-1}.

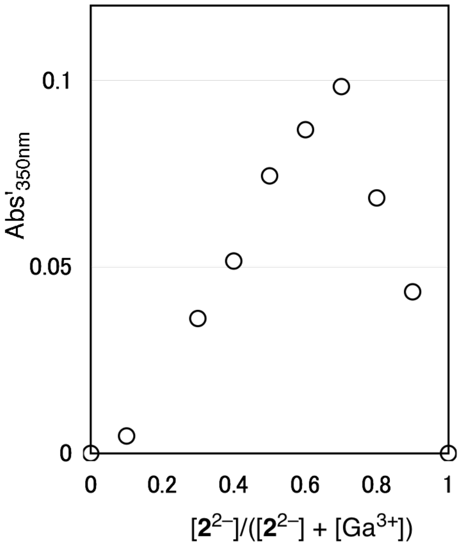


Figure S2. Job plot for dianion 2^{2-} with $Ga(acac)_3$ in CH_3OH at 298 K.

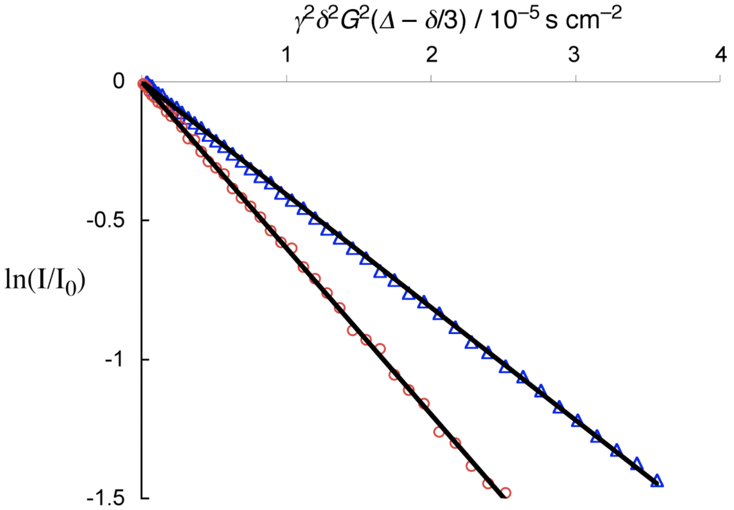


Figure S3. Stejskal-Tanner plots for $\mathbf{1_a}$ (red circle) and **2** (blue triangle).

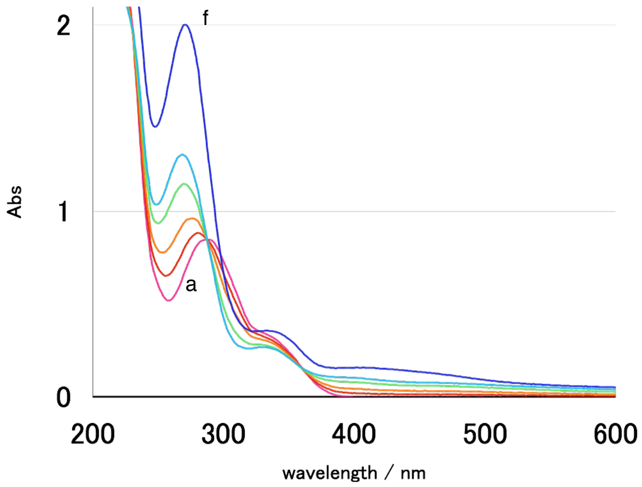


Figure S4. Absorption spectra of dianion 2^{2-} (3.9×10^{-5} mol L^{-1}) in the presence of $Fe(acac)_3$ in CH_3OH at 298K. The concentrations of $Fe(acac)_3$ are from the bottom (a) 0.0, (b) 0.8×10^{-5}, (c) 2.0×10^{-5}, (d) 2.6×10^{-5}, (e) 3.9×10^{-5}, (f) 7.8×10^{-5} mol L^{-1}.

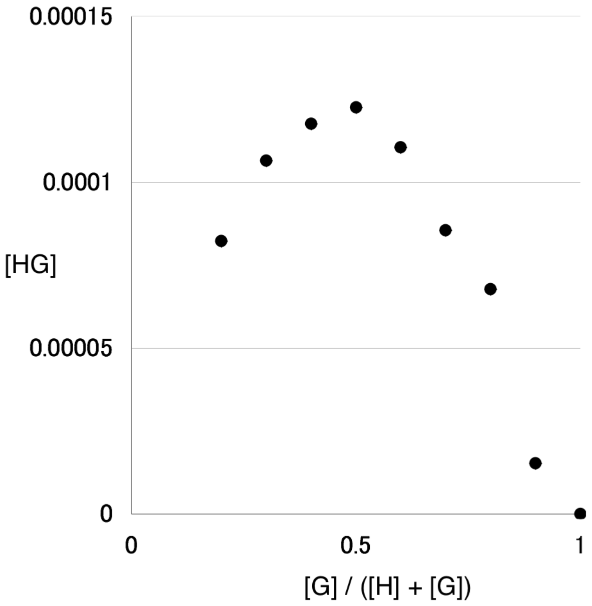


Figure S5. Job plot for $\mathbf{1}_a$ with guest **3** in methanol-d_4 at 293 K.

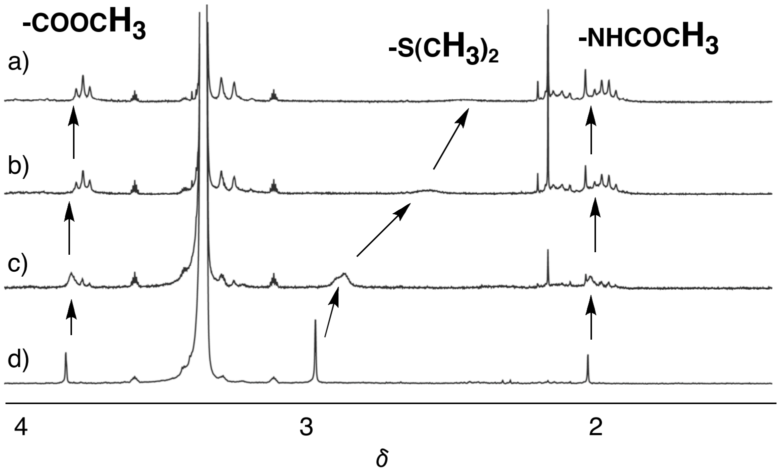


Figure S6. ^{1}H NMR spectra of **3** (0.9 mmol L^{-1}) in the presence of $\mathbf{1_a}$ in CD_3OD at 298K. The concentrations of $\mathbf{1_a}$ are (a) 0.0, (b) 0.09, (c) 0.45, (d) 0.9 mmol L^{-1}.

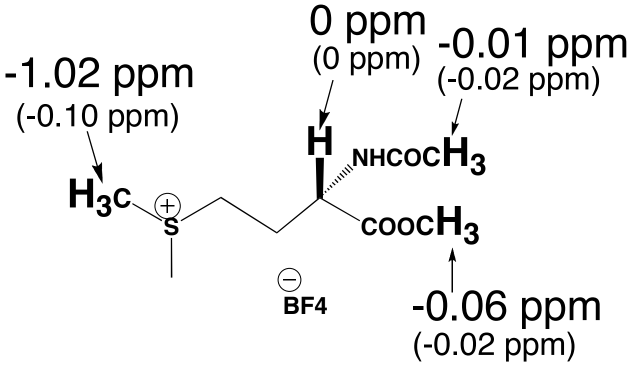


Figure S7. The CIS of the protons of **3** during the complexation with $\mathbf{1_a}$. The values in the parentheses indicate the CIS of the protons upon the addition of the large excess of $K_6Ga(cat)_3$ instead of $\mathbf{1_a}$.

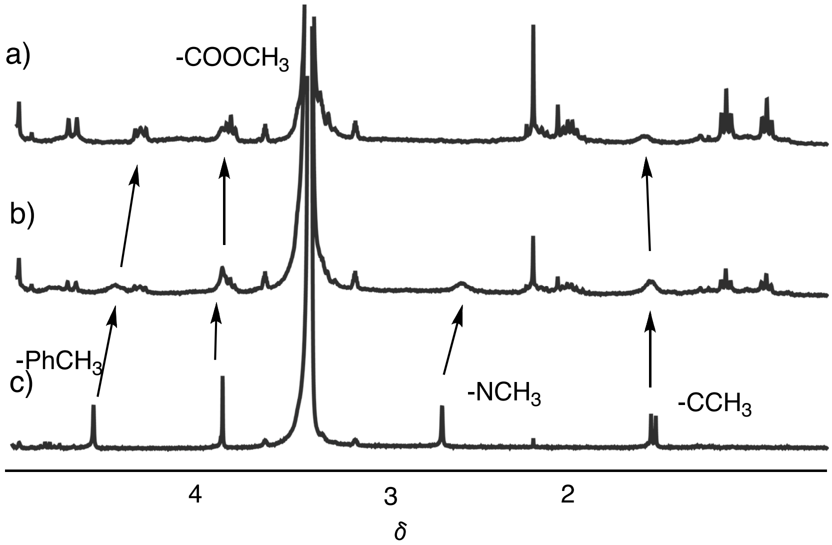


Figure S8. ^{1}H NMR spectra of **4** (5.8 mmol L^{-1}) in the presence of $\mathbf{1_a}$ in CD_3OD at 298K. The concentrations of

$\mathbf{1}_\mathrm{a}$ are (a) 0.0, (b) 0.58, (c) 1.74 mmol L^{-1}.

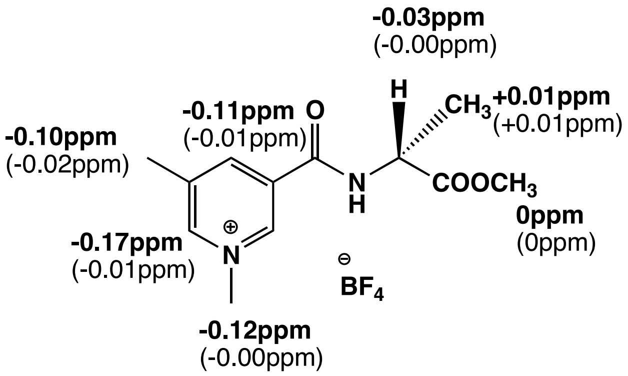


Figure S9. The CIS of the protons of **4** upon the addition of 0.1 equivalent of $\mathbf{1}_\mathrm{a}$. The values in the parentheses indicate the CIS of the protons upon the addition of 0.1 equivalent of $K_6Ga(cat)_3$ instead of $\mathbf{1}_\mathrm{a}$.

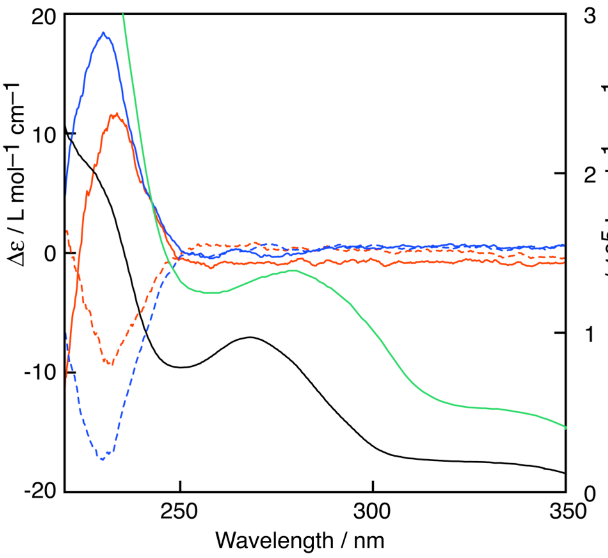


Figure S10. Absorption and circular dichroism spectra of $\mathbf{1}_\mathrm{a}$ (black), $\mathbf{1}_\mathrm{b}$ (green), $\mathbf{1}_\mathrm{a}$ (0.0066 mmol L^{-1}) with 197 eq. of *D*-**3** (blue solid) and with 197 eq. of *L*-**3** (blue dash), $\mathbf{1}_\mathrm{b}$ (0.0063 mmol L^{-1}) with 206 eq. of *D*-**3** (red solid) and with 206 eq. of *L*-**3** (red dash) in methanol at 273K.