Supplementary Information

Supramolecular chiroptical switching of helical-sense preferences through the two-way intramolecular transmission of a single chiral source associated with a dynamic helical loop

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Supplementary Figures

**Fig. S1** Partial $^1$H NMR spectra (400 MHz) of (R,R)-1,\(^1\) measured in chloroform-\(d\) at 223-293 K.

**Fig. S2a** Titration curves for the complexation of 3 with (R,R)-4 and the 1:1 binding constant, obtained by a curve fitting method,\(^2\) based on changes in the chemical shift for protons H\(D\) (blue), H\(E\) (yellow) and H\(F\) (green) upon complexation.
**Fig. S2b** Partial $^1$H NMR spectra (400 MHz) of ($R,R$)-1 ([1] = 1.06 mM) in the presence of 2 $^3$ [0 (1 only)-3 equiv.], measured in chloroform-$d$ at 303 K.

**Fig. S3** Titration curves for the complexation of 3 with ($R,R$)-4 and the 1:1 binding constant, obtained by a curve fitting method,$^2$ based on changes in the induced CD ($\Delta\varepsilon$) at 280 (blue), 298 (yellow), 313 (green) and 337 (red) nm upon complexation.
Fig. S4 (a) Partial $^1$H NMR spectra (400 MHz) of 3 in the presence of a monotopic guest (R)-8$^4$ [0 (3 only) and 6.8 equiv.], measured in chloroform-$d$ at 303 K; (b) UV spectrum of 3 (1.79×10$^{-4}$ M) in the presence of (R)-8 [0 (3 only, thin line), 8 and 16 (bold lines) equiv.]; (c) CD spectra of 3 (1.79×10$^{-4}$ M) in the presence of (R)-8 (8 and 16 equiv.). UV and CD spectra were measured in dichloromethane at room temperature.

**Experimental**

Preparation of 3

To a solution of 6 (183 mg, 0.731 mmol) and 7b (824 mg, 1.90 mmol) in THF/Et$_3$N (7 mL/7 mL) were added Pd(PPh$_3$)$_4$ (45 mg, 0.039 mmol) and CuI (13 mg, 0.068 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 50 °C for 20 hours. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (ethyl acetate/dichloromethane/hexane), followed by GPC (chloroform) to give 3 (470 mg) as a yellow solid in 75% yield. An analytical sample was obtained as a white solid by recrystallization from ethanol. 3: mp 139-140 °C; elemental analyses Found: C, 86.11; H, 6.10; N, 3.69. Calc. for C$_{54}$H$_{44}$N$_2$O$_2$: C, 86.14; H, 5.89; N 3.72%; IR (KBr) $\nu_{\text{max}}$/cm$^{-1}$ 3059, 2959, 2928, 2860, 2215, 1644, 1599, 1510; $^1$H NMR $\delta_H$(400 MHz, CDCl$_3$, Me$_4$Si)/ppm 7.54-7.51 (4H, m), 7.42 (4H, d, $J = 8.8$ Hz), 7.37 (2H, dt, $J = 1.2$, 7.6 Hz), 7.32 (2H, dt, $J = 1.6$, 7.6 Hz), 7.27-7.25 (4H, m), 7.22-7.17 (2H, m), 7.15-7.11 (4H, m), 6.95 (4H, d, $J = 8.8$ Hz), 3.88 (4H, t, $J = 7.6$ Hz), 1.61-1.53 (4H, m), 1.39-1.29 (4H, m), 0.90 (6H, t, $J = 7.6$ Hz); $^{13}$C NMR $\delta_C$(100 MHz, CDCl$_3$)/ppm 170.1, 143.7, 136.0, 132.6, 132.6, 131.6, 129.6, 129.0, 128.6, 128.1, 127.8, 127.4, 126.8, 124.4, 120.9, 93.5, 88.5, 81.4, 77.8, 50.1, 29.8, 20.1, 13.8; FD-LRMS $m/z$ 755.3 ([M+3]$^+$, 4%), 754.2 ([M+2]$^+$, 19), 753.2 ([M+1]$^+$, 61), 752.2 (M$^+$, 100); UV $\lambda_{\text{max}}$(CH$_2$Cl$_2$)/nm (log $\varepsilon$) 372 (sh, 4.03), 346 (sh, 4.42), 319 (sh, 4.60), 297 (4.73), 259 (4.76).
$^1$H NMR (400 MHz) spectrum of (R,R)-1, measured in chloroform-d at room temperature.$^1$

$^{13}$C NMR (100 MHz) spectrum of (R,R)-1, measured in chloroform-d at room temperature.$^1$
$^1$H NMR (400 MHz) spectrum of 3, measured in chloroform-$d$ at room temperature.

$^{13}$C NMR (100 MHz) spectrum of 3, measured in chloroform-$d$ at room temperature.
References and note


2. S. Akine, TitrationFit, program for analyses of host-guest complexation, Kanazawa University, Kanazawa, Japan, 2013.

