# **Supporting Information**

# Guest-induced Supramolecular Chirality in Ditopic Azoprobe/Cyclodextrin Complex in Water

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#### 1. Materials and Measurements.

All chemicals were obtained as special-grade reagents from Wako Pure Chemical Industries Ltd, and used as received. Water was doubly distilled and deionized by a Mill-Q water system (WG222, Yamato Sci. Co. Ltd. and Autopure WR-600G, Millipore).

<sup>1</sup>H NMR spectra were obtained with a JMN-ECX300 (JEOL Ltd.). UV-Vis spectra were recorded with a HITACHI U-3900 spectrometer (HITACHI Corp.) at room temperature (298 K). Quarts cuvette with a 1-cm path length was used. The ICD spectra were obtained with a J-820 spectrophotometer (JASCO Corp.) using a 1.0-cm quartz cell. The scan speed was 120 nm min<sup>-1</sup>.

#### 2. Syntheses of azoprobes.



Scheme S1 Synthesis route of **15C5-Azo-dpa**.

2.1. N-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15yl)azo-4-phenol (15C5-Azo-Ph). To 3.8 mL of water containing 4'-aminobenzo-15crown-5 (0.50 g, 1.76 mmol) and conc. HCl (0.43 mL), sodium nitrite (0.12 g, 1.76 mmol) in cold water (0.7 mL) was added and the solution was stirred for 1.0 h in an ice bath (0-2°C). Then phenol (0.16 g, 1.76 mmol) in cold water (1.0 mL) and aqueous NaOH solution (0.50 M, 5.0 mL) were added dropwise to the solution, followed by stirring for an additional 1.0 h. The yellow precipitate was filtered, rinsed with water, and dried *in vacuo*. The solid product was recrystallized from aqueous methanol to give yellow plate crystals (0.52 g, 76%)<sup>2</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 270 MHz)  $\delta$  10.16 (s, 1H, OH), 7.73 (d, *J* = 8.6 Hz, 2H, ArH), 7.47 (dd, *J* = 8.6 Hz, J=2.2 Hz, 1H, ArH), 7.37 (d, *J* = 2.2 Hz, 1H, ArH), 7.10 (d, *J* = 8.6 Hz, 1H, ArH), 6.90 (d, *J* = 8.6 Hz, 2H, ArH), 4.12 (m, 4H, CH<sub>2</sub>), 3.79 (m, 4H, CH<sub>2</sub>), 3.62 (m, 8H, CH<sub>2</sub>). Anal. Calcd. for  $C_{20}H_{24}N_2O_60.2H_2O$ : C, 61.27; H, 6.22; N, 7.15%. Found: C, 61.15; H, 6.31; N, 7.12%.

**15C5-Azo-Ph** was prepared by azo coupling of 4'-aminobenzo-15-crown-5 with phenol, followed by recrystallization from aqueous methanol solution<sup>2</sup>. The yield of **15C5-Azo-ph** was 53.0 % (0.748 g, 1.930 mmol).

2.2. N-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)azo-4-phenylbromoethylether (15C5-Azo-Br).

15C5-Azo-Br was prepared by procedure<sup>1</sup>, with some modifications 1,2-dibromoetane (1.562 g, 8.405 mmol) was slowly added (rate: about 3 seconds per one drop) and refluxed for 9 h. The yield of 15C5-Azo-Br was 51.5 % (0.490 g, 0.990 mmol).
2.3. (E)-2-(4-((2,3,5,6,8,9,11,12-1)))

octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecin-15-yl)diazenyl)phenoxy)-N,N-bis(pyridin-2-ylmethyl)ethan-1-amine. (15C5-Azo-dpa). The mixture, 0.090 g of 15C5-Azo-Br (0.182 mmol), 2.639 g (19.14 mmol) of K<sub>2</sub>CO<sub>3</sub> and 0.370 g (2.23 mmol) of KI were dissolved in 50 cm<sup>3</sup> acetonitrile with stirring. Then, 0.036 g of bis(2pyridylmethyl)amine (0.184mmol) added. After stirring for 24 h, the solution was filtrated and the solvent was removed under vacuo to obtain orange solid product. The product was purified by column chromatography (silica gel/dichloromethane : methanol = 9: 1). The product was obtained from the third fraction after removing the eluent under vacuo. The yield of 15C5-Azo-dpa was 46.6 % (0.052 g, 0.0848 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.50-8.45 (dd,  $J_{lk}$  = 4.8 Hz,  $J_{li}$  = 1.3 Hz, 2H, ArH<sub>1</sub>), 7.82-7.72 (d,  $J_{de} = 8.7$  Hz, 2H, ArH<sub>d</sub>), 7.76-7.71 (dd,  $J_{ik} = 8.4$ ,  $J_{il} = 1.3$ Hz, 2H, ArH<sub>i</sub>), 7.59-7.55 (d, J<sub>ij</sub> = 7.8 Hz, 2H, ArH<sub>i</sub>), 7.53-7.48 (dd, J<sub>ba</sub> = 8.4 Hz, , J<sub>bc</sub> = 2.4 Hz, 1H, ArH<sub>b</sub>), 7.40-7.39 (d,  $J_{cb} = 2.4$  Hz, 1H, ArH<sub>c</sub>), 7.26-7.20 (ddd,  $J_{kj} = 8.4$  Hz,  $J_{kl} = 4.8$  Hz,  $J_{ki} = 4.8$ 1.4 Hz, 2H, ArH<sub>k</sub>), 7.14-7.10 (d,  $J_{ab} = 8.4$ , 1H, ArH<sub>a</sub>), 7.07-7.03 (d,  $J_{ed} = 8.7$ , 2H, ArHe), 4.21 (t, 2H, Hf), 4.15-4.01 (m, 4H, Hn), 3.84-3.77 (m, 4H, Hm), 3.67-3.54 (m, 8H,  $H_{0,p}$ ), 2.93 (t, 2H,  $H_g$ ), negative ESI-MS (*m*/*z*): Calcd. for C<sub>34</sub>H<sub>39</sub>N<sub>5</sub>O<sub>6</sub> Na (M<sup>-</sup>): 613.7, Found: 613. Anal. Calcd. for C<sub>34</sub>H<sub>39</sub>N<sub>5</sub>O<sub>6</sub>: C, 66.48; H, 6.36; N, 11.41%. Found: C, 66.07; H, 6.43; N, 11.66%.



Fig. S1. Structure of 15C5-Azo-dpa.



Fig. S2 <sup>1</sup>H NMR spectrum of **15C5-Azo-dpa** (300 MHz in CDCI<sub>3</sub>).



Fig. S3 ESI-MS spectrum of **15C5-Azo-dpa**.

### 3. Job's plot analysis for 15C5-Azo-dpa/ $\gamma$ -CyD complex.



Fig. S4 ICD spectra of **15C5-Azo-dpa**/ $\gamma$ -CyD sensors (upper), [**15C5-Azo-dpa**] = 10-70  $\mu$ M, [ $\gamma$ -CyD] = 10-70  $\mu$ M, [Zn<sup>2+</sup>] = 100  $\mu$ M, [K<sub>2</sub>CO<sub>3</sub>] = 50 mM, in 4% DMSO aq., pH = 11.0 at 25°C; (M = mol dm<sup>-3</sup>). Job's plot calculated with the ICD spectra at 395 nm (bottom).

### 4. Binding constant of 15C5-Azo-dpa/y-CyD complex.

Host = H, Guest = G Host · Guest = HG  $\begin{array}{c} K\\ [H] + [G] \rightleftharpoons [HG] \\ \hline \\ K = [HG] / [H] [G] \\ [Ht] = [H] + [HG] \\ (2) \\ [Gt] = [G] + [HG] \\ (3) \\ \theta = \varepsilon_{H} [H]d + \varepsilon_{HG} [HG]d \\ (4) \\ \end{array}$ from equation (1), (2), (3), (4)  $\theta = (\theta_{0} + \theta_{\lim} K [G_{t}]) / (1 + K [G_{t}]) \\ ([G] \gg [H]) \end{array}$ 

The ICD spectrum changes at 395 nm are shown in Fig. S5 and Fig. S6 as a function of carbonate  $(CO_3^{2-})$  or acetate  $(CH_3CO_2^{-})$  ion concentration, and the observed results were well fitted with the theoretical curves (solid lines in Fig. S5, Fig. S6).



Fig. S5 ICD spectrum of **15C5-Azo-dpa**/ $\gamma$ -CyD sensors, [**15C5-Azo-dpa**] = 40  $\mu$ M, [Zn<sup>2+</sup>] = 40  $\mu$ M, [K<sub>2</sub>CO<sub>3</sub>] = 0 - 80 mM, [KCI] = 0 - 80 mM, [ $\gamma$ -CyD] = 5 mM, in 4% DMSO aq., pH = 11.0 at 25°C; (M = mol dm<sup>-3</sup>).



Fig. S6 ICD spectrum of **15C5-Azo-dpa**/ $\gamma$ -CyD sensors, [**15C5-Azo-dpa**] = 40  $\mu$ M, [Zn<sup>2+</sup>] = 40  $\mu$ M, [CH<sub>3</sub>CO<sub>2</sub>K] = 0 - 100 mM, [KNO<sub>3</sub>] = 0 - 100 mM, [ $\gamma$ -CyD] = 5 mM, in 4% DMSO aq., pH = 7.0 at 25°C; (M = mol dm<sup>-3</sup>).

## 5. <sup>1</sup>H NMR analysis of 15C5-Azo-dpa/*y*-CyD complex with H-H COSY.



Fig. S7 H-H COSY spectrum of **15C5-Azo-dpa**/ $\gamma$ -CyD sensors, adding Zn<sup>2+</sup>, K<sup>+</sup>, CO<sub>3</sub><sup>2-</sup> at 22.8°C, 500 MHz, scans:64, acquisition time; 0.1271 sec, relaxation delay; 1 sec, repetition time; 1.1271, data points:512x512.

## 6. <sup>1</sup>H NMR analysis of 15C5-Azo-dpa/*p*-CyD complex with NOESY.



Fig. S8 NOESY spectra of **15C5-Azo-dpa**/ $\gamma$ -CyD sensors, (a) none, (b) adding Zn<sup>2+</sup>, (c) adding Zn<sup>2+</sup>, K<sup>+</sup>, CO<sub>3</sub><sup>2-</sup> at 22.8°C, 500 MHz, scans:128, acquisition time; 0.1422 sec, relaxation delay; 1 sec, mixing time; 500 msec.

### References

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