## 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).
${ }^{1} \mathrm{H}$ 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 $1-\mathrm{cm}$ path length was used. The ICD spectra were obtained with a J-820 spectrophotometer (JASCO Corp.) using a $1.0-\mathrm{cm}$ quartz cell. The scan speed was 120 $\mathrm{nm} \min ^{-1}$.

## 2. Syntheses of azoprobes.





Scheme S1 Synthesis route of 15C5-Azo-dpa
2.1. $\mathbf{N}-(\mathbf{2 , 3 , 5}, 6,8,9,11,12-o c t a h y d r o-1,4,7,10,13-b e n z o p e n t a o x a c y c l o p e n t a d e c i n-15-~$ yl)azo-4-phenol (15C5-Azo-Ph). To 3.8 mL of water containing 4 '-aminobenzo-15-crown-5 $(0.50 \mathrm{~g}, 1.76 \mathrm{mmol})$ and conc. $\mathrm{HCl}(0.43 \mathrm{~mL})$, sodium nitrite $(0.12 \mathrm{~g}, 1.76$ $\mathrm{mmol})$ in cold water $(0.7 \mathrm{~mL})$ was added and the solution was stirred for 1.0 h in an ice bath $\left(0-2^{\circ} \mathrm{C}\right)$. Then phenol $(0.16 \mathrm{~g}, 1.76 \mathrm{mmol})$ in cold water $(1.0 \mathrm{~mL})$ and aqueous NaOH solution ( $0.50 \mathrm{M}, 5.0 \mathrm{~mL}$ ) 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 $(0.52 \mathrm{~g}, 76 \%)^{2} .{ }^{1} \mathrm{H}$ NMR (DMSO- $\left.d_{6}, 270 \mathrm{MHz}\right) \delta 10.16$ (s, $1 \mathrm{H}, \mathrm{OH}$ ), 7.73 (d, $J=8.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}$ ), 7.47 (dd, $J=8.6 \mathrm{~Hz}, \mathrm{~J}=2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 7.37 (d, $J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 7.10 (d, $J=8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 6.90 (d, $J=8.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}$ ),
$4.12\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.79\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.62\left(\mathrm{~m}, 8 \mathrm{H}, \mathrm{CH}_{2}\right)$. Anal. Calcd. for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{6} 0.2 \mathrm{H}_{2} \mathrm{O}: \mathrm{C}, 61.27$; 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 ${ }^{2}$. The yield of 15C5-Azoph was $53.0 \%(0.748 \mathrm{~g}, 1.930 \mathrm{mmol})$.
2.2. $\mathrm{N}-(\mathbf{2 , 3 , 5 , 6 , 8 , 9 , 1 1 , 1 2 - o c t a h y d r o - 1 , 4 , 7 , 1 0 , 1 3 - b e n z o p e n t a o x a c y c l o p e n t a d e c i n - 1 5 -}$ yl)azo-4-phenylbromoethylether ( $15 \mathrm{C} 5-\mathrm{Azo}-\mathrm{Br}$ ).
15C5-Azo- Br was prepared by procedure ${ }^{1}$, with some modifications 1,2-dibromoetane $(1.562 \mathrm{~g}, 8.405 \mathrm{mmol}$ ) was slowly added (rate: about 3 seconds per one drop) and refluxed for 9 h . The yield of $\mathbf{1 5 C 5}-\mathbf{A z o}-\mathrm{Br}$ was $51.5 \%(0.490 \mathrm{~g}, 0.990 \mathrm{mmol})$.
2.3.
(E)-2-(4-( $(2,3,5,6,8,9,11,12-$ 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 $\mathbf{1 5 C 5}-\mathrm{Azo}-\mathrm{Br}(0.182 \mathrm{mmol}), 2.639 \mathrm{~g}(19.14 \mathrm{mmol})$ of $\mathrm{K}_{2} \mathrm{CO}_{3}$ and $0.370 \mathrm{~g}(2.23$ mmol ) of KI were dissolved in $50 \mathrm{~cm}^{3}$ acetonitrile with stirring. Then, 0.036 g of bis(2pyridylmethyl)amine $(0.184 \mathrm{mmol})$ 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 $46.6 \%(0.052 \mathrm{~g}, 0.0848 \mathrm{mmol}) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right) \delta 8.50-8.45\left(\mathrm{dd}, J_{l k}=4.8 \mathrm{~Hz}, J_{l j}=1.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}_{1}\right), 7.82-$ $7.72\left(\mathrm{~d}, J_{d e}=8.7 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}_{\mathrm{d}}\right), 7.76-7.71\left(\mathrm{dd}, J_{j k}=8.4, J_{j l}=1.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}_{\mathrm{j}}\right), 7.59-$ $7.55\left(\mathrm{~d}, J_{i j}=7.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}_{\mathrm{i}}\right), 7.53-7.48\left(\mathrm{dd}, J_{b a}=8.4 \mathrm{~Hz}, J_{b c}=2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}_{\mathrm{b}}\right)$, $7.40-7.39\left(\mathrm{~d}, J_{c b}=2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}_{\mathrm{c}}\right), 7.26-7.20\left(\mathrm{ddd}, J_{k j}=8.4 \mathrm{~Hz}, \quad J_{k l}=4.8 \mathrm{~Hz}, J_{k i}=\right.$ $1.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}_{\mathrm{k}}$ ), 7.14-7.10 (d, $J_{a b}=8.4,1 \mathrm{H}, \mathrm{ArH}_{\mathrm{a}}$ ), 7.07-7.03 (d, $J_{e d}=8.7,2 \mathrm{H}$,
 $8 \mathrm{H}, \mathrm{H}_{\mathrm{o}, \mathrm{p}}$ ), $2.93\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{H}_{\mathrm{g}}\right)$, negative ESI-MS ( $\mathrm{m} / \mathrm{z}$ ): Calcd. for $\mathrm{C}_{34} \mathrm{H}_{39} \mathrm{~N}_{5} \mathrm{O}_{6} \mathrm{Na}\left(\mathrm{M}^{-}\right)$: 613.7, Found: 613. Anal. Calcd. for $\mathrm{C}_{34} \mathrm{H}_{39} \mathrm{~N}_{5} \mathrm{O}_{6}$ : 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 ${ }^{1} \mathrm{H}$ NMR spectrum of 15 C 5 -Azo-dpa $\left(300 \mathrm{MHz}\right.$ in $\left.\mathrm{CDCl}_{3}\right)$.


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] $=$ $10-70 \mu \mathrm{M},[\gamma \mathrm{CyD}]=10-70 \mu \mathrm{M},\left[\mathrm{Zn}^{2+}\right]=100 \mu \mathrm{M},\left[\mathrm{K}_{2} \mathrm{CO}_{3}\right]=50 \mathrm{mM}$, in $4 \% \mathrm{DMSO}$ aq., $\mathrm{pH}=11.0$ at $25^{\circ} \mathrm{C}$; $\left(\mathrm{M}=\mathrm{mol} \mathrm{dm}^{-3}\right)$. Job's plot calculated with the ICD spectra at 395 nm (bottom).

## 4. Binding constant of $15 \mathrm{C} 5-\mathrm{Azo}-\mathrm{dpa} / \gamma$-CyD complex.

$$
\begin{align*}
& \text { Host }=\mathrm{H} \text {, Guest }=\mathrm{G} \\
& \text { Host } \cdot \text { Guest }=\text { HG } \\
& {[\mathrm{H}]+[\mathrm{G}] \stackrel{K}{\rightleftarrows}[\mathrm{HG}]} \\
& K=[\mathrm{HG}] /[\mathrm{H}][\mathrm{G}]  \tag{1}\\
& {[\mathrm{Ht}]=[\mathrm{H}]+[\mathrm{HG}]}  \tag{2}\\
& \text { [Gt] }=[\mathrm{G}]+[\mathrm{HG}]  \tag{3}\\
& \theta=\varepsilon_{\mathrm{H}}[\mathrm{H}] \mathrm{d}+\varepsilon_{\mathrm{HG}}[\mathrm{HG}] \mathrm{d}  \tag{4}\\
& \text { from equation (1), (2), (3), (4) } \\
& \theta=\left(\theta_{0}+\theta_{\text {lim }} \mathrm{K}\left[\mathrm{G}_{\mathrm{t}}\right]\right) /\left(1+\mathrm{K}\left[\mathrm{G}_{\mathrm{t}}\right]\right) \\
& \text { ([G] > [H]) }
\end{align*}
$$

The ICD spectrum changes at 395 nm are shown in Fig. S5 and Fig. S6 as a function of carbonate $\left(\mathrm{CO}_{3}{ }^{2-}\right)$ or acetate $\left(\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right)$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] $=40 \mu \mathrm{M}$, $\left[\mathrm{Zn}^{2+}\right]=40 \mu \mathrm{M},\left[\mathrm{K}_{2} \mathrm{CO}_{3}\right]=0-80 \mathrm{mM},[\mathrm{KCl}]=0-80 \mathrm{mM},[\gamma-\mathrm{CyD}]=5 \mathrm{mM}$, in $4 \%$ DMSO aq., $\mathrm{pH}=11.0$ at $25^{\circ} \mathrm{C}$; $\left(\mathrm{M}=\mathrm{mol} \mathrm{dm}^{-3}\right)$.


Fig. S6 ICD spectrum of 15C5-Azo-dpa $/ \gamma$-CyD sensors, [15C5-Azo-dpa] $=40 \mu \mathrm{M}$, $\left[\mathrm{Zn}^{2+}\right]=40 \mu \mathrm{M},\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{~K}\right]=0-100 \mathrm{mM},\left[\mathrm{KNO}_{3}\right]=0-100 \mathrm{mM},[\gamma-\mathrm{CyD}]=5 \mathrm{mM}$, in $4 \%$ DMSO aq., $\mathrm{pH}=7.0$ at $25^{\circ} \mathrm{C}$; $\left(\mathrm{M}=\mathrm{mol} \mathrm{dm}^{-3}\right)$.
5. ${ }^{1} \mathrm{H}$ NMR analysis of $15 \mathrm{C} 5-\mathrm{Azo}-\mathrm{dpa} / \gamma$ - CyD complex with $\mathrm{H}-\mathrm{H}$ COSY.


Fig. S7 H-H COSY spectrum of 15C5-Azo-dpa $/ \gamma-\mathrm{CyD}$ sensors, adding $\mathrm{Zn}^{2+}, \mathrm{K}^{+}$, $\mathrm{CO}_{3}{ }^{2-}$ at $22.8^{\circ} \mathrm{C}, 500 \mathrm{MHz}$, scans: 64 , acquisition time; 0.1271 sec , relaxation delay; 1 sec , repetition time; 1.1271, data points: $512 \times 512$.
6. ${ }^{1} \mathrm{H}$ NMR analysis of $15 \mathrm{C} 5-\mathrm{Azo}-\mathrm{dpa} / \gamma-\mathrm{CyD}$ complex with NOESY.


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

## References

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