Electronic Supplementary Information for:

Helicity Induction on Water-Soluble Oligoresorcinols in Alkaline Water and Their Application to Chirality Sensing

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1. Experimental Procedures

Instruments. Melting points were measured on Yanaco MP-500D melting point apparatus (Kyoto, Japan) and were uncorrected. The solution pH was measured with a B-211 pH meter (Horiba, Japan) or a GST-5428S pH meter (DKK-TOA, Tokyo, Japan). NMR spectra were taken on a Varian UNITY INOVA-500S spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. Chemical shifts are reported in parts per million (δ) downfield from acetone dissolved in D_2O. Absorption and CD spectra were measured in a 1.0-mm quartz cell on a Jasco V-570 spectrophotometer and a Jasco J-820 spectropolarimeter, respectively. The temperature was controlled by a JASCO PTC-423L apparatus (0 to 25 °C).

Materials. Oligoresorcinols (**3merH**, **6merH**, and **9merH**) were synthesized according to the previously reported method.[1] All reagents and solvents were purchased from Wako (Osaka, Japan), Tokyo Kasei Kogyo (TCI, Tokyo, Japan), and Aldrich and were used as received unless otherwise noted. Distilled water (Wako, Osaka, Japan) and D_2O (99.9 atom %D) (CIL, Andover, MA, USA) were degassed with argon and used throughout for all experiments. (*R*)- and (*S*)-**2**,[2] and (*S*)-**3**[3] were prepared by the reaction of (*R*)- and (*S*)-*N*,*N*-dimethyl-1-phenylethylamine, and *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine with iodomethane (Wako), respectively.

Typical Experimental Procedure for pH Titrations. An aqueous solution of **9merH** (2.0 mg/10 mL, 1.8 mM unit^{-1}) was prepared in a 30-mL flask equipped with a stopcock. The pH and absorption spectrum of the solution were measured using a GST-5428S pH meter and Jasco V-570 spectrophotometer with a 1.0-mm cell, respectively. After 5–30 μL of 0.1 M NaOH aqueous solution was added, the resulting solution was subjected to pH and absorption spectrum measurements. This procedure was repeated until the added 0.1 M NaOH amounted to 540 μL.

Typical Experimental Procedure for CD Measurements. The concentrations of oligoresorcinols were calculated based on the monomer units and were 0.2 mg/mL (1.8 mM unit^{-1}, 1.0-mm cell) unless otherwise stated. Stock solutions of **9merH** (3.0 mg/3 mL, 9 mM unit^{-1}) and (*S*)-**2** (6.6 mg/mL, 4.5 mM) were prepared in 3 and 5-mL flasks equipped with stopcocks, respectively. The **9merH** solution (0.1 mL) was placed in a 1.0-mm cell with a

stopcock. 0.2 mL of the (*S*)-**2** solution and 0.2 mL of degassed, distilled water were added to the solution, so that the [**9merH**] and the [(*S*)-**2**]/[**9merH**] were adjusted to 1.8 mM (monomer unit) and 2, respectively. The solution pH was adjusted with 0.1 M and 1 M NaOH aqueous solutions (Wako), while the solution pH was measured with a B-211 pH meter.

Absorption Titrations and Hill Plots. Stock solutions of **9merH** (3.0 mg/3 mL, 9 mM unit^{-1}) and (*S*)-**2** (6.6 and 65.5 mg/mL, 4.5 and 45 mM) were prepared in 3- and 5-mL flasks equipped with stopcocks, respectively. 0.1 mL of the **9merH** solution was placed in a 1.0-mm cell with a stopcock. Increasing amounts of the stock solution of (*S*)-**2** were added to the cell; the molar ratios of (*S*)-**2** to **9merH** are 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.075, 0.1, 1.5, 0.2, 0.3, 0.4, 0.5, 0.75, 1, 2 (4.5 mM) and 5, 10, 20 (45 mM), and the resulting solutions were diluted with water to make [**9merH**] at 1.8 mM unit^{-1}. To the solution was added 3 μL of 1 M NaOH aqueous solution and the absorption spectra were taken to determine the changes in the absorbance at 360 nm, while the solution pH was measured with a B-211 pH meter.
Plots of the absorbance at 360 nm of **9merH** versus the concentration of (*S*)-**2** gave a saturation binding isotherm at 25 °C. The Hill plot analysis of the data gave an apparent binding constant (K) according to the Hill equation, $\log(Y/(1-Y)) = n\log[G] + n\log K$, where Y, n, and [G] represent the fractional saturation, the Hill coefficient, and the concentration of the guest, respectively.

Molecular Modeling and Calculations. Molecular modeling and molecular mechanics calculations were performed with COMPASS and pcff force fields as implemented in Materials Studio software (version 4.0; Accerlys Inc.). The models of **9merH** were constructed using Materials Visualizer in Materials Studio. The main chain conformation of **9merH** is defined as a conformation of a rotational single bond between neighboring benzene rings. The initial dihedral angles of a single bond from planarity were set to 40°. The constructed models were accomplished by Smart Minimizer method using a Discover module. The energy minimization was continued until the root-mean-square (rms) value became less than 0.1 kcal mol^{-1} Å^{-1}.

References

1. H. Goto, H. Katagiri, Y. Furusho and E. Yashima, *J. Am. Chem. Soc.*, 2006, **128**, 7176-7178.
2. I. Angres and H. E. Zieger, *J. Org. Chem.*, 1975, **40**, 1457-1460.
3. M. A. Petti, T. J. Shepodd, R. E. Barrans and D. A. Dougherty, *J. Am. Chem. Soc.*, 1988, **110**, 6825-6840.

2. Potentiometric pH Titration of 3merH and 6merH

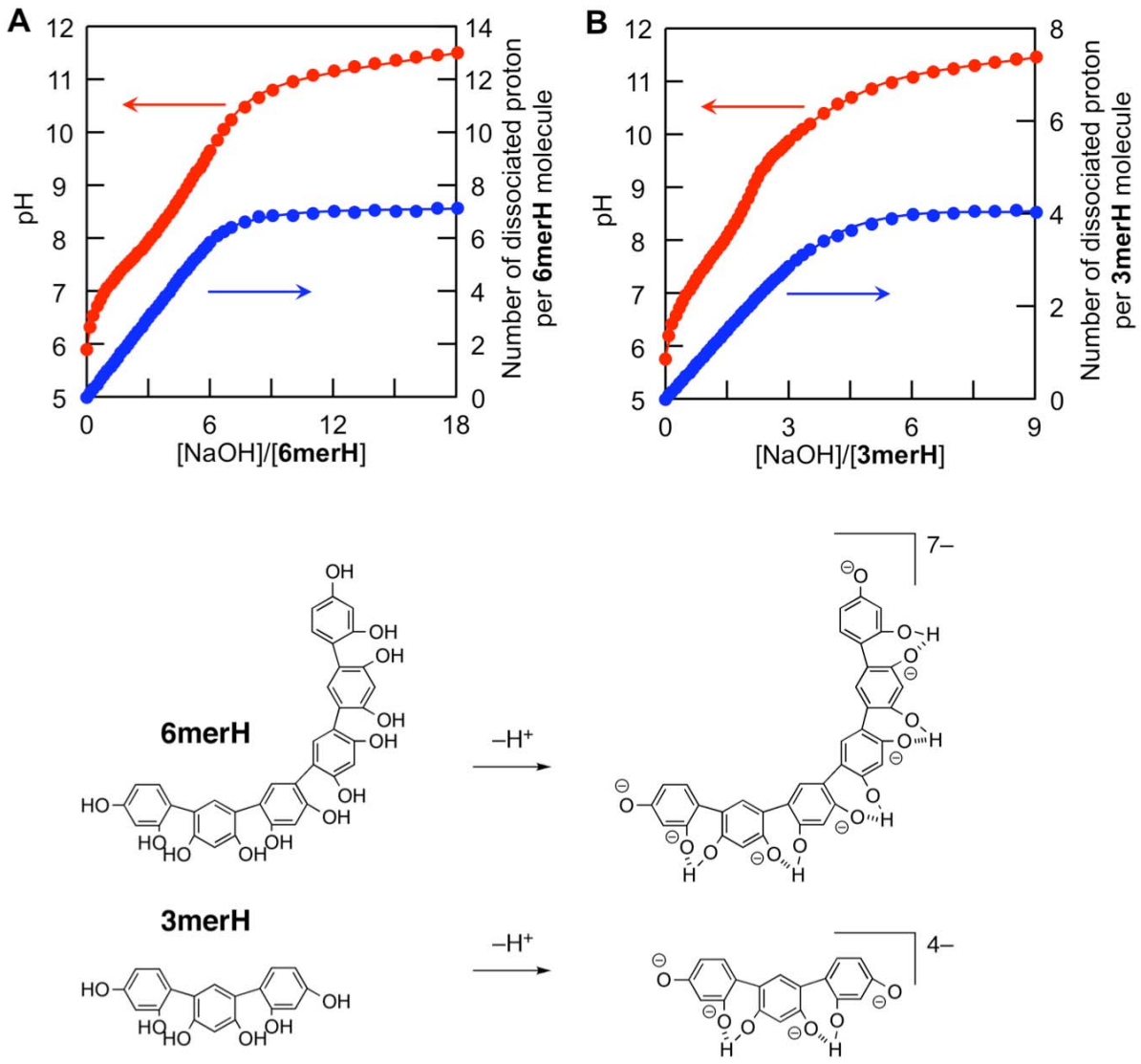

Fig. S1. Changes of pH and number of dissociated OH protons of **6merH** (A) and **3merH** (B) plotted against the amount of added NaOH at *ca*. 25 °C. [**6merH**] = 0.3 mM and [**3merH**] = 0.6 mM.

3. Molecular-Mechanics Calculation of the Single Helix of 9merH

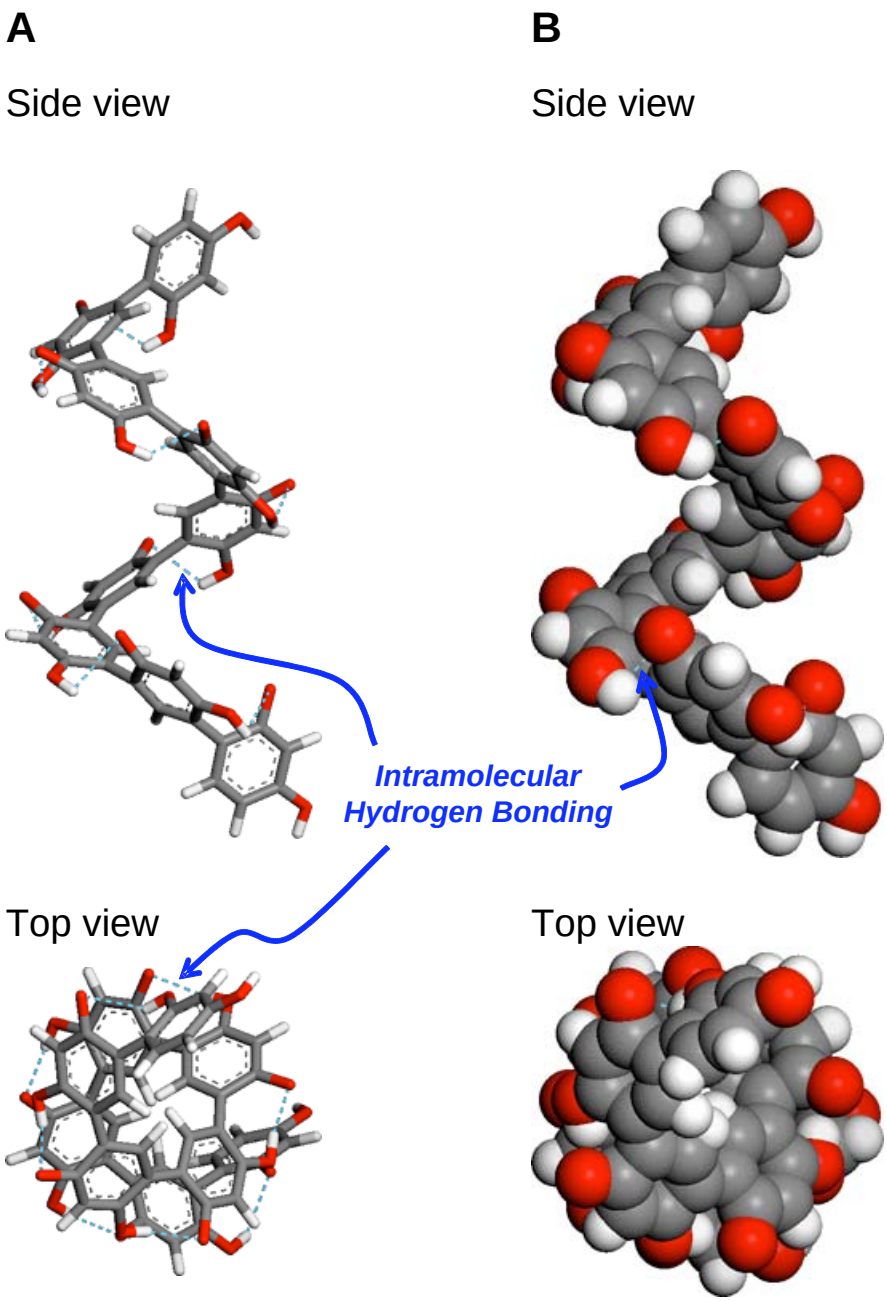

Fig. S2. A calculated structure of **9merH** anion molecule ([**9merH**]$^{10-}$) using MM calculation (stick (A) and CPK (B) models). The dashed blue lines show the intramolecular hydrogen bonds.

4. NOESY Spectrum of 9merH

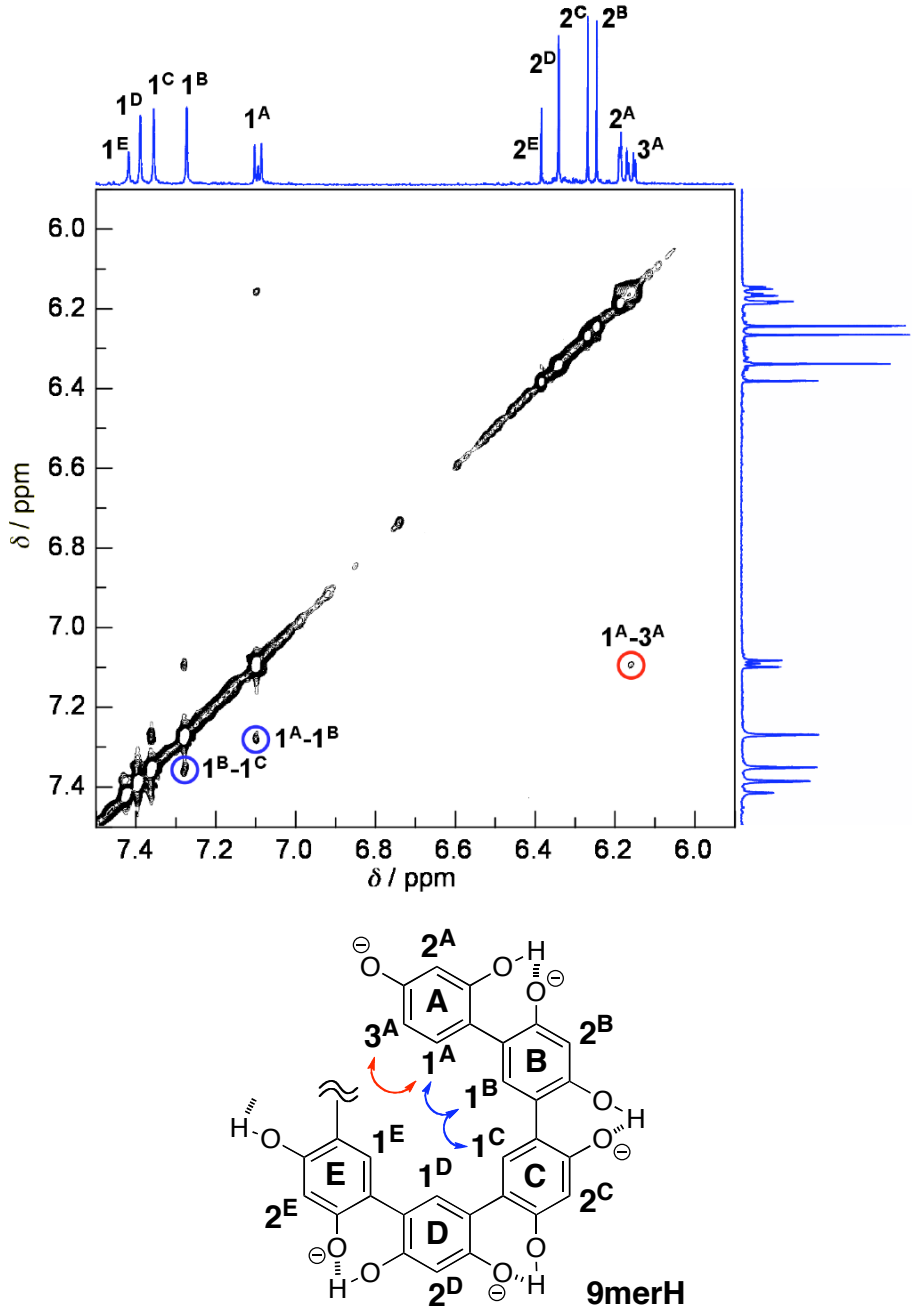

Fig. S3. Partial NOESY spectrum of **9merH** in NaOD/D_2O (pD = 11.9) at 25 °C (mixing time = 0.1 s). [**9merH**] = 9 mM unit^{-1}.

5. ^{1}H NMR Spectra of 9merH with (*S*)-2

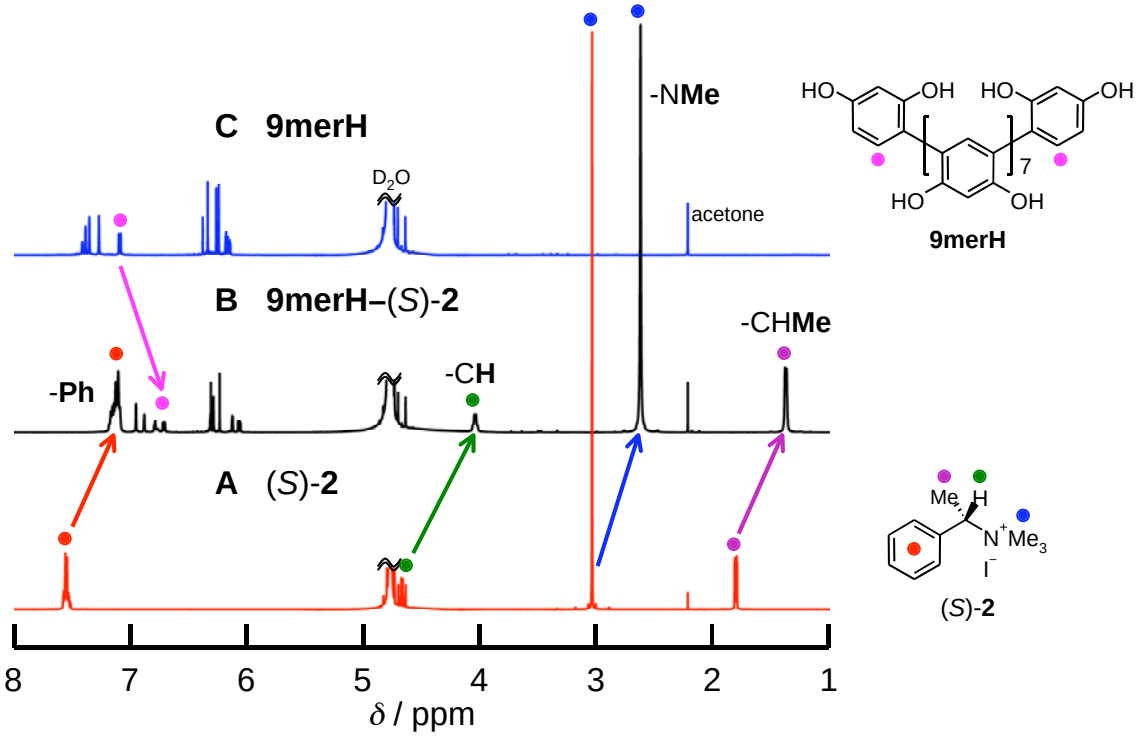

Fig. S4. ^{1}H NMR spectra of (*S*)-**2** (A), **9merH**–(*S*)-**2** complex (B), and **9merH** (C) in NaOD/D_2O (pD = 11.8–11.9) at 25 °C. [**9merH**] = 9 mM unit^{-1} and [(*S*)-**2**] = 4.5 mM.

6. ROESY Spectra of 9merH with (*S*)-2

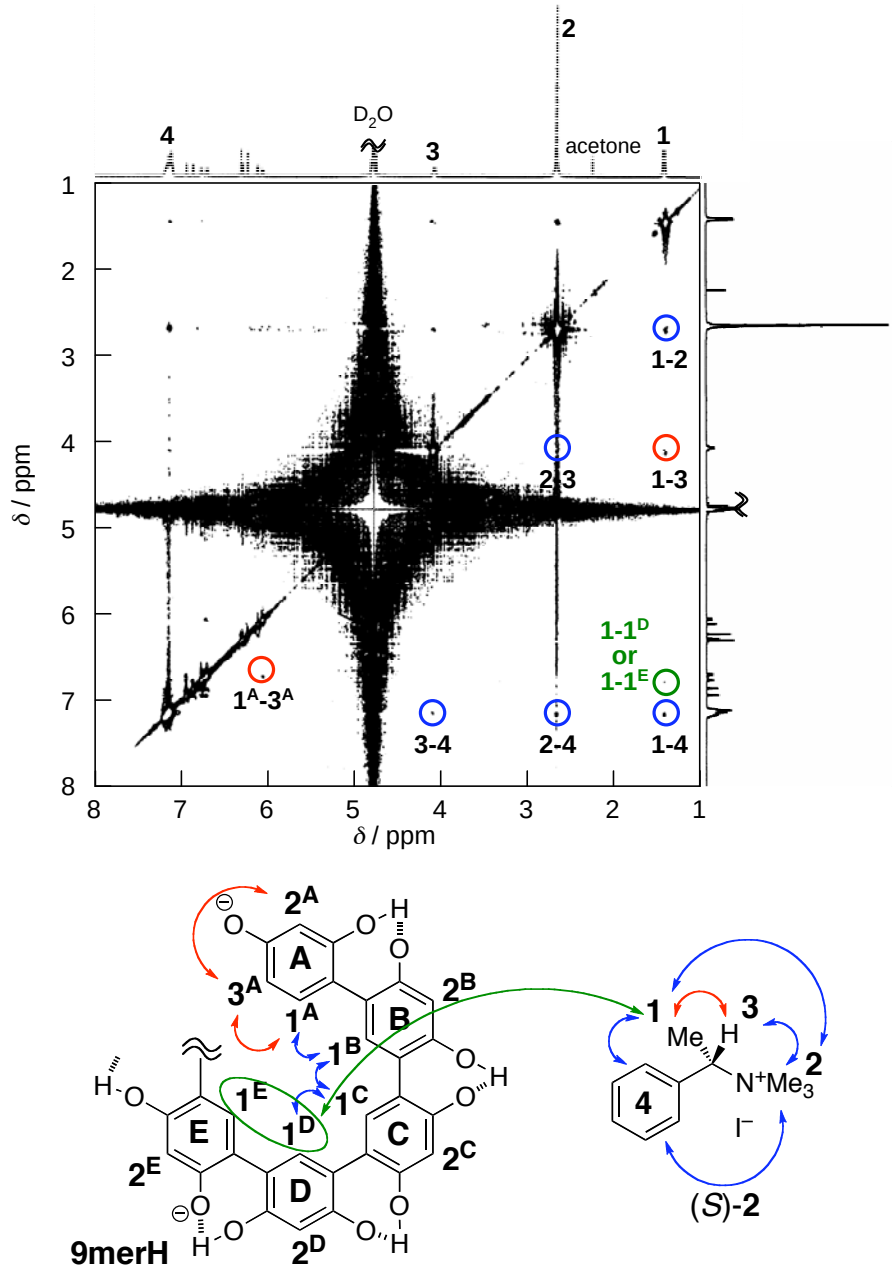

Fig. S5. ROESY spectrum of **9merH**–(*S*)-**2** complex in NaOD/D_2O (pD = 11.8) at 25 °C (mixing time = 0.1 s). [**9merH**] = 9 mM unit^{-1} and [(*S*)-**2**]/[**9merH**] = 0.5.

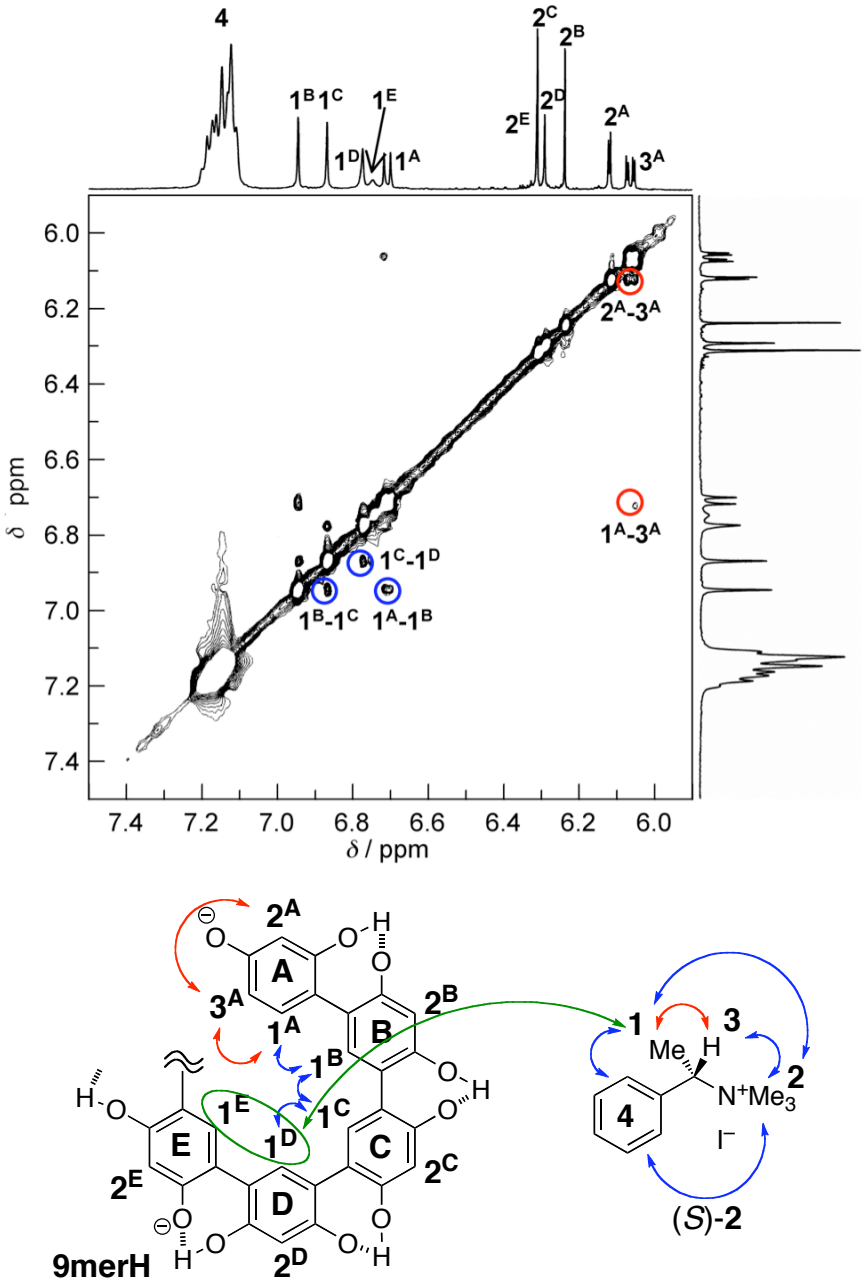

Fig. S6. Partial ROESY spectrum of **9merH**–(*S*)-**2** complex in NaOD/D_2O (pD = 11.8) at 25 °C (mixing time = 0.1 s). [**9merH**] = 9 mM unit^{-1} and [(*S*)-**2**]/[**9merH**] = 0.5.

7. pH Dependence of ICD Intensity Change

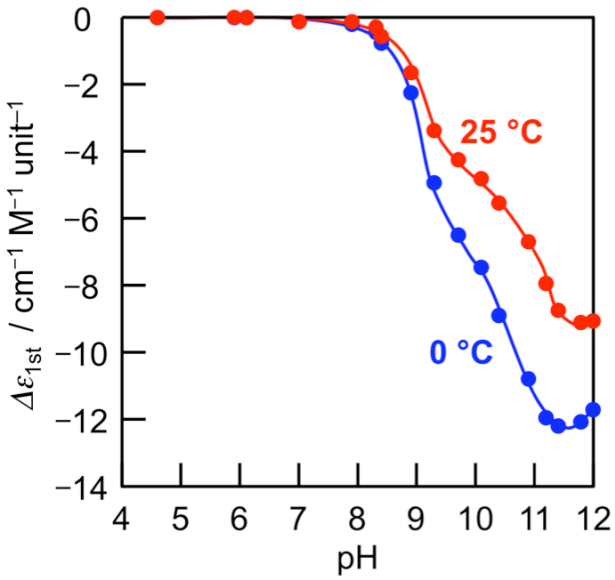

Fig. S7. The pH dependence of ICD intensity ($\Delta\varepsilon_{1st}$) of **9merH** in the presence of (*S*)-**2** in H_2O (pH = 4.5–12.0) at 0 (**blue**) and 25 °C (**red**). [**9merH**] = 1.8 mM unit^{-1} and [**2**]/[**9merH**] = 2. The pH was adjusted with 0.1 M HCl and 1 M NaOH at room temperature.

8. Determination of the Binding Constants of 9merH and 6merH for (*S*)-2

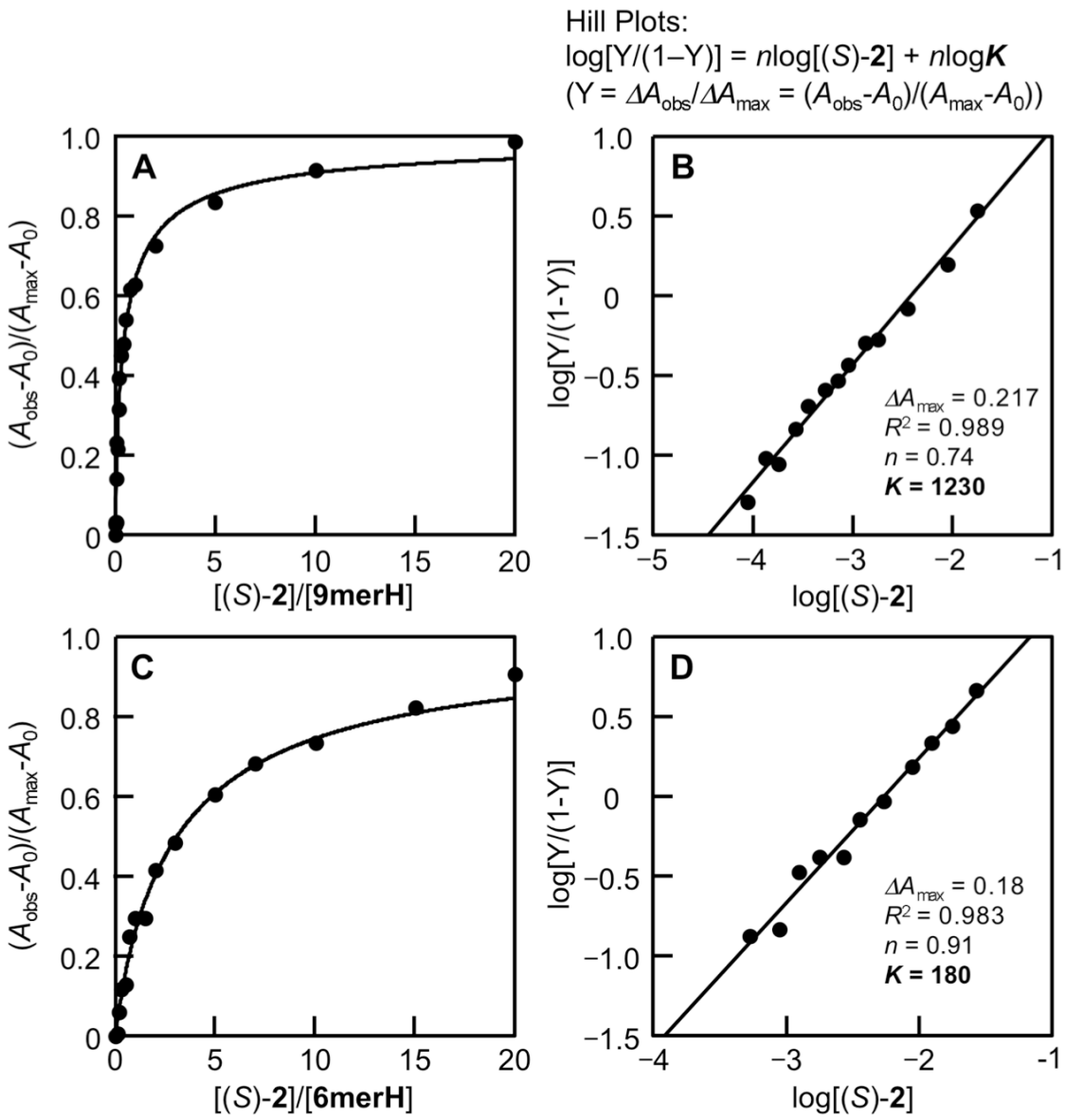

Fig. S8. The Hill plot analysis of the complexation of **9merH** (A, B) and **6merH** (C, D) with (*S*)-**2** in H_2O (pH = 11.3–11.5) at 25 °C (λ = 360 nm). [**9merH**] = [**6merH**] = 1.8 mM unit^{-1} and [(*S*)-**2**]/[**9merH**] = [(*S*)-**2**]/[**6merH**] = 0–20.