Electronic Supplementary Information for:

Double helix formation of poly(*m*-phenylene)s bearing achiral oligo(ethylene oxide) pendants and transformation into an excess one-handed single helix through cholate binding in water

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1. Instruments

The solution pH was measured with a B-211 pH meter (Horiba, Japan) or a GST-5428S pH meter (DKK-TOA, Tokyo, Japan). The NMR spectra were taken on a Varian UNITY INOVA-500S spectrometer operating at 500 MHz for ¹H and 125 MHz for ¹³C. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (TMS) as the internal standard in CDCl₃, and from acetone dissolved in D₂O. The DOSY experiments were carried out by using pulsed field gradient with the BPPSTE pulse sequence.^{1,2} The electron spray ionization mass spectra (ESI-MS) were recorded on a JEOL JMS-T100CS spectrometer (Akishima, Japan). The matrix-assisted laser desorption-ionization time-of-flight mass spectra (MALDI-TOF-MS) were measured using a Shimadzu AXIMA-CFR Plus spectrometer (Kyoto, Japan). The elemental analyses were performed by the laboratory of elemental analyses in the Department of Agriculture, Nagoya University. The IR spectra were recorded using a JASCO Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). The absorption and CD spectra were measured in a 1 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 (-10 to 90 °C). The dynamic light scattering (DLS) measurements were performed using an Otsuka Photal DLS-7070YN spectrometer equipped with a 10mW He-Ne laser (632.8 nm).

References

1 Y. Cohen, L. Avram and L. Frish, *Angew. Chem.*, *Int. Ed.*, 2005, **44**, 520-554.

2 P. S. Pregosin, P. G. A. Kumar and I. Fernandez, *Chem. Rev.*, 2005, **105**, 2977-2998.

2. Molecular Modeling and Calculations

The molecular modeling and molecular mechanics calculations were performed using the Compass Force Field as implemented in the Materials Studio software (version 4.0; Accerlys Software Inc.). The single-stranded helical structure of 5-methoxy-*m*-phenylene 30-mer (**PMP**₃₀) as a model of **P1**_H and the inclusion complex of **PMP**₃₀ and sodium cholate (2) were constructed using Materials Visualizer in the Materials Studio. The parameter, "relative electric" was set to 4 which is the recommended value for the calculations in water. The energy minimization of **PMP**₃₀ and the inclusion complex of **PMP**₃₀ with 2 was performed using the Smart Minimizer of the Discover module until the root-mean-square value became less than 0.1 kcal·mol⁻¹.

3. Materials

All starting materials and dehydrated solvents were purchased from Aldrich, Wako Pure Chemical Industries (Osaka, Japan), and Tokyo Kasei Kogyo (TCI) (Tokyo, Japan) unless otherwise noted. Triethylamine (NEt₃) was distilled over CaH₂ under Ar after being stirred with KOH pellets overnight under Ar. The distilled water and D₂O (99.9 atom %D) purchased from Wako and Cambridge Isotope Laboratories (Andover, MA, USA), respectively, were degassed with Ar and used throughout all the experiments. Silica gel (SiO₂) and aminopropyl-modified silica gel (NH-SiO₂) for the flash chromatography were purchased from Merck and Fuji Silysia Chemical Ltd. (Kasugai, Japan), respectively.

4. Synthesis of Poly(*m*-phenylene)s

3,5-Dibromo-(2-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)benzene (1): To a solution of 3,5-dibromophenol (5.49 g, 21.8 mmol), tetraethylene glycol monomethyl ether (5.00 g, 24.0 mmol), and PPh₃ (6.25 g, 23.8 mmol) in dehydrated THF (200 mL) was added dropwise a solution of diisopropyl azodicarboxylate (4.81 g, 23.8 mmol) in THF (125 mL) over 30 min with a water bath (*ca.* 20 °C), and the mixture was stirred at ambient temperature for 1 day. After evaporation, EtOAc was added to the dried residue, and then the EtOAc-insoluble fraction was removed by Celite[®] filtration. After the filtrate was concentrated *in vacuo*, the residue was purified by SiO₂ chromatography (*n*-hexane/EtOAc (1/1, v/v)) to afford **1** as a slightly yellow oil (6.83 g, 15.4 mmol, 70.6% yield). IR (neat, cm⁻¹): 2873, 1584, 1557, 1437, 1419, 1257, 1108, 1056, 955, 832, 742, 669. ¹H NMR (CDCl₃): δ 3.37 (s, OCH₃, 3H), 3.83 (m, CH₂, 2H), 3.6–3.8 (m, CH₂, 10H), 3.83 (t, *J* = 4.8 Hz, CH₂, 2H), 7.01 (d, *J* = 1.5 Hz, Ar-H_{2 and 6}, 2H), 7.24 (t, *J* = 1.5 Hz, Ar-H₄, 1H). ¹³C NMR (CDCl₃): δ 59.02, 68.10, 69.41, 70.52, 70.62, 70.64, 70.90, 71.94, 117.13, 123.03, 126.57, 160.00. ESI-MS (CH₃OH, positive): Calcd for C₁₅H₂₂Br₂O₅Na [1+Na]⁺: *m/z* = 464.97. Found: *m/z* = 464.92. Elemental Anal. Calcd for C₁₅H₂₂Br₂O₅: C, 40.75; H, 5.02. Found: C, 40.75; H, 5.06.

Polymerization of Monomer (1) with Ni(0) **Complex:** То solution of а bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)₂) (1.20 g, 4.36 mmol) and 2,2'-bipyridyl (680 mg, 4.35 mmol) in dehydrated DMF (2.4 mL) was added 1,5-cyclooctadiene (cod) (0.51 mL, 4.16 mmol), and the mixture was aged at 80 °C for 1 h. To the resultant purple nickel solution was added 1 (530 mg, 1.20 mmol), and the mixture was stirred at 80 °C overnight to obtain a deep purple suspension. After cooling to room temperature, conc. HCl aq. was added to the mixture until it turned to a green clear solution. After neutralization with NEt₃, the volatile components were completely removed in vacuo. THF was added to the dried residue, and then the THF-insoluble fraction was removed by

Celite[®] filtration. After the filtrate was concentrated *in vacuo*, the residue was purified by chromatography (NH-SiO₂, MeOH) to obtain **P1** as a slightly brown oil (340 mg, 1.20 mmol, quant.). The **P1** was subjected to recycling SEC to afford a high molecular weight part, **P1_H** (76 mg, 0.268 mmol, 22.3% yield; $M_n = 1.51 \times 10^4$, $DP_n = 53$, $M_w/M_n = 1.46$) and a low molecular weight part, **P1_L** (255 mg, 0.903 mmol, 75.3% yield; $M_n = 0.32 \times 10^4$, $DP_n = 11$, $M_w/M_n = 1.06$).

P1_H: IR (neat, cm⁻¹): 2873, 1582, 1455, 1387, 1193, 1105, 849. ¹H NMR (CDCl₃): δ 3.32 (s, OCH₃, 3H), 3.50 (t, J = 4.5 Hz, CH₂, 2H), 3.60 (t, J = 4.5 Hz, CH₂, 2H), 3.63 (d, J = 4.5 Hz, CH₂, 2H), 3.65 (t, J = 4.5 Hz, CH₂, 2H), 3.68 (t, J = 4.5 Hz, CH₂, 2H), 3.75 (t, J = 4.5 Hz, CH₂, 2H), 3.92 (t, J = 4.5 Hz, CH₂, 2H), 4.27 (t, J = 4.5 Hz, CH₂, 2H), 7.20 (s, Ar-H_{4 and 6}, 2H), 7.45 (s, Ar-H₂, 1H). ¹³C NMR (CDCl₃): δ 58.97, 67.76, 69.77, 70.47, 70.59, 70.83, 71.88, 112.96, 119.06, 142.99, 159.54. Elemental Anal. Calcd for (C₁₅H₂₂O₅)_n: C, 63.81; H, 7.85. Found: C, 63.71; H, 7.85.



Fig. S1. SEC profiles of **P1**s before and after fractionation (A) and ¹H NMR (B), MALDI-TOF-MS (C), and ESI-MS (D) spectra of $P1_{H}$ and $P1_{L}$.

5. Investigation of Single- and Double-stranded Helix Formation of $\text{P1}_{\rm H}$

5-1. Solvent Effect



Fig. S2. ¹H NMR (A) and absorption (B) spectra of $\mathbf{P1}_{\mathbf{H}}$ in CDCl₃, CD₃OD, and D₂O at 25 °C; [$\mathbf{P1}_{\mathbf{H}}$] = 1 mM unit⁻¹. Plots of the chemical shifts of Ar-H₂ (blue circles), Ar-H_{4,6} (green circles), and the pendant methyl group (red circles) (C) and the molar absorptivities (ε_{max} , black full circles) and the wavelengths (λ_{max} , black open circles) at *ca*. 300 nm (D) of **P1**_H in various solvent mixtures.

5-2. DLS Measurements



Fig. S3. Histogram analysis of DLS measurement of $P1_{H}$ in H₂O (2.9 mM / unit⁻¹) at *ca.* 25 °C.

6. Inclusion Complexation of $\text{P1}_{\rm H}$ with 2

6-1. Titration Experiment of 2 to $\mathrm{P1}_{\mathrm{H}}$



Fig. S4. Plots of the molar absorptivities at 300 nm (ε_{300}) of **P1**_H upon the addition of **2** in H₂O (pH = 6.1–6.5) at 25 °C. [**P1**_H] = 0.2 mM (5 unit⁻¹) and [**2**] = 0–69 mM. The solid line in the UV titration curve represents the nonlinear curve fitting result.

6-2. Temperature Effect of $2 \cdot P1_H$ Complex



Fig. S5. (A) Changes in the CD and absorption spectra of $\mathbf{P1}_{\mathbf{H}}$ with **2** in H₂O (pH = 6.1) at various temperatures (5–75 °C). [**P1**_H] = 1 mM unit⁻¹ and [**2**] = 69 mM. (B) Plots of the molar circular dichroisms at 264 nm ($\Delta \varepsilon_{264}$) and the molar absorptivities at 300 nm (ε_{300}) against temperature.



Fig. S6. Full (A) and partial (B) NOESY spectra of $\mathbf{P1}_{\mathbf{H}}$ with **2** in D₂O (pD = 6.5) at 25 °C. [$\mathbf{P1}_{\mathbf{H}}$] = 60 mM unit⁻¹, [**2**] = 1 mM, and mixing time = 0.3 s.

	concentration	$D (10^{-10} \text{ m}^2 \text{ s}^{-1})$		
system	(mM)	P1 _H	Guest	water
P1 _H	60	0.56	_	18.8
2	1	_	4.29	20.4
P1 _H /2	60/1	0.60	1.68	18.2
$\eta({\rm H_2O}) = 0.895 \text{ mPa}\cdot \text{s.}$				

Table S1. Diffusion Coefficients (*D*) of $\mathbf{P1}_{\mathbf{H}}$, **2**, and Their Complexes in D₂O at 25 °C.