Supporting Information

Synthesis of head-to-tail-type cyclodextrin-based insulated molecular wire

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General Comments

6-O-monotosyl permethylated α -cyclodextrin 1 was prepared by the reported procedure.¹ Other reagents were purchased from commercial sources and used without further purification. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra was obtained with α -cyano-4-hydroxycinnamic acid as a matrix and NaTFA as a cationization reagent on a SHIMADZU KRATOS TOF MASS spectrometer AXIMA-CFR Plus. ¹H NMR for 400 MHz and ¹³C NMR for 100 MHz spectra were recorded by a JEOL JNM-Alice 400 spectrometer. 2D-COSY, ROESY, and TOCSY for 600MHz were recorded by a Varian INOVA-600. Elemental analysis was carried out at the Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. GC analysis was carried out using a Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-5, 0.25 mm i.d. \times 25 m). The HPLC separation was performed on a Japan Analytical Industry Co. Ltd. LC-9204 recycling preparative HPLC equipped with JAIGEL-1H and -2H columns or LC-908 recycling preparative HPLC equipped with JAIGEL-2.5H and -3H columns using CHCl₃ as the eluent. Analytical size-exclusion chromatography (SEC) was carried out on a GL-Science GL-7400 HPLC System equipped with a GL-7410 HPLC pump, a GL-7400 UV detector, and GL-7454 RI detector through a column set consisting of Shodex KF-801, -802, -802.5, -803, -804 using THF as the eluent at a flow rate of 0.6 mL min⁻¹. Average molecular weights and the polydisperse index (PDI) of polyrotaxanes were estimated with polystylene standards as calibration standards. The absolute quantum yields were determined using a calibrated integrating sphere system (HAMAMATSU Quantaurus-QY).

Synthesis of 2.



2-Iodo-5-nitrophenol (3.0 g, 11.0 mmol), 6-*O*-monotosyl α -cyclodextrin permethylate **1** (10.0 g, 7.32 mmol), and dry K₂CO₃ (2.10 g, 14.6 mmol) were placed in a round-bottom flask and dried at 100 °C *in vacuo*. The mixture was dissolved in DMF (60 mL) and stirred at 85 °C overnight. The mixture was diluted with EtOAc and washed with saturated aqueous NaHCO₃ and brine. The organic layer was separated and dried over Na₂SO₄. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as eluent to give **2** (10.5 g, orange solid, 98%); ¹H NMR (400 MHz, CDCl₃, 23.7 °C): δ (ppm) = 7.65 (d, *J* = 8.4 Hz, 1H, ArH), 7.36 (d, *J* = 8.4 Hz, 1H, ArH), 7.12 (dd, *J* = 2.1, 8.4 Hz, 1H, ArH), 5.12-5.00 (m, 6H, CD-H₁), 4.44-3.10 (m, 87H, CD-H, OCH₃); ¹³C NMR (100 MHz, CDCl₃, 23.7 °C): δ (ppm) = 158.84, 138.74, 138.6-138.5 (several peaks overlapped), 113.57, 113.50, 104.46, 104.46, 100.6-99.7 (several peaks overlapped), 70.45, 69.72, 61.87, 59.2-59.0 (several peaks overlapped), 58.79, 58.72, 57.9-57.8 (several peaks overlapped).

Synthesis of 3.



To a solution of **2** (8.1 g, 5.55 mmol) in $NH^{i}Pr_{2}$ (40 mL) was added $Pd(PPh_{3})_{2}Cl_{2}$ (156 mg, 0.22 mmol), CuI (10.5 mg, 0.055 mmol), and 1-ethynyl-4-(trimethylsilylethynyl)benzene (1.20 g, 6.1 mmol) under nitrogen. After

stirring for 10 h at 50 °C, the mixture was filtered through a Celite pad and concentrated, followed by a chromatographic purification on silica gel with EtOAc-EtOH (9:1) as eluent to give **3** (4.64 g, orange solid, 95%). MALDI-TOF MS: (*m/z*) 1551 ([M+Na]⁺, $C_{72}H_{109}NO_{32}SiNa$, calcd. 1551); ¹H NMR (400 MHz, CDCl₃, 23.2 °C): δ (ppm) = 7.96 (d, *J* = 8.4 Hz, 1H, ArH), 7.64 (d, *J* = 2.4 Hz, 1H, ArH), 7.61 (dd, *J* = 2.4, 8.4 Hz, 1H, ArH), 7.28-7.23 (m, 2H, ArH), 7.20-7.16 (m, 2H, ArH), 5.17-5.00 (m, 6H, CD-H₁), 4.60-3.04 (m, 87H, CD-H, OCH₃), -0.06 (s, 9H, (CH₃)₃Si); ¹³C NMR (100 MHz, CDCl₃, 23.2 °C): δ (ppm) = 160.12, 139.74, 133.25, 131.86, 131.34, 123.70, 122.40, 110.73, 108.42, 105.85, 104.21, 100.47, 100.09, 99.54, 96.08, 92.93, 88.12, 82.6-82.0 (several peaks overlapped), 81.55, 81.37, 81.12, 71.7-71.3 (several peaks overlapped), 70.74, 67.64, 62.0-61.6 (several peaks overlapped), 57.31, 0.00.

Synthesis of 4.



3 (2.0 g, 1.31 mmol) was added to a mixture of 0.1N HCl aq (140 mL), benzene (50 mL), and MeOH (12.5 mL), and then Fe (3.07 g, 55.0 mmol) and FeSO₄ • 7H₂O (947 mg, 3.41 mmol) were added with vigorous stirring, and the whole was refluxed for 3 h. The mixture was diluted with EtOAc and washed with saturated aqueous NaHCO₃ and brine. The organic layer was separated and dried over Na₂SO₄. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as eluent to give **4** (1.94 g, yellow solid, 99%). MALDI-TOF MS: (*m/z*) 1520 ([M+Na]⁺, C₇₂H₁₁₁NO₃₀SiNa, calcd. 1521); ¹H NMR (400 MHz, CDCl₃, 20.2 °C): δ (ppm) = 7.44 (d, *J* = 8.4 Hz, 2H, ArH), 7.36 (d, *J* = 8.4 Hz, 2H, ArH), 7.22 (d, *J* = 2.4 Hz, 1H, ArH), 7.21 (d, *J* = 8.4 Hz, 1H, ArH), 7.15 (dd, *J* = 2.4, 8.4 Hz, 1H, ArH), 5.16-5.01 (m, 6H, CD-H₁), 4.58-3.02 (m, 87H, CD-H, OCH₃), -0.03 (s, 9H, (CH₃)₃Si); ¹³C NMR (100 MHz, CDCl₃, 20.8 °C): δ (ppm) = 158.02, 138.64, 134.22, 130.88, 130.35, 123.86, 123.59, 112.85, 109.37, 105.84, 102.71, 101.57, 100.16, 99.75, 97.07, 93.91, 87.12, 82.5-82.2 (several peaks overlapped), 81.76, 81.55, 81.23, 71.5-71.1 (several peaks overlapped), 70.66, 67.60, 62.1-61.8 (several peaks

overlapped), 59.2-59.0 (several peaks overlapped), 58.56, 58.24, 58.0-57.8 (several peaks overlapped), 57.36, -0.06.

Synthesis of 5.



4 (2.0 g, 1.33 mmol) was dissolved in 20% H₂SO₄ (50mL) and cooled to 0-5 °C. The solution was added drop wise a cold solution of NaNO₂ (101 mg, 1.46 mmol) in H₂O (20 mL). The reaction mixture was stirred at 0-5 °C for 1 h, and then the mixture was added to a solution of KI (1.08 g, 6.5 mmol). After the resulting mixture was stirred at room temperature for 1 h, the mixture was filtered. The brown solid was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as eluent to give monoiodide 5' (1.07 g, yellow solid, 50%). MALDI-TOF MS: (m/z) 1631 $([M+Na]^+,$ C₇₂H₁₀₉IO₃₀SiNa, calcd. 1631). To a solution of 5' (300 mg, 0.186 mmol) in MeOH (7 mL), and H₂O (1.5 mL) was added K₂CO₃ (258 mg, 1.86 mmol). After stirring for 1 h at room temperature, the mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as an eluent to give 5 (223 mg, brilliant yellow solid, 78%). MALDI-TOF MS: (m/z) 1561 ([M+Na]⁺, C₆₉H₁₀₁IO₃₀Na, calcd. 1560); ¹H NMR (400 MHz, CDCl₃, 22.1 °C): δ (ppm) = 7.55 (d, J = 8.4 Hz, 2H, ArH), 7.44 (d, J = 8.4 Hz, 2H, ArH), 7.28 (d, *J* = 8.4 Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.16 (d, *J* = 8.4 Hz, 1H, ArH), 5.11-5.03 (m, 6H, CD-H₁), 4.99-3.03 (m, 88H, CD-H, CC-H); δ (ppm) = 162.35, 138.21, 132.07, 131.158, 124.38, 123.26, 122.76, 112.85, 101.63, 100.721, 99.77, 98.00, 82.3-82.2 (several peaks overlapped), 71.4-71.1 (several peaks overlapped), 72.05, 70.03, 61.76, 59.3-59.0 (several peaks overlapped); Anal. Calcd for $C_{69}H_{101}IO_{30}$: C, 53.90; H, 6.62%; Found: C, 53.77; H, 6.74%.

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Synthesis of 7.



5 (350 mg, 0.22 mmol) was dissolved in MeOH (35 mL) under a nitrogen atmosphere and degassed water (35 mL) was added in the solution. This suspended solution was stirred at 60 °C for 1 h. After cooled to ambient temperature, were added K₂CO₃ (188 mg, 1.36 mmol) into the solution. Then the catalyst solution of Pd(OAc)₂ (1.17 mg, 5.2 µmol), TXPTS (6.7 mg, 0.01 mmol) and CuI (0.25 mg, 1.3 µmol) in water (1.0 mL), and triethylamine (350 µL) were added. The mixture was stirred at room temperature for 1 d. The reaction mixture was extracted with CHCl₃. The combined organic layer was washed with saturated aqueous NaCl solution and dried over anhydrous Na₂SO₄, and filtered to remove insoluble fractions. The solvent was removed under reduced pressure and subjected to preparative SEC using CHCl₃ as eluent and evaporated to give 283 mg of 7 as a yellow solid in 88% yield ($M_w = 3.2 \times 10^4$, PDI = 2.51, $\tilde{n} = 22$); ¹H NMR (400 MHz, CD₂Cl₂) δ (ppm) = 8.08 (br, ArH), 7.69 (br, ArH), 7.63 (br, ArH), 7.50 (br, ArH), 7.25 (br, ArH), 4.96-4.48 (m, CD-H), 4.04-2.68 (m, CD-H, OCH₃-H).

Synthesis of 8.



5 (200 mg, 0.13 mmol) was dissolved in NH'Pr₂ (50 mL) and THF (10 mL) under a nitrogen atmosphere. The solution was added Pd(PPh₃)₂Cl₂(9.1 mg, 0.013 mmol) and CuI (0.4 mg, 2.1 μ mol). The mixture was stirred at 50 °C for 1 d. The reaction mixture was extracted with CHCl₃. The combined organic layer was washed with saturated aqueous NaCl solution and dried over anhydrous Na₂SO₄, and filtered to remove

insoluble fractions. The solvent was removed under reduced pressure and subjected to preparative SEC using CHCl₃ as eluent and evaporated to give 153 mg of **8** as a yellow solid in 83% yield ($M_w = 4.5 \times 10^4$, PDI = 2.43, $\tilde{n} = 32$); ¹H NMR(400 MHz, CD₂Cl₂) $\delta = 7.59$ (br, ArH), 7.43 (br, ArH), 7.13 (br, ArH), 7.07 (br, ArH), 4.97-4.49 (m, CD-H), 4.01-2.68 (m, CD-H, OCH₃-H).

Fig. S1 <u>400-MHz ROESY NMR spectrum of inclusion complex 6 in $D_2O:CD_3OD = 1:3 \text{ at } 25 \text{ °C.}$ </u>







Fig. S3 MALDI-TOF mass spectrum of 7.



Fig. S4 Space-filling model of IMW 7.



Fig. S5 <u>¹H NMR (400 MHz) Spectra of uninsulated monomer 5, insulated monomer 6,</u> insulated polymer 7, and uninsulated polymer 8.



The solution properties of 7 and 8 in the unperturbed worm-like cylinder model of the Yamakawa-Fujii-Yoshizaki theory.

The solution properties of polymers in the unperturbed worm-like cylinder model of the Yamakawa-Fujii-Yoshizaki theory² can be described as an analytical function of the intrinsic viscosity $[\eta]$ and the molecular weight (M_w) , according to Bushin et al.³ and Bohdanecky,⁴ if the persistence length (q), the diameter of the cylinder (d), and the molar mass per unit contour length (M_L) , which eventually leads to the monomer unit height (h), are given. Therefore the relationship between the intrinsic viscosity $[\eta]$ and the absolute molecular weight of 7 and 8 was explored in chloroform by SEC equipped with refractive index and light scattering detectors and a viscometer, and the results were analyzed to estimate the q, d, and M_L values in order to investigate the global conformational properties of these polymers (Fig. S6).

The solid curves in the plots were calculated using the parameters determined from the fits between the theoretical and experimental $[\eta]$ values over the entire M_w studied range. The calculated q values of 7 and 8 are 3.41 and 1.79 nm, respectively, indicating that the origin of the main chain rigidity of 7 may be largely attributed to the intramolecular inclusion of the polymer main chain in the cyclodextrin cavity.



Fig. S6 Double-logarithmic plots of the intrinsic viscosity vs molecular weight of 7 (green points), and **8** (black points), taken at 40 °C in chloroform. Solid curves (green and black lines) were obtained from the wormlike cylinder theory and fit well with the experimental data.

Flash-photolysis time-resolved microwave conductivity measurement (FP-TRMC).

The nanosecond laser pulses from a Nd: YAG laser (third harmonic generation, THG (355 nm) from Spectra Physics, INDY-HG, FWHM 3-5 ns) have been used as excitation sources. The photon density of the laser was set at $9.0 \times 10^{15} - 2.7 \times 10^{17}$ photons/cm². For time-resolved microwave conductivity (TRMC) measurement, the microwave frequency and power were set at ~ 9.1 GHz and 3 mW respectively, and the film of the samples (casted from 1~2 wt% CHCl₃ solutions at 0.2-0.4 µm thick) was set at the electric field maximum in the cavity. The TRMC signal picked up by a diode (rise time < 1 ns) is monitored by a digital oscilloscope (Tektronix, TDS3032B, rise time 1.4 ns). All the above experiments were carried out at room temperature. The transient photoconductivity ($\Delta \sigma$) of the samples is related to the reflected microwave power ($\Delta P_r/P_r$) and sum of the mobilities of charge carriers via:

$$<\Delta\sigma>=\frac{1}{A}\frac{\Delta P_r}{P_r}$$
 (1)

$$\Delta \sigma = e \sum \mu \phi N \tag{2}$$

where A, e, ϕ , N, and $\Sigma\mu$ are a sensitivity factor, elementary charge of electron, photo carrier generation yield (quantum efficiency), the number of absorbed photons per unit volume, and sum of mobilities for negative and positive carriers respectively. The number of photons absorbed by the sample was estimated based on the power loss of an incident laser pulses averaged over 100 shots. The values of ϕ in the polymer films were determined by transient absorption spectroscopy (TAS) and integration of transient current in direct-current time-of flight (DC-TOF) measurement. The other details of the set of apparatus were described elsewhere.⁵⁻⁹

Transient absorption spectroscopy measurement (TAS)

The TRMC measurement directly gives the value of $\phi\Sigma\mu$, which is the product of the quantum yield of charge carriers (ϕ) and the sum of their mobilities ($\Sigma\mu$). In-situ TAS measurement assigns the conductivity kinetics to negative or positive charge species and to determine its concentration quantitatively. The THG laser pulses from the nanosecond laser were used as excitation light sources. The incident photon densities in the present paper were set at 2.7×10^{17} photon/cm². The same films used in the TRMC measurement were irradiated with continuum white light for absorption spectroscopy perpendicularly with respect to the laser pulse. The spot size of the light probe was approximately 1 mm in diameter at the sample. After passing through the sample, the white light and/or emission was led to a grating unit (Hamamatsu, C5094) and scanned by a wide-dynamic-range streak camera (Hamamatsu, C7700). The streak image was collected via a CCD camera (Hamamatsu, C4742-98).¹⁰

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