

Electronic Supplementary Information (ESI)

**Cyclodextrin-grafted poly(phenylene ethynylene) with
chemically-responsive properties**

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Synthetic Procedures

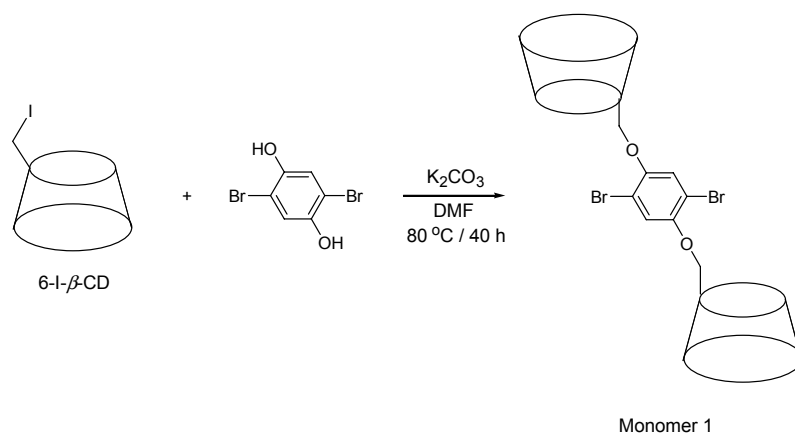
Materials.

All solvents and reagents were used as supplied except the following. Dimethylformamide (DMF) was dried and distilled over magnesium sulfate under reduced pressure and stored under argon atmosphere. Diisopropylamine was dried and distilled over KOH and stored under nitrogen atmosphere. Toluene was dried and distilled over sodium and stored under argon atmosphere. Milli-Q water was used for preparation of aqueous solutions. Ethanol was dried and distilled over magnesium ethoxide and stored under argon atmosphere.

6-Iodo- β -CD (6-I- β -CD). 6-I- β -CD was prepared from 6-tosyl- β -CD (6-TsO- β -CD) as a starting material. 6-TsO- β -CD was synthesized according to the literature previously reported.¹ To 100 mL of DMF, 6-TsO- β -CD (10.6 g, 8.20 mmol) and potassium iodide (21.0 g, 0.130 mol) were added. The mixture was heated at 100 °C

for 6 h. The resulting yellow solution was poured into acetone (1 L). The white precipitate was collected by filtration and dried in a vacuum oven at 60 °C. The white solid was dissolved in water, then excess amount of tetrachloroethylene was added to the aqueous solution. The solid precipitated was collected by filtration and washed by acetone (8.40 g, yield 82.0%). ¹H NMR (400 MHz, DMSO-*d*₆) δ, 3.20 – 4.20 (m, β-CD), 4.78 – 4.90 (m, 7H, C₁H protons of β-CD), 5.59 – 5.80 (m, 14H, OH groups of β-CD). Positive ion MALDI-TOF mass m/z = 1275 (M+Na)⁺.

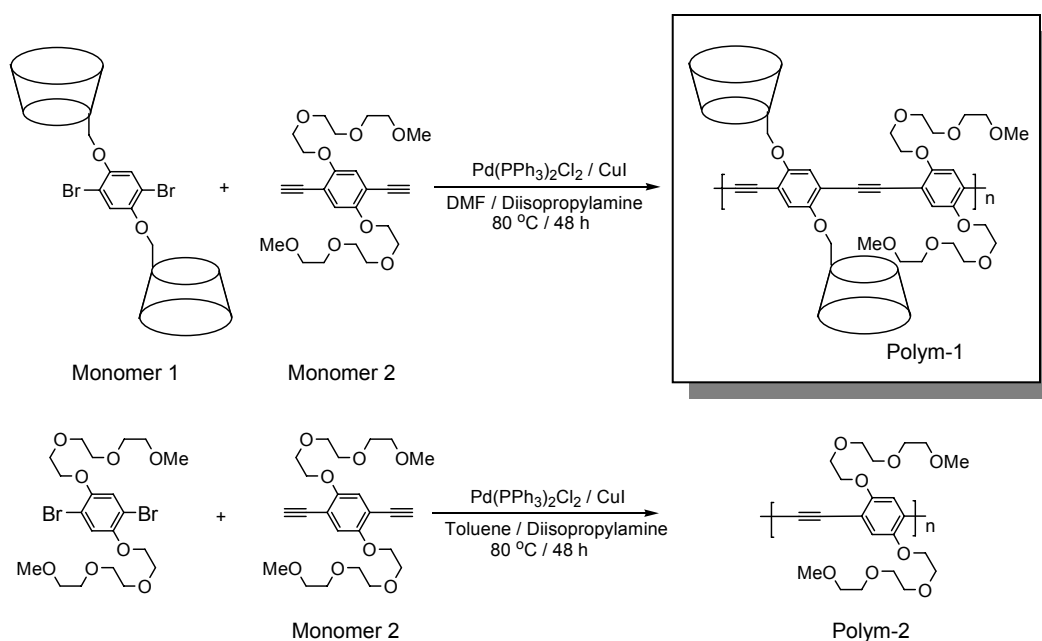
β-CD Modified Monomer (Monomer 1). Novel monomer having two β-CD groups (Monomer 1) was prepared. 2,5-Dibromobenzene-1,4-diol was prepared according to the procedure described in the literature.² To a solution of 2,5-dibromobenzene-1,4-diol (0.269 g, 1.00 mmol) in DMF (50 mL), K₂CO₃ (0.700 g, 5.07 mmol) was added under nitrogen atmosphere. The mixture was stirred at 80 °C for 1 h, then 6-I-β-CD (5.00 g, 4.02 mmol) was added to the reaction solution and additionally heated at 80 °C for 40 h. The resulting mixture was neutralized by aqueous hydrochloric acid. After removal of insoluble salts by filtration, the filtrate was reprecipitated with acetone. The solid precipitated was redissolved in water and poured into ethyl acetate. The white precipitation was collected by filtration and



finally purified with HPLC (160 mg, 6.28%). $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 3.20 – 4.20 (m, $\beta\text{-CD}$), 4.79 – 4.89 (m, 7H, C_1H of $\beta\text{-CD}$), 5.67 – 5.75 (m, 14H, OH groups of $\beta\text{-CD}$), 7.32 (s, 2H, aromatic protons). UV-Vis (DMF): $\lambda_{\text{max}} = 297$ nm. Positive ion MALDI-TOF mass $m/z = 2530$ (M) $^+$.

1,4-Bis((triethylene glycol monomethyl ether)oxy)-2,5-diethynylbenzene (Monomer 2). 1,4-Bis((triethylene glycol monomethyl ether)oxy)-2,5-diethynylbenzene (Monomer 2) was prepared according to the detailed experimental procedure described in a previous paper.³

Polym-1. Polym-1 was synthesized by Sonogashira-Hagiwara reaction. A mixture of Monomer 1 (30.0 mg, 11.8 μmol), Monomer 2 (5.31 mg, 11.8 μmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (1.99 mg, 2.83 μmol), PPh_3 (2.30 mg, 8.77 μmol), CuI (0.550 mg, 2.89 μmol), diisopropylamine (1.00 mL) and DMF (3.00 mL) was placed in a 10 mL of Schlenk flask equipped with a magnetic stirring bar under nitrogen atmosphere. The



reaction carried out at 80 °C for 48 h with stirring. After the reaction mixture was cooled, precipitated ammonium salts were filtrated off. The filtrate was poured into acetone to precipitate the polymer. The resulting polymer was filtrated, and then dissolved in water. The mixture was reprecipitated with methanol twice. The solid thus precipitated was filtered off and dried in a vacuum to yield Polym-1 as a brown solid (11.4 mg, 32.2%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 3.00 – 4.60 (br, protons of β-CD and triethylene oxide moieties), 4.70 – 4.95 (br, C₁H of β-CD), 5.45 - 5.92 (br, OH group of β-CD), 7.03 (br, aromatic protons), 7.31 (br, aromatic protons). FT-IR (KBr) 3410 cm⁻¹ (s, –OH), 2145 cm⁻¹ (v, –C≡C–). UV-Vis (DMF): λ_{max} = 443 nm. SEC analysis (THF, polystyrene standards) : $M_w = 16,000$, $M_w / M_n = 1.49$.

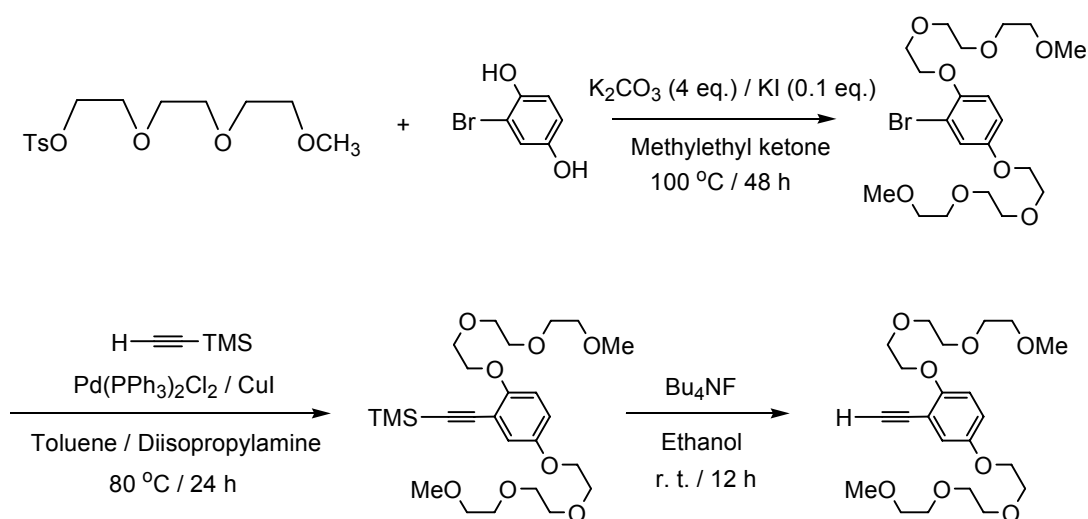
Polym-2. 1,4-Bis((triethylene glycol monomethyl ether)oxy)-2,5-dibromobenzene (592 mg, 1.00 mmol), Monomer 2 (451 mg, 1.00 mmol), Pd(PPh₃)₂Cl₂ (70.0 mg, 0.100 mmol), PPh₃ (52.0 mg, 0.198 mmol) and CuI (19.0 mg, 0.100 mmol) were combined in a mixture of toluene (10.0 mL) and diisopropylamine (5.00 mL) under nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 48 h. The resulting solution was reprecipitated with methanol three times. The solid precipitated was filtered off. After drying under vacuum, Polym-2 was obtained as a red-brown solid (212 mg, 20.3%). FT-IR (KBr) 2196 (v, –C≡C–). UV-Vis (DMF): λ_{max} = 433 nm. ¹H NMR (400 MHz, DMSO-*d*₆) δ 3.29 – 4.19 (br, protons of triethylene oxide moiety), 7.15 (s, aromatic protons). SEC analysis (THF, polystyrene standards) : $M_w = 18,000$, $M_w / M_n = 2.04$.

1,4-Bis((triethylene glycol monomethyl ether)oxy)-2-bromobenzene. Triethylene glycol monomethyl ether *p*-toluenesulfonate was prepared according to the detailed

experimental procedure described in a previous literature.⁴ Bromohydroquinone (1.04 g, 5.52 mmol), triethylene glycol monomethyl ether *p*-toluenesulfonate (7.02 g, 22.1 mmol), K₂CO₃ (3.06 g, 22.1 mmol) and KI (92.0 mg, 0.550 mmol) were combined in methylethyl ketone (50 mL) and refluxed for 48 h under nitrogen atmosphere and then cool to room temperature. The solvent was removed *in vacuo*, and the residue was dissolved in CH₂Cl₂, followed by rinsing with 10% KOH aqueous solution, distilled water. The organic layer was separated, washed with saturated aqueous NaCl, and then dried with Na₂SO₄, and concentrated under reduced pressure to give colorless oil. Chromatography (80% CH₂Cl₂ / 10% ethyl acetate / 10% hexane) afforded a colorless oil (1.94 g, 3.78 mmol, yield 68.5%). ¹H NMR (400 MHz, CDCl₃) δ 3.35 (m, 6H, -OCH₃), 3.51 – 4.10 (m, protons of triethylene oxide moiety), 6.77 – 6.85 (m, 2H, aromatic protons), 7.11 (d, 1H, aromatic proton).

1,4-Bis((triethylene glycol monomethyl ether)oxy)-2-(trimethylsilyl)ethynylbenzene.

To the mixture of toluene (10 mL) and diisopropylamine (15 mL), 1,4-bis((triethylene glycol monomethyl ether)oxy)-2-bromobenzene (1.94 g, 3.78

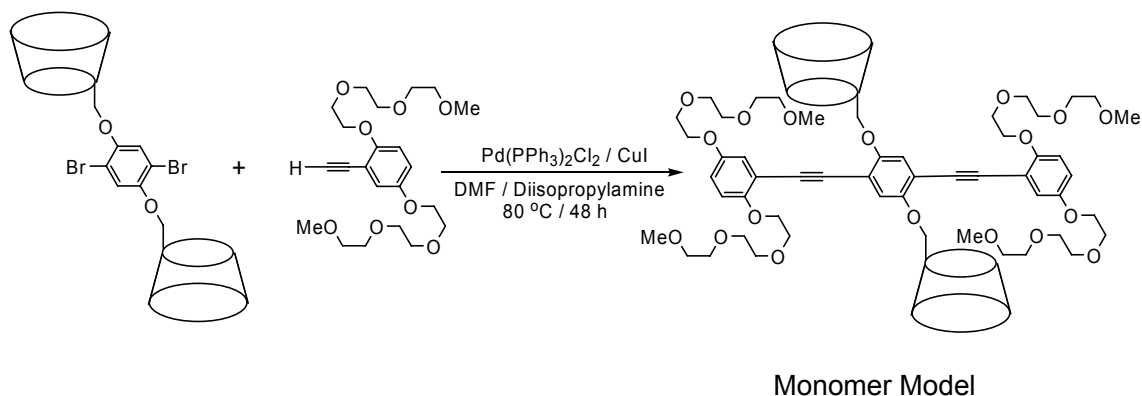


mmol), (trimethylsilyl)acetylene (2.00 mL, 14.2 mmol), Pd (PPh₃)₂Cl₂ (0.230 g, 0.328 mmol), PPh₃ (0.17 g, 0.648 mmol) and CuI (0.060 g, 0.315 mmol) were added under nitrogen atmosphere. The reaction mixture was heated at 80 °C for 40 h. The solvent was removed under reduced pressure. Chromatography (8% CH₂Cl₂ / 25% ethyl acetate / 67% hexane) afforded a yellow oil (0.731 g, 1.37 mmol, yield 36.2%). ¹H NMR (400 MHz, CDCl₃) δ 0.20 – 0.37 (m, 9H, -SiCH₃), 3.38 (m, 6H, -OCH₃), 3.50 – 4.10 (m, protons of triethylene oxide moiety), 6.60 – 6.90 (m, 3H, aromatic protons).

1,4-Bis((triethylene glycol monomethyl ether)oxy)-2-ethynylbenzene. To ethanol (15 mL), 1,4-bis((triethylene glycol monomethyl ether)oxy)-2-(trimethylsilyl)ethynylbenzene (0.731 g, 1.37 mmol) and tetrabutylammonium fluoride hydrate (1.00 g, 3.79 mmol) were added under nitrogen atmosphere. The resulting solution was stirring at room temperature for 20 h. The red solution was concentrated under reduced pressure and the residue was dissolved in CH₂Cl₂ and partitioned saturated aqueous NaCl and dried with Na₂SO₄ and concentrated *in vacuo*. Flash chromatography (95% CH₂Cl₂ / methanol 5%) afforded a brown oil (0.50 g, 1.09 mmol, yield 79.6%). ¹H NMR (400 MHz, CDCl₃) δ 3.16 (s, 1H, acetylene proton), 3.29 (m, 6H, -OCH₃), 3.45 – 4.08 (m, protons of triethylene oxide moiety), 6.75 – 6.77 (m, 2H, aromatic protons), 6.91 (d, 1H, aromatic proton). Anal. Calc. for C₂₂H₃₄O₈: C 61.95, H 8.04, O 30.01; found C 62.26, H 7.95. FAB-mass calculated for C₂₂H₃₄O₈ (M)⁺: 426.5 ; found 426.4.

Monomer Model. To the solution of DMF (1 mL) and diisopropylamine (5 mL), 1,4-bis((triethylene glycol monomethyl ether)oxy)-2-ethynylbenzene (60.0 mg, 0.130

mmol), Monomer 1 (60.0 mg, 0.0237 mmol), Pd (PPh₃)₂Cl₂ (70.0 mg, 0.100 mmol), PPh₃ (52.0 mg, 0.198 mmol) and CuI (19.0 mg, 0.100 mmol) were added. The resulting solution was degassed and heated at 80 °C for 40 h with stirring. The resulting solution was reprecipitated with acetone and methanol three times to remove remaining 1,4-bis((triethylene glycol monomethyl ether)oxy)-2-ethynylbenzene. The slight yellow precipitation was collected by centrifugation and finally purified with HPLC (40.0 mg, 51.3%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 3.56 – 4.54 (m, protons of β-CD and triethylene oxide moieties), 4.84 – 4.94 (br, 14H, C₁H protons of β-CD), 5.58 – 5.84 (br, 28H, OH groups of β-CD), 6.96 – 7.12 (m, 8H, aromatic protons),. UV-Vis (DMF): λ_{max} = 362 nm. Fluorescence (DMF, excited at 360 nm) λ_{max} = 409 nm. Positive ion MALDI-TOF mass m/z = 3219 (M)⁺.



1-Adamantyl-(1-methyl-4-(1'-methyl-4'-pyridinium)pyridinium)ketone (AdBpyMe), Adamantane carbomethylpyridinium bromide (AdPy) were prepared according to a previous paper.⁵

Optical Properties of Polymers

Table S1. UV-Vis absorption and fluorescence properties in DMF

Polymer	λ_{\max} (nm)	FL ^b (nm)	$\Phi_{\text{fl}}^{\text{a}}$
Polym-1	443	481	0.24
Polym-2	433	473	0.41

^a The quantum efficiency (Φ_{unk}) of an unknown sample was calculated by the following equation: $\Phi_{\text{unk}} = \Phi_{\text{std}} [A_{\text{std}} F_{\text{unk}} / A_{\text{unk}} F_{\text{std}}] [n_{\text{D,unk}} / n_{\text{D,std}}]^2$ where A_{std} and A_{unk} are the absorbance of the standard and unknown samples, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_{D} is the refractive index [CH_2Cl_2 ($n_{\text{D}} = 1.424$) and DMF ($n_{\text{D}} = 1.430$) were used]. 9-Anthracene carboxylic acid was used as a standard.

^b Excited at 400 nm.

¹H NMR Spectra of Polym-1 in DMSO-*d*₆ and D₂O

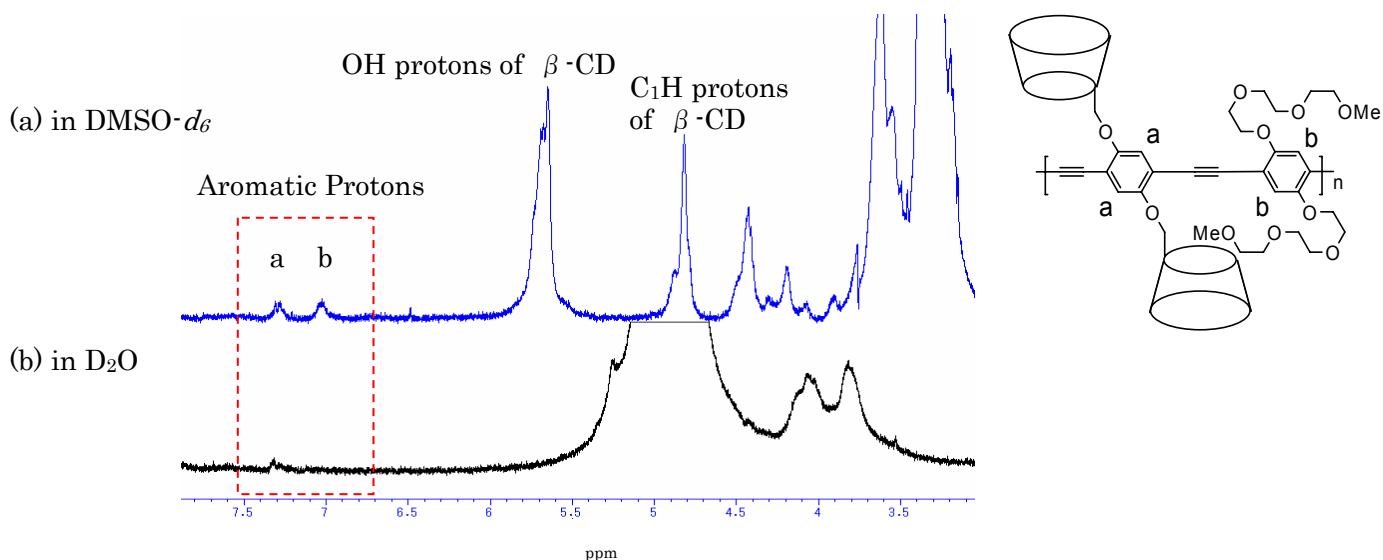


Figure S1. 400 MHz ¹H NMR spectra of Polym-1 in (a) DMSO-*d*₆ and (b) D₂O at 30 °C.

^1H NMR Spectra of Polym-1 with Guest Compounds

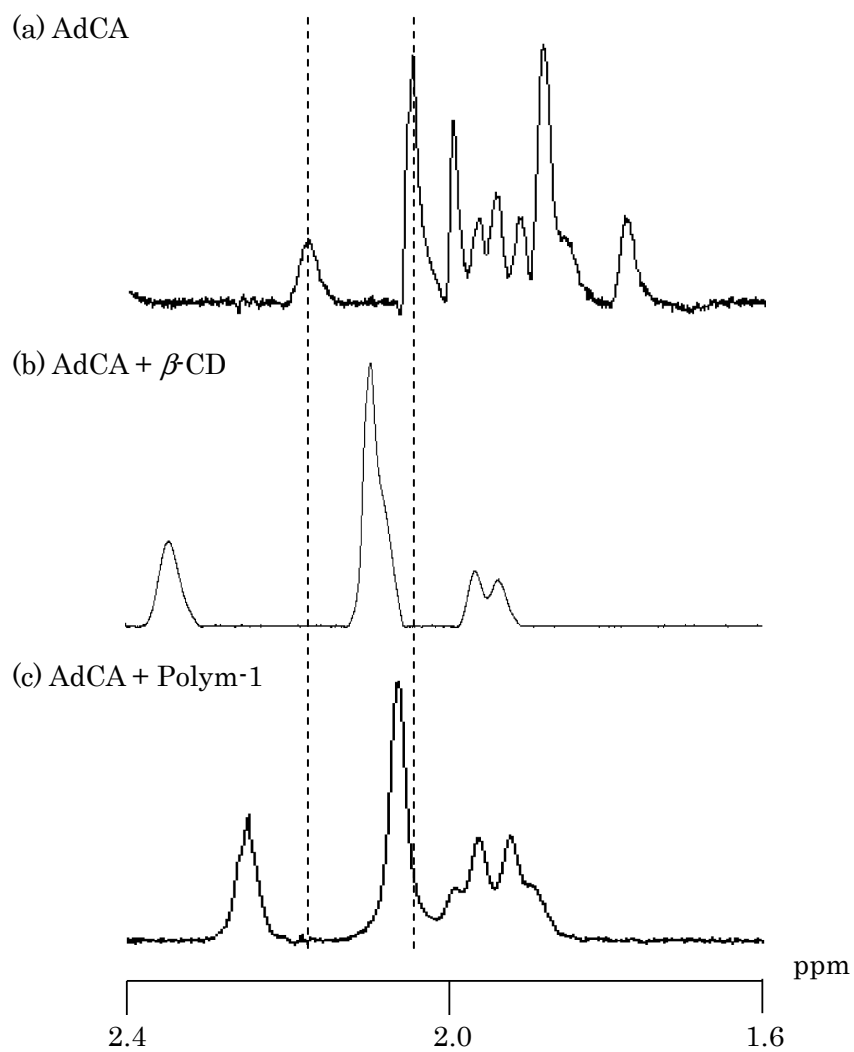


Figure S2. 400 MHz ^1H NMR spectra of (a) AdCA, (b) AdCA + β -CD and (c) AdCA + Polym-1 in D_2O .

References

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