Supplementary information

**Thermally responsive poly(ethylene oxide)-based polyrotaxanes bearing hydrogen-bonding pillar[5]arene rings**

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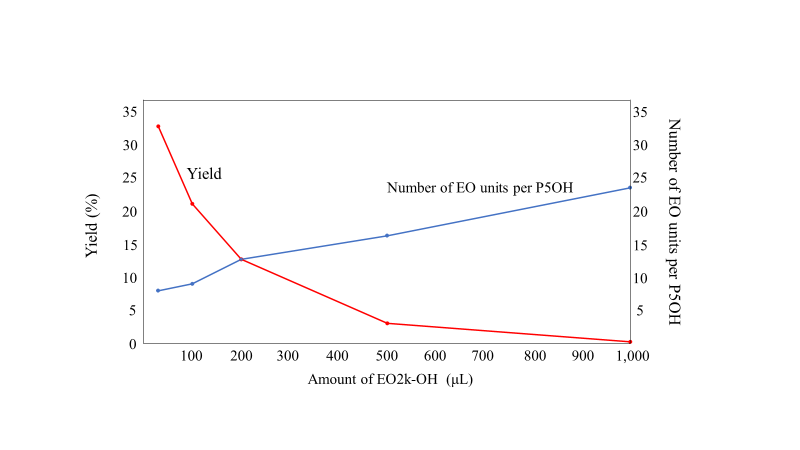
**1. Synthetic procedures**

**Supplementary Table 1** Poly(ethylene oxide)s (PEOs) used in this study

|  |  |  |
| --- | --- | --- |
| Types of PEOs | Product Name | Product Number |
| PEO2k-OH | Polyethylene Glycol 2,000 | Wako (165-09105) |
| PEO4k-OH | Polyethylene Glycol 4,000 | Wako (162-09115) |
| PEO6k-OH | Polyethylene Glycol 6,000 | Wako O (169-09125) |
| PEO20k-OH | Polyethylene Glycol #20,000 | Nacalai Tesque (28223-85) |
| PEO100k-OH | Polyethylene Oxide, M.W. 100,000 | Aldrich (42236) |
| PEO500k-OH | Polyethylene Glycol 500,000 | Wako (160-18521) |
| PEO2k-NH2 | Poly (ethylene glycol) diamine | Aldrich (753084-1G) |
| PEO2k-OMe | Poly (ethylene glycol) dimethyl ether | Aldrich (445908-50G) |
| PEO2k-OTs | PEG-ditosylate | Aldrich (719080-5G) |

**1.1 Effect of the amount of PEO2k-OH**

10 mL (10 mmol/L) of **P5OH** solution in methanol and water [1/1 (v/v)] was mixed with a varying amount (20 μL, 30 μL, 50 μL, 100 μL, 200 μL, 500 μL, 1,000 μL) of **PEO2k-OH** solution (833 mmol/L) in the same solvent. Then, the resulting pseudopolyrotaxanes were obtained by following the procedure described in the main text. The molar ratios of EO units to **P5OH** were determined by 1H NMR spectroscopy (Supplementary Table 2 and Supplementary Fig. 1).



**Supplementary Fig. 1** PEO amount-dependent changes in yield (left) and number of EO units per **P5OH** (right) of pseudopolyrotaxane **P5OH•PEO2k-OH**

**Supplementary Table 2** Effect of the amount of **PEO2k-OH** solution

|  |  |  |
| --- | --- | --- |
| Added PEO solution | Yield (%) | Number of EO units per **P5OH** |
| 30 μL | 33 | 8 |
| 100 μL | 21 | 11 |
| 200 μL | 13 | 13 |
| 500 μL | 3 | 16 |
| 1000 μL | <1 | 23 |

**1.2 Effect of the molecular weight and terminal groups of PEOs**

10 mL (10 mmol/L) of **P5OH** solution in methanol and water [1/1 (v/v)] was mixed with 0.60 mL of **PEO4k-OH, 6k-OH, 20k-OH, 100k-OH,** and **500k-OH** solution (42 mmol/L) in the same solvent. The resulting pseudopolyrotaxanes were obtained by following the procedure described in the main text.The molar ratios of ethylene oxide units to **P5OH** were also determined by 1H NMR spectroscopy. Further, the effect of PEO’s terminal groups was studied using solutions of Poly (ethylene glycol) diamine (**PEO2k-NH2**), Poly (ethylene glycol) dimethyl ether (**PEO2k-OMe**), and PEG-ditosylate (**PEO2k-OTs**), on the basis of the same method.

**Supplementary Table 3** Effect of the molecular weight and terminal groups of PEOs

|  |  |  |
| --- | --- | --- |
| Types of PEOs | Yield (%) | Number of EO units per **P5OH** |
| **PEO2k-OH** | 32 | 8 |
| **PEO4k-OH** | 32 | 12 |
| **PEO6k-OH** | 74 | 15 |
| **PEO20k-OH** | 70 | 19 |
| **PEO100k-OH** | 45 | Unmeasurable\* |
| **PEO500k-OH** | 76 | Unmeasurable\* |
| **PEO2k-NH2** | 28 | 2.5 |
| **PEO2k-OMe** | 12 | 9 |
| **PEO2k-OTs** | 41 | 8 |
| **PEO20k-COOH** | 19 | 4.2 |
| **PEO500k-COOH** | 18 | 14 |

\*These pseudopolyrotaxanes could not be dissolved in deuterated solvents enough for NMR studies.

**1.3 Competition with adiponitrile**

10 mL (10 mmol/L) of **P5OH** solution in methanol and water [1/1 (v/v)] was mixed with 0.60 mL of **PEO2k-OH** solution (42 mmol/L) in the same solvent and adiponitrile (0.050 mL, 0.45 mmol). The resulting mixture was vigorously sonicated for 1 h. The mixture was allowed to stand overnight and then centrifuged. The resulting supernatant was removed to give crude pseudopolyrotaxane as a precipitate, which was washed with water. Removal of water *in vacuo* afforded pseudopolyrotaxane (0.004 g, 3.2%). The molar ratio of EO units to **P5OH** was determined to be 27.

**1.4 Effect of pH**

**P5OH** (0.075 g, 0.10 mmol) was dissolved in a NaOH solution in a mixed solvent of methanol and water (10 mL, 1/1 (v/v), pH = 12). **PEO2k-OH** (0.500 g, 0.25 mmol) was also dissolved in the same NaOH solution (6.0 mL, 42 mmol/L, pH = 12) in another vial. The **PEO2k-OH** solution (0.60 mL) was added to the **P5OH** solution (10 mL) and the resulting mixture was vigorously sonicated for 1 h. The mixture was allowed to stand overnight and then centrifuged. The resulting supernatant was removed to give crude pseudopolyrotaxane as a precipitate. The precipitate was washed with water and dried *in vacuo*, affording pseudopolyrotaxane (0.011 g, 8.8%). The molar ratio of EO units to **P5OH** was determined to be 193.

**1.5 COOH-terminated PEO (PEO20k-COOH)**S1



**PEO20k-OH** (10 g), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 100 mg, 0.640 mmol), and NaBr (100 mg, 0.9.72 mmol) were suspended in water (100 mL), to which aqueous NaClO solution (available chlorine > 5.0%, 10 mL) was added. After stirring at room temperature for 30 min, the mixture was quenched with ethanol and acidified with dilute aqueous HCl solution to become pH < 2. The mixture was extracted with 100 mL of CH2Cl2 three times and the combined organic layers were evaporated under reduced pressure. The residue was dissolved in hot ethanol, followed by precipitation in a freezer overnight to yield **PEO20k-COOH** (9.10 g, 91%) as a white solid.

Following the same method, **PEO500k-OH** (10 g) was converted to **PEO500k-COOH** (7.57 g, 76%).

**1.6 Effect of solvents used in capping reactions**

1-Adamantanamine (16 mg, 0.11 mmol), BOP reagent (48 mg, 0.11 mmol), and EDIPA (0.019 mL, 0.12 mmol) were dissolved in various solvents (10 mL). The solution was cooled to 0 °C with an ice bath, to which **P5OH•PEO20k-COOH** (ca. 150 mg) were added. The reaction mixture was allowed to warm up to room temperature and stirred overnight at that temperature. After the solvent was removed under reduced pressure, the residue was washed with acetone to yield polyrotaxanes as brown solids. The yield and molar ratios of ethylene oxide units to **P5OH** were displayed in Supplementary Table 4.

**Supplementary Table 4** Effect of solvents used in capping reactions

|  |  |  |  |
| --- | --- | --- | --- |
| Dry solvent | **P5OH•PEO20k-COOH**  (mg) | Yield  (%) | Number of EO units  per **P5OH** |
| Acetonitrile | 154 | 32 | 34 |
| DMF | 150 | 28 | 28 |
| THF | 163 | 38 | 20 |
| Acetone | 152 | 43 | 9 |

**1.7 Polyrotaxanes of α-CD and PEO (α-CD•PEO500k-CONHAd)**S1

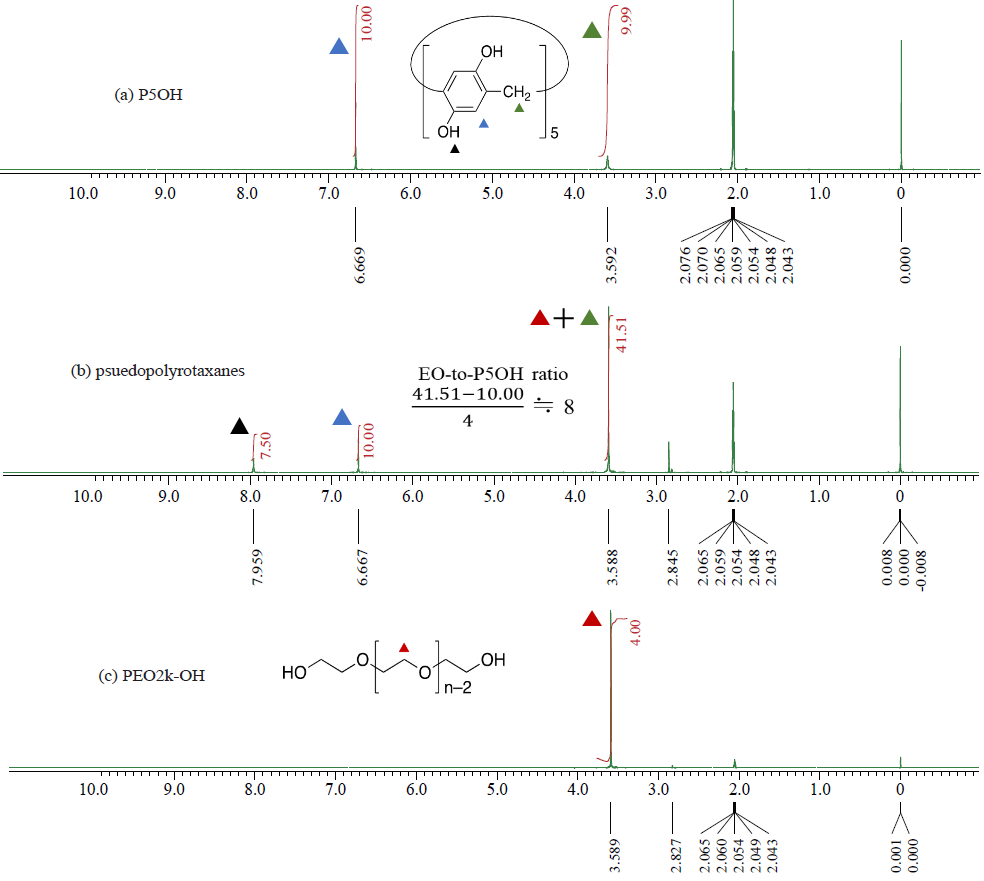
**PEO500k-COOH** (3.0 g, 6.0 μmol) and α-cyclodextrin (**α-CD**, 12 g, 12 mmol) were dissolved in water (100 mL) and kept in a refrigerator overnight, giving a white paste-like inclusion complex. The solution was cooled to 0 °C with an ice bath, to which 1-Adamantanamine (0.16 g, 1.1 mmol), BOP reagent (0.48 g, 1.1 mmol), and EDIPA (0.19 mL, 1.2 mmol) dissolved in dehydrated DMF (100 mL) were added. The slurry-like mixture was allowed to react at 4 °C overnight, followed by washing with DMF/methanol [1/1 (v/v)] and methanol. Precipitation of the DMSO solution (80 mL) of the obtained solid into water (800 mL), repeated washing with water to yield **α-CD•PEO20k-CONHAd** as a white solid (10.3 g, yield 98%, EO-to-**α-CD** ratio: 7).

**1.8 Polyrotaxanes of P5OEt and PEO (P5OEt•PEO20k-CONHAd)**

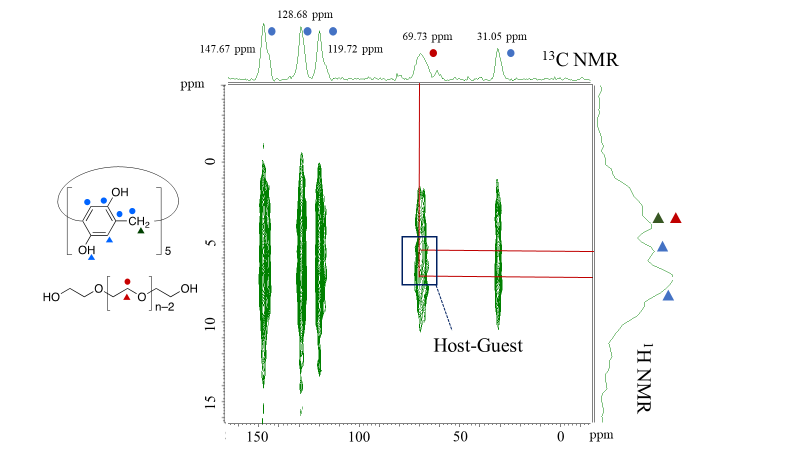
**PEO20k-COOH** (2.9 g, 0.145 mol) was melted at 80 °C, to which **P5OEt** (640 mg, 0.72 mmol) was immersed for 2.5 h. The complex was left at room temperature overnight, followed by washing with water to remove uncomplexed **PEO20k-COOH** to yield **P5OEt•PEO20k-COOH** as a white solid (510 mg, yield 14% EO-to-**P5OEt** ratio: 17).S2

1-Adamantanamine (16 mg, 0.11 mmol), BOP reagent (48 mg, 0.11 mmol), and EDIPA (0.019 mL, 0.12 mmol) were dissolved in super dehydrated acetone, chloroform or THF (10 mL). The solution was cooled to 0 °C with an ice bath, to which **P5OEt•PEO20k-COOH** (150 mg) was added. The reaction mixture was allowed to warm up to room temperature and stirred overnight at that temperature. Removal of the solvent under reduced pressure gave crude materials as pale orange solids, which were characterized by 1H NMR spectroscopy and GPC analysis. No signals assigned to the threaded **P5OEt** were detected, which suggested that polyrotaxanes were not contained in the solids.

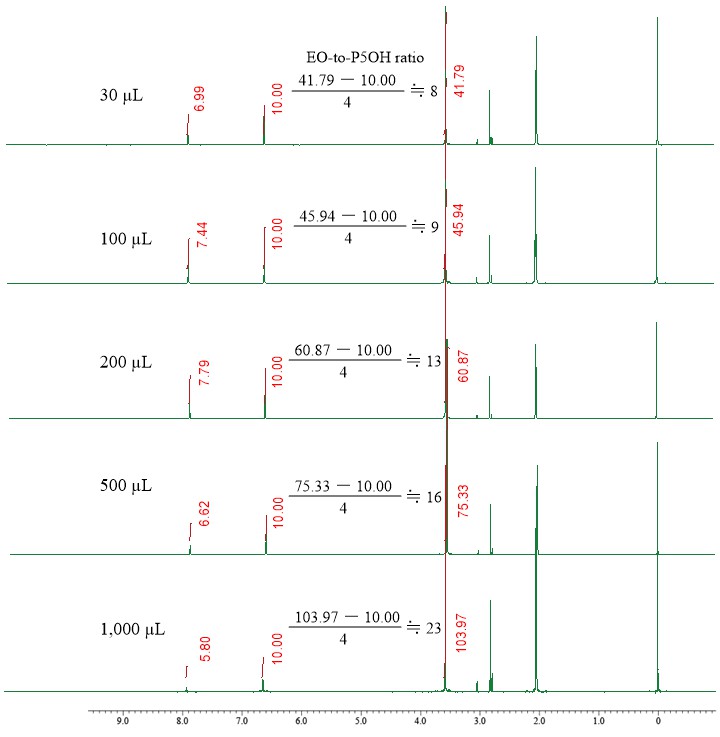
**2. NMR spectra**

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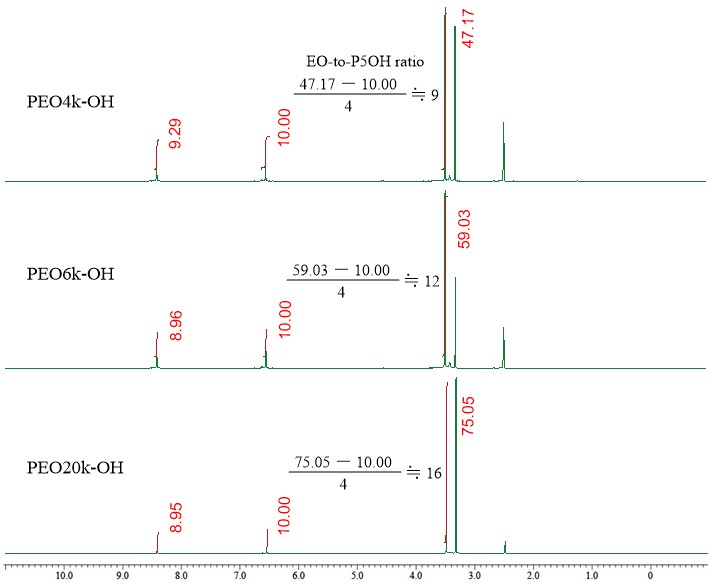
**Supplementary Fig. 2** 1H NMR spectra of **a** **P5OH**, **b** **P5OH•PEO2k-OH** (de-threading gave free **P5OH** and **PEO2k-OH**), and **c PEO2k-OH** (acetone-*d*6, 25°C)

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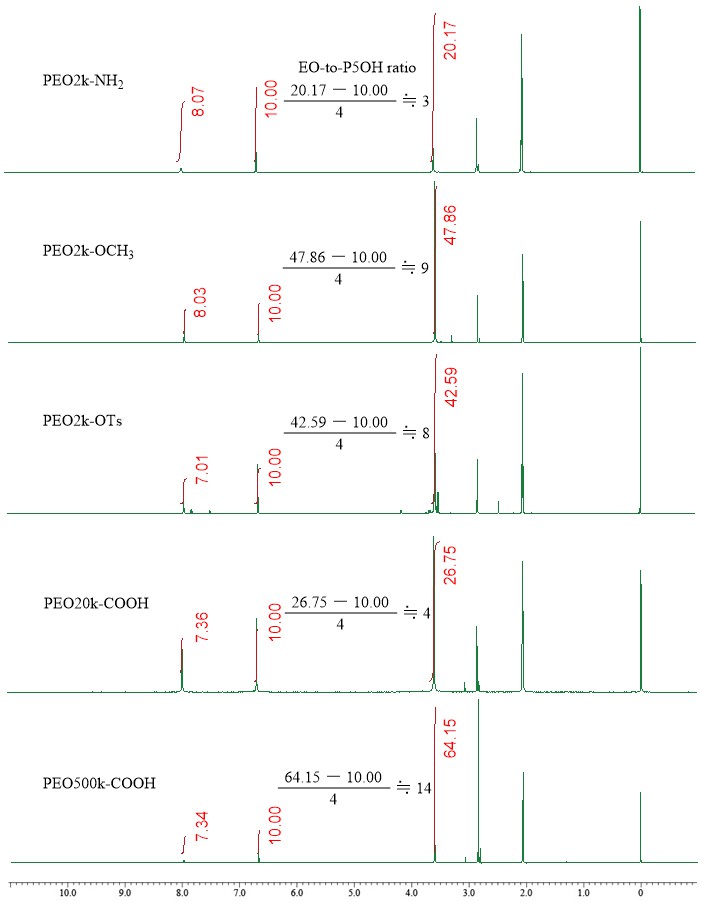
**Supplementary Fig. 3** Solid-state 2D 1H/13C hetero-correlated NMR spectrum of **P5OH•PEO2k-OH**



**Supplementary Fig. 4** 1H NMR spectra of pseudopolyrotaxanes prepared in **1.1** (acetone-*d*6, 25°C)

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**Supplementary Fig. 5** 1H NMR spectra of pseudopolyrotaxanes with various PEO molecular weight (DMSO-*d*6, 25 °C)



**Supplementary Fig. 6** 1H NMR spectra of pseudopolyrotaxanes with different terminal groups (acetone-*d*6, 25°C)



**Supplementary Fig. 7** 1H NMR spectrum of **P5OH•PEO20k-CONHAd** (DMSO-*d*6, 25°C)



**Supplementary Fig. 8** 1H NMR spectrum of polyrotaxanes prepared in **1.6** using acetonitrile as the reaction solvent (DMSO-*d*6, 25°C)



**Supplementary Fig. 9** 1H NMR spectrum of polyrotaxanes prepared in **1.6** using DMF as the reaction solvent (DMSO-*d*6, 25°C)



**Supplementary Fig. 10** 1H NMR spectrum of polyrotaxanes prepared in **1.6** using THF as the reaction solvent (DMSO-*d*6, 25°C)



**Supplementary Fig. 11** 1H NMR spectrum of polyrotaxanes prepared in **1.6** using acetone as the reaction solvent (DMSO-*d*6, 25°C)



**Supplementary Fig. 12** 1H NMR spectrum of **P5OH•PEO500k-CONHAd** (DMSO-*d*6, 25°C)



**Supplementary Fig. 13** 1H NMR spectrum of **α-CD•PEO500k-CONHAd** (DMSO-*d*6, 25°C)

**3. GPC charts**

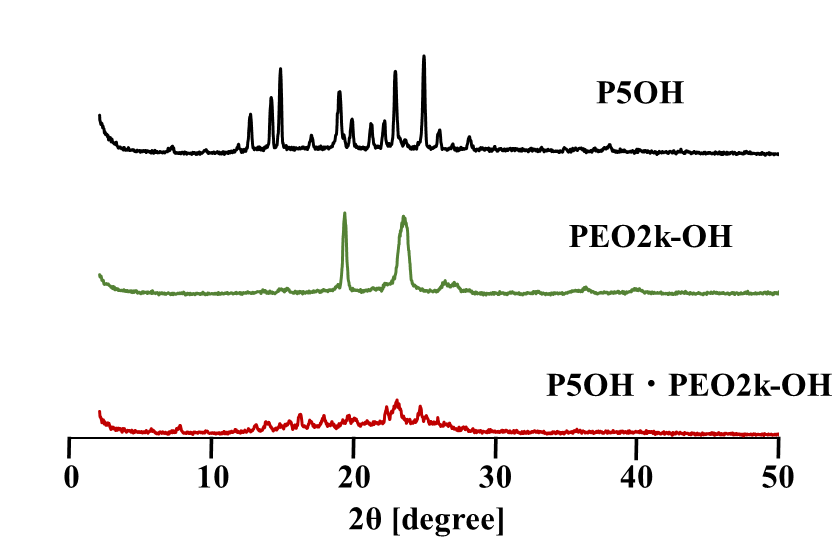


**Supplementary Fig. 14** GPC-UVtraces of **P5OH**, **PEO20k-OH**, and **P5OH•PEO20k-CONHAd** using DMF (10 mM LiBr) as the eluent



**Supplementary Fig. 15** GPC-UV traces of **P5OEt** and crude materials prepared in **1.8** using acetone, chloroform and THF as the reaction solvent. For GPC-UV measurements, THF was used as the eluent

**4. PXRD analysis**



**Supplementary Fig. 16** PXRD patterns of **P5OH** (top), **PEO2k-OH** (middle), and **P5OH•PEO2k-OH** (bottom)



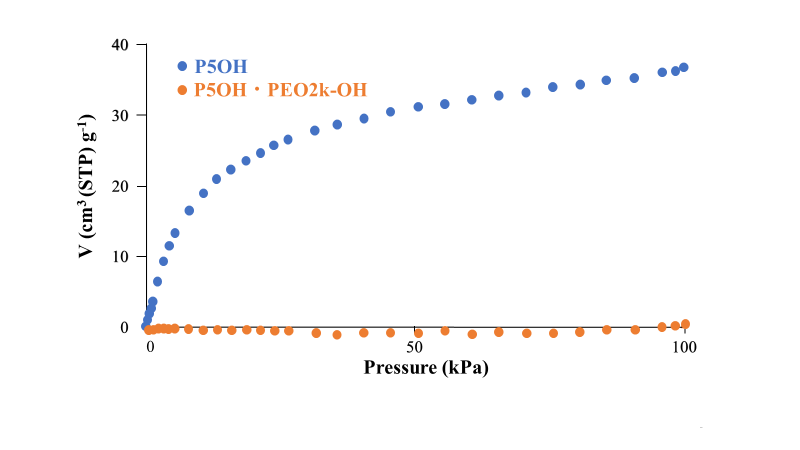






**Supplementary Fig. 17** Variable-temperaturePXRD patterns of **a**,**b** **PEO500k-COOH** and **c**,**d P5OH•PEO500k-CONHAd**. **a**,**c** Heating from 30 °C to 100 °C and **b**,**d** cooling from 100 °C to 30 °C

**5. CO2 gas adsorption measurements**

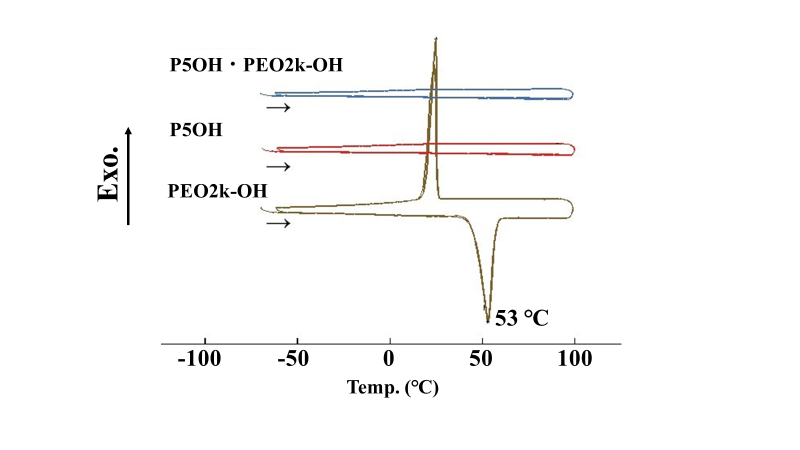


**Supplementary Fig. 18** CO2 adsorption curvilinear diagrams of **P5OH** (blue) and **P5OH•PEO2k-OH** (orange)

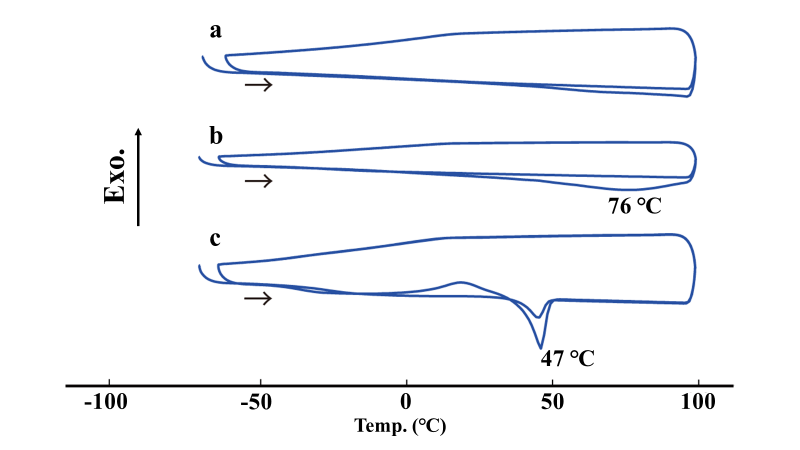


**Supplementary Fig. 19** CO2 adsorption curvilinear diagrams of **P5OH** (blue) and **P5OH•PEO20k-CONHAd** (green)

**6. DSC**

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**Supplementary Fig. 20** DSC graphs of **P5OH•PEO2k-OH** (top), **P5OH** (middle), and **PEO2k-OH** (bottom). Samples were heated from –70 °C to 100 °C and cooled back to –70 °C under N2. This cycle was repeated twice at the heating/cooling rate of 10 °C/min

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**Supplementary Fig. 21** DSC graphs of pseudopolyrotaxanes prepared in **1.1**. The molar ratios of EO units to **P5OH** were **a** 8, **b** 13, and **c** 15. Scanning conditions were the same as those for Supplementary Fig. 20

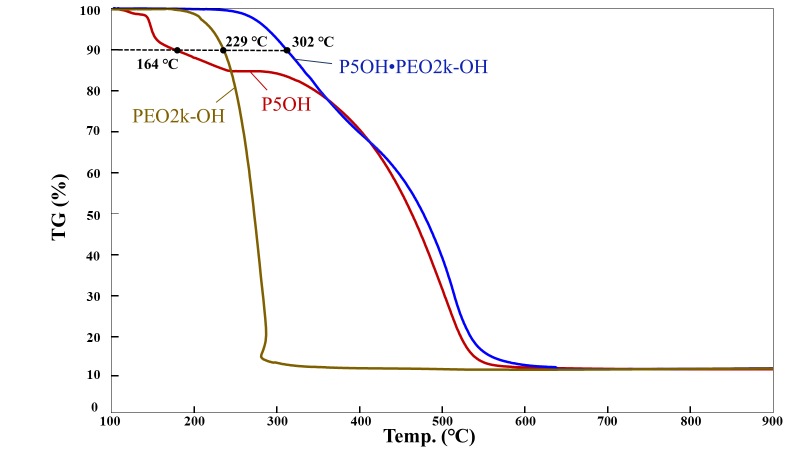






**Supplementary Fig. 22** DSC graphs of **a** **PEO500k-OH**, **b** **P5OH•PEO500k-CONHAd**, and **c** **α-CD•PEO500k-CONHAd**. Samples were heated from 0 °C to 160 °C and cooled back to 0 °C under N2. This cycle was repeated twice at the heating/cooling rate of 10 °C/min. For all materials, no peaks were detected in the regions of 0 °C to 20 °C and 70 to 160 °C

**7. TGA**

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**Supplementary Fig. 23** TGA traces of **PEO2k-OH**, **P5OH**, and **P5OH•PEO2k-OH**. Before the measurement, samples were heated to 100 °C and kept this temperature for 60 min to release the residual solvent under air. Then, the samples were heated from 100 °C to 700 °C at the rate of 10 °C/min under air



**Supplementary Fig. 24** TG traces of polyrotaxanes prepared in **1.6** using various reaction solvents. After heating at 100 °C for 15 min under N2, the samples were heated from 100 °C to 300 °C at the rate of 1.0 °C/min and from 300 °C to 900 °C at the rate of 10 °C/min under N2. The molar ratio of EO units to **P5OH** and their 10% weight loss temperature were 34 and 270 °C (acetonitrile), 28 and 273 °C (DMF), 20 and 253 °C (THF), and 9 and 198 °C (acetone), respectively. These values were between those of uncomplexed **P5OH** (125 °C) and **PEO20k-OH** (371 °C)



**Supplementary Fig. 25** TG traces of **P5OH•PEO500k-CONHAd** and **α-CD•PEO500k-CONHAd**. After being heated at 100 °C for 15 min under N2, the samples were heated from 100 °C to 300 °C at the rate of 1.0 °C/min and from 300 °C to 900 °C at the rate of 10 °C/min under N2

**8. Supplementary references**

1. Araki, J., Zhao, C. & Ito, K. Efficient Production of Polyrotaxanes from α-Cyclodextrin and Poly(ethylene glycol). *Macromolecules* **38**, 7524–7527 (2005).
2. Ogoshi, T. et al. Molecular weight fractionation by confinement of polymer in one-dimensional pillar[5]arene channels. *Nat. Commun.* **10**, 479 (2019).