Electronic Supplementary Information

Polypseudorotaxanes Constructed from Pillar[n]arenes and Polyamides by Interfacial Polymerization

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1. Materials

All solvents and reagents were used as supplied. Per-ethylated pillar[5]arene (**P5A**) was synthesized according to the previous paper.[1]

2. Measurements and Experiments

The ^{1}H NMR spectra were recorded at 500 MHz with a JEOL-ECA500 spectrometer. Diffuse reflectance spectra were recorded with a JASCO V-670 spectrometer. Differential scanning calorimetry (DSC) was performed using a PerkinElmer Jade DSC calorimeter equipped with an Intracooler II under a flow of dry nitrogen and with a heating rate of 10 °C/min. The FT-IR spectra were obtained using a JASCO FT-IR460 plus infrared spectrometer. Powder X-ray diffraction (PXRD) patterns were measured using Smart Lab (Rigaku). Solid-state NMR experiments were carried out at 6.9 T (74.18 MHz for ^{13}C) using a JEOL-ECA-300 NMR spectrometer and a 4.0 mm CP-MAS probe. All samples were spun at a frequency of 5.0 kHz. All sample temperatures were between 300 and 302 K calibrated by $Pb(NO_3)_2$. ^{13}C chemical shifts are presented in ppm relative to tetramethylsilane using the ^{13}C chemical shift for the methine ^{13}C of solid adamantine (29.5 ppm) as an external reference standard. For ^{13}C 1D spectra, the variable-amplitude cross polarization and total suppression of spinning sidebands sequences were used to excite ^{13}C magnetization. In all ^{13}C NMR experiments, ^{13}C signals were detected under ^{1}H-^{13}C heteronuclear decoupling with SPINAL64 sequence using a ^{1}H decoupling frequency of 60 kHz. In ^{1}H-^{13}C heteronuclear two-dimensional experiments, ^{1}H signals were detected using Phase Modulated Lee-Goldburg (PMLG) homonuclear decoupling.

Synthetic Procedure of Polypseudorotaxane

In a 100 mL beaker, dichloride (1.11 mmol) and **P5A** (1.00 g, 1.11 mmol) were dissolved in chloroform (10 mL). In a 50 mL beaker, diamine (1.11 mmol) and NaOH (0.018 g, 0.45 mmol) were dissolved in water (5 mL). The aqueous solution in the 50 mL beaker was slowly added to the chloroform solution in 100 mL beaker at room temperature, and allowed it to stand at room temperature for 1 h. After 1 h, a film was formed at the interface between chloroform and water. The film was pulled continuously from the interface in an unstirred reaction, forming ropes of polymeric film. To remove salts and unreacted dicarbonyl chloride and diamine, the polymer film was washed with hot water and methanol. To remove un-complexed P5A, the film was washed with chloroform, in which P5A is highly soluble.

Table S1. Synthesis of polypseudorotaxanes *via* interfacial polymerization using linear dicarbonyl chlorides (**Cn-COCl**)[a]

Entry	**Cn-COCl**	**P5A** (Equiv. to **Cn-COCl**)	Cover Ratio (number of units covered by one **P5A** ring)[c]	Yield (mg)
1	**C4-COCl**	0.1	55	47
2	**C4-COCl**	0.3	18	25
3	**C4-COCl**	0.5	15	39
5	**C6-COCl**	1	33	32
6	**C8-COCl**	1	22	49
7	**C10-COCl**	1	55	30
8	**C8-COCl**	4	3.2	48
9	**C8-COCl**	10	2.8	32

[a] 1 equiv. of **C6-NH$_2$** relative to **Cn-COCl** was used as the diamine.

3. ^{1}H NMR Titrations

NMR titrations were done with solutions which had a constant concentration of pillar[5]arene (1 mM) and varying concentrations of dicarbonyl chloride. By the non-linear curve-fitting methods, the association constants were estimated for 1:1 stoichiometry. The non-linear curve-fitting was based on the equation:[2]

$$\Delta\delta_{obs} = \frac{\Delta\delta_{11}}{2K[H]_0}\left[1 + K[H]_0 + K[G]_0 - \{(1 + K[H]_0 + K[G]_0)^2 - 4K^2[H]_0[G]_0\}^{1/2}\right]$$

Where $\Delta\delta_{obs}$ is the chemical shift change of phenyl proton signal (Figs. S1-S4, peak A) of pillar[5]arene at $[G]_0$, $\Delta\delta_{11}$ is the chemical shift change of pillar[5]arene proton resonance when pillar[5]arene is completely complexed, $[G]_0$ is the initial concentration of the axle, and $[H]_0$ is the fixed initial concentration of pillar[5]arene.

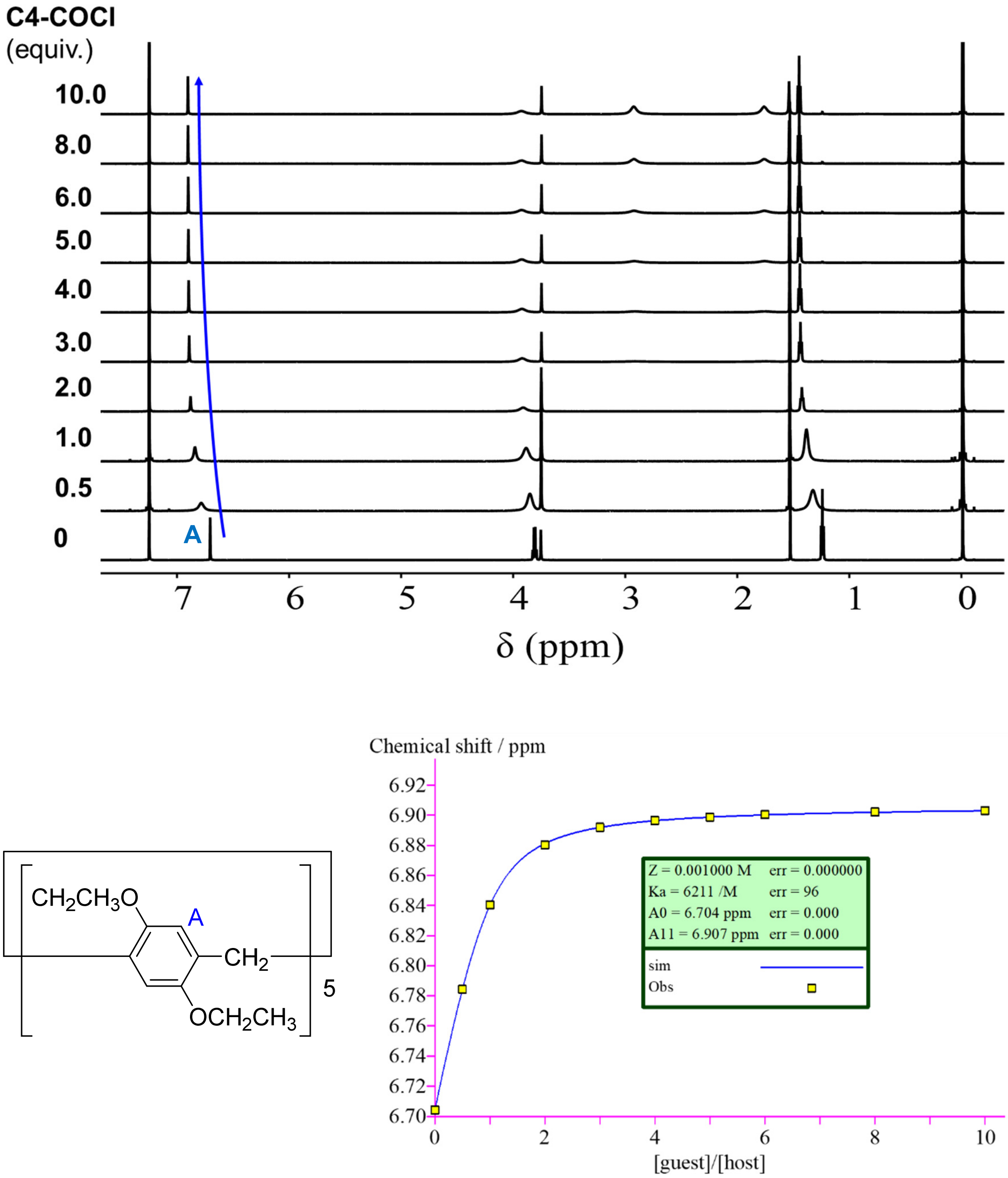


Fig. S1 ^{1}H NMR titrations ($CDCl_3$, 25 °C) of **P5A** (1 mM) with **C4-COCl** (0 equiv. to 10 equiv.).

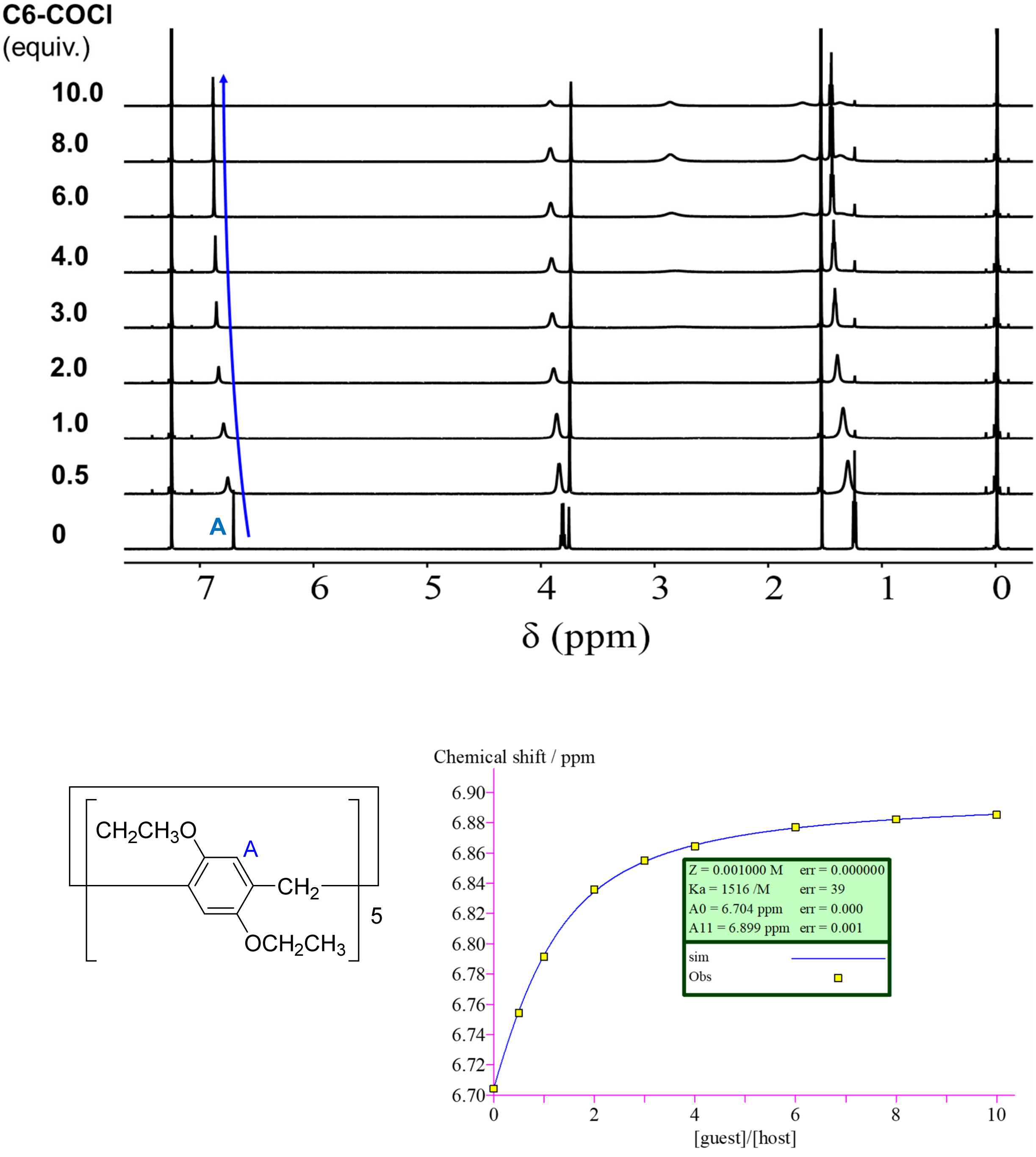


Fig. S2 ^{1}H NMR titrations ($CDCl_3$, 25 °C) of **P5A** (1 mM) with **C6-COCl** (0 equiv. to 10 equiv.).

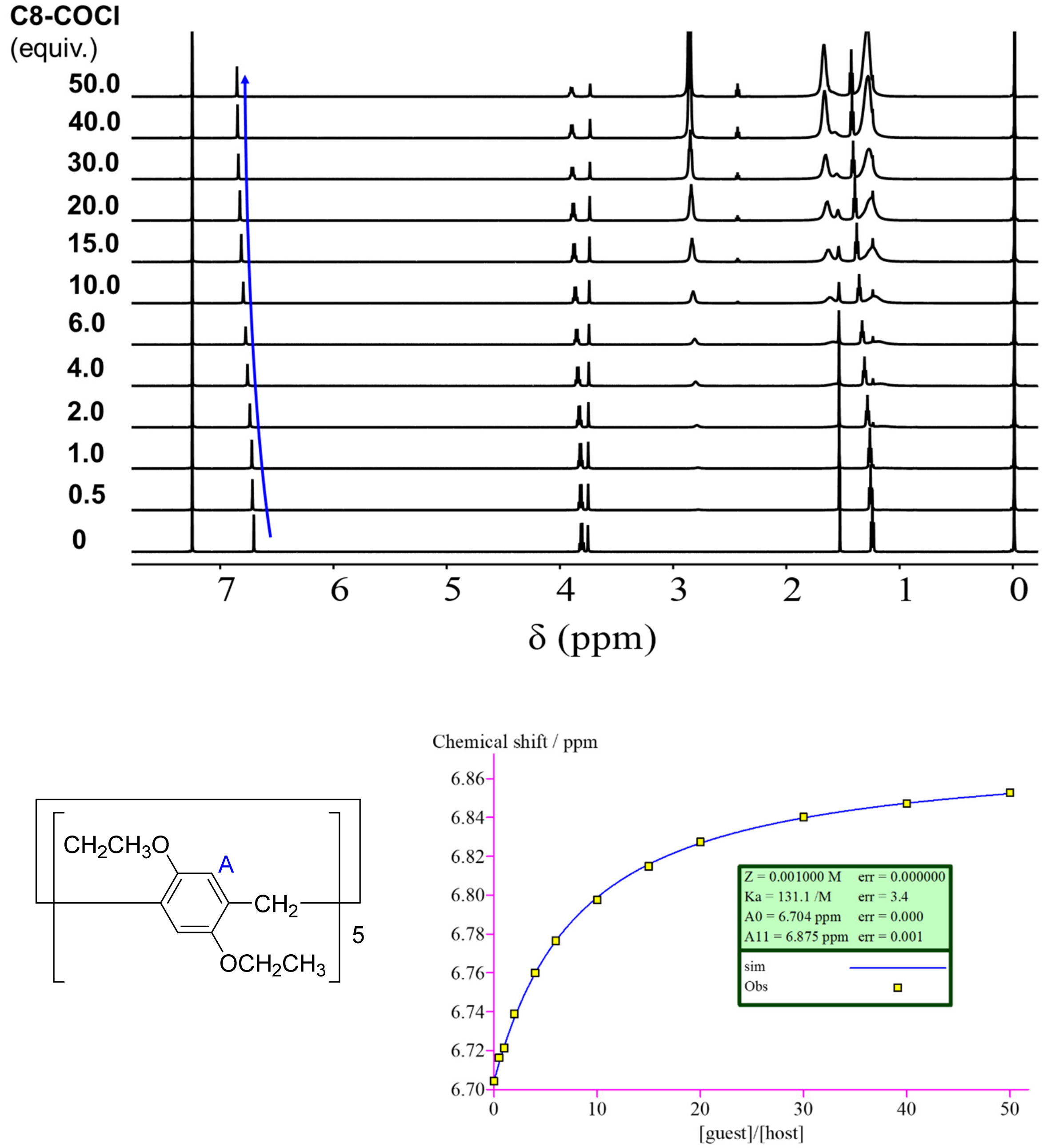


Fig. S3 ^{1}H NMR titrations ($CDCl_3$, 25 °C) of **P5A** (1 mM) with **C8-COCl** (0 equiv. to 50 equiv.).

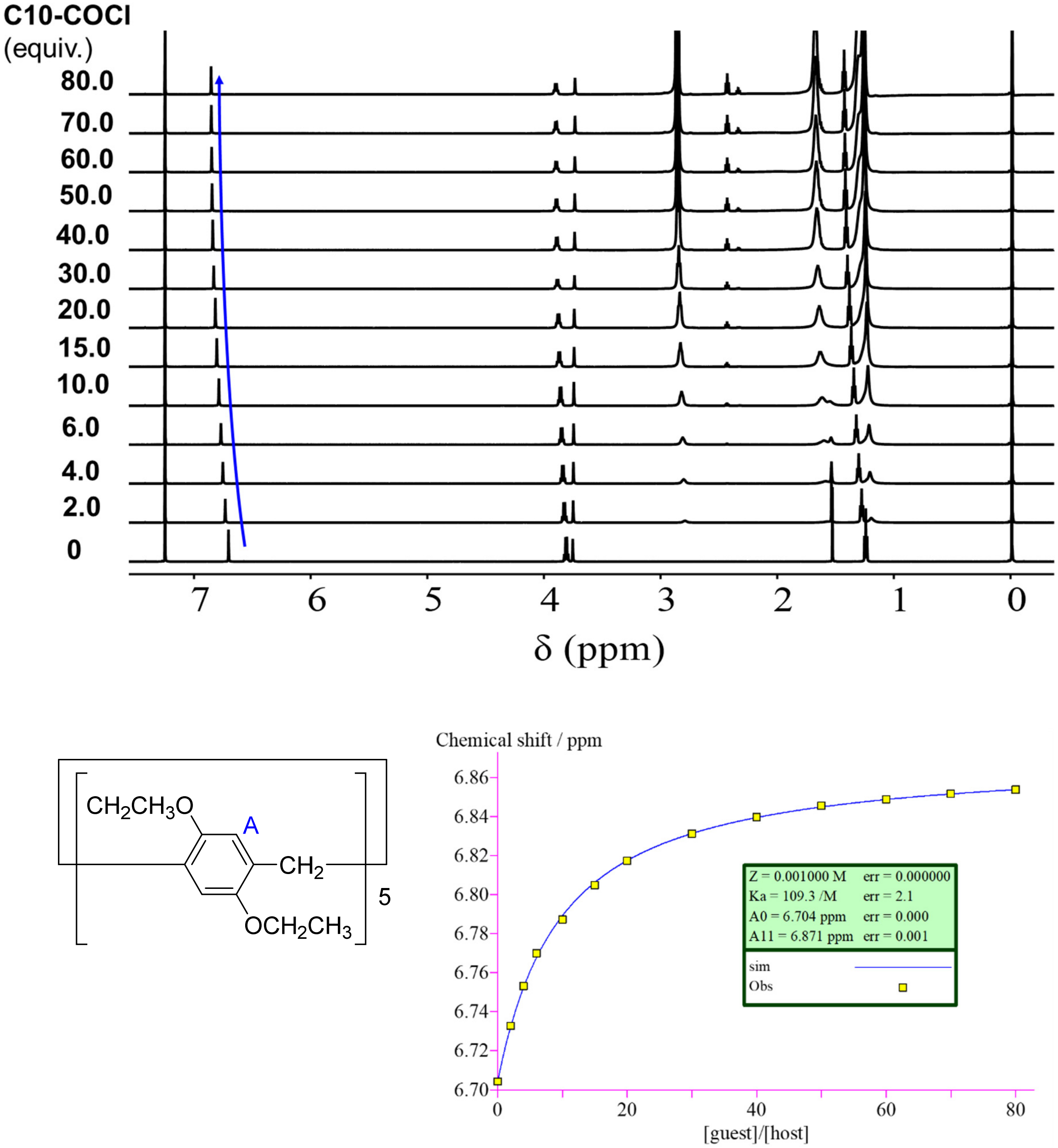
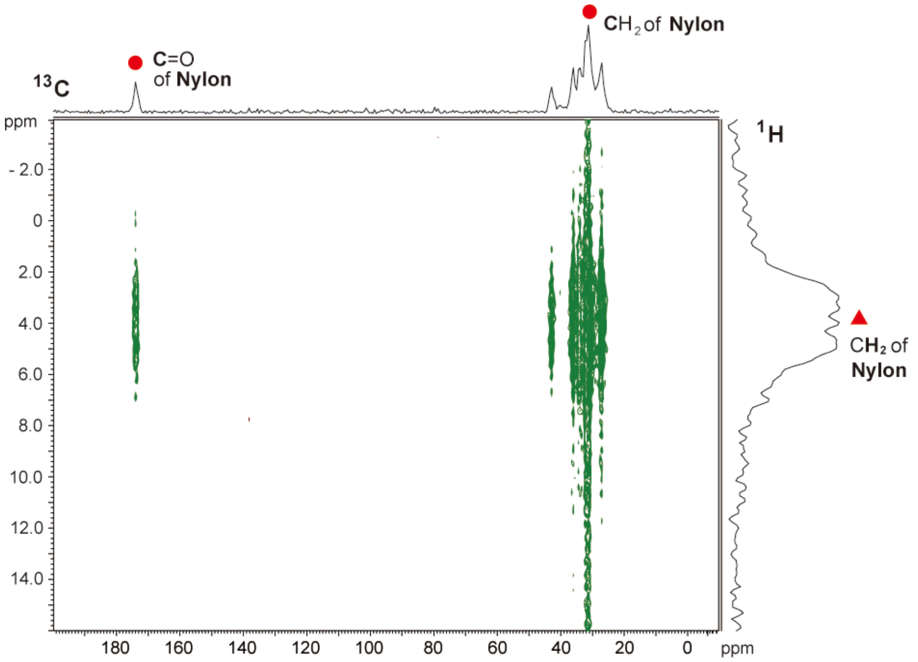


Fig. S4 ^{1}H NMR titrations ($CDCl_3$, 25 °C) of **P5A** (1 mM) with **C10-COCl** (0 equiv. to 80 equiv.).

4. Magnetic angle spinning 2D heterocorrelated NMR spectra

(a) Polyamide



(b) **P5A**

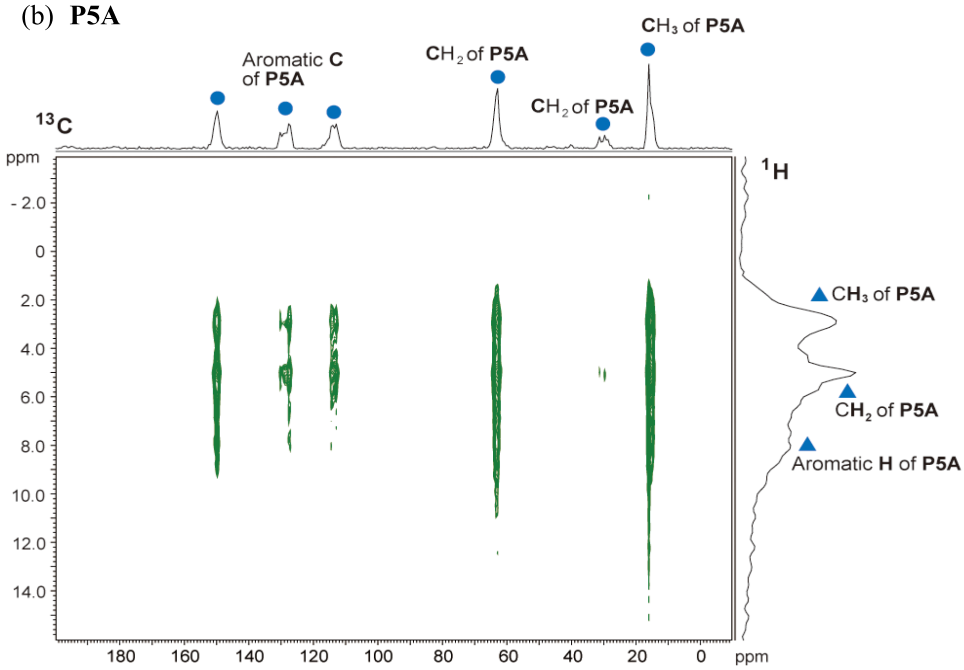


Fig. S5 Magnetic angle spinning 2D heterocorrelated NMR spectra of (a) polyamide (nylon 6,10) and (b) **P5A** with PMLG homonuclear decoupling (ct = 1 ms).

5. FT-IR

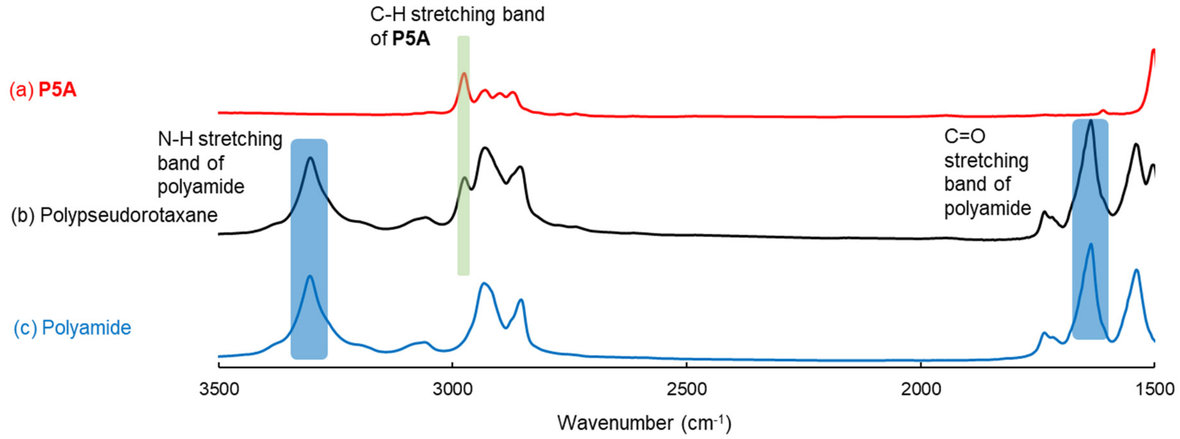


Fig. S6 FT-IR spectra of (a) **P5A**, (b) polypseudorotaxane (entry 8) and (c) polyamide (nylon 6,10).

6. PXRD Patterns

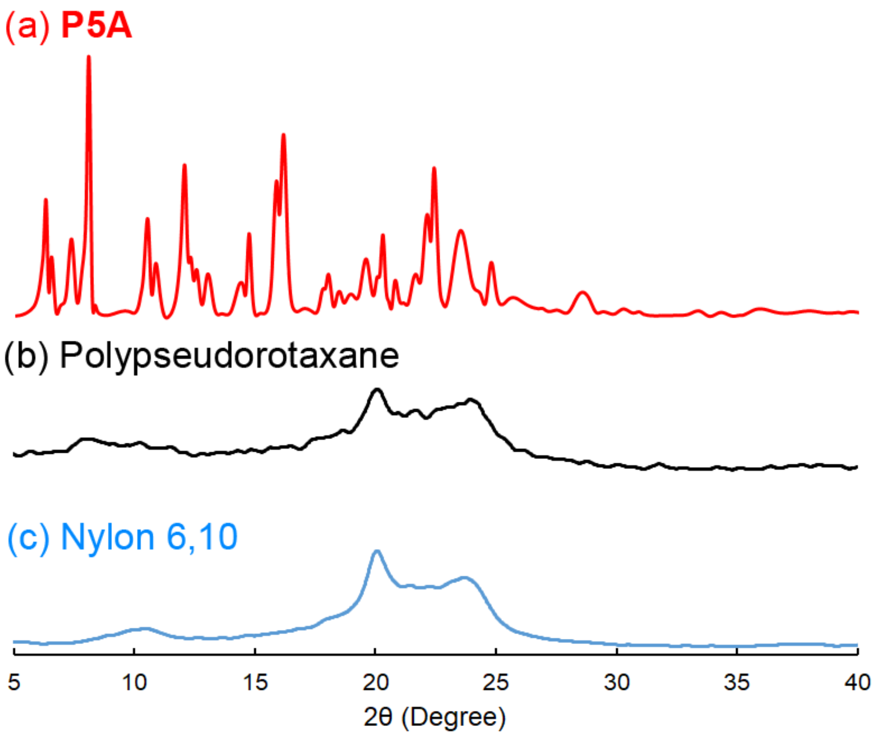


Fig. S7 Powder X-ray diffraction (PXRD) patterns of (a) **P5A**, (b) polypseudorotaxane (entry 8) and (c) polyamide (nylon 6,10).

7. DSC Traces

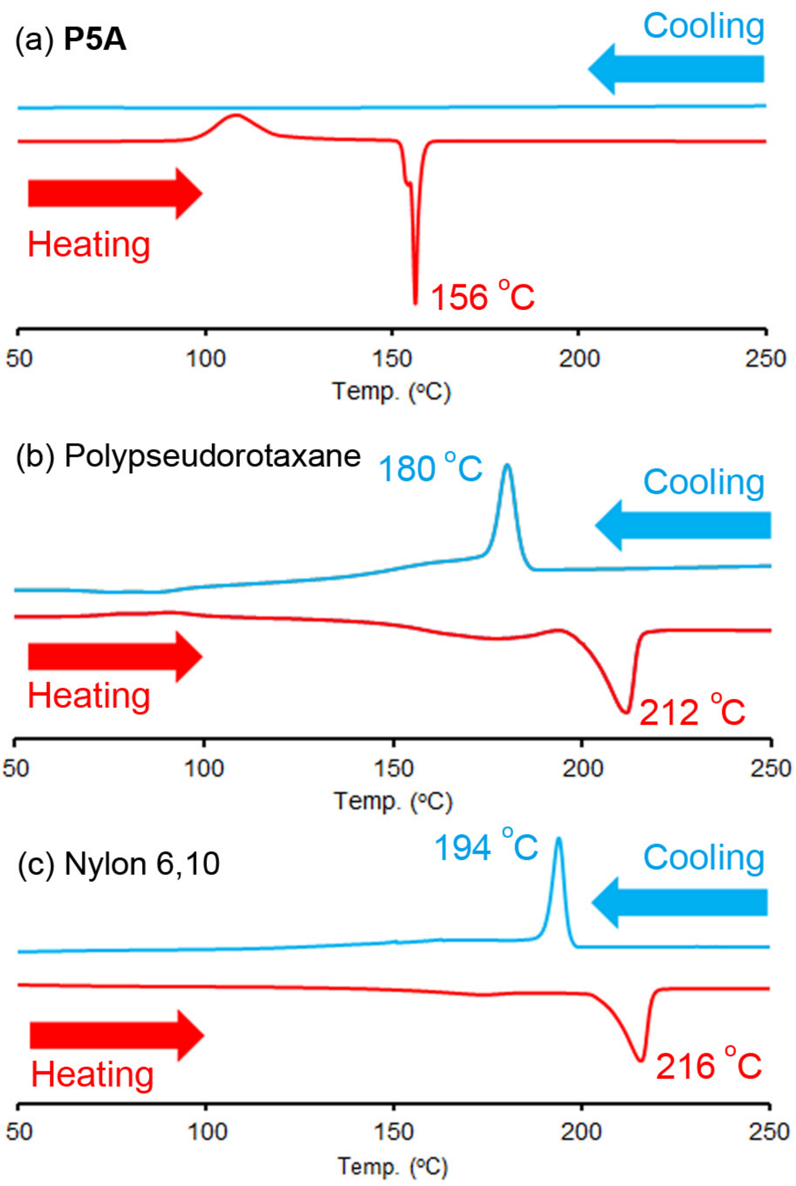


Fig. S8 DSC traces of (a) **P5A**, (b) polypseudorotaxane (entry 8) and (c) polyamide (nylon 6,10).

8. Polypseudorotaxane Synthesis Using Other Amines

Table S2. Synthesis of polypseudorotaxanes using other amines *via* interfacial polymerization with linear **C8-COCl**[a]

Entry	Diamine	Cover Ratio (number of units covered by one **P5A** ring)[b]	Yield (mg)
12	**C4**	19	26
13	**C8**	31	21
14	*p*-phenylene diamine	36	16

[a] 1 equiv. of the diamine relative to **Cn-COCl** was used. [b] Cover ratios (number of nylon units covered by one **P5A** molecule) were determined by elemental analysis.

9. References

1) T. Ogoshi, K. Kitajima, T. Aoki, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Org. Chem.*, 2010, **75**, 3268.

2) P. R. Ashton, R. Ballardini, V. Balzani, M. Bělohradský, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.,* 1996, **118**, 4931.