Molecular weight fractionation by confinement of polymer in one-dimensional pillar[5]arene channels

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Confinement of polymers in nano-spaces can induce unique molecular dynamics and properties. Here we show molecular weight fractionation by the confinement of single polymer chains of poly(ethylene oxide) (PEO) in the one-dimensional (1D) channels of crystalline pillar[5]arene. Pillar[5]arene crystals are activated by heating under reduced pressure. The activated crystals are immersed in melted PEO, causing the crystals to selectively take up PEO with high mass fraction. The high mass fractionation is caused by the greater number of attractive CH/π interactions between PEO C-H groups and the π-electron-rich 1D channel of the pillar[5]arene with increasing PEO chain length. The molecular motion of the confined PEO (PEO chain thickness of ~3.7 Å) in the 1D channel of pillar[5]arenes (diameter of ~4.7 Å) is highly restricted compared with that of neat PEO.
Confinement of polymers in nanometer scale spaces can increase understanding of the intrinsic properties of single polymer chains, control the molecular motion of polymer chains and provide new polymer properties. Zeolites, mesoporous silica, organic crystal hosts, and porous coordination polymers/metal–organic frameworks have been used as nanoporous materials to confine polymers\(^1\text{–}^4\).

Pillar[n]arenes, which were introduced by our group in 2008\(^9\), are pillar-shaped macrocyclic hosts that feature methylene bridge linkages at the para-positions of 2,5-dialkoxybenzene constituent units\(^10\text{–}^17\). Their pillar-shaped structures provide high \(\pi\)-electron density inside their cavities, giving rise to excellent host–guest properties. Pillar[n]arenes can form host–guest complexes with not only cationic guests via charge-transfer interactions, but also neutral guests through multiple \(\text{CH}/\pi\) interactions\(^11\text{,}^18\). However, almost all host–guest complexation experiments using pillar[n]arenes have been carried out in solution systems. Recently, we investigated crystal-state host–guest complexation using pillar[n]arenes\(^19\text{–}22\). We discovered that host–guest complexation could be achieved using pillar[n]arene crystals that were activated by drying solvates in the crystals by heating under reduced pressure. Immersing activated crystals of pillar[n]arenes have been carried out in solution systems. Recently, we investigated crystal-state host–guest complexation using pillar[n]arenes\(^19\text{–}22\). We discovered that host–guest complexation could be achieved using pillar[n]arene crystals that were activated by drying solvates in the crystals by heating under reduced pressure. When the activated crystals were immersed in bulk guest solvents in the crystals by heating under reduced pressure.

**Results**

**Encapsulation of PEO in the 1D channel of crystalline P5.** The host–guest complexation between P5 (Fig. 1a) and PEO (Fig. 1b) in solution was investigated by \(^1\text{H} NMR\) spectroscopy (Supplementary Fig. 2). When PEO with OH end groups (\(M_0 = 1000\), PEO1000-OH, where 1000 is molecular weight of PEO and OH is end groups of PEO) was mixed with P5 in CDCl\(_3\), neither peak shifts nor new peaks were observed, indicating that host–guest complexation hardly took place in CDCl\(_3\). When \(n\)-alkanes were used as the guest, complexation occurred in CDCl\(_3\)\(^23\text{,}^24\). Thus, the negatively charged oxygen atoms in the PEO chain inhibited the complexation in this case\(^25\). Next, we investigated the host–guest complexation of PEO with crystals of P5. First, crystals of P5 were activated according to the reported method\(^19\). PEO melted when heated at 80 °C. The activated P5 crystals were immersed in an excess amount of melted PEO at 80 °C (Fig. 1c; we determined a suitable PEO/P5 feed ratio, Supplementary Fig. S4). Crystals of P5 were insoluble in melted PEO, which means that the complexation proceeded in a heterogeneous system. After immersion in PEO, the crystals were isolated from the mixture by filtration and then washed with water to remove un-complexed PEO (Fig. 1d). The components of the host–guest complex crystals were dissolved in CDCl\(_3\) (PEO and P5 are all highly soluble in CDCl\(_3\)) and then investigated by \(^1\text{H} NMR\) spectroscopy. Proton signals from PEO were clearly observed (Supplementary Fig. 3), despite the fact that the crystals were washed with water to remove un-complexed PEO, indicating that activated crystals of P5 took up PEO during the immersion. As shown in Supplementary Fig. 2, P5 hardly formed any host–guest complexes with PEO in solvent. Therefore, the crystalline-state complexation is a useful method to obtain host–guest complex crystals containing PEO. We monitored the time-dependent uptake of PEO in the crystalline-state complexation using \(^1\text{H} NMR\) spectroscopy (Fig. 2a, Supplementary Fig. 3 and Supplementary Note 1).

Rapid uptake of PEO was observed for activated crystals of P5; it took ca. 10 min to reach an equilibrium state. In the equilibrium state, the PEO uptake amount ratio (PEO unit/host molar ratio) for P5 crystals was ca. 4.0. The efficiency of the complexation of P5 with PEO was also determined by organic vapor sorption experiments. Activated crystals of P5 took up one \(n\)-hexane molecule per cavity upon exposing activated crystals of P5 to \(n\)-hexane vapor\(^19\text{,}^20\). However, P5 \(\supset\) PEO complex crystals did not take up \(n\)-hexane vapor (Supplementary Fig. 5), indicating that all cavities in the P5 crystals after PEO uptake are filled with PEO chains. The P5 \(\supset\) PEO complex crystals were washed with water to ensure that there was no leakage of PEO from the pillar[5]arene cavities.

The complexation of PEO with P5 in crystalline state was confirmed directly by magic angle spinning 2D heterocorrelated NMR study (Fig. 2b). The cross peak observed can be assigned to inter-molecular host–guest correlations of the CH\(_3\) proton groups of P5 and the carbon atoms of PEO, indicating the inclusion of PEO chain in the cavity of P5. From the previous reports\(^26\text{,}^27\), carbon signals of PEO in non-crystalline and crystalline phases were observed at 72.0 and 71.2 ppm, respectively. The chemical shift of neat PEO was observed at 72.0 ppm (Fig. 2c, top), indicating formation of crystalline phase. In contrast, the chemical shift observed in P5 \(\supset\) PEO complex crystals (Fig. 2c, bottom) was ca. 70 ppm, which was remarkably lower than 71.2 ppm and 72.0 ppm assigned to PEO carbon in non-crystalline
and crystalline phases, respectively. Therefore, the upper chemical shift of the $5 \supset PEO$ complex crystals would result from aromatic shielding of PEO upon incorporation into the cavities of $P5$.

To investigate the assembled structures of $5 \supset PEO$ complex, powder X-ray diffraction patterns (PXRD) were measured. The PXRD pattern of $5 \supset PEO$ complex crystals was quite different from that of activated $P5$ crystals (Supplementary Fig. 7), indicating that a crystal transformation underwent by the PEO uptake. PXRD patterns of the host–guest complex crystals using $P5$ can be classified as two major classes, i.e., 1D channel and herringbone structures. As a rule, when the length of the $n$-alkanes was increased, $5 \supset n$-alkane complexes changed from a herringbone to a 1D channel structure to cover the protruding part of the $n$-alkane molecule. $5 \supset n$-hexane complex forms herringbone structure, but $5 \supset n$-octane complex forms 1D channel structure. The PXRD pattern of $5 \supset PEO$ complex in low angles was similar to that of $5 \supset n$-octane complex, but not similar to that of $5 \supset n$-hexane complex. These data indicates that $P5$ molecules in the crystals after the PEO uptake also assembled to form 1D channels containing PEO chains. PEO is long linear chain guest, thus formation of the 1D channels should be reasonable.

**Molecular weight fractionation by activated $P5$ crystals.** Activated crystals of $P5$ are able to take up PEO when they are immersed in melted PEO. Next, we turned our attention to the dependence of PEO uptake efficiency on the molecular weight of PEO. PEO uptake time was monitored by $^1H$ NMR spectroscopy. As the molecular weight of PEO increased, complexation took a longer time to reach the equilibrium state (Supplementary Fig. 8). To form a complex, an end group of PEO needs to thread into a $P5$ crystal. The number of end groups of PEO decreases as the molecular weight of PEO increases. Therefore, the complexation took a longer time to form as the molecular weight of PEO increased.

We investigated the uptake of PEO with different molecular weights by activated crystals of $P5$. $5 \supset PEO$ complex crystals containing PEO10000-OH were prepared by immersing activated crystals $P5$ in melted PEO1000-OH. Subsequently, the $P5$ crystals complexed with PEO1000-OH were immersed in melted PEO1000-OH. The molecular weight of PEO encapsulated in the host–guest complex crystals was evaluated by liquid chromatography. Peaks from PEO10000-OH were observed, whereas those from PEO1000-OH were not (Supplementary Fig. 9 and Supplementary Note 3), indicating that the guest PEO1000-OH was replaced with PEO10000-OH. In contrast, a similar guest replacement event did not occur when $5 \supset PEO$ complex crystals containing PEO10000-OH were immersed in melted PEO1000-OH (Supplementary Fig. 10 and Supplementary Note 4). These results indicate that activated $P5$ crystals interact more strongly with PEO of higher mass fraction than with PEO of lower mass fraction. Next, activated $P5$ crystals were immersed in an equal-weight mixture of PEO with different molecular weights (Fig. 3a, top, PEO1000-OH, PEO4000-OH, PEO6000-OH, and PEO10000-OH). The host–guest complex crystals formed after the immersion showed peaks from PEO with high mass fraction, mainly PEO6000-OH and PEO10000-OH (Fig. 3a, bottom), indicating that activated $P5$ crystals selectively took up PEO with high mass fraction from the PEO mixture with a wide molecular weight dispersion. The selectivity was independent of the immersion time (Supplementary Fig. 11). When activated crystals of $P5$ were immersed in another equal-weight mixture of PEO (Fig. 3b, top, PEO1000-OH, PEO4000-OH, and PEO6000-OH), $P5$ crystals selectively took up PEO with a high mass fraction, mainly PEO6000-OH (Fig. 3b, bottom). The high mass fractionation was also confirmed by $^1H$ NMR (Supplementary Fig. 12 and Supplementary Note 5). These results demonstrate that activated crystals of $P5$ are able to sort PEO with high mass fraction from PEO mixtures with high polydispersity.

To better understand the molecular weight fractionation, we calculated binding energies of various model complexes using...
molecular mechanics (MM) simulations (Fig. 3c). The binding energies between a PEO 10-mer and model 1D channel constructed from pillar[5]arene molecules were almost constant (blue diamonds, −86.8 to −87.6 kcal/mol) and did not increase even when the number of pillar[5]arene molecules in the 1D channel was increased from five to eight. This is because the PEO 10-mer is already fully covered by the 1D channel constructed from five pillar[5]arene molecules (Supplementary Fig. 13), so a further increase of the number of pillar[5]arene molecules did not provide additional stabilization. However, as the number of pillar[5]arene molecules was increased from five to eight, the binding energy between a PEO 20-mer and the 1D channel increased accordingly from −140.3 to −163.0 kcal/mol (red squares). The PEO 20-mer was longer than the 1D channel of five pillar[5]arene molecules, so the PEO 20-mer was not completely covered by pillar[5]arene molecules (Supplementary Fig. 13). In contrast, the PEO 20-mer was fully covered by the 1D channels constructed from eight pillar[5]arene molecules (Supplementary Figs 14–16), thus resulting in a larger stabilization effect. This explains why the binding energy of the PEO 20-mer changed noticeably with the length of the 1D channel. Multiple attractive van der Waals interactions exist between a PEO chain and a 1D channel. Therefore, effective coverage of PEO by a channel results in a high binding energy. In addition, the PEO 20-mer can form a larger number of interactions with a pillar[5]arene channel than the PEO 10-mer, even when the channel length is the same. Consequently, the binding energy of the PEO 20-mer is always larger than that of the PEO 10-mer; that is, the longer PEO 20-mer binds more strongly to the 1D channel than the PEO 10-mer. The calculation results are thus consistent with the observed high mass fractionation.

**Effect of end groups on PEO uptake by activated P5 crystals.**

We also investigated the effect of the end groups of PEO on its PEO uptake by activated crystals of P5. PEO with methoxy (OMe), amine (NH2), tosyl, and carboxylic acid (COOH) end groups were used. The rapid complexation occurred in PEO with OMe ends (Fig. 4, 3 min to reach equilibrium), which was faster than that in PEO with OH end groups (10 min) and NH2 end groups (20 min). In the cases of the OH and NH2 end groups, OH/O and NH/O hydrogen-bonding interactions between the OH or NH2 end groups of PEO and O atoms of P5 may slow the threading of P5 on the polymeric chains. In the case of PEO with COOH end groups, the amount of PEO taken up was small (guest/host ratio = ca. 1), and the PEO uptake did not reach the saturated state even after 3 h. The cavities of pillar[5]arenes are electron-rich; therefore, electronic repulsion between the electron-rich pillar[5]arene cavities and electron-rich carboxyl groups of the COOH end groups would hinder the complexation.
The same behavior was reported for the host–guest complexes formed between a viologen guest containing COOH end groups and a pillar[5]arene. When we used PEO with tosyl end groups, the PEO uptake was slow compared with that of PEO with OH end groups. Tosyl end groups are bulky compared with OH ones, so steric hindrance would slow complexation in this case.

**Dynamics of PEO confined in the 1D channel of crystalline P5.** We envisioned that the encapsulation may also influence the thermal transition behavior and dynamics of PEO. To evaluate the thermal transition behavior of PEO, differential scanning calorimetry (DSC) measurements were performed (Fig. 5a).

The DSC scans for neat PEO and activated P5 crystals yielded endothermic peaks at 40 and 156 °C, respectively, corresponding to the melting temperatures of these materials. In contrast, the P5 ⊃ PEO complex crystals did not show these endothermic peaks; instead, a new endothermic peak appeared at 179 °C. The data indicates that PEO confined in the 1D channel of pillar[5]arenes exhibits different thermal transition behavior compared with that of neat PEO. The dynamics of PEO confined in the 1D channel was evaluated by solid-state cross polarization-magic angle spinning (CP-MAS) $^{13}$C NMR spectroscopy (Fig. 5b). Peaks corresponding to PEO chains accommodated in the channels were detected at around 70 ppm (Fig. 2c). For neat PEO, the half-width at half-maximum (HWHM) values of the PEO peak were around 50–100 Hz (filled circles). In stark contrast, the HWHM values for PEO encapsulated in the 1D channel of P5 were ca. 300 Hz, and remained almost constant at different temperatures (open circles). This indicates that the mobility of a PEO chain in the 1D channel of P5 was much lower than that of a PEO chain in the neat environment. We also measured variable temperature $^{13}$C spin-lattice relaxation time ($T_1$) to investigate the mobility of PEO (Fig. 5c). For the $T_1$ measurements of the P5 ⊃ PEO complex, PEO1000-OH was used.

**Fig. 4** Effect of end groups on PEO uptake. Uptake ratio of PEO with a, OMe (PEO1000-OMe), b, OH (PEO1000-OH), c, NH$_2$ (PEO1000-NH$_2$), d, tosyl (PEO1000-Ts), and e, COOH (PEO1000-COOH) end groups by activated crystals of P5

**Fig. 5** Thermal transitions and molecular dynamics of PEO confined in 1D pillar[5]arene channels. a, DSC heating curves of P5, P5 ⊃ PEO, and PEO. PEO1000-OH was used. b, Plots of the half-width at half-maximum (HWHM) values of the signal from complexed and un-complexed PEO (Fig. 2b) at different temperatures (open circles = P5 ⊃ PEO complex and filled circles = neat PEO). c, Arrhenius plot of $^{13}$C $T_1$ as a function of temperature (open circles = P5 ⊃ PEO complex and filled circles = neat PEO)
complex crystals, we used CP-MAS method. However, we could not use CP-MAS method for the T1 measurements of neat PEO. Therefore, we performed DD-MAS method for the T1 measurements of neat PEO, which indicated that mobility of neat PEO was remarkably higher than PEO in the 1D channels of P5. In the measurement temperatures, T1 values of neat PEO were shorter than that of the P5 ⊂ PEO complex crystals, indicating that neat PEO has higher mobility than PEO in the 1D channels of P5. The data also suggests that the mobility of a PEO chain in the 1D channel of P5 was much lower than that of a PEO chain in the neat environment. We performed molecular dynamics (MD) simulations of a model PEO molecule in an isolated state and in a 1D channel of pillar[5]arenes. The torsion angles of PEO in the MD trajectories were also analysed. The MD studies showed that PEO in P5 favors the all-anti conformation (Supplementary Fig. 19). The simulation results therefore suggest that PEO is considerably restrained within the pillar[5]arene channel, which is consistent with the dynamics of PEO measured by solid-state 13C NMR.

Discussion

We demonstrated the unique complexation behavior of the linear polymer PEO with activated pillar[5]arene crystals. In view of the fact that the complexation did not occur in a common host–guest complexation system using a solvent, the crystalline-state complexation presented in this study offers a useful strategy that allows complexation between PEO and pillar[5]arenes, although complexation of specific cationic polymers with pillar[n]arenes in solution has been reported29,30. Various types of PEO are commercially available, and PEO has high functionality and good solubility in various solvents; thus we believe that the poly-pseudorotaxanes consisting of pillar[5]arenes and PEO should be useful for material applications.

The activated pillar[5]arene crystals selectively took up PEO with high mass fraction from mixtures of PEO with high polydispersity. Our MM calculation indicated that the formation of multiple CH/π interactions between the PEO chain and pillar[5]arene 1D channel increases the binding energy of the complex, which contributes to the selectivity for high mass PEO sorting. The end groups of PEO influenced its uptake. Complexation was slower for PEO with OH and NH2 end groups compared with that of PEO with OMe end groups. The uptake of PEO with COOH and tosyl end groups was slow compared with that of PEO with OH end groups.

Thermal transitions of PEO in the 1D channels of P5 occurred at higher temperature compared with that of neat PEO. The motion of PEO confined in the 1D channel of P5 was extremely limited compared with neat PEO because PEO chain fitted snugly into the 1D channel of P5. Understanding the thermal transition and dynamic behavior of a single polymer chain encapsulated in the channel of a pillar[5]arene should have considerable implications for their potential application as single polymer transporters, lubricants, and connectors in molecular-based devices. In this respect, we believe that our results provide new insights into the polymer dynamics within a 1D channel.

Methods

Materials. All solvents and reagents were used as supplied. P5 was synthesized according to the previous report31. Supplementary Table S1 shows product information of poly(ethylene oxide) (PEO) used in this study. PEO with COOH ends (PEO-1000-OOCH) was prepared from PEO1000-OH according to the previous report28.

Solution NMR. Solution 1H NMR spectra were recorded at 500 MHz with a JEOL ECA-300 spectrometer operating at 7.175 MHz. High-resolution solid-state NMR spectra were obtained using magic-angle spinning (MAS) and by proton 1D dipole decoupling (DD). Cross-polarization (CP) was used for signal enhancement. The sample was packed into a 4 mm diameter zirconia rotor. The total suppression of sidebands (TOSS) sequence was used to suppress spinning sidebands25. The MAS rate was set to 5 kHz. 13C chemical shifts were expressed as values relative to tetramethylsilane (TMS) using the 29.50 ppm line of adamantane as an external reference. The Torchia pulse sequence was used for 13C spin-lattice relaxation time (T1) measurement of P5 ⊂ PEO complex34. The inversion recovery method based on DD-MAS was used for 13C T1 measurement of neat PEO. In the 1H–13C heterocorrelated 2D NMR measurement, the 1H signals were detected using Phase Modulated Lee–Goldburg (PMLG) homonuclear decoupling35.

Powder X-ray diffraction. Laboratory powder X-ray diffraction (PXRD) measurements were performed on a Rigaku Smart Lab high-resolution diffractometer.

Organic vapor sorption experiments. Organic vapor sorption isotherms were obtained by a BELSORP-max (BEL Japan Inc., Osaka, Japan) sorption analyzer.

Liquid chromatography. Liquid Chromatography (LC) analyses were performed on a Thermo Fisher Scientific chromatograph (UltiMate3000 Thermo Fisher Scientific column; Accucore C18) with a Corona VeoRS detection. Mixture of water and acetonitrile were used as eluents. The gradient program of eluents for molecular weight distribution of PEO is shown in Supplementary Fig. 1.

Activation of P5 crystals. Crystals of P5 were activated according to the previous report19. P5 was dissolved in acetone, and then the evaporation of acetone afforded crystals. Drying under vents was enough for 24 h was sufficient to desolvate all the acetone molecules and afforded activated crystals of P5. Removing acetone was confirmed by 1H NMR measurement.

Complexation of PEO with activated P5 crystals. Activated crystals of P5 (64 mg) were immersed in a sealed 5 mL vial containing melted PEO (500 mg) at 80 °C. The feed ratio [PEO]/[P5] = 500/64 (wt/wt) was determined by evaluating the feed ratio on the PEO uptake time-dependency and amount at equilibrium state (Supplementary Fig. 4 and Supplementary Note 2). The heterogeneous mixture was heated at 80 °C. To remove un-complexed PEO, the crystals were washed with water. The amount of PEO taken up by activated crystals of P5 was monitored by completely dissolving the crystals in CDCl3, and measuring the ratio of proton signals from ethylene moieties of PEO to that from phenyl groups of P5 by 1H NMR spectroscopy (Fig. 2a and Supplementary Fig. 3). P5 ⊂ PEO host–guest complex crystals for vapor sorption experiments (Supplementary Fig. 5), PXRD (Supplementary Fig. 7), DSC, and solid state NMR (Fig. 5) were prepared by immersing activated crystals of P5 in melted PEO1000-OH for 12 h.

Competitive PEO uptake with different molecular weights. 64 mg of the host–guest complex crystals of P5 containing PEO1000-OH, which was prepared by immersing activated crystals of P5 in melted PEO1000-OH at 80 °C for 12 h, was immersed in 500 mg of melted PEO1000-OH at 80 °C for 12 h. Molecular weights of PEO in the crystals after the immersion was investigated by liquid chromatography (Supplementary Fig. 9). 64 mg of the host–guest complex crystals of P5 containing PEO1000-OH, which was prepared by immersing activated crystals of P5 in melted PEO1000-OH at 80 °C for 12 h, was immersed in 500 mg of melted PEO1000-OH at 80 °C for 12 h. Molecular weights of PEO after the immersion was investigated by liquid chromatography (Supplementary Fig. 10).

Molecular weight fractionation using activated P5 crystals. Activated P5 crystals (50 mg) were immersed in a sealed 5 mL vial containing an equal-weight mixture of melted PEO with different molecular weights (160 mg × 4 in Fig. 3a, and 160 mg × 3 in Fig. 3b) at 80 °C for 12 h. To remove uncomplexed PEO, the crystals were washed with water. The molecular weight of PEO molecules encapsulated in the host–guest complex crystals was evaluated by liquid chromatography (Fig. 3a, b). The selectivity was independent of the immersing time (Supplementary Fig. 11).

Molecular mechanics (MM) calculations. We used molecular mechanics (MM) to calculate binding energies between PEO (PEO 10-mer or 20-mer) and P5. For this purpose, the Forcite program implemented in Materials Studio 8.0 was used16, and molecules were described by use of the COMPASS II (version 1.2) force field37. Models 1 (PEO 10-mer and 20-mer) were prepared from the crystal structure of PEO in the bulk state36, and PEO is a helical structure in the bulk state. Models 2 for P5 were built from the X-ray structure of P5 ⊂ n-octane complex. In Models 3, PEO is in the cavity of P5. Binding energies were calculated using the following equation:

\[
E_{\text{bind}} = E(\text{Model3}) - [E(\text{Model1}) + E(\text{Model2})]
\]

where the E values are energies of geometry-optimized molecules.
Conformations of PEO in P5. To find a stable conformation of PEO in pillar[5]arene, we performed additional MM calculations. Here, we evaluated the binding energy between 3 pillar[5]arenes and PEO 10-mer in the linear or helical geometry.

The linear geometry has all-anti conformations at heavy atoms, while the helical conformation contains gauche conformations. In the case of P5, the binding energy was calculated as $-87.8 \text{kcal/mol}$ in the linear geometry, while the binding energy was $-82.8 \text{kcal/mol}$ in the helical geometry. These results indicate that PEO favors the linear conformation within P5.

Molecular dynamics (MD) simulations. For molecular dynamics (MD) simulations, we used a short PEO model (Supplementary Fig. 17). Periodic models of free PEO and P5-3 PEO complex were also built (Supplementary Fig. 18). The free PEO model contained 16 PEO molecules in a cubic cell with a size of 50 × 50 × 50 Å$^3$. The supercell models of pillar[5]arene complexes were built from X-ray structures. All simulations were performed with the Forcite module of Materials Studio 8.0. The COMPASS II (version 1.2) force field$^{37,38}$ was used with the force-field-assigned atomic charges.

Prior to MD simulations, we performed energy minimization calculations for 5000 cycles with the smart algorithm. Subsequently, we performed MD simulations for 10 ns in constant NPT conditions. MD trajectories were analyzed to determine the distributions of different torsion angles (Supplementary Fig. 19).

Data availability

The authors declare that all data supporting the findings of this study are available within the Article and its Supplementary Information. The raw data generated in this study is available from the corresponding author upon reasonable request.

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References

1. Wu, C.-G. & Bein, T. Conducting polyaniline. Acc. Chem. Res. 51, 1656–1666 (2018).
2. Nguyen, T.-Q., Wu, J., Doan, V., Schwartz, B. J. & Tolbert, S. H. Control of stacking in polyaniline nanostructures. J. Am. Chem. Soc. 130, 1757–1759 (2014).
3. Comotti, A. et al. Conformation and molecular dynamics of single polystyrene macrocycles for supramolecular chemistry. Acc. Chem. Res. 43, 381–390 (2010).
4. Ogoshi, T., Nishida, Y., Yamagishi, T. & Nakamoto, Y. Polypseudorotaxane constructed from pillar[5]arene and viologen polymer and stabilization of its radical cation. Macromolecules 43, 7088–7072 (2010).
5. Ogoshi, T., Nishida, Y., Yamagishi, T. & Nakamoto, Y. Polypseudorotaxane constructed from pillar[5]arene and viologen polymer. Macromolecules 43, 3145–3140 (2010).
6. Ogoshi, T. et al. Synthesis and conformational characteristics of alkyl-substituted pillar[5]arenes. J. Org. Chem. 75, 3268–3273 (2010).
7. Araki, L. Zhao, C. & Ito, K. Efficient production of polypseudorotaxanes from a cycloextrin and poly(ethylene glycol). Macromolecules 38, 7524–7527 (2005).
8. Dixon, W. T., Schafer, J. S., Sefcik, M. D., Stejskal, E. O. & McKay, R. A. Total suppression of sidebands in CP MAS C-13 NMR. J. Magn. Reson. 49, 341–345 (1982).
9. Torchica, D. A. The measurement of proton-enhanced carbon-13 T values by an NMR method which suppresses artifacts. J. Magn. Reson. 40, 613–616 (1978).
10. Vinogradov, E., Madhu, P. K. & Vega, S. High-resolution proton solid-state NMR spectroscopy by phase-modulated Lee-Goldburg experiment. Chem. Phys. Lett. 314, 443–450 (1999).
11. Sun, H. COMPASS II: an ab initio force-field optimized for condensed-phase applications - overview with details on alkane and benzene compounds. J. Phys. Chem. B 102, 7338–7364 (1998).
12. Sun, H. et al. COMPASS II: extended coverage for polymer and drug-like molecule databases. J. Mol. Model. 22, 47 (2016).
13. French, A. C., Thompson, A. L. & Davis, B. G. High-purity discrete PEG oligomers allow structural insight. Angew. Chem. Int. Ed. 48, 1248–1252 (2009).

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Author contributions

T.O. conceived the project and designed the experiments. R.S. M.Y., R.K. and T.Y. investigated crystalline state complexation with PEO. K.D. A.K.T. and H.H. performed M.M. and M.D. calculations. Y.S. and S.A. measured X-ray single-crystal structures and M.M. performed the solid-state NMR measurements. All authors analysed and discussed the results, and co-wrote the paper.
Additional information

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