Supplementary Material (ESI) for Chemical Communications

Supporting Information

Construction of polyrotaxane via reversible chain exchange between acylhydrazone bonds

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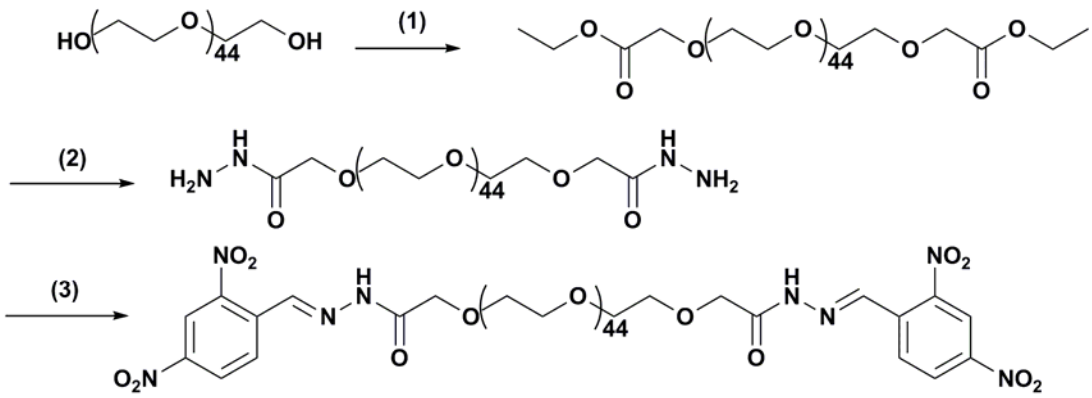
Part I: PEG end-modified with 2, 4-dinitrobenzaldehyde

SI-1. Preparation of PEG derivatives



(1) ethyl 2-bromoacetate,Potassium ter-butanolate,toluene solution, r.t, dropwise, 24 hours
(2) hydazine hydrate, methanol solution, r.t, 24 hours
(3) 2,4-dinitrobenzaldehyde, ethanol solution ,reflux, 24 hours

Fig. S1 Synthesis routes for PEG2k derivatives

SI-1.1. Materials

All chemicals were purchased from Alfa Aesar, Aldrich and SCRC and used without further purification unless noted. α-Cyclodextrin (α-CD) was kindly donated by Rohm Hass Company. Potassium tert-butanolate, 2, 4-dinitrobenzaldehyde, 2, 4-dinitrofluorobenzene, and 9-anthraldehyde were attained from Alfa Aesar Company. Poly(ethylene glycol) (PEG2k, Mn=2,000), ethyl 2-bromoacetate, hydrazine hydrate (85%) and other reagents were purchased from a local company named Shanghai Sinopharm Chemical Reagent Co., Ltd (SCRC).

SI-1.2. General Methods

Some ^{1}H NMR spectra of PEG derivatives were recorded on a *MERCURY plus-400* spectrometer (Varian, Inc., USA), with a spinning rate of 20 Hz, while other ^{1}H NMR spectra of mixtures of PEG2k derivatives and α-CD were recorded on a *AVANCE III-400M* spectrometer (Bruker BioSpin Group, Switz.) without spinning. Solid-state ^{13}C CP/MAS NMR spectra were also measured on the *AVANCE III-400M* spectrometer with a single contact time of 1 ms and a spinning rate of 5 kHz. Wide-angle X-ray diffraction (WAXD) scans were taken by a *D/max-2200/PC* Diffractometer (Rigaku, Japan), using Cu-Kα radiation. Differential scanning calorimetric (DSC) measurements were conducted at a heating rate of 20 ^{o}C/min on a *Modulated Differential Scanning Calorimetry Q2000* (TA Instruments, USA), calibrated with In and Zn standards respectively. UV-Vis tests were carried out on a *Lambda 20* spectroscopy (Perkin Elmer, USA).

SI-1.3. Synthetic procedure of PEG2k acylhydrazide derivatives[1, 2, 3]

After PEG2k (Mn=2000, 5.2 g, 2.6 mmol) was fully dissolved in toluene (100 ml), the tert-butyl alcohol (20 ml) solution in which potassium tert-butanolate (2.05 g, 18 mmol) dissolved was added. Then, ethyl 2-bromoacetate (3.2 ml, 28 mmol) was added dropwise over a period of 30 minutes under inert atmosphere. The solution was stirred at room temperature for 24 hours, and then filtered, concentrated and precipitated into diethyl ether three times to obtain solid product. Subsequently, the residue was dissolved in methanol (100 ml), and then hydrazine hydrate methanol solution (30 ml hydrazine hydrate dissolved in 40 ml methanol) was added dropwise. After stirring at room temperature for 24 hours, the solution was filtered and concentrated, and then extracted with CH_2Cl_2. The organic layer obtained was washed with water several times and dried by anhydrous magnesium sulfate. After solvent evaporation, the concentrated solution was poured into excess amount of diethyl ether to precipitate the product. After dried in vacuum at room temperature, the PEG2k derivative with acylhydrazide end group (PEG2k-$NHNH_2$) was obtained (Yield: 2.85 g, 57%).
^{1}H NMR (DMSO-d_6): δ (ppm): 3.88 (s, -OC*H*$_2$CO-), 3.26-3.67 (m, -OC*H*$_2$C*H*$_2$O- of PEG), 8.80 (br, -N*H*N*H*$_2$).

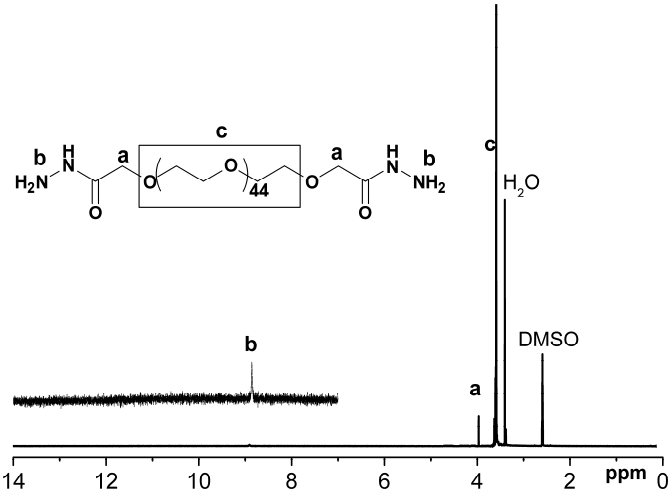


Fig. S2 ^{1}H NMR spectrum of PEG2k-$NHNH_2$ in DMSO-d_6

SI-1.4. End-capping PEG2k-$NHNH_2$ with 2, 4-dinitrobenzadehyde

PEG2k-$NHNH_2$ (1.05 g, 0.5 mmol) was dissolved in anhydrous ethanol solution (100 ml), and then 2, 4-dinitrobenzadehyde (0.981 g, 5 mmol) was added. The reaction was stirred and refluxed at 78 ^{o}C for 24 hours under inert atmosphere. After cooled down to room temperature, the reaction solution was filtered and concentrated, and then precipitated in excess diethyl ether three times. The yellow product was dried in vacuum at room temperature, and the 2, 4-dinitrobenzadehyde end-capped PEG2k (PEG2k-2DNBA) was attained. (Yield: 0.61 g, 58%)

^{1}H NMR (DMSO-d_6): δ (ppm): 8.27-8.79 (m, -2, 4-C$_6H_3$ (NO$_2$)$_2$), 11.84-11.89 (d, -N*H*N=C-), 8.35 (br, -N=C*H*-), 4.12 (s, -OCH_2CO-), 3.26-3.68 (m, -OCH_2CH_2O- of PEG)

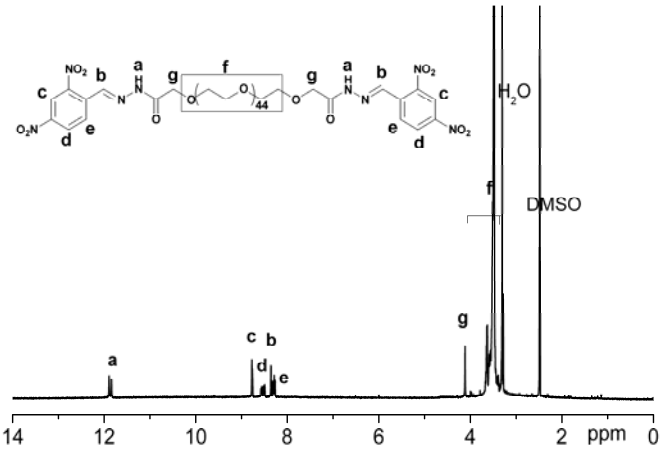


Fig. S3 ^{1}H NMR spectrum of PEG2k-2DNBA in DMSO-d_6

SI-2. NMR diffusion-ordered spectroscopy (DOSY) experiments

The DOSY experiments were carried out on the Bruker *AVANCE III-400M* spectrometer with the gradient strength in z-direction of about 50 G cm^{-1}.The gradients (G) were incremented from 1 to 47.5 G cm^{-1} in 16 steps. All spectra were measured at 300K with 16 accumulations. The diffusion coefficients, D, have been determined for all the samples according to the equation $I=I_0\times\exp[-D\times\gamma^2\times G^2\times\delta^2\times(\Delta-\delta/3)]$, where I is the observed intensity; I_0, the reference intensity; G, the gradient amplitude; δ, the duration of the gradient; γ, the gyromagnetic ratio; Δ, the diffusion time. Samples were dissolved in DMSO-d_6, with the concentration of 10 mg/ml.

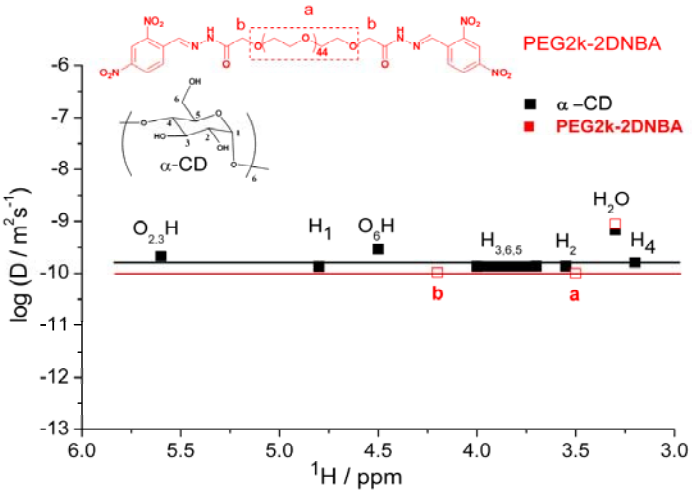


Fig. S4 2D-DOSY spectra of pure α-CD and PEG2k-2DNBA in DMSO-d_6

Table S-1 Diffusion coefficients (D, $\times 10^{-10}$ m^2s^{-1}) observed at 300 K*

^{1}H (ppm) / D	δ	Δ	$O_{2,3}H$	H_1	O_6H	$H_{3,6,5}$	H_2	H_{PEG}	H_{PEG}	H_2O	H_4
	ms	ms	**5.6**	**4.8**	**4.5**	**4.0-3.6**	**3.55**	**4.1**	**3.5**	**3.3**	**3.25**
Pure α-CD	5.6	120	2.1	1.34	2.93	1.36	1.35	/	/	6.73	1.6
Pure PEG2k-2DNBA	5	100	/	/	/	/	/	1.03	0.989	8.83	/
PEG2k-2DNBA/α-CD[a]	5	100	1.24	1.17	1.16	1.16	1.15	/	0.905	9.24	1.14
ethylene glycol units/α-CDs=9:1[b]	5	100	0.651	0.611	0.593	0.656	0.657	/	0.656	8.73	0.665
ethylene glycol units/α-CDs=2:1[c]	5	100	0.576	0.548	0.530	0.561	0.560	/	0.567	9.47	0.560

* Calculation error of D= ± 5%
[a]. physical mixture, ethylene glycol units/α-CDs=2:1, stored at r.t. without heating
[b]. purified product from PEG2k-2DNBA and α-CDs (ethylene glycol units/α-CDs =9:1) kept at 120 °C for 32 hours
[c]. purified product from PEG2k-2DNBA and α-CDs (ethylene glycol units/α-CDs =2:1) kept at 120 °C for 32 hours

SI-3. Determination of the number of α-CDs in the polyrotaxane

The number of α-CDs in the polyrotaxane was estimated by the ^{1}H NMR spectrum of the polyrotaxane in DMSO-d_6. For example, a comparison between the integral of the peak of the H_1 of α-CD (I_{H_1}, 4.8 ppm) and that of H_{PEG} ($I_{H^{PEG}}$, 3.50 ppm) gave the number of α-CDs included in the PEG chain as following:

$$N_{\alpha-CD} = (\frac{180}{6}) * (\frac{I_{H_1}}{I_{H_{PEG}}}) = (\frac{180}{6}) * (\frac{I_{H_1}}{I_{4.1-3.0} - I_{H_2O} - I_{H_{3,6,5}} - I_{H_{2,4}}})$$

$$= (\frac{180}{6}) * (\frac{I_{H_1}}{I_{4.1-3.0} - I_{H_2O} - 6I_{H_1}})$$

The exemplified ^{1}H NMR spectrum of the polyrotaxane in DMSO-d_6 and its stoichiometry was shown as following:

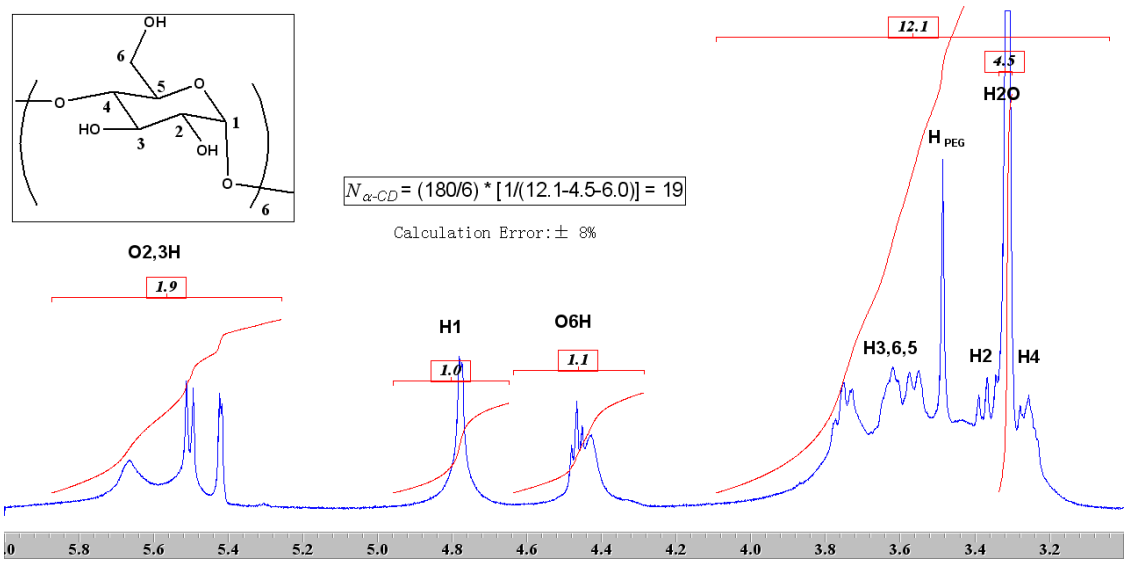


Fig. S5 Stoichiometry calculation of the polyrotaxane formed by mixture of PEG2k-2DNBA and α-CDs kept at 120 °C for 32 hours (ethylene glycol units/α-CDs=1:1; the product was purified and dried before NMR experiment; calculation error: ± 8%)

Table S-2 Calculated Number of α-CDs in the Polyrotaxane*

Molar Ratio (Ethylene Glycol Units/α-CDs)	**1:1**	**1.5:1**	**1.8:1**	**2:1**	**4.5:1**	**9:1**
Weight Ratio	**1:24**	**1:16**	**1:13**	**1:12**	**1:5**	**1:2.5**
$I_{4.1\text{-}3.0}$	12.1	11.8	10.5	12.0	10.1	12.6
I_{H2O}	4.5	4.1	2.7	4.1	1.3	2.2
$N_{\alpha\text{-}CD}$	19(±8%)	18(±8%)	17(±8%)	16(±8%)	11(±8%)	7(±8%)
Stoichiometry	2.36	2.50	2.64	2.81	4.09	6.43

* Molar ratio: the molar amount of the PEG repeat units/molar amount of α-CDs
Weight ratio: the weight amount of PEG/ weight amount of α-CDs
All products were obtained from mixtures of PEG2k-2DNBA and α-CD kept at 120 °C for 32 hours. The products were purified and dried before NMR experiments.

SI-4. Real-time WAXD scans of PEG2k derivative and α-CD mixtures

All of the mixtures with the different molar ratio (ethylene glycol units (PEG repeat units)/α-CDs) were fully grinded before heating. The grinded powders were flattened in the standard XRD sample container. Then, the containers were placed in the oven and heated at desired temperature. After heating for a certain period of time, the sample containers were took out and cooled down to room temperature in the desiccator. The heated mixtures were grinded again before WAXD scans.

SI-4.1. Mixtures heated at 120 °C

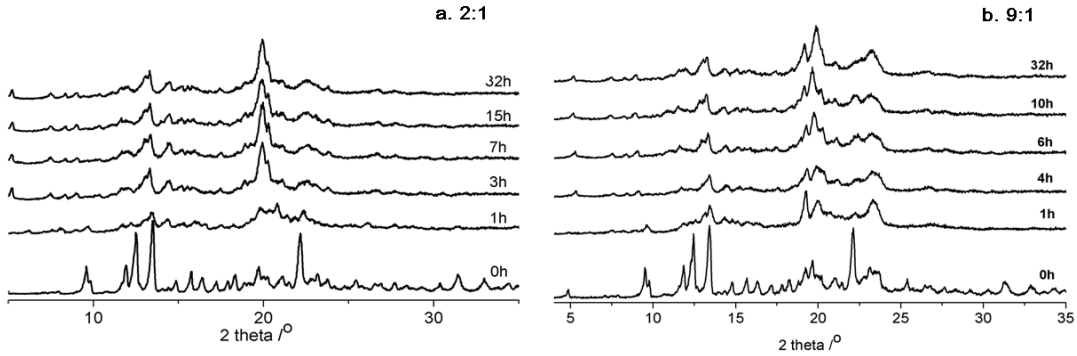


Fig. S6 Real-time WAXD spectra of (a) mixture of PEG2k-2DNBA and α-CD (ethylene glycol units/α-CDs=2:1), kept at 120 °C, and (b) mixture of PEG2k-2DNBA and α-CD (ethylene glycol units/α-CDs=9:1), kept at 120 °C

SI-4.2. Mixture heated at 80 °C

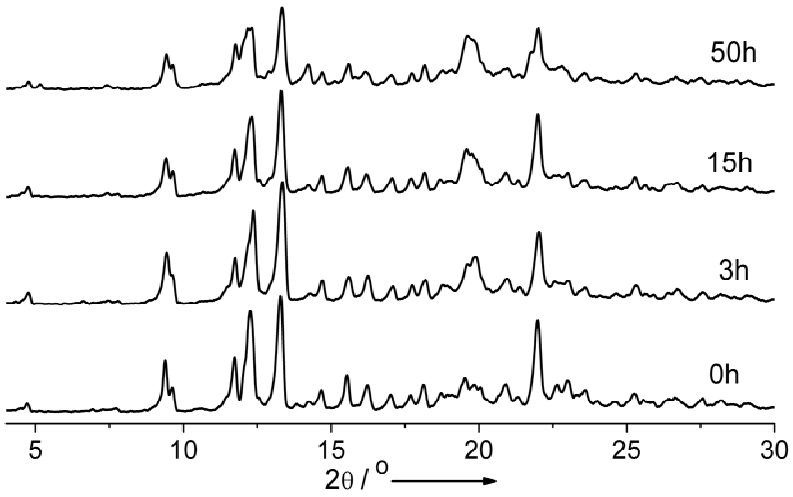


Fig. S7 Real-time WAXD spectra of PEG2k-2DNBA and α-CD mixture (ethylene glycol units/α-CDs=2:1), kept at 80 °C

SI-4.3. Mixture heated at 50 ^{o}C

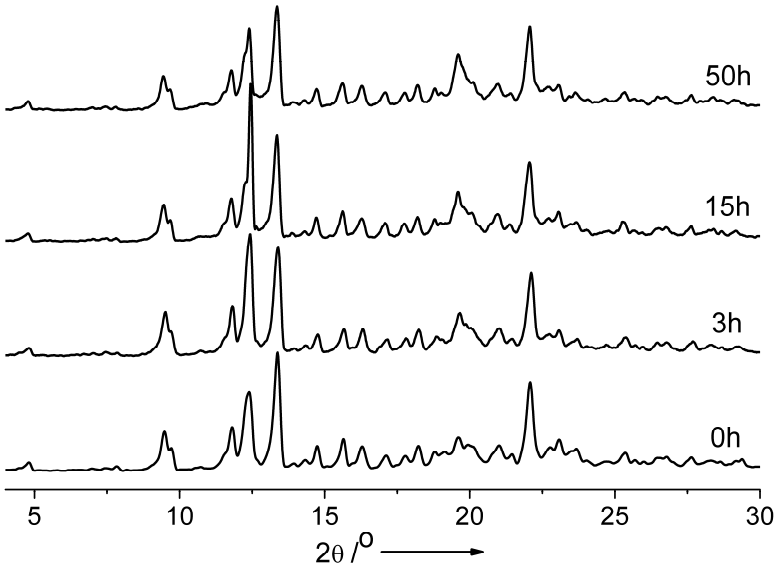


Fig. S8 Real-time WAXD spectra of PEG2k-2DNBA and α-CD mixture (ethylene glycol units/α-CDs=2:1), kept at 50 ^{o}C

SI-4.4. Stored at room temperature

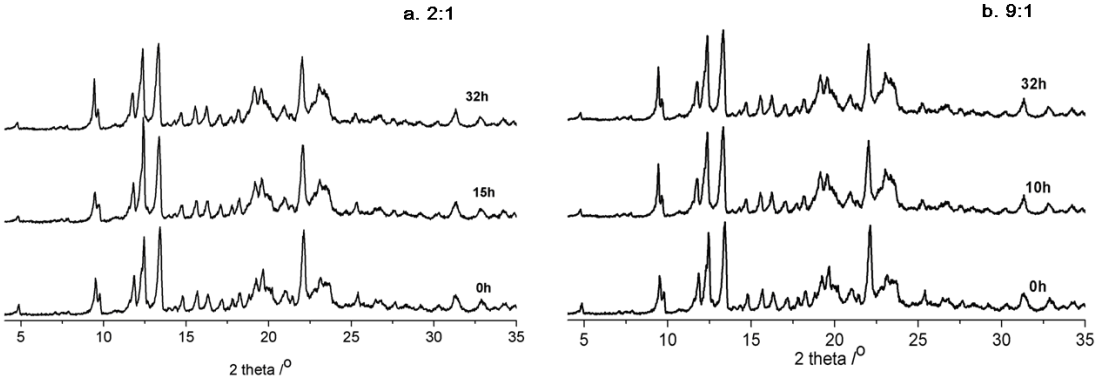


Fig. S9 Real-time WAXD spectra of (a) PEG2k-2DNBA and α-CD mixture (ethylene glycol units/α-CDs=2:1), kept at r.t. and (b) PEG2k-2DNBA and α-CD mixture (ethylene glycol units/α-CDs=9:1), kept at r.t.

SI-4.5. Comparison of mixtures heated at different temperature

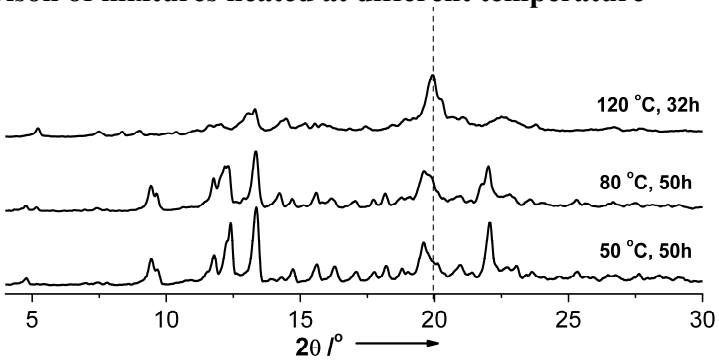


Fig. S10 Comparison of PEG2k-2DNBA and α-CD mixtures (ethylene glycol units/α-CDs=2:1) heated at different temperature

Fig. S10 shows the WAXD results of PEG2k-2DNBA and α-CD mixtures (ethylene glycol units/α-CDs=2:1) heated at different temperature. For the mixtures heated at 120 ^{o}C for 32 hours, there is clearly channel-like diffraction at the peak around 20^{o} (2θ). However, the channel-like diffraction becomes weaker when the mixtures heated at 50 ^{o}C and 80 ^{o}C. We suggest that the exchange of acylhydrazone bonds is limited when the heating temperature is low, so there are less α-CD pass through the reversible bonds. As a result, it would be proper to construct polyrotaxane at 120 ^{o}C. This fact is also quite consistent with the results proved by Lehn and coworkers (T. Ono, T. Nobori, J.-M. Lehn, *Chem. Commun.*, 2005, **12**, 1522).

SI-5. ^{1}H NMR spectra of PEG2k-2DNBA/α-CD mixtures in DMSO-d$_6$

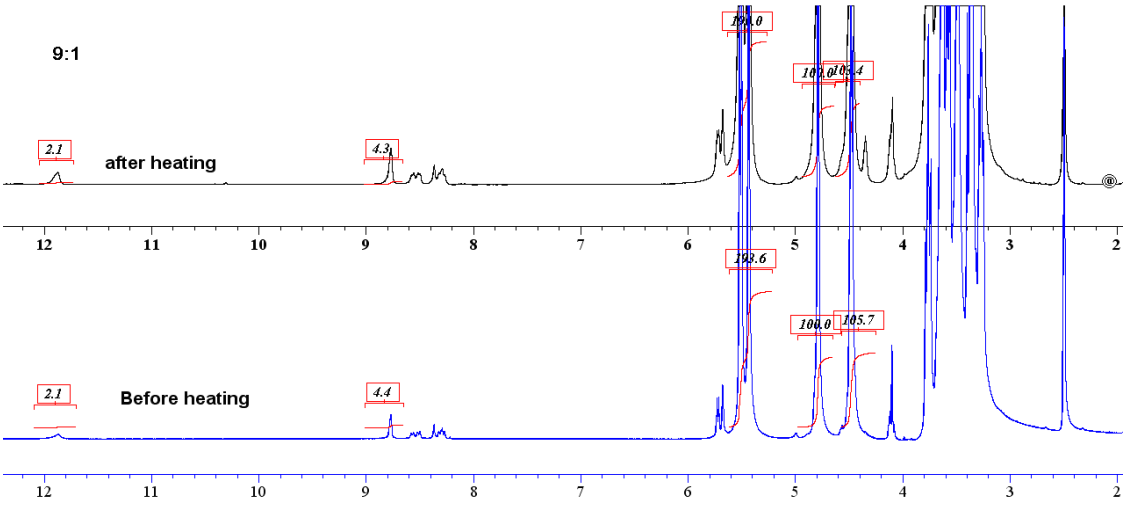


Fig. S11 ^{1}H NMR spectra of PEG2k-2DNBA and α-CD mixture before and after keeping at 120 ^{o}C for 32 hours (ethylene glycol units/α-CDs=9:1; integral error: ± 5%; concentration: 600 mg/ml)

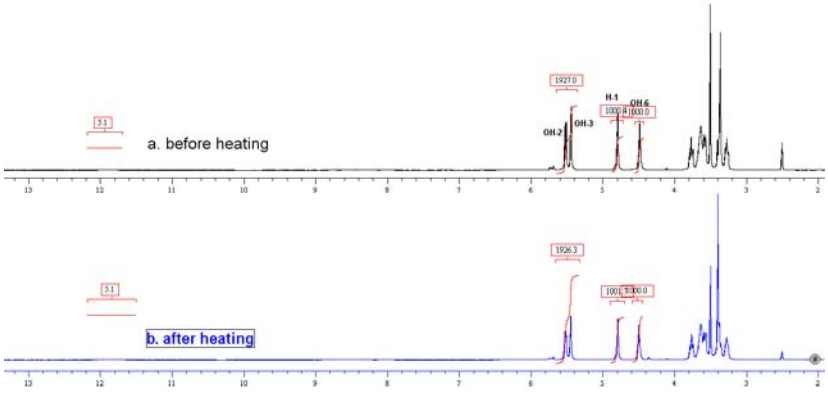


Fig. S12 ^{1}H NMR spectra of PEG2k-2DNBA and α-CD mixture before and after heating (ethylene glycol units/α-CDs=2:1): (a) before heating and (b) after keeping at 120 ^{o}C for 32 hours. (Integral error: ± 5%, concentration: 600 mg/ml)

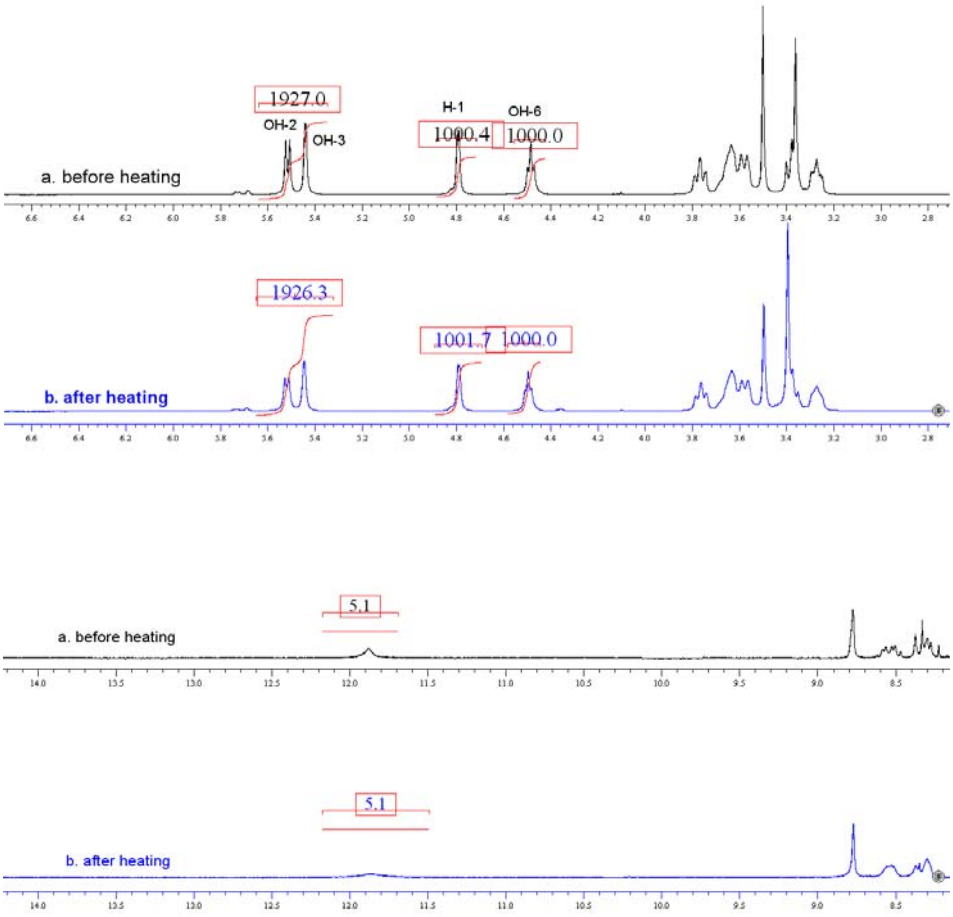


Fig. S13 ^{1}H NMR spectra of PEG2k-2DNBA and α-CD mixture before and after heating (ethylene glycol units/α-CDs=2:1): (a) before heating, and (b) kept at 120 ^{o}C for 32 hours (part of Fig. 9, enlarged, Integral error: ± 5%, concentration: 600 mg/ml)

SI-6. Solid-state ^{13}C CP/MAS spectra of α-CD and its mixtures with PEG2k derivatives

Fig. S14 gives the solid-state ^{13}C CP/MAS NMR spectra of pure α-CD and its mixtures with PEG2k derivatives. The peaks around 100 and 78 ppm in the spectrum of pure α-CDs are assigned to the conformational strained glycosidic linkage. Fig. S14b shows that α-CDs remain the same conformation in the PEG2k-2DNBA/α-CD mixtures stored at room temperature, indicating the absence of inclusion complexes. However, when the mixtures are heated at 120 ^{o}C for 32 hours, these two characteristic peaks disappear. It demonstrates that the PEG chains are included in many α-CDs. Moreover, the smoothness of peaks assigned to C-1, C-4 and C-6 of α-CD also prove the formation of inclusion complexes. Comparing to the spectra shown in Fig. S14c and Fig. S14d, the solid-state ^{13}C CP/MAS NMR signal of PEG2k/α-CD mixtures in Fig. S14e has fewer splits, illustrating the formation of more perfect channel-like structures. Apparently, the reversible reorganization of the bulky stoppers in PEG2k-2DNBA prevents from the incorporation of more α-CDs into the PEG chain[4].

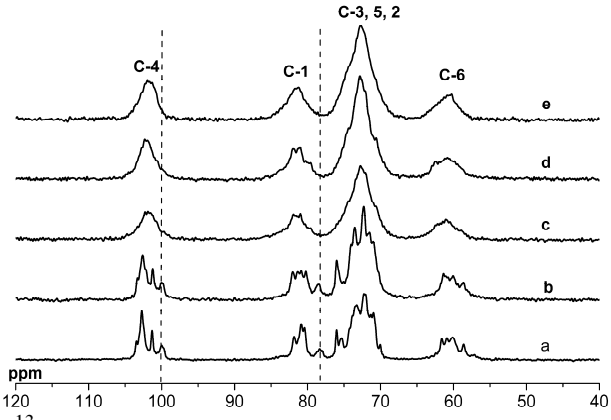


Fig. S14 Solid-state ^{13}C CP/MAS spectra of (a) pure α-CD, r.t., (b) PEG2k-2DNBA/α-CDs (ethylene glycol units/α-CDs=9:1), stored at r.t., (c) PEG2k-2DNBA/α-CDs (ethylene glycol units/α-CDs=9:1), kept at 120 ^{o}C for 32 hours, (d) PEG2k-2DNBA/α-CDs (ethylene glycol units/α-CDs=2:1), kept at 120 ^{o}C for 32 hours, and (e) PEG2k/α-CDs (ethylene glycol units/α-CDs=2:1), kept at 120 ^{o}C for 32 hours

SI-7. DSC tests of PEG2k-2DNBA/α-CD mixtures

Differential scanning calorimetry (DSC) analysis of α-CDs and PEG2k-2DNBA mixtures in Fig. S15 also confirms the formation of CD inclusion complexes via chain exchange at high temperature. For pure PEG2k-DNBA, the crystallization peak temperature and the correspondent melting point are located at 13.1 and 40.3 ^{o}C, respectively. When mixing PEG2k-2DNBA with α-CDs (ethylene glycol units/α-CDs=9:1) at 120 ^{o}C for 32 hours, the crystallization peak temperature moves to -7.2 ^{o}C and the melting enthalpy decreases. It can be attributed to the fact that the formation of inclusion complexes between linear polymers with α-CDs reduces the crystallization of PEG derivatives. If we further increase the dosage of α-CDs (ethylene glycol units/α-CDs=2:1) at high temperature, the crystallization and melting peaks totally disappear, as shown in Fig. S15c. However, for

the PEG2k-2DNBA/α-CD mixtures stored at room temperature, it is hard to form polyrotaxane due to the absence of acylhydrazone exchange at low temperature. Therefore, both crystallization and melting can be observed clearly in Fig. S15d.

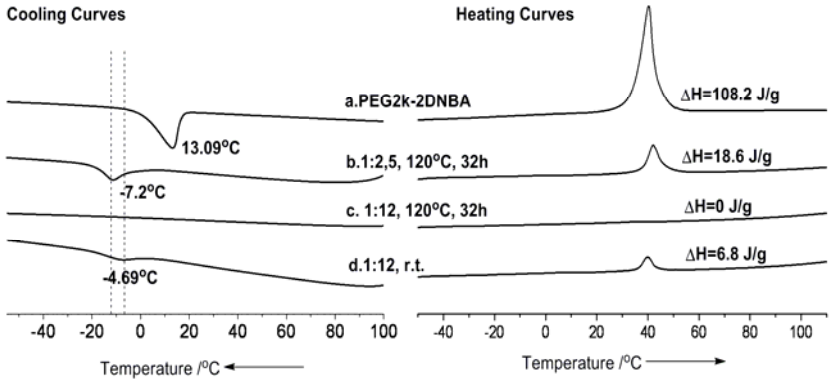


Fig. S15 DSC spectra of (a) pure PEG2k-2DNBA, (b) PEG2k-2DNBA/α-CD (ethylene glycol units/α-CDs=9:1), kept at 120 °C for 32 hours, (c) PEG2k-2DNBA/α-CD (ethylene glycol units/α-CDs=2:1), kept at 120 °C for 32 hours, and (d) PEG2k-2DNBA/α-CD (ethylene glycol units/α-CDs=2:1), stored at r.t**.**

SI-8. UV-Vis tests of PEG2k-2DNBA/α-CD mixtures

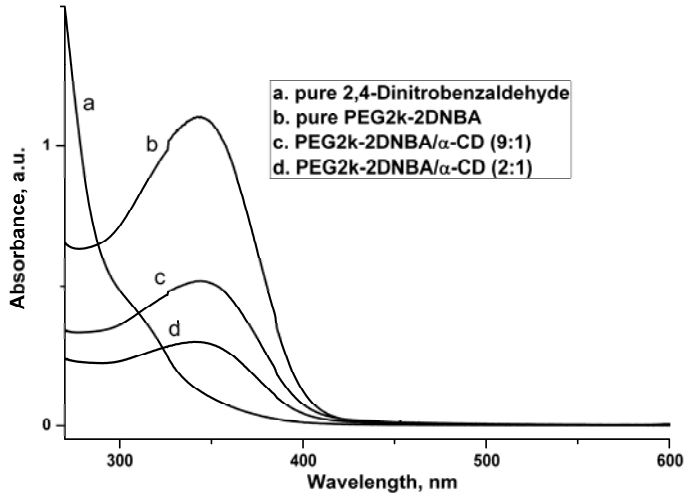


Fig. S16 UV-Vis spectra of (a) pure 2, 4-dinitrobenzaldehyde, (b) pure PEG2k-2DNBA, (c) PEG2k-2DNBA/α-CD (ethylene glycol units/α-CDs=9:1), kept at 120 °C for 32 hours and (d) PEG2k-2DNBA/α-CD (ethylene glycol units/α-CDs=2:1), kept at 120 °C for 32 hours. (All samples were dissolved in dimethyl sulfoxide solution)

Fig. S16 shows the UV-Vis tests of PEG2k-2DNBA and α-CD mixtures. In contrast to the pure 2, 4-dinitrobenzaldehyde, which has no absorbance around 343 nm, the mixtures heated at 120 °C for 32 hours have a noticeable absorbance as the pure PEG2k-2DNBA. It suggests that the bulky stoppers are still located on the PEG ends after heating treatment.

Part II: PEG end-modified with 2, 4-dinitrofluorobenzene

SII-1. Synthetic procedure of PEG2k-2DNFB

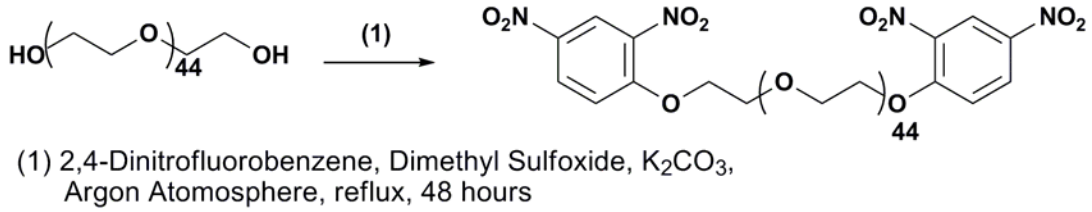


Fig. S17 Synthesis route for PEG2k-2DNFB

PEG2k (1.05 g, 0.5 mmol) was dissolved in anhydrous dimethyl sulfoxide solution (100 ml), and then 2, 4-dinitrofluorobenzene (1.5 g, 8.1 mmol) and K_2CO_3 (1.4 g, 10 mmol) was added. The reaction was stirred and refluxed at 80 ^oC for 48 hours under argon atmosphere. After cooled down to room temperature, the reaction solution was filtered and concentrated with the vacuum distillation, and then dissolved in water and extracted with CH_2Cl_2. The solution obtained was concentrated and then precipitated in excess diethyl ether three times. The yellow product obtained was dialyzed in water for 4 days. After freeze-drying, the 2, 4-dinitrofluorobenzene end-capped PEG2k (PEG2k-2DNFB) was attained. (Yield: 0.4 g, 38%)
^{1}H NMR (DMSO-d_6): δ (ppm): 7.51-8.79 (m, -2, 4-$C_6H_3(NO_2)_2$), 4.45 (s, -OCH_2CO-), 3.26-3.80 (m, -OCH_2CH_2O- of PEG)

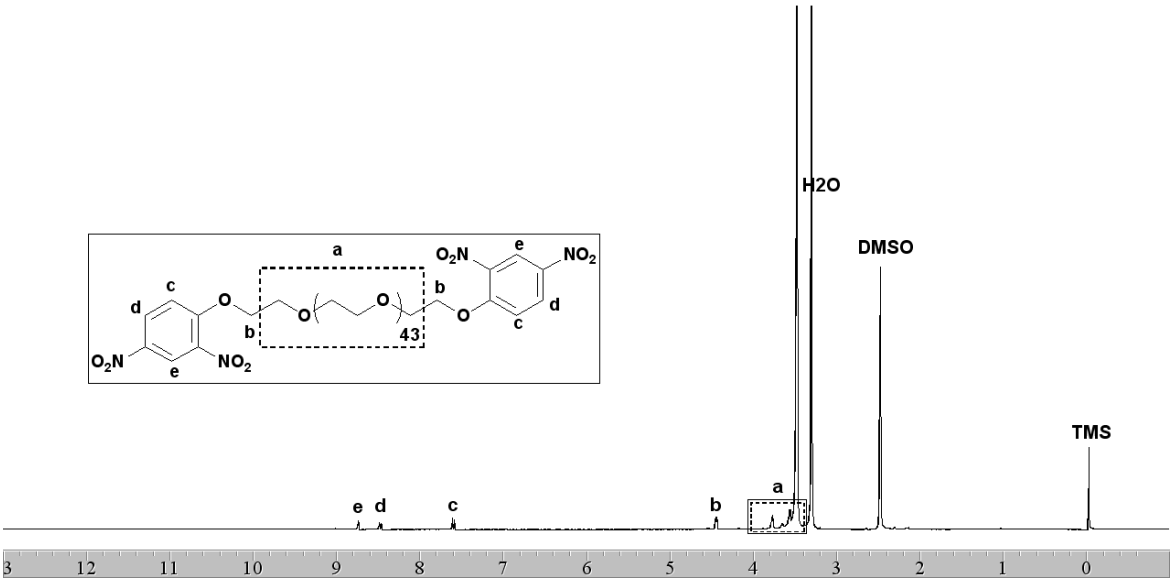


Fig. S18 ^{1}H NMR spectrum of PEG2k-2DNFB in DMSO-d_6

SII-2. Real-time WAXD scans of PEG2k-2DNFB/α-CD mixtures

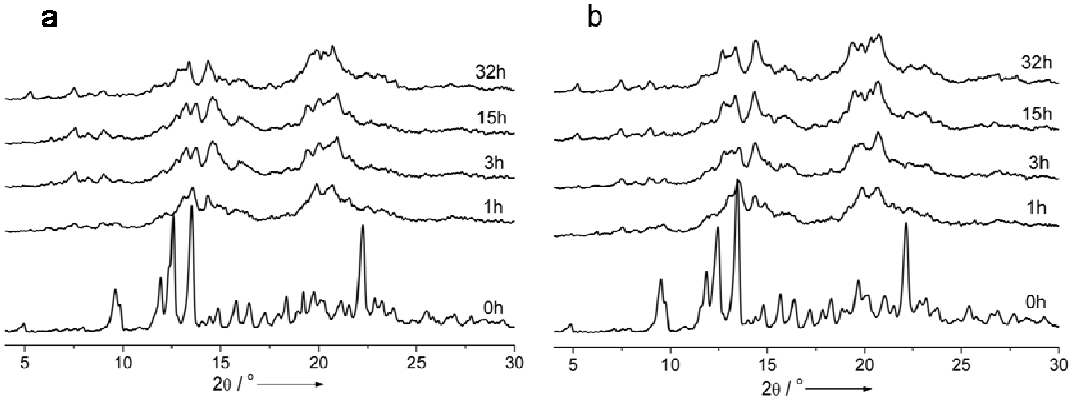


Fig. S19 Real-time WAXD spectra of (a) PEG2k-2DNFB/α-CD (ethylene glycol units/α-CDs=9:1), kept at 120 °C and (b) PEG2k-2DNFB/α-CD (ethylene glycol units/α-CDs=2:1), kept at 120 °C

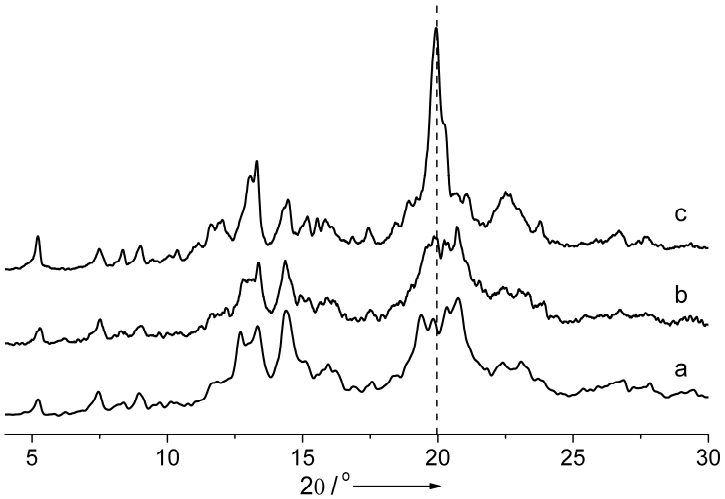


Fig. S20 WAXD spectra of (a) PEG2k-2DNFB/α-CD (ethylene glycol units/α-CDs=9:1) kept at 120 °C for 32 hours, (b) PEG2k-2DNFB/α-CD (ethylene glycol units/α-CDs=2:1), kept at 120 °C for 32 hours, and (c) PEG2k-2DNBA/α-CD (ethylene glycol units/α-CDs=2:1), kept at 120 °C for 32 hours

Fig S19 and Fig. S20 give the WAXD results of PEG2K-2DNFB and α-CD mixtures heated at 120 °C. The lack of diffraction peak around 20° in the mixtures of PEG2K-2DNFB and α-CDs heated for 32 hours indicate there wasn't any inclusion complexes formed during the heating treatment, which clearly proves that the 2, 4-dinitrophenyl group is big enough to prevent α-CDs from slipping over the PEG ends to thread onto the dumbbell chain.

Part III: PEG end-modified with 9-anthraldehyde

SIII-1. Synthetic routes for PEG2k-2AD

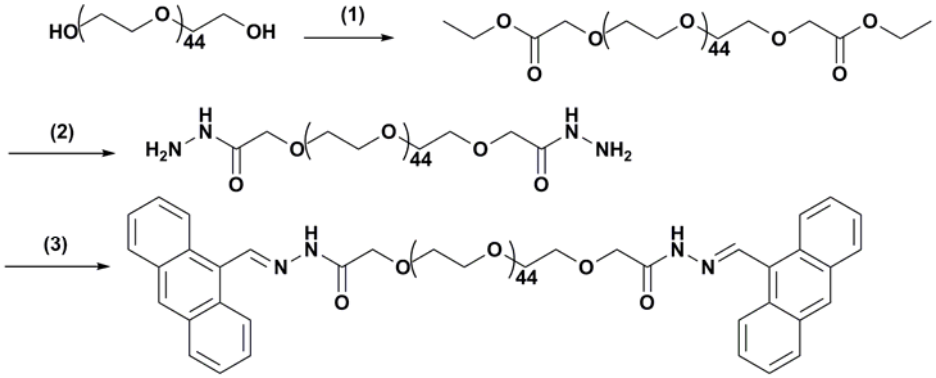


Fig. S21 Synthesis routes for PEG2k-2AD

PEG2k-$NHNH_2$ (1.05 g, 0.5 mmol) was dissolved in anhydrous $CHCl_3$ solution (100 ml), and then 9-anthraldehyde (1.03 g, 5 mmol) was added. The reaction was stirred and refluxed at 65 ^oC for 24 hours under inert atmosphere. After cooled down to room temperature, the reaction solution was filtered and concentrated, and then precipitated in excess diethyl ether three times. The yellow product was dissolved in water and extracted with CH_2Cl_2. After filtered, the obtained solution was concentrated and precipitated in excess diethyl ether. The product obtained was dried in vacuum at room temperature, and the 9-anthraldehyde end-capped PEG2k (PEG2k-2AD) was attained. (Yield: 0.3 g, 20%)
^{1}H NMR (DMSO-d_6): δ (ppm): 7.6-8.8 (m, -9-anthracene), 11.3-11.7(d, -N*H*-N=C-), 9.2-9.6 (d, -N=C*H*-), 4.1-4.6 (s, -OCH_2CO-), 3.26-3.68 (m, -OCH_2CH_2O- of PEG)

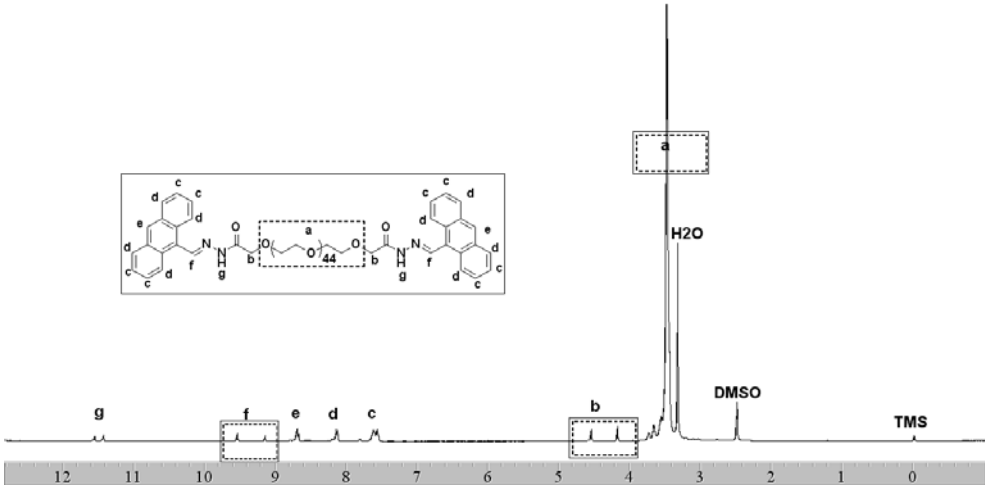


Fig. S22 ^{1}H NMR spectrum of PEG2k-2AD in DMSO-d_6

SIII-2. WAXD spectra of PEG2k-2AD/α-CD mixtures

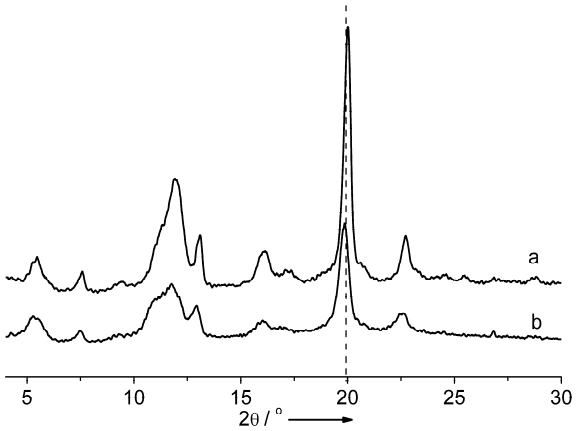


Fig. S23 WAXD spectra of (a) purified product from mixture of PEG2k-2AD and α-CDs (ethylene glycol units/α-CDs=2:1) kept at 120 °C for 32 hours, and (b) purified product from mixture of PEG2k-2AD and α-CDs (ethylene glycol units/α-CDs=4.5:1) kept at 120 °C for 32 hours

Fig. S23 gives the WAXD spectra of purified products of PEG2k-2AD and α-CDs which had been kept at 120 °C for 32 hours. The purification procedure was as follows: the heated mixtures were dissolved in dimethyl sulfoxide solution and washed with water (twice), methanol (twice) and diethyl ether (three times). After purification treatment, the products obtained were fully grinded and flattened in the standard XRD sample container before WAXD scans. The appearance of strong diffraction peak around 20° (2θ) proves the formation of inclusion complexes by PEG2k-2AD and α-CDs through acylhydrazone exchange when heated at 120 °C.

SIII-3. ^{1}H NMR spectra of polyrotaxane of PEG2k-2AD with α-CDs

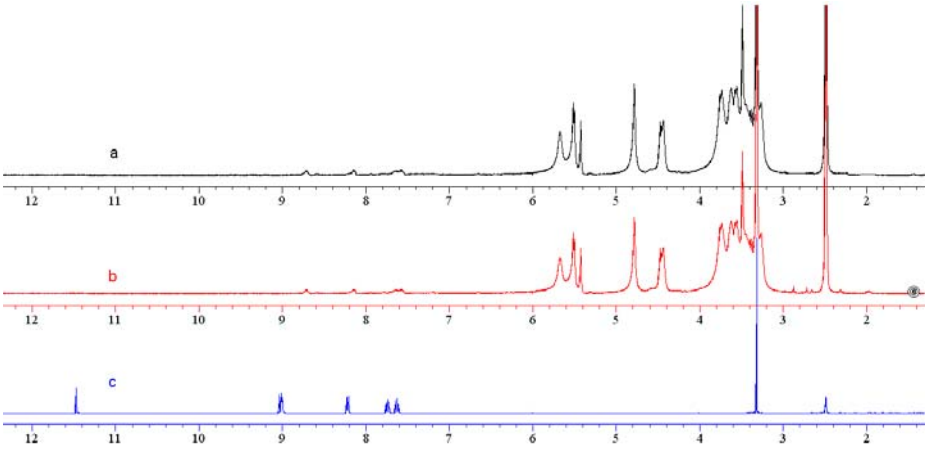


Fig. S24 ^{1}H NMR spectra of (a) purified product from mixture of PEG2k-2AD and α-CDs (ethylene glycol units/α-CDs=2:1) kept at 120 °C for 32 hours, (b) purified product from mixture of PEG2k-2AD and α-CDs (ethylene glycol units/α-CDs=4.5:1) kept at 120 °C for 32 hours, and (c) 9-anthraldehyde (in DMSO-d_6)

Fig. S24 gives the ^{1}H NMR spectra of the purified products formed by heated mixture of PEG2k-2AD with α-CDs. The spectra (a) and (b) show clear signals of 9-anthracene group around 7.5-8.8 ppm and signals assigned to α-CD at 5.4-5.8 ppm and 3.0-4.1 ppm, as well as signals assigned to PEG at 3.5 ppm. This is the evidence that the end groups are still fixed at the PEG chain.

SIII-4. UV-Vis spectra of polyrotaxane formed by PEG2k-2AD and α-CDs

Fig. S25 gives the UV-Vis spectra of pure PEG2k-2AD and the purified products formed by mixture of PEG2k-2AD and α-CDs kept at 120 ^{o}C for 32 hours. Comparing to the pure PEG2k-2AD, the purified products obtained have the same absorbance around 390 nm, which proves the bulky stoppers are still fixed on the polymer ends.

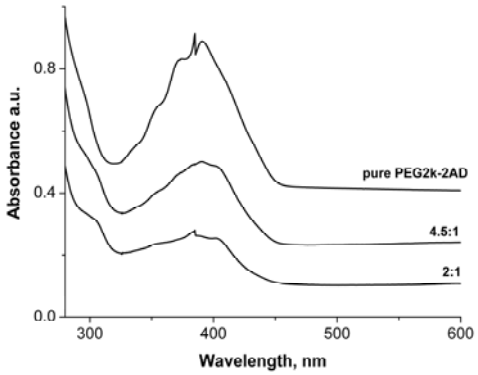


Fig. S25 UV-Vis spectra of PEG2k-2AD and the purified products obtained from the heated mixtures of PEG2k-2AD and α-CDs. (All samples were dissolved in dimethyl sulfoxide solution)

SIII-5. DSC spectra of polyrotaxane formed by PEG2k-2AD and α-CDs

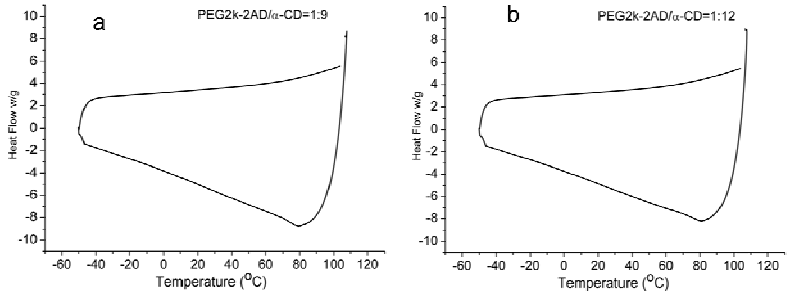


Fig. S26 DSC spectra of (a) purified product from mixture of PEG2k-2AD and α-CDs (ethylene glycol units/α-CDs=4.5:1) kept at 120 ^{o}C for 32 hours and (b) purified product from mixture of PEG2k-2AD and α-CDs (ethylene glycol units/α-CDs=2:1) kept at 120 ^{o}C for 32 hours

Fig. S26 gives the DSC spectra of the purified products from the heated mixture of PEG2k-2AD and α-CDs. Both the melting peak in heating curve and the crystalline peak in cooling curve disappear, indicating the formation of α-CD based polyrotaxane.

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