Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

High-yield one-pot synthesis of polyrotaxanes with tunable well-defined threading ratios over a wide range

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NMR spectra of PR-hpCD

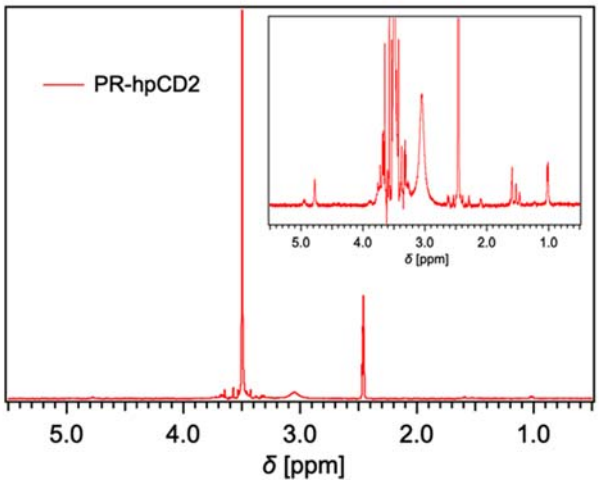

Fig. S1. ^{1}HNMR spectrum of PR-hpCD2.

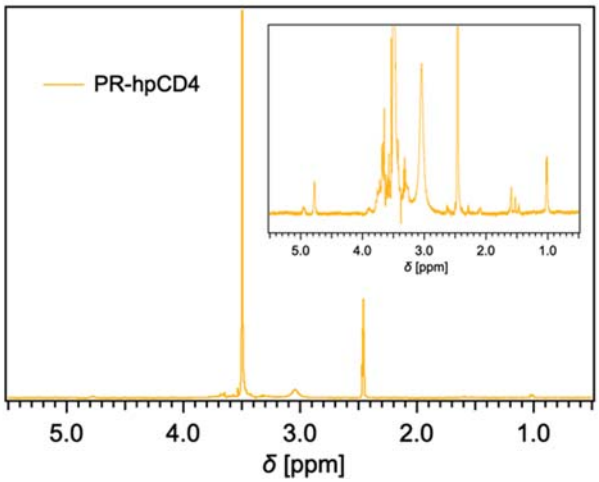

Fig. S2. ^{1}HNMR spectrum of PR-hpCD4.

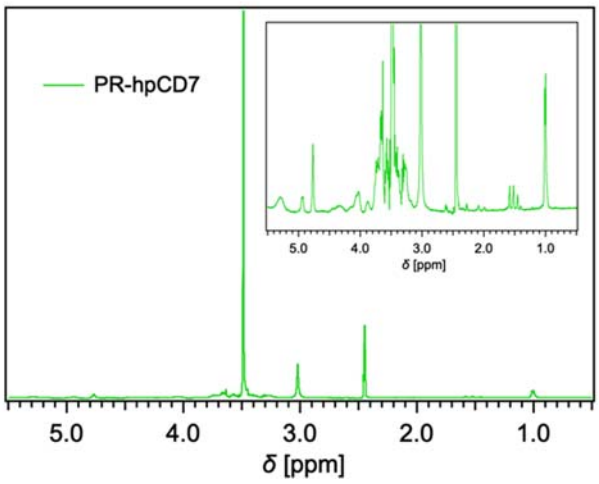

Fig. S3. ^{1}HNMR spectrum of PR-hpCD7.

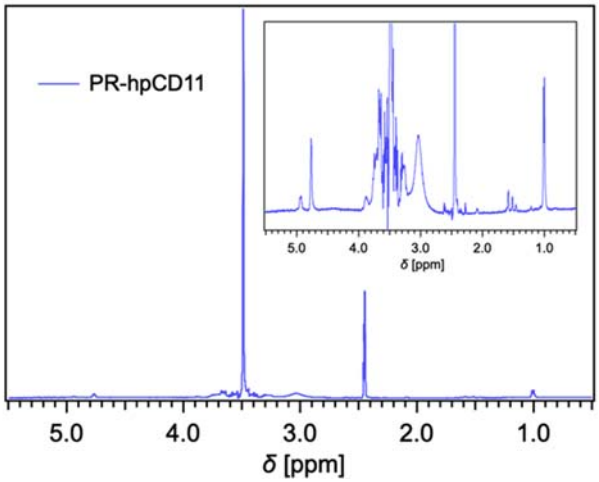

Fig. S4. ^{1}HNMR spectrum of PR-hpCD11.

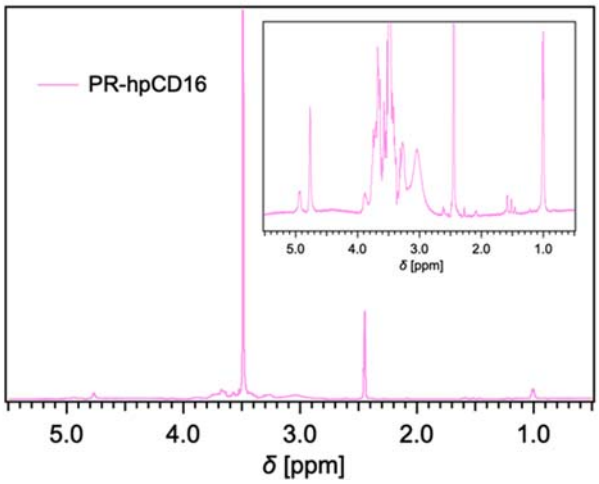

Fig. S5. ^{1}HNMR spectrum of PR-hpCD16.

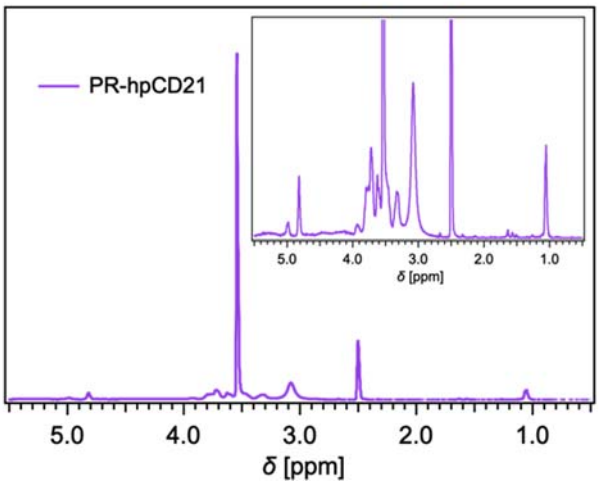

Fig. S6. ^{1}HNMR spectrum of PR-hpCD21.

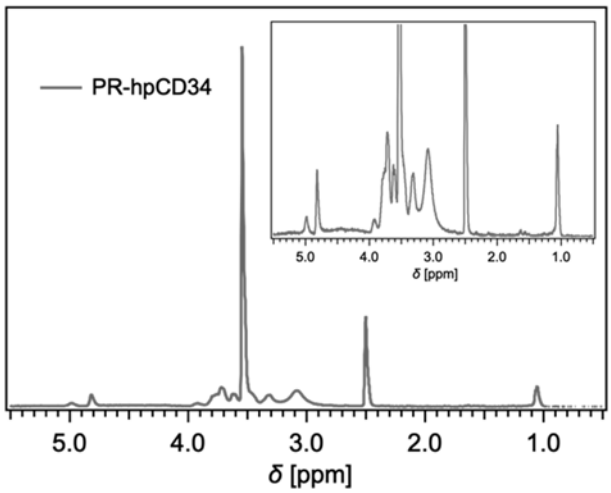

Fig. S7. ^{1}HNMR spectrum of PR-hpCD34.

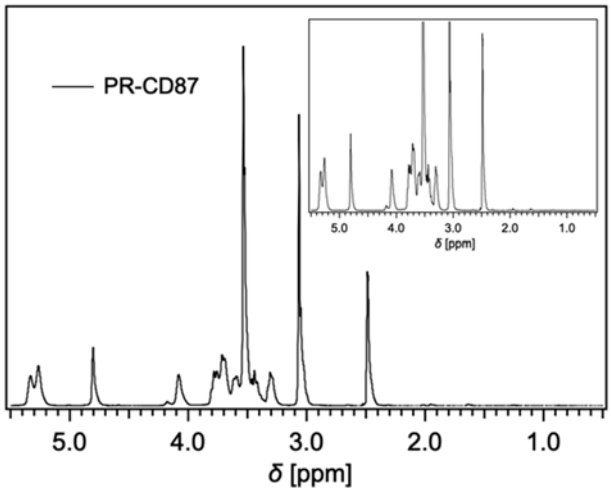

Fig. S8. ^{1}HNMR spectrum of PR-CD87.

Thermogravimeter-Differential Thermal Analyzer (TG-DTA) measurement of PR-hpCD

TG-DTA measurements were performed to evaluate the ratio of hpCD and PEG molecules in the PR samples using a Rigaku Thermo Plus EVO TG-DTA. The measurement temperature was controlled from room temperature to 773 K to measure the molecular content ratio (hpCD or CD : PEG) in each sample. hpCD or CD molecules and PEG in PR were detected at approximately 300 and 400 °C, respectively. Each molecular ratio for calculating the threading ratio was obtained from the weight change percentage by combustion.

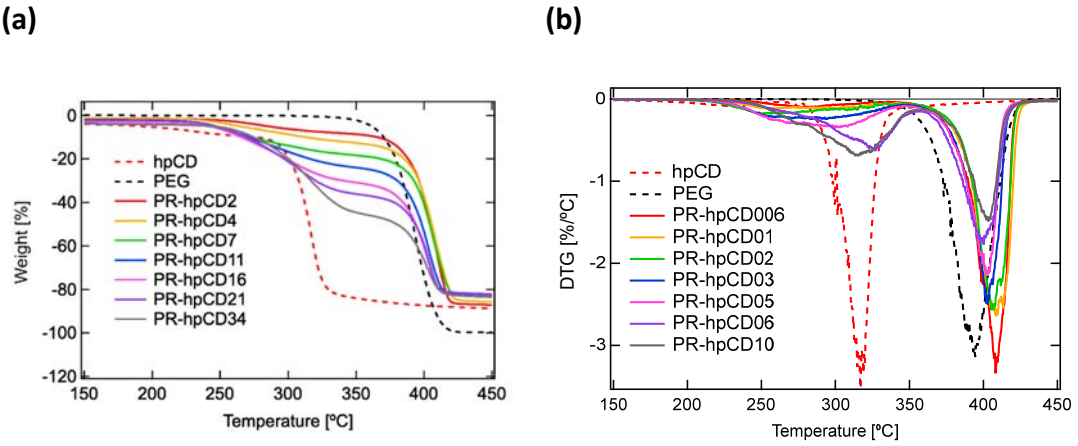

Fig. S9. TG-DTA curves for hpCD, PEG, and PR-hpPRs prepared at various hpCD concentrations.

Table S1. Comparison of threading ratios calculated from ^{1}H-NMR and TG-DTA.

Sample name	Calculated by ^{1}H-NMR		Calculated by TG-DTA	
	Threading ratio [%]	Number of CD per PEG	Threading ratio [%]	Number of CD per PEG
PR-hpCD2	0.64	2.2	0.62	2.1
PR-hpCD4	1.09	3.7	1.09	3.7
PR-hpCD7	2.05	7.0	1.82	6.2
PR-hpCD11	3.09	10.5	2.74	9.3
PR-hpCD16	4.81	16.4	4.06	13.8
PR-hpCD21	6.03	20.6	5.05	17.2
PR-hpCD34	10.0	34.2	8.43	28.7

Synthesis of PR-hpCD at various PEG concentrations

Table S2. Synthesis of PR-hpCD at various PEG concentrations

hpCD [mol/L]	PEG (*10^{-3}) [mol/L]	Threading ratio [%]	Number of hpCD per PEG N_{CD}	*M*w [*10^4]	*M*n [*10^4]	*M*w/*M*n	Yield [%]
0.44	1.1	5.49	18.7	5.46	5.07	1.08	75.9
0.44	2.3	4.27	14.6	4.78	5.18	1.08	93.0
0.44	4.5	4.81	16.4	5.04	4.68	1.08	98.9

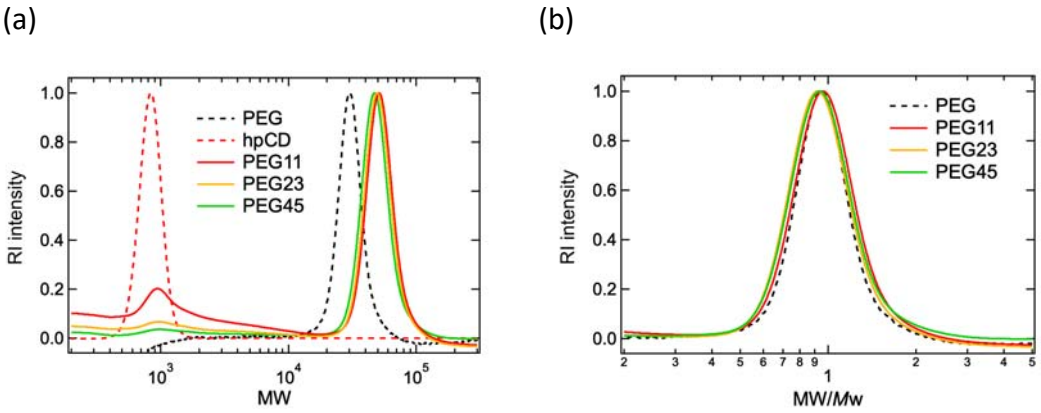

Fig. S10. Distribution of (a) molecular weight MW and (b) MW normalized by average molecular weight M_w for PEG and PR-hpCDs prepared at various PEG concentrations.

Synthesis of PR-hpCD at various temperatures

Table S3. Synthesis of PR-hpCD at various temperatures.

Temperature [K]	Threading ratio [%]	Number of hpCD per PEG	*M*w [*10^4]	*M*n [*10^4]	*M*w/*M*n	Yield [%]
277	4.81	16.4	5.04	4.68	1.08	98.9
298	5.20	17.7	5.19	4.83	1.08	91.5
333	5.81	19.8	5.01	4.66	1.08	88.6
353	5.46	18.6	5.46	4.78	1.08	96.7

(a) (b)

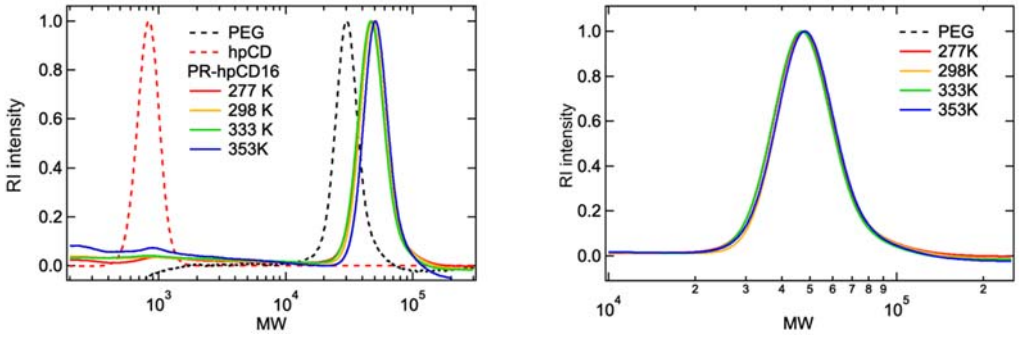

Fig. S11. Distribution of (a) molecular weight MW and (b) MW normalized by average molecular weight M_w for PEG and PR-hpCDs prepared at various temperatures.

SAXS and WAXS profiles of hpCD and pPR-hpCD solutions

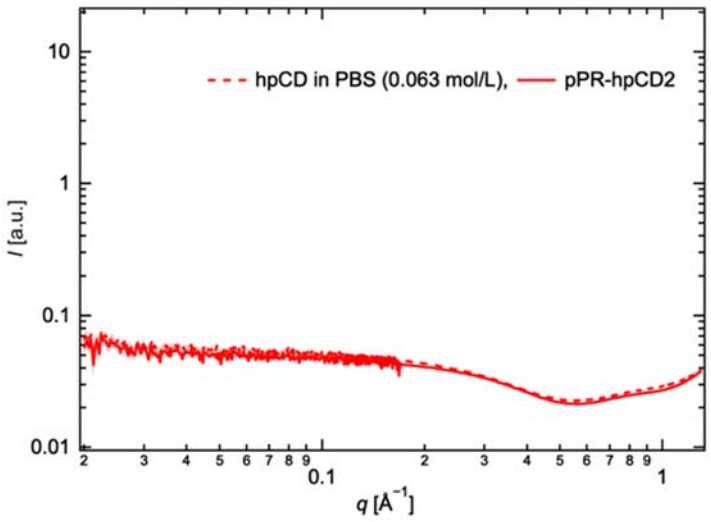

Fig. S12. X-ray scattering profile of hpCD and pPR-hpCD2.

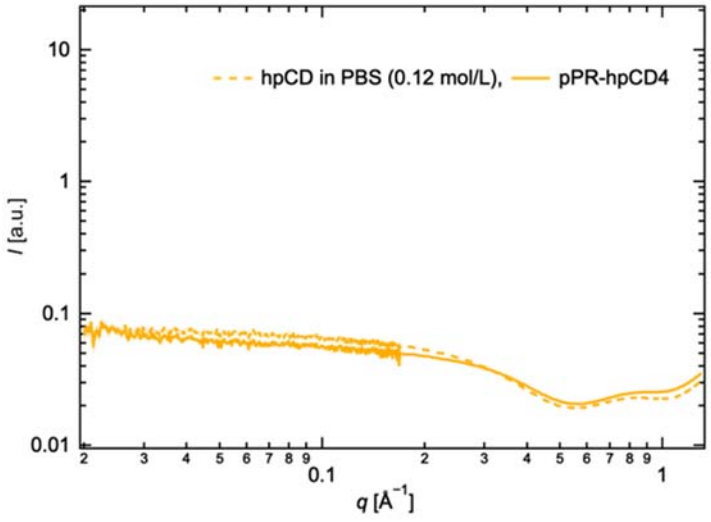

Fig. S13. X-ray scattering profile of hpCD and pPR-hpCD4.

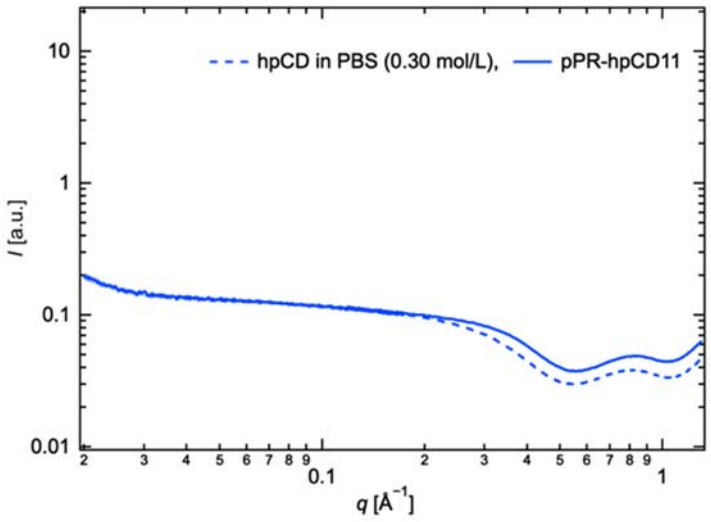

Fig. S14. X-ray scattering profile of hpCD and pPR-hpCD11.

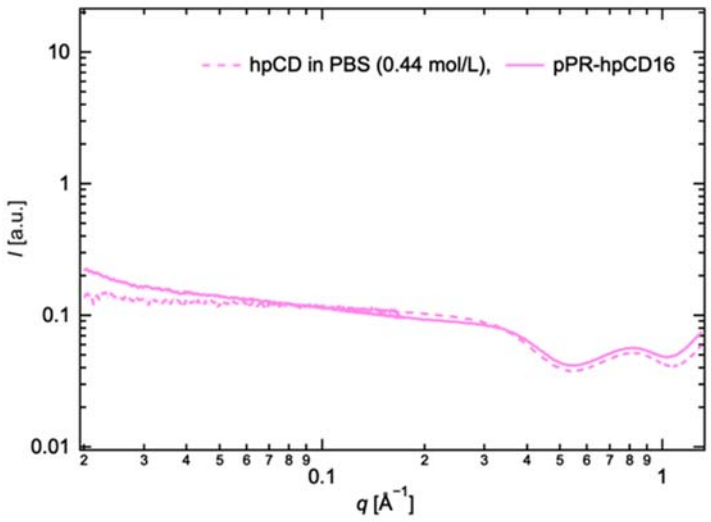

Fig. S15. X-ray scattering profile of hpCD and pPR-hpCD16.

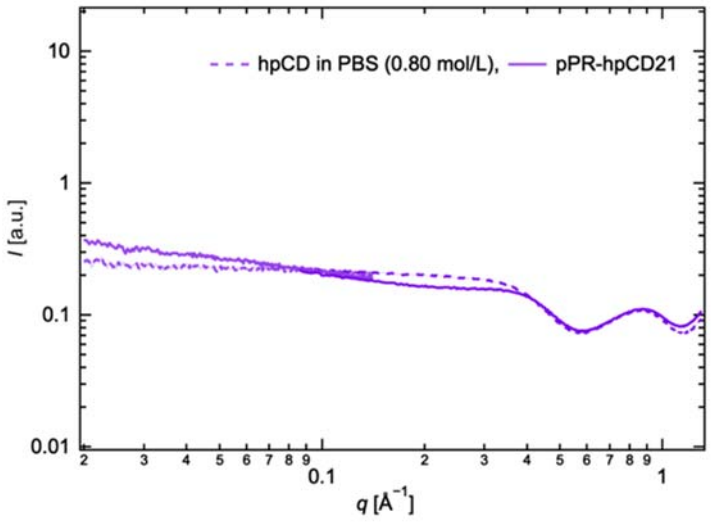

Fig. S16. X-ray scattering profile of hpCD and pPR-hpCD21.

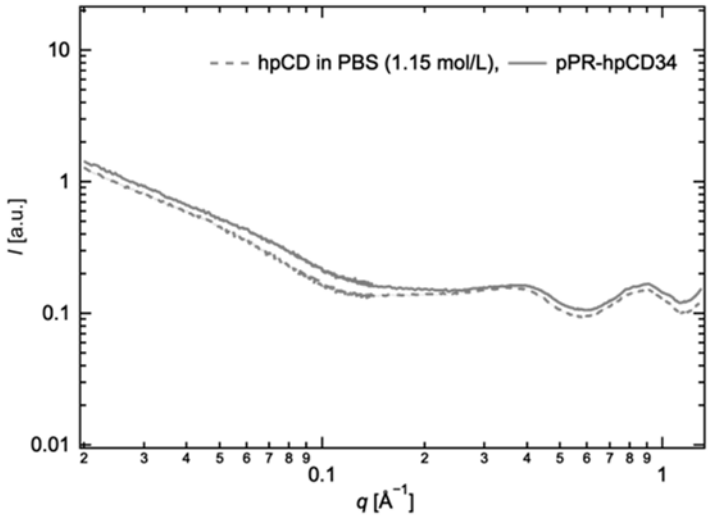

Fig. S17. X-ray scattering profile of hpCD and pPR-hpCD34.

SANS measurements of PR-hpCD solution

Small-angle neutron scattering (SANS) measurements on PEG and PR-hpCD solutions were performed using the SANS-U spectrometer of the Institute for Solid State Physics, the University of Tokyo, located at the JRR-3M research reactor of Japan Atomic Energy Agency in Tokai, Japan. For the SANS experiments, PEG and PR-hpCD were dissolved in D2O with the concentration of 1 wt%. The neutron wavelength was 7.0 Å, and the sample-to-detector distances were 8 and 1 m. After the subtraction of background and cell scattering, the scattered intensity was normalized to the absolute intensity. The corrected 2-dimensional scattering pattern was converted to 1-dimentional scattering profile, I(q) vs q by circular averaging, followed by incoherent scattering subtraction. The temperature of the sample was set to be 25 °C.

Fig. S.18 shows the SANS profiles of the PEG and PR-hpCD solutions. All the scattering profiles of PR-hpCDs with various threading ratios were overlapped with each other and close to that of PEG. This suggests that the conformation of PR-hpCD does not change with the threading ratio in the range from 0.7% to 10% (N_{CD} = 2 to 11).

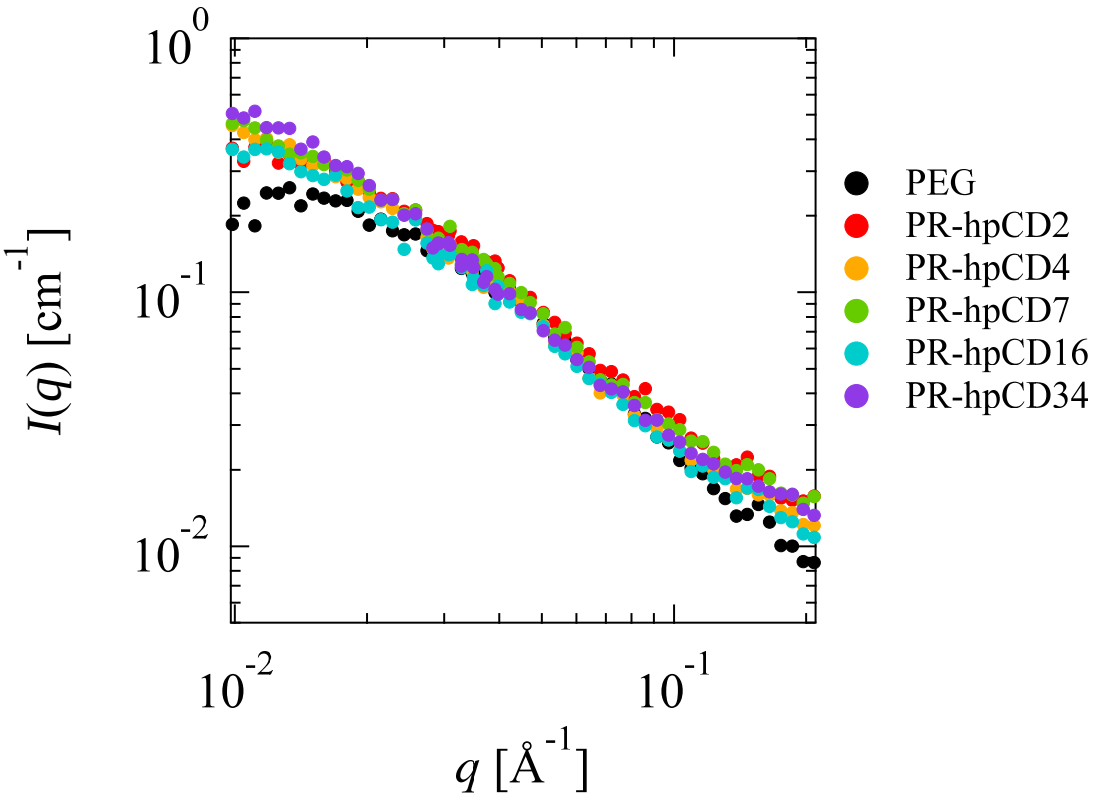

Fig. S18. SANS profiles of PEG and PR-hpCD.