

Supporting Information

High-performance cationic polyrotaxanes terminated with polypeptides as promising nucleic acid delivery systems

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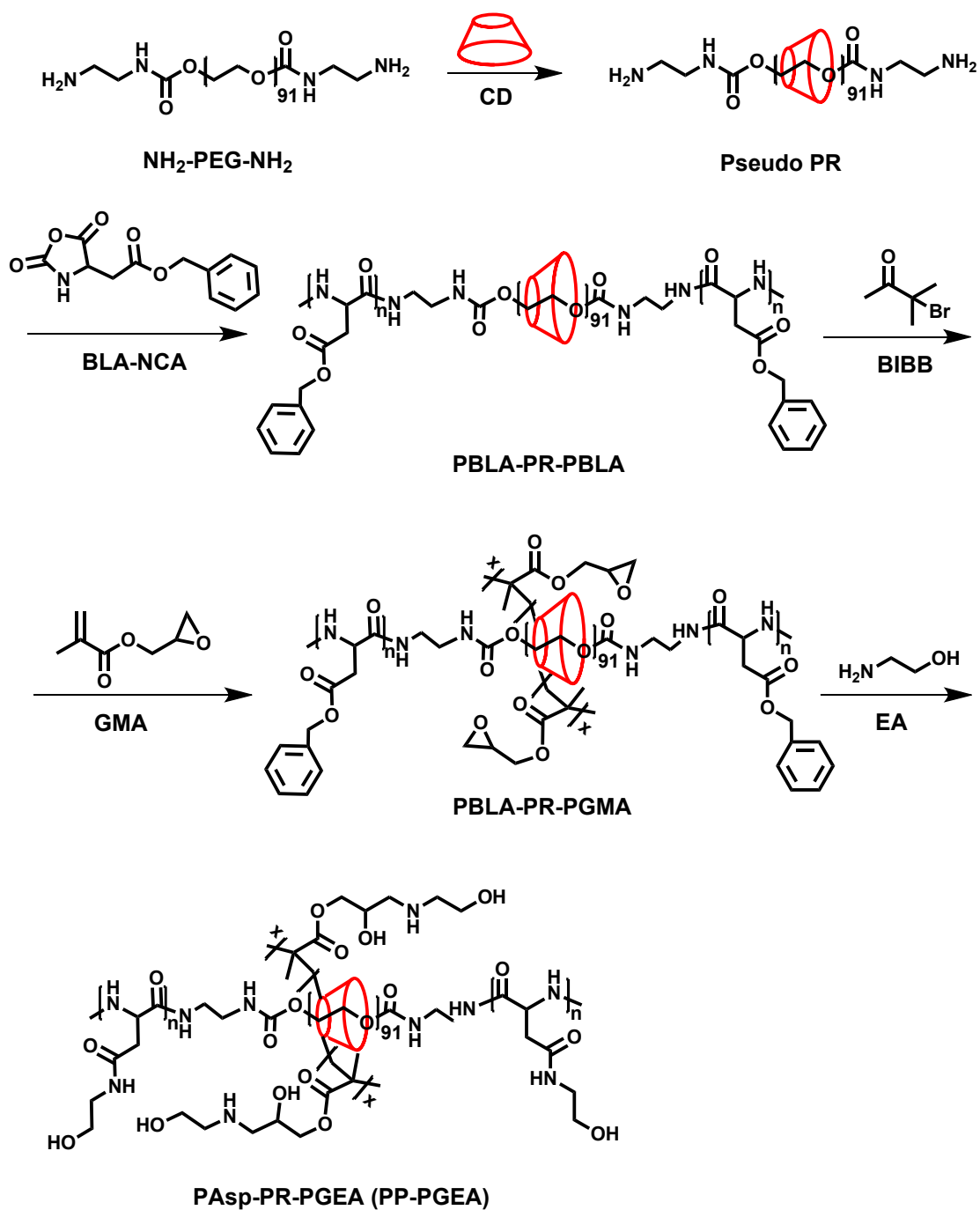


Fig. S1. Chemical scheme of the synthesis process of cationic polyrotaxanes PP-PGEA.

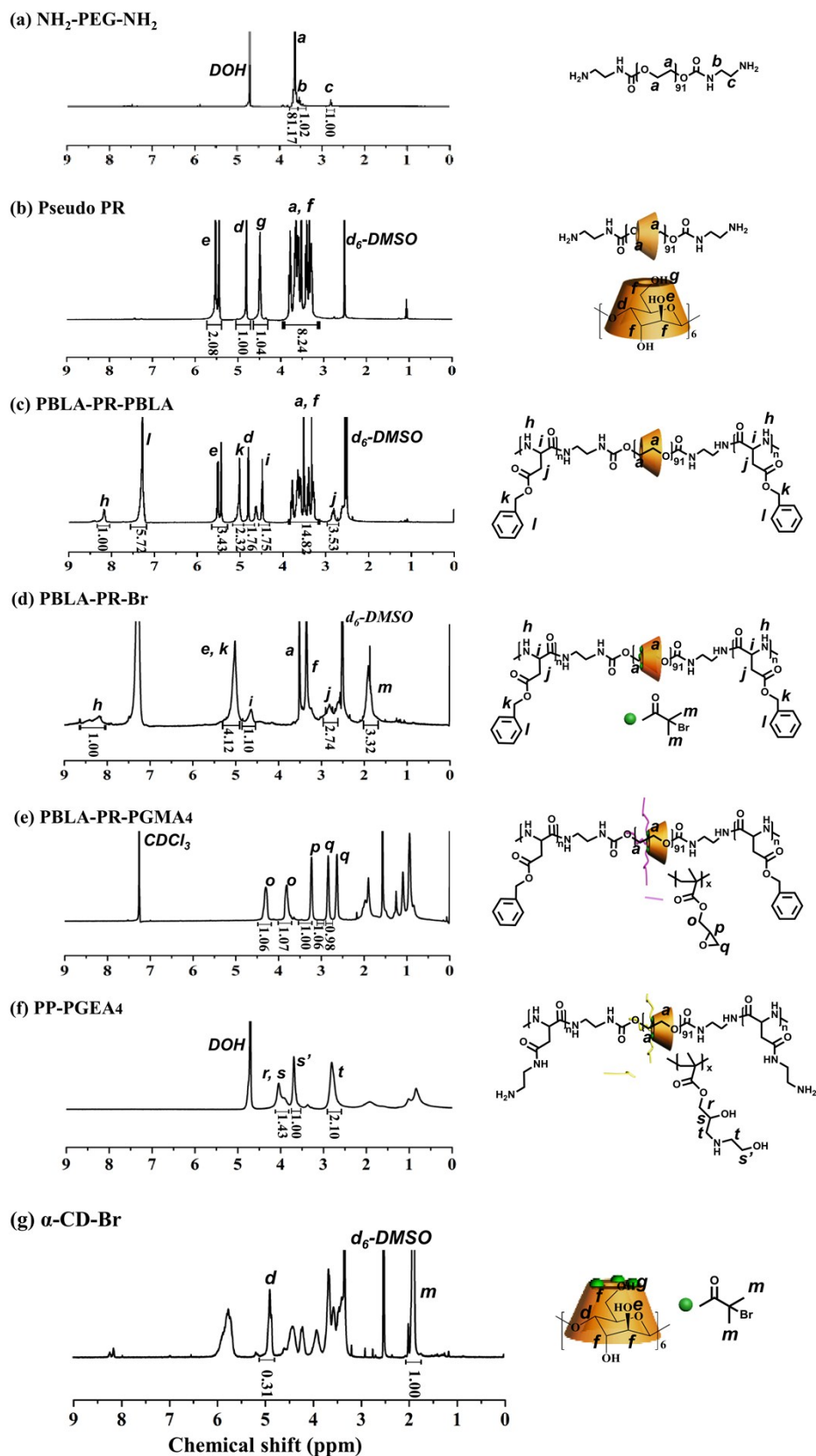


Fig. S2. ^1H NMR spectra of (a) $\text{NH}_2\text{-PEG-NH}_2$ in D_2O , (b) Pseudo PR in $d_6\text{-DMSO}$, (c) PBLA-PR-PBLA in $d_6\text{-DMSO}$, (d) PBLA-PR-Br in $d_6\text{-DMSO}$, (e) PBLA-PR-PGMA₄ in CDCl_3 , (f) PP-PGEA₄ in D_2O , and (g) $\alpha\text{-CD-Br}$ in $d_6\text{-DMSO}$.

The representative chemical structures of NH₂-PEG-NH₂, pseudo PR, PBLA-PR-PBLA, PBLA-PR-Br, PBLA-PR-PGMA₄, PP-PGEA₄, and α-CD-Br were characterized by ¹H NMR (Fig. S2). For NH₂-PEG-NH₂ (Fig. S2(a)), the peak at δ = 3.6 ppm was associated with methylene protons of PEG (*a*, O-CH₂-CH₂). The peaks at 2.8 and 3.47 ppm were assigned to the protons of methylene adjacent to amide (*b*, CH₂-NH-CO) and amino groups (*c*, CH₂-NH₂), respectively. For pseudo PR (Fig. S2(b)), the peaks at the scope of 5.46-5.53 ppm were associated with the hydroxyl protons adjacent to the methylidyne moieties (*e*, CH-OH) of glucose units. The peak at δ = 4.8 ppm was related to the unique methylidyne protons between the oxygen moieties (*d*, O-CH-O) of glucose. The chemical shift at δ = 4.5 ppm was mainly attributable to the hydroxyl protons adjacent to the methylene moieties (*g*, CH₂-OH). The broad peaks at the scope of 3.20-3.84 ppm were attributed to the methylidyne and methylene protons (*f*, CH-O and CH₂-O) of α-CD units and methylene protons (*a*, CH₂-O) of PEG units. For PBLA-PR-PBLA (Fig. S2(c)), the signals at 4.59, 8.13, 2.85, and 5.08 ppm belonged to the protons of methylidyne adjacent to amide groups (*i*, CO-CH(CH₂)-NH), protons of amide groups (*h*, CO-NH-CH), protons of methylene groups adjacent to methylidyne groups (*j*, CH-CH₂-CO), and protons of methylene groups adjacent to phenyl groups (*k*, C₆H₅-CH₂), respectively. The peak *d* at 4.81 ppm was attributed to the methylene protons of α-CD. Based on the characteristic peak areas of α-CD (peak *d*) and PEG (at 3.6 ppm, a+f-6d), the number of α-CD threaded onto PEG was about 23 after PEG were end-capped with PBLA chains.

For PBLA-PR-Br (Fig. S2(d)), the peak at δ = 1.99 ppm was associated with the methyl proton (*m*, OC-C(CH₃)₂-Br) of the 2-bromoisobutyryl groups. The substitution degree of the hydroxyl groups on the outside α-CD surface is determined to be about

3 from the area ratio of peak *m* and *e*. For PBLA-PR-PGMA (Fig. S2(e)), the signals at $\delta = 3.8$ and $\delta = 4.3$ ppm were attributed to methylene protons adjacent to oxygen moieties of the ester linkages (*o*, $\text{CH}_2\text{OC}=\text{O}$). The peak at $\delta = 3.2$ and peaks at $\delta = 2.6$ and 2.8 ppm could be assigned to the methyldyne (*p*, $\text{CH}_2\text{CH}(\text{O})\text{CH}_2$) and methylene (*q*, $\text{CHCH}(\text{O})\text{CH}_2$) protons of the epoxy ring, respectively. The area ratio *o:p:q* was 2:1:2, which demonstrated that the epoxy groups in the PBLA-PR-PGMA₄ were not damaged throughout ATRP. After the ring-opening and aminolysis reactions of PBLA-PR-PGMA with excess EA, the peaks *o* and *p* which represented the epoxy groups of PBLA-PR-PGMA disappeared completely (Fig. S2(f)). The peaks *q* at 3.8 ppm and 4.3 ppm were combined into one peak *r* ($\delta = 4.0$ ppm). The chemical shift of $\delta = 3.6$ ppm mainly corresponded to the resultant methyldyne protons adjacent to the hydroxyl groups (*s*, CHOH). The signal at 2.9 ppm was attributable to the methylene protons adjacent to the amine groups (*t*, $\text{CH}(\text{OH})\text{CH}_2\text{NH}$). The ¹H NMR results indicated that PP-PGEA was prepared successfully. For the control α -CD-Br, the substitution degree of the hydroxyl groups on the outside α -CD surface is determined to be about 3 from the area ratio of peak *m* and *d* (Fig. S2(g)).