Supplementary Information

Block catiomers with flanking hydrolyzable tyrosinate groups enhance *in vivo* mRNA delivery *via* π–π stacking-assisted micellar assembly

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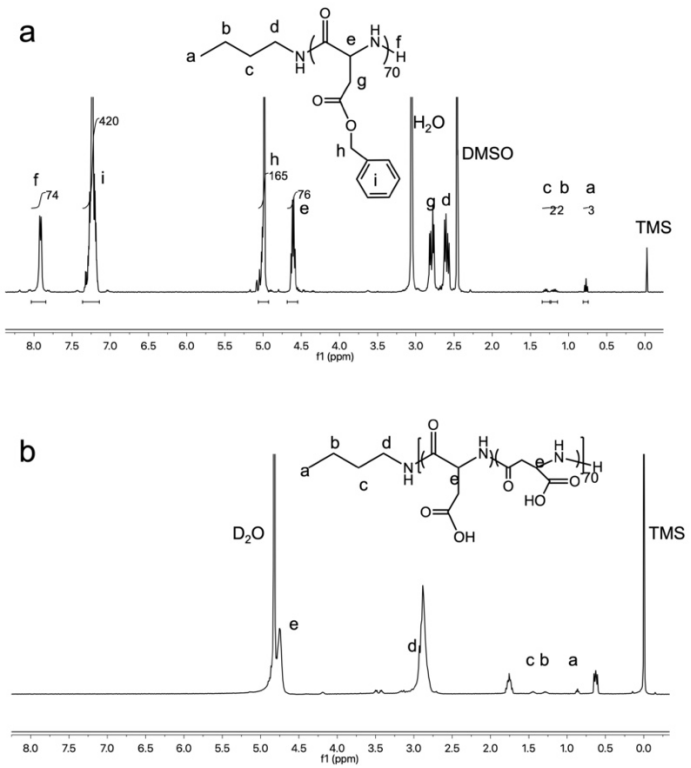
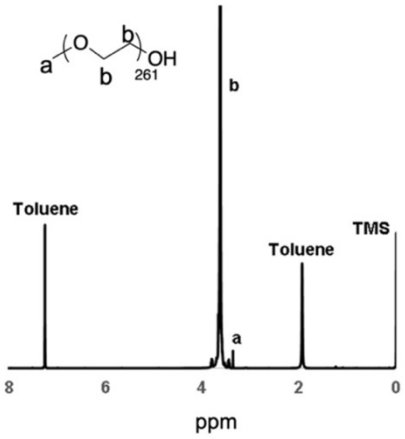
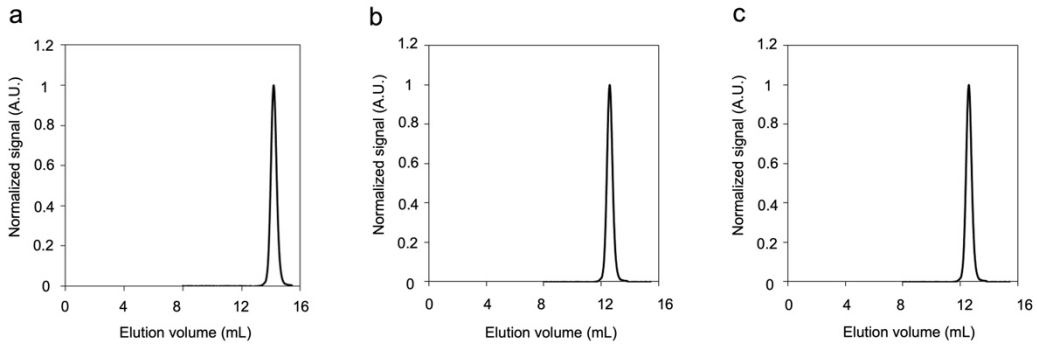


Supplementary Figure 1. [1]H-NMR of a) Homo-PBLA (polymer concentration: 10 mg/mL, solvent: DMSO, and temperature: 80 °C), b) Homo-PAsp (polymer concentration: 10 mg/mL, solvent: D_2O, and temperature: 25 °C)



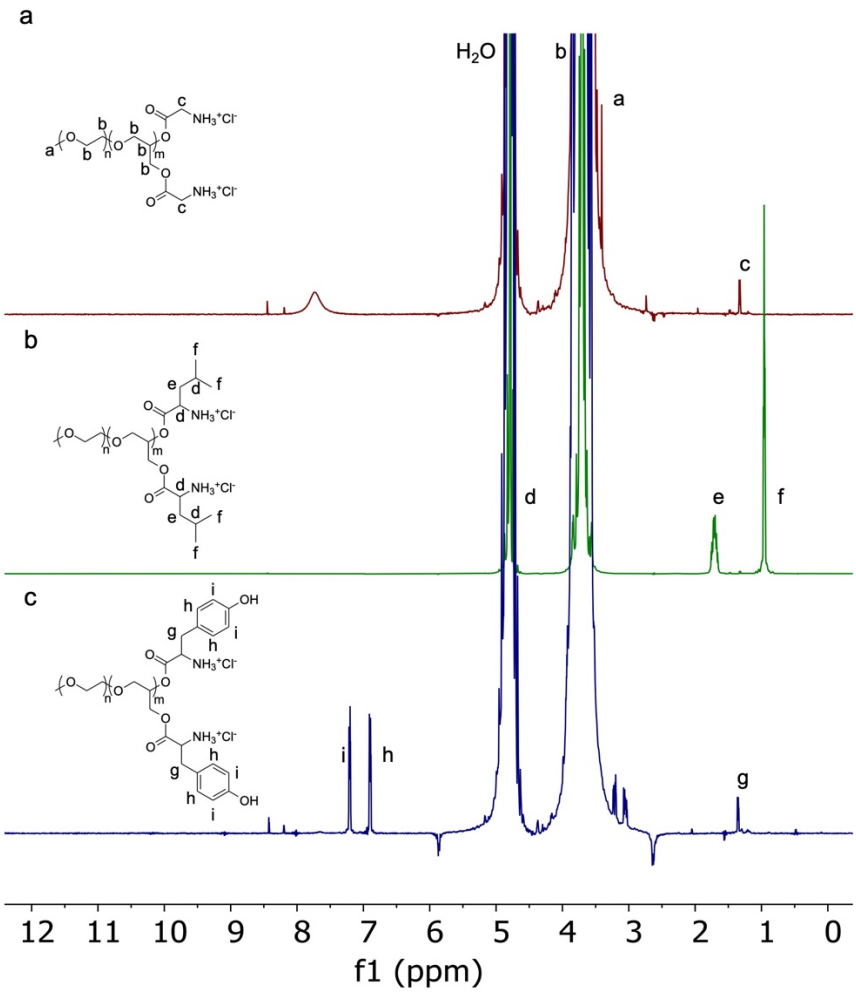
Supplementary Figure 2. [1]H-NMR of PEG-OH (polymer concentration: 10 mg/mL, solvent: Toluene-d8, and temperature: 80 °C).



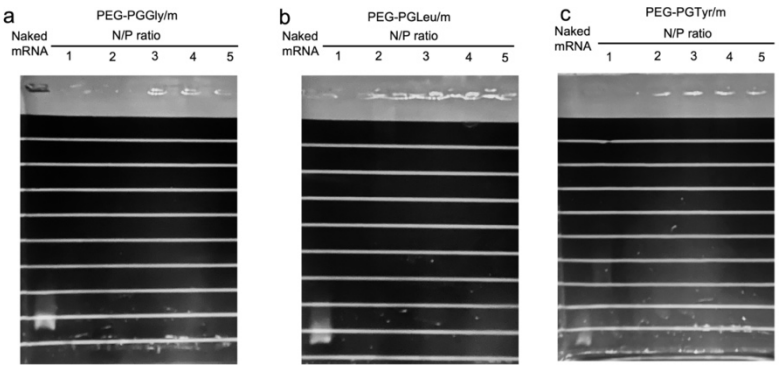
Supplementary Figure 3. SEC curves of (a) PEG-OH, (b) PEG-PECH, and (c) PEG-PG (Polymer concentration: 1 mg/mL, solvent: DMF with 10 mM lithium chloride, temperature: 40 °C).

Supporting Table 1. Elementary analysis of PEG-PECH

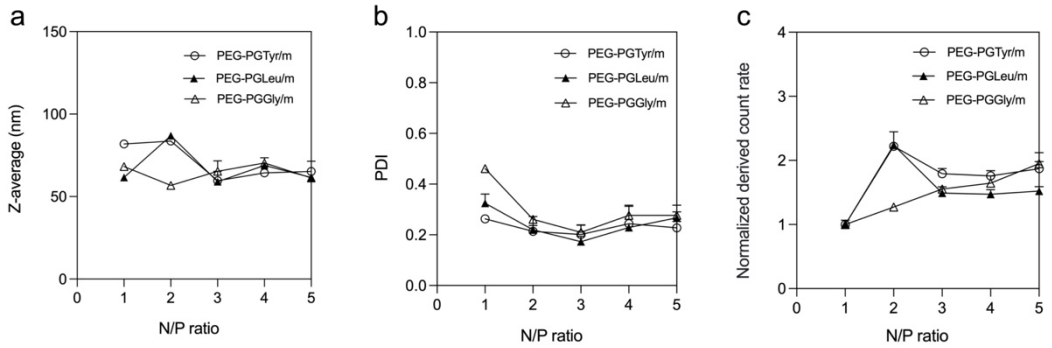
Polymer	Cl (%)	C (%)	H (%)	O (%)
PEG-PECH	14.7	48.6	7.67	29.0



Supplementary Figure 4. ^{1}H-NMR of a) PEG-PGGly, b) PEG-PGLeu and c) PEG-PGTyr (polymer concentration: 10 mg/mL, solvent: D_2O, and temperature: 25 °C).



Supplementary Figure 5. Electrophoretic analysis of the PEG-PGGly/m (a), PEG-PGLeu/m (b) and PEG-PGTyr/m (c) at N/P ratios ranging from 1 to 5 on 1% agarose gel (15 µL sample solution containing 500 ng of mRNA were applied to each well and mRNA was visualized using Midori Green Direct dye).



Supplementary Figure 6. DLS characterization of micelles from PEG-PGGly, PEG-PGleu and PEG-PGTyr. (a) Z-average diameter, (b) polydispersity index (PDI), and (c) normalized derived count rate (normalization with derived count rate of N/P = 1) of micelles in 10 mM HEPES buffer.