

Supporting Information

**Polypeptides with Quaternary Phosphonium Side Chains: Synthesis,  
Characterization, and Cell-Penetrating Properties**

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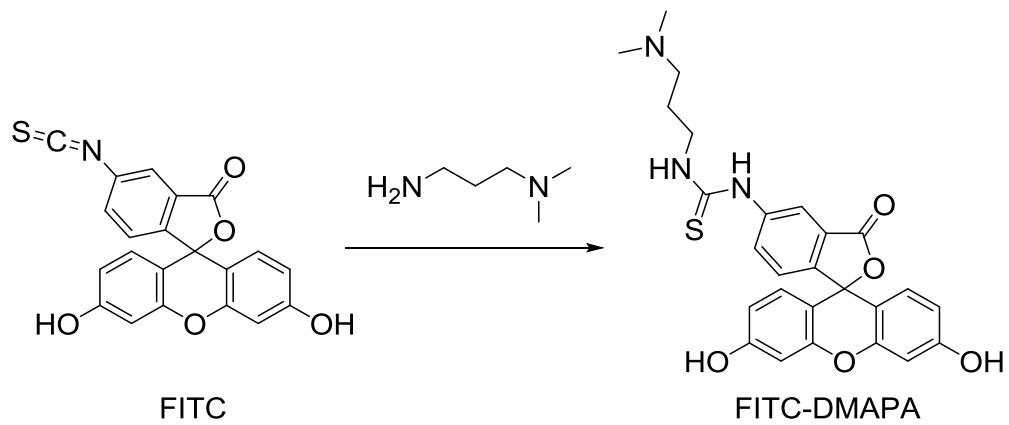
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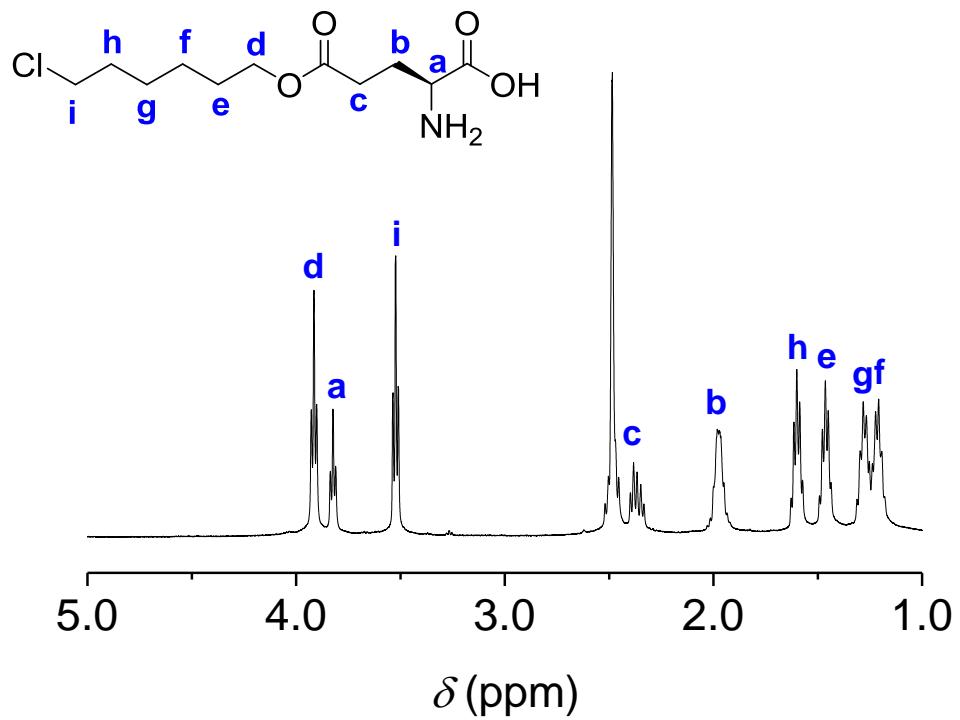
**Table S1.** Synthesis of polypeptides with chloroalkyl side chains<sup>a</sup>

entry	monomer	M/I	$M_n (M_n^*)^{b,c}$ (kDa)	$M_w/M_n^c$
1	CP-L-Glu-NCA	40/1	8.1 (8.2)	1.02
2	CH-L-Glu-NCA	40/1	10.0 (9.9)	1.02
3	CH-DL-Glu-NCA	40/1	9.7 (9.9)	1.10

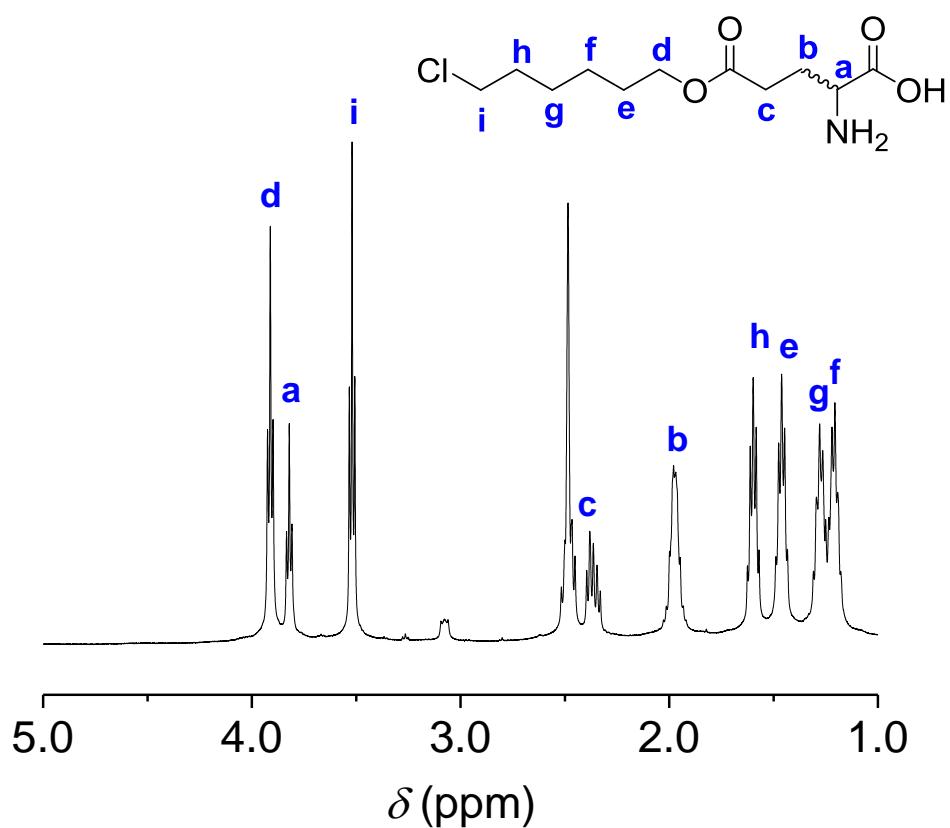
<sup>a</sup> Polymerizations were carried out at room temperature for 48 h. Monomer conversions were all above 99% as indicated by FTIR. <sup>b</sup> Obtained MW (expected MW). <sup>c</sup> Determined by GPC.



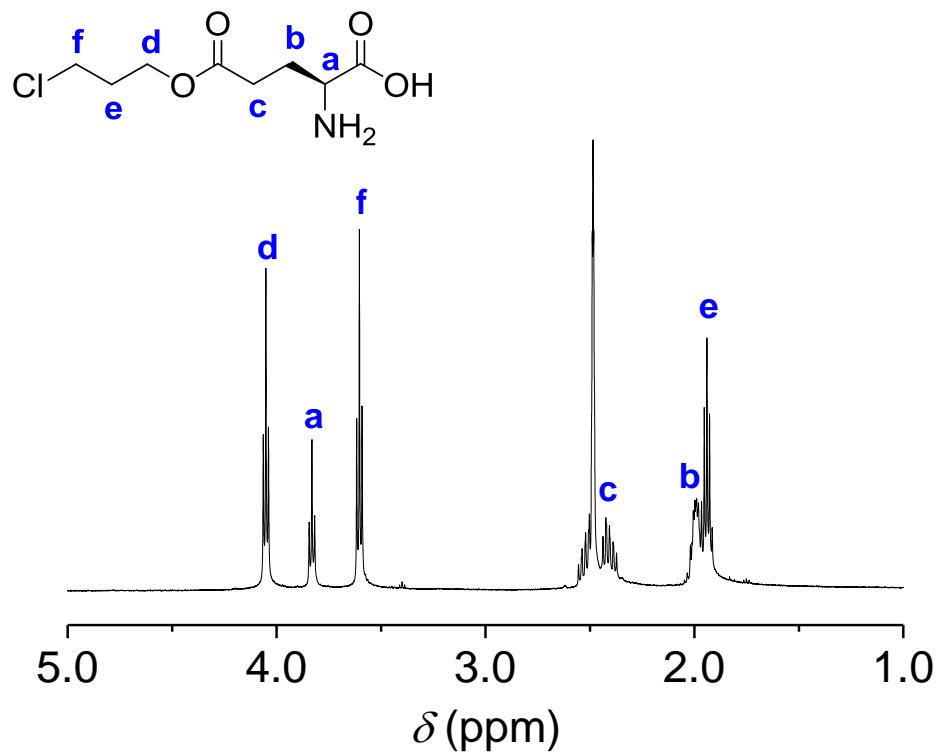
**Scheme S1.** Synthesis of fluorescein-functionalized tertiary amine (FITC-DMAPA).



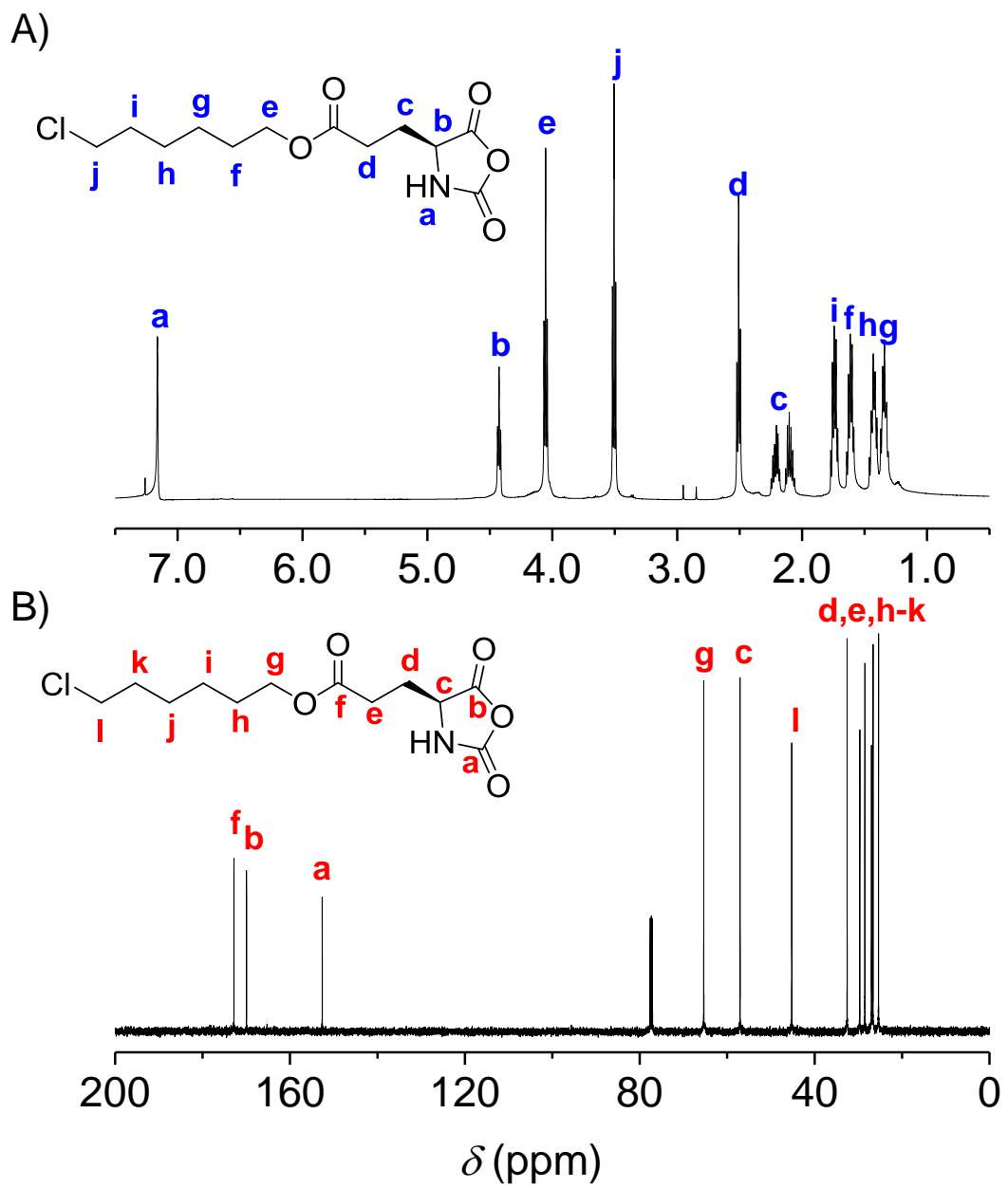
**Figure S1.**  $^1\text{H}$  NMR spectrum of CH-L-Glu in  $\text{DMSO}-d_6/\text{D}_2\text{O}-\text{DCl}$  (9:1, v/v).



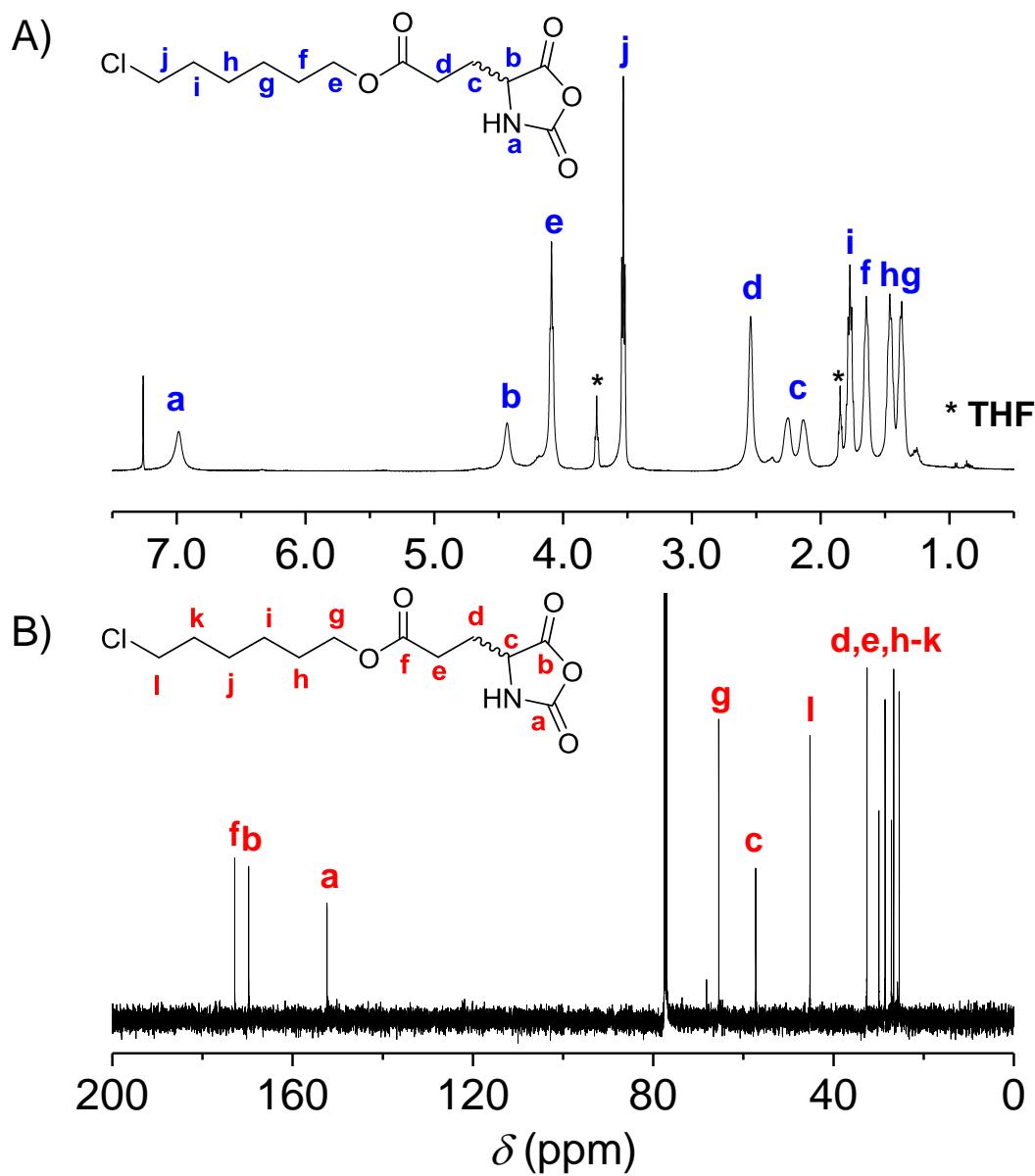
**Figure S2.**  $^1\text{H}$  NMR spectrum of  $\text{CH-DL-Glu}$  in  $\text{DMSO}-d_6/\text{D}_2\text{O-DCl}$  (9:1, v/v).



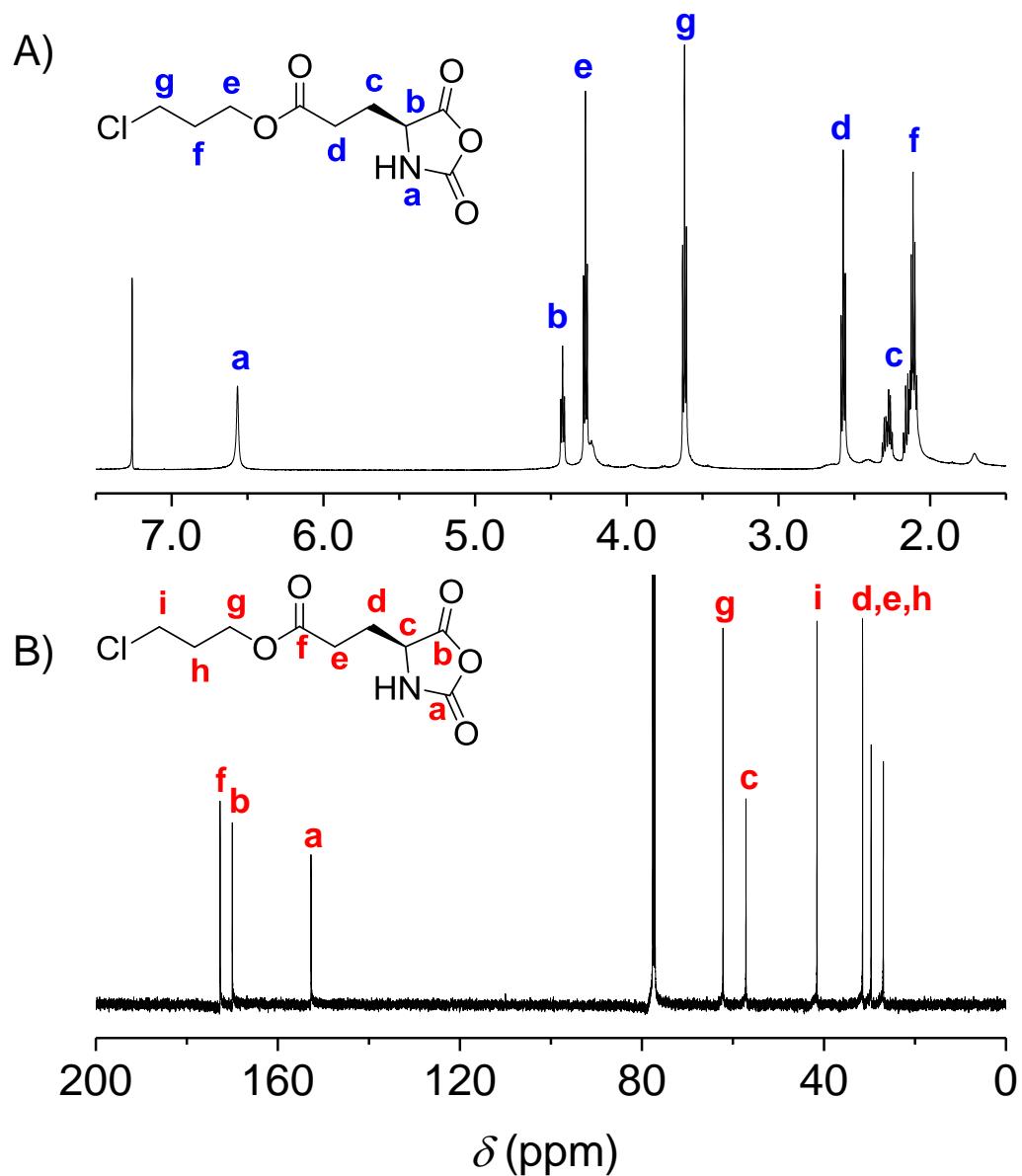
**Figure S3.**  $^1\text{H}$  NMR spectrum of CP-L-Glu in  $\text{DMSO}-d_6/\text{D}_2\text{O-DCl}$  (9:1, v/v).



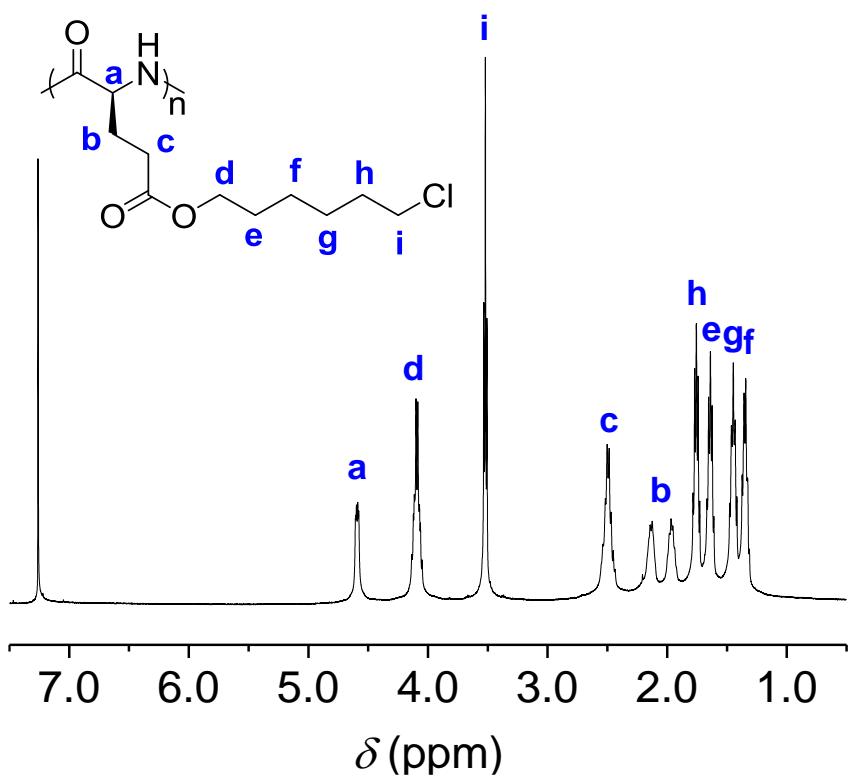
**Figure S4.**  $^1\text{H}$  (A) and  $^{13}\text{C}$  (B) NMR spectra of CH-L-Glu-NCA in  $\text{CDCl}_3$ .



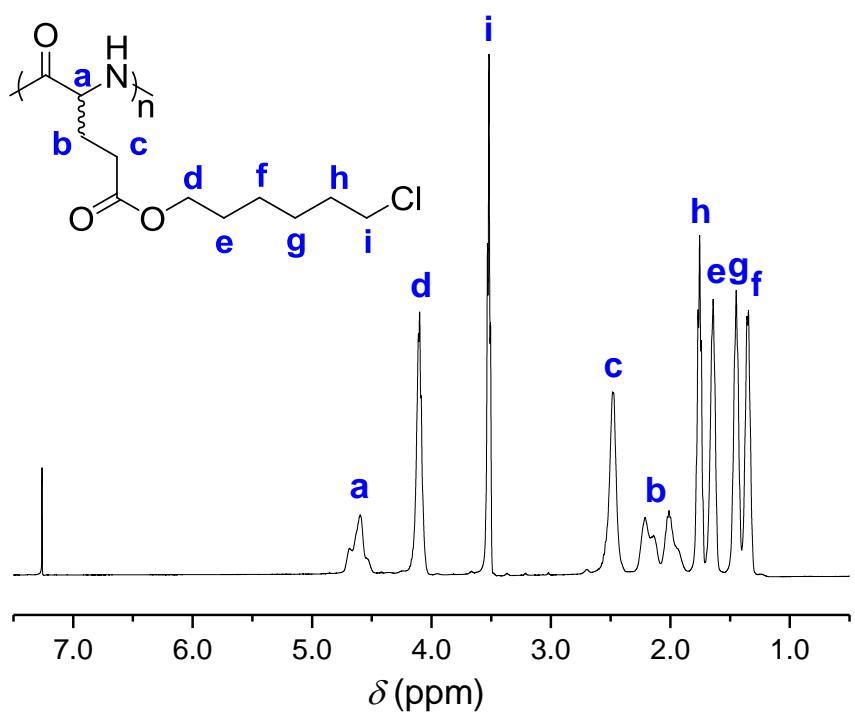
**Figure S5.**  $^1\text{H}$  (A) and  $^{13}\text{C}$  (B) NMR spectra of CH-DL-Glu-NCA in  $\text{CDCl}_3$ .



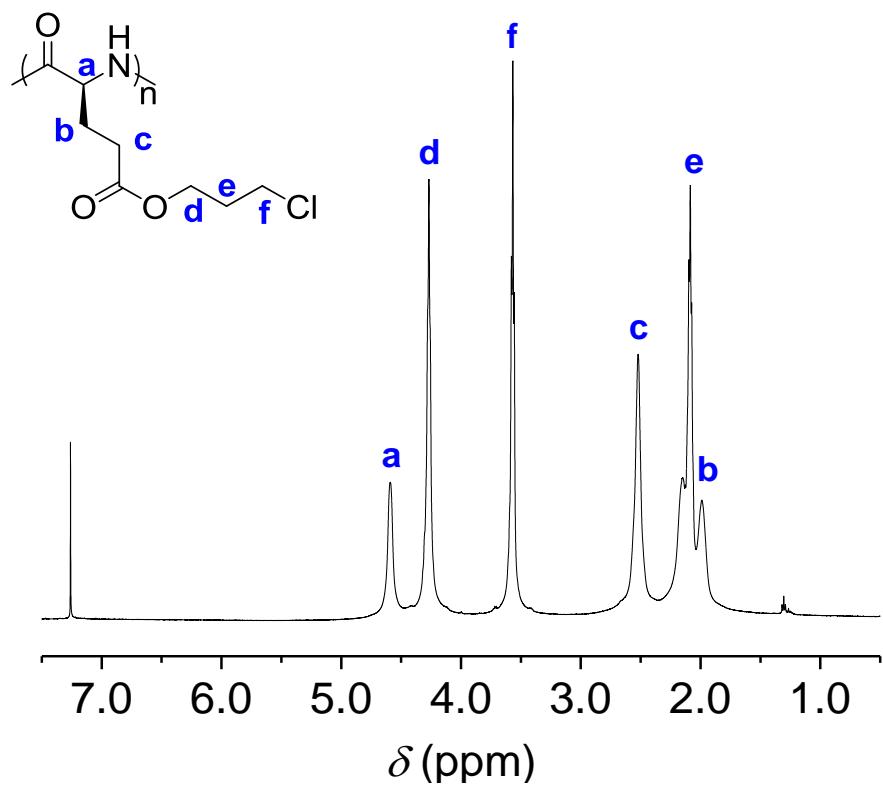
**Figure S6.**  $^1\text{H}$  (A) and  $^{13}\text{C}$  (B) NMR spectra of CP-L-Glu-NCA in  $\text{CDCl}_3$ .



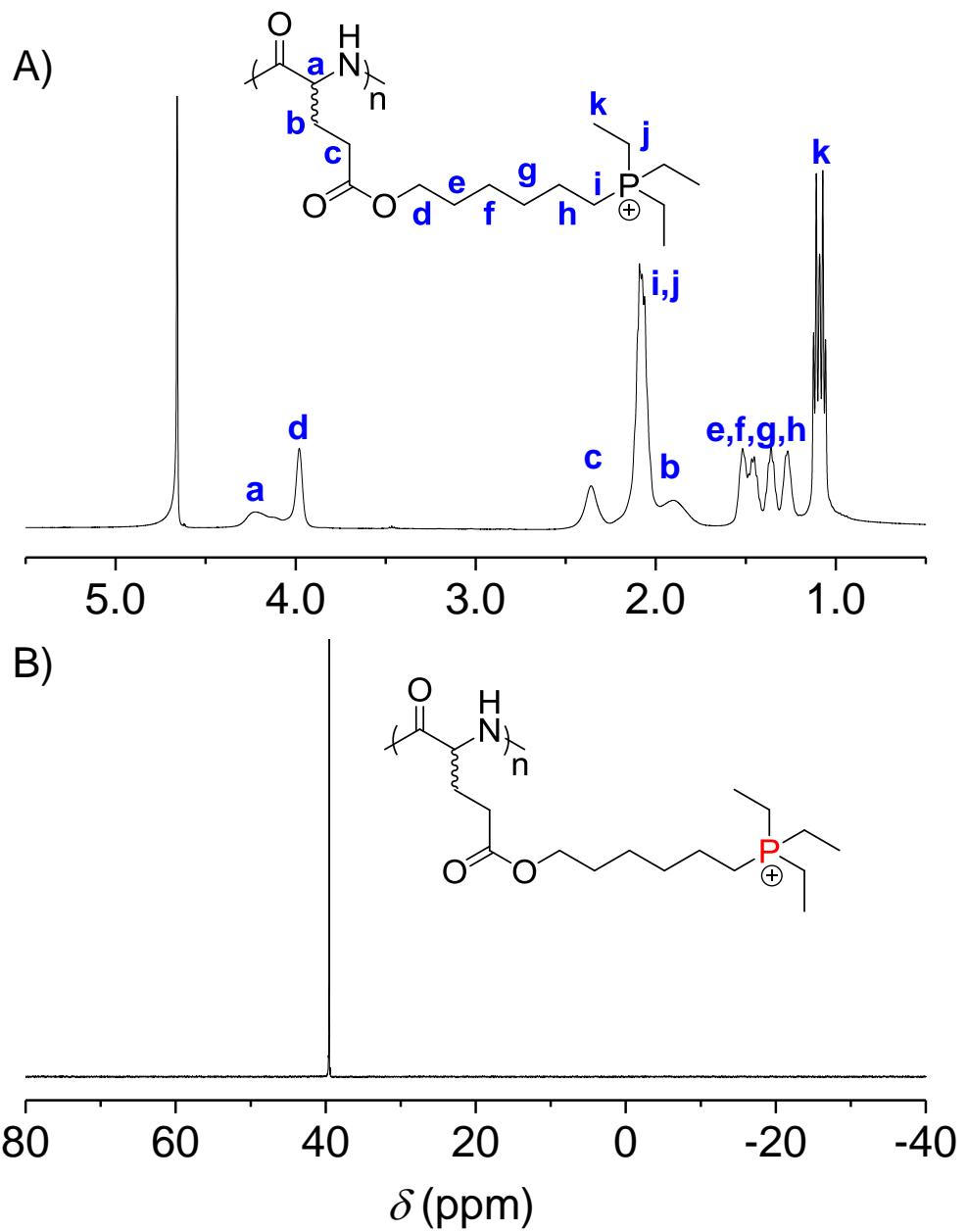
**Figure S7.**  $^1\text{H}$  NMR spectrum of PCHLG in  $\text{CDCl}_3/\text{TFA}-d$  (85:15, v/v).



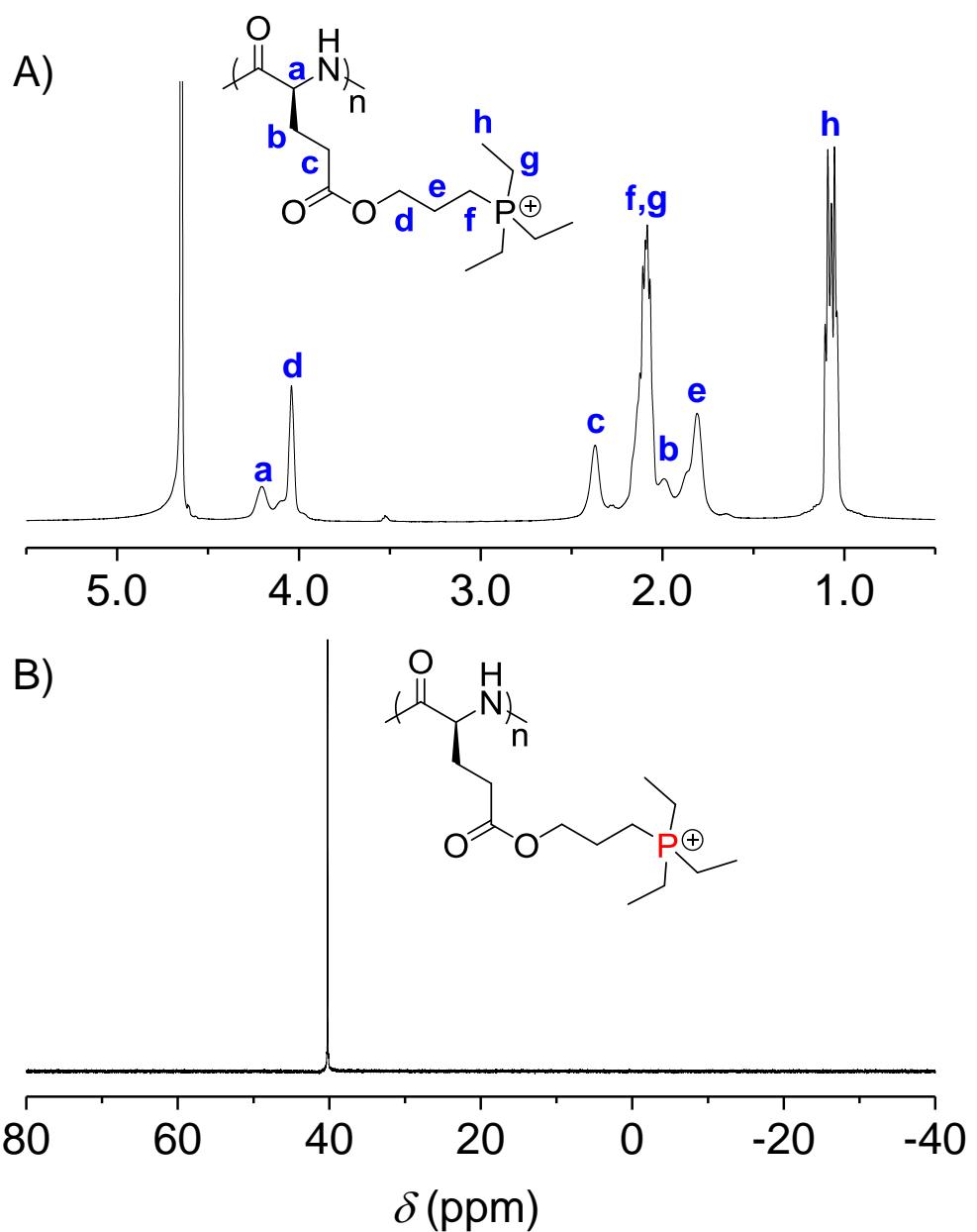
**Figure S8.**  $^1\text{H}$  NMR spectrum of PCHDLG in  $\text{CDCl}_3/\text{TFA}-d$  (85:15, v/v).



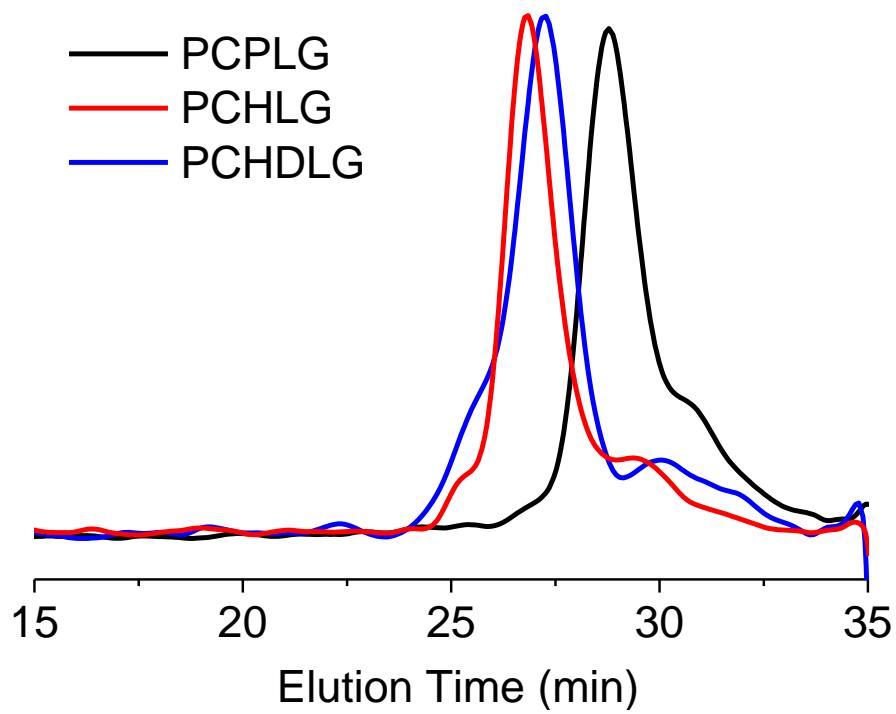
**Figure S9.**  $^1\text{H}$  NMR spectrum of PCPLG in  $\text{CDCl}_3/\text{TFA}-d$  (85:15, v/v).



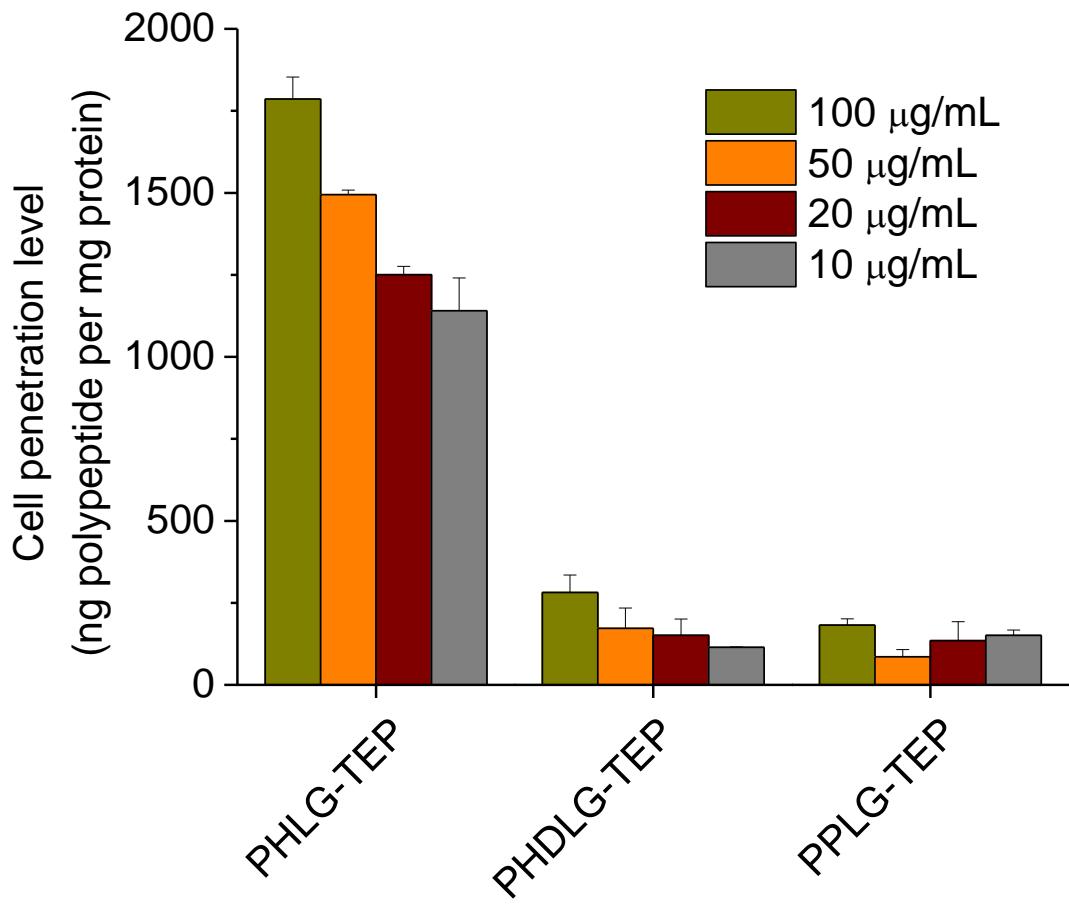
**Figure S10.**  $^1\text{H}$  (A) and  $^{31}\text{P}$  (B) NMR spectra of PHDLG-TEP in  $\text{D}_2\text{O}$ .



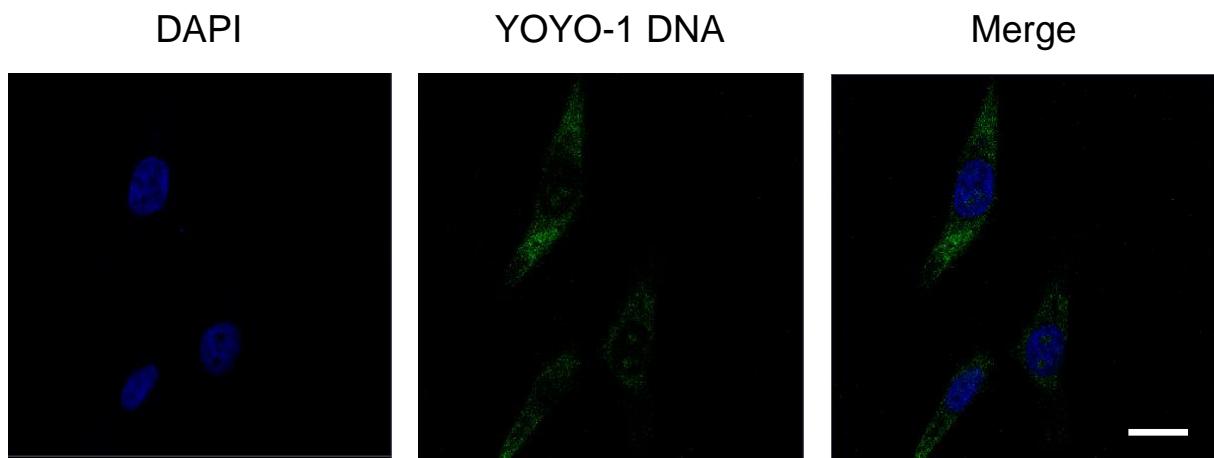
**Figure S11.**  $^1\text{H}$  (A) and  $^{31}\text{P}$  (B) NMR spectra of PPLG-TEP in  $\text{D}_2\text{O}$ .



**Figure S12.** GPC traces of polypeptides with chloroalkyl side chains.



**Figure S13.** Uptake level of fluorescein-labeled polypeptides in HeLa cells at different polypeptide concentrations ( $n = 3$ ). The incubation time was maintained constant at 2 h.



**Figure S14.** CLSM images of HeLa cells incubated with PHLG-TEP and YOYO-1-labeled DNA complex at 37 °C for 4 h (bar = 20 μm).