Supporting Information

Thermo and pH Dual Responsive Polypeptide Derived from "Clickable" Poly(γ-3-methylthiopropyl-_L-glutamate)

Chenglong Ge, Liang Zhao, Ying Ling, and Haoyu Tang*

Key Laboratory of Polymeric Materials and Application Technology of Hunan Province, Key Laboratory of Advanced Functional Polymer Materials of Colleges and Universities of Hunan Province, College of Chemistry, Xiangtan University, Xiangtan, Hunan, 411105, China

Correspondence to: Haoyu Tang (Email: <u>htang@xtu.edu.cn</u>)



Figure S1. (a) Optical image and (b) FTIR spectrum of MTPLG-NCA in the solid state.



Figure S2. ¹H NMR spectra of PMTPLG samples prepared from ring-opening polymerizations with different initial monomer to initiator ratios ($[M]_0/[I]_0$, asterisks signify DMF and diethyl ether signals).



signals).

moretres							
samples	TCM	THF	DMF	DMSO	H_2O	MeOH	EtOH
PMTPLG	S	S	S	S	Ι	Ι	Ι
PPLG-DMS-I	Ι	Ι	S	S	S	U	Ι
PPLG-DMS-BF ₄	Ι	Ι	S	S	S	U	Ι
PPLG-MBS-Br	S	S	S	S	Ι	U	U
PPLG-MBS-I	S	S	S	S	Ι	U	Ι
PPLG-MBS-BF ₄	S	S	S	S	Ι	Ι	Ι
PPLG-MPS-Br	S	S	S	S	Ι	U	U
PPLG-MPS-I	S	S	S	S	Ι	U	Ι
PPLG-MPS-BF ₄	S	S	S	S	Ι	Ι	Ι
PPLG-MSEA-Cl	Ι	Ι	S	S	S	Ι	Ι
PPLG-MSEA-BF ₄	Ι	Ι	S	S	S	Ι	Ι

Table S1. Solubility of PMTPLG and polypeptides bearing various sulfonium moieties

TCM = trichloromethane or chloroform; THF = tetrahydrofuran; DMF = N,Ndimethylformamide; DMSO = dimethyl sulphoxide; MeOH = methanol; EtOH = ethanol; S = soluble; I = insoluble; U = UCST-type phase transition (concentration = 1 mg·mL⁻¹).



Figure S5. (a) Representative optical images of PPLG-MSEA-BF₄ aqueous solution at pH = 7.50 at different temperature to demonstrate the reversible UCST-type phase behavior. (b) Representative plot of transmittance at $\lambda = 500$ nm *versus* temperature for PPLG-MSEA-BF₄ aqueous solutions at pH = 7.50 in a cooling/heating cycle (polymer concentration = 5 mg·mL⁻¹).



Figure S6. Plots of transmittance at $\lambda = 500$ nm *versus* temperature for PPLG-MSEA-BF₄ aqueous solutions with decreasing the pH values (polymer concentration = 5 mg·mL⁻¹).



Figure S7. Plots of transmittance at $\lambda = 500$ nm *versus* temperature for PPLG-MSEA-BF₄ aqueous solutions at pH = 7.50 with different polymer concentrations.



Figure S8. Plots of transmittance at $\lambda = 500$ nm *versus* temperature for PPLG-MSEA-BF₄ aqueous solutions at pH = 7.50 with increasing the concentration of (a) NaCl or (b) NaBF₄ (polymer concentration = 5 mg·mL⁻¹).