Supporting Information

Synthesis and self-assembly of a dual-responsive monocleavable ABCD star

quaterpolymer

Huanhuan Liu,^{a,b} Jian Zhang,^a Wenxue Dai^a and Youliang Zhao*a

^a Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. Tel: +86-512-65882045; E-mail: ylzhao@suda.edu.cn

^b College of Pharmacy, Anhui University of Chinese Medicine, Hefei 230012, China



Scheme S1 Synthetic routes to 2-azidomethyl-2-bromomethyl-3-hydroxypropyl 4-(benzodithioyl)-4-cyanopentanoate (ABCP).



Fig. S1 1 H (a) and 13 C (b) NMR spectra of ABCP.



Fig. S2 FT-IR spectrum of ABCP.



Fig. S3 GPC traces of ABCD₁ star ($M_{n,LS} = 24200 \text{ g mol}^{-1}$, D = 1.09) and ABC star ($M_{n,LS} = 17300 \text{ g mol}^{-1}$, D = 1.10) obtained by DTT-triggered cleavage of disulfide linkage of ABCD₂ star and removal of PAA by precipitation into water, in which A = PEG, B = PSt, C = PCL, D₁ = P*t*BA, and D₂ = PAA.



Fig. S4 ¹H NMR spectra of PDMA (a) in CDCl₃ and P(DMA-*co*-QDMA) (abbreviated as PDQ, b) in DMSO- d_6 .



Fig. S5 Influence of $[QDMA^+]/[COO^-]$ ratio (*r*) and pH on DLS plots of copolymer coaggregates formed from PEG-PSt-PCL-PAA star ($c_{star} = 0.50 \text{ mg mL}^{-1}$) and P(DMA-*co*-QDMA) mixtures in aqueous solution at 25 °C.