Supporting Information

Synthesis and self-assembly of hyperbranched multiarm copolymer peptide conjugates based on light-induced metal-free ATRP

Yue Zhang*, Rong Zhao, Yan Qin, Jianguo Yi, Jimin Zhang* and Xiaoai Chen

Characterization: ^{1}H NMR measurements were carried out on a 400 MHz Varian UNITY-plus NMR spectrometer. The M_n and the dispersity were measured by a Hitachi gel permeation chromatography (GPC) with DMF as the mobile phase and PMMA as the standards. The GPC was equipped with a Hitachi L-2490 refractive index detector and a Viscotek 270 dual detector. Scanning electron microscopy (SEM) was measured with an FEI Apreo S LoVac electron microscope. Transmission electron microscopy (TEM) was measured with a Tecnai G2 F20 electron microscope under 200 kV operating voltage. The hydrodynamic diameters (D_h), the polydispersities (PDI) and the Zeta potentials of the assemblies were measured by a Malvern Zetasizer Nano-ZS. The UV-vis absorbance spectra were collected on a Shimadzu UV-2450 spectrophotometer. Confocal images of the aggregates were obtained with a ZEISS LSM800 CLSM.

Table S1. Polymerization recipe of the hyperbranched polymers

	DEGMA (mL)	BMA (g)	PTH (mg)	DMF (mL)	Time (h)
h_1PDEGMA	2.70	0.4	4.4	3.1	11
h_2PDEGMA	2.15	0.4	3.6	2.5	13
h_3PDEGMA	1.35	0.4	2.4	1.7	12

Table S2. Polymerization recipe of the hyperbranched multiarm copolymers

	hPDEGMA (g)	DSMA (g)	PTH (mg)	DMF (mL)
h_1PDEGMA-*star*-PDSMA	0.15	0.233	1.3	1.5
h_2PDEGMA-*star*-PDSMA	0.15	0.328	1.7	1.5
h_3PDEGMA-*star*-PDSMA	0.15	0.179	1.0	1.5

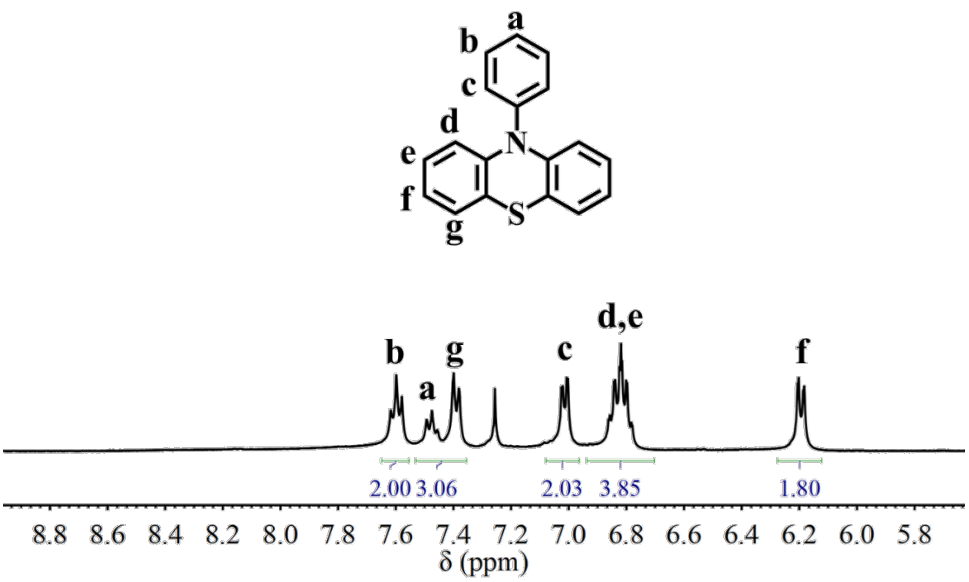

Figure S1. ^{1}H NMR spectrum of PTH in $CDCl_3$.

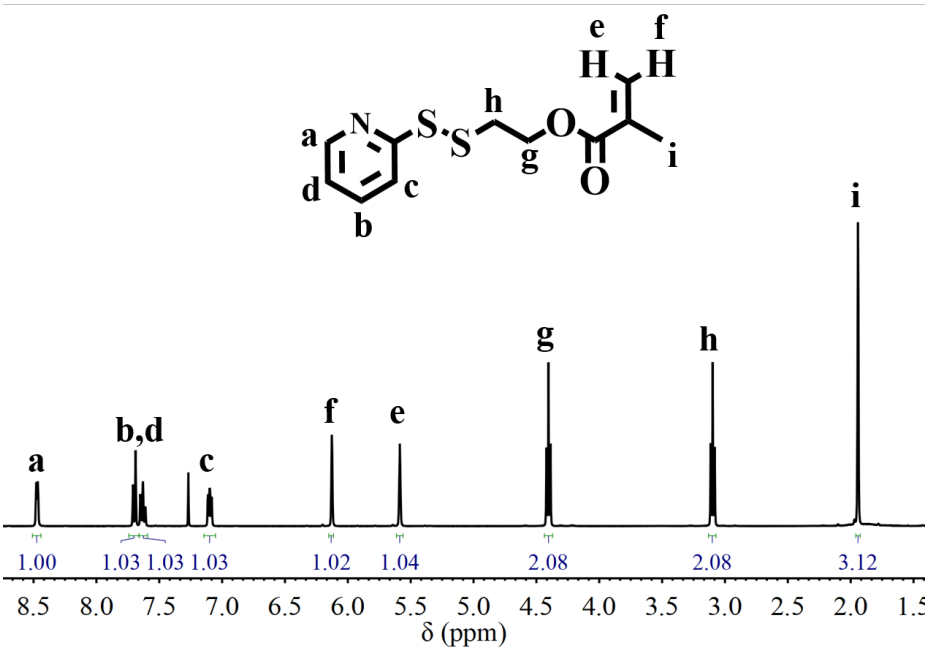

Figure S2. ^{1}H NMR spectrum of DSMA in $CDCl_3$.

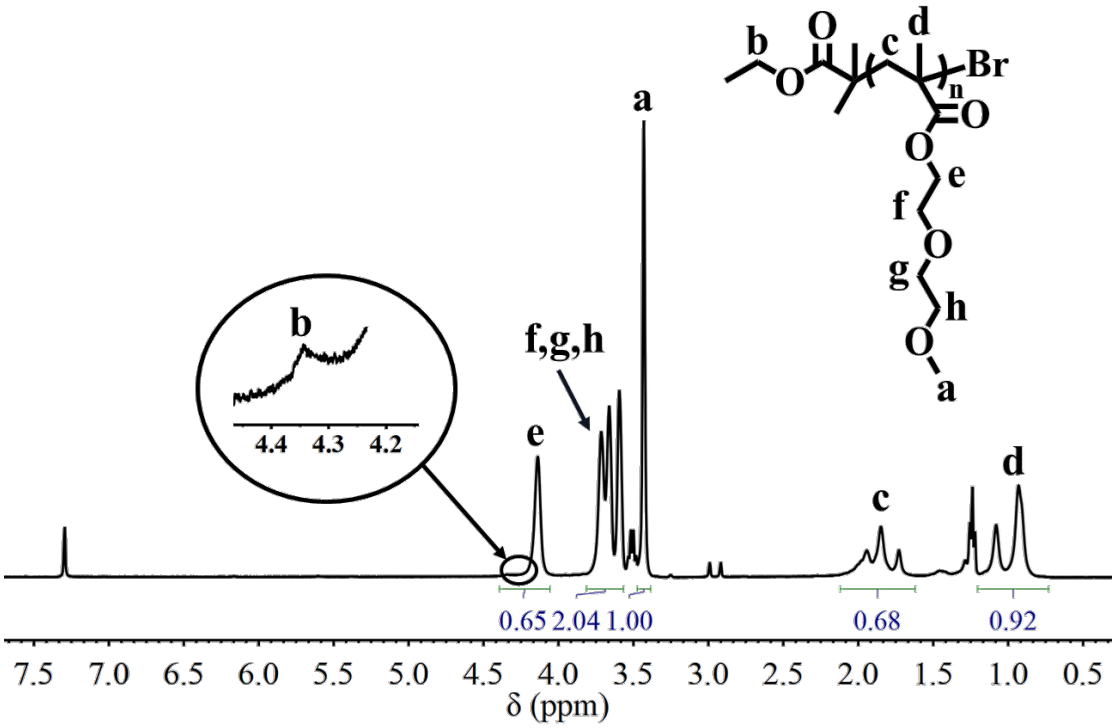

Figure S3. ^{1}H NMR spectrum of PDEGMA in $CDCl_3$.

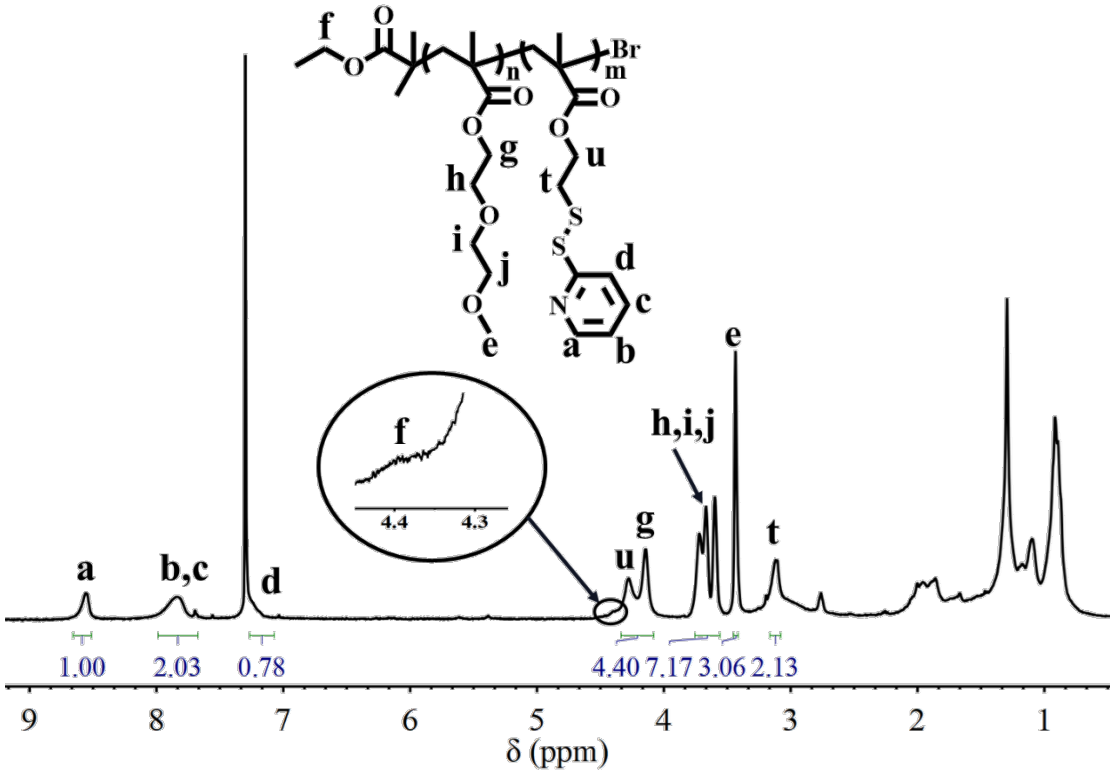

Figure S4. ^{1}H NMR spectrum of PDEGMA-*b*-PDSMA in $CDCl_3$.

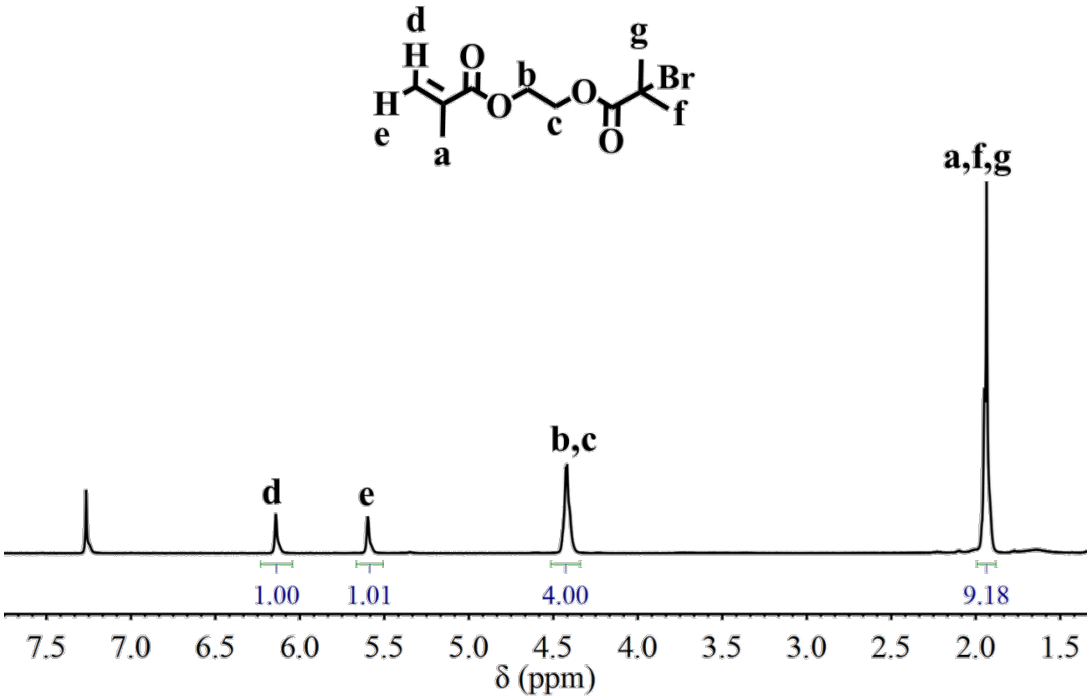

Figure S5. ^{1}H NMR spectrum of BMA in $CDCl_3$.

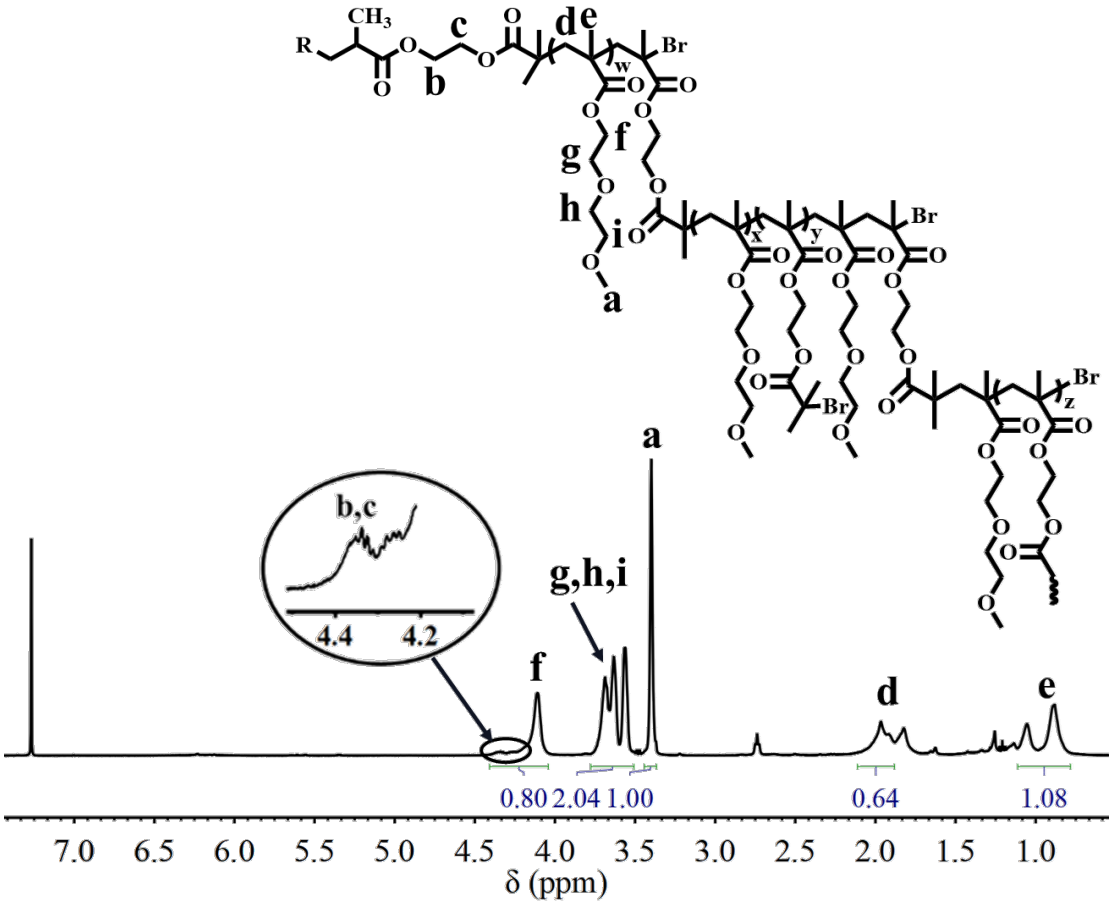

Figure S6. ^{1}H NMR spectrum of h_1PDEGMA in $CDCl_3$.

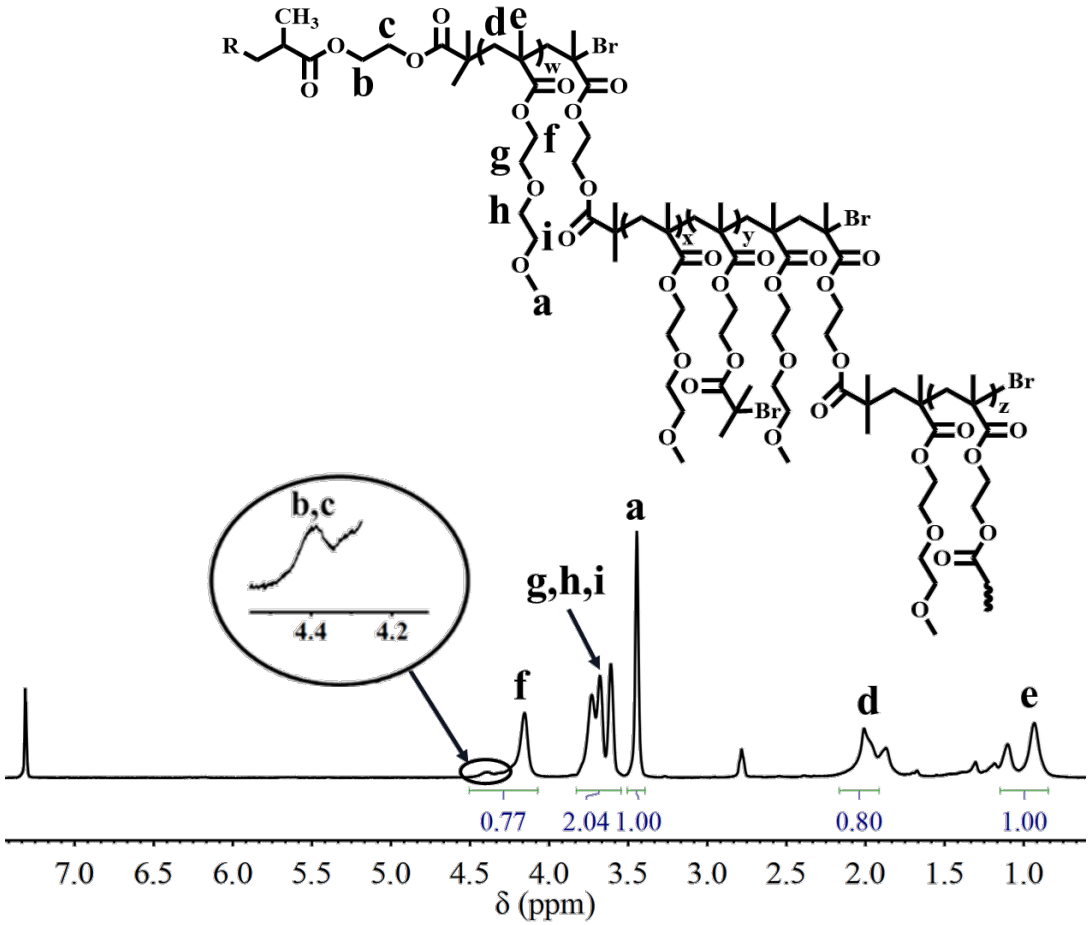

Figure S7. ^{1}H NMR spectrum of h_2PDEGMA in $CDCl_3$.

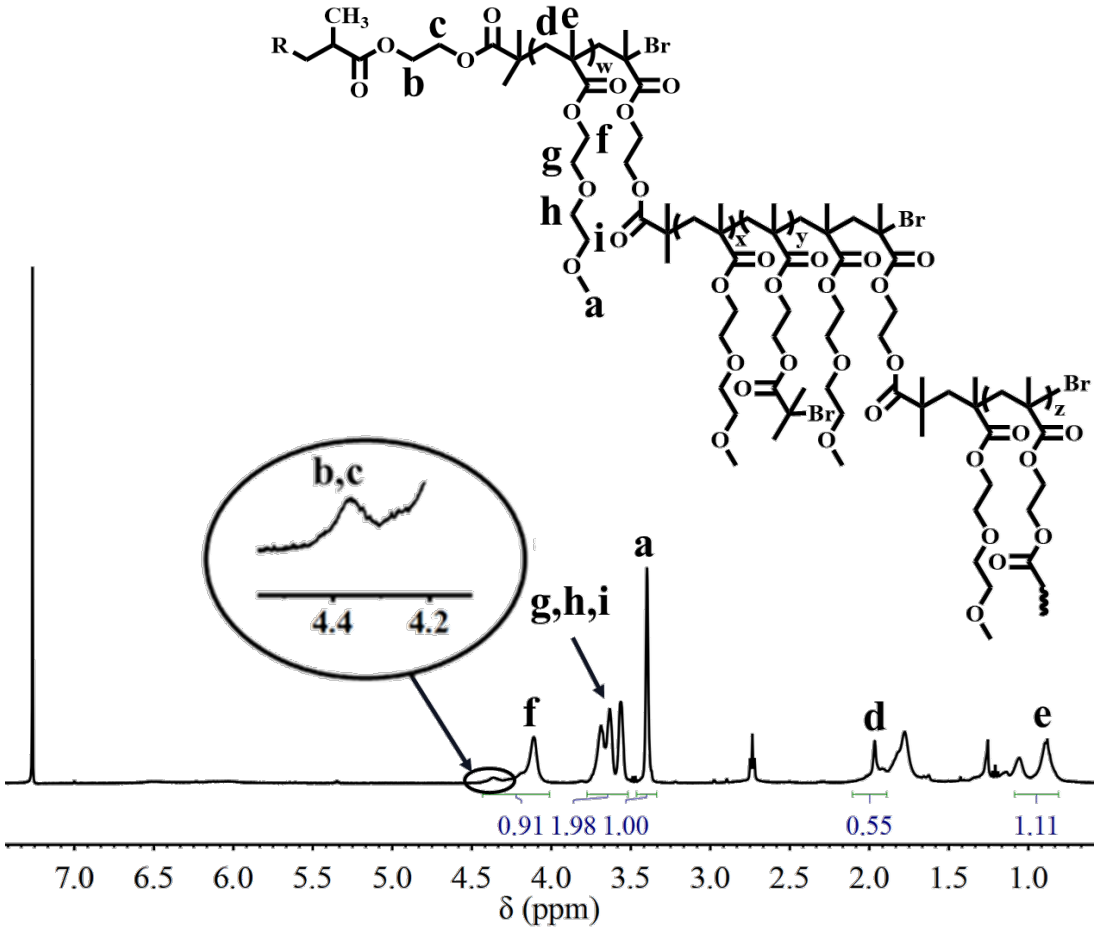

Figure S8. ^{1}H NMR spectrum of h_3PDEGMA in $CDCl_3$.

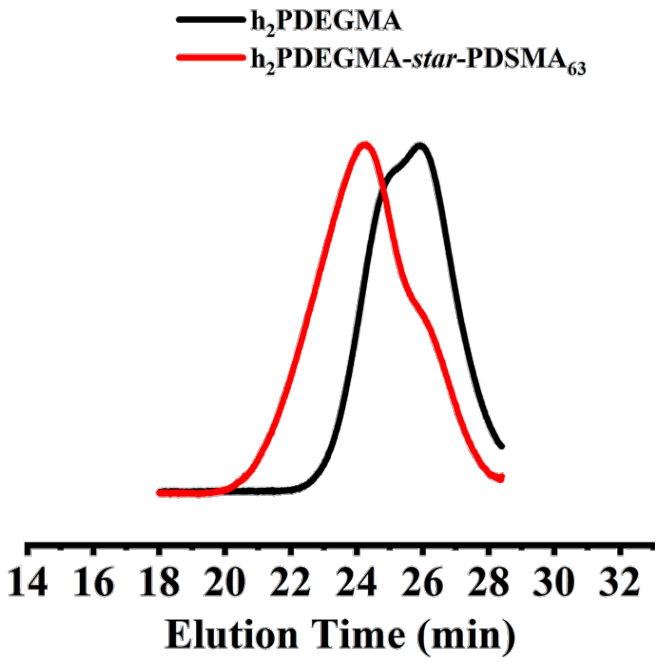

Figure S9. GPC curves of h_2PDEGMA (black line) and h_2PDEGMA-*star*-PDSMA$_{63}$ (red line).

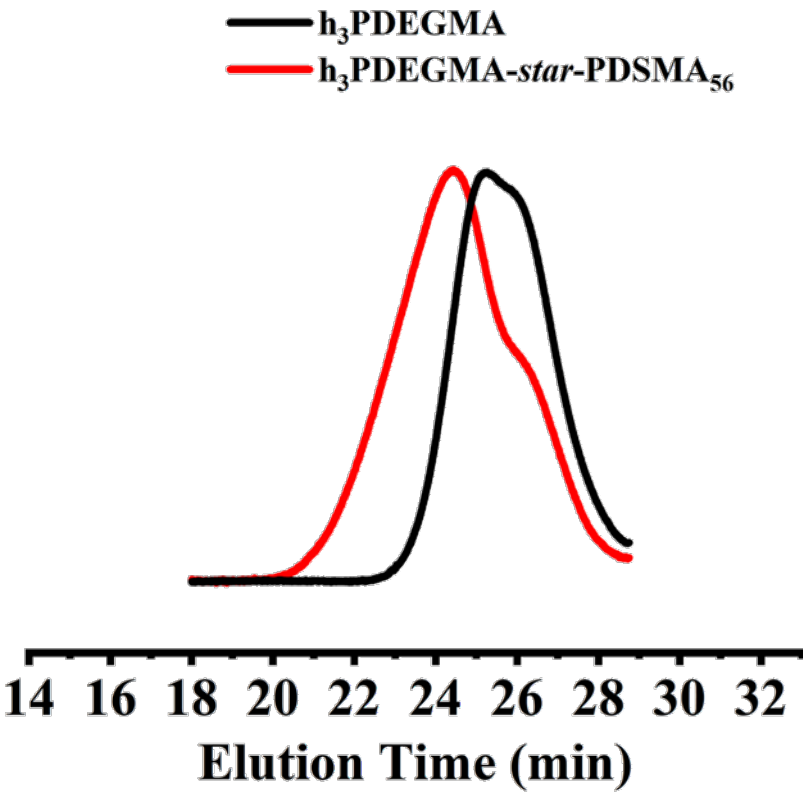

Figure S10. GPC curves of h_3PDEGMA (black line) and h_3PDEGMA-*star*-PDSMA$_{56}$ (red line).

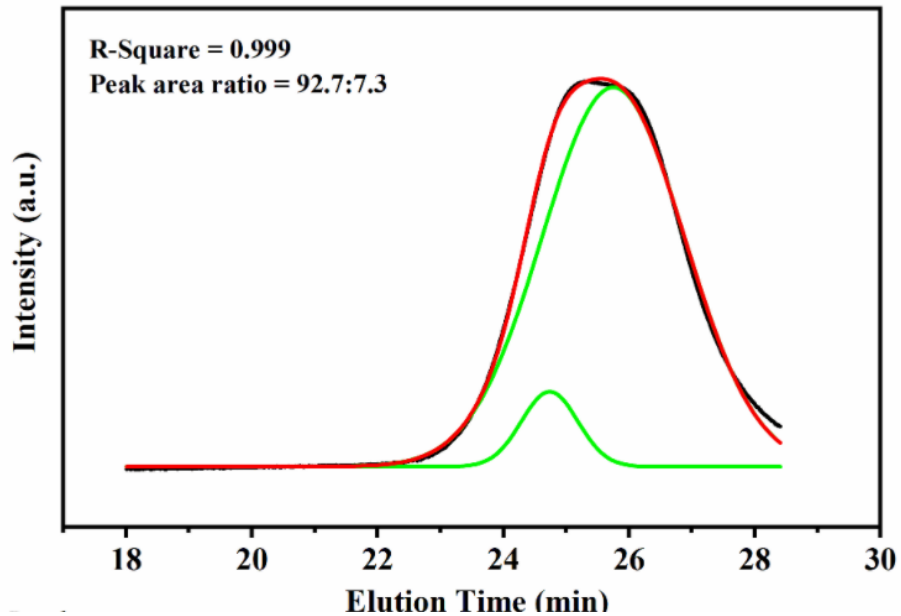

Figure S11. Fitting result of the GPC curve of h_1PDEGMA. The M_ns of the two peaks are 12.8 and 23.7 kDa.

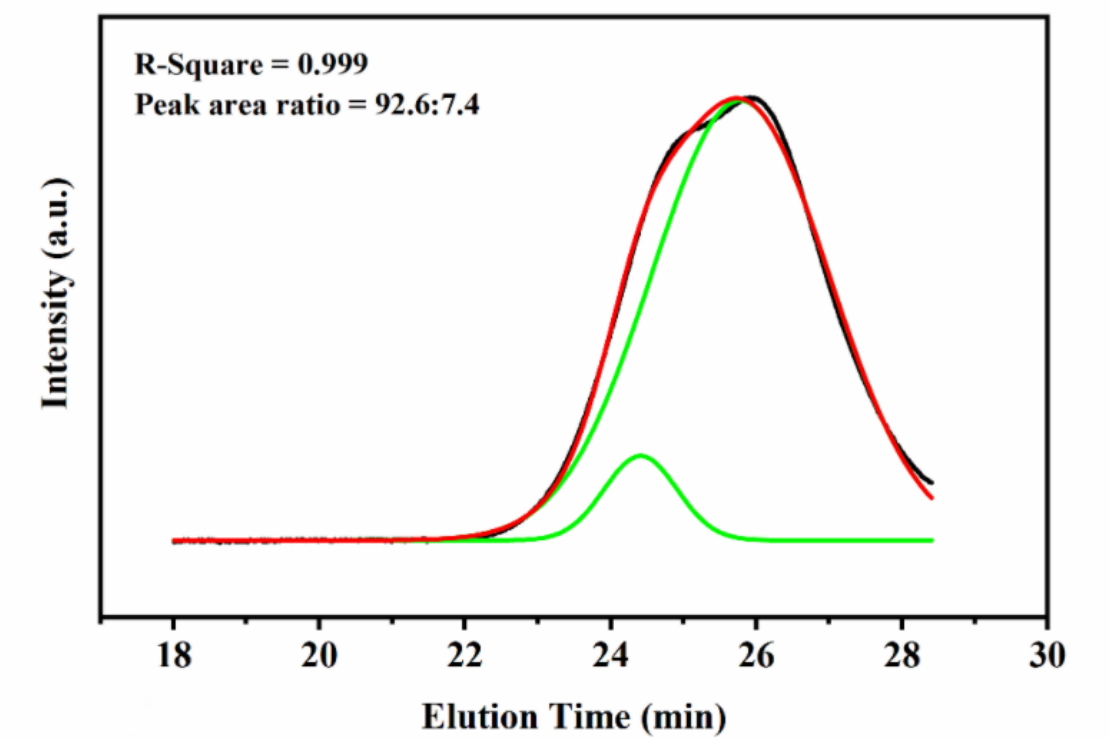

Figure S12. Fitting result of the GPC curve of h_2PDEGMA. The M_ns of the two peaks are 12.6 and 28.8 kDa.

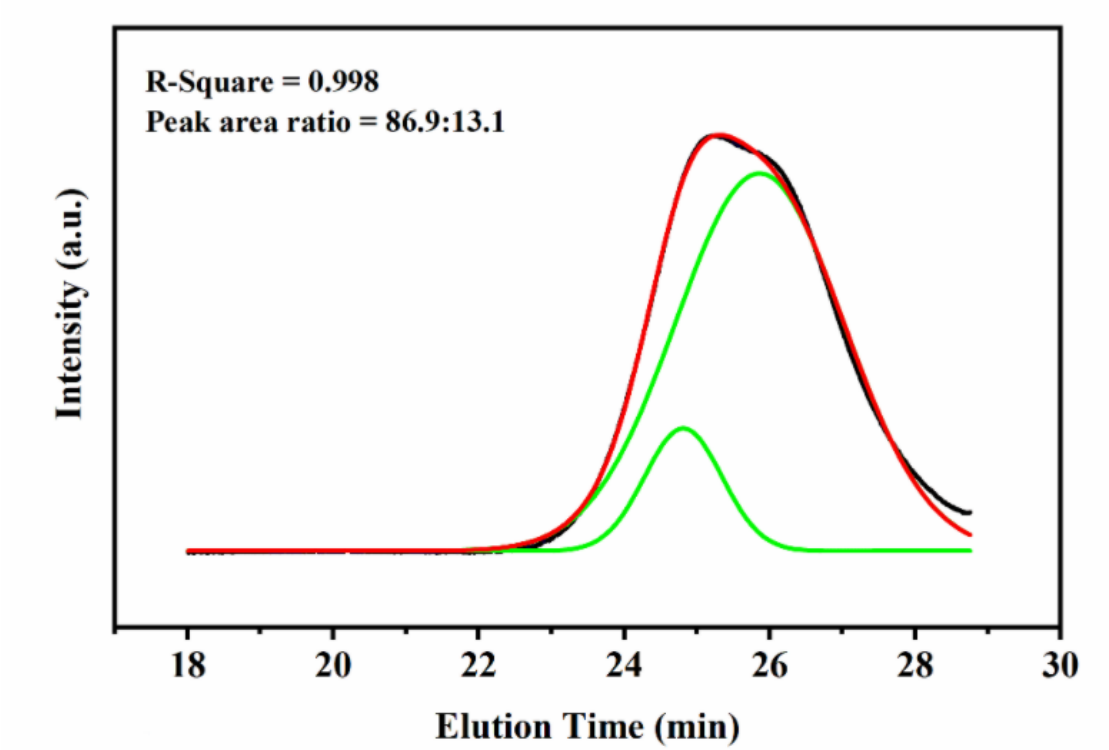

Figure S13. Fitting result of the GPC curve of h_3PDEGMA. The M_ns of the two peaks are 12.0 and 22.6 kDa.

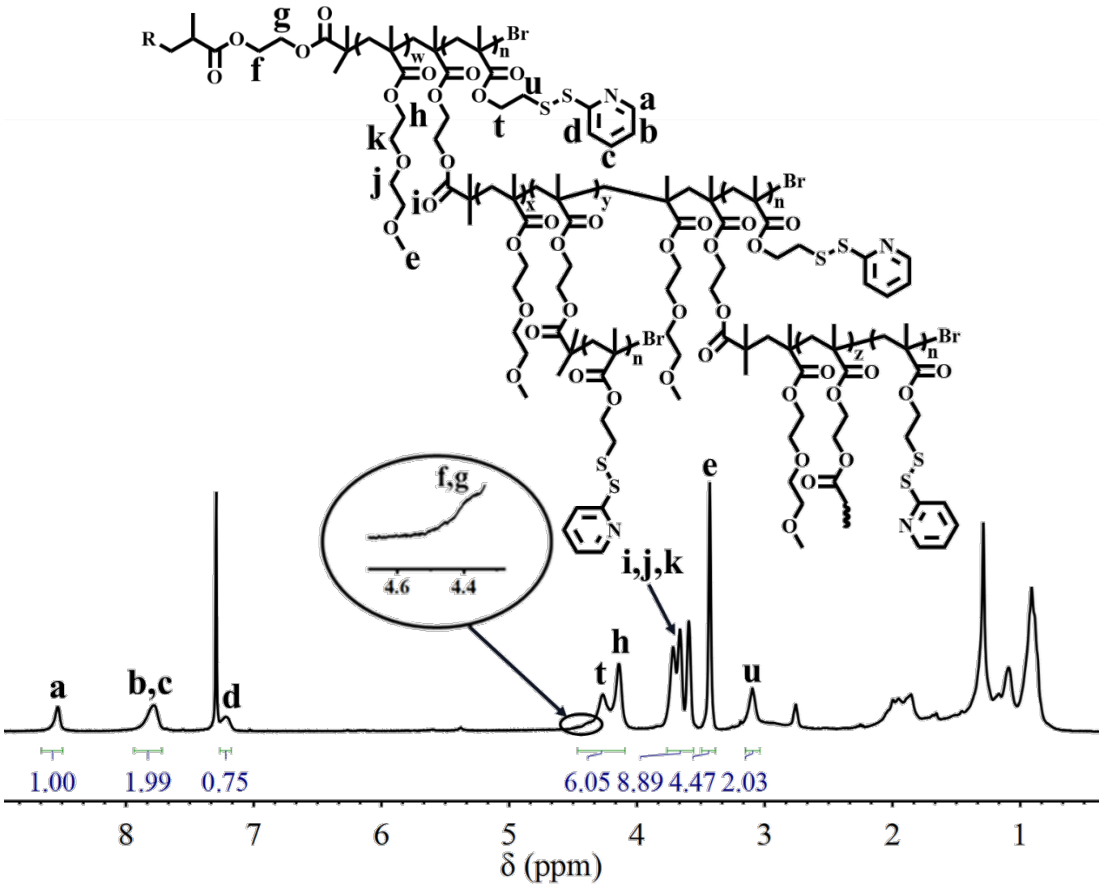

Figure S14. ^{1}H NMR spectrum of h_1PDEGMA-*star*-PDSMA$_{56}$ in $CDCl_3$.

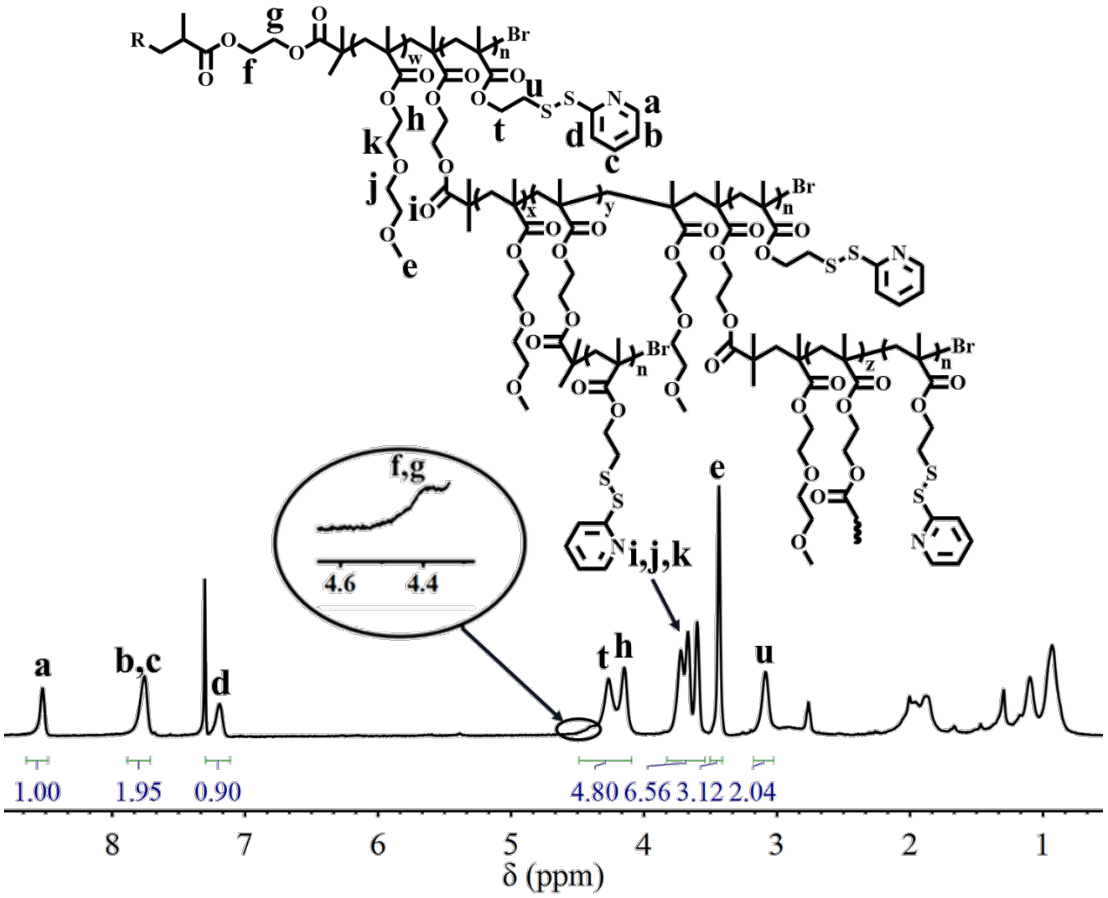

Figure S15. ^{1}H NMR spectrum of h_2PDEGMA-*star*-PDSMA$_{63}$ in $CDCl_3$.

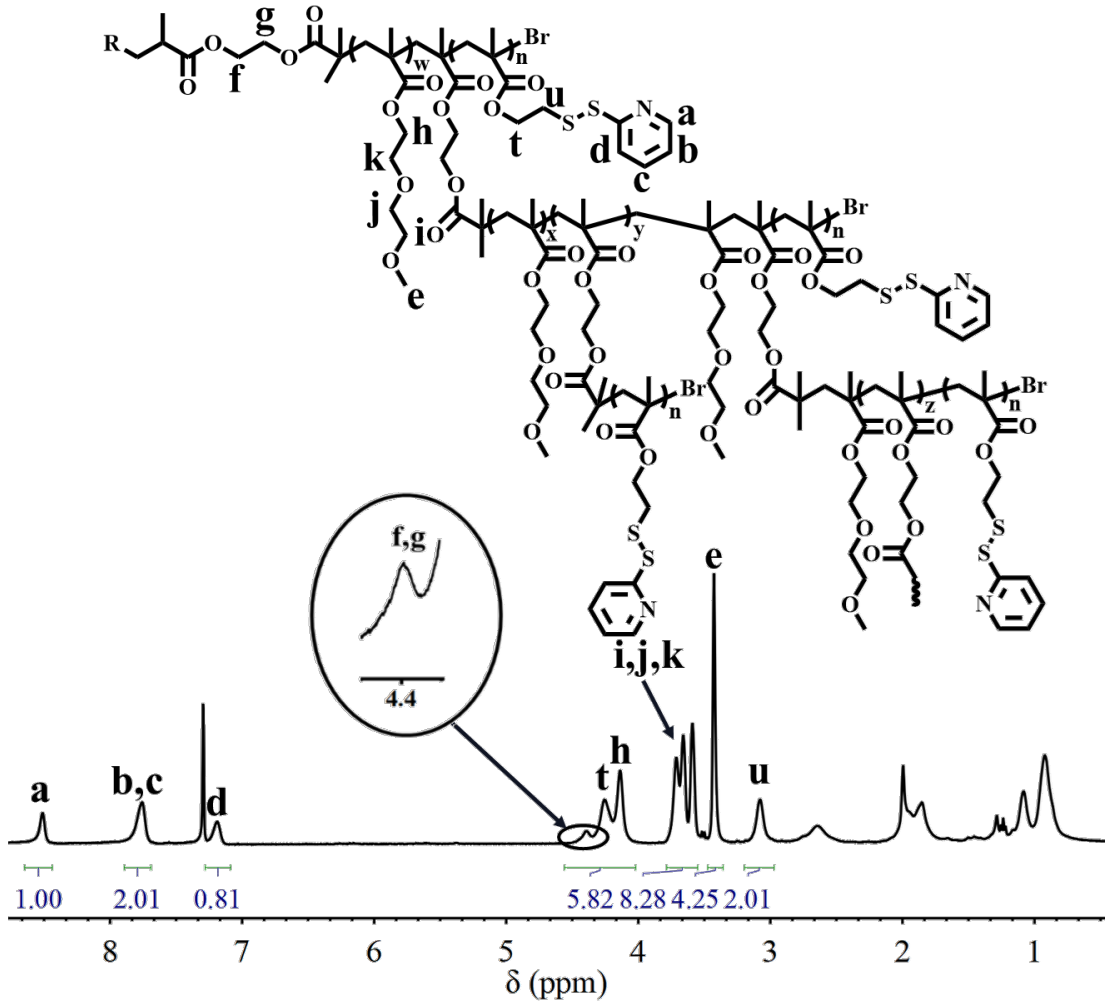

Figure S16. ^{1}H NMR spectrum of h_3PDEGMA-*star*-PDSMA$_{56}$ in $CDCl_3$.

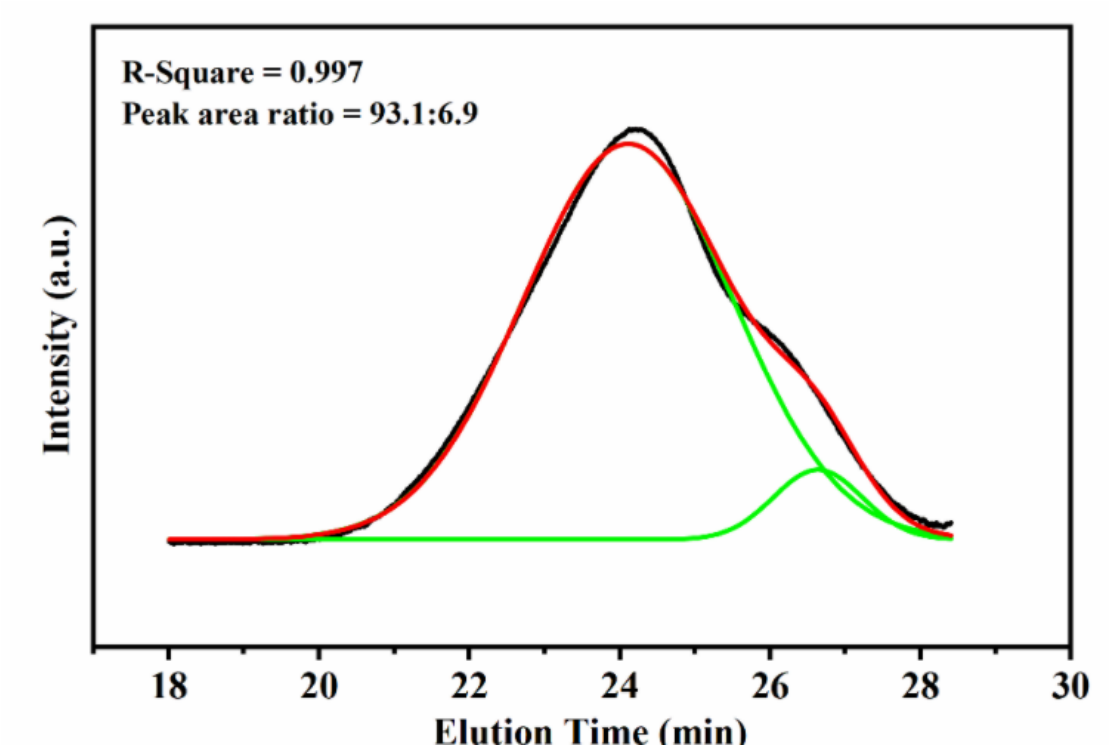

Figure S17. Fitting result of the GPC curve of h_1PDEGMA-*star*-PDSMA$_{56}$. The M_ns of the two peaks are 7.5 and 34.5 kDa.

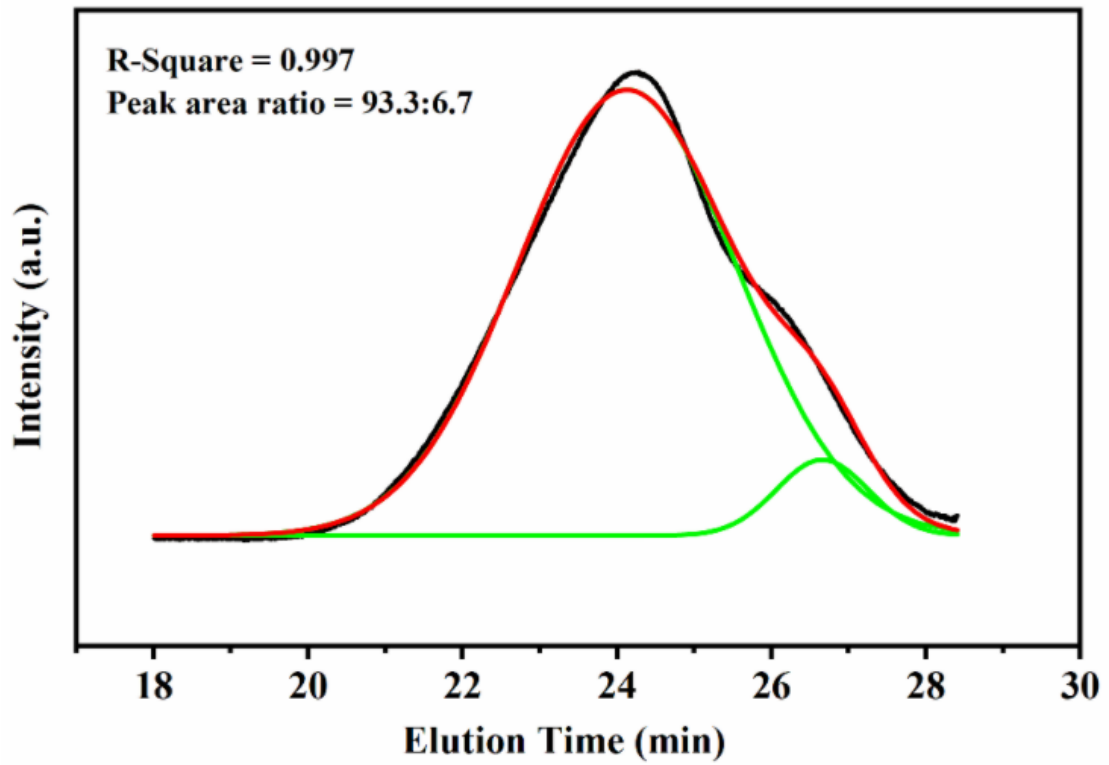

Figure S18. Fitting result of the GPC curve of h_2PDEGMA-*star*-PDSMA$_{63}$. The M_ns of the two peaks are 7.4 and 34.2 kDa.

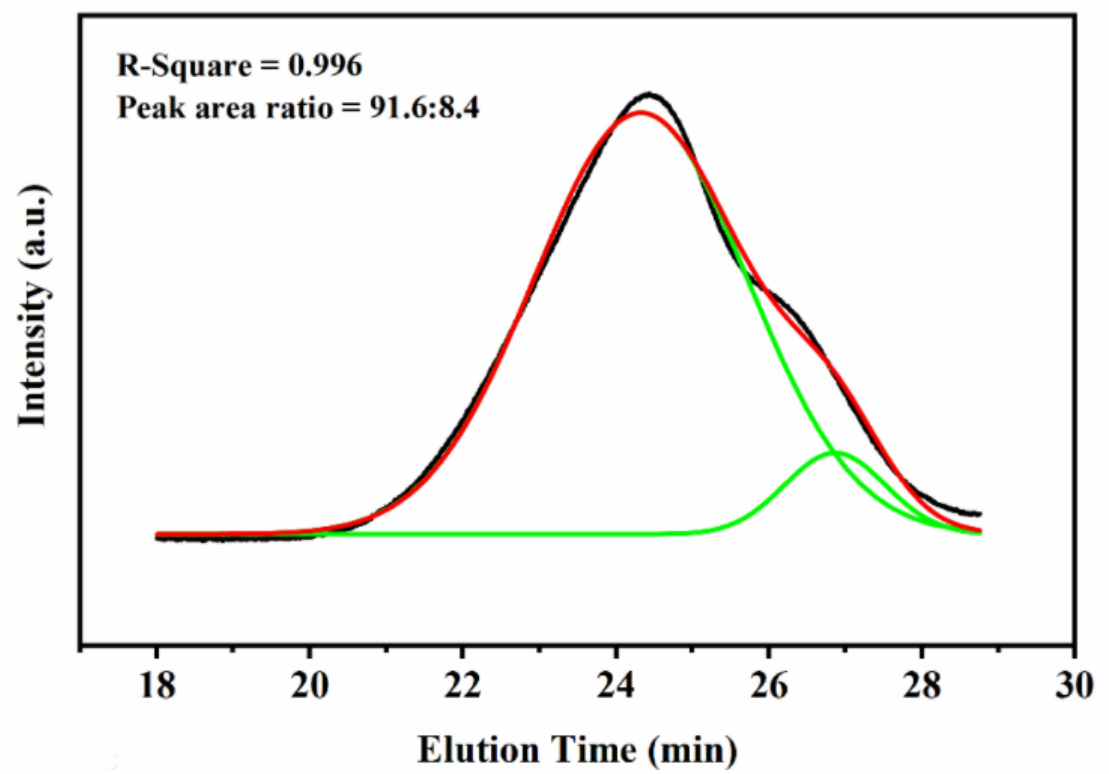

Figure S19. Fitting result of the GPC curve of h_3PDEGMA-*star*-PDSMA$_{56}$. The M_ns of the two peaks are 6.5 and 30.4 kDa.

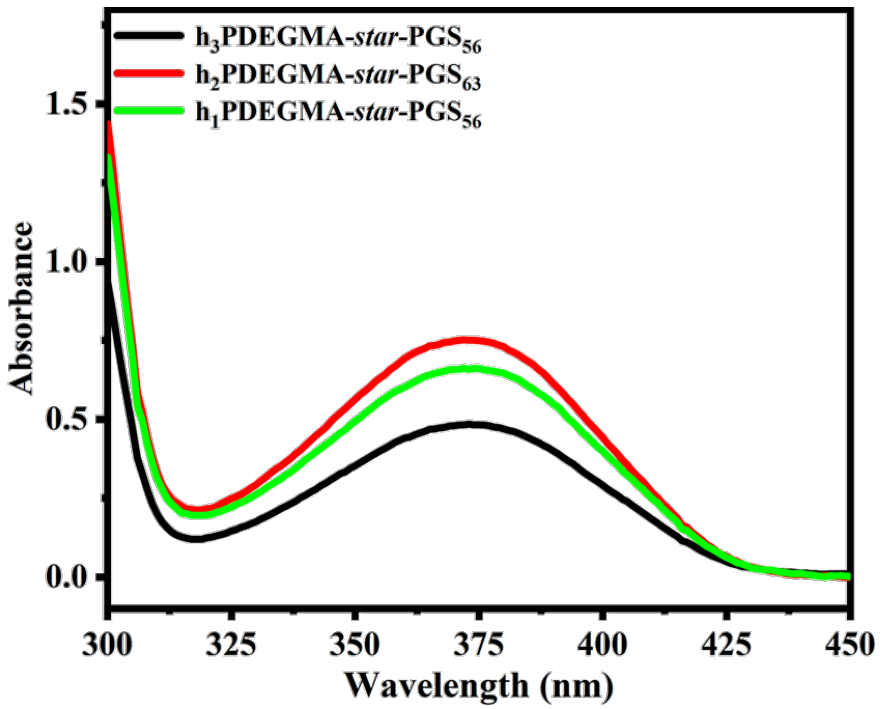

Figure S20. UV-vis absorbance spectra of 2-mercaptopyridine in water as a byproduct of h_1PDEGMA-*star*-PGS$_{56}$ (green line), h_2PDEGMA-*star*-PGS$_{63}$ (red line), and h_3PDEGMA-*star*-PGS$_{56}$ (black line).

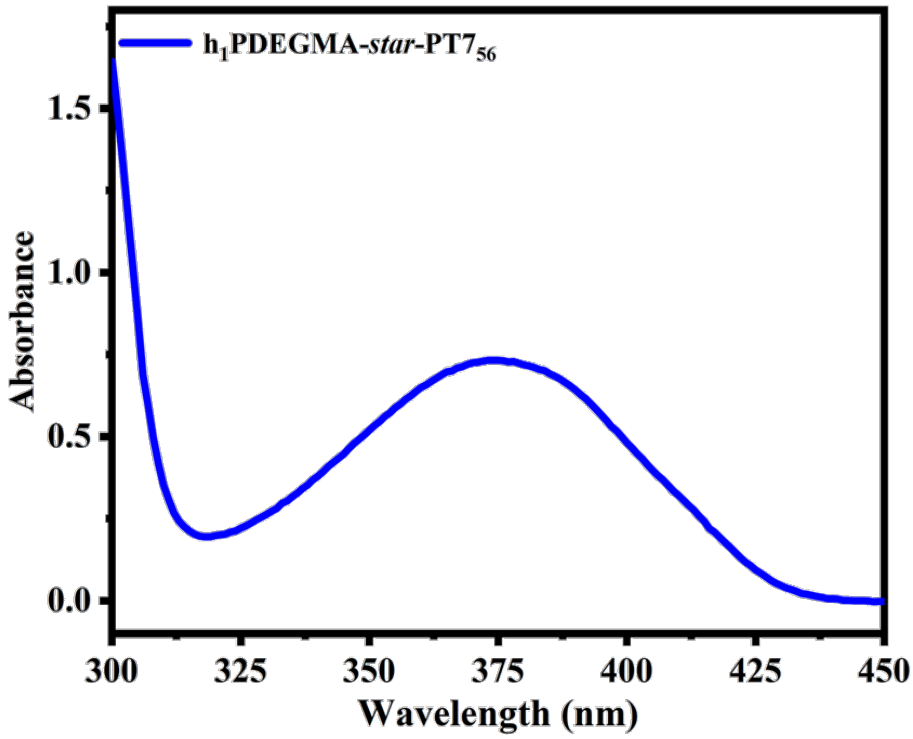

Figure S21. UV-vis absorbance spectrum of 2-mercaptopyridine in water as a byproduct of h_1PDEGMA-*star*-PT7_{56}.