

Electronic Supporting Information for:

**AIE-Active Miktoarm Star Polymer Nanoassemblies: Structure-
Dependent Self-assembly and Photoluminescence Behavior**

Xuehui Liu,^a Qian Li,^a Ranran Gao,^a Qu Wang,^a Li Wang,^{*a} and Wantai Yang^{*abc}

^a. State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

^b. Beijing Engineering Research Center for the Syntheses and Applications of Waterborne Polymers, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

^c. Beijing Advanced Innovation Centre for Soft Matter Science and Engineering, Beijing 100029, China.

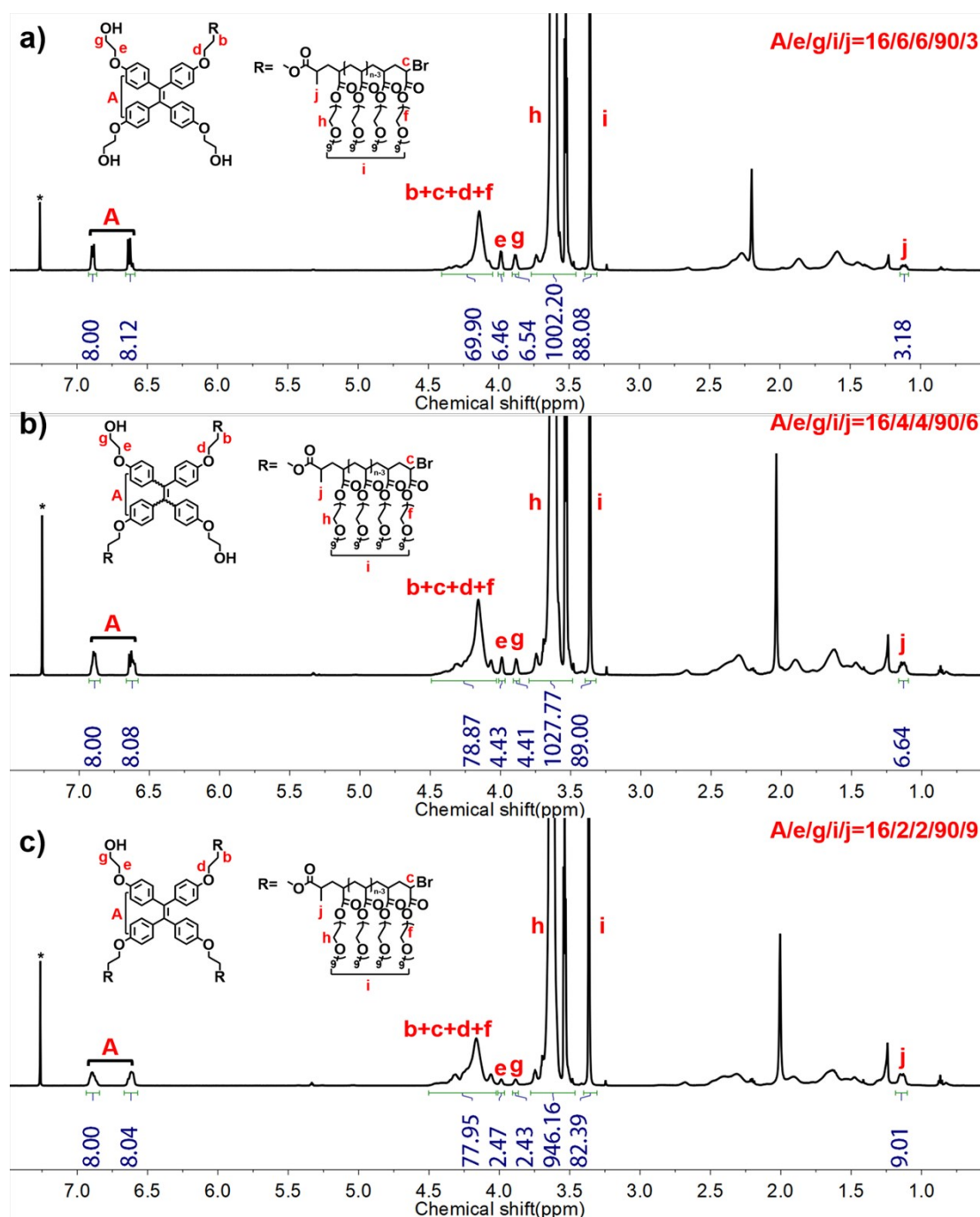


Fig. S1 ^1H NMR spectra of (a) TPE-POEGA₂₉-3OH, (b) TPE-(POEGA₁₅)₂-2OH, and (c) TPE-(POEGA₉)₃-1OH in CDCl_3 . ^1H NMR resonances from residual solvent in CDCl_3 are indicated by an asterisk (*). The ratios on the top right are theoretical values obtained assuming 100% conversion of OEGA and initiation efficiency $f = 1$.

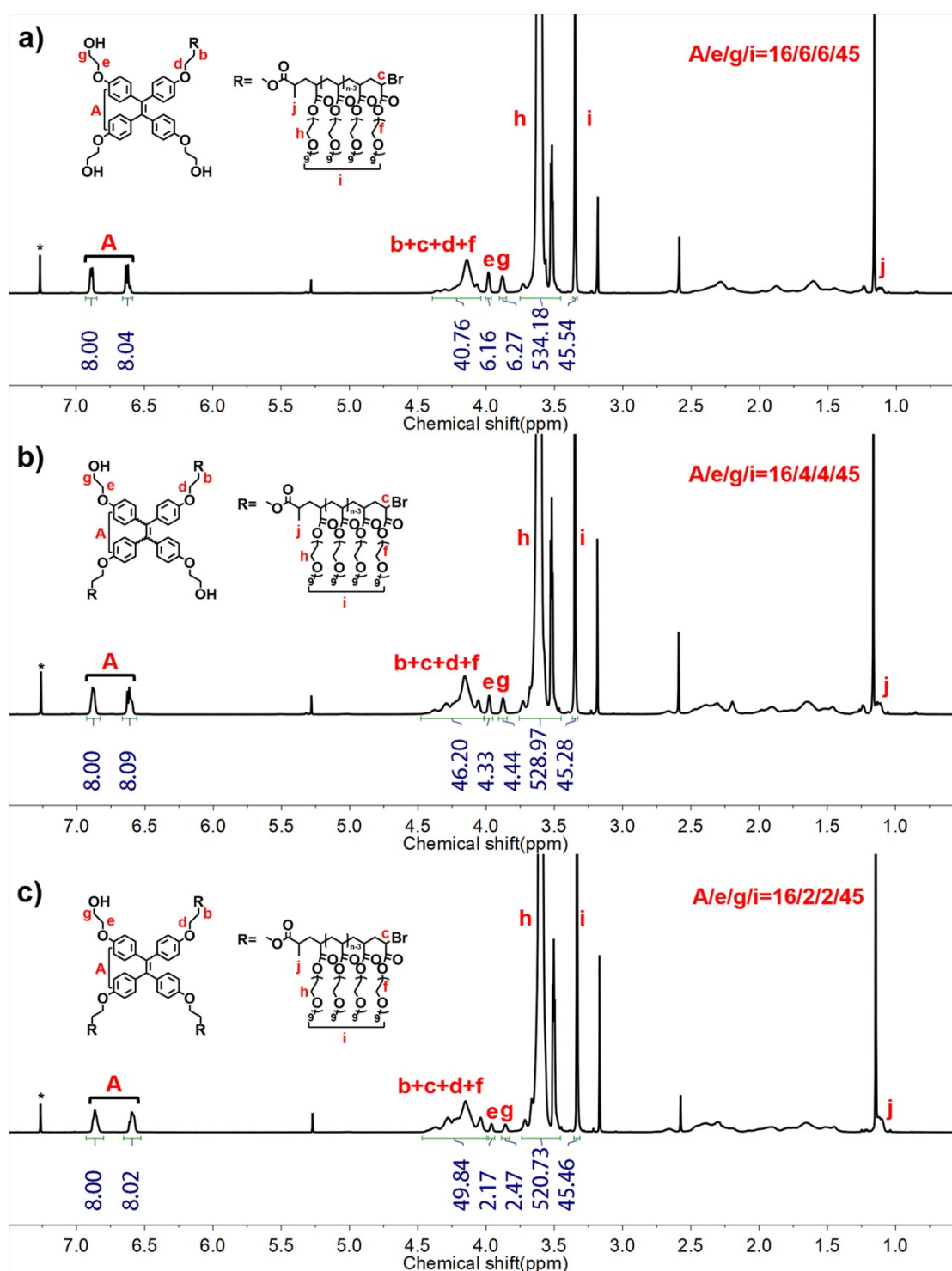


Fig. S2 ^1H NMR spectra of (a) TPE-POEGA₁₅-3OH, (b) TPE-(POEGA_{7.5})₂-2OH, and (c) TPE-(POEGA₅)₃-1OH in CDCl₃. ^1H NMR resonances from residual solvent in CDCl₃ are indicated by an asterisk (*). The ratios on the top right are theoretical values obtained assuming 100% conversion of OEGA and initiation efficiency $f = 1$.

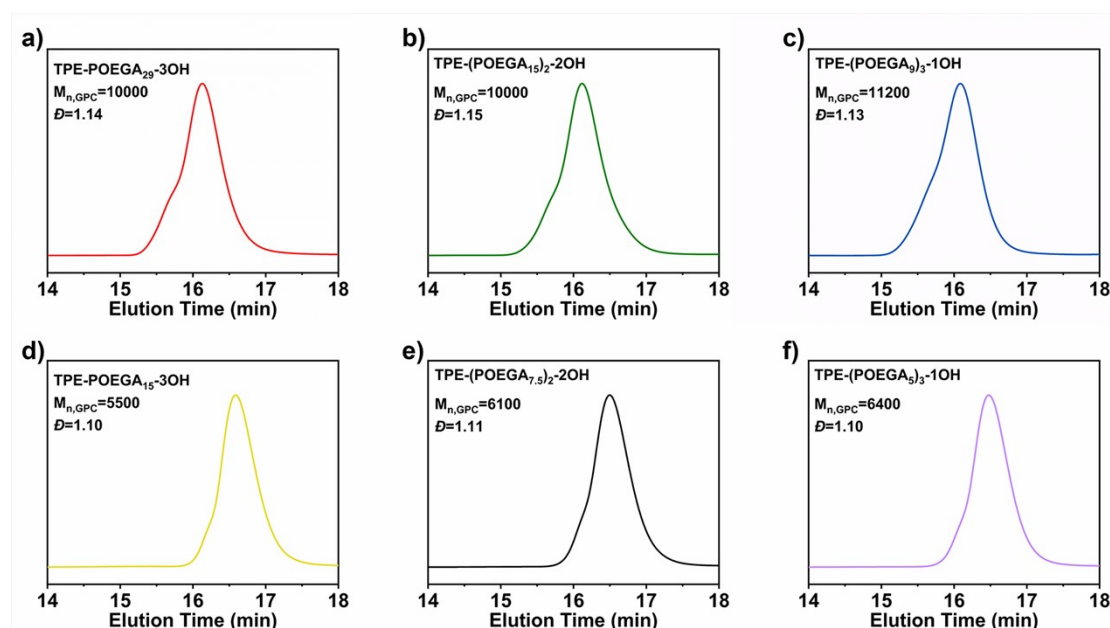


Fig. S3 GPC traces of (a) TPE-POEGA₂₉-3OH, (b) TPE-(POEGA₁₅)₂-2OH, (c) TPE-(POEGA₉)₃-1OH, (d) TPE-POEGA₁₅-3OH, (e) TPE-(POEGA_{7.5})₂-2OH, and (f) TPE-(POEGA₅)₃-1OH.

Table S1 Characterization results of TPE-(POEGA)_n-(4-n)CDPA (n = 1–3)

	DP ^a	M _{n,NMR} (g/mol) ^b	M _{n,GPC} (g/mol) ^c	Đ
TPE-POEGA ₂₉ -3CDPA	29	15800	13700	1.14
TPE-(POEGA ₁₅) ₂ -2CDPA	30	16000	12900	1.15
TPE-(POEGA ₉) ₃ -1CDPA	27	14300	12900	1.15
TPE-POEGA ₁₅ -3CDPA	15	9070	5900	1.10
TPE-(POEGA _{7.5}) ₂ -2CDPA	15	8810	6000	1.10
TPE-(POEGA ₅) ₃ -1CDPA	15	8570	6200	1.10

^a Theoretical DP of POEGA; ^b M_n calculated by ¹H NMR; ^c M_n measured by GPC.

Polymerization conditions: [TPE-(POEGA)_n-(4-n)OH]/[CDPA]/[DCC]/[DMAP] = 1/3/3/0.3, 40 °C, 48 h.

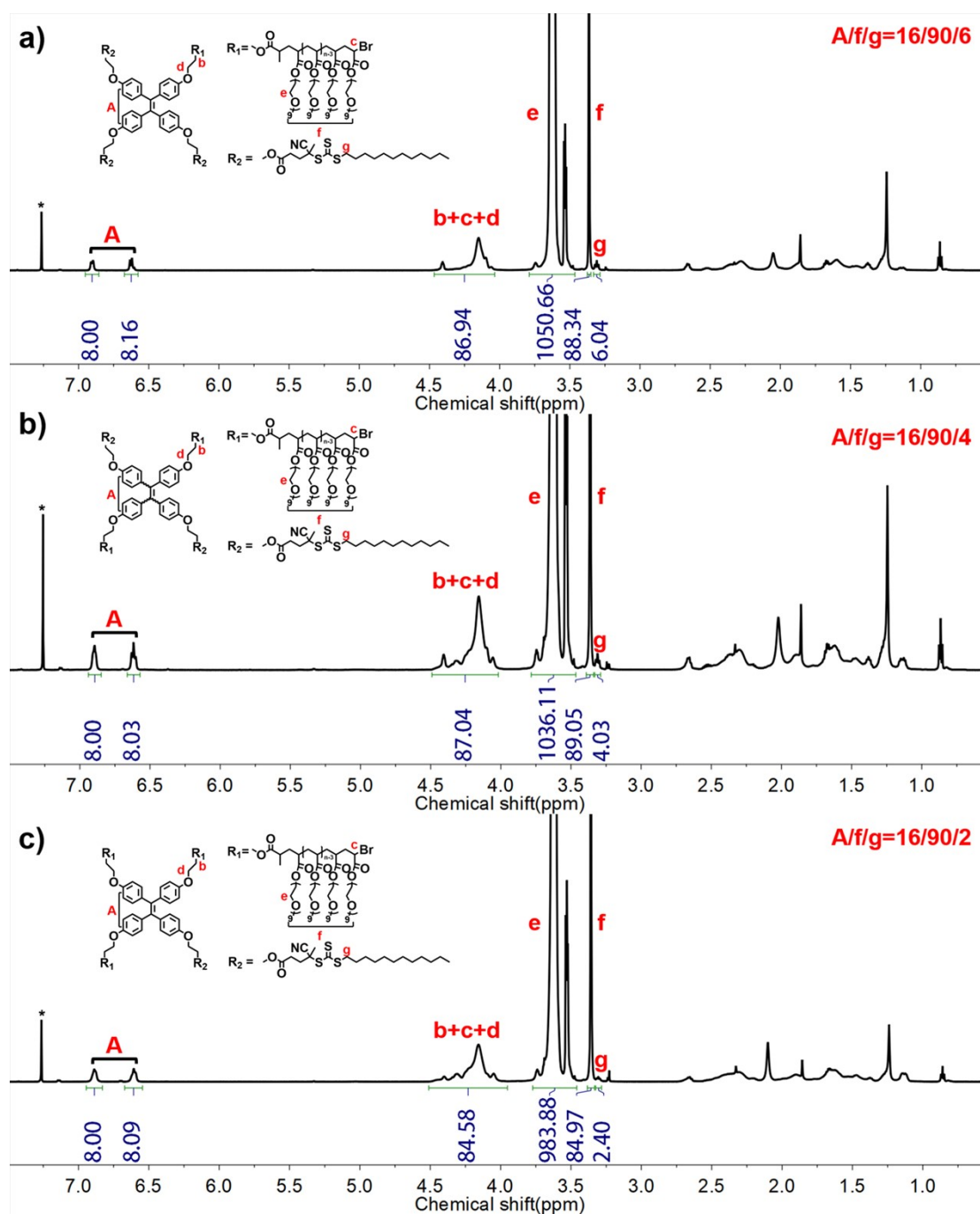


Fig. S4 ^1H NMR spectra of (a) TPE-POEGA₂₉-3CDPA, (b) TPE-(POEGA₁₅)₂-2CDPA, and (c) TPE-(POEGA₉)₃-1CDPA in CDCl_3 . ^1H NMR resonances from residual solvent in CDCl_3 are indicated by an asterisk (*).

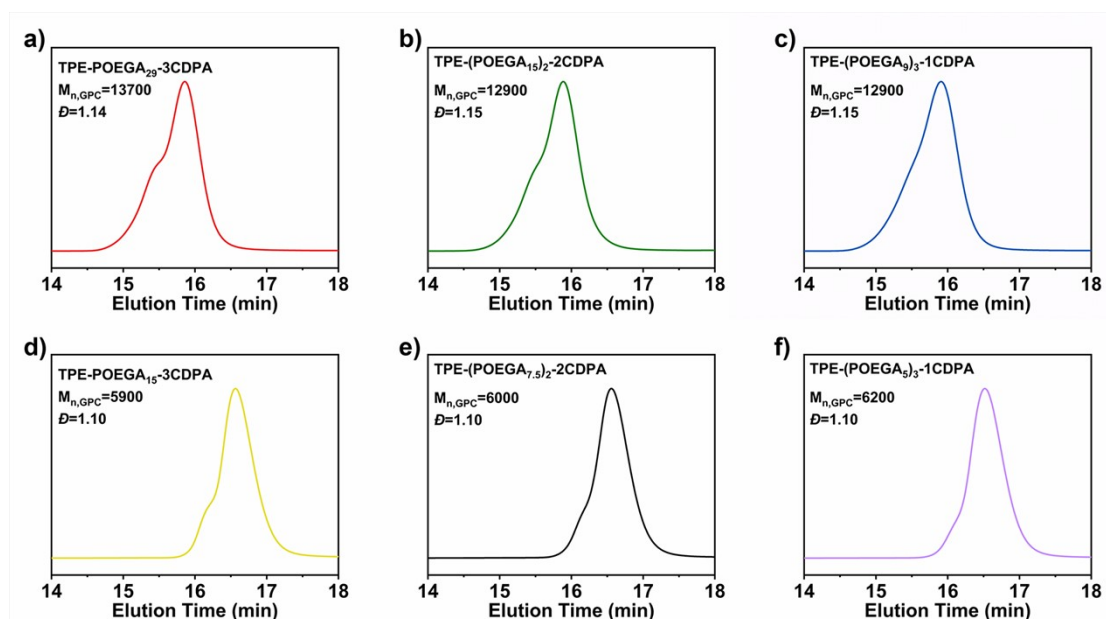


Fig. S5 GPC traces of (a) TPE-POEGA₂₉-3CDPA, (b) TPE-(POEGA₁₅)₂-2CDPA, (c) TPE-(POEGA₉)₃-1CDPA, (d) TPE-POEGA₁₅-3CDPA, (e) TPE-(POEGA_{7.5})₂-2CDPA, and (f) TPE-(POEGA₅)₃-1CDPA.

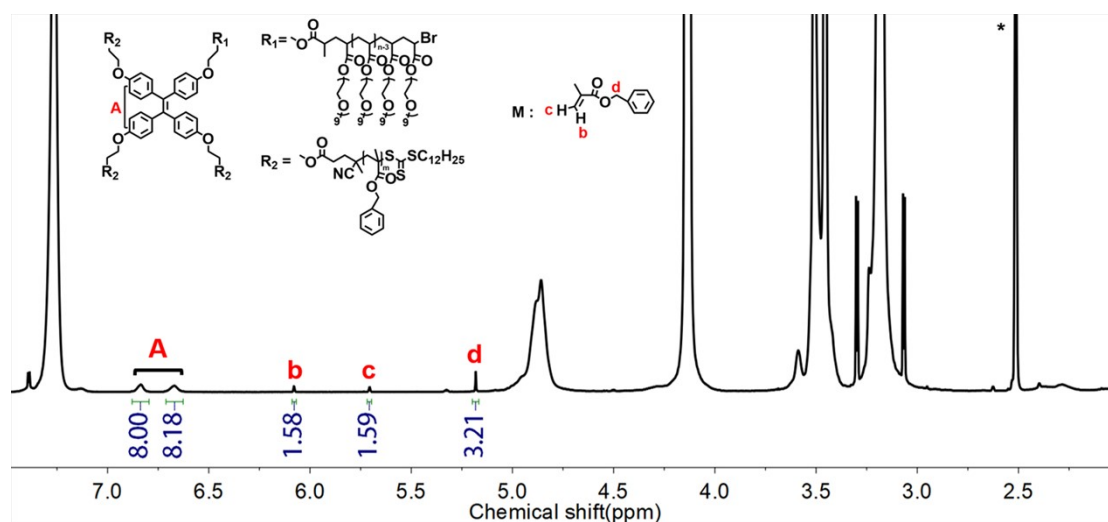


Fig. S6 ^1H NMR spectra for TPE-POEGA₁₅-3CDPA mediated RAFT dispersion polymerization of BzMA. ^1H NMR resonances from residual solvent in DMSO- d_6 are indicated by an asterisk (*).

$$\text{Conversion}\% = \frac{DP_{\text{design}} - S_b}{DP_{\text{design}}}$$

Equation S1. Calculation of conversion by ^1H NMR.

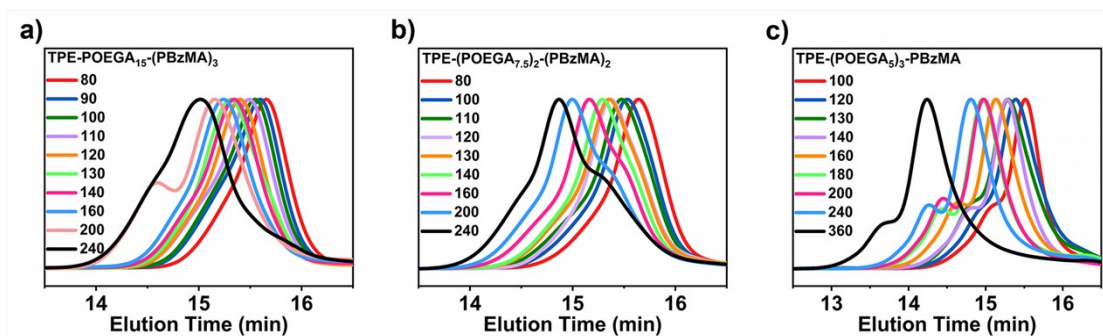


Fig. S7 GPC traces of TPE-(POEGA)_{*n*}-(PBzMA)_{4-*n*}.

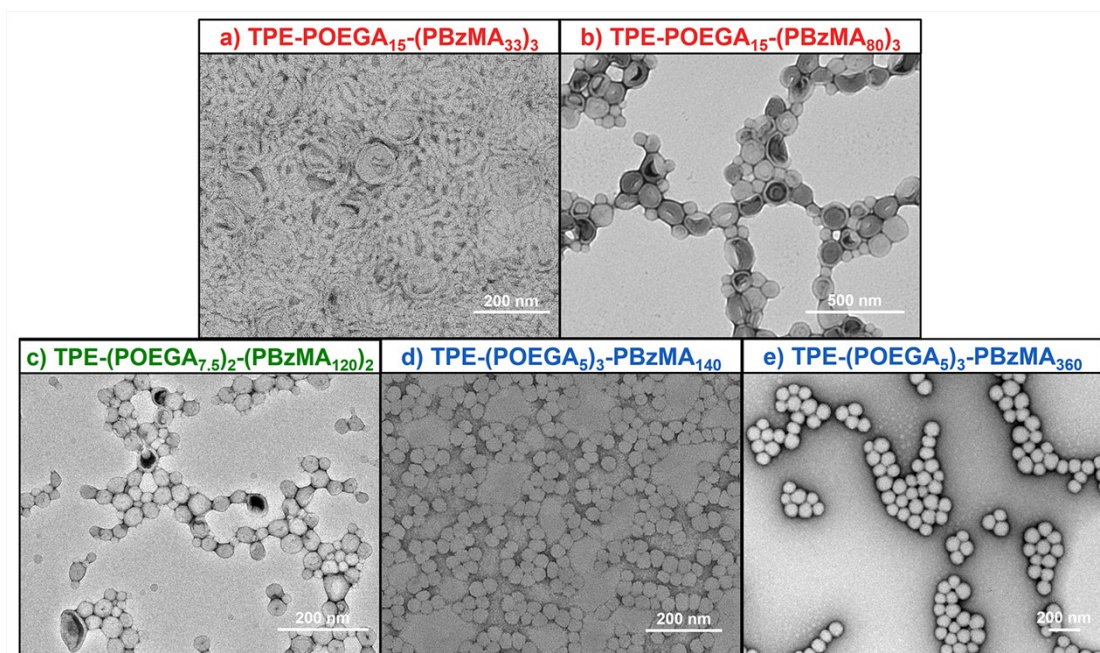


Fig. S8 TEM micrographs of (a, b) TPE-POEGA₁₅-(PBzMA)₃, (c) TPE-(POEGA_{7.5})₂-(PBzMA)₂, and (d, e) TPE-(POEGA₅)₃-PBzMA nanoassemblies with different DP of PBzMA.

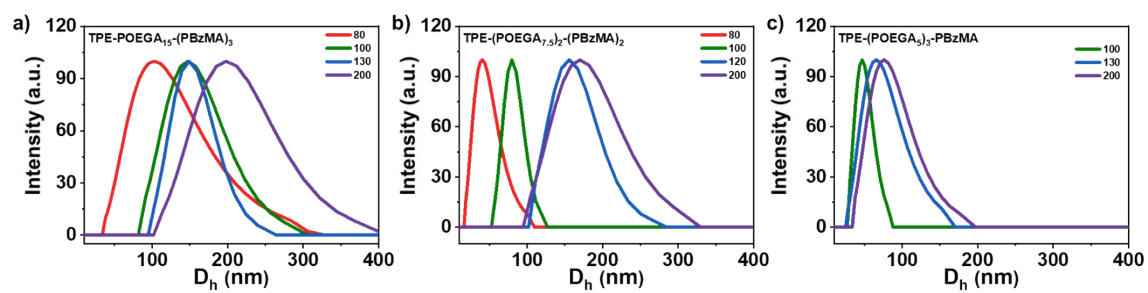


Fig. S9 Representative DLS traces of (a) TPE-POEGA₁₅-(PBzMA)₃, (b) TPE-(POEGA_{7.5})₂-(PBzMA)₂, and (c) TPE-(POEGA₅)₃-PBzMA nanoassemblies with different DP_{PBzMA} .

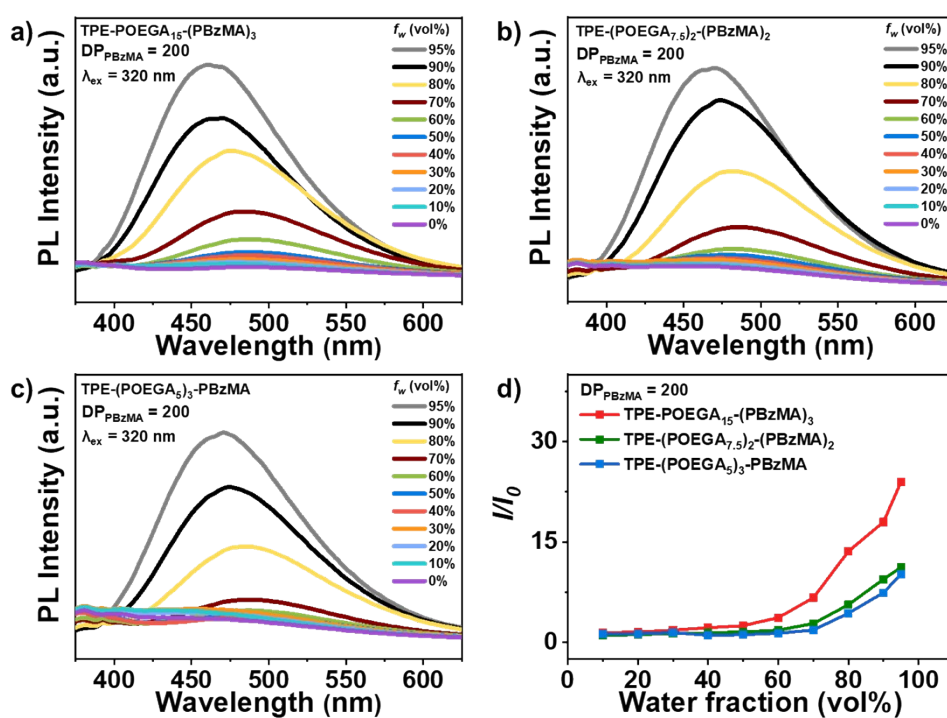


Fig. S10 Fluorescence spectra of (a) TPE-POEGA₁₅-(PBzMA)₆₆)₃, (b) TPE-(POEGA_{7.5})₂-(PBzMA₁₀₀)₂, and (c) TPE-(POEGA₅)₃-PBzMA₂₀₀ in THF/H₂O mixture with different volume fraction of H₂O. (d) Plots of I/I_0 versus the volume fraction of water (f_w). [TPE] = 20 μ M; excitation wavelength = 320 nm; I_0 : PL intensity of the polymer in pure THF.

Scheme S1 Schematic illustration of the three stereoisomers of TPE-(POEGA_{7.5})₂-(PBzMA)₂.

