SUPPORTING INFORMATION

Aggregation-Induced Emission Polymer Nanoparticles with pH-Responsive Fluorescence

Yuming Zhao,^{a,c} Wen Zhu,^a Lixia Ren,^b Ke Zhang*a

^a State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, The Chinese Academy of

Sciences, Beijing 100190, China.

^b School of Materials Science and Engineering, Tianjin University, No. 92 Weijin Road, Tianjin 300072, China.

^c University of Chinese Academy of Sciences, Beijing 100049, China.

Corresponding author: Fax: +86-010-62559373; E-mail: kzhang@iccas.ac.cn



Figure S1. ¹H-NMR spectra of M1 (A) and the corresponding raw poly(M1)₁₀ polymerization solution (B) in CDCl₃.



Figure S2. ¹H-NMR spectra of **M2** (A), **M3** (B), and the corresponding raw poly(**M1**)₁₀-*b*-poly(**M2**₁₀₀-*co*-**M3**₅) polymerization solution (C) in CDCl₃.



Figure S3. (A) GPC curves of poly(M1)₁₀ (black) and poly(M1)₁₀-*b*-poly(M2₈₀-*co*-M3₄) (red), in which THF was used as the eluent and PS standards were used for the calibration. (B) ¹H-NMR spectra of poly(M1)₁₀-*b*-poly(M2₈₀-*co*-M3₄) in CDCl₃.



Figure S4. (A) GPC curves of poly(M1)₁₀ (black) and poly(M1)₁₀-*b*-poly(M2₅₀-*co*-M3_{2.5}) (red), in which THF was used as the eluent and PS standards were used for the calibration. (B) ¹H-NMR spectra of poly(M1)₁₀-*b*-poly(M2₅₀-*co*-M3_{2.5}) in CDCl₃.



Figure S5. TEM images of crosslinked PNPs from $poly(M1)_{10}-b-poly(M2_{50}-co-M3_{2.5})$ (A), $poly(M1)_{10}-b-poly(M2_{80}-co-M3_4)$ (B), and $poly(M1)_{10}-b-poly(M2_{100}-co-M3_5)$ (C) dispersed in THF/H₂O (v/v = 85/15).



Figure S6. DLS characterization of the PNPs in THF before (black) and after (red) cross-linking from $poly(M1)_{10}-b-poly(M2_{50}-co-M3_{2.5})$ (A), $poly(M1)_{10}-b-poly(M2_{80}-co-M3_4)$ (B), and $poly(M1)_{10}-b-poly(M2_{100}-co-M3_5)$ (C).



Figure S7. (A) FT-IR spectra of $poly(M1)_{10}$ -*b*- $poly(M2_{50}$ -*co*- $M3_{2.5}$) (black) and the resultant spherical micelles post-functionalized by DEDA (red) and Ala (blue). (B) FT-IR spectra of $poly(M1)_{10}$ -*b*- $poly(M2_{80}$ -*co*- $M3_4$) (black) and the resultant cylindrical micelles post-functionalized by DEDA (red) and Ala (blue).



Figure S8. TEM images of post-functionalized PNPs stored in water after two months: DEDA post-functionalized PNPs from $poly(M1)_{10}$ -*b*- $poly(M2_{50}$ -*co*- $M3_{2.5})$ (A), $poly(M1)_{10}$ -*b*- $poly(M2_{80}$ -*co*- $M3_4)$ (B), and $poly(M1)_{10}$ -*b*- $poly(M2_{100}$ -*co*- $M3_5)$ (C); Ala post-functionalized PNPs from $poly(M1)_{10}$ -*b*- $poly(M2_{50}$ -*co*- $M3_{2.5})$ (D), $poly(M1)_{10}$ -*b*- $poly(M2_{80}$ -*co*- $M3_4)$ (E), and $poly(M1)_{10}$ -*b*- $poly(M2_{100}$ -*co*- $M3_5)$ (F).



Figure S9. Fluorescence spectra of DEDA post-functionalized spherical micelles from $poly(M1)_{10}$ -*b*- $poly(M2_{50}$ -*co*- $M3_{2.5})$ in water with a concentration of 20 mg/L at varied pH from 2 to 11 (A) and the corresponding fluorescence intensity ratio (I/I₀) at the given pH values, in which the fluorescence intensity at pH = 2 was chosen as I₀ (B). Fluorescence spectra of Ala post-functionalized spherical micelles from $poly(M1)_{10}$ -*b*- $poly(M2_{50}$ -*co*- $M3_{2.5})$ in water with a concentration of 20 mg/L at varied pH from 2 to 11 (C) and the corresponding fluorescence intensity ratio (I/I₀) at the given pH values, in which the fluorescence intensity at pH = 11 was chosen as I₀ (D). The inserted pictures in (B) and (D) were taken from the UV (365 nm) irradiated vesicle aqueous solutions at pH = 2 and pH = 11.



Figure S10. (A) Fluorescence spectra of DEDA post-functionalized cylindrical micelles from poly(M1)₁₀-*b*-poly($M2_{80}$ -*co*- $M3_4$) in water with a concentration of 20 mg/L at varied pH from 2 to 11 (A) and the corresponding fluorescence intensity ratio (I/I₀) at the given pH values, in which the fluorescence intensity at pH = 2 was chosen as I₀ (B). Fluorescence spectra of Ala post-functionalized cylindrical micelles from poly(M1)₁₀-*b*-poly($M2_{80}$ -*co*- $M3_4$) in water with a concentration of 20 mg/L at varied pH from 2 to 11 (C) and the corresponding fluorescence intensity ratio (I/I₀) at the given pH values, in which the fluorescence intensity at pH = 11 was chosen as I₀ (D). The inserted pictures in (B) and (D) were taken from the UV (365 nm) irradiated vesicle aqueous solutions at pH = 2 and pH = 11.



Figure S11. Fluorescence spectra of self-assemblies from $poly(M1)_{10}$ -b- $poly(M2_{50}$ -co- $M3_{2.5})$ (A), $poly(M1)_{10}$ -b- $poly(M2_{80}$ -co- $M3_4)$ (B), and $poly(M1)_{10}$ -b- $poly(M2_{100}$ -co- $M3_5)$ (C) in water before (black) and after (red) UV irradiation for 30 min.



Figure S12. Fluorescence spectra of the post-functionalized vesicles from $poly(M1)_{10}$ -b- $poly(M2_{100}$ -co- $M3_5)$ in water before (black) and after (red) UV irradiation for 30 min: Ala post-functionalized vesicles at pH = 7 (A) and pH = 2 (B), DEDA post-functionalized vesicles at pH = 7 (C) and pH = 11 (D).