## Supporting Information

# Crosslinking Induced Self-organization of Polymers into Degradable Assemblies 

Conghui Yuan $\digamma^{*}$, Bihong Hong $\nleftarrow$, Ying Chang $\nleftarrow$, Jie Mao $\%$, Yang Li $\%$, Yiting<br><br>$\dagger$ College of Materials, Xiamen University, Xiamen, 361005, China<br>$\ddagger$ Fujian Provincial Key Laboratory of Fire Retardant Materials, College of Materials,<br>Xiamen University, Xiamen, 361005, China<br>§ INSA de Lyon, IMP, Villeurbanne F-69621, France<br>Corresponding author E-mail address:<br>*Conghui Yuan, E-mail: yuanch@xmu.edu.cn; *Lizong Dai, E-mail: lzdai@xmu.edu.cn




Scheme S1. Synthetic procedures of BP and CP.


Figure S1. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{P}(\mathrm{APMA}-c o-\mathrm{MAPEG})$ in $\mathrm{CDCl}_{3}$.


Figure $\mathrm{S} 2 .{ }^{1} \mathrm{H}$ NMR spectrum of BP in methanol- $\mathrm{D}_{4}$.


Figure S3. ${ }^{1} \mathrm{H}$ NMR spectrum of CP in methanol- $\mathrm{D}_{4}$.


Figure S4. FT-IR (a) and UV-vis spectra (b) of BP, CP and BP-CP assemblies. The absorption peaks were tentatively assigned to the corresponding groups as shown in (b).


Figure S5. SEM image of bundle-like assemblies redispersed in water solution (a) and the corresponding EDX line scan analyses (b).


Figure S6. TEM images of bundle-like assemblies (a) formed in dichloromethane with a concentration of BP+CP $2.0 \mathrm{mg} / \mathrm{mL}$, and spherical assemblies (b) formed in a mixed solvent (the volume ratio of methanol to water is $1: 1$ ) with $2.0 \mathrm{mg} / \mathrm{mL} \mathrm{BP}+\mathrm{CP}$.


Figure S7. UV-vis spectrum evolution of bundle-like assemblies at $\mathrm{pH}=7.4$ without D-glucose. Bundle-like assemblies were prepared by using $0.2 \mathrm{mg} / \mathrm{mL}$ of BP and CP .


Figure S8. UV-vis spectrum evolution of bundle-like assemblies under different stimuli: (a) $\mathrm{pH}=5.0$, (b) $\mathrm{pH}=6.0$ with 0.1 mM of D-glucose, (c) $\mathrm{pH}=6.0$ with 0.6 mM of D-glucose. Bundle-like assemblies were prepared by using $0.2 \mathrm{mg} / \mathrm{mL}$ of BP and CP.


Figure S9. UV-vis spectrum evolution of spherical assemblies under different stimuli: (a) $\mathrm{pH}=6.0$, (b) $\mathrm{pH}=5.0$, (c) $\mathrm{pH}=6.0$ with 0.1 mM of D -glucose and (d) $\mathrm{pH}=5.0$ with 0.6 mM of D-glucose. Spherical assemblies were prepared by using $0.2 \mathrm{mg} / \mathrm{mL}$ of BP and CP .


Figure S10. TEM images of bundle-like assemblies after staying in a solution with 0.1 mM of D -glucose at $\mathrm{pH}=5.0$ for 2.0 h (a) and 8.0 h (b). Bundle-like assemblies were prepared by using $0.2 \mathrm{mg} / \mathrm{mL}$ of BP and CP .


Figure S11. Fluorescence spectrum evolution of DiI encapsulated in bundle-like assemblies in a solution at $\mathrm{pH}=7.4$ without D-glucose (a). Fluorescence spectra trace the release of DiI from bundle-like assemblies in response to different stimuli: (b) $\mathrm{pH}=5.0$, (c) $\mathrm{pH}=6.0$ with 0.1 mM of D -glucose, (d) $\mathrm{pH}=6.0$ with 0.6 mM of D-glucose. Bundle-like assemblies were prepared by using $0.2 \mathrm{mg} / \mathrm{mL}$ of BP and CP.


Figure S12. Fluorescence spectra trace the release of DiI from spherical assemblies in response to different stimuli: (a) $\mathrm{pH}=6.0$, (b) $\mathrm{pH}=5.0$, (c) $\mathrm{pH}=6.0$ with 0.1 mM of D-glucose, (d) $\mathrm{pH}=5.0$ with 0.1 mM of D-glucose. Spherical assemblies were prepared by using $0.2 \mathrm{mg} / \mathrm{mL}$ of BP and CP .


Figure S13. Stability of spherical and bundle-like assemblies against dilution: (a) in water solution with $\mathrm{pH}=7.4$, (b) in PBS solution with $\mathrm{pH}=7.4$. Both spherical and bundle assemblies were prepared by using $0.2 \mathrm{mg} / \mathrm{mL} \mathrm{BP}+\mathrm{CP}$. Therefore, in this measurement, samples before dilution, diluted 2 times and diluted 20 times represented assembly concentration of $0.2,0.1$ and $0.01 \mathrm{mg} / \mathrm{mL}$, respectively. The DLS tests were conducted 24 h after dilution.


Figure S14. CLSM images of Hela cells incubated with spherical assemblies prepared by using $0.2 \mathrm{mg} / \mathrm{mL}$ of BP and CP . For each panel, the images from left to right show cell nuclei stained with 2-(4-amidinophenyl)-6-indolecarbamidine dihydrochloride (DAPI, blue), DiI loaded BP-CP assemblies (red) in cells, and overlays of the two images.

