

Supporting Information

Polymer nanoparticles self-assembled from photo-, pH- and thermo-responsive azobenzene-functionalized PDMAEMA

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1. The GPC profile of PDMAEMA.

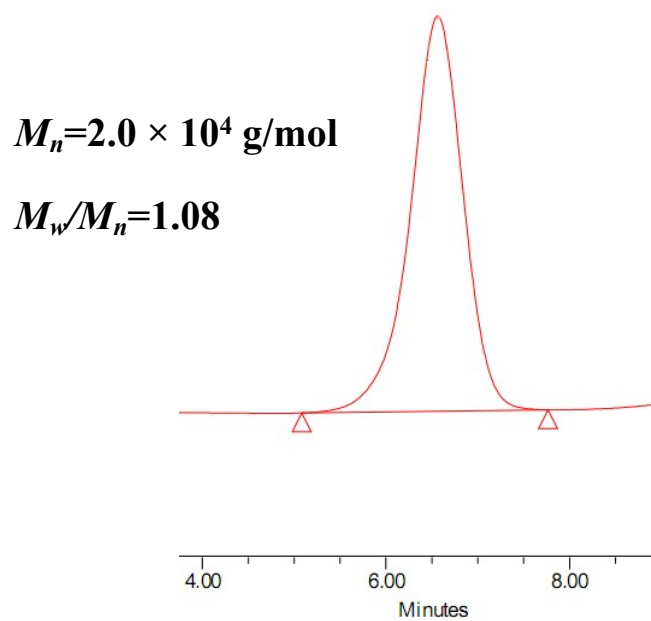


Figure S1. GPC profile of the synthesized polymer PDMAEMA.

2. ^1H NMR spectrum of the polymer with DF of 17% in CDCl_3 .

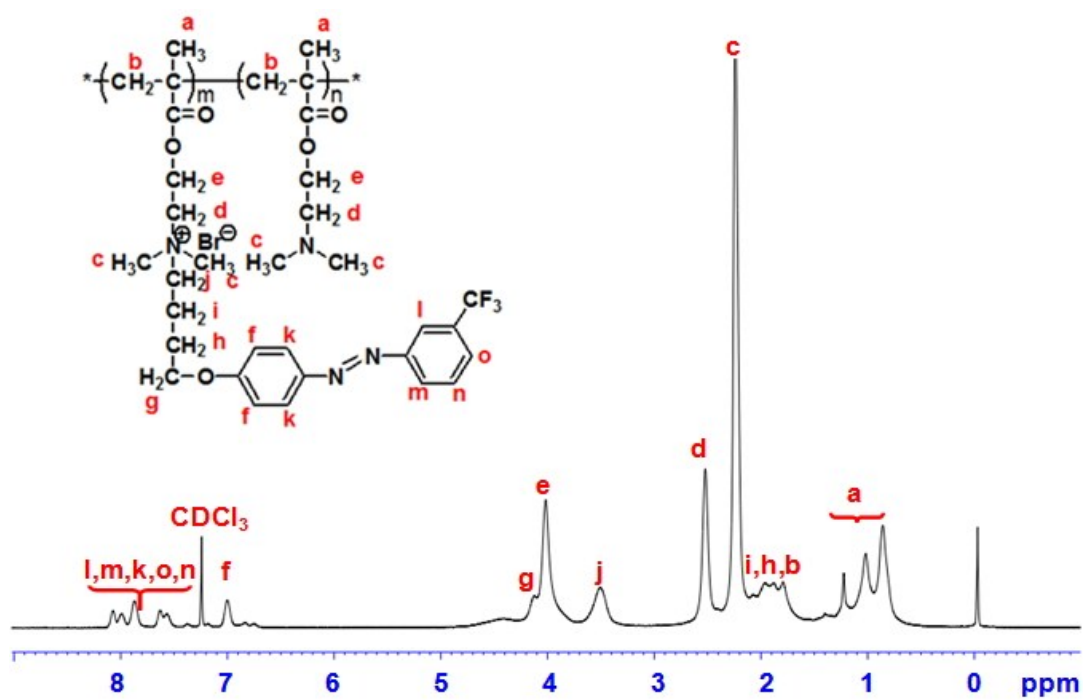


Figure S2. ^1H NMR spectrum of PDMAEMA-AZO with DF of 17% in CDCl_3 .

3. FTIR spectra of PDMAEMA and PDMAEMA-AZO.

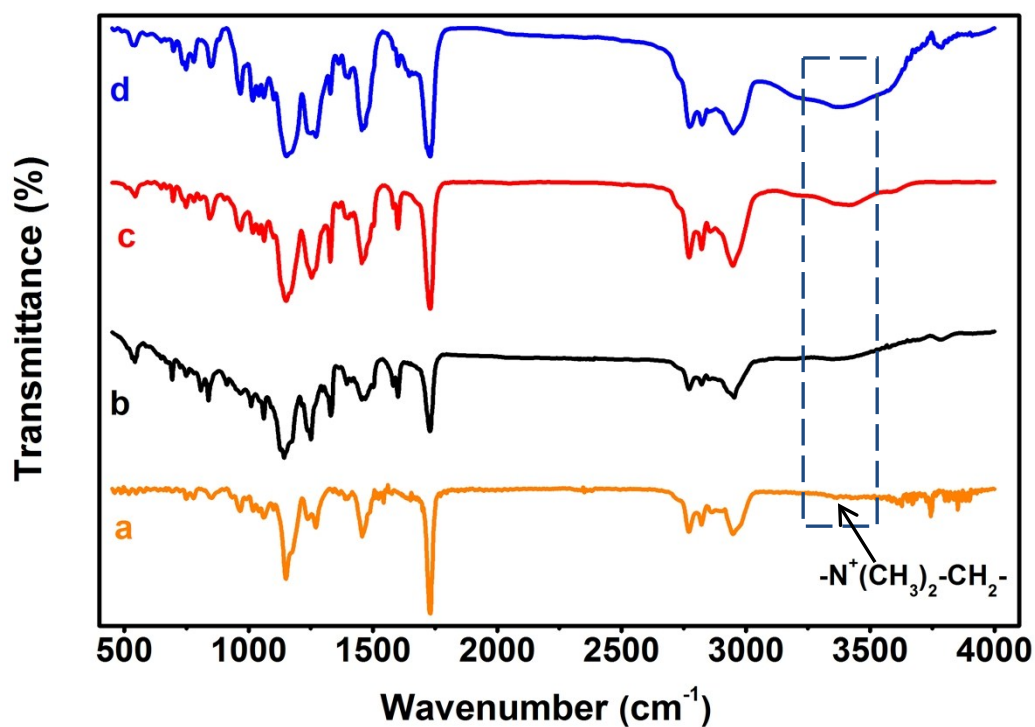


Figure S3. FTIR spectra of (a) PDMAEMA, (b) PDMAEMA-AZO with DF of 4%, (c) PDMAEMA-AZO with DF of 9% and (d) PDMAEMA-AZO with DF of 17%.

Compared with the spectrum of PDMAEMA, a carbon-nitrogen vibration peak from the ammonium groups at 3420 cm⁻¹ appeared and increased with the increase of the DF for the azobenzene-functionalized copolymers, shown in Figure S3.

4. The critical aggregation concentration (CAC) of the azobenzene-functionalized polymers with DF of 9% and 17%.

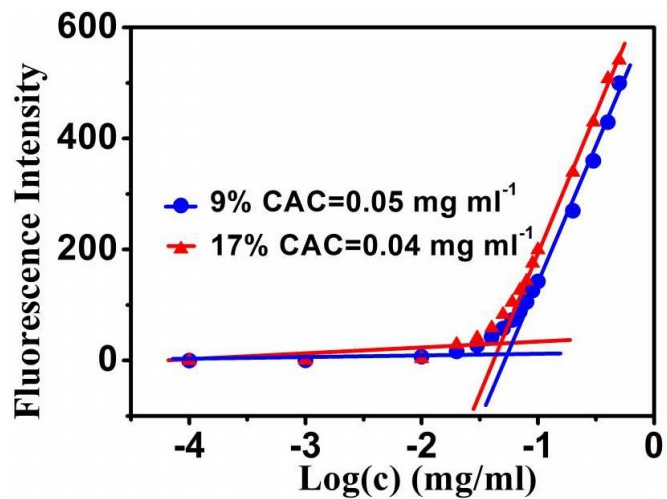


Figure S4. Plot of the maximum fluorescence emission intensity of Nile Red ($\lambda_{ex}=550$ nm) vs the log of concentration of the polymer PDMAEMA-AZO with DF of 9% and 17%.

5. TEM images of the nanoparticles self-assembled from the copolymer with DF of 9% under different stimuli.

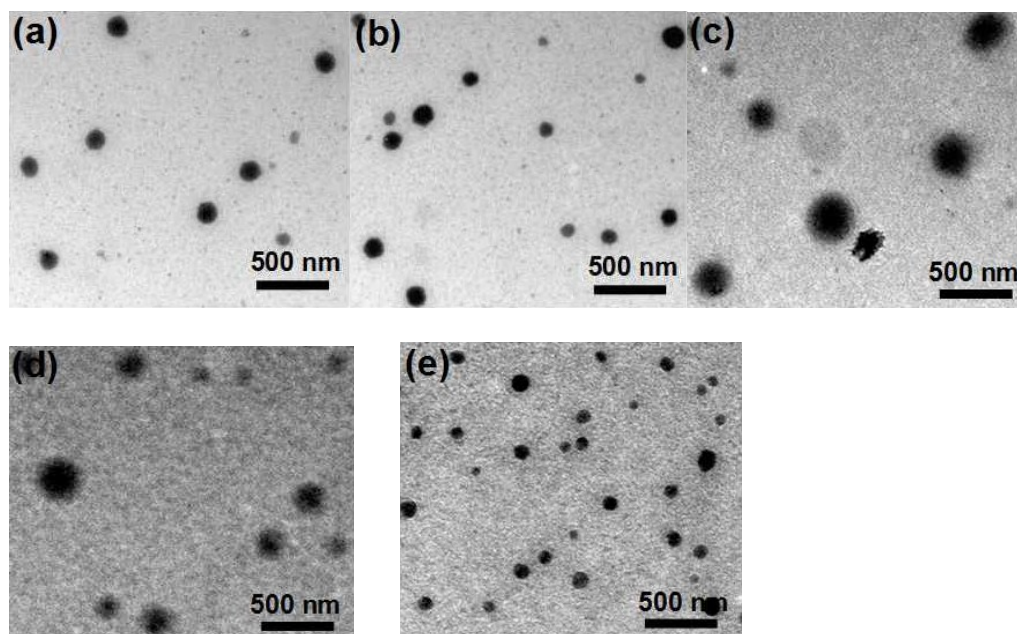


Figure S5. TEM images of the nanoparticles self-assembled from the copolymer with DF of 9% under different stimuli: (a) before stimulus presentation; (b) after UV light irradiation; (c) at pH 3; (d) at pH 10; (e) at 60 °C.

The diameter of the nanoparticles from the copolymer PDMAEMA-AZO with DF of 9% was approximately 120 nm before stimulus presentation, as shown in Figure S5a. After UV light irradiation, the spherical morphology of polymer nanoparticles could be still observed and the size of the nanoparticles increased to 125 nm (Figure S5b). At pH 3, the nanoparticles were swollen greatly, the diameter of which increased to about 290 nm (Figure S5c). At pH 10, the large nanoparticles with diameter of 450 nm appeared, corresponding to the complex aggregates for the deprotonation of the PDMAEMA segments, shown in Figure S5d. When the nanoparticles were heated to 60 °C, the diameter decreased to 100 nm, shown in Figure S5e.

6. TEM images of the nanoparticles self-assembled from the copolymer with DF of 17% under different stimuli.

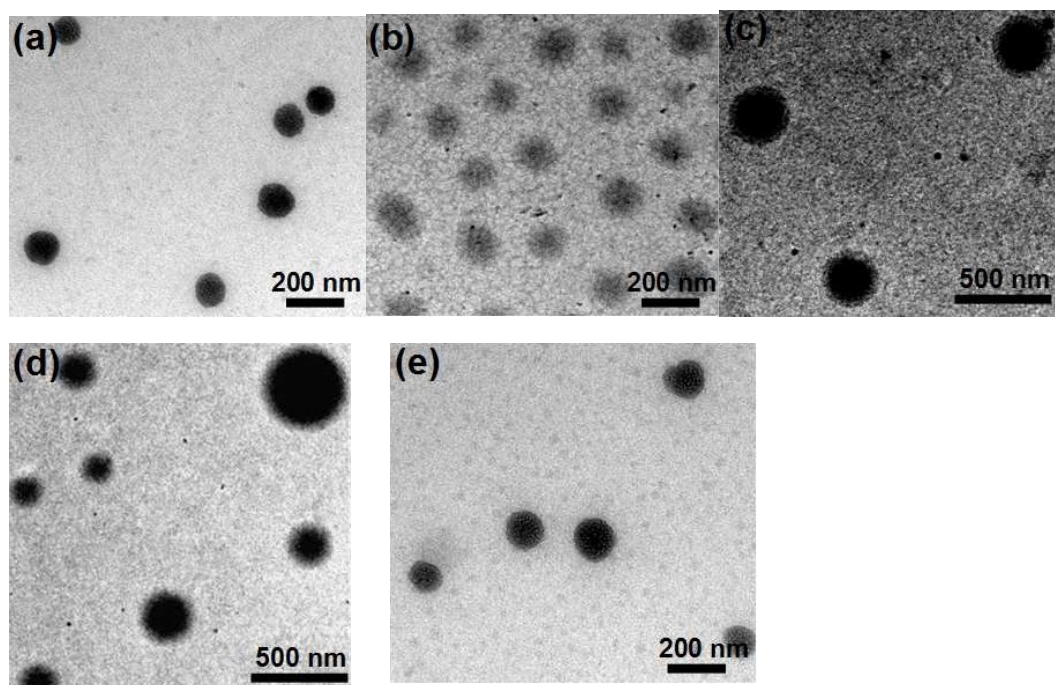


Figure S6. TEM images of the nanoparticles self-assembled from the copolymer PDMAEMA-AZO with DF of 17% under different stimuli: (a) before stimulus presentation; (b) after UV light irradiation; (c) at pH 3; (d) at pH 10; (e) at 60 °C.

The diameter of the nanoparticles from the copolymer PDMAEMA-AZO with DF of 17% was approximately 130 nm before stimulus presentation, as shown in Figure S6a. After UV light irradiation, the spherical morphology of polymer nanoparticles could be still observed and the size of the nanoparticles increased to 135 nm (Figure S6b). At pH 3, the nanoparticles were swollen greatly, the diameter of which increased to about 290 nm (Figure S6c). At pH 10, the large nanoparticles with diameter of 480 nm appeared, corresponding to the complex aggregates for the deprotonation of the PDMAEMA segments, shown in Figure S6d. When the nanoparticles were heated to 60 °C, the diameter decreased to 120 nm, shown in Figure S6e.

7. UV-vis spectra and fluorescence emission spectra of Nile Red in THF under UV light and visible light irradiation.

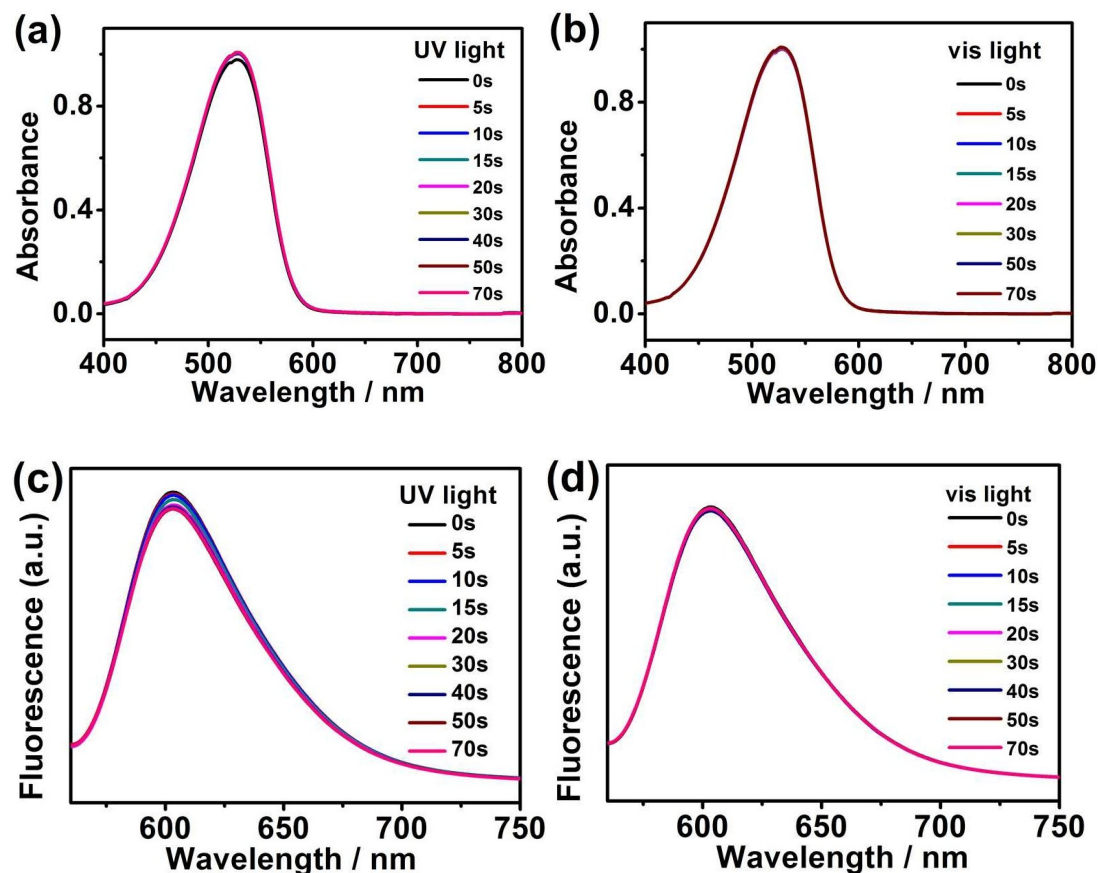


Figure S7. (a) and (b) UV-vis spectra of the Nile Red in THF under UV light irradiation (365 nm, 5 mW cm⁻²) and visible light irradiation (450 nm, 7mW cm⁻²), respectively. (c) and (d) Fluorescence spectra of the Nile Red under UV light irradiation (365 nm, 5 mW cm⁻²) and visible light irradiation (450 nm, 7mW cm⁻²).

Figure S7 shows the UV-vis spectra and fluorescence emission spectra of Nile Red in THF under UV light and visible light irradiation, from which it can be seen that the absorption and fluorescence of Nile Red changed little upon UV and visible light irradiation.

8. Fluorescence emission spectra of the nanoparticles self-assembled from the azobenzene-functionalized polymers with DF of 4% loaded with pyrene under UV light irradiation and visible light irradiation.

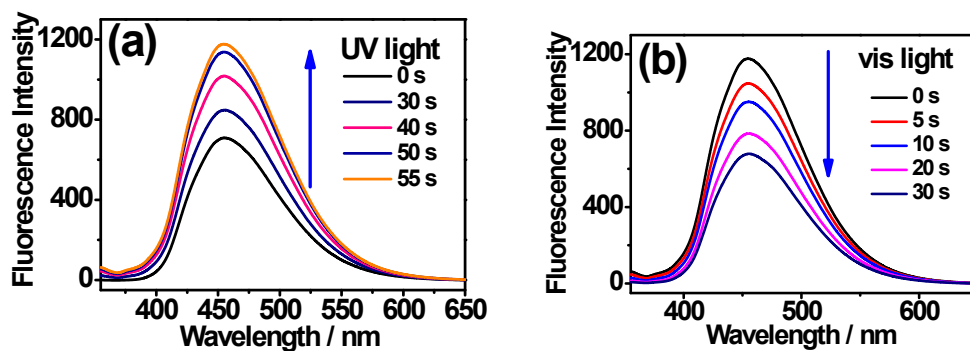


Figure S8. (a) and (b) Fluorescence spectra ($\lambda_{\text{ex}}=345$ nm) of the nanoparticles of the copolymer with DF of 4% loaded with pyrene under UV light irradiation (365 nm, 5 mW cm^{-2}) and visible light irradiation (450 nm, 7 mW cm^{-2}), respectively.

Figure S8 shows the fluorescence change of encapsulated pyrene upon light irradiation. The emission band centered at 450 nm is ascribed to the pyrene excimer emission.¹ The excimer emission increased when increasing UV irradiation time, where the hydrophilicity increased since the trans azobenzene changed to the cis; while the excimer emission decreased when irradiating with visible light, where the hydrophilicity decreased since the cis isomer changed to the trans.

9. UV-vis spectra of the nanoparticles self-assembled from the azobenzene-functionalized polymers with DF of 9% and 17% loaded with Nile Red under UV light irradiation.

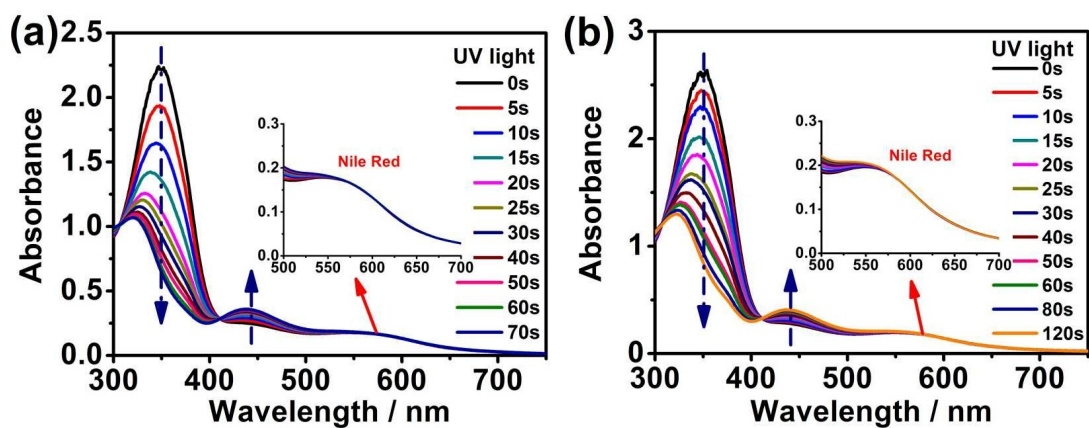


Figure S9. UV-vis spectra of the nanoparticles self-assembled from the azobenzene-functionalized polymers with DF of 9% (a) and 17% (b) loaded with Nile Red under UV light irradiation.

10. UV-vis spectra of the nanoparticles self-assembled from the azobenzene-functionalized polymers with DF of 4% loaded with Nile Red at pH 7, pH 5 and under the combined stimulation of pH 5 and UV light irradiation.

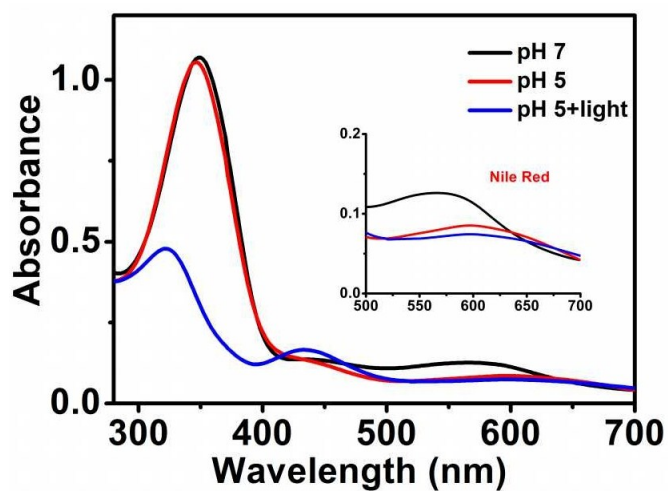


Figure S10. UV-vis spectra of the nanoparticles self-assembled from the azobenzene-functionalized polymers with DF of 4% loaded with Nile Red at pH7, pH 5 and the combined stimulation of pH 5 and UV light irradiation.

Figure S10 shows that the release could be enhanced indeed upon the combined stimulation compared with those under single stimulation.

11. Fluorescence emission spectra of the nanoparticles self-assembled from the azobenzene-functionalized polymers with DF of 9% and 17% loaded with Nile Red under UV light irradiation and visible light irradiation.

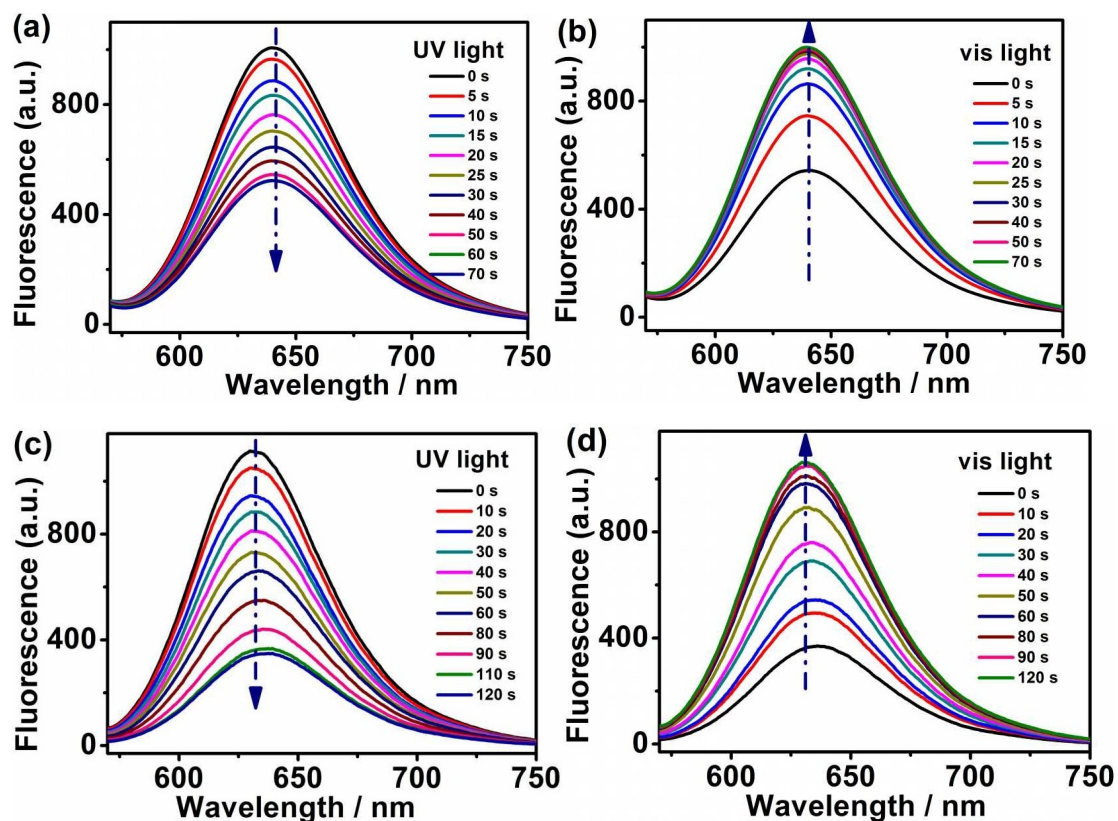


Figure S11. (a) and (b) Fluorescence spectra ($\lambda_{\text{ex}}=550$ nm) of the nanoparticles self-assembled from the copolymer with DF of 9% loaded with Nile Red under UV light irradiation (365 nm, 5 mW cm⁻²) and visible light irradiation (450 nm, 7mW cm⁻²), respectively. (c) and (d) Fluorescence spectra ($\lambda_{\text{ex}}=550$ nm) of the nanoparticles self-assembled from the copolymer with DF of 17% loaded with Nile Red under UV light irradiation (365 nm, 5 mW cm⁻²) and visible light irradiation (450 nm, 7mW cm⁻²), respectively.

12. UV-vis spectra and Fluorescence emission spectra of Nile Red in THF at different pH.

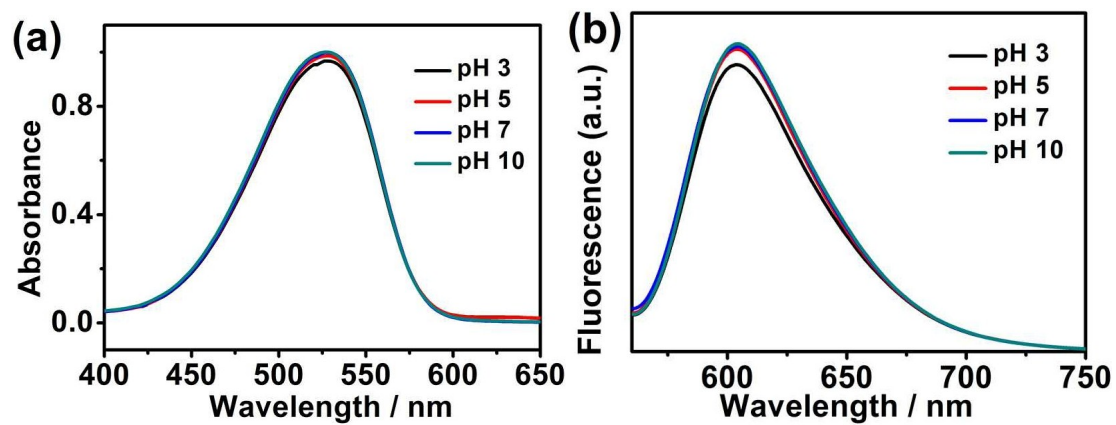


Figure S12. UV-vis spectra (a) and fluorescence emission spectra (b) of Nile Red in THF at different pH.

Figure S12 shows the UV-vis spectra and fluorescence emission spectra of Nile Red in THF at different pH, from which it can be seen that the absorption and fluorescence of Nile Red changed little at different pH.

13. UV-vis spectra of the nanoparticles self-assembled from the azobenzene-functionalized polymer with DF of 4% loaded with Nile Red through a heating process.

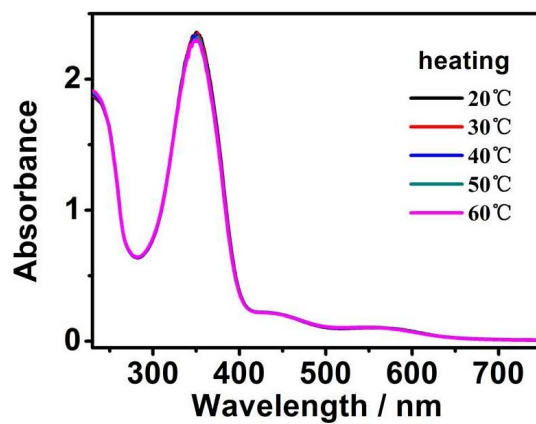


Figure S13. UV-vis spectra of the nanoparticles of the copolymer PDMAEMA-AZO with DF of 4% loaded with Nile Red through a heating process from 20 to 60 °C.

14. UV-vis absorption spectra and fluorescence emission spectra of Nile Red in THF upon heating and cooling process.

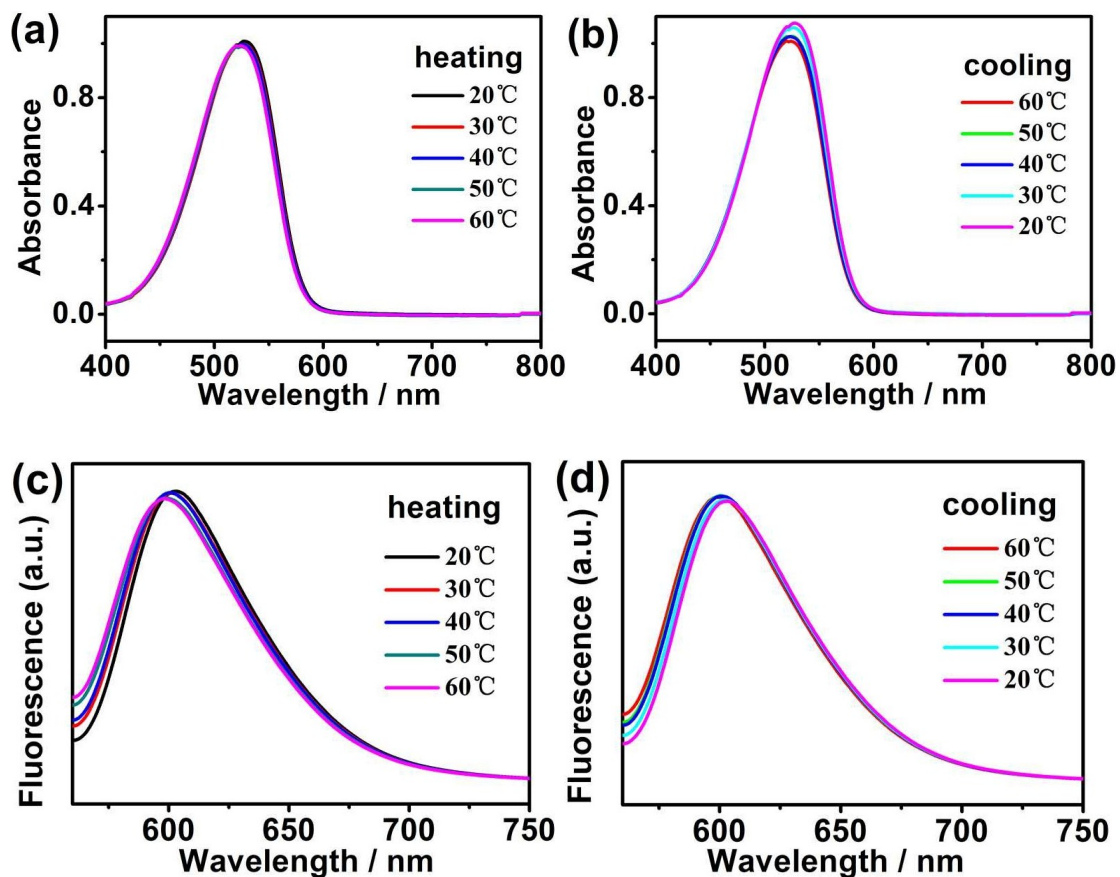


Figure S14. (a) and (b) UV-vis absorption spectra of Nile Red in THF upon heating and cooling process, respectively. (c) and (d) Fluorescence spectra ($\lambda_{\text{ex}}=550$ nm) of Nile Red in THF upon heating and cooling process, respectively.

15. Fluorescence emission spectra of the nanoparticles self-assembled from the azobenzene-functionalized polymers with DF of 9% and 17% loaded with Nile Red under temperature stimulation.

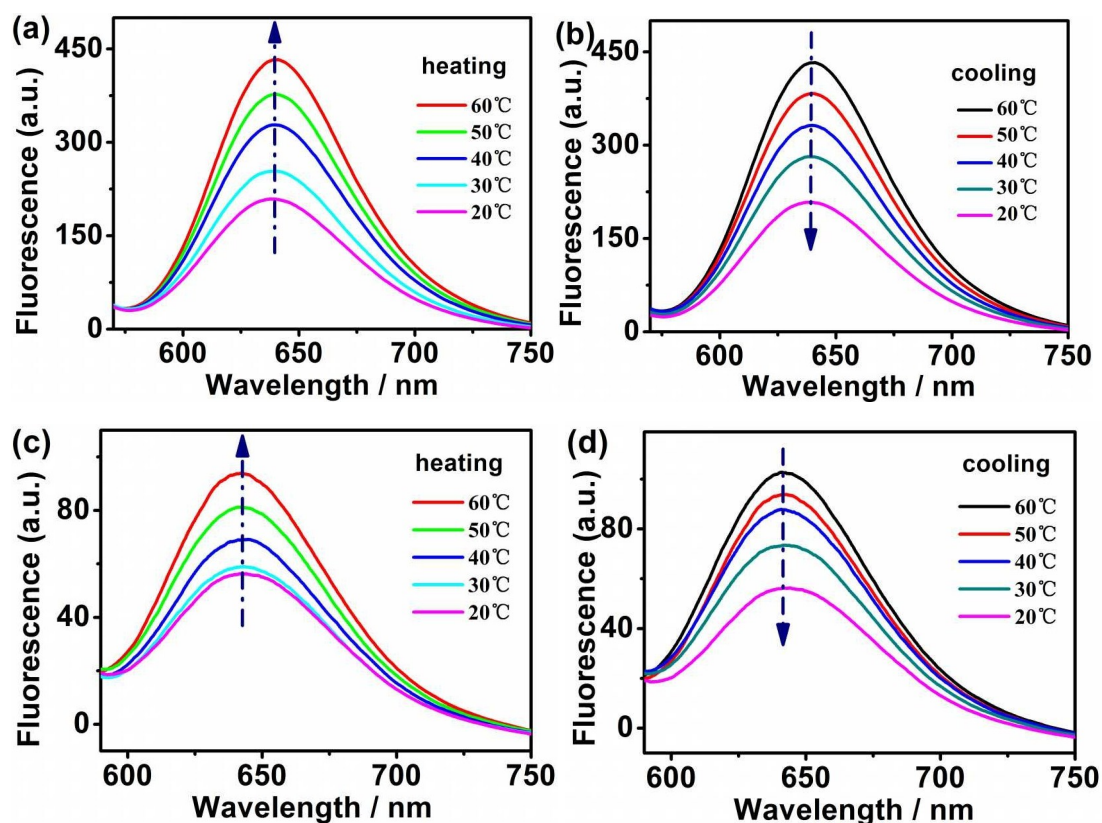


Figure S15. (a) and (b) Fluorescence spectra ($\lambda_{ex}=550$ nm) of the nanoparticles self-assembled from the copolymer PDMAEMA-AZO with DF of 9% loaded with Nile Red upon heating and cooling process, respectively. (c) and (d) Fluorescence spectra ($\lambda_{ex}=550$ nm) of the nanoparticles self-assembled from the copolymer PDMAEMA-AZO with DF of 17% loaded with Nile Red upon heating and cooling process, respectively.

Reference

- 1 G. J. Wang, G. V. Bobkov, S. N. Mikhailov, G. Schepers, A. Van Aerschot, J. Rozenski, M. Van der Auweraer, P. Herdewijn and S. De Feyter, *ChemBioChem*, 2009, **10**, 1175-1185.