Supplementary Information (SI)

Reversibly Photoswitchable Dual-Color Fluorescence and Controlled Release Properties of Polymeric Nanoparticles

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Synthesis of Spiropyran Derivative (SP-Br). SP-OH (1.056 g, 3×10^{-3} mol) and Et_3N (2 mL) were dissolved in DCM (40 mL) at 0 °C. Subsequently, bromoacetyl bromide (1 mL, 1.3×10^{-3} mol) was dissolved in DCM (5 mL) and added dropwise to the above solution, followed by stirring at room temperature for 24 h. Then the mixed solution was neutralized with saturated sodium bicarbonate solution and wished with deionized water. The collected organic layer was dried over anhydrous $MgSO_4$, and the DCM was removed at 40 ℃ by rotary evaporation under reduced pressure to obtain the red product SP-Br.

Synthesis of Poly(ethylene glycol) methyl ether acrylate (MPEG-A). Briefly, MPEG (1.9 g, 1×10^{-3} mol), dissolved in anhydrous DCM (10 mL), was mixed with triethylamine (0.55 mL, 4×10^{-3} mol) and cooled to 0 °C. Following the dropwise addition of acryloyl chloride (0.24 mL, 3×10^{-3} mol), the mixture was stirred at 0 °C for 2 h, then stirred for 24 h at room temperature. Then the mixture was washed with dilute HCl and precipitated with hexane to obtain poly(ethylene glycol) methyl ether acrylate (MPEG-A).

Synthesis of Naphthalimide Derivative (NAPH-Br). The synthesis of NAPH-Br included: (i) 4-bromo-1,8-naphthalimide was prepared starting from 4-bromo-1,8-naphthalic anhydride (5.54 g, 2×10^{-2} mol) with aqueous ammonia (30 mL) at 45 °C for 8 h. The residue was washed with water and dried to obtain the crude product as brown powder. (ii) 4-hexylamino-1,8-naphthalimide was prepared starting from 4-bromo-1,8-naphthalimide (2.76g, 1×10^{-2} mol) with hexylamine (3.03 g, 3×10^{-2} mol) in DMSO (50 mL) at 100 ℃ for 4 h. Then the reaction system was first cooled to room temperature, and the mixture was poured into deionized water (500 mL). The precipitate was filtered and washed with deionized water, and dried to give orange product 4-hexylamino-1,8-naphthalimide. (iii) 4-hexylamino-1,8-naphthalimide (1.48 g, 5×10^{-3} mol) and K_2CO_3 (1.03 g, 7.5×10^{-3} mol) were added to DMF (10 ml), and the mixed mixture was stirred at 60 ℃ for 20 min, then adding 1,4-dibromobutane (4 mL) at 40 °C for 24 h (monitored by TLC, eluent, chloroform/methanol, 40/1, v/v). The reaction solution was added to DCM (100 mL) and washed with deionized water (500 mL). Then the collected organic

layer was concentrated with rotary-evaporator to gain the crude product. The crude product was further purified by column chromatography (ethyl acetate/petroleum ether, 1/5, v/v) to yield yellow product NAPH-Br.

Preparation of Polymeric Nanoparticles and Controlled Release of Coumarin 102. In a typical experiment, the copolymer (2 mg) was dissolved in DMF (1 mL). Then under vigorous stirring, deionized water (1 mL) was added to the solution to induce the formation of nanoparticles. After stirring for 3h, the formation was stabilized by quickly adding another 9 mL of deionized water. Finally, the solution was added to dialysis sack (Mw, 500) and dialyzed against deionized water for 24 h to remove DMF. As to the nanoparticles encapsulated with Coumarin 102, the copolymer (2 mg) and Coumarin 102 (0.5 mg) was fully dissolved in DMF (1 mL). Similarly, deionized water was added and DMF was removed to obtain the nanoparticles solution loaded with Coumarin 102. When Coumarin 102 is encapsulated into nanoparticles, it can exhibit a strong emission, while the emission intensity of Coumarin 102 decreases drastically when it is released from the nanoparticles since Coumarin 102 is almost insoluble in water. The controlled release behaviors of Coumarin 102 under the stimuli of pH and UV irradiation were investigated according to the change of fluorescence intensity. For the controlled release under UV irradiation, the nanoparticles solution loaded with Coumarin 102 was placed under a LED lamp (365 nm, 30 mW/cm^2) at pH 7. For the controlled release at pH 5.5, the sample was adjusted to pH 5.5 by adding aqueous HCl solutions. For the controlled release under combined stimulation, the sample was adjusted to pH 5.5 and irradiated with UV light. After each stimulation for an appropriate time interval, the corresponding fluorescence spectra were recorded.

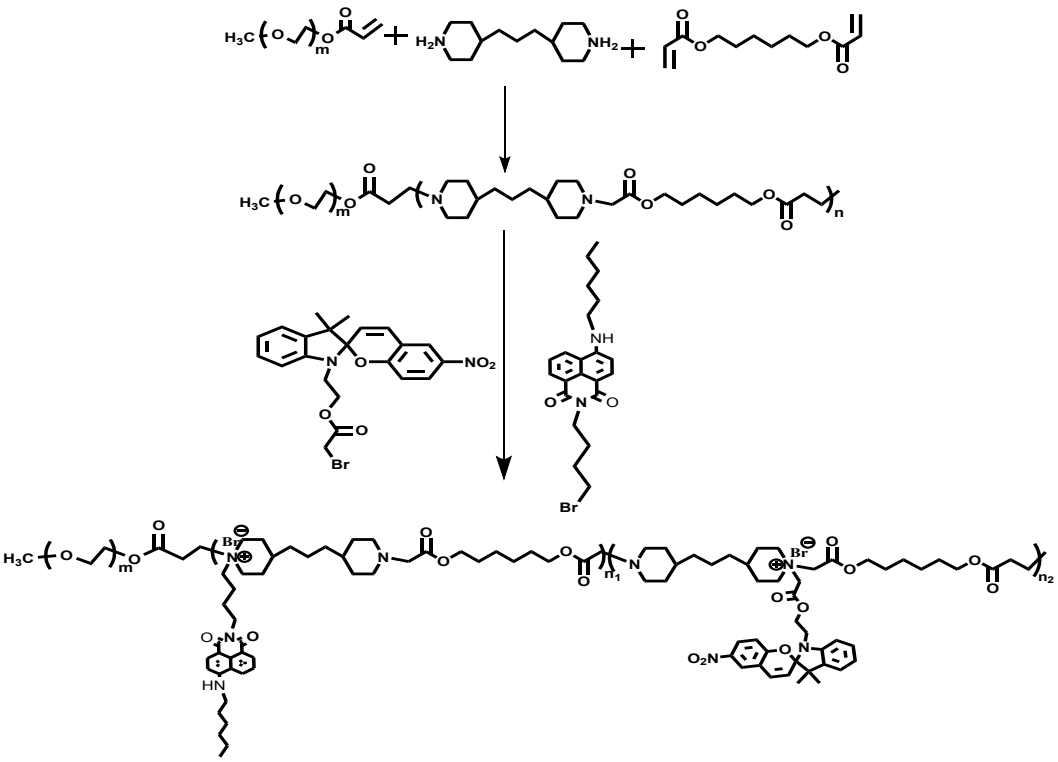

Figure S1. Synthetic route of the copolymers P1 and P2.

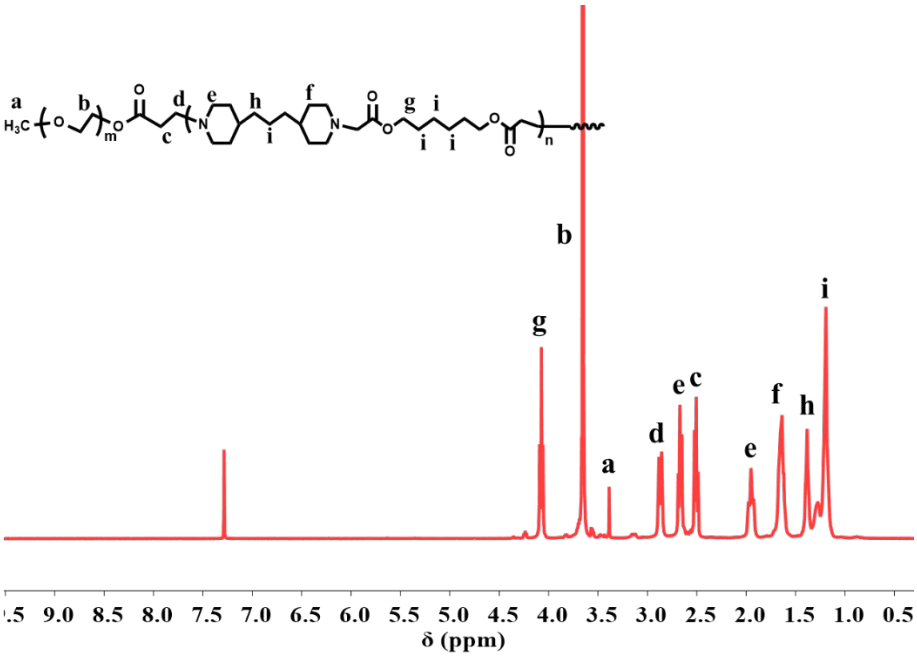

Figure S2. ^{1}H NMR spectrum of MPEG-PAE.

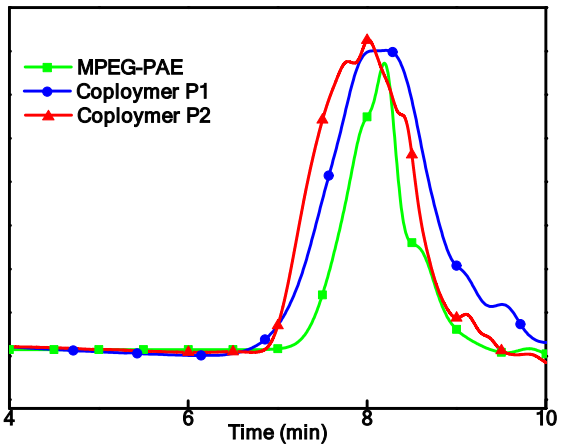

Figure S3. GPC traces of MPEG-PAE and the Copolymers P1 and P2.

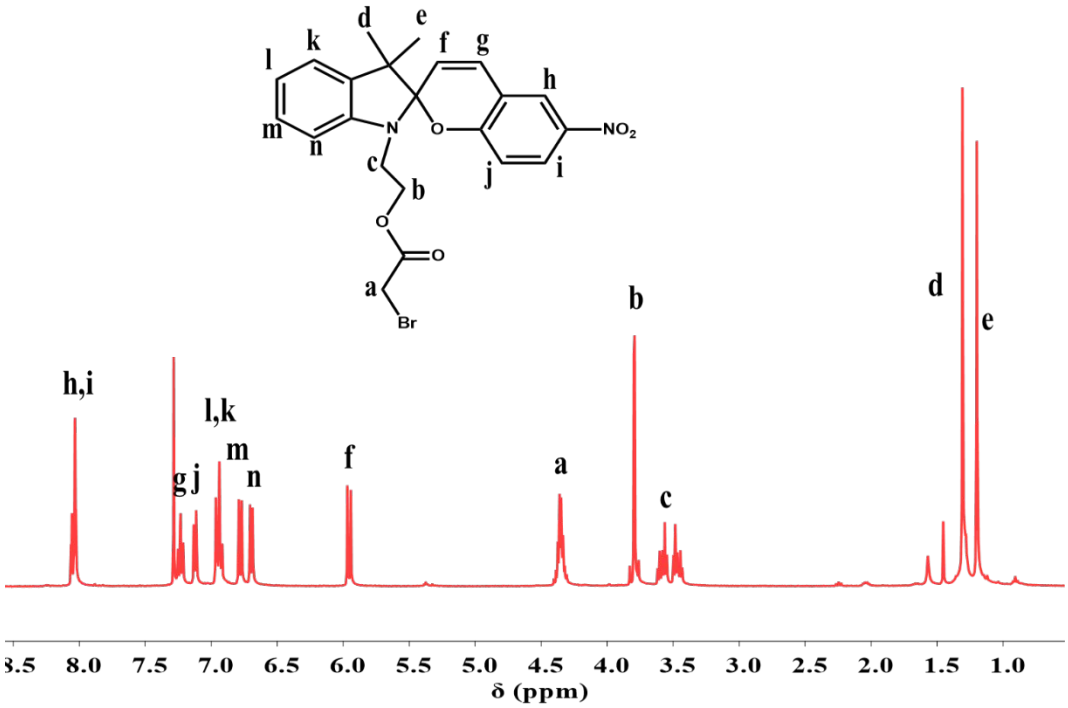

Figure S4. ^{1}H NMR spectrum of SP-Br.

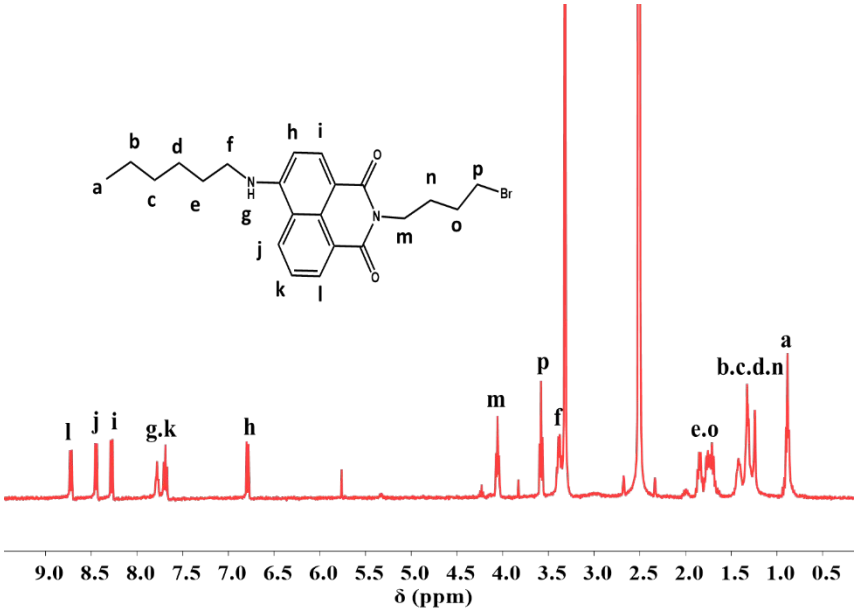

Figure S5. ^{1}H NMR spectrum of NAPH-Br in DMSO.

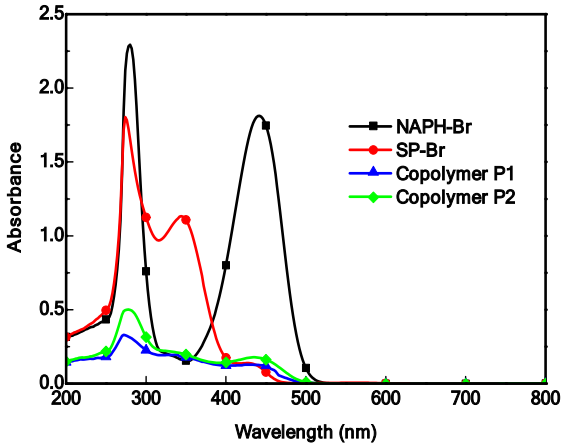

Figure S6. UV-Vis absorbance spectra of Copolymers P1and P2, SP-Br and NAPH-Br with concentration of 0.05 mg/ml in DMF.

Figure S6 shows the absorbance spectra of Copolymers P1and P2, SP-Br and NAPH-Br with same concentration. The molar absorptivity ε (λ_{max}) of the spiropyran and naphthalimide chromophores in the copolymers can be considered to be the same as that of the corresponding molecules SP-Br and NAPH-Br. The degrees of functionalization (DF) of SP and NAPH in the copolymer P1 were calculated to be 9.5 % and 4.8 % respectively, by contrasting the intensity of absorption band at 340 nm belonging to SP and 440 nm belonging to NAPH. Correspondingly, the DF of SP and NAPH in the copolymer P2 were calculated to be 9.7 % and 9.3 %, respectively.

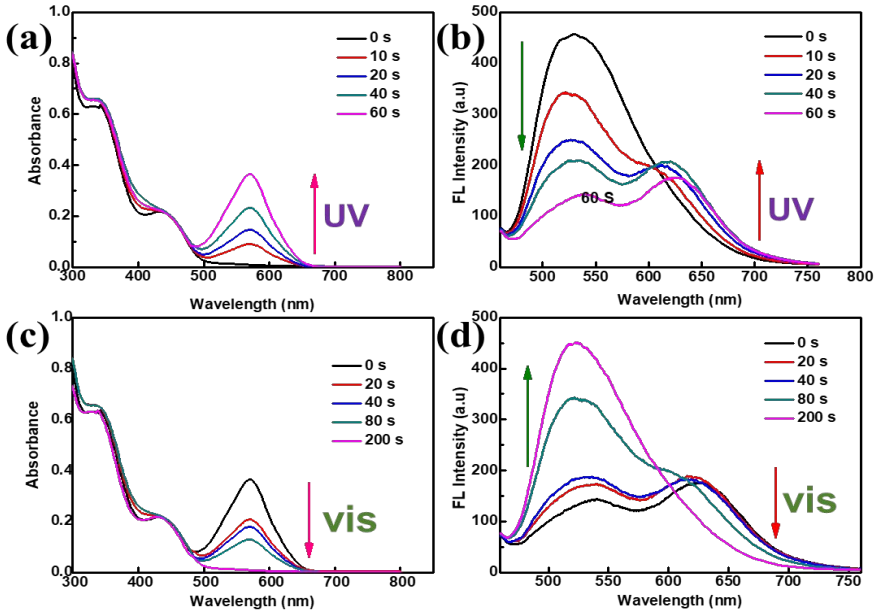

Figure S7. (a) UV-Vis spectra of the nanoparticles of P1 under the irradiation of UV light (365 nm, 30 mW/cm^2) for different time; (b) Fluorescence spectra of the nanoparticles of P1 under the irradiation of UV light (365 nm, 30 mW/cm^2) for different time (excited at 440 nm); (c) UV-Vis spectra of the nanoparticles of P1 after UV irradiation and then under the irradiation of green light (520 nm, 30 mW/cm^2); (d) Fluorescence spectra of the nanoparticles of P1 after UV irradiation and then under the irradiation of green light (520 nm, 30 mW/cm^2) for different time (excited at 440 nm).

Table S1. The photophysical properties of nanoparticles of P2.

Fluorophore	λ_{ab} (nm)[a]	λ_{em}, nm (Φ_F, %)[b]	λ_{em}, nm (Φ_F, %)[c]
NAPH-Br (donor)	440	550 (10.4)	550 (4.12)
SP-Br (acceptor)	365	--	630 (3.71)

[a] Determined in DMF.

[b] Emission maximum in nanoparticles before UV irradiation.

[c] Emission maximum in nanoparticles after 40 s UV irradiation (365 nm, 30 mW/cm^2).

Note: the quantum yields (Φ_F) are determined by using fluorescein in sodium hydroxide solution (0.1 M, Φ_R=0.95) and rhodamine B in deionized water (Φ_R=0.31) as reference, respectively.

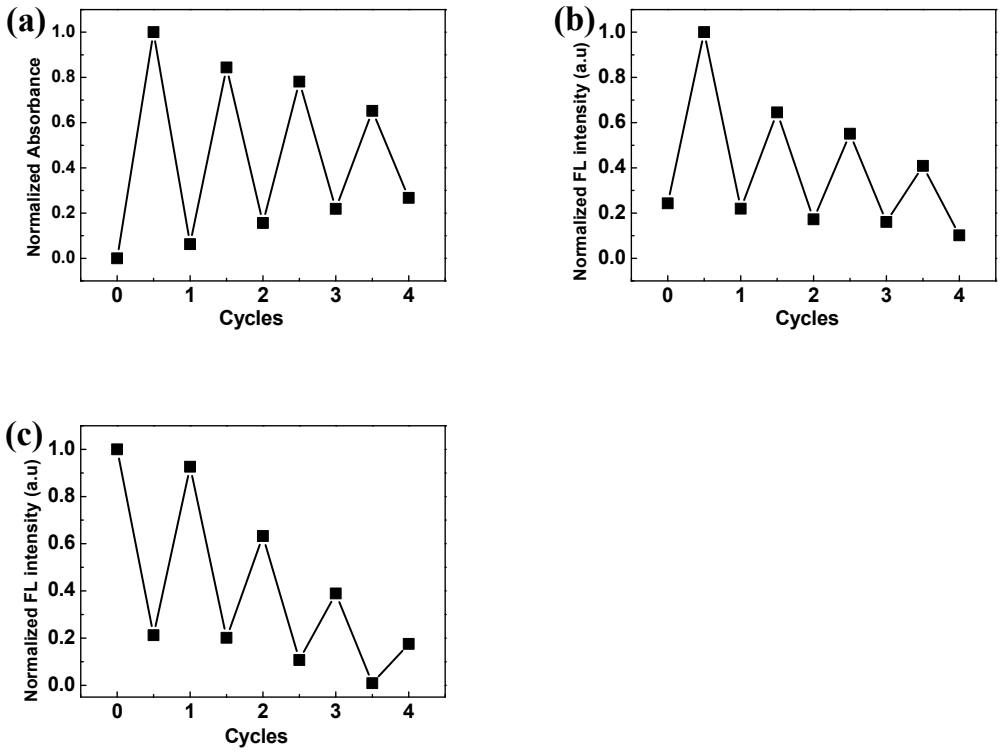

Figure S8. (a) UV-Vis absorbance changes of the nanoparticles of P2 at 530 nm upon alternate UV (40 s) and visible light (200 s) irradiation cycles. (b) Fluorescence changes of the nanoparticles of P2 at 630 nm upon alternate UV (40 s) and visible light (200 s) irradiation cycles. (c) Fluorescence changes of the nanoparticles of P2 at 550 nm upon alternate UV (40 s) and visible light (200 s) irradiation cycles.

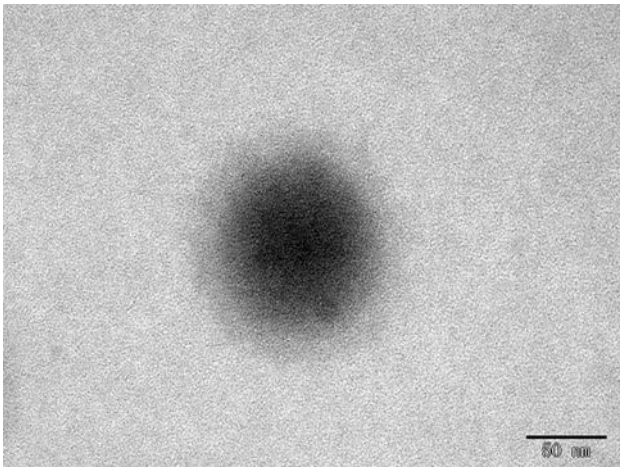

Figure S9. High-resolution TEM image of the initial nanoparticle.

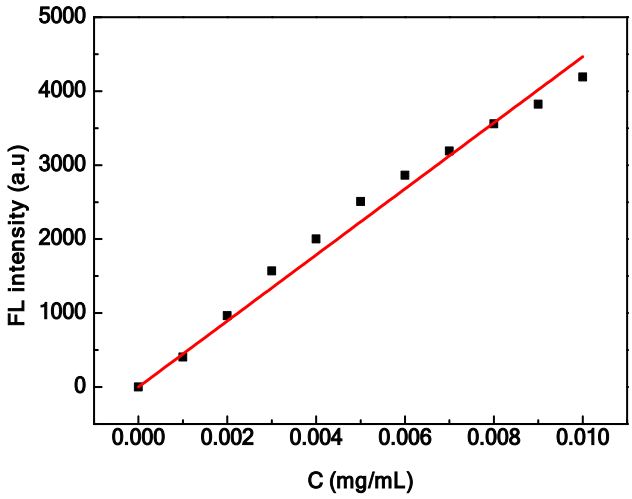

Figure S10. Plots of fluorescence emission intensity of Coumarin 102 at 490 nm at low concentrations in DMF.

Figure S10 shows that the fluorescence emission intensity increases with the increase of the concentration of Coumarin 102 linearly at low concentrations. The loading efficiency of Coumarin 102 in nanoparticles of P2 is 1.0 %, evaluated by the fluorescence intensity at 490 nm. The release profiles of Coumarin 102 from the polymeric nanoparticles was calculated from the fluorescence decrease divided by the primary fluorescence intensity.

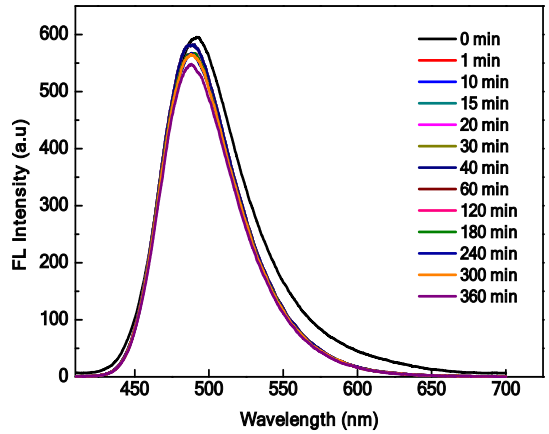

Figure S11. Fluorescence spectra of nanoparticles loaded with Coumarin 102 in water without stimulation for different time.

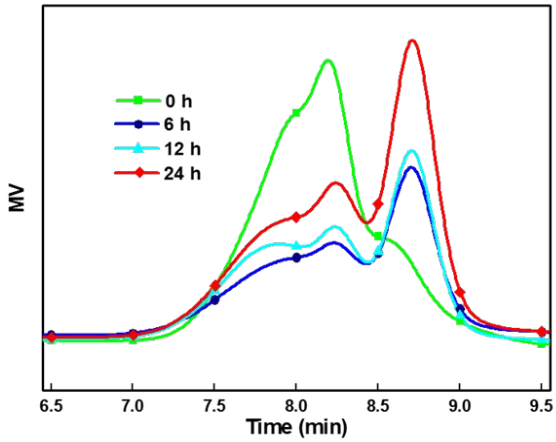

Figure S12. Normalized GPC traces of the synthesized MPEG-PAE hydrolyzed for different time in pH 5.5 at 25 °C.

Figure S10 shows the normalized GPC traces of the synthesized MPEG-PAE hydrolyzed for different time in pH 5.5 at 25°C, from which it can be seen that the ratio of integral areas of the peak centered at 8.7 minutes to integral areas of the peak centered at 8.3 minutes gradually increased with the increase of time, which were attributed to the degradation of PAE by hydrolysis of ester bonds.

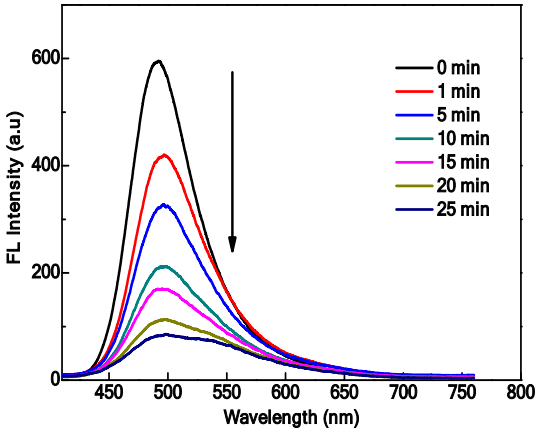

Figure S13. Fluorescence spectra of nanoparticles loaded with Coumarin 102 under UV light irradiation at pH 5.5 for different time.

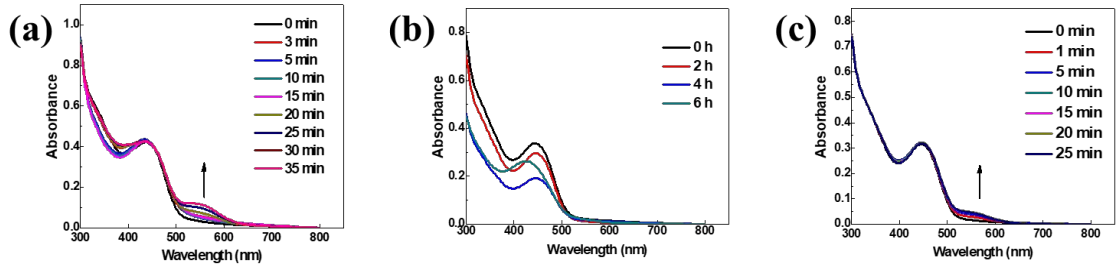

Figure S14. Absorbance spectra of nanoparticles loaded with Coumarin 102 under the stimuli: (a) UV light irradiation (30 mW/cm^2) at pH 7; (b) at pH 5.5; (c) UV light irradiation (30 mW/cm^2) at pH 5.5.