

## Supplementary Information (SI)

### **Micellar assembly of a photo- and temperature-responsive amphiphilic block copolymer for controlled release**

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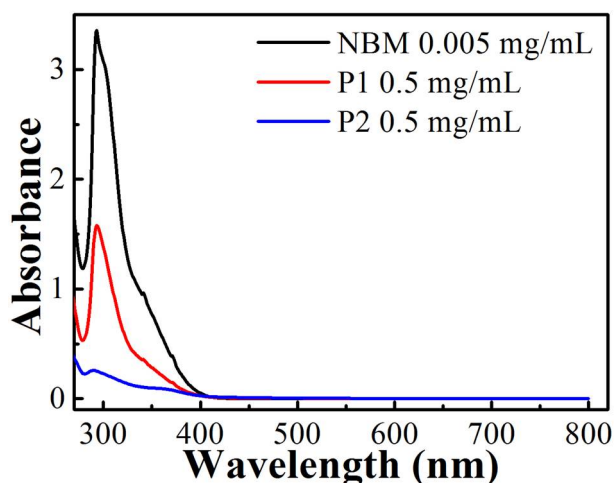
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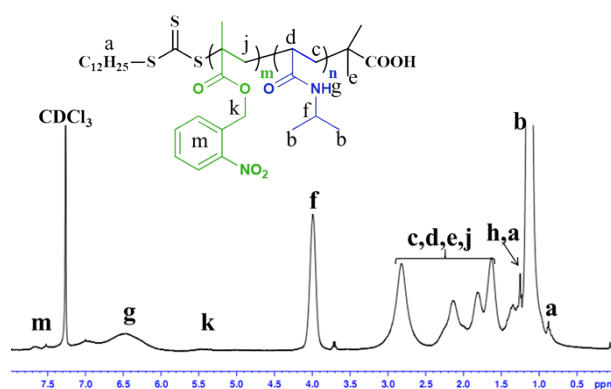
### 1. UV-vis spectra of NBM, P1 and P2 in THF

Figure S1 shows the UV-vis absorbance spectra of the copolymers (P1 and P2, 0.5 mg/mL) and 2-nitrobenzyl methacrylate (NBM, 0.005 mg/mL) in THF, from which the molar ratio between NIPAM and NBM in P1 and P2 could be determined (1.65:1 and 34:1, respectively).



**Figure S1.** UV-vis absorbance spectra of the synthesized copolymers (P1 and P2) and 2-nitrobenzyl methacrylate (NBM) in THF.

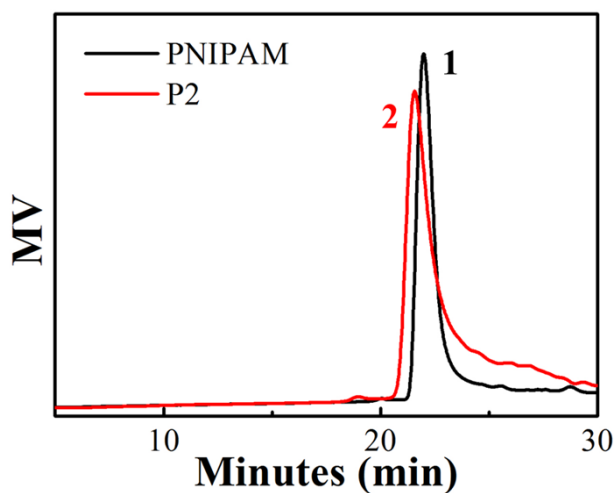
### 2. $^1\text{H}$ NMR spectrum of P2



**Figure S2.**  $^1\text{H}$  NMR spectrum of the copolymer PNIPAM<sub>74</sub>-*b*-PNBM<sub>2</sub> (P2) in  $\text{CDCl}_3$ .

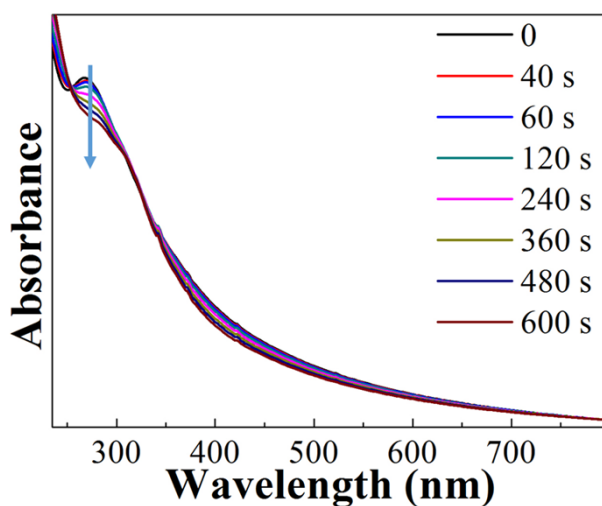
### 3. GPC traces of PNIPAM and P2

The  $M_n$  and  $M_w/M_n$  of P2 were about 9380 g/mol and 1.18, respectively.



**Figure S3.** GPC traces of the polymer PNIPAM (curve 1) and copolymer P2 (curve 2)

#### 4. UV-vis absorbance spectra of P1 aqueous solution under UV light irradiation

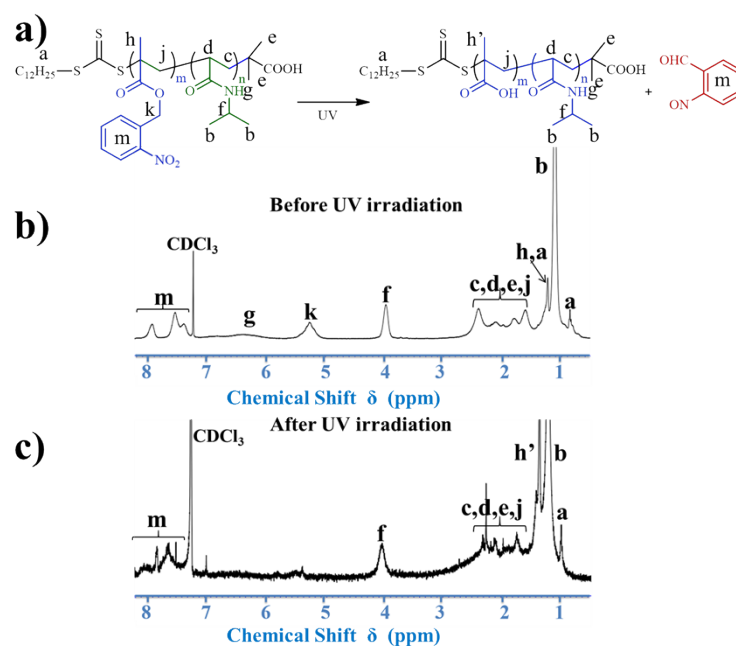


**Figure S4.** UV-Vis absorbance spectra of the copolymer P1 aqueous solution (0.2 mg/mL) under UV light irradiation.

Figure S4 shows the UV-Vis absorbance spectra of the copolymer P1 aqueous solution (0.2 mg/mL) under UV light irradiation. It can be seen that the characteristic absorption intensity of NBM at about 280 nm progressively decreased and then leveled off with increasing UV irradiation time.

## 5. Photolysis process and $^1\text{H}$ NMR spectra of P1 before and after UV light irradiation

As shown in Figure S5, the detachment of nitrobenzyl groups from the polymer upon UV irradiation was confirmed by  $^1\text{H}$  NMR. In this experiment, in order to better observe the spectral changes, the sample was prepared using a higher polymer concentration of 1.0 mg/mL in  $\text{CDCl}_3$ . The intensity of UV irradiation was  $75 \text{ mW/cm}^2$ . Before UV irradiation, the absorption band of aromatic protons ( $\delta$  7.32 ~ 8.02 ppm) and that of methylene protons ( $\delta$  5.13-5.45) were broad; while after UV irradiation, the broad absorption band of aromatic protons turned to be multi-peaks and that of methylene protons disappeared, which demonstrated the photo-induced cleavage reaction of nitrobenzyl esters.<sup>1</sup>

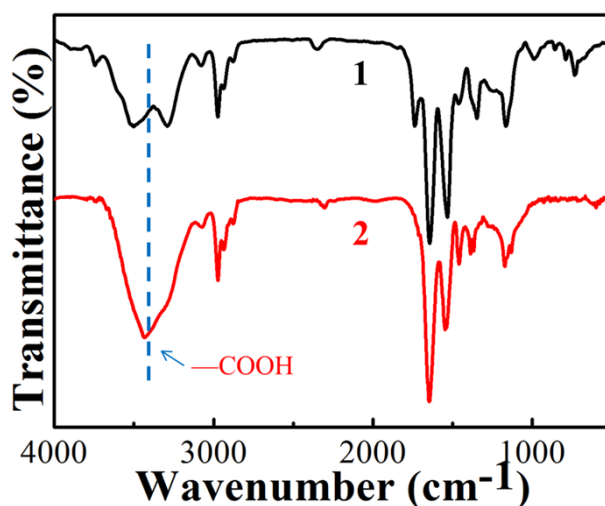


**Figure S5.** (a) Photolysis process of the 2-nitrobenzyl-containing amphiphilic copolymer. (b) and (c)  $^1\text{H}$  NMR spectra of the block copolymer P1 in  $\text{CDCl}_3$  before and after UV irradiation, respectively.

## 6. FTIR measurements

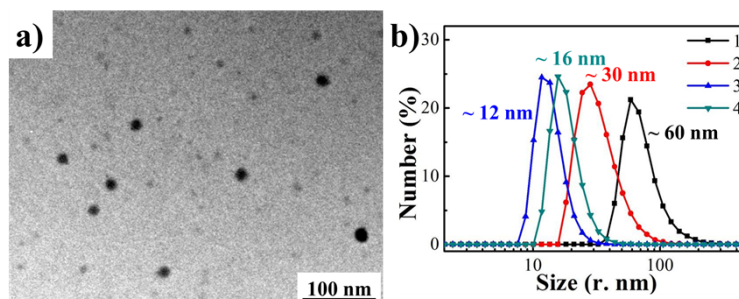
Infrared spectroscopy was also used to prove the photo-reaction of P1. The FTIR

spectra of P1 before and after UV irradiation (Figure S6) clearly revealed the change of the broad absorbance band ranging from 3150 to 3700  $\text{cm}^{-1}$ , which confirmed the presence of carboxylic acid groups after UV light irradiation.<sup>2</sup>



**Figure S6.** FTIR spectra of P1 before (curve 1) and after (curve 2) UV light irradiation.

## 7. TEM image and DLS data of P2

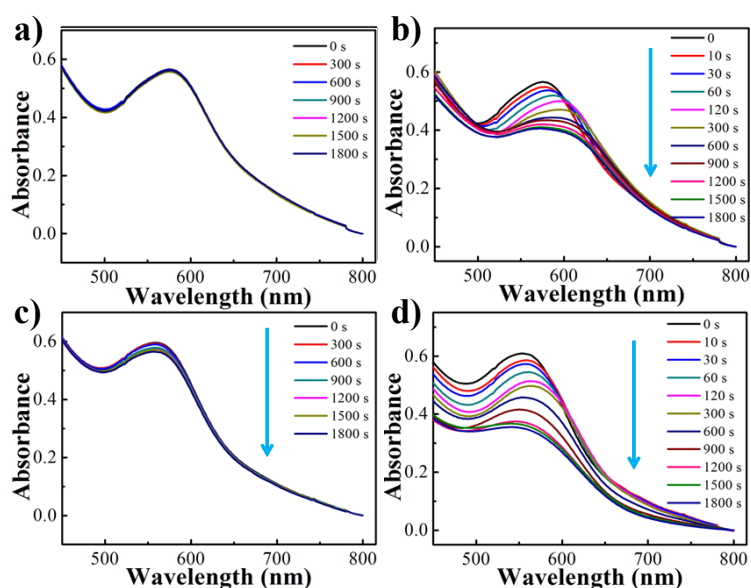


**Figure S7:** (a) TEM image of the primary assemblies of the copolymer P2 and (b) DLS curves of P2 assemblies: primary micellar nanoparticles (curve 1), under the stimulation of UV light irradiation for 30 min (curve 2), under the stimulation of temperature at 37 °C (curve 3) and under the combined stimulations of UV and temperature at 37 °C (curve 4).

Figure S7 shows the morphology and size distribution of the self-assemblies of P2 measured by TEM and DLS. DLS reveals that the diameter of the nanoparticles of P1

was about 60 nm, which was smaller than that of P1 (120 nm), since P1 possesses a longer PNBM chain.<sup>3</sup> After UV light irradiation, the  $D_h$  decreased to ~ 30 nm. At 37 °C, the  $D_h$  decreased to ~ 12 nm. Under the combined stimulation, the  $D_h$  decreased to ~ 16 nm.

#### 8. UV-Vis absorbance spectra of the polymeric nanoparticles of P1 loaded with Nile Red under the stimulation of UV light and temperature change



**Figure S8.** UV-Vis absorbance spectra of the polymeric nanoparticles of P1 loaded with Nile Red: (a) without stimulation; (b) under the stimulation of temperature at 37 °C; (c) under the stimulation of UV light irradiation; (d) under the combined stimulation of temperature at 37 °C and UV light irradiation.

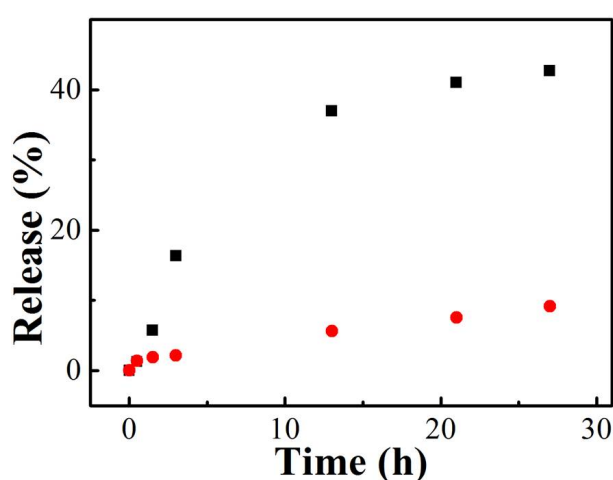
The absorption band of NR is overlapped with that of the segments PNBM containing nitrobenzene. The absorption intensity of NR at 560 nm was calculated by subtracting the absorption of PNBM. The release amount was calculated as:

$$\text{Cumulative NR release [\%]} = (A_0 - A_t / A_0) \times 100 \%$$

Where  $A_0$  and  $A_t$  are the absorption intensities of NR before and after stimulation, respectively.

## 9. Release profiles of NR encapsulated in the polymeric nanoparticles of P1 at different temperature

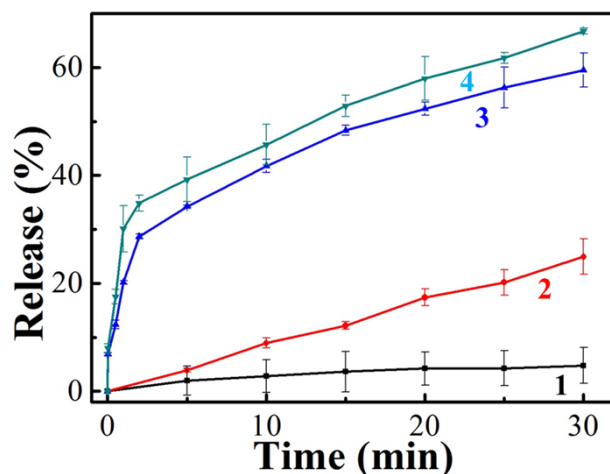
Figure S9 shows that the release profiles of NR encapsulated in the polymeric nanoparticles of P1 under temperature change stimulation for 27 h, from which it can be seen that 40% of NR could be released from the nanoparticles at 37 °C for 27 h, while no more than 10% of NR could be released at room temperature.



**Figure S9.** Release profiles of NR encapsulated in the polymeric nanoparticles of P1: (■) at room temperature and (●) at 37 °C for 27 h.

## 10. Release profiles of NR encapsulated in the polymeric nanoparticles of P2 under the stimulation of UV light and temperature change

Figure S10 shows the release profiles of NR encapsulated in the polymeric nanoparticles of P2. Without any stimulation, the release was negligible at room temperature (25°C). Under UV irradiation for 30 min, about 60 % of NR could be released. When incubating the nanoparticles at 37 °C for 30 min, about 20 % of NR could be released. Under the combined stimulation of UV light and 37 °C for 30 min, the release amount could increase to 65%.



**Figure S10.** Release profiles of NR encapsulated in the polymeric micellar nanoparticles of P2: without stimulation (curve 1); under the stimulation of temperature at 37 °C (curve 2); under the stimulation of UV light irradiation (curve 3); under the combined stimulation of UV light irradiation and temperature at 37 °C (curve 4).

## References

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- 2 E. Cabanel, V. Malinova and W. Meier, *Macromol. Chem. Phys.*, 2010, **211**, 1847-1856.
- 3 L. Sun, B. Zhu, Y. Su and C Dong, *Polym. Chem.*, 2014, **5**, 1605-1613.