

**Supplementary Information (SI)**

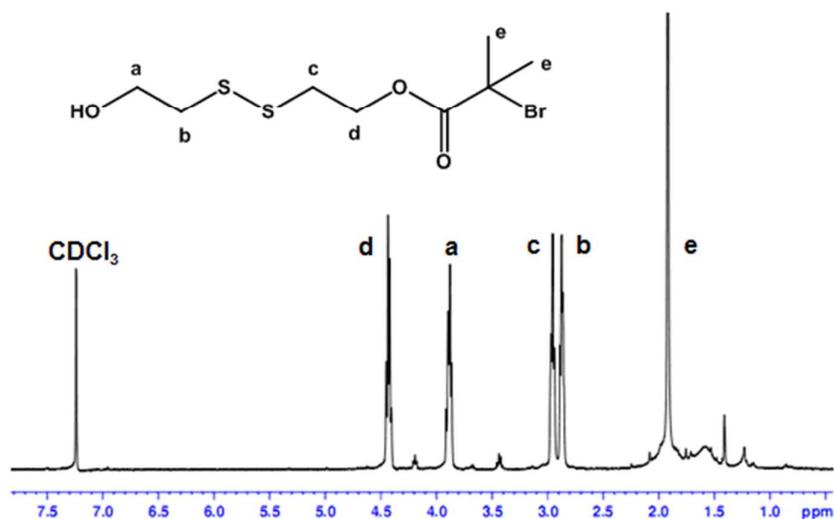
**Quadruple Stimuli Sensitive Polymeric Nanocarriers for  
Controlled Release under Combined Stimulation**

**Ziquan Cao, Hao Wu, Jie Dong, Guojie Wang\***

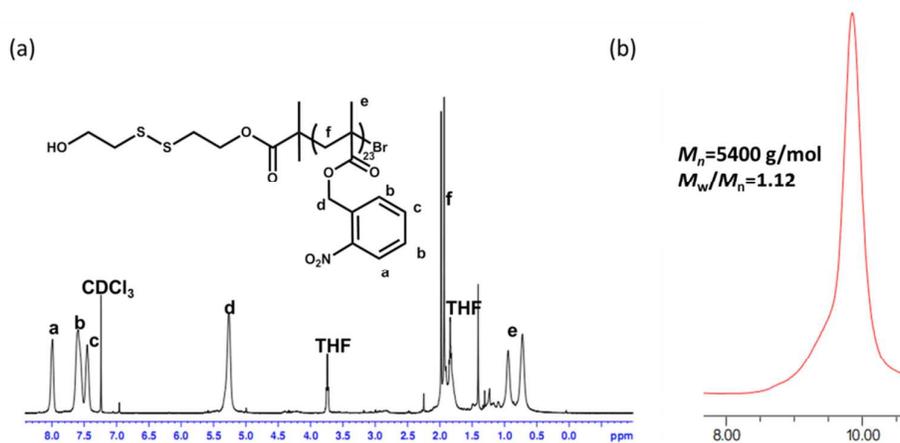
*School of Materials Science and Engineering, University of Science and Technology*

*Beijing, Beijing 100083, China;*

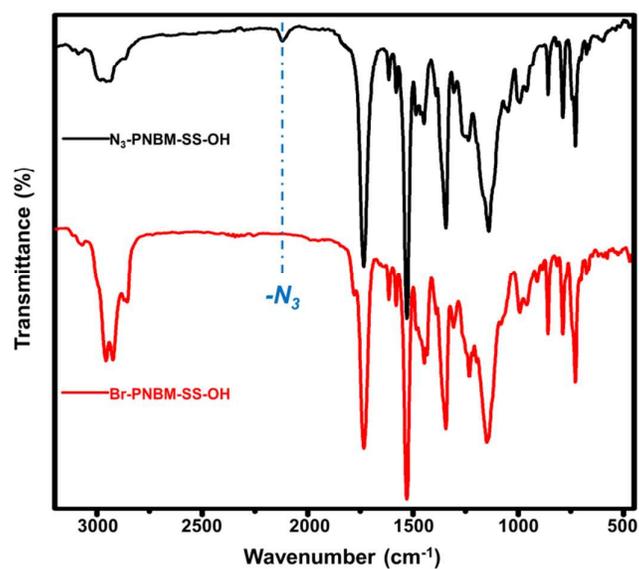
AUTHOR EMAIL ADDRESS: *guojie.wang@mater.ustb.edu.cn*



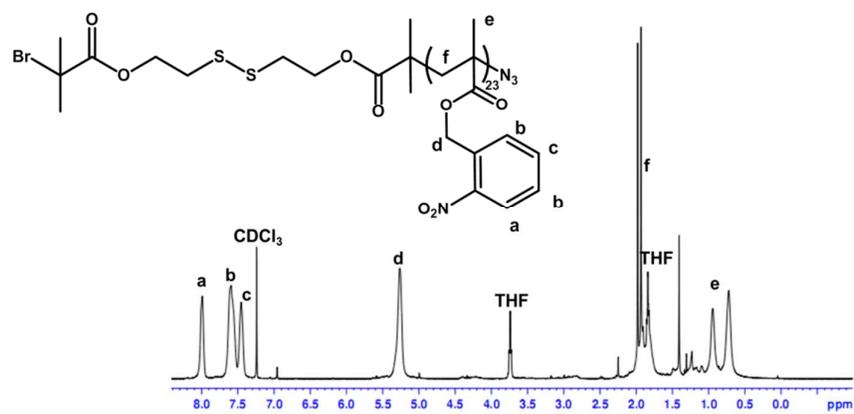
**Fig. S1** <sup>1</sup>H NMR spectrum of HO-SS-iBuBr.



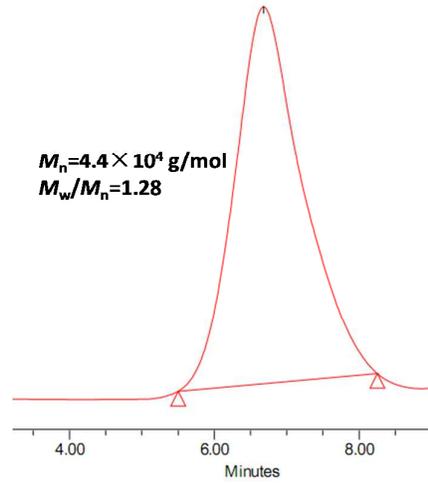
**Fig. S2** (a) <sup>1</sup>H NMR spectrum of Br-PNBM-SS-OH in CDCl<sub>3</sub>; (b) GPC profile of Br-PNBM-SS-OH.



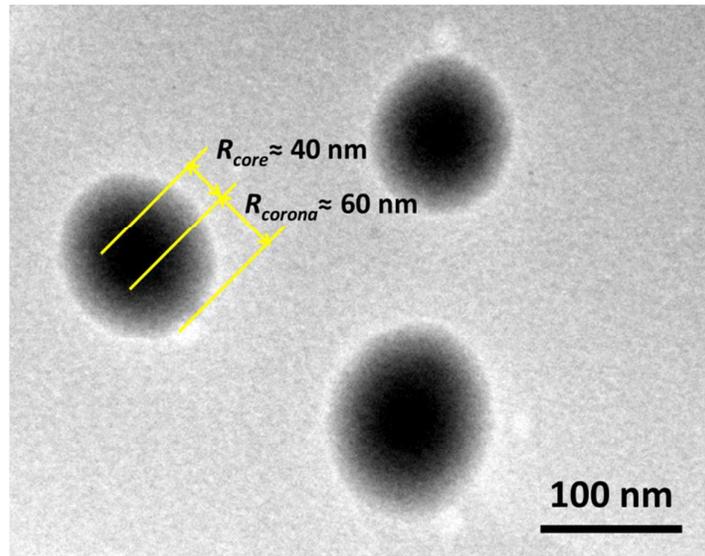
**Fig. S3** FTIR spectra of Br-PNBM-SS-OH and N<sub>3</sub>-PNBM-SS-OH.



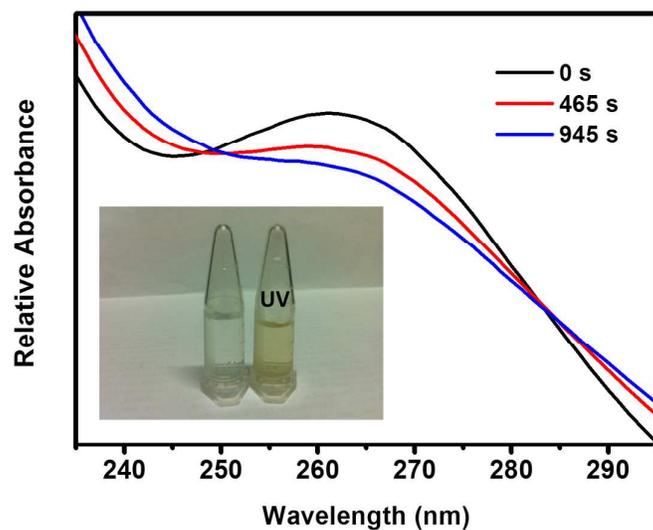
**Fig. S4** <sup>1</sup>H NMR spectrum of N<sub>3</sub>-PNBM-SS-iBuBr in CDCl<sub>3</sub>.



**Fig. S5** GPC profile of the copolymer PNBM-SS-PDMAEMA.

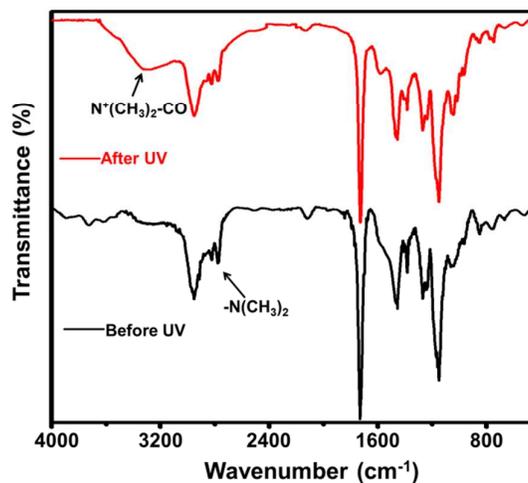


**Fig. S6** High-resolution TEM image of PNBM-SS-PDMAEMA nanoparticles.



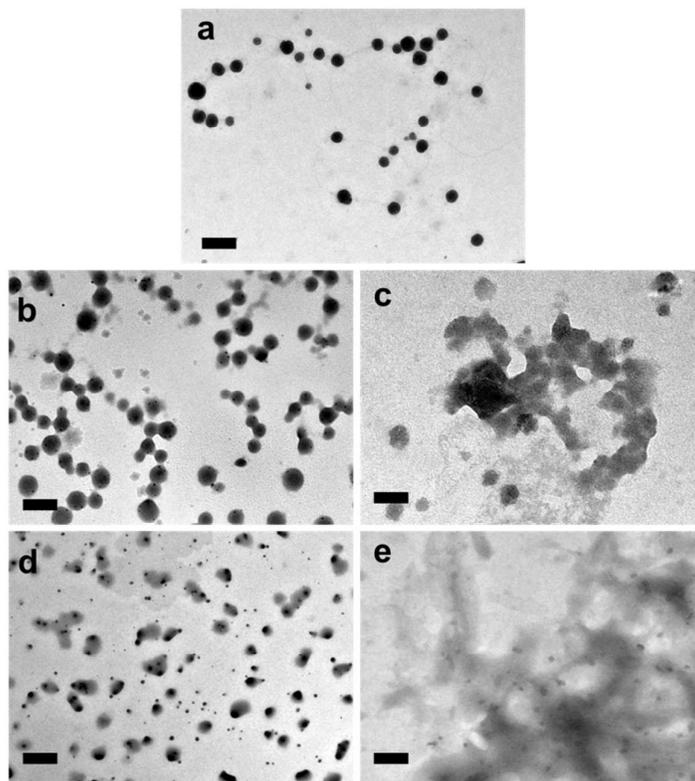
**Fig. S7** UV-vis absorption spectra of the polymer nanoparticles in water (pH 7, 0.5 mg/mL) recorded at various UV irradiation times (inset: photograph of the nanoparticle solution before (left) and after (right) UV irradiation).

It is well known that *o*-nitrobenzyl alcohol derivatives can be cleaved when exposed to 300-365 nm light. The photocleavage of the polymer nanoparticles in this study was confirmed by the UV-vis spectra under UV irradiation at 365 nm (light intensity, 45 mW/cm<sup>2</sup>) (Fig. S7). It is found that the characteristic absorption band of NBM near 262 nm decreased with the increase of the UV irradiation time and the color of the solution changed to yellow after UV irradiation.

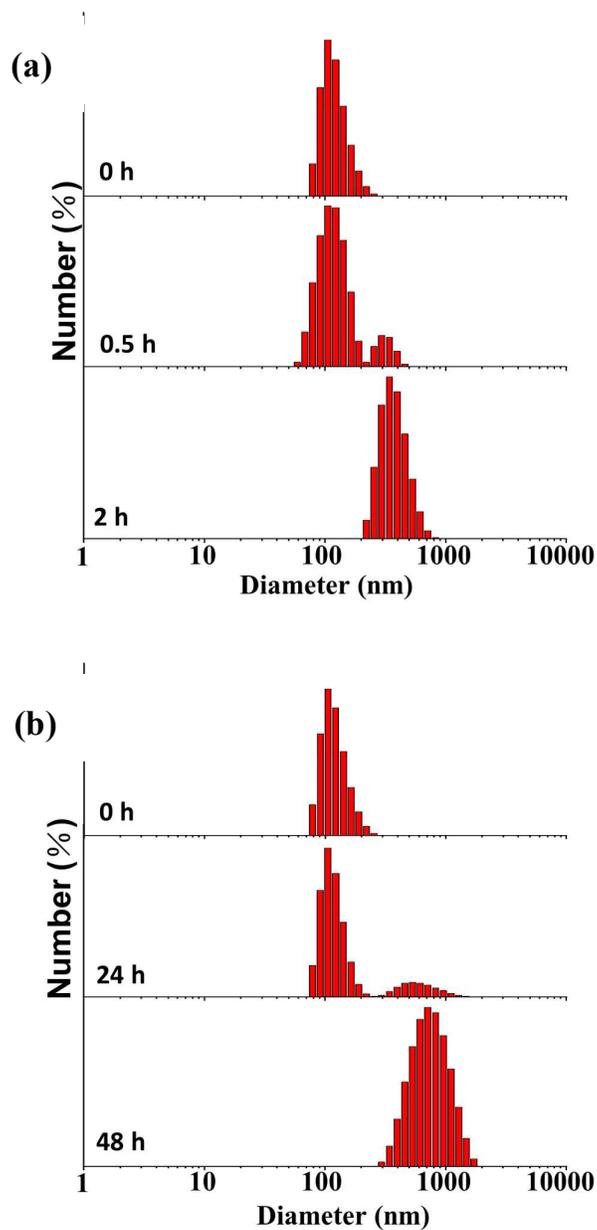


**Fig. S8** FTIR spectra of the block copolymer before and after UV irradiation.

The reaction between the amine groups and carboxylic acid groups generated after UV irradiation was confirmed by FTIR spectra. 5 mg of the copolymer and 1 mL of THF were placed in a standard cuvette and the solution was exposed to UV light (365 nm, 45 mW/cm<sup>2</sup>) for 2 h. Then the solvent was evaporated and the aggregates were dried at 70 °C before FTIR measurements. Fig. S8 shows that the carbon-nitrogen vibration peak from the amino groups at 2800 cm<sup>-1</sup> decreased and a carbon-nitrogen vibration peak from the ammonium groups appeared at 3400 cm<sup>-1</sup> after UV irradiation. The FTIR changes proved the reaction between the amine groups and the carboxylic acid groups after UV irradiation.

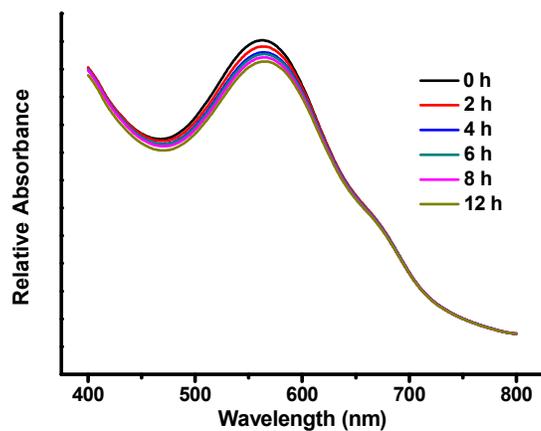


**Fig. S9** TEM images of (a) the block copolymer PNBM-SS-PDMAEMA assemblies without any treatment; (b) after UV irradiation for 30 min, (c) after UV irradiation for 2 h ( $45 \text{ mW/cm}^2$ ); (d) after 10 mM DTT treatment for 24 h without UV irradiation, (e) after 10 mM DTT for 48 h without UV irradiation, scale bar denoting 200 nm.

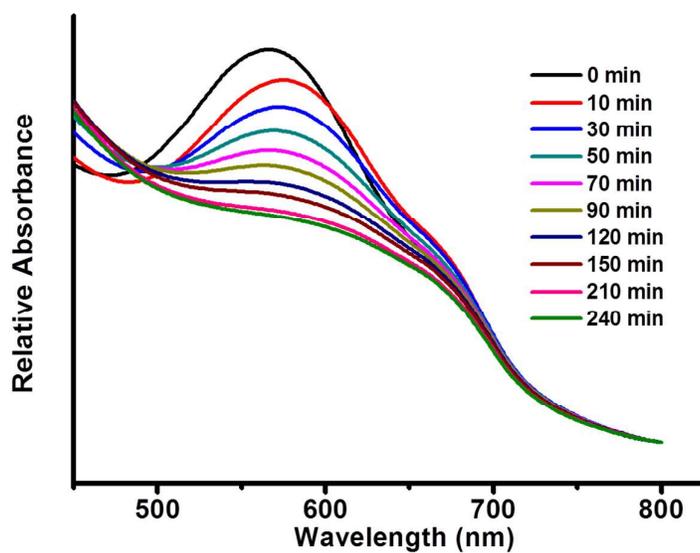


**Fig. S10** Number average size distributions for the polymer nanoparticles of PNBM-SS-PDMAEMA under different stimulation time (a) upon UV irradiation; (b) in the presence of 10mM DTT over a 48 h period.

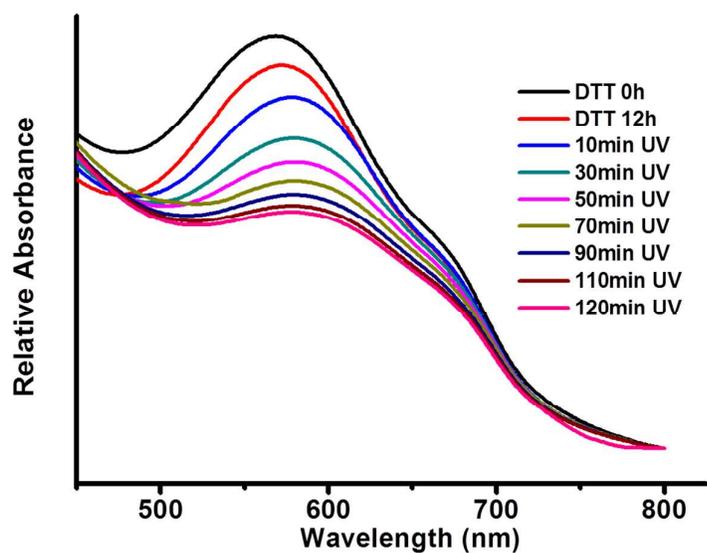
The results monitored by DLS showed that the hydrodynamic diameter of block copolymer PNBM-SS-PDMAEMA nanoparticles gradually increased with the stimulation time under UV irradiation and in the presence of 10 mM DTT.



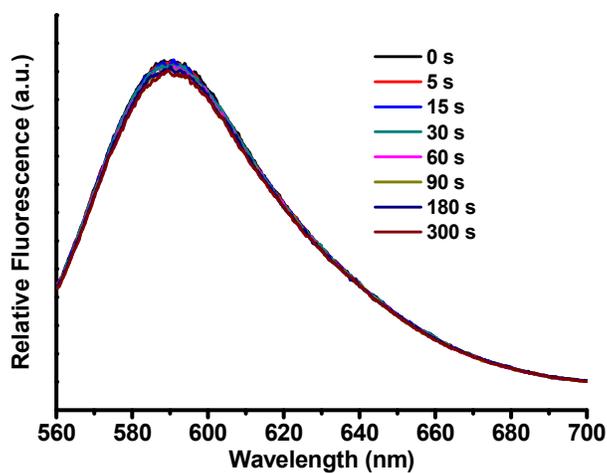
**Fig. S11** UV-vis absorbance spectra of NR-loaded nanoparticles in aqueous solution at pH 3 for different time.



**Fig. S12** UV-vis absorbance spectra of NR-loaded nanoparticles in aqueous solution at pH 3 with UV light irradiation.



**Fig. S13** UV-vis absorbance spectra of NR-loaded nanoparticles in aqueous solution at pH 3 and with 20 mM DTT first for 12 h and then under UV irradiation.



**Fig. S14** Fluorescence spectra of Nile Red mixed with the copolymer PNBM-SS-PDMAEMA (0.01 mg/mL) in THF solution upon UV light irradiation (45 mW/cm<sup>2</sup>). The fluorescence of NR was stable when the system was irradiated with UV light, which indicated that the photocleavage of the copolymer has little effect on the fluorescence of NR.