

## Supplementary Information

# Synthesis of Crosslinkable Diblock terpolymers PDPA-*b*-P(NMS-*co*-OEG) and Preparation of Shell- Crosslinked pH/Redox-Dual Responsive Micelles as Smart Nanomaterials

Jingjing Sun<sup>1,2</sup>, Zhao Wang<sup>2,3</sup>, Amin Cao<sup>2\*</sup>, Ruilong Sheng<sup>1,2,4\*</sup>

1. Department of Radiology, Shanghai Tenth People's Hospital, School of Medicine, Tongji University, Shanghai 200072, China.

2. Key Laboratory of Synthetic and Self-assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, CAS. Lingling Road 345, Shanghai, 200032, China.

3. Department of Materials, Jinling Institute of Technology, Nanjing, 211169, China.

4. CQM - Centro de Química da Madeira, Universidade da Madeira, Campus da Penteada, 9000-390, Funchal, Portugal.

**S1.** Synthesis of the functional monomers: **Figure S1.** <sup>1</sup>H NMR (a) and <sup>13</sup>C NMR (b) spectrum of the NMS monomer in CDCl<sub>3</sub>

**Figure S2.** Plots of fluorescence excitation intensity ratio ( $I_{337}/I_{333}$ ) of pyrene probe versus mass concentration of the PDPA<sub>33</sub>-*b*-P(NMS<sub>22</sub>-*co*-OEG<sub>25</sub>) (P3) copolymers

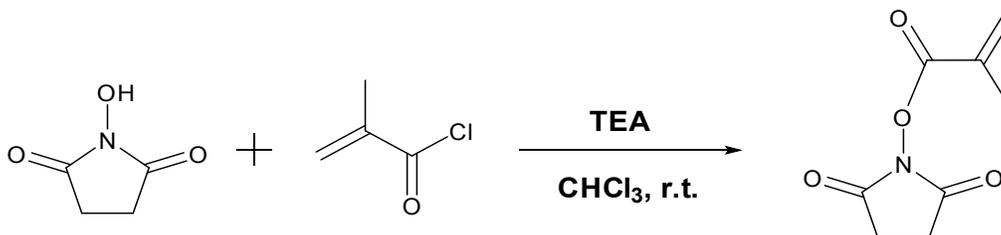
**Figure S3.** Plots of fluorescence excitation intensity ratio ( $I_{337}/I_{333}$ ) of pyrene-loaded NCL-P3 micelles

**Figure S4.** Protonation of the SCL-P3 micelles under various pH by Zeta potential measurement

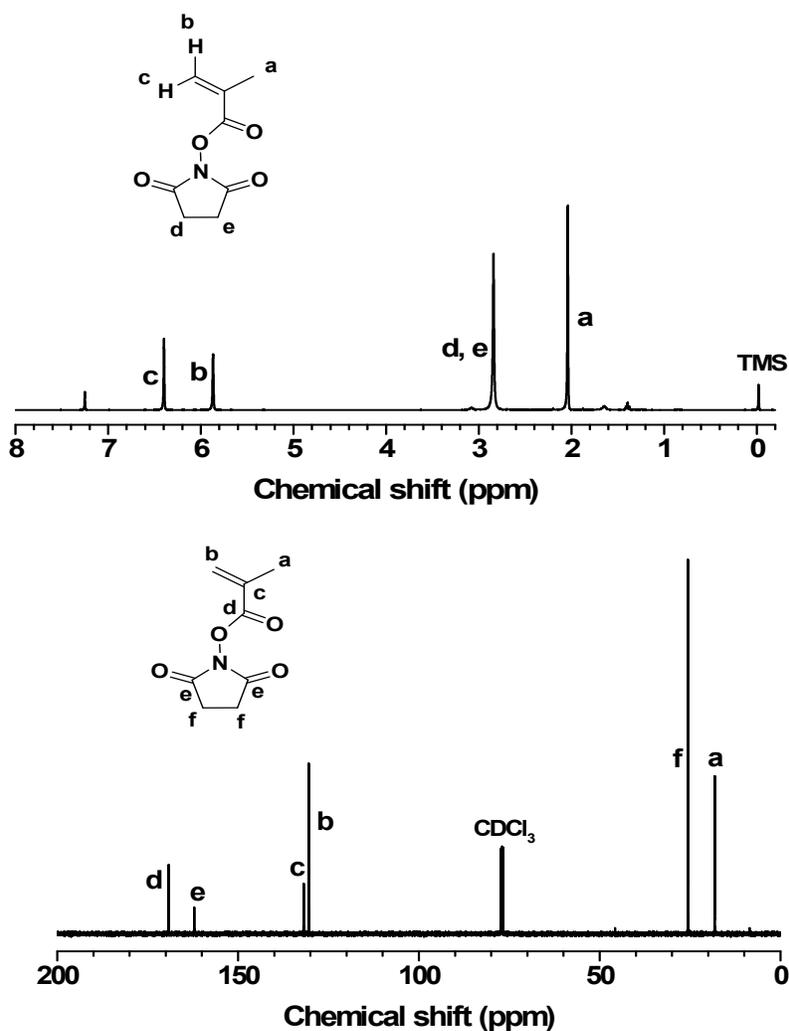
**Figure S5.** Particle sizes and their distribution of the CPT-loaded uncross-linked and cross-linked micelles (NCL-P3 and SCL-P3)

**Figure S6.** UV-Vis absorption of the CPT standard solutions

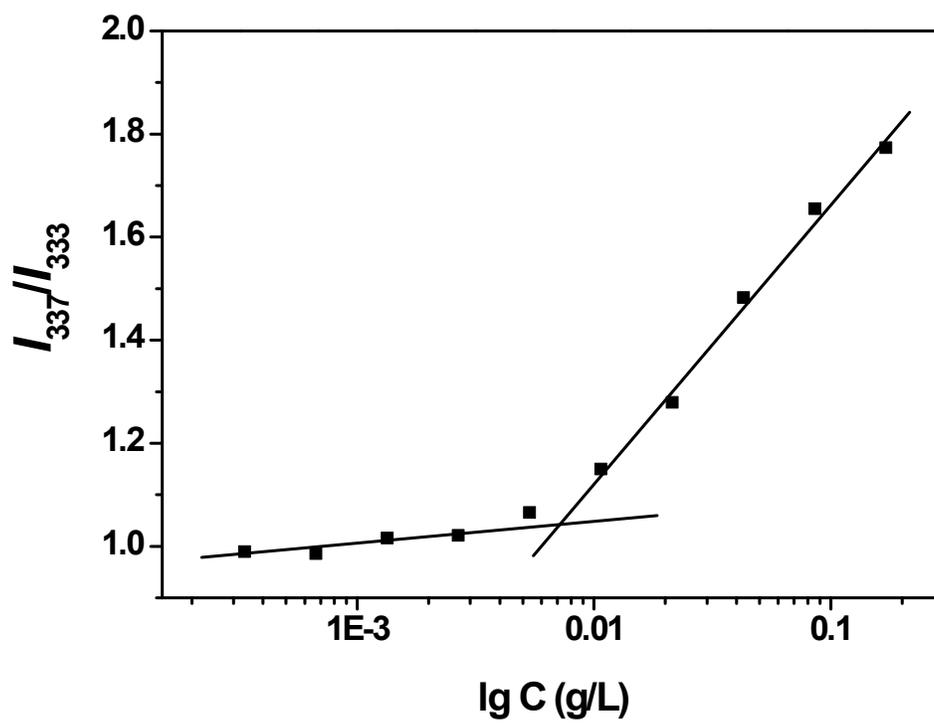
### S1. Synthesis of the NMS monomer



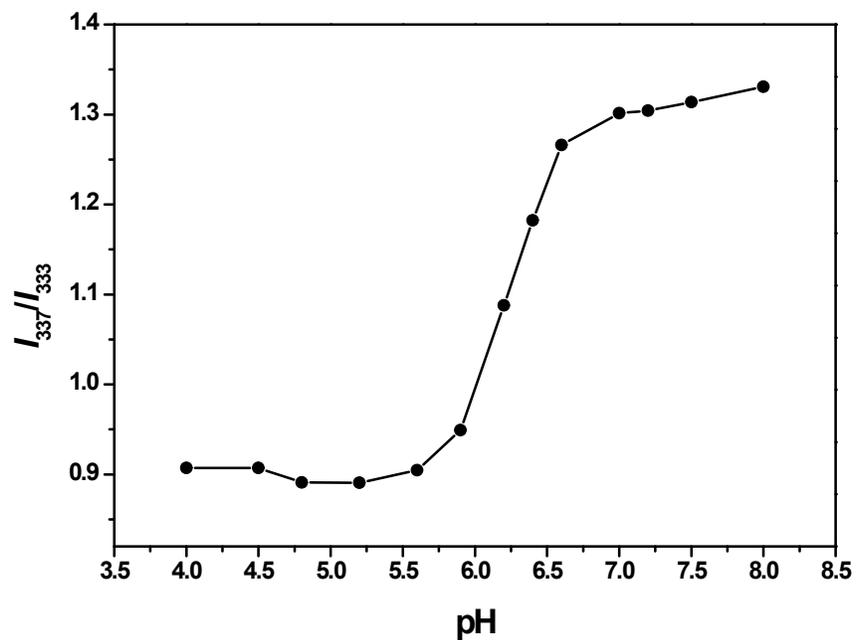
N-hydroxysuccinimide (9.6 g, 0.083 mol) and triethylamine (8.4 g, 0.083 mol) dissolved in 150 mL chloroform, the methylacryloyl chloride (10.4 g, 0.1 mol) in 150 mL chloroform was added dropwise at 0°C for 7 h, the organic layer washed by 10% sodium bicarbonate and distilled water, and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed under reduced pressure and the residue was recrystallized by ethyl acetate/hexane to get white crystals (10.6 g, Yield: 70%).



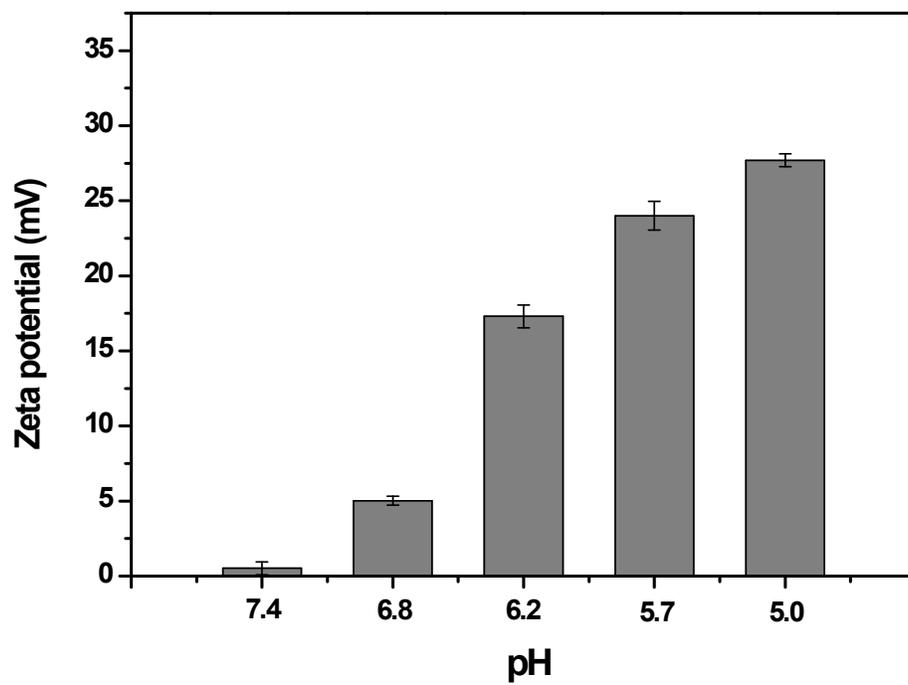
**Figure S1.** <sup>1</sup>H NMR (a) and <sup>13</sup>C NMR (b) spectrum of the NMS monomer in CDCl<sub>3</sub>



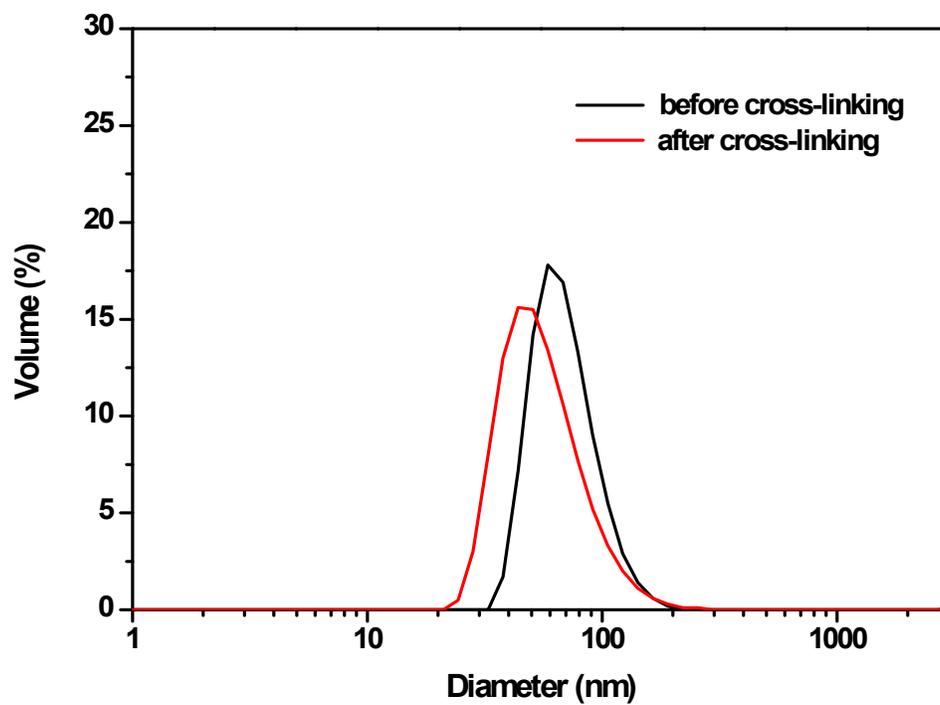
**Figure S2.** Plots of fluorescence excitation intensity ratio ( $I_{337}/I_{333}$ ) of pyrene probe versus mass concentration of the PDPA<sub>33</sub>-*b*-P(NMS<sub>22</sub>-*co*-OEG<sub>25</sub>) (P3) copolymers



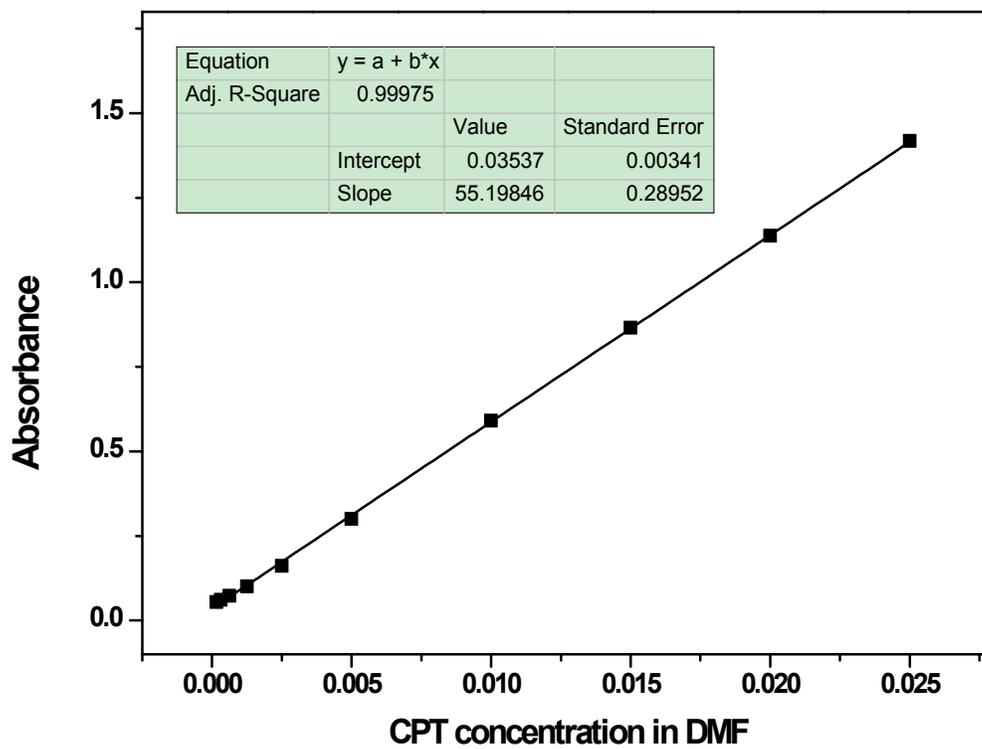
**Figure S3.** Plots of fluorescence excitation intensity ratio ( $I_{337}/I_{333}$ ) of pyrene-loaded NCL-P3 micelles versus different pH value



**Figure S4.** Protonation of the SCL-P3 micelles under various pH by Zeta potential measurement



**Figure S5.** Particle size and distribution of the CPT-loaded uncrosslinked and crosslinked micelles (NCL-P3 and SCL-P3)



**Figure S6.** UV-Vis absorption of the CPT standard solutions