

**Supporting information for**

**Dual responsive Pickering emulsions stabilized by the  
constructed core crosslinked polymer nanoparticles *via*  
reversible covalent bonds**

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## S1. The $^1\text{H}$ NMR spectra of EMP (A) and APBA (B)

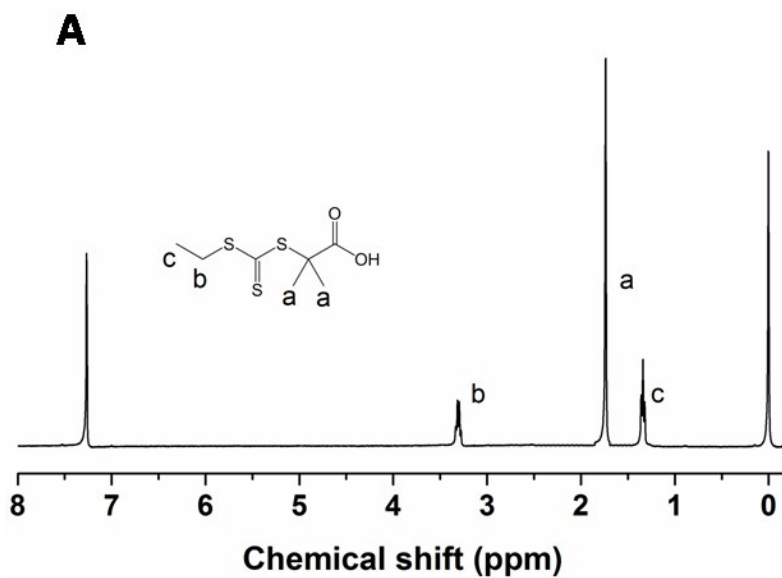


Fig. S1.  $^1\text{H}$  NMR spectrum of EMP

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =3.30 (q, 2H,  $\text{SCH}_2$ ), 1.73 (s, 6H,  $\text{C}(\text{CH}_3)_2$ ), 1.34 (t, 3H,  $\text{CH}_2\text{CH}_3$ ).

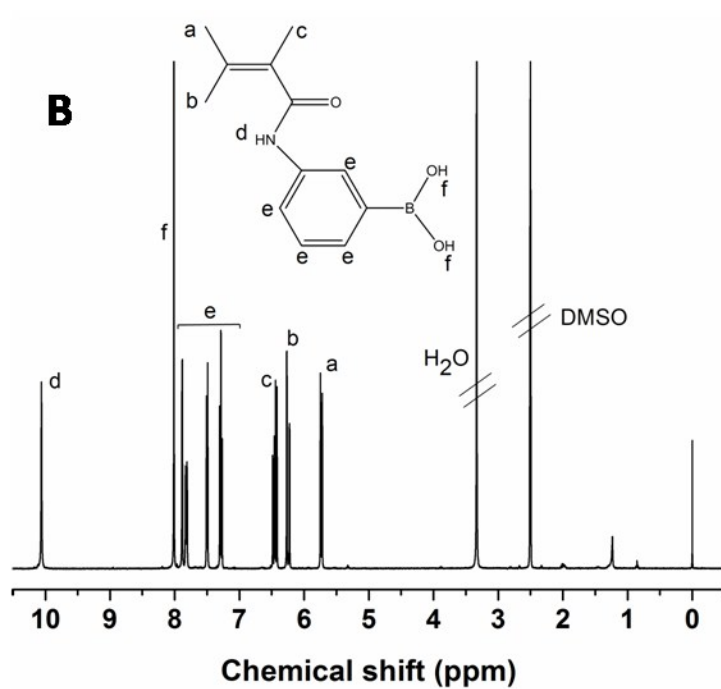


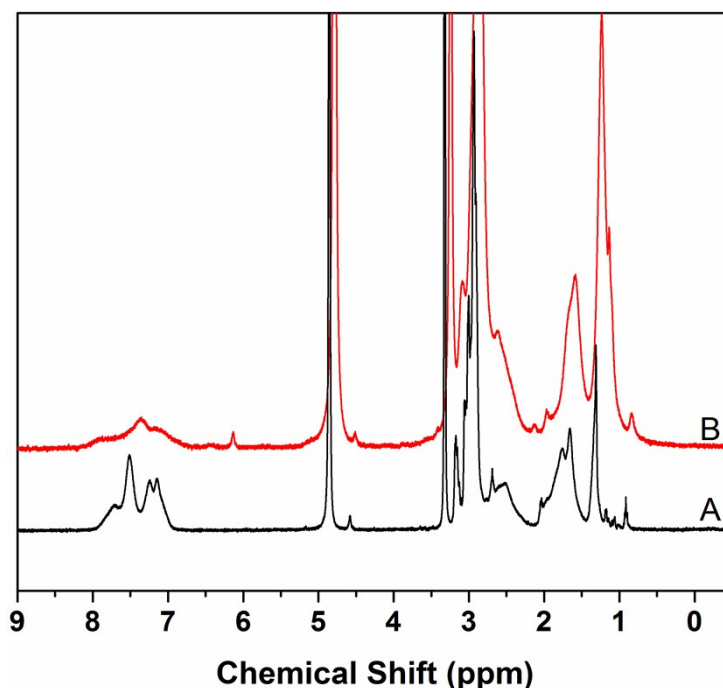
Fig. S2.  $^1\text{H}$  NMR spectrum of APBA

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ): 10.07 (s, 1H, NH), 8.00 (s, 2H,  $\text{B}(\text{OH})_2$ ), 7.89, 7.83-7.81, 7.51-7.49, 7.31-7.29 (s, d, d, t, 1H each, ArH), 6.46-6.42, 6.27-6.22 (2d, dd, 1H each,  $-\text{CH}_2-$ ),

5.75-5.72 (dd, 1H, -CH-).

## S2. The protection of PDMA-*b*-PAPBA diblock copolymer by pinacol

A protection procedure is implemented as described previously elsewhere [1]. PDMA-*b*-PAPBA (0.10 g, 0.005 mmol), pinacol (0.6 g, 5.0 mmol), and molecular sieves (4Å) were placed in a round-bottom flask. Anhydrous DMF (10 mL) was added, and the mixture was stirred under N<sub>2</sub> at 90 °C for 24 h. The mixture was filtered, and the polymer was precipitated into cold diethyl ether.



**Fig. S2.** <sup>1</sup>H NMR spectra of PDMA-*b*-PAPBA diblock copolymer (A) before and (B) after protection by pinacol.

<sup>1</sup>H NMR spectroscopy was used to confirm the successful protection. Fig.S2 showed the <sup>1</sup>H NMR spectra of the original PDMA-*b*-PAPBA diblock copolymer and the PDMA-*b*-PAPBA protected by pinacol. An obvious resonance peak at  $\delta = 1.26$  ppm, corresponding to the ester methyl protons, appeared in the <sup>1</sup>H NMR spectroscopy of the protected PAPBA-*b*-PDMA.

### S3. Dependence of size of CCPNs on the ratio of the mass of PVA to that of diblock copolymer and the composition of diblock copolymer

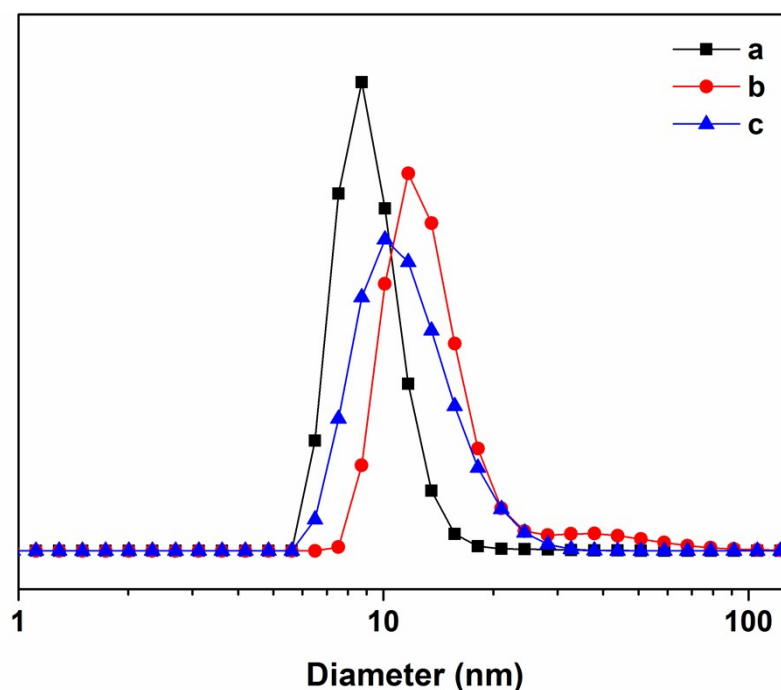
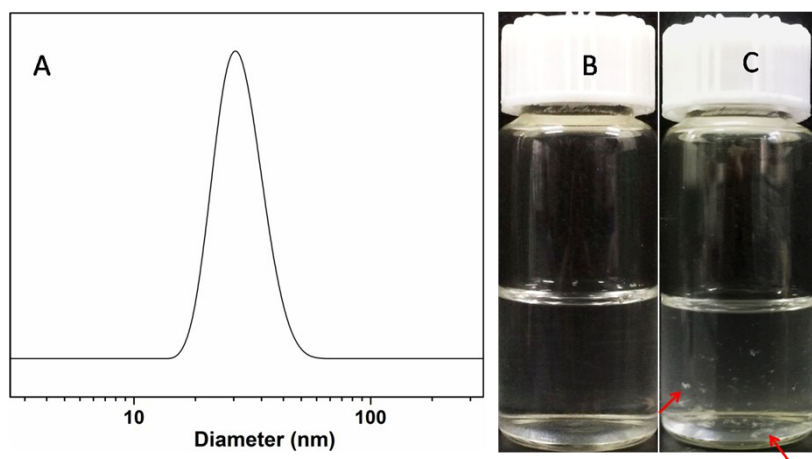


Fig.S3. DLS traces of CCPNs formed at varied conditions

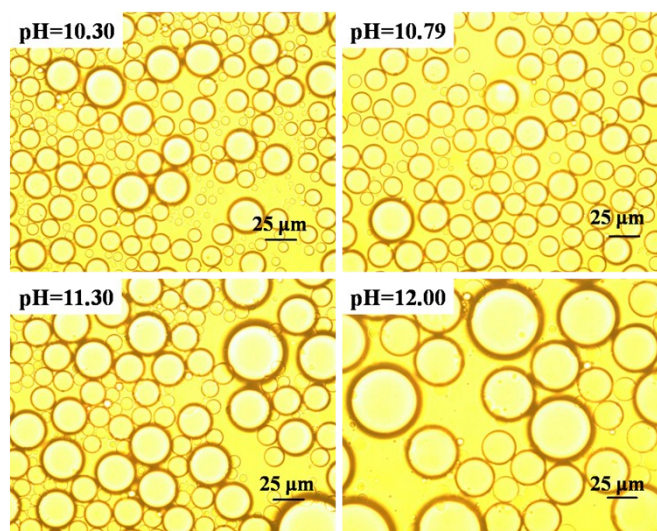
The size of CCPNs was dependent on both the ratio of the mass of PVA to that of the diblock copolymer and the composition of diblock copolymer. For PDMA<sub>29</sub>-*b*-PAPBA<sub>19</sub>, the  $\langle D_h \rangle$  values of the formed CCPNs were about 9 (trace a) and 13 nm (trace b) when the mass ratios of PVA to PDMA<sub>29</sub>-*b*-PAPBA<sub>19</sub> diblock copolymer were 1/20 and 3/20, respectively. For a fixed mass ratio of PVA to diblock copolymer of 1/5, the  $\langle D_h \rangle$  of the formed CCPNs was ~12 nm with a broader distribution when PDMA<sub>29</sub>-*b*-PAPBA<sub>10</sub> was used for the formation of CCPNs (trace c). The DLS measurements were conducted after 24 h of stirring at room temperature.

### S4. Micelles formed by self assembly PDMA<sub>29</sub>-*b*-PAPBA<sub>19</sub> diblock copolymers in the selected solvent of water and their structure transition with the variation of pH



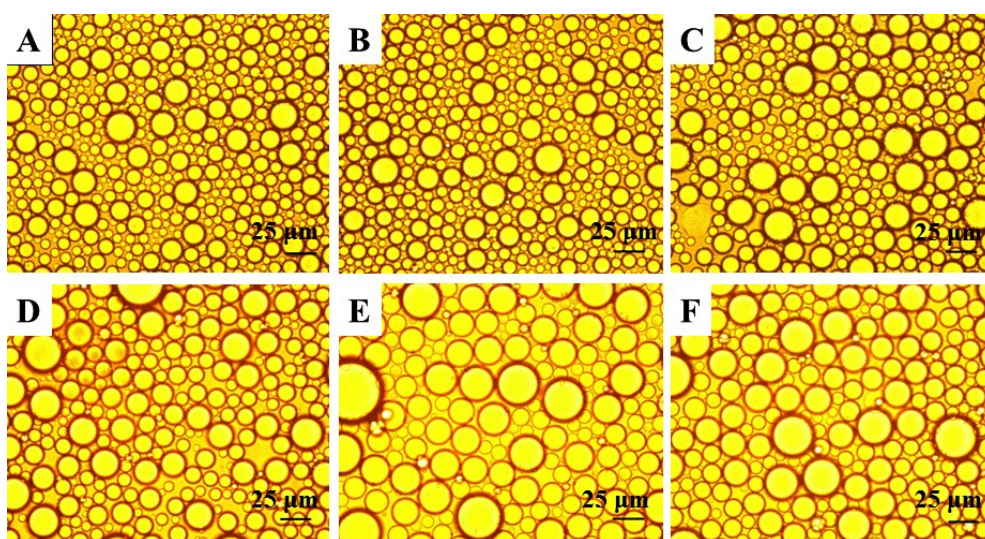
**Fig.S4.** (A) DLS curve of micelles formed by the self assembly PDMA<sub>29</sub>-*b*-PAPBA<sub>19</sub> diblock copolymers in the selected solvent of water; (B) The photograph of PDMA<sub>29</sub>-*b*-PAPBA<sub>19</sub> micelles (pH=7.63) aqueous dispersion at a concentration of 2 mg/mL; (C) The PDMA<sub>29</sub>-*b*-PAPBA<sub>19</sub> micelles disassociated completely into polymer unimers when pH was improved from 7.63 to about 12. Meanwhile, the polymer was found to be precipitated because of the salt effect when pH was readjusted back to ~7.63, as indicated by arrow in Fig.S4C.

**S5. The effect of pH on the stabilities of Pickering emulsions stabilized by 0.16% of CCPNs**



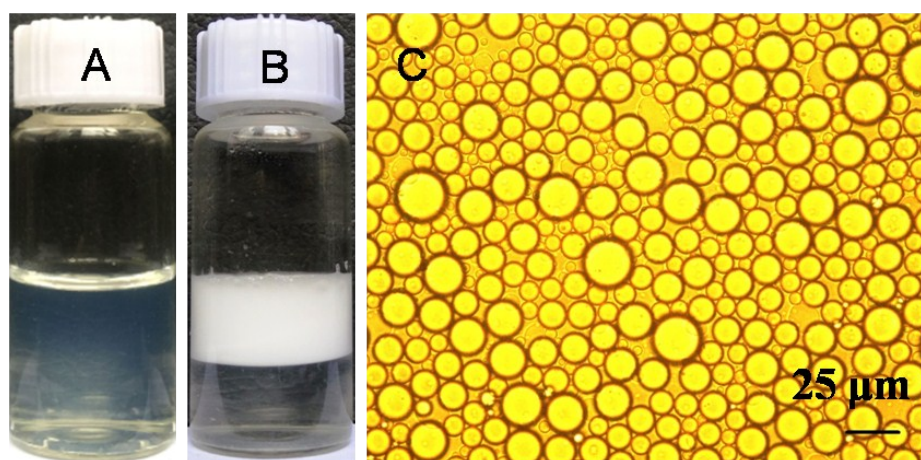
**Fig. S5.** The optical microscope images of the Pickering emulsion droplets stabilized by 0.16% of CCPNs at different pHs. The average size of emulsion droplets were about 15, 16, 18 and 27  $\mu\text{m}$ , corresponding to pHs of 10.3, 10.79, 11.3 and 12, respectively.

**S6. The optical microscope images of the emulsion droplets corresponding to the different emulsification/deemulsification cycles**



**Fig. S6.** The optical microscope images of the emulsion droplets corresponding to the different emulsification/deemulsification cycles of A: the primary emulsion; B: the first cycle; C: the second cycle; D: the third cycle; E: the fourth cycle; F: the fifth cycle. The CCPNs content: 0.16%. With the increase of cycle number, the salt concentration increased. The droplets also showed a slight increase in the average size.

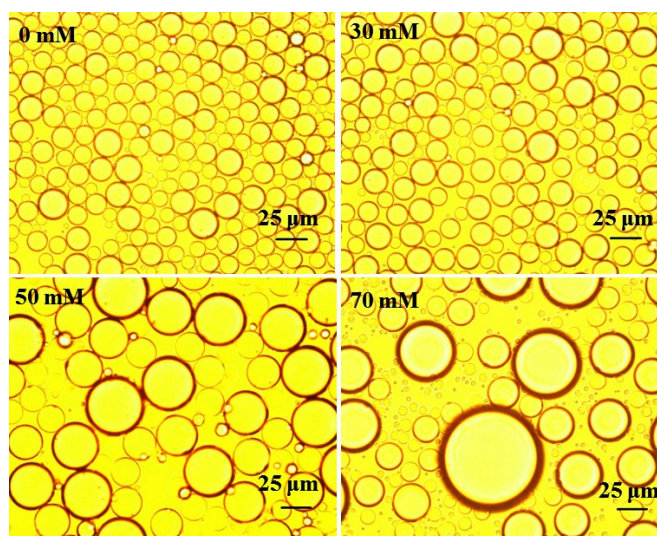
**S7. Pickering emulsion stabilized by 0.16% of PDMA<sub>29</sub>-*b*-PAPBA<sub>19</sub> micelle nanoparticles with PVA chains in cores, which were originated from the transition of CCPNs**



**Fig.S7.** (A) The photograph of PDMA<sub>29</sub>-*b*-PAPBA<sub>19</sub> micelles with PVA chains in cores; (B) Pickering emulsion stabilized by 0.16% of PDMA<sub>29</sub>-*b*-PAPBA<sub>19</sub> micelles

with PVA chains in cores; (C) The optical microscope images of the emulsion droplets. The average diameter of the droplets was about 11.6  $\mu\text{m}$ , and the value was almost the same as that of Pickering emulsion stabilized by 0.16% of CCPNs. The photograph of Pickering emulsion was taken after 24 h of placement.

### S8. Glucose-induced deemulsification of CCPNs stabilized Pickering emulsions at pH 10.79



**Fig.S8.** The optical microscope images of the Pickering emulsion droplets at pH 10.79 stabilized by 0.16% of CCPNs in the presence of different concentrations of glucose of A: 0 mM; B: 30 mM; C: 50 mM; and D: 70 mM. The average droplet size showed an obvious increase with the increase of the concentration of glucose. The average droplet size was about 16  $\mu\text{m}$  for A, 17  $\mu\text{m}$  for B, 28  $\mu\text{m}$  for C, and 31  $\mu\text{m}$  for D, respectively, indicating the coalescence of the droplets after the addition of glucose. After the solid glucose was added, the emulsion was stirred for 30 min, and the image was randomly taken for each sample. The content of CCPNs was 0.16% for all the Pickering emulsions.

#### Reference

1. D. Roy, J. N. Cambre, B. S. Sumerlin, Sugar-responsive block copolymers by direct RAFT polymerization of unprotected boronic acid monomers. *Chemical Communications*, 2477-2479 (2008).