# Supporting information

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### **Experimental section**

Milli-Q water was used throughout all experiments, all of chemical reagents were used without further purification. N,N'-isopropylacrylamide (NIPAM, 97%), N,N'- methylenebisacrylamide (MBA, 99%), toluene (99.7%), rhodamine b, 1-octadecene, anthracene, sodium hydroxide, hydrochloric acid (32%), potassium persulfate (APS), potassium chloride were purchased from Sigma-Aldrich; Span 80 was used as surfactant and obtained from Fluka, and acrylic acid (AA, 99.5%) were purchased from Acros.

## 1. Synthesis of particles

(a) Bi-compartmental copolymer particles

P(NIPAMA-co-AA) copolymer particles were synthesized using a 100 mL three-neck flask under flowing nitrogen atmosphere. Span 80 was used as surfactant and mixed with toluene; monomers with a certain molar ratio, APS and hydrochloric acid were put into water phase. The system was emulsified before polymerization. In all experiments, the concentration of hydrochloric acid, APS and monomers were respectively kept at 1M, 4 mM and 0.5 M. Typically, Span 80, the water phase and toluene were mixed with a volume ratio of 1:8:100, while the molar ratio among NIPAM, AA and MBA is 15:5:1. After deoxygenation by N<sub>2</sub> for 1 hour, the polymerization was initiated by heating the mixture to 70°C. Polymer particles were collected by centrifugation after polymerization. The liquid was decanted and the product was dispersed into solvent and centrifuged again. After washing enough with toluene, acetone and water, a gel-like product was obtained.

## (b) Pure PNIPAM particles and PAA particles

Pure PNIPAM particles were synthesized by acid emulsion polymerization of NIPAM and MBA with the ratio at 20:1. The feed ratio of surfactant, the content of acid, the ratio of toluene to water and all reaction conditions were the same as described in the synthesis of bi-compartmental particles. The preparation of PAA particles was the same as the synthesis of PNIPAM by using AA as monomers.

#### 2. Instruments

All SEM images were obtained by environmental scanning electron microscope Philips XL 30 ESEM-FEG under vacuum. Transmission electron microscopy (TEM) micrographs were obtained with a JEOL 2100 instrument. The Atomic Force Microscope (AFM) images of polymer bi-compartmental particles were recorded by a digital multimode Nanoscope III (Digital Instruments, Santa Barbara, CA) scanning force microscope, equipped with a J-scanner. All measurements were performed using a SiC tip with tapping mode at room temperature. The sizes of the particles were measured by dynamic light scattering analysis on a Zetatrac and Nanotrac by Anaspec operating with a Microtrac FLEX Operating Software. <sup>1</sup>H nuclear magnetic resonance spectra were recorded on a BrukerAscend <sup>TM</sup> 400 NMR spectrometer using deuterated methanol-D4 as solvent. IR spectrum was measured by an Nicolet 6700 FTIR spectrometer. The content of carboxyl groups in bi-compartmental particles was measured in water by potential titration using a digital pH meter equipped with a glass electrode. The optical photographs were taken by Cannon digital camera. The fluorescent images were taken by an Olympus IX71 fluorescent microscope.

#### Supporting figures and data analysis

## 1. The size of bi-compartmental particles



Fig. S1 The hydrodynamic size of bi-compartmental copolymer particles in water, which was measured by DLS. Particles were the same as that in figure 1, which were synthesized in acid/toluene emulsion by polymerization for 2h at 70°C with the ratio of NIPAMA to AA at 3.

### 2. Measurement of the composition of bi-compartmental particles

The composition of bi-compartmental particles was characterized by IR, <sup>1</sup>H NMR and potential titration.

(a) <sup>1</sup>H NMR and IR spectra of bi-compartmental particles



Fig. S2 A) Infrared spectrum measured by using pure particles dried, where carboxyl group derived from AA and amide group derived from NIPAM was shown clearly. B) 1H-NMR spectrum of bi-compartmental copolymer particles measured in deuterated d4-methanol. Particles were synthesized with ratio of NIPAM to AA at 3. These spectra reveal that particles chemical composition is P(NIPAM-AA).

(b) Analysis of particles composition

Infrared spectrum (IR) indicated a typical P(NIPAM-AA) copolymer. In figure S2A, the strong absorption at 1626 and 1547 cm-1 are attributed to amide I band (C=O stretching) and amide II (N-H bending) band, respectively, which derived from NIPAM; the absorption at 1717 cm<sup>-1</sup> is attributed to C=O stretching of carboxyl group, which resulted from AA. Nuclear magnetic resonance spectrum (<sup>1</sup>H NMR) was measured in deuterated methanol (figure S2B). The peaks at 3.0-3.5 ppm and the peak at 4.8-5.2 ppm were respectively ascribed to methanol and water, which were removed from the spectrum. The chemical shifts at 1.2, 4.0 ppm were respectively from CH<sub>3</sub> and CH of amide group in NIPAM, and 2.7 ppm resulted from AA according to literature<sup>i</sup>. The peak at  $\delta$ =1.6 ppm and  $\delta$ = 2.2 ppm was respectively ascribed to backbone CH<sub>2</sub> and backbone CH. The result indicates a typical P(NIPAM-co-AA) polymer. The content of NIPAM was evaluated by comparing the integral areas between the peak of NIPAM units at 4.0 ppm and the peak of backbone CH<sub>2</sub> at 1.6 ppm, which is around 67 mol.%.

(c) Potentiometric Titration of AA Content

In order to investigate the ratio of two parts in bi-compartmental particles dependent on the feed ratio of AA, a series of bi-compartmental particles were synthesized by acid emulsion polymerization for 4 hours with different feed ratio of monomers, whereof the AA feed ratio was respectively 17 wt.%, 36 wt.%, 60 wt.%, while the feed of crosslinker MBA was kept at 5 mol%. AA content of P(NIPAM-co-AA) was measured using potentiometric titration according to literature<sup>ii</sup>. Because particles were prepared in HCl solution, so they were used directly after the products were washed enough with organic solvent, e.g. toluene, ethanol and acetone and dried at 100 °C under vacuum. For pH titration, the particles were suspended in 100 mM KCl at a concentration of 1 mg/mL and titrated with 100 mM NaOH and 100mM HCl solution. The titration was carried out two circles by pH meter from Mettler Toledo GmbH. The content of AA units was respectively 20 wt%, 38 wt% and 58 wt%; which is basically in agreement with the feed ratio.

#### 3. The shape of bi-compartmental particles



Fig. S3 Bi-compartmental polymer particles. A) SEM image of particles with larger view-field; B) TEM image of particles. Particles were the same as that in figure 1. TEM sample was stained with uranyl acetate.



4. Recovered shape of bi-compartmental particles

Fig. S4 (A) SEM image of bi-compartmental polymer particles dried out of acetone dispersion; (B) SEM image of bi-compartmental polymer particles dried from water after treated with acetone, which means that the alteration of shape is reversible. The particles are the same as those in Fig. 1 A/B, which were just dispersed into acetone before put into water and dried. The result exhibits that bi-compartmental particles could change their shape when the solvent changed from water to acetone, and the alteration was reversible.

## 5. Composition analysis of bi-compartmental particles by monomers ratio



Fig. S5 The ratio of two compartments in particles dependent on the content of AA. A-F) SEM images of polymer particles with different content of AA units. A, D) 20%; B, E) 38%; C, F) 58%; G) Relationship between the ratio of R/r and the concentration of carboxyl groups in polymer. The polymerization temperature is 70°C and reaction time is 4 hours. R and r is respectively the diameter of dark part and bright part;  $C_{COOH}$  is the content of AA units measured by potentiometric titration. All samples were prepared by using different feed ratio of NIPAM to AA from 75:25 to 25:75 when the feed ratio of MBA was fixed at 5 mol%. The results indicates that the ratio of dark area to the bright area increase with the feed ratio of AA to NIPAM, which means that the two part respectively derived from two different monomers: AA and NIPAM.

### 6. The influence of crosslinker MBA on particles shape



Fig. S6 SEM images of polymer particles prepared in acid emulsion with different feed ratio of crosslinker (MBA) to monomers (the ratio of NIPAM to AA was kept at 3). A, D) 2.5 mol%; B, E)10 mol%; C, F) 20 mol%. The diameter ratio of two parts is basically kept constant, which further proves that the two parts mainly derived from NIPAM and AA. The result indicates that the alteration of two parts is not related with crosslinker.

<sup>&</sup>lt;sup>i</sup>S. Chen, L. Jiang, Y. Dan, J. Appl. Polym. Sci., 2011, **121**, 3322.

<sup>&</sup>quot;T. Hoare, R. Pelton, *Langmuir*, 2004, **20**, 2123.