

Electronic Supplementary Materials:

**Polymeric Core-Shell Stars with a Novel Fluorescent, Cross-Linked
and Swollen Core: Their Efficient One-Step Preparation, Further
Self-Assembly into Superparticles and Application as a Chemosensor**

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S1. Static light scattering results of the pure block polymer and the aggregates resulted from the reaction between P4VP-b-PS and PB in DMF for 50 hours

M_w s of the pure block polymer and the aggregates were measured by SLS to be $1.35E5$ g/mol and $4.58E6$ g/mol (Figure S1A and Figure S1B), respectively. Assuming 100% quaternization of pyridine unit of the block polymer by PB, the aggregation number of the core-shell stars was then calculated to be 26.

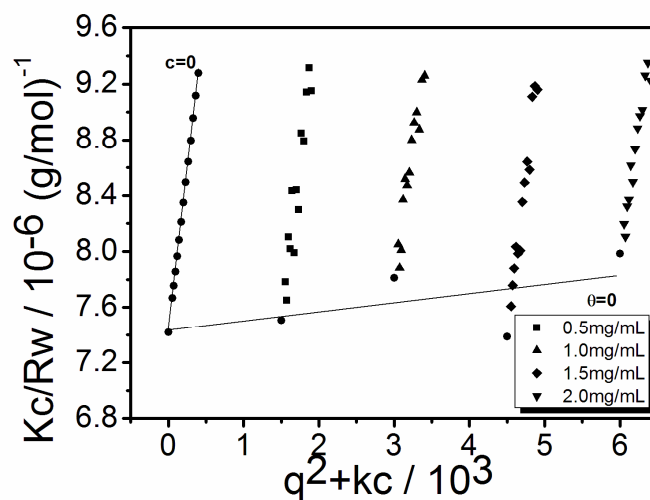


Figure S1A. SLS curve of the block polymer.

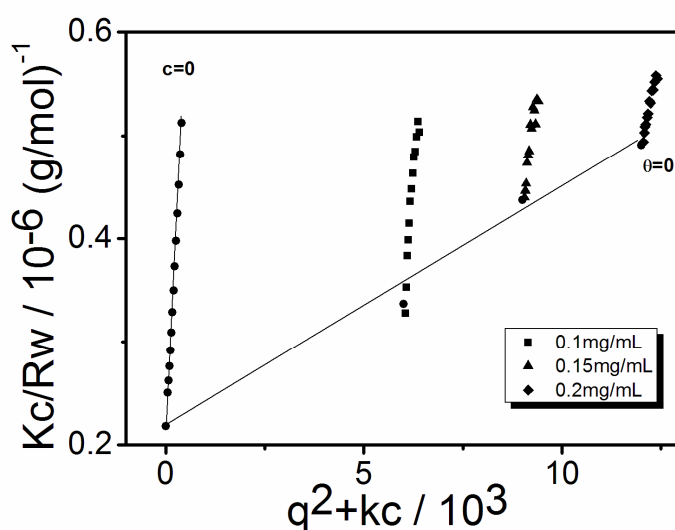


Figure S1B. SLS curve of the aggregates.

S2. Control experiment of the reaction between P4VP and PB

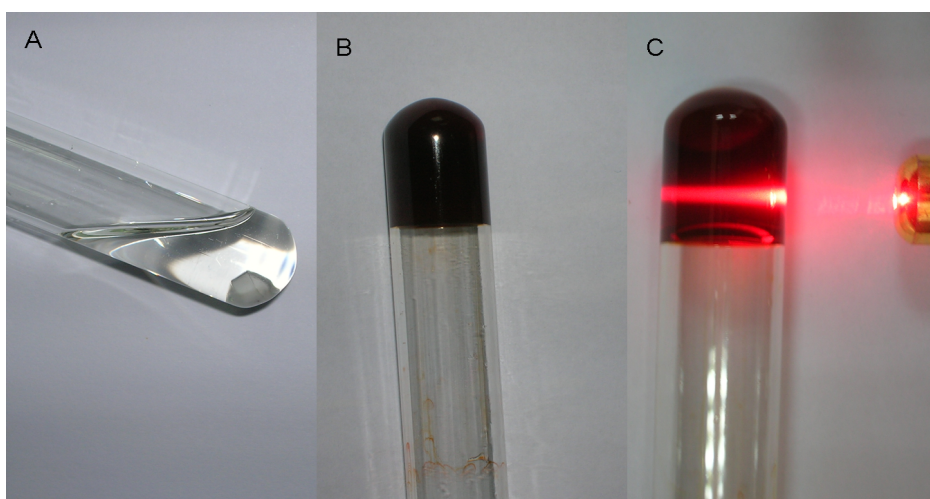


Figure S2. Control experiment. (A) Solution of P4VP in DMF, (B, C) the gel formed after the reaction between PB and P4VP in DMF at 60 °C for 10 hours. The P4VP ($M_w=42500$, $M_w / M_n=1.17$) used here was purchased from Polymer Source Inc. The molar ration between the 4VP units and PB is 1:1.

S3. Determination of the content of the alkyne groups:

Pyridinium signal at 8.67 ppm in the ^1H NMR spectra is used for the determination of the content of residual alkyne groups. All pyridinium groups in the nanoparticles can be divided into two parts: pyridinium groups connected to unpolymerized propargyl (i.e., the remaining alkyne groups), and those to polymerized propargyl. In the ^1H NMR spectrum in deuterated DMF, the pyridinium groups that connected to polymerized propargyl are as the cross-linking points to form the cross-linked network. Therefore, their mobility is seriously restricted so

that the pyridinium groups connected to polymerized propargyl are undetectable by the liquid ^1H NMR. Whereas, the pyridinium groups that are connected to unpolymerized propargyl groups are soluble in the medium and are detectable by the liquid ^1H NMR, as indicated in the text. This pyridinium signal (at 8.67 ppm) can be used for determination of the propargyl groups (the molar ratio of detectable pyridinium groups to the remaining alkyne groups should be 1:1). Assuming that all the pyridine groups were reacted, the intensity ratio of the pyridinium signal in the spectrum of the nanoparticles to the pyridine signal in the spectrum of the primary block copolymer should be the molar ratio of the remaining alkyne groups within the particle to the sum of unpolymerized and polymerized grafted propargyl groups, which is determined to be 28% using S_d/S_a .

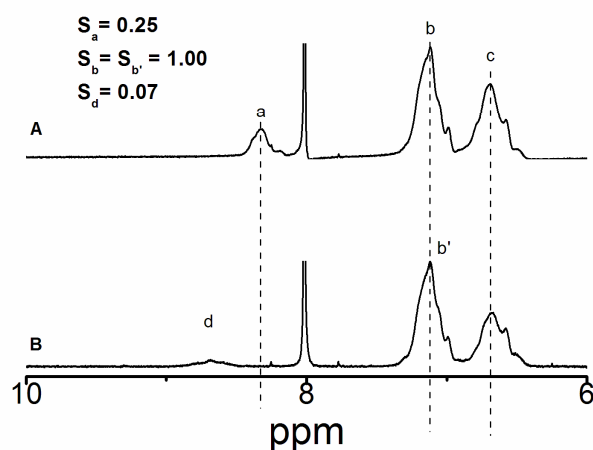


Figure S3. ^1H NMR spectra in DMF-d_7 of the PS-b-P4VP (A) and the PS-b-P4VP/PB nanoparticles after reaction time of 50h (B). S_a , S_b , $S_{b'}$ and S_d represent the peak areas of peak, a, b, b' and d, respectively.

S4. Number-averaged DLS curve of the primary core-shell stars formed at $t=50$ h

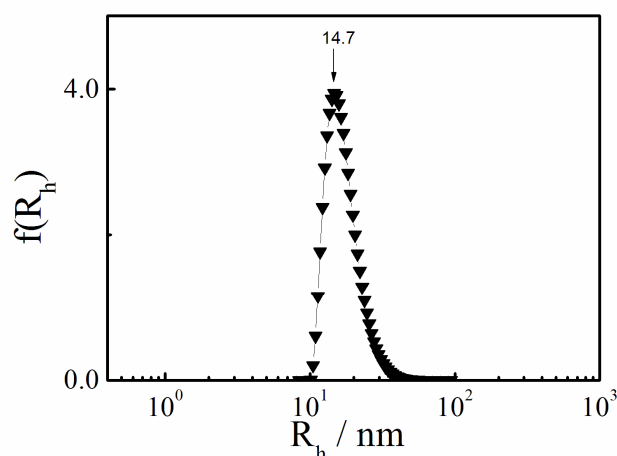


Figure S4. Number-averaged DLS curve of the primary core-shell stars

S5 Discussion on the mechanism for stabilization of the superparticles in water:

We measured the ^1H -NMR spectrum of superparticles in D_2O . However, in the spectrum, no any signal can be seen. It is noted that although the pyridinium groups of unpolymerized propargylpyridinium give a signal in the ^1H NMR spectrum of the primary particles in deuterated DMF, they are undetectable in the ^1H NMR spectrum of the superparticles in D_2O . It seems that the propargylpyridinium groups, as a whole, are insoluble in water due to the existence of the hydrophobic propargyl groups that are soluble in DMF but insoluble in water. The statement that “the hydrophilic pyridinium stabilized PS core” in the original manuscript is incorrect. To reveal the mechanism for stabilization of the superparticles in water, we measured the zeta potential of the aqueous suspension of the superparticles (at 0.5 mg/mL) to be about 40 mV (measured at 25 °C on a ZetaSizer Nano ZS90 (Malvern Instruments) equipped with a 4mWHe-Ne Laser (λ 633 nm) using the technique of laser Doppler electrophoresis). According to literature, this zeta potential value is large enough to stabilize the superparticles in water. Therefore, the superparticles are actually stabilized by the charges contributed by the pyridinium groups. We revised the sentence “the hydrophilic pyridinium stabilized PS core” as “the charges contributed by the pyridinium groups stabilized the superparticles in water”.

S6. Discussion on the resource of the fluorescent emission:

The resource of the fluorescent emission should be polyacetylene, as stated in the text. This is based on the experimental data and also consistent with the results reported in literature. 1): Propargyl bromide molecules can quaternize pyridine groups in the repeat units of the P4VP, grafting propargyl groups onto the P4VP block chains. This is confirmed by appearance of pyridinium signals in both the FT-IR spectrum (as indicated in Figure 2 in the text) and ^1H NMR spectrum (peak d in Figure 3 in the text). 2): (a) The polymerization of the acetylene groups in the grafted propargyl groups into polyacetylene was demonstrated by appearance of the relatively strong signal of carbon-carbon double bonds in the FT-IR spectrum of the nanoparticles (indicated in Figure 2 in the text). (b) The polymerization of acetylene groups in propargylpyridinium chloride into polyacetylene was reported by Kabanov et al. (US patent, 3658942, 1972; J. Appl. Polym. Sci., 1975, 19, 1275). (c) In our control experiment of reacting pyridine with propargyl bromide in DMF, a fluorescent polymer with a molecular weight about 18,000 was formed. This fluorescent polymer should result from the polymerization of the acetylene groups in the propargylpyridinium bromide, which leads to a substituted polyacetylene. 3): The fluorescence of polyacetylene has been reported in a lot of research papers.

S7. UV-visible spectrum

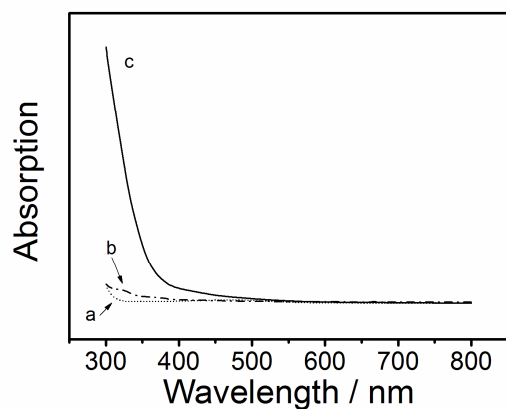


Figure S5. UV-visible spectrum of PB (a), Block Polymer (5 mg/mL, b) and the core-shell stars (1 mg/mL, c) in solvent DMF.

S8. Z-averaged distribution of hydrodynamic radius of the core-shell stars at different concentrations

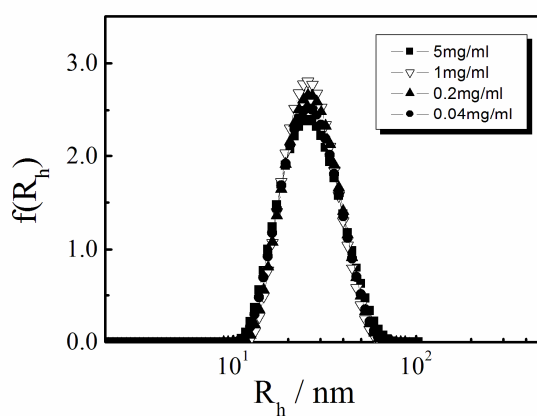


Figure S6. Z-averaged distribution of hydrodynamic radius of the core-shell stars at different concentrations.