Supporting Information

The fabrication of amphiphilic double dynamers for the responsive Pickering emulsifiers

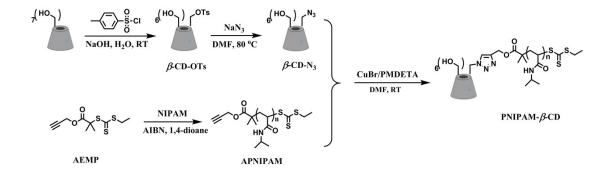
Ting Zeng,^a Duanguang Yang^a, Huaming Li^{a,b}, Chong Cheng ^{c*}, and Yong Gao^{a,b*}

^a College of Chemistry, Xiangtan University, Xiangtan, Hunan Province 411105, China;

^bKey Lab of Environment-friendly Chemistry and Application in Ministry of Education; Key Laboratory of Polymeric Materials & Application Technology of Hunan Province, Key Laboratory of Advanced Functional; Polymeric Materials of College of Hunan Province, Xiangtan, Hunan Province 411105, China; ^cDepartment of Chemical and Biological Engineering, University at Buffalo, The

State University of New York, Buffalo, New York 14260, USA.

* Corresponding author: ccheng8@buffalo.edu; gydx.1027@163.com



S2. The ¹H NMR proof for the formation of the inclusions

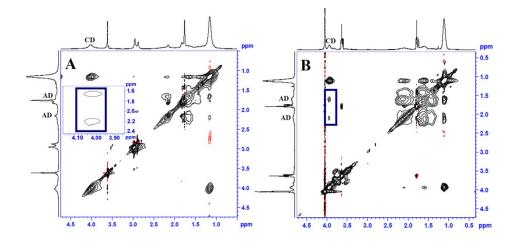


Fig. S1. 2D ¹H NOESY spectra of the PNIPAM- β -CD host and PMMA-b-PAMPMA guest in different media: ((A) d_4 -THF, (B) the mixture of d_4 -THF and D₂O (d_4 -THF/D₂O = 10:1 (v/v))

A weak NOESY cross-peak between the β -CD and the AD was monitored in d_{4^-} THF, however, a strong NOESY cross-peak signal occurred at $\delta = 1.60-2.16$ ppm was observed in the d_4 -THF/D₂O (v/v, 10:1).

S3. DLS traces of polymer particles in different media (A: THF/water (1:1, v/v) before dialysis; B: pure water; C: THF/water (1:1, v/v))

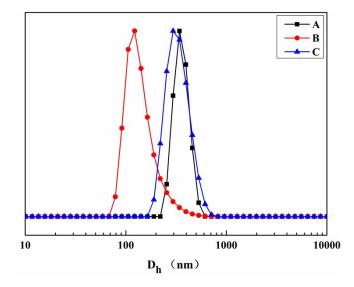


Fig. S2. DLS traces of polymer particles in different solvents, A: THF/water (1:1, v/v) before dialysis; B: pure water; C: THF/water (1:1, v/v)

The average size of the aggregates was about 360 nm in the THF/H₂O mixture with 50% of water content (trace A). After the complete removal of THF by dialysis against the water, the final size of the aggregates was about 145 nm in the pure water (trace B). Upon the addition of THF into the dispersion of polymer particles in the pure water, and the final volume fraction of THF reached 50%. After 30 min of gentle stirring at room temperature, $D_{h,N}$ of the polymer particles was about ~340 nm (trace C), showing a $D_{h,N}$ very similar to the value before dialysis. This suggested in turn that the remarkable size reduction of polymer particles was mainly ascribed to the shrinking of the core, which was the result of the removal of the good solvent of THF for core during the dialysis.

S4. Size and morphologies of the polymer particles obtained by self-assembly of the double dynamers under different conditions

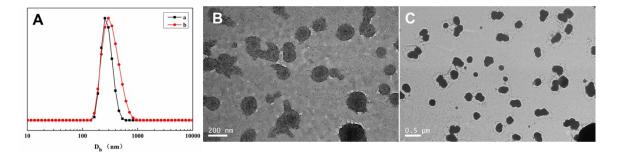


Fig .S3. (A) DLS traces and (B and C) TEM images of the polymer particles obtained by self-assembly of the double dynamers under different conditions. Conditions: a and B: mole ratio of β -CD/AD was 0.5 and the M_n of PNIPAM was 3400 g/mol; b and C: mole ratio of β -CD/AD was 1, and the M_n of PNIPAM was 9500 g/mol.

S5. The photos of the morphological transition of the polymer particles in response to the external stimuli



Fig.S4. The photograph of polymer particles in pure water at different conditions: (A) room temperature and pH 7; (B) 38 °C and pH 7; (C) cooling from 38 °C to room temperature and pH 7; (D) room temperature and pH 5

S6. The variation of the average hydrodynamic diameters $(D_{h,N})$ of polymer particles in water at pH5

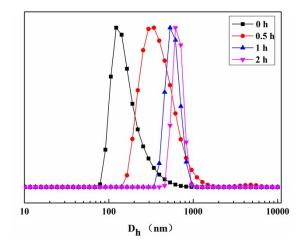


Fig. S5. Time-dependence of $D_{h,N}$ of polymer particles in water solution at pH 5

Upon decreasing the pH value from 7 to 5, the size of the polymer particles showed a remarkable increase within a short time. Finally, the precipitation of polymer was observed.

S7. The DLS proof for the insolubility of the PMMA-b-PAMPMA in xylene

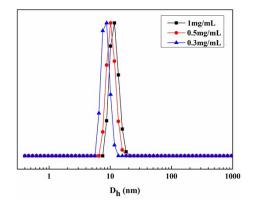


Fig.S6. The DLS traces of PMMA-b-PAMPMA in xylene at different concentrations

PMMA-*b*-PAMPMA diblock copolymers could not be molecularly dissolved in xylene. DLS measurement indicated that D_h of PMMA-*b*-PAMPMA at 0.3, 0.5 and 1.0

mg/mL was ~8.6, ~10.9 and ~11.7 nm, respectively, which were all remarkably larger than its D_h of ~3.1 nm in THF.

S8. The emulsifying results of P2 and P3

Fig. S7 The photographs of Pickering emulsions and the corresponding optical microscope images of droplets of the Pickering emulsions stabilized by P2 (A, B) and P3 (C, D)