

Supplementary Information for

Mussel-Inspired Chemistry for Dual-Responsive Capsules with Tunable Low Critical Solution Temperatures and Their Loading and Release Behavior

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Figure S1. The effects of pH value on loading kinetics at $T > \text{LCST}$ (capsule 1).

Figure S2. The effects of pH value on loading kinetics of capsule 2 (A) and capsule 3 (B) at $T < \text{LCST}$.

Figure S3. The effects of pH value on release kinetics at $T > \text{LCST}$ (capsule 1).

Figure S4. The effects of pH value on release kinetics of capsule 2 (A) and capsule 3 (B) at $T < \text{LCST}$.

Figure S5. (A) The effects of pH value on uptake kinetics at $T > \text{LCST}$. MO loading profile recorded by switching the buffer solution pHs: (B) pH=4.6, (C) pH=7.0 and (D) pH=8.6.

Figure S6. (A) The effects of pH value on release kinetics at $T > \text{LCST}$. MO loading profile recorded by switching the buffer solution pHs: (B) pH=4.6, (C) pH=7.0 and (D) pH=8.6.

Experimental

Materials

Dopamine hydrochloride (DA), copper (I) bromide, 2- (2- methoxyethoxy) ethyl methacrylate (MEO₂MA), oligo (ethylene glycol) methacrylate (OEGMA) and Rhodamine 6G (Rh6G) were purchased from Aldrich. 2- Bromoisobutryl bromide (BIBB), and 4- (Dimethylamino) pyridine (DMAP) were provided by Alfa Aesar. 2, 2'- Bipyridine (bpy), and Methyl Orange (MO) were provided by J&K Chemical Ltd. Tetraethyl orthosilicate (TEOS, FuChen Chemical Reagents Factory, Tianjin, China) was purified by vacuum distillation. All the water used was de-ionized, and all other chemicals were analytical grade and used as received.

Preparation of SiO₂ templates

The silica core with diameters about 360 nm was synthesized according to the Stöber method. 5.6 mL TEOS was diluted with 30 mL ethanol and added to a solution containing 28 mL of ethanol, 26 mL of deionized water and 10 mL of ammonia. The reaction was allowed to proceed at room temperature under magnetic stirring for two hours. The silica spheres were centrifuged and washed with ethanol three times and dried.

Preparation of Pdop coated SiO₂ (SiO₂@Pdop)

2 g silica cores were placed into a glass beaker with 100 mg DA dissolved in 200 mL Tris-HCl (pH=8.5), the solution was stirred for 24 h at room temperature. After centrifugation and water washing cycles, the products were vacuum dried at 45°C.

Preparation of SiO₂@Pdop supported initiator

100 mL flask containing 2 g SiO₂@Pdop, 20.0 mL of CH₂Cl₂, 0.5 g DMAP, and 1 mL of TEA were evacuated and thrice filled with argon. Afterwards 1 mL of BIBB dissolved in 20 mL of CH₂Cl₂ was added dropwise at 0°C for 60 minutes. Later, the resulting mixture reacted at room temperature for 23 h. The products were separated by centrifuged and thoroughly washed with acetone and methanol, respectively. The solid was dried overnight under vacuum at 45°C. These resultant samples were denoted as SiO₂@Pdop-Br.

Preparation of dual-responsive capsules

Three kinds of tunable thermo-sensitivity capsules were produced through control the different ratios of MEO₂MA: OEGMA and denoted as capsule 1 to 3. For example, the capsule1 was produced as the fellow: 2 g of SiO₂@Pdop-Br, 13 mg (0.09 mmol) of CuBr, 28.3 mg (0.18 mmol) of bpy were added to a Schlenk flask sealed with a rubber plug, which was equipped with a magnetic stirring bar. The flask was evacuated and filled with argon thrice. 1.52 g OEGMA (10 equiv), 0.427 g MEO₂MA (90 equiv) and 2.4 mL of ethanol were added in another flask. Degas the mixture monomer using three freeze-pump-thaw cycles, then the degassed monomer was injected to the Schenck flask with double-ended needles performed under argon. The flask was heated at 60 °C in an oil bath. After reaching the desired reaction time, the substrates were removed from the polymerization solution, exhaustively rinsed with water, then the silica cores were removed using 2 % HF solution, after centrifugation/water washing cycles the dual-responsive capsules were obtained after dried in a vacuum oven overnight at room temperature.

Loading behavior of dual-responsive capsules

Before the loading and release behaviors were studied, the standard curve between the absorbance and the concentrations of dye in different solvents were measured. The loading behaviors of dual-responsive capsules were carried out as follows: 10 mg capsules were added into conical flasks with 100 mL dye solution (10 μ M) in three types of buffer solutions (pH=4.6, 7.0 and 8.5), respectively. Then the flasks were divided into two groups, shaken at the temperatures of $T < \text{LCST}$ and $T > \text{LCST}$. For regular intervals, the suspension was withdrawn and determined by UV-Vis spectra at a wavelength of 525 nm (Rh6G) and 465 (MO). The suspension then was added into the system to maintain a constant amount of solvent.

Release behavior of dual-responsive capsules

The test molecule was encapsulated in multi-responsive capsules by the following process: 150 mg capsules were immersed in 250 mL alkaline phosphate buffer of Rh6G (25×10^{-6} M) and 250 mL acid phosphate buffer of MO (25×10^{-6} M), respectively. The mixture was agitated for 24 h at a low temperature (below the LCST of the thermo-responsive layer), then the dye-loaded capsules were separated from the dye solution and dipped in water at a high temperature (above the LCST) to allow the corona OEGMA-based layer to collapse and thus entrap the dye. Afterward, the dye-loaded capsules were thoroughly rinsed with water at temperature above LCST. The sample was denoted as Rh6G-loaded capsules and MO-loaded capsules.

For the release behavior of capsules, the dye-loaded capsules were immersed in a solvent to study the effects of pH and temperature on release kinetics. The release

profiles of the dye were determined by soaking 10 mg of dye-loaded capsules in 100 mL of the release mediums at different pH values (pH=4.6, 7.0 and 8.5) under stirring at 120 rpm in a flask. The temperature of the suspension was kept at a certain value. After that, the supernatant fluid centrifuged and taken out, the absorbance values was measured with UV-Vis, for regular intervals.

Characterization

Turbidity of the resultant capsules given in nephelometric turbidity units (NTU) was measured as a function of temperature measured for aqueous solutions (1 mg mL^{-1}) using WGZ-3 turbidimeter (ShangHai XinRui Instrument & Meter CO., LTD.). Thermal stability was determined by thermogravimetric analyzer (TGA, Netzsch STA449F3) over a temperature range of 40-1000°C at a heating rate of 10 °C/min under N₂ atmosphere. Relative molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI). Transmission electron microscopy (TEM, Hitachi H-600) was used to observe the morphology of products. UV-Vis measurements were conducted using an ultraviolet visible spectrophotometer (UV-3200, Shanghai MeiPuDa Company).

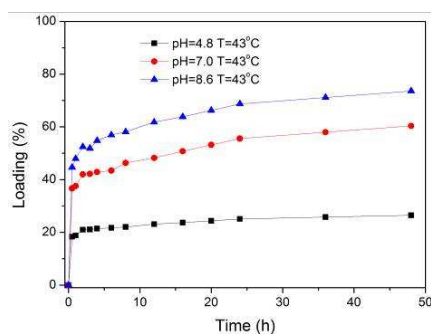


Figure S1. The effects of pH value on loading kinetics at $T > \text{LCST}$ (capsule 1).

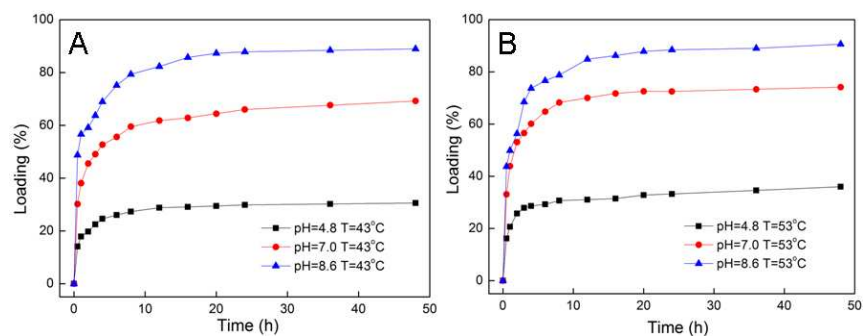


Figure S2. The effects of pH value on loading kinetics of capsule 2 (A) and capsule 3 (B) at $T < LCST$.

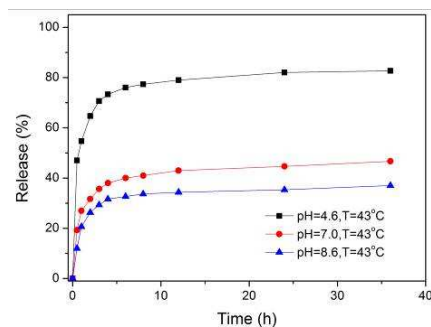


Figure S3. The effects of pH value on release kinetics at $T > LCST$ (capsule 1).

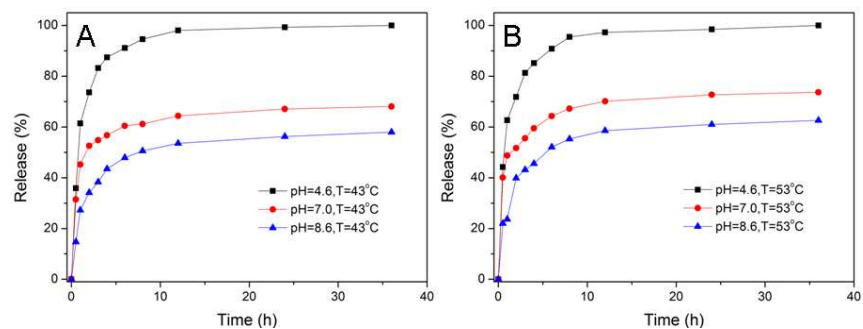


Figure S4. The effects of pH value on release kinetics of capsule 2 (A) and capsule 3 (B) at $T < LCST$.

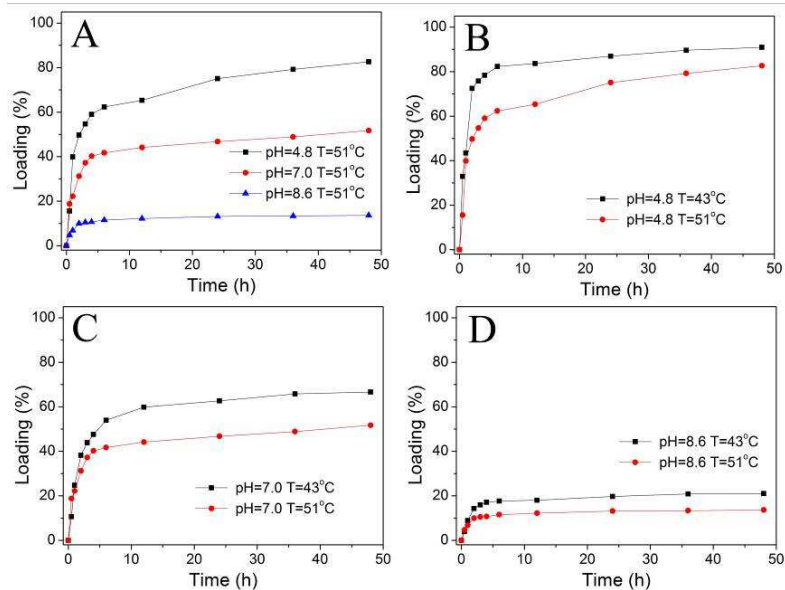


Figure S5. (A) The effects of pH value on uptake kinetics at $T > \text{LCST}$. MO loading profile recorded by switching the buffer solution pHs: (B) pH=4.6, (C) pH=7.0 and (D) pH=8.6.

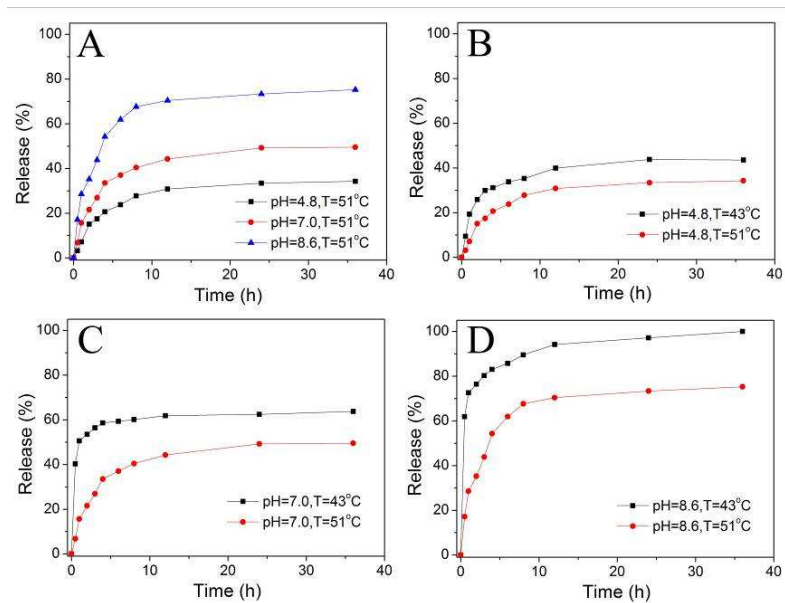


Figure S6. (A) The effects of pH value on release kinetics at $T > \text{LCST}$. MO loading profile recorded by switching the buffer solution pHs: (B) pH=4.6, (C) pH=7.0 and (D) pH=8.6.