Supporting Information

Interfacial Assembly and Jamming of Polyelectrolyte Surfactants: A Simple Route To Print Liquids in Low Viscosity Solution

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Experimental Section

Materials. Carboxymethyl cellulose (CMC) with M_w = 250,000 g/mol, was dispersed in 18.2 Ω ultrapure water at a series of concentrations from 4.0 × 10^{-4} to 4.0 × 10^{-3} mM, and was purchased from Aladdin. The pH of the dispersions was adjusted using 1.0 M HCl or 1.0 M NaOH directly prior to testing and printing. Toluene was obtained from Sigma Aldrich. Amine-terminated polystyrene (PS-NH_2, M_w = 1500 g/mol) and amine-terminated polyhedral oligomeric silsesquioxanes (POSS-NH_2, M_w = 874.58 g/mol) were purchased from Polymer Source and Hybrid Plastics, respectively. The p*K*a of CMC is 3.0 ~ 4.0 (*Materials* **2013**, *6*, 738-781), and the p*K*a of amine group in POSS-NH_2 and PS-NH_2 is ~ 9.0 (*Langmuir* **2014**, *30*, 1072−1079; *Angew. Chem. Int. Ed.* **2019**, *58*, 18171 –18176). PS-NH_2 and POSS-NH_2 were dissolved in dry toluene to obtain required solutions. Congo red and Nile blue were purchased from Alfa Aesar and dissolved in ultrapure water. All reagents were used as received without treatment.

Characterization. The interfacial tension (γ) was analyzed by a multi-functional tensiometer (Krüss DSA30) using a pendent-drop method, where the evolution of γ with time was recorded after the water phase was slowly injected into the toluene phase. The deformation and wrinkle behavior were recorded as an image or video with a digital camera. The Plateau–Rayleigh instability fluid jetting from the syringe was generated with tensiometer under flush mode (flow rate = 2.0 mL/min). The morphologies of tubule liquids were characterized by polarized optical microscopy (ZEISS Imager.A2) or confocal fluorescence microscopy (Leica SP8). Imaging of the moment of fluid tubular break-up was performed by using a high-speed camera (Phantom, Miro LAB310, Ametek). Zeta-potential was measured using a zeta-potential ZetaPlus analyzer (Brookhaven, USA).

All-liquid 3D Printing. A commercially available JGAURORA 3D printer was modified to produce water-in-oil tubules. The print head nozzle was replaced by a stainless steel syringe needle (gauge 25, 23 or 22, internal diameter = 0.26, 0.34, or 0.41 mm) and attached to a syringe pump. The trajectories of the print head were controlled by G-Code commands using software of Repetier-Host and 3ds Max. Depending on the desired feature sizes, the print head velocity was 900 ~ 4000 mm/min and the CMC aqueous solutions was injected at a flow rate of 1.0 ~ 3.5 mL/min. The aqueous dye solution was pumped through the tubule. To achieve flow through the entire tubule, two stainless steel syringe needles (gauge 25) were inserted into both ends of the printed tubule and attached to syringe pumps, and the dye solution must be infused and extracted at the same rate (1 ~ 10 mL/h). No leakage was observed from the tubule during transportation. For FITC-BSA adsorption, the tubule was first washed with water (pH = 3.0) for 0.4 h to remove excess CMC in solution, then the solution of FITC-BSA ([FITC-BSA] = 0.1 mg/mL, pH = 3.0) was injected into the tubule for 0.4 h to achieve the adsorption of BSA on the wall. Finally, the tubule was washed with water for 0.4 h again to remove the excess BSA in solution.

All-liquid Molding. To obtain the liquid letters, an aqueous CMC solution ([CMC] = 4.0×10^{-3} mM) with traces of dye (Nile blue) was placed into the mold with a pattered trench, which had been prewetted with CCl_4 solution of POSS-NH_2 ([POSS-NH_2] = 2.3 mM). After waiting for assembly and molding for about 2 minutes, the filled mold was then immersed in an CCl_4 solution of POSS-NH_2 ([POSS-NH_2] = 2.3 mM), producing liquid with desired shapes (*Adv. Mater.* **2018**, *30*, 1705800).

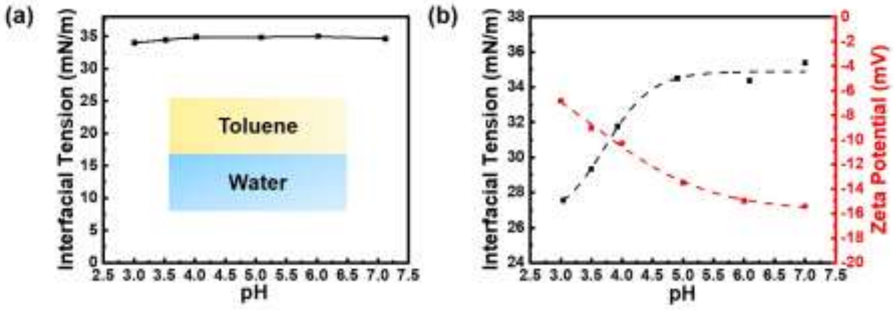

Figure S1. a) Equilibrium interfacial tension between water and toluene at different pH values; b) equilibrium interfacial tension between CMC aqueous solution and pure toluene, and zeta potential of CMC dissolved in water at different pH values. [CMC] = 4.0×10^{-4} mM.

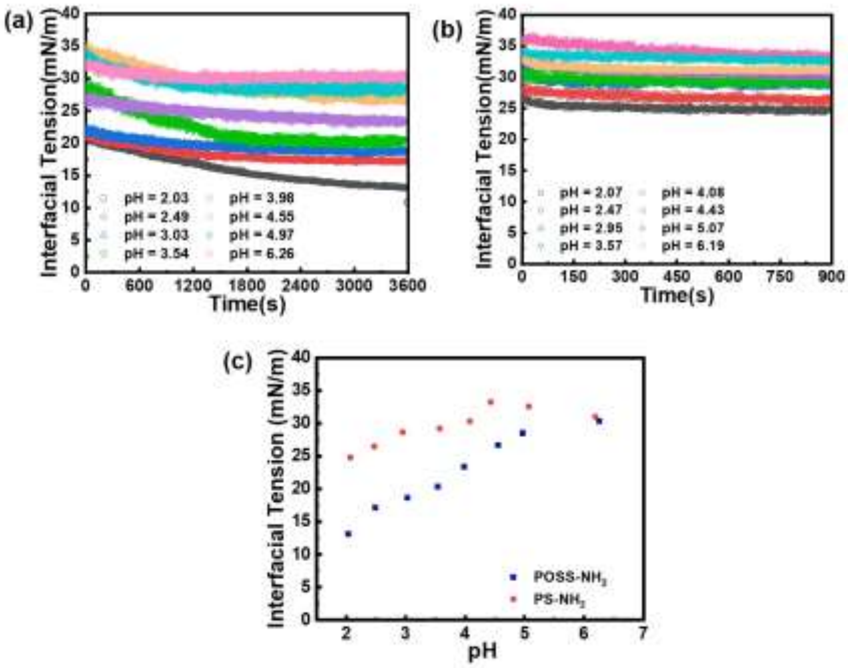

Figure S2. Time-evolution of the interfacial tension of a) POSS-NH_2 and b) PS-NH_2 dissolved in toluene against a pure water phase with different pH values; c) equilibrium interfacial tension with different pH values. [PS-NH_2] = 0.10 mM, [POSS-NH_2] = 0.10 mM.

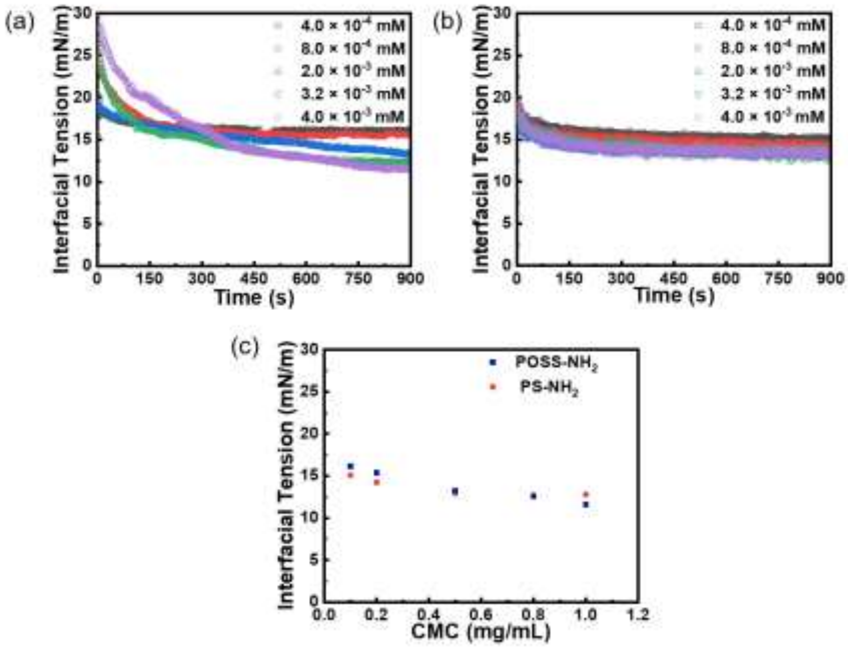

Figure S3. Time-evolution of the interfacial tension at different concentrations of CMC dissolved in water against toluene dissolving a) POSS-NH_2 and b) PS-NH_2; c) equilibrium interfacial tension in a) and b). [CMC] = $4.0 \times 10^{-4} \sim 4.0 \times 10^{-3}$ mM, [PS-NH_2] = 0.10 mM, [POSS-NH_2] = 0.10 mM, pH = 3.0.

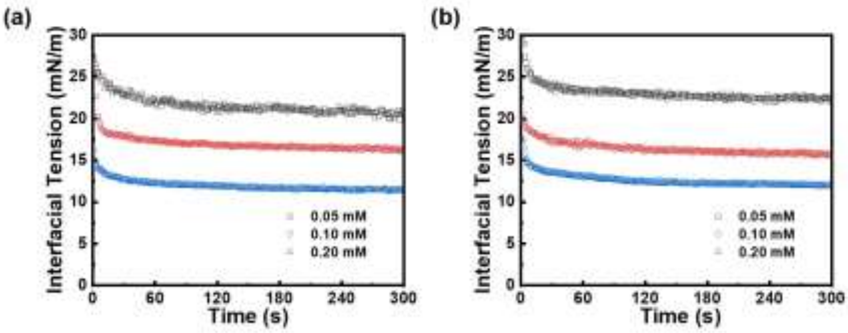

Figure S4. Time-evolution of the interfacial tension at different concentrations of a) POSS-NH_2 and b) PS-NH_2 dissolved in toluene against water phase dissolving CMC. [CMC] = 4.0×10^{-4} mM, [PS-NH_2] = 0.05 ~ 0.20 mM, [POSS-NH_2] = 0.05 ~ 0.20 mM, pH = 3.0.

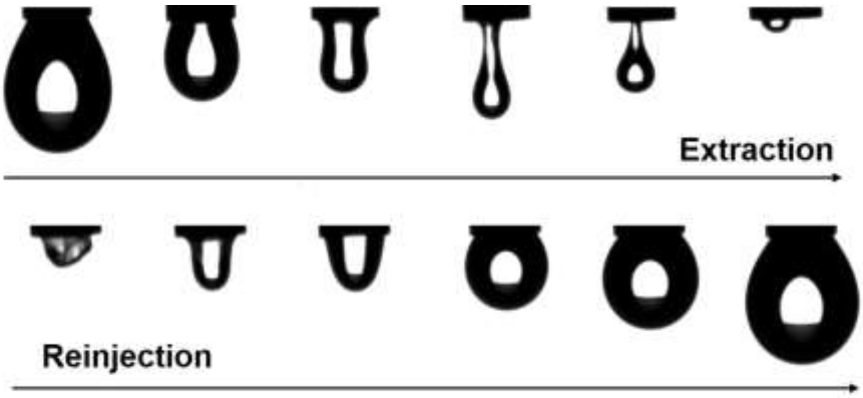

Figure S5. Snapshots of droplet's morphology evolution in an extraction-reinjection process, [CMC] = 4.0×10^{-3} mM, [PS-NH_2] = 1.0 mM, pH = 3.0.

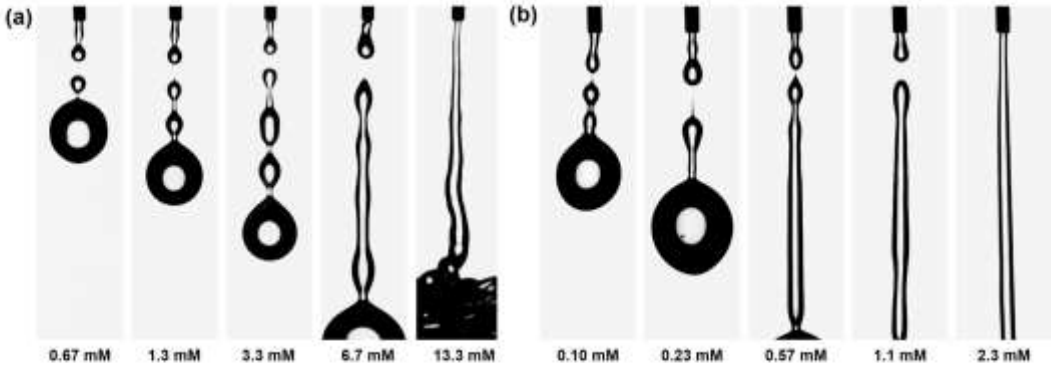

Figure S6. High speed photography of an aqueous CMC solution falling in toluene solution containing a) PS-NH_2 and b) POSS-NH_2, [CMC] = 4.0×10^{-3} mM, [PS-NH_2] = 0.67 ~ 13.3 mM, [POSS-NH_2] = 0.10 ~ 2.3 mM, pH = 3.0, flow rate = 2.0 mL/min.

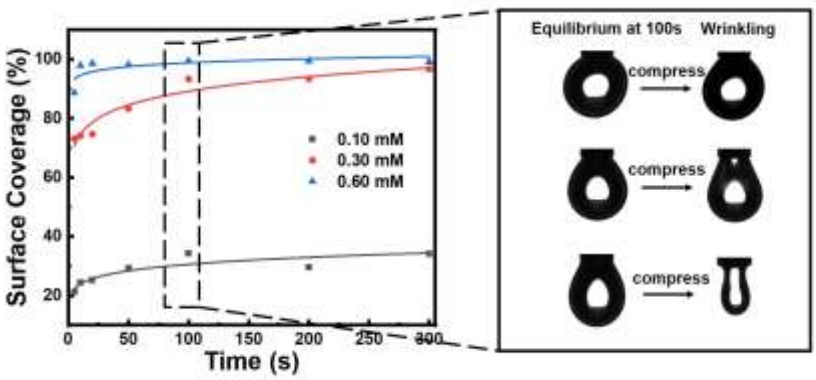

Figure S7. Surface coverage variation of the droplets with increasing assembly time with different concentrations of POSS-NH_2. [CMC]= 4.0×10^{-3} mM, pH = 3.0.

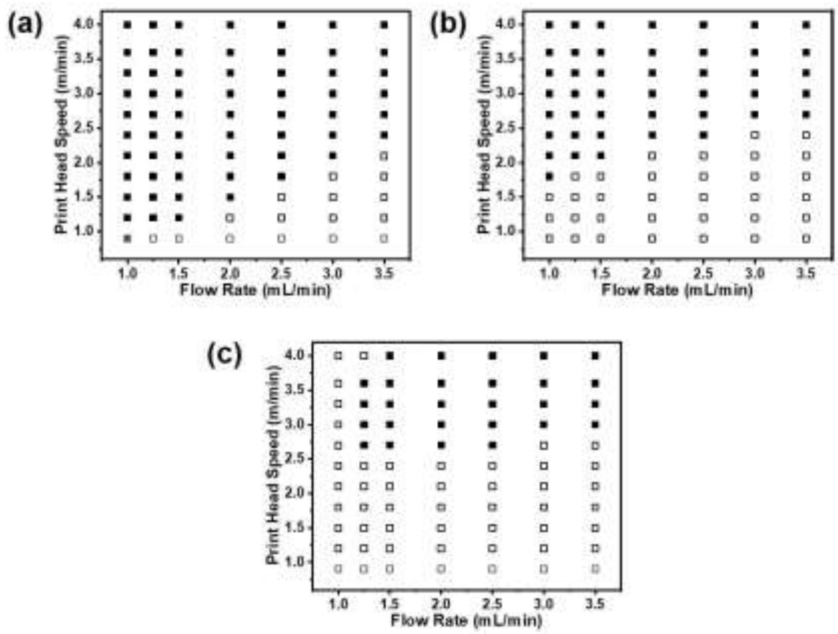

Figure S8. Stable state for printing at different needle internal diameter of a) 0.26, b) 0.34, and c) 0.41 mm, respectively, marked as black filled square.

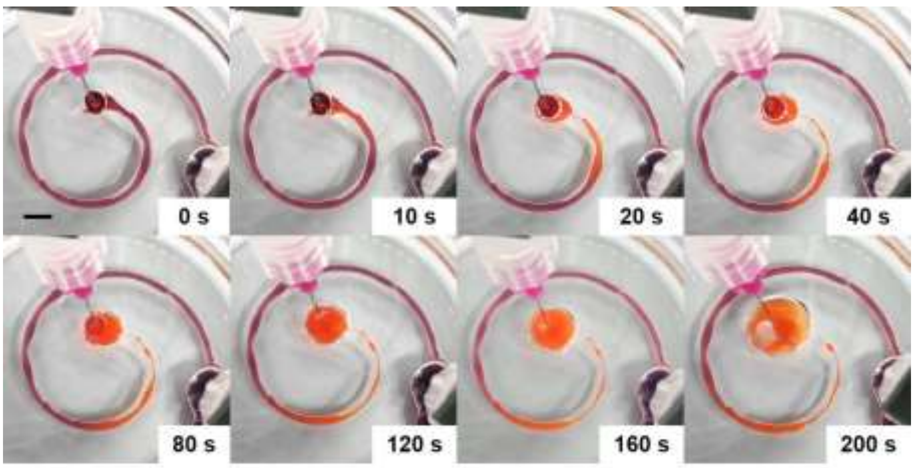

Figure S9. An aqueous solution of NaOH (1.0 M) is injected into the tubule liquid, resulting in the piecewise narrowing and damage of the structure, and a change in color (to red) of the dye. [Congo red] = 0.07 mM, transmission rate = 5 mL/h. Scale bar: 5 mm.

Video S1 (am0c00577_si_002): Morphology evolution of droplets under compression (with only CMC assembled at the interface), showing a liquid-like behavior (MP4)

Video S2 (am0c00577_si_003): Morphology evolution of droplets under compression (with CMC/POSS-NH_2 or CMC/PS-NH_2 assembled at the interface), showing different surface coverage (MP4)

Video S3 (am0c00577_si_004): Contact, compression, and separation process of the needle and droplet, showing an elastic behavior (MP4)

Video S4 (am0c00577_si_005): Contact, compression, and separation process of the needle and droplet, showing a solid-like behavior (MP4)

Video S5 (am0c00577_si_006): Morphology evolution of droplets in an extraction−reinjection process with no evidence of cracking, indicating the robust nature of the assemblies (MP4)

Video S6 (am0c00577_si_007): Morphology evolution of droplets in an extraction−reinjection process, where wrinkles are observed at large compression ratios and an elongation of the droplet is observed (MP4)

Video S7 (am0c00577_si_008): Formation of tubules by injecting an aqueous CMC solution into POSS-NH2 toluene solution (MP4)

Video S8 (am0c00577_si_009): Process of all-liquid 3D printing (MP4)

Video S9 (am0c00577_si_010): Transmission of a dye solution (MP4)

Video S10 (am0c00577_si_011): Piecewise narrowing and damage of the structure with an injection of NaOH solution into the tubule liquid (MP4)

Video S11 (am0c00577_si_012): Process of all-liquid molding (MP4)