Supporting Information

Structured Liquids stabilized by Polyethyleneimine Surfactants

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EXPERIMENTAL SECTION

Materials. Sodium borohydride (NaBH$_4$, 98%), l-lactic acid (LLA, 98%), poly-l-lactic acid (PLLA, M_n = 3.0 K), ferrocene methanol (97%), tin 2-ethylhexanoate catalyst (96%), nile red and sodium hypochlorite (NaClO, 8% available chlorine), were purchased from J&K. β-cyclodextrin(β-CD) and branched polyethyleneimine (PEI, M_n = 10 K, 99%) were purchased from Energy Chemical. p-toluenesulfonyl chloride (PTSC, 99%), sodium hydroxide (NaOH, 99%) and hydrochloric acid (HCl, 99%) were purchased from Aladdin. Fluorescein sodium was purchased from TCI. Rose bengal and methylene blue were purchased from Heowns. The above reagents were used as received unless otherwise noted. All anhydrous solvents (toluene, dichloromethane (DCM), N, N-dimethylformamide (DMF), n-hexane, acetone, methanol, ethanol) were purchased on commercially and used without further purification.

Characterization. The apparent number-average molecular weights (M_n) and dispersity (M_w/M_n) were measured by size-exclusion chromatography (SEC), which was conducted with THF as the eluent. Polymerization was monitored by ^{1}H NMR spectroscopy using a Bruker Advance 400 MHz NMR spectrometer with D$_2$O, CDCl$_3$ and DMSO-d$_6$ as solvent. Fourier transform infrared spectra (FTIR) was recorded on a Spectrum One spectrophotometer by 64 scans from 4000 to 500 cm^{-1} with a resolution of 4.0 cm^{-1}. The concentration of the feed dyes and filtrate dyes solutions were measured via ultraviolet (UV) visible spectroscopy (SHIMADZU-3600 model). 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 images or videos with a digital camera. The morphology of emulsions was characterized by fluorescence

microscopy (ZEISS Imager.A2). Electrochemical redox experiments were obtained using CHI 660E electrochemical workstation (Chenhua Instrument, Shanghai, China).

Surface coverage calculation. For the calculation of surface coverage of PEIS-based assemblies, a pendant droplet is first made by injecting a PEI-β-CD-containing aqueous solution at a given volume into Fc-PLLA-containing toluene solution. With time, PEISs form at the toluene-water interface, then assemble into membranes. At a certain assembly time, if the PEISs are uniformly distributed over the interface (termed the "free" state), then as the volume, therefore, the surface area of the pendant droplet is reduced, the areal density of the PEIS increases, and eventually they lose mobility, "jamming" on the interface. Wrinkling happens when PEIS are closely jammed together at the interface. Therefore, the coverage (C) of PEIS on the droplet surface in the "free" state could be estimated as $C \approx S_J/S_F$, where S_J and S_F are surface areas for the jammed and free states respectively, which can be achieved by tensiometer directly. By measuring the surface coverage at different assembly time, the evolution of surface coverage as a function of time can be achieved.

Voltage-responsive experiments. Electrochemical redox experiments are measured on a CHI 660E electrochemical workstation (Chenhua Instrument, Shanghai, China) at ambient temperature. A traditional three-electrode system with a Pt electrode as the counter electrode, Ag/AgCl as the reference electrode, and glassy carbon as the working electrode. The supporting electrolyte was 0.1 mol L^{-1} KNO$_3$ and the scanning rate was 0.10 V s^{-1}. The electrochemical stimuli were conducted by inserting three electrodes into the O/W emulsions at ambient temperature.

All-liquid molding. To construct liquid letters, an aqueous PEI-β-CD solution was placed into the mold with a pattered trench, which had been prewetted with toluene solution of Fc-PLLA. After

assembling for 30 minutes, the filled mold was immersed in CCl$_4$ solution, producing liquids with desired shapes. [PEI-β-CD] = 5.0 mg mL^{-1}, [Fc-PLLA] = 5.0 mg mL^{-1}.[1]

All-liquid 3D printing. A commercial JGAURORA 3D printer was modified to print aqueous tubules in toluene solution. The print head nozzle was replaced by a stainless syringe needle and connected with the syringe pump. The movement of the print head was controlled by Repetier-Host software. PEI-β-CD aqueous solution was injected into Fc-PLLA toluene solution at a flow rate of 60 mL h^{-1}. [PEI-β-CD] = 20 mg mL^{-1}, [Fc-PLLA] = 20 mg mL^{-1}.[2]

Adsorption efficiency calculation. A concentration–absorbance calibration curve is first obtained by measuring the absorption intensity of dye in aqueous solution at different concentrations. The adsorption efficiency (η) can be estimated as $\eta = (C_0-C_i)/C_0$, where C_0 is the dye concentration before adsorption and C_i is the dye concentration after adsorption.[3]
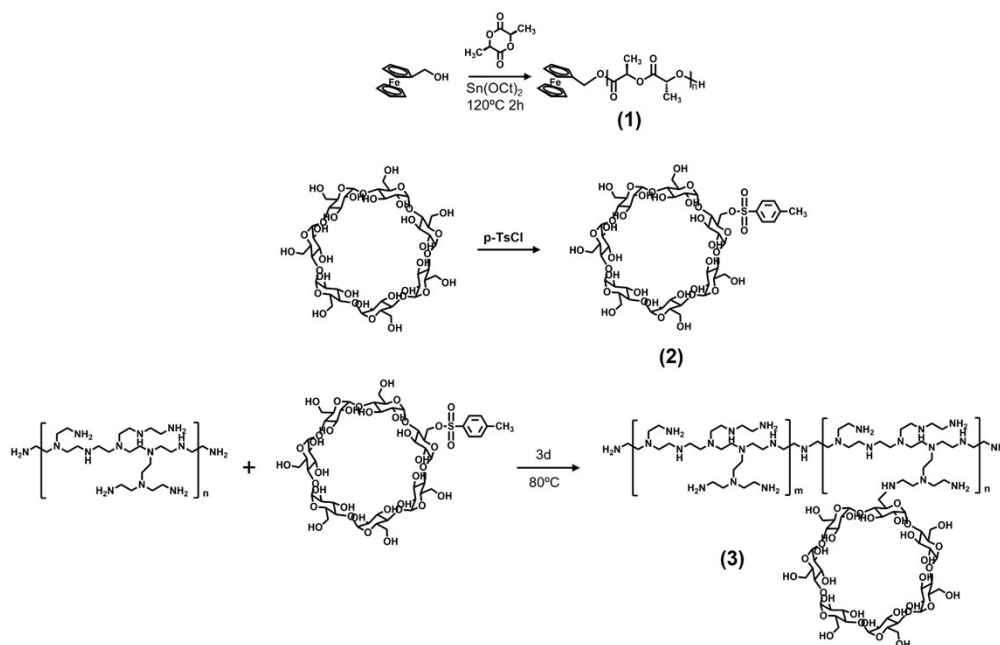
Scheme S1. Synthetic route of Fc-PLLA and PEI-β-CD.

Synthesis of Ferrocene-terminated Poly-l-lactic acid (Fc-PLLA) (1)[4,5]

2.9 g l-lactic acid (LLA) and 0.2 g ferrocene methanol were added into a 25 mL Schlenk flask. Three freeze-pump-thaw cycles were performed to remove the oxygen. The flask was immersed into an oil bath at 120 °C with vigorous magnetic stirring for 5.0 min. Then 4.0 mg tin 2-ethylhexanoate catalyst in dry 0.2 mL DMF was added to the mixture via a microsyringe. After reacting for 2.0 h at 120 °C, the crude product was dissolved in hot DCM, and the solution was precipitated into n-hexane. The product was washed for three times. The final product was dried in vacuum, yielding a light yellow solid (2.4 g, 83% yield). FT-IR (KBr, cm^{-1}): 693, 756 (V_{C-H} in Fc), 1456 ($V_{C=O}$ in PLLA), 1622 ($V_{C=C}$ in Fc), 2946 (V_{C-H} in PLLA), 2998 (V_{C-H} in PLLA). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 5.2 (s, 2H), 1.84-1.14 (m, 6H). $M_n = 3200$, $M_w = 3500$, PDI = 1.1.

Synthesis of Mono-(6-O-(p-tolylsulfonyl))-β-Cyclodextrin (β-CD-OTS) (2)[6,7]

β-CD (50 g, 44.0 mmol) was dissolved in 500 mL solution of sodium hydroxide (0.4 M) under ice-bath, p-toluensulfonyl chloride (35 g, 184 mmol) was added in small portions over a period of 5 min to the vigorously stirred solution. The mixture was stirred at 5 °C for 30 min and then filtered. The filtrate was neutralized with concentrated hydrochloric acid and stirred for 1 h. After filtering the mixture and washing for 3 times with water, the white precipitate was obtained and dried overnight at 60 °C (14.32 g, 26% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$, δ): 7.76 (d, 2H), 7.42(d, 2H), 6.03-5.33 (m, 14H), 4.83 (t, 5H), 4.77 (d, 2H) ,4.47-4.14(d, 6H), 3.73-3.49(m, 28H), 2.43 (s, 3H).

Synthesis of β-cyclodextrin-modified polyethyleneimine (PEI-β-CD) (3)[8]

β-CD-OTS (1.07 g, 0.82 mmol) was dissolved in 10 mL DMF solution and sonicated for 8 min. After completely dissolved, the DMF solution of β-CD-OTS was added dropwise to 10 mL DMF solution including 0.4 g (0.04 mmol) PEI (M_n = 10 K) for 1 h. The resultant solution was stirred for 3 days at 80 °C under N_2, and the mixture was added to 1.0 L acetone to precipitate. The sediments were separated by centrifugation and re-dissolved in 5 mL DI water, washed with 500 mL acetone twice and dried to get the crude products. The purified solution was collected and lyophilized to get the products (0.26 g, 18% yield). FT-IR (KBr, cm^{-1}): 1031 (V_{C-O} in β-CD), 1405 (V_{C-C} in β-CD), 2928 (V_{-CH3}, V_{-CH2} in β-CD), 3420 (V_{O-H} in β-CD). ^{1}H NMR (400 MHz, D_2O, δ): 4.99(s, H), 3.99-3.69(m, H), 3.62-3.45(m, H), 2.62(m, H).
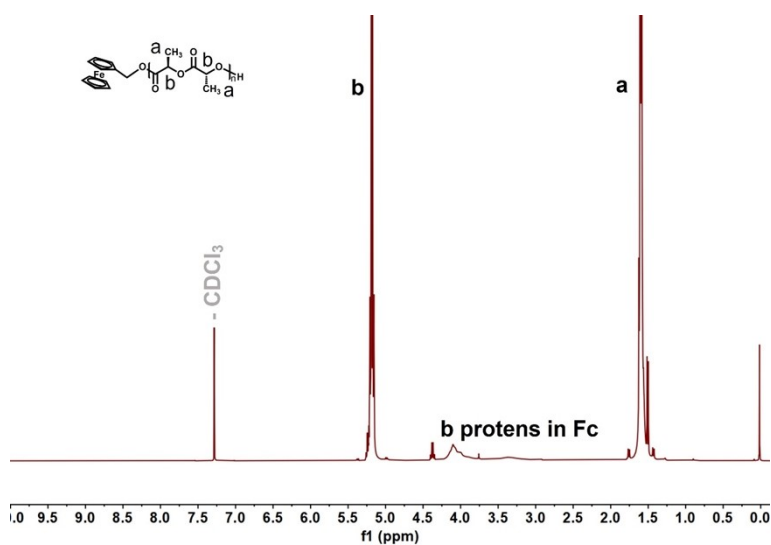
Fig. S1 ^{1}H NMR spectrum of Fc-PLLA in CDCl$_3$.
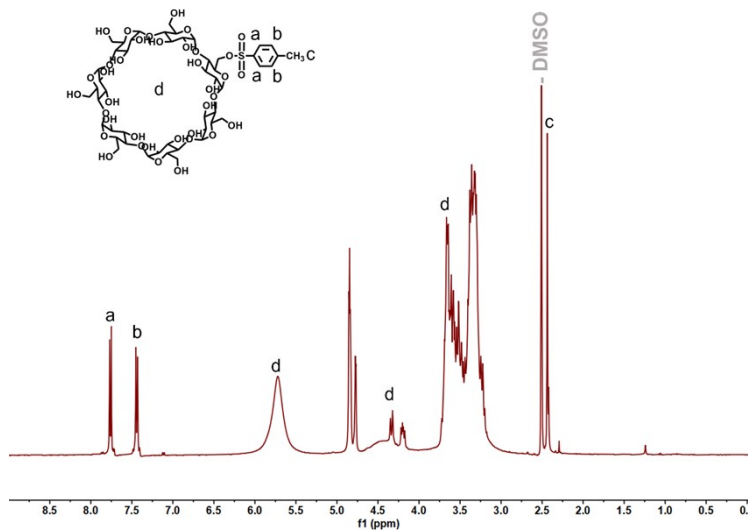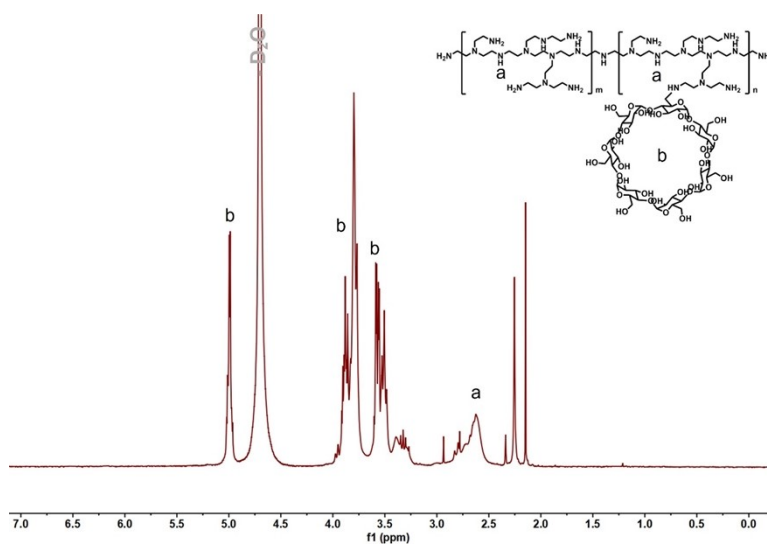
Fig. S2 ^{1}H NMR spectrum of β-CD-OTS in DMSO-d_6.

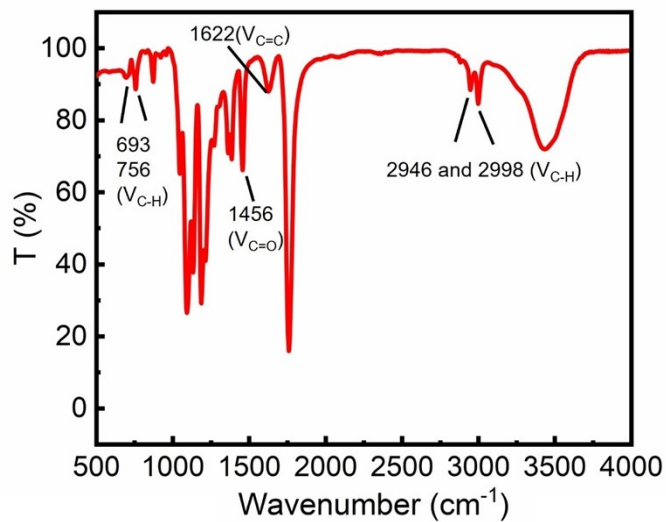**Fig. S3** ^{1}H NMR spectrum of PEI-β-CD in D$_2$O.

Fig. S4 FTIR spectrum of Fc-PLLA.
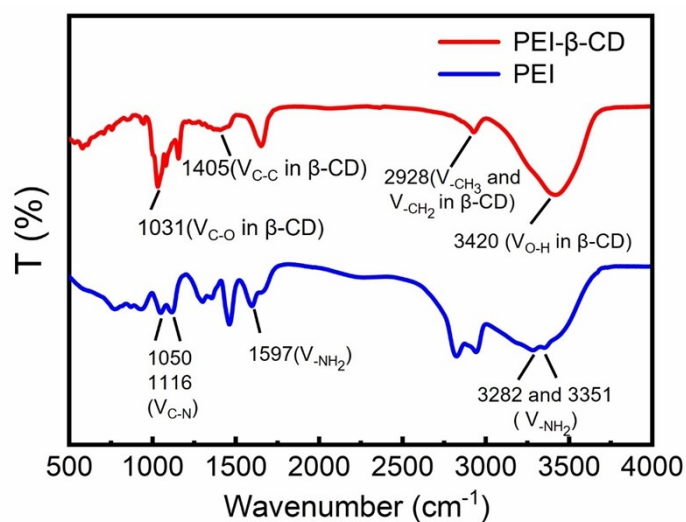

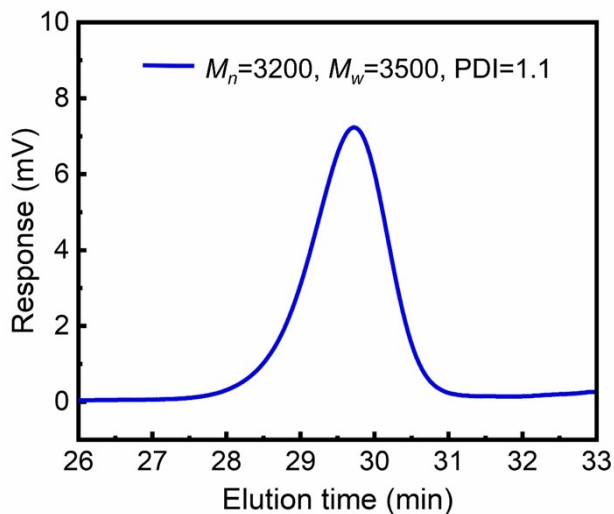**Fig. S5** FTIR spectra of PEI and PEI-β-CD.
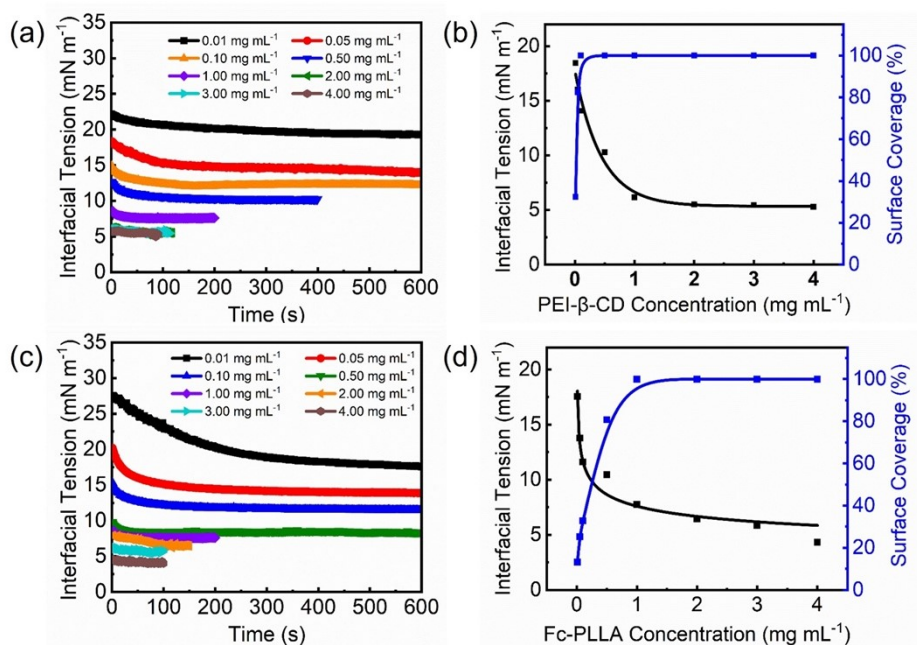
Fig. S6 SEC spectrum of Fc-PLLA.

Fig. S7 (a) Time evolution of interfacial tension with different concentrations of PEI-β-CD from 0.01 to 4.0 mg mL^{-1}, [Fc-PLLA] = 1.0 mg mL^{-1}; (b) equilibrium interfacial tension and surface coverage as a function of PEI-β-CD concentration; (c) time evolution of interfacial tension with different concentrations of Fc-PLLA from 0.01 to 4.0 mg mL^{-1}, [PEI-β-CD] = 1.0 mg mL^{-1}; (d) equilibrium interfacial tension and surface coverage as a function of Fc-PLLA concentration.
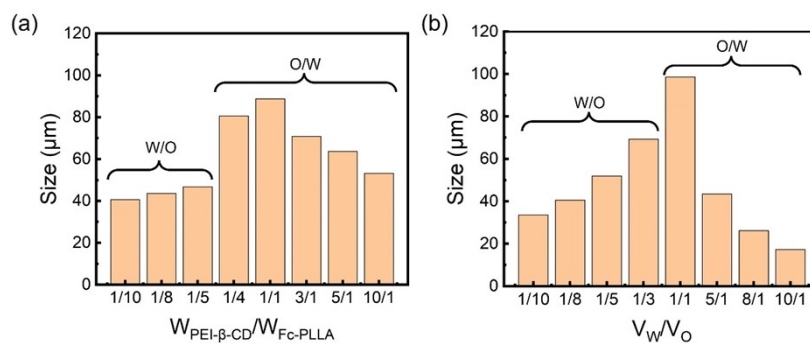
Fig. S8 (a) Size distribution of emulsion droplets at different PEI-β-CD/Fc-PLLA mass ratios from 1/10 to 10/1 at a constant 1/1 volume ratio of water and toluene. (b) Size distribution of emulsion droplets at different water/toluene volume ratios from 1/10 to 10/1 at fixed PEI-β-CD/Fc-PLLA concentration ($[PEI-β-CD] = 1.0$ mg mL^{-1}, $[Fc-PLLA] = 1.0$ mg mL^{-1}). Shear rate = 15000 rpm, shear time = 2.0 min.
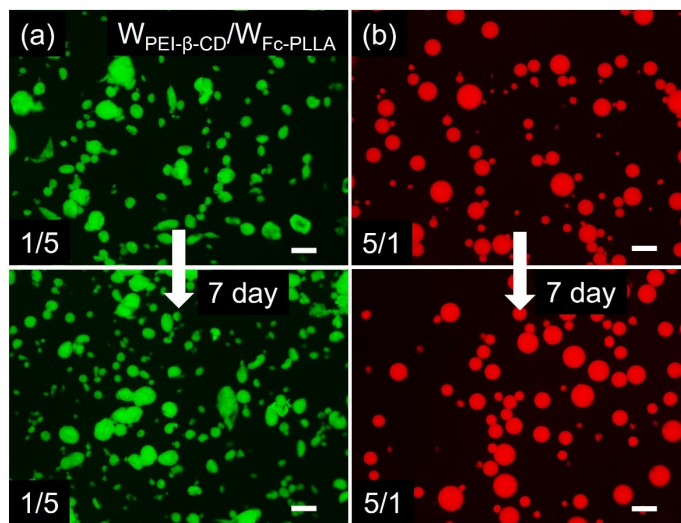

Fig. S9 Fluorescence microscopy images showing the stability of (a) W/O emulsions at PEI-β-CD/Fc-PLLA mass ratio of 1/5 and (b) O/W emulsions at PEI-β-CD/Fc-PLLA mass ratio of 5/1. $V_W/V_O = 1:1$, Fluorescein sodium is loaded in water, Nile red is loaded in toluene, [Fluorescein sodium] = 0.5 mg mL^{-1}, [Nile red] = 0.5 mg mL^{-1}, scale bar: 100 μm.
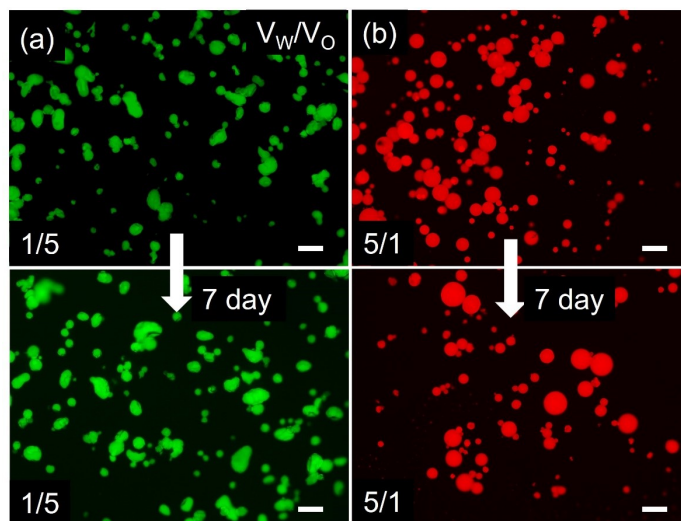
Fig. S10 Fluorescence microscopy images showing the stability of (a) W/O emulsions at water/toluene volume ratio of 1/5 and (b) O/W emulsions at water/toluene volume ratio of 5/1. Nile red is loaded in toluene, Fluorescein sodium is loaded in water, $[\text{PEI-}\beta\text{-CD}] = 1.0$ mg mL^{-1}, $[\text{Fc-PLLA}] = 1.0$ mg mL^{-1}, $[\text{Fluorescein sodium}] = 0.5$ mg mL^{-1}, $[\text{Nile red}] = 0.5$ mg mL^{-1}, scale bar: 100 μm.
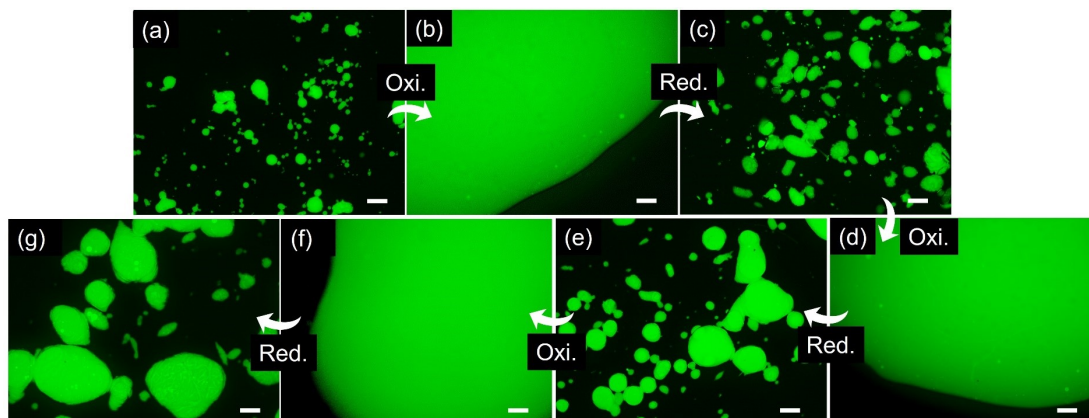

Fig. S11 Fluorescence microscopy images of emulsions during three redox cycles by the addition of redox reagents. Fluorescein sodium is loaded in water, $[\text{PEI-}\beta\text{-CD}] = 1.0$ mg mL^{-1}, $[\text{Fc-PLLA}] = 1.0$ mg mL^{-1}, $[\text{NaClO}] = 2.0$ mg mL^{-1}, $[\text{NaBH}_4] = 4.0$ mg mL^{-1}, $[\text{Fluorescein sodium}] = 0.5$ mg mL^{-1}, $V_W/V_O = 1:6$, shear rate = 15000 rpm, shear time = 2.0 min, scale bar: 200 μm.
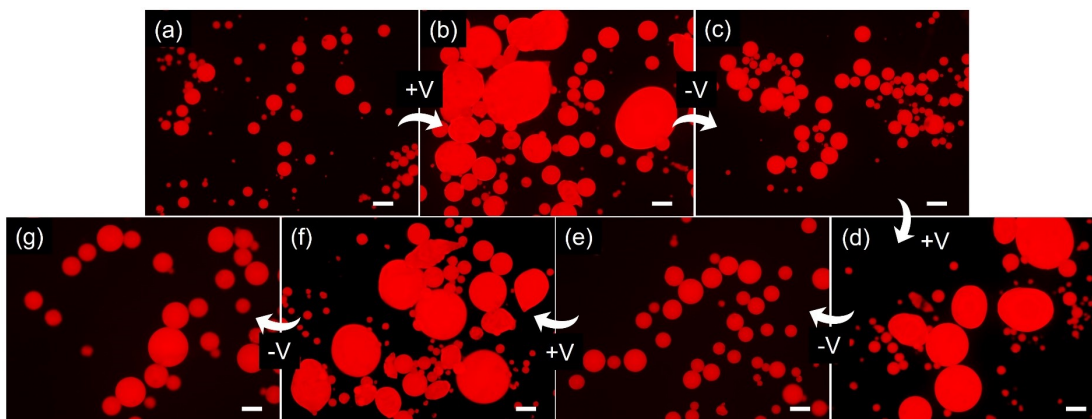
Fig. S12 Fluorescence microscopy images of emulsions during three redox cycles by applying voltage. Nile red is loaded in toluene, [PEI-β-CD] =1.0 mg mL^{-1}, [Fc-PLLA] =1.0 mg mL^{-1}, [Nile red] = 0.5 mg mL^{-1}, V_W/V_O = 2:1, shear rate = 15000 rpm, shear time = 2.0 min, scale bar: 200 μm.
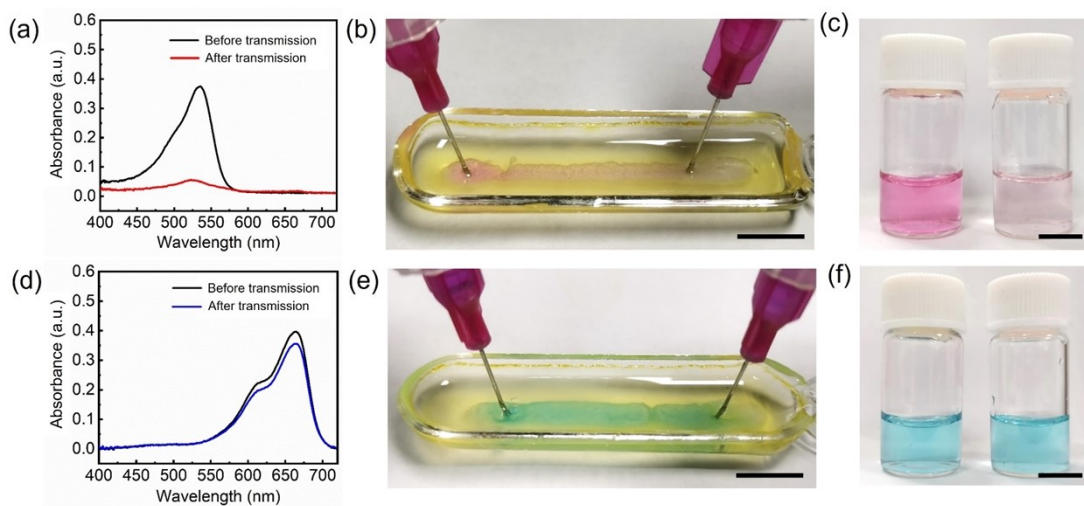

Fig. S13 (a) UV-vis absorption spectra of RB-containing aqueous solutions before and after transmission; (b) optical image showing the transmission of RB-containing aqueous solutions in a 3D printed all-liquid microfluidic chip; (c) optical image showing the color of RB-containing aqueous solutions before and after transmission; (d) UV-vis absorption spectra of MB-containing aqueous solutions before and after transmission; (e) optical image showing the transmission of

MB-containing aqueous solutions in a 3D printed all-liquid microfluidic chip; (f) optical image showing the color of MB-containing aqueous solutions before and after transmission. Flow rate = 3 mL h^{-1}, [PEI-β-CD] = 20 mg mL^{-1}, [Fc-PLLA] = 20 mg mL^{-1}, RB = 0.025 mg mL^{-1}, MB = 0.0084 mg mL^{-1}, scale bar: 1 cm.

References

[1] S. W. Shi, X. B. Liu, Y. N. Li, X, F. Wu, D. Wang, J. Forth and T. P. Russell, *Adv. Mater.*, 2018, **30,** 1705800.

[2] J. Forth, X. B. Liu, J. Hasnain, A. Toor, K. Miszta, S. W. Shi, P. L. Geissler, T. Emrick, B. A. Helms and T. P. Russell, *Adv. Mater.*, 2018, **30,** 1707603.

[3] R. Krishnamoorthi, R. Anbazhagan, H.C. Tsai, C. F. Wang and J. Y. Lai, *J. Taiwan. Inst. Chem. E.,* 2021, **118,** 325-333.

[4] H. L. Sun, M. W. Li, L. S. Li, T Liu, Y. Z. Luo, T. P. Russell and S. W. Shi, *J. Am. Chem. Soc.,* 2021, **143** (10), 3719-3722.

[5] Y. Xia, B. D. Olsen, J. A. Kornfield and R. H. Grubbs, *J. Am. Chem. Soc.*, 2009, **131** (51), 18525-18532.

[6] S. Amajjahe, S. Choi, M. Munteanu and H. Ritter, *Angew. Chem. Int. Ed.*, 2008, **47,** 3435-3437.

[7] A. C. Feng, Q. Yan, H. J. Zhang, L. Peng and J. Y. Yuan, *Chem. Commun.*, 2014, **50**(36), 4740-4742.

[8] P. Lv, C. Zhou, Y. L. Zhao, X. L, Liao and B. Yang, *Carbohydr. Polym.*, 2017, ***168,*** 103-111.