Supplementary Information for
Polymerizable bijels prepared by a direct-mixing method

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1. Materials and methods

1.1 Materials

Silicon particles (~ 20 nm in diameter) and aminopropyl terminated polydimethyl siloxane (diNH_2-PDMS) with Mw of 3000 and fluorescein sodium (FLS) were purchased from Macklin (Shanghai, China). Polydimethylsiloxane acrylate (PDMS-AR) (JHB-170) was obtained from Mingcheng Plastic Chemical Auxiliary (Guangdong, China). 2, 2-Diethoxyacetophenone (GC) was produced from Aladdin Industrial Co., Ltd. (China). N, N-bis (2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-3,4,9,10-perylenetetracarboxylic diimide (ROT 300) was produced by J&K Scientific Ltd. (Beijing, China). The deionized water with a resistivity of 18.2 MΩ·cm (25 °C) was obtained from UPH-IV ultrapure water apparatus (China). All reagents were used directly without further purification.

1.2 Sample preparation

The sample of bijel was prepared as follows: different amounts of diNH_2-PDMS, PDMS-AR with 2 wt% 2, 2-Diethoxyacetophenone were mixed uniformly in a 5 mL slender glass bottle. Next, appropriate amounts of SiO_2 and H_2O were added, and then the mixture was stirred for 2 minutes using the vortex. The polymerizable bijel can be obtained by placing the resulting emulsion under a xenon lamp (PLS-SEX300/300UV, Beijing) and initiating polymerization with 365nm UV light for 2 hours. The final solid sample was placed in air for one week to obtain aerogel sample.

1.3 Characterizations

Fourier transform infrared spectroscopy measurements (FTIR, VERTEX-70/70v

spectrometer, Bruker Optics, Germany) were utilized to analyze the characteristic groups of functional polymers and SiO_2. Zeta potential were measured on a Zetasizer Nanoseries (Malvern Instruments Ltd). The three-phase contact angles were tested by a contact angle analyzer instrument (Krüss DSA100, Germany), for which the same sample was repeatedly measured three times. For measurements, the particles were pressed to be flat discs and immersed in oil, and then the water phase was dropped onto the flat disc to test the contact angles (θ). The interfacial tension was tested by surface tension meter (Dataphysics DCAT21, Germany) with hanging plate method. Super-resolution laser confocal scanning microscope (TCS SP8, Leica, Germany) was used to view the structures of emulsion samples. The freshly prepared sample was placed on a microscopy slide, and the observation was carried out before the sample starts to dry in the air. The 525 nm and 488 nm lasers were respectively provided to excitate the fluorescence of oil-soluble ROT 300 and water-soluble FLS. Rheological measurements were performed on a HAAKE RS75 rheometer with a cone-plate system (C35/1°Ti L07116, diameter: 35 mm, core angle: 1°). In oscillatory measurements, a stress sweep at a fixed frequency of 1 Hz was carried out to select a stress in a linear viscoelastic region, which was unchangeable in the frequency sweep ranging from 0.1 to 10 Hz. The microstructures of polymerized samples were characterized by scanning electron microscope (ZEISS G300, Germany) and super-resolution laser scanning confocal microscope (TCS SP8, Leica, Germany).

1.4 Image analysis

The 3D construction of bijel was obtained by 3D viewer plugin of image J2 [1] through laser confocal section images, and the channel diameters were also measured by image J2. The curvatures were analyzed by Avizo software. A series of appropriate slices were imported to generate 3D ortho slice and allow the software to process interactive thresholding, following the thresholded images can be obtained (Fig. S9a). Then the surface was extracted by generating surface module (Fig. S9b) and the curvature could be calculated. The more accurate thresholded images can be produced by adjusting interactive thresholding module to resemble to the original bijel as well as reducing the occurrence of surface discontinuities.

2. Supplementary Figures, Table and Video

Table S1 The interface tension of water-oil (PDMS-AR) interface under different additives.

Interface	Interface tension (mN m^{-1})
Water/PDMS-AR	22.06 ± 0.01
SiO_2 (0.5 wt%) in water/PDMS-AR	21.51 ± 0.03
SiO_2 (0.5 wt%) in water/diNH_2-PDMS (7.5 wt%) in PDMS-AR	5.20 ± 0.01

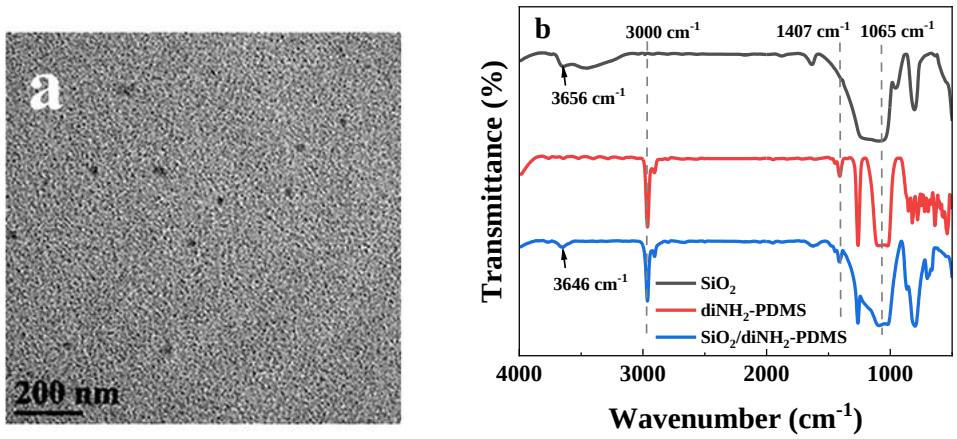


Fig. S1 (a) TEM image of primitive SiO_2 particles; (b) FT-IR spectra of SiO_2, diNH_2-PDMS and SiO_2/diNH_2-PDMS mixtures.

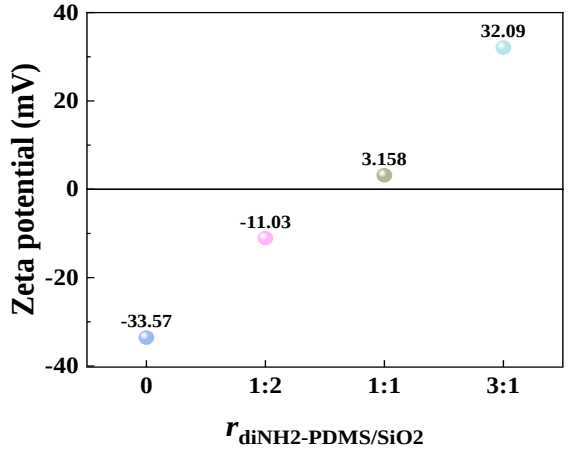


Fig. S2 Zeta potential of SiO_2 particles at different mass ratios (r) of diNH_2-PDMS to SiO_2 particles. pH = 7.

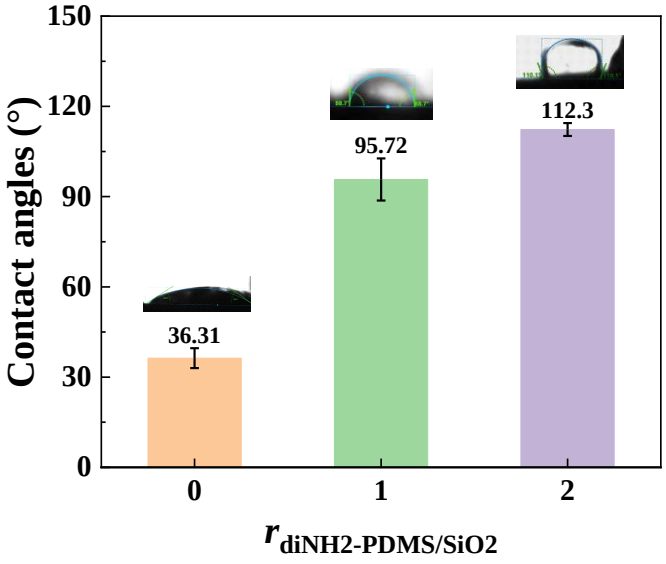


Fig. S3 The water-(PDMS-AR)-particle contact angles of stabilizers with different mass ratios of $diNH_2$-PDMS to SiO_2 at pH = 7. T = 25.0 °C.

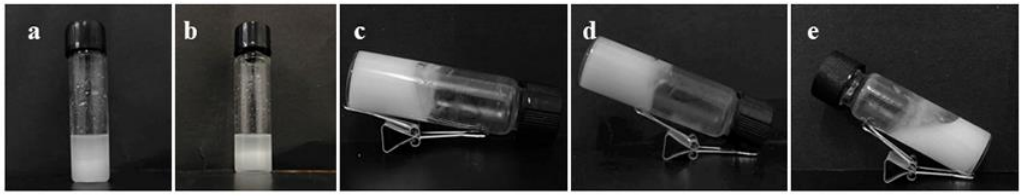
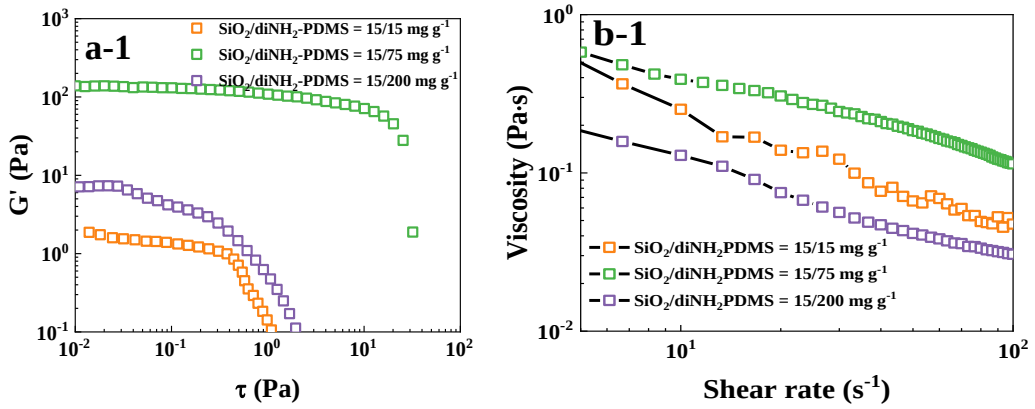


Fig. S4 Photographs of samples stabilized by (a) SiO_2 (15 mg g^{-1}), (b) $diNH_2$-PDMS (75 mg g^{-1}), (c) SiO_2/$diNH_2$-PDMS (mass concentration, 15/15 mg g^{-1}), (d) SiO_2/$diNH_2$-PDMS (mass concentration, 15/75 mg g^{-1}) and (e) SiO_2/$diNH_2$-PDMS (mass concentration, 15/200 mg g^{-1}). pH = 7.



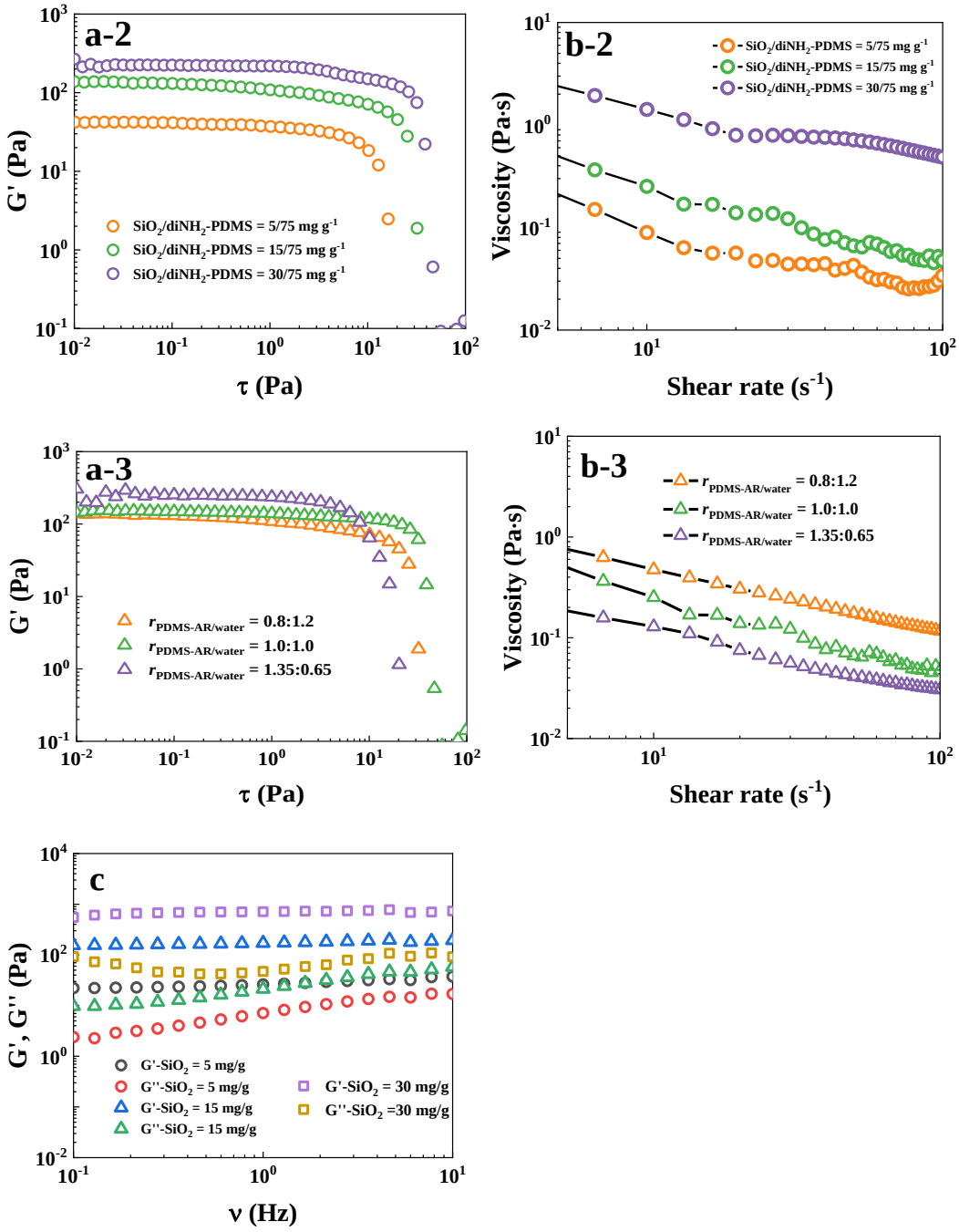


Fig. S5 (a) Stress sweep and (b) steady-state shear of emulsion samples: (a-1, b-1) 15 mg g^{-1} SiO_2 with different concentrations of $diNH_2$-PDMS; (a-2, b-2) 75 mg g^{-1} $diNH_2$-PDMS with different concentrations of SiO_2; (a-3, b-3) 15 mg g^{-1} SiO_2 and 75 mg g^{-1} $diNH_2$-PDMS with different mass ratios ($r_{PDMS\text{-}AR/water}$) of PDMS-AR to water; (c) frequency sweep of emulsion samples stabilized by 75 mg g^{-1} $diNH_2$-PDMS with different concentrations of SiO_2, $r_{PDMS\text{-}AR/water}$ = 1:1.

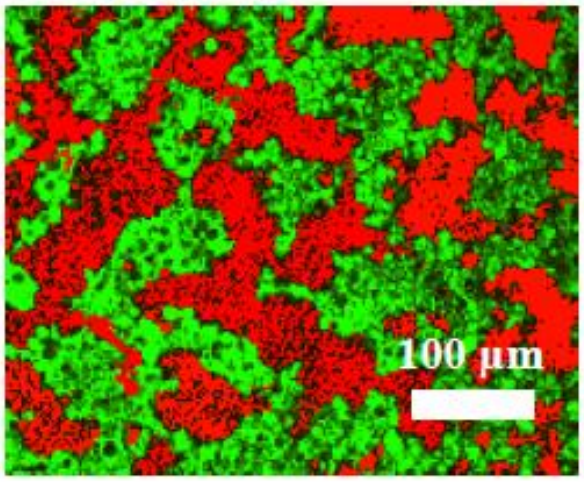


Fig. S6 The laser confocal microscopy image of Bijel stabilized by 15 mg g^{-1} SiO_2 with 75 mg g^{-1} diNH_2-PDMS at $r_{PDMS\text{-}AR/water}$ = 1:1. The oil and water were stained by ROT 300 and fluorescein sodium (FLS) with the red and green emission, respectively.

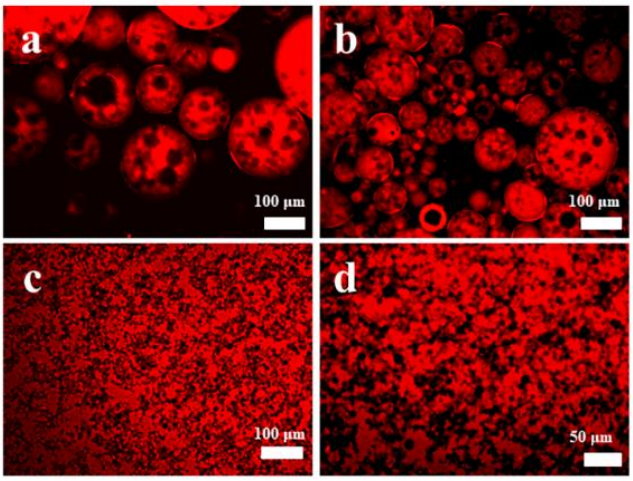


Fig. S7 Inverted fluorescence microscopy images of sample under specific shear force applied at different durations (a) 15 s, (b) 30 s, (c) 60 s and (d) 120 s. Emulsion was stabilized by 15 mg g^{-1} SiO_2 with 75 mg g^{-1} diNH_2-PDMS, $r_{PDMS\text{-}AR/water}$ = 1:1. The oil was stained by ROT 300 with the red emission.

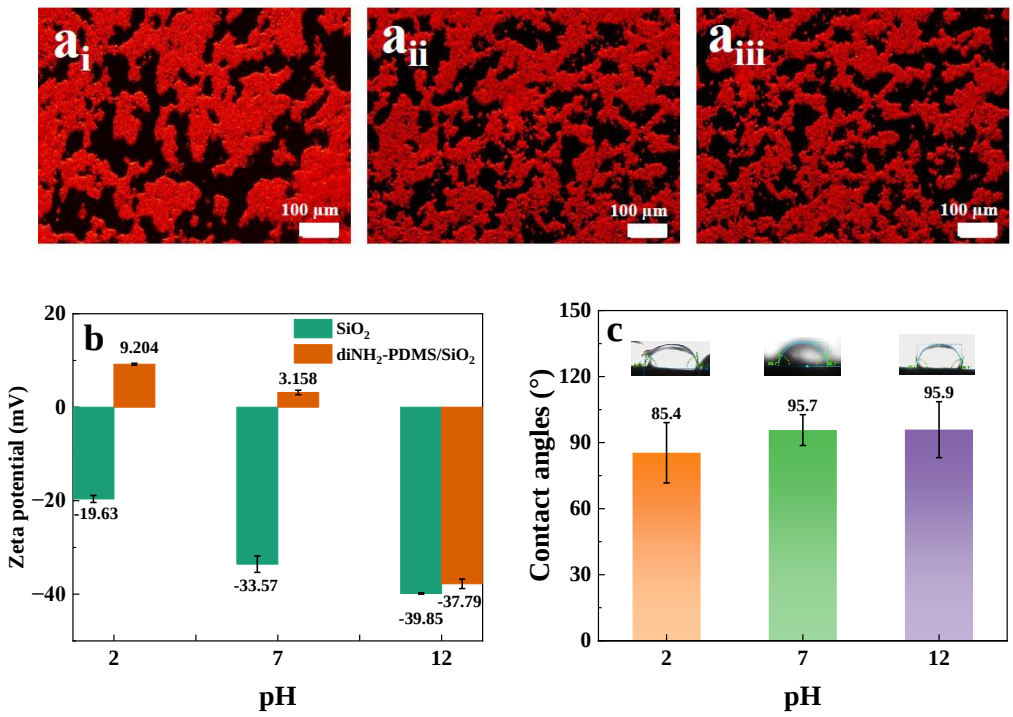


Fig. S8 Laser confocal microscopy images of Bijels at different pH: (a_i) pH = 2, (a_{ii}) pH = 7 and (a_{iii}) pH = 12; (b) zeta potential of SiO_2 and $diNH_2$-PDMS/SiO_2 at different pH; (c) water-(PDMS-AR)-particle contact angles at different pH ($r_{diNH2\text{-}PDMS/SiO2}$ = 1:1). Emulsions were stabilized by 15 mg g^{-1} SiO_2 with 75 mg g^{-1} $diNH_2$-PDMS, $r_{PDMS\text{-}AR/water}$ = 1:1. The oil was stained by ROT 300 with red emission.

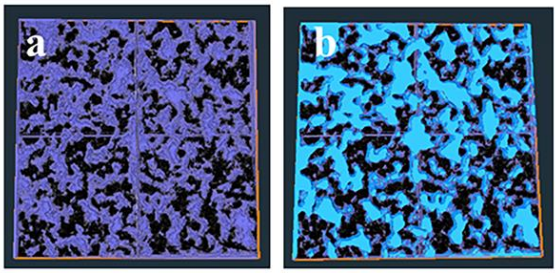
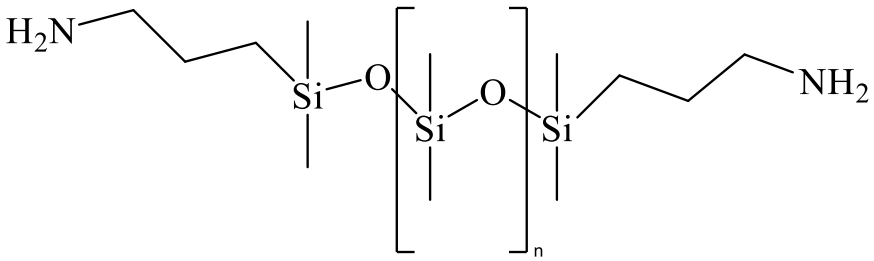


Fig. S9 (a) Thresholded bijel image and (b) extracted surface image by Avizo software.



Scheme S1 The chemical structure of diNH_2-PDMS.

Video S1 The reconstruction movie of bijel sample by imageJ software.

References

1. M. Reeves, K. Stratford and J. H. Thijssen, *Soft Matter*, 2016, **12**, 4082-4092.