Electronic Supporting Information

Bioorganometallic Ferrocene-Tripeptide Nanoemulsions

Xuejiao Yang, ‡ª Yuefei Wang, ‡ª, c Wei Qi, *a, b, c Rongxin Su, a, b, c Zhimin Heª

^aState Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China.

^bCollaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China.

^cTianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin 300072, P. R. China.

*qiwei@tju.edu.cn

[‡]These authors contributed equally.

Supplementary Figures



Fig. S1 Static water contact angle in air of the obtained a) Fc-FFH, b) Fc-FFD, c) Fc-FFF, and d) Fc-FFS nanoemulsions prepared at a 7:3 aqueous/organic volume ratio, indicating the four kinds of nanoemulsions were oil-in-water.



Fig. S2 Confocal laser scanning microscopy (CLSM) images of the a) Fc-FFH, b) Fc-FFD, c) Fc-FFF, and d)

Fc-FFS nanoemulsions prepared at a 7:3 aqueous/organic volume ratio under bright field.



Fig. S3 CLSM a) and SEM b) images of the FFH self-assemblies prepared at a 7:3 aqueous/organic volume ratio.



Fig. S4 The top optical photographs showed tripeptide nanoemulsions freshly prepared at 7:3 aqueous/organic volume ratio, and the bottom showed the four samples incubated for 4 months at room temperature (T=25 °C). From left to right, the samples are Fc-FFH, Fc-FFD, Fc-FFF, and Fc-FFS nanoemulsions, respectively.



Fig. S5 High-magnification SEM images of the a) Fc-FFD, b) Fc-FFF, and c) Fc-FFS nanoemulsions prepared at a 7:3 aqueous/organic volume ratio.



Fig. S6 High-magnification TEM images of the a) Fc-FFD, b) Fc-FFF, and c) Fc-FFS nanoemulsions prepared at a 7:3 aqueous/organic volume ratio.



Fig. S7 Size distribution of the Fc-FFD, Fc-FFF, and Fc-FFS nanoemulsions prepared at a 7:3 aqueous/organic volume ratio derived from the DLS analysis.



Fig. S8 a) The change in the average diameter of Fc-FFH nanoemulsions as a function of the aqueous/organic volume ratio. b) Histogram of the normalized size distribution of the Fc-FFH nanoemulsions prepared in a 7:3 aqueous/organic volume ratio, derived from the TEM image. The red curve is the size distribution of Fc-FFH nanoemulsions prepared in a 7:3 aqueous/organic volume ratio, derived from DLS.



Fig. S9 The change in the average diameter of a) Fc-FFD, b) Fc-FFF, and c) Fc-FFS nanoemulsions as a function of the aqueous/organic volume ratio. As the aqueous/organic volume ratio altered from 1:9 to 9:1, the average diameter changed from 5391 nm, 928 nm, 375 nm, 158 nm, to 127 nm for Fc-FFD nanoemulsions, from 5555 nm, 916 nm, 396 nm, 181 nm, to 158 nm for Fc-FFF nanoemulsions, and changed from 5407 nm, 795 nm, 357 nm, 217 nm, to 180 nm for Fc-FFS nanoemulsions, respectively. The insets of the images are the photographs which show the oil-in-water nanoemulsions (yellow milky layer) prepared by homogenizing ethyl acetate with 1 mg mL⁻¹ Fc-FFD, Fc-FFF, and Fc-FFS phosphate buffer solution (50 mM, pH 7.20). From left to right, the volume ratio of phosphate buffer to ethyl acetate was altered from 1:9, 3:7, 5:5, 7:3, to 9:1, and the total volume was 1 mL.



Fig. S10 High-magnification TEM images of a) Fc-FFH, b) Fc-FFD, c) Fc-FFF, and d) Fc-FFS nanoemulsions prepared at a 7:3 aqueous/organic volume ratio incubated for 4 months at room temperature.



Fig. S11 Size distribution of the Fc-FFH, Fc-FFD, Fc-FFF, and Fc-FFS nanoemulsions prepared at a 7:3 aqueous/organic volume ratio incubated for 4 months derived from the DLS analysis. The average diameter of Fc-FFH, Fc-FFD, Fc-FFF, and Fc-FFS nanoemulsions is 556 nm, 480 nm, 532 nm, and 498 nm, respectively.



Fig. S12 High-magnification SEM images of Fc-FFH hydrogels and nanoemulsions prepared at a 7:3 aqueous/organic volume ratio incubated at a) 10 °C, b) 40 °C, and c) 60 °C for 3 hours.



Fig. S13 Optical photographs of Fc-FFD, Fc-FFF, and Fc-FFS nanoemulsions prepared at a 7: 3 aqueous/organic volume ratio incubated at increasing temperatures for 3 hours. Even at 70 °C, the three kinds of nanoemulsions still maintain stable, indicating that the nanoemulsions have a strong tolerance to high temperature.



Fig. S14 High-magnification TEM images of a) Fc-FFD, b) Fc-FFF, and c) Fc-FFS nanoemulsions prepared at

a 7:3 aqueous/organic volume ratio incubated at 70 °C for 3 hours.



Fig. S15 The change in the average diameter of Fc-FFD, Fc-FFF, and Fc-FFS nanoemulsions prepared at a 7:3 aqueous/organic volume ratio as the function of temperature.



Fig. S16 2-D X-ray diffraction pattern of Fc-FFH nanoemulsions prepared at a 7:3 aqueous/organic volume ratio at room temperature.



Fig. S17 Standard curve for the relation between monomer concentration and peak ratio (D₂O/Fc) derived from Nuclear Magnetic Resonance (NMR) spectroscopy analysis.



Fig. S18 High-magnification SEM image of oxidized Fc-FFH nanoemulsions prepared at a 7:3 aqueous/organic volume ratio using electrochemical method.



Fig. S19 Standard curve for the relation between the absorbance at 400 nm in UV-visible spectroscopy and the concentration of PNP which dissolved in 50 mM, pH 7.20 phosphate buffer.

Supplementary Tables

	Peak Ratio (D ₂ O/Fc)	Monomer Concentration (mM)
Nanoemulsions	242.45	0.71
Hydrogels	258.30	0.33

Table S1 Monomer concentration of nanoemulsions and hydrogels calculated according to Fig. S17.