

Electronic Supplementary Information

Vesicles of 2-Ketooctanoic Acid in Water: A Plausible Protocell Model

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Measurements

Nuclear magnetic resonance (NMR) Spectroscopy. ^1H NMR spectra were recorded at 25.0 ± 0.1 °C on a Brüker Advance 400 spectrometer (Brüker, Switzerland) equipped with a pulse field gradient module (Z-axis), using a 5 mm BBO probe at a frequency of 400.13 MHz. Samples for ^1H NMR were prepared in D_2O .

Electrospray Ionization Mass (ESI-MS) Spectrometry. ESI-MS spectra were recorded on an Agilent 6510 Q-TOF mass spectrometer (Agilent, USA).

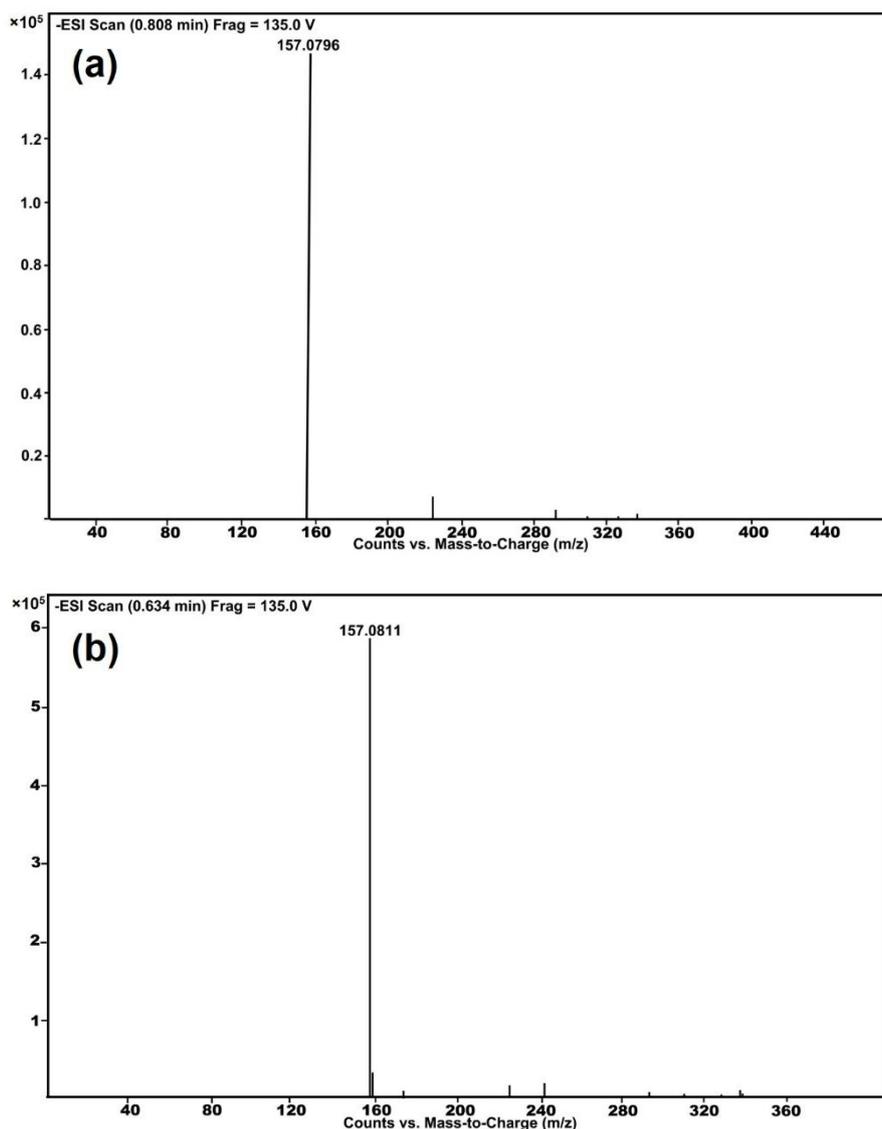


Fig. S1 ESI-MS spectra of KOCOOH solution (a) before and (b) after the experiments. No chemically bonded KOCOOH-KOCOOH dimers ($317.2 m/z$) were detected, and only a single peak of KOCOOH monomer ($157.1 m/z$) was observed. Small peaks (at m/z close to 220, 240 etc) probably arise from contaminants existing in the KOCOOH sample, as suggested by Griffith et al. (Photoinitiated synthesis of self-assembled vesicles, *J. Am. Chem. Soc.* **2014**, *136*, 3784–3787).

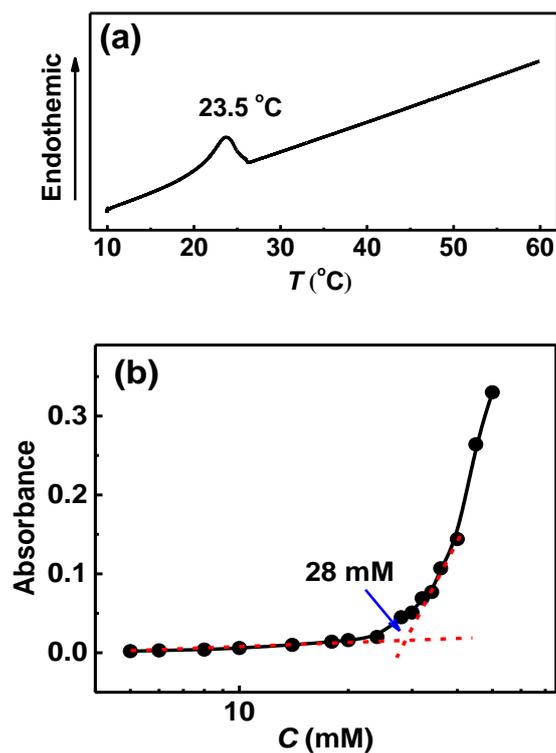


Fig. S2 (a) DSC trace of KOCOOH reagent. (b) Absorbance (at 400 nm) of KOCOOH aqueous solutions as a function of concentration.

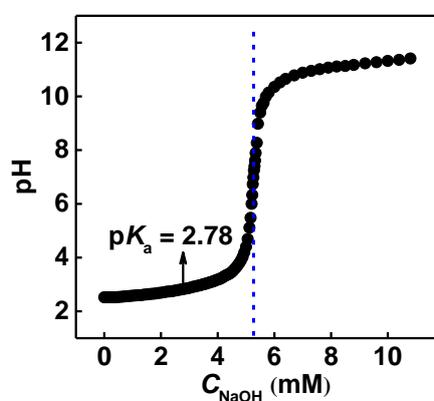


Fig. S3 pH titration curve of KOCOOH solution (6 mM) at $25\text{ }^{\circ}\text{C}$. The inflection points (at $\text{pH} \sim 7$ in our case) of pH titration curves are commonly thought to correspond to the complete ionization of weakly acidic surfactants, and the pH values (~ 2.78 in our case) at half the ionization volume (i.e., half the NaOH volume required to reach the complete ionization end point) are defined as the $\text{p}K_a$ of the surfactants.

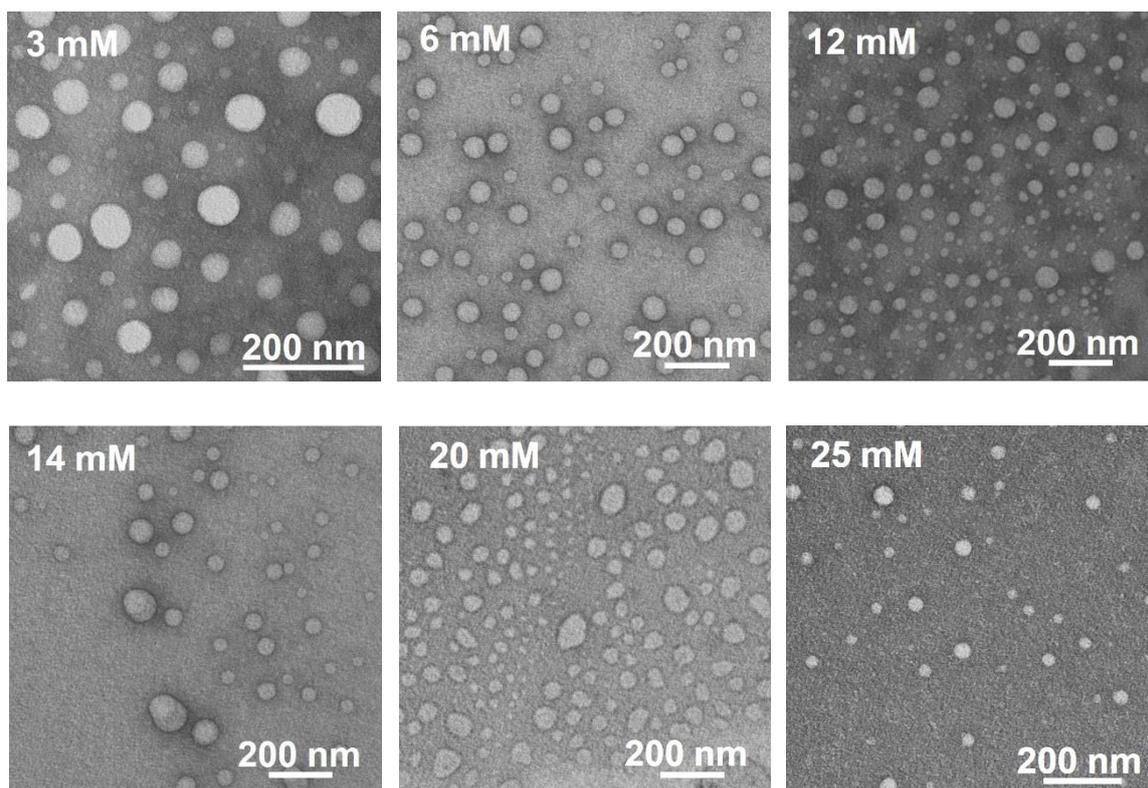


Fig. S4 NS-TEM images of KOCOOH solutions with various concentrations.

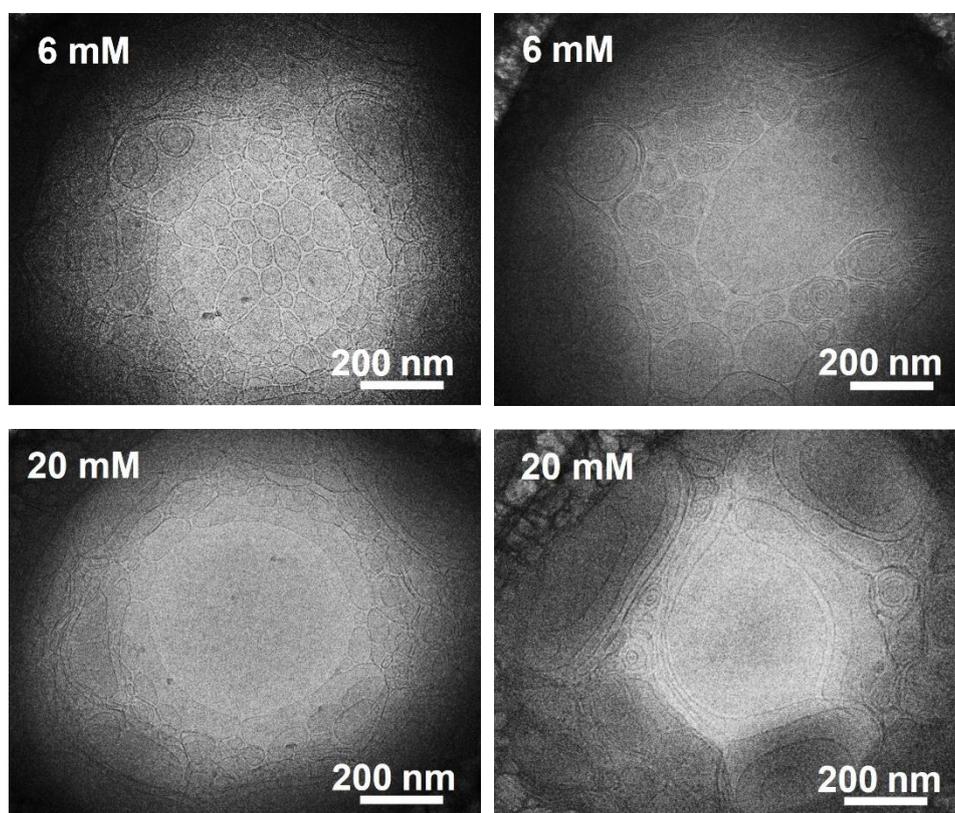


Fig. S5 Cryo-TEM images of KOCOOH solutions with 6 and 20 mM.

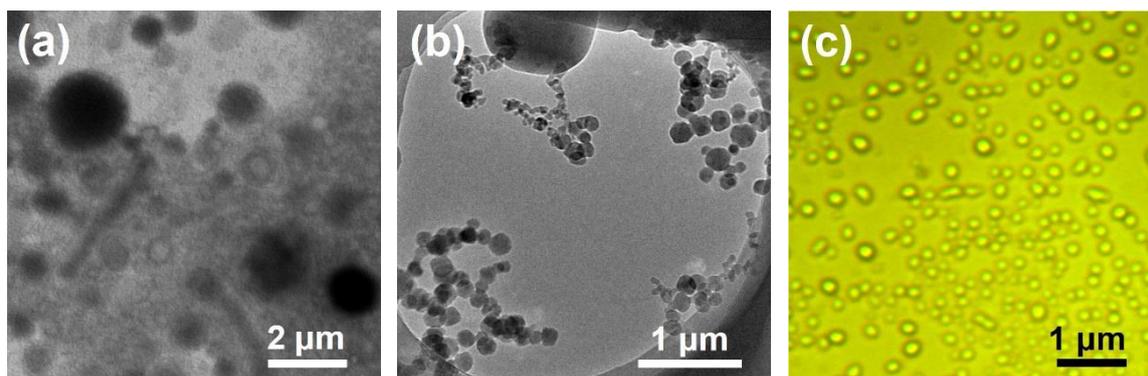


Fig. S6 (a) NS-TEM, (b) cryo-TEM images and (c) optical photograph of KOCOOH solution with 50 mM.

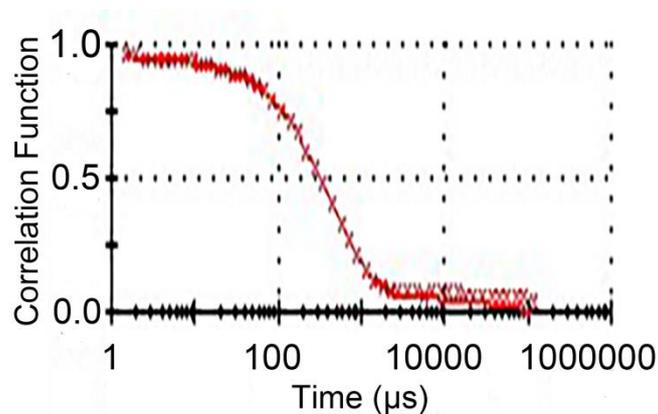


Fig. S7 Correlation function of KOCOOH aqueous solution (20 mM, pH = 2.2).

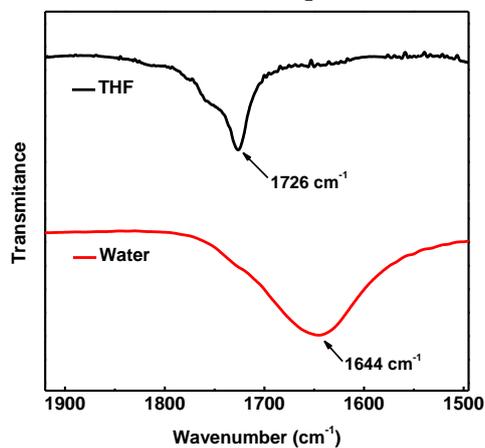


Fig. S8 FTIR spectra of KOCOOH in THF and water. The absorption peak corresponding to carbonyl stretching appears at $\sim 1726\text{ cm}^{-1}$ in THF, while shifts to 1644 cm^{-1} in water. This suggests that there exists hydrogen bonding between head groups (carboxyl groups) in vesicles, based on the previous reports (Ref. 45, Mondal et al., Langmuir, 2013, 29, 6746–6753).

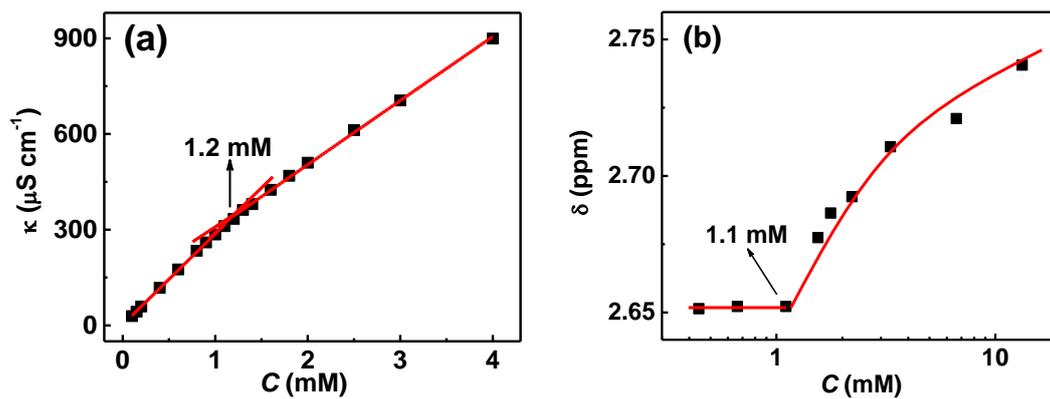


Fig. S9 (a) Change in conductivity (κ) of KOCO₂H solutions versus concentration. (b) Change in chemical shift (δ) of β -methylene protons of KOCO₂H in D₂O versus concentration. Breakpoints can be observed, indicating that aggregation of KOCO₂H molecules occurred.

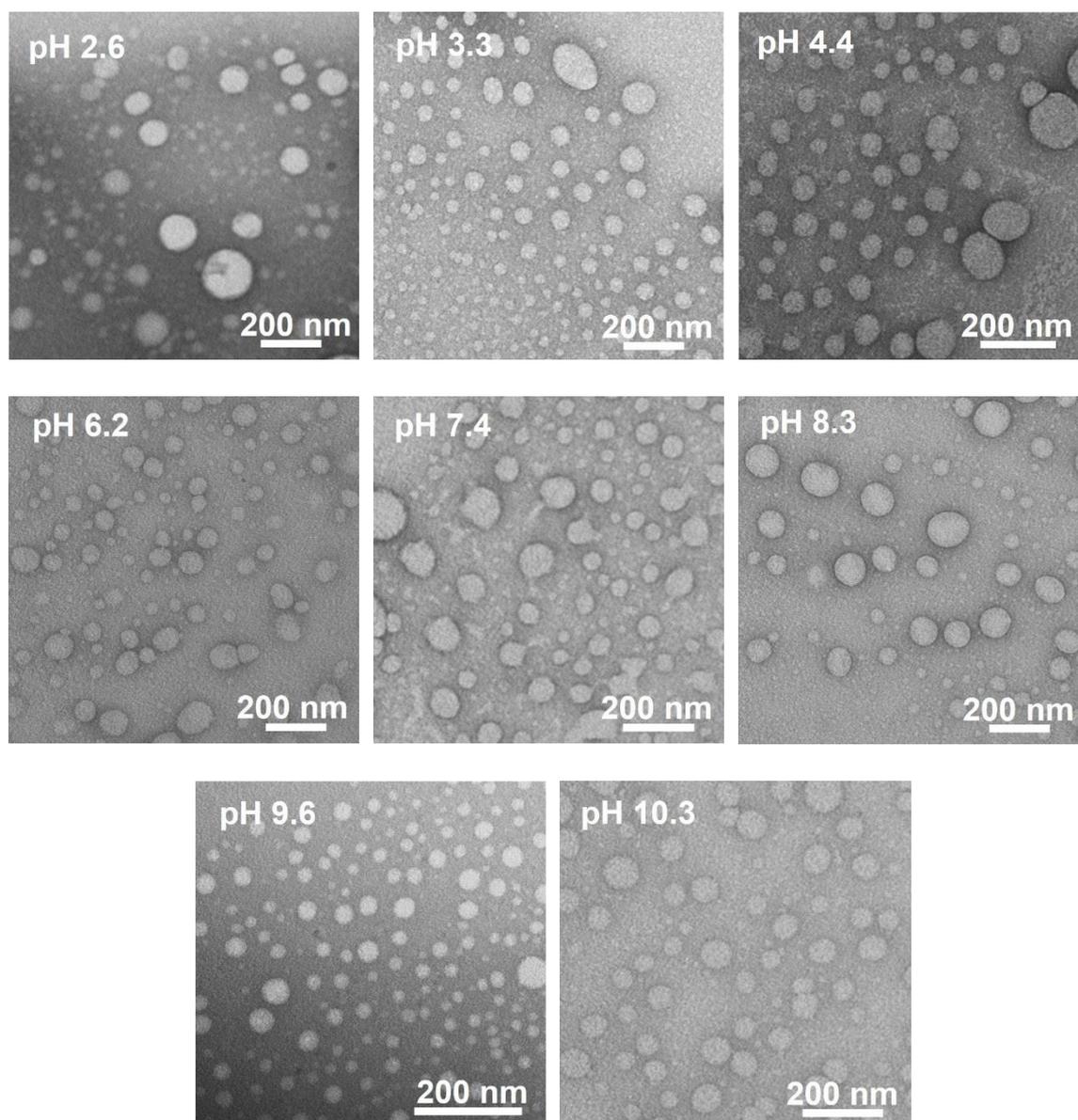


Fig. S10 NS-TEM images of KOCOOH solutions (6 mM) at various pH.

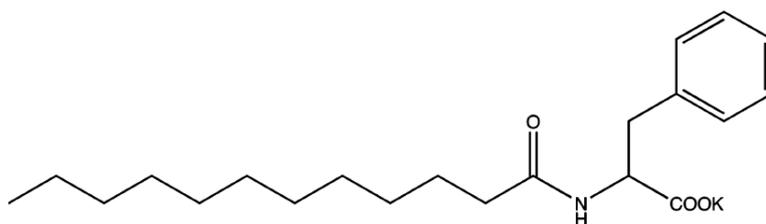


Fig. S11 Chemical structure of potassium *N*-dodecanoyl *L*-phenylalaninate.