Supporting Information For:

Discrete Single Entity Electrochemistry of Pickering Emulsions

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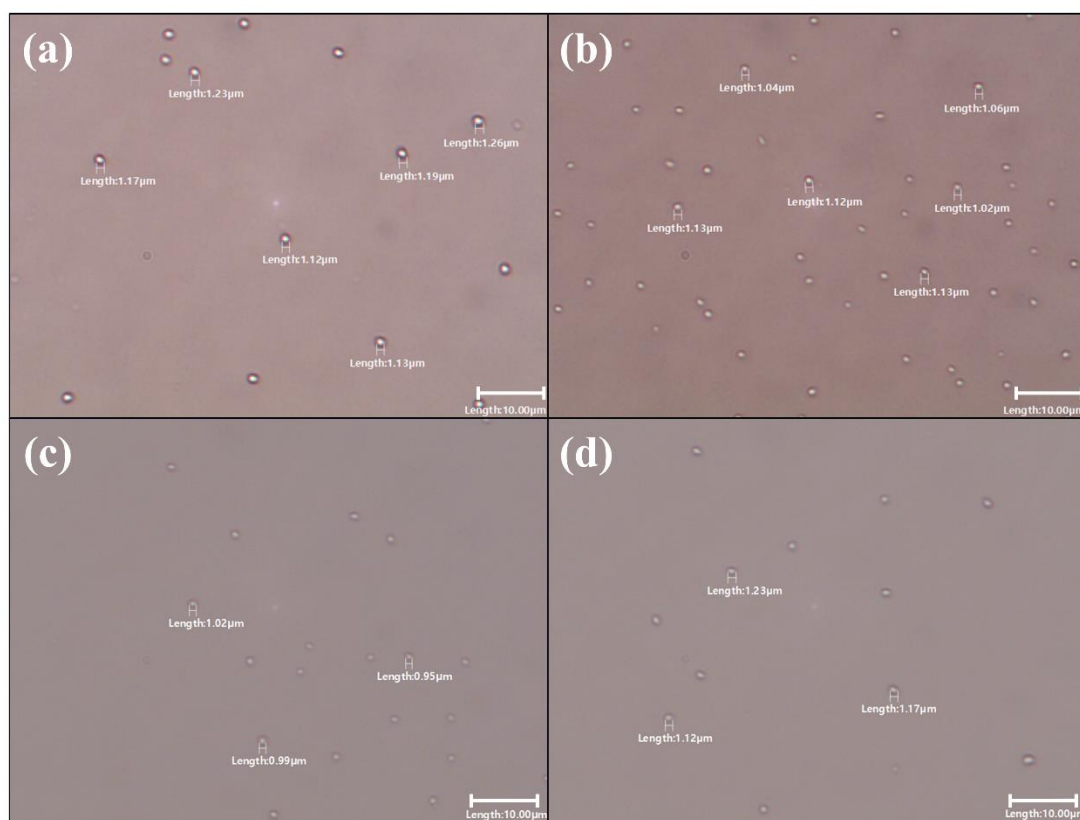*bDepartment of Chemistry, Sookmyung Women's University, Seoul 04310, Republic of Korea*
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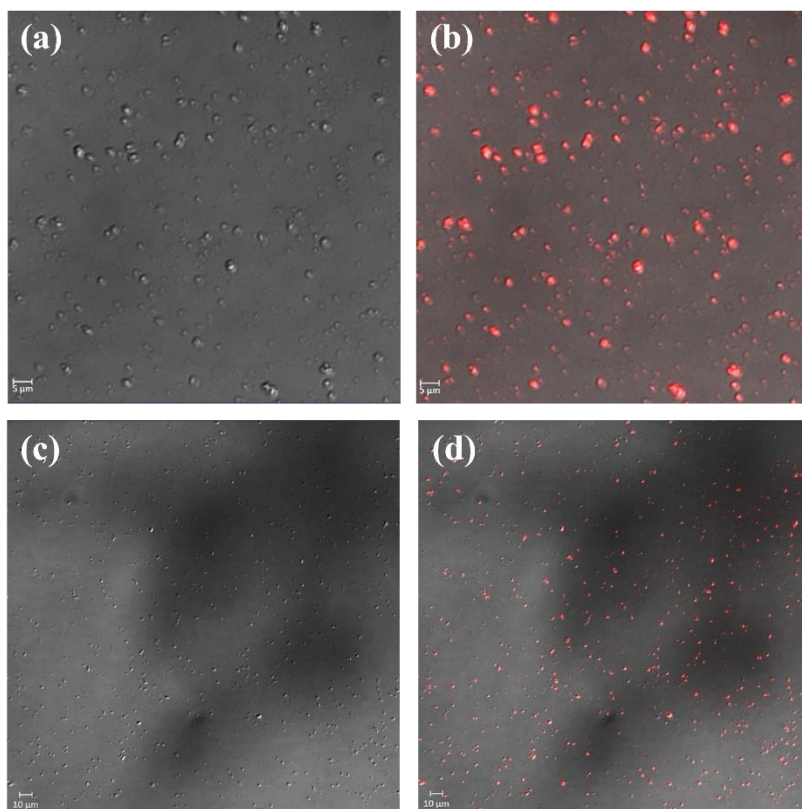
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Figure S1. **(a)**-**(c)** Optical microscopy images of synthesized Pickering emulsions dispersed in toluene, **(d)** optical image of Pickering emulsions dispersed in toluene/chloroform mixture (0.01 M TBAP).

Figure S2. (a), **(c)** Confocal laser scanning microscopy images of Pickering emulsions containing Rhodamine 6G in water phase obtained by T-PMT mode of confocal laser scanning microscope. **(b)**, **(d)** Confocal micrographs of Pickering emulsions when fluorescence activated.
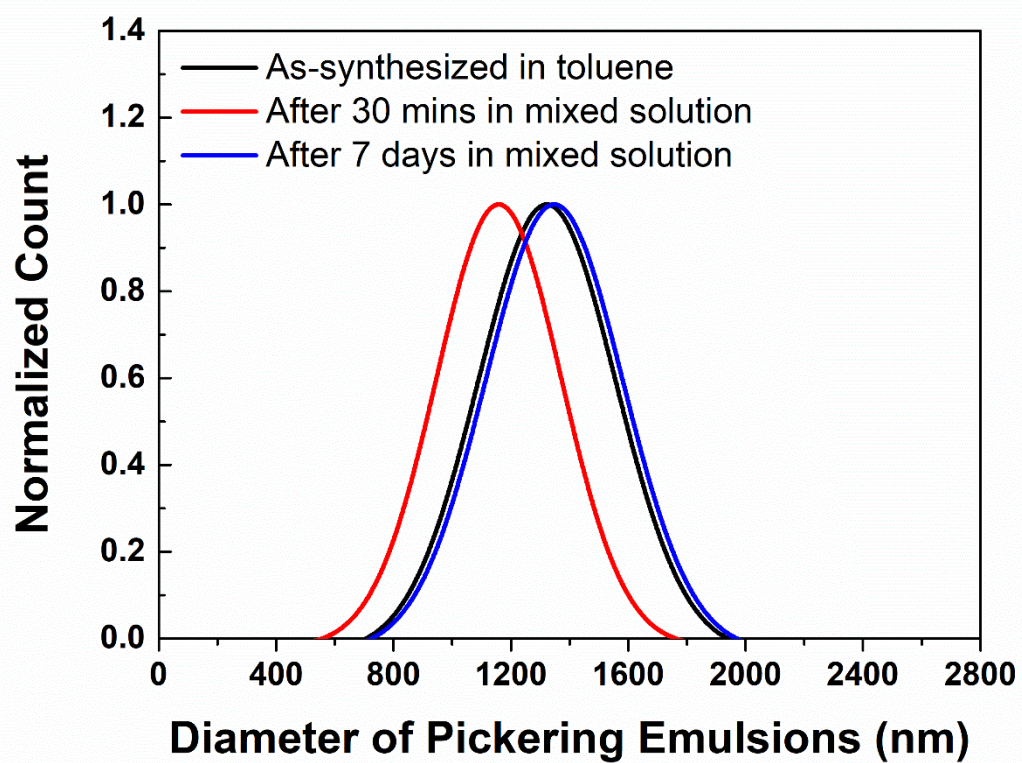
Figure S3. Size distribution of Pickering emulsions in experimental solution determined by DLS exhibiting their stability. The stability of Pickering emulsions were maintained over 7 days.

Calculation of Expected Collision Frequency of Pickering Emulsions

The expected frequency of the Pickering emulsions colliding with the working electrode can be estimated by the following formula.[S1]

$$f_{P.E.} = 4D_{P.E.}C_{P.E.}r_{elec}N_A$$

$C_{P.E.}$ is the concentration of the Pickering emulsions.

$$C_{P.E.} = \frac{\frac{V_{aq}}{V_{P.E.}}}{N_A} \cdot \frac{1}{V_s} \cdot \frac{V_{in}}{V_{total}} = \frac{\frac{1 \times 10^{-6}\ m^3}{\frac{4}{3}\pi \times (5.5 \times 10^{-7}\ m)^3}}{(6.0221 \times 10^{23}\ mol^{-1})} \times \frac{1}{0.0051\ L} \times \frac{0.3\ mL}{6.3\ mL}$$

$$= 2.34 \times 10^{-12}\ M$$

V_{aq} is the volume of aqueous solution added when synthesizing the Pickering emulsions, V_s is the sum of aqueous solution and toluene volumes, $V_{P.E.}$ is the volume of the synthesized Pickering emulsions, N_A is Avogadro's number, V_{in} is the volume of the Pickering emulsions injected in the experiment, V_{total} is the total volume of the experimental solution.

The diffusion coefficient of the Pickering emulsions dispersed in a mixed solution of chloroform and toluene, $D_{P.E.}$, was obtained using the Stokes-Einstein equation.[S1] The viscosity of the mixed solution of chloroform and toluene was calculated using the Gambill method.[S2] η is the kinetic viscosity, and x is the mass fraction. In the formula, a and b were chloroform and toluene, respectively.

$$D_{P.E.} = \frac{k_B T}{6\pi\eta r_{P.E.}}$$

$$\eta^{1/3} = x_a \eta_a^{1/3} + x_b \eta_b^{1/3}$$

$$\eta^{1/3} = \left\{ 0.775 \times (5.42 \times 10^{-4}\ Pa \cdot s)^{1/3} \right\} + \left\{ 0.225 \times (5.6 \times 10^{-4}\ Pa \cdot s)^{1/3} \right\}$$

$$\eta = 5.46 \times 10^{-4}\ Pa \cdot s$$

$$D_{P.E.} = \frac{(1.381 \times 10^{-23}\ kg \cdot m^2 \cdot s^{-2} \cdot K^{-1}) \times (298\ K)}{6\pi \times (5.46 \times 10^{-4}\ kg \cdot m^{-1} \cdot s^{-1}) \times (5.5 \times 10^{-7}\ m)} = 7.27 \times 10^{-13}\ m^2 s^{-1}$$

r_{elec} is the radius of ultramicroelectrode, therefore, the expected collision frequency is,

$$f_{P.E.} = 4D_{P.E.}C_{P.E.}r_{elec}N_A$$

$$= 4 \times (7.27 \times 10^{-13}\ m^2 \cdot s^{-1}) \times (2.34 \times 10^{-12}\ mol \cdot m^{-3}) \times (1.25 \times 10^{-5}\ m)$$

$$\times (6.0221 \times 10^{23}\ mol^{-1}) = 0.0512\ s^{-1}$$
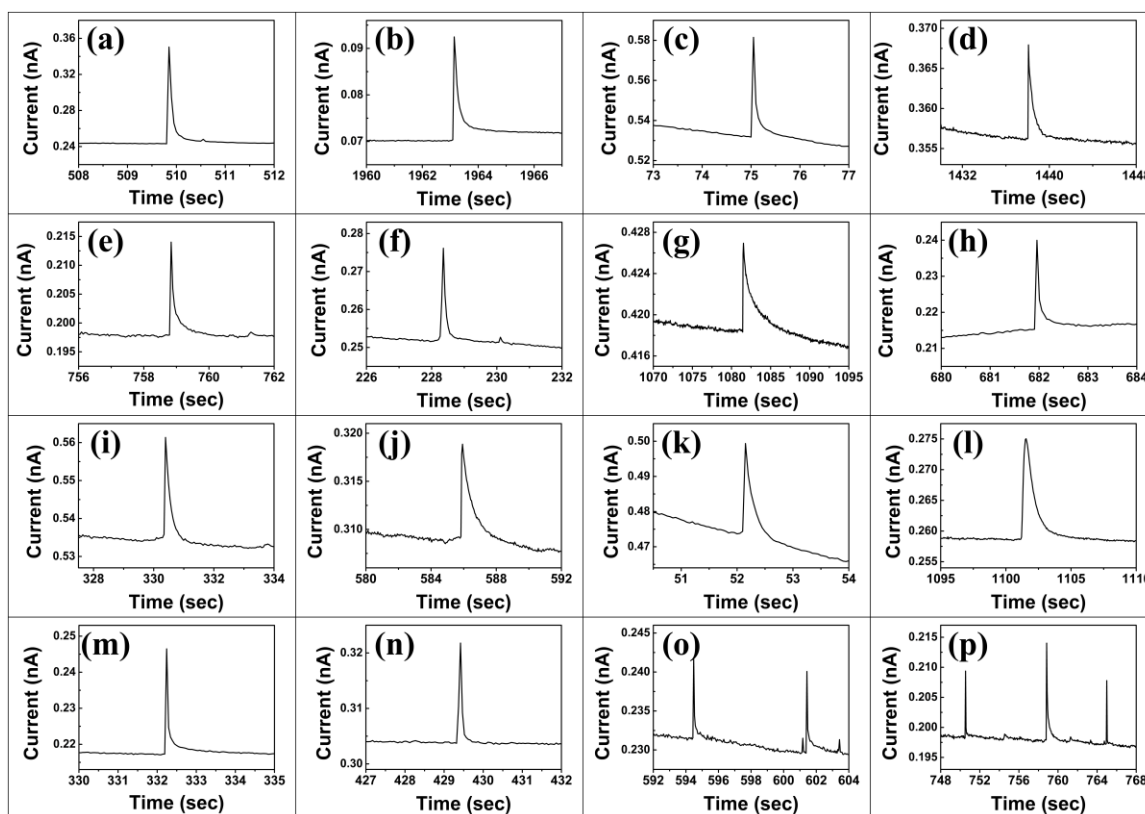
Figure S4. Chronoamperograms exhibiting individual collision events of Pickering emulsions containing 0.1 M ferricyanide. The size distribution of the colliding Pickering emulsions can be estimated by integrating the area under each current signal.
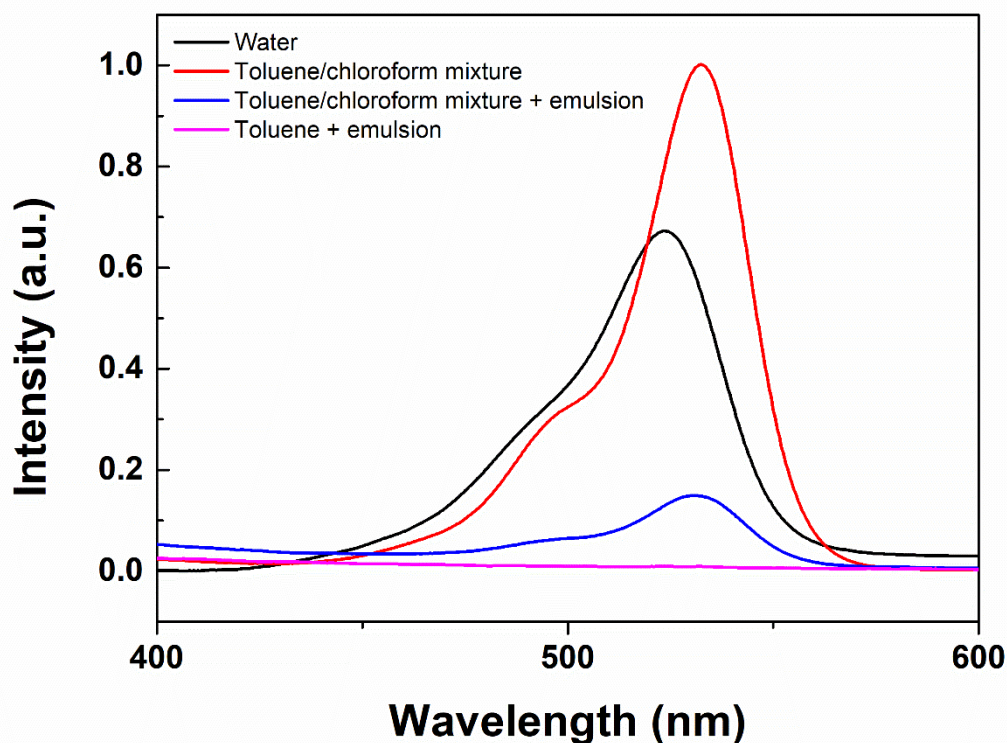
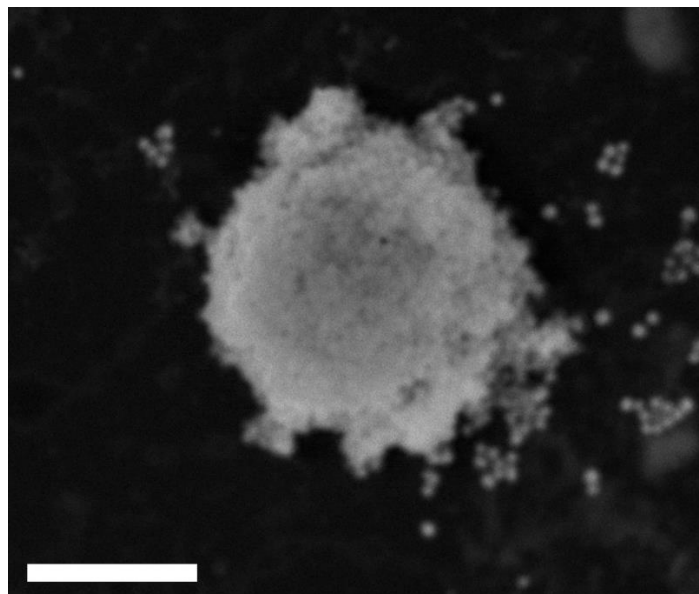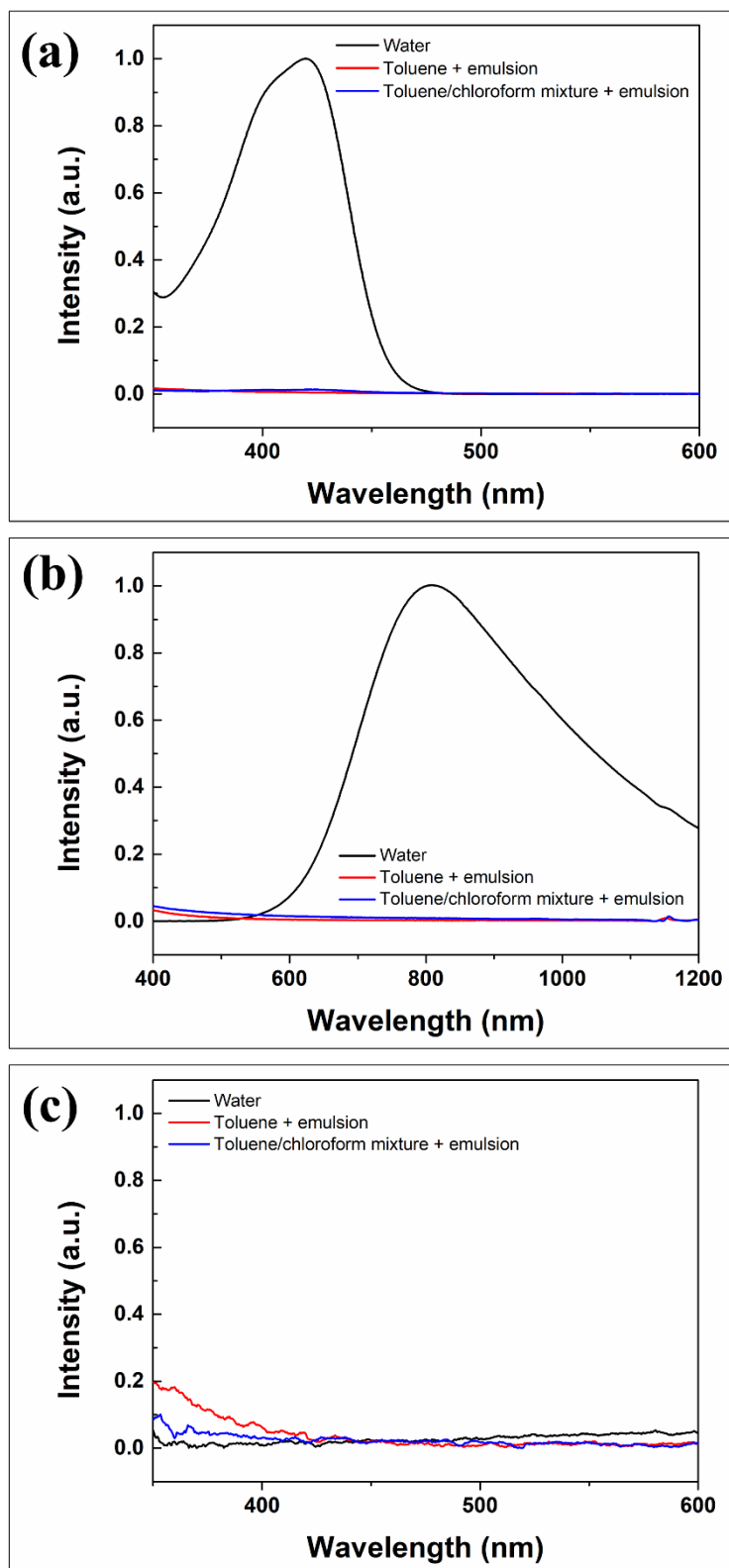**Figure S5.** UV-visible absorption spectrum of Rhodamine 6G in water (black trace) showing a strong absorption centered around 550 nm. The magenta trace is that of the continuous phase when the Pickering emulsions were dispersed in toluene continuous phase. Due to the poor solubility of Rhodamine 6G in toluene, negligible absorption occurred, consistent with our confocal microscopy results. Black and red traces are that of 5 mM Rhodamine 6G dissolved in water and 2:1 v/v mixture of chloroform and toluene, respectively. Appreciable solubility was observed in the mixed solvent system. Blue trace was obtained when Pickering emulsions containing 10 mM Rhodamine 6G in their aqueous phase was dispersed in chloroform/toluene, similar to the solvent in the electrochemistry experiments. Rhodamine 6G molecules escaped the Pickering emulsions into the continuous phase, as evidenced by the absorption at 550 nm.

Figure S6. SEM image of a Pickering emulsion droplet (stabilized by 12 nm silica) adsorbed to a glassy carbon electrode. The scale bar is 1 μm.
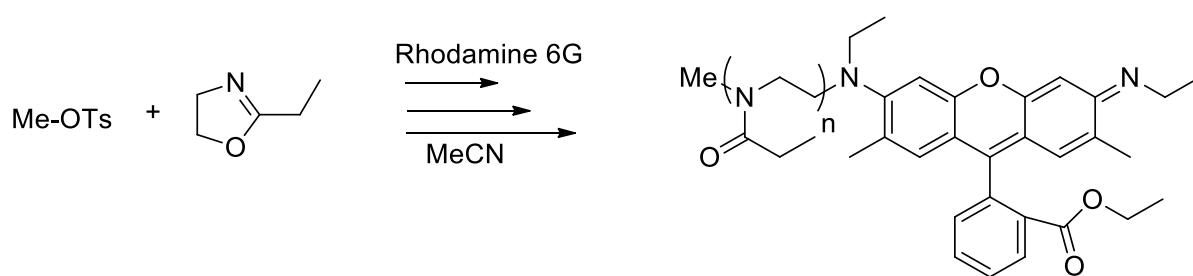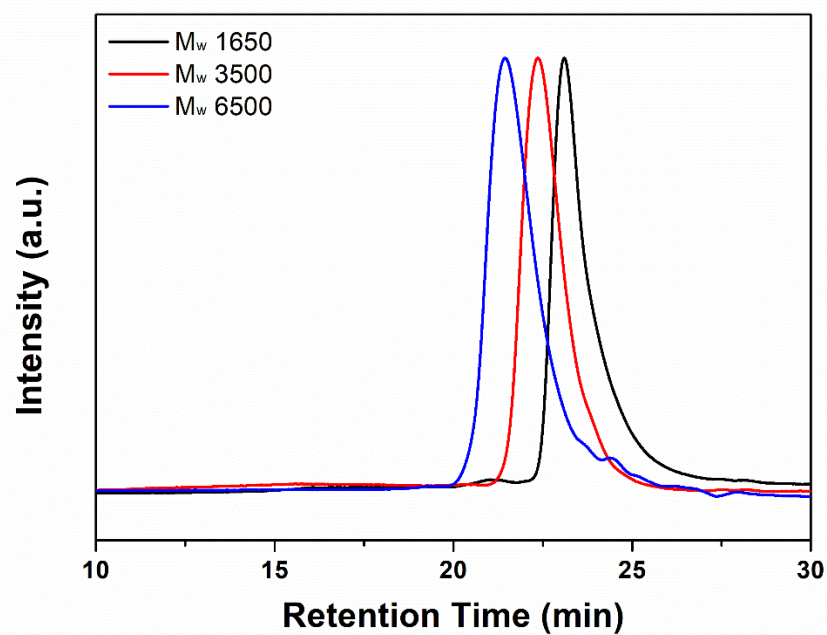
Figure S7. UV-visible absorption spectra of Pickering emulsions containing electroactive species of **(a)** 0.1 M [Fe(CN)$_6$]$^{3-}$, **(b)** 0.1 M Cu(NO$_3$)$_2$, **(c)** 0.1 M AgNO$_3$. None of the species were able to escape Pickering emulsions to toluene/chloroform continuous phase.

Synthesis of Methyl-PEtOx-R6G Dye molecules

The synthesis process for Methly-PEtOx-R6G is summarized in Scheme S1. A Schlenk flask was degassed under high vacuum and backfilled with N_2. A solution of initiator methyl p-toluenesulfonate (0.2 g, 1 eq) in MeCN (1.6 mL to 7.1 mL) was placed in the Schlenk flask, and then a solution of 2-ethyl-2-oxazoline (EtOx) (1.1 mL, 10 to 45 eq) was added. The mixture was stirred at 60 °C under a N_2 atmosphere for 24 h. The reaction was monitored by analytical SEC. When target molecular weight (1650, 3500, 6500) was reached, a solution of Rhodamine 6G (0.5 g, 1 eq) in MeOH (1 mL) was added as terminator to the reaction mixture, which was further stirred at 60 °C for 24 h. The mixture was poured into DCM and washed with brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by recycling preparative SEC using $CHCl_3$ as eluent to afford Methyl-PEtOx-R6G as a pink powder.

Scheme S1. Synthesis of Methyl-PEtOx-R6G polymers

Figure S8. Size exclusion chromatographs of methyl-PEtOx-R6G polymers in CHCl$_3$ with varying molecular weight: **(a)** 1650, **(b)** 3500, **(c)** 6500. Polystyrene standards were used for analysis.
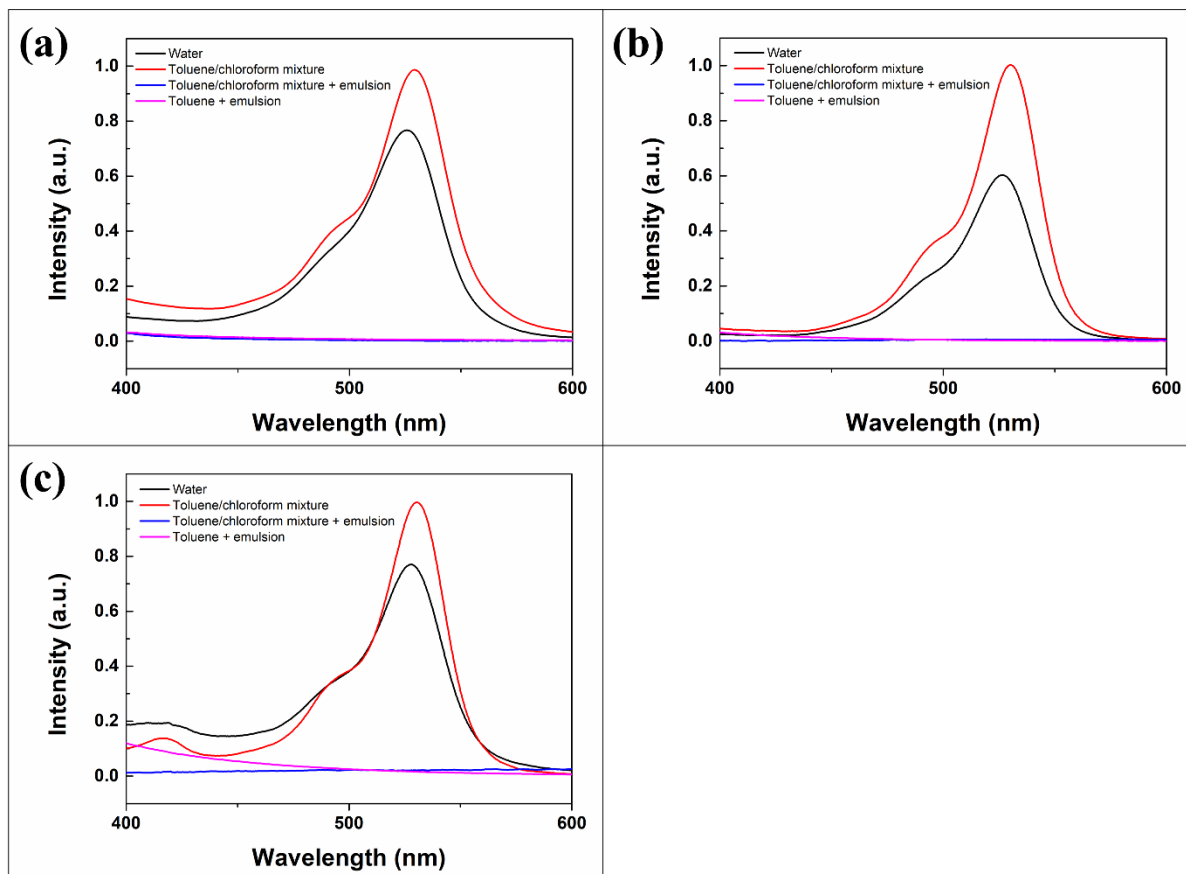
Figure S9. UV-visible absorption spectra of Pickering emulsions containing 3 mM methyl-PEtOx-R6G polymers in varying molecular weights of **(a)** 1650, **(b)** 3500, **(c)** 6500. None of the dye molecules were able to escape to toluene/chloroform continuous phase in conditions of electrochemistry experiments.

Calculation of Diameter of Pickering Emulsions Based on EDR

The diameter of synthesized Pickering emulsions can be estimated by following equation.

$$d_{P.E.} = 2\sqrt[3]{\frac{3Q}{4\pi F C_{redox}}}$$

By integrating the area of single collision signal of chronoamperogram, the amount of charge, Q can be obtained. F is Faraday constant, and C_{redox} is the concentration of the reactant (0.1 M ferricyanide in EDR) contained in the Pickering emulsions. For a spike current signal, the calculated droplet diameter when a total charge of 8.75 pC passes through is,

$$d_{P.E.} = 2\sqrt[3]{\frac{3 \times 8.75 \times 10^{-12}\ C}{4 \times \pi \times 96485\frac{C}{mol} \times 0.1\frac{mol}{L} \times \frac{1\ L}{1000\ cm^3}}} \times \frac{1\ m}{100\ cm}$$

$$= 1.2 \times 10^{-6}\ m$$

## Calculation of Projected Average Diameter of the Synthesized Nanoparticles

The average diameter of the nanoparticles electrodeposited on an electrode as a result of Pickering emulsion collisions can be calculated according to the equations below.[S2] In the case of Ag nanoparticle synthesis, the concentration of $AgNO_3$ in an emulsion droplet is 100 mM. Assuming close packed spherical geometry,

$$V_{NP} = \frac{4\pi \times (5.50 \times 10^{-7}\ m)^3}{3} \times \frac{10^3\ L}{1\ m^3} \times (1.0 \times 10^{-1})\ \frac{mol}{L}$$

$$\times (6.0221 \times 10^{23})\ \frac{1}{mol} \times \frac{4\pi \times (1.72 \times 10^{-10}\ m)^3}{3}$$

$$= 8.95 \times 10^{-22}\ m^3$$

$$d_{NP} = 2 \times \sqrt[3]{\frac{3 \times (8.95 \times 10^{-22}\ m^3)}{4\pi}} = 1.20 \times 10^{-7}\ m$$
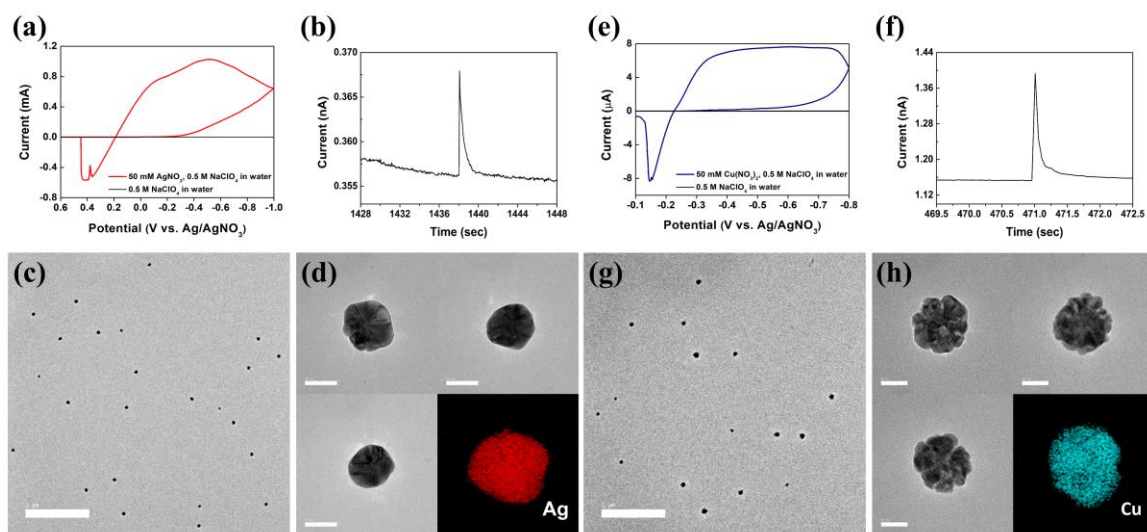
Figure S10. Cyclic voltammogram corresponding to the reduction of 50 mM **(a)** AgNO₃, **(e)** CuNO₃ obtained at 9 µm carbon UME in N₂ saturated aqueous solution. **(b)**, **(f)** The synthesis process of each nanoparticle by Pickering emulsion collision events are monitored *in-situ* through amperometry. **(c)**, **(d)** TEM and elemental mapping images of Pickering emulsion synthesized Ag nanoparticles. **(g)**, **(h)** TEM and elemental mapping images of Pickering emulsion synthesized Cu nanoparticles. Scale bars in **(c)** and **(g)** are 1 µm in length, and those in **(d)** and **(h)** are 50 nm in length.
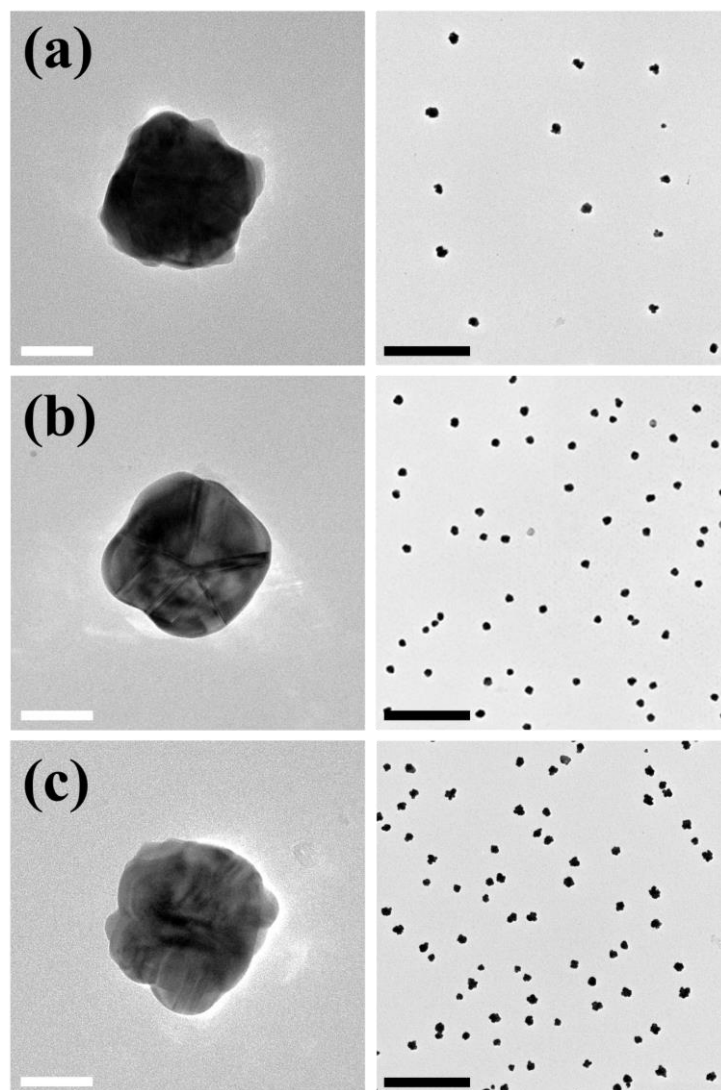
Figure S11. TEM micrographs of Ag nanoparticles synthesized *via* Pickering emulsion electrolysis by repeating electrodeposition cycles: **(a)** 1, **(b)** 2, **(3)** 3 times. The white scale bars are 50 nm and the black scale bars are 1 µm.

References

(1) B.-K. Kim, J. Kim and A. J. Bard, *J. Am. Chem. Soc.*, 2015, **137**, 2343–2349.

(2) Y. E. Jeun, B. Baek, M. Y. Lee and H. S. Ahn, *Chem. Commun.*, 2018, **54**, 10052-10055.

(3) J. M. Park, Y. J. Kim and W.-D. Jang, *ACS Appl. Polym. Mater.*, 2020, **2**, 3535–3542.