Supporting Information

Towards Ultralow Detection Limits of Aromatic Toxicants in Water using Pluronic Nanoemulsions and Single-Entity Electrochemistry

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1. Characterization of NEs by Dynamic Light Scattering (DLS)

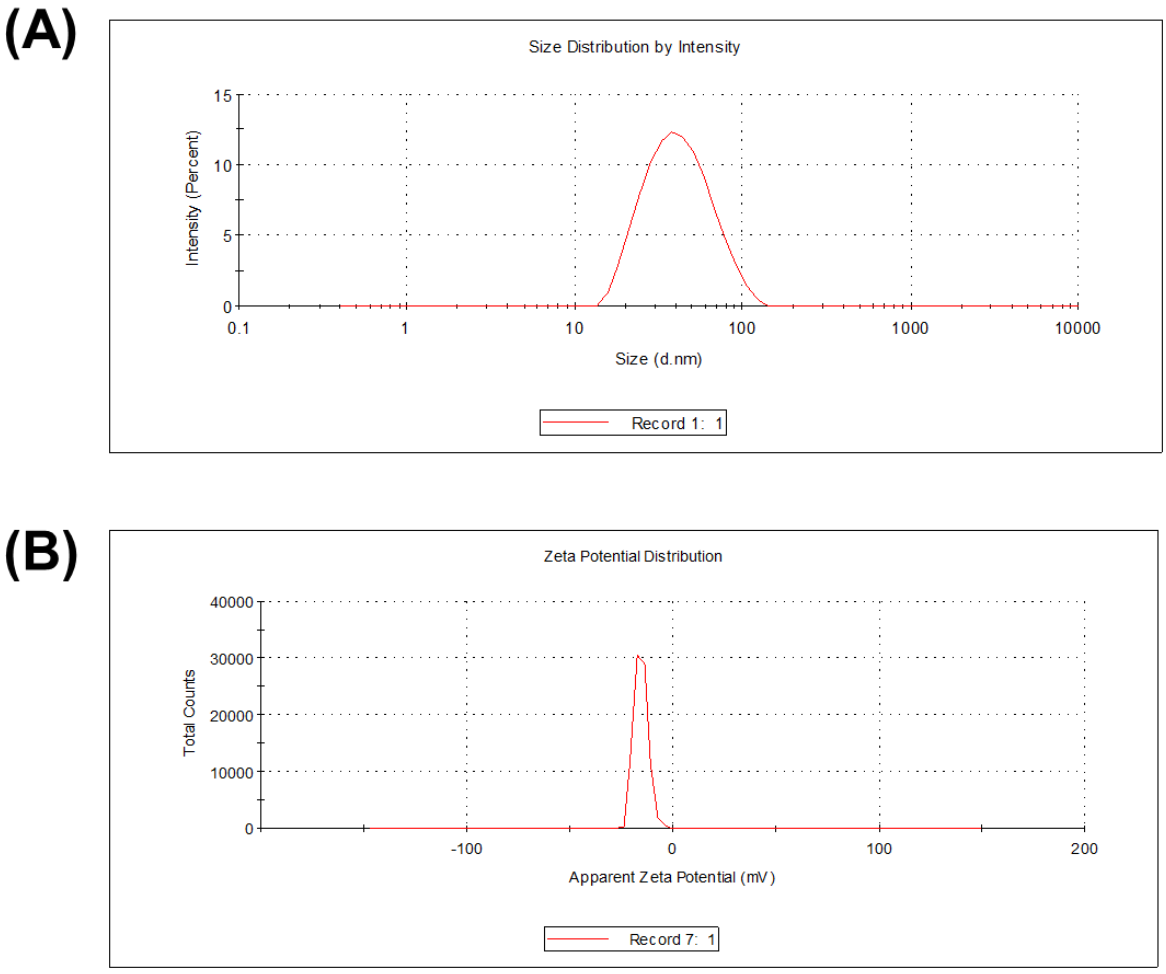

Figure S1. DLS results of (A) Average diameter, 38 nm with polydispersity index (PDI) 0.17, (B) Average zeta potential, −17 mV.

2. Additional Experimental Data

	8 pM NEs	0.8 pM NEs	80 fM NEs
V_{NE} (mL)	1.607×10^{-6}	1.607×10^{-7}	1.607×10^{-8}
V_{aq} (mL)	10.00	10.00	10.00
V_{total}(mL)	$V_{aq} + V_{NE}$	$V_{aq} + V_{NE}$	$V_{aq} + V_{NE}$

Table S1. Experimental parameters for estimating a partition coefficient, *P*.

3. Fitting *i-t* Decay with Bulk Electrolysis Model.

This collisional response, *i-t* decay was fitted with bulk electrolysis model as below [S1,S2]

$$i(t) = i_p e^{-\frac{mA}{V}t} \quad (1)$$

$$m = \frac{4D_{\mathrm{FcMeOH}}}{\pi r_c} \quad (2)$$

where, i_p (= 0.23 pA) is the initial peak current, t is the time (s), m is the mass-transfer coefficient, r_c (=19 pm) and A (=1.13×10^{-17} cm^2) are a contact radius and area between an UME and a NE, respectively, V (=2.87×10^{-17} cm^3 for 19 nm radius NE) is a NE volume, and D_{FcMeOH} (=1×10^{-7} cm^2/s) is the diffusion coefficient of FcMeOH in the castor oil inside a NE determined by Stoke-Einstein equation. In Figure S3, we show a good agreement between the experimental *i-t* curve (black solid lines) and the simulation (red open circles), thus validating bulk electrolysis of FcMeOH inside a ~38 nm diameter NE.

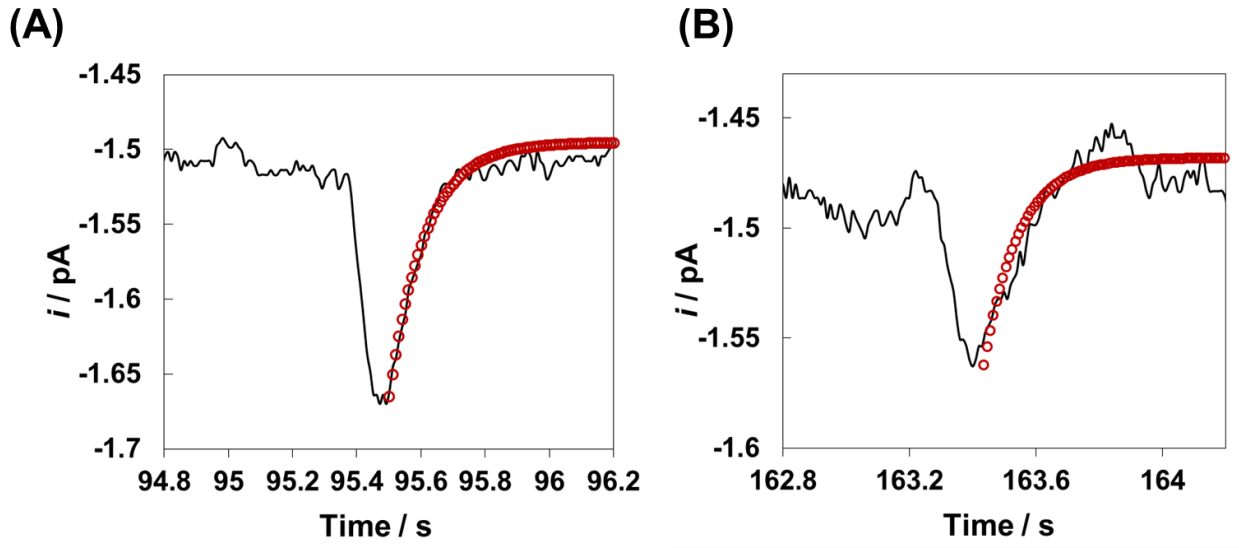

Figure S2. (A) (B) Magnified *i-t* curves of a FcMeOH partitioned NE colliding onto Pt UME under 0.40 V vs Pt QRE, shown in Figure 2B inset II and III, respectively. The experimental data is fitted with simulated *i-t* behavior for the first order homogeneous electrolysis reaction shown by red open circles.

4. Additional SEE Data with FcMeOH

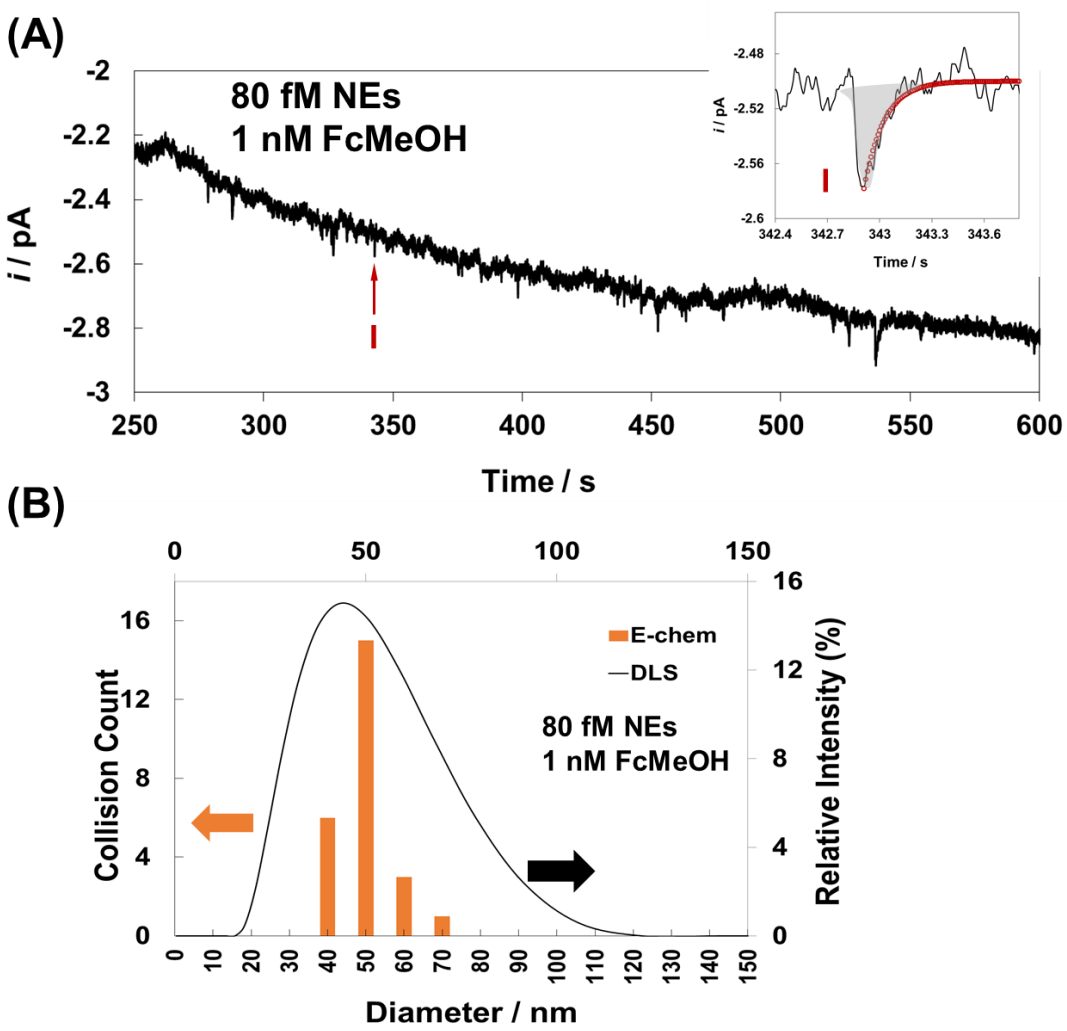

Figure S3. *I-t* curves in the presence of 1 nM FcMeOH with 80 fM NEs ((E_{tip} = 0.4 V vs Pt QRE). The insets magnified typical current spikes fitted with bulk electrolysis model (red open circles). (B) Size distribution curves of NEs based on the electrochemical measurements (orange bars) from (A) and DLS measurements (black solid lines).

5. Electrochemistry of 2-ABP in THF Cocktail Solution.

Based on the results in cyclic voltammetry with 2-ABP in THF cocktail solution, 0.85 V vs Pt QRE has been selected to perform the following SEE measurements. Note that 0.85V vs Pt QRE does not trigger the electropolymerization of 2-ABP, thus simplifying the electrochemical oxidation of 2-ABP during SEE measurements.

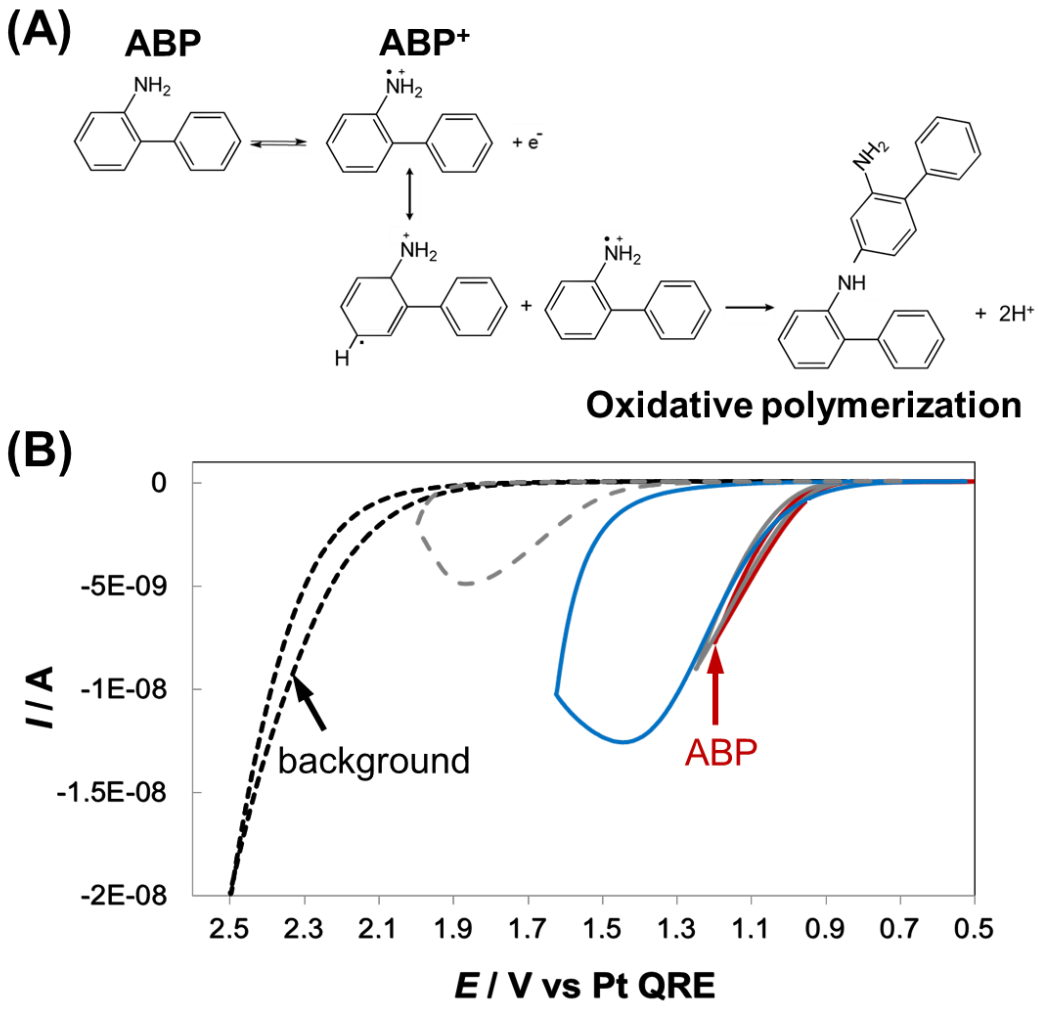

Figure S4. (A) A mechanistic scheme of electrochemical oxidation of 2-ABP with one electron transfer, which can further undergo electropolymerization reaction. (B) Cyclic voltammograms of 2-ABP in THF cocktail solutions.

6. Calibration Curves for 2-ABP with 8 pM, 0.8 pM, 80 fM NEs

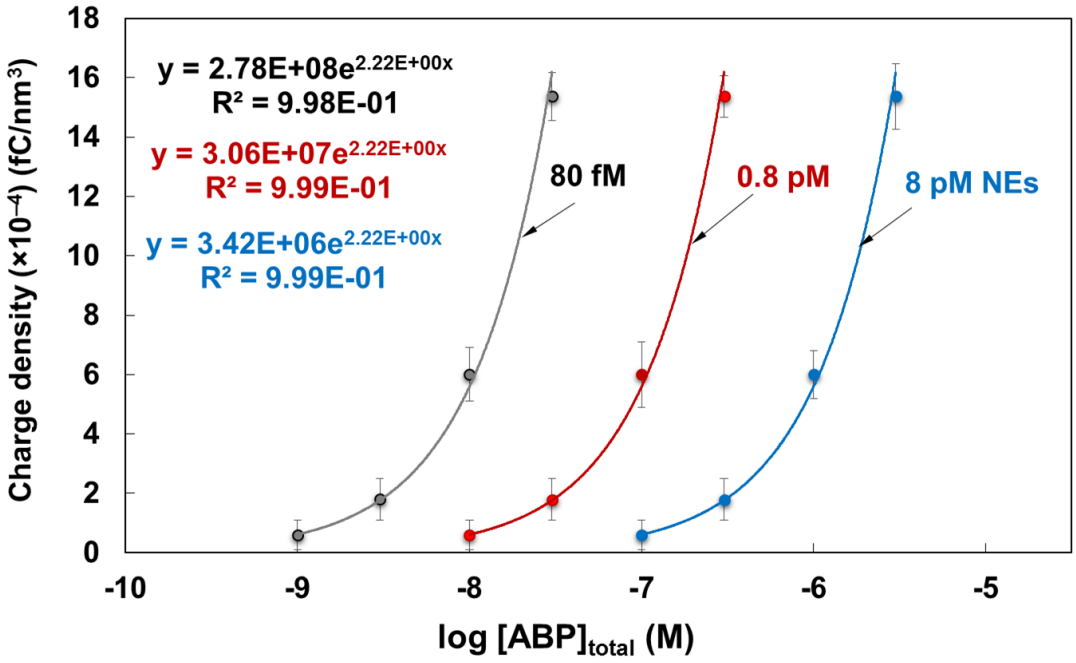

Figure S5. Calibration curves for 2-ABP with 8 pM, 0.8 pM, 80 fM NEs, respectively. Calibration curves are plotted within the dynamic range in Figure 5C, where calibration equations are obtained by fitting with exponential functions.

6. *i-t* Curves with NEs added to the Blank Aqueous Solution Containing no FcMeOH.

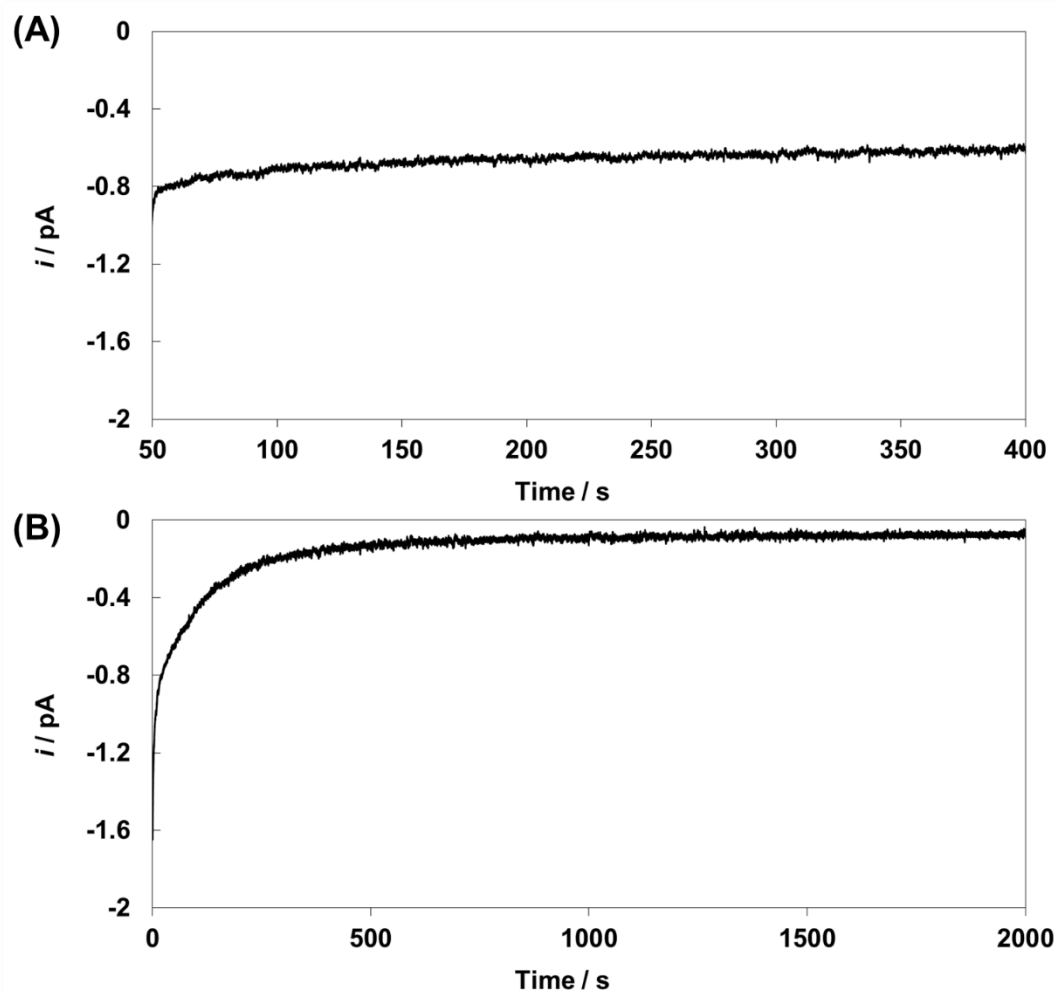

Figure S6. (A), (B) *i-t* curves of blank aqueous solutions in the presence of NEs. The constant potential, 0.4 V vs. Pt QRE were applied. The noise level ranges 20 ~ 50 fA.

S1 . Kim, B.K.; Boika, A.; Kim, J.; Dick, J.E.; Bard, A.J., Characterizing Emulsions by Observation of Single Droplet Collisions- Attoliter Electrochemical Reactors, *J. Am. Chem. Soc.*, **2014**, 136, 4849-4852.

S2. Bard, A. J.; Faulkner, L. R., "Electrochemical Methods: Fundamental and Applications", **2004**, 2nd Ed., John Wiley & Sons INC.