



## Supporting Information

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### **Simultaneous Detection of Single Attoliter Droplet Collisions by Electrochemical and Electrogenerated Chemiluminescent Responses\*\***

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## Supporting Information

**Emulsion synthesis and characterization:** The emulsion preparation is based on a previously reported method.<sup>1</sup> In brief, in a vial containing 100 µL of 15 mM rubrene (Aldrich, St. Louis, MO) in toluene (>99.9%, Sigma Aldrich, St. Louis, MO), 5 mL of deionized Milli-Q water (> 18 MΩ.cm, MilliQ Reagent Water System, Millipore, Billerica, MA) is added. Then, 30 µL of ionic liquid trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide (Aldrich, St. Louis, MO) and 50 µL of tri-*n*-propylamine (TCI co. LTD, Tokyo, Japan) are successively injected in the vial. Finally the content of the vial is sonicated with a horn ultrasonicator (Q500 ultrasonic processor with a microtip probe, Qsonica, Newtown, CT) to form a finely dispersed emulsion with a milky orange color. A visual examination of the emulsion indicated that this latter is stable over at least 5 h. The droplets size distribution was measured by dynamic light scattering (Zetasizer Nano ZS, Malvern, Westborough, MA) less than 1 h after the sonication of the emulsion. The concentration of droplets in the emulsion is roughly estimated by dividing the total volume of toluene and TPrA (150 µL) by the average volume of a droplet (440 aL if we consider only 945 nm diameters droplets) and the total volume of solution in the vial (5.15 mL). A value of 110 pM is obtained. The diameter of the droplets obtained by electrochemistry is higher than the diameter obtained by DLS (270 and 730 nm) and thus the concentration is probably overestimated. The polydispersive index (PDI) of the reported DLS data is 0.18.

**Experimental setup for simultaneous ECL and current measurement:** The experimental setup is presented in Figure S1. Briefly, a 1 cm path length plastic cuvette (Fisher Scientific, Waltham, MA) was used to fabricate the spectroelectrochemical cell. The UME was inserted in the cuvette via a hole drilled in one face of the cuvette. The distance between the surface of the UME and the opposite cuvette wall is c.a. 1-2 mm. First, the cell was filled with 2 mL of a 5 mM phosphate buffer pH 7 solution ( $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$  are purchased from Sigma Aldrich, St. Louis, MO) and then an appropriate volume of the stock solution emulsion (at 110 pM) was added to achieve the desired final emulsion concentration in the cell. A platinum

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<sup>1</sup> a.) B.-K. Kim, A. Boika, J. Kim, J. E. Dick, A. J. Bard, *Journal of the American Chemical Society* **2014**, *136*, 4849. b.) J. E. Dick, C. Renault, B.-K. Kim, A. J. Bard, *submitted*.

wire (counter electrode) and Ag/AgCl 1 M KCl reference electrode (CH Instrument, Austin, TX) were inserted via the top of the cuvette. The distance between the UME surface and the PMT is c.a. 1-2 cm. The PMT (Hamamatsu R4220, Tokyo, Japan) was powered at -700 V using a Kepco DC power supply (New York, NY). The signal of the PMT was read with an electrometer (Keithley 6517, Solon, OH) and then digitalized using an analogue to digital converter (ADC 164, Eco Chemie Autolab, Utrecht, Netherlands) integrated the potentiostat (Eco Chemie Autolab PGSTAT100, Utrecht, Netherlands). A home-made program (made with Nova® v1.7) was used to synchronize the current and ECL measurements. The spectroelectrochemical cell was placed in a Faraday cage placed itself in a light-tight box to ensure low background noise on both the current and ECL signals. The sampling interval for both current and ECL signals was set to 50 ms. The experiment is realized in a room maintained at 20°C.

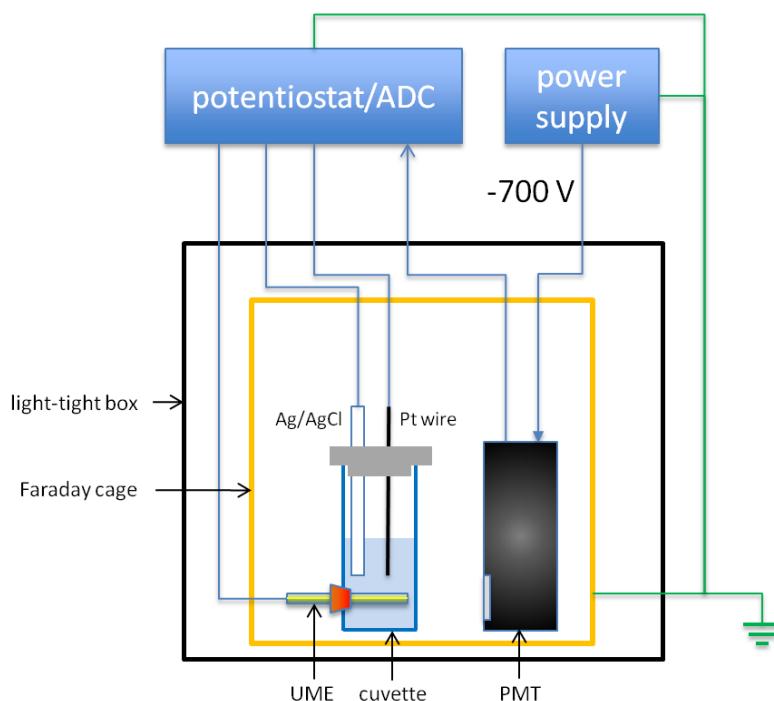


Figure S1. Schematic of the experimental setup used to measure the current and ECL signal of single droplet collision.

**Calculation of the diffusion coefficient of droplets:** The droplets are assumed to be perfectly spherical and rigid. The diffusion coefficient,  $D_{ems}$ , is calculated using the Stokes-Einstein equation.

$$D_{ems} = \frac{k_b T}{6\pi\eta r_{ems}}$$

Here,  $k_b$  is the Boltzman constant,  $T$  is the temperature (298 K),  $\eta$  is the dynamic viscosity (8.9 Pa.s for water at 25°C) and  $r_{ems}$  is the radius of the emulsion droplet (472 nm from electrochemical data). We obtain a value of  $D_{ems}$  of  $5 \times 10^{-9}$  cm<sup>2</sup>/s for a 945 nm diameter droplet in water. Droplet concentration is calculated by assuming a 945 nm diameter droplet, calculating its volume, and dividing this volume into the total volume of the organic phase (toluene + TPrA).