Supporting Information

**Single Fusion Events at Polarized Liquid–Liquid Interfaces**

*Eduardo Laborda,* אנגела מולינה, ונסה ז'ואנדה אספין, פרFragmentManager-אורטי, ג'וז'ה גאצ'ה דה ל'טור, ורייצ'רד ג'קוומטון

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SUPPORTING INFORMATION

S1. Potential window available and transfer of tetramethylammonium in Cell I

S2. DLS number and intensity size distributions obtained with different emulsion samples. Comparison with the size distribution obtained electrochemically with the new method

S3. Dynamic light scattering (DLS) measurements of microparticle size standards

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**Figure S1.** *(Black line)* Potential window available with the water/DCE cell employed for the electrochemical measurements (Cell I); *(Red line)* Cyclic voltammogram corresponding to the transfer of the cation tetramethylammonium present in the aqueous phase of Cell I at 0.5 mM concentration. Scan rate = 10 mVs⁻¹.
S2. DLS number and intensity size distributions obtained with different emulsion samples. Comparison with the size distribution obtained electrochemically with the new method

**Sample 1**

**Sample 2**

**Sample 3**

*Figure S2*. Comparison of the droplet size distributions obtained electrochemically and by DLS of different samples of DCE-in-water emulsions with the DCE droplets bearing 0.35M TDACl (Emulsion1). Error bars represent the standard deviations obtained from 5 measurements of the same sample within a period of 40min. The number size distributions, which are more sensitive to smaller particles than intensity-based distributions, point out the absence of any droplet population of submicrometer size in the samples.
S3. Dynamic light scattering measurements of microparticle size standards

Figure S3. DLS intensity particle size distributions obtained with three polystyrene latex standard of 1.0 µm, 3.0 µm and 4.0 µm particle diameter diluted in a 10 mM ionic strength water solution. Data acquisition time = 300 s. Error bars represent the standard deviation obtained from 3 measurements.