

## Supporting Information

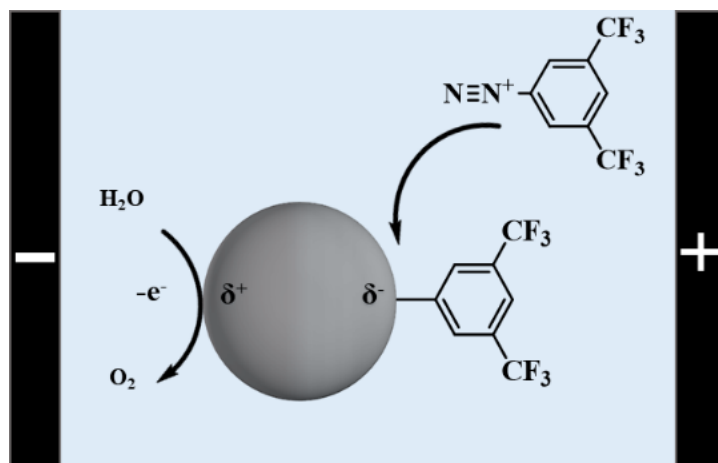
### **Bipolar Electrochemiluminescence at the Water/Organic Interface**

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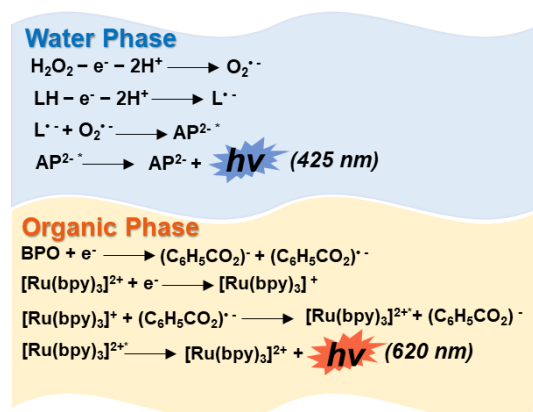
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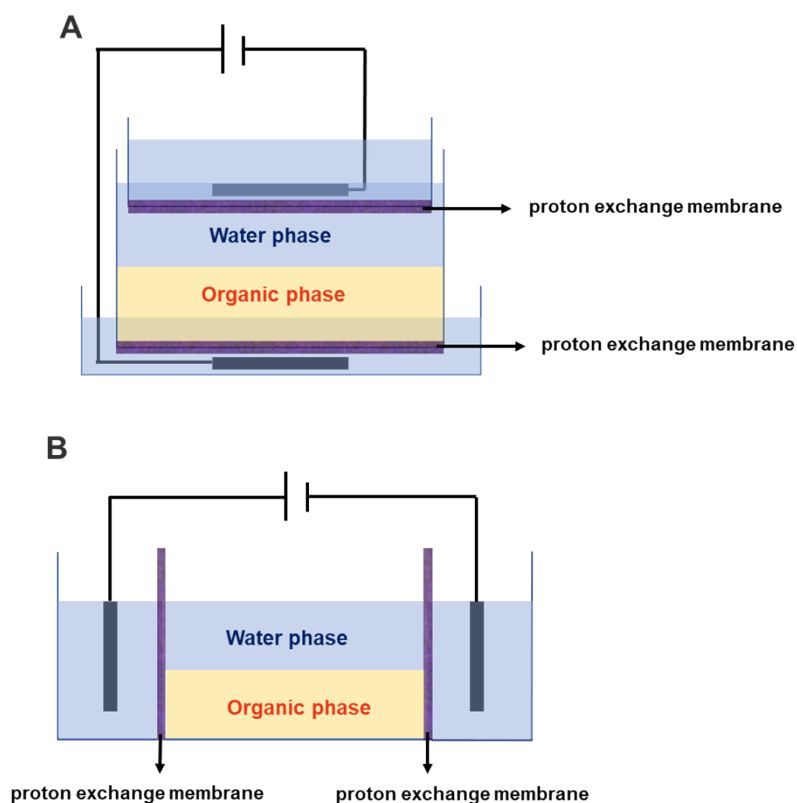


**Scheme S1.** Preparation of amphiphilic Janus particles by bipolar electrochemistry.

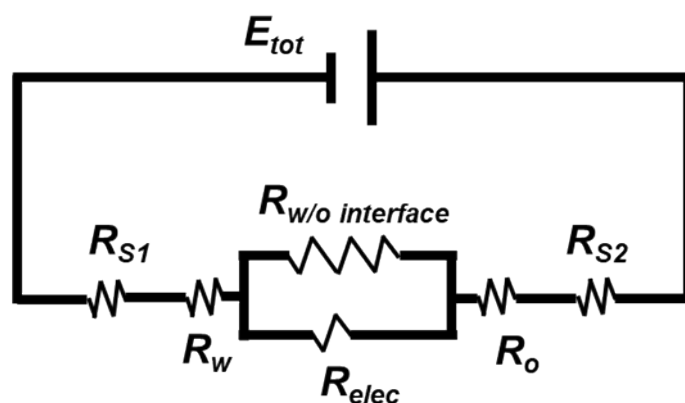
In **Scheme S1**, the amphiphilic Janus particles are prepared by bipolar electro-grafting a hydrophobic 3,5-bis(trifluoromethyl)phenyl layer.



**Scheme S2.** ECL mechanisms occurring at amphiphilic Janus particles located at the w/o interface operating in the water and organic phases, respectively.<sup>1-3</sup>

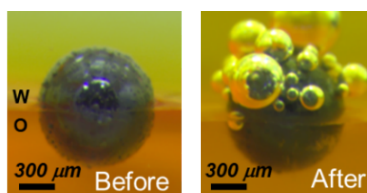


**Scheme S3.** Schematic illustration of the bipolar ECL set-up with (A) Route 1: the direction of the electric field is perpendicular to the w/o interface (cell 2), (B) Route 2: the direction of the electric field is parallel to the w/o interface.

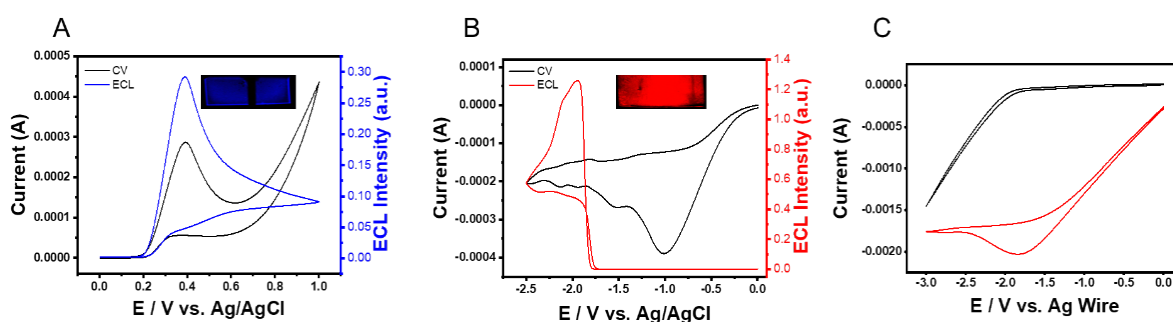


**Scheme S4.** The physical schematics of amphiphilic microbead-base BPE-ECL system.

$E_{tot}$ : applied potential,  $R_{S1}$  and  $R_{S2}$ : resistance of the feeder electrode chamber solution,  $R_{elec}$ : total resistance to electronic current posed by the bipolar electrode,  $R_w$ : resistance of water phase solution,  $R_o$ : resistance of organic phase solution,  $R_{w/o}$  interface: resistance of ions across the w/o interface.



**Figure S1.** Images of the Janus microbeads under white light before and after the bipolar ECL experiment.



**Figure S2.** Cyclic voltammograms and ECL intensity recorded with a GC plate ( $1 \times 2 \text{ cm}^2$ ) (A) in aqueous solution containing 5 mM luminol, 50 mM  $\text{H}_2\text{O}_2$  and 0.1 M NaOH. The scan rate was 100 mV/s. (B) in DCE containing 1 mM  $\text{Ru}(\text{bpy})_3\text{PF}_6$ , 20 mM BPO and 200 mM TBAPF<sub>6</sub> under  $\text{N}_2$  atmosphere. The scan rate was 100 mV/s. (C) Cyclic voltammograms recorded with a GC plate ( $1 \times 2 \text{ cm}^2$ ) in DCE containing 100 mM TBAPF<sub>6</sub> with (red line) and without (black line) 20 mM BPO under  $\text{N}_2$  atmosphere. The scan rate was 50 mV/s. Inset: optical images of ECL emission on GC plate under different conditions.

## References

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- 2 S. J. He, K. Chu, J. M. Wong, L. Q. Yang, J. R. Adsetts, R. Z. Zhang, Y. H. Chen and Z. F. Ding, *J. Anal. Test.*, 2020, **4**, 257–263.
- 3 A. B. Nepomnyashchii, R. J. Ono, D. M. Lyons, C. W. Bielawski, J. L. Sessler and A. J. Bard, *Chem. Sci.*, 2012, **3**, 2628–2638.