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## Electronic Supporting Information

### **An electrochemiluminescent sensor based on functionalized conjugated polymer dots for the ultrasensitive detection of Cu<sup>2+</sup>**

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## 45 **1. Experimental**

### 46 **1.1 Chemical and Reagents.**

47 PFO (MW 20000) was provided by ADS Dyes, Inc. (Quebec, Canada). Aladdin  
48 Ltd. (Shanghai, China) provided poly(styrene-co-maleicanhydride) (PSMA). The  
49 average MW and styrene content of PSMA were 1700 and 68%, respectively.  
50 Acetonitrile (MeCN) was purchased from Kelong Chemical Co., Ltd. (Chengdu,  
51 China). Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) and tetrahydrofuran  
52 (THF) were provided by Sigma Chemical Co. (St. Louis, MO, USA). Chitosan  
53 solution (0.20%) was prepared by dissolving chitosan powder in hydrochloric acid  
54 (1.0%) and then adjusting pH to 6.5 with NaOH solution. 0.10 M phosphate-buffered  
55 saline (PBS) solution was used as detection solution. For the ECL measurements in  
56 MeCN system, TBAPF<sub>6</sub> was dissolved in MeCN to make TBAPF<sub>6</sub> stock solutions  
57 (0.10 M), which served as the supporting electrolyte.

### 58 **1.2 Apparatus.**

59 A MPI-E electrochemical analyser, which was provided from Xi'an Remax  
60 Analyse Instrument Co. Ltd, was used to monitor the ECL emission. The CHI600D  
61 electrochemical work station was from Shanghai CH Instruments Co. China, and used  
62 to perform electrochemical measurement. An IFS 66 V/S (Bruker) IR spectrometer  
63 was used to record Fourier transform infrared spectroscopy (FT-IR). A FR-5301-PC  
64 spectrophotometer was provided from Shimadzu (Tokyo, Japan), which was used to  
65 achieve fluorescence spectrometry at room temperature with the range of 420~550 nm.

66 A Lambda 17 UV-vis spectrometer 8500 (PECo., USA) was used to record the  
67 UV-visible (UV-vis) spectrometry in the range of 200~600 nm. A Hitachi H-800  
68 microscope (Japan) was used to obtain the transmission electron microscopy (TEM)  
69 images.

### 70 **1.3 Preparation of PS-COOH-co-PFO dots.**

71 PS-COOH-co-PFO dots were synthesized according to the literature<sup>1</sup> with some  
72 changes. In brief, PFO and PSMA were dissolved in tetrahydrofuran (THF) to make  
73 stock solutions with a concentration of 1.0 mg/mL, respectively. Then 4.0 mL of the  
74 prepared PFO and 800  $\mu$ L of PSMA were mixed and sonicated to form a  
75 homogeneous solution. Subsequently, 10 mL ultrapure water was injected into above  
76 solution and stirred overnight. Finally, THF was removed by partial vacuum  
77 evaporation to obtain PS-COOH-co-PFO dots, which were redispersed in ultrapure  
78 water. The obtained dispersion was stored for further use.

### 79 **1.4 Preparation of sensor**

80 After polished with alumina powders (average diameters: 0.30  $\mu$ m and 0.050  $\mu$ m),  
81 the glassy carbon electrode (GCE,  $\Phi$ =4.0 mm) was ultrasonically cleaned with  
82 ultrapure water and ethanol in turn. Then, it was modified with 15  $\mu$ L of  
83 PS-COOH-co-PFO dispersion. Following by drying in air, the modified electrode was  
84 cast with 2.0  $\mu$ L of chitosan solution. Dried in air, a sensor (PS-COOH-co-PFO /GCE)  
85 was obtained.

### 86 **1.5 Experimental determination**

87 The ECL and cyclic voltammetry (CV) measurements were performed in 3.0 mL  
88 PBS (0.10 M). A modified GCE, platinum wire and Ag/AgCl (saturated KCl) served

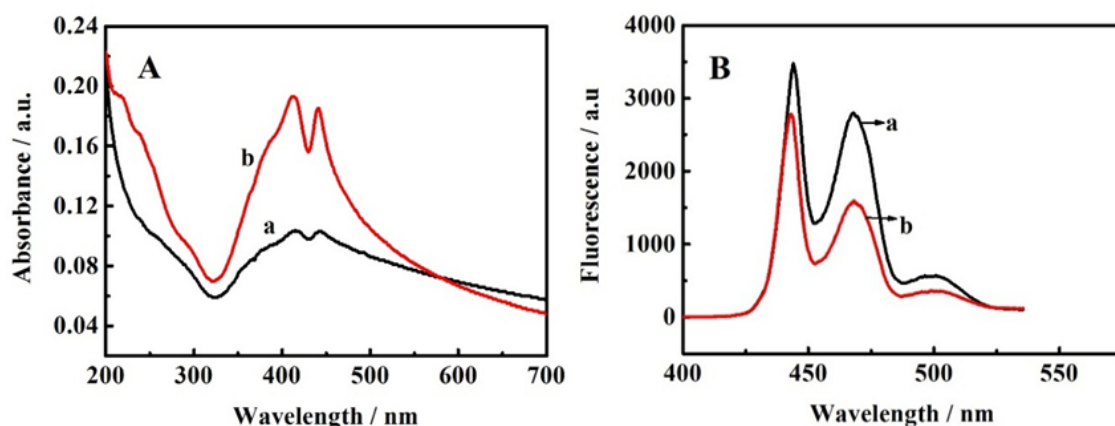
89 as working electrode, auxiliary electrode, and reference electrode, respectively. The  
90 voltage of photomultiplier tube (PMT) was set at 800 V and the sweep speed was set  
91 at  $0.30 \text{ V}\cdot\text{s}^{-1}$  during the detection. Additionally, for the ECL measurements in MeCN  
92 system, MeCN solutions containing TBAPF<sub>6</sub> as the supporting electrolyte were used.

## 93 2. Results and discussion

### 94 2.1 Characterization of nanomaterials

95 UV-Vis absorption spectroscopy was performed to identify the formation of  
96 PS-COOH-co-PFO dots. Fig. S1A presents the corresponding results. For PFO (curve  
97 a), a peak located at 415 nm was attributed to the  $\pi$ - $\pi^*$  transition of the fluorene units.  
98 The peak at 442 nm was due to the formation of poly fluorene's crystal line  $\beta$  phase.  
99 Compared with PFO, the UV-Vis spectra of PS-COOH-co-PFO (curve b) was almost  
100 unchanged except for the enhanced absorption intensity.

101 The fluorescence (FL) spectra also were performed and Fig. S1B displays the  
102 results. As observed from curve a, PFO showed three well resolved vibronic peaks at  
103 443nm, 468 nm and 497 nm, respectively. Observed three peaks were consistent with  
104 the previous reports<sup>2</sup>. Compared with PFO (curve a), the FL spectra of  
105 PS-COOH-co-PFO (curve b) was also almost unchanged.

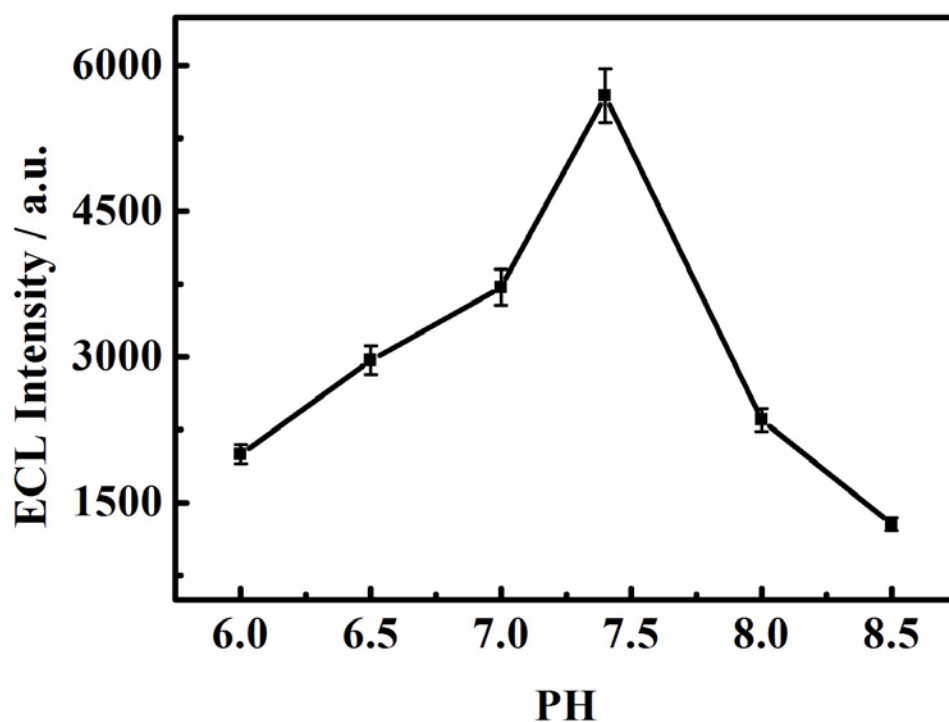


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107 **Fig. S1** (A) UV-vis spectra and (B) FL spectra of (a) PFO and (b) PS-COOH-co-PFO  
108 dots

## 109 2.2 Optimization of experimental conditions

110 The pH of PBS solution and CV scan rate were optimized for detecting  $\text{Cu}^{2+}$ . pH  
111 influence was investigated in range of pH 6.0-8.5 and Fig. S2 presents corresponding  
112 results. As observed, the ECL intensity increased with increasing pH from 6.0 to 7.4,  
113 and then dropped at pH 7.4 to 8.5. Thus, pH 7.4 was chosen as the optimal pH for the  
114 detection of  $\text{Cu}^{2+}$ .

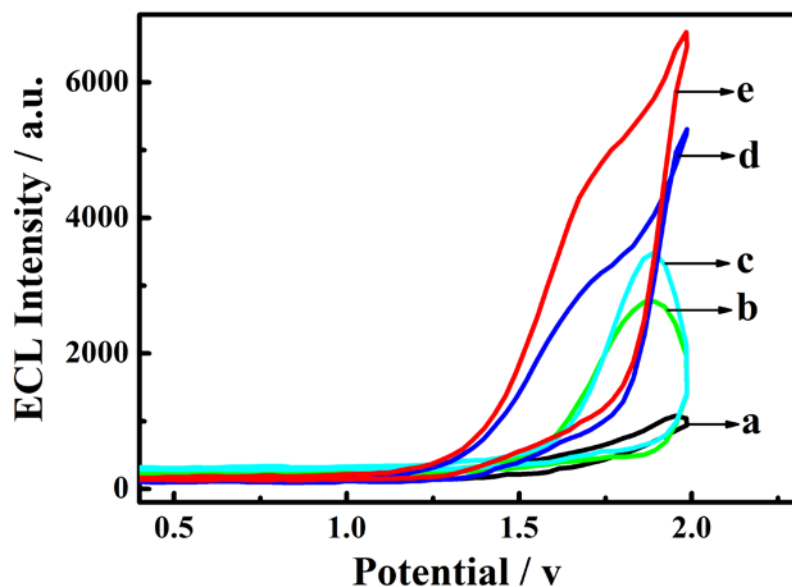


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116 **Fig. S2** Effect of the pH of PBS on the ECL intensity of PS-COOH-co-PFO/GCE

117 3. The ECL response of PS-COOH-co-PFO/GCE without co-reactant and PFO/GCE

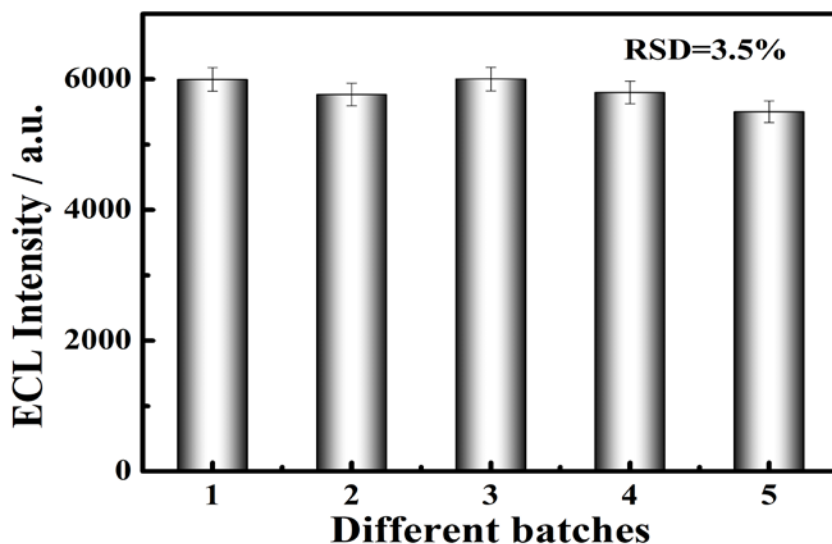
118 with the commonly used co-reactants toward PFO



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120 **Fig. S3** ECL response of PFO/GCE without adding any co-reactant (a), PFO/GCE  
 121 with 0.50 mM H<sub>2</sub>O<sub>2</sub> (b), PFO/GCE with 0.050 M SO<sub>3</sub><sup>2-</sup> (c), PFO/GCE with 0.050 M  
 122 C<sub>2</sub>O<sub>4</sub><sup>2-</sup> (d) and PS-COOH-co-PFO dots/GCE without adding any co-reactant (e) in  
 123 PBS (0.10 M, pH 7.4)

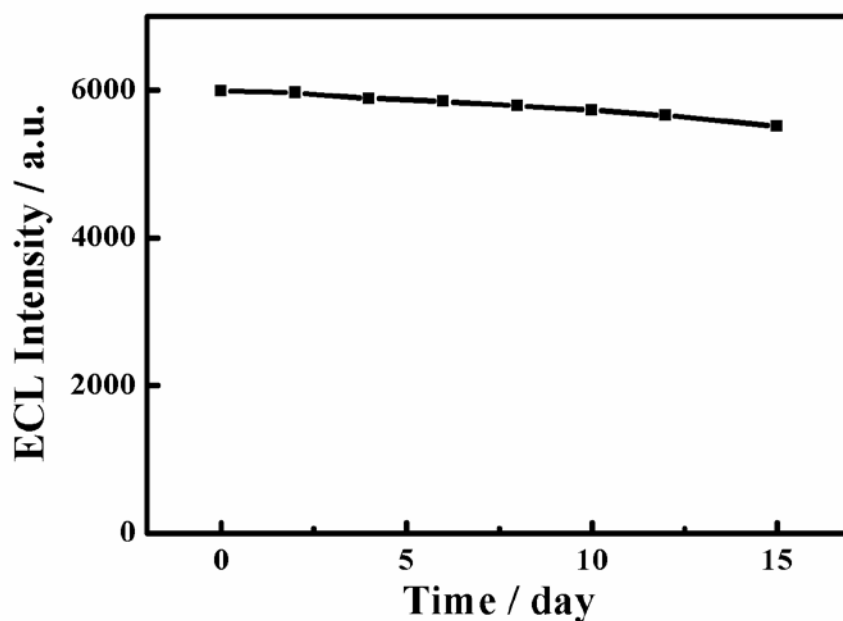
124 **4. Reproducibility of the proposed ECL sensor**



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126 **Fig. S4** Reproducibility of the proposed ECL sensor using five different batches  
 127 sensors with 1.0 nM Cu<sup>2+</sup> under the same conditions

128 **5. The longterm stability of the proposed sensor**



130

131 **Fig. S5** The longterm stability of the proposed sensor in the presence of 1.0 nM Cu<sup>2+</sup>

132 in PBS (0.10 M, pH 7.4)

133 **6. Table S1** Recovery experiments of the proposed ECL sensor in real water samples

Samples	Added/nM	Found/nM	Recovery/%
1	0.0050	0.0051	102.1
2	0.050	0.049	98.4
3	0.100	0.098	98.2
4	1.000	1.035	103.5
5	50.00	50.45	100.9

134 **Notes and references**135 1 C.F. Wu and D.T. Chiu, *Angew. Chem. Int. Ed.*, 2013, 52, 3086-3109.136 2 C. F. Wu, B. Bull, C. Szymanski, K. Christensen and Jason McNeill, *ACS NANO*, 2008,

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