## **Supporting Information**

## High sensitive sensor with HEPES-enhanced electrochemiluminescence of benzo[3]uril for Fe<sup>3+</sup> and its application in human serum

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Figure S1. <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>: CD<sub>3</sub>OD = 6:1) of benzo[3]uril.



Figure S2. <sup>13</sup>C NMR spectra (100 MHz,  $CDCl_3$ :  $CD_3OD = 6:1$ ) of benzo[3]uril.



Figure S3. HRMS spectra of benzo[3]uril.



**Figure S4.** Effects of different electrolytes (0.1 M CBS, Tris-HCl, PBS, BBS, pH = 7.4), containing 0.050 M HEPES on the ECL intensity with the decorated electrode.



**Figure S5.** The ECL intensity of decorated electrode in the 0.1M PBS buffer (pH = 7.4) containing 0.050 M HEPES with different scan rates.



**Figure S6.** Cyclic voltammograms of benzo[3]uril and with the incubation of  $Fe^{3+}$  in the 0.05M HEPES in the PBS solution at pH=7.4.



**Figure S7.** Effects of the incubation time of the decorated electrode into  $Fe^{3+}$  aqueous solution (5min, 10min, 20min, 30min, 40min) to the ECL intensity of the sensor in 0.10 M PBS (pH = 7.4) containing 0.050 M HEPES, and scan rate 100 mV/s<sup>-1</sup>.



Figure S8. Competitive selectivity of the ECL sensor toward metal cations.



Figure S9. Competitive interferences of the ECL sensor toward  $Fe^{3+}$  in the presence of other metal cations



Figure S10. The reproducibility of the proposed ECL modified electrodes.

## Description of the source of human serum and preparation for the Fe<sup>3+</sup> solution

Samples of deproteinized human serum were obtained from the Hospital of Guizhou University, which was applied for analysis without any further process.

The solution of  $Fe^{3+}$  was prepared by deionized water without acidification, and we did not observe the formation of any deposits by hydrolysis of the metal cations.