## Supporting Information

## High sensitive sensor with HEPES-enhanced electrochemiluminescence of benzo[3]uril for $\mathrm{Fe}^{3+}$ and its application in human serum

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Figure S1. ${ }^{1} \mathrm{H}$ NMR spectra ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}: \mathrm{CD}_{3} \mathrm{OD}=6: 1$ ) of benzo[3]uril.


Figure S2. ${ }^{13} \mathrm{C}$ NMR spectra $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}: \mathrm{CD}_{3} \mathrm{OD}=6: 1\right)$ 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, $\mathrm{pH}=7.4$ ), containing 0.050 M HEPES on the ECL intensity with the decorated electrode.


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


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


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


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


Figure S9. Competitive interferences of the ECL sensor toward $\mathrm{Fe}^{3+}$ 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 $\mathbf{F e}^{\mathbf{3 +}}$ 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 $\mathrm{Fe}^{3+}$ was prepared by deionized water without acidification, and we did not observe the formation of any deposits by hydrolysis of the metal cations.

