

## Electronic supplementary information

### An ON<sup>1</sup>–OFF–ON<sup>2</sup> Electrochemiluminescence Response: Combining the Intermolecular Specific Binding with Radical Scavenger

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#### Experimental details

**Chemicals.** Ionic liquid 1-butyl-3-methylimidazolium chloride salt ([BMIM]Cl) was purchased from Shanghai Cheng Jie Chemical Co. LTD (China). Cobalt phthalocyanine (CoPc), ethoprophos (EP), profenofos (PF), parathion-methyl (PM), dylox (DL) and pentachlorophenol (PCP) were purchased from Sigma-Aldrich (USA) and used as received. The standard solution of EP ( $2.5 \times 10^{-4}$  M) was prepared by dissolving EP with acetonitrile was prepared and then diluted with water to the desired concentrations. Stock solution of luminol was prepared by dissolving luminol in 0.1 M NaOH solution and was kept at 4 °C when not in use. All chemicals were of analytical reagent grade and used without further purification.

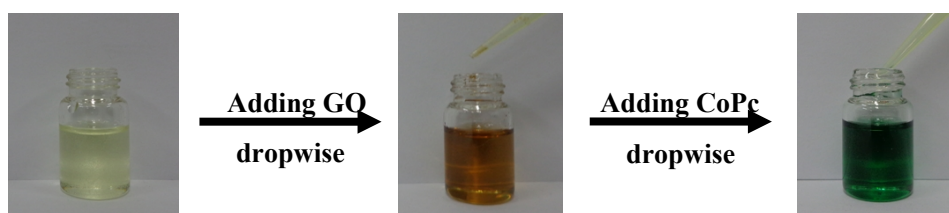
**Apparatus.** The transmission electron microscopy (TEM) image was taken with a JEOL 2100 TEM (JEOL, Japan) operated at 200 kV. X-ray diffraction (XRD) spectra analysis was conducted on a Bruker D8 diffractometer with high-intensity Cu K $\alpha$  ( $\lambda$  = 1.54 Å). The Raman spectra were obtained from RM 2000 microscopic confocal Raman spectrometer. The UV-vis spectra were conducted on a Perkin-Elmer Lambda 18 UV-vis-NIR spectrometer (USA). Thermogravimetric analysis (TGA) of the sample was performed on a Pyris 1 TGA Instrument (PE, USA).

Cyclic voltammograms (CVs) were recorded using CHI660 B electrochemical analyzer (Chen Hua Instruments, China) and ECL signals were recorded by a Model MPI-A ECL analyzer system with a photomultiplier tube (PMT) biased at 800 V. Electrochemical impedance spectroscopy (EIS) was performed in 0.1 M KCl solution containing 5 mM Fe(CN) $_6^{3-/4-}$  with a frequency range from 0.01 Hz to 10 kHz, and the amplitude of the applied sine wave potential in each case was 5 mV which was taken with a ZENNIUM electrochemical workstation (Zahner Instruments, Germany). All electrochemical and ECL curves were recorded by a conventional three-electrode system where glassy carbon electrode (GCE, 3 mm in diameter) was used as working electrode, Ag/AgCl (saturated KCl solution) as reference electrode and platinum wire as counter electrode, respectively. All the experiments were performed at room temperature (25  $\pm$  1.0 °C). All solutions were prepared with double distilled water.

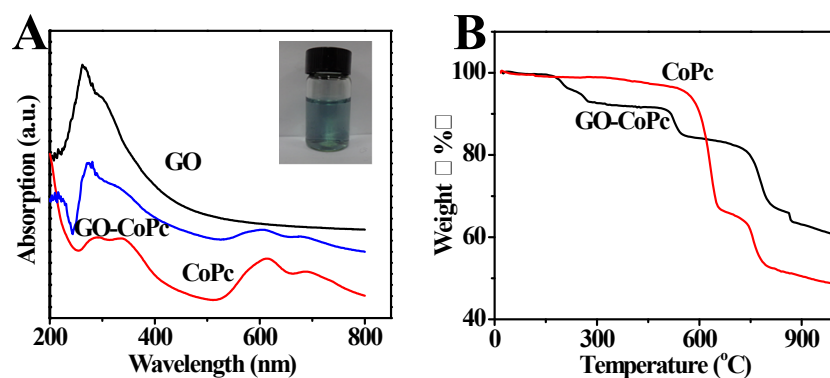
**Synthesis and Characterization of the GO-CoPc hybrid.** GO was prepared from purified natural graphite by the modified Hummers method.<sup>S1</sup> As shown in Fig. S1, the GO-CoPc hybrid could be facilely fabricated by adding the aqueous solution of

GO and CoPc into the [BMIM]Cl dropwise, successively. The opaque system with a yellowish and aquamarine blue color was obtained in sequence, respectively, after the dropwise addition of the aqueous solution of GO nanosheet and CoPc into the [BMIM]Cl solution. The obtained product solution was further dialyzed in a dialysis bag (retained molecular weight: 8000–14000 Da) for 7 days. Finally the product was dried under vacuum at 333 K for 24 h.

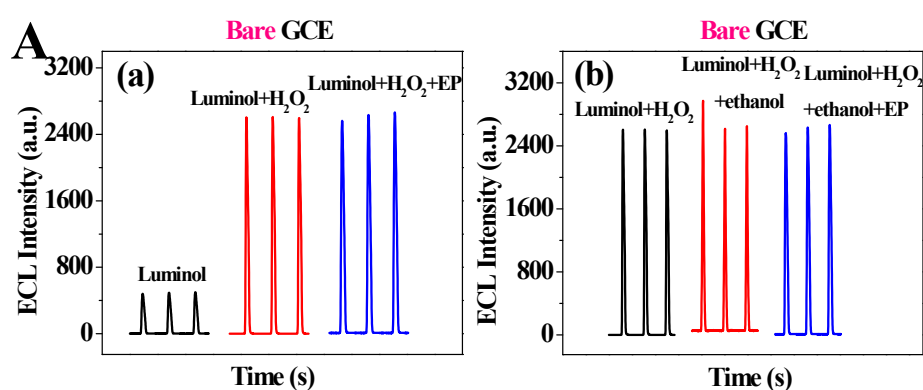
**Fabrication of the modified electrode.** The surface of the GCE (diameter = 3 mm) was polished successively with 0.3 and 0.1  $\mu\text{m}$  alumina paste (Struers, Copenhagen, Denmark) to obtain a mirror finish and then cleaned in water under the ultrasonication. 2  $\text{mg mL}^{-1}$  GO-CoPc hybrid suspension was prepared by dispersing 2.0 mg GO-CoPc hybrid in 1.0 mL water with ultrasonic agitation for about 2 min. 6  $\mu\text{L}$  of the prepared GO-CoPc hybrid suspension was cast on the surface of GCE and dried in the air for the use to obtain the GO-CoPc hybrid modified GCE (denoted as GO-CoPc/GCE). In our work, the CoPc contents were 80 % for GO-CoPc hybrid. In order to keep the constant amount of CoPc, 0.4  $\text{mg mL}^{-1}$  GO suspension, 1.6  $\text{mg mL}^{-1}$  CoPc suspension and 2  $\text{mg mL}^{-1}$  GO-CoPc suspension were prepared to fabricate the GO/GCE, CoPc/GCE and GO-CoPc/GCE, respectively.



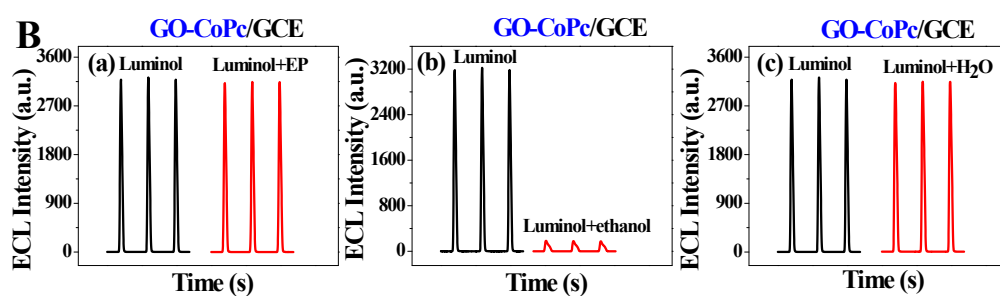
**Fig. S1** Typical picture indicates the preparation of GO-CoPc hybrid nanocomposites via an ionic liquid system at room temperature.



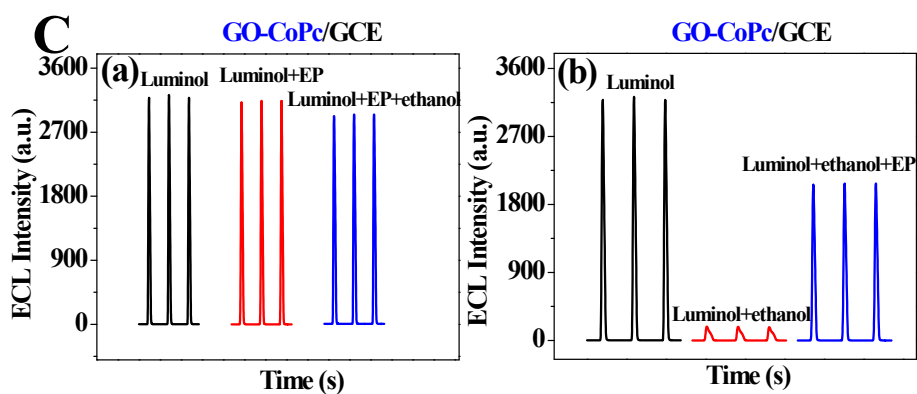
**Fig. S2** UV-vis spectra (A) and TGA (B) of CoPc and GO-CoPc.



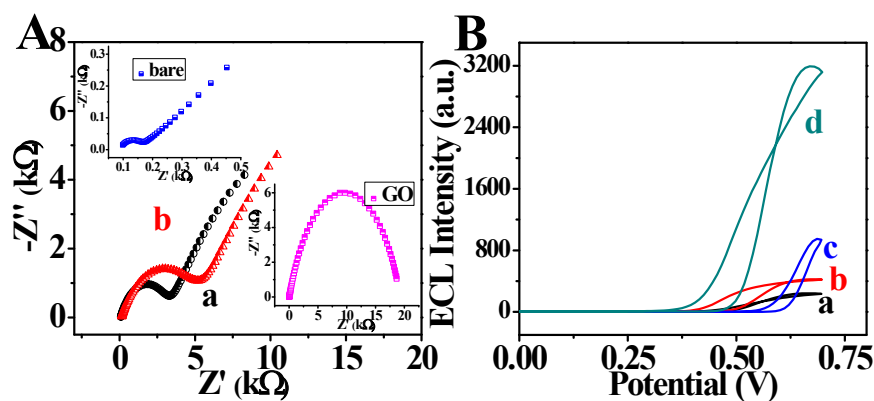
**Fig. S3A** The ECL intensities from the bare/GCE in different solution. PBS: (0.10 M, pH 7.4); luminol: 0.10 mM; ethanol: 1.2 mM; EP: 5 nM.



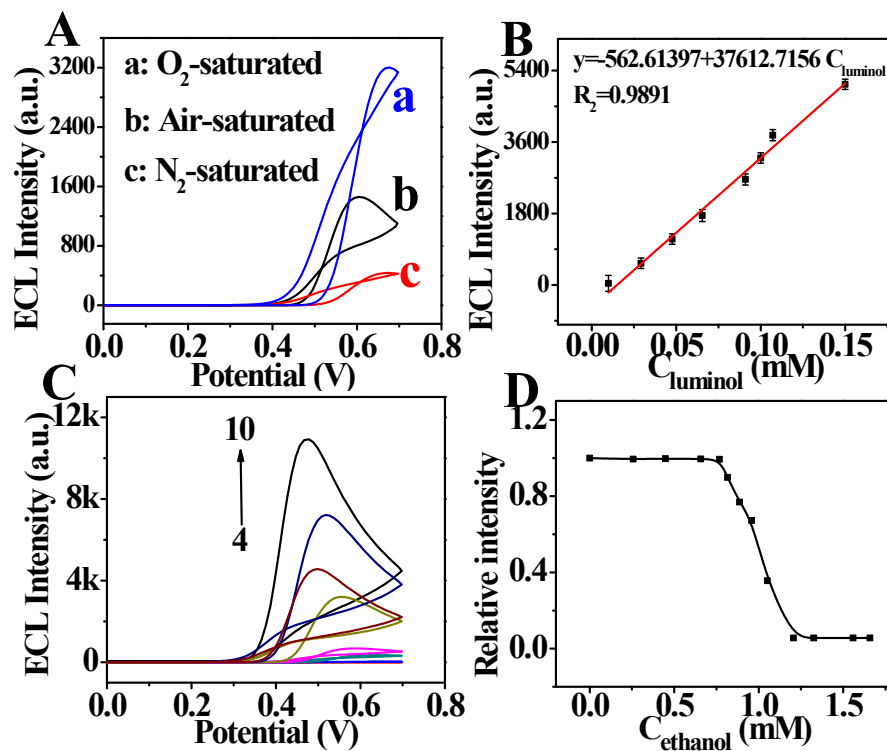
**Fig. S3B** The ECL performances from the GO-CoPc/GCE in different solution. PBS: (0.10 M, pH 7.4); luminol: 0.10 mM; ethanol: 1.2 mM; EP: 5 nM.



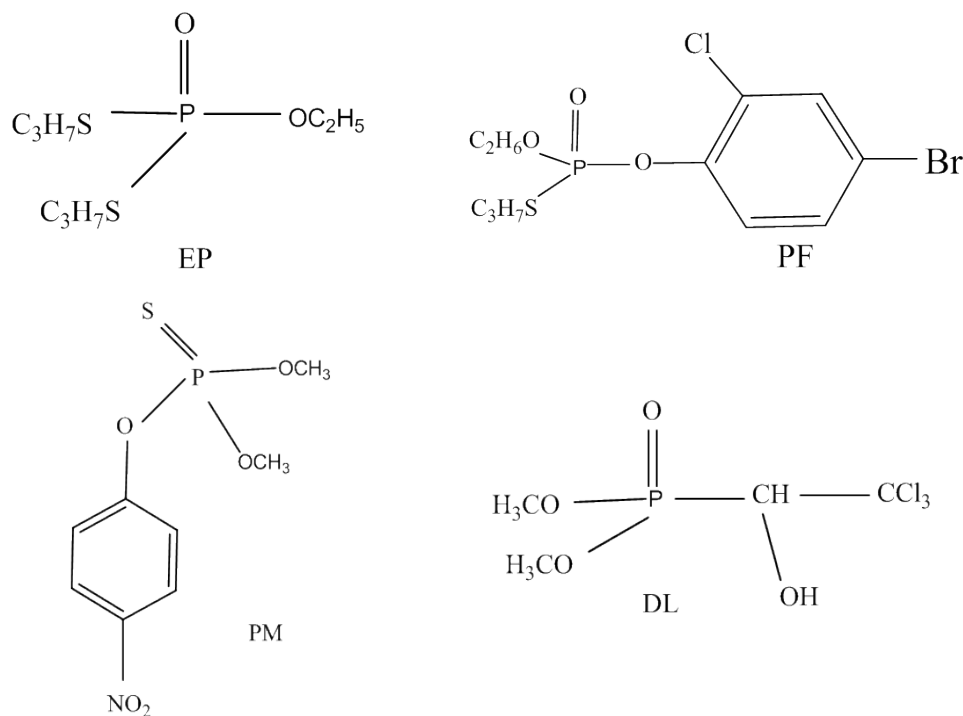
**Fig. S3C** The ECL responses from the GO-CoPc/GCE in different batches. PBS: (0.10 M, pH 7.4); luminol: 0.10 mM; ethanol: 1.2 mM; EP: 5 nM.



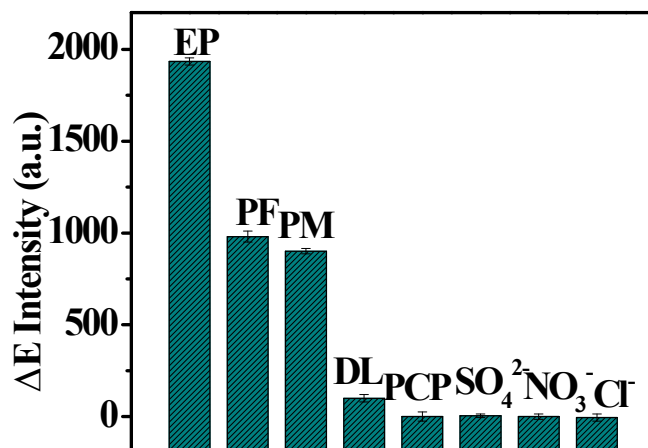
**Fig. S4** (A) EIS of bare electrode, GO, CoPc (a), GO-CoPc (b) modified electrodes in 5 mM  $\text{Fe(CN)}_6^{3-/4-}$  solution; (B) ECL of 0.10 mM luminol at a bare/GCE (a), GO/GCE (b), CoPc/GCE (c) and GO-CoPc/GCE.



**Fig. S5** Effects of O<sub>2</sub> (A), luminol concentration (B), pH (C) and ethanol concentration (D) on ECL responses.



**Fig. S6** Molecular structures of four typical organophosphate pesticide EP, PF, PM and DL.



**Fig. S7** Comparison of the ECL responses of various pesticides (0.4 nM): EP, PF, PM, DL, PCP, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> on the luminol GO-CoPc-ethanol ECL sensor. The ECL responses is determined in terms of ΔE, which is the difference value between E<sub>0</sub> and E (E<sub>0</sub> and E are the ECL intensity in the absence and presence of pesticides, respectively).

### Discussion on the ECL Mechanism of GO-CoPc/Luminol System

According to previous reports,<sup>S2,S3</sup> the equations of ECL mechanism in our work can be listed as follows:



Actually, in order to investigate the relating ECL mechanism, some essential experiments have been designed and implemented in our studies. Fig. S3 could be summarized as follows:

Section A:

- (a) bare/GCE/Luminol/PBS + H<sub>2</sub>O<sub>2</sub> + EP aqueous solution → ECL no change
- (b) bare/GCE/Luminol/PBS + H<sub>2</sub>O<sub>2</sub> + EP ethanol solution → ECL no change

Section B:

- (a) GO-CoPc/GCE/Luminol/PBS + EP aqueous solution → ECL no change
- (b) GO-CoPc/GCE/Luminol/PBS + ethanol → ECL quenching
- (c) GO-CoPc/GCE/Luminol/PBS + H<sub>2</sub>O → ECL no change

Section C:

- (a) GO-CoPc/GCE/Luminol/PBS + ethanol + EP aqueous solution → ECL enhancing
- (b) GO-CoPc/GCE/Luminol/PBS + EP aqueous solution + ethanol → ECL no change

As shown in Section A, EP could not be detected through the traditional ECL reaction of the luminol–H<sub>2</sub>O<sub>2</sub> whether adding aqueous solution or ethanol solution and the dissolved oxygen played an important role in our work. From Section B, there was no enhanced light emission when first adding EP. Besides, ethanol has been reported as a radical scavenger and readily reacts with superoxide anions,<sup>S4</sup> leading to the quenching of ECL emission due to the loss of superoxide anions. For further understanding the function of ethanol, we studied the effect of water and ethanol on ECL emission (Section B: b and c). In Section C: a, there was no enhanced light emission when first adding EP and no obvious intensity decrease was observed after



adding ethanol. The experimental results of the Section C: b demonstrated that as the Scheme 1 showed, there was only weak light emission (“OFF” state) because of the consumption of superoxide anions and the strong light emission appeared again when adding EP (“ON<sup>2</sup>” state), which might be attributed to that specific molecules possess much stronger binding capacity than ethanol and can obstruct the approaching of ethanol to superoxide anions.<sup>S5</sup> As a result, introducing the EP inhibited the consumption of the superoxide anions and we identified that the superoxide anions were wrapped the pesticide EP inside as shown in Scheme 1. In summary, the above experimental results proved the-proposed mechanism hypothesis.

### **ECL Performances of Different Modified Electrodes**

The comparison experiments of ECL performances of different modified electrodes have been made in our experiment as depicted in Fig. S4B. Fig. S4B showed that the onset potential of CoPc/GCE shifted more positively compared with bare GCE. That is to say, the component CoPc in GO-CoPc hybrids catalyzed the luminol reaction and enhanced the ECL emission of luminol, which is attributed to that the CoPc could catalyze the luminol reaction due to it reacts with dissolved oxygen to produce more OH<sup>-</sup>, facilitating the ECL of luminol.<sup>S6,S7</sup>

On the other hand, previous studies demonstrated that GO not only acted as an immobilization platform for nanomaterials, but also served as a good ECL signal amplifier which would greatly enhance the sensitivity of ECL detection.<sup>S8</sup> In our work (Fig. S3B), the ECL performances of GO-CoPc hybrids exhibited more excellent ECL activities with not only the lower onset potential of luminol and more enhanced ECL

emission, which was attributed to that GO could provide larger surfaces area in the hybrids films and accelerate the radical species generation.<sup>S8,S9</sup>

### **The Reproducibility of the Proposed ECL Sensor**

The reproducibility of the proposed ECL sensor was examined by measuring the current responses upon 1 pM EP in 0.10 M PBS (pH 7.4) containing 0.10 mM luminol and 1.2 mM ethanol. In a series of five electrodes prepared in the same way, a relative standard deviation (RSD) of 4.2 % was obtained, indicating the reliability of this method. Besides, 5 measurements for an electrode were made upon the addition of 1 pM EP in 0.10 M PBS (pH 7.4) containing 0.10 mM luminol and 1.2 mM ethanol with RSD of 2.9 %, indicating excellent reproducibility.

### **References**

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