# **Supplementary information**

A metal-organic framework regulated graphdiyne-based electrochemiluminescence sensor with constraint and self-accelerating effect for the detection of di(2-ethylhexyl) phthalate

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#### **Experimental section**

#### **Materials and Reagents**

All reagents are analytical grade and are ready for use without any treatment. Ultrapure water was used in all experiments. Bisphenol A (BPA), bisphenol B (BPB), nonylphenol (NP), dibutyl phthalate (DBP), dibutyl phthalate (2-ethylhexyl) ester (DEHP) diethylstilbestrol (DES), 2-amino-terephthalic acid(2-NH<sub>2</sub>-BDC), tetrabutylammonium fluoride (TBAF) and methanol were purchased from Aladdin. sodium ascorbate (NaAsc), sodium hydroxide (NaOH), Pyridine, tetrahydrofuran (THF), disodium hydrogen phosphate dodecahydrate (Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O), sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), N, Ndimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,2,3,4,5,6-hexakis[2-(trimeyhylsilyl)ethynyl] benzene purchased from shanghai haohong scientific co., ltd. The aptamers had the following sequence: 5'-COOH-ATG CGA AGC TTG CGC-3'.1 A lyophilized powder of the aptamers was dissolved in Tris-EDTA buffer and diluted to the preferred concentration.

#### Apparatus

The microstructure and morphology of the material were characterized by scanning electron microscopy (SEM) (SUPRA-55, Germany) and transmission electron microscope (TEM) (HT-7800, Japanese). The energy-dispersed spectrum (EDS) (JSM-6360LA, Japanese) were received at 5 kV. The UV-vis absorption spectra were carried out by an UV-2450 spectrophotometer (Shimadzu, Japan) with a 1 cm square quartz

cell and fluorescence spectrum were detected on the Hitachi F-4500 fluorescence spectrophotometer (Tokyo, Japan). Fourier transform infrared spectroscopy (FT-IR) characterizations were presented by Nicolet In10 (Thermo Fisher Scientific, USA) using a liquid-nitrogen-cooled detector. The phase and crystallinity of the material were analyzed by X-ray diffraction (XRD, Rigaku Smart Lab SE, Japan) with Cu-Ka rays as the light source. The elements and valence states of the material were analyzed using the excitation source as Al Ka ray X-ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha). ECL measurements were performed on MPI-B multifunctional ECL system (Xi'an Ruimai Analytical Instrument Co., Ltd.) with three-electrode system, which chosen glassy carbon electrode (GCE) as a working electrode, platinum wire as a counter electrode and Ag/AgCl as a reference electrode for ECL detection. Electrochemical impedance spectroscopy (EIS) were studied by CHI660D electrochemical workstation (Shanghai CH Instrument Co., Ltd., China) in 5.0 mM  $Fe(CN)_{6}^{3-/4-}$  containing 0.1 M KCl solution with an AC signal amplitude of 23 mV in the frequency range from 0.1 to  $10^5$  Hz. High performance liquid chromatography (HPLC) was performed on Agilent 1200 and the mobile phase was methanol and acetonitrile with a flow rate of 0.6 mL/min. The chromatographic column was C18 (150  $\times$  4.6 mm<sup>2</sup>).

#### Synthesis of graphdiyne

GDY was synthesized by cross-coupling reaction with hexaethynylbenzene as precursor, copper foil as catalyst and substrate.<sup>2</sup> Hexaethynylbenzene monomer was simply synthesized by stirring the mixture of tetrahydrofuran (THF) solution of hexa-[ (trimethylsilyl) ethyl] benzene with tetrabutylammonium fluoride (TBAF) for 10 min at 8 °C. In the presence of pyridine, GDY was grown on the surface of copper foil by cross-coupling reaction of hexaethynylbenzene monomer under nitrogen atmosphere at 60 °C for 72 h. The black film grown on copper foil was ultrasonically washed with acetone, and then hot dimethylformamide (DMF; 80 °C) ultrasonic washing for 1 h, and the black solid was peeled off. At 100 °C, the solid was refluxed in NaOH (4 M), HCl (6 M) and NaOH (4 M) for 2 h to remove residual copper and other impurities. The product was collected by centrifugation, washed with hot DMF (80 °C) and hot ethanol (70 °C), and finally dried in a vacuum oven overnight to obtain GDY powder.

# Preparation of functionalized zirconium-metal organic framework (NH<sub>2</sub>-Zr-MOF)

The synthesis of NH<sub>2</sub>-Zr-MOF is consistent with previous literature reports.<sup>3</sup> 2-Aminoterephthalic acid (31 mg, 0.17 mmol) was added to 20 mL mixed DMF solution of zirconium tetrachloride (80 mg, 0.34 mmol) and lauric acid (2.4 g, 12 mmol). After ultrasonic mixing, it was transferred to a hydrothermal autoclave and reacted at 120 °C for 12 h. The precipitate was centrifuged with DMF and ethanol, washed and vacuum dried for 6 h to obtain yellow powder.

#### Synthesis of NH<sub>2</sub>-Zr-MOF/GDY

20 mg GDY and 20 mg  $NH_2$ -Zr-MOF were added to 40 mL DMF solution. The mixed solution was ultrasonically treated for 4 h, and then stirred in a magnetic stirrer at a stirring speed of 1000 rpm for 6 h. After stirring, centrifugal separation was carried out. The product was washed with DMF and deionized water respectively. Finally, the washed product was dried in a drying oven at 60 °C to obtain a black powder, and 10 mg of the composite material was dispersed in 10 mL of DMF for subsequent experiments.



Scheme. S1 Schematic diagram of ECL reaction (A), workstation (B) and Micro-nanobubble generator (C).



Fig. S1 (A)The EDS and (B) X-ray photoelectron spectroscopy (XPS) analysis analyses of NH<sub>2</sub>-Zr-

MOF/GDY; (C) Elemental mapping of GDY and NH<sub>2</sub>-Zr-MOF/GDY.



Fig. S2 The Zeta-potential of GDY, NH2-Zr-MOF, NH2-Zr-MOF/GDY and Apt.



Fig. S3 CV profiles of bare GCE (a), GDY/GCE (b), NH2-Zr-MOF/GCE (c), NH2-Zr-





Fig. S4 (A) The ECL emission spectra of GDY, NH2-Zr-MOF; (B) The ECL stability diagram of

GDY under different ventilation conditions: Oxygen (a), Nitrogen (b) and Nitrogen nanobubbles

(c).



Fig. S5 The ECL stability diagram of NH2-Zr-MOF/GCE (a), GDY/GCE (b) and NH2-Zr-



**Optimization of experimental conditions** 

**Fig. S6** Optimization of experimental conditions of (A) sodium ascoibate concentration, (B) nitrogen nanobubble ventilation time in co-reactant solution, (C) aptamer modification concentration and (D) assay binding time (D).

A series of experimental conditions were optimized to construct the aptamer sensor with excellent performance. First, as the concentration of NaAsc increased, the ECL intensity rose and then slightly fell after 16 M (Fig. S6A). This was considered to the admission of NaAsc as a co-reaction accelerator into the  $K_2S_2O_8$  reaction system, which encouraged the conversion of  $S_2O_8^{2-}$  to  $SO_4^{+-}$ , and when the concentration of NaAsc was too high, it would consume strong oxidizing SO4<sup>+-</sup> radicals. In order to obtain the best luminescence effect, we selected 16 µM as the optimal concentration of sodium ascorbate in the co-reactant solution. Second, the appropriate breathing time of nitrogen nanobubbles was established by varying the intensity of the ECL signal (Fig. S6B). The ECL intensity gradually increases over 3-12 min, possibly because of the steady depletion of dissolved oxygen in the solution caused by the addition of nitrogen nanobubbles. It tended to be stable at 12 min, which might be due to the gradual increase of the temperature of the solution with the nitrogen nanobubbles, resulted in the decomposition of the potassium persulfate solution; secondly, probably because the nitrogen concentration in the solution has reached saturation, the nitrogen capacity would not change with the increase of time. Therefore, 12 min was the best ventilation time for nitrogen nanobubbles. Furthermore, we explored the effect of different aptamer concentrations on the ECL signal. The extent of the ECL steadily broken down, accompanied by an increase in the concentration of aptamers in the range of 0.5-9.0 µM (Fig. S6C). However, the ECL signal did not change significantly when the concentration was about 3.0 µM, indicated that the saturated concentration reached when 3.0  $\mu$ M aptamer solution was immobilized on the working electrode. Finally, the effect of incubation time on ECL intensity was studied. The aptamer modified electrode had a significant growth trend within 20 min (Fig. S6D) and ECL decreased slightly after 20 min. Therefore, the optimal incubation time was 20 min.

	Linear range	Detection limit	Reference	
Methods	$(ng mL^{-1})$ $(ng mL^{-1})$			
GC-MS	25-5000	13.3	4	
SERS	0.0031-71	0.0031	5	
EIS Apt	78.1-468.7	3.9	6	
ECL Apt	0.1-5000	0.04	7	
FL Apt	0.01~100	1.008 ×10 <sup>-6</sup>	8	
This work	0.000001-100	2.43×10 <sup>-7</sup>	-	

Table. S1 The comparison of different methods to determine DEHP



Fig. S7 Repeatability of Apt sensor and DEHP detection by 6 parallel measurements

Sample	Added		ECL			HPLC	
(ng/L)	(ng/L)	Found	Recovery	RSD	Found	Recovery	RSD
		(ng/L)	%	(%)	(ng/L)	%	(%)
				(n=3)			(n=3)
River	0	None	-	-	None	-	-
water		None	-			-	
	1.0	1.01	101	2.13	0.99	99	2.18
		0.98	98		0.96	96	
	10.0	10.3	103	2.59	10.3	103	2.26
		9.93	99.3		9.98	99.8	
Urban	0	None	-	-	None	-	-
drinkin		None	-			-	
g water	1.0	1.02	102	2.11	1.01	101	2.13
		0.99	99		0.98	98	
	10.0	10.2	102	2.90	10.3	103	2.37
		9.79	97.9		9.96	99.6	

**Table. S2.** Analytical data of DEHP in the river water and Urban drinking water

samples with the ECL and HPLC (n=3).

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