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Supplementary Information

Ultrathin alkynylation phthalocyanine-conjugated organic polymer nanosheets for constructing a sensitive electrochemiluminescence sensor

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1. Reagents and chemicals

Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70-230 mesh) with the indicated eluents. Tetrahydrofuran (THF) was distilled from sodium. All other chemicals were of analytical grade and used as received without further purification. Iron powder, hydrochloric acid, sulfuric acid, sodium nitrite, KI, CuI, NaOH, $AgNO_3$, anhydrous magnesium sulfate, sodium thiosulfate and copper foil were brought from Beijing Chemical Reagent Co. (Beijing, China). 0.5% Nafion solution was purchased from Dupont China Holding Co., LTd. 1,8-diazabicyclo[5,4,0]undec-7-ene (99%), tri-n-propylamine (TPrA), n-pentanol, n-hexane, toluene, CH_3OH, $Pd(PPh_3)_2Cl_2$, methyl butynol, triethylamine (Et_3N), 4-nitrophthalonitrile, and methylmalonic acid (MMA) were brought from Acros Organics Co., Ltd (USA). Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 99%), alumina slurries (0.3 μm and 0.05 μm), dichloromethane (HPLC), acetonitrile and THF were all purchased from Aladin Co., Ltd. (Shanghai, China). Healthy human serum samples were obtained from Fujian Medical University Union Hospital. The compounds of 4-iodophthalonitrile, 2(3),9(10),16(17),23(24)-tetraiodophthalocyanine ($H_2Pc(I)_4$), 4,4',4'',4'''-(phthalocyanine-2(3),9(10),16(17),23(24)-tetrayl)tetrakis(2-methylbut-3-yn-2-ol) ($H_2Pc(etynol)_4$) and 2(3),9(10),16(17),23(24)-tetraethynylphthalocyanine ($H_2Pc(ethynyl)_4$) were prepared according to the published procedure[1].

2. Characterization

The X-ray photoelectron spectroscopy (XPS) data were carried out on ESCALAB 250Xi (Thermo Scientific, USA) using 200 W monochromated Al Kα radiation. Raman spectra were taken on a Horiba LabRAM Hp Evolution Raman spectrometer with an excitation wavelength at 473 nm from an Ar laser at the resolution of 2 cm^{-1}. A PerkinElmer Frontier Fourier transform infrared (FT-IR) spectrometer was used to conduct FT-IR spectra. The ultraviolet-visible (UV–vis) absorption spectra were collected by a PerkinElmer Lambda 950 ultraviolet-visible spectrophotometer. An Agilent Cary Eclipse fluorescence spectrophotometer was used to detect the photoluminescence (PL) spectrum. The high-resolution transmission electron microscopy images (HRTEM) were collected on a JEOL-1400 microscope (JEOL, Japan) with an accelerating voltage of 200 kV. Scanning electron micrographs (SEM) were obtained with a SUPRA 55 field emission scanning electron microscope (Carl Zeiss AG, Germany). Atomic force microscope (AFM, Multimode VIII Bioscope Catalyst, Brugg Group Co., Ltd., Swiss) was taken to detect the thickness of TAPc-COPs nanosheets. N_2 adsorption-desorption isotherms and pore size distribution were detected on autosorb iQ (Quantachrome Instruments Co., USA). The pore volume of samples was obtained from the Barrett-Joyner-Halenda (BJH) method. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were measured on a CHI 760e electrochemical workstation (Chenghua Co., Ltd., Shanghai, China) by a three-electrode electrochemical cell system which was composed of a modified glass carbon electrode (GCE) (5 mm diameter) as the working electrode, an Ag/Ag^+ electrode as the reference electrode, and a Pt wire (1 mm diameter) as the counter electrode. Electrochemiluminescence (ECL) was performed with a homemade ECL analyzer which contained a CHI 760e electrochemical workstation and an ultraweak chemiluminescence (CL) analyzer (IFFM-E, Xi'an Remex Analytical Instrument Co., Ltd., China). The electrochemical workstation equipped with the above three-electrode system was utilized to apply the designed voltage. CL analyzer was utilized to take ECL images.

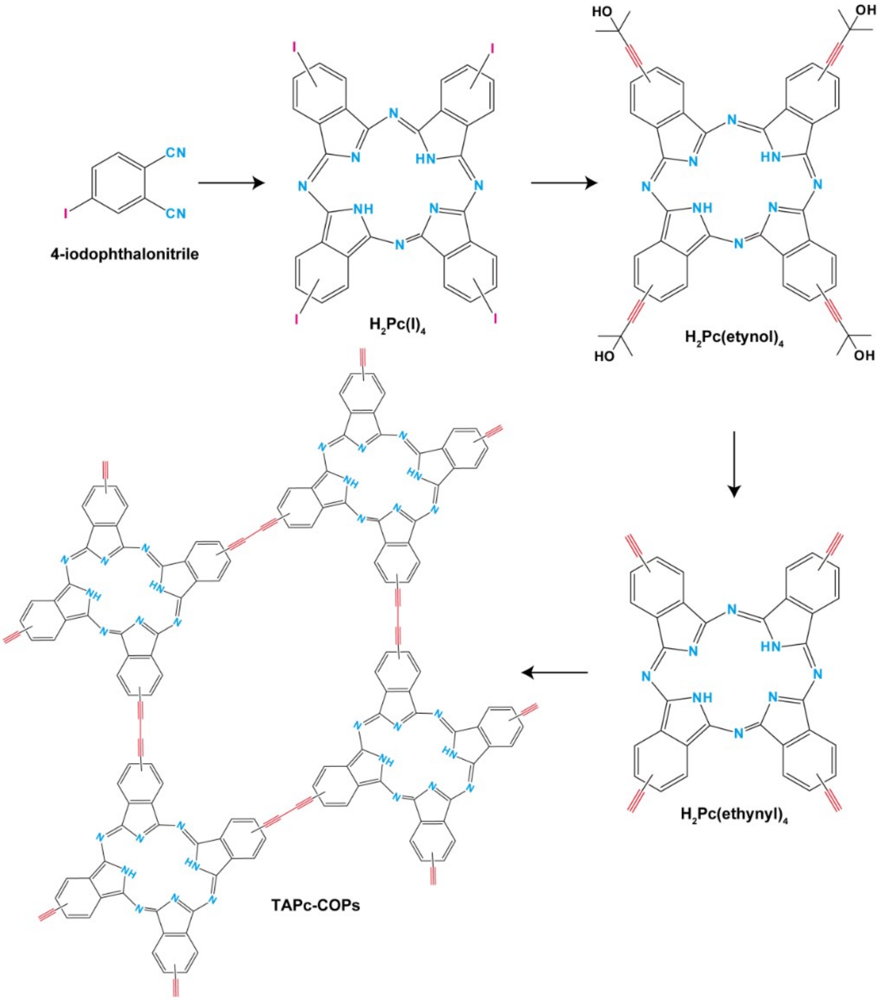
3. Synthesis of 4-iodophthalonitrile

Scheme S1. Synthetic route of 4-iodophthalonitrile.

The synthetic route of 4-iodophthalonitrile was listed in Scheme S1. (1) Synthesis of 4-aminophthalonitrile: 4-nitrophalonitrile (2.34 g, 13.5 mmol), CH_3OH (48 mL) and iron powder (2.27 g, 40.5 mmol) were put into a 500 mL reaction flask. Then, the mixture was refluxed at 85 °C. 12 mL hydrochloric acid (12 M) was added dropwise into the flask accompanying with an intense stir. The reaction was kept for 30 min. Then, the mixture was cooled to room temperature. Cold water (300 mL) was added to wash them. The resultant product was filtered swiftly and repeatedly with cold water. Finally, the filter cake was dried at 40 °C in a vacuum oven for 48 h to obtain 4-aminophthalonitrile.

(2) Synthesis of 4-iodophthalonitrile: 4-aminophthalonitrile (25.8 mmol, 3.7 g) was dissolved in 25% sulfuric acid solution (51 mL). Sodium nitrite (2.07 g) was dissolved in deionized water (6 mL) and was slowly dropped into the previous solution at -5 °C with stirring for 30 min. Then, KI solution (4.66 g in 30 mL H_2O) was added to the reaction. The reaction was kept for 1.5 h. The resultant mixture was washed with cool water and dispersed by ultra-dry dichloromethane and anhydrous magnesium sulfate. Column chromatography was used to purify the product using dichloromethane as eluent. The effluent was washed with saturated sodium thiosulfate solution and cold water, and then dried with anhydrous magnesium sulfate and recrystallized with dichloromethane:*n*-hexane (V:V, 1:3) to get 4-iodophthalonitrile.

4. Synthetic route of TAPc-COPs



Scheme S2. Synthetic route of TAPc-COPs.

5. Pore structure of powdered TAPc-COPs

Powdered TAPc-COPs was used to make know the sample pore structure because the quantity of TAPc-COPs collected on the surface of copper foil was not enough for Brunauet-Emmett-Teller (BET) analysis. N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves were detected and shown in Fig. S1. The main mesopore size was distributed within 3-30 nm and the average pore size was 26.34 nm.

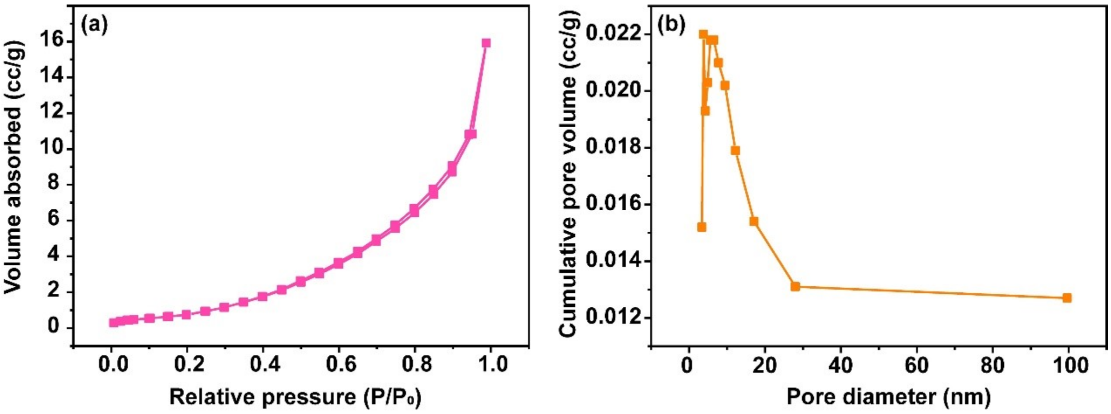


Fig. S1 The detection of pore structure of powdered TAPc-COPs. (a) N_2 adsorption-desorption isotherms; (b) the corresponding pore size distribution curves.

6. ECL on bare GCE

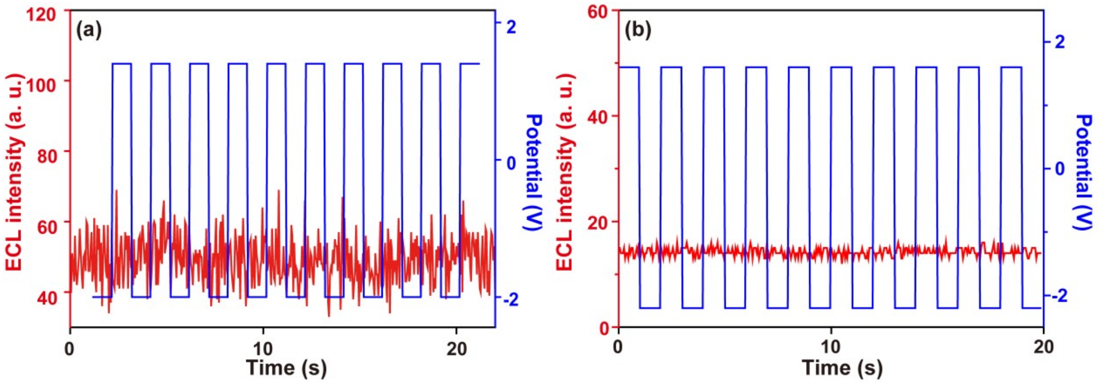


Fig. S2 ECL on bare GCE. (a) Electron injection initialed ECL transients of bare GCE. The pulse potential was stepped from -2.2 V to 1.6 V (vs Ag/Ag$^+$) with a period of 1 s. (b) Hole injection initialed ECL transients of bare GCE. The pulse potential was stepped from 1.6 V to -2.2 V (vs Ag/Ag$^+$) with a period of 1 s. Solution: air-free dichloromethane containing 0.1 M TBAPF$_6$. The voltage of photomultiplier tube (PMT) was set at 700 V.

7. ECL spectra of TAPc-COPs

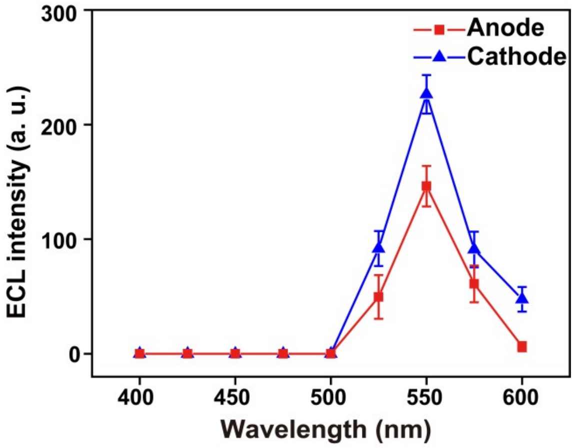


Fig. S3 ECL spectra of TAPc-COPs. The pulse potential was stepped from -2.2 V to 1.6 V (vs Ag/Ag$^+$) with a period of 1 s. Solution: air-free dichloromethane containing 0.1 M TBAPF$_6$. The voltage of PMT was set at 700 V.

8. ECL processes on the TAPc-COPs|GCE for MMA detection

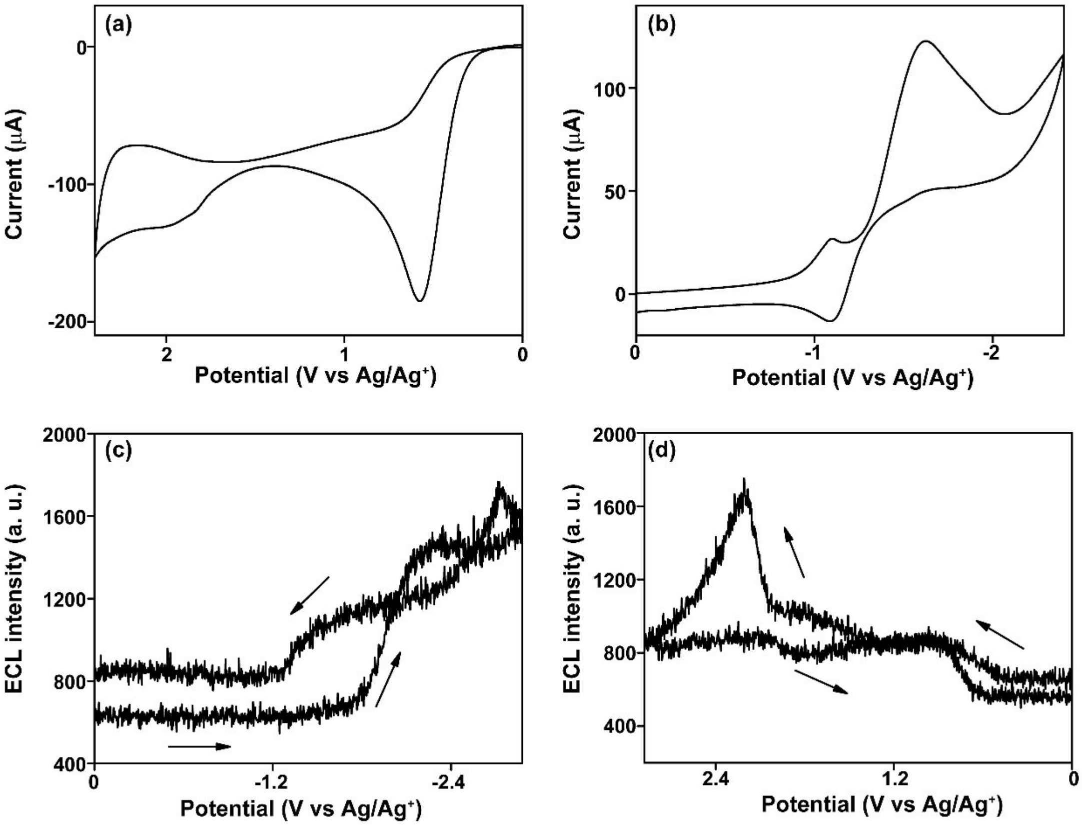


Fig. S4 ECL properties of TAPc-COPs|GCE in solutions containing MMA. (a) Anodic and (b) cathodic CV profiles of TAPc-COPs|GCE in air-free acetonitrile containing 0.1 M $TBAPF_6$, 10 mM TPrA and 0.01 mM MMA at 50 mV s^{-1}. (c) Corresponding anodic and (d) cathodic ECL profiles of TAPc-COPs|GCE in air-free acetonitrile containing 0.1 M $TBAPF_6$, 10 mM TPrA and 0.01 mM MMA at 50 mV s^{-1}.

9. Stability and reproducibility of the ECL sensor

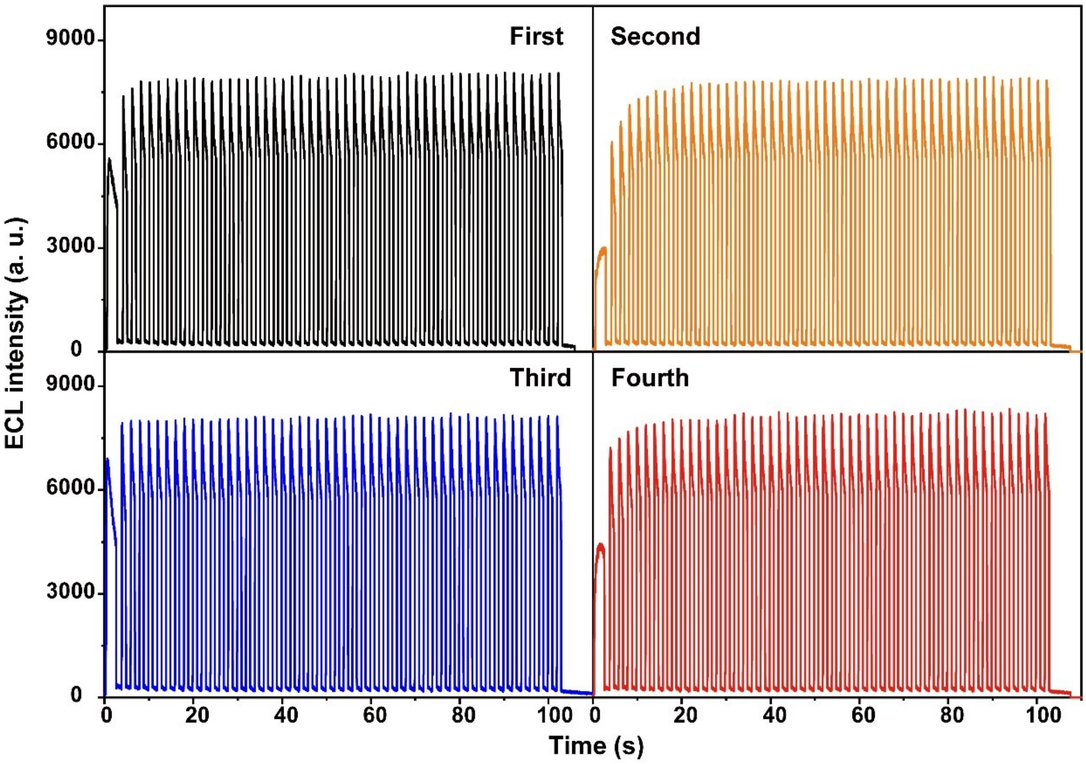


Fig. S5 Stability of the ECL sensor based on TAPc-COPs|GCE. Solution contained 10 μM MMA and was detected with a period of 1 s. The detection process lasted for 100 s.

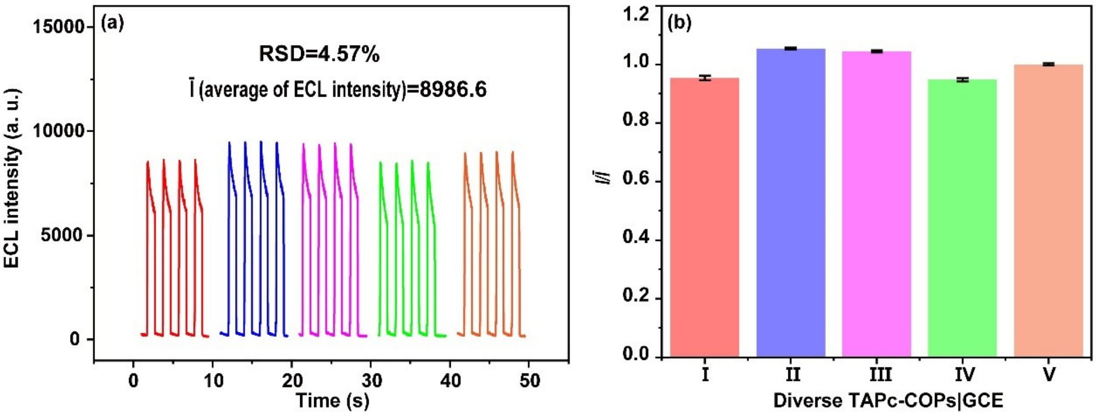


Fig. S6 Reproducibility of the ECL sensor based on TAPc-COPs|GCE. (a) The ECL intensity of five diverse TAPc-COPs|GCE and (b) the corresponding bar graphs of $I/\bar{I}$.

References:

1. W. Liu, H. Pan, C. Liu, C. Su, W. Liu, K. Wang and J. Jiang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 11466-11473.