

Electronic Supplementary Information

Ultra-high Sensitive and Selective Self-enhanced AIECL Sensor for Public Security Early Warning in Nuclear Emergency *via* a Co-reactive Group Poisoning Mechanism

Ziyu Wang, Meiyun Xu, Nan Zhang, Jian-Bin Pan*, Xinqi Wu, Peng Liu, Jing-Juan Xu* and Daoben Hua*

Content

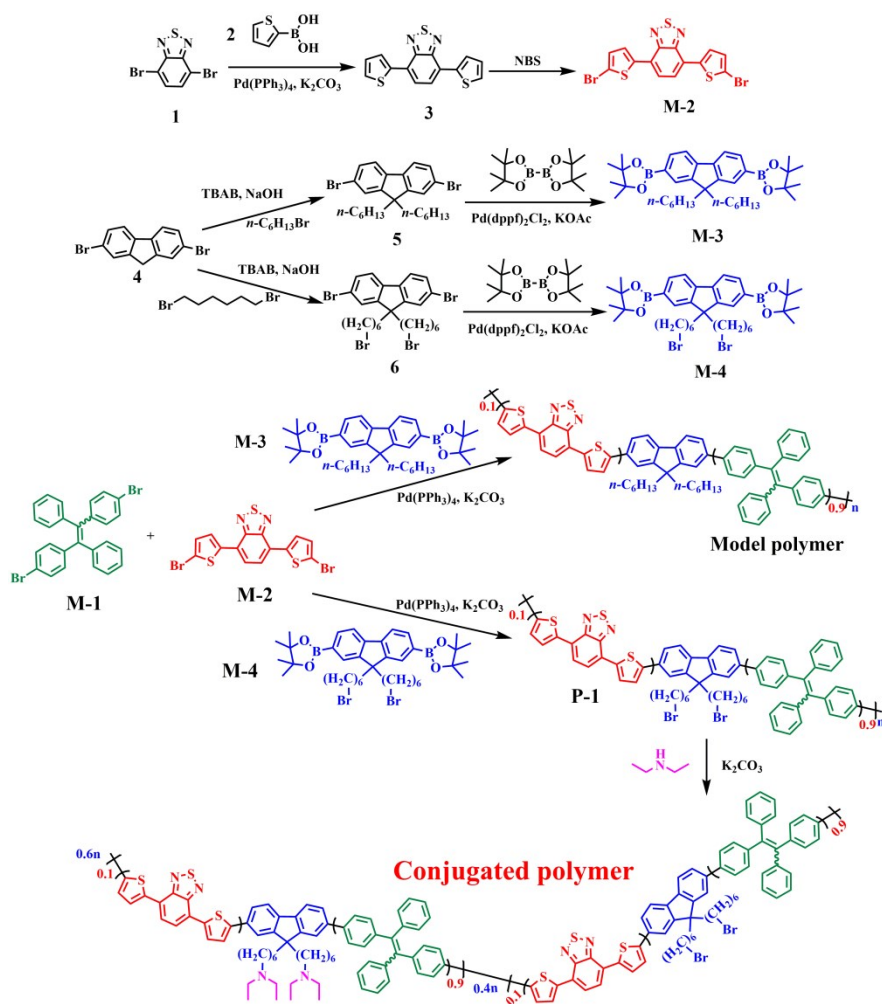
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Supplemental Experimental Procedures

Materials and apparatus

All solvents and reagents were commercially available and of analytical reagent grade. NMR spectra were obtained using a Bruker Advance 400 spectrometer at 400 MHz for ^1H NMR and reported as parts per million (ppm) from the internal standard TMS. UV-*vis* absorbance spectra were obtained on a Thermo Nanodrop 2000c spectropolarimeter. The fluorescence emission and ECL spectra were measured using a Hitachi F4700. The molecular weight was determined through gel permeation chromatography (GPC) using a Waters 244 HPLC pump, and THF was used as the solvent relative to the polystyrene standards. Electrochemical and ECL emission measurements were conducted on an ECL analyzer equipped with a CHI-600 E electrochemical station (supplied by the State Key Laboratory of Analytical Chemistry for Life Science, Nanjing University). The spectral width of the photomultiplier tube (PMT) was 350–650 nm, and the PMT voltage was set to 600 V during the detection process.

Synthesis Procedure



Scheme S1. Detailed synthetic route of model polymer and conjugated polymer

For the synthesis of the model polymer, **M-1** (0.101 g, 0.207 mmol), **M-2** (0.011 g, 0.023 mmol), **M-3** (0.113 g, 0.23 mmol) and Pd(PPh₃)₄ (0.030 g, 5% e.q.) were dissolved in 10 mL of toluene, 5 mL of ethanol, and K₂CO₃ (1.30 g) in water (5 mL). The mixture was refluxed for 48 h under an Ar atmosphere. The organic phase was dried using Na₂SO₄, and the solvent was removed. The resulting mixture was then dissolved in 2 mL THF and dropped into 300 mL of hexane. The product was filtered to give red solid model polymer as the product (0.11 g, 75.8%). ¹H NMR (400 MHz, CDCl₃) δ 7.77 - 7.69 (m, 2H), 7.60 - 7.51 (m, 4H), 7.50 - 7.44 (m, 3H), 7.22 - 7.10 (m, 16.8H), 2.24 - 1.82 (m, 4H), 1.82 - 1.49 (m, 2H), 1.33 - 1.27 (m, 1H), 1.16 - 1.01 (m, 10H), 0.79 - 0.68 (m, 9H). GPC data: M_w = 11740, M_n = 8940, PDI = 1.31.

Preparation of Pdots

PEG5k (100 µg) and conjugated/model polymer (100 µg) was dissolved in 1.0 mL of THF. After 5.0 mL of Milli-Q water was degassed by ultrasonication for 20 min, the THF solution was rapidly injected in and sonicated for another 4 min. Pdots dispersion was concentrated by removing the THF and then infiltrated to give 100 ppm Pdots (1.0 mL).

Preparation of modified electrodes

Glassy carbon electrodes (GCE, 5 mm in diameter) were polished with a 0.02–0.05 µm alumina slurry (Gauss Union, Wuhan) and then sonicated in Milli-Q water, ethanol, and Milli-Q water. The electrodes were then rinsed thoroughly with ultrapure water and dried under a N₂ flow. Pdots were modified on the GCEs (at 10 µL per electrode) and dried at 37 °C.

Formula for calculating the mass of radioactive elements

$$A(\text{Bq}) = \ln 2 / T_{1/2}(\text{s}) \times m(\text{g}) / M(\text{g/mol}) \times N_A$$

A is radioactivity of ¹³¹I; T_{1/2} is half-life value of ¹³¹I; m is mass of ¹³¹I; M is relative molecular mass of ¹³¹I; N_A is Avogadro constant. (D. Halliday, R. Resnick, J. Walker, Fundamental of Physics 7th, USA: John Wiley and Sons, Inc.: 2005, 1173-1175, 2005, ISBN 0-471-23231-9)

Supplemental Data Items

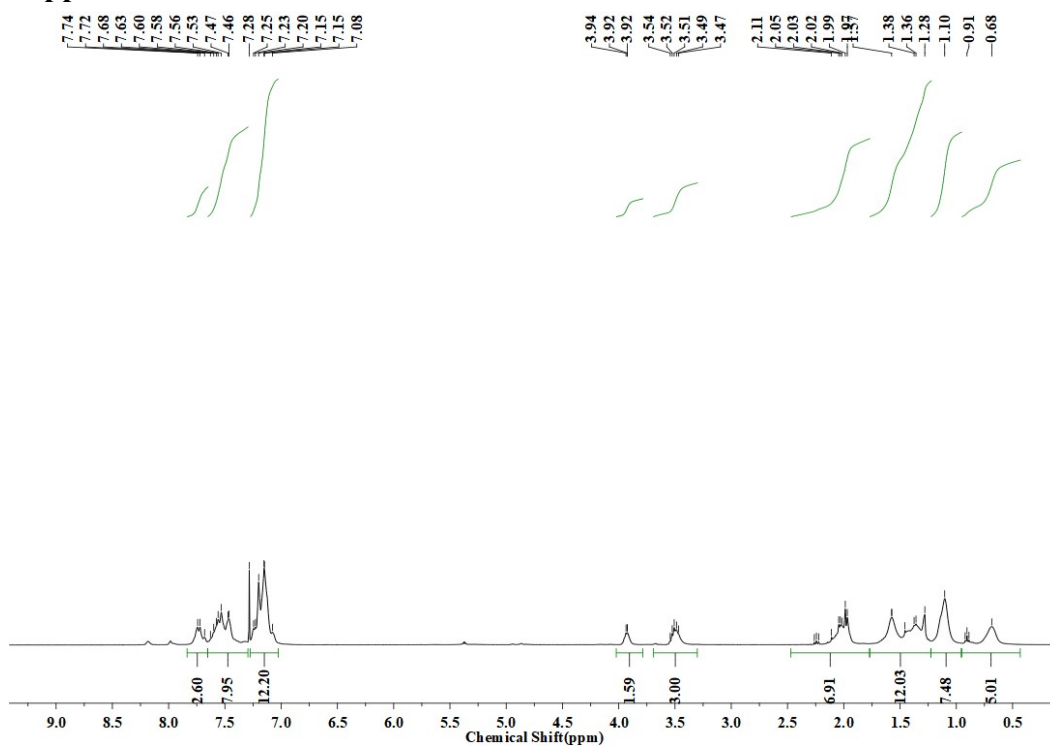


Fig. S1. ^1H NMR spectrum of conjugated polymer

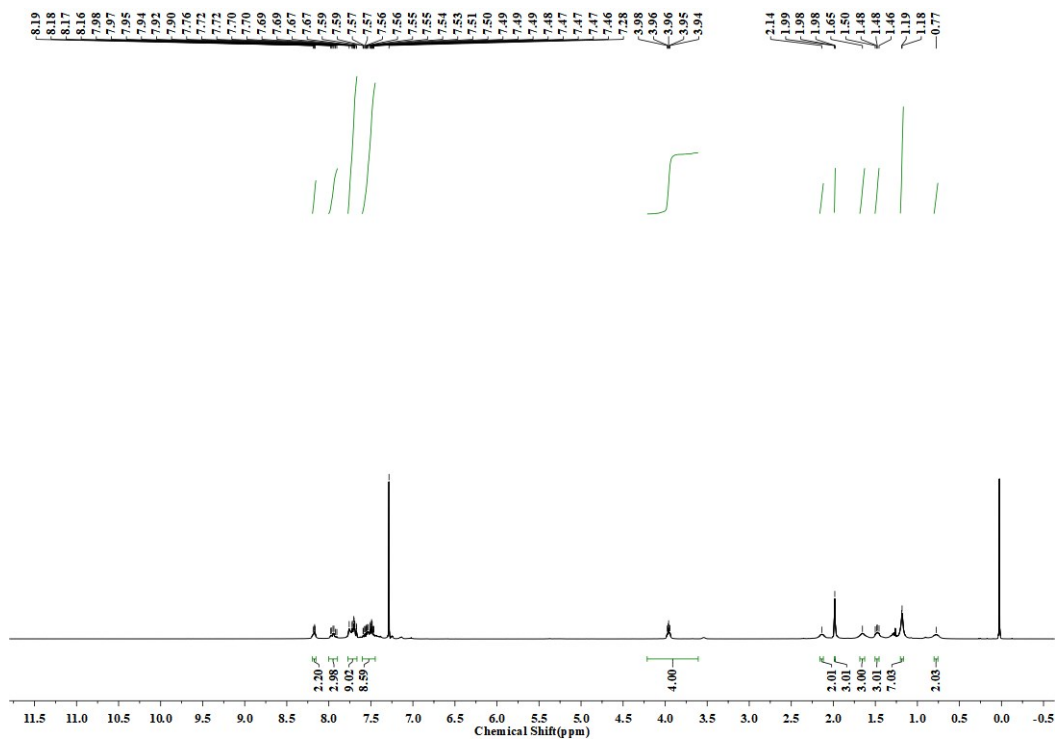


Fig. S2. ^1H NMR spectrum of P-1

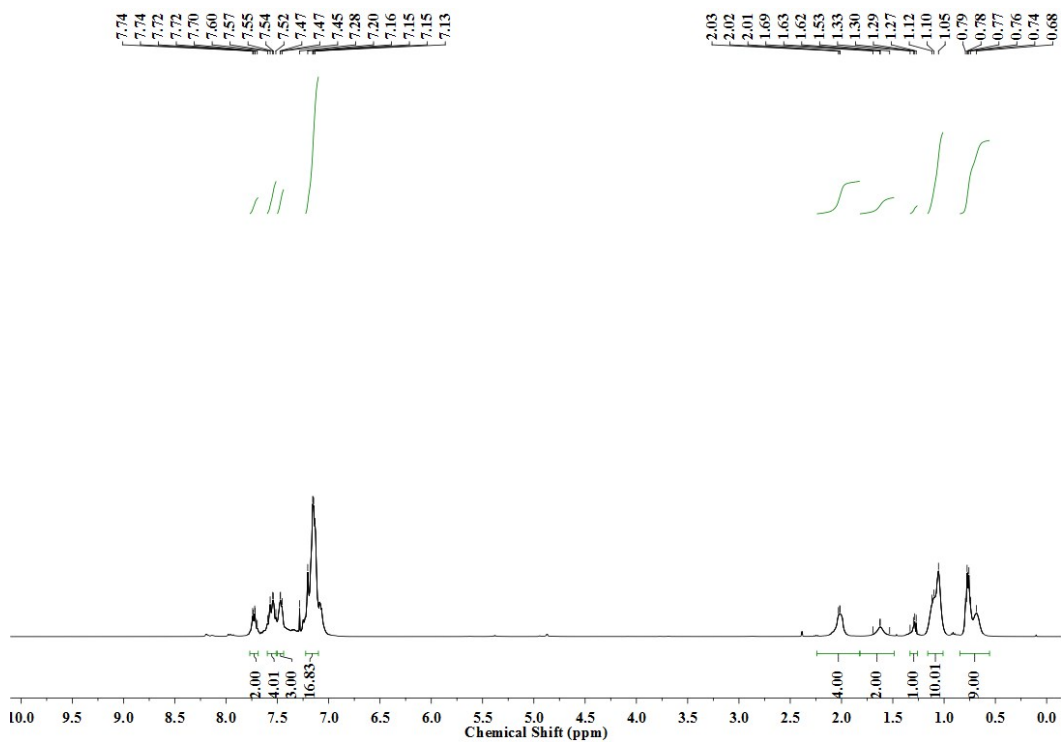


Fig. S3. ¹H NMR spectrum of model polymer

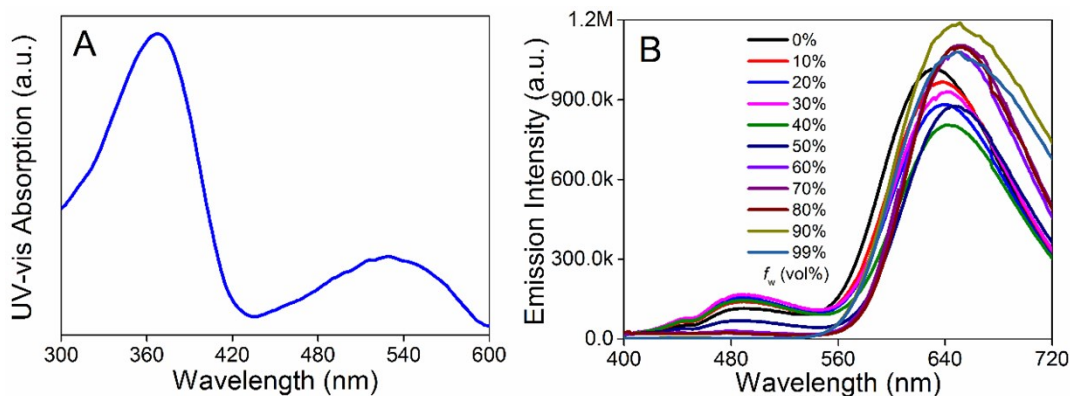


Fig. S4. UV-vis absorption spectrum in THF (A) and fluorescence spectra in THF-H₂O mixtures with different water fraction (f_w) (B) of conjugated polymer. Polymer concentration: 1×10^{-5} mol L⁻¹ corresponding to fluorene moiety.

(As is shown in Fig. S3A, the conjugated polymer exhibited two obvious absorbance peaks centered at 368 nm and 529 nm, respectively. The peak at 368 nm could be assigned to the conjugated backbone while the long wavelength peak could be attributed to the intramolecular charge transfer (ICT) process from electron donor to acceptor.¹ The fluorescence spectra were carried out in Fig. S3B and showed obvious AIE behavior in red colored region. The emission peak appeared at 650 nm and gave the strongest fluorescence signal when $f_w = 90\%$. Then the fluorescence signal exhibited slight quenching due to the decreased effective polymer concentration induced by large-sized aggregates in aqueous solution.²⁾

Table S1. Electrochemical data and calculated energy levels of conjugated polymer.

	E_{Onset}^{Ox} (V ^a)	E_{Onset}^{Red} (V ^a)	HOMO (eV ^b)	LUMO (eV ^b)	E_g (eV ^b)
Conjugated polymer	+0.36	-0.83	-5.19	-3.85	1.19

^a Potential was versus Ag/Ag⁺ in CH₂Cl₂. ^b The energy levels were calculated using the following equations: $E_{HOMO} = -(E_{onset}^{Ox} - E_{Fc/Fc^+} + 4.8)$ eV, $E_{LUMO} = -(E_{onset}^{Red} - E_{Fc/Fc^+} + 4.8)$ eV, $E_g = E_{LUMO} - E_{HOMO}$. E_{Fc/Fc^+} was reported as +0.12 V vs. Ag/Ag⁺.^[1]

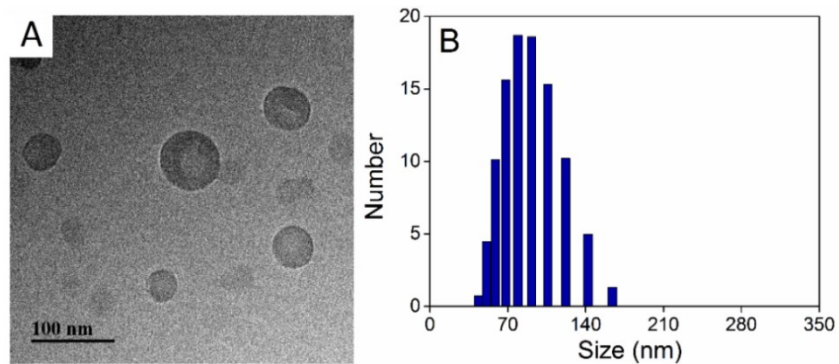


Fig. S5. TEM image (A) (Plotting scale: 100 nm) and DLS data (B) of model polymer Pdots.

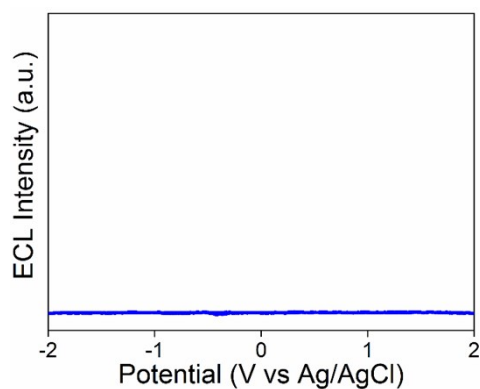


Fig. S6. ECL of model polymer Pdots in 0.1 M pH 7.4 PBS. Pdots concentration: 100 ppm, PMT = 750 V, scan rate = 100 mV s⁻¹.

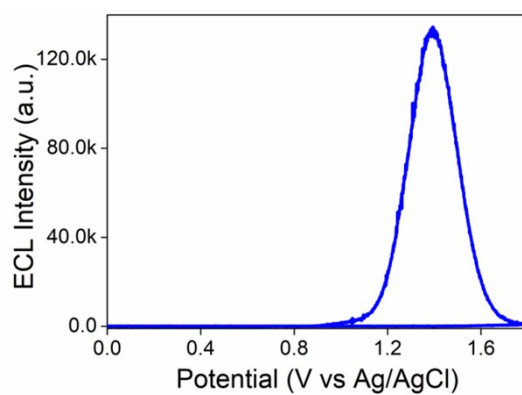


Fig. S7. ECL of model polymer Pdots in 0.1 M pH 7.4 PBS with 25 mM TEA as co-reactant reagent. Pdots concentration: 100 ppm, PMT = 600 V, scan rate = 100 mV s⁻¹.

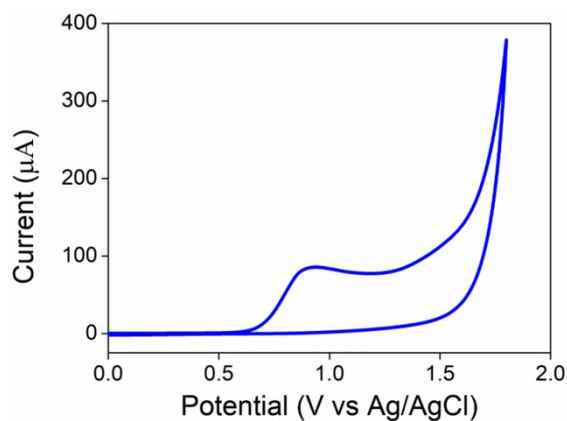


Fig. S8. CV data of 25 mM TEA, scan rate = 100 mV s⁻¹.

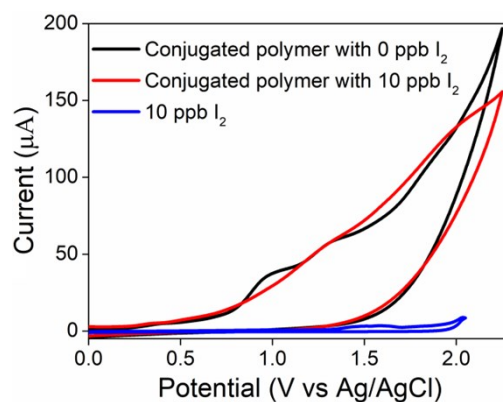


Fig. S9. CV of conjugated polymer with different I₂ concentrations in CH₂Cl₂ solution with 0.1 M Bu₄NBF₄, polymer concentration: 300 ppm; CV of I₂ in CH₂Cl₂ with 0.1 M Bu₄NBF₄, scan rate = 50 mV s⁻¹.

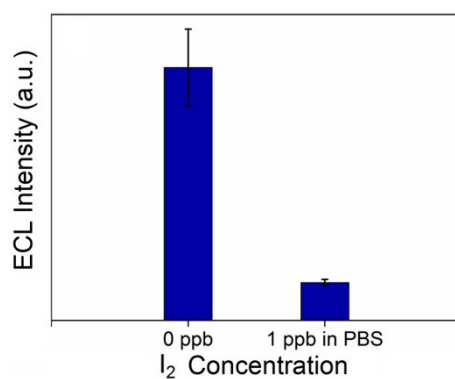


Fig. S10. ECL signals of model polymer Pdots modified GCE in 0.1 M pH 7.4 PBS with 25 mM I₂ treated TEA. Polymer concentration: 1 mM corresponding to fluorene moiety; scan rate = 100 mV s⁻¹, Pdots concentration: 100 ppm.

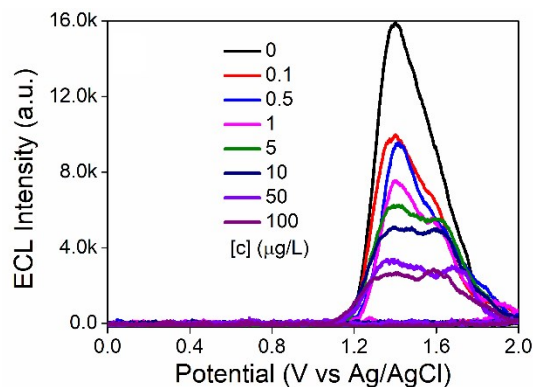


Fig. S11. ECL signals of conjugated polymer Pdots modified GCE treated by I₂ vapor in different concentration in 0.1 M pH 7.4 PBS, PMT = 850 V, scan rate: 100 mV s⁻¹.

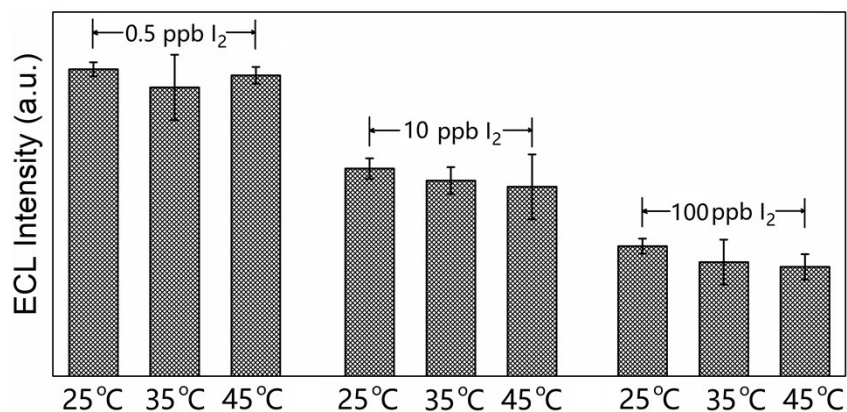


Fig. S12. ECL intensity values of conjugated polymer Pdots modified GCE treated by I₂ vapor in different concentration in 0.1 M pH 7.4 PBS under different temperature, PMT = 850 V, scan rate: 100 mV s⁻¹.

Reference

- [1] Z. Wang, C. Wang, Q. Gan, Y. Cao, H. Yuan, D. Hua, *ACS Appl. Mater. Interfaces* 2019, **11**, 41853.
- [2] E. Wang, J. W. Y. Lam, R. Hu, C. Zhang, Y. S. Zhao, B. Z. Tang, *J. Mater. Chem. C* 2014, **2**, 1801.