

Supporting Information

Molecular Engineering of Polymer Dots for Electrochemiluminescent Emission

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Experimental Section

Materials and Reagents

Triethylamine (TEA, $\geq 99\%$), tri-*n*-propylamine (TPrA), tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), tetrahydrofuran (THF, anhydrous, $\geq 99.9\%$, inhibitor-free) were purchased by Sigma-Aldrich Co. Ltd (Shanghai, China). All other reagents were of analytical grade and directly used without further purification. Phosphate buffer saline (PBS, 0.1 M) was prepared by mixing stock solutions of NaH_2PO_4 and Na_2HPO_4 . Ultrapure water obtained from a Millipore water purification system ($\geq 18 \text{ M}\Omega \text{ cm}$, Milli-Q, Millipore) was used in all tests.

Apparatus.

Transmission electron microscopic (TEM) images were acquired on a FEI Tecnai F20 transmission electron microscope (Thermo Fisher Scientific, U.S.A.). Dynamic light scattering (DLS) and Zeta potential analysis were performed on a 90 Plus/BI-MA Sequipment (Brookhaven, U.S.A.). The UV-vis absorption spectra were obtained using a UV-3600 UV-vis-NIR spectrophotometer (Shimadzu Co.). Fluorescence measurements were conducted on an F-7000 fluorescence spectrometer (Hitachi Co., Japan) equipped with a xenon lamp. The absolute photoluminescence quantum yields (Φ_F) and the decay lifetimes was measured with HORIBA FL-3 fluorescence spectrometer. The NMR spectra were obtained from a Bruker Advance 400 spectrometer (Bruker, German) with 400 MHz for ^1H NMR reported as parts per million (ppm) from the internal standard tetramethylsilane (TMS). Molecular weight was determined by gel permeation chromatography (GPC) with a Waters 244 HPLC pump, and THF was used as the solvent relative to polystyrene standards. Electrochemical experiments were performed on a CHI 660a electrochemical workstation (CH Instruments Inc., China). Electrochemical impedance spectroscopic (EIS) measurements were performed on a PGSTAT30/FRA2 system (Autolab, the Netherlands) in 0.1 M KCl aqueous solution containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6 / \text{K}_4\text{Fe}(\text{CN})_6$ (1:1). ECL measurements were carried out in a self-made cell on MPI-E multifunctional

electrochemical and chemiluminescent analytical system (Xi'an Remex Analytical Instrument Co., Ltd. China). The visual ECL images of these Pdots were collected by Olympus DP71 CCD. Ultrasonic synthesis experiments were conducted on the sonicator (Elmasonic P30H, Germany).

Preparation of Electrodes.

Glassy carbon electrode (GCE, 3 mm in diameter) was polished on a microcloth to a mirror surface using 0.02 - 0.05 μm alumina slurry, followed by sonication in water, water/ethanol (1:1), and water, successively. These electrodes were washed thoroughly with ultrapure water and dried in a steam of nitrogen for next experiments.

Electrochemical and ECL Measurements.

The cyclic voltammograms (CVs) were examined using a conventional three-electrode system, where the modified glassy carbon electrode (GCE, 3 mm in diameter) was used as a working electrode, a platinum wire was used as an auxiliary electrode, and an Ag/AgCl electrode (saturated KCl) was used as the reference electrode.

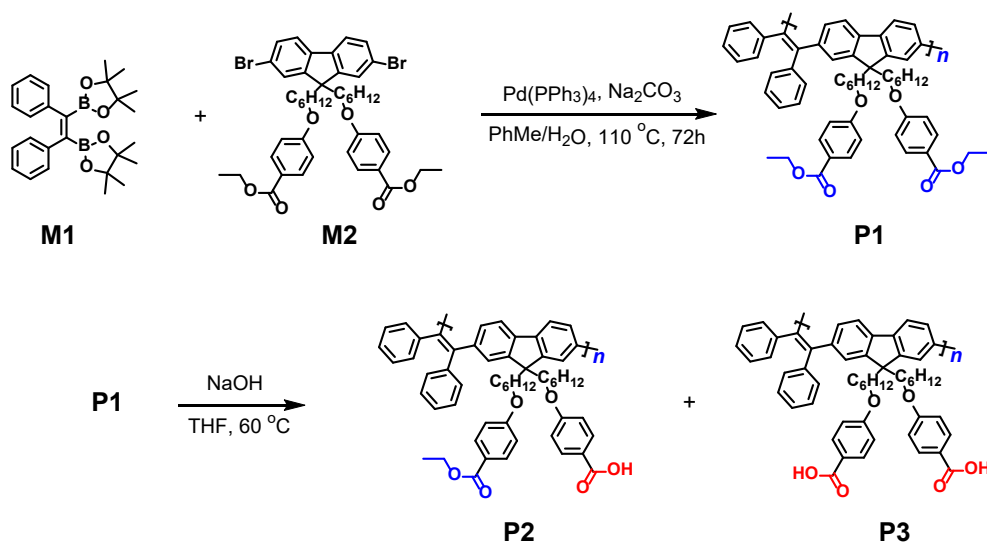
The glass carbon electrodes modified with Pdots were prepared by dropping 10 μL of 60 μM corresponding Pdots solution on an activated GCE and dried under 35 $^{\circ}\text{C}$. The ECL curves were obtained by scanning from 0 to +1.50 V in 0.1 M PBS (pH 7.4) containing 25 mM TEA as anodic co-reactant. Unless otherwise stated, the ECL window was placed in front of the photomultiplier tube (PMT) biased at 400 V with a scan rate of 100 mV s^{-1} . The ECL emission spectra of **Pdots1**, **Pdots2**, and **Pdots3** were obtained by a self-made ECL spectrum analyzer consisting of a CHI-660D electrochemical workstation and a FLS-980 fluorescence spectrophotometer. The ECL spectra of these Pdots modified electrodes were recorded in 0.1 M pH 7.4 PBS containing 25 mM TEA at +1.4 V for **Pdots1**, + 1.3 V for **Pdots2**, and + 1.2 V for **Pdots3** for 10s, respectively.

ECL Efficiency of Pdots/GCE. The ECL efficiency of these Pdots/GCE systems was calculated relative to $\text{Ru}(\text{bpy})_3^{2+}$ /solution system. The relative ECL quantum efficiency was calculated applying the relation below:¹

$$\Phi_x = \Phi_{st} \left(\frac{\int_0^t I dt}{\int_0^t i dt} \right)_x / \left(\frac{\int_0^t I dt}{\int_0^t i dt} \right)_{st} = \Phi_{st} \left(\frac{\int_a^b I dv}{\int_a^b i dv} \right)_x / \left(\frac{\int_a^b I dv}{\int_a^b i dv} \right)_{st} \quad (\text{Eq S1})$$

Here, Φ_{st} was the ECL efficiency of 0.1 mM Ru(bpy)₃²⁺/(25 mM TPrA in 0.1 M PBS with pH 7.4) with the value of 100% used as the standard (st), i is current value, I is ECL intensity, and x is the sample.

Synthesis Procedures of the Polymers.



Scheme S1. The synthesis routes of P1-P3.

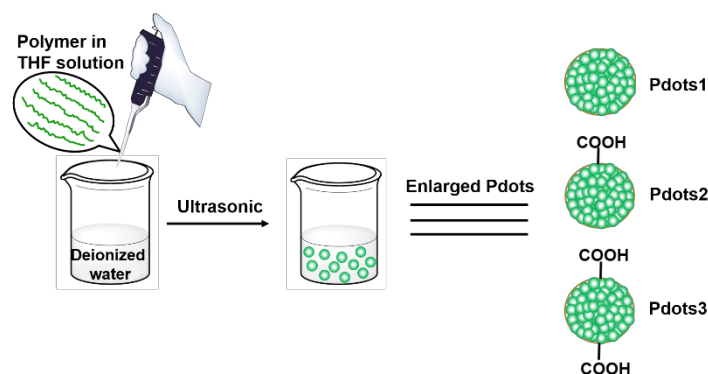
P1: A mixture of (Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**M1**, 100.0 mg, 0.23 mmol), diethyl 4,4-(((2,7-dibromo-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(oxy))dibenzoate (**M2**, 189.9 mg, 0.23 mmol), Pd(PPh₃)₄ (26.6 mg, 2.3% mmol), and Na₂CO₃ (243.8 mg, 2.3 mmol) in PhMe/H₂O (8 mL: 2 mL) in a Schlenk tube was stirred at 110 °C for 72 h under an argon atmosphere. After reaction, the resulting polymers were purified by being precipitated in methanol twice as green solid. Yield: 81%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.99 - 7.28 (m, 8H), 7.16 - 6.79 (m, 16H), 4.35 - 4.30 (m, 4H), 3.92 - 3.79 (m, 4H), 1.79 - 1.43 (m, 7H), 1.39 - 1.29 (m, 6H), 1.14 - 0.41 (m, 13H). GPC data: $M_n = 17240$, PDI = 2.38.

P2: The above polymer of **P1** (100 mg, 0.11 mmol) and NaOH (6.8 mg, 0.17 mmol) were mixed into THF (15 mL) and heated at 50 °C for 24 hours. After the mixture was cooled, 0.1 mol/L HCl was added to adjust the solution pH about 5. Then, the solvent was removed and the resulting crude product was purified by being precipitated in

methanol twice as green solid. Yield: 90%. ^1H NMR ((400 MHz, *d*-DMSO) δ (ppm): 12.53 (s, 1H), 7.84 - 6.88 (m, 24H), 4.25 - 4.22 (m, 2H), 3.83 - 3.79 (m, 4H), 1.61 - 0.15 (m, 23H). GPC data: $M_n = 18320$, PDI = 1.97.

P3: The synthesized method was similar to **P2**. The above polymer of **P1** (100 mg, 0.11 mmol) and NaOH (22 mg, 0.55 mmol) were mixed into THF (15 mL) and heated at 50 °C for 72 hours. After the mixture was cooled, 0.1 mol/L HCl was added to adjust the solution pH about 2. Then, the solvent was removed and resulting crude product was purified by being precipitated in methanol twice as green solid. Yield: 88%. ^1H NMR ((400 MHz, *d*-DMSO) δ (ppm): 12.57 (s, 2H), 7.86 - 6.87 (m, 24H), 3.95 - 3.79 (m, 4H), 2.01 - 0.15 (m, 20H). GPC data: $M_n = 16240$, PDI = 1.76.

Preparation of Pdots.



Scheme S2. The preparation of Pdots.

These Pdots were prepared by nanoprecipitation method according to the literature with minor modification.² In brief, 1.5 mL of 0.6 mM polymers of **P1-P3** in THF were prepared diluted to 15 mL, and ultrasonically degassed for 3 min under room temperature (Elmasonic P30H, Germany). Then, 2 mL of the mixture was quickly added to 10 mL of water under sonication. The THF solvent was removed by rotary evaporation under vacuum, followed by filtration through a 0.22 μm poly(ether sulfones) (PES) syringe filter (Millex-GP Filter, Millipore). The obtained solution of 60 μM **Pdots1** – **Pdots3** was colorless and transparent.

2. Supplementary Figures and Tables.

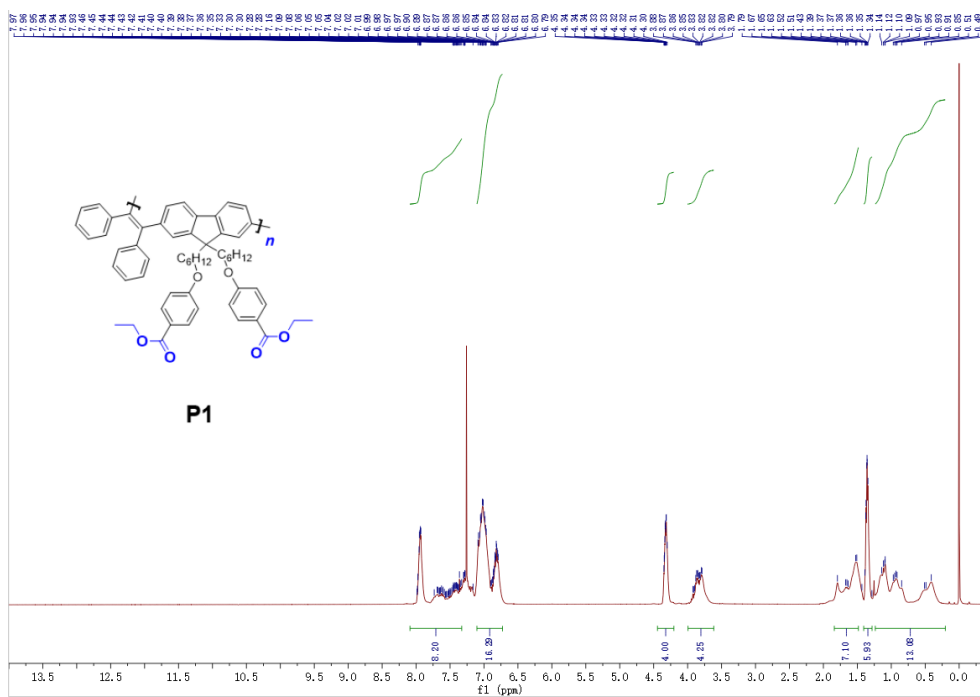


Figure S1. ¹H NMR of P1.

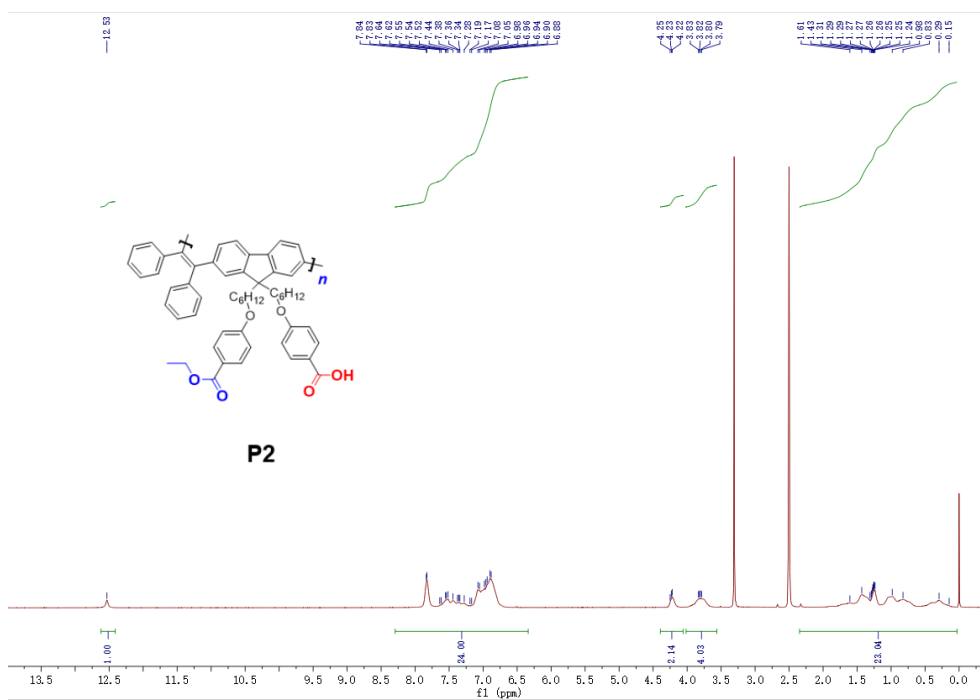


Figure S2. ¹H NMR of P2.

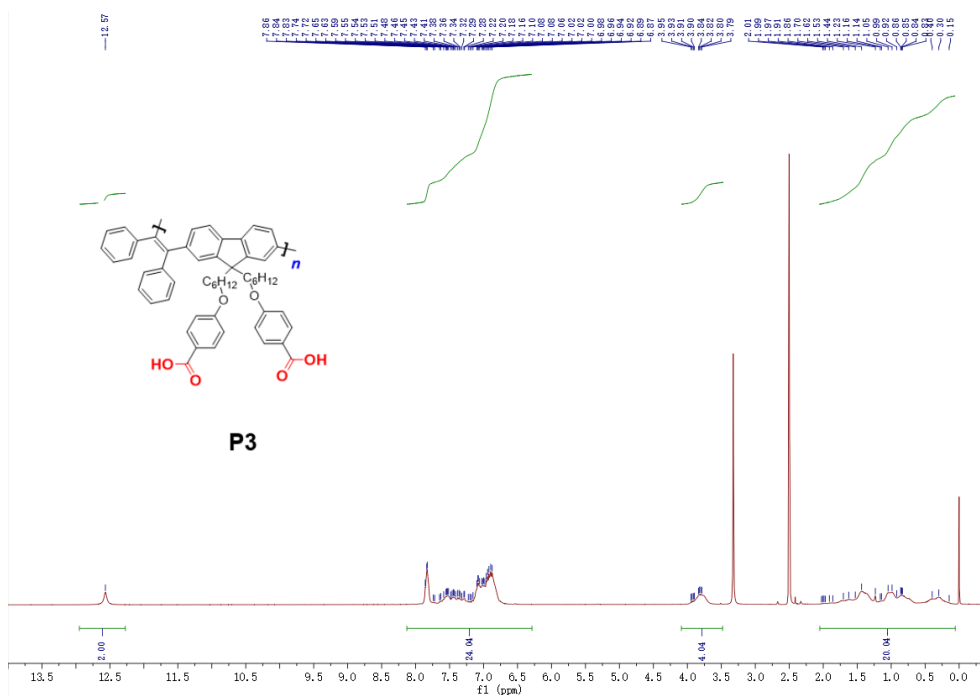


Figure S3. ¹H NMR of P3.

Table S1. Yield and GCP data.

Polymer	Yield	Mw	Mn	PDI
P1	81	41110	17240	2.38
P2	90	36150	18320	1.97
P3	88	28651	16240	1.76

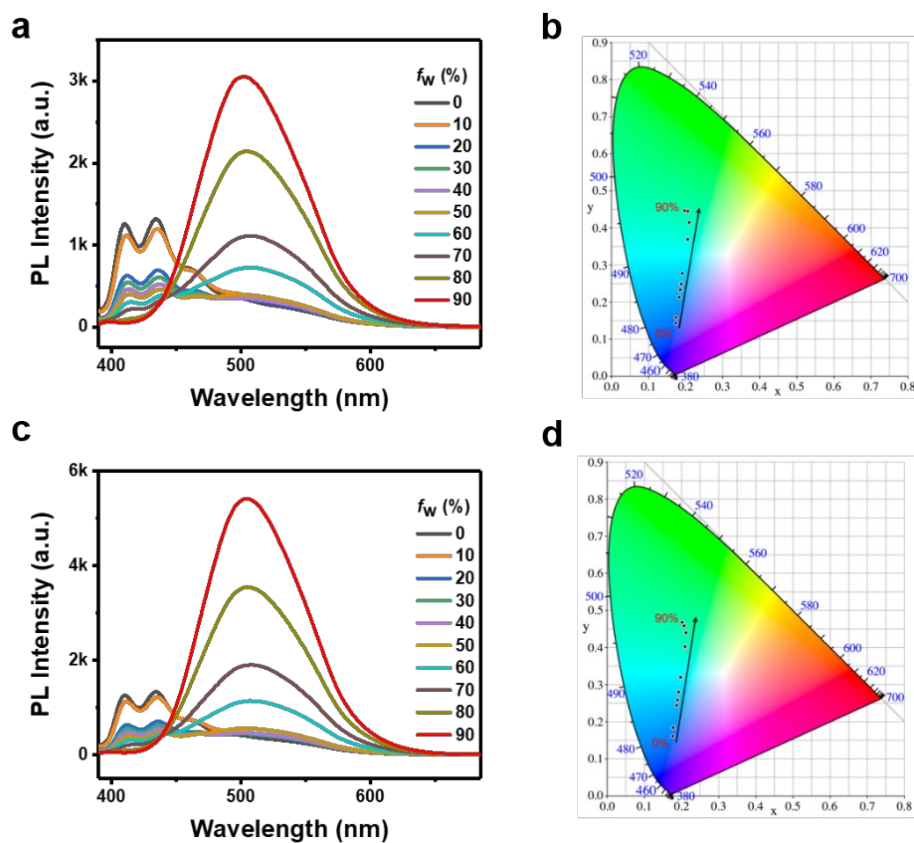


Figure S4. Fluorescence spectra and CIE color diagram for the emission of **P1** (a, b) and **P2** (c, d) in the mixtures with different composition of H₂O/THF.

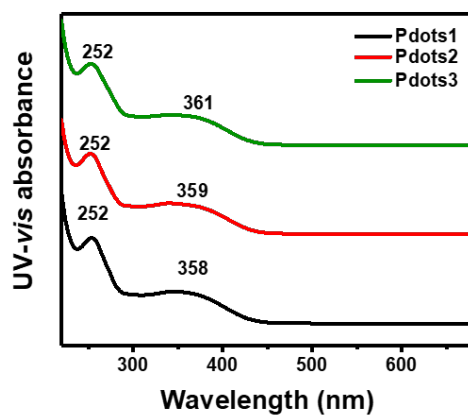


Figure S5. UV-vis absorption spectra of **Pdots1-Pdots3**.

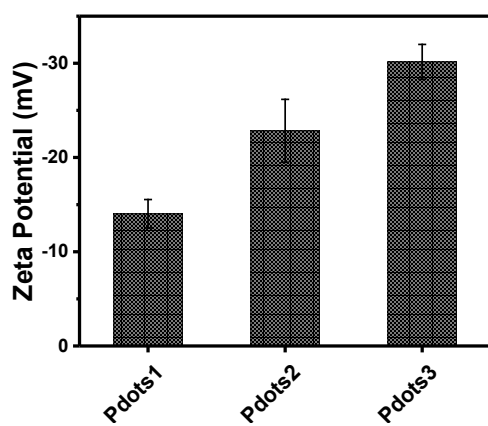


Figure S6. Zeta potentials of Pdots1-Pdots3.

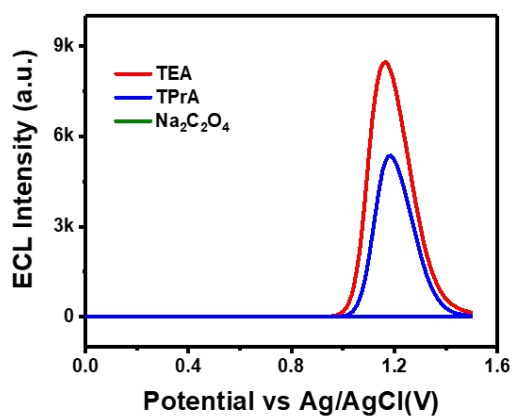


Figure S7. ECL intensity of Pdots3/GCE in 0.1 M pH 7.4 PBS with different 25 mM oxidative-reductive coreactants.

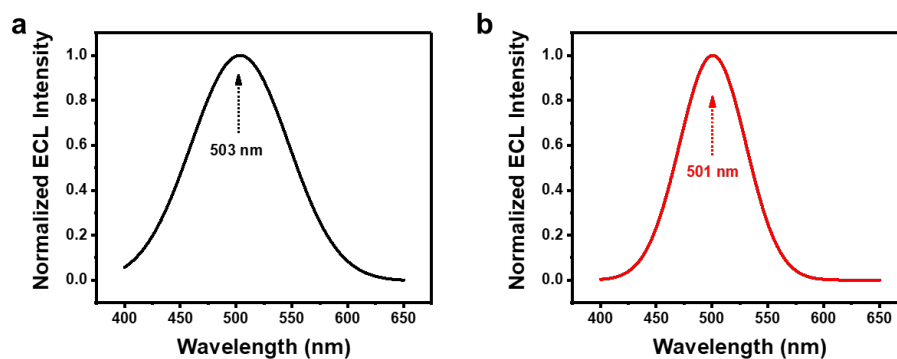


Figure S8. ECL spectra of Pdots1/GCE (a) and Pdots2/GCE (b).

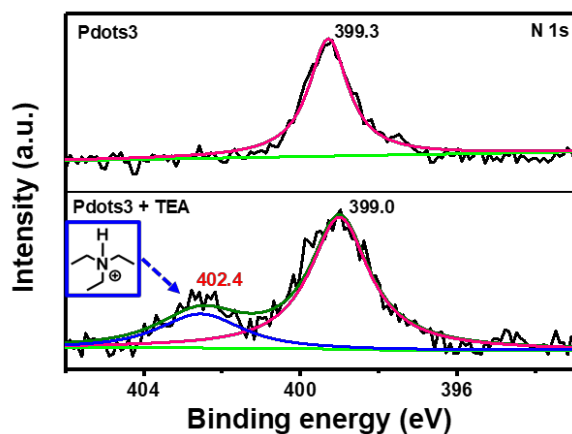


Figure S9. N 1s XPS spectra of **Pdots3** and the mixture of **Pdots3** and TEA.

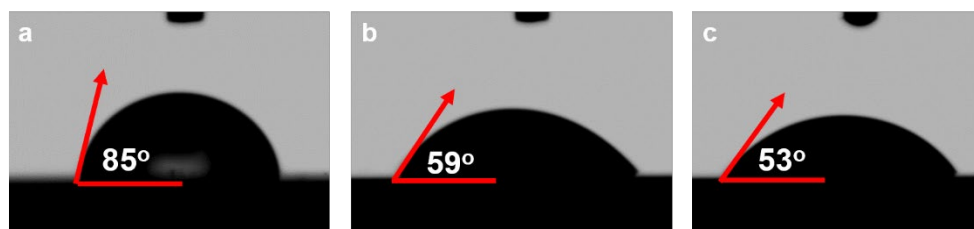


Figure S10. Contact angle of **Pdots** modified glass slide: (a) **Pdots1**, (b) **Pdots2**, and (c) **Pdots3**.

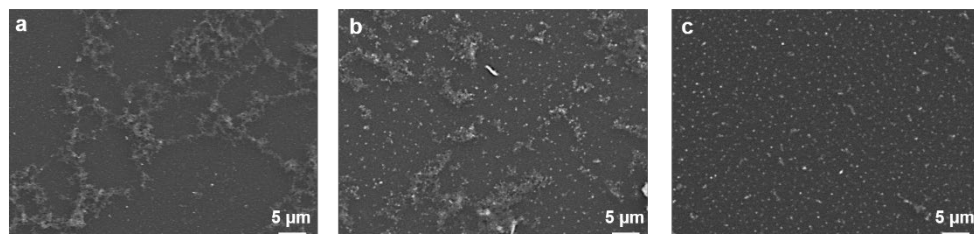


Figure S11. SEM images of these Pdots modified electrode: (a) **Pdots1**, (b) **Pdots2**, and (c) **Pdots3**.

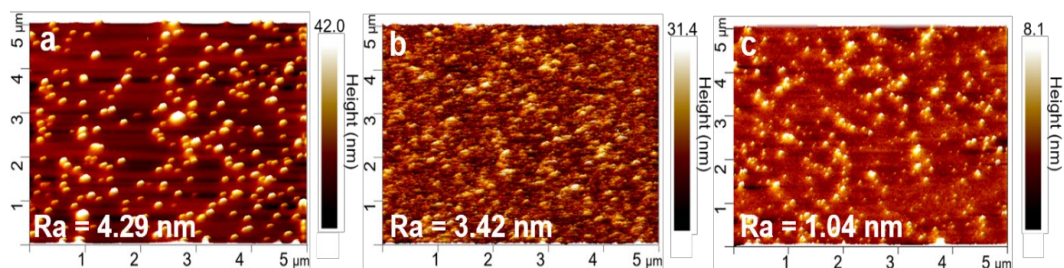


Figure S12. AFM images of these Pdots modified electrode: (a) **Pdots1**, (b) **Pdots2**, and (c) **Pdots3**. Ra means average roughness.

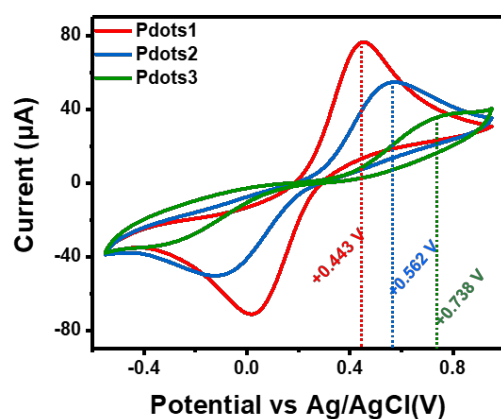


Figure S13. CV curves of 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl solution at Pdots/GCE. Scan rate: 0.1 V s^{-1} .

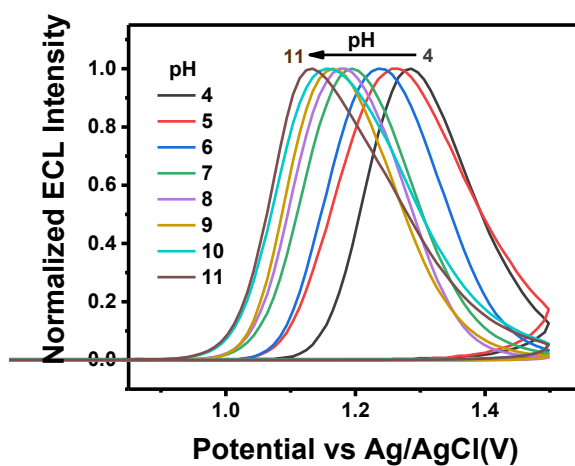


Figure S14. ECL curves Pdots3 modified GCE in 0.1 M PBS containing 25 mM TEA at different solution pH.

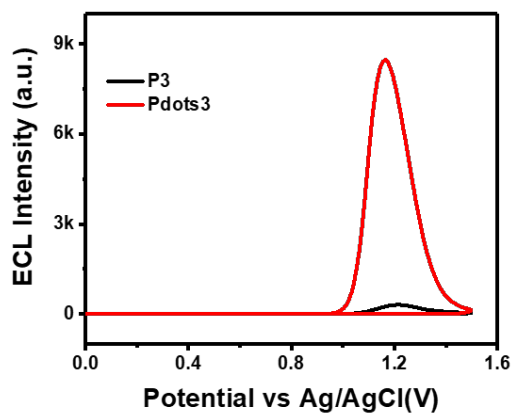


Figure S15. ECL curves of Pdots3/GCE and P3/GCE in 0.1 M PBS containing 25 mM TEA.

Table S2. Comparison of relative ECL Efficiencies for Different ECL Systems.

Material (environment)^a		Ø_{ECL} (%)	Ref.
TPE nanocrystals	TEA	1.35	3
ATPP Dots	K ₂ S ₂ O ₈	34	4
HPS Dots	K ₂ S ₂ O ₈	37.8	5
TPE-CMP	TPrA	1.72	6
CN-PPV Pdots	K ₂ S ₂ O ₈	11.2	7
	TPrA	1.84	
PFBT Pdots	TPrA	1.2	8
TPE-based Pdots	TPrA	0.5	9
	TPrA	23.1	10
	TPrA	11.8	11
	TEA	11	12
	Pdots2/Pdots3	TEA	44.3/54.7

^aATPP= 5-(4-aminophenyl)-10,15,20-triphenylporphyrin; HPS= 1,1,2,3,4,5-hexaphenylsilole; CMP = conjugated microporous polymer; CN-PPV = poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-(1-cyanovinylene-1,4-phenylene)]; PFBT = poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(1,4-benzo-{2,1',3}-thiadiazole)].

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