

## Supporting Information

### Near-Infrared II Aggregation-Induced Electrochemiluminescence of Organic Dots

Hang Gao,<sup>a</sup> Jia-Bao Lin,<sup>a</sup> Shu-Min Wang,<sup>a</sup> Qian-Qian Tao,<sup>a</sup> Ben-Zhong Tang,<sup>\*b</sup> Hong-Yuan Chen,<sup>a</sup> and Jing-Juan Xu<sup>\*a</sup>

<sup>a</sup>State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

<sup>b</sup>Shenzhen Institute of Molecular Aggregate Science and Engineering, School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen, Guangdong 518172, China

Corresponding Authors: xujj@nju.edu.cn (Jing-Juan Xu); tangbenz@cuhk.edu.cn (Ben-Zhong Tang)

## **Table of contents:**

### **1. Experimental Section**

**Materials and Reagents**

**Apparatus**

**Computational Methods**

**Preparation of Electrodes**

**Electrochemical and ECL Measurements**

**ECL Efficiency of ODs/GCE**

**Synthetic Procedure of TPE-BBTD**

**Preparation of ODs**

### **2. Supplementary Schemes and Figures**

**Schemes S1 and S2**

**Figures S1-S10**

### **3. Supplementary Table**

**Table S1**

# 1. Experimental Section

## Materials and Reagents.

4,4,5,5-Tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane was purchased from Bide Pharmatech Ltd. (Shanghai, China). Compound **1** was purchased from Zhengzhou Ruke Biological Co., Ltd. Tri-*n*-propylamine (TPrA), Triethylamine (TEA), H<sub>2</sub>O<sub>2</sub> and Tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) was bought from Shanghai J&K Scientific Ltd. Tetrahydrofuran (THF) was received from Sigma-Aldrich Co. Ltd (Shanghai, China). Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) and potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) were purchased from Shanghai Macklin Biochemical Co., Ltd. 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<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>. Ultrapure water obtained from a Millipore water purification system (≥18 MΩ 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.). Steady-state fluorescence spectra and transient decay spectra were measured in Edinburgh Instruments FLS980 spectrometer. The 400 MHz <sup>1</sup>H and 101 MHz <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 400 spectrometer (Bruker, German) in deuterated chloroform with tetramethylsilane (TMS) as an internal reference. High-resolution mass spectrometry (HRMS) spectrum was measured by Q-TOF (6530B, Agilent Technologies, Inc., Santa Clara, U.S.A.) mass spectrometer. Electrochemical experiments were performed on a CHI 660a electrochemical workstation (CH Instruments Inc., China). ECL measurements were carried out on an MPI-E multifunctional electrochemical and chemiluminescent analytical system (Xi'an Remex Analytical Instrument Co., Ltd. China). Ultrasonic synthesis experiments were conducted on the sonicator (Elmasonic P30H, Germany).

## Computational Methods.

All quantum calculations were carried out by using the Gaussian 16 program.<sup>1</sup> The molecular conformation and single-point energies of neutral molecules and cationic radicals were optimized at the level of M06-2X density functional combined with the 6-31+G(*d,p*) standard basis set.<sup>2</sup> In addition, the single point energy of all stationary points was further refined under the same method. The dispersion correction schemes by Grimme (denoted as D3) were used to account for the van der Waals interactions.<sup>3</sup> For the geometry optimization procedure, the structures were optimized until the forces were < 10<sup>-5</sup> hartree/bohr and the energy change was < 10<sup>-7</sup> hartree. The convergence criterion for the energy calculation during the self-consistent-field procedure was set for < 10<sup>-8</sup> hartree.

## Preparation of Electrodes.

Glassy carbon electrode (GCE, 3 mm in diameter) was polished successively with 0.3 and 0.05 μm alumina powder, 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 the next experiments.

## Electrochemical and ECL Measurements.

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

The glass carbon electrodes modified with ODs were prepared by dropping 10  $\mu\text{L}$  of 34  $\mu\text{M}$  corresponding ODs solution on an activated GCE and dried under 35  $^{\circ}\text{C}$ . The ECL curves were obtained by potential scanning from 0 to +1.40 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 800 V with a scan rate of 100  $\text{mV s}^{-1}$ . ECL spectra were recorded on a homemade ECL spectrum analyzer consisting of a Princeton Acton P-2300 monochromator equipped with a grating (grating density: 150  $\text{g mm}^{-1}$ ; blazed wavelength: 600 nm), a liquid  $\text{N}_2$  cooled Princeton PyLoN digital charge-coupled device (CCD) detector, and a CHI-660D electrochemical workstation.

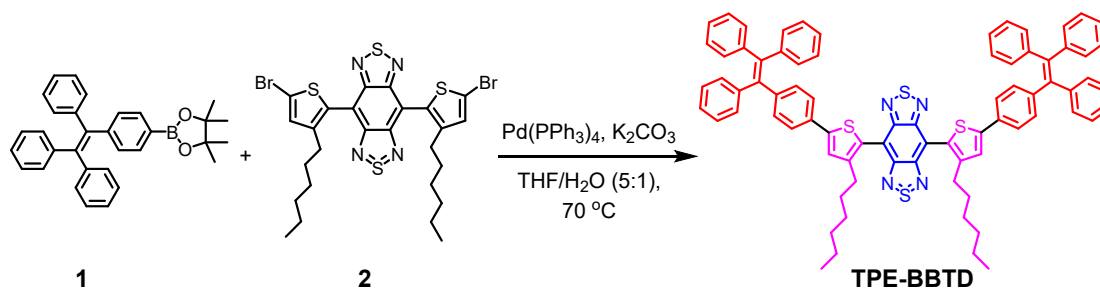
## ECL Efficiency of ODs/GCE.

The ECL efficiency of these ODs/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:<sup>4</sup>

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

Here,  $\Phi_{st}$  is the ECL efficiency of 33.7  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$ /(25 mM TEA in 0.1 M PBS with pH 7.4), where the concentration of  $\text{Ru}(\text{bpy})_3^{2+}$  is equal to TPE-BBTD ODs and the  $\Phi_{st}$  value is recognized as 100%;  $i$  is current value,  $I$  is ECL intensity, and  $x$  was the sample.

## Synthetic Procedure of TPE-BBTD.

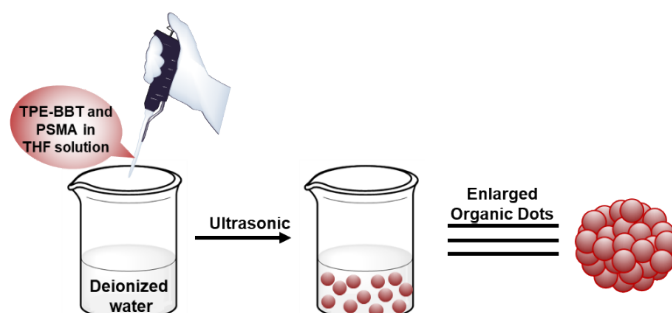


**Scheme S1.** Synthetic route of TPE-BBTD.

TPE-BBTD was synthesized with reference to previous reports using similar strategy.<sup>5</sup> A mixture of **1** (267.7 mg, 0.584 mmol), **2** (400.0 mg, 0.584 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (67.5 mg, 0.058 mmol),  $\text{K}_2\text{CO}_3$  (161.4 mg, 1.168 mmol), and THF/ $\text{H}_2\text{O}$  (5 mL: 1 mL) was stirred under argon at 70  $^{\circ}\text{C}$  for 12 h. After the mixture was cooled, the solvent was removed by evaporation under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, v/v, 20:1) to afford TPE-BBTD as deep-blue solid, yield:41%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.46 – 7.40 (m, 6H), 7.15 – 7.04 (m, 34H), 2.56 (t,  $J = 8.0$  Hz, 4H), 1.64 – 1.57 (m, 4H), 1.17 – 1.03 (m, 12H), 0.73 (t,  $J = 8.0$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 153.23, 145.64, 143.68, 143.66, 143.51, 143.46, 131.44, 131.37,

127.83, 127.74, 127.66, 125.02, 116.14, 31.50, 30.41, 30.25, 29.09, 22.46, 13.99. HRMS (ESI,  $m/z$ ):  $[M+Na]^+$  calculated, 1209.4068; found, 1209.3981.

### Preparation of ODs.



### Scheme S2. Preparation of TPE-BBTD organic dots.

These organic dots were prepared by nanoprecipitation method according to the literature with minor modification.<sup>6</sup> In brief, 1 mL of 337.0  $\mu$ M TPE-BBTD in THF and 80  $\mu$ L of 1.0 mg/mL PSMA solution were mixed, where PSMA was 20% w.t of TPE-BBT, then diluted to 10 mL, and ultrasonically degassed for 3 min under room temperature (Elmasonic P30H, Germany). Then, 2 mL of the above mixture was quickly added to 10 mL of water under sonication. After sonicating for 6 min, the THF solvent was removed by rotary evaporation under vacuum, and the mixture was concentrated to 2 mL, followed by filtration through a 0.22  $\mu$ m poly(ether sulfones) (PES) syringe filter (Millex-GP Filter, Millipore). The obtained solution of 33.7  $\mu$ M TPE-BBTD ODs was blue and transparent.

## 2. Supplementary Figures.

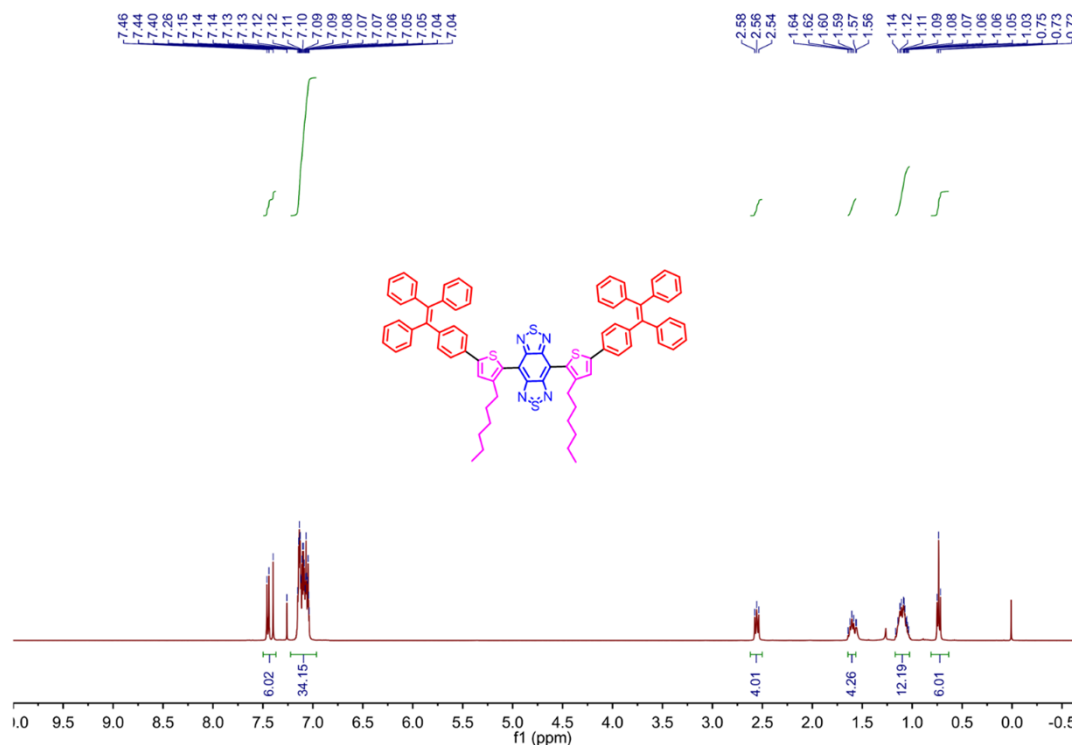


Fig. S1 <sup>1</sup>H NMR spectrum of TPE-BBTD.

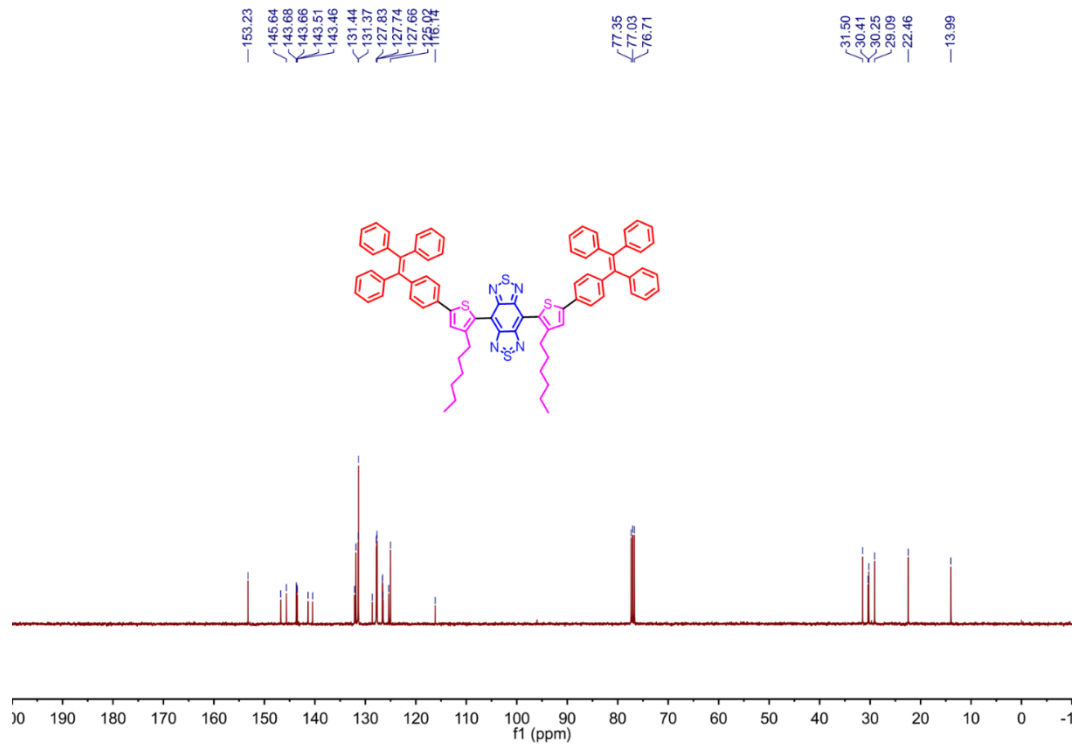


Fig. S2  $^{13}\text{C}$  NMR spectrum of TPE-BBTD.

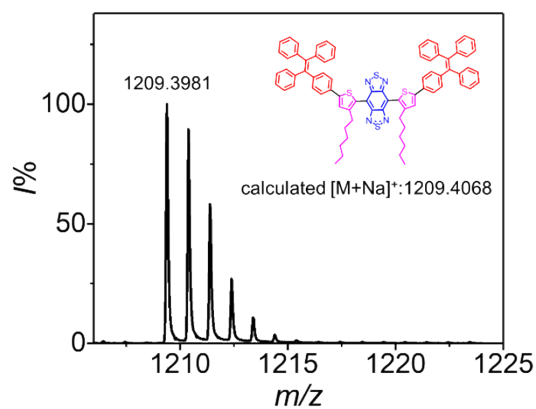


Fig. S3 HRMS spectrum of TPE-BBTD.

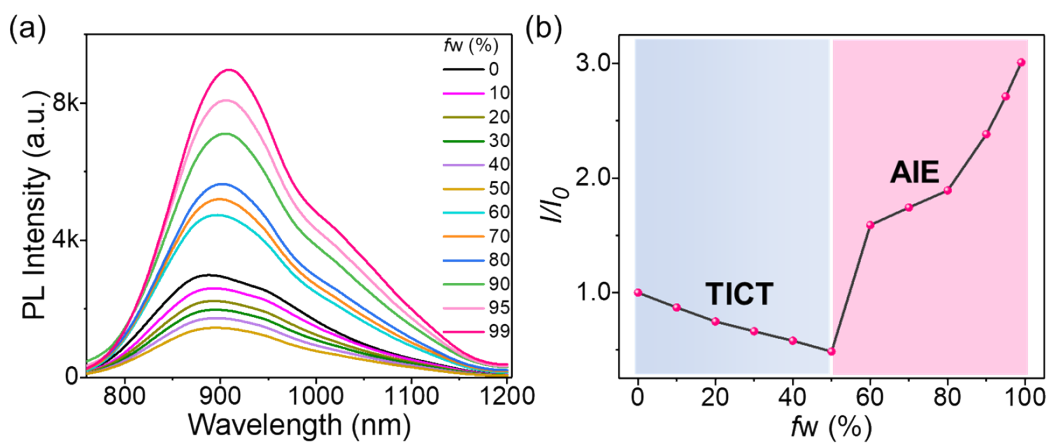
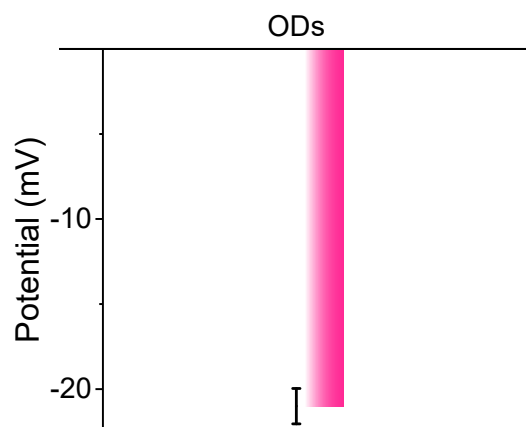
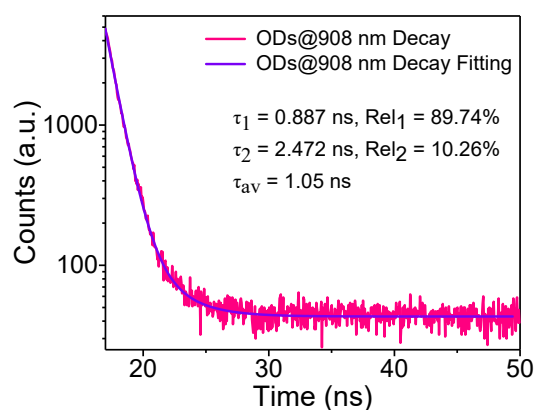


Fig. S4 (a) PL spectra of TPE-BBTD in THF/water mixtures with different water fractions ( $fw$ ). (b) Plots of  $I/I_0$  vs  $fw$  for TPE-BBTD, where  $I_0$  and  $I$  are the PL intensities in pure THF and THF/water mixtures, respectively.

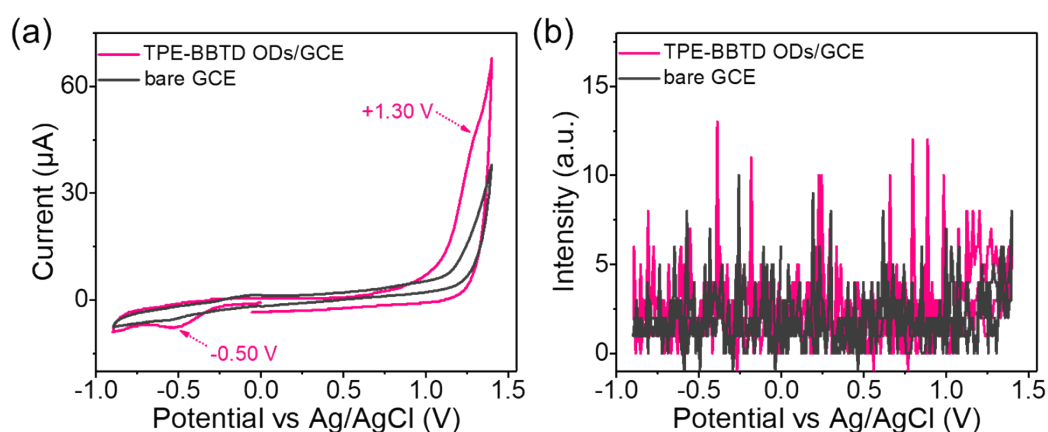


**Fig. S5** Zeta potential of TPE-BBTD ODs.

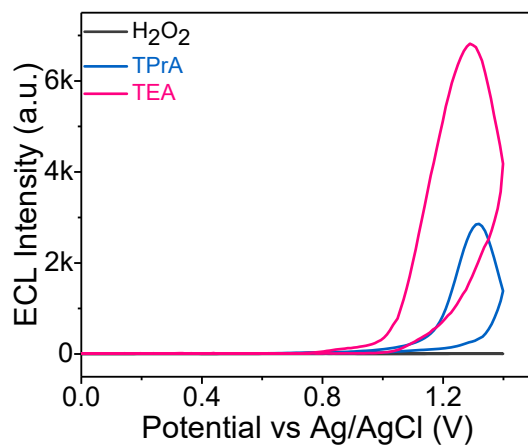


**Fig. S6** Transient PL spectrum of TPE-BBTD ODs collected at 908 nm.

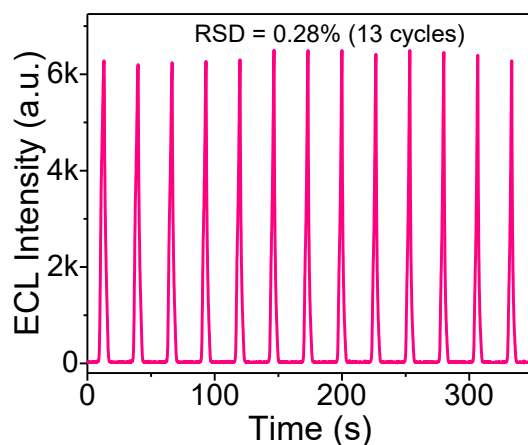
The decay curve of TPE-BBTD ODs is fitted by double-exponential function, and the  $\tau_{\text{aver}}$  is calculated according to following equation:  $\tau_{\text{aver}} = \tau_1 \times \text{Rel}_1 + \tau_2 \times \text{Rel}_2$ , where  $\text{Rel}_1$  and  $\text{Rel}_2$  are component ratio for  $\tau_1$  and  $\tau_2$ , respectively. As shown in Figure S6, the lifetime of  $\tau_1$  as well as  $\tau_2$ , and its relative ratio ( $\text{Rel}_1$  and  $\text{Rel}_2$ ) are calculated to be 0.887 ns (89.74%) and 2.472 ns (10.26%), respectively. Eventually, the average lifetime ( $\tau_{\text{aver}}$ ) of TPE-BBTD ODs with emission at 908 nm is calculated to be 1.05 ns.



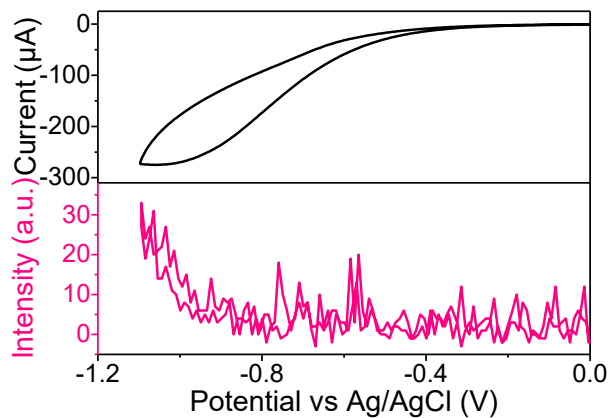
**Fig. S7** CV (a) and corresponding ECL-potential curve (b) of TPE-BBTD ODs/GCE and bare GCE in 0.1 M PBS without co-reactant; Potential window: -0.90 V - +1.40 V.



**Fig. S8** ECL-potential curves of TPE-BBTD ODs/GCE in 0.1 M PBS with different co-reactants (25 mM).



**Fig. S9** ECL signals of TPE-BBTD ODs/GCE under continuous potential scan between 0 and +1.40 V.



**Fig. S10** CV and corresponding ECL-potential curve of TPE-BBTD ODs/GCE in 0.1 M PBS with 25 mM K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as co-reactant; potential window: 0 – -1.10 V.



### 3. Supplementary Table.

**Table S1.** Calculated relative ECL efficiency.

System	$\int_a^b I dv$	$\int_a^b i dv$	$\Phi$
Ru(bpy) <sub>3</sub> <sup>2+</sup> /TEA	1.843×10 <sup>5</sup>	0.5554	100%
TPE-BBTD ODs/TEA	1.692×10 <sup>3</sup>	0.7815	0.65%

#### References:

1. Frisch MJ, T. G., Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Peralta Jr JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam NJ, Klene M, Knox JE, Cross JB., Bakken V, Adamo C, Jaramillo J, Gomperts RE, Stratmann O, Yazyev AJ, Austin R, Cammi C, Pomelli JW, Ochterski R, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. , Gaussian, Inc, Wallingford CT,. *Gaussian 09, Revision A.02* **2009**.
2. A. McLean and G. Chandler, Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z= 11–18. *J. Chem. Phys.* **1980**, 72, 5639-5648.
3. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, A Consistent and Accurate *ab initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, 132, 154104.
4. M. Hesari, M. S. Workentin and Z. Ding, Highly Efficient Electrogenerated Chemiluminescence of Au<sub>38</sub> Nanoclusters. *ACS Nano* **2014**, 8, 8543–8553.
5. H. Shen, F. Sun, X. Zhu, J. Zhang, X. Ou, J. Zhang, C. Xu, H. H. Y. Sung, I. D. Williams, S. Chen, R. T. K. Kwok, J. W. Y. Lam, J. Sun, F. Zhang and B. Z. Tang, *J. Am. Chem. Soc.* **2022**, 144, 15391-15402.
6. H. Gao, S. Y. Shi, S. M. Wang, Q. Q. Tao, H. L. Ma, J. Hu, H. Y. Chen and J. J. Xu, *Aggregate*, **2023**, e394.