Electronic Supplementary Information

Near-Infrared Aggregation-Induced Enhanced Electrochemiluminescent Tetraphenylethylene Nanocrystals: A New Generation of ECL emitter

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Reagents and Materials. Tetraphenylethylene (TPE) was purchased from TCI Development Co., Ltd. (Shanghai, China). Triethylamine (TEA) was received from Kelong Chemical Inc. (Chengdu, China). Bovine serum albumin (BSA, 96-99%) was provided by Sigma-Aldrich Co. (St. Louis, MO, USA). The deionized water was purified by water purification system with an electrical resistance of 18.2 $M\Omega\cdot cm^{-1}$. The phosphate buffered solutions (PBS), pH 7.4 (0.1 M Na_2HPO_4, 0.1 M KH_2PO_4 and 0.1 M KCl, using 0.1 M HCl or 0.1 M NaOH solution to adjust pH) were used in this work.

Apparatus. The scanning electron microscope (SEM) images of the materials were characterized by S-4800 scanning electron microscopy (Hitachi, Tokyo, Japan). The crystal structure was carried out by X-ray diffraction (XRD) (Bruker, D8-Advance X-ray diffractometer, Cu Kα radiation, Germany). UV-vis absorption spectra were characterized by a UV-2450 UV-vis spectrophotometer (Shimadzu, Tokyo, Japan). Fluorescence spectra were characterized by FL-5700 spectrophotometer (Hitachi, Tokyo, Japan). The size distribution of TPE NCs was characterized by dynamic light scattering (DLS) on a Nano-ZS90 particle size analyzer (Malvern, England). The electrochemical measurements were performed on a CHI 660C electrochemistry workstation (Shanghai CH Instruments, China). ECL emission spectra were measured on a Newton EMCCD spectroscopy detector (Andor Co., England) combined with an electrochemical workstation based on a conventional three-electrode system (a bare or modified GCE (Φ=4 mm) as the working electrode, Ag/AgCl (saturated KCl) as the reference electrode, and a Pt wire as counter electrode).

Fabrication of Modified GCE. Before the modification, the glassy carbon electrode (GCE, Φ = 4 mm) was polished and rinsed as the previous method.[1] Then, the bare GCE was coated with 5 μL of TPE NCs and dried at room temperature to form a thin film.

Measurement Procedure. The ECL response of the proposed modified GCE was measured at the potential from 0 to 1.6 V in 2 mL of detection solution (0.1 M PBS (pH 7.4) containing 18 mM TEA with the voltage of the PMT high-voltage at 800 V.

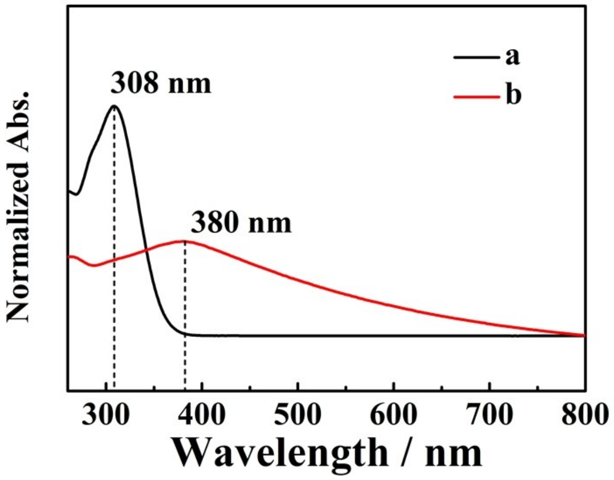

Fig. S1 UV-vis absorption spectra of (a) TPE dissolved in THF, (b) TPE NCs.

Electroluminescence (EL) emission peak of TPE film. The electroluminescence (EL) emission peak of TPE film was investigated in an OLED device with the configuration of ITO/PEDOT/TCTA (60 nm) /TPE (~120 nm) /BCP (80 nm) /LIF (10 nm)/Al (100 nm). As shown in Fig. S2, the black line is the raw data. After fitting, the EL emission peak of TPE located at 442 nm (skyey line, basically consistent with the PL spectra) and 492 nm (blue line, the exciplex emission).

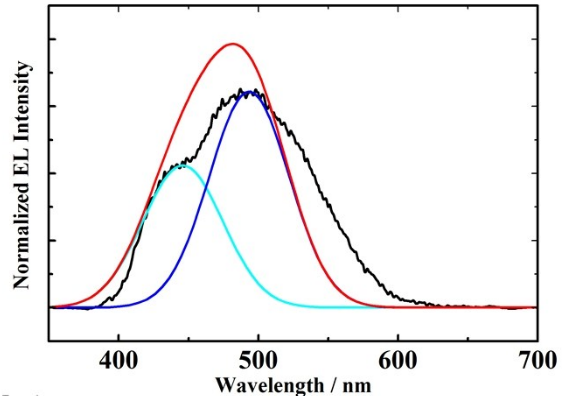

Fig. S2 The electroluminescence (EL) spectra of TPE film.

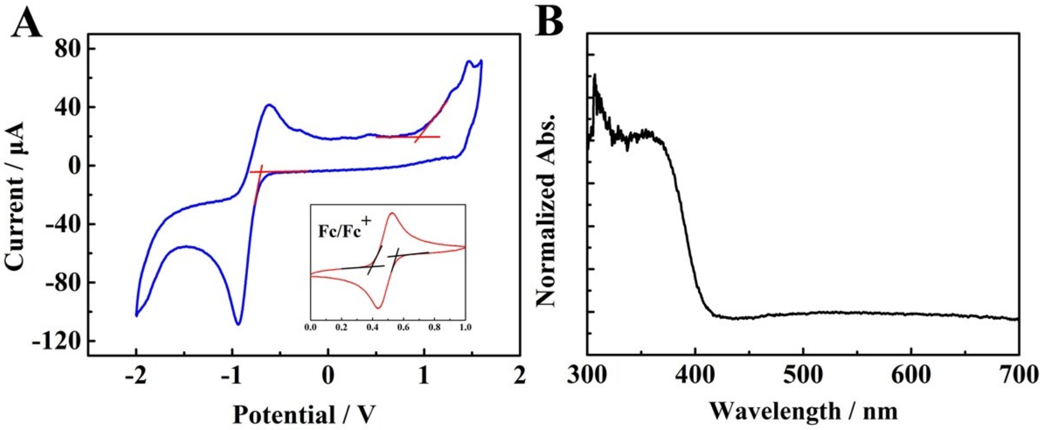

Fig. S3 (A) CV curves (blue line) of TPE NCs, and the inset of (A): the CV curves (red line) of 1 mM ferrocene in 0.1 M Bu_4NBF_4 acetonitrile solution (potential was versus Ag/Ag^+). The energy levels were calculated using the following equations: $E_{VB} = -(E_{onset}{}^{Ox} - E_{Fc/Fc+} + 4.8)$ eV, $E_{CB} = -(E_{onset}{}^{Red} - E_{Fc^+/Fc} + 4.8)$ eV. Ag/Ag^+ vs NHE is 0.197 V, and the energy level of NHE is -4.5 eV in the vacuum. (B) UV-vis diffuse reflectance spectra (DRS) of TPE NCs. The band gap was calculated using the following equations: Eg (eV)=hc / λ= 1240 / 408 = 3.04 eV.

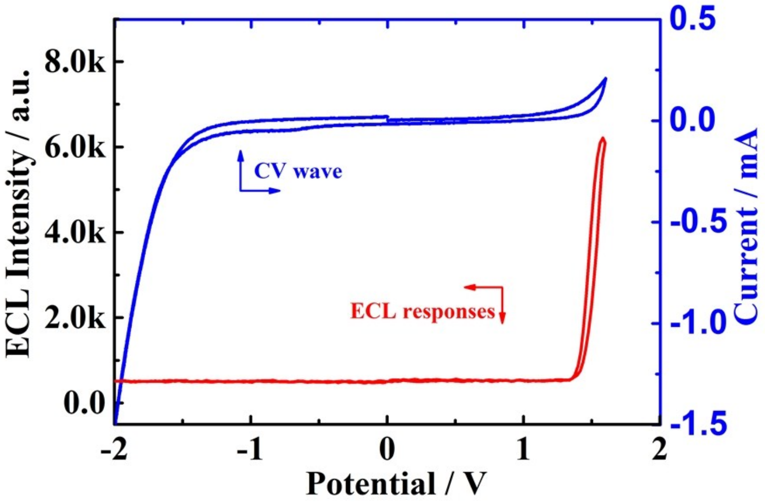

Fig. S4 ECL-potential profiles (red line) and its corresponding CV curves (blue line) of the TPE NCs in 0.1 M PBS (pH 7.4).

ECL efficiency of the TPE NCs. The relative ECL efficiency of TPE NCs was calculated by comparing the ratio of the integrated ECL intensity of the TPE NCs in reference to that of $[Ru(bpy)_3]^{2+}$/TPA system as the following equation:

$$Q = \frac{\varnothing_x}{\varnothing_0} = \left(\frac{\int_0^t I \, dt}{\int_0^t i \, dt}\right)_x \Bigg/ \left(\frac{\int_0^t I \, dt}{\int_0^t i \, dt}\right)_0$$

Here, $\varnothing_x$ is the ECL quantum efficiency of TPE NCs, $\varnothing_0$ is the ECL quantum efficiency of $[Ru(bpy)_3]^{2+}$ (1 mM). Where “I” is ECL intensity, “i” is current value.

REFERENCES

(1) W. B. Liang, M. Z. Yang, Y. Zhuo, Y. N. Zheng, Y. Q. Chai, R. Yuan, Chem. Sci. 2016, 7, 7094-7100.