Supporting Information

Mechano-chromic and mechano-enhanced electrogenerated

chemiluminescence of tetra[4-(4-cyanophenyl)phenyl]ethene

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1. Experimental Procedures

1.1 Apparatus

A MPI-E ECL detector (Xi'an Remax Analysis Instruments Co. Ltd., China) and CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) were used for ECL and electrochemical measurements. ECL spectra were recorded on Princeton Instruments PyLon 100BX CCD camera coupled with an Acton SP2300 monochromator (Trenton, USA). The ECL images were captured using an Olympus IX 73 inverted microscopy (Olympus, Japan) coupled with Prime 95B complementary metal-oxide-semiconductor (Photometrics, USA). The ultraviolet-visible absorption spectra, fluorescence (FL) spectra, FL quantum yields (Φ) and lifetime (τ) were recorded on Fluorolog-3 fluorescence spectrophotometer (Horiba JY, USA). A time-correlated single photon counting (TCSPC) equipment was used to collect the lifetime data using a 401-nm laser as the excitation source (pulse duration <200 ps), and lifetimes were calculated using decay analysis software (DAS6) according to triexponential decay function. Absolute fluorescence quantum yields were determined with a calibrated integrating sphere system (errors <3%) under air conditions. The morphology of crystal and ground TCPPE powder were obtained from SU8220 scanning electron microscopy (HITACHI, Japan). The powder X-ray diffraction spectra were recorded on D8 Quest single-crystal X-ray Diffractometer (Brooker Co. Ltd., Germany). The thermal analysis data were recorded on were recorded on a SETARAM (C80) instrument (Setaram Co. Ltd., France).

1.2 Preparation of samples

Ground TCPPE powder was obtained by grinding 20 mg crystal TCPPE powder with a mortar and pestle. The grinding time was controlled by the observation of the FL emission color of TCPPE powders under UV lamp illumination. 1.0 mg crystal TCPPE powder (or 1.0 mg ground TCPPE powder) was dispersed into 1 mL water with ultrasonic to get 1.0 mg/mL TCPPE powder dispersion.

1.3 ECL measurements and ECL imaging

A traditional three-electrode configuration was employed in the ECL experiment, in which a glassy carbon electrode (GCE, 2 mm in diameter, unless stated otherwise) functioned as the working electrode, an Ag/AgCl (saturated KCl) electrode functioned as the reference electrode and a Pt wire functioned as the counter electrode.

For ECL measurement of crystal, ground, annealed and fumed TCPPE powder, $10 \ \mu L$ of $1.0 \ mg/mL$ crystal, ground, annealed and fumed TCPPE powder dispersion was dropped onto the surface of GCE and dried at room temperature for measurement.

For simultaneous ECL imaging of both crystal and ground TCPPE powder modified GCE, the fabricated process is following. Firstly, a thin glass slice was pasted on the surface of GCE (3 mm in diameter) vertically to make it into two equal parts. Then 5 μ L of 1.0 mg/mL crystal TCPPE powder suspension was dropped onto upper half part of GCE and 5 μ L of 1.0 mg/mL ground TCPPE powder suspension was dropped onto bottom half part of GCE. When the modified GCE dried as a thin film, the thin glass slice was taken out and a sticker of hollow "3" was pasted on the surface of modified GCE. So the upper half part of "3" was filled with crystal TCPPE powder and the bottom half part of "3" was filled with ground TCPPE powder. Multi-potential steps technique was applied between 0 V and -1.75 V in 0.1 M PBS (pH 7.4) containing 50 mM K₂S₂O₈ and the exposure time is 3 s.

2. Supplementary Figures



S1 FL data of crystal, ground, annealed and fumed TCPPE powder

Fig. S1 FL spectra of crystal, ground, annealed and fumed TCPPE powder.



Fig. S2 Switching of (A) FL maximum wavelength and (B) FL intensity of TCPPE powder by repeated grinding-annealing process and grinding-fuming process.



Fig. S3 FL stability of (A) crystal and (B) ground TCPPE powder in air at room temperature.



Fig. S4 Lifetime decay curve of crystal, ground, annealed and fumed TCPPE powder in air at room temperature.

	Crystal	Ground	Annealed	Fumed
	TCPPE powder	TCPPE powder	TCPPE powder	TCPPE powder
λ _{em} (nm, FL)	480	530	477	480
λ_{em} (nm, ECL)	478	528	478	478
$\Phi_{ m FL}$	73.4%	89.5%	72.9%	73.2%
$\Phi_{ m ECL}$	12.1%	75.5%	12.0%	12.4%
Lifetime (ns)	0.9 (0.3, 17.79%;	2.3 (0.3, 1.77%;	0.9 (0.3, 15.90%;	1.1 (0.6, 20.69%;
	1.1, 53.02%;	2.0, 52.53%;	1.0, 53.02%;	1.2, 56.53%;
	2.7, 29.13%)	4.5, 45.70%)	3.0, 31.07%	3.3, 22.77%)



S2 Electrochemistry and ECL data of crystal and ground TCPPE powder

Fig. S5 (A) Cyclic voltammograms for bare GCE, crystal and ground TCPPE powder modified GCE in 0.1 M PBS (pH 7.4) containing 50 mM K₂S₂O₈. Scan rate: 0.1 V/s. (B) ECL intensity vs. potential profiles for bare GCE, crystal and ground TCPPE powder modified GCE in 0.1 M PBS (pH 7.4) containing 50 mM K₂S₂O₈. PMT= -500 V.



Fig. S6 ECL stability of six (A) crystal and (B) ground TCPPE powder modified GCE in 0.1 M PBS (pH 7.4) containing 50 mM K₂S₂O₈. PMT= -500 V. ECL peak intensiy was recorded at about -1.75 V using cyclic voltammetry technique.



Fig. S7 ECL intensity vs. time profiles of one (A) crystal and (B) ground TCPPE powder modified GCE in 0.1 M PBS (pH 7.4) containing 50 mM K₂S₂O₈. PMT= -500 V. Multi-potential steps technique was applied, low potential: -1.75 V; high potential: 0 V; pulse time: 0.3 s.



S3 Gray value for crystal and ground TCPPE powder modified GCE

Fig. S8 Gray value of FL and ECL images for crystal and ground TCPPE powder modified GCE.

S4 Crystal data and structure refinement for TCPPE

CCDC number	2089575		
Empirical formula	C ₆₁ H ₄₇ Cl ₃ N ₆ O ₂		
Formula weight	1002.39		
Temperature/K	152.0		
Crystal system, space group	Monoclinic, P21/n		
a/Å	20.0178 (11)		
b/Å	8.9301(5)		
c/Å	30.0676 (17)		
a/°	90		
β/°	102.188 (3)		
$\gamma/^{\circ}$	90		
Volume/Å ³	5253.8 (5)		
Z	4		
$ ho_{cale} g/cm^3$	1.267		
μ/mm^{-1}	1.970		
F(000)	2088.0		
Radiation	$CuK\alpha$ ($\lambda = 1.54178$)		
2θ range for data collection/°	4.868 to 136.71		
Index ranges $-24 \le h \le 24, -10 \le k \le 10, -36 \le l \le 34$			
Reflections collected	flections collected 75138		
Independent reflections	9623 [$R_{int} = 0.0675, R_{sigma} = 0.0377$]		
Data/restraints/parameters	9623/294/726		
Goodness-of-fit on F ²	1.647		
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.1193, wR_2 = 0.3483$		
Final R indexes [all data]	$R_1 = 0.1343, wR_2 = 0.3731$		
Largest diff. peak/hole / e Å-3	1.24/-1.48		

Table S2 Crystal data and structure refinement for TCPPE