Supporting Information

Anodic, Cathodic and Annihilation Electrochemiluminescence Emissions from Hydrophilic Conjugated Polymer Dots in Aqueous Medium

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§1. Core-shell structure of Triton X-100 modified CP-dots

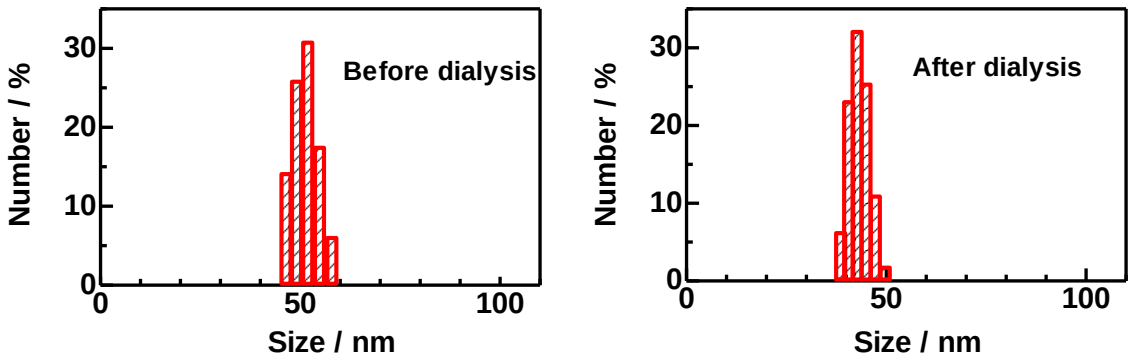

Figure S1. The size distribution of MEH-PPV CP-dots before dialysis and after dialysis for 64 hours.

The encapsulation efficiency of Triton X-100 on the CP-dots was approximately estimated as follow. First, the free Triton-X 100 was removed by being dialyzed with the 10000 Da MWCO membrane. The dialysis process was monitored by investigating the decrease in the characteristic UV absorption of Triton X-100 peak at 275 nm (Figure S2). The complete removal of free Triton X-100 from a 2 mL mixed solution containing 3 μg/mL MEH-PPV polymer (i.e. total 6 μg MEH-PPV) was finished within 64 h. The immobilized Triton X-100 on the surfaces of CP-dots can be calculated by the small UV absorption at 275 nm (left inset of Figure S2) with help of calibration curve (right inset of Figure S2). The total amount of Triton-X 100 capped on the surface of CP-dots was calculated to be 6.12 μg. For approximately calculation, we assumed that the density of the core (twisted MEH-PPV strain) was the same as the shell (compact Triton X-100 layer), i.e. 1 g/cm^3. Then each Triton-X-100-capped CP-dot after dialysis (with average diameter of 44 nm) had a core of 35 nm diameter (c.a. 160 chains of MEH-PPV polymer with average MW of 70000-100000), and a shell thickness of 4.5 nm (approximately one-chain length of Triton X-100, and c.a. 21000 molecules of Triton X-100), as shown in Figure S3. Based on this estimation, the core of Triton-X-100-capped CP-dot before ultrafiltration (with average diameter of 50 nm) had a core of 35 nm diameter and a shell thickness of 7.5 nm (approximately two-chain length of Triton X-100). These results suggest that the hydrophilic CP-dots might be coated respectively with two and one molecule layer of Triton X-100 before and after dialysis (Figure S3). The encapsulation efficiency of MEH-PPV core by Trion X-100 was estimated to be 5.5 molecules /nm^2 after dialysis.

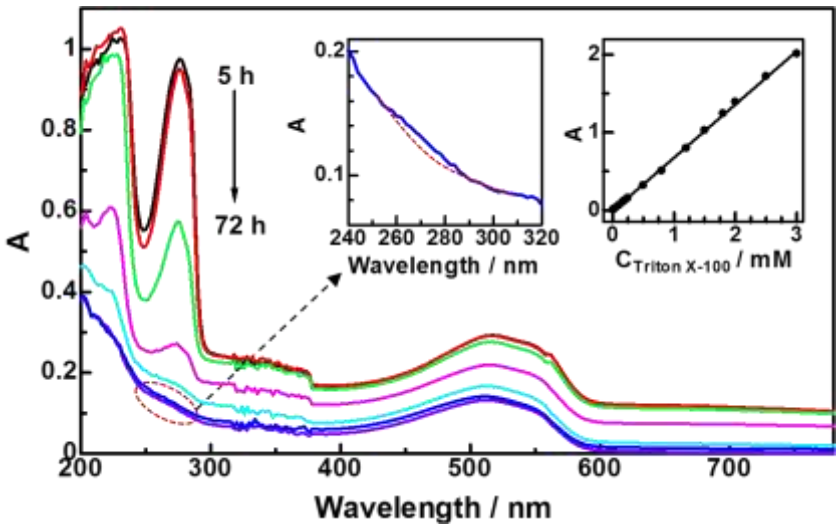

Figure S2. UV-Vis absorption spectra of Triton X-100 functionalized MEH-PPV CP-dots mixed solution dialyzed against pure water after 5 h, 8 h, 20 h, 32 h, 48 h, 64 h and 72 h. Inset: Amplified absorption curve in the range from 240 nm to 320 nm for that sample dialyzing 72 h (left); The calibration curve for Triton X-100 (right). The concentration of Triton X-100 was calculated by the absorption peak at 275 nm subtracted by the absorption background (red dashed line in left inset).

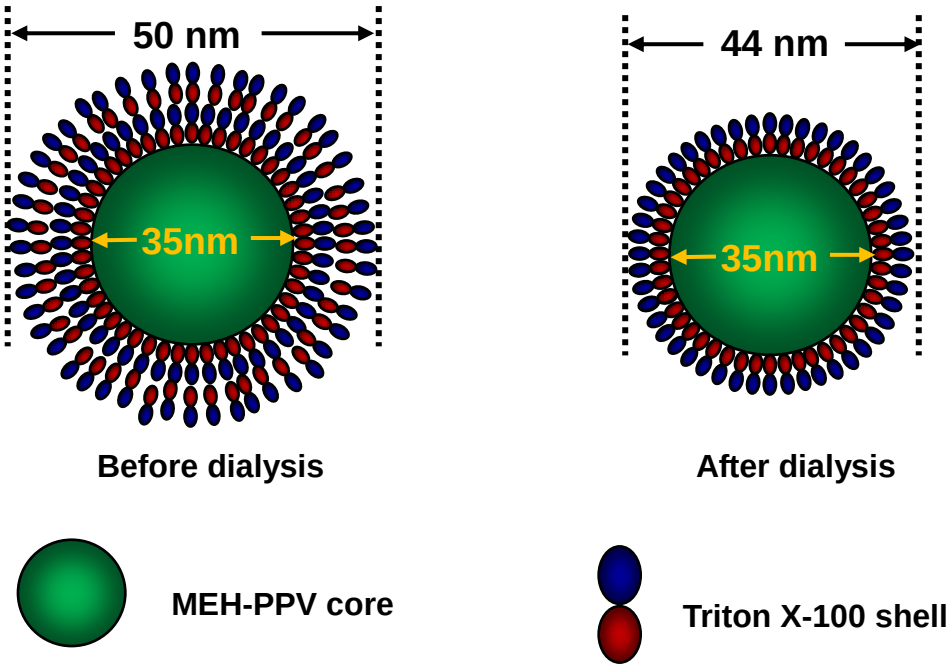

Figure S3. Schematic core-shell structures and sizes of Triton X-100 functionalized CP-dots before and after dialysis.

§2. Value comparison of the function: f(x)=1-exp(-x) at x_1=k$_1$τ and x_2=k$_2$τ

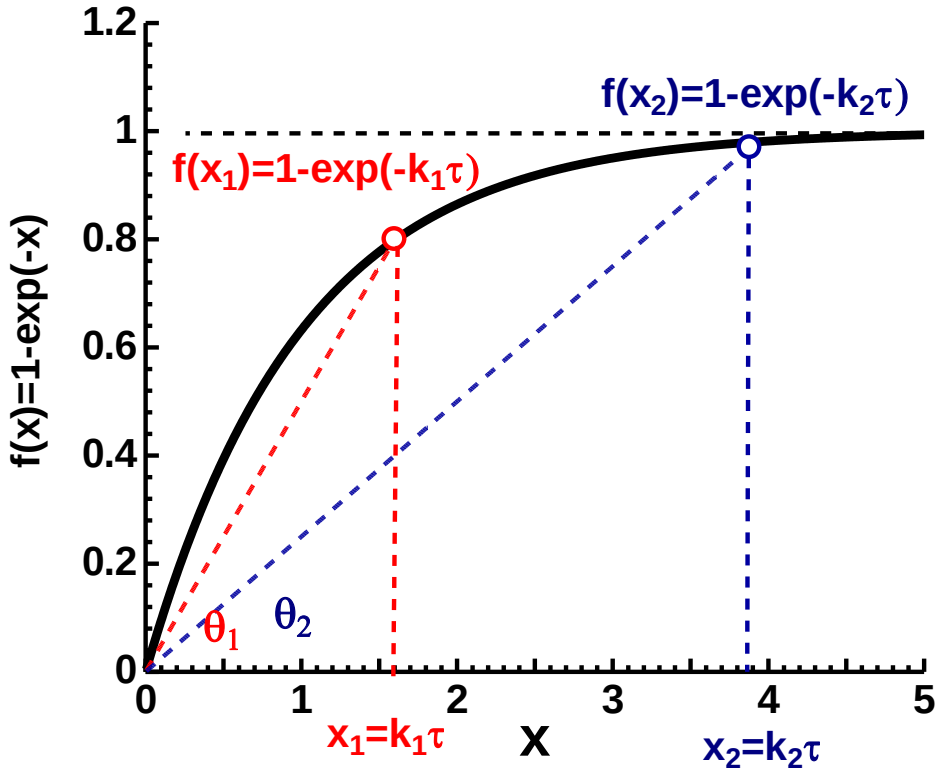

Figure S4. The curve of the function: f(x)=1-exp(-x) and the values at x_1=k$_1$τ and x_2=k$_2$τ

The black curve in Figure S4 is the plot of the function: f(x)=1-exp(-x) vs x.

When 0<k$_1$ < k$_2$, and τ >0, then x_1=k$_1$τ < x_2=k$_2$τ). Apparently, θ$_1$ >θ$_2$,

Then $tg\theta_1 = \dfrac{1-\exp(-k_1\tau)}{k_1\tau} > tg\theta_2 = \dfrac{1-\exp(-k_2\tau)}{k_2\tau}$

Then $\dfrac{1-\exp(-k_1\tau)}{1-\exp(-k_2\tau)} > \dfrac{k_1}{k_2}$

Then $R = \dfrac{k_2}{k_1} \bullet \dfrac{1-\exp(-k_1\tau)}{1-\exp(-k_2\tau)} > \dfrac{k_2}{k_1} \bullet \dfrac{k_1}{k_2} = 1 \qquad (when \quad k_2 > k_1)$

§3. Stability of Triton X-100-capped CP-dots film at the GC electrode surface

In order to investigate the stability of Trion X-100-capped CP-dots film at the GC electrode surface, We recorded the anodic ECL intensity after the modified electrode was immersed in test solution containing 5 mM TPrA and 0.1 M PBS, and the results were shown in Figure S4. Since cathodic ECL and annihilation ECL of Trion X-100-capped CP-dots basically have similar variation trend as anodic ECL, only the anodic ECL was investigated for stability.

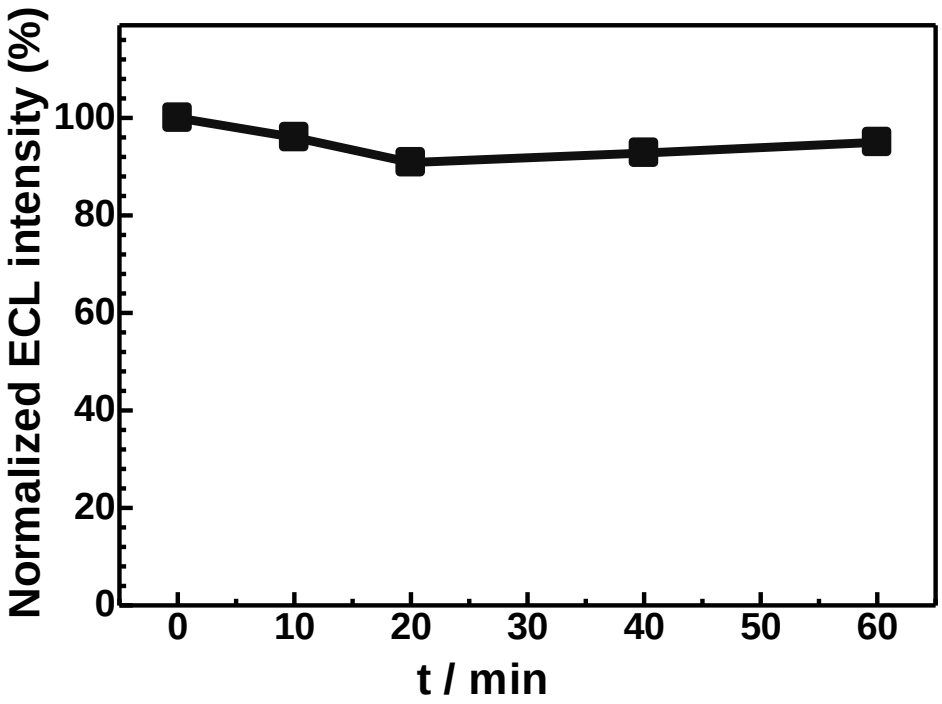

Figure S5. Relative ECL intensity of anodic ECL emission of Triton X-100-capped CP-dots film at the GC electrode surface recorded after the modified electrode was immersed into the test solution (pH 9 PBS containing 5 mM TPrA) for different time.

§4. Effect of surfactant type on ECL of CP-dots

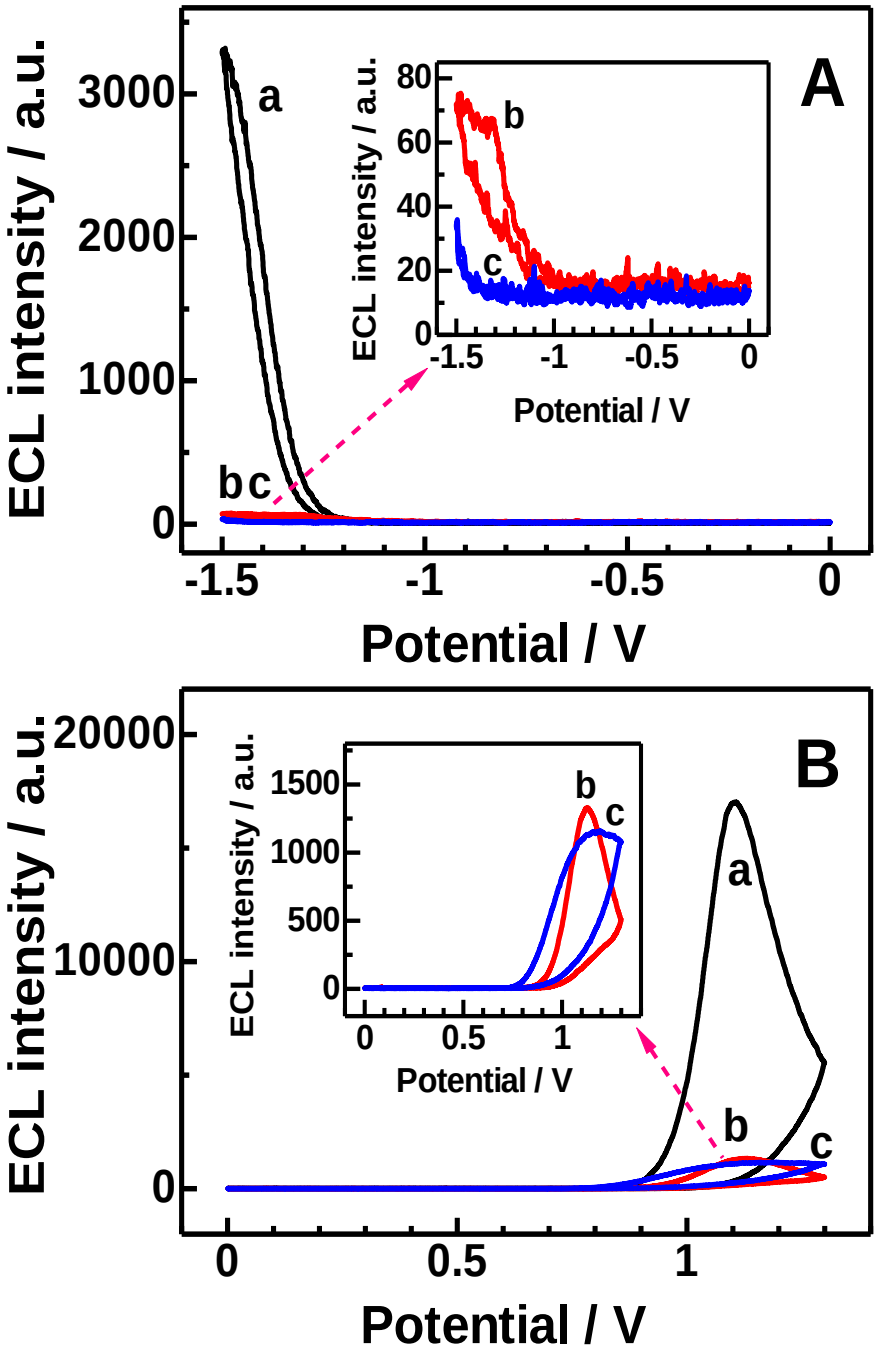

Figure S6. (A) Cathodic ECL responses obtained at GC electrodes for systems containing 5 mM $K_2S_2O_8$ and CP-dots capped by (a) Triton X-100; (b) Pluronic F-127; (c) PSMA. (B) Anodic ECL responses obtained for system containing 5 mM TPrA and CP-dots which capped by (a) Triton X-100;(b) F-127; (c) PSMA. Inset: amplified curves b and c.

§5. Effect of oxygen on ECL of CP-dots

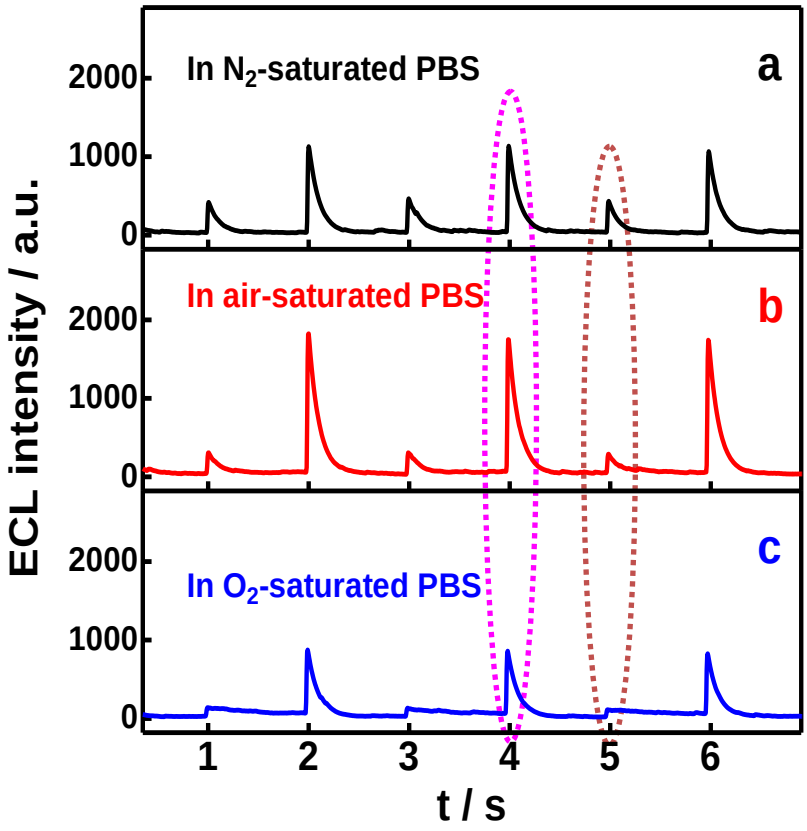

Figure S7. Annihilation ECL emission obtained for the CP-dots by stepping (1 Hz) potential between + 0.7 and −1.4 V at GC electrodes in aqueous solutions (0.1 M phosphate) saturated with nitrogen (a), air (b), and oxygen (c). The higher ECL peaks (cycled by pink dash line) and the lower ECL peaks (cycled by brown dash lines) were cathodic and anodic annihilation ECL processes, respectively.

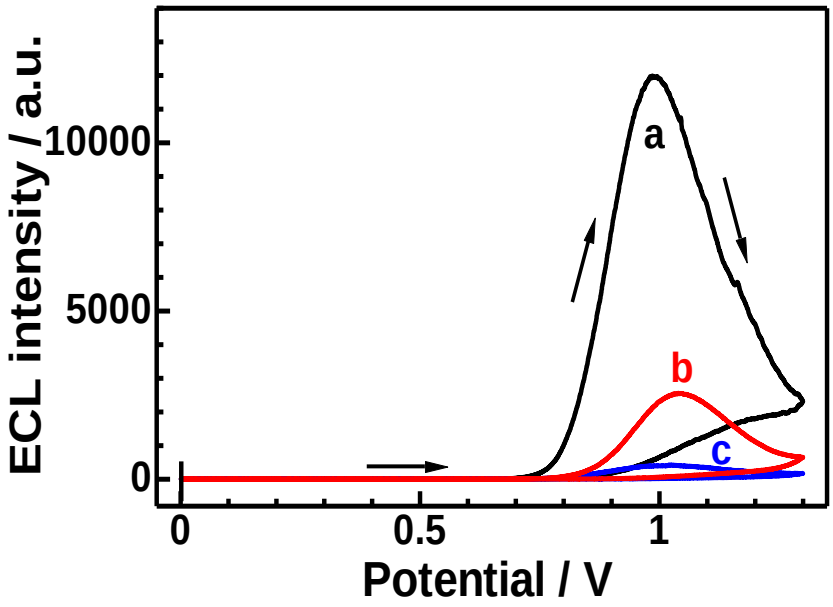

Figure S8. Anodic ECL responses of the CP-dots—$K_2S_2O_8$ system at GC electrodes in aqueous solutions (0.1 M phosphate, pH 9.0) saturated with nitrogen (a), air (b), and oxygen (c). The concentration of $K_2S_2O_8$ was 5 mM. The scan rate was 0.1 V/s

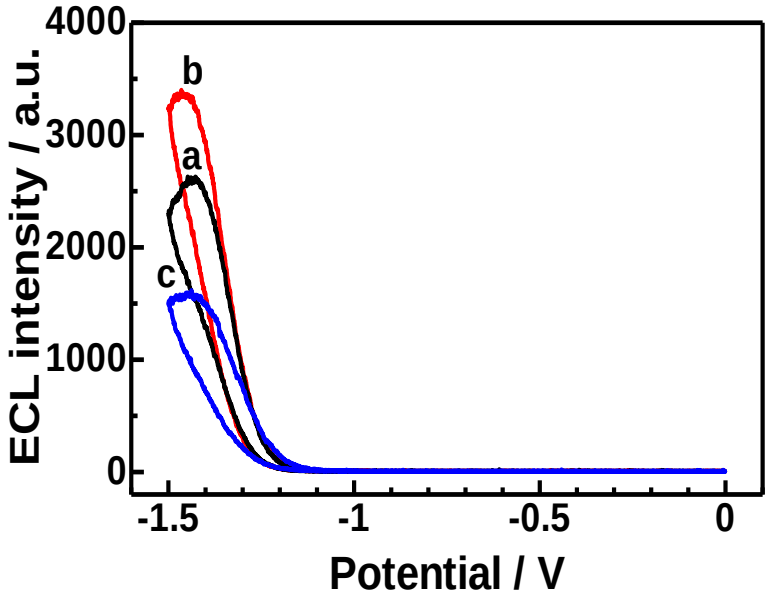

Figure S9. Cathodic ECL responses of the CP-dots—TPrA system at GC electrodes in aqueous solutions (0.1 M phosphate, pH 9.0) saturated with nitrogen (a), air (b), and oxygen (c). The concentration of TPrA was 5 mM. The scan rate was 0.1 V/s