Supporting information

The Scaffold of Thermally Activated Delayed Fluorescence Polymer Dots Towards Aqueous Electrochemiluminescence and Biosensing Application

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1. Supplementary Figures

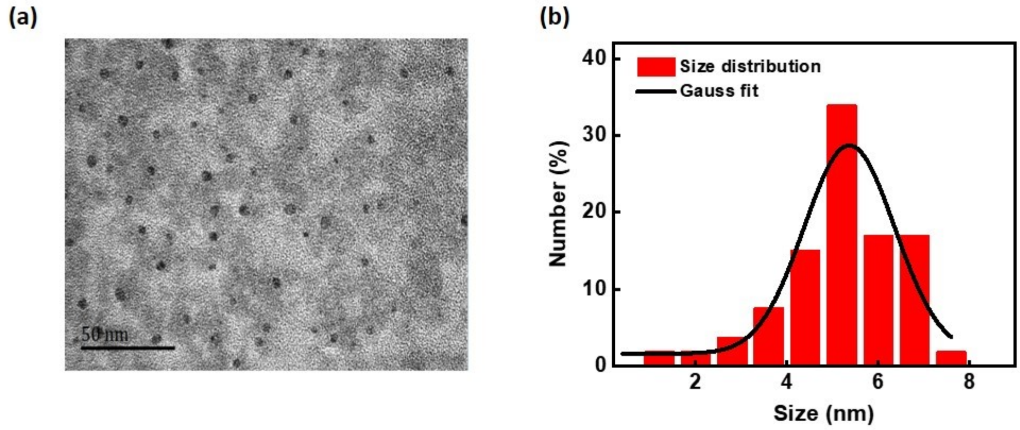

Figure S1. TEM image (bar scale: 50 nm.) and the size distribution of PAPTC TADF Pdots.

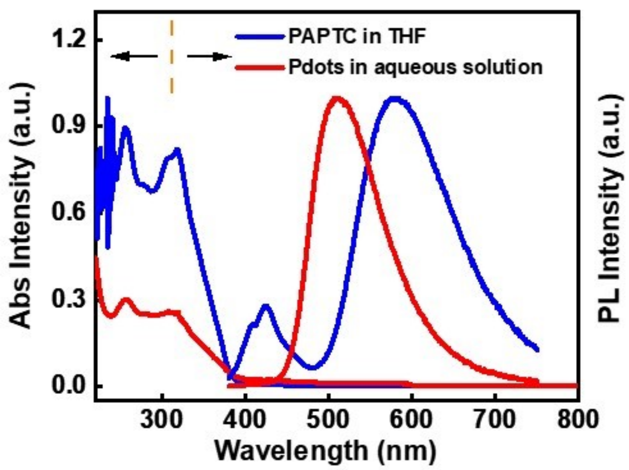

Figure S2. UV-visible absorption and steady-state PL spectra of PAPTC polymer in THF or the corresponding Pdots in aqueous solution.

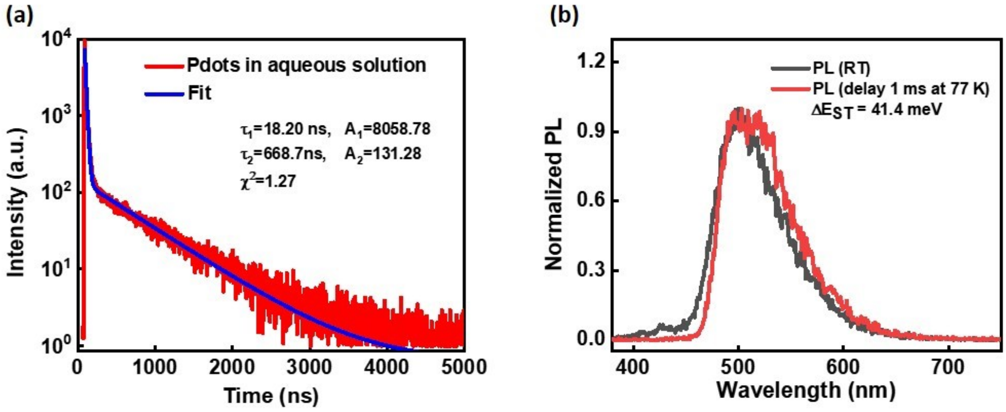

Figure S3. (a) transient PL decay curves of Pdots aqueous solution. (b) PL spectra at room temperature or 77K with a delayed 1ms (λ_{Ex} = 363nm).

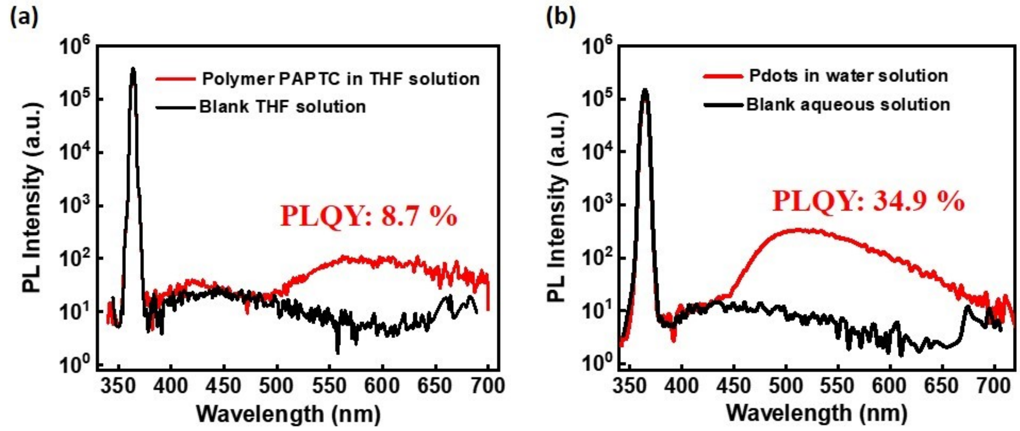

Figure S4. absolute PL quantum efficiency measurement for PAPTC polymer in THF (a) or the Pdots in water solution (b).

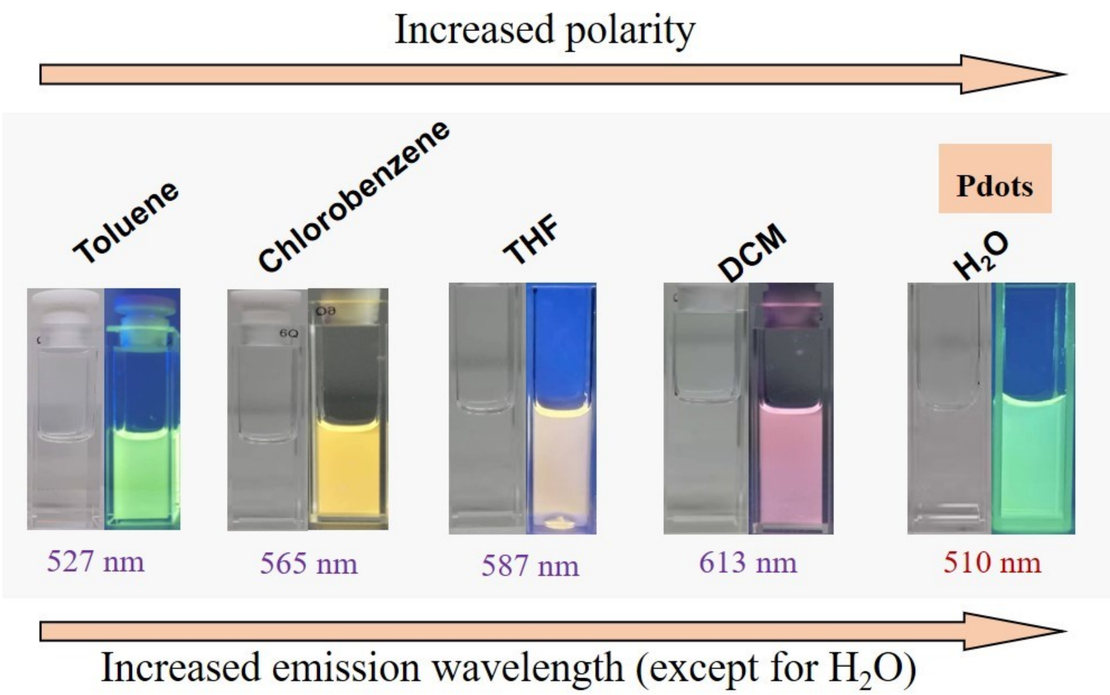

Figure S5. photograph of PAPTC polymer in different solvent under daylight (left) and 363 nm excitation (right).

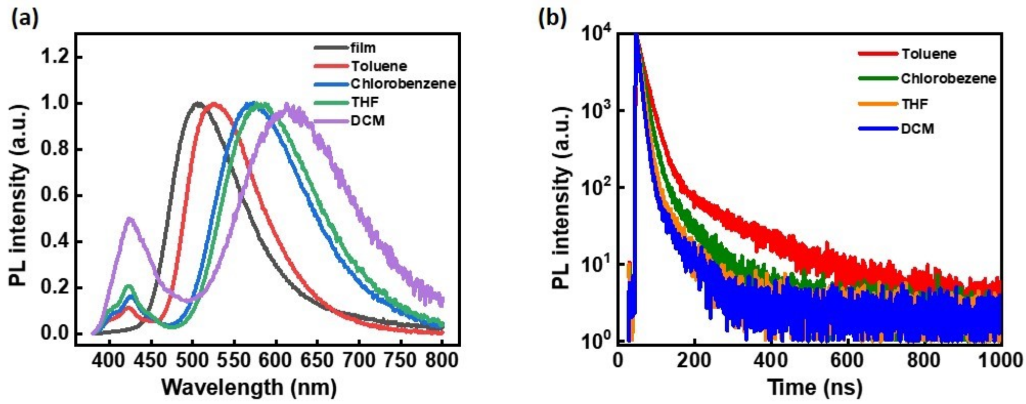

Figure S6. PL spectra (a) and transient PL decay (b) curves of PAPTC polymer in different solvent, including toluene, chlorobenzene, THF, and DCM in atmosphere. λ_{Ex} = 363nm.

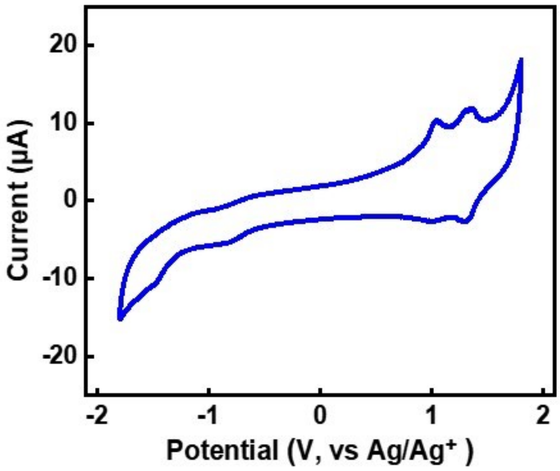

Figure S7. cyclic voltammograms of Pdots films in ACN containing 0.1 M $TBAPF_6$. Measured in a glove box.

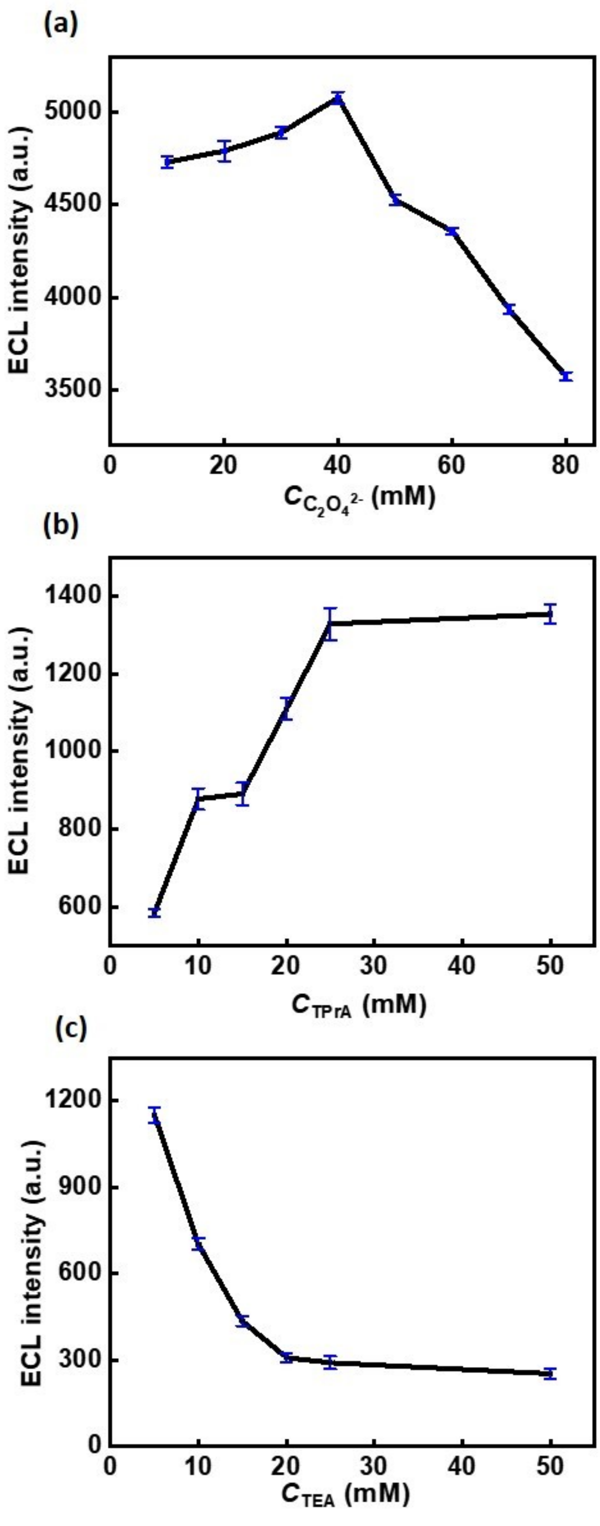

Figure S8. the effects of concentration of co-reactant (a) $Na_2C_2O_4^{2-}$, (b) TPrA and (c) TEA on the ECL intensity.

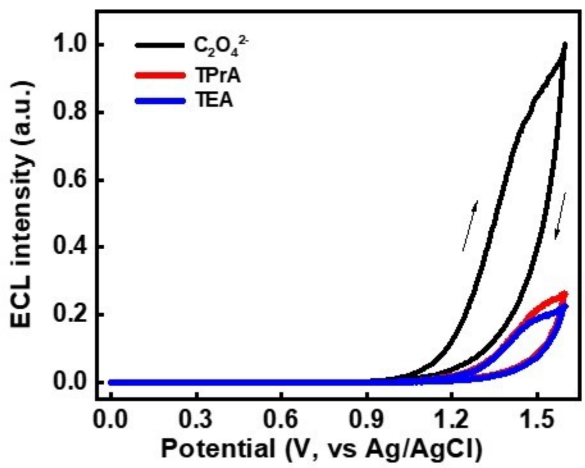

Figure S9. ECL-potential curves of Pdots-modified GCE/different co-reactant at their respective optimal concentration conditions, i.e. $C_2O_4^{2-}$ (black), TPrA (red) or TEA (blue) (0.1 M PBS, pH= 7.45, containing 0.1 M KNO_3).

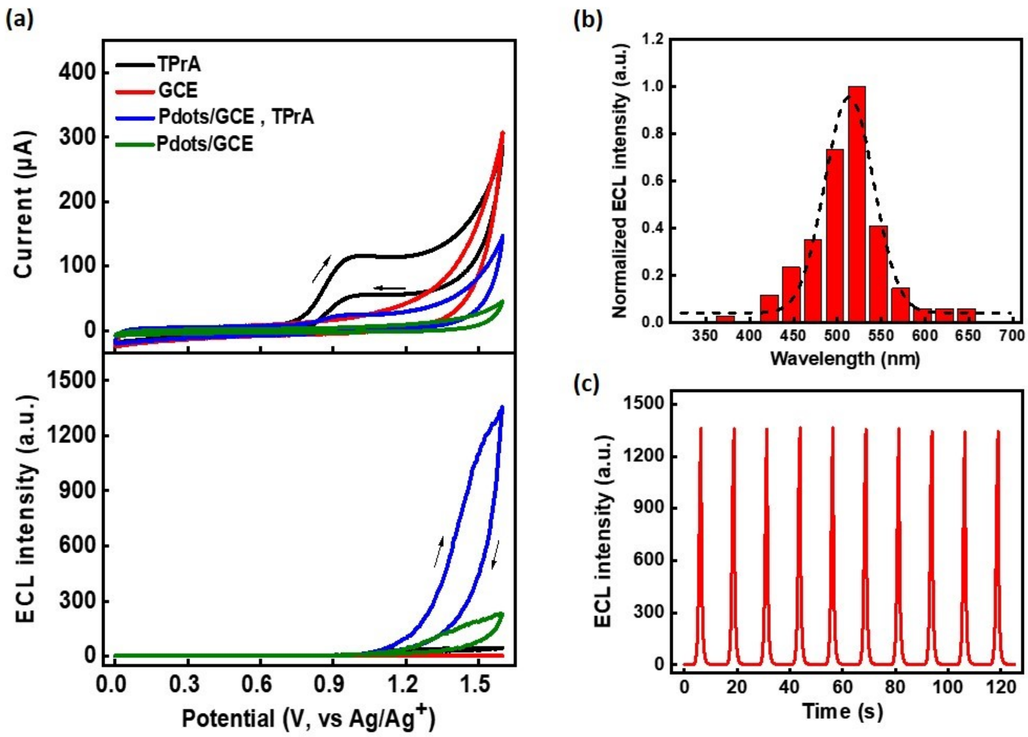

Figure S10. (a) CV and ECL responses at different conditions (in PBS), i.e. 25 mM TPrA only (black), bare GCE (red), P-dots/25 mM TPrA couple (blue) or P-dots only (green). (b) ECL spectrum of Pdots/25 mM TPrA couple. (c) co-reactant ECL stability (10 cycles) of Pdots/25 mM TPrA couple. PBS (0.1 M, pH = 7.45) contains 0.1 M KNO_3. scan rate: 250mV s^{-1}.

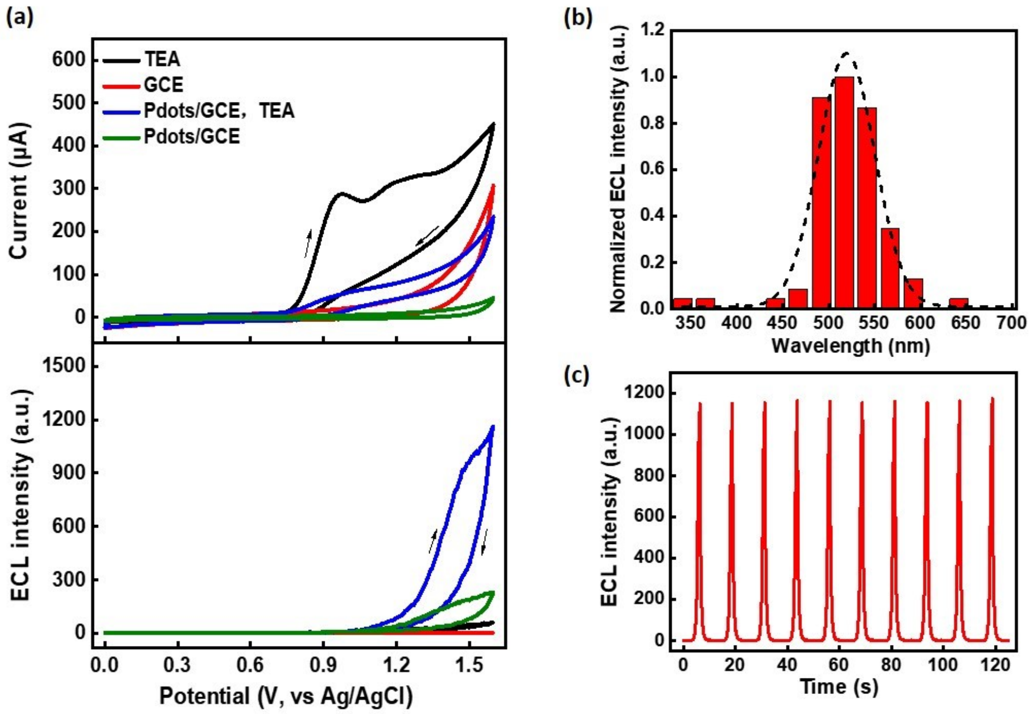

Figure S11. (a) CV and ECL responses at different conditions (in PBS): 5 mM TEA only(black), bare GCE (red), Pdots/5 mM TEA couple (blue), Pdots only (green). (b) the corresponding ECL spectrum of Pdots/5 mM TEA couple. **(c)** Co-reactant ECL stability (10 cycles) of Pdots with 5 mM TEA in PBS. PBS (0.1 M, pH = 7.45) contains 0.1 M KNO_3. scan rate：250mV s^{-1}.

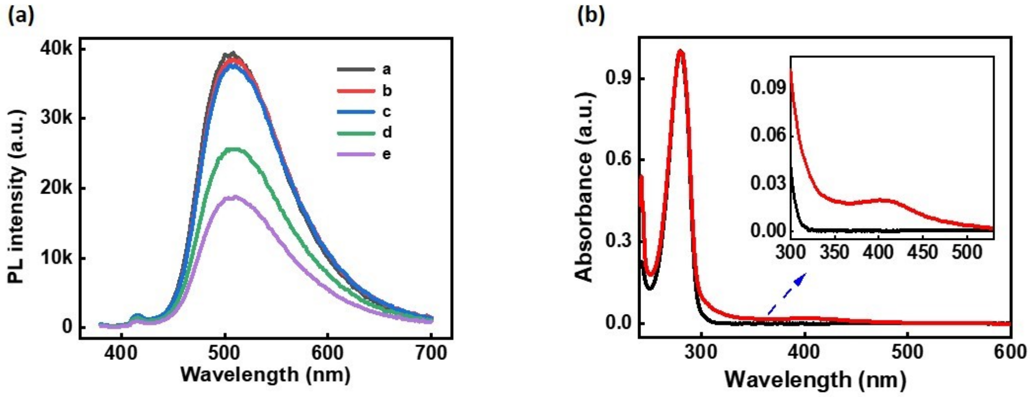

Figure S12. (a) PL spectra of Pdots in (a) absence and (b-d) presence of 200 (b) or 500 μM (c) dopamine , and 200 (d) or 500 μM oxidized dopamine (e). **(b)** UV-vis absorption spectra of dopamine (black curve) and oxidized dopamine (red curve).

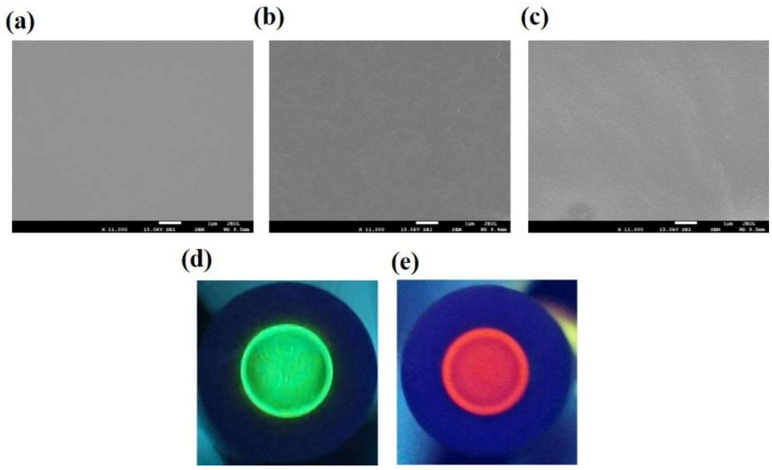

Figure S13. SEM image of bare GCE (a), Pdot/Nafion-modified GCE (b) and $Ru(bpy)_3^{2+}$/Nafion-modified GCE(c); UV-lamp (365nm) excited PL image of Pdot/Nafion-modified GCE (d) and $Ru(bpy)_3^{2+}$/Nafion-modified GCE(e), respectively.

2. Supplementary Tables

Table S1. Photophysical properties of PAPTC in differnt conditons.

Conditions	λ_{PL} ^{b} [nm]	Fwhm [nm]	Φ_{PL} ^{c} [%]	τ_p ^{d} [ns]	τ_d ^{d} [ns]	Φ_{PF} ^{e} [%]	Φ_{DF} ^{e} [%]	Φ_{DF}/Φ_{PF}	k_f ^{f} [10^7 s^{-1}]	k_{ISC} ^{g} [10^7 s^{-1}]	k_{RISC} ^{h} [10^5 s^{-1}]
film[a]	506	100	28	13.8	680	24.8	3.92	0.16	1.80	5.45	3.13
Toluene (N_2) [a]	510	-	40	12.6	230	23.2	16.8	0.72	1.84	6.10	40.7
Toluene	527	101	16.8	19.9	158	14.8	2.00	0.14	0.74	4.27	10.4
chlorobenzene	565	127	15.1	14.72	76.1	13.6	1.47	0.11	0.93	5.87	16.7
THF	587	130	8.7	11.11	75	8.13	0.59	0.07	0.73	8.27	10.1
DCM	613	154	3.89	9.29	40	3.54	0.35	0.10	0.38	10.38	25.9
Pdots	510	100	34.9	18.2	670	21.8	13.1	0.60	1.20	4.30	11.5

[a]From ref. results.[1] [b]Measured at room temperature in air. [c]Absolute PL quantum efficiency (Φ_{PL}) evaluated using an integrating sphere under air atmosphere. [d]The prompt fluorescence lifetime (τ_p) and the delayed fluorescence lifetime (τ_d) calculated by transient PL decay curves under air atmosphere at room temperature, the average lifetime calculated by $\tau_{av} = \Sigma A_i\tau_i^2/\Sigma A_i\tau_i$, where A_i is the pre-exponential for lifetime τ_i. [e]The fractional contributions of the prompt fluorescence (Φ_{PF}) and delayed fluorescence (Φ_{DF}) to the total Φ_{PL} calculated by transient PL decay curves under air atmosphere. $\Phi_{PL} = \Phi_{PF} + \Phi_{DF}$, $\Phi_{PF} = r_p \times \Phi_{PL}$, $r_p = \tau_1A_1/(\tau_1A_1+ \tau_2A_2+ \tau_3A_3)$, $\Phi_{DF} = r_d \times \Phi_{PL}$, $r_d = 1 - r_p$. [f]The fluorescence rate constants k_f (S_1 to S_0) calculated using equation of $k_f = \Phi_{PF}/\tau_p$. [g]The rate constants of ISC calculated using equation of $k_{ISC} = k_p\cdot(1-\Phi_{PF})$. [h]The rate constant of RISC rate was calculated using equation of $k_{RISC} = (k_p\cdot k_d)/k_{ISC} \times (\Phi_{DF}/\Phi_{PF})$, in which $k_p = 1/\tau_p$, $k_d = 1/\tau_d$.

Table S2. ECL efficiency of different couple, vs. $Ru(bpy)_3^{2+}$/ TPrA (25 mM) reference.

System	$\int_a^b I^o dt$	$\int_a^b i^o dt$	$\int_a^b I dt$	$\int_a^b i dt$	$\Phi_{ECL}(\%)$
Pdots/$C_2O_4^{2-}$ (40 mM)	16425.56	1.59	7242.92	6.04	11.73
Pdots/TPrA (25 mM)	16425.56	1.59	1610.93	4.12	3.78
Pdots/TEA (5 mM)	16425.56	1.59	1426.12	7.21	1.91

Note: such Φ_{ECL} calculation refers to the reference reports.[2]

Reference:
1. Y. Zhu, Y. Zhang, B. Yao, Y. Wang, Z. Zhang, H. Zhan, B. Zhang, Z. Xie, Y. Wang and Y. Cheng, *Macromolecules*, 2016, **49**, 4373-4377.
2. S. Y. Ji, W. Zhao, H. Gao, J. B. Pan, C. H. Xu, Y. W. Quan, J. J. Xu and H. Y. Chen, *iScience*, 2020, **23**, 100774.