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Triphenothiazinyl triazacoronenes: Donor−acceptor molecular graphene exhibitng multiple fluorescence and electrogenerated chemiluminescence emissions

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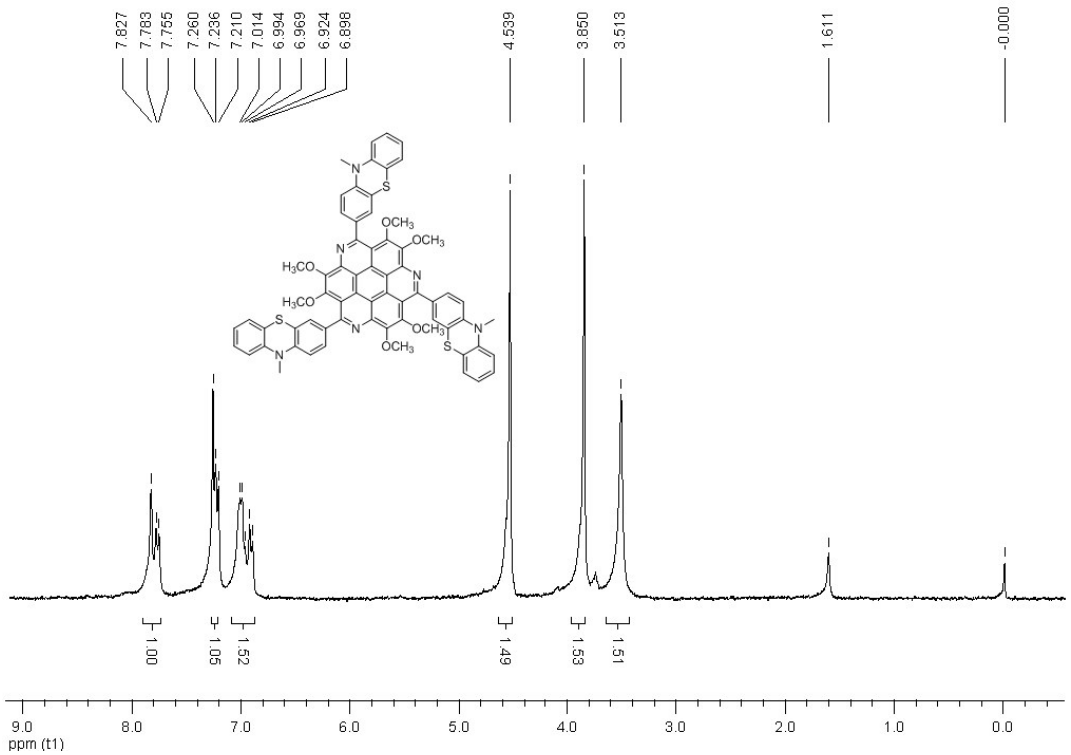


Figure S-1. ^{1}H NMR spectrum of TPTZ-TAC1 recorded in $CDCl_3$

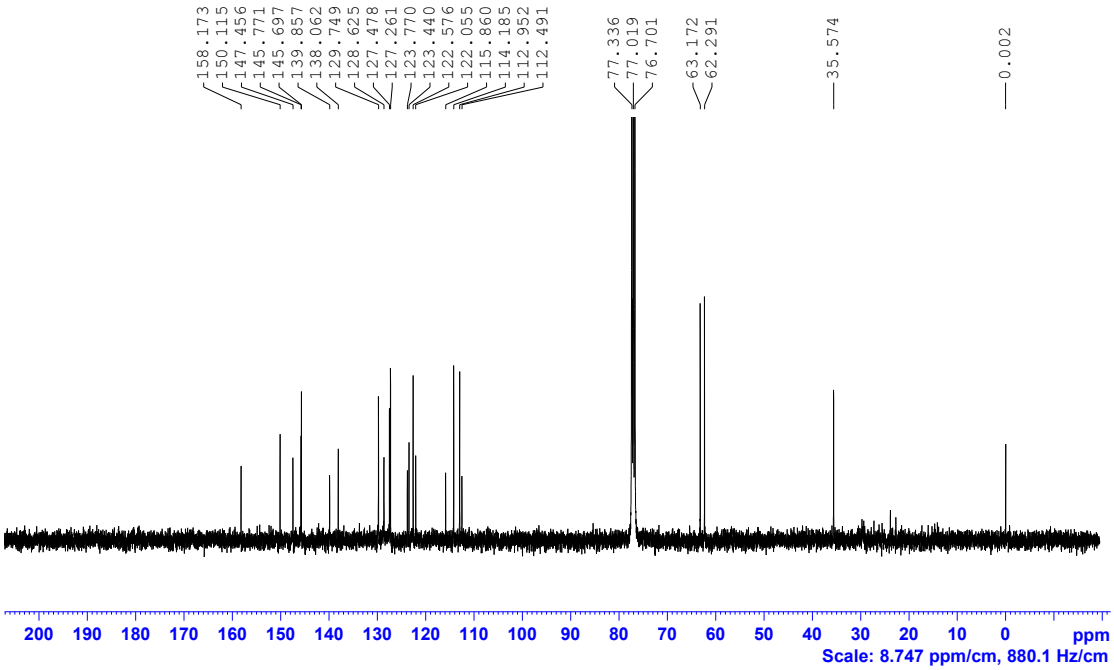


Figure S-2. ^{13}C NMR spectrum of TPTZ-TAC1 recorded in $CDCl_3$.

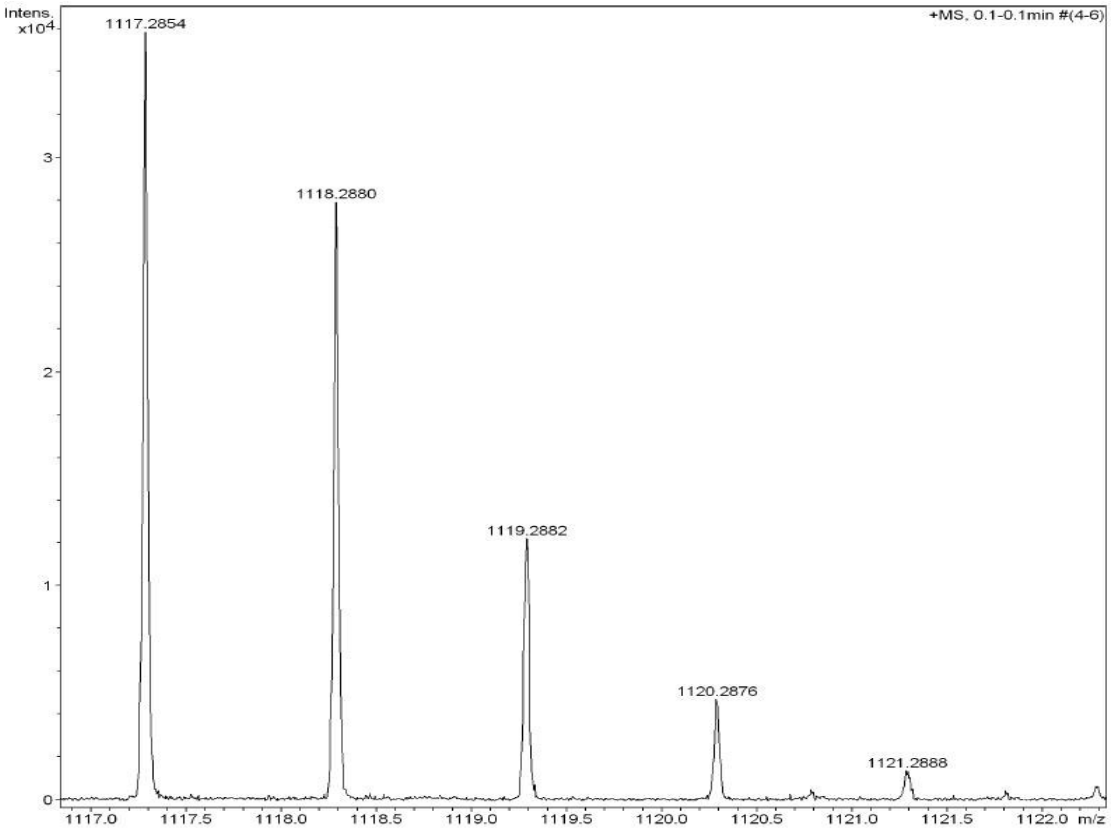


Figure S-3. HRMS (ESI) spectrum of TPTZ-TAC1 recorded in THF/CH_3CN.

Figure S-4. Photo of 1×10^{-5} M PTZ, TAC and TPTZ-TAC1 in benzene: MeCN (*v*:*v*=1:1) from left to right.

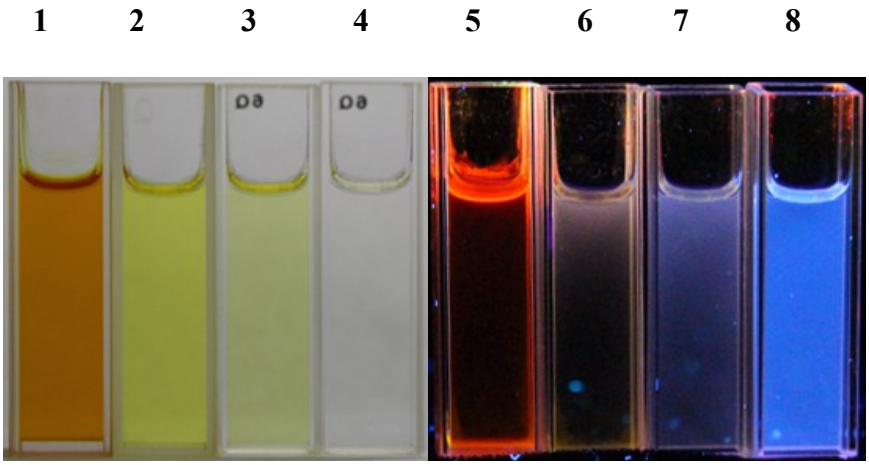


Figure S-5. Photo of 1×10^{-3} M, 2×10^{-5} M, 1×10^{-5} M, 5×10^{-7} M TPTZ-TAC1 in benzene: MeCN (*v*:*v*=1:1) from left to right. 1-4 in bright light, 5-8 excited in 365 nm UV lamp in dark condition.

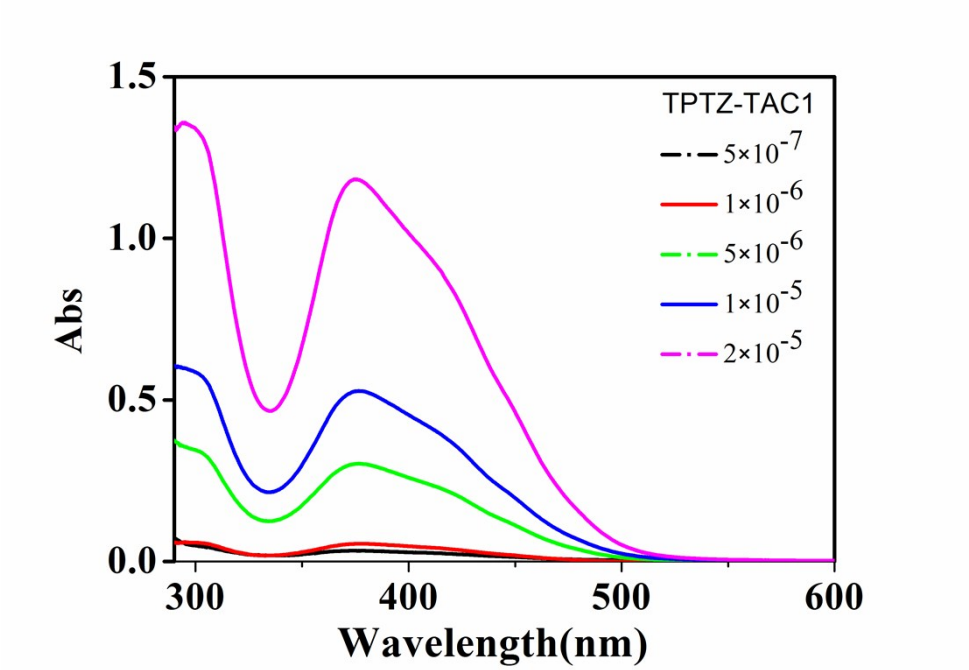


Figure S-6. Absorption spectra of TPTZ-TAC1 at different concentrations in benzene: MeCN (*v*:*v*=1:1).

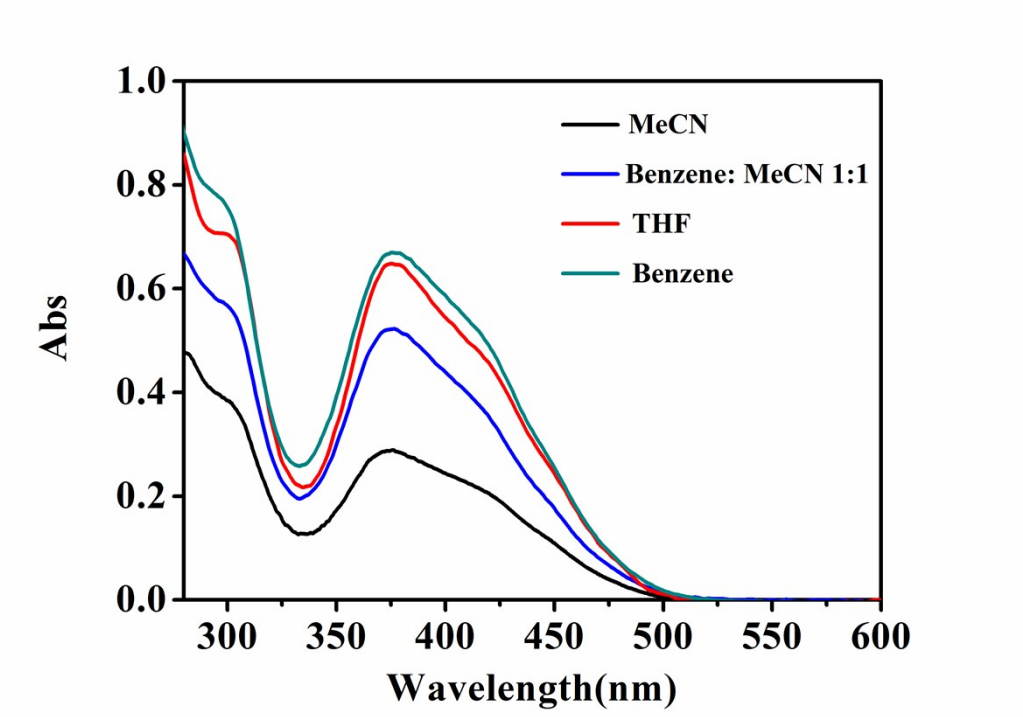


Figure S-7. Absorption spectra of 10 μM TPTZ-TAC1 in different solvents.

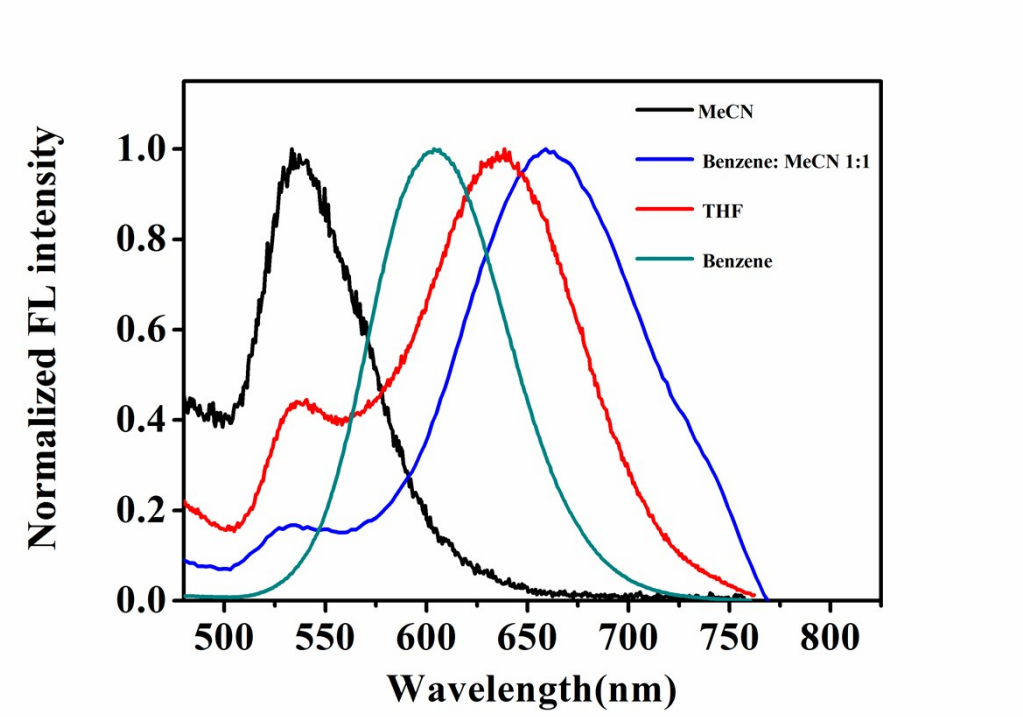
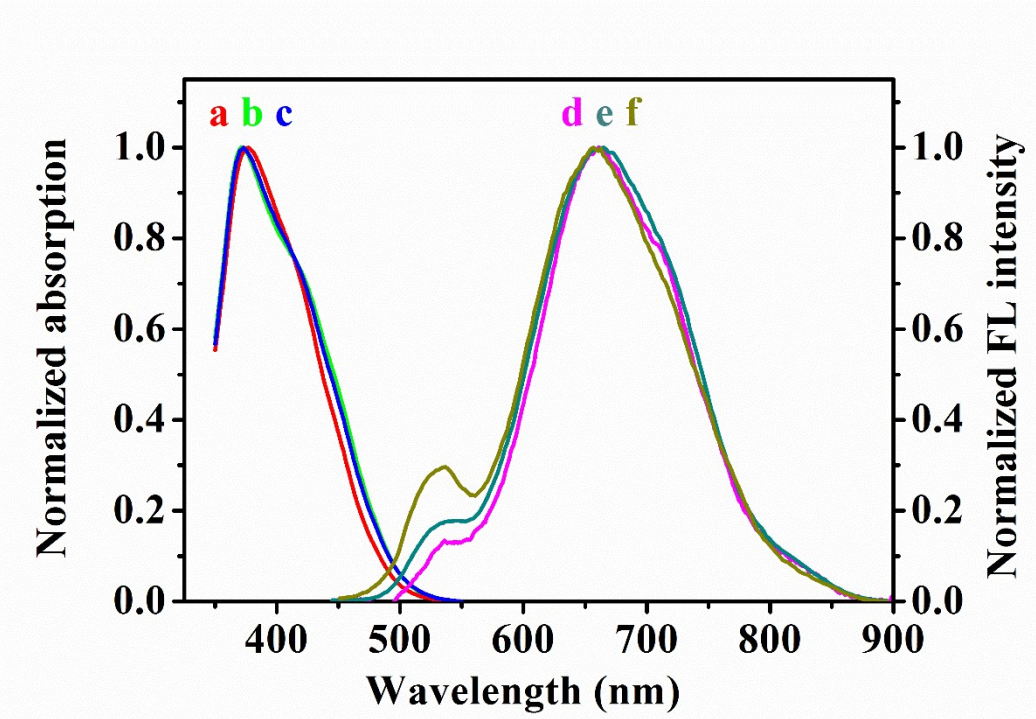


Figure S-8. Normalized fluorescence spectra for 20 μM TPTZ-TAC1 in different solvents. Fluorescence emissions were excited at the absorption maximum wavelength.



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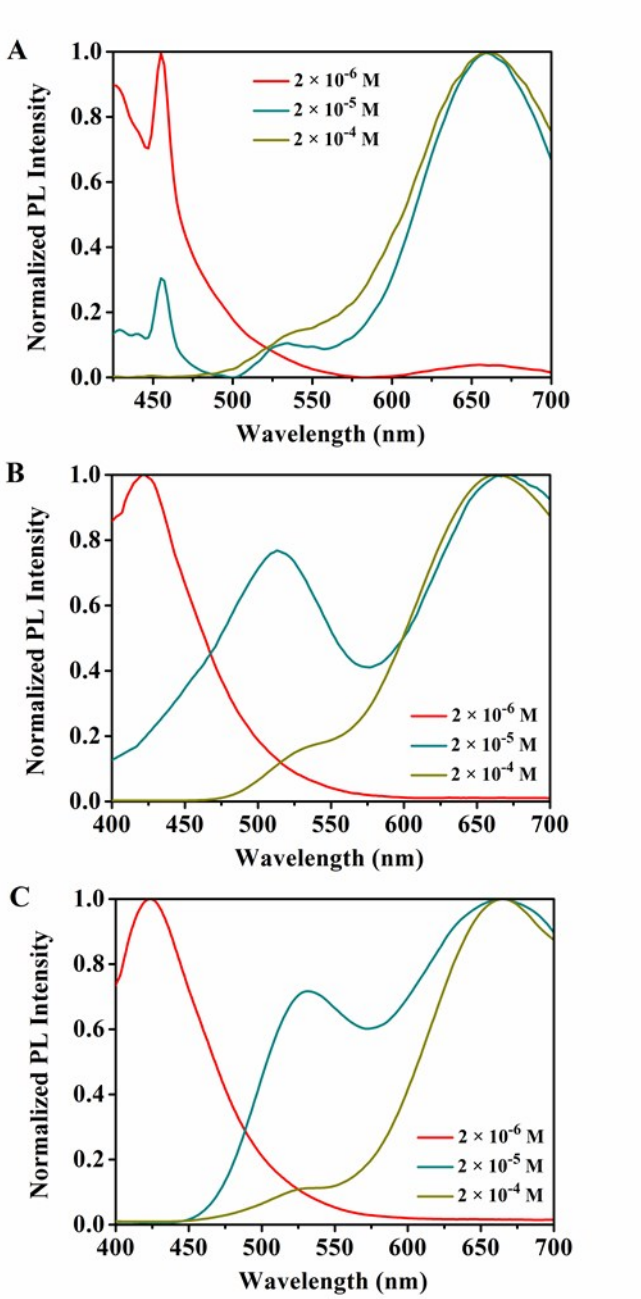

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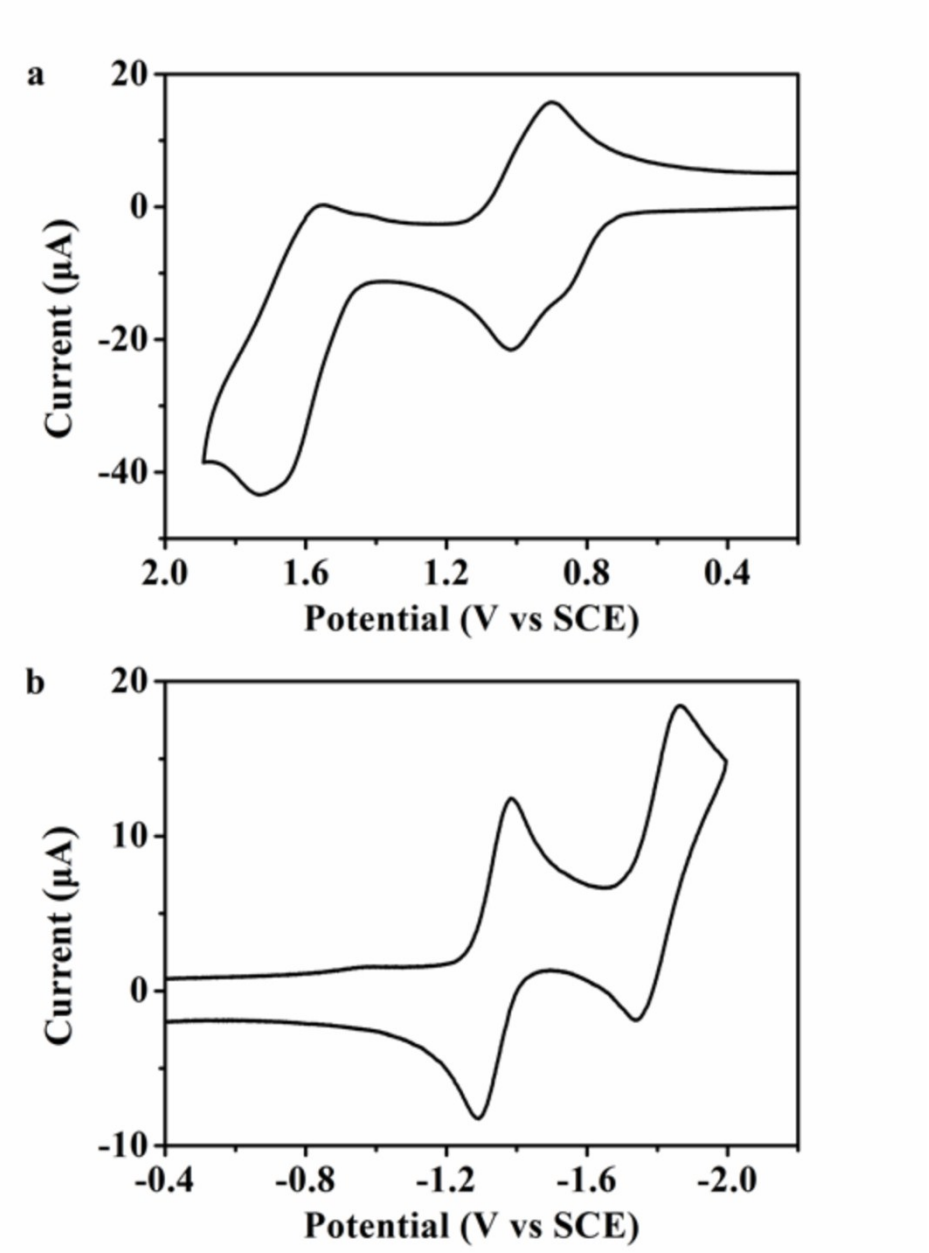

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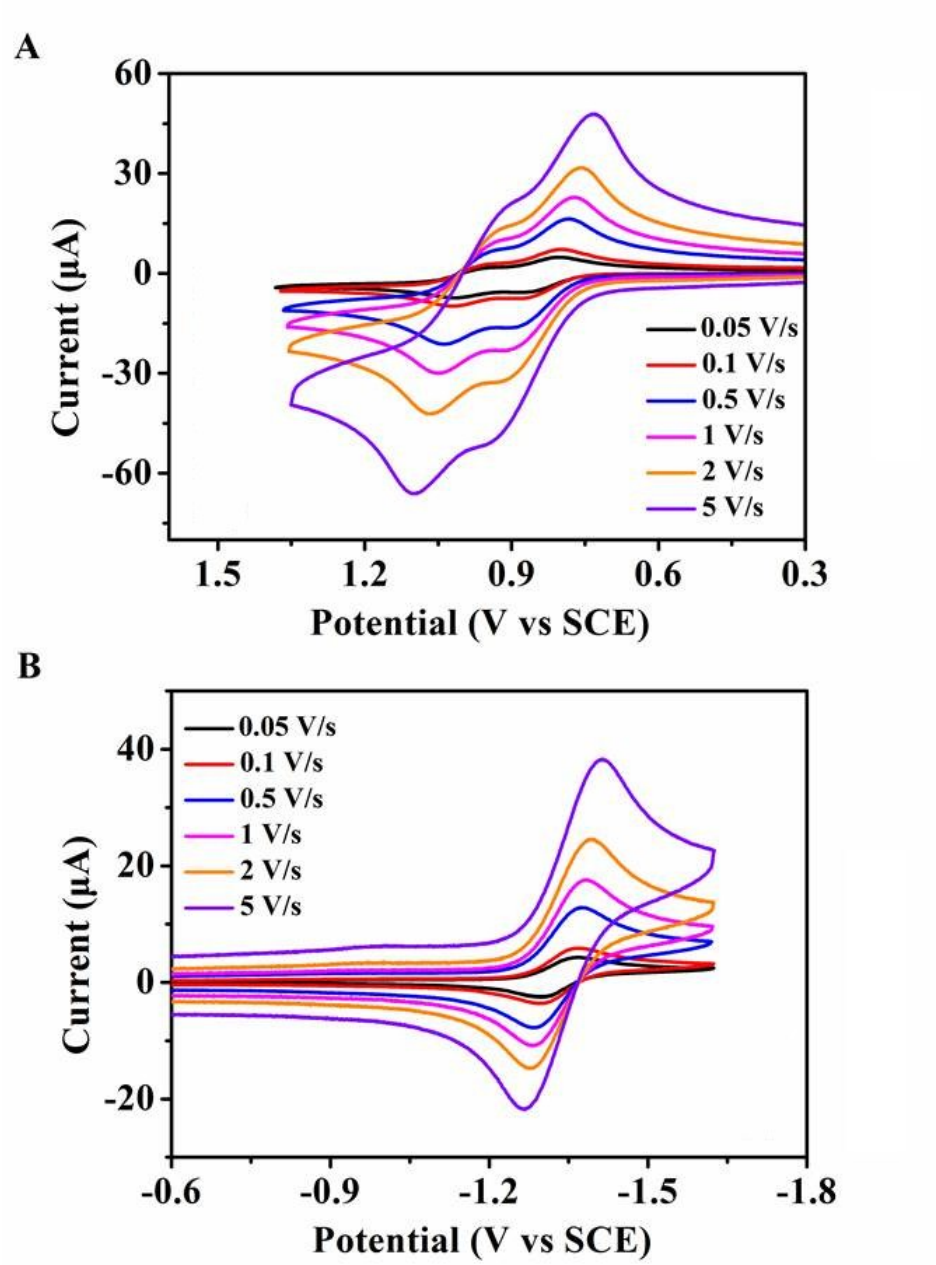
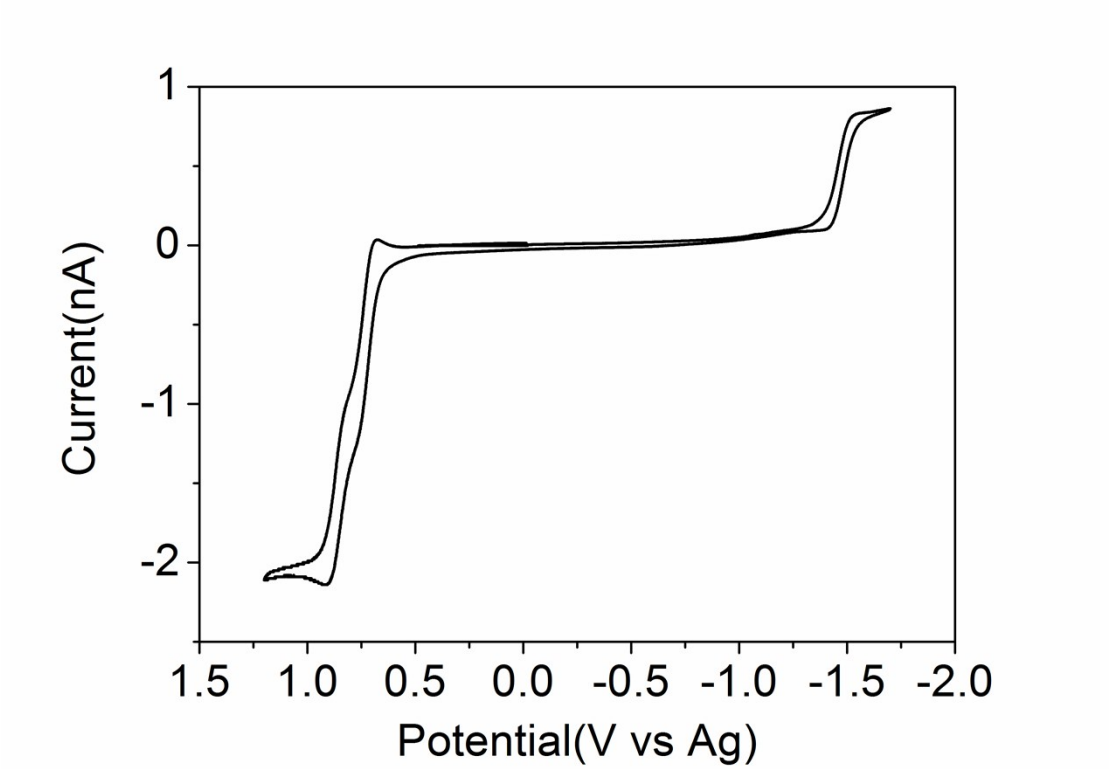


Figure S-12. Cyclic voltammograms of 1.5 mM TPTZ-TAC1 in benzene: MeCN (*v*:*v*=1:1) containing 0.1 M $TBAPF_6$ at a Pt electrode (electrode area is 0.027cm^2) with different scan rates.



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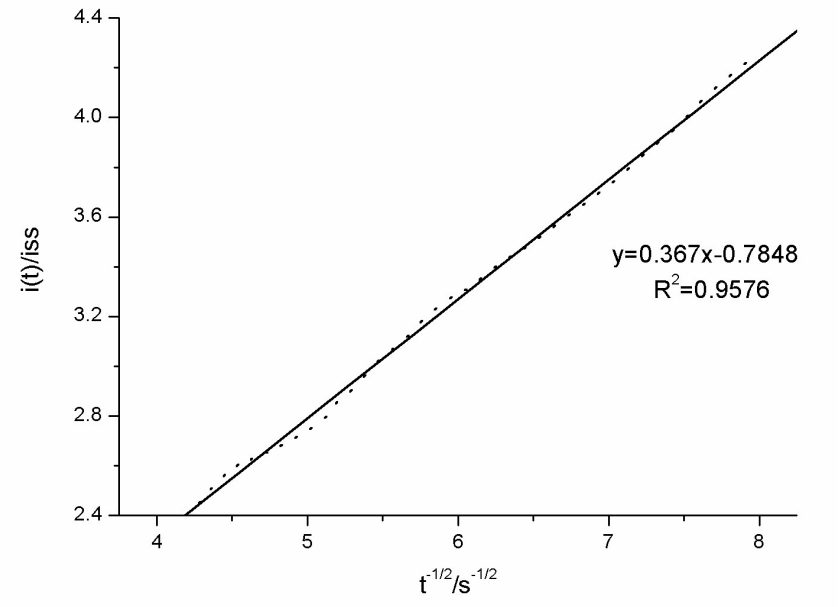

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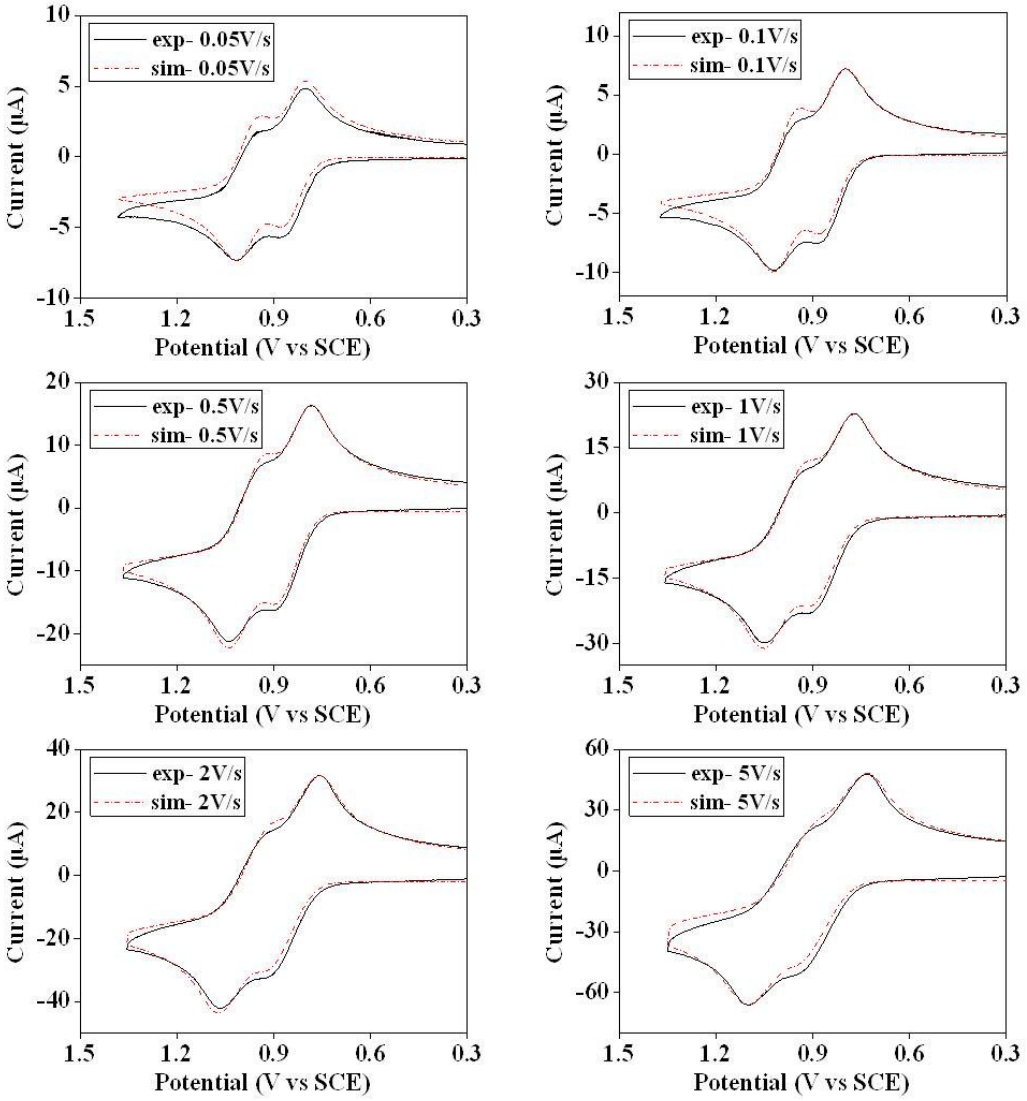

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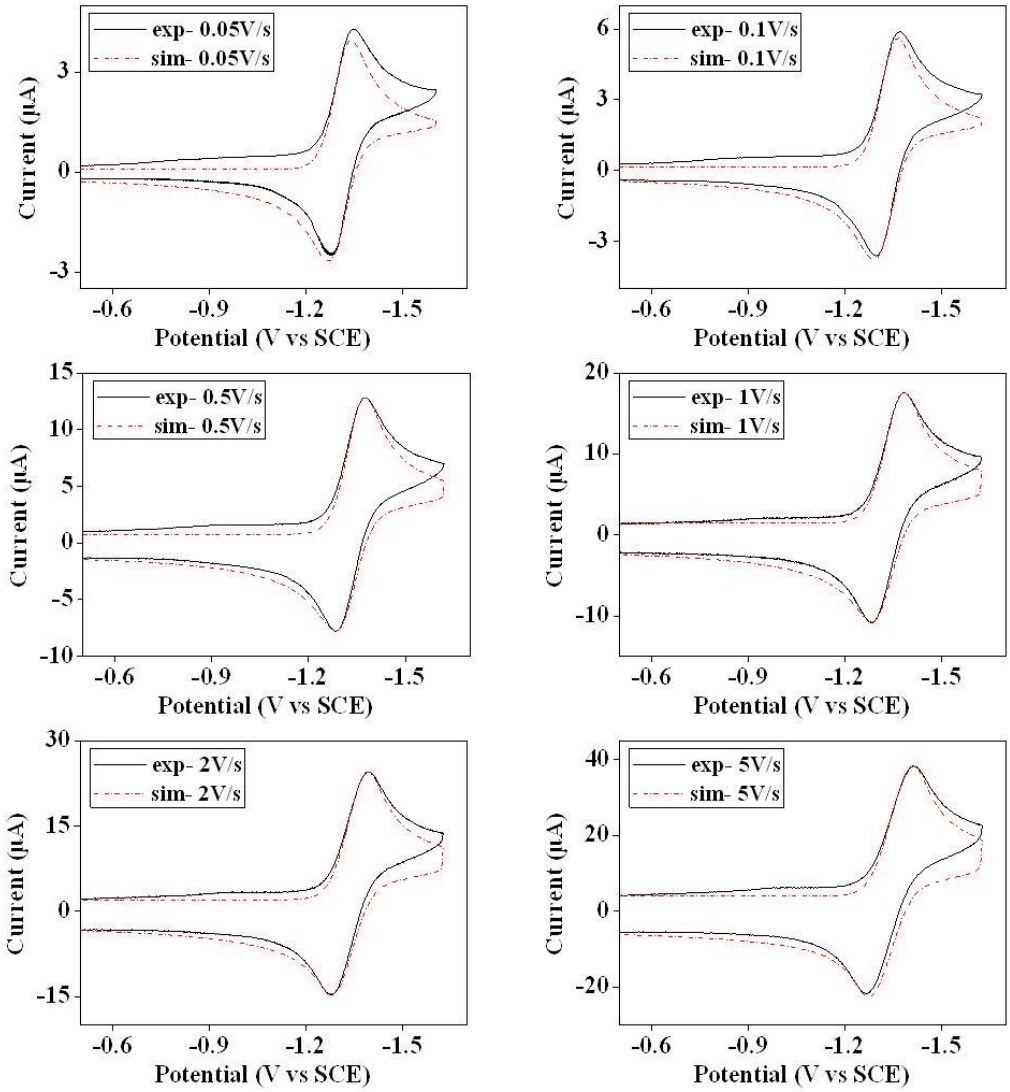

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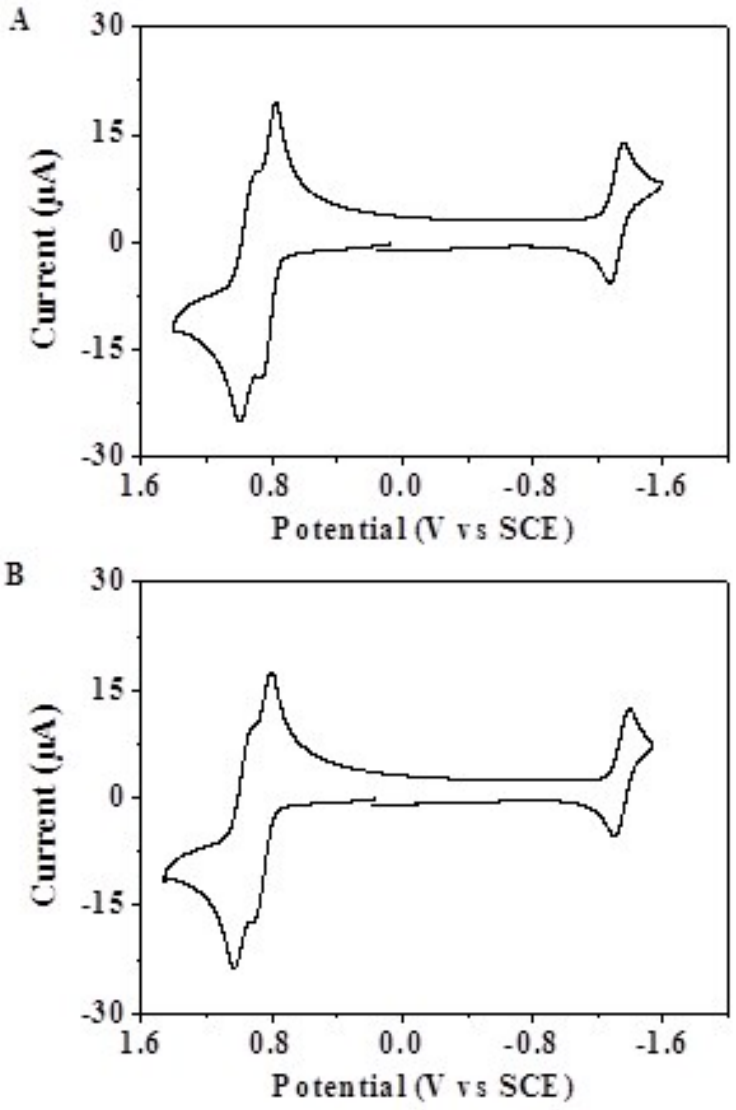
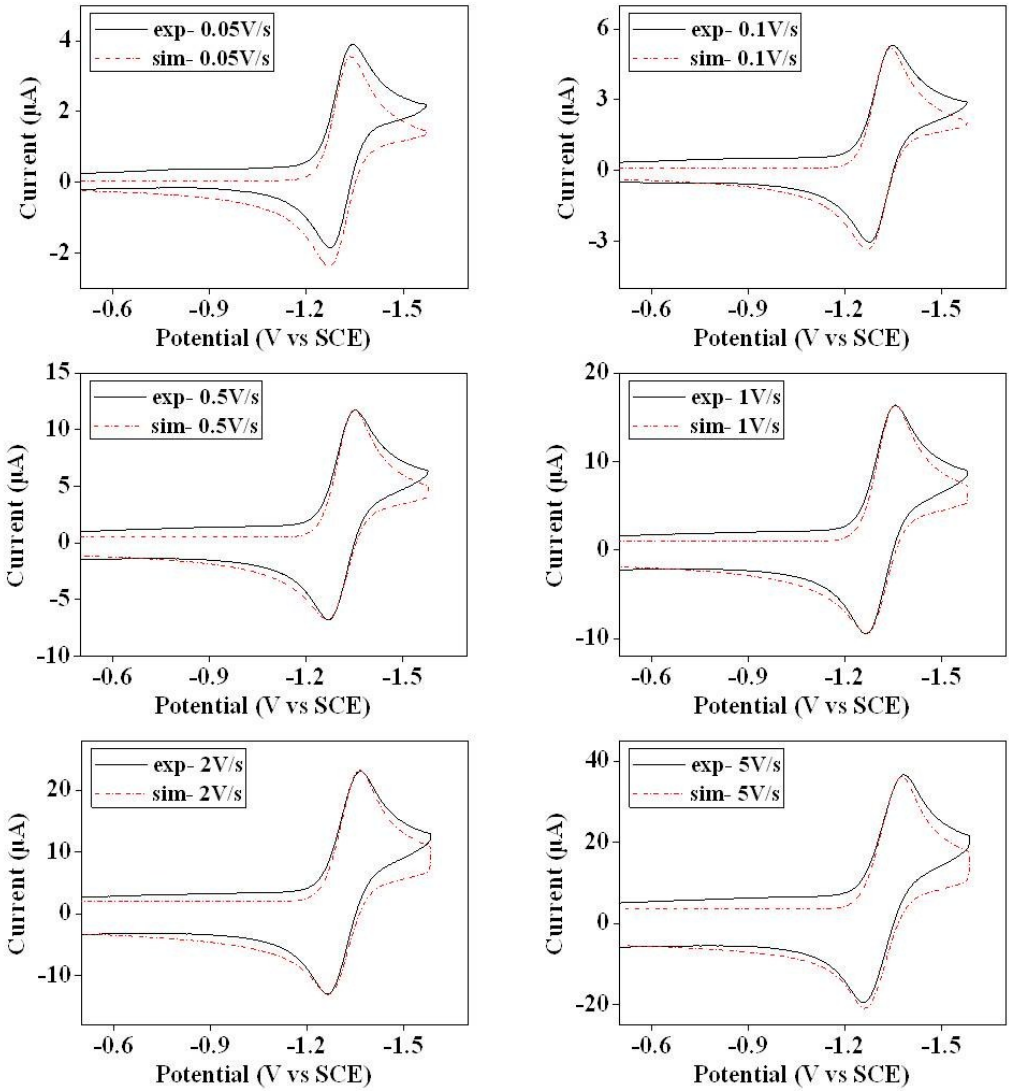


Figure S-17. Cyclic voltammograms of 1.5 mM TPTZ-TAC2 (A) and 1.5 mM TPTZ-TAC3 (B) in benzene: MeCN (*v*:*v*=1:1) containing 0.1 M $TBAPF_6$ at platinum electrode with scan rate of 0.5 V/s (electrode area is 0.027 cm^2).



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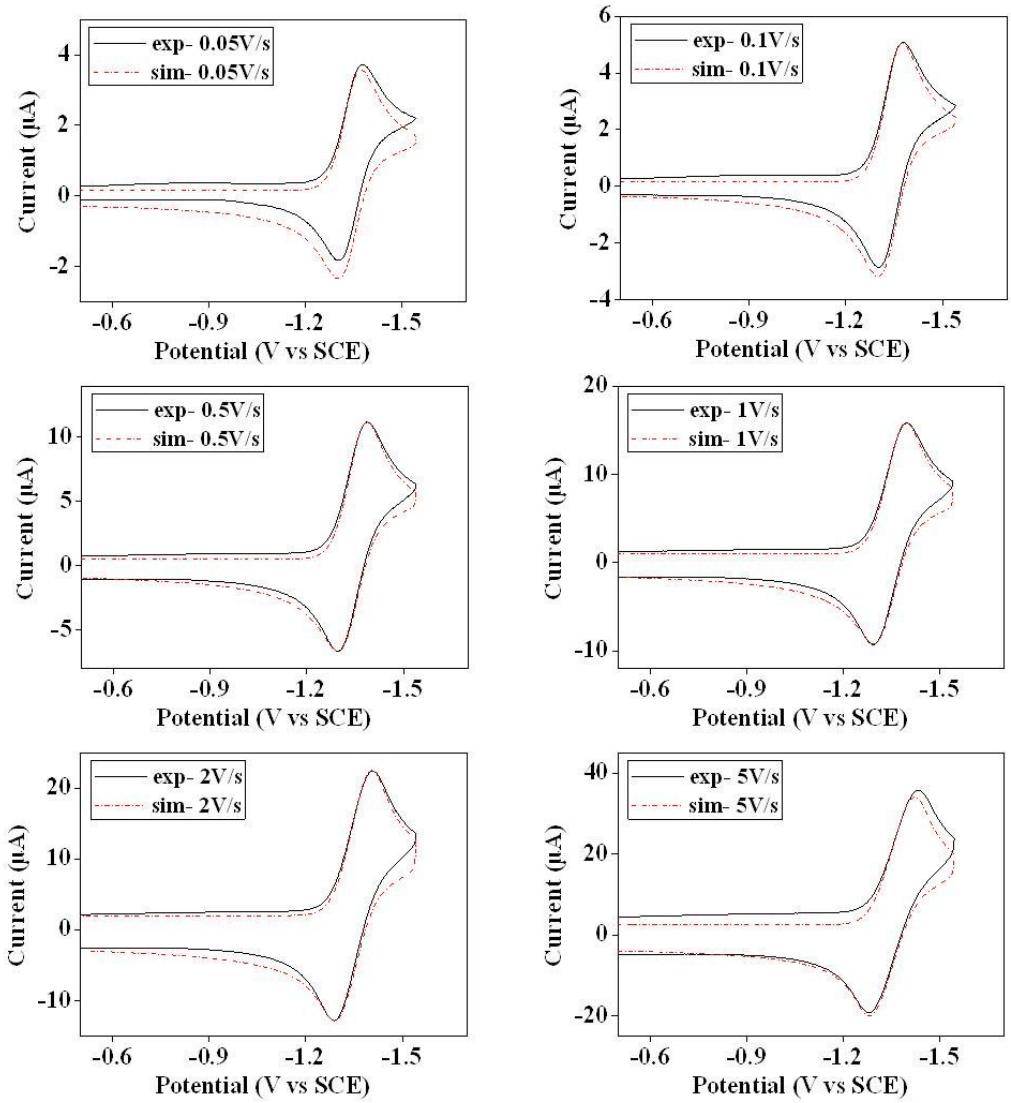

Figure S-19. Comparison between simulated and experimental reduction waves for 1.5 mM TPTZ-TAC3 at different scan rates. The model for these reduction simulations: EC, with n = 1, with a heterogeneous rate constant, α = 0.5, $k^0 = 1\times10^4$ cm/s and a homogeneous forward rate constant, k_{eq} = 0.4, k_f = 8 s^{-1}. Simulated data: E^o = -1.35 V vs SCE; Diffusion coefficient: 7.00 × 10^{-6} cm^2/s, uncompensated resistance 883 Ω, capacitance 3×10^{-6} F. Experimental conditions: solvent: benzene: MeCN (*v*:*v*=1:1), supporting electrolyte: 0.1 M $TBAPF_6$, Pt electrode area 0.027 cm^2.

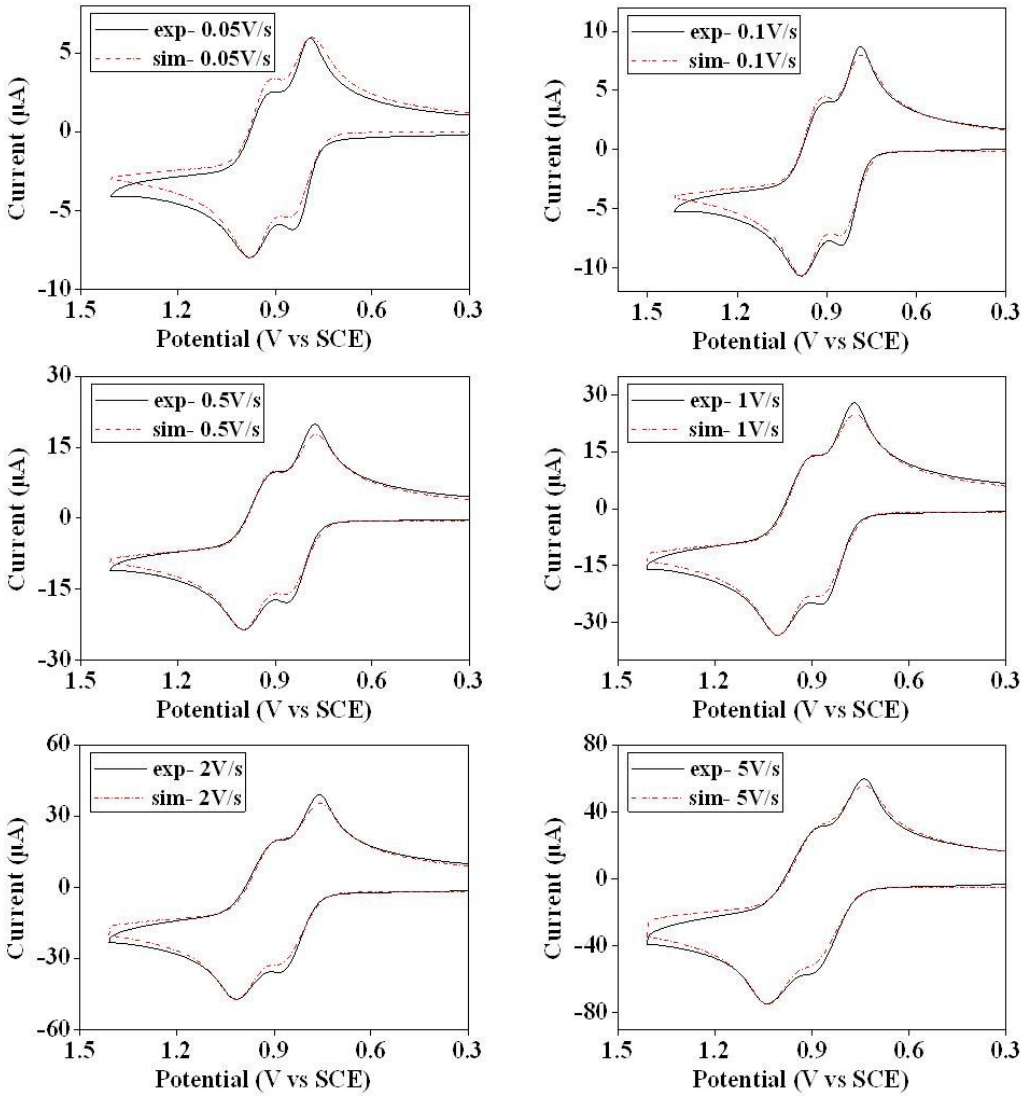

Figure S-20. Comparison between simulated and experimental oxidation waves for 1.5 mM TPTZ-TAC2 at different scan rates. The model for these oxidation simulations: ECE, with n = 2, with a heterogeneous rate constant, α = 0.5, k_1^0 = 0.1 cm/s, k_2^0 = 0.1 cm/s. Simulated data: E_1^o = 0.82 V vs SCE, E_2^o = 0.95 V vs SCE; Diffusion coefficient: 7.01×10^{-6} cm^2/s, uncompensated resistance 1129 Ω, capacitance 1×10^{-6} F. Experimental conditions: solvent: benzene: MeCN (v:v=1:1), supporting electrolyte: 0.1 M $TBAPF_6$, Pt electrode area 0.027 cm^2.

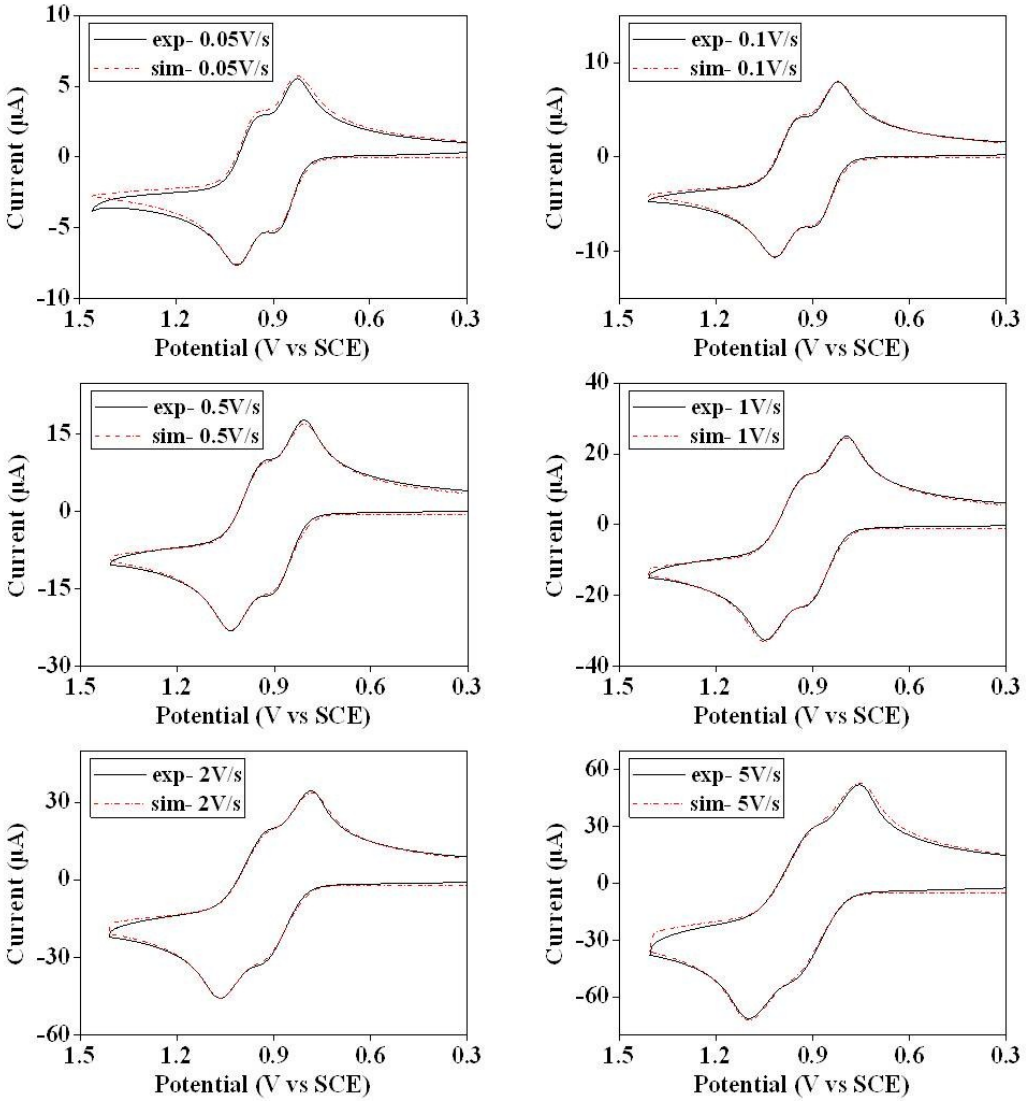

Figure S-21. Comparison between simulated and experimental oxidation waves for 1.5 mM TPTZ-TAC3 at different scan rates. The model for these oxidation simulations: ECE, with n = 2, with a heterogeneous rate constant, α = 0.5, k_1^0 = 0.1 cm/s, k_2^0 = 0.1 cm/s. Simulated data: E_1^o = 0.86 V vs SCE, E_2^o = 0.97 V vs SCE; Diffusion coefficient: 7.00×10^{-6} cm^2/s, uncompensated resistance 1060 Ω, capacitance 1×10^{-6} F. Experimental conditions: solvent: benzene: MeCN (v:v=1:1), supporting electrolyte: 0.1 M $TBAPF_6$, Pt electrode area 0.027 cm^2.

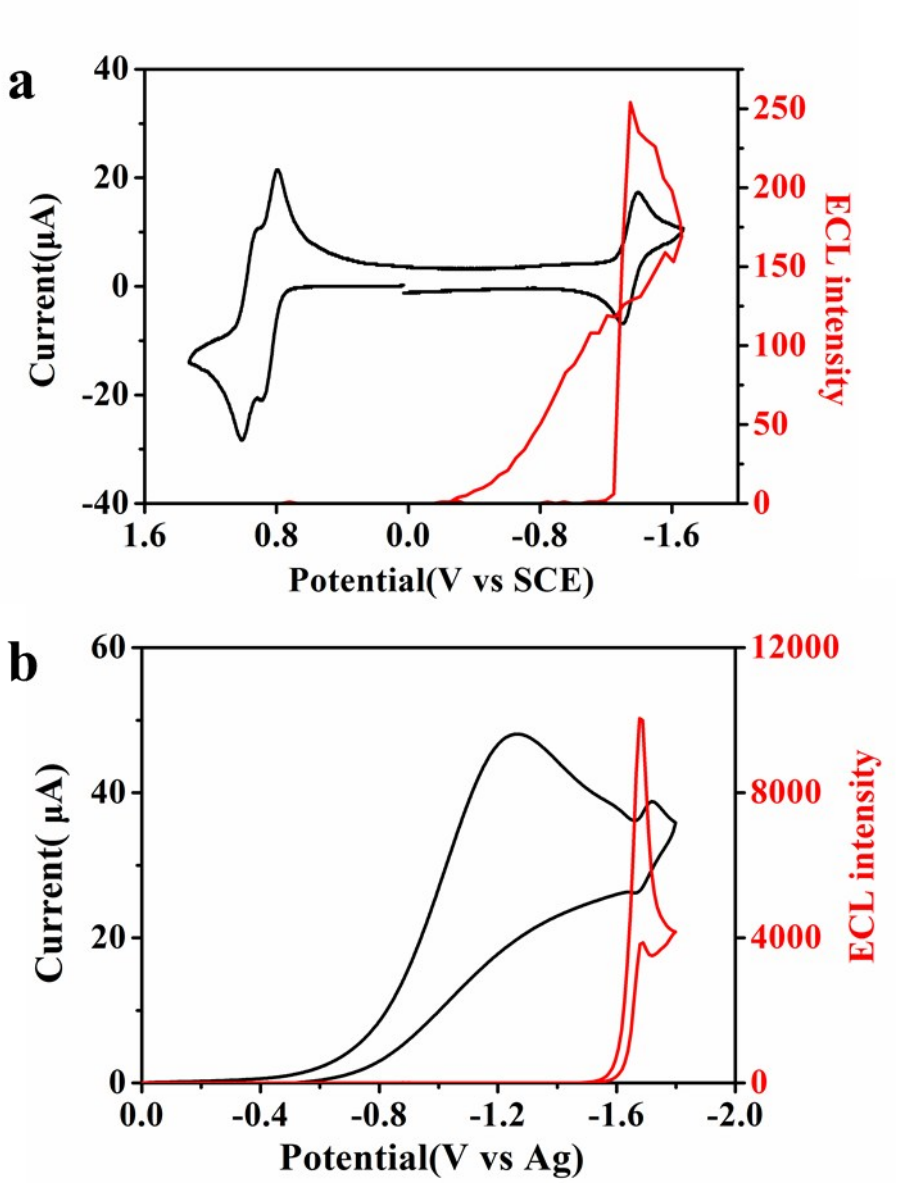

Figure S-22. ECL (red) and CV (black) simultaneous measurements for 1.5 mM TPTZ-TAC1 in the absence (a) and in the presence (b) of 10 mM benzoyl peroxide (BPO), Experimental conditions: solvent: benzene: MeCN (*v*:*v*=1:1), supporting electrolyte: 0.1 M $TBAPF_6$, negative high-voltage: 600 V, Pt electrode area 0.027 cm^2.

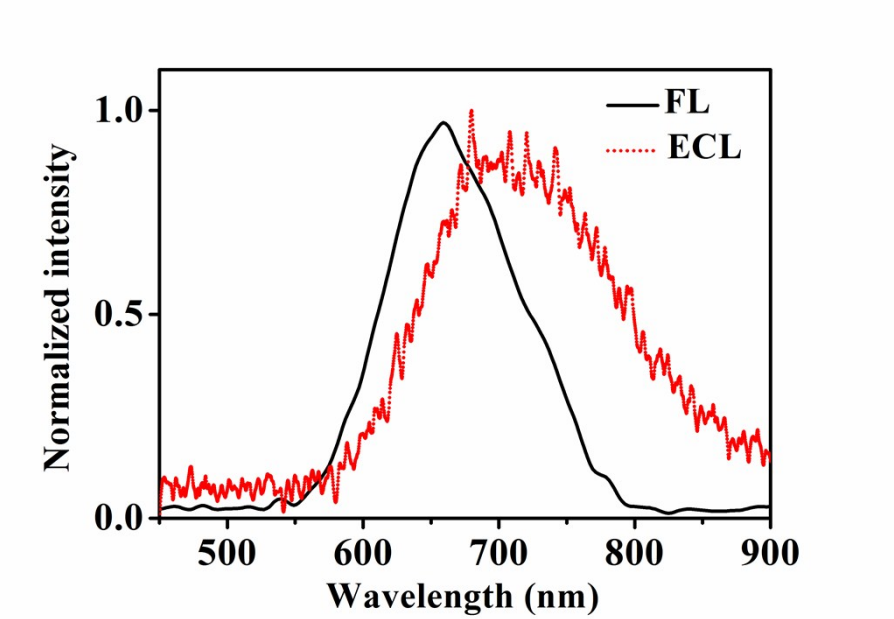

Figure S-23. Normalized fluorescence (solid, black) and ECL (short dot, red) spectra of TPTZ-TAC1 in benzene: MeCN (*v*:*v*=1:1) solution; ECL conditions were same as Figure 5. The concentration of TPTC-TAC1 is 1 $\times 10^{-3}$ M for fluorescence and ECL spectrum. Slit width is 5 nm for fluorescence and 20 nm for ECL spectrum.

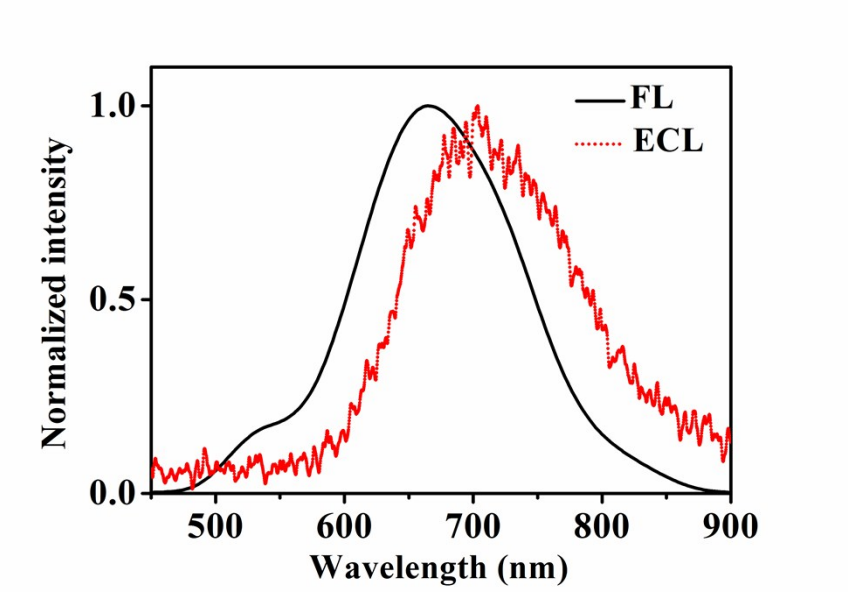

Figure S-24. Normalized fluorescence (solid, black) and ECL (short dot, red) spectra of TPTZ-TAC2 in benzene: MeCN (*v*:*v*=1:1) solution; ECL conditions were same as Figure 5. The concentration of TPTC-TAC2 is 1 $\times 10^{-3}$ M for fluorescence and ECL spectrum.

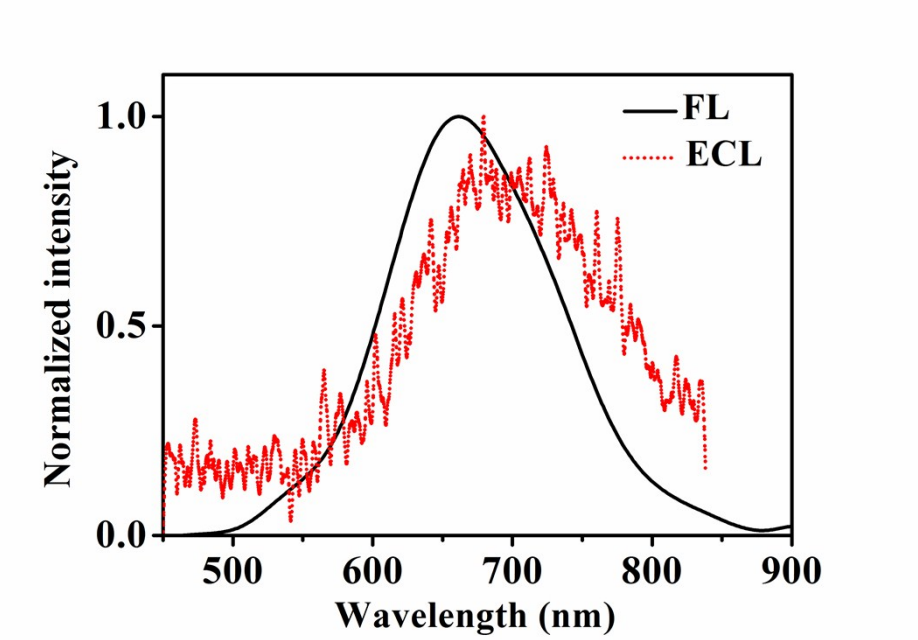

Figure S-25. Normalized fluorescence (solid, black) and ECL (short dot, red) spectra of TPTZ-TAC3 in benzene: MeCN (*v*:*v*=1:1) solution; ECL conditions were same as Figure 5. The concentration of TPTC-TAC3 is 1 $\times 10^{-3}$ M for fluorescence and 1 $\times 10^{-3}$ M for ECL spectrum.