Supporting Information

Water-Compatible Electrogenerated Chemiluminescence Effect Derived from Readily Accessible Tripyridinium Salts

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General Information

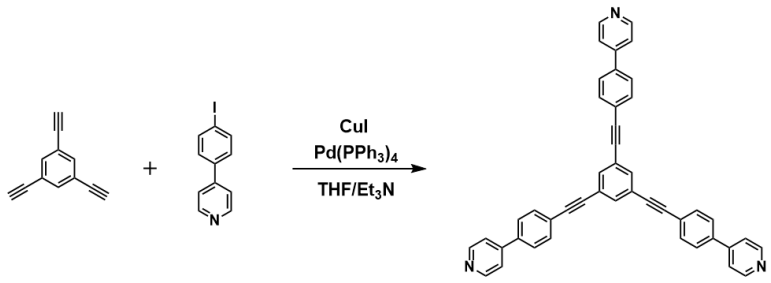
Chemicals

Unless stated otherwise, all chemicals were analytical grade at least and used directly without further purification. The osmosis Milli-Q water (18 MΩ, Millipore, Bedford, USA) was used throughout. 1,3,5-Tri(pyridin-4-yl)benzene, 1,3,5-tris(pyridin-4-ylethynyl)benzene, 4,4'-(5'-(4-(pyridin-4-yl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)dipyridine, copper iodide (CuI), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), 1,3,5-triethynylbenzene, 4-(4-bromophenyl)pyridine, iodomethane, lithium bis((trifluoromethyl)sulfonyl)amide ($LiNTf_2$), potassium hexafluorophosphate (KPF_6), potassium persulfate ($K_2S_2O_8$), hydrogen peroxide solution (30%), tripropylamine, sodium oxalate, and lithium perchlorate were purchased from Aladdin Industrial Inc. (China).

Instruments

^1H and ^{13}C NMR were recorded on a Bruker 400 MHz nuclear magnetic resonance (NMR) spectrometer (Bruker, Switzerland) with trimethylsilylation (TMS) as the internal standard. Peak multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet). UV−visible absorption and fluorescence spectra were recorded on a UV-1700 UV−vis spectrophotometer (Shimadzu, Japan) and a LS-55 fluorescence spectrometer (PerkinElmer, USA) equipped with a 1 cm quartz cell, respectively. Electrochemical measurements were carried out on a CHI 660D electrochemical workstation (CH Instruments, Inc., China) coupled with a three-electrode system (a wire auxiliary electrode (AE), a saturated calomel reference electrode (RE), and a working glassy carbon electrode (GCE)). The ECL experiments were performed on a MPI-E multifunctional electrochemical and chemiluminescent analytical system (Xi'an Remex Analytical Instrument Co., Ltd. China).

Synthesis of ***triYnPhPy***



triYnPhPy

To an oven-dried 100 mL Schlenk tube under a nitrogen atmosphere equipped with a magnetic bar were added $Pd(PPh_3)_4$ (0.116 g, 0.1 mmol), CuI (0.019 g, 0.1 mmol), 1,3,5-triethynylbenzene (0.3 g, 2 mmol), 4-(4-bromophenyl)pyridine (2.34 g, 10 mmol), and the mixed solvents of THF/EtN_3 (*v*/*v* = 1/1, 50 mL). The mixture was stirred at 60 °C in an oil bath for 48 h. After reaction, the crude sample was chromatographed on silica gel (CH_2Cl_2/methanol/Et_3N = 100/3/1) to afford **triYnPhPy** as a light red solid (0.464 g, 38%). ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.72-8.70 (m, 6H), 7.74 (s, 3H), 7.69-7.66 (m, 12H), and 7.55-7.52 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.5, 150.4, 147.3, 138.2, 134.4, 134.3, 132.5, 132.4, 127.1, 127.0, 124.0, 123.6, 121.5, 121.4, 90.2, and 89.3. MS (ESI) *m*/*z* calcd for triYnPhPy $C_{45}H_{27}N_3$; $[M + H]^+$: 610.118, found 610.225.

Fig. S1 ^{1}H and ^{13}C NMR of **triPy**$^{+}$ in DMSO-d_6.

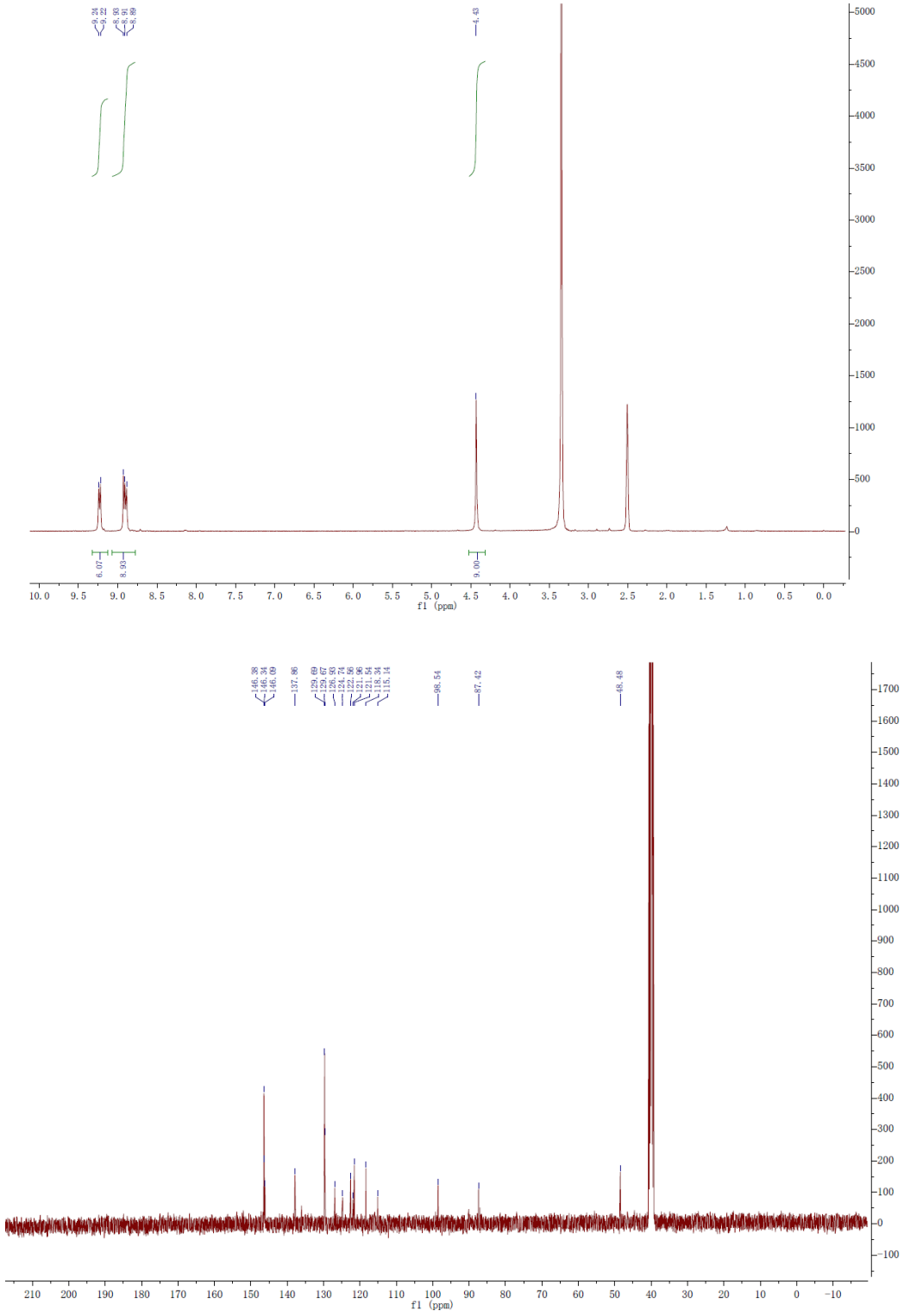
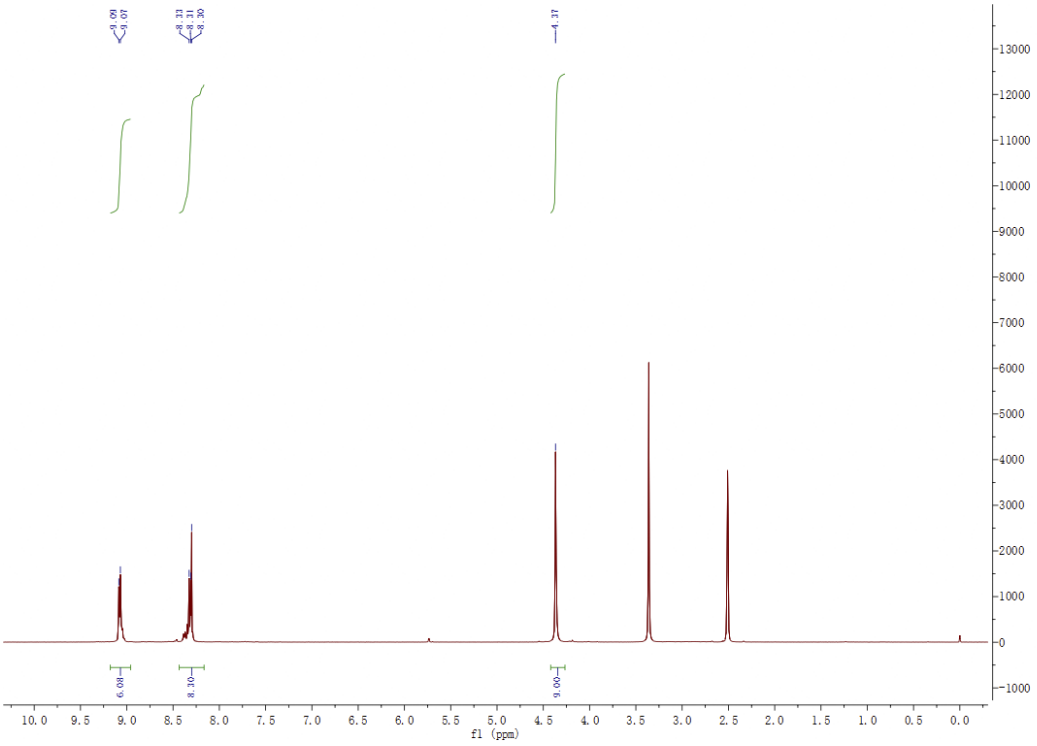


Fig. S2 ^{1}H and ^{13}C NMR of **triYnPy**$^{+}$ in DMSO-d_6.



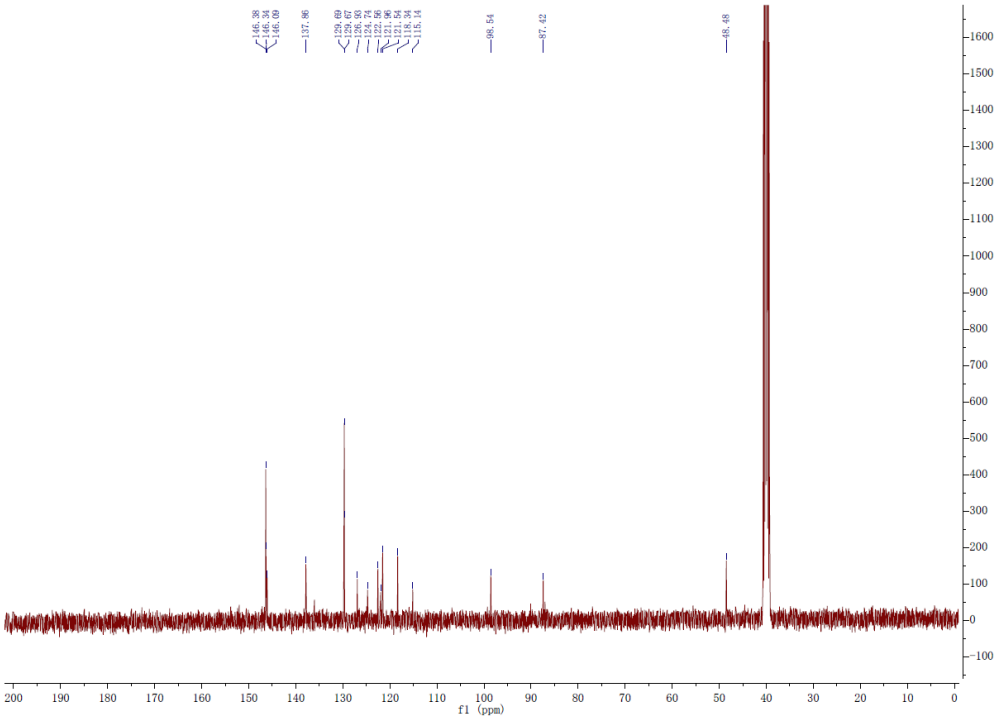
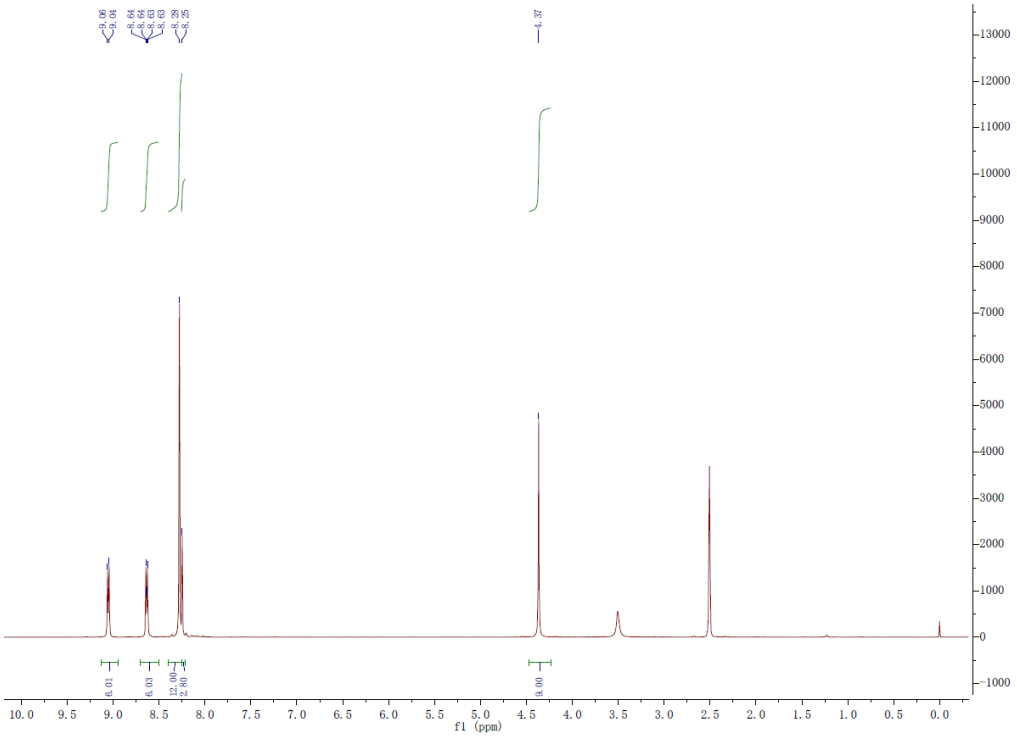


Fig. S3 ^{1}H and ^{13}C NMR of **triPhPy**$^{+}$ in DMSO-d_6.



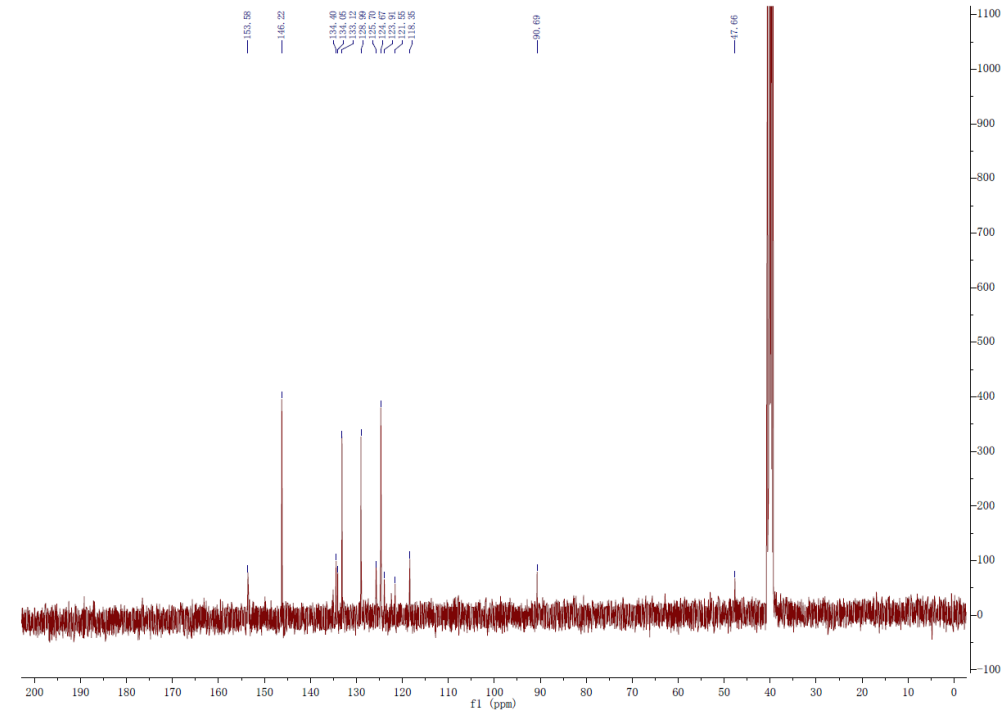
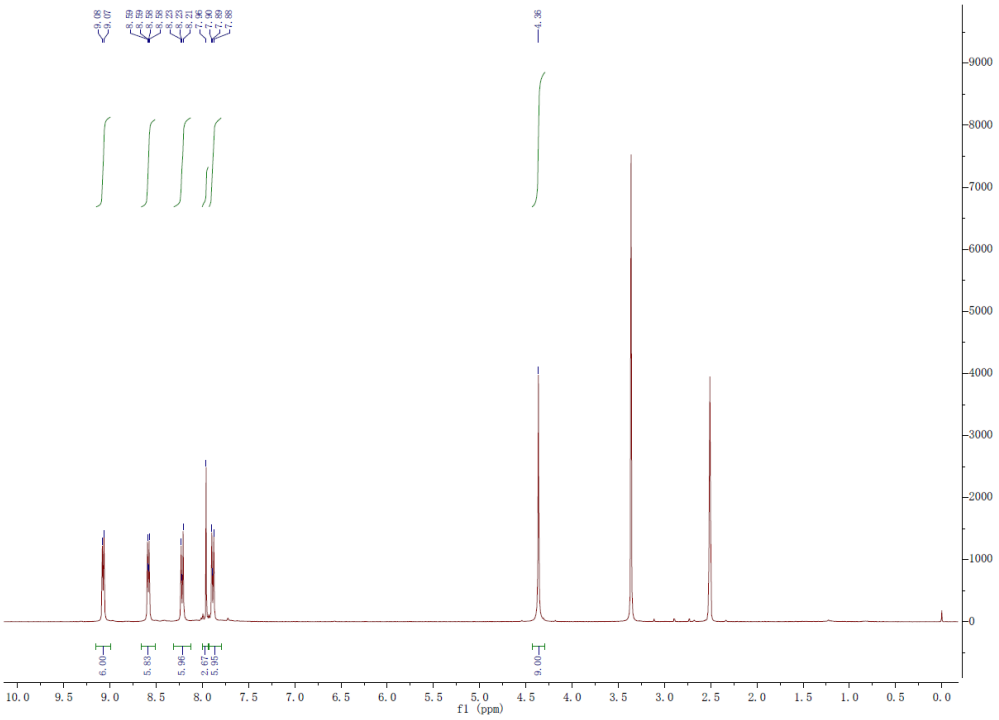


Fig. S4 ^{1}H and ^{13}C NMR of **triYnPhPy**$^{+}$ in DMSO-d_6.



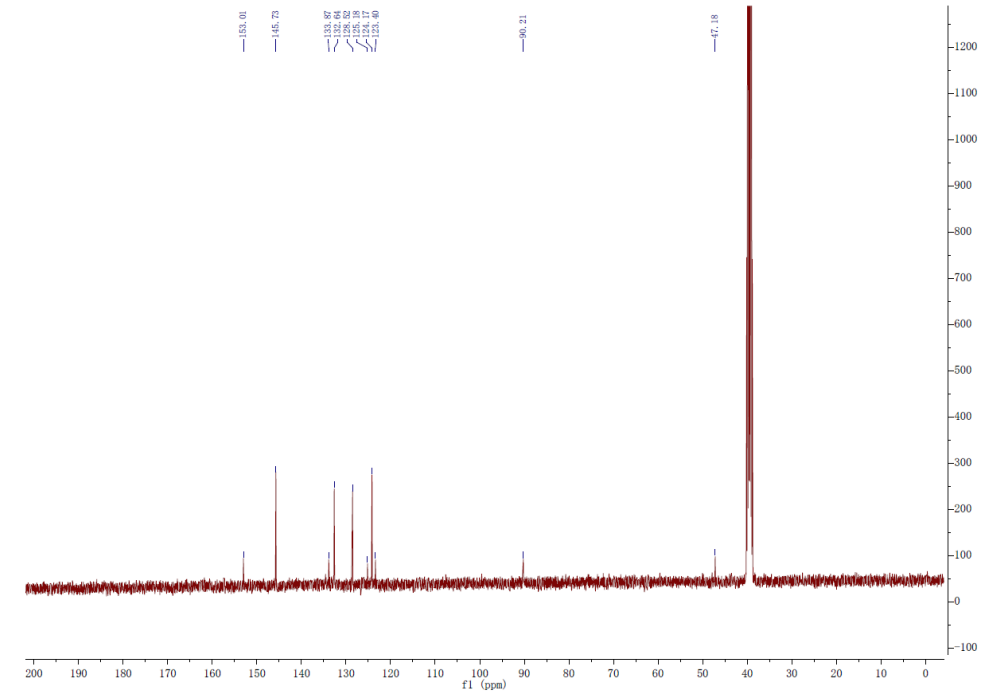
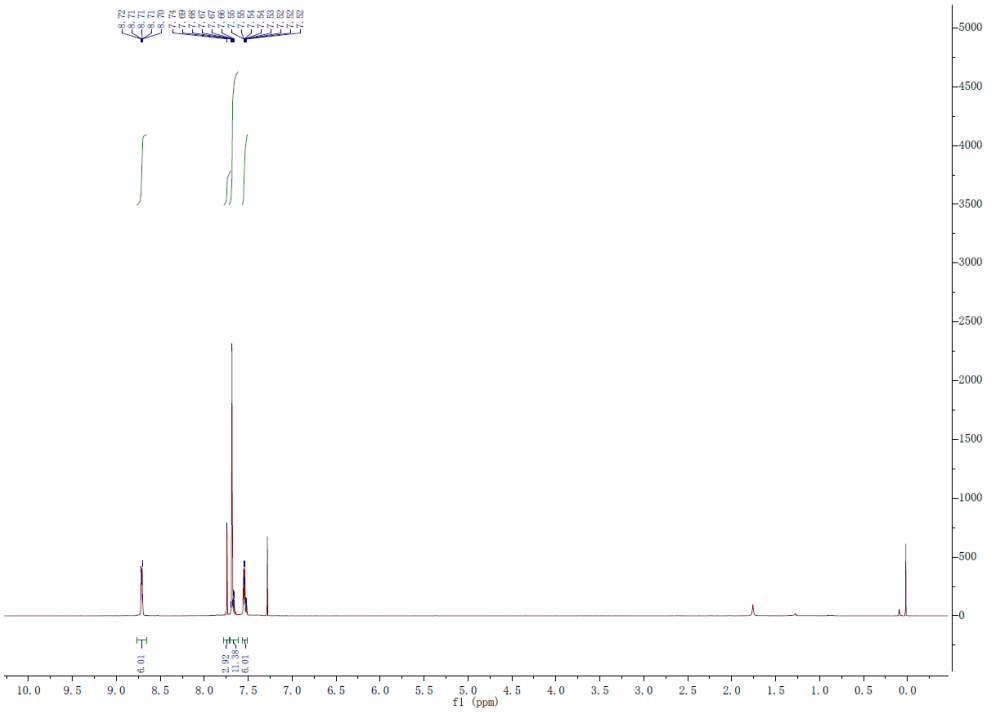


Fig. S5 ^{1}H and ^{13}C NMR of **triYnPhPy** in $CDCl_3$.



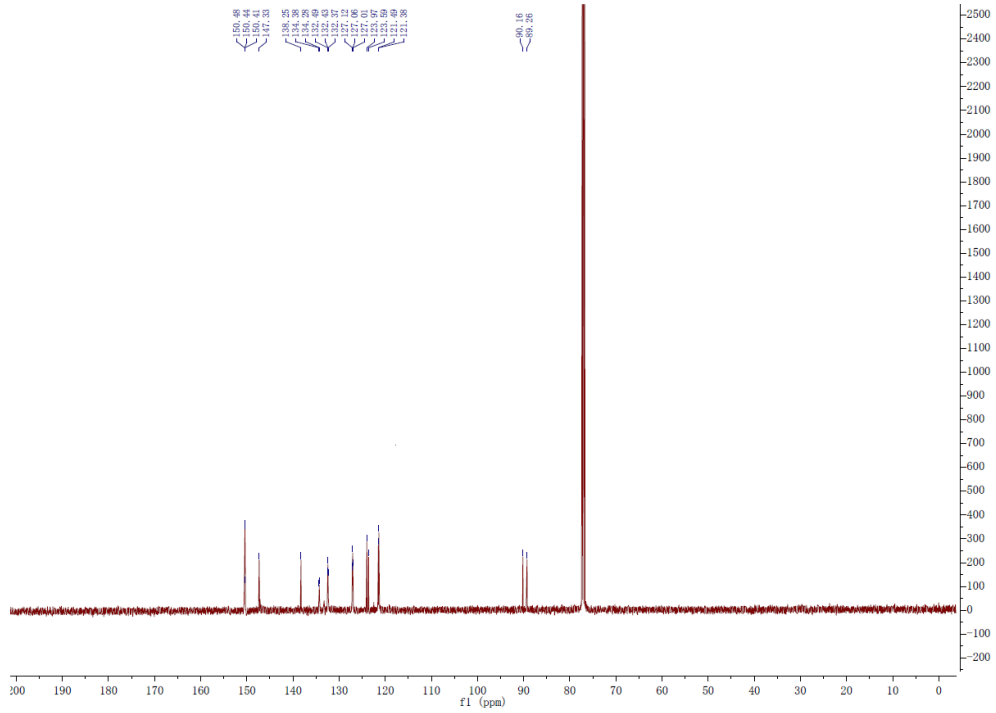


Fig. S6 Normalized UV−vis absorption spectra of **triPy**$^{+}$, **triYnPy**$^{+}$, **triPhPy**$^{+}$, and **triYnPhPy**$^{+}$ in the addition of $NaBH_4$.

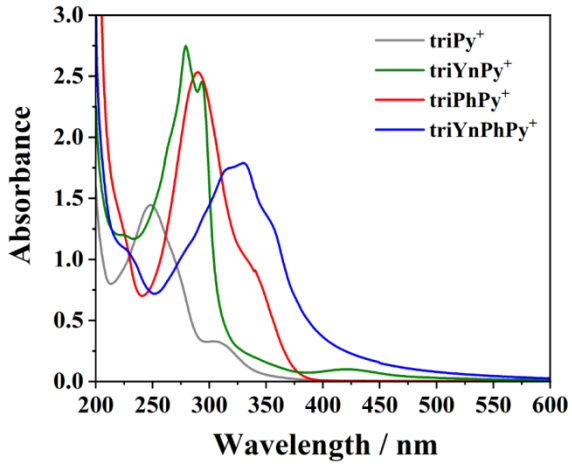


Fig. S7 Fluorescence photographs of **triPy**$^{+}$, **triYnPy**$^{+}$, **triPhPy**$^{+}$, and **triYnPhPy**$^{+}$ irradiated under 365 nm light.

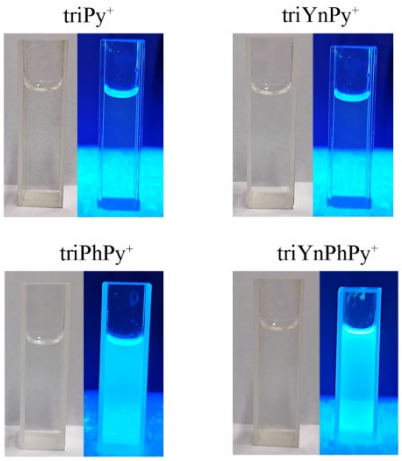


Fig. S8 PL decay profiles of **triPy**$^+$, **triYnPy**$^+$, **triPhPy**$^+$, and **triYnPhPy**$^+$ in CH_3CN/H_2O (1/1, *v*/*v*).

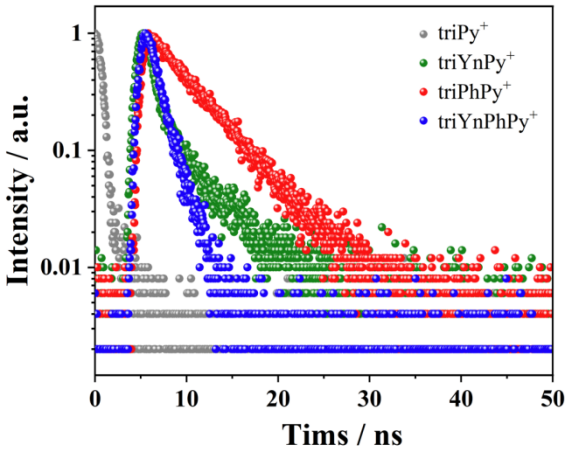


Table S1. Parameters of the PL decay profile curves for triPy$^+$, triYnPy$^+$, triPhPy$^+$, and triYnPhPy$^+$.

	$R(t) = B_1 e^{\left(\frac{-t}{\tau_1}\right)} + B_2 e^{\left(\frac{-t}{\tau_2}\right)}$					
	τ_1 / ns	τ_2 / ns	B_1	B_2	x^2	τ_{ave} / ns
triPy$^+$	0.6245(97.23%)	3.35(2.77%)	235.8	1.25	0.89	0.7
triYnPy$^+$	1.2817(63.33%)	8.4684(36.67%)	484.2	42.4	0.91	3.9
triPhPy$^+$	1.3812(69.41%)	12.5574(30.59%)	516.9	25.0	0.89	4.8
triYnPhPy$^+$	0.5262(95.19%)	20.0(4.81%)	702.1	0.93	0.93	1.5

Fig. S9 Differential pulse voltammetry measurements of **triPy**$^{+}$ in CH_3CN/H_2O (1/1, *v*/*v*) with $LiClO_4$ as supporting electrolyte.

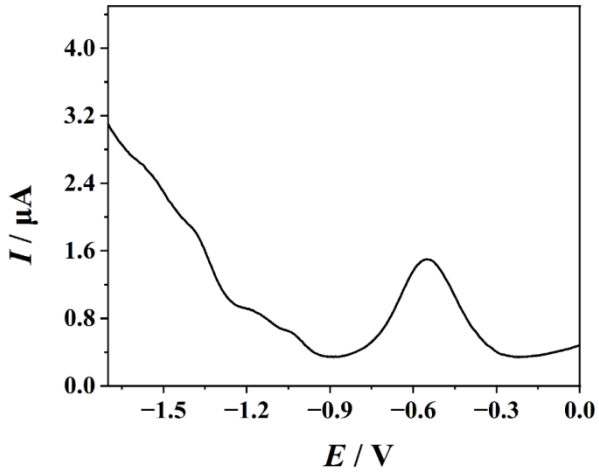


Fig. S10 Differential pulse voltammetry measurements of **triYnPy**$^{+}$ in CH_3CN/H_2O (1/1, *v*/*v*) with $LiClO_4$ as supporting electrolyte.

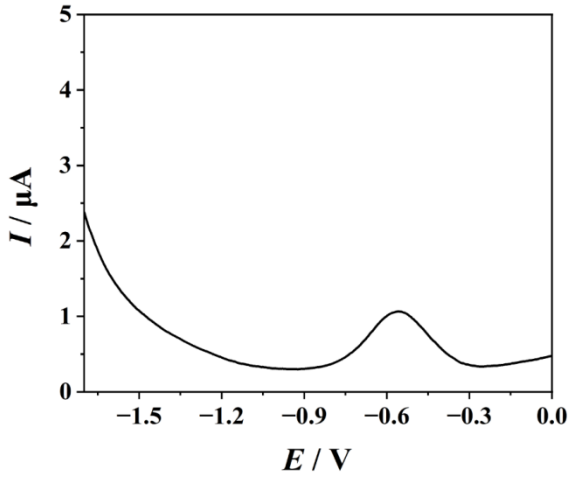


Fig. S11 Differential pulse voltammetry measurements of **triPhPy**$^{+}$ in CH_3CN/H_2O (1/1, *v*/*v*) with $LiClO_4$ as supporting electrolyte.

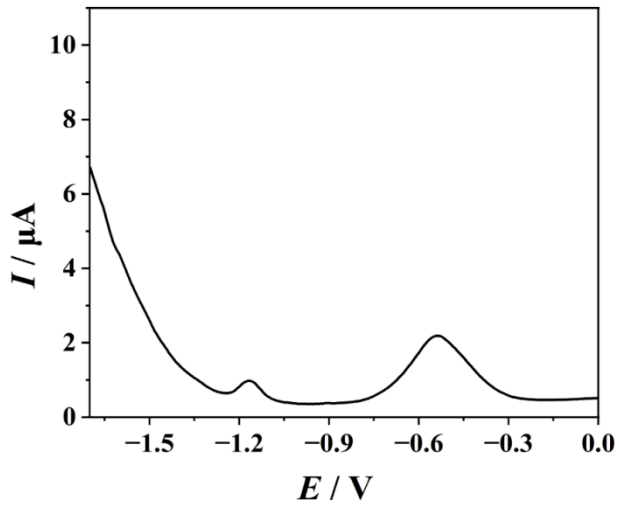


Fig. S12 Differential pulse voltammetry measurements of **triYnPhPy**$^{+}$ in CH_3CN/H_2O (1/1, *v*/*v*) with $LiClO_4$ as supporting electrolyte.

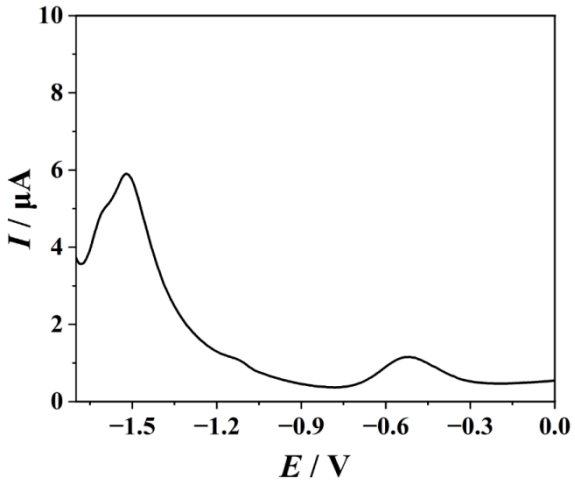


Fig. S13 ECL curves of **triPhPy**$^{+}$ in the presence of different co-reactants ($K_2S_2O_8$, $Na_2C_2O_4$, TPrA, and H_2O_2).

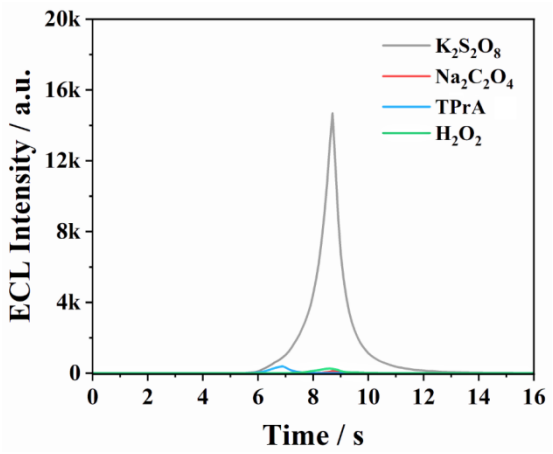


Fig. S14 ECL curves of **triPhPy**$^{+}$ coupled with the counterions including I^{-}, PF_6^{-}, and $[NTf_2]^{-}$.

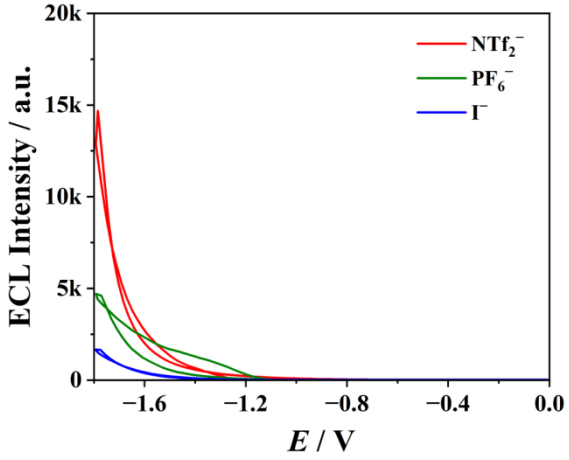


Fig. S15 ECL curves of **triPhPy**$^{+}$ in the addition of $K_2S_2O_8$ in various concentration.

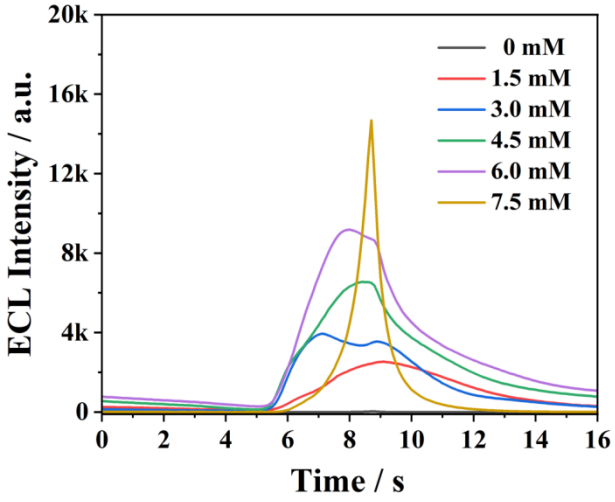


Fig. S16 ECL curves of **triPhPy**$^{+}$ operated at different scan rate (0.05, 0.1, 0.2, 0.5 V s^{-1}).

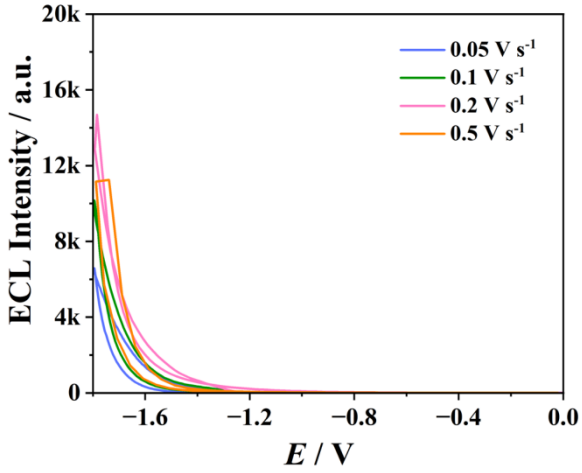


Fig. S17 ECL curves of **triPhPy**$^{+}$ at different pH.