Supplementary Information for Self-Enhanced Electrogenerated Chemiluminescence of Ruthenium (II) Complexes Conjugated with Schiff Bases

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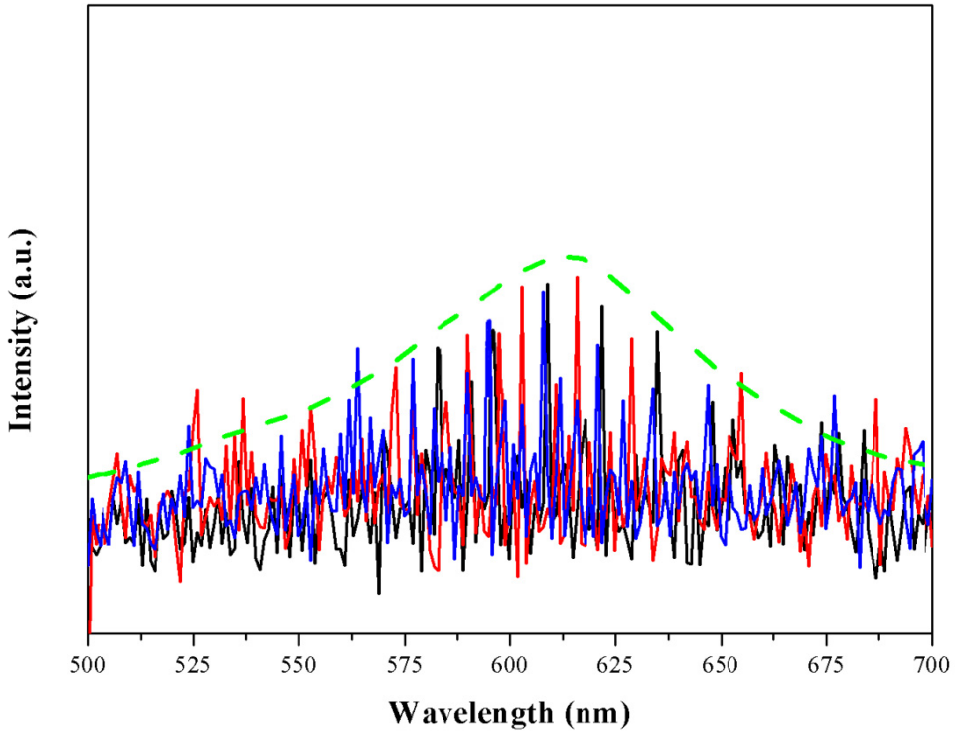

Fig. S1 ECL spectrum was obtained via CV between -1.4 V and 1.3 V in 0.2 M phosphate buffer solution (pH = 7.2) cotaining 90 μM Ru-PBI.

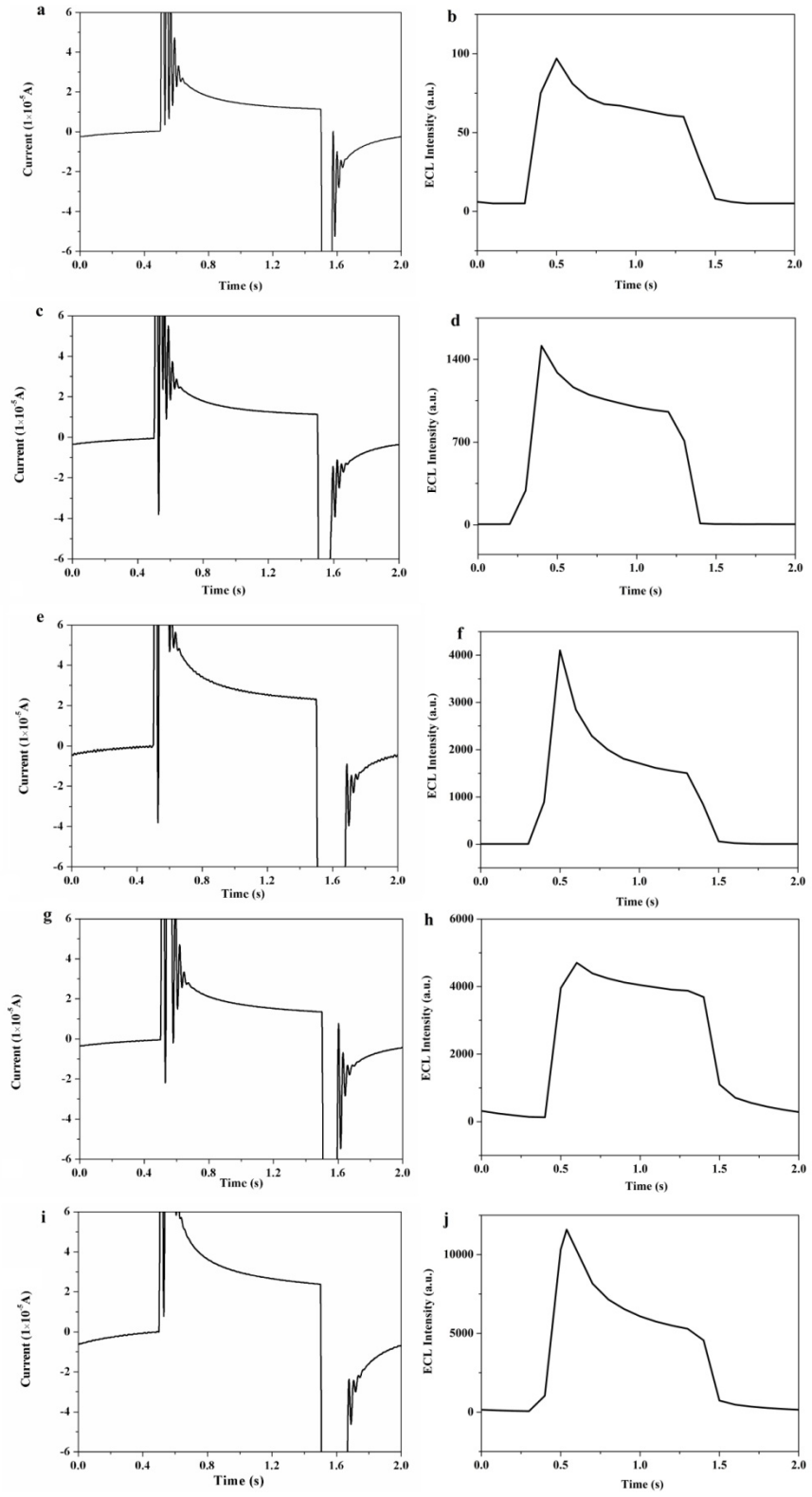

Fig. S2. a), c), e), g) and i) were obtained based on step potential chronoamperometry to count coulombs (integral areas of curves), respectively from 0.2 M PBS of 4.5 μM Ru-BP, Ru-PBI-M, Ru-BP with addition of 16 μM TPrA, Ru-PBI-H and Ru-BP with addition of 36 μM. b), d), f), h) and j) were corresponding ECL intensitys of a), c), e), g) and i) (integral areas of curves). The applied potential of step potential chronoamperometry is 1.2 V and the pulse time is 1.0 s. All data were gained at room temperature (25 ℃)

Table S1. The values of integral areas separately.

Curves	Integral areas
a (Q^0)	1.88
c (Q^1)	1.81
e (Q^2)	3.49
g (Q^3)	2.22
i (Q^4)	3.71
b (I^0)	79.15
d (I^1)	1113.8
f (I^2)	2131.5
h (I^3)	4506.5
j (I^4)	7374.5

Table S2. Energy band structures of Ru-BP, Ru-PBI and Ru-PBI-M-Co.

Complexes	Ru-BP	Ru-PBI	Ru-PBI-Co
$E^{ox\,\theta}$ (V)	1.447	0.847	0.917
E_{HOMO}[a] (eV)	-5.947	-5.347	-5.417
$E^{red\,\theta}$ (V)	-1.123	-0.853	-0.973
E_{LUMO}[b] (eV)	-3.377	-3.647	-3.527
E_g[c] (eV)	2.57	1.70	1.89
E_{HOMO}[d] (eV)	-5.967	-2.299	—
E_{LUMO}[d] (eV)	-2.492	-1.465	—
E_g[d] (eV)	3.475	0.834	—

[a] $|E_{HOMO}| = E^{ox\theta} + 4.5eV$, $E_{HOMO} < 0$.

[b] $|E_{LUMO}| = E^{red\theta} + 4.5eV$, $E_{LUMO} < 0$. Where $E^{ox\,\theta}$ and $E^{red\,\theta}$ are the first oxidation potentials and the first reduction potentials versus NHE.

[c] $E_g = E_{LUMO} - E_{HOMO}$.

[d] theoretical values obtained via Gaussian09 package.

Table S3. Composition (%) of frontier molecular orbitals of Ru-BP and Ru-PBI.

Complexes	HOMO			LUMO		
	Ru	**bpy**	**PBI**	**Ru**	**bpy**	**PBI**
Ru-BP	80.27	19.73	—	1.229	98.77	—
Ru-PBI	0.02261	0.03739	99.94	7.603	33.65	58.75

Table S4. The coordinates of the optimized structures for Ru-BP and Ru-PBI (the geometries were optimized at the B3LYP/6-31G level in Gaussian09 package).

Coordinates of Ru-BP:

N	7.7496	-1.7454	16.8376
C	8.6678	-2.6395	16.3656
C	8.9443	-3.8121	17.0647
H	9.5678	-4.4164	16.733
C	7.1352	-2.0213	18.0011
H	6.5105	-1.4163	18.3265
C	8.2924	-4.0755	18.2489
H	8.4608	-4.8625	18.7128
C	7.3889	-3.1611	18.7359
H	6.9577	-3.3076	19.5484
N	9.0149	1.0149	16.8376
C	9.33	2.2572	16.3656
C	10.2073	3.0829	17.0647
H	10.4189	3.9251	16.733
C	9.561	0.6208	18.0011
H	9.3494	-0.2227	18.3265
C	10.7614	2.65	18.2489
H	11.3588	3.1893	18.7128
C	10.4212	1.4104	18.7359
H	10.7637	1.1102	19.5484
N	5.9917	0.7305	16.8376
C	4.7583	0.3823	16.3656
C	3.6046	0.7292	17.0647
H	2.7694	0.4914	16.733
C	6.06	1.4005	18.0011
H	6.8963	1.639	18.3265
C	3.7024	1.4255	18.2489
H	2.9367	1.6732	18.7128
C	4.9461	1.7507	18.7359
H	5.0348	2.1974	19.5484
N	9.0149	-1.0149	14.6549
C	9.33	-2.2572	15.1269
C	10.2073	-3.0829	14.4278
H	10.4189	-3.9251	14.7595
C	9.561	-0.6208	13.4914
H	9.3494	0.2227	13.166
C	10.7614	-2.65	13.2436
H	11.3588	-3.1893	12.7797
C	10.4212	-1.4104	12.7566
H	10.7637	-1.1102	11.9441

N	5.9917	-0.7305	14.6549
C	4.7583	-0.3823	15.1269
C	3.6046	-0.7292	14.4278
H	2.7694	-0.4914	14.7595
C	6.06	-1.4005	13.4914
H	6.8963	-1.639	13.166
C	3.7024	-1.4255	13.2436
H	2.9367	-1.6732	12.7797
C	4.9461	-1.7507	12.7566
H	5.0348	-2.1974	11.9441
N	7.7496	1.7454	14.6549
C	8.6678	2.6395	15.1269
C	8.9443	3.8121	14.4278
H	9.5678	4.4164	14.7595
C	7.1352	2.0213	13.4914
H	6.5105	1.4163	13.166
C	8.2924	4.0755	13.2436
H	8.4608	4.8625	12.7797
C	7.3889	3.1611	12.7566
H	6.9577	3.3076	11.9441
Ru	7.5854	0	15.7462

Coordinates of Ru-PBI:

C	-0.63167	3.47298	0.17784
C	0.6307	2.9154	0.06569
C	0.7593	1.50523	-0.05682
C	-0.43448	0.74299	-0.06764
C	-1.77809	2.65132	0.15994
C	2.04004	0.85111	-0.15063
C	-0.38812	-0.67238	-0.23472
C	0.86241	-1.34424	-0.3675
C	2.09779	-0.57164	-0.26726
C	0.79453	-2.73269	-0.66038
H	1.69625	-3.30059	-0.83647
C	-0.44368	-3.36699	-0.75435
C	-1.6239	-2.65434	-0.54451
H	-0.75707	4.54538	0.2778
H	1.53809	3.5082	0.06207
H	-2.77642	3.05882	0.24266
H	-0.49778	-4.42406	-0.98973
H	-2.59861	-3.11925	-0.58499
N	-1.60312	-1.31825	-0.28875
N	-1.68422	1.31592	0.02773
C	-5.13442	-2.38164	0.77425
C	-6.1628	-3.29415	0.59576
C	-6.80318	-3.35908	-0.66659
C	-6.37612	-2.52441	-1.68328
C	-5.31351	-1.61119	-1.46928
H	-4.62606	-2.28059	1.72437
H	-6.47313	-3.92744	1.41798
H	-7.61529	-4.05789	-0.83563
H	-6.84782	-2.57225	-2.65795
C	-4.73144	-0.77072	-2.47358
C	-5.15097	-0.69828	-3.82612
C	-4.44558	0.06091	-4.74188
H	-6.02863	-1.25076	-4.1416
C	-2.92602	0.69378	-2.97911
C	-3.2901	0.7625	-4.31462
H	-4.76825	0.11244	-5.77612
H	-2.06551	1.23033	-2.60065
H	-2.69965	1.35016	-5.00692
C	-5.97496	2.40345	2.23806
C	-4.98496	1.47717	1.815
C	-5.47005	2.02982	-0.4455
C	-6.4451	2.94012	-0.06796
C	-6.70047	3.12942	1.3135

H	-6.15342	2.54395	3.29763
H	-5.24118	1.84992	-1.48727
H	-7.00007	3.48267	-0.82353
H	-7.45432	3.83727	1.6411
C	-4.16385	0.69616	2.69397
C	-4.25249	0.70136	4.1094
C	-2.34552	-0.82865	2.83926
C	-3.38162	-0.0544	4.87295
H	-5.01166	1.30464	4.59308
C	-2.39161	-0.83323	4.22536
H	-1.61495	-1.41646	2.29888
H	-3.45474	-0.04796	5.95513
H	-1.68134	-1.42567	4.789
N	-4.70482	-1.54584	-0.20993
N	-3.6257	-0.0197	-2.05394
N	-4.74165	1.30463	0.44752
N	-3.206	-0.10967	2.06926
N	3.35018	-1.14733	-0.35886
N	3.09979	1.73765	-0.10749
C	3.72729	-2.31211	0.09673
C	4.36691	1.49536	0.04593
C	5.48323	-4.02567	0.43985
C	6.77592	-4.52817	0.21548
C	7.67659	-3.85008	-0.60217
C	7.2655	-2.64684	-1.20802
C	5.98752	-2.144	-0.99307
C	5.06645	-2.82024	-0.154
H	8.67308	-4.23697	-0.77798
H	7.95597	-2.11583	-1.85481
H	5.65679	-1.22851	-1.46829
C	7.80748	2.99049	0.13839
C	7.57529	4.36904	-0.00729
C	6.2627	4.81118	-0.13464
C	5.1695	3.9192	-0.12408
C	5.39309	2.5328	0.01901
C	6.7398	2.10254	0.15161
H	8.82384	2.62561	0.24048
H	8.40455	5.0659	-0.01736
H	6.92193	1.03785	0.26088
O	4.61454	-4.7317	1.26018
H	5.0749	-5.53436	1.58537
O	3.90222	4.46164	-0.24676
H	4.00517	5.43576	-0.33396
H	4.74473	0.48481	0.20287

Ru	-3.26169	-0.0759	-0.01181
H	3.08858	-2.93105	0.72808
H	6.96093	-5.44873	0.72856
H	5.96086	5.83155	-0.24707

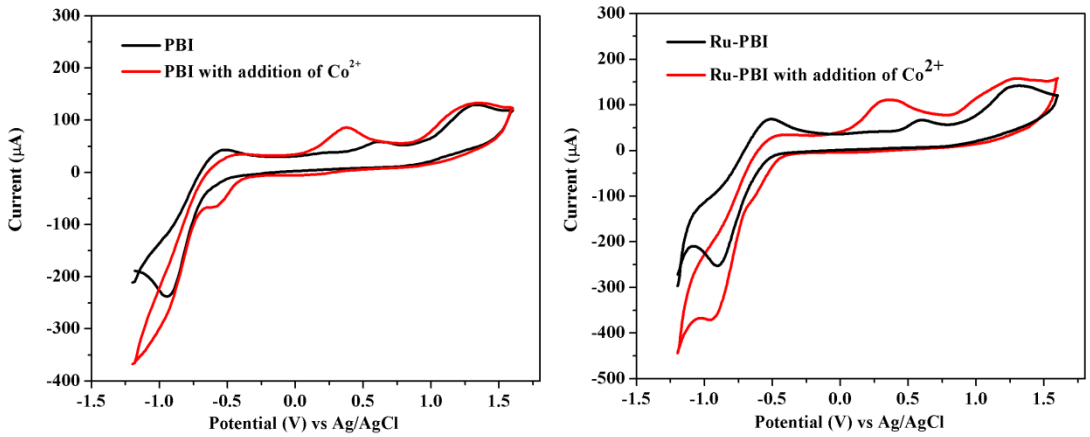

Fig. S3 CVs of Ru complex and the Schiff base ligand before and after addition of Co^{2+} in MeCN (90 uM PBI and Ru-PBI with addition of 180 uM Co^{2+} respectively, Ag/AgCl electrode as reference, 0.1M $TBAClO_4$ as supporting electrolyte) with the scan rate of 200 mV s^{-1}.

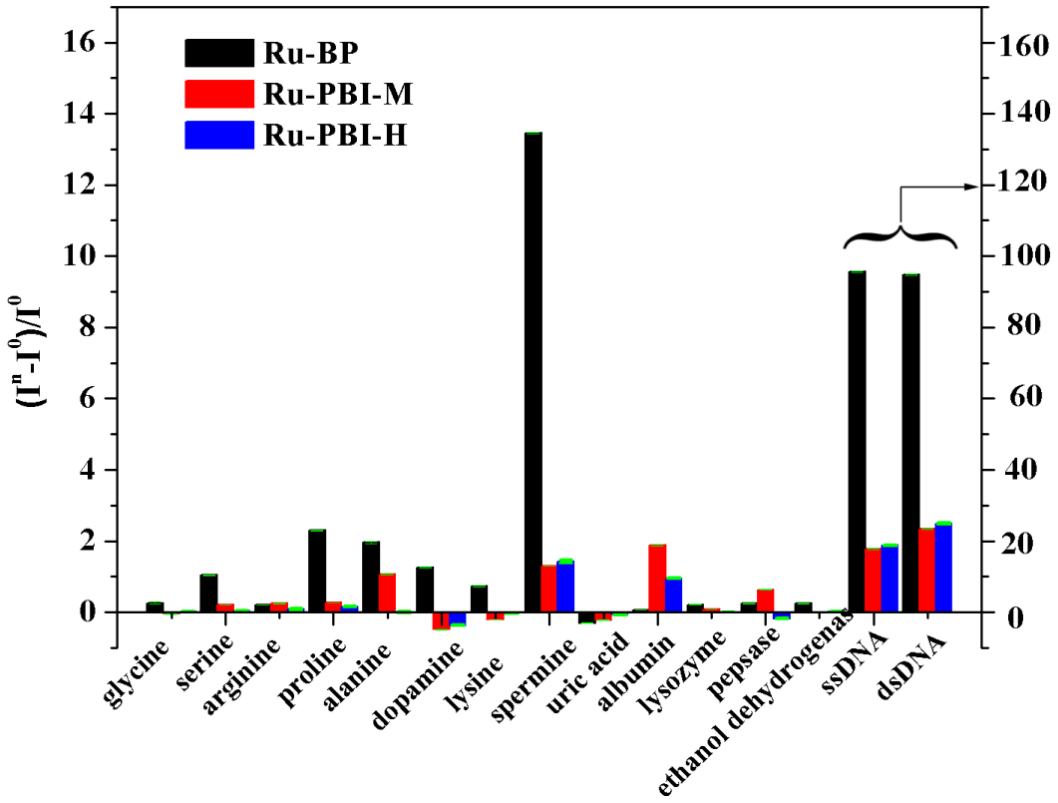

Fig. S4 Interference of some amine derivatives (glycine, serine, arginine, proline, alanine, dopamine, lysine, spermine and uric acid with the same concentration of 18 uM and albumin, lysozyme, pepsase, ethanol dehydrogenase with 4 mg L^{-1} and ssDNA, dsDNA with 2 uM) for ECL intensity of Ru-BP, Ru-PBI-M and Ru-PBI-H (I^n is the ECL intensity after the addition of 18 uM amine derivatives and I^0 is the initial intensity).

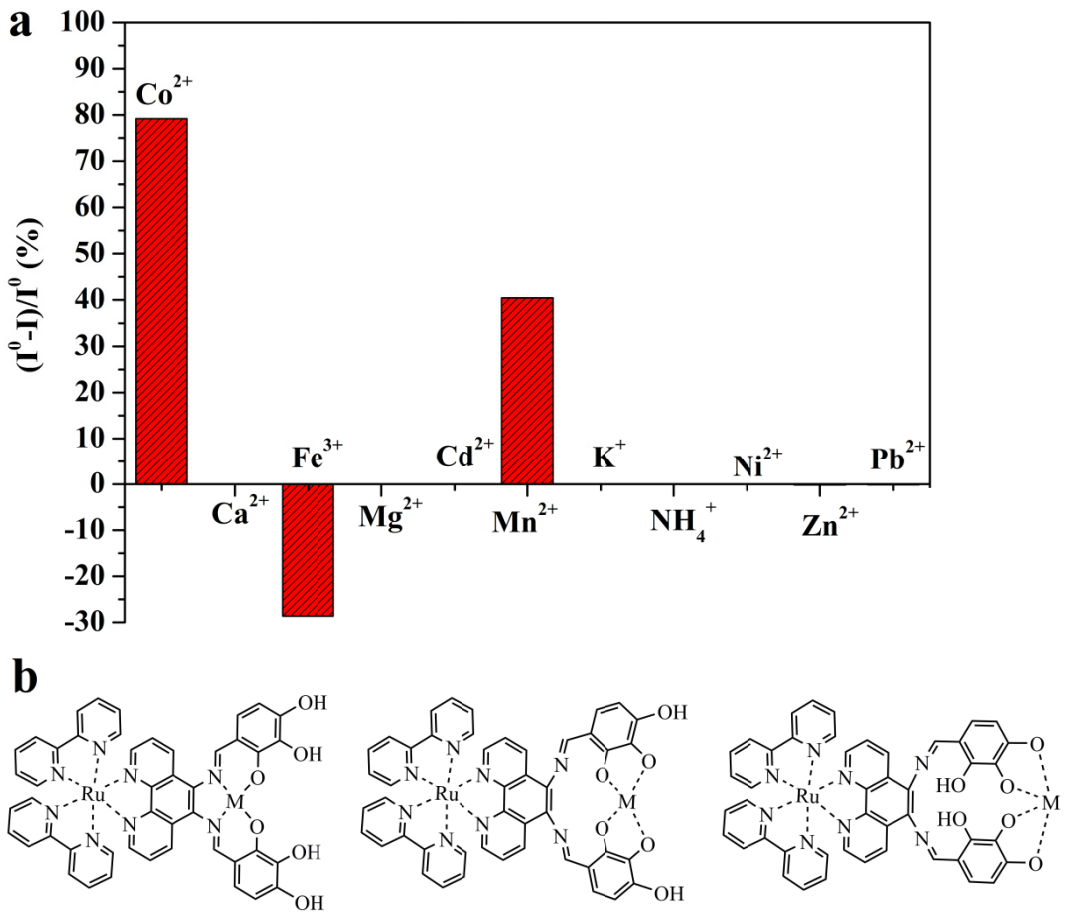

Fig. S5 a) Quenching efficiency on ECL intensity of 45 μM various metal ions adding to 4.5 μM Ru-PBI-H in 0.2M PBS (pH = 7.2). b) Probable bonding modes of metal ions for Ru-PBI-H.

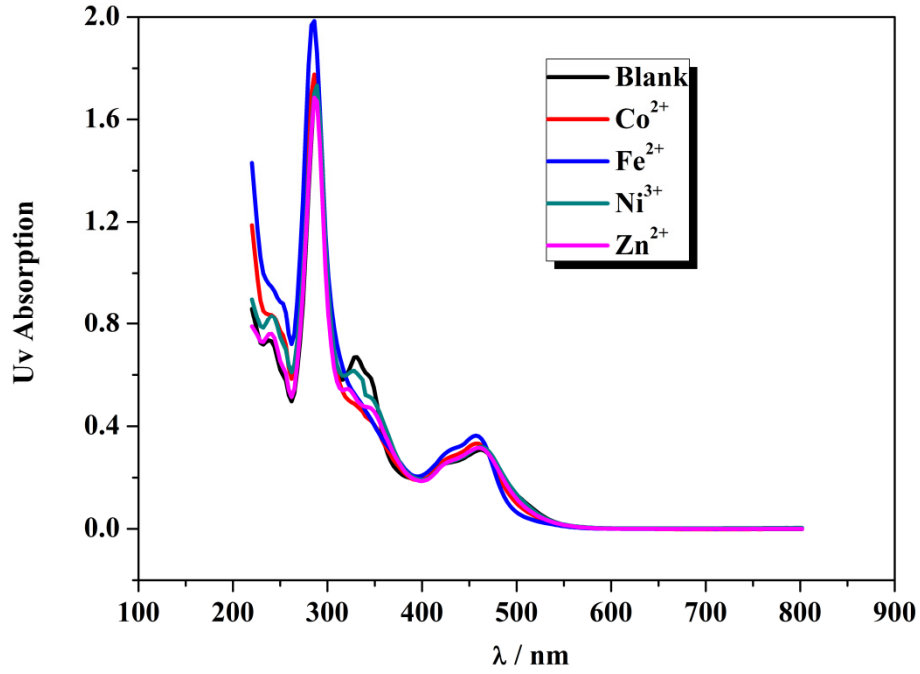

Fig. S6 UV-Vis spectra of Ru-PBI-M (blank) in ethanol and Ru-PBI-M bonding with Co^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}(2 eq. metal ions involved related to Ru-PBI-M).

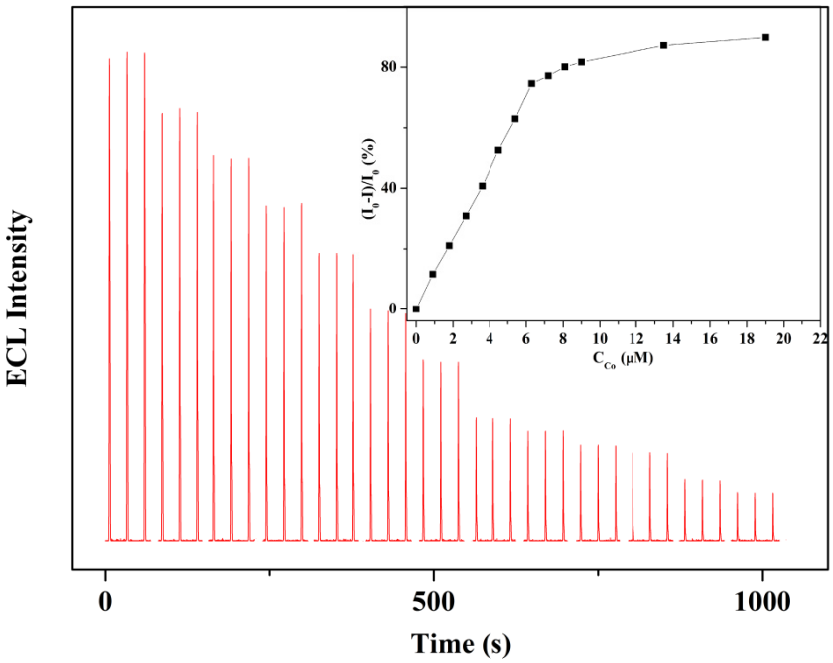

Fig. S7 ECL peak intensity with the addition of different Co^{2+} concentration. Inset is the correlation between the Co^{2+} concentration and the ECL quenching efficiency. ECL experiments were conducted in 0.2 M PBS (pH = 7.2) including 4.5 μM Ru-PBI-M.

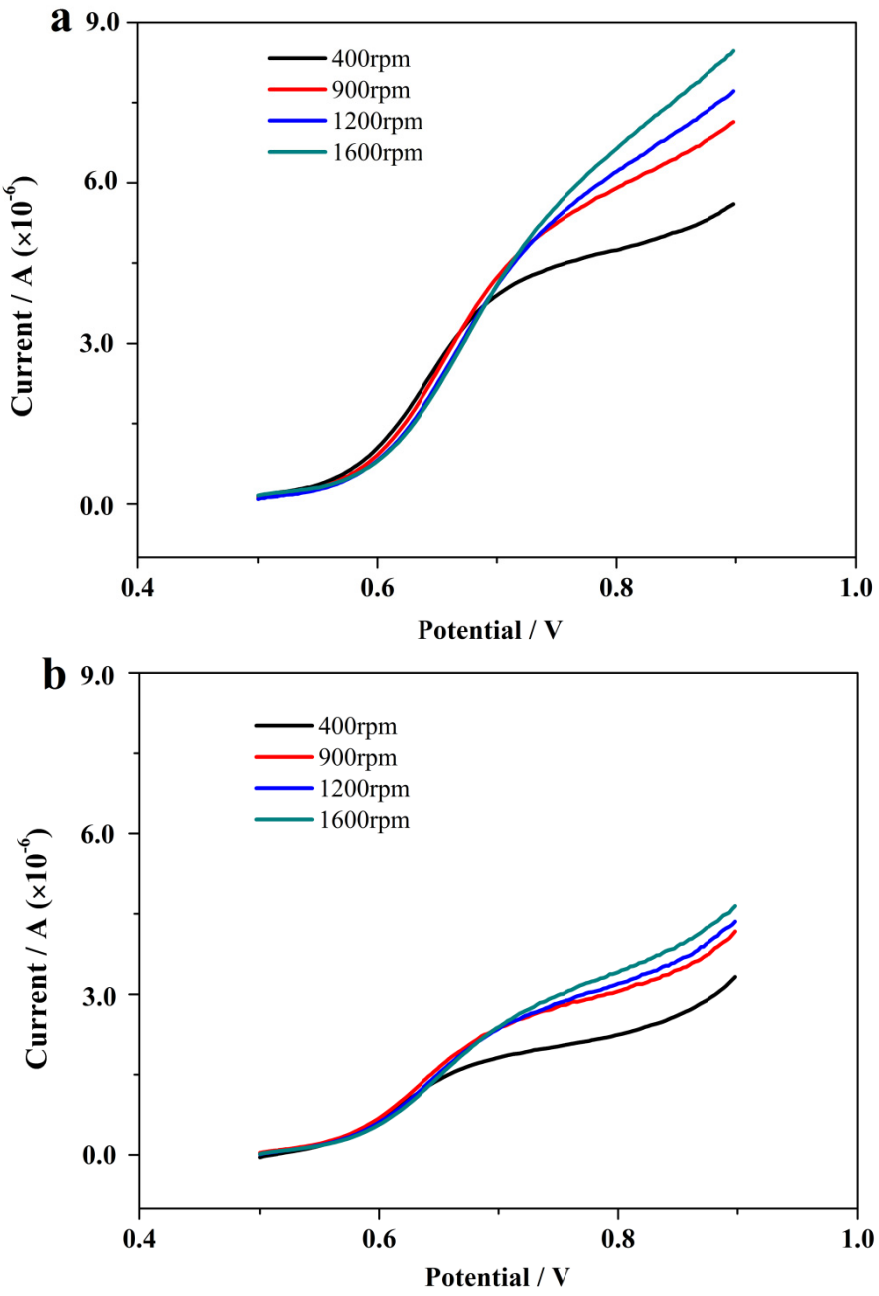

Fig. S8 Polarization curves of Ru-PBI-M (a) and Ru-PBI-M-Co (b) at different rotation (rates scan rate is kept at 5 mV s^{-1}).

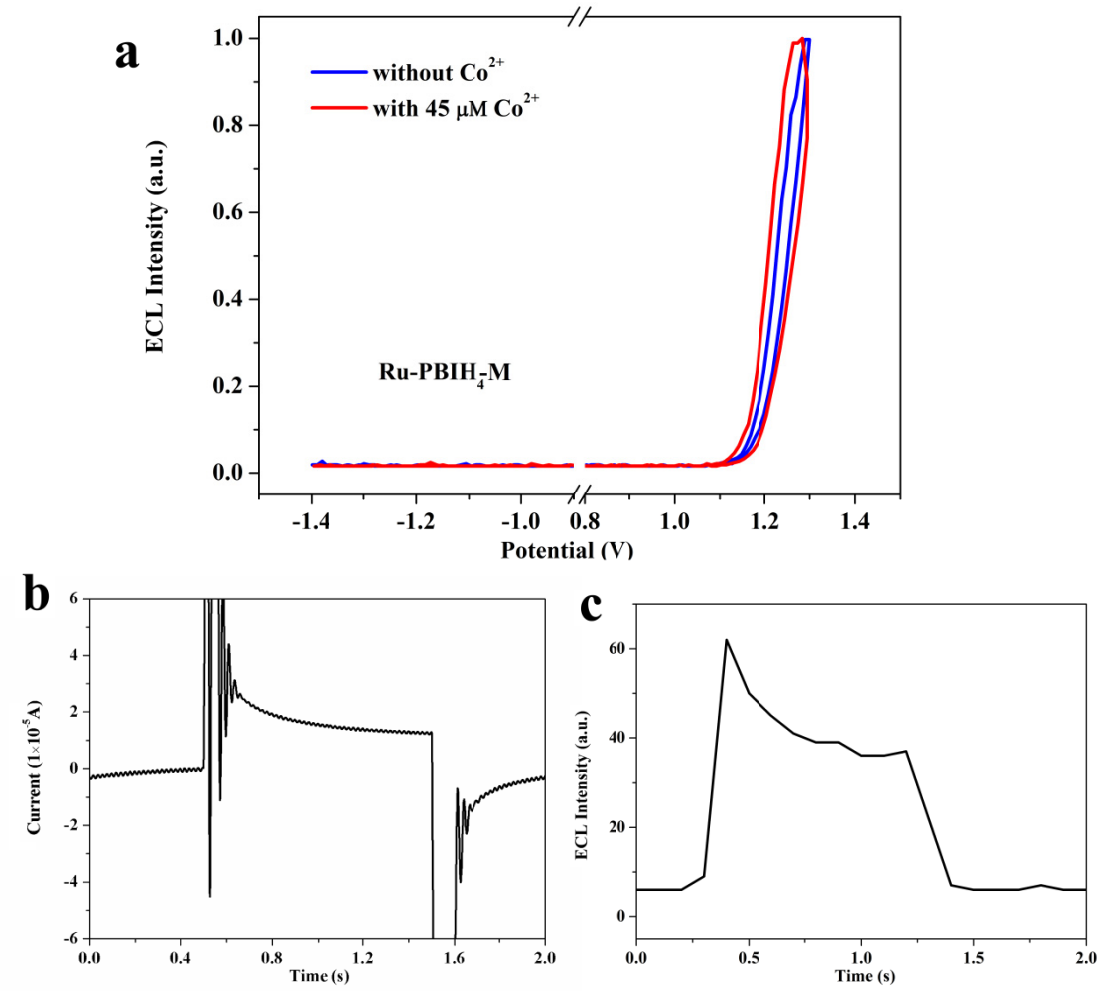

Fig. S9 Co^{2+} recognition of Ru-$PBIH_4$-M (a), step potential (b) and corresponding ECL intensity (c) of 4.5 μM Ru-$PBIH_4$-M in 0.2 M PBS. Measuring method is in accordance with Fig. S2.

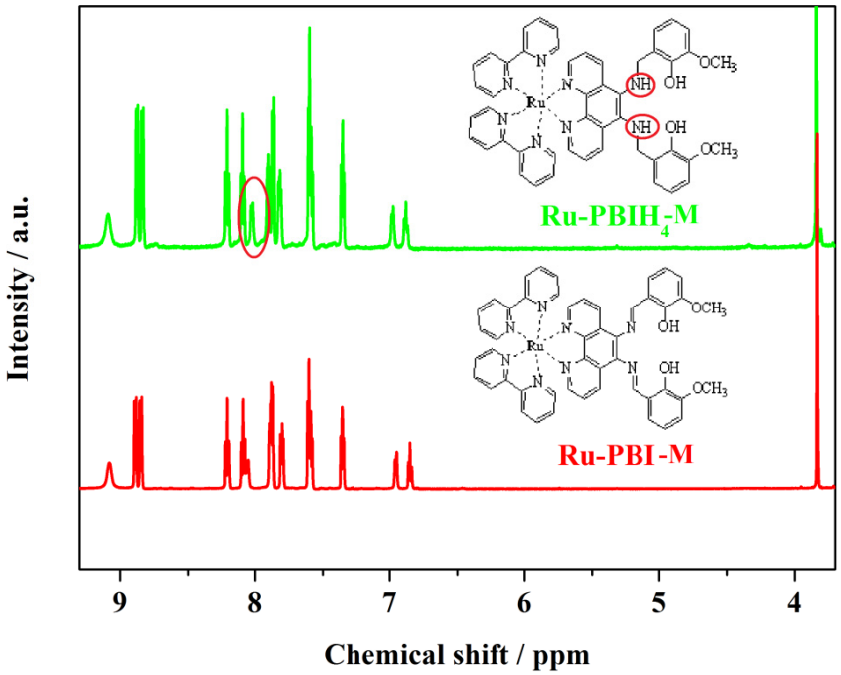

Fig. S10 ^{1}H NMR of Ru-PBIH$_4$-M and Ru-PBI-M.

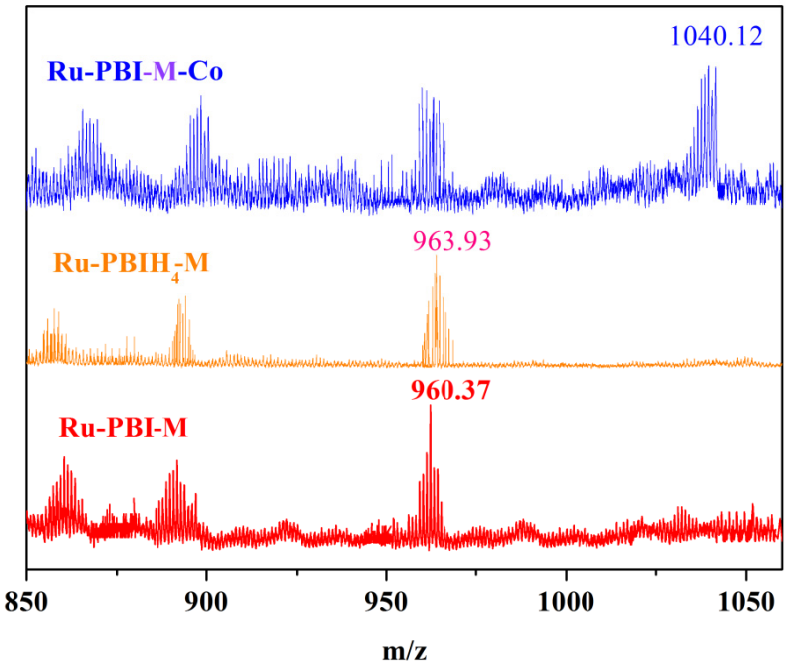

Fig. S11 MALDI-TOF-MS of Ru-PBI-M-Co, Ru-PBIH$_4$-M and Ru-PBI-M.