Supporting Information

Influence of reaction temperature and stoichiometry on the coordination mode of a multidentate pyridylpyrazole ligand in Co(II) complexes: from 0D mononuclear to 3D frameworks

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Table S1a. Selected bond lengths (Å) and angles (°) for complex **1**.

1			
Co1−O1	2.0966(13)	Co1−O3	2.1164(14)
Co1−N	2.1119(14)	Co1−O1^{a}	2.0966(13)
Co1−O3^{a}	2.1164(14)	Co1−N1^{a}	2.1119(14)
O1−Co1−O3	172.46(5)	O1−Co1−N1	77.99(5)
O1−Co1−O1^{a}	94.74(5)	O1−Co1−O3^{a}	89.35(5)
O1−Co1−N1^{a}	96.72(5)	O3−Co1−N1	95.27(5)
O1^{a}−Co1−O3	89.35(5)	O3−Co1−O3^{a}	87.32(5)
O3−Co1−N1^{a}	90.32(5)	O1^{a}−Co1−N1	96.72(5)
O3^{a}−Co1−N1	90.32(5)	N1−Co1−N1^{a}	172.29(6)
O1^{a}−Co1−O3^{a}	172.46(5)	O1^{a}−Co1−N1^{a}	77.99(5)
O3^{a}−Co1−N1^{a}	95.27(5)		
Symmetry code: a = 1−x, y, 1/2−z			

Table S1b. Selected bond lengths (Å) and angles (°) for complex **2**.

2			
Co1−O2	2.0656(12)	Co1−N1	2.2226(14)
Co1−O2^{a}	2.0656(12)	Co1−N1^{a}	2.2226(14)
Co1−N3^{b}	2.1411(16)	Co1−N3^{c}	2.1411(16)
O2−Co1−N1	76.50(5)	O2−Co1−O2^{a}	166.15(5)
O2−Co1−N1^{a}	93.23(5)	O2−Co1−N3^{b}	87.90(6)
O2−Co1−N3^{c}	101.94(6)	O2^{a}−Co1−N1	93.23(5)
N1−Co1−N1^{a}	85.51(5)	N1−Co1−N3^{b}	164.34(5)
N1−Co1−N3^{c}	94.21(5)	O2^{a}−Co1−N1^{a}	76.50(5)
O2^{a}−Co1−N3^{b}	101.94(6)	O2^{a}−Co1−N3^{c}	87.90(6)
N1^{a}−Co1−N3^{b}	94.21(5)	N1^{a}−Co1−N3^{c}	164.34(5)
N3^{b}−Co1−N3^{c}	90.23(6)		
Symmetry code: a = −x, y, 1/2−z; b = −1/2+x, 1/2+y, z; c = 1/2−x, 1/2+y, 1/2−z			

Table S1c. Selected bond lengths (Å) and angles (°) for complex **3**.

		3	
Co1−Cl1	2.4576(13)	Co1−O2	2.085(3)
Co1−O3	2.157(3)	Co1−N1	2.171(3)
Co1−N3[a]	2.153(3)	Co1−O1[b]	2.027(3)
Cl1−Co1−O2	87.16(9)	Cl1−Co1−O3	175.61(10)
Cl1−Co1−N1	91.11(11)	Cl1−Co1−N3[a]	92.20(10)
Cl1−Co1−O1[b]	93.83(8)	O2−Co1−O3	88.57(13)
O2−Co1−N1	77.86(12)	O2−Co1−N3[a]	88.83(12)
O1[b]−Co1−O2	176.96(11)	O3−Co1−N1	86.99(14)
O3−Co1−N3[a]	88.73(13)	O1[b]−Co1−O3	90.48(12)
N1−Co1−N3[a]	166.10(13)	O1[b]−Co1−N1	104.97(13)
O1[b]−Co1−N3[a]	88.27(12)		
Symmetry code: a = 1/2+x, –1/2+y, z; b = –1/2+x, 3/2–y, –1/2+z			

Table S2 Hydrogen bond parameters for complexes **1**–**3**.

D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	D–H…A (°)
1				
N2−H2…O2[a]	0.8600	1.8500	2.697(2)	167.00
O3−H3A…N3[b]	0.8200	2.0100	2.804(2)	164.00
O3−H3B…O1[a]	0.8400	2.3700	3.0556(19)	139.00
O3−H3B…O2[a]	0.8400	2.2300	3.043(2)	162.00
C9−H9…O2[a]	0.9300	2.5300	3.427(3)	162.00
Symmetry code: a = 1/2+x,1/2+y,z; b = x,1–y,1/2+z				
2				

N2−H2…O1[a]	0.8600	1.9300	2.687(2)	145.00
C7−H7…O2[b]	0.9300	2.3700	2.904(3)	116.00
C9−H9…O2[a]	0.9300	2.5700	3.454(2)	158.00

Symmetry code: a = 1/2+x, 1/2–y, 1/2+z; b = 1/2+x, –1/2+y, z

3

N2−H2A…Cl1[a]	0.8600	2.8000	3.638(4)	166.00
N2−H2A…O2[a]	0.8600	2.4700	2.978(4)	118.00
O3−H3A…Cl1[b]	0.8000	2.4900	3.267(4)	165.00
O3−H3B…Cl1[c]	0.6800	2.7100	3.287(4)	145.00
C7−H7…O2[d]	0.9300	2.4600	2.981(5)	115.00
C9−H9…Cl1[a]	0.9300	2.8000	3.691(4)	161.00

Symmetry code: a = –1/2+x, 3/2–y, –1/2+z; b = 1/2+x, 3/2–y, –1/2+z; c = x, y, –1+z; d = –1/2+x, 1/2+y, z

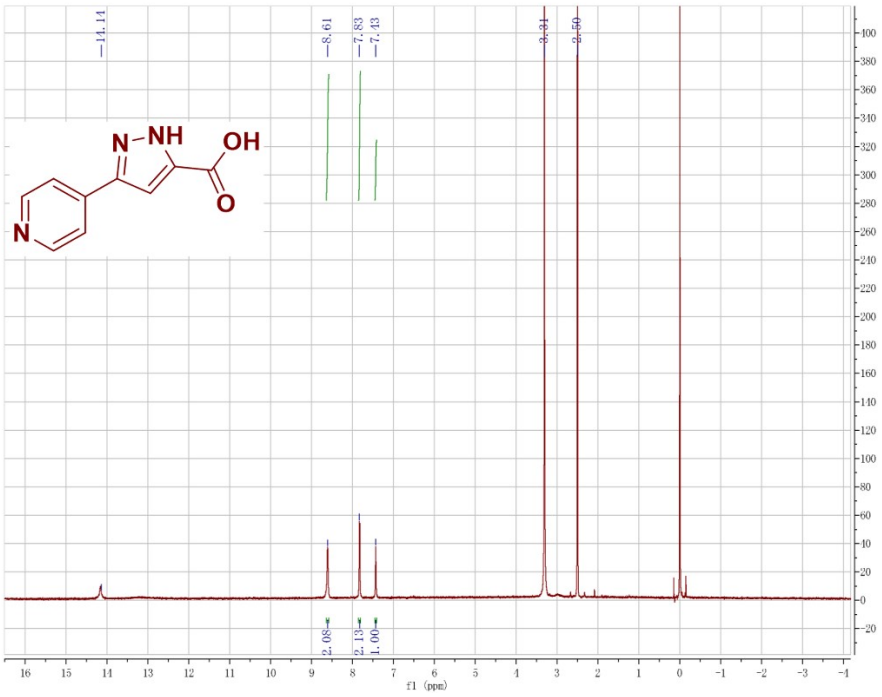


Fig. S1 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of H_2ppza.

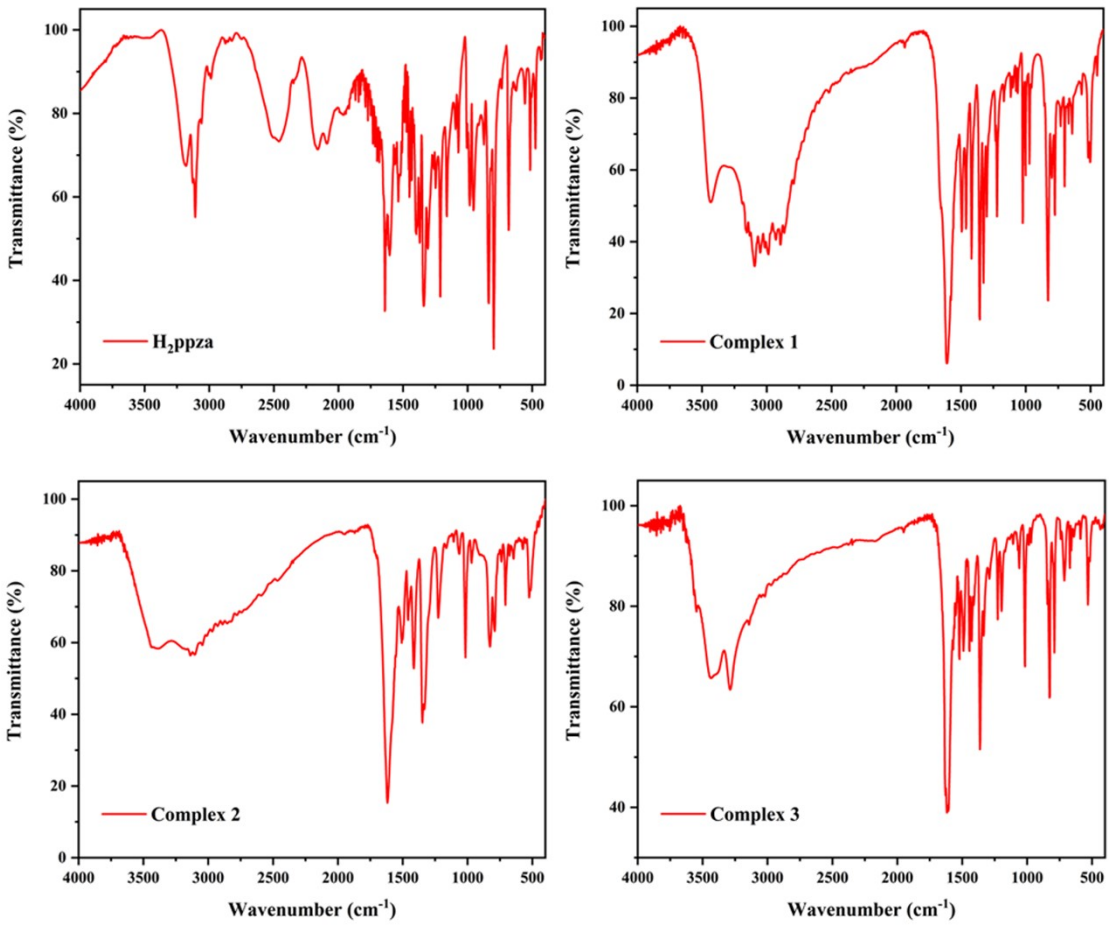
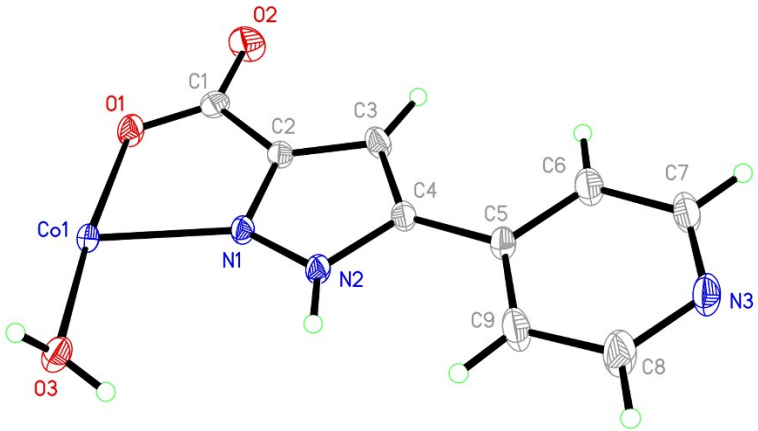
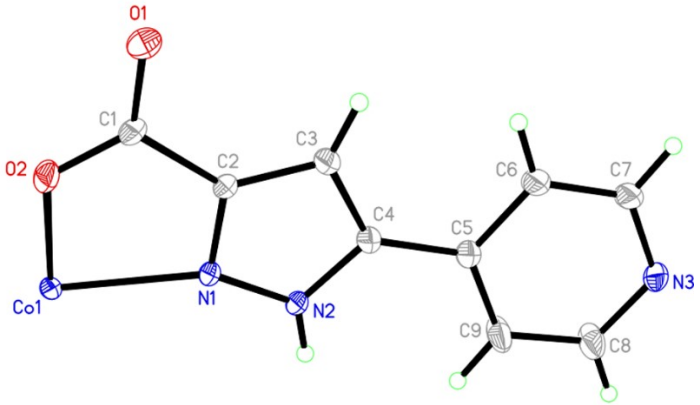


Fig. S2 IR spectra of H_2ppza ligand and complexes 1–3 from 400 cm^{-1} to 4000 cm^{-1}.

Complex **1**



Complex **2**



Complex **3**

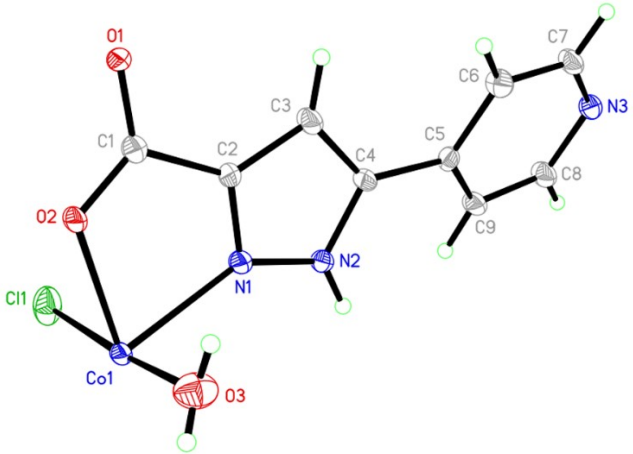
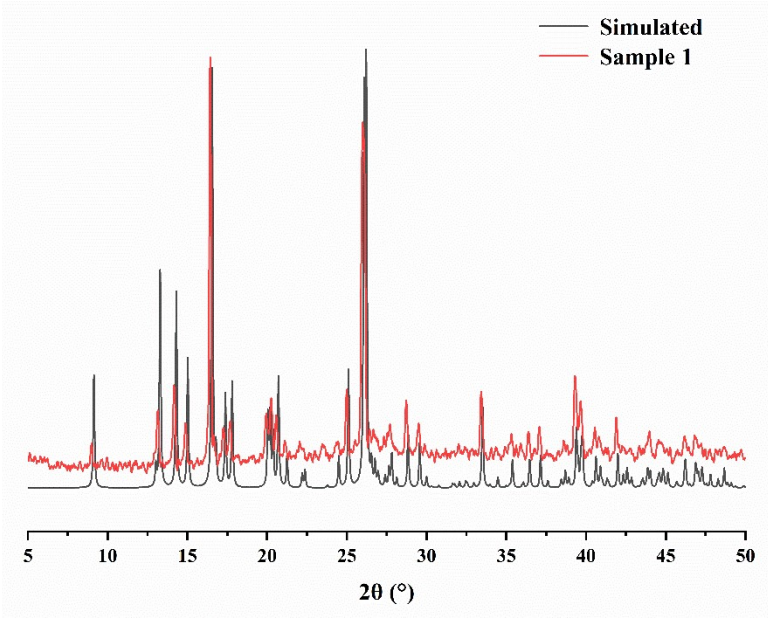


Fig. S3 Asymmetric unit of **1**–**3**, drawn with displacement ellipsoids at 30% probability level.



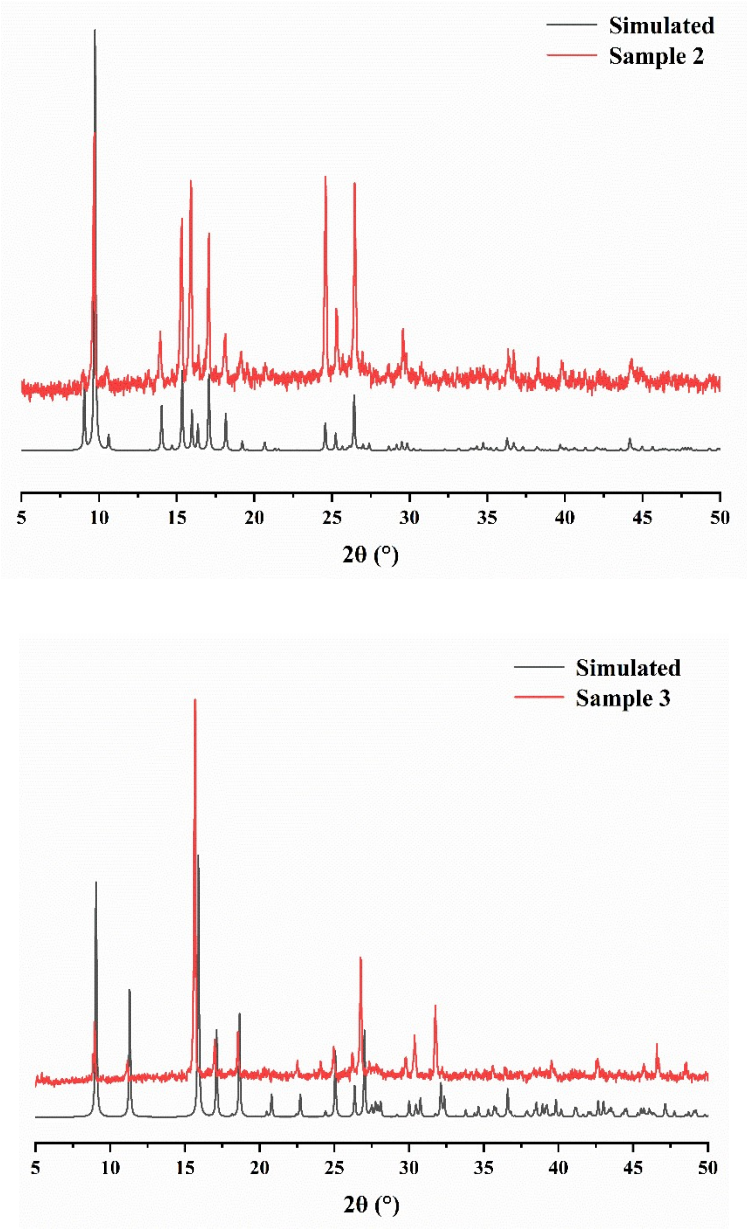


Fig. S4 PXRD patterns of simulated and experimental crystals of complexes **1**–**3**.

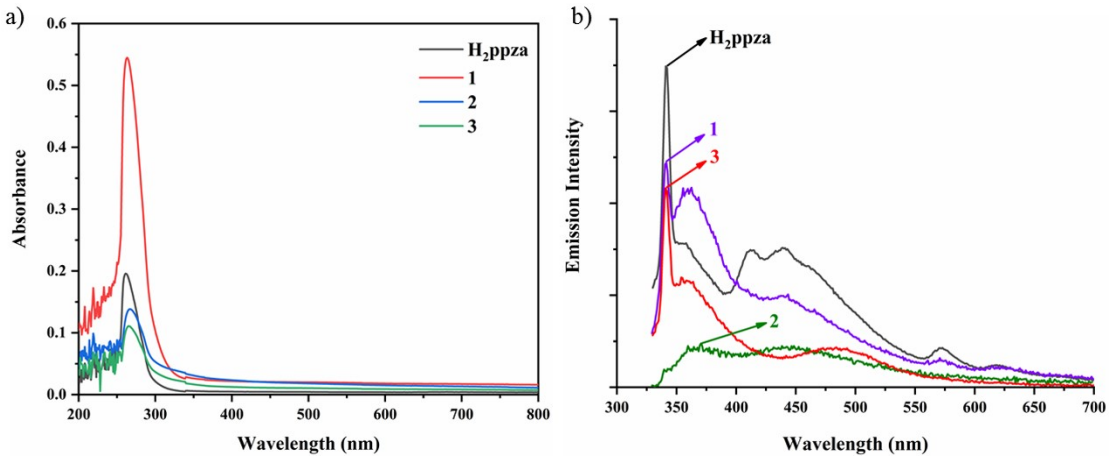


Fig. S5 (a) UV-Vis absorption spectra and (b) luminescence spectra of 10^{-5} M DMSO solutions of H_2ppza and its corresponding complexes **1**–**3**.

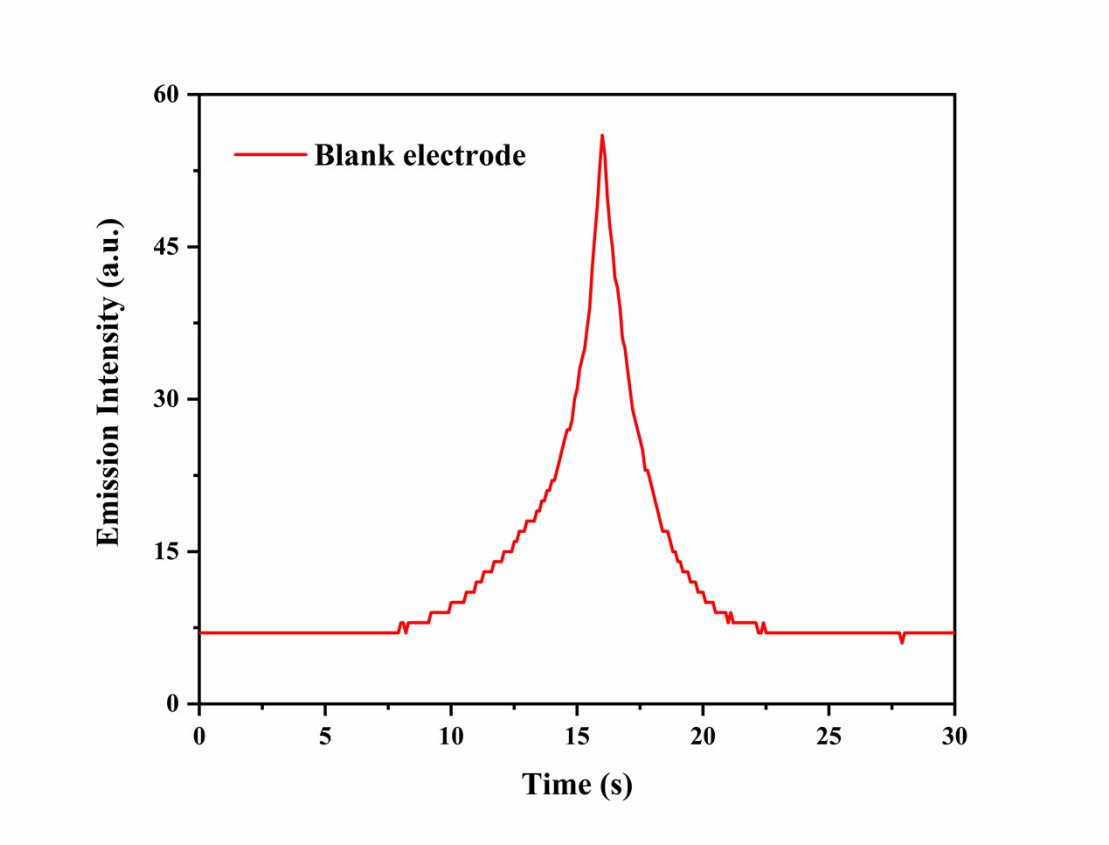


Fig. S6 ECL intensity–time profile of blank electrode.

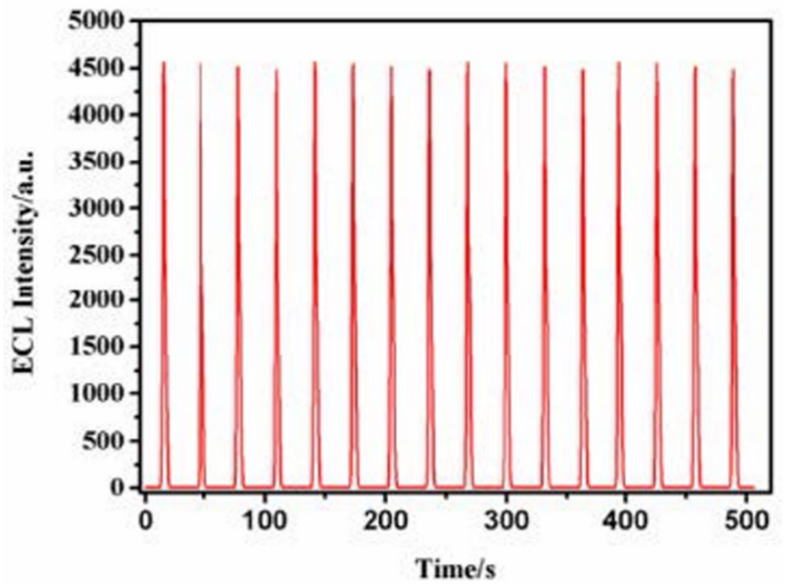


Fig. S7 Electrochemiluminescence for $Ru(bpy)_3^{2+}$.