

New Journal of Chemistry

Supporting Information

**Hydrogen photogeneration catalyzed by a cobalt complex of pentadentate
aminopyridine-based ligand**

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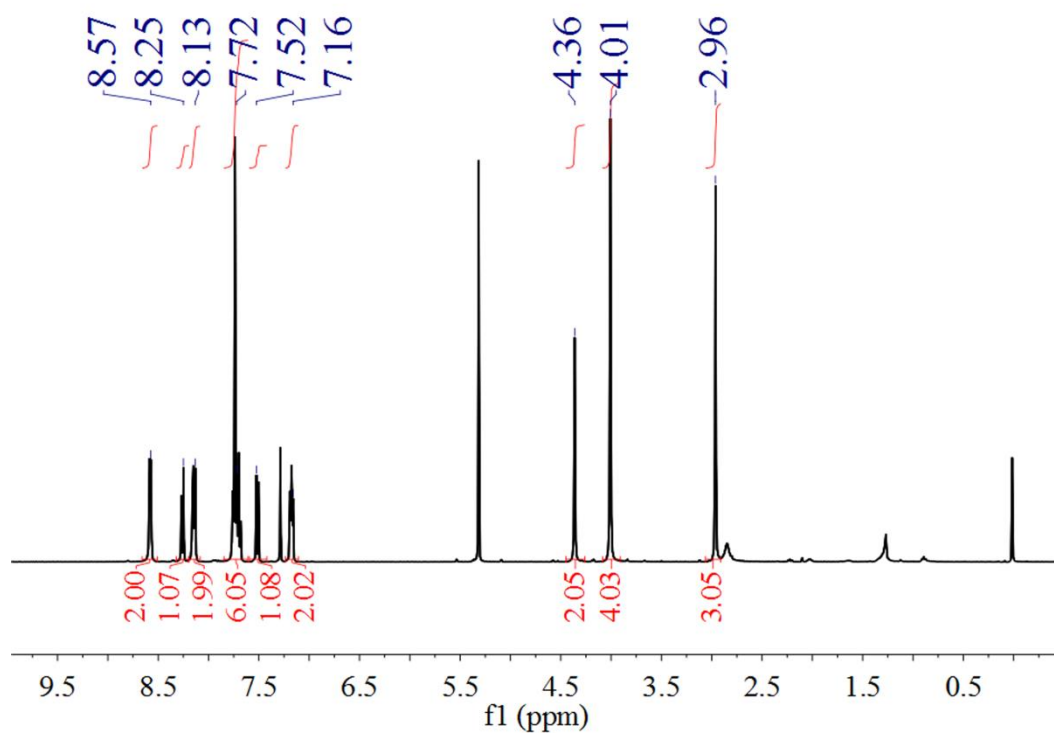


Fig. S1 $^1\text{H-NMR}$ of prepared ligand Dmphen-DPA

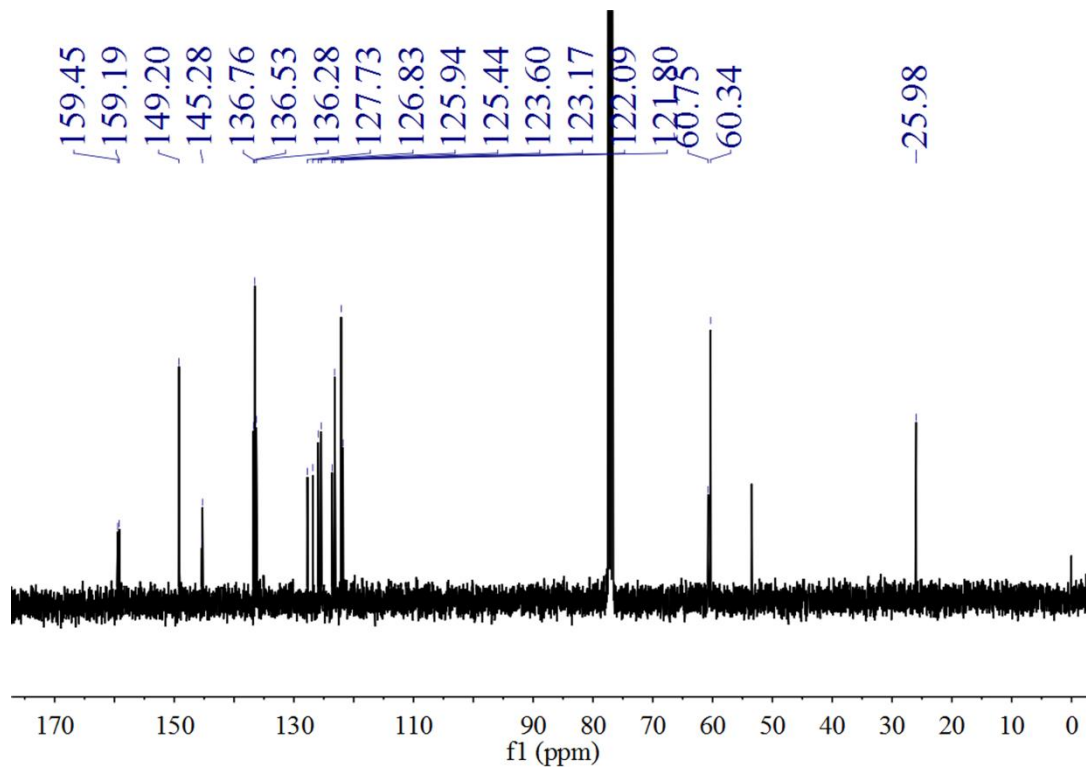


Fig. S2 ^{13}C -NMR of prepared ligand Dmphen-DPA

Ndpmp #65 RT: 0.98 AV: 1 NL: 1.03E6
T: + c ESI Full ms [50.00-500.00]

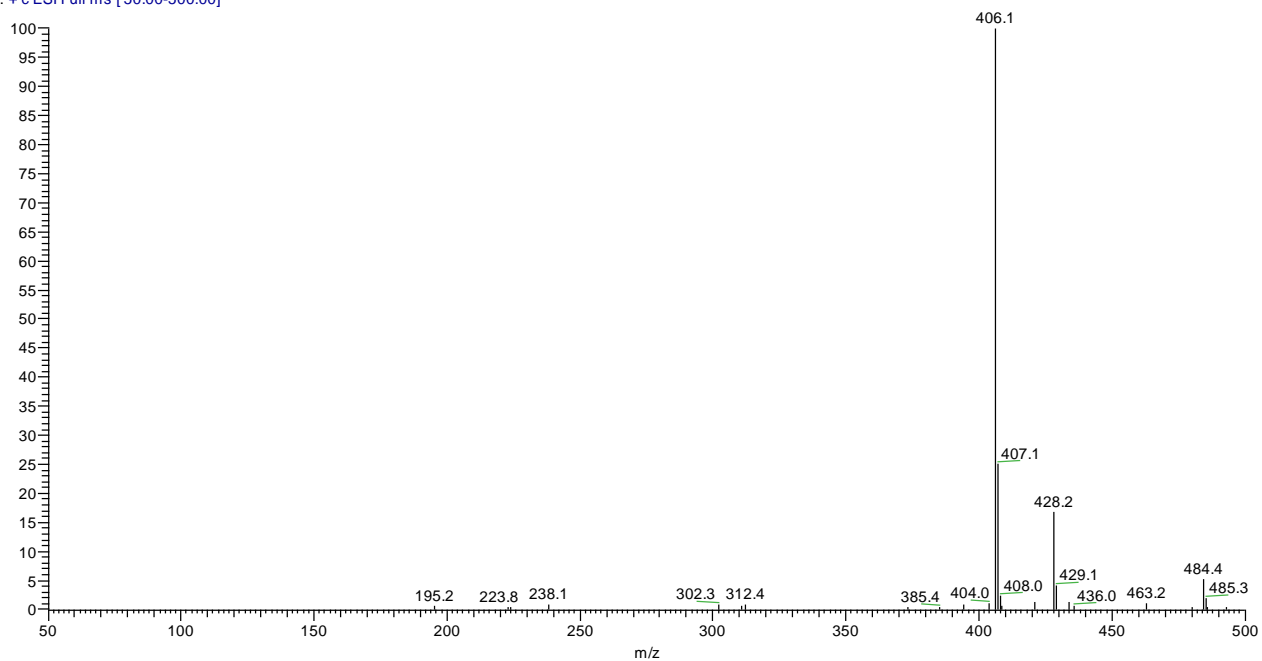


Fig. S3 The ESI-MS spectrometry of ligand Dmphen-DPA.

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CONN4 #115 RT: 2.90 AV: 1 NL: 4.82E6
T: + c ESI Full ms [50.00-1000.00]

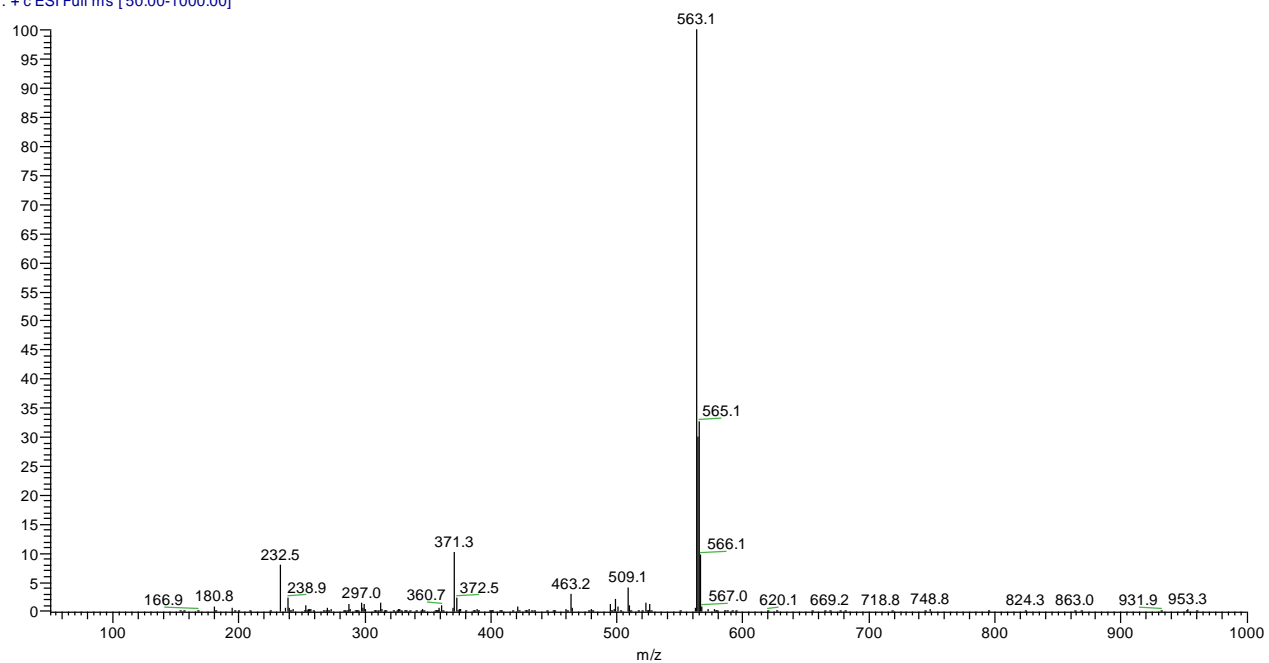


Fig. S4 The ESI-MS spectrometry of complex **1**.

D:\Data\CCR\NiNN4
N

20140821 11:00:01 AM

NiNN4

NiNN4 #218 RT: 6.37 AV: 1 SB: 18 0.08-0.37 NL: 1.62E6
T: + c ESI Full ms [50.00-1000.00]

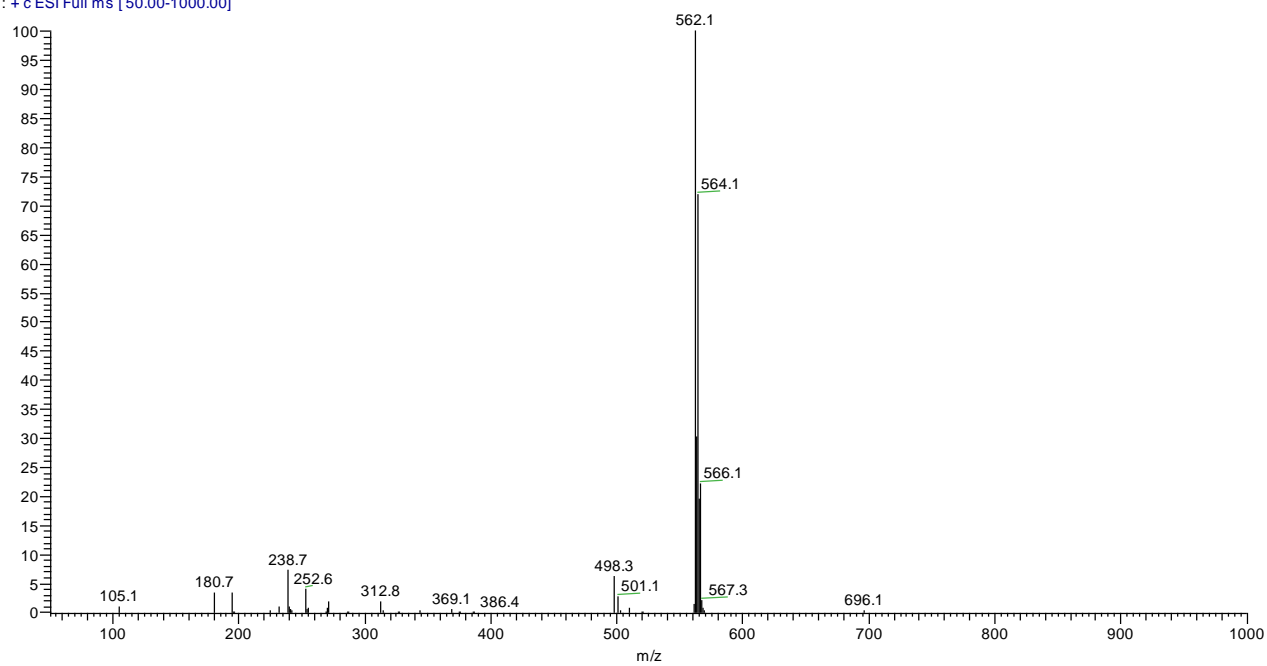


Fig. S5 The ESI-MS spectrometry of complex 2.

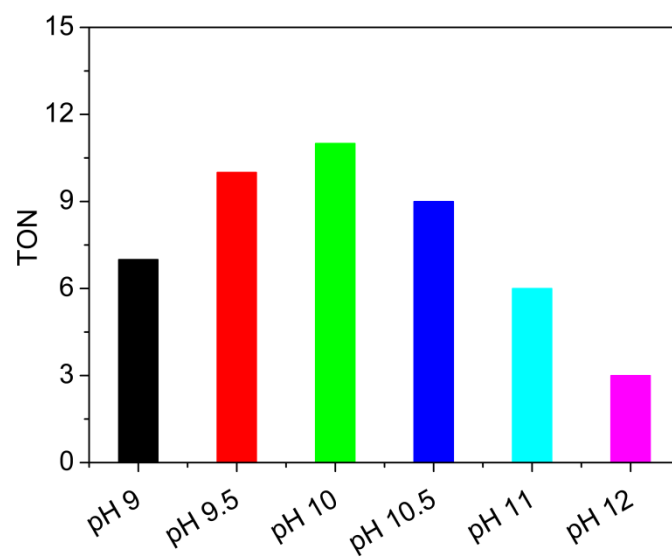


Fig. S6 pH dependence on the hydrogen production over [Ir(ppy)₂(bpy)]PF₆/2/TEA system under the following conditions: TEA (10 vol%), **2** (0.1 mM) and [Ir(ppy)₂(bpy)]PF₆ (0.5 mM) in CH₃CN-H₂O (1/3, v/v) solution; irradiation time 4 h.

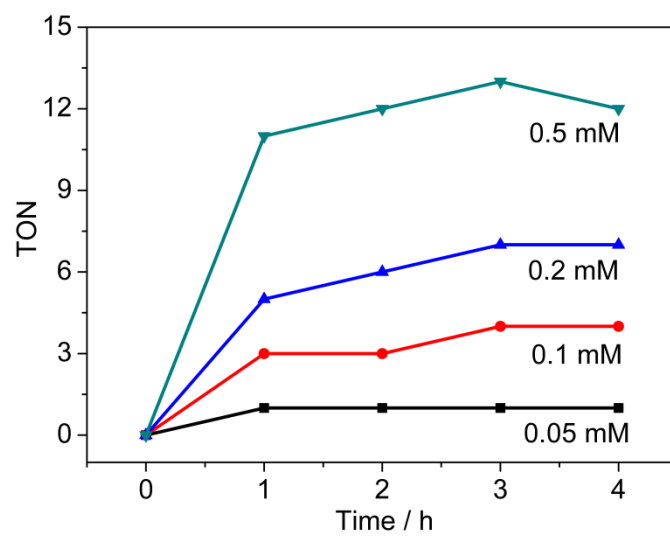


Fig. S7 the dependence of H₂ evolution on the concentration of [Ir(ppy)₂(bpy)](PF₆) from 0.05 mM to 0.5 mM, **2** (0.1 mM), 10 vol% TEA and pH 10 in CH₃CN-H₂O (1/3, v/v) solution.

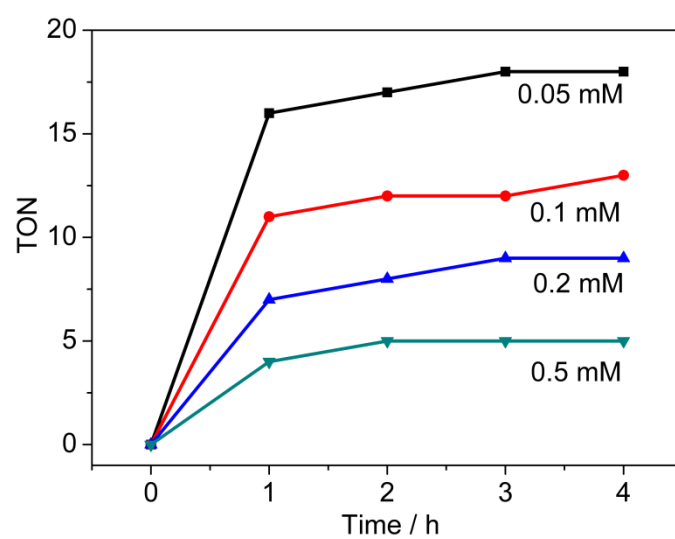


Fig. S8 the dependence of H₂ evolution on the concentration of **2** from 0.05 mM to 0.5 mM, [Ir(ppy)₂(bpy)](PF₆) (0.5 mM), 10 vol% TEA and pH 10 in CH₃CN-H₂O (1/3, v/v) solution.

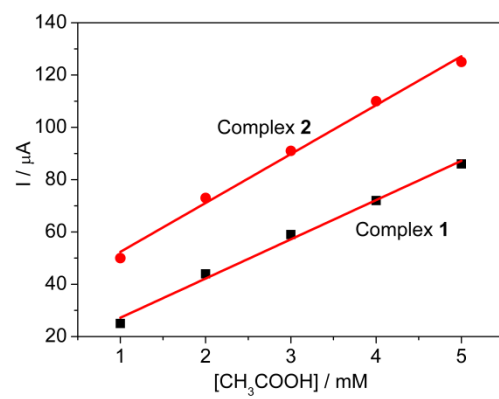


Fig. S9 Acetic acid concentration dependence of the peak current at -2.1 V (vs. Fc^+/Fc) for complexes **1** and **2**

Table S1 Selected bond lengths (Å) and angles (°) for **1** and **2**

1					
Co(1)-N(1)	2.2153(16)	N(1)-Co(1)-N(3)	77.95(6)	N(2)-Co(1)-O(9)	86.81(6)
Co(1)-N(2)	2.1272(17)	N(1)-Co(1)-N(4)	78.48(6)	N(3)-Co(1)-N(4)	94.86(6)
Co(1)-N(3)	2.1169(16)	N(1)-Co(1)-N(5)	155.36(6)	N(3)-Co(1)-N(5)	103.51(6)
Co(1)-N(4)	2.0414(16)	N(1)-Co(1)-O(9)	100.84(6)	N(3)-Co(1)-O(9)	88.70(6)
Co(1)-N(5)	2.2292(16)	N(2)-Co(1)-N(3)	155.55(6)	N(4)-Co(1)-N(5)	76.88(6)
Co(1)-O(9)	2.0701(14)	N(2)-Co(1)-N(4)	89.32(6)	N(4)-Co(1)-O(9)	176.13(6)
N(1)-Co(1)-N(2)	79.32(6)	N(2)-Co(1)-N(5)	100.91(6)	N(5)-Co(1)-O(9)	103.78(6)
2					
Ni(1)-N(1)	2.150(2)	N(1)-Ni(1)-N(3)	79.63(8)	N(2)-Ni(1)-O(9)	86.27(8)
Ni(1)-N(2)	2.082(2)	N(1)-Ni(1)-N(4)	80.50(9)	N(3)-Ni(1)-N(4)	95.22(9)
Ni(1)-N(3)	2.068(2)	N(1)-Ni(1)-N(5)	158.94(8)	N(3)-Ni(1)-N(5)	102.42(9)
Ni(1)-N(4)	1.982(2)	N(1)-Ni(1)-O(9)	99.02(8)	N(3)-Ni(1)-O(9)	88.27(8)
Ni(1)-N(5)	2.211(2)	N(2)-Ni(1)-N(3)	158.96(9)	N(4)-Ni(1)-N(5)	78.44(9)
Ni(1)-O(9)	2.0683(19)	N(2)-Ni(1)-N(4)	90.05(9)	N(4)-Ni(1)-O(9)	176.32(9)
N(1)-Ni(1)-N(2)	81.19(8)	N(2)-Ni(1)-N(5)	98.59(8)	N(5)-Ni(1)-O(9)	101.99(8)

Table S2 Redox potentials observed in CH₃CN (0.1 M NBu₄PF₆) for complexes **1** and **2**.

complex	E ^{1/2} (ox1)	E ^{1/2} (red1)	E (red2) ^a	E (red3) ^a
1	-0.02	-1.43	-2.22	-
2	-	-1.42	-2.08	-2.21

^a Irreversible reduction wave