# Supplementary materials

# Three novel $d^7/d^{10}$ metal complexes with N-heterocyclic ligand of 2,6-bis(3-pyrazolyl)pyridine: Synthesis, structure, surface photovoltage spectroscopy and photocatalytic activity

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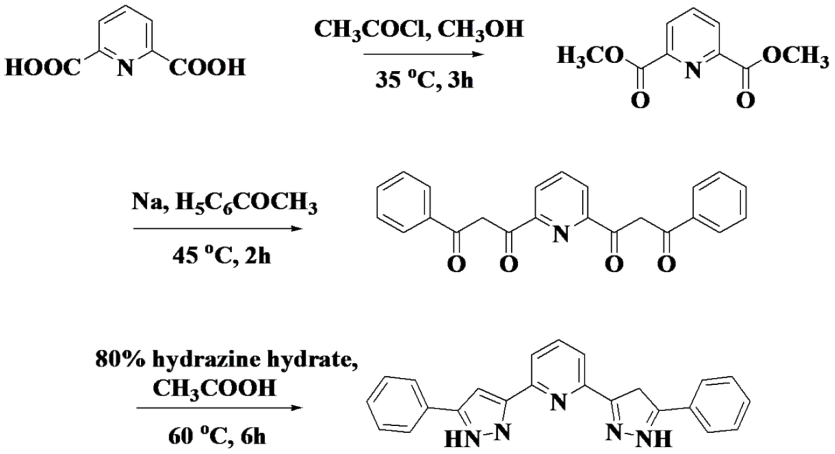
1. The detail synthesis method of the ligand




**Scheme.S1** The synthesis method of the $H_2L$ ligand in detail.

2.The PXRD patterns of complex **1-3**

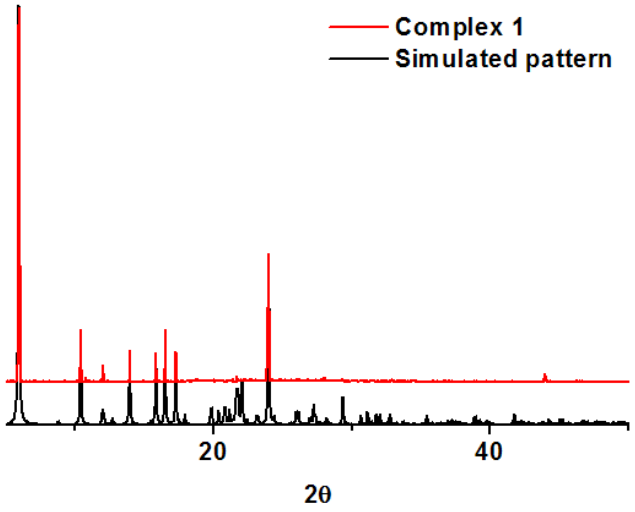



**Figure.S1** The comparison of simulated and measured patterns of complex **1**.

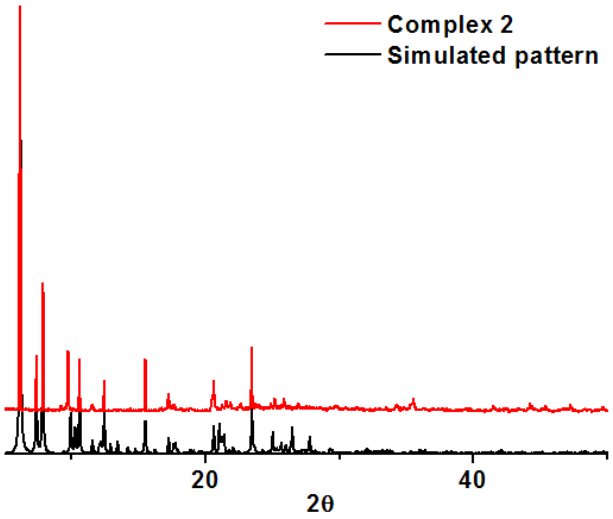



**Figure.S2** The comparison of simulated and measured patterns of complex **2**.

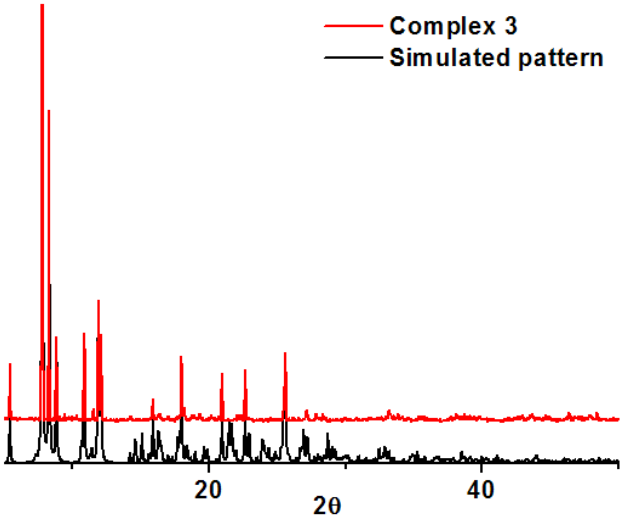



**Figure.S3** The comparison of simulated and measured patterns of complex **3**.

3. The IR spectra of complex **1-3**

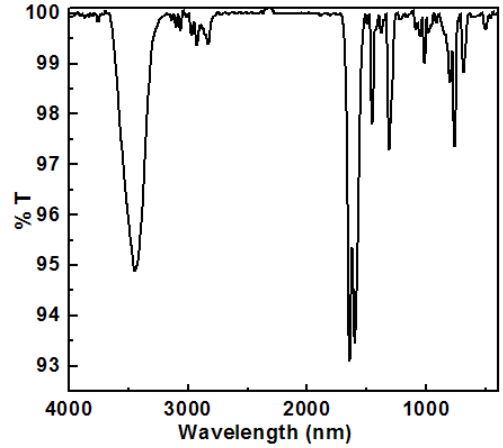



**Figure.S4** The IR spectra of complex **1.**

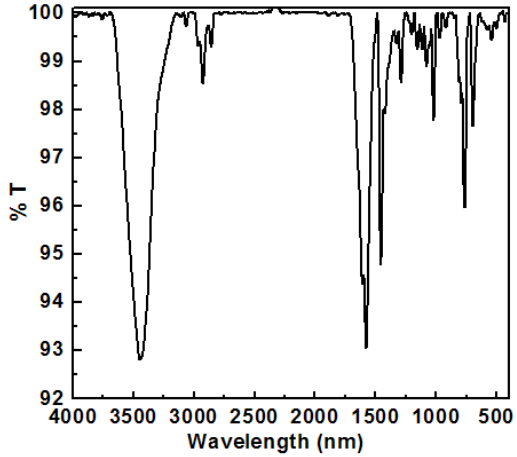



**Figure.S5** The IR spectra of complex **2.**

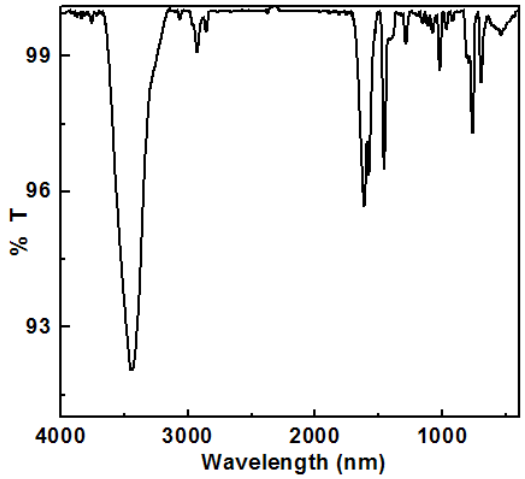



**Figure.S6** The IR spectra of complex **3.**

4. Selected Bond Distances (Å) and Angles（°) of Complexes **1-3***

**Table S1** Selected Bond Distances (Å) and Angles（°) of Complexes **1-3***

| | | | |
|---|---|---|---|
| Complex **1** | | | |
| Co1-O2 | 2.048(11) | Co2-O7 | 2.004(11) |
| Co1-O3 | 2.059(11) | Co2-N3 | 2.054(13) |
| Co1-O4 | 2.066(9) | Co2-O5 | 2.099(9) |
| Co1-N8 | 2.142(10) | Co2-O6 | 2.099(10) |
| Co1-N7 | 2.148(13) | Co2-N2 | 2.191(14) |
| Co1-N9 | 2.199(15) | Co2-N4 | 2.277(14) |
| O2-Co1-O3 | 168.7(4) | O7-Co2-N3 | 102.6(5) |
| O2-Co1-O4 | 90.1(4) | O7-Co2-O5 | 90.7(4) |
| O3-Co1-O4 | 78.8(4) | N3-Co2-O5 | 166.4(4) |
| O2-Co1-N8 | 103.1(5) | O7-Co2-O6 | 171.6(4) |
| O3-Co1-N8 | 87.7(4) | N3-Co2-O6 | 85.7(5) |
| O4-Co1-N8 | 165.6(4) | O5-Co2-O6 | 81.0(4) |
| O2-Co1-N7 | 93.7(4) | O7-Co2-N2 | 91.1(4) |
| O3-Co1-N7 | 92.1(5) | N3-Co2-N2 | 74.6(5) |
| N8-Co1-N7 | 75.7(5) | O5-Co2-N2 | 108.5(5) |
| O2-Co1-N9 | 96.0(5) | O6-Co2-N2 | 92.5(4) |
| O4-Co1-N7 | 109.4(5) | O7-Co2-N4 | 96.3(5) |
| O3-Co1-N9 | 83.9(5) | N3-Co2-N4 | 75.7(5) |
| O4-Co1-N9 | 99.8(5) | O5-Co2-N4 | 100.1(4) |
| N8-Co1-N9 | 73.6(5) | O6-Co2-N4 | 84.2(5) |
| N7-Co1-N9 | 149.1(5) | N2-Co2-N4 | 150.3(5) |
| Complex **2** | | | |
| Co1-O2 | 2.006(4) | Co2-O1 | 2.003(4) |
| Co1-N10 | 2.028(5) | Co2-N5 | 2.014(5) |
| Co1-N3 | 2.071(5) | Co2-N8 | 2.066(5) |
| Co1-N2 | 2.105(5) | Co2-N9 | 2.128(5) |
| Co1-N4 | 2.132(5) | Co2-N7 | 2.187(5) |
| O2-Co1-N10 | 103.56(19) | O1-Co2-N5 | 104.91(18) |
| O2-Co1-N3 | 123.19(19) | O1-Co2-N8 | 124.63(17) |
| N10-Co1-N3 | 132.69(19) | N5-Co2-N8 | 130.27(18) |
| O2-Co1-N2 | 96.89(18) | O1-Co2-N9 | 99.66(18) |
| N10-Co1-N2 | 107.0(2) | N5-Co2-N9 | 93.60(18) |
| N3-Co1-N2 | 76.46(19) | N8-Co2-N9 | 75.5(2) |
| O2-Co1-N4 | 95.49(18) | O1-Co2-N7 | 94.93(17) |
| N10-Co1-N4 | 94.81(19) | N5-Co2-N7 | 106.59(18) |
| N3-Co1-N4 | 75.33(18) | N8-Co2-N7 | 75.7(2) |
| N2-Co1-N4 | 151.56(18) | N9-Co2-N7 | 151.11(19) |
| Complex **3** | | | |
| Zn1-O1 | 1.981(11) | N7-Zn2 | 2.125(8) |
| Zn1-N10 | 1.984(7) | N8-Zn2 | 2.104(8) |
| Zn1-N3 | 2.109(7) | N9-Zn2 | 2.164(7) |
| Zn1-O1A$^{\#1}$ | 2.12 (2) | N5-Zn2 | 2.018(7) |
| Zn1-N4 | 2.131(7) | O2-Zn2 | 2.024(7) |
| Zn1-N2 | 2.205(7) | N4-Zn1-N2 | 148.6(3) |
| O1-Zn1-N10 | 105.5(4) | N3-Zn1-N2 | 73.5(3) |
| O1-Zn1-N3 | 124.2(4) | O1A$^{\#1}$-Zn1-N2 | 88.6(6) |
| N10-Zn1-N3 | 130.1(3) | N5-Zn2-O2 | 103.1(3) |
| N7-Zn2-N9 | 149.9(3) | N5-Zn2-N8 | 134.6(3) |
| N10-Zn1-O1A$^{\#1}$ | 100.4(7) | O2-Zn2-N8 | 121.6(3) |
| N3-Zn1-O1A$^{\#1}$ | 129.2(7) | N5-Zn2-N7 | 109.5(3) |
| O1-Zn1-N4 | 98.5(4) | O2-Zn2-N7 | 95.2(3) |
| N10-Zn1-N2 | 107.3(3) | N8-Zn2-N7 | 76.4(3) |
| N3-Zn1-N2 | 73.5(3) | N5-Zn2-N9 | 93.6(3) |

| | | | |
|---|---|---|---|
| O1A$^{\#1}$-Zn1-N2 | 88.6(6) | O2-Zn2-N9 | 98.1(3) |
| O1-Zn1-N2 | 97.0(4) | N8-Zn2-N9 | 73.7(3) |

* Symmetry transformation used to generate equivalent atoms: #1: -x+1,-y, -z+1.

## 5. The detailed attribution of IR ($cm^{-1}$) for complex **1**-**3**

**Table S2** The detailed attribution of IR ($cm^{-1}$) for complex **1**-**3**

| Complex | **1** | **2** | **3** |
|---|---|---|---|
| ν(N-H) | 3439 | 3439 | 3440 |
| ν(Ar-H) | 3137 | 3161 | 3161 |
| ν(C-H) | 3061 | 2962 | 2924 |
| $\nu_{as(COO^-)}$ | 1310 | 1450 | 1423 |
| $\nu_{s(COO^-)}$ | 1598 | 1574 | 1576 |
| ν(C=C) | 1644 | 1618 | 1601 |
| ν(C=N) | 1448 | 1473 | 1451 |