# Electronic Supplementary Information

# Reaction Controlled Assemblies and Structural Diversities of Seven Co(II)/Cu(II) Complexes Based on a Bipyridine-dicarboxylate N-oxide Ligand

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**Table S1** Crystallographic data and structure refinement parameters for complexes **1-5**

| complex | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| chemical formula | $C_{14}H_{11}CoN_3O_8$ | $C_{12}H_8CuN_2O_7$ | $C_{48}H_{28}Cu_2N_8O_{12}$ | $C_{48}H_{48}Cu_2N_8O_{22}$ | $C_{44}H_{40}Cu_2N_8O_{18}$ |
| formula weight | 408.17 | 355.74 | 1035.86 | 1216.02 | 1095.92 |
| crystal shape | columnar | block | columnar | block | block |
| crystal color | red | bright green | blue | blue | blue |
| temperature (K) | 296(2) | 296(2) | 296(2) | 296(2) | 296(2) |
| crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic | Triclinic |
| space group | *C*2/*m* | *P*2(1)/*n* | *P*2(1)/*n* | *P*-1 | *P*-1 |
| *a*/Å | 14.462(2) | 5.8488(13) | 9.3276(10) | 9.213(2) | 9.357(4) |
| *b*/Å | 15.486(3) | 16.227(4) | 11.9664(13) | 12.190(3) | 11.325(5) |
| *c*/Å | 7.4899(12) | 13.164(3) | 19.099(2) | 12.635(3) | 12.540(5) |
| $\alpha$ (°) | 90 | 90 | 90 | 109.362(4) | 64.338(6) |
| $\beta$ (°) | 96.971(3) | 91.507(3) | 92.947(2) | 109.077(4) | 69.757(6) |
| $\gamma$ (°) | 90 | 90 | 90 | 91.212(4) | 75.003(6) |
| *V*/Å$^3$ | 1665.0(5) | 1249.0(5) | 2128.9(4) | 1251.8(5) | 1114.4(8) |
| *Z* | 4 | 4 | 2 | 1 | 1 |
| density (mg/m$^3$) | 1.620 | 1.892 | 1.616 | 1.613 | 1.633 |
| $\mu$ (mm$^{-1}$) | 1.080 | 1.790 | 1.078 | 0.944 | 1.044 |
| *F*(000) | 820 | 716.0 | 1052 | 626 | 562 |
| reflections collected | 4251 | 6642 | 10555 | 6190 | 5612 |
| $R_{int}$ | 0.0504 | 0.0335 | 0.0463 | 0.0212 | 0.0247 |
| number of parameters | 129 | 199 | 316 | 361 | 325 |
| Goodness-of-fit on F^2 | 1.075 | 1.075 | 1.002 | 1.052 | 1.028 |
| $R_1$[a], $wR_2$[b] [$I>2\sigma(I)$ ] | 0.0642, 0.1755 | 0.0408, 0.1228 | 0.0410, 0.0877 | 0.0450, 0.1330 | 0.0559, 0.1634 |
| $R_1$, $wR_2$ (all data) | 0.0897, 0.1940 | 0.0656, 0.1756 | 0.0659, 0.0978 | 0.0538, 0.1567 | 0.0741, 0.2373 |

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

**Table S2** The selected bond lengths (Å) and angles (º) for complexes **1**-**5**.

| | | | |
|---|---|---|---|
| | | **1** | |
| Co(1)-O(2)#1 | 2.080(4) | Co(1)-O(2)#2 | 2.080(4) |
| Co(1)-O(2)#3 | 2.080(4) | Co(1)-O(2) | 2.080(4) |
| Co(1)-O(4) | 2.138(5) | Co(1)-O(4)#1 | 2.138(5) |
| Co(2)-O(3) | 2.075(4) | Co(2)-O(3)#4 | 2.075(4) |
| Co(2)-O(3)#5 | 2.075(4) | Co(2)-O(3)#6 | 2.075(4) |
| Co(2)-N(1) | 2.115(8) | Co(2)-N(1)#4 | 2.115(8) |
| O(2)#1-Co(1)-O(2)#2 | 90.6(3) | O(2)#1-Co(1)-O(2)#3 | 89.4(3) |
| O(2)#2-Co(1)-O(2)#3 | 180 | O(2)#1-Co(1)-O(2) | 180 |
| O(2)#2-Co(1)-O(2) | 89.4(3) | O(2)#3-Co(1)-O(2) | 90.6(3) |
| O(2)#1-Co(1)-O(4) | 92.48(2) | O(2)#2-Co(1)-O(4) | 87.52(2) |
| O(2)#3-Co(1)-O(4) | 92.48(2) | O(2)-Co(1)-O(4) | 87.52(2) |
| O(2)#1-Co(1)-O(4)#1 | 87.52(2) | O(2)#2-Co(1)-O(4)#1 | 92.48(2) |
| O(2)#3-Co(1)-O(4)#1 | 87.52(2) | O(2)-Co(1)-O(4)#1 | 92.48(2) |
| O(4)-Co(1)-O(4)#1 | 180 | O(3)-Co(2)-O(3)#4 | 180 |
| O(3)-Co(2)-O(3)#5 | 93.6(2) | O(3)#4-Co(2)-O(3)#5 | 86.4(2) |
| O(3)-Co(2)-O(3)#6 | 86.4(2) | O(3)#4-Co(2)-O(3)#6 | 93.6(2) |
| O(3)#5-Co(2)-O(3)#6 | 180 | O(3)-Co(2)-N(1) | 95.31(2) |
| O(3)#4-Co(2)-N(1) | 84.69(2) | O(3)#5-Co(2)-N(1) | 95.31(2) |
| O(3)#6-Co(2)-N(1) | 84.69(2) | O(3)-Co(2)-N(1)#4 | 84.69(2) |
| O(3)#4-Co(2)-N(1)#4 | 95.31(2) | O(3)#5-Co(2)-N(1)#4 | 84.69(2) |
| O(3)#6-Co(2)-N(1)#4 | 95.31(2) | N(1)-Co(2)-N(1)#4 | 180 |
| | | **2** | |
| Cu(1)-O(3)#1 | 1.929(4) | Cu(1)-O(6)#2 | 1.973(3) |
| Cu(1)-O(5)#2 | 1.974(3) | Cu(1)-O(1) | 1.977(3) |
| Cu(1)-O(7) | 2.363(5) | | |
| O(3)#1-Cu(1)-O(6)#2 | 90.86(2) | O(3)#1-Cu(1)-O(5)#2 | 158.55(2) |
| O(6)#2-Cu(1)-O(5)#2 | 90.57(2) | O(3)#1-Cu(1)-O(1) | 88.75(2) |
| O(6)#2-Cu(1)-O(1) | 177.36(2) | O(5)#2-Cu(1)-O(1) | 90.75(2) |
| O(3)#1-Cu(1)-O(7) | 108.09(2) | O(6)#2-Cu(1)-O(7) | 87.17(2) |
| O(5)#2-Cu(1)-O(7) | 93.36(2) | O(1)-Cu(1)-O(7) | 90.47(2) |
| | | **3** | |
| Cu(1)-O(1) | 1.933(2) | Cu(1)-O(2) | 2.645(3) |
| Cu(1)-O(3)#1 | 1.954(2) | Cu(1)-O(4)#1 | 2.585(2) |
| Cu(1)-N(3) | 2.000(3) | Cu(1)-N(4) | 2.005(3) |
| O(1)-Cu(1)-O(3)#1 | 91.72(9) | O(1)-Cu(1)-N(3) | 172.85(1) |
| O(3)#1-Cu(1)-N(3) | 93.88(1) | O(1)-Cu(1)-N(4) | 93.61(1) |

| | | | |
|---|---|---|---|
| O(3)#1-Cu(1)-N(4) | 167.25(1) | N(3)-Cu(1)-N(4) | 81.83(1) |
| | | **4** | |
| Cu(1)-O(1) | 1.929(3) | Cu(1)-O(2) | 2.856(3) |
| Cu(1)-O(4)#1 | 1.961(2) | Cu(1)-N(4) | 2.005(3) |
| Cu(1)-N(3) | 2.027(3) | Cu(1)-O(1W) | 2.439(3) |
| O(1)-Cu(1)-O(4)#1 | 91.21(1) | O(1)-Cu(1)-N(4) | 175.37(1) |
| O(4)#1-Cu(1)-N(4) | 92.71(1) | O(1)-Cu(1)-N(3) | 94.60(1) |
| O(4)#1-Cu(1)-N(3) | 165.02(1) | N(4)-Cu(1)-N(3) | 82.20(1) |
| O(1)-Cu(1)-O(1W) | 90.19(1) | O(4)#1-Cu(1)-O(1W) | 94.16(1) |
| N(4)-Cu(1)-O(1W) | 87.06(1) | N(3)-Cu(1)-O(1W) | 99.61(1) |
| | | **5** | |
| Cu(1)-O(1) | 1.945(4) | Cu(1)-O(3)#1 | 1.961(4) |
| Cu(1)-N(4) | 1.997(4) | Cu(1)-N(3) | 2.022(4) |
| Cu(1)-O(1W) | 2.420(4) | Cu(1)-O(2) | 2.797(6) |
| O(1)-Cu(1)-O(3)#1 | 90.94(2) | O(1)-Cu(1)-N(4) | 170.91(2) |
| O(3)#1-Cu(1)-N(4) | 93.65(2) | O(1)-Cu(1)-N(3) | 94.34(2) |
| O(3)#1-Cu(1)-N(3) | 173.58(2) | N(4)-Cu(1)-N(3) | 80.63(2) |
| O(1)-Cu(1)-O(1W) | 92.06(2) | O(3)#1-Cu(1)-O(1W) | 93.31(2) |
| N(4)-Cu(1)-O(1W) | 95.50(2) | N(3)-Cu(1)-O(1W) | 90.15(2) |

Symmetry codes: For **1**, #1 -*x*, -*y*+1, -*z*+1; #2 *x*, -*y*+1, *z*; #3 -*x*, *y*, -*z*+1; #4 -*x*, -*y*, -*z*; #5 *x*, -*y*, *z*; #6 -*x*, *y*, -*z*. For **2**, #1 *x*+1, *y*, *z*; #2 *x*+1/2, -*y*+1/2, *z*+1/2. For **3**, #1 -*x*+2,-*y*+1,-*z*+2; For **4**, #1 -*x*+1, -*y*, -*z*; For **5**, #1 -*x*+1,-*y*+1,-*z*+1.

**Table S3** Hydrogen bond geometries in the crystal structure of **1-5**.

| D−H···A | D−H | H···A | D···A(Å) | D−H···A(°) |
|---|---|---|---|---|
| | | **1** | | |
| C(4)−H(4)···O(1)#1 | 0.93 | 2.42 | 3.146(7) | 135 |
| C(8)−H(8A)···O(4)#2 | 0.96 | 2.54 | 3.356(17) | 142 |
| | | **2** | | |
| O(7)−H(7A)···O(2)#1 | 0.86 | 2.39 | 3.160(7) | 150 |
| O(7)−H(7B)···O(1) | 0.86 | 2.47 | 3.093(6) | 130 |
| O(7)−H(7B)···O(2) | 0.86 | 1.90 | 2.704(8) | 156 |
| | | **3** | | |
| C(1)−H(1)···O(6)#1 | 0.93 | 2.19 | 2.927(4) | 136 |
| C(2)−H(2)···O(4)#2 | 0.93 | 2.57 | 3.376(3) | 145 |
| C(9)−H(9)···O(5)#3 | 0.93 | 2.25 | 3.095(4) | 150 |

| | | | | |
|---|---|---|---|---|
| C(18)−H(18)···O(2)#4 | 0.93 | 2.40 | 2.995(5) | 121 |
| | | **4** | | |
| O(1W)−H(1A)···O(5)#1 | 0.86 | 1.89 | 2.711(6) | 160 |
| O(1W)−H(1B)···O(3W) | 0.85 | 2.13 | 2.983(6) | 179 |
| O(2W)−H(2A)···O(2) | 0.86 | 2.03 | 2.888(5) | 179 |
| O(2W)−H(2B)···O(4W)#2 | 0.86 | 2.05 | 2.908(7) | 178 |
| O(3W)−H(3A)···O(3)#3 | 0.86 | 1.94 | 2.801(5) | 179 |
| O(3W)−H(3B)···O(5)#4 | 0.85 | 1.85 | 2.698(6) | 179 |
| O(4W)−H(4A)···O(6)#3 | 0.87 | 1.90 | 2.772(6) | 179 |
| O(4W)−H(4B)···O(3W) | 0.85 | 2.08 | 2.925(6) | 178 |
| O(5W)−H(5A)···O(3)#5 | 0.85 | 1.91 | 2.760(7) | 180 |
| O(5W)−H(5B)···O(1W)#6 | 0.85 | 2.15 | 2.995(9) | 180 |
| C(8)−H(8)···O(4W)#6 | 0.93 | 2.39 | 3.312(7) | 170 |
| C(22)−H(22)···O(1W)#6 | 0.93 | 2.52 | 3.376(6) | 154 |
| | | **5** | | |
| O(1W)−H(1WA)···O(4)#1 | 0.86 | 2.14 | 2.717(7) | 124 |
| O(1W)−H(1WB)···O(5)#2 | 0.86 | 2.18 | 2.828(7) | 133 |
| O(2W)−H(2A)···O(2) | 0.86 | 2.00 | 2.852(8) | 178 |
| O(2W)−H(2B)···O(3W) | 0.86 | 1.97 | 2.829(8) | 179 |
| O(3W)−H(3A)···O(6)#3 | 0.85 | 1.97 | 2.818(8) | 180 |
| O(3W)−H(3B)···O(4) | 0.85 | 2.08 | 2.930(8) | 180 |
| C(8)−H(8)···O(6)#4 | 0.93 | 2.25 | 3.172(8) | 169 |
| C(19)−H(19)···O(2W)#5 | 0.93 | 2.31 | 3.175(7) | 155 |

Symmetry codes: For **1**, #1 1/2+*x*, 1/2-*y*, *z*; #2 1/2-*x*, -1/2+*y*, 1-*z*. For **2**, #1 –*x*+2, -*y*+1, -*z*+2. For **3**, #1 3/2-*x*, 1/2+*y*, 3/2-*z*; #2 -1+*x*, *y*, *z*; #3 5/2-*x*, -1/2+*y*, 3/2-*z*; #4 2-*x*, -*y*, 2-*z*; For **4**, #1 –*x*+1, -*y*, -*z*; #2 *x*, *y*, *z*-1; #3 *x*+1, *y*, *z*+1; #4 *x*, *y*, *z*+1; #5 *x*+1, *y*+1, *z*+1; #6 –*x*+1, -*y*+1, -*z*+1. For **5**, #1 –*x*+1, -*y*+1, -*z*+1; #2 *x*, *y*+1, *z*; #3 *x*-1, *y*, *z*; #4 2-*x*, 1-*y*, -*z*; #5 1-*x*, 2-*y*, -*z*.

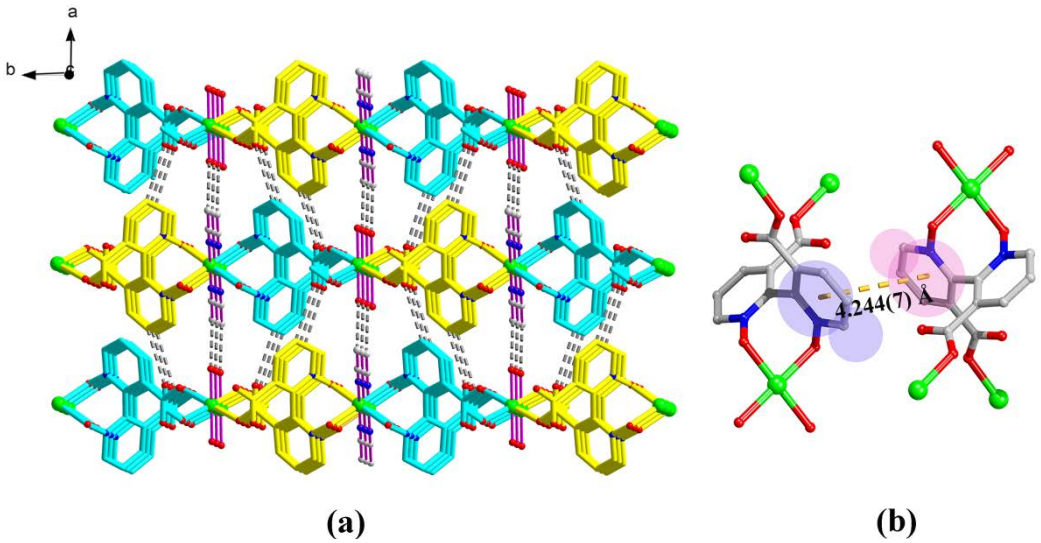



**Fig. S1** (a) A view of the 3D supramolecular network of complex **1** constructed through hydrogen bonds (C-H···O) and (b) the weak $\pi$-$\pi$ stacking interactions between the adjacent 2D layers. The broken lines are on behalf of the hydrogen bonds and $\pi\cdots\pi$ interactions, and the hydrogen atoms are omitted for clarity.

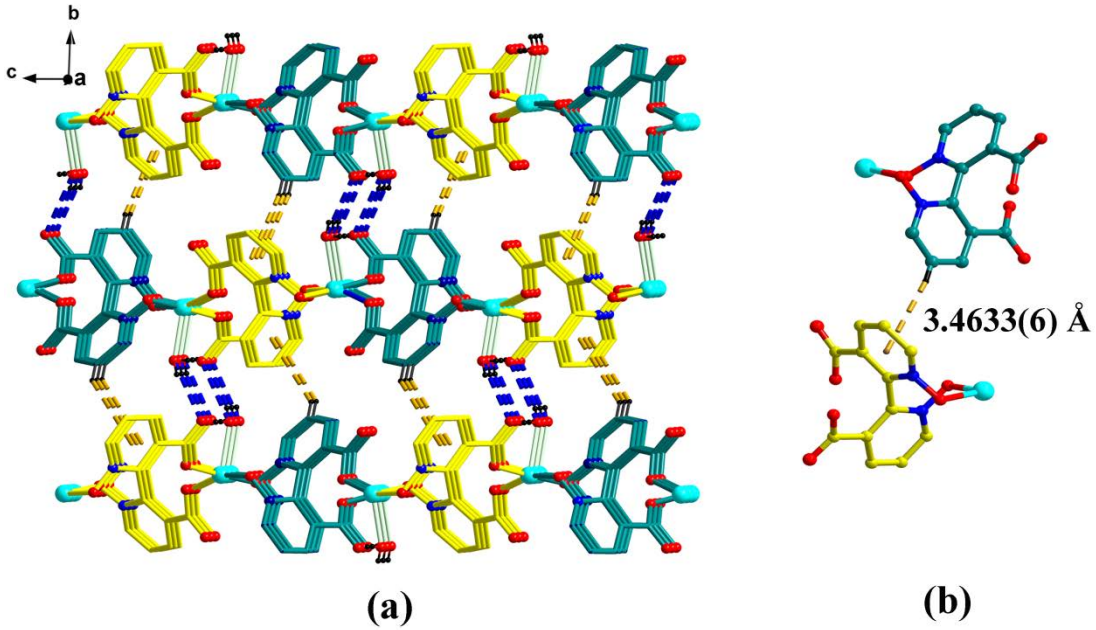



**Fig. S2** (a) A view of the 3D supramolecular network of complex **2** constructed through hydrogen bonds (O-H···O) and (b) C-H···$\pi$ interactions between the adjacent 2D layers. The broken lines are on behalf of the hydrogen bonds and C-H···$\pi$ interactions, and the hydrogen atoms are omitted for clarity.

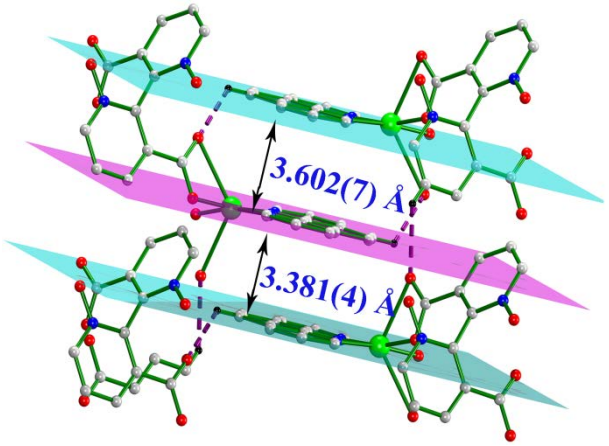



**Fig. S3** The $\pi$-$\pi$ stacking interactions can be observed in the 2D layers of complex **3**. The broken lines are on behalf of the hydrogen bonds, and the hydrogen atoms are omitted for clarity.

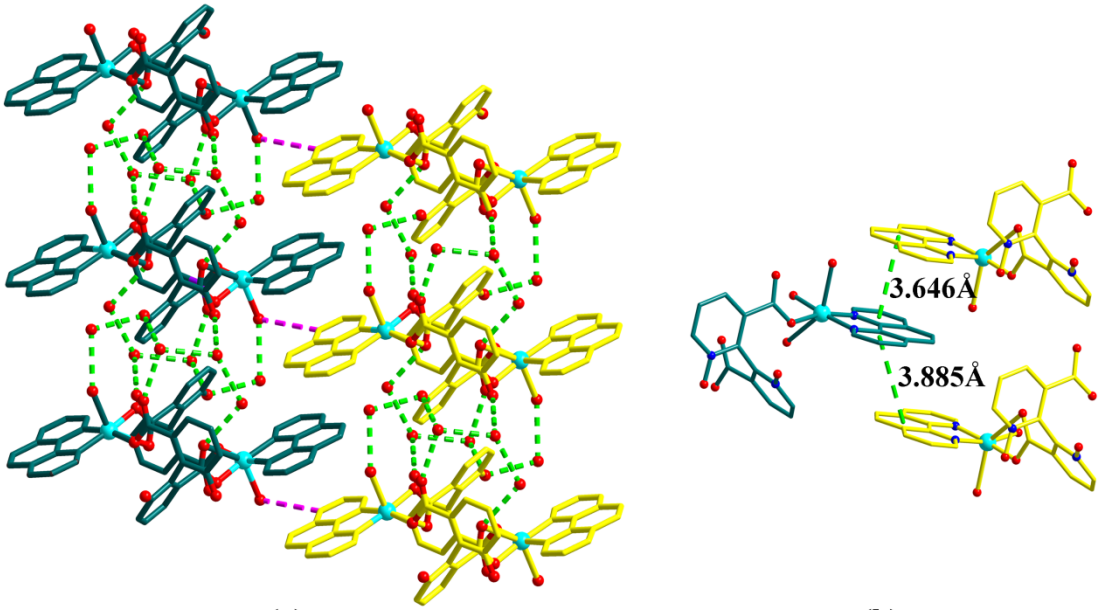



**Fig. S4** A view of 2D layer of complex **4** constructed by hydrogen bonds (O-H···O and C-H···O) and $\pi\cdots\pi$ staking interactions between two neighboring phen ligands with the centroids distance of 3.646 Å and 3.885 Å. The broken lines are on behalf of the hydrogen bonds and $\pi\cdots\pi$ interactions, and the hydrogen atoms are omitted for clarity.

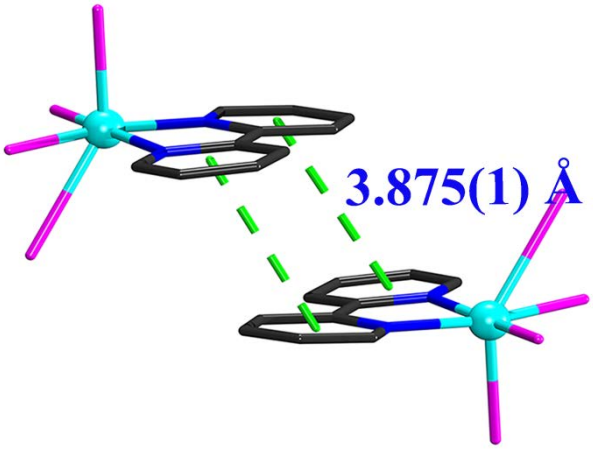
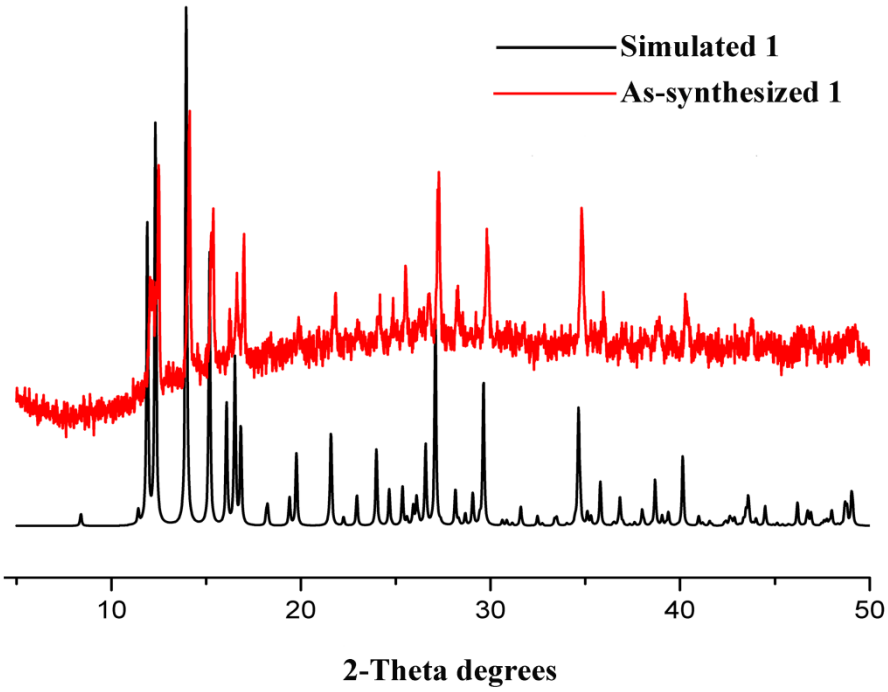
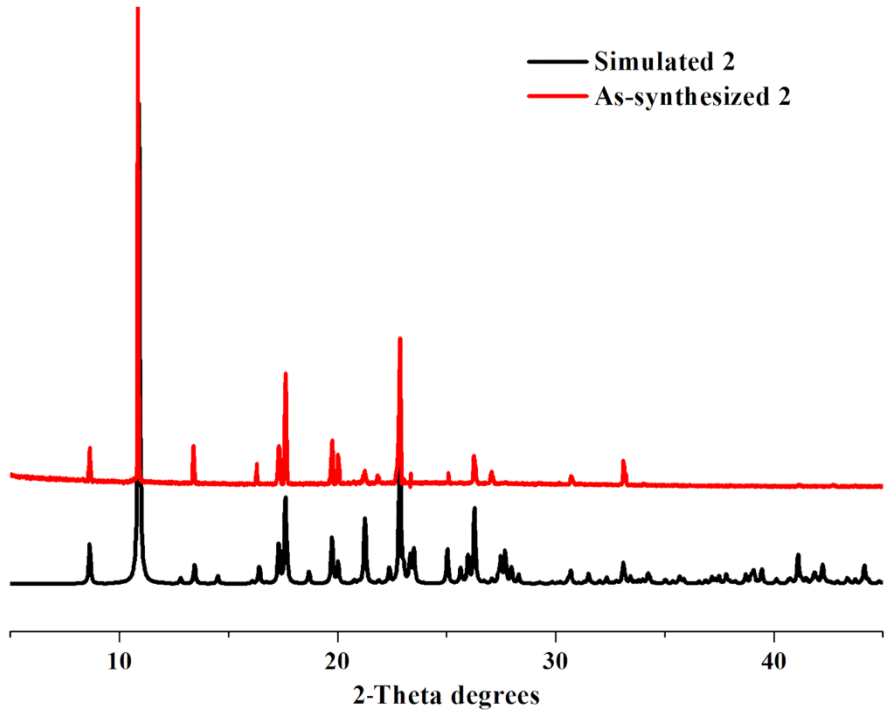
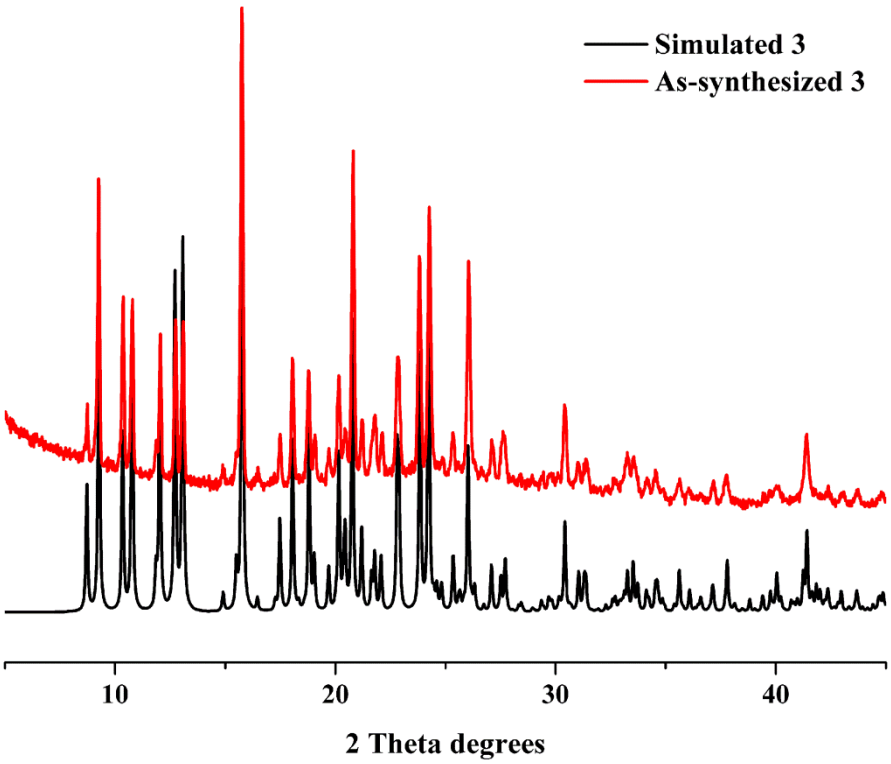
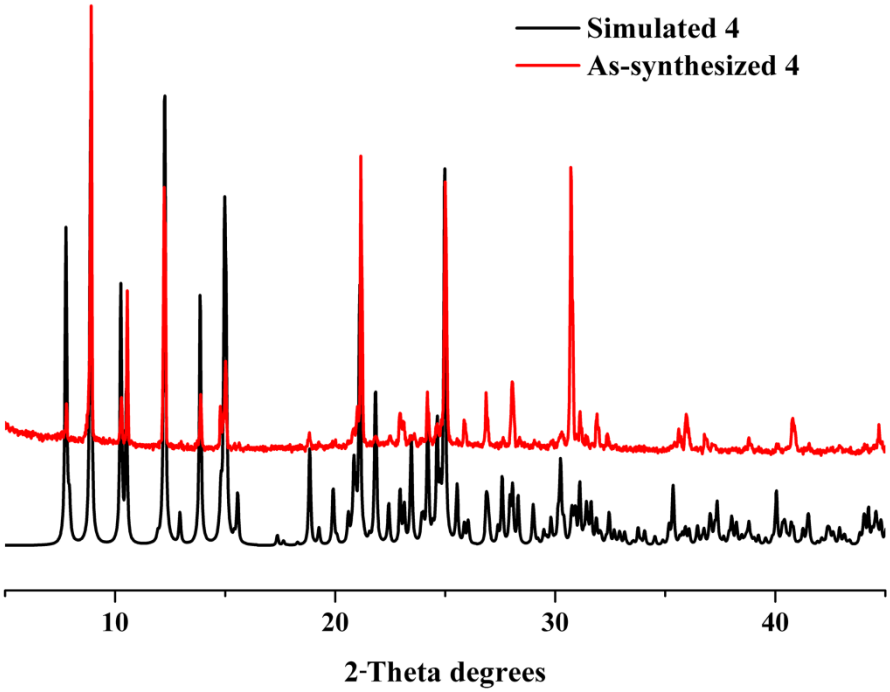



**Fig. S5** The $\pi$-$\pi$ stacking interactions can be seen between the 2D layers of complex **5**. The broken lines are on behalf of the$\pi\cdots\pi$ interactions, and the hydrogen atoms and (*R*, *S*)-bpdado ligands are omitted for clarity.




Simulated 2
As-synthesized 2
10
20
30
40
2-Theta degrees


Simulated 3
As-synthesized 3
10
20
30
40
2 Theta degrees



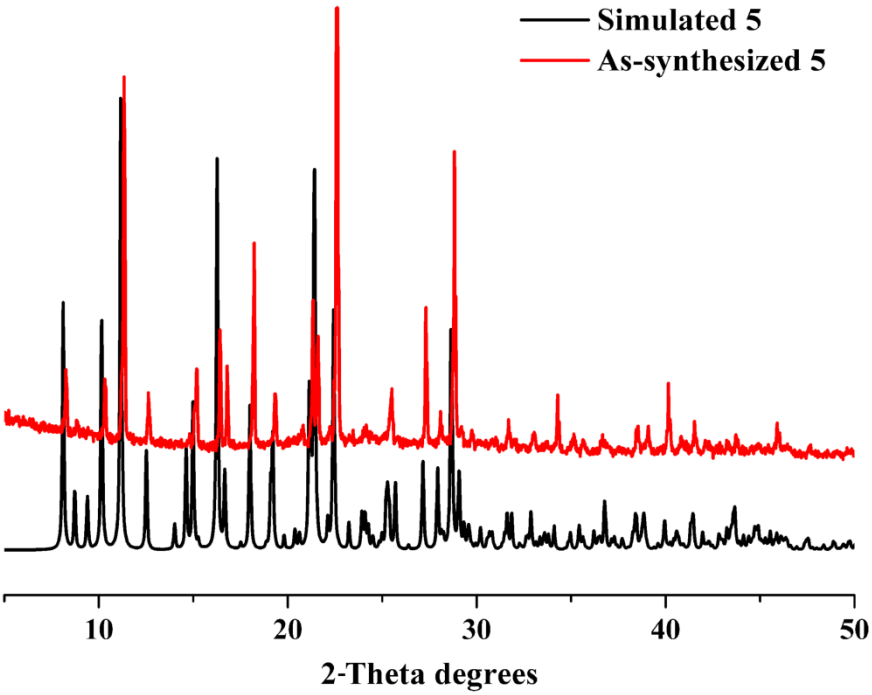
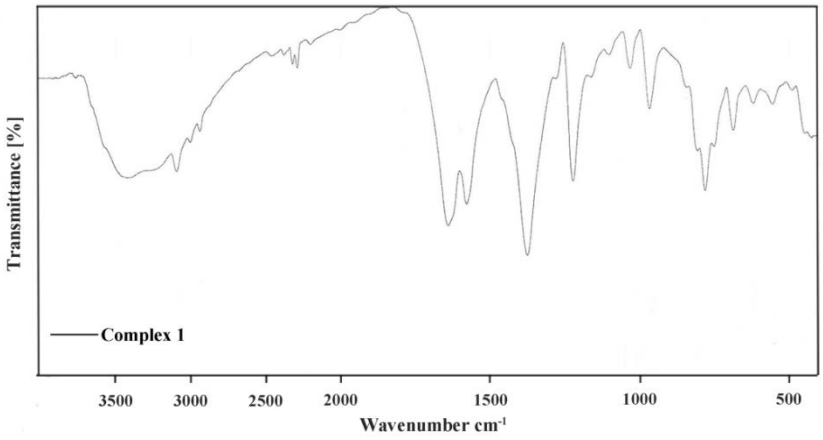
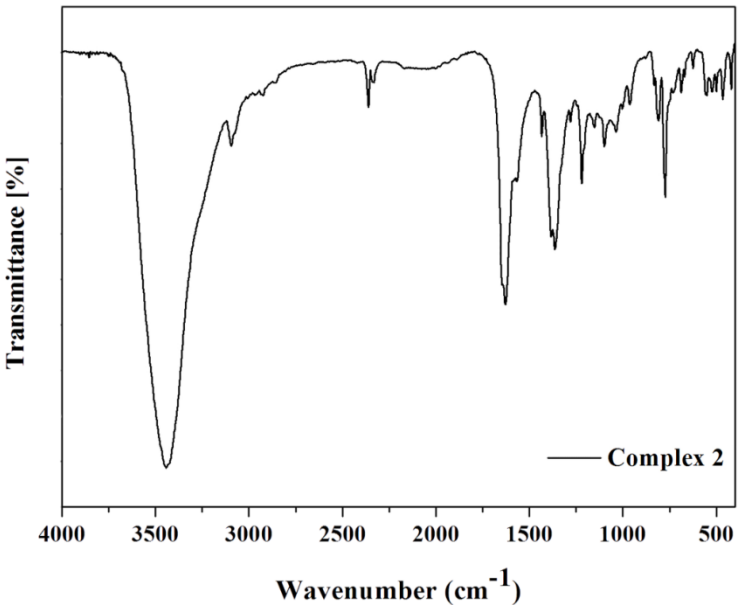
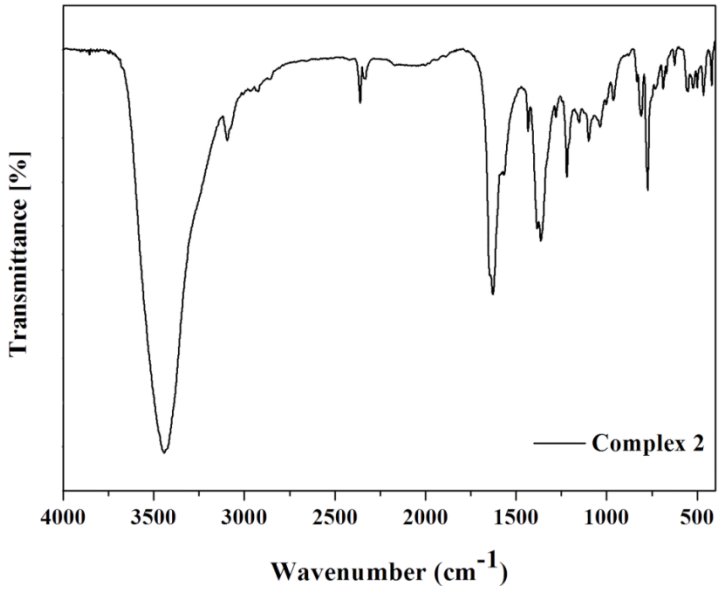
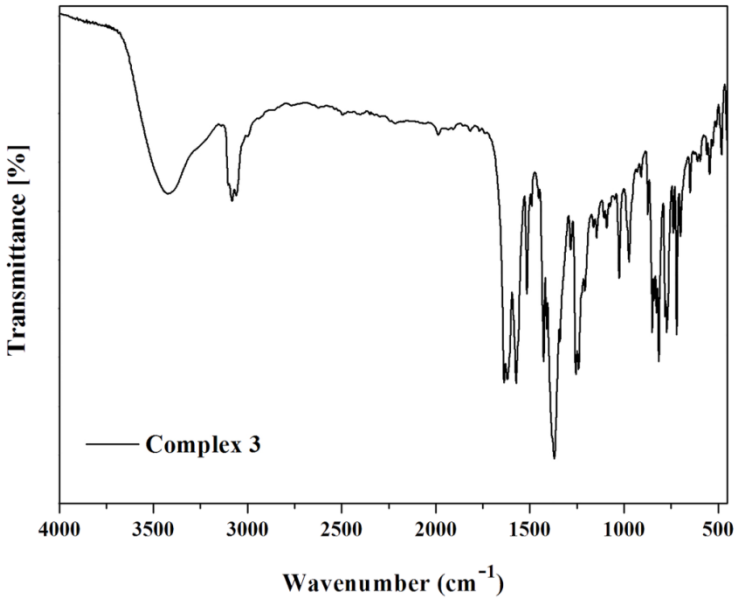



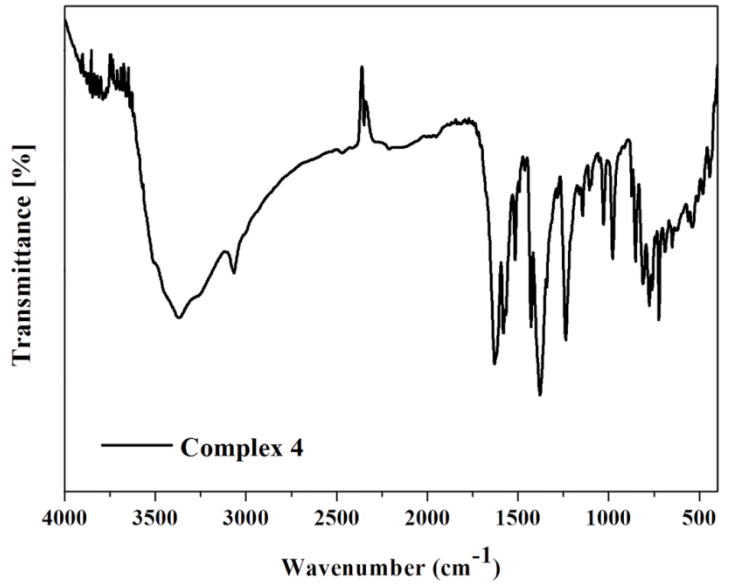

**Fig.S6** Comparisons of XRD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized products in complexes **1**-**5**.


Transmittance [%]
Complex 1
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


Transmittance [%]
Complex 2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


Transmittance [%]
Complex 2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)



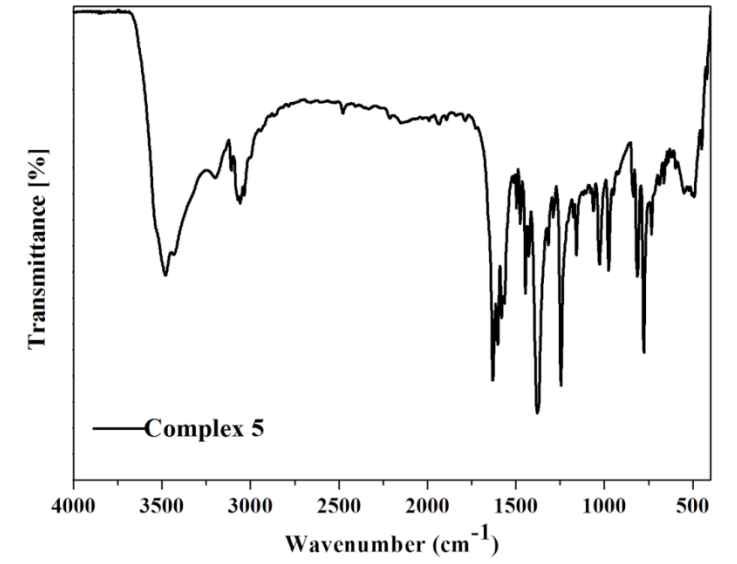




**Fig.S7** IR for complexes **1**-**5**.