Supporting Information

The Homocoupling Reaction of Aryl Halides Catalyzed by Metal Cations in Isostructural Coordination Polymers

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Synthesis of $[Zn(pypa)_2(H_2O)_2]_n$ (5)

Table S1. Crystallographic Data and Refinement Parameters for 5.

Figure S1. Supporting structure figures.

Figure S2. The 3D supermolecular structure by hydrogen bonds of 3.

Figure S3. PXRD data of 1-4.

Figure S4. Thermogravimetric curve of 1-4.

Figure S5. The SEM images of 1-4.

Figure S6. Characterization Data of Biaryl

Table S2. Selected bond lengths (Å) and bond angles (deg) for 1-5.

Table S3. Comparison of selected bond lengths (Å) of optimized by DFT calculations with experimental X-ray Diffraction Data.

Table S4. Hydrogen Bonds of 3.

Synthesis of $[Zn(pypa)_2(H_2O)_2)]_n$ (5) A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (29.7 mg, 0.1 mmol), Hpypa (10.8 mg, 0.05 mmol), dimethyl sulfoxide (4 mL) and H_2O (4 mL) was placed in a 25 mL Teflon-lined stainless steel container. The container was sealed and heated at 130 °C for 3 days. After the mixture had cooled to ambient temperature at a rate of 5 °C/h, light yellow crystals of **5** were obtained with a yield of 81% (based on Hpypa). Anal. Calcd (%) for $C_{22}H_{24}N_6ZnO_6$: C, 49.50; H, 4.53; N, 15.74. Found: C, 49.63; H, 4.59; N, 15.81. IR (KBr, cm^{-1}): 3412(s), 3139(s), 3102(s), 2156(m), 1632(s), 1567(s), 1492(m), 1413(s), 1402(s), 1327(s), 1208(m), 1112(m), 1013(w), 847(m).

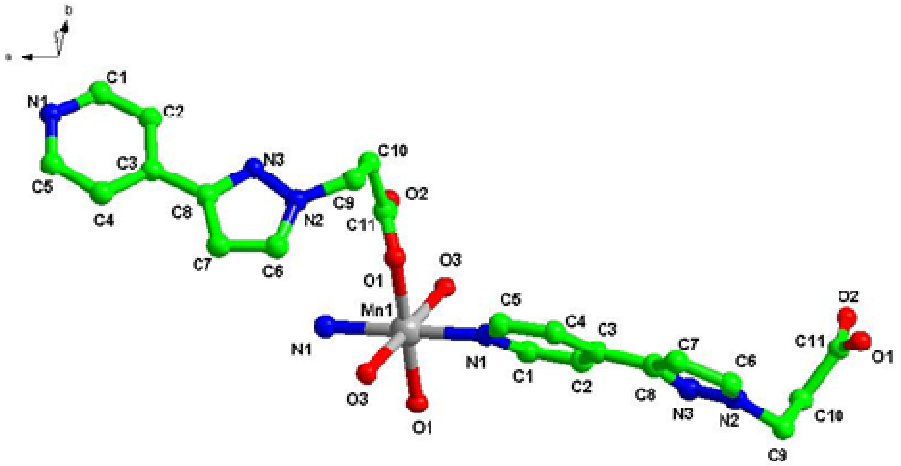
Crystal Structures. Single-crystal X-ray diffraction analysis reveals that complexes **5** are isostructural with **1-4**, thus **5** doesn't discussed here in detail.

Catalytic Capacity of 5. As expect, **5** shows no catalytic activity for any of the tested aromatic halides. According to the reference, Zn salt also has no catalytic activity in the homo-coupling reaction.

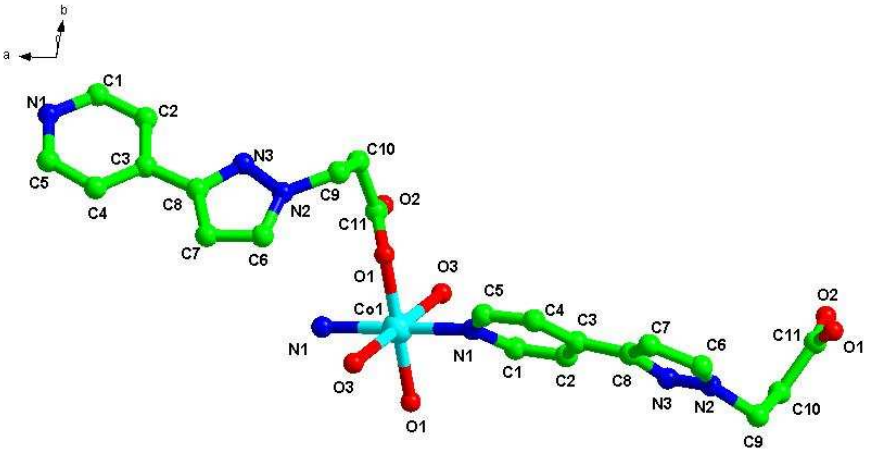
Table S1. Crystallographic Data and Refinement Parameters for **5**.

	5
Formula	$C_{22}H_{24}N_6Zn$
Fw	531.83
temp (K)	298(2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	12.219(2)
b (Å)	8.6730(17)
c (Å)	11.713(2)
α (deg)	90
β (deg)	111.50(3)
γ (deg)	90
V (Å^3)	1154.9(4)
Z	2
Dc (g cm^{-3})	1.529
μ (mm^{-1})	1.115
F(000)	548
GOF on F^2	0.975
no. of reflections	9281
no. of unique reflections	2744
R_1, wR_2 [I > 2σ(I)]	0.0589, 0.1515

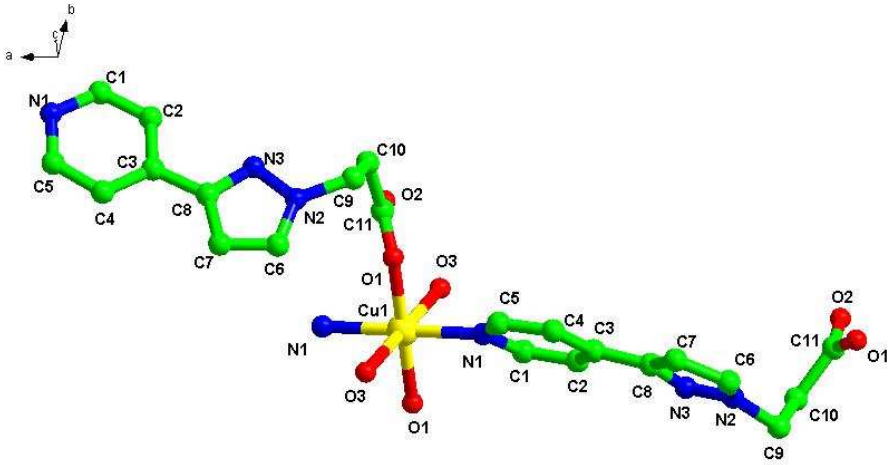
(a)


b
a
N1
C1
C2
C3
C5
C4
C8
N3
N2
C9
C10
O2
C11
C7
C6
O1
O3
Mn1
N1
O3
O1
C5
C4
C3
N1
C1
C2
C7
C6
C8
N3
N2
C10
C9
C11
O2
O1

(b)


b
a
N1
C1
C2
C3
C5
C4
C8
N3
N2
C9
C10
O2
C11
C7
C6
O1
O3
Co1
N1
O3
O1
C5
C4
C3
N1
C1
C2
C7
C6
C8
N3
N2
C10
C9
C11
O2
O1

(c)


b
a
N1
C1
C2
C3
C5
C4
C8
N3
N2
C9
C10
O2
C11
C7
C6
O1
O3
Cu1
N1
O3
O1
C5
C4
C3
N1
C1
C2
C7
C6
C8
N3
N2
C10
C9
C11
O2
O1

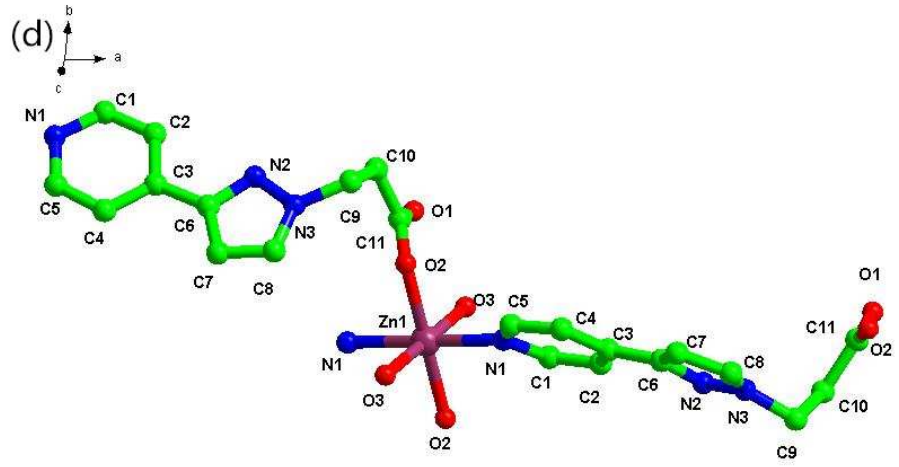


Figure S1. (a) Coordination environment around Mn^{2+} in **1;** (b) Coordination environment around Co^{2+} in **2;** (c) Coordination environment around Cu^{2+} in **4;** (d) Coordination environment around Zn^{2+} in **5**

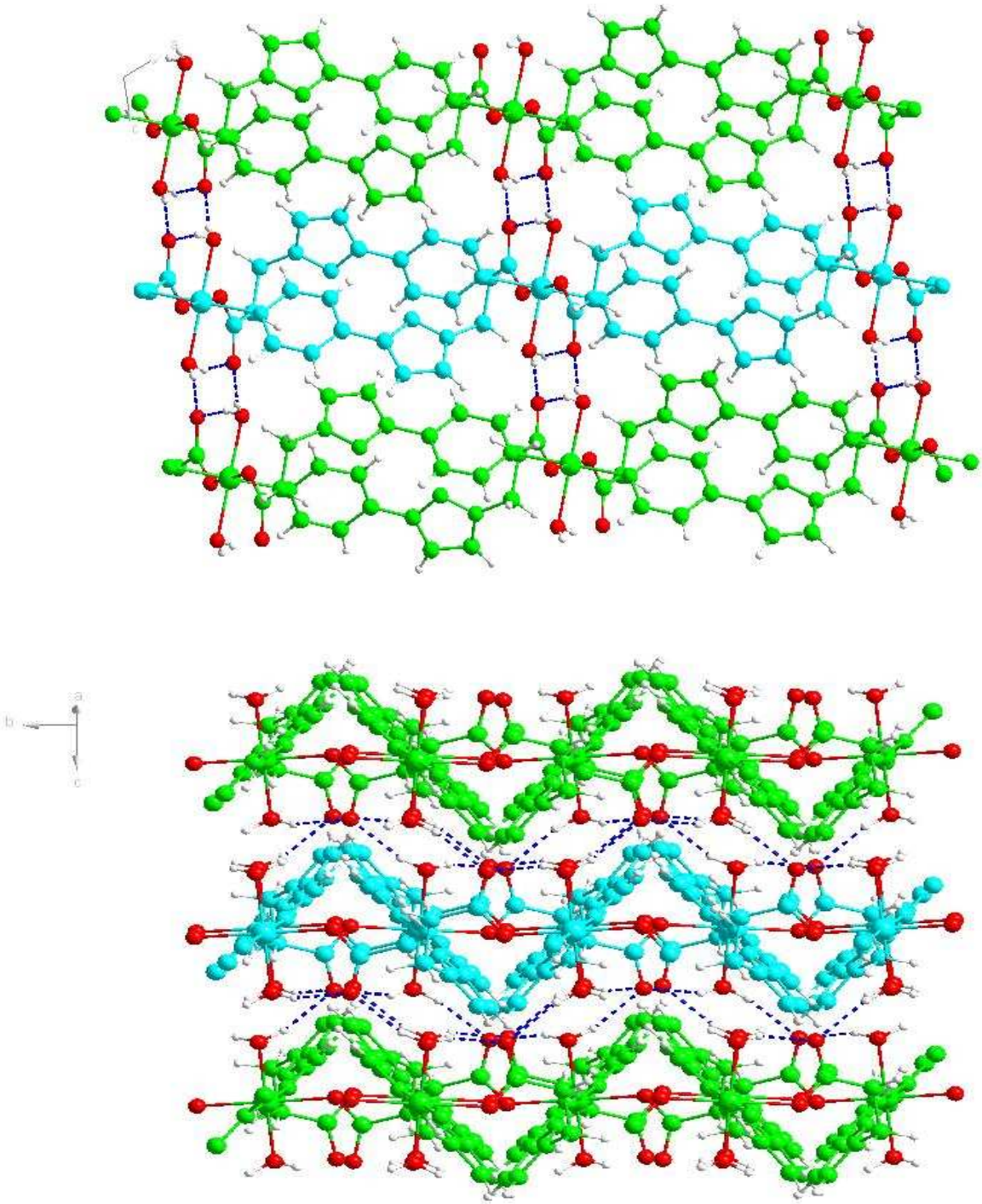
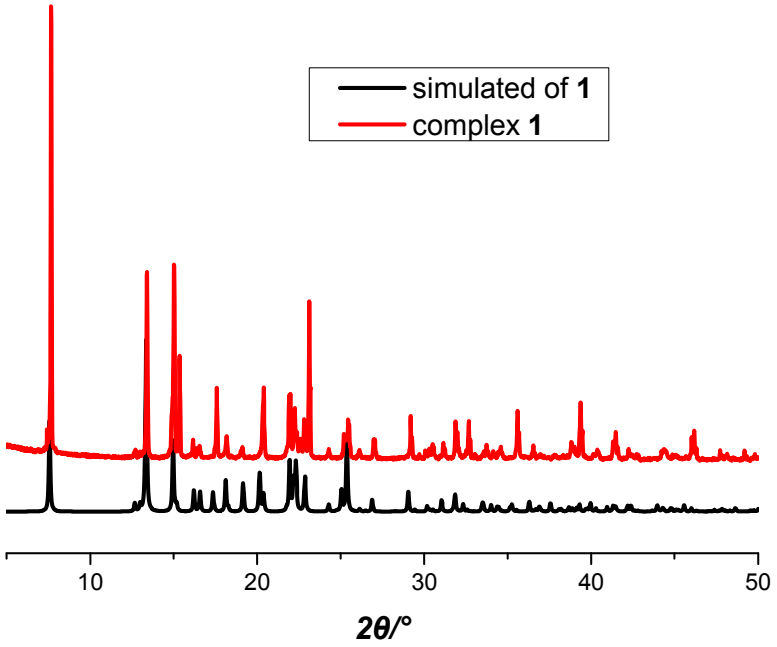
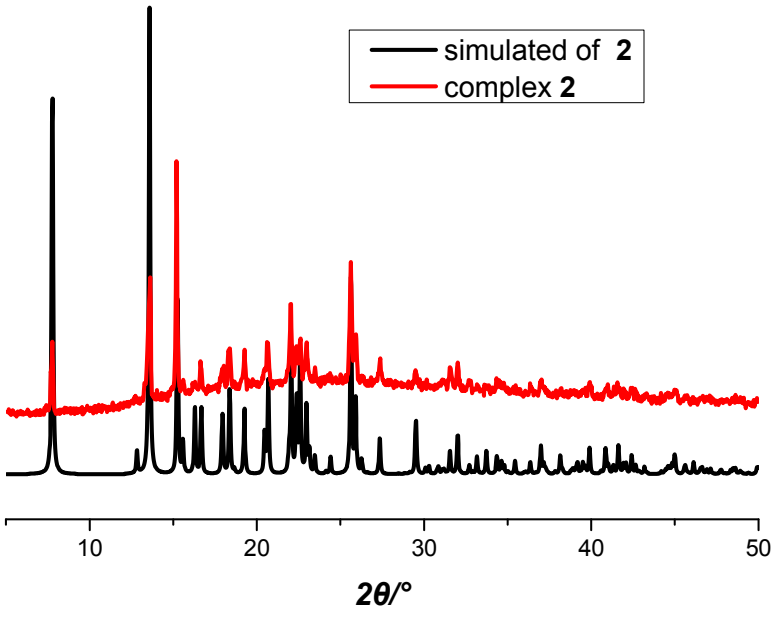
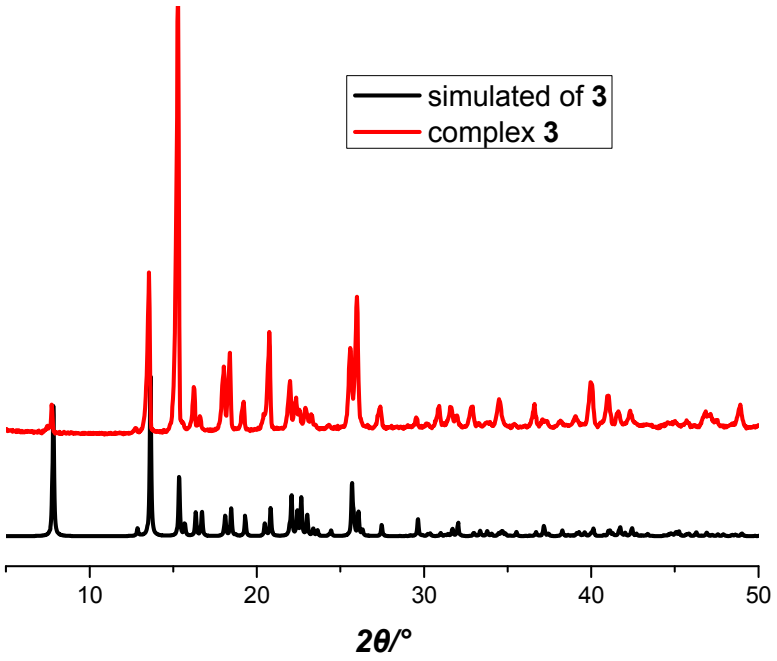


Figure S2. View of hydrogen bond in **3.**


simulated of 1
complex 1
10
20
30
40
50
2θ/°


simulated of 2
complex 2
10
20
30
40
50
2θ/°



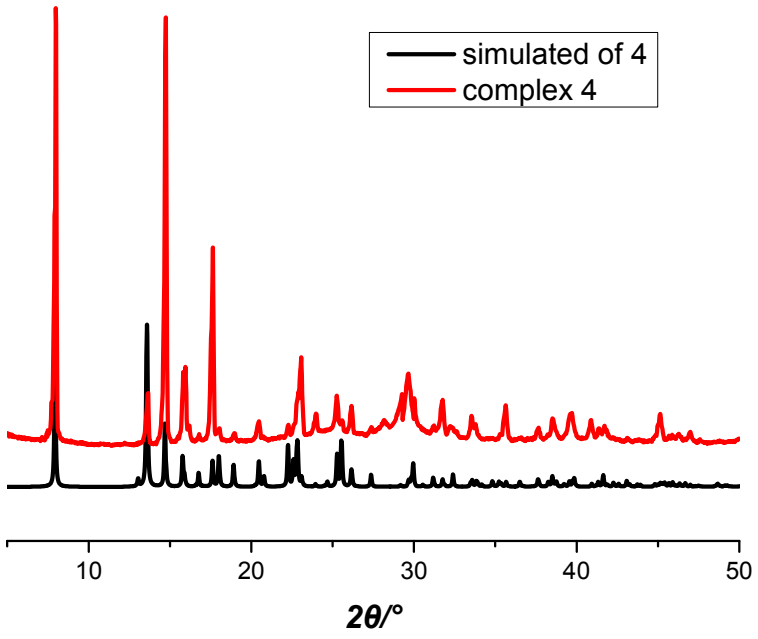


Figure S3. Simulated and experimental PXRD data for **1, 2, 3** and **4**

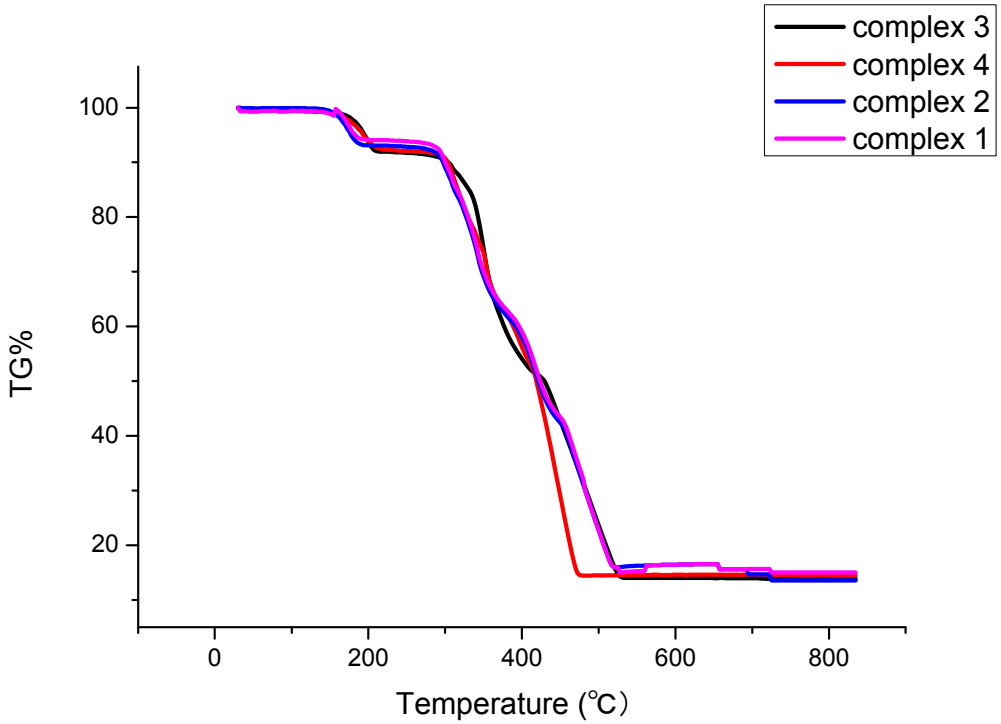


Figure S4. Thermogravimetric analyses of **1, 2, 3** and **4.**

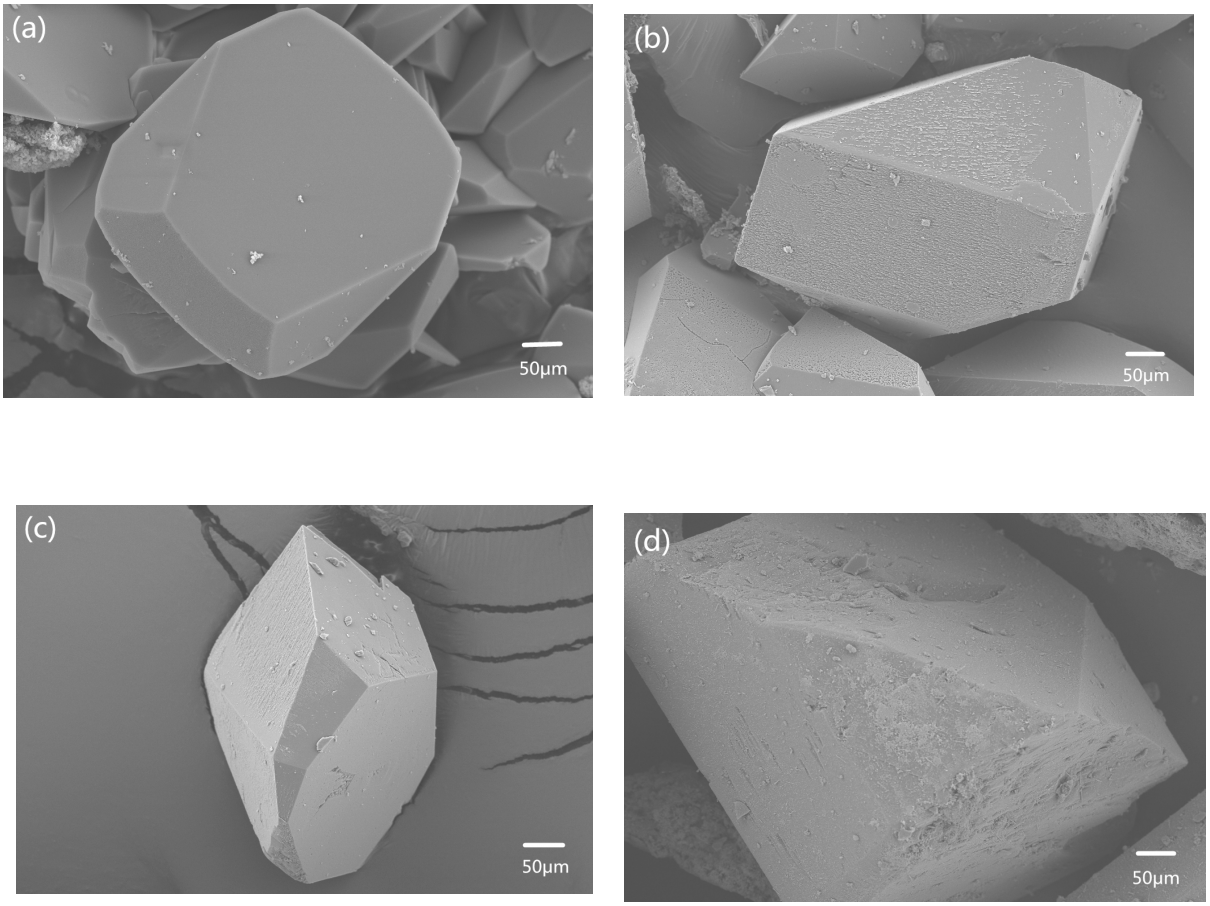
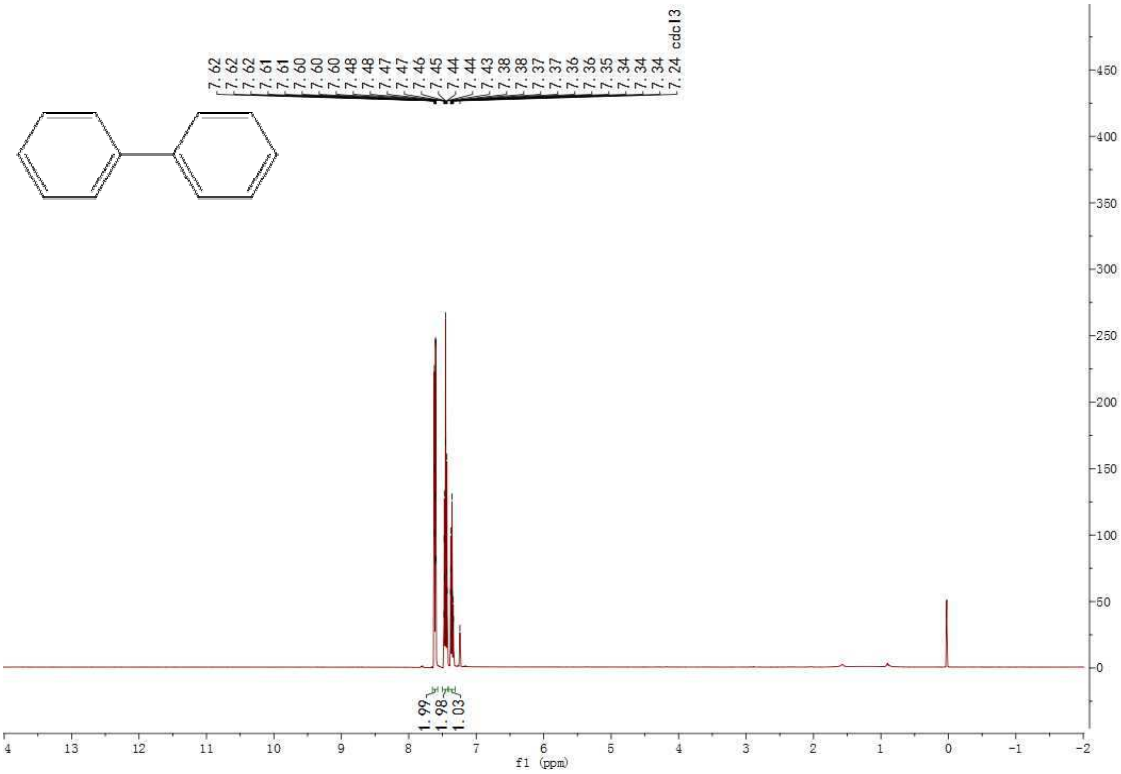
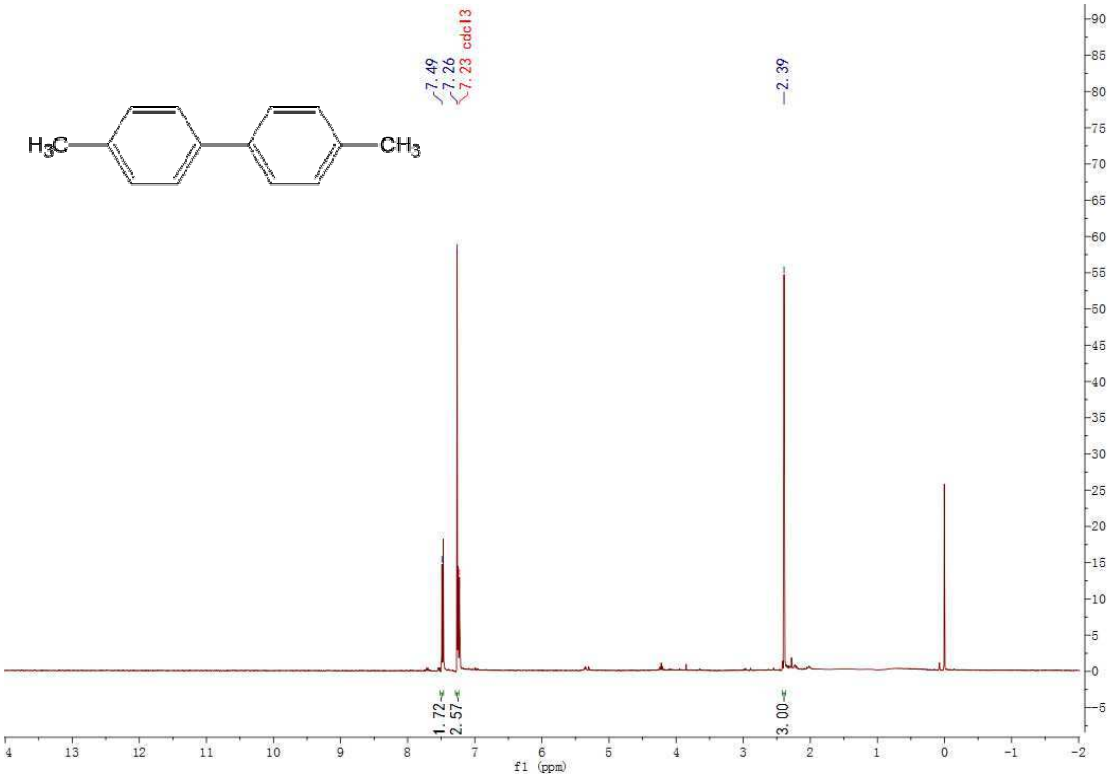
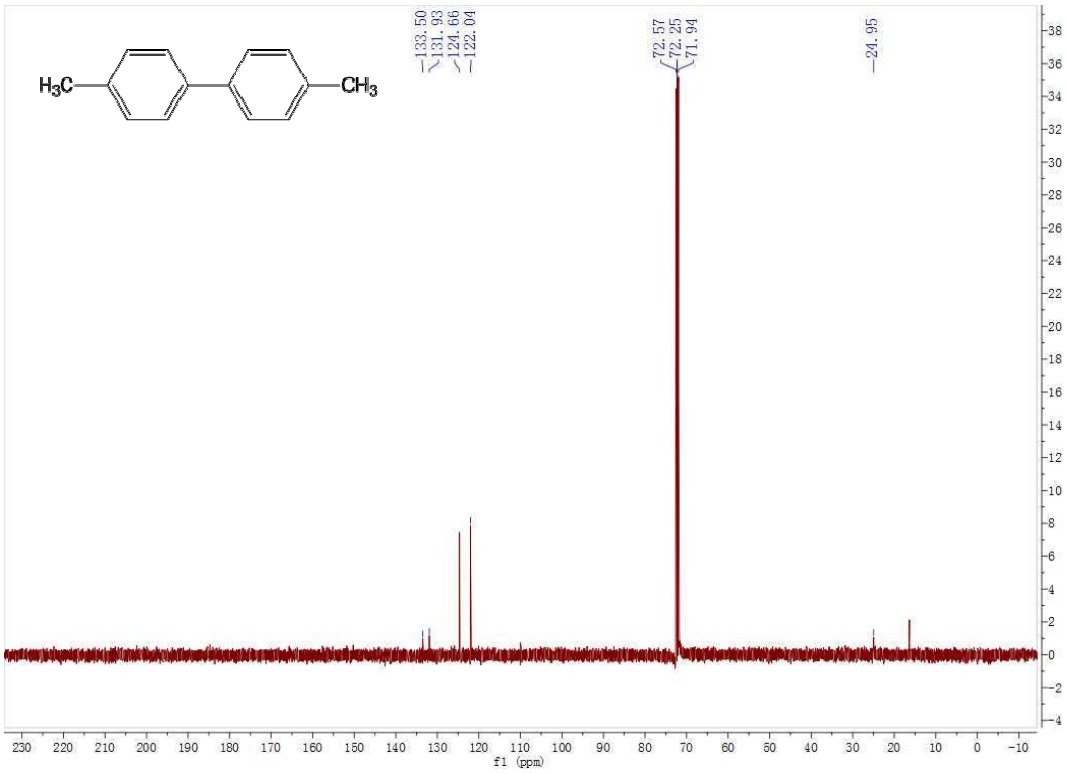


Figure S5. (a) The morphologies and particle sizes of **1;** (b) The morphologies and particle sizes of **2;** (c) The morphologies and particle sizes of **3;** (d) The Morphologies and particle sizes of **4.**


7.62
7.62
7.62
7.61
7.61
7.60
7.60
7.60
7.48
7.48
7.47
7.47
7.46
7.45
7.44
7.44
7.43
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.24 cdcl3
1.99
1.98
1.03
f1 (ppm)


H3C
CH3
7.49
7.26
7.23 cdcl3
2.39
1.72
2.57
3.00
f1 (ppm)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CH3
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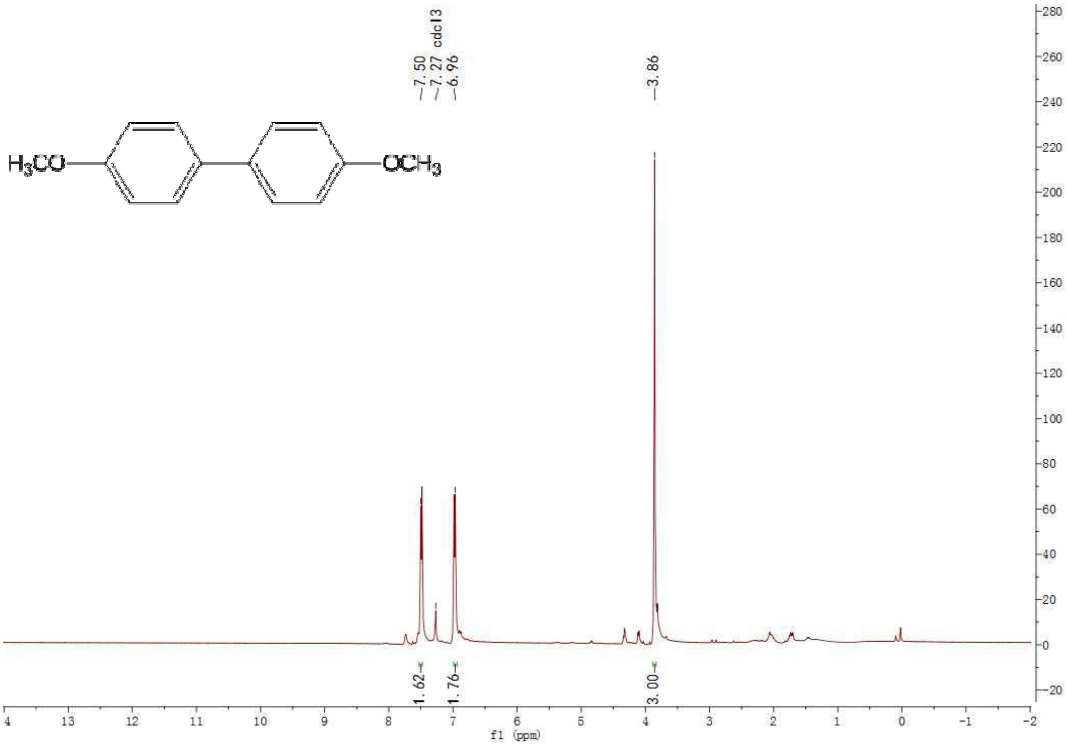
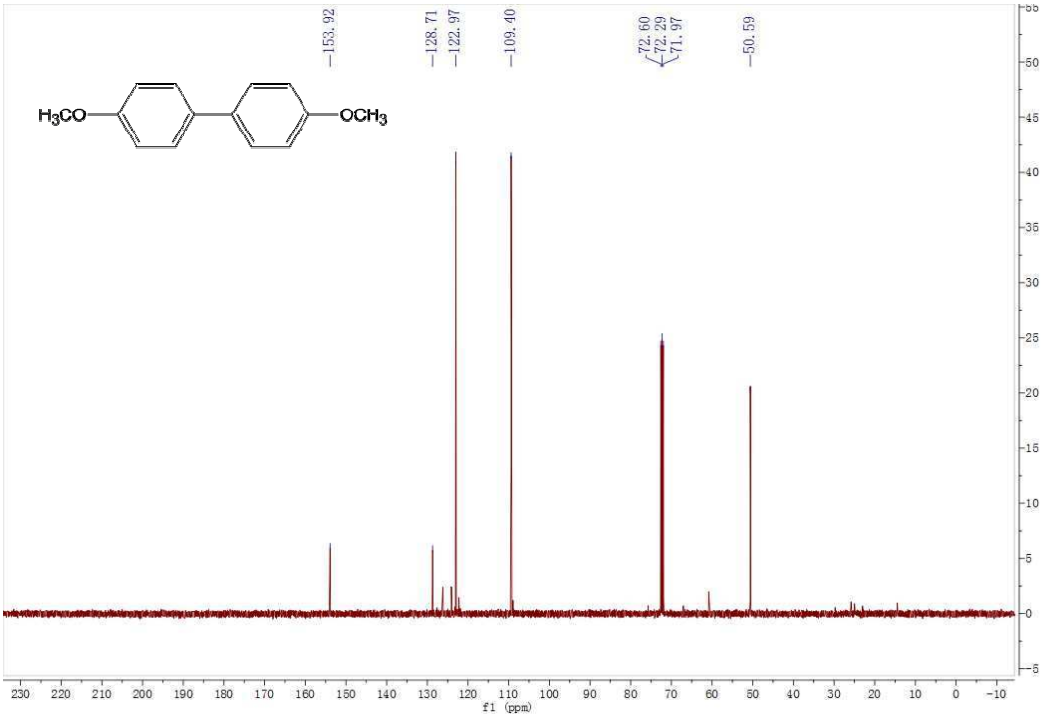
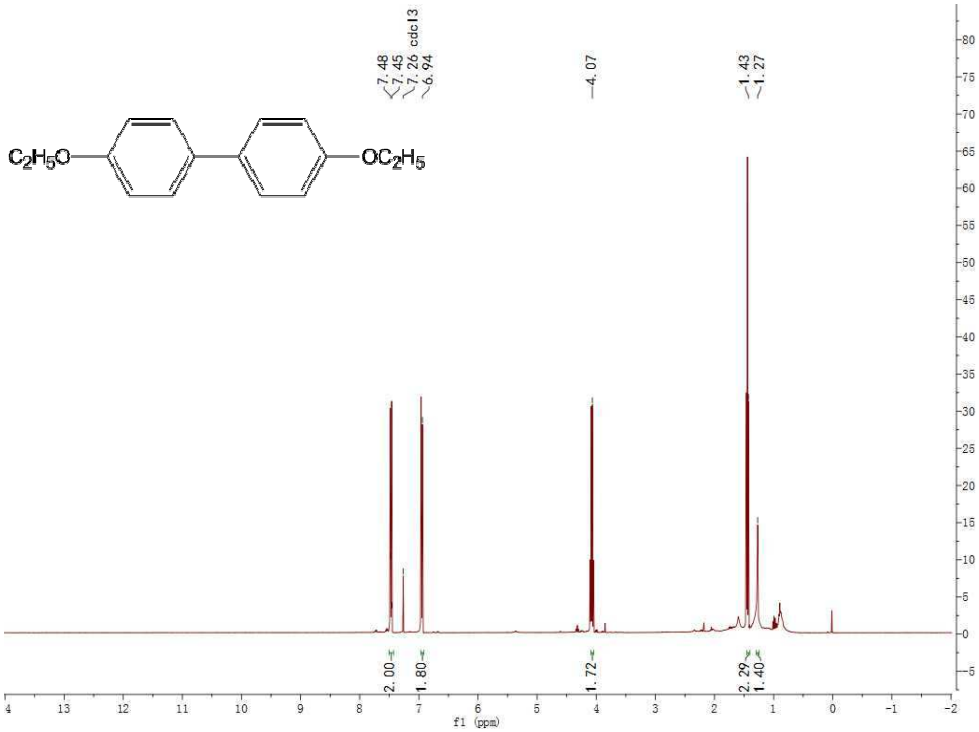
131.93
124.66
122.04
72.57
72.25
71.94
24.95
f1 (ppm)


H3CO
OCH3
7.50
7.27 cdcl3
6.96
3.86
1.62
1.76
3.00
f1 (ppm)


153.92
128.71
122.97
109.40
72.60
72.29
71.97
50.59
H3CO
OCH3
f1 (ppm)


7.48
7.45
7.26 cdcl3
6.94
4.07
1.43
1.27
C2H5O
OC2H5
2.00
1.80
1.72
2.29
1.40
f1 (ppm)

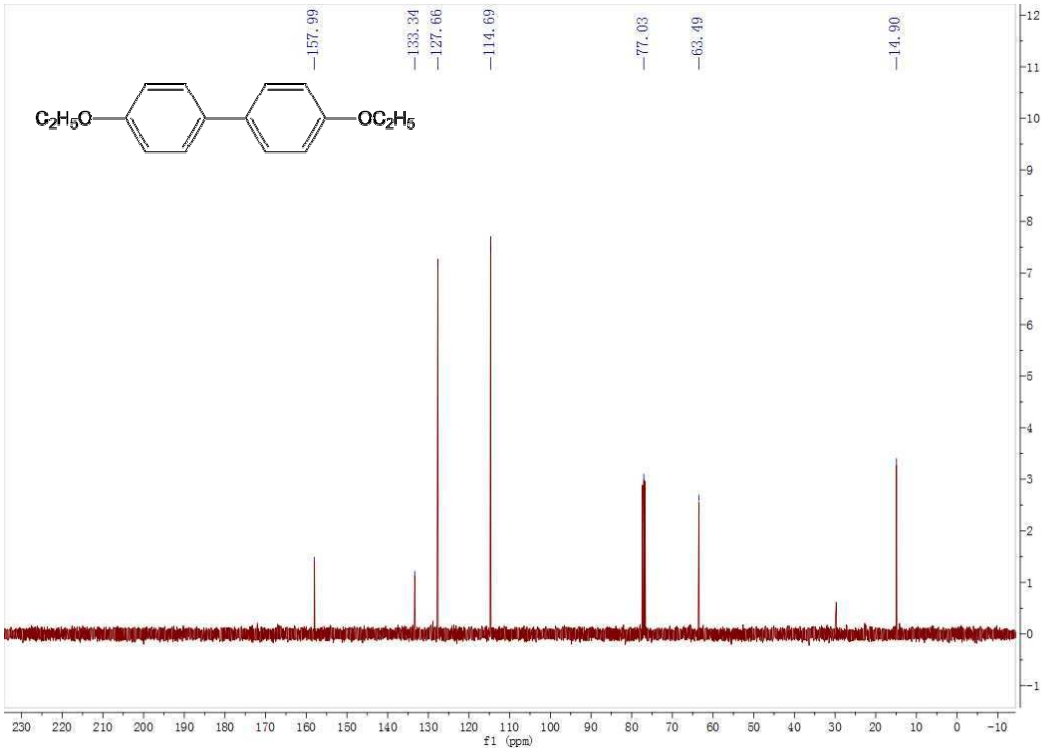


Figure S6. Characterization Data of Biaryl

Table S2. Selected bond lengths [Å] and angles [°] for coordination polymers **1-5.**

1			
Mn(1)-O(1)#1	2.1437(14)	C(1)-O(1)-Mn(1)#4	128.89(13)
Mn(1)-O(1)#2	2.1437(14)	Mn(1)-O(3)-H(3W1)	109.5
Mn(1)-O(3)#3	2.1854(16)	Mn(1)-O(3)-H(3W2)	100(2)
Mn(1)-O(3)	2.1854(16)	H(3W1)-O(3)-H(3W2)	116.2
Mn(1)-N(1)	2.3016(19)	C(11)-N(1)-C(9)	116.42(19)
Mn(1)-N(1)#3	2.3016(19)	C(11)-N(1)-Mn(1)	125.91(14)
O(1)-C(1)	1.252(2)	C(9)-N(1)-Mn(1)	117.41(15)
O(1)-Mn(1)#4	2.1437(14)	C(6)-N(2)-N(3)	104.72(18)
O(2)-C(1)	1.259(2)	C(4)-N(3)-N(2)	112.26(18)
O(3)-H(3W1)	0.82	C(4)-N(3)-C(3)	128.53(19)
O(3)-H(3W2)	0.856(16)	N(2)-N(3)-C(3)	118.86(19)
N(1)-C(11)	1.331(3)	O(1)-C(1)-O(2)	124.74(18)
N(1)-C(9)	1.343(3)	O(1)-C(1)-C(2)	118.21(18)
N(2)-C(6)	1.339(3)	O(2)-C(1)-C(2)	117.03(18)
N(2)-N(3)	1.344(2)	C(1)-C(2)-C(3)	115.71(18)
N(3)-C(4)	1.340(3)	C(1)-C(2)-H(2A)	108.4
N(3)-C(3)	1.459(3)	C(3)-C(2)-H(2A)	108.4
C(1)-C(2)	1.512(3)	C(1)-C(2)-H(2B)	108.4
C(2)-C(3)	1.513(3)	C(3)-C(2)-H(2B)	108.4
C(2)-H(2A)	0.97	H(2A)-C(2)-H(2B)	107.4
C(2)-H(2B)	0.97	N(3)-C(3)-C(2)	112.65(18)
C(3)-H(3A)	0.97	N(3)-C(3)-H(3A)	109.1
C(3)-H(3B)	0.97	C(2)-C(3)-H(3A)	109.1
C(4)-C(5)	1.369(3)	N(3)-C(3)-H(3B)	109.1
C(4)-H(4)	0.93	C(2)-C(3)-H(3B)	109.1
C(5)-C(6)	1.398(3)	H(3A)-C(3)-H(3B)	107.8
C(5)-H(5)	0.93	N(3)-C(4)-C(5)	107.2(2)
C(6)-C(7)	1.469(3)	N(3)-C(4)-H(4)	126.4
C(7)-C(10)	1.382(3)	C(5)-C(4)-H(4)	126.4
C(7)-C(8)	1.389(3)	C(4)-C(5)-C(6)	104.8(2)
C(8)-C(9)	1.373(3)	C(4)-C(5)-H(5)	127.6
C(8)-H(8)	0.93	C(6)-C(5)-H(5)	127.6
C(9)-H(9)	0.93	N(2)-C(6)-C(5)	110.97(19)
C(10)-C(11)	1.383(3)	N(2)-C(6)-C(7)	118.68(19)
C(10)-H(10)	0.93	C(5)-C(6)-C(7)	130.3(2)
C(11)-H(11)	0.93	C(10)-C(7)-C(8)	117.05(19)
		C(10)-C(7)-C(6)	122.4(2)
O(1)#1-Mn(1)-O(1)#2	180.00(8)	C(8)-C(7)-C(6)	120.48(19)
O(1)#1-Mn(1)-O(3)#3	88.97(6)	C(9)-C(8)-C(7)	119.7(2)
O(1)#2-Mn(1)-O(3)#3	91.03(6)	C(9)-C(8)-H(8)	120.1
O(1)#1-Mn(1)-O(3)	91.03(6)	C(7)-C(8)-H(8)	120.1
O(1)#2-Mn(1)-O(3)	88.97(6)	N(1)-C(9)-C(8)	123.5(2)
O(3)#3-Mn(1)-O(3)	180.00(11)	N(1)-C(9)-H(9)	118.2
O(1)#1-Mn(1)-N(1)	92.12(6)	C(8)-C(9)-H(9)	118.2
O(1)#2-Mn(1)-N(1)	87.88(6)	C(7)-C(10)-C(11)	119.4(2)
O(3)#3-Mn(1)-N(1)	92.08(7)	C(7)-C(10)-H(10)	120.3

O(3)-Mn(1)-N(1)	87.92(7)	C(11)-C(10)-H(10)	120.3
O(1)#1-Mn(1)-N(1)#3	87.88(6)	N(1)-C(11)-C(10)	123.78(19)
O(1)#2-Mn(1)-N(1)#3	92.12(6)	N(1)-C(11)-H(11)	118.1
O(3)#3-Mn(1)-N(1)#3	87.92(7)	C(10)-C(11)-H(11)	118.1
O(3)-Mn(1)-N(1)#3	92.08(7)		
N(1)-Mn(1)-N(1)#3	180.00(13)		

Symmetrycodes: #1 x-1,-y+1/2,z-1/2；#2 -x+1,y-1/2,-z+1/2；#3 -x,-y,-z；#4 -x+1,y+1/2,-z+1/2

2			
Co(1)-O(1)#1	2.0809(14)	C(11)-O(1)-Co(1)#4	128.14(12)
Co(1)-O(1)#2	2.0809(14)	Co(1)-O(3)-H(3W1)	122.4(17)
Co(1)-O(3)#3	2.1110(14)	Co(1)-O(3)-H(3W2)	98.8(18)
Co(1)-O(3)	*2.1110(14)*	H(3W1)-O(3)-H(3W2)	111.4(19)
Co(1)-N(1)#3	2.1660(18)	C(5)-N(1)-C(1)	116.04(17)
Co(1)-N(1)	2.1660(18)	C(5)-N(1)-Co(1)	125.27(13)
O(1)-C(11)	1.254(2)	C(1)-N(1)-Co(1)	118.53(14)
O(1)-Co(1)#4	2.0809(14)	C(6)-N(2)-N(3)	104.79(17)
O(2)-C(11)	1.260(2)	C(8)-N(3)-N(2)	112.37(17)
O(3)-H(3W1)	0.846(15)	C(8)-N(3)-C(9)	128.52(18)
O(3)-H(3W2)	0.855(15)	N(2)-N(3)-C(9)	118.74(18)
N(1)-C(5)	1.331(3)	N(1)-C(1)-C(2)	123.65(19)
N(1)-C(1)	1.350(3)	N(1)-C(1)-H(1)	118.2
N(2)-C(6)	1.338(3)	C(2)-C(1)-H(1)	118.2
N(2)-N(3)	1.346(2)	C(1)-C(2)-C(3)	119.94(19)
N(3)-C(8)	1.340(3)	C(1)-C(2)-H(2)	120
N(3)-C(9)	1.461(3)	C(3)-C(2)-H(2)	120
C(1)-C(2)	1.368(3)	C(2)-C(3)-C(4)	116.96(18)
C(1)-H(1)	0.93	C(2)-C(3)-C(6)	120.66(18)
C(2)-C(3)	1.389(3)	C(4)-C(3)-C(6)	122.29(18)
C(2)-H(2)	0.93	C(5)-C(4)-C(3)	119.17(19)
C(3)-C(4)	1.389(3)	C(5)-C(4)-H(4)	120.4
C(3)-C(6)	1.470(3)	C(3)-C(4)-H(4)	120.4
C(4)-C(5)	1.384(3)	N(1)-C(5)-C(4)	124.17(18)
C(4)-H(4)	0.93	N(1)-C(5)-H(5)	117.9
C(5)-H(5)	0.93	C(4)-C(5)-H(5)	117.9
C(6)-C(7)	1.403(3)	N(2)-C(6)-C(7)	110.91(18)
C(7)-C(8)	1.372(3)	N(2)-C(6)-C(3)	118.71(18)
C(7)-H(7)	0.93	C(7)-C(6)-C(3)	130.30(19)
C(8)-H(8)	0.93	C(8)-C(7)-C(6)	104.8(2)
C(9)-C(10)	1.514(3)	C(8)-C(7)-H(7)	127.6
C(9)-H(9A)	0.97	C(6)-C(7)-H(7)	127.6
C(9)-H(9B)	0.97	N(3)-C(8)-C(7)	107.17(19)
C(10)-C(11)	1.515(3)	N(3)-C(8)-H(8)	126.4
C(10)-H(10A)	0.97	C(7)-C(8)-H(8)	126.4
C(10)-H(10B)	0.97	N(3)-C(9)-C(10)	112.58(17)
		N(3)-C(9)-H(9A)	109.1
O(1)#1-Co(1)-O(1)#2	180.00(7)	C(10)-C(9)-H(9A)	109.1
O(1)#1-Co(1)-O(3)#3	87.74(6)	N(3)-C(9)-H(9B)	109.1

O(1)#2-Co(1)-O(3)#3	92.26(5)	C(10)-C(9)-H(9B)	109.1
O(1)#1-Co(1)-O(3)	92.26(6)	H(9A)-C(9)-H(9B)	107.8
O(1)#2-Co(1)-O(3)	87.74(6)	C(9)-C(10)-C(11)	115.98(17)
O(3)#3-Co(1)-O(3)	180.00(10)	C(9)-C(10)-H(10A)	108.3
O(1)#1-Co(1)-N(1)#3	88.62(6)	C(11)-C(10)-H(10A)	108.3
O(1)#2-Co(1)-N(1)#3	91.38(6)	C(9)-C(10)-H(10B)	108.3
O(3)#3-Co(1)-N(1)#3	87.84(6)	C(11)-C(10)-H(10B)	108.3
O(3)-Co(1)-N(1)#3	92.16(6)	H(10A)-C(10)-H(10B)	107.4
O(1)#1-Co(1)-N(1)	91.38(6)	O(1)-C(11)-O(2)	125.19(17)
O(1)#2-Co(1)-N(1)	88.62(6)	O(1)-C(11)-C(10)	117.96(16)
O(3)#3-Co(1)-N(1)	92.16(6)	O(2)-C(11)-C(10)	116.83(17)
O(3)-Co(1)-N(1)	87.84(6)		
N(1)#3-Co(1)-N(1)	180.00(12)		

Symmetrycodes: #1 x-1,-y+1/2,z-1/2；#2 -x+1,y-1/2,-z+1/2；#3 -x,-y,-z；#4 -x+1,y+1/2,-z+1/2

3			
Ni(1)-O(2)#1	2.0541(18)	C(11)-O(2)-Ni(1)#4	127.87(17)
Ni(1)-O(2)#2	2.0541(18)	Ni(1)-O(3)-H(3W1)	109.5
Ni(1)-O(3)	2.0825(19)	Ni(1)-O(3)-H(3W2)	98(3)
Ni(1)-O(3)#3	2.0825(19)	H(3W1)-O(3)-H(3W2)	115.3
Ni(1)-N(1)#3	2.110(2)	C(5)-N(1)-C(1)	116.4(2)
Ni(1)-N(1)	2.110(2)	C(5)-N(1)-Ni(1)	124.51(18)
O(1)-C(11)	1.264(3)	C(1)-N(1)-Ni(1)	118.99(18)
O(2)-C(11)	1.252(3)	C(6)-N(2)-N(3)	104.8(2)
O(2)-Ni(1)#4	2.0541(18)	C(8)-N(3)-N(2)	112.4(2)
O(3)-H(3W1)	0.82	C(8)-N(3)-C(9)	128.3(2)
O(3)-H(3W2)	0.82(4)	N(2)-N(3)-C(9)	119.0(2)
N(1)-C(5)	1.336(3)	N(1)-C(1)-C(2)	123.7(3)
N(1)-C(1)	1.346(3)	N(1)-C(1)-H(1)	118.2
N(2)-C(6)	1.335(4)	C(2)-C(1)-H(1)	118.2
N(2)-N(3)	1.344(3)	C(1)-C(2)-C(3)	119.9(3)
N(3)-C(8)	1.341(4)	C(1)-C(2)-H(2)	120.1
N(3)-C(9)	1.460(4)	C(3)-C(2)-H(2)	120.1
C(1)-C(2)	1.365(4)	C(4)-C(3)-C(2)	116.9(3)
C(1)-H(1)	0.93	C(4)-C(3)-C(6)	122.4(3)
C(2)-C(3)	1.395(4)	C(2)-C(3)-C(6)	120.6(3)
C(2)-H(2)	0.93	C(5)-C(4)-C(3)	119.3(3)
C(3)-C(4)	1.389(4)	C(5)-C(4)-H(4)	120.3
C(3)-C(6)	1.473(4)	C(3)-C(4)-H(4)	120.3
C(4)-C(5)	1.383(4)	N(1)-C(5)-C(4)	123.8(3)
C(4)-H(4)	0.93	N(1)-C(5)-H(5)	118.1
C(5)-H(5)	0.93	C(4)-C(5)-H(5)	118.1
C(6)-C(7)	1.401(4)	N(2)-C(6)-C(7)	111.1(3)
C(7)-C(8)	1.374(4)	N(2)-C(6)-C(3)	118.7(3)
C(7)-H(7)	0.93	C(7)-C(6)-C(3)	130.1(3)
C(8)-H(8)	0.93	C(8)-C(7)-C(6)	104.7(3)
C(9)-C(10)	1.518(4)	C(8)-C(7)-H(7)	127.7
C(9)-H(9A)	0.97	C(6)-C(7)-H(7)	127.7

C(9)-H(9B)	0.97	N(3)-C(8)-C(7)	107.0(3)
C(10)-C(11)	1.511(4)	N(3)-C(8)-H(8)	126.5
C(10)-H(10A)	0.97	C(7)-C(8)-H(8)	126.5
C(10)-H(10B)	0.97	N(3)-C(9)-C(10)	112.4(2)
		N(3)-C(9)-H(9A)	109.1
O(2)#1-Ni(1)-O(2)#2	180	C(10)-C(9)-H(9A)	109.1
O(2)#1-Ni(1)-O(3)	87.46(8)	N(3)-C(9)-H(9B)	109.1
O(2)#2-Ni(1)-O(3)	92.54(8)	C(10)-C(9)-H(9B)	109.1
O(2)#1-Ni(1)-O(3)#3	92.54(8)	H(9A)-C(9)-H(9B)	107.9
O(2)#2-Ni(1)-O(3)#3	87.46(8)	C(11)-C(10)-C(9)	116.0(2)
O(3)-Ni(1)-O(3)#3	180	C(11)-C(10)-H(10A)	108.3
O(2)#1-Ni(1)-N(1)#3	91.11(8)	C(9)-C(10)-H(10A)	108.3
O(2)#2-Ni(1)-N(1)#3	88.89(8)	C(11)-C(10)-H(10B)	108.3
O(3)-Ni(1)-N(1)#3	92.49(9)	C(9)-C(10)-H(10B)	108.3
O(3)#3-Ni(1)-N(1)#3	87.51(9)	H(10A)-C(10)-H(10B)	107.4
O(2)#1-Ni(1)-N(1)	88.89(8)	O(2)-C(11)-O(1)	125.3(2)
O(2)#2-Ni(1)-N(1)	91.11(8)	O(2)-C(11)-C(10)	118.0(2)
O(3)-Ni(1)-N(1)	87.51(9)	O(1)-C(11)-C(10)	116.6(2)
O(3)#3-Ni(1)-N(1)	92.49(9)		
N(1)#3-Ni(1)-N(1)	180.00(17)		

Symmetrycodes: #1 -x+1,y-1/2,-z+3/2; #2 x-1,-y+1/2,z-1/2; #3 -x,-y,-z+1; #4 -x+1,y+1/2,-z+3/2

4			
Cu(1)-O(1)#1	1.9819(19)	C(11)-O(1)-Cu(1)	126.62(18)
Cu(1)-O(1)	1.9819(19)	Cu(1)-O(3)-H(3W1)	109.5
Cu(1)-N(1)#1	2.025(2)	Cu(1)-O(3)-H(3W2)	87(3)
Cu(1)-N(1)	2.025(2)	H(3W1)-O(3)-H(3W2)	116.2
Cu(1)-O(3)	2.438(2)	C(5)-N(1)-C(1)	116.8(2)
Cu(1)-O(3)#1	2.438(2)	C(5)-N(1)-Cu(1)	123.42(19)
O(1)-C(11)	1.264(3)	C(1)-N(1)-Cu(1)	119.7(2)
O(2)-C(11)	1.249(3)	N(3)-N(2)-C(6)	112.3(2)
O(3)-H(3W1)	0.82	N(3)-N(2)-C(9)	118.6(3)
O(3)-H(3W2)	0.845(17)	C(6)-N(2)-C(9)	128.8(3)
N(1)-C(5)	1.334(4)	C(8)-N(3)-N(2)	104.9(3)
N(1)-C(1)	1.348(4)	N(1)-C(1)-C(2)	123.3(3)
N(2)-N(3)	1.344(3)	N(1)-C(1)-H(1)	118.4
N(2)-C(6)	1.343(4)	C(2)-C(1)-H(1)	118.4
N(2)-C(9)	1.462(4)	C(1)-C(2)-C(3)	120.0(3)
N(3)-C(8)	1.331(4)	C(1)-C(2)-H(2)	120
C(1)-C(2)	1.364(4)	C(3)-C(2)-H(2)	120
C(1)-H(1)	0.93	C(4)-C(3)-C(2)	116.9(3)
C(2)-C(3)	1.398(4)	C(4)-C(3)-C(8)#2	123.0(3)
C(2)-H(2)	0.93	C(2)-C(3)-C(8)#2	120.0(3)
C(3)-C(4)	1.379(4)	C(3)-C(4)-C(5)	119.6(3)
C(3)-C(8)#2	1.471(4)	C(3)-C(4)-H(4)	120.2
C(4)-C(5)	1.390(4)	C(5)-C(4)-H(4)	120.2
C(4)-H(4)	0.93	N(1)-C(5)-C(4)	123.3(3)

C(5)-H(5)	0.93	N(1)-C(5)-H(5)	118.3
C(6)-C(7)	1.378(4)	C(4)-C(5)-H(5)	118.3
C(6)-H(6)	0.93	N(2)-C(6)-C(7)	107.0(3)
C(7)-C(8)	1.401(4)	N(2)-C(6)-H(6)	126.5
C(7)-H(7)	0.93	C(7)-C(6)-H(6)	126.5
C(8)-C(3)#3	1.471(4)	C(6)-C(7)-C(8)	104.4(3)
C(9)-C(10)	1.517(5)	C(6)-C(7)-H(7)	127.8
C(9)-H(9A)	0.97	C(8)-C(7)-H(7)	127.8
C(9)-H(9B)	0.97	N(3)-C(8)-C(7)	111.4(3)
C(10)-C(11)	1.513(4)	N(3)-C(8)-C(3)#3	118.6(3)
C(10)-H(10A)	0.97	C(7)-C(8)-C(3)#3	129.9(3)
C(10)-H(10B)	0.97	N(2)-C(9)-C(10)	112.3(2)
		N(2)-C(9)-H(9A)	109.2
O(1)#1-Cu(1)-O(1)	180	C(10)-C(9)-H(9A)	109.2
O(1)#1-Cu(1)-N(1)#1	90.29(9)	N(2)-C(9)-H(9B)	109.2
O(1)-Cu(1)-N(1)#1	89.71(9)	C(10)-C(9)-H(9B)	109.2
O(1)#1-Cu(1)-N(1)	89.71(9)	H(9A)-C(9)-H(9B)	107.9
O(1)-Cu(1)-N(1)	90.29(9)	C(9)-C(10)-C(11)	116.2(3)
N(1)#1-Cu(1)-N(1)	180.000(1)	C(9)-C(10)-H(10A)	108.2
O(1)#1-Cu(1)-O(3)	86.09(8)	C(11)-C(10)-H(10A)	108.2
O(1)-Cu(1)-O(3)	93.91(8)	C(9)-C(10)-H(10B)	108.2
N(1)#1-Cu(1)-O(3)	93.76(9)	C(11)-C(10)-H(10B)	108.2
N(1)-Cu(1)-O(3)	86.24(9)	H(10A)-C(10)-H(10B)	107.4
O(1)#1-Cu(1)-O(3)#1	93.91(8)	O(2)-C(11)-O(1)	125.4(3)
O(1)-Cu(1)-O(3)#1	86.09(8)	O(2)-C(11)-C(10)	117.7(3)
N(1)#1-Cu(1)-O(3)#1	86.24(9)	O(1)-C(11)-C(10)	116.9(3)
N(1)-Cu(1)-O(3)#1	93.76(9)		
O(3)-Cu(1)-O(3)#1	180		
Symmetrycodes: #1 -x+1,-y,-z+2 ； #2 x-1,-y+1/2,z-1/2 ； #3 x+1,-y+1/2,z+1/2			

5			
Zn(1)-O(1)#1	2.088(3)	C(4)-O(1)-Zn(1)	127.9(2)
Zn(1)-O(1)	2.088(3)	Zn(1)-O(3)-H(3)	109.5
Zn(1)-O(3)#1	2.122(3)	O(1)-C(4)-O(2)	125.3(3)
Zn(1)-O(3)	2.122(3)	O(1)-C(4)-C(16)	117.7(3)
Zn(1)-N(1)	2.188(3)	O(2)-C(4)-C(16)	116.9(3)
Zn(1)-N(1)#1	2.188(3)	C(11)-N(1)-C(9)	116.8(4)
O(1)-C(4)	1.247(4)	C(11)-N(1)-Zn(1)	125.0(3)
O(2)-C(4)	1.263(4)	C(9)-N(1)-Zn(1)	118.1(3)
O(1)#1-Zn(1)-O(1)	180.000(1)	N(2)-C(14)-H(14B)	109.1
O(1)#1-Zn(1)-O(3)#1	91.82(11)	C(16)#2-C(14)-H(14B)	109.1
O(1)-Zn(1)-O(3)#1	88.18(11)	H(14A)-C(14)-H(14B)	107.9
O(1)#1-Zn(1)-O(3)	88.18(11)	C(9)-C(15)-C(7)	120.1(4)
O(1)-Zn(1)-O(3)	91.82(11)	C(9)-C(15)-H(15)	119.9
O(3)#1-Zn(1)-O(3)	180	C(7)-C(15)-H(15)	119.9
O(1)#1-Zn(1)-N(1)	88.58(12)	Zn(1)-O(3)-H(3)	109.5
O(1)-Zn(1)-N(1)	91.42(12)	O(3)-Zn(1)-N(1)#1	92.10(12)

O(3)#1-Zn(1)-N(1)	92.10(12)	C(9)-C(15)-C(7)	120.1(4)
O(3)-Zn(1)-N(1)	87.90(12)	N(1)-Zn(1)-N(1)#1	180.00(12)
O(1)#1-Zn(1)-N(1)#1	91.42(12)	O(3)#1-Zn(1)-N(1)#1	87.90(12)
O(1)-Zn(1)-N(1)#1	88.58(12)		

Symmetry codes: #1 -x,-y,-z+1；#2 x+1,-y+1/2,z+1/2；#3 x-1,-y+1/2,z-1/2

Table S3. Comparison of selected bond lengths (Å) of optimized by DFT calculations with experimental X-ray Diffraction Data.

Bond	X-ray structure(Å)	Optimized structure(Å)
Ni(1)-O(2)#1	2.054	2.090
Ni(1)-O(2)#2	2.054	2.091
Ni(1)-O(3)#1	2.082	2.109
Ni(1)-O(3)#2	2.082	2.105
Ni(1)-N(1)#1	2.110	2.150
Ni(1)-N(1)#2	2.110	2.150
O(1)-C(11)	1.264	1.280
O(2)-C(11)	1.252	1.252

Bond	X-ray structure(Å)	Optimized structure(Å)
Co(1)-O(1)#1	2.081	1.987
Co(1)-O(1)#2	2.081	1.987
Co(1)-O(3)#1	2.111	2.185
Co(1)-O(3)#2	2.111	2.183
Co(1)-N(1)#1	2.166	2.102
Co(1)-N(1)#2	2.166	2.102
O(1)-C(11)	1.254	1.285
O(2)-C(11)	1.260	1.246

Bond	X-ray structure(Å)	Optimized structure(Å)
Mn(1)-O(1)#1	2.144	2.137
Mn(1)-O(1)#2	2.144	2.137
Mn(1)-O(3)#1	2.185	2.094
Mn(1)-O(3)#2	2.185	2.093
Mn(1)-N(1)#1	2.302	2.257
Mn(1)-N(1)#2	2.302	2.246
O(1)-C(1)	1.252	1.280
O(2)-C(1)	1.259	1.254

Bond	X-ray structure(Å)	Optimized structure(Å
Cu(1)-O(1)#1	1.982	2.017
Cu(1)-O(1)	1.982	2.018
Cu(1)-N(1)#1	2.025	2.085
Cu(1)-N(1)	2.025	2.085
Cu(1)-O(3)	2.438	2.398
Cu(1)-O(3)#1	2.438	2.397
O(1)-C(11)	1.264	1.287
O(2)-C(11)	1.249	1.244

Table S4. Hydrogen bonds of **3**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3W2)...O(1)#2	0.82(4)	1.88(4)	2.671(3)	160(4)
O(3)-H(3W1)...O(1)#5	0.82	1.95	2.747(3)	163.5