Supporting Information

Structures and Catalytic Oxidative Coupling Reaction of Four Co-MOFs Modified by R-isophthalic acid (R=H, OH and COOH) and Trigonal ligands

Qing Liu[a], Lin-Yan Zhang,[a] Yu-Mei Bao,[a] Na Zhang*,[a], Jian-Yong Zhang*,[a], Yuan-Yuan Xing[a], Wei Deng,[a] Zhen-Jiang Liu*,[a]

[a] School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418 (P. R. China).
E-mail: nzhang@sit.edu.cn, jianyong1106@163.com, zjliu@sit.edu.cn

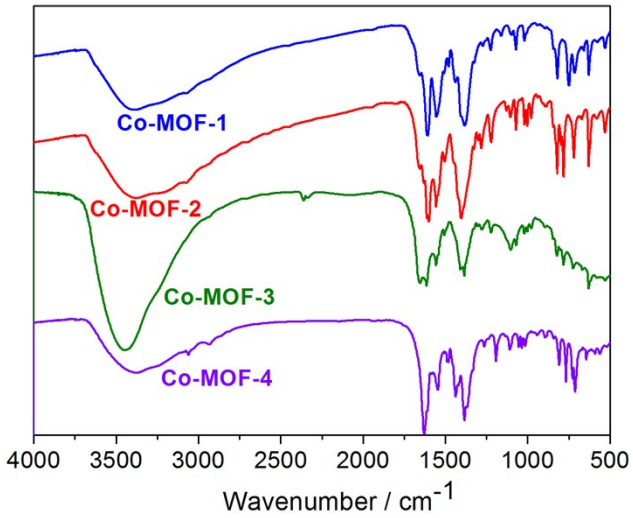


Fig. S1. The FT- IR spectra of the four **Co-MOFs** presented in this paper.

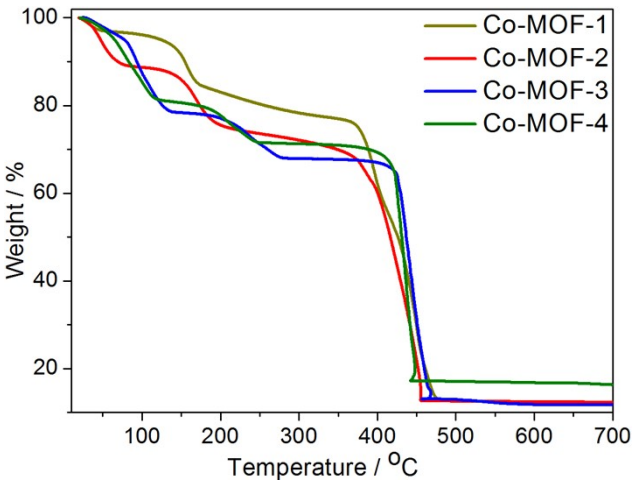
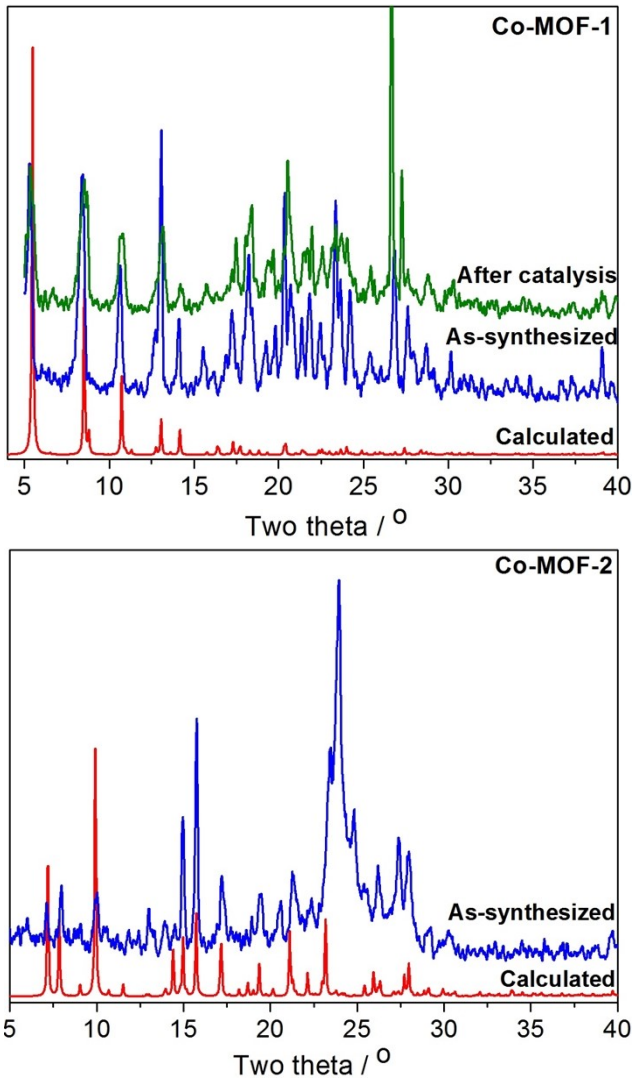


Fig. S2. The TGA curves for the reported four **Co-MOFs** in this paper.



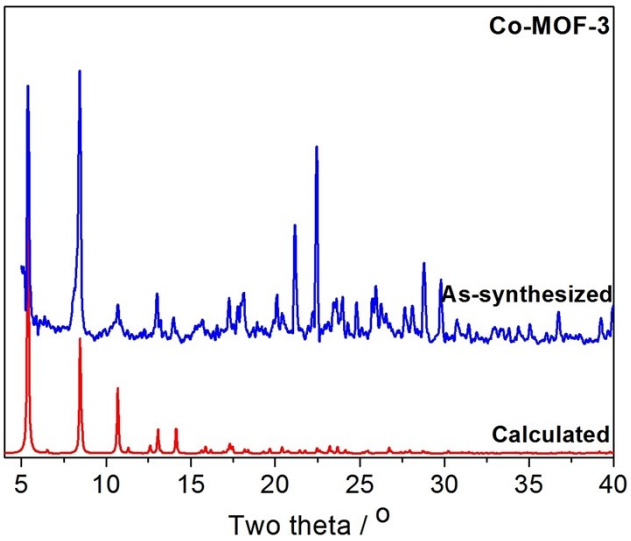


Fig. S3. The comparison of the observed and calculated PXRD patterns from the **Co-MOFs**.

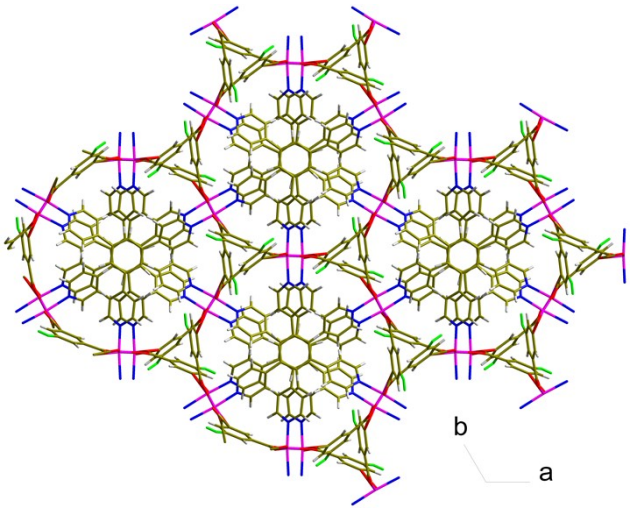


Fig. S4. The 3D framework of **Co-MOF-3**, showing the uncoordinated –OH groups in OH-BDC^{2-} ligands (highlighted in green color).

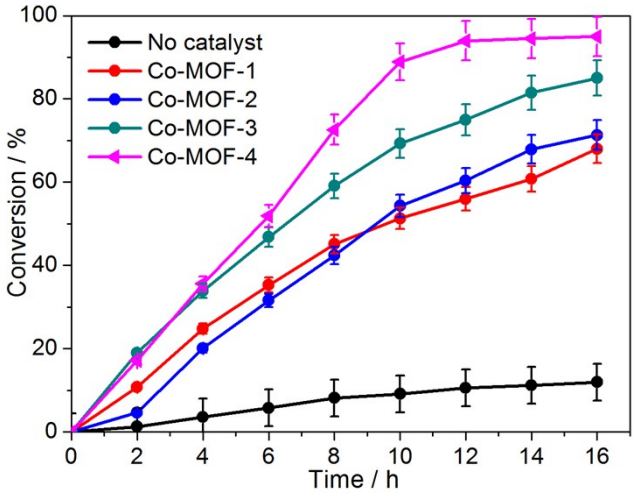


Fig. S5. Time dependence of conversion using different **Co-MOFs** as catalysts.

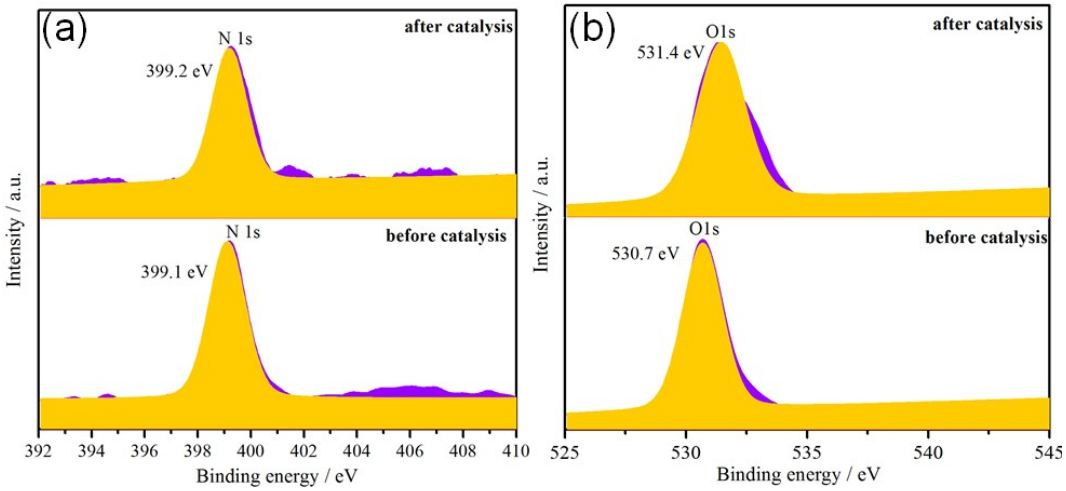


Fig. S6. The XPS survey spectra for N 1s (a) and O1s (b) of **Co-MOF-4** catalyst before and after catalysis reaction.

Table S1. Selected bond [Å] and angles [º] for **Co-MOFs**.

Co1-O1	2.154(3)	Co1-O2	2.193(4)
Co1-O3#1	2.019(4)	Co1-O4#1	2.060(3)
Co1-N1	2.118(3)	Co1-N2	2.159(3)
O1-Co1-N1	98.70(12)	O3#1-Co1-O4#2	119.66(14)
O3#2-Co1-N1	92.20(13)	O4#2-Co1-N1	89.77(12)
O3#1-Co1-O1	89.16(14)	O4#2-Co1-O1	149.75(14)
O3#1-Co1-N2	89.22(14)	O4#2-Co1-N2	84.97(12)
N1-Co1-N2	174.56(13)	O1-Co1-N2	86.56(12)
O3#1-Co1-O2	148.93(12)	O4#2-Co1-O2	91.41(13)
N1-Co1-O2	87.48(14)	O1-Co1-O2	60.28(12)
N2-Co1-O2	94.01(14)		

Symmetry codes for **Co-MOF-1**: #1 -x+y+2/3, -x+1/3, z+1/3; #2 x-y+1/3, x-1/3, -z+5/3.			
Co1-O1#1	1.997(3)	Co1-O2	1.998(3)
Co1-O3#3	2.201(3)	Co1-O4#3	2.249(3)
Co1-N1	2.153(3)	Co1-N3#2	2.147(3)
O1#1-Co1-O2	120.73(13)	O1#1- Co1-N3#2	93.43(12)
O2-Co1-N3#2	88.97(12)	O1#1- Co1-N1	88.68(12)
O2-Co1-N1	88.01(12)	N3#2-Co1-N1	176.91(12)
O1#1-Co1-O3#3	87.21(13)	O2-Co1-O3#3	151.40(13)
N3#2-Co1-O3#3	95.77(12)	N1-Co1-O3#3	86.59(12)
O1#1-Co1-O4#3	146.25(12))	O2-Co1-O4#3	92.61(12)
N3#2-Co1-O4#3	92.16(12)	N1-Co1-O4#3	87.32(12)
O3#3-Co1-O4#3	59.11(12)		
Symmetry code for **Co-MOF-2**: #1 -x+1/2, -y+1/2, -z; #2 x-1/2, -y+1/2, z-1/2; #3 -x+1/2, y+1/2, -z+1/2.			
Co1-O3#1	2.199(3)	Co1-O4#1	2.178(3)
Co1-O1	2.008(3)	Co1-O2#2	2.048(2)
Co1-N1	2.160(3)	Co1-N2	2.137(3)
O1-Co1-O2#2	118.29(11)	O1-Co1-N2	92.53(12)
O2#2-Co1-N2	89.92(10)	O1-Co1-N1	89.55(11)
O2#2-Co1-N1	85.13(10)	N2-Co1-N1	175.04(10)
O3#1-Co1-O2#2	150.15(12)	O2#2-Co1-O4#1	92.18(11)
N2-Co1-O4#1	87.55(12)	N1-Co1-O4#1	92.94(12)
O3#1-Co1-O1	90.20(12)	O4#1-Co1-O3#1	59.70(11)
N2-Co1-O3#1	98.00(11)	N1-Co1-O3#1	86.49(11)
Symmetry code for **Co-MOF-3**: #1 –x+y+2/3, -x+4/3, z+1/3; #2 –x+4/3, -y+5/3, -z+2/3.			
Co1-O1	2.0001(10)	Co1-O2#1	2.0082(8)
Co1-O6#2	2.1219(8)	Co1-O5#2	2.2833(10)
Co1-N1	2.1756(11)	Co1-N2#2	2.1627(12)
Co2-O3	2.0810(8)	Co2-O7	2.1096(11)
Co2-N3#4	2.1633(11)		
O1-Co1-O2#1	113.13(4)	O1- Co1-O6#2	91.80(4)
O2#1-Co1-O6#2	154.95(4)	O1- Co1-N2#2	91.10(5)
O2#2-Co1-N2#2	89.43(4)	O6#2-Co1-N2#2	87.62(4)
O1-Co1-N1	89.20(5)	O2#1-Co1-N1	90.47(4)
O6#2-Co1-N1	92.34(4)	N2#2-Co1-N1	179.70(4)
O1-Co1-O5#2	150.93(4)	O2#1-Co1-O5#2	95.92(3)
O6#2-Co1-O5#2	59.25(3)	N2#2-Co1-O5#2	90.38(4)
N1-Co1-O5#2	89.34(4)	O3-Co2-O3#3	180.00(5)
O3-Co2-O7	88.94(4)	O3#3-Co2-O7	91.05(4)
O7-Co2-O7#3	180.0	O3-Co2-N3#4	91.21(4)
O3#3-Co2-N3#4	88.79(4)	O7-Co2-N3#4	89.33(5)

O7#3-Co2-N3#4	90.67(5)	N3#4-Co2-N3#5	180.0
Symmetry code for **Co-MOF-4**: #1 -x+1, -y, -z+1; #2 -x, -y, -z+1; #3 -x+1, -y+1, -z; #4 -x, -y+1, -z+1; #5 x+1, y, z-1.			

Table S2. Effect of the reaction temperature and time for the oxidative coupling reaction.[a]

Entry	Catalyst	Base	Temp.(°C)	Time (h)	Conv.(%)[b]
1				2	7
2	**Co-MOF-4**	KOH	rt.	6	30
3				12	50
4				2	13
5	**Co-MOF-4**	KOH	60	6	42
6				12	76
7				2	18
8	**Co-MOF-4**	KOH	100	6	54
9				8	73
10				2	48
11	**Co-MOF-4**	KOH	120	8	85
12				12	74

[a] 1a (1.0 mmol), 2a (1.5 mmol), **Co-MOF-4** (0.2 mmol%), KOH (0.1 mmol), pyrene (100 μL, as an internal standard), solvent-free conditions; [b] determined by GC-MS.

The computed results of the (3,8)-connected net of **Co-MOF-1** and **Co-MOF-3** by TOPOS 4.0 are as follows:

Topology for Sc1

Atom Sc1 links by bridge ligands and has

Common vertex with R(A-A)

V 2 0.3333 0.6667 0.4161 (0 0 0) 7.920A 1

V 2 0.0000 0.0000 0.2506 (0 0 0) 7.920A 1

V 1 0.0000 0.0000 0.4281 (0-1 0) 7.984A 1

V 1 0.3333 0.6667 0.2386 (0 0 0) 7.984A 1

Sc 1 0.5000 0.5000 0.0000 (0 0-1) 10.591A 1

Sc 1 -0.1667 0.1667 0.6667 (0 0 1) 10.591A 1

Sc 1 0.3333 0.1667 0.6667 (0 0 1) 10.591A 1

Sc 1 0.0000 0.5000 0.0000 (0 0-1) 10.591A 1

Topology for V1

Atom V1 links by bridge ligands and has

Common vertex with R(A-A)

Sc 1 0.6667 0.8333 0.3333 (1 1 0) 7.984A 1

Sc 1 0.1667 0.8333 0.3333 (0 1 0) 7.984A 1

Sc 1 0.1667 0.3333 0.3333 (0 0 0) 7.984A 1

Topology for V2

Atom V2 links by bridge ligands and has

Common vertex with R(A-A)

Sc 1 -0.3333 -0.1667 0.3333 (0 0 0) 7.920A 1

Sc 1 0.1667 -0.1667 0.3333 (0 0 0) 7.920A 1

Sc 1 0.1667 0.3333 0.3333 (0 0 0) 7.920A 1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with V4Sc3

Coordination sequences

Sc1: 1 2 3 4 5 6 7 8 9 10

Cum 9 33 89 195 363 605 937 1371 1923 2605

V1: 1 2 3 4 5 6 7 8 9 10

Num 3 16 41 86 145 221 302 406 515 647

Cum 4 20 61 147 292 513 815 1221 1736 2383

V2: 1 2 3 4 5 6 7 8 9 10

Num 3 16 41 86 145 221 302 406 515 647

Cum 4 20 61 147 292 513 815 1221 1736 2383

TD10=2478

Vertex symbols for selected sublattice

Sc1 Point (Schlafli) symbol:{4^12;6^10;8^6}

Extended point symbol:[4.4.4.4.4.4.4.4.4(2).4(2).4(2).4(2).6(3).6(3).6(3).6(3).6(3).6(3).6(3).6(3).6(3).6(6).6(6).8(12).8(12).8(12).8(12).8(66).8(66)]

V1 Point (Schlafli) symbol:{4^3}

Extended point symbol:[4(2).4(2).4(2)]

V2 Point (Schlafli) symbol:{4^3}

Extended point symbol:[4(2).4(2).4(2)]

Point (Schlafli) symbol for net: {4^12;6^10;8^6}3{4^3}4

3,8-c net with stoichiometry (3-c)4(8-c)3; 2-nodal net