Supporting Information

MOFs Assembled from C_3 Symmetric Ligands: Structure, Iodine Capture and as Bifunctional Catalyst towards Oxidation-Knoevenagel Cascade Reaction

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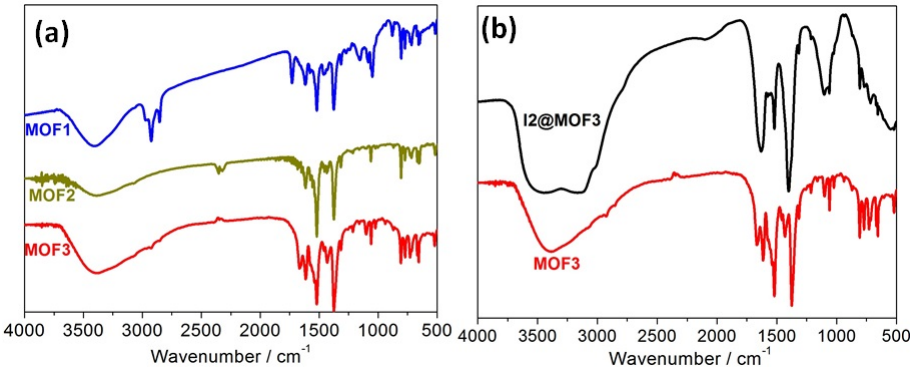


Figure S1. The FT- IR spectra of the three MOFs presented in this paper.

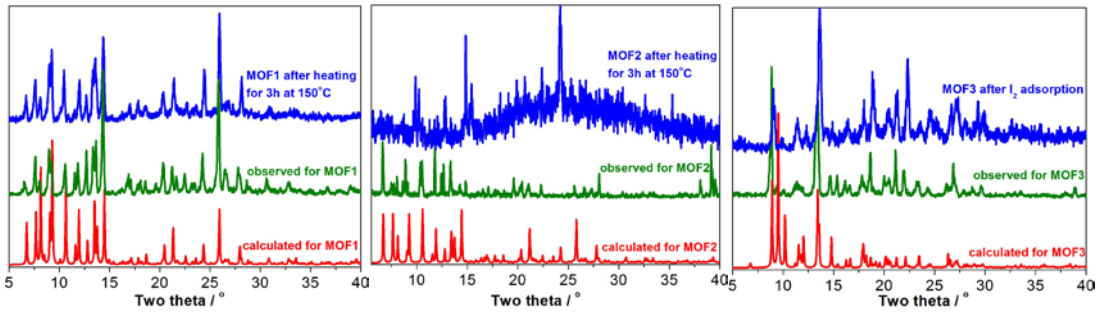


Figure S2. The comparison of the observed, calculated and PXRD patterns after heating or I_2 adsorption for the three reported MOFs.

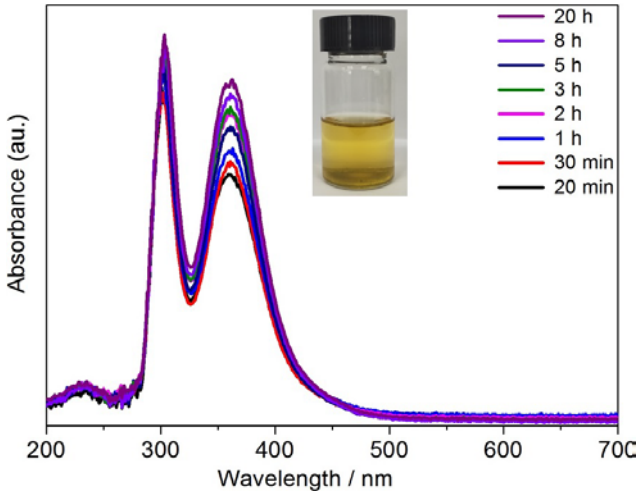


Figure S3. The UV-vis spectra of I_2 release process in ethanol.

Table S1. Crystal data and structure refinements of three MOFs.

Compound	**MOF1**	**MOF2**	**MOF3**[b]
Formula	$C_{47}H_{38.5}N_{12.5}O_{10.5}Ni_2$	$C_{47}H_{38.5}N_{12.5}O_{10.5}Co_2$	$C_{54}H_{45}N_{12}O_{19.5}Ni_3$
Formula weight	1063.82	1064.26	1350.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	17.5508(6)	17.6225(4)	10.144(2)
b, Å	13.8259(4)	13.8371(3)	26.077(5)
c, Å	20.8220(6)	20.9929(4)	15.602(3)
α, °	90	90	90
β, °	92.7240(10)	92.6410(10)	101.362(7)
γ, °	90	90	90
Z	4	4	2
V, Å^3	5046.9(3)	5113.56(19)	4046.2(13)
ɵ range (°)	2.32 - 26.01	2.31- 26.01	2.35 - 26.01
D_c, g cm^{-3}	1.400	1.382	1.108
μ, mm^{-1}	0.816	0.717	0.753
Reflections collected	118241	123858	83056
Unique reflections	9923	10034	7969
R_{int}	0.0720	0.0401	0.0991
GOF on F^2	1.049	0.878	1.086
R_1,wR_2[$I>2\sigma(I)$][a]	0.0562, 0.1824	0.0445, 0.1380	0.0519, 0.1408
R_1,wR_2(all data)[a]	0.0702, 0.1929	0.0525, 0.1476	0.0624, 0.1460

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR_2 = |\Sigma w(|F_0|^2 - |F_c|^2)^2/\Sigma|w(F_0^2)^2|^{1/2}$.

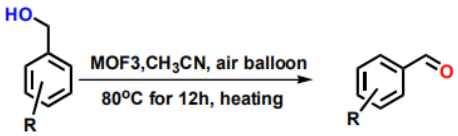
[b] The values in parenthesis are for the refinement after the SQUEEZE routine.

Table S2. Selected bond [Å] and angles [º] for MOF**1**-**3**.

Ni1-O1	1.987(2)	Ni1-O5#1	2.199(3)
Ni1-O6#1	2.101(3)	Ni1-O7	1.967(2)
Ni1-N1	2.126(3)	Ni1-N2#2	2.133(3)
Ni2-O2	2.069(2)	Ni2-O3#3	2.078(2)
Ni2-O7	2.018(2)	Ni2-O8	2.091(3)
Ni2-N7	2.086(3)	Ni2-N8#2	2.078(3)
O1-Ni1-O7	97.98(10)	O7-Ni1-O6#1	103.45(9)
O1-Ni1-O6#1	158.39(11)	O7-Ni1-N1	87.07(11)
O1-Ni1-N1	91.22(12)	O6#1-Ni1-N1	87.17(11)
O7-Ni1-N2#2	94.68(11)	O1-Ni1-N2#2	90.71(12)
O6#1-Ni1-N2#2	90.28(11)	N1-Ni1-N2#2	177.19(12)
O7-Ni1-O5#1	164.86(10)	O1-Ni1-O5#1	97.02(10)
O6#1-Ni1-O5#1	61.47(10)	N1-Ni1-O5#1	90.57(12)
N2#2-Ni1-O5#1	87.17(12)	O7-Ni2-O2	97.90(9)
O7-Ni2-O3#3	174.54(11)	O2-Ni2-O3#3	84.83(10)
O7-Ni2-N8#2	87.68(11)	O2-Ni2-N8#2	89.00(12)
O3#3-Ni2-N8#2	87.68(11)	O7-Ni2-N7	93.36(11)
O2-Ni2-N7	89.88(12)	O3#3-Ni2-N7	91.37(12)
N8#2-Ni2-N7	178.56(13)	O7-Ni2-O8	86.60(11)
O2-Ni2-O8	175.12(12)	O3#3-Ni2-O8	90.53(12)
N8#2-Ni2-O8	89.30(14)	N7-Ni2-O8	91.75(14)
Symmetry codes for MOF**1**: #1 -x+1/2, y-1/2, -z+1/2; #2 x+1/2, -y+3/2, z+1/2; #3 -x+1, -y+2, -z.			
Co1-O1	2.0019(18)	Co1-O5#1	2.282(2)
Co1-O6#1	2.1110(18)	Co1-O7	1.9624(15)
Co1-N1	2.191(2)	Co1-N2#2	2.191(2)
Co2-O2	2.0959(18)	Co2-O3#3	2.0915(18)
Co2-O7	2.0359(15)	Co2-O8	2.136(2)
Co2-N7	2.137(2)	Co2-N8#2	2.135(2)
O1-Co1-O7	100.23(7)	O7- Co1-O6#1	104.77(7)
O1-Co1-O6#1	154.70(8)	O7- Co1-N1	87.15(8)
O1-Co1-N1	91.13(9)	O6#1-Co1-N1	86.28(8)
O7-Co1-N2#2	95.39(8)	O1-Co1-N2#2	90.71(9)
O6#1-Co1-N2#2	90.81(8)	N1-Co2-N2#2	176.55(8)
O7-Co1-O5#1	164.50(7)	O1-Co1-O5#1	95.20(7)
O6#1-Co1-O5#1	59.74(7)	N1-Co1-O5#1	91.10(9)
N2-Co1-O5#1	85.83(8)	O7-Co2-O2	97.78(7)
O7-Co2-O3#3	173.18(8)	O2-Co2-O3#3	86.65(7)
O7-Co2-N8#2	87.32(8)	O2-Co2-N8#2	88.63(9)
O3#3-Co2-N8#2	87.60(9)	O7-Co2-O8	85.42(8)
O2-Co2-O8	176.21(9)	O3#3-Co2-O8	89.97(8)
N8#2-Co2-O8	89.51(10)	O7-Co2-N7	93.55(8)

O2-Co2-N7	89.93(9)	O3#3-Co2-N7	91.63(9)
N8#2-Co2-N7	178.41(9)	O8-Co2-N7	91.89(10)
Symmetry code for MOF**2**: #1 -x+1/2,y-1/2,-z+1/2; #2 x+1/2,-y+3/2,z+1/2; #3 -x+1,-y+2,-z.			
Ni1-O1	2.149(2)	Ni1-O2	2.094(2)
Ni1-O4#1	2.019(2)	Ni1-O7	2.049(2)
Ni1-N1	2.090(2)	Ni1-N3#2	2.102(2)
Ni2-O8	2.061(3)	Ni2-O9	2.049(3)
Ni2-N2	2.109(3)		
O4#1-Ni1-O7	96.15(9)	O4#1-Ni1-O2	163.44(9)
O7-Ni1-O2	100.33(9)	O4#1-Ni1-N1	87.70(10)
O7-Ni1-N1	90.99(10)	O2-Ni1-N1	93.67(9)
O4#1-Ni1-N3#2	86.24(10)	O7-Ni1-N3#2	94.24(10)
O2-Ni1-N3#2	90.84(9)	N1-Ni1-N3#2	172.39(10)
O4#1-Ni1-O1	101.48(8)	O7-Ni1-O1	162.34(9)
O2-Ni1-O1	62.02(8)	N1-Ni1-O1	90.66(9)
N3#2-Ni1-O1	86.04(9)	O9-Ni2-O9#3	180.0
O9-Ni2-O8#3	89.04(12)	O9-Ni2-O8	90.96(12)
O8#3-Ni2-O8	180.0	O9-Ni2-N2#3	89.36(11)
O9-Ni2-N2	90.64(11)	O8-Ni2-N2	89.98(12)
O8#3-Ni2-N2	90.02(12)	N2#3-Ni2-N2	180.0
Symmetry code for MOF**3**: #1 x+1, y, z; #2 -x+1/2, y+1/2, -z+3/2; #3 -x, -y, -z.			

Table S3. The alcohol oxidation of different substituted benzyl alcohol to benzaldehyde catalyzed by activated **MOF3**[a].



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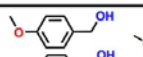
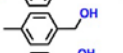
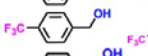
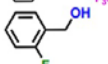
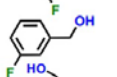
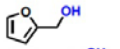
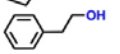
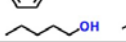
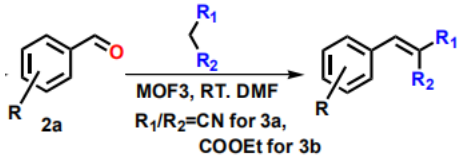
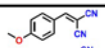
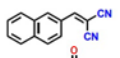
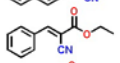
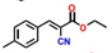
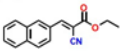
1			6	95	>99
2			6	92	>99
3			6	*NR*	--
4			12	41	>99
5			12	63	>99
6			12	54	>99
7			16	*NR*	--
8			16	*NR*	--
9			16	*NR*	--

[a] The reactions were carried out under the optimized conditions: 80ºC for 12 h, catalyst (0.25 mmol%), CH_3CN (5 mL) as solvent, *n*-dodecane (400 μL, as internal standard), air balloon. [b] determined by GC-MS on the basis of area %.

Table S4. The Knoevenagel reaction of different alcohol and methylene substrates catalyzed by activated **MOF3**.[a]



Entry	2a	3a/3b	Product	Time (h)	Conversion (%)[b]	Selectivity (%)
1				6	94	>99
2				6	92	>99
3				12	55	>99
4				6	86	>99
5				6	71	>99
6				12	34	99

[a] The reactions were carried out under the optimized conditions: 2a (1.0 mmol), 3a or 3b (1.5 mmol), catalyst (0.25 mmol%), DMF (5 mL) as solvent, *n*-dodecane (400 μL, as internal standard), room temperature. [b] determined by GC-MS on the basis of area %.

The computed results of the (3,5)-connected net of MOF**1** and **2** by TOPOS 4.0 are as follows:

Topology for Ti1

Atom Ti1 links by bridge ligands and has

Common vertex with					R(A-A)	
V	1	0.3371	1.1232	0.1071	(0 1 0)	5.159A 1
V	1	0.1629	0.6232	0.3929	(0 0 0)	7.180A 1
V	1	0.6629	0.8768	-0.1071	(1 1 0)	7.273A 1
Ti	1	-0.0899	0.7333	-0.3527	(-1 1-1)	13.398A 1
Ti	1	0.9101	0.7333	0.6473	(0 1 0)	13.398A 1

Topology for V1

Atom V1 links by bridge ligands and has

Common vertex with R(A-A)

Ti 1 0.4101 -0.2333 0.1473 (0-1 0) 5.159A 1

Ti 1 0.0899 0.2667 0.3527 (0-1 0) 7.180A 1

Ti 1 0.5899 0.2333 -0.1473 (1 1 0) 7.273A 1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with V, Ti

Coordination sequences

Ti1: 1 2 3 4 5 6 7 8 9 10

Num 5 13 28 49 75 108 145 189 240 295

Cum 6 19 47 96 171 279 424 613 853 1148

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

Num 3 11 28 47 75 106 145 189 238 295

Cum 4 15 43 90 165 271 416 605 843 1138

TD10=1143

Vertex symbols for selected sublattice

Ti1 Point symbol:{4.6^6.8^3}

Extended point symbol:[4.6.6.6.6.6(2).6(2).8.8(5).8(8)]

V1 Point symbol:{4.6^2}

Extended point symbol:[4.6(2).6(2)]

Point symbol for net: {4.6^2}{4.6^6.8^3}

3,5-c net with stoichiometry (3-c)(5-c); 2-nodal net

ATTENTION! If the name below is written in a long notation s/... or s-d-G-n, this net is a subnet of the net s (see Manual for details)

Topological type: fsc-3,5-Cmce-2 (binodal.ttd) {4.6^2}{4.6^6.8^3} - VS [4.6(2).6(2)] [4.6.6.6.6.6(2).6(2).8.8(3).8(4)] (78929 types in 11 databases)

The computed results of the (3,4)-connected net of MOF**3** by TOPOS 4.0 are as follows:

Topology for Ti1

Atom Ti1 links by bridge ligands and has

Common vertex with					R(A-A)	
V	1	0.3764	0.6986	0.7205	(0 0 1)	7.697A	1
V	1	0.1236	1.1986	0.7795	(0 1 0)	7.745A	1
Ti	1	-0.1774	1.0419	-0.4971	(0 2 0)	15.374A	1

Topology for V1

Atom V1 links by bridge ligands and has

Common vertex with					R(A-A)	
Ti	1	0.3226	0.4581	1.0029	(0-1 1)	7.697A	1
Ti	1	0.1774	-0.0419	0.4971	(0-1 0)	7.745A	1
V	1	1.1236	0.1986	0.7795	(1 0 0)	10.144A	1
V	1	-0.8764	0.1986	0.7795	(-1 0 0)	10.144A	1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with V, Ti

There are 3 interpenetrating nets

FIV: Full interpenetration vectors

[0,0,1] (15.60A)

PIC: [0,0,3][1,0,0][0,1,0] (PICVR=3)

Zt=3; Zn=1

Class Ia Z=3

Coordination sequences

Ti1:	1	2	3	4	5	6	7	8	9	10
Num	3	8	20	38	59	82	111	146	182	224
Cum	4	12	32	70	129	211	322	468	650	874

V1:	1	2	3	4	5	6	7	8	9	10
Num	4	10	20	34	54	80	108	140	180	222
Cum	5	15	35	69	123	203	311	451	631	853

TD10=863

Vertex symbols for selected sublattice

Ti1 Point symbol:{6.8^2}

Extended point symbol:[6(2).8(4).8(4)]

V1 Point symbol:{6^4.8.10}
Extended point symbol:[6.6.6.6.8(2).10(4)]

Point symbol for net: {6.8^2}{6^4.8.10}
3,4-c net with stoichiometry (3-c)(4-c); 2-nodal net
ATTENTION! If the name below is written in a long notation s/... or s-d-G-n, this net is a subnet of the net s (see Manual for details)
Topological type: fsg-3,4-Cmmm (binodal.ttd) {6.8^2}{6^4.8.10} - VS [6(2).8(4).8(4)][6.6.6.6.10(2).*] (78929 types in 11 databases)