Electronic Supporting Information (ESI) for Inorganic Chemistry Frontiers

Hexagonal Co_6 and Zigzag Co_4 Clusters Based Magnetic MOFs with *pcu* Net for Selective Catalysis

Ru-Xin Yao, Xiao-Hui Qiao, Xin Cui, Xiao-Xia Jia and Xian-Ming Zhang*

Department of Chemistry & Material Science,

Shanxi Normal University, Linfen 041004, P. R. China

Supplementary Index

in the allylic oxidation of cyclohexene

13. **Table S3**. Bond lengths [Å] and angles [deg] data for **1** and **2**

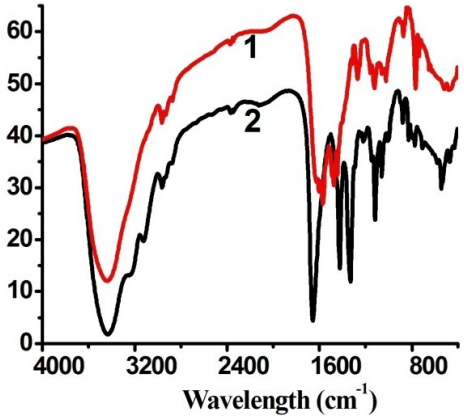


Fig. S1 IR spectra of **1** and **2**.

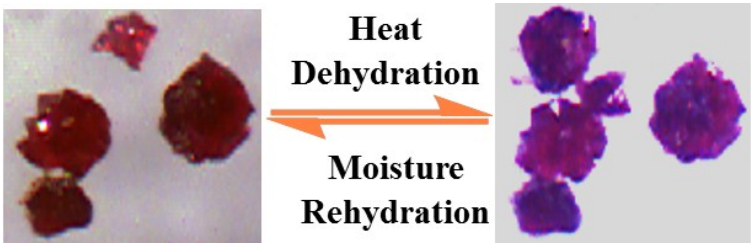


Fig. S2 Crystal photographs of **1** and activated **1** at heat and moisture conditions, respectively.

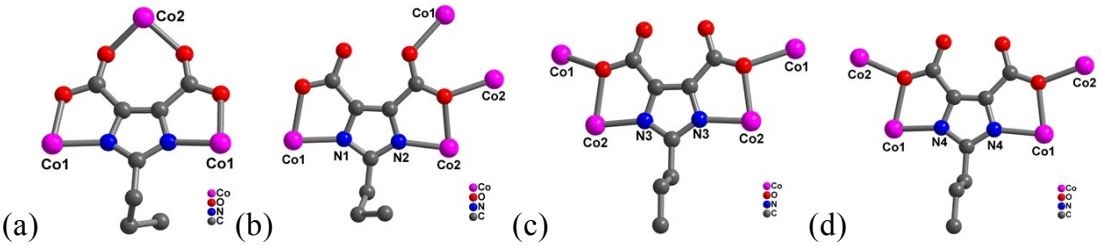


Fig. S3 Four coordination modes of $Hpimdc^{2-}$ ligands, (a) μ_3-*kN,O: kO′,O″: kN′,O‴*, (b) μ_4–*kN,O : kO′ : kO″: kN′,O″* , (c,d) μ_4–*kN,O : kO : kO′ : kN′,O′*.

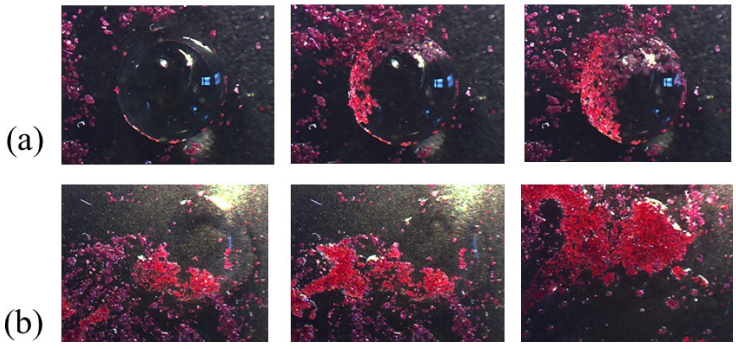
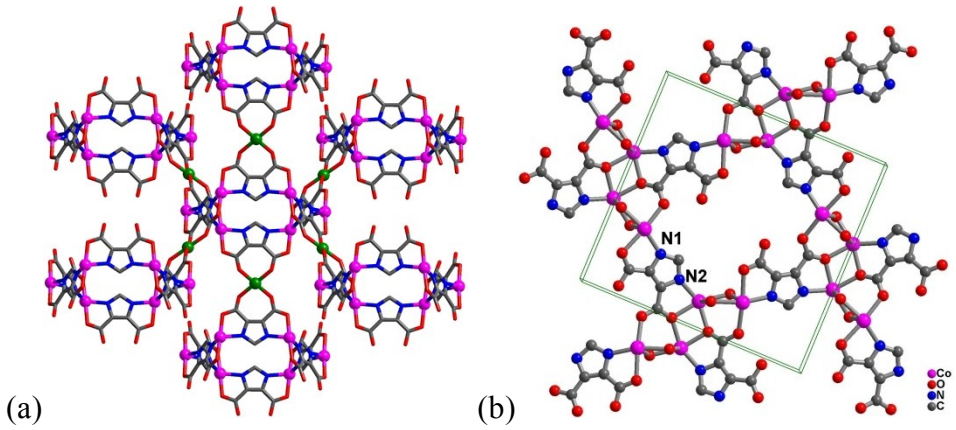
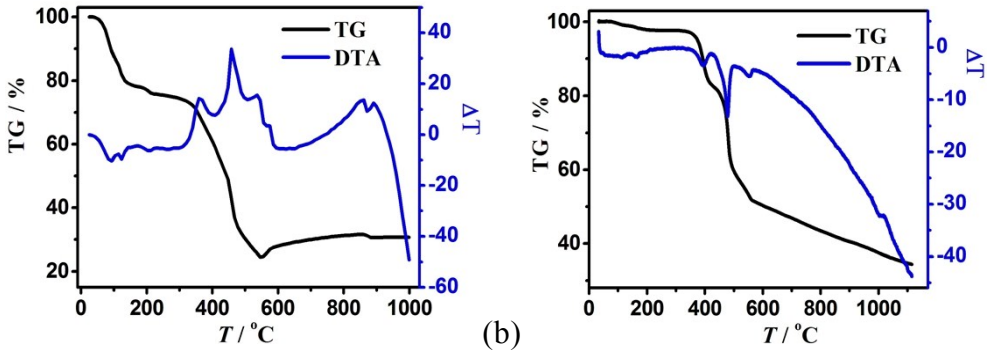


Fig. S4 Contact angle images of (a) water and (b) ethanol droplets balanced on the powders of **1.**



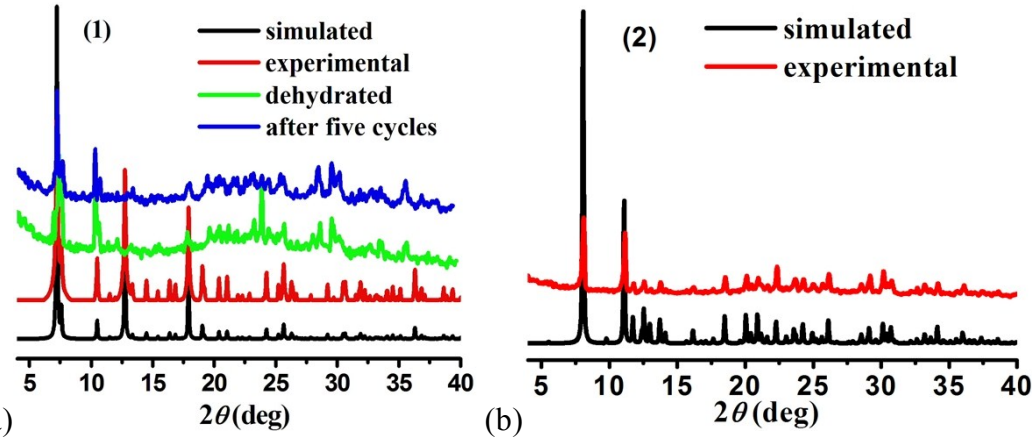
(a) (b)

Fig. 5 (a) $Co_6(pimdc)_6$ unit linked with six Co_6 unit through Co2 atoms in **1,** (b) 2D rhombic grid along *c*-axis direction in **2** (propyl group is deleted for clearity).



(a) (b)

Fig. S6 The TG/DTA plots of **1** and **2.**



(a) (b)

Fig. S7 The PXRD patterns of simulated and experimental for **1** and **2**, and that of after five catalytic cycles for catalyst **1.**

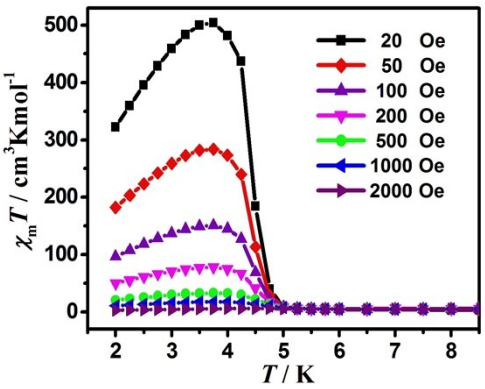


Fig. S8 Temperature dependence of the susceptibility in different applied magnetic fields for **2**.

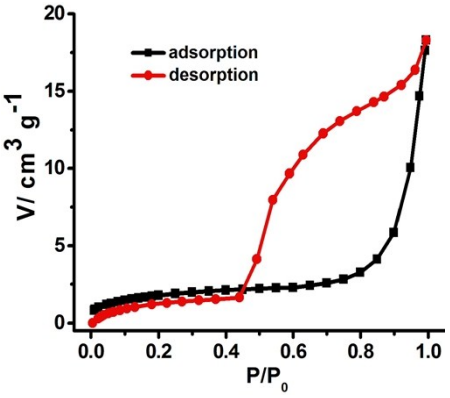


Fig. S9 N_2 sorption isotherms for **1** at 77 K.

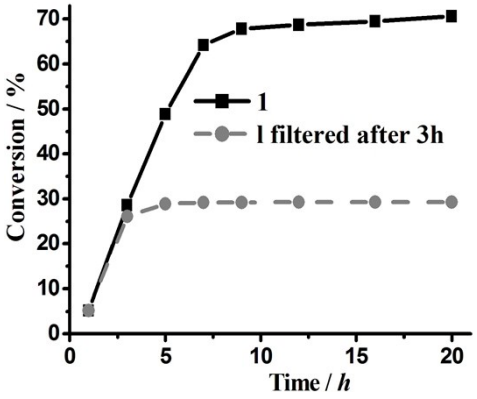
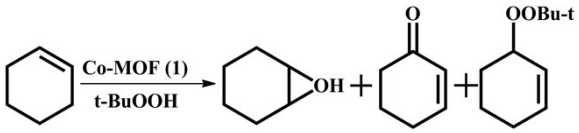


Fig. S10 The allylic oxidation of cyclohexene with activated **1** as catalyst (black) and filtration of **1** (gray).

Table S1. The optimization of reaction condition for the allylic oxidation of cyclohexene with activated **1** as catalyst.



Entry	Particle	Temp. (°C)	Cat (mmol)	Con (%)	Selectivity (%) A	B	C	TON[b]
1	unground[a]	50	0.15	28.6	48.3	28.6	23.1	91
2	ground	50	0.15	37.5	51.8	26.4	21.8	103
3	ground	50	0.10	41.6	54.6	29.7	15.7	118
4	ground	50	0.05	31.8	46.3	28.1	20.6	96
5	ground	60	0.10	56.4	57.8	25.3	17.9	123
6	ground	70	0.10	70.6	61.2	23.5	15.3	148
7	ground	80	0.10	25.6	46.9	27.4	22.9	85
8	ground	70	0.10 (hydrated **1**)	3.8	4.2	2.8	1.2	34
9	ground	70	0.10 (**2**)	3.3	3.7	2.3	1.1	30
10	------	70	-----	1.8	3.2	2.1	0.9	28

[a]Reaction conditions: cyclohexene (3.6 mmol), *t*-BuOOH (12 mmol), 1,2,4-trichlor-obenzene (1 mmol; as internal standard), Temp = 70°C, solvent-free. [b]TON (turnover number) = moles converted / moles of active Co sites. Entry 6 is the optimization of reaction condition.

Table S2. Comparison catalytic performances of activated **1** with other catalysts in the allylic oxidation of cyclohexene

Catalyst	*T*, °C (time, h)	Solvent	Con (%)	Selectivity (%) A	B	C	Ref
activated **1**	70 (20)	free	70.6	61.2	23.5	15.3	
TM salts (Co)	homogeneous		> 99	50			[24]
Fe^{III}/SiO_2	78 (10)	CH_3CN	98	76	5	--	[25]
Co-MOF	35 (24)	CH_3CN	35	16	--	76	[26]
Cr-MIL-101	60 (16)	free	16	56	--	6	[27]

Table S3. Bond lengths [Å] and angles [deg] for **1** and **2**.

Compound 1			
Co(1)-N(1)	2.0673(19)	Co(2)-O(2b)	2.0361(16)
Co(1)-N(2a)	2.0638(18)	Co(2)-O(2)	2.0361(16)
Co(1)-O(4a)	2.1332(16)	Co(2)-O(3b)	2.0785(16)
Co(1)-O(1)	2.1451(16)	Co(2)-O(3)	2.0784(16)
Co(1)-O(1w)	2.1650(17)	Co(2)-O(3wb)	2.148(2)
Co(1)-O(2w)	2.1861(17)	Co(2)-O(3w)	2.148(2)
N(2a)-Co(1)-N(1)	104.98(8)	O(2b)-Co(2)-O(2)	180.00(0)
N(2a)-Co(1)-O(4a)	78.37(6)	O(2b)-Co(2)-O(3b)	93.36(7)
N(1)-Co(1)-O(4a)	106.86(7)	O(2)-Co(2)-O(3b)	86.65(7)
N(2a)-Co(1)-O(1)	100.97(7)	O(2b)-Co(2)-O(3)	86.64(7)
N(1)-Co(1)-O(1)	78.48(6)	O(2)-Co(2)-O(3)	93.36(7)
O(4a)-Co(1)-O(1)	174.64(6)	O(3b)-Co(2)-O(3)	180.00(0)
N(2a)-Co(1)-O(1W)	91.97(7)	O(2b)-Co(2)-O(3Wb)	87.99(7)
N(1)-Co(1)-O(1W)	159.82(7)	O(2)-Co(2)-O(3Wb)	92.00(7)
O(4a)-Co(1)-O(1W)	86.97(7)	O(3)-Co(2)-O(3Wb)	91.85(8)
O(1)-Co(1)-O(1W)	87.74(6)	O(3b)-Co(2)-O(3Wb)	88.15(8)
N(2a)-Co(1)-O(2W)	167.02(7)	O(2b)-Co(2)-O(3W)	92.01(7)
N(1)-Co(1)-O(2W)	83.57(7)	O(2)-Co(2)-O(3W)	88.00(7)
O(4a)-Co(1)-O(2W)	89.89(6)	O(3b)-Co(2)-O(3W)	91.85(8)
O(1)-Co(1)-O(2W)	90.20(6)	O(3)-Co(2)-O(3W)	88.15(8)
O(1W)-Co(1)-O(2W)	81.80(7)	O(3Wb)-Co(2)-O(3W)	180.00(0)

Symmetry codes: a) x-y+2/3, x+1/3, 4/3-z; b) 1-x, 1-y, 1-z.

Compound 2			
Co(1)-N(1)	2.058(4)	Co(2)-N(2b)	2.052(4)
Co(1)-N(4)	2.092(4)	Co(2)-N(3)	2.074(3)
Co(1)-O(5)	2.146(3)	Co(2)-O(8)	2.102(3)
Co(1)-O(8)	2.171(3)	Co(2)-O(1a)	2.135(3)
Co(1)-O(2a)	2.178(3)	Co(2)-O(1b)	2.141(3)

Co(1)-O(4)	2.225(4)	Co(2)-O(5)	2.174(3)
N(1)-Co(1)-N(4)	107.03(16)	N(2b)-Co(2)-N(3)	101.43(14)
N(1)-Co(1)-O(5)	97.14(14)	N(2b)-Co(2)-O(8)	90.13(14)
N(4)-Co(1)-O(5)	152.84(14)	N(3)-Co(2)-O(8)	155.60(13)
N(1)-Co(1)-O(8)	165.75(16)	N(2b)-Co(2)-O(1a)	149.15(14)
N(4)-Co(1)-O(8)	77.88(13)	N(3)-Co(2)-O(1a)	98.73(13)
O(5)-Co(1)-O(8)	75.79(12)	O(8)-Co(2)-O(1a)	80.66(12)
N(1)-Co(1)-O(2a)	105.41(15)	N(2b) -Co(2)-O(1b)	78.16(13)
N(4)-Co(1)-O(2a)	95.76(15)	N(3)-Co(2)-O(1b)	98.67(12)
O(5)-Co(1)-O(2a)	89.45(12)	O(8)-Co(2)-O(1b)	104.75(12)
O(8)-Co(1)-O(2a)	87.09(13)	O(1a) -Co(2)-O(1b)	75.91(14)
N(1)-Co(1)-O(4)	78.39(15)	N(2b) -Co(2)-O(5)	119.48(14)
N(4)-Co(1)-O(4)	88.44(16)	N(3)-Co(2)-O(5)	78.97(12)
O(5)-Co(1)-O(4)	84.38(14)	O(8)-Co(2)-O(5)	76.63(12)
O(8)-Co(1)-O(4)	88.50(13)	O(1a) -Co(2)-O(5)	87.10(12)
O(2a)-Co(1)-O(4)	173.15(14)	O(1b)-Co(2)-O(5)	162.35(12)

Symmetry codes: a) -x+1/2, y+1/2, z; b) x-1/2, -y+1/2, z.