Supporting Information

Pillar-Layered Metal-Organic Frameworks Based on Hexaprismane [$Co_6(\mu_3\text{-}OH)_6$] Cluster: Structural Modulation and Catalytic Performance in Aerobic Oxidation Reaction

Xiuling Zhang,[a] Yong-Zheng Zhang,*[ab] Yao-Qiang Jin,[a] Longlong Geng,[a] Da-Shuai Zhang,[a] Hui Hu,[a] Tingting Li,[a] Bin Wang,[c] and Jian-Rong Li*[b]

[a]*College of Chemistry and Chemical Engineering, Dezhou University, Dezhou, 253023, P. R. China*

[b]*Beijing Key Laboratory for Green Catalysis and Separation, Beijing University of Technology, Beijing 100124, P. R. China*

[c]*Fujian Provincial Key Laboratory of Polymer Materials, College of Chemistry and Materials Science, Fujian Normal University, 32 Shangsan Road, Fuzhou 350007, PR China.*

*E-mail: zhangyongzheng23@163.com

*E-mail: jrli@bjut.edu.cn

Section 1. Additional Figures

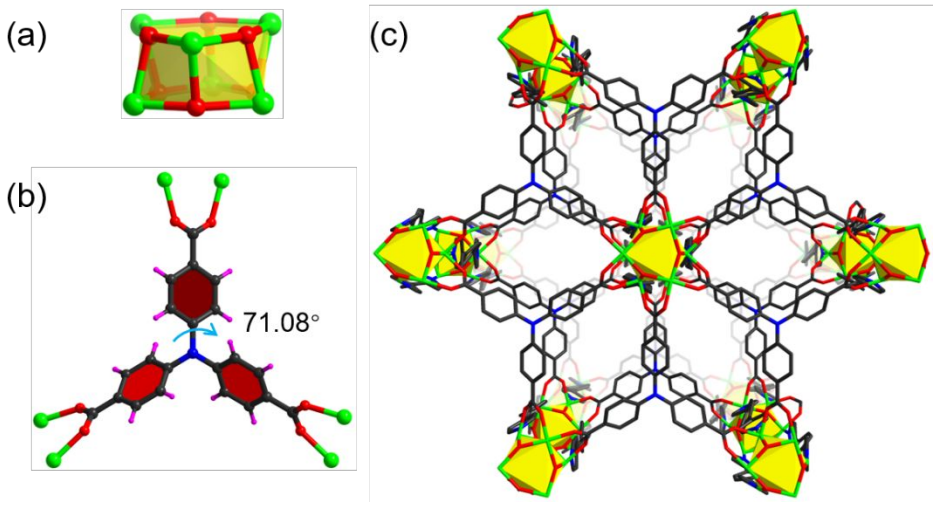

Figure S1. (a) The hexaprismane $Co_6(\mu_3\text{-}OH)_6$ cluster, (b) carboxylate of the TCA^{3-} ligand with $\mu_2\text{-}\eta^1\text{:}\,\eta^1$ coordinating mode, and (c) 3D framework network of Co_6-MOF-3 with 1D channel along the (001) direction.

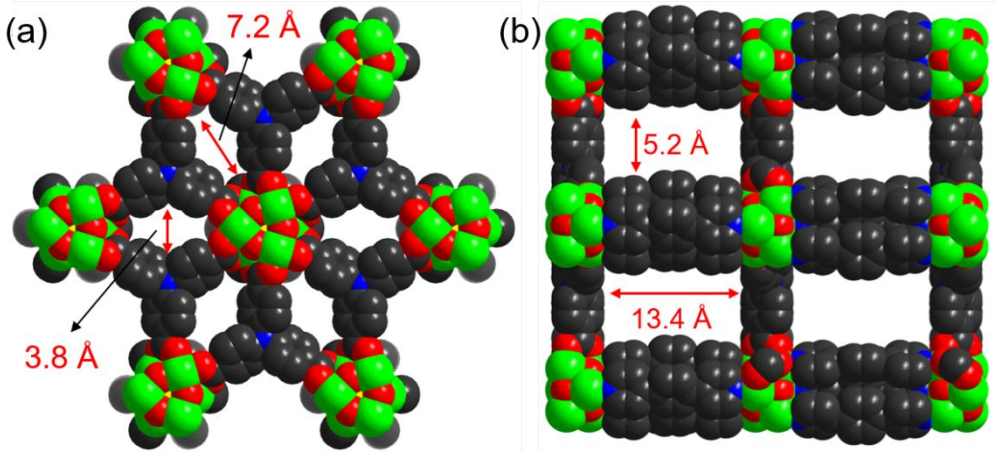

Figure S2. Space-filling view of 1D channels along the (a) (100), and (b) (001), directions in Co_6-MOF-3.

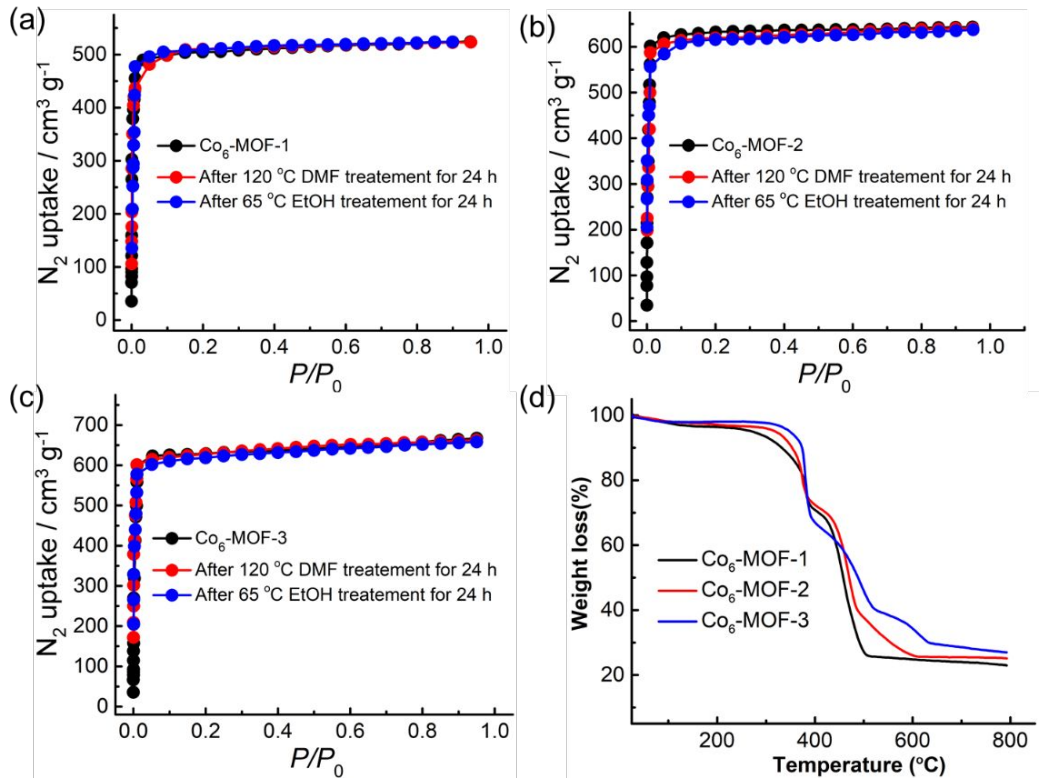

Figure S3. N_2 adsorption isotherms at 77 K of (a) Co_6-MOF-1, (b) Co_6-MOF-2, and (c) Co_6-MOF-3, as well as their samples treated under different conditions, respectively. (d) TGA curves of three Co_6-MOFs.

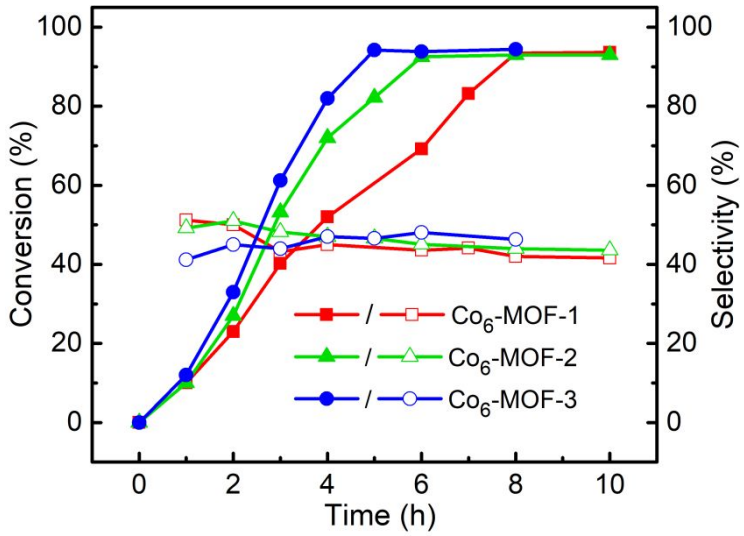

Figure S4. The epoxidation of styrene catalyzed by Co_6-MOFs with O_2 as the oxidant source. Reaction conditions: styrene (1 mmol), DMF (10 mL), the amount of catalyst: $[Co_6(\mu_3\text{-}OH)_6]$ /substrate % = 0.37 mol%, T = 80 °C, O_2 (1 atm).

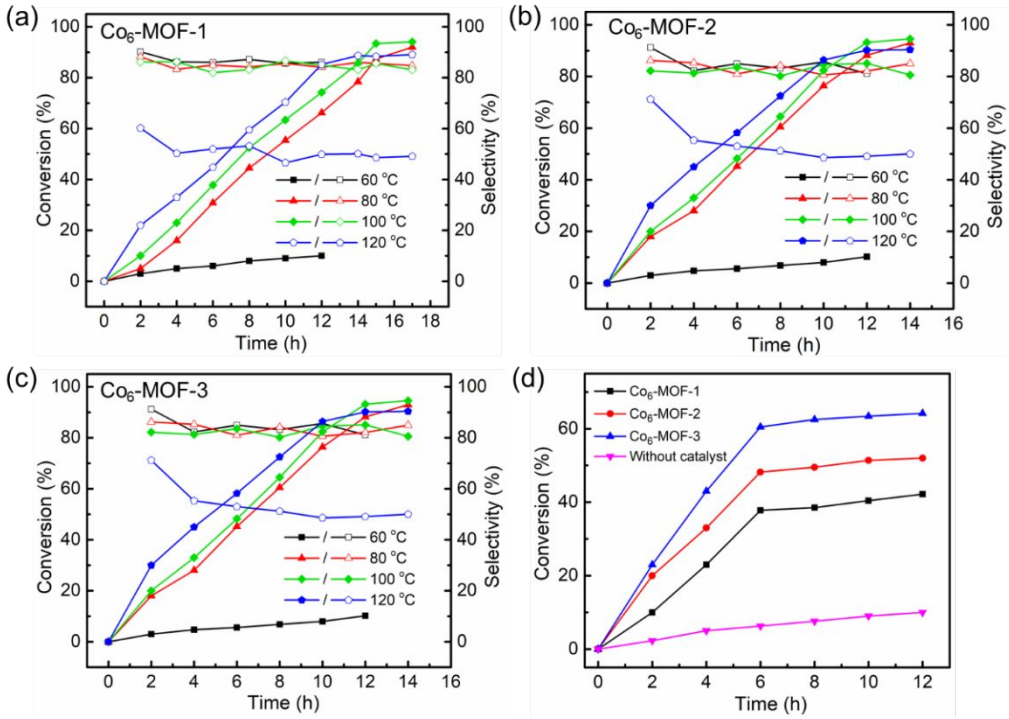

Figure S5. Influence of the temperature on the epoxidation of styrene catalyzed by Co_6-MOFs. Reaction conditions: styrene (1 mmol), DMF (10 mL). the amount of catalyst: $[Co_6(\mu_3\text{-}OH)_6]$ /substrate % = 0.37 mol%, Air (1 atm), (a) Co_6-MOF-1 (b) Co_6-MOF-2 (c) Co_6-MOF-3, (d) Hot filtration test of the epoxidation of styrene catalyzed by Co_6-MOFs catalysts, respectively.

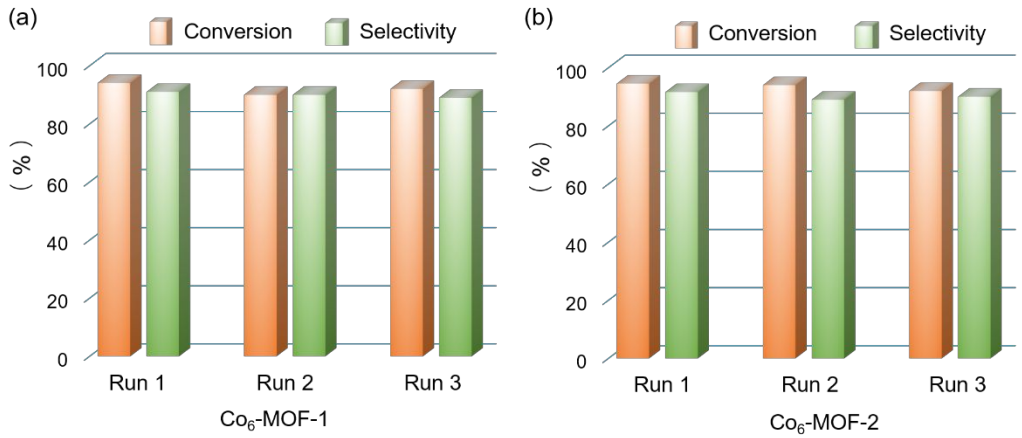

Figure S6. Conversion and selectivity in three cycles of styrene epoxidation catalyzed by (a) Co_6-MOF-1 (b) Co_6-MOF-2. Reaction conditions: styrene (3 mmol), DMF (30 mL). the amount of catalyst: $[Co_6(\mu_3\text{-}OH)_6]$ /substrate % = 0.37 mol%, Air (1 atm), T = 100 °C.

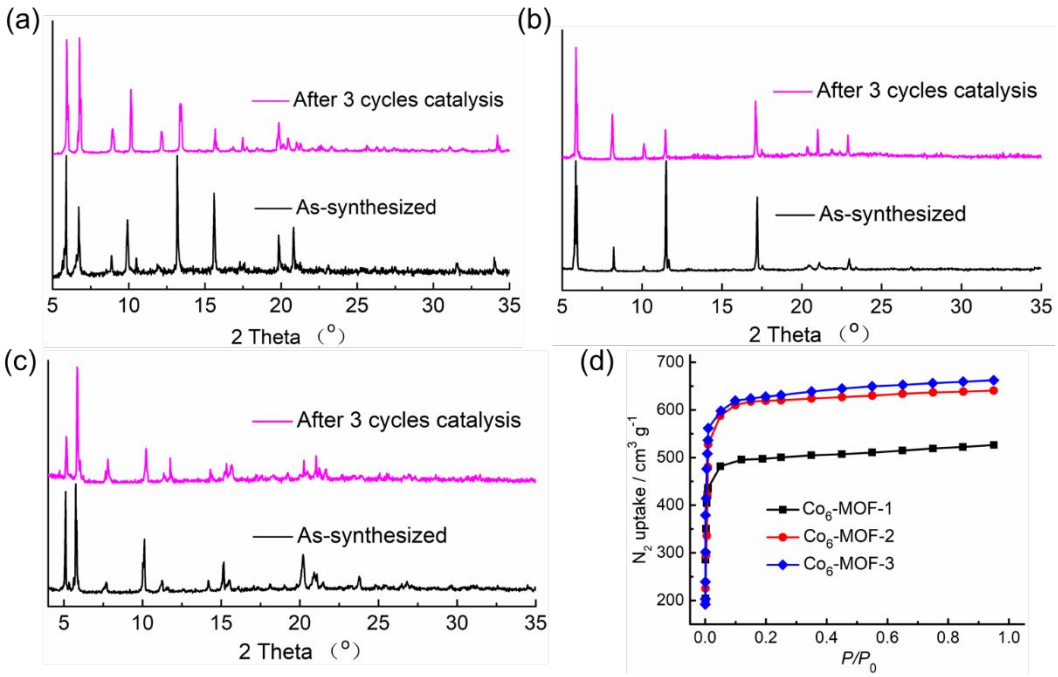

Figure S7. The PXRD patterns of (a) Co_6-MOF-1, (b) Co_6-MOF-2, and (c) Co_6-MOF-3 after 3 catalytic cycles, respectively. (d) N_2 adsorption isotherms at 77 K of Co_6-MOFs after 3 catalytic cycles, respectively.

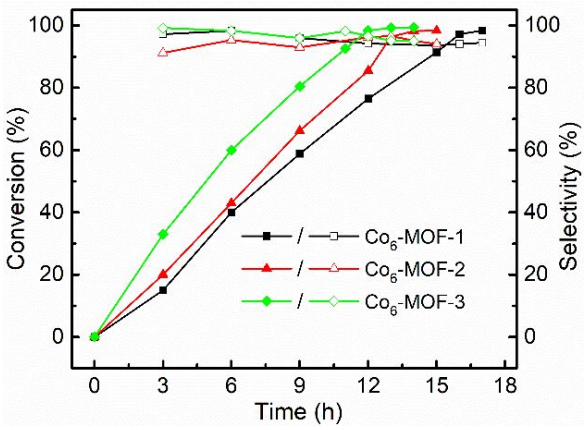

Figure S8. The oxidation of benzyl alcohol catalyzed by Co_6-MOFs with O_2 as the oxidant source. Reaction conditions: benzyl alcohol (1 mmol), DMF (10 mL), the amount of catalyst: $[Co_6(\mu_3\text{-}OH)_6]$ /substrate % = 0.43 mol%, T = 80 °C, O_2 (1 atm).

Section 2. Additional Tables

Table S1. Crystal data and structure refinements of **Co_6-MOF-1**, **-2**, and **-3**.

	Co_6-MOF-1	Co_6-MOF-2	Co_6-MOF-3
Empirical formula	$C_{36}H_{27}N_4O_9Co_3$	$C_{13}H_8N_{1.33}O_3Co$	$C_{36}H_{33}N_4O_9Co_3$
Formula weight	836.29	1990.89	843.29
Temperature (K)	150	243	243
Crystal system	hexagonal	hexagonal	hexagonal
Space group	*P*6$_3$/*mcm*	*P*6$_3$/*mc*m	*P*6$_3$/*mcm*
a (Å)	17.7315 (9)	17.7204 (5)	17.7496 (5)
c (Å)	26.666 (3)	31.2804 (11)	35.3261 (15)
Volume (Å^3)	7260.8 (11)	8506.5(6)	9638.4 (5)
Z	4	12	4
D_c (g cm^{-3})	0.762	0.679	0.649
2θ angle range (°)	4.046 to 54.99	6.95 to 57.872	2.65 to 54.96
Absorption correction	Semi-empirical from equivalents		
Refinement method	Full-matrix least-squares on F^2		
Goodness-of-fit on F^2	1.071	1.128	1.104
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	R_1 = 0.0749, wR_2 = 0.2392	R_1 = 0.0921, wR_2 = 0.2019	R_1 = 0.0928, wR_2 = 0.2593
R_1[a], wR_2[b] (all data)	R_1 = 0.0869, wR_2 = 0.2515	R_1 = 0.1183, wR_2 = 0.3280	R_1 = 0.1036, wR_2 = 0.2728
Largest diff. peak and hole (e/Å^{-3})	1.49/-1.25	1.39/-0.86	1.20/-1.21

[a]$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and [b]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/[w(Fo^2)^2]\}^{1/2}$, $[F_o > 4\sigma(F_o)]$.

The B level alert in Co_6-MOF-1 cif and its explanation:

Alert level B

PLAT420_ALERT_2_B D-H Without Acceptor O2 --H2. Please Check

The acceptor of O2--H2 in Co_6-MOF-1 could be attributed to the disordered guest molecule (DMA or H_2O), which were treated by using the MASK routine in the Olex2 software package.

Table S2. Influence of the Co_6-MOF catalyst on the epoxidation of styrene.

Catalyst[#]	oxidant	Conversion (%)	Selectivity (%)	TON	TOF (h)
Co_6-MOF-1	O_2	93.2	51.2	128.9	16.1
	air	94.1	90.8	230.9	15.4
Co_6-MOF-2	O_2	95.2	50.3	129.4	21.6
	air	94.5	90.2	230.4	19.2
Co_6-MOF-3	O_2	96.1	52.1	135.3	27.1
	air	95.6	91.8	237.2	23.7
blank	O_2	10.5	66.3	–	–
	air	5.6	75.4	–	–

Reaction conditions: 100 °C, O_2 / air (1 atm), styrene (0.5 mmol), DMF (10 mL). [#] the amount of catalyst: $[Co_6(\mu_3\text{-}OH)_6]$ / substrate % = 0.37 mol%

Section 3. Conversion, Selectivity and Yield

To determine conversion, selectivity and yield, the GC was calibrated. Therefore, five standard solutions containing authentic samples of starting material (styrene) and product (styrene oxide) were prepared and measured. Calibration curves were obtained by plotting the ratio of internal standard peak area to the mass of internal standard in

the solution against the ratio of analyte peak area to the mass of analyte. The slope of the calibration lines, received by linear fit, is the response factor R_x, which takes into account the differences in the detector response between the analyte and the standard:

$$R_x = \frac{A_{is}/m_{is}}{A_x/m_x}$$

with Ais: peak area of the internal standard, Ax: peak area of the analyte, mis: mass of the internal standard, and mx: mass of the analyte. Masses then were calculated using the following equation:

$$m_x = \frac{m_{is}}{A_{is}} * A_x * R_x$$

Conversion, yield and selectivity were calculated as follows:

$$conversion = \left(\frac{n_0(styrene) - n_i(styrene)}{n_0(styrene)}\right) * 100$$

$$yield = \left(\frac{n(styrene\ oxide}{n_0(styrene)}\right) * 100$$

$$selectivity = \left(\frac{yield}{conversion}\right) * 100$$

TONs were calculated using the following equation: $TON = \frac{n(product)}{n(catalyst)}$

TOFs were calculated using the following equation:

$$TOF = \frac{TON}{reaction\ time}$$