Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Metal phosphonates as heterogeneous catalysts for highly efficient chemical fixation of CO_2 under mild conditions

Yi-xin Wang, Jing-hui Zhou, Jun Xiong, Wan-qi Huang, Quan Li, Xue Min* and Ming Li *

School of Chemistry and Chemical Engineering, Hubei Key Laboratory of Biomass Fibers and Eco-dyeing & Finishing, Wuhan Textile University, Wuhan 430200, China, E-mail: xmin@wtu.edu.cn

Supplementary Index

Contents

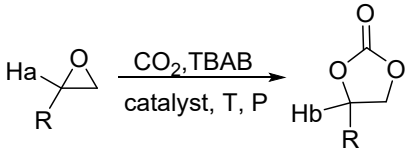
S1. Methods

1.1 General information

Powder X-ray diffraction (PXRD) was carried out with a MiniFlex 600 X-ray powder diffractometer equipped with a Cu sealed tube (λ = 1.541 78 Å) at 40 kV and 40 mA. Inductively coupled plasma (ICP) analyses of Cu and elemental analyses of C, H, and N were conducted on a Perkin-Elmer Optima 3300DV spectrometer and a Perkin-Elmer 2400 elemental analyzer, respectively. Thermal gravimetric analysis (TGA) was conducted under an N_2 atmosphere with a heating rate of 10℃/min on a SDT 2960 Simultaneous DSC-TGA of TA instruments up to 800℃. The infrared $(IR)^{-1}$ spectra (diamond) were recorded on a Nicolet 7600 FT-IR spectrometer within the 4000-500 cm^{-1} region. ^1H NMR spectra were carried out in $CDCl_3$ solvent on a Bruker 400 MHz spectrometer. The chemical shift is given in dimensionless δ values and is referenced relative to TMS in ^1H spectroscopy.

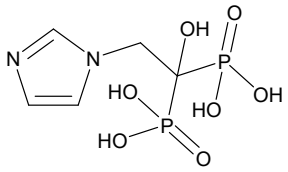
1.2 Cycloaddition of CO_2 to epoxides

The yield was calculated from H NMR according to the following equation.



$$\text{Yield}=\frac{^1Hb}{^1Ha+^1Hb}$$

S2 Supplementary tables and figures



zoledronic acid

Scheme S1. Chemical structure of ligand

Table S1 Selected bond lengths (Å) and angles (deg) for **1**

Co1-O4	2.083(4)	Co1-O4A	2.083(4)
Co1-O2	2.083(4)	Co1-O2A	2.083(4)
Co1-O12	2.132(5)	Co1-O12A	2.132(5)
Co2-O6B	2.021(4)	Co2-O7C	2.186(4)
Co2-O3C	2.119(5)	Co2-O3	2.078(5)
Co2-O5C	2.150(4)	Co2-O9	2.099(6)
O4-Co1-O4A	180.00(19)	O4A-Co1-O12A	87.21(18)
O41-Co1-O12	92.79(18)	O4-Co1-O12A	92.79(18)

O4-Co1-O12	87.21(18)	O2-Co1-O4	91.34(17)
O2A-Co1-O4A	91.34(17)	O2-Co1-O4A	88.66(17)
O2A-Co1-O4	88.66(17)	O2A-Co1-O2	180.0
O2A-Co1-O12	89.33(18)	O2-Co1-O12	90.67(18)
O2A-Co1-O12A	90.67(18)	O2-Co1-O12A	89.33(18)
O12-Co1-O12A	180.0	O6B-Co2-O7C	94.02(17)
O6B-Co2-O33	177.39(17)	O6B-Co2-O3	96.89(18)
O6B-Co2-O5C	95.31(17)	O6B-Co2-O9	94.1(3)
O3C-Co2-O7C	83.55(17)	O3-Co2-O7C	167.26(17)
O3-Co2-O3C	85.41(18)	O3-Co2-O5C	91.93(18)
O3C-Co2-O5C	83.34(18)	O3-Co2-O9	94.3(3)
O5C-Co2-O7C	80.50(16)	O9-Co2-O7C	91.4(2)
O9-Co2-O3C	86.9(3)	O9-Co2-O5C	168.0(2)

[a]Symmetry code A: 1-x, 1-y, 2-z; B: -1+x, y, z; C: 1-x, -y, 2-z

Table S2 Selected bond lengths (Å) and angles (deg) for **2**

Cd2-O5A	2.210(3)	Cd1-O7	2.260(3)
Cd2-O5	2.210(3)	Cd1-O4B	2.352(3)
Cd2-O9	2.363(4)	Cd1-O4	2.331(3)
Cd2-O9A	2.363(4)	Cd1-O6C	2.295(3)
Cd2-O8A	2.293(3)	Cd1-O3D	2.289(3)
Cd2-O8	2.293(3)	Cd1-N1E	2.264(4)
O5A-Cd2-O5	180.0	O7-Cd1-O4B	163.57(11)
O5-Cd2-O9A	90.10(11)	O7-Cd1-O4	86.01(11)
O5ACd2-O9	90.10(11)	O7-Cd1-O6C	82.54(10)
O5A-Cd2-O9A	89.90(11)	O7-Cd1-O3D	101.74(11)
O5-Cd2-O9	89.90(11)	O7-Cd1-N1E	89.68(12)
O5A-Cd2-O8	90.02(11)	O4-Cd1-O4B	83.88(10)
O5-Cd2-O8	89.98(11)	O6C-Cd1-O4B	82.84(10)
O5-Cd2-O8A	90.02(11)	O6C-Cd1-O4	79.02(10)
O5A-Cd2-O8A	89.98(11)	O3D-Cd1-O4B	92.39(11)
O9-Cd2-O9A	180.0	O3D-Cd1-O4	97.33(10)
O8A-Cd2-O9A	92.65(15)	O3D-Cd1-O6C	174.24(11)
O8A-Cd2-O9	87.35(15)	N1E-Cd1-O4B	99.48(12)
O8-Cd2-O9A	87.35(15)	N1E-Cd1-O4	174.38(11)

O8-Cd2-O9	92.65(15)	N1E-Cd1-O6C	96.85(12)
O8-Cd2-O8A	180.0	N1E-Cd1-O3D	87.08(12)

[a]Symmetry code A:1-x,1-y,-z; B:2-x,1-y,-1-z; C:1+x,+y,+z; D:1-x,1-y,-1-z; E:+x,1+y,+z

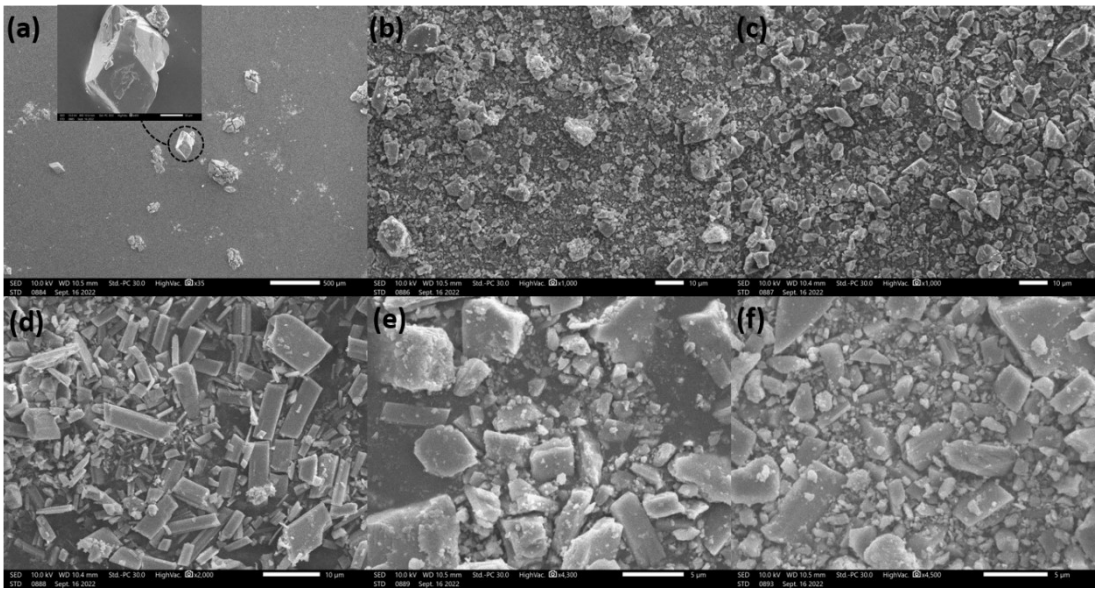


Figure S1 SEM diagram of compound 1 before (a; inset a: one crystal of compound 1 at the 50um scale) and after (b) grinding and after catalytic reaction (c); SEM diagram of compound 2 before (d) and after (e) grinding and after catalytic reaction (f).

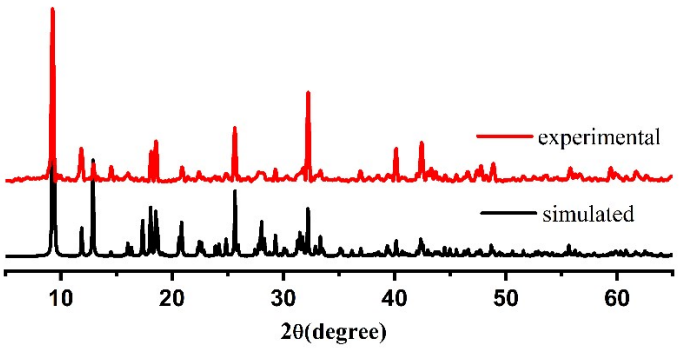


Figure S2 PXRD patterns of compound 1.

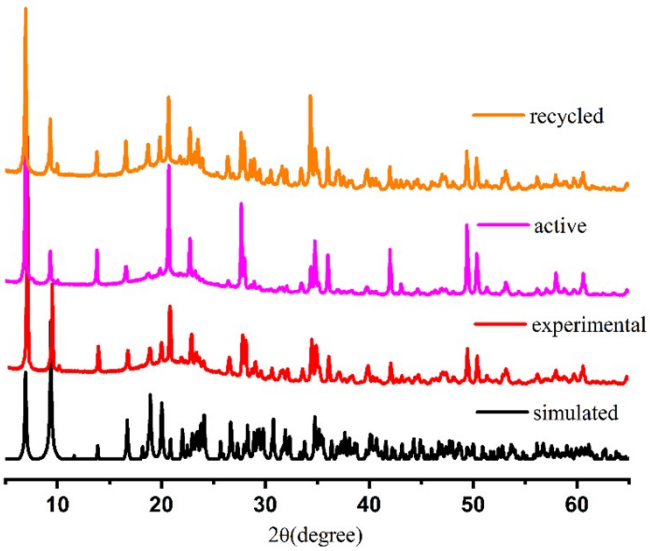


Figure S3 PXRD patterns of compound 2.

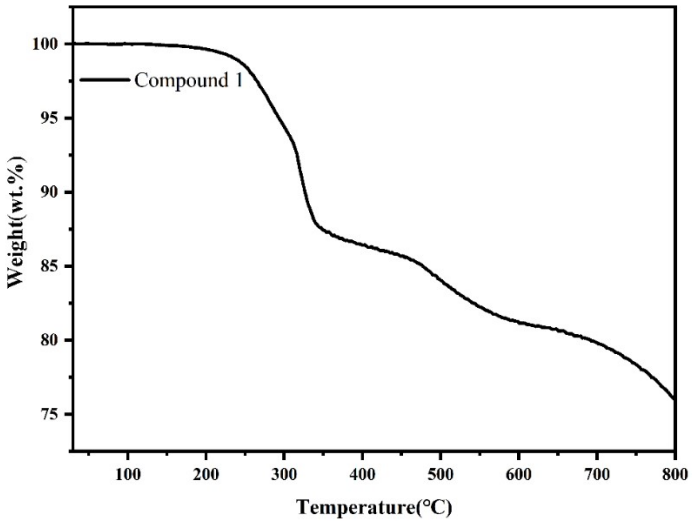


Figure S4 TGA curve of compound 1.

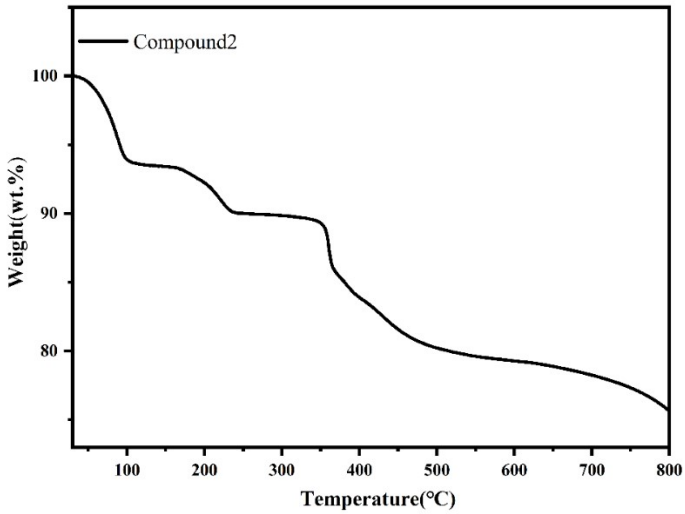


Figure S5 TGA curve of compound 2.

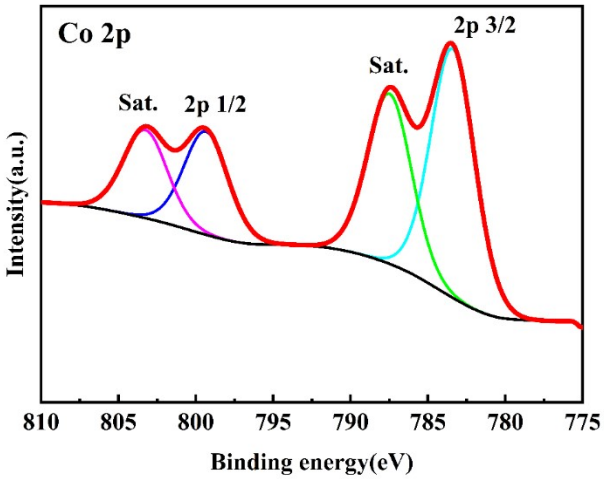


Figure S6 High-resolution XPS spectra of compound 1 in the Co 2p region.

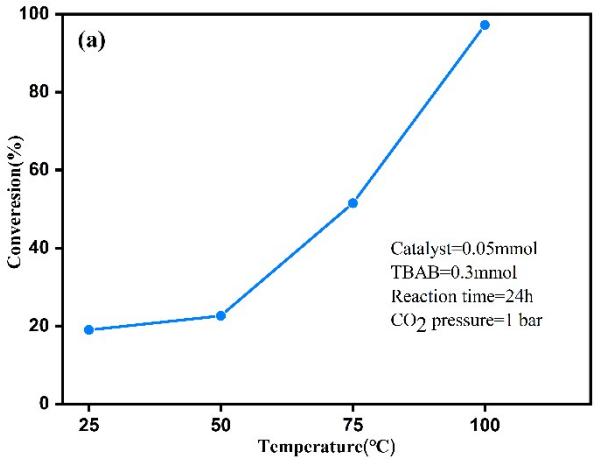


Figure S7 Reaction temperature that affect the cycloaddition of SO and CO_2.

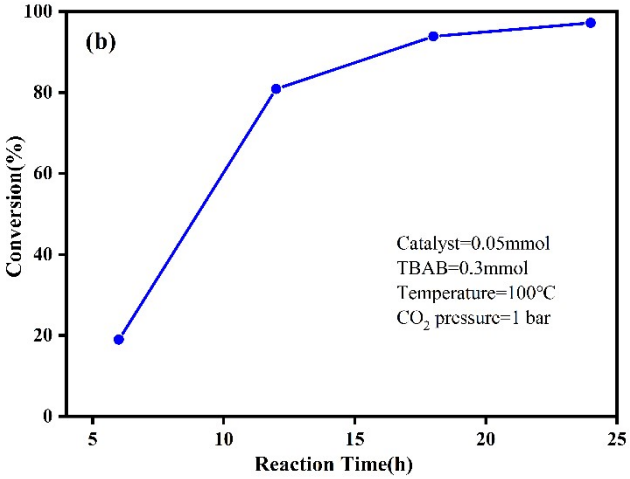


Figure S8 Reaction time that affect the cycloaddition of SO and CO_2.

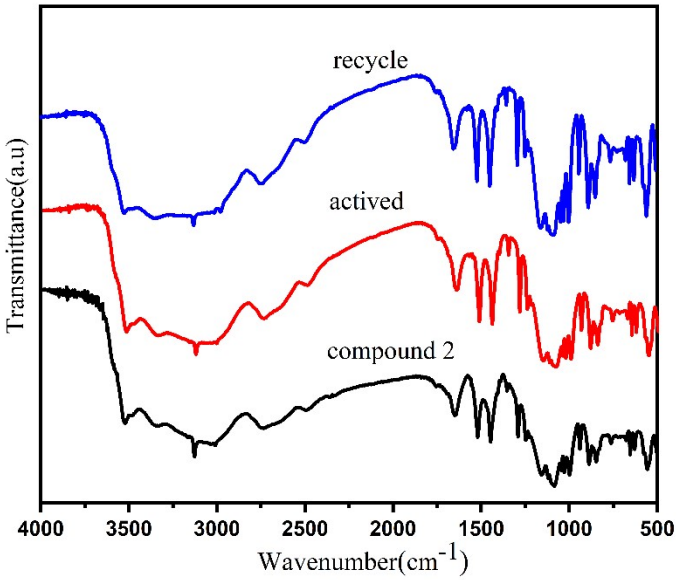


Figure S9 Infrared spectra of compound **2**.

Table S3 Compound 2 catalytic of cycloaddition of CO_2 to styrene epoxide[a]

Entry	Catalyst	Co-catalyst	Substrate	Time(h)	Conversion(%)[b]
1	0.05	none	SO	12	4.3
2	none	0.3	SO	12	17.9
3	0.05	0.3	SO	12	97.5
4	0.05[c]	0.3	SO	12	52.2
5	0.025	0.15	SO	12	79.2
6	0.05	0.3	BGE	12	92.5

[a]Reaction conditions: epoxide=10 mmol (SO, styrene epoxide; BGE, butyl glycidyl ether), compound 2 (0.05mmol), and TBAB(0.3mmol) under 1atm CO_2, 100℃. [b]Determined by GC. [c]Reuse1.

Table S4 Comparative catalytic performance of 1 with others previously reported Co-MOFs catalysts for cycloaddition of epoxides with CO_2.

NO.	catalyst Co based MOFs	Co-catalyst	Temperature (°C)	Pressure (MPa)	Time (h)	Yield (%)	Ref.
1	Co-MOF-74(M)	-	100	2	4	96	32a
2	ZIF-67	-	120	1	6	87	32b
3	Co/ZIF-8	-	120	0.7	8	96.8	32c
4	TPPCoCl	TBAI	120	1.8	12	24.1	32d
5	Co-MOF-184	TBAB	80	0.1	6	72	32e
6	$Co(XN)(HCOO)_2$	TBAB	90	0.1	12	99	32f
7	$Co(TCPB)_{0.5}$	TBAB	80	0.1	9	80.8	32g

8	Co(BDC)(L)	TBAB	40	0.1	12	99	32h
9	Co(OBA)(L')	TBAB	60	0.1	24	99	32i
10	Co(μ_3-L'')	TBAB	50	0.1	36	94.3	32j
11	Co(L''')	TBAB	RT	0.1	8	91.7	32k
12	Compound 1	TBAB	100	0.1	24	97.4	This work

S3. The NMR spectrums

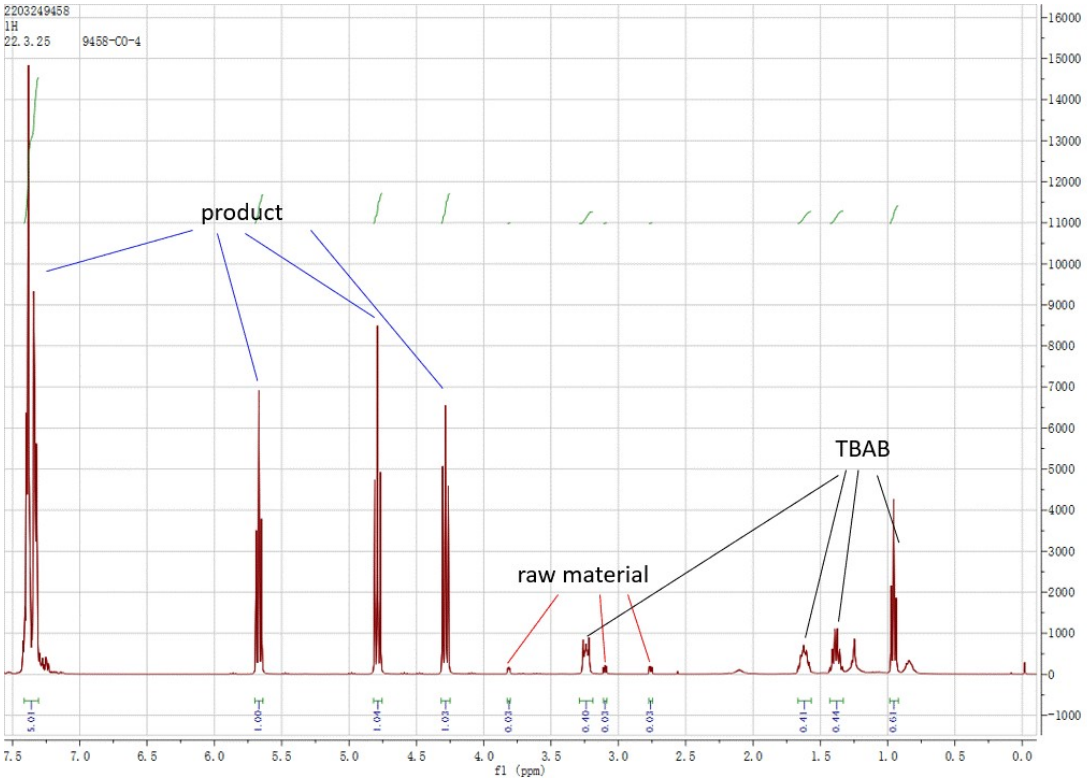


Figure S9 The 1H NMR results of Catalytic Styrene oxide cycloaddition with CO_2 using compound 1 as catalyst under the optimized reaction conditions mentioned in main body.