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Supporting Information

2 **Bifunctional Chlorhexidine-Based Covalent Organic Polymers for**

3 **CO₂ Capture and Conversion without Co-catalyst**

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1 **1. Materials**

2 All reagents and chemicals were purchased from commercial vendors and could be
3 used directly without further purification. Chlorhexidine (CHX) and imidazole were
4 purchased from Shanghai Meryer Chemical Technology Co., Ltd. $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
5 was purchased from Boka (Shanghai) Chemical Technology Co., Ltd.
6 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and triethylamine (TEA) was purchased from Sinopharm Chemical
7 Reagent Co., Ltd. 1, 2-epoxybutane was purchased from Adamas Chemical Reagent
8 Co., Ltd. N-butyl glycidyl ether was obtained from TCI (Shanghai) Development Co.,
9 Ltd. Cyanogen chloride were purchased from Aladdin Bio-Chem (Shanghai)
10 Technology Co., Ltd. Epichlorohydrin and propylene oxide were purchased from
11 Jining Huake New Material Co. Ltd. Epoxy styrene was purchased from Jinjinle
12 (Hunan) Chemical Co., Ltd. Methanol and DMF were purchased from Tianjin
13 Yongda Chemical Reagent Co., Ltd. Ethanol was purchased from Shanghai Macklin
14 Biochemical Technology Co., Ltd.

15 **2. Characterizations**

16 Powder X-ray diffraction (PXRD) was carried out with a Bruker AXS D8 advanced
17 automatic diffractometer. Fourier transform infrared (FT-IR) spectrum
18 characterization was performed using a Nicolet 5DX spectrometer.
19 Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris1
20 TGA7. The sample was heated to 800 °C at a rate of 5 °C min⁻¹ under N₂ atmosphere.
21 Glass transition point was detected by differential scanning calorimeter (NEXTA
22 DSC 600). Catalytic reaction conversion was measured by SP-2100A gas
23 chromatography (GC). The molecular weight was tested by gel permeation
24 chromatography (AMERICAN Waters 1525). The morphologies were recorded by
25 transmission electron microscopy (TEM; JEOL, JEM-2010) and scanning electron
26 microscopy (COP-Co: SEM, FEI Quanta 250F; COP-Zn: SEM, HITACHI SU8010).
27 EDS elemental-mapping images were acquired by SEM. Nitrogen adsorption and
28 desorption isotherms were determined by Beishide-3H 2000PS1. X-ray photoelectron
29 spectroscopy (XPS) was performed by UIVAC-PHI Quantum 2000. The solid-state
30 high resolution nuclear magnetic resonance (¹³C-NMR) spectrometer was assessed with
31 Bruker 400 M (spinning speed: 10 kHz; recovery time: 4 s; pulse program for
32 acquisition: cp; pre-scan delay: 6.5 μs).

1 **3. Experimental section**

2 **Synthesis of tris(1H-imidazol-1-yl) triazine (TIT).** The TIT was synthesized based
3 on a procedure we have reported earlier.¹ Imidazole (15 mmol) and TEA (15 mmol)
4 were dissolved into a 50 mL tetrahydrofuran solution. The mixture was heated to 50
5 °C in N₂ atmosphere and stirred until dissolved. After 1 h, cyanogen chloride (5 mmol,
6 0.92 g) was dissolved in 25 mL tetrahydrofuran solution, and the solution was added
7 to the flask drop by drop with a needle. The mixture was further heated to 75 °C and
8 stirred for 2 h. After the reactants were cooled, tetrahydrofuran was removed by
9 evaporation. The crude product was rinsed with deionized water three times and then
10 dried overnight to obtain a white solid product.

11 **Synthesis of CHX-Co.** Firstly, the ethanol (30 mL) and CHX (1 mmol) were added to
12 a three-mouth flask and heated to 40 °C. Then Co(NO₃)₂·3H₂O (1 mmol) was added
13 to the white suspension and stirred for 12 h. Then the suspension was filtered and
14 washed with anhydrous ethanol three times. After drying at room temperature, a
15 thistle-colored solid was obtained.

16 **Synthesis of CHX-Zn.** Firstly, the Ethanol (30 mL) and CHX (1 mmol) were added
17 to a three-mouth flask and heated to 40 °C. Then Zn(NO₃)₂·6H₂O (1 mmol) was added
18 to the white suspension and stirred for 12 h. The suspension was filtered and washed
19 with anhydrous ethanol for three times. After drying at room temperature, the white
20 solid product was obtained.

21 **Synthesis of COP-Co.** Firstly, the CHX-Co (1.2 mmol) and TIT (1.5 mmol) were
22 added into a mixture of DMF (20 mL) and ethanol (20 mL). The suspension was
23 heated to 110 °C and refluxed for 3 days. Then the mixture was filtered and washed
24 three times under ultrasonic conditions with DMF and methanol. After drying at 60 °C
25 for 12 h, the indigo solid COP-Co was obtained.

26 **Synthesis of COP-Zn.** Firstly, the CHX-Zn (1.3 mmol) and TIT (1.6 mmol) were
27 added into a mixture of DMF (30 mL) and ethanol (30 mL). The suspension was
28 heated to 110 °C and refluxed for 3 days. Then the mixture was then filtered and
29 washed three times under ultrasonic conditions with DMF and methanol. After drying
30 at 60 °C for 12 h, the white solid COP-Zn was obtained.

1 **Cycloaddition of CO₂ with epoxides** Firstly, the COP-Co and COP-Zn catalysts
2 were vacuumed at 110 °C for 12 h to remove the remaining guest molecules on their
3 surfaces. 50 mg catalyst and 10 mmol substrate (propylene oxide, epichlorohydrin, 1,
4 2-epoxy-butane, N-butyl glycidyl ether, and epoxy styrene) were added to a 20 mL
5 high-pressure reactor. Then the mixture was reacted at 90 °C and 1 MPa CO₂ for 12 h,
6 and the stirring speed of the reactor was set at 350 rpm. After the reaction, the reactor
7 was quickly cooled to room temperature, and the conversion was determined by gas
8 chromatography.

9 **Cycle experiments** The COP-Co and COP-Zn catalysts were recovered by
10 centrifugation and washed abundantly with methanol for three times. Then the COP-
11 Co and COP-Zn catalysts were vacuum-dried at 60 °C overnight. Finally, the
12 recovered catalysts were conducted for the next five cycles. Specifically, 50 mg
13 catalyst and 10 mmol propylene oxide were added to a 20 mL high-pressure reactor.
14 Then the mixture was reacted at 90 °C and 1 MPa CO₂ for 12 h, and the stirring speed
15 of the reactor was set at 350 rpm. Finally, the reactor was quickly cooled to room
16 temperature, and the conversion was determined by gas chromatography.

17 **4. The Langmuir model**

18 The mathematical expression of Langmuir equation is the following:

$$19 \quad q_e = \frac{q_L K_L P_{CO_2}}{1 + K_L P_{CO_2}} \quad \text{Equation S1}$$

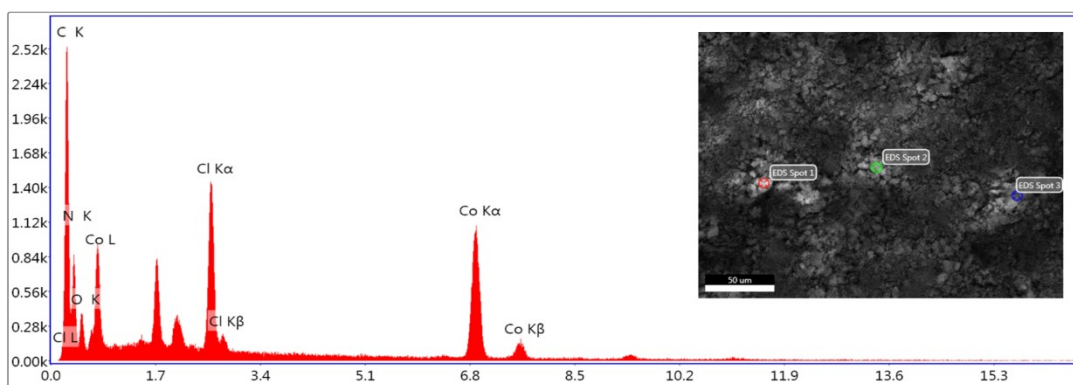
20 where q_L (mL g⁻¹) is the maximum monolayer adsorption capacity of the adsorbent,
21 P_{CO_2} (atm) is the equilibrium pressure of the gas adsorbed, whilst K_L (atm⁻¹) is the
22 Langmuir adsorption constant or the affinity constant.²

23 **5. The GC determination**

$$24 \quad \text{Conversion (\%)} = \frac{S_B + S_C}{S_A} \quad \text{Equation S2}$$

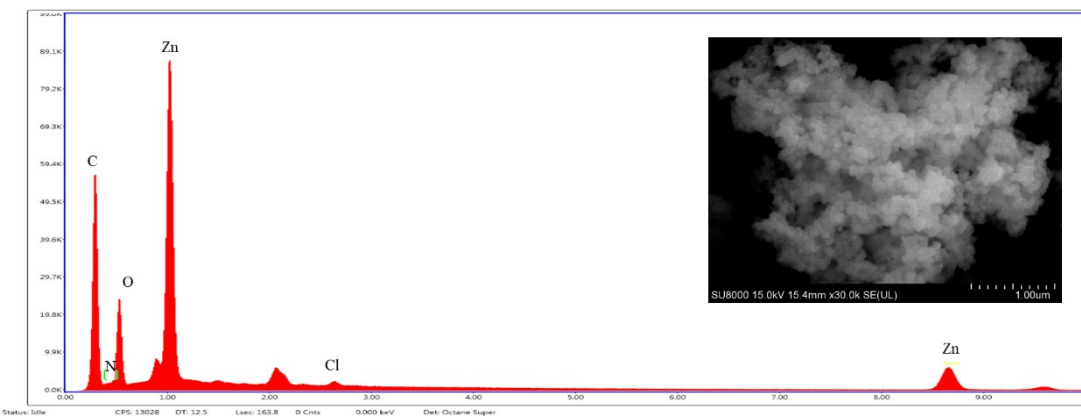
25 where S_A , S_B , and S_C are denoted as the integral area values of epoxide,
26 cyclocarbonate, and by-product, respectively.

1 **6. Figures**



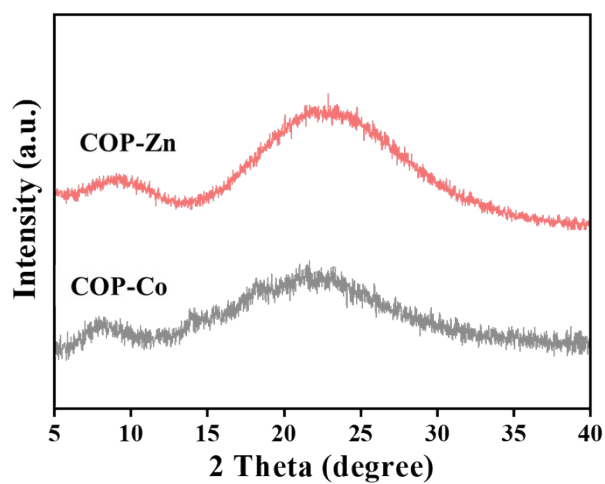
2 活时间 (秒) : 30.0 0 Cnts 0.000 keV 探测器: Apollo XL-SDD Det

3 **Fig. S1. SEM-EDS element analysis of COP-Co.**



4 Status: Idle CPS: 13028 DT: 12.5 Lvol: 163.8 0 Cnts 0.000 keV Det: Oxford Super

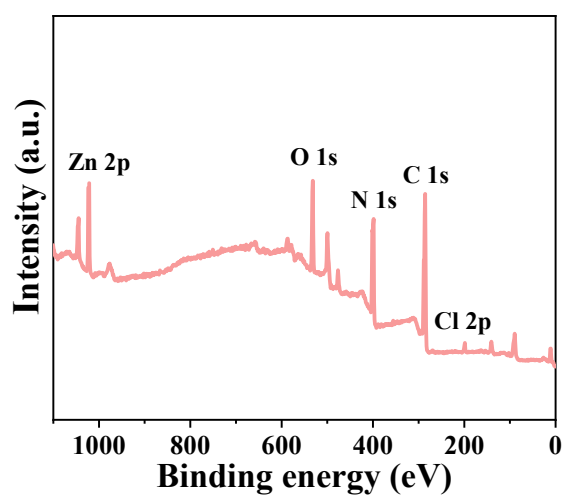
5 **Fig. S2. SEM-EDS element analysis of COP-Zn.**



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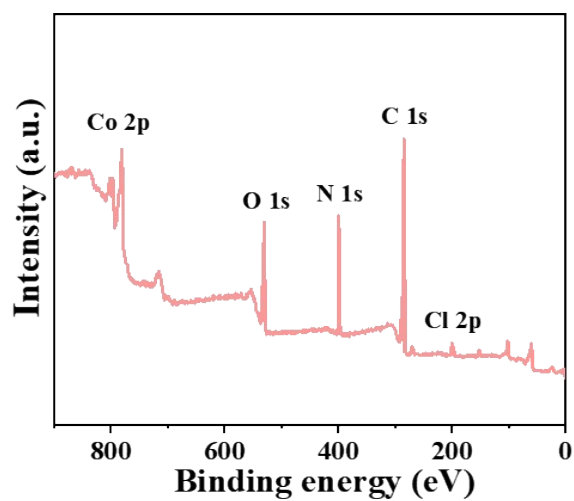
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Fig. S3. Power XRD patterns of COP-Co and COP-Zn.



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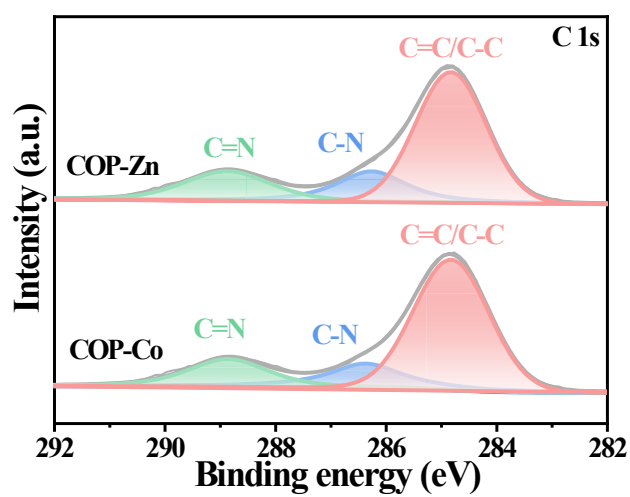
4 **Fig. S4.** XPS survey of COP-Zn with Ar ion etching 50 nm.



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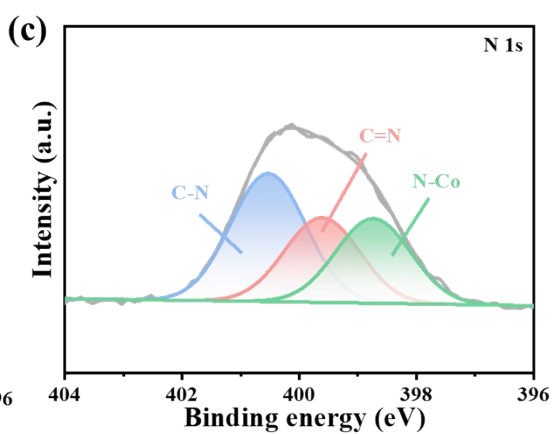
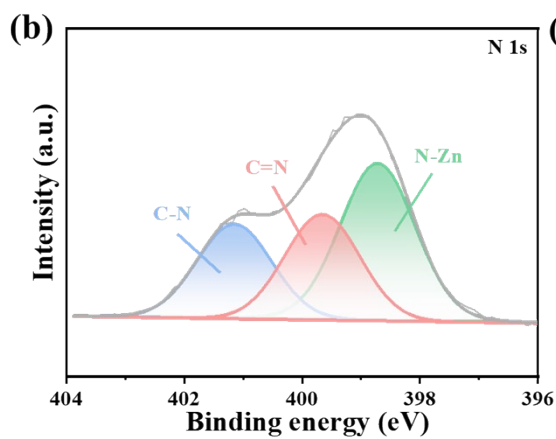
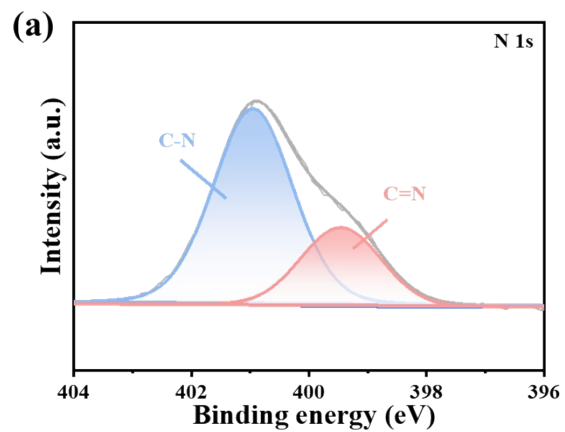
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Fig. S5. XPS survey of COP-Co with Ar ion etching 50 nm.



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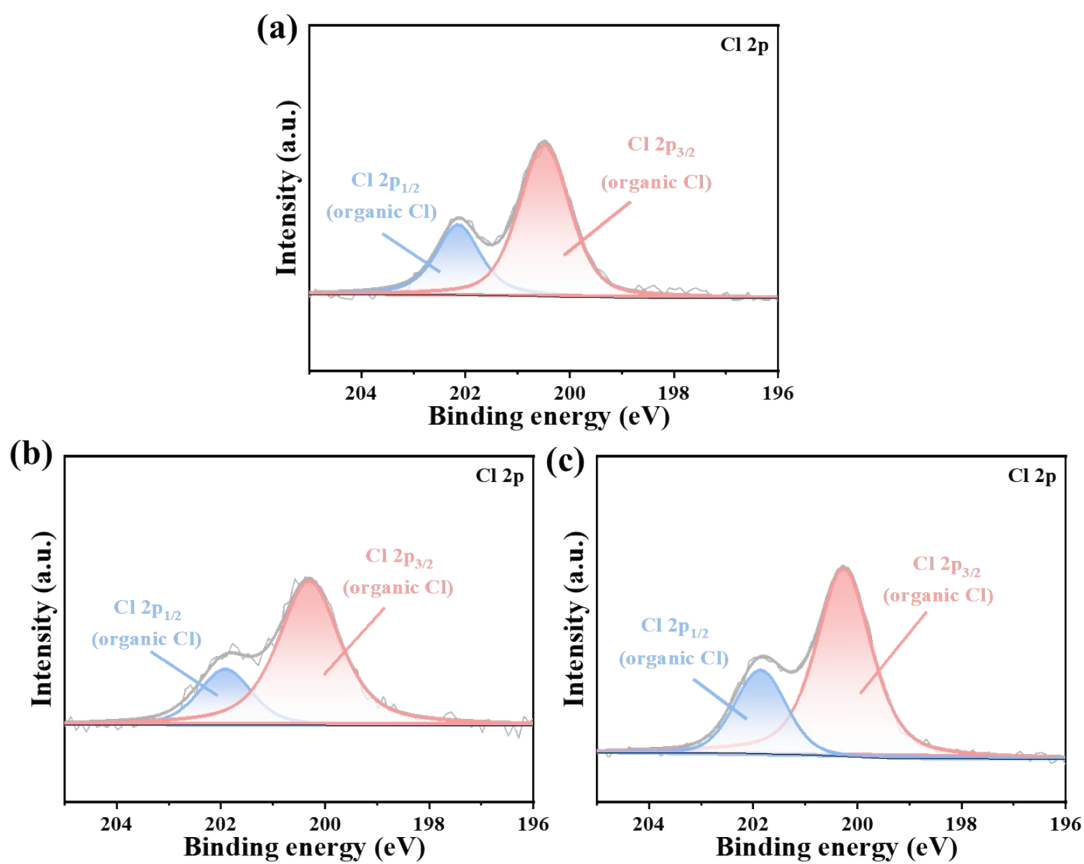
4 **Fig. S6.** High-resolution C 1s XPS spectra of COP-Zn and COP-Co.



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1 **Fig. S7.** High-resolution N 1s XPS spectra of (a) CHX, (b) CHX-Zn, and (c) CHX-Co.

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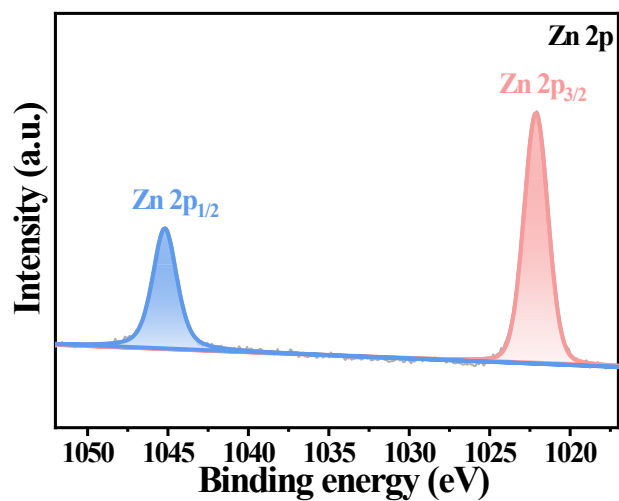


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4 **Fig. S8.** High-resolution Cl 2p XPS spectra of (a) CHX, (b) CHX-Zn, and (c) CHX-

5

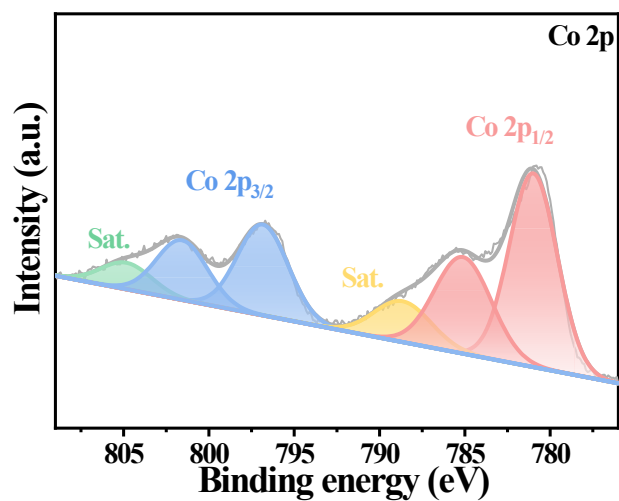
Co.



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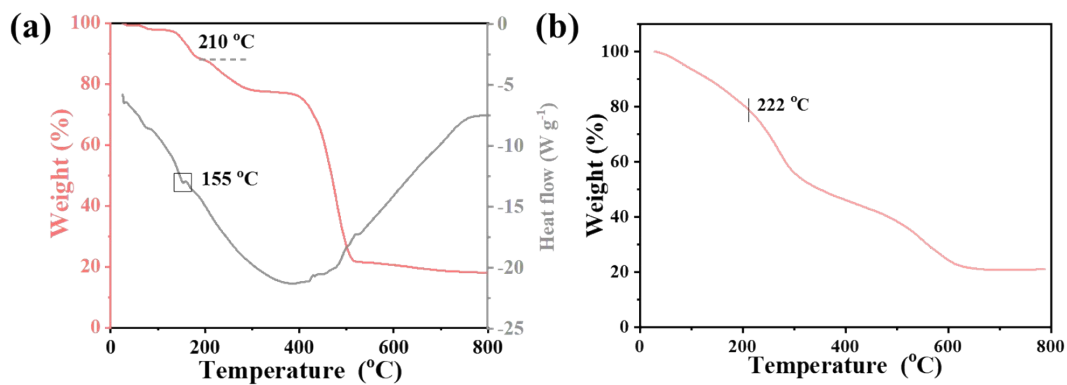
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Fig. S9. High-resolution Zn 2p XPS spectra of COP-Zn.



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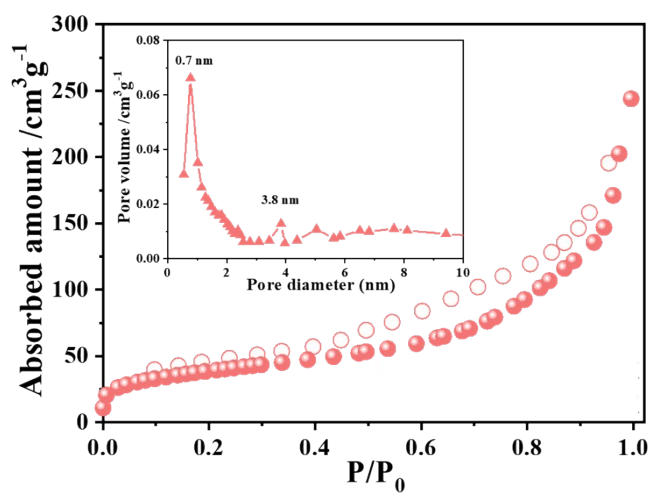
4 **Fig. S10.** High-resolution Co 2p XPS spectra of COP-Co.



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Fig. S11. TGA curves of (a) COP-Co and (b) COP-Zn.

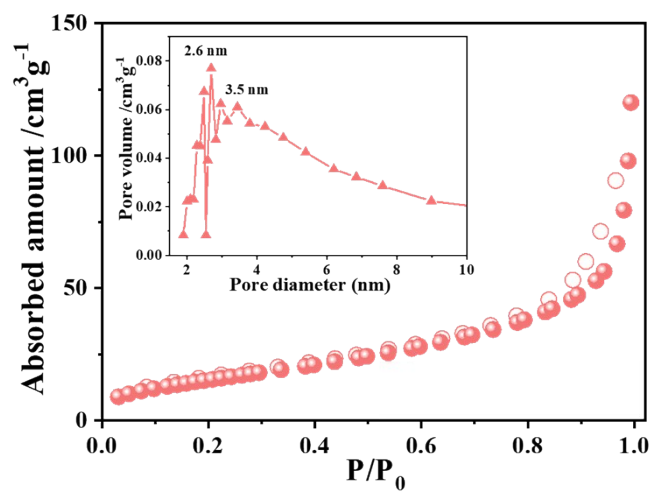


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Fig. S12. N₂ adsorption/desorption isotherms and pore diameter distribution of COP-

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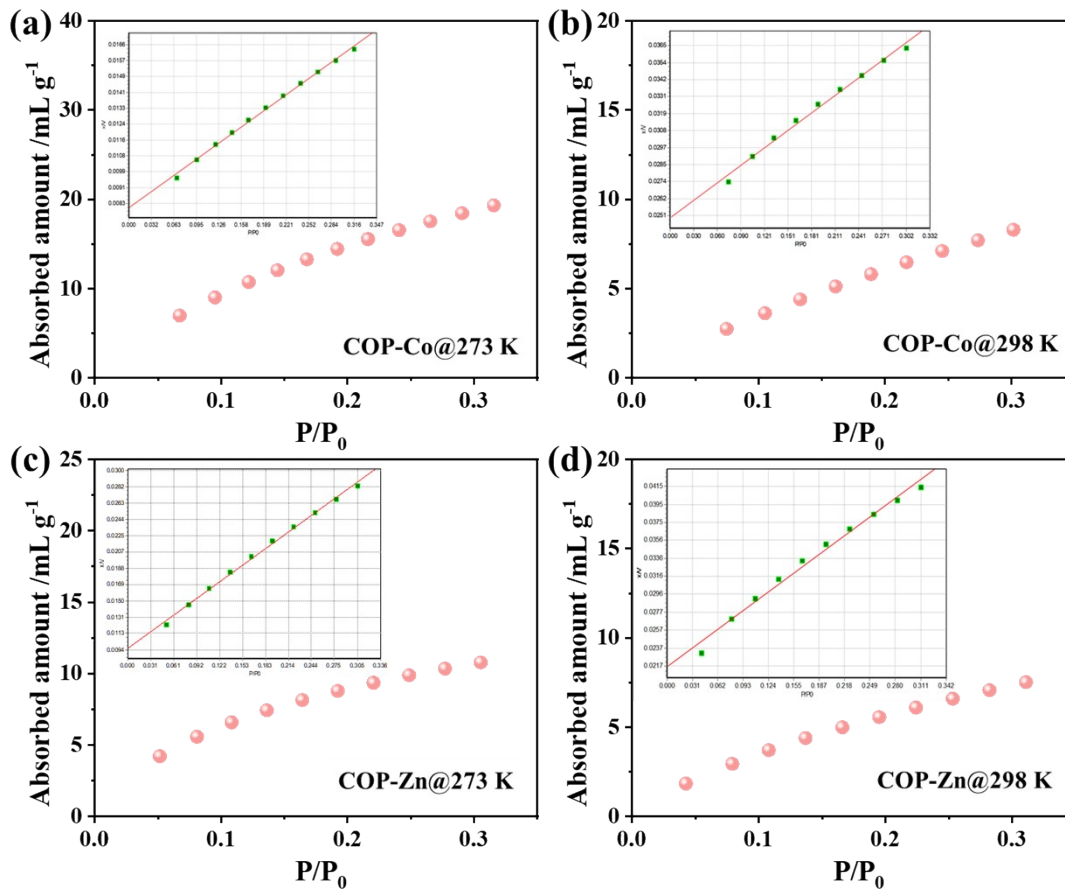
Co at 77 K.



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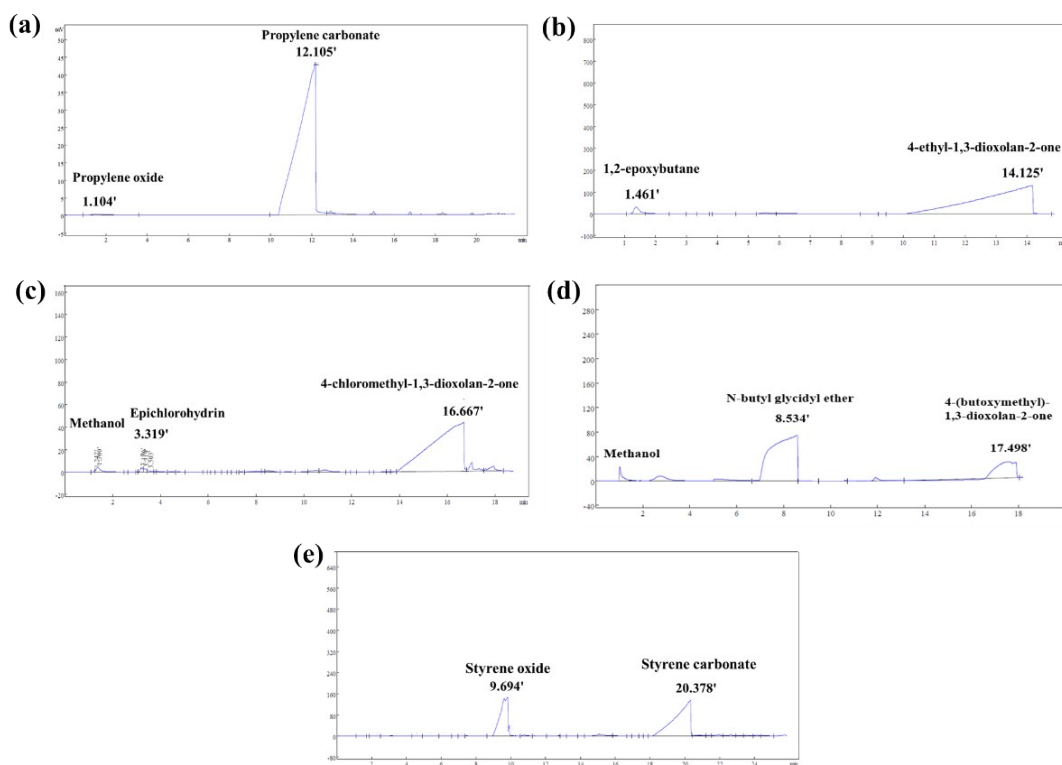
2 **Fig. S13.** N_2 adsorption/desorption isotherms and pore diameter distribution of COP-

3 Zn at 77 K.



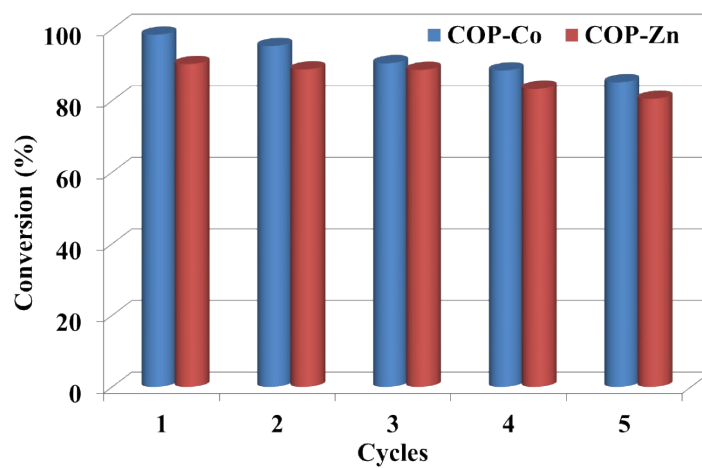
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2 **Fig. S14.** CO₂ uptake isotherms and fitted curves at the temperature of of (a) COP-Co
 3 at 273 K, (b) COP-Co at 298 K, (c) COP-Zn at 273 K, and (d) COP-Zn at 298 K.



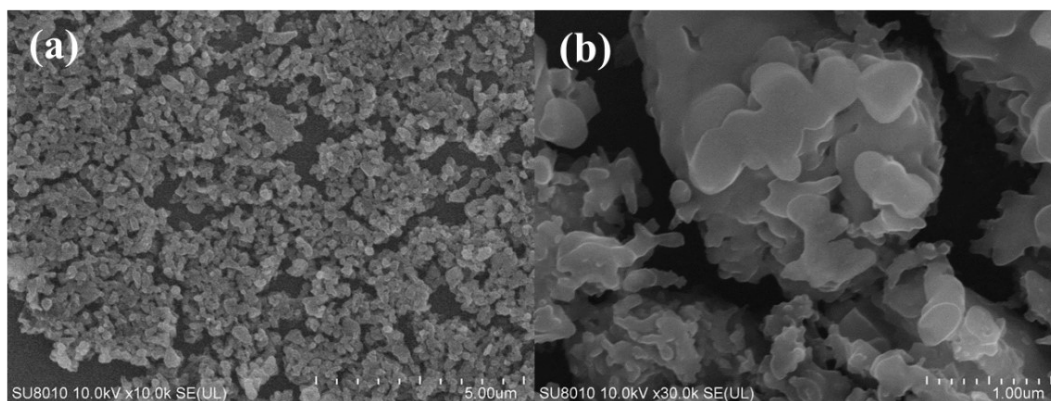
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2 **Fig. S15.** GC chromatograms of (a) CO₂-propylene oxide, (b) CO₂-epichlorohydrin,
 3 (c) CO₂-1, 2-epoxybutane, (d) CO₂-n-butyl glycidyl ether, (e) CO₂-styrene oxide
 4 reaction mixtures. Injection amount : 1 μL. GC program: Set point (Initial): 60 °C,
 5 Hold time (Initial): 2 min, Ramp: 10 °C min⁻¹; Set point (Step I): 240 °C, Hold time
 6 (Step I): 10 min; Set point (Step II/Final): 260 °C, Hold time (Step II/Final): 10 min,
 7 FID temperature 280 °C.



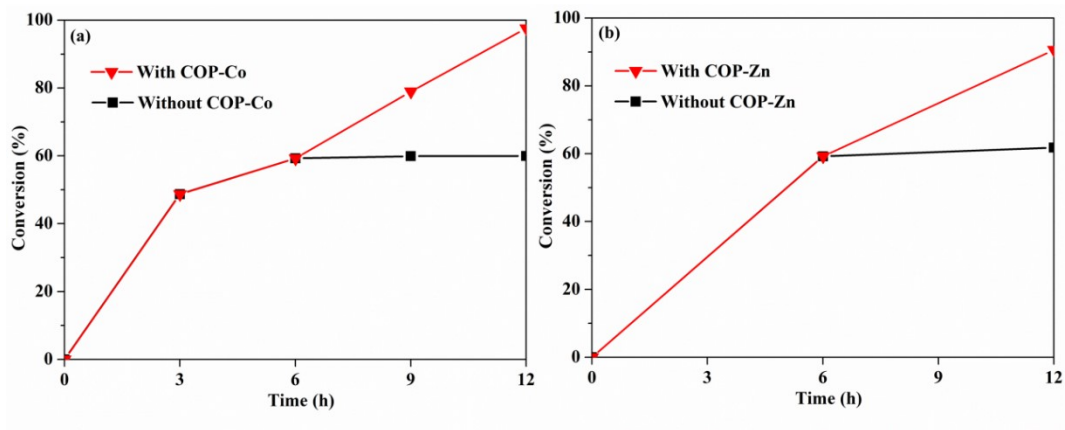
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2 **Fig. S16.** Recycling test of COP-Co and COP-Zn for the cycloaddition of CO₂ with
 3 PO.



4

5 **Fig. S17.** SEM of (a) COP-Co and (b) COP-Zn after five cycles.



1

2 **Fig. S18.** Leaching performance tests of (a) COP-Co and (b) COP-Zn.

1 **7. Table**

2 **Table S1.** Adsorption isotherm fitting parameters of using COP-Co and COP-
3 Zn based on Langmuir model.

Sample	T (K)	q_L (mL g ⁻¹)	K_L	R^2	q_e (mL g ⁻¹)	q_e (mg g ⁻¹)
COP-Co	273	37.4	3.3	99.9	28.7	57.3
COP-Co	298	25.7	1.6	99.6	15.8	31.2
COP-Zn	273	15.9	6.6	99.9	13.8	27.6
COP-Zn	298	15.1	3.1	99.4	11.4	22.5

4

1 **Table S2.** Comparison of the cycloaddition of propylene oxide and CO₂ with
 2 previously reported catalysts under the co-catalyst-free condition.

Entry	Cat. ^a	Tem. ^b (°C)	Pre. ^c (MPa)	T. ^d (h)	Con. ^e (%)	Y. ^f (%)	S. ^g (%)	TON	Ref.
1	COP-Co	90	1	12	98.4	/	>99	164	This work
2	COP-Zn	90	1	12	90.2	/	>99	150	This work
3	CNT-OH@ PV ₃ Br-0.7	100	0.2	3	/	94. 5	99.6	158	3
4	HIP-COOH-TMG	110	1	8	85	/	99	/	4
5	UMCM-15-OH	60	1	30	92	/	/	567	5
6	[o-MBzMIM]Cl	130	2	4	/	94. 9	/	380	6
7	{[Co ₂ (tzpa)(OH) (H ₂ O)]. DMF} _n	25	0.1	48	/	94	/	94	7
8	ZnAl-RM	25	1	12	<5	/	/	/	8
9	(I)Meim-UiO-66	120	0.1	24	77	/	62	119	9
10	NU-1000 (Zr)/cat 1	80	0.4	4	98	98	/	98	10
11	{[Co ₆ (TATAB) ₄ (D ABCO) ₃ (H ₂ O) ₃] ₁₂ DMF·9H ₂ O	80	0.1	15	94.6	/	/	473	11
12	POF-[Cellmim] [Br]	120	2	4	/	97	99	32	12
13	MA-PDA IL@COF	70	0.1	14	/	76	>99	95	13
14	Complex Zn-3	80	1	6	100	95	/	95	14

3 ^aCatalyst; ^bTemperature; ^cPressure; ^dTime; ^eConversion; ^fYield; ^gSelectivity.

1 **8. References**

- 2 1 R. Y. Zhang, Y. Zhang, J. Tong, L. Liu, Z. B. Han, *Catal. Lett.*, 2021, 18, 2833-
3 2841.
- 4 2 F. Raganati, M. Alfe, V. Gargiulo, R. Chirone, P. Ammendola., *Chem. Eng. Res.*
5 *Des.*, 2018, **134**, 540–552; H. J. Esfahani, A. Ghaemi, S. Shahhosseini, *Sci. Rep-*
6 *UK*, 2024, **14**, 18871.
- 7 3 Y.-L. Wan, J. Zhang, L. Wang, Y.-Z. Lei, L.-L. Wen, *J. Colloid Interf. Sci.*, 2024,
8 **653**, 844-856.
- 9 4 M. Li, L. Shi, Y. Liu, S. Li, W. Cui, W. Li, Y. Zhi, S. Shan, Y. Miao, *Chem. Eng.*
10 *J.*, 2024, **481**, 148550.
- 11 5 M. Saghian, S. Dehghanpour, M. Sharbatdaran, *Micropor. Mesopor. Mat.*, 2024,
12 **366**, 112955.
- 13 6 T. Wang, D. Zheng, Y. Ma, J. Guo, Z. He, B. Ma, L. Liu, T. Ren, L. Wang, J.
14 Zhang, *J. CO₂ Util.*, 2017, **22**, 44-52.
- 15 7 R. S. S. Pillai, D. Kim, D. Mathew, R. R. Kuruppathparambil, T. M. Robert, S. K.
16 B. Pillai, S. K. K. Shankaranarayanan, *J. CO₂ Util.*, 2022, **59**, 101951.
- 17 8 Y. Chen, P. Xu, M. Arai, J. Sun, *Adv. Synth. Catal.*, 2019, **361**, 335-344.
- 18 9 J. Liang, R.-P. Chen, X.-Y. Wang, T.-T. Liu, X.-S. Wang, Y.-B. Huang, R. Cao,
19 *Chem. Sci.*, 2017, **8**, 1570-1575.
- 20 10 M. Pander, M. Janeta, W. Bury, *ACS Appl. Mater. Interfaces*, 2021, **13**, 8344-
21 8352.
- 22 11 B. Ugale, S. Kumar, T. J. D. Kumar, C. M. Nagaraja, *Inorg. Chem.*, 2019, **58**,
23 3925-3936.
- 24 12 Y. Yang, Y. Guo, C. Gao, M. North, J. Yuan, H. Xie, Q. Zheng, *ACS Appl.*
25 *Energy Mater.*, 2023, **6**, 2634-2646.
- 26 13 S. Sarkar, S. Ghosh, R. Sani, J. Seth, A. Khan, S. M. Islam, *ACS Sustainable*
27 *Chem. Eng.*, 2023, **11**, 14422-14434.
- 28 14 B. Wang, L. Wang, J. Lin, C. Xia, W. Sun, *ACS Catal.*, 2023, **13**, 10386-10393.