

## Supporting information

# Synthesis of covalent organic frameworks via in-situ salen skeleton formation for catalytic applications

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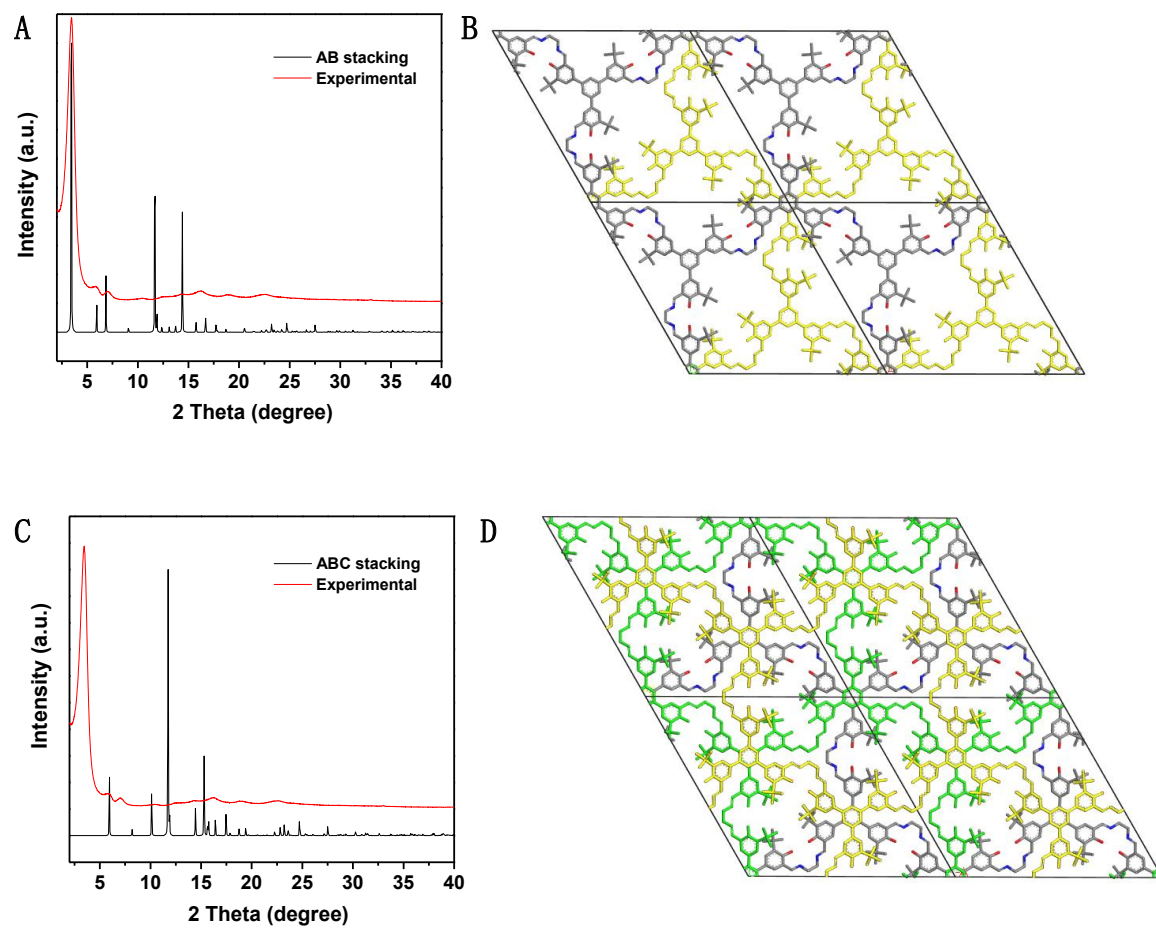
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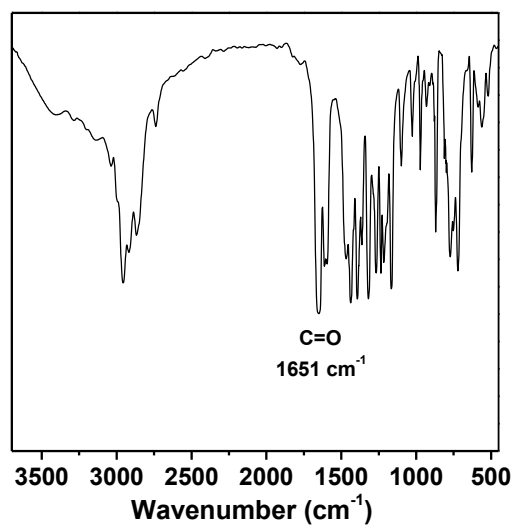
**Table S1.** Synthesis of COF-salen under different conditions.

Sample	Solvent (v : v : v)	State
a	Dioxane : EtOH : 3 M CH <sub>3</sub> COOH = 4 : 1 : 1	Crystalline solid
b	DMF : EtOH : 3 M CH <sub>3</sub> COOH = 4 : 1 : 1	Crystalline solid
c	THF : EtOH : 3 M CH <sub>3</sub> COOH = 4 : 1 : 1	Crystalline solid
d	Dioxane : EtOH : 3 M CH <sub>3</sub> COOH = 4 : 1 : 0	Crystalline solid
e	DMF : EtOH : 3 M CH <sub>3</sub> COOH = 4 : 1 : 0	Crystalline solid
f	THF : EtOH : 3 M CH <sub>3</sub> COOH = 4 : 1 : 0	Crystalline solid
g	THF : EtOH : 3 M CH <sub>3</sub> COOH = 4 : 0 : 1	Amorphous solid

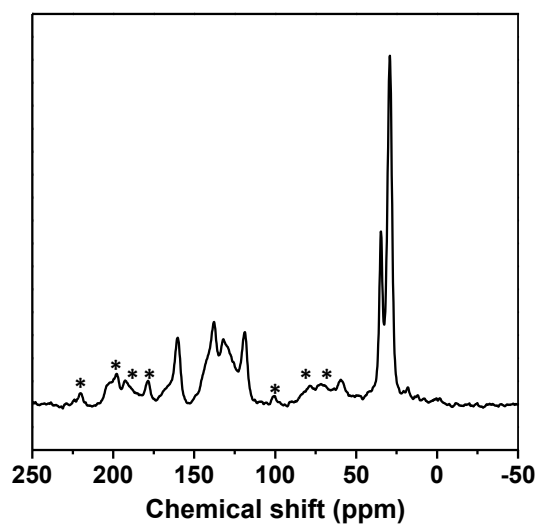
Conditions: TBHFPB (182 mg), ethylenediamine (30  $\mu$ L), solvent A (6.4 mL), EtOH (1.6 mL), 3 M CH<sub>3</sub>COOH (1.6 mL), air, 120 °C, 3 d.



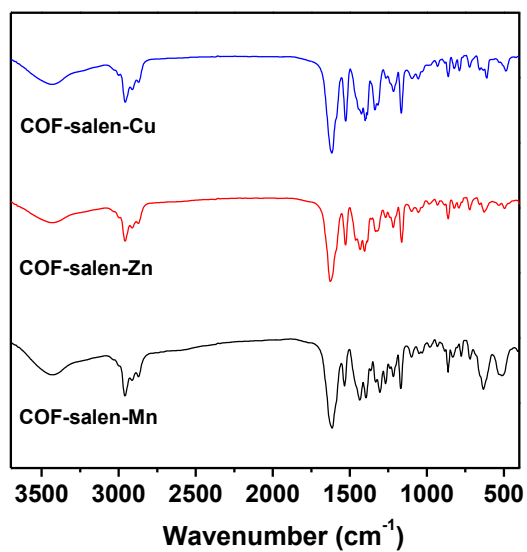
**Figure S1.** (A, C) Simulated PXRD patterns of COF-salen using different stacking in comparison with the experimental pattern, (B, D) space-filling models of COF-salen in (B) AB stacking and (D) ABC stacking.



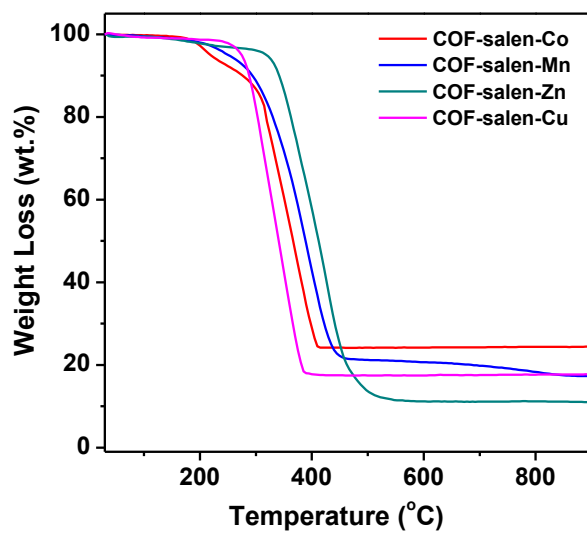
**Figure S2.** The FT-IR spectrum of TBHFPB.



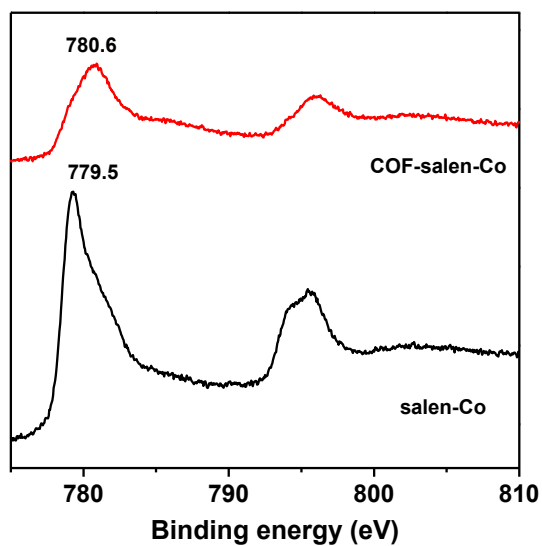
**Figure S3.** <sup>13</sup>C CP MAS NMR spectrum of the amorphous organic polymer POF-salen.



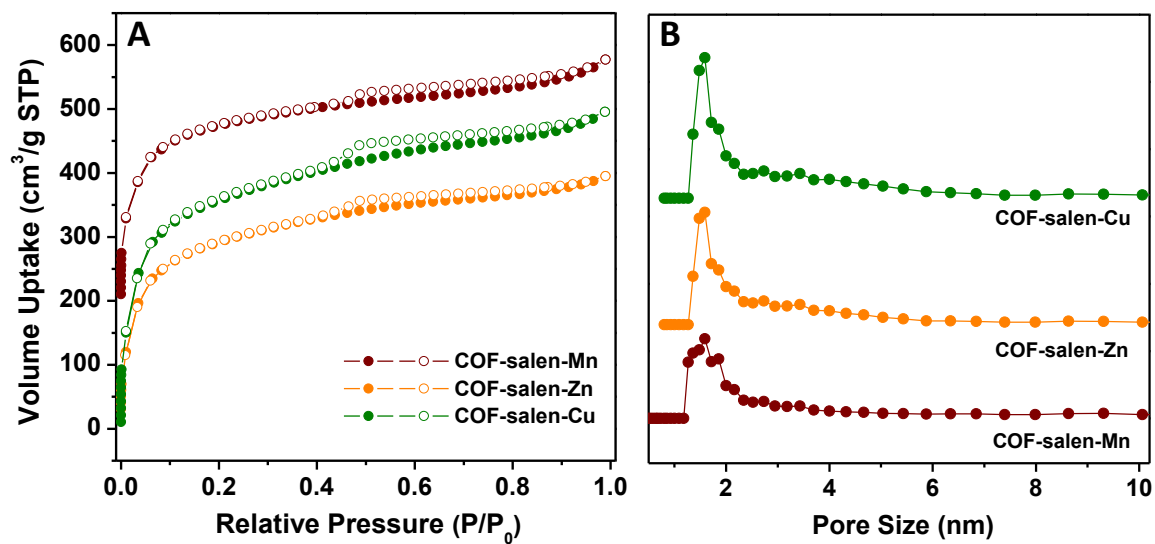
**Figure S4.** The FT-IR spectra of COF-salen-M.



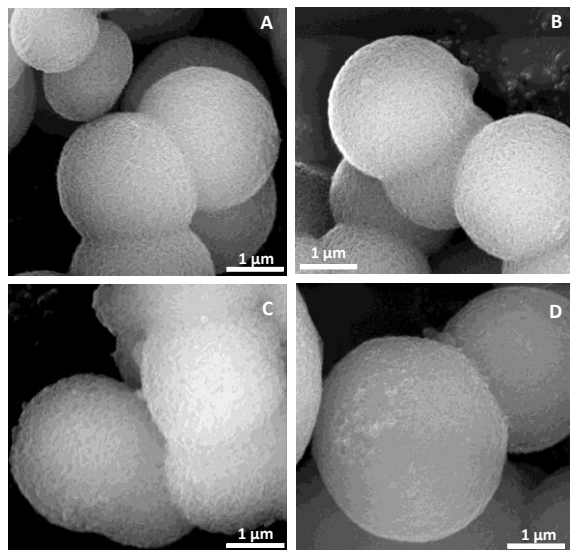
**Figure S5.** TGA curves of COF-salen-M.



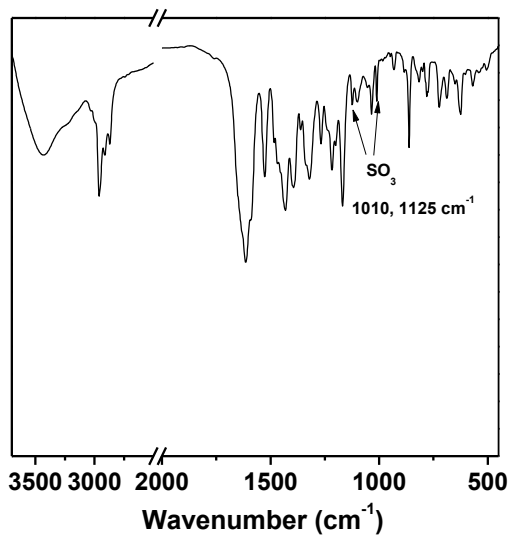
**Figure S6.** Co 2p XPS spectra of COF-salen-Co and the homogeneous counterpart salen-Co (II).



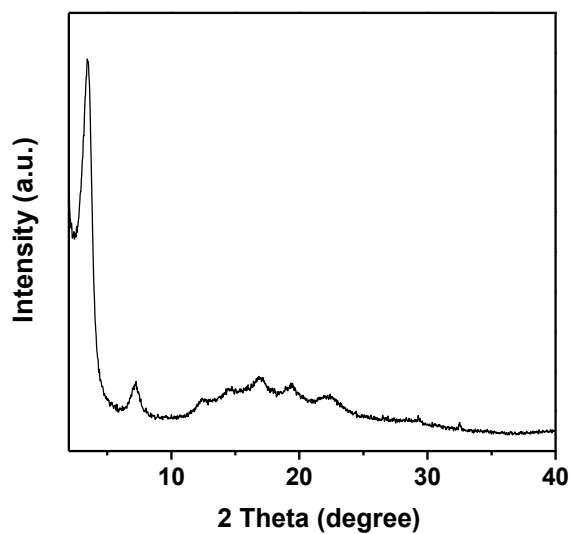
**Figure S7.** (A) N<sub>2</sub> sorption isotherms (measured at 77 K) and (B) NLDFT pore size distribution curves of COF-salen-Mn, COF-salen-Zn and COF-salen-Cu.



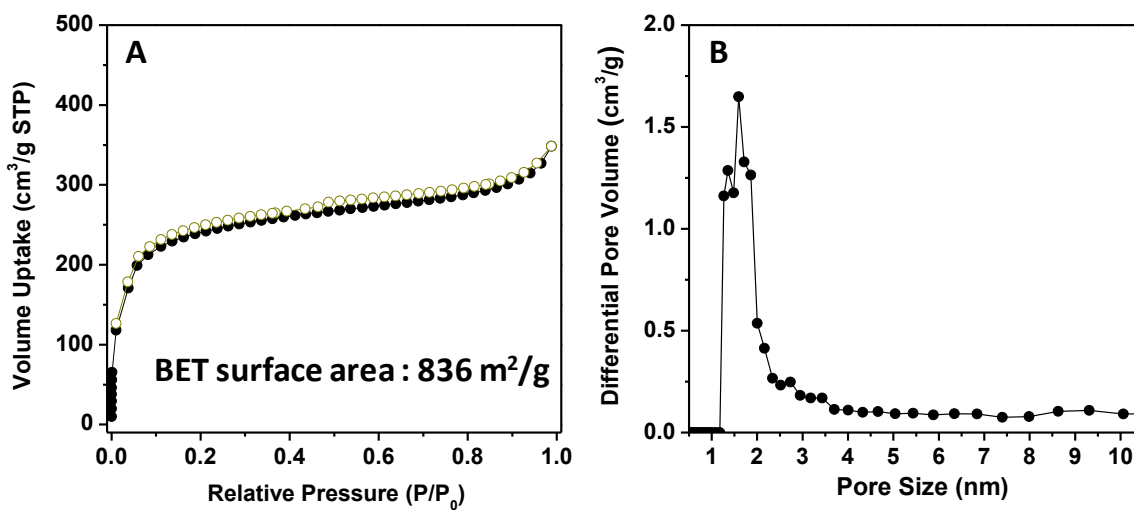
**Figure S8.** SEM pictures of (A) COF-salen-Co, (B) COF-salen-Mn, (C) COF-salen-Cu, (D) COF-salen-Zn.



**Figure S9.** FT-IR spectrum of COF-salen-Co(III).

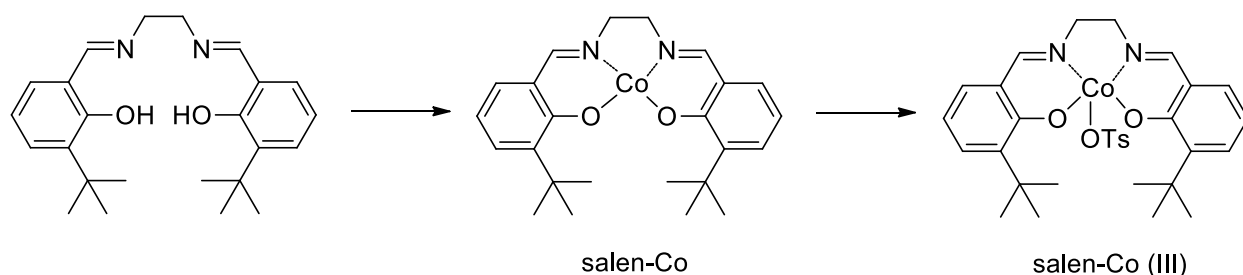


**Figure S10.** PXRD pattern of COF-salen-Co(III).



**Figure S11.** (A) N<sub>2</sub> sorption isotherms (measured at 77 K) and (B) NLDFT pore size distribution curves of COF-salen-Co(III).

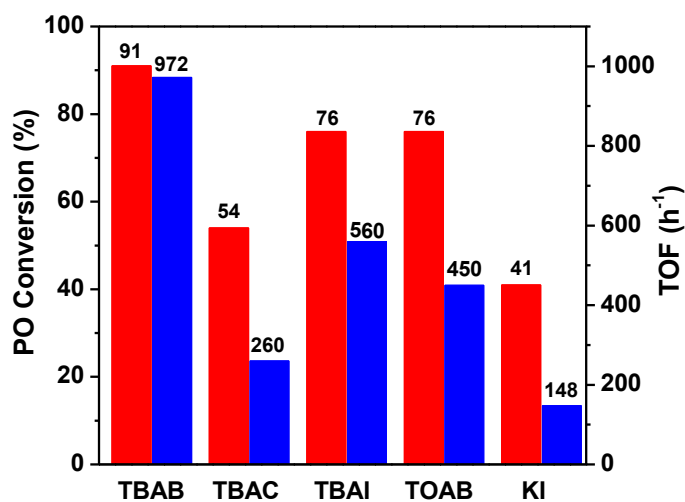




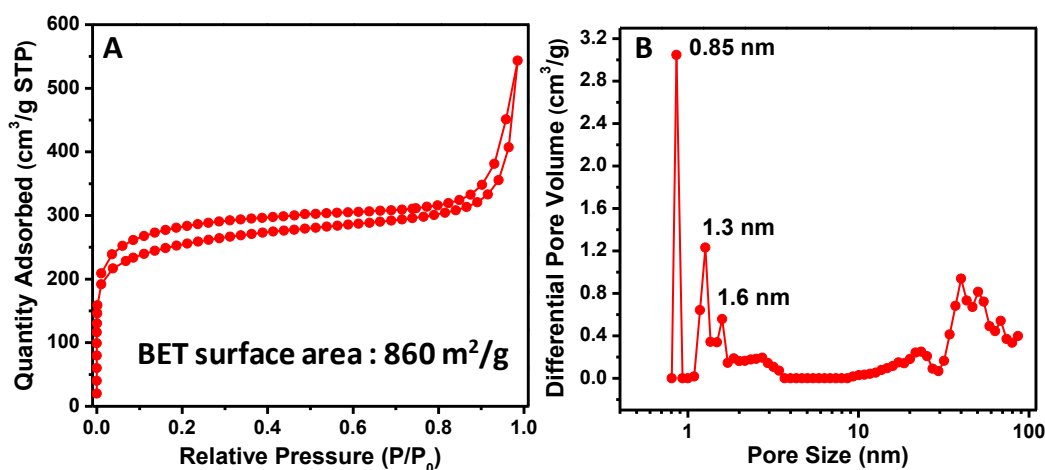
**Scheme S1.** Synthesis of the homogeneous catalyst salen-Co and salen-Co(III).

### Synthetic Procedures of salen-Co(III):

0.1 mmol of salen-Co was dissolved in 2 mL  $\text{CH}_2\text{Cl}_2$ , to this solution, a solution of PTSA (0.1 mmol) dissolved in 2 mL EtOH was added and the mixture was stirred under air atmosphere at room temperature for 12 h. The solid formed was collected by filtration, washed with ether and dried under vacuum at room temperature.



**Figure S12.** Cycloaddition reactions of PO and  $\text{CO}_2$  catalyzed by COF-salen-Co using different co-catalysts (red column: PO conversion, blue column: TOF). Reaction conditions: PO (8 mmol), COF-salen-Co (8  $\mu\text{mol}$ ), co-catalyst (80  $\mu\text{mol}$ ), 100  $^\circ\text{C}$ , 3 h, 2 MPa of  $\text{CO}_2$ .

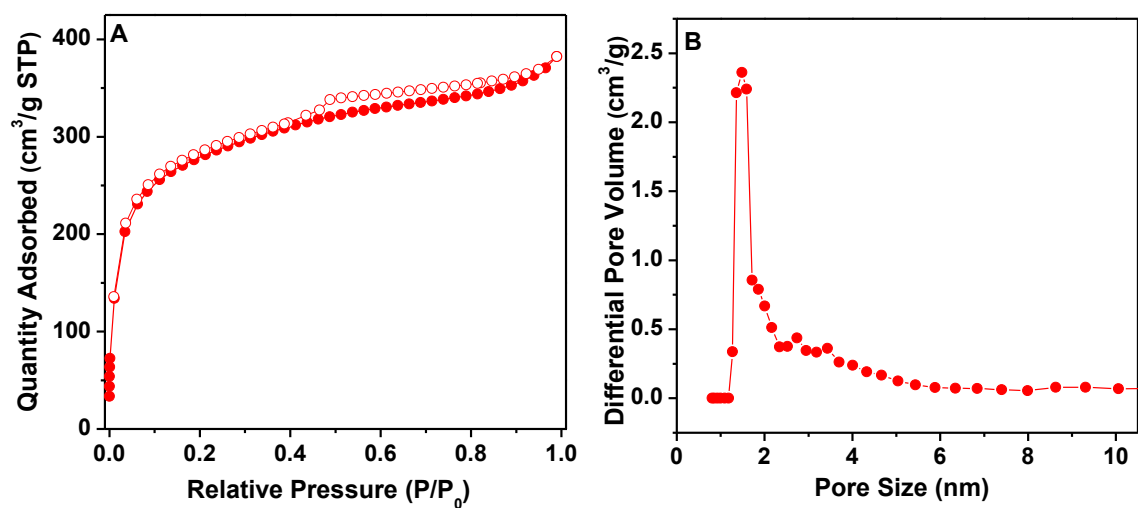


**Figure S13.** (A) N<sub>2</sub> sorption isotherms (measured at 77 K) and (B) NLDFT pore size distribution curves of POF-salen-Co.

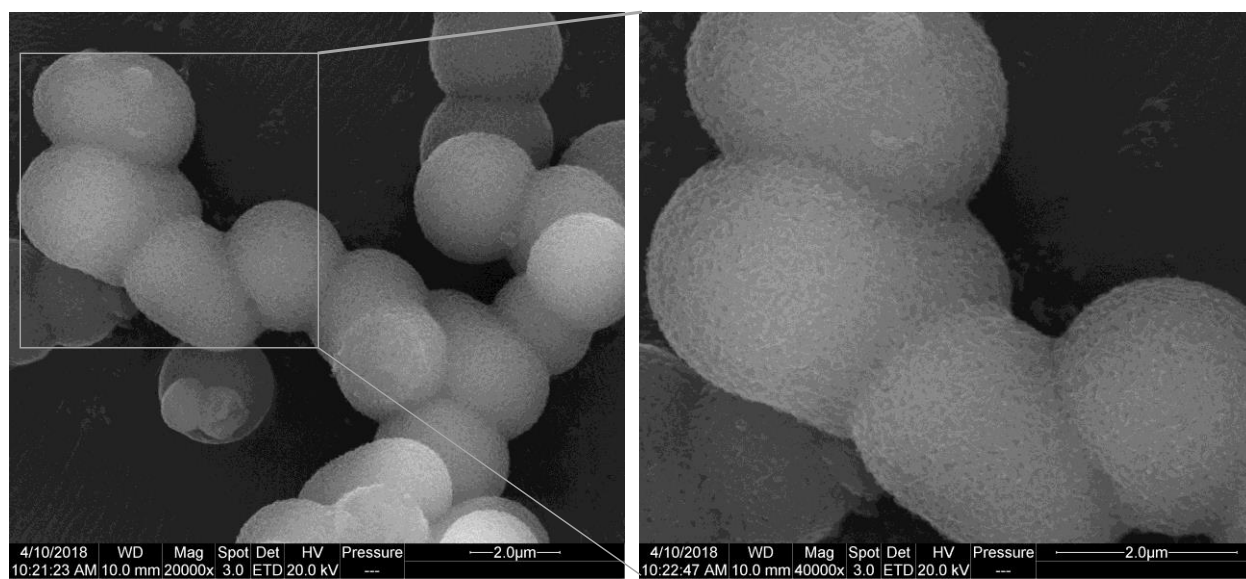
**Table S2.** Comparison of the activity of COF-salen-Co in the PO cycloaddition reaction with the reported MOFs or POPs catalysts.

Catalyst	S/C	TBAB (x mol%)	T (°C)	Pressure (MPa)	Time (h)	Yield (%)	TOF (h <sup>-1</sup> )	Ref.
COF-salen-Co	1000	1	100	2	3	91	972	This work
COF-salen-Co	1000	1	120	2	3	95	1440	This work
NH <sub>2</sub> -MIL-101(Al)	590	0.14	120	1.8	6	96	21.7	1
Co-MON	2000	0.15	60	1	12	75	125	2
Bp-Zn@MA	1160	0.55	100	1	1.5	99	2252	3
Zn(Por)OP	1000	5	120	3	2.5	95	1628	4
Al-CMP	2000	0.5	100	3	5	91	364	5
In-MOF	770	2.5	80	2	4	57.2	110	6
Zn-CMP	1000	1.8	120	3	1	74.8	748	7
gea-MOF-1	667	0.15	120	2	6	88	98	8
(NH <sub>4</sub> ) <sub>3</sub> [In <sub>3</sub> Cl <sub>2</sub> (BPDC) <sub>5</sub> ]	1000	1	80	2	24	98	40.8	9
COF-salen-Co <sup>a</sup>	1000	1	25	0.1	144	96	26	This work
Co-POP-Bpy <sup>a</sup>	400	3.5	29	0.1	24	50.3	8.4	10
Cu-pbpta <sup>a</sup>	1000	7.2	25	0.1	48	94.3	-	11

<sup>a</sup> EPH as substrate.



**Figure S14.** (A) N<sub>2</sub> sorption isotherms (measured at 77 K) and (B) NLDFT pore size distribution curves of COF-salen-Co after 5 cycles.



**Figure S15.** SEM pictures of COF-salen-Co after 5 cycles.

## References for Supporting Information.

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