

Supporting Information

Cobalt porphyrin-based hypercrosslinked ionic polymers as biomimetic nanoreactors for CO₂ conversion to cyclic carbonates

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1. Materials and apparatus

Propylene oxide, epichlorohydrin, epibromohydrin, allyl glycidyl ether, *n*-butyl glycidyl ether, glycidyl methacrylate, styrene oxide and cyclohexene oxide were purchased from J&K Scientific Ltd. 1,2-Epoxybutane and 1,2-epoxyhexane were used as received from TCI Shanghai Ltd.. 1-Benzyl-3-methylimidazolium bromide was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (CAS). Other chemicals were obtained from commercial suppliers and directly used without purification.

Fourier Transform infrared spectroscopy (FT-IR) was carried out by a Nicolet 6700 research-based infrared spectrometer. The chemical structure of the catalyst was measured by solid-state ¹³C NMR spectroscopy taken by a 600 MHz digital superconducting nuclear magnetic resonance spectrometer (NMR). X-ray photoelectron spectroscopy (XPS) was obtained by Escalab 250Xi (Thermo Fisher). An inductively coupled plasma mass spectrometer, the ICAP RQ (Thermo Fisher) S-3 inductively coupled plasma (ICP-MS), was used for the determination of metal content.

Ion chromatography (IC) was used to determine the content of halogen ions by a Thermo Scientific ICS100 ion chromatograph with a column model of 11-HC. Field emission transmission electron microscopy (TEM) and element distribution energy spectrum (EDS-mapping) were used to test the obtained materials (Talos F200S). Thermogravimetric analysis (TGA) was performed by the STA449F5 thermogravimetric analyzer. The samples were tested by the ASAP2020 surface area meter and the microporous physical adsorption meter, and then analyzed by the Brunauer-Emmett-Teller (BET) method and the non-local density functional theory (NLDFT) method to obtain the results of specific surface area and pore size analysis. The CO₂ adsorption experiment was also carried out on the ASAP2020 automatic physical adsorption instrument. The experimental conditions were CO₂ 1 bar, the pretreatment temperature was 273 K or 298 K, and the temperature was 150 °C. The yields and selectivities of the products were measured by a PANNA-A60 gas chromatograph equipped with an Rtx-5 (30 m*0.32 mm*0.25 μm) capillary column.

2. Experimental section

2.1 Synthesis of tetraphenylporphyrin (TPP)

A mixture of benzaldehyde (10.6 g, 100 mmol) in propionic acid (400 mL) was added to a 500 mL round-bottomed flask under nitrogen atmosphere. After the reaction solution was heated up to 130 °C, the freshly distilled pyrrole (6.7 g, 100 mmol) was added dropwise via syringe. Then, the mixture was stirred at 140 °C for 2 h. After cooling to room temperature, the dark precipitate was filtered and washed with methanol. ¹H NMR (400 MHz, CDCl₃) δ -2.70 (s, 2H), 8.90 (s, 8H), 8.27 (d, 8H), 7.78-7.76 (m, 12H).

2.2 Synthesis of aluminum tetraphenylporphyrin Chloride (AlTPP)

A solution of TPP (1.0 g, 1.6 mmol) in anhydrous dichloromethane was charged into a 50 mL round-bottomed flask under nitrogen atmosphere. After a solution of diethylaluminum chloride (Et₂AlCl 0.9 M solution in toluene, 2.0 mL, 1.8 mmol) was added slowly, the reaction solution was heated to room temperature and stirred for additional 4 h. The solvent was evaporated to afford AlTPP as purple powder. ¹H NMR (400 MHz, DMSO-d₆) δ 8.98 (s, 8H), 8.19 (d, 8H), 7.88- 7.82 (m, 12H).

2.3 Synthesis of cobalt tetraphenylporphyrin (CoTPP)

A solution of TPP (0.31 g, 0.5 mmol) and Co(OAc)₂·4H₂O (0.75 g, 3.0 mmol) in 30 mL of chloroform and propionic acid (1/1, v/v) was charged into a 50 mL round-bottomed flask under N₂ atmosphere. The reaction solution was heated to 120 °C and stirred for 2 h, the resulted precipitate was filtered and washed with methanol (30 mL ×3).

2.4 Synthesis of cobalt tetraphenylporphyrin chloride (CoTPP(Cl))

A suspension of CoTPP (0.34 g, 0.5 mmol) in 300 mL of dichloromethane and methanol was charged into a 500 mL round-bottomed flask. The concentrated hydrochloric acid (HCl, 0.25 mL, 2.5 mmol) was added dropwise to the stirring mixtures. Then, the reaction solution was stirred at room temperature for 24 h under air atmosphere. The solvent was evaporated and the residue was washed with water until filtrate was neutral. After dried at 40 °C in a vacuum for 12 h, the desired purple crystals

were obtained.

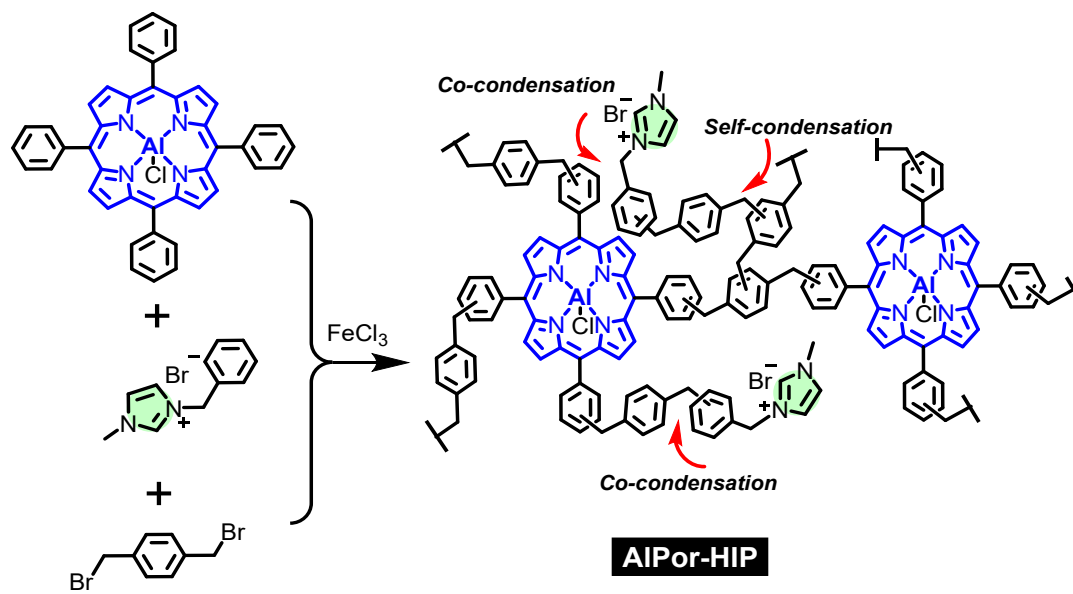
2.5 Synthesis of CoPor-HIP, AlPor-HIP and Co-Im-HCP

Take **CoPor-HIP** for an example: 1-Benzyl-3-methylimidazolium bromide (0.5 mmol, 126 mg), CoTPP (0.25 mmol, 168 mg), DBX (2 mmol, 522 mg) and anhydrous FeCl₃ (2 mmol, 326 mg) were added to the Schleck tube (15 mL) under nitrogen atmosphere. Then, ultra-dry dichloroethane (10 mL) was added through a syringe. The reaction mixture was stirred at 0 °C for 30 min, and then heated to 40 °C for 12 h, finally heated to 80 °C for 24 h. After the reaction is complete, the reactor is cooled in an ice-water mixed bath. The resulting suspension is washed with deionized water, methanol, dichloroethane, ethyl acetate and N,N-dimethylformamide for several times. The resulting solid is dried overnight under vacuum at 65 °C and then further purified by Soxhlet extraction for 24 h to remove trace impurities. Similarly, AlTPP was used to prepare **AlPor-HIP** instead of CoTPP and *N*-methylimidazole was used to prepare **Co-Im-HCP** instead of 1-benzyl-3-methylimidazolium bromide under identical conditions.

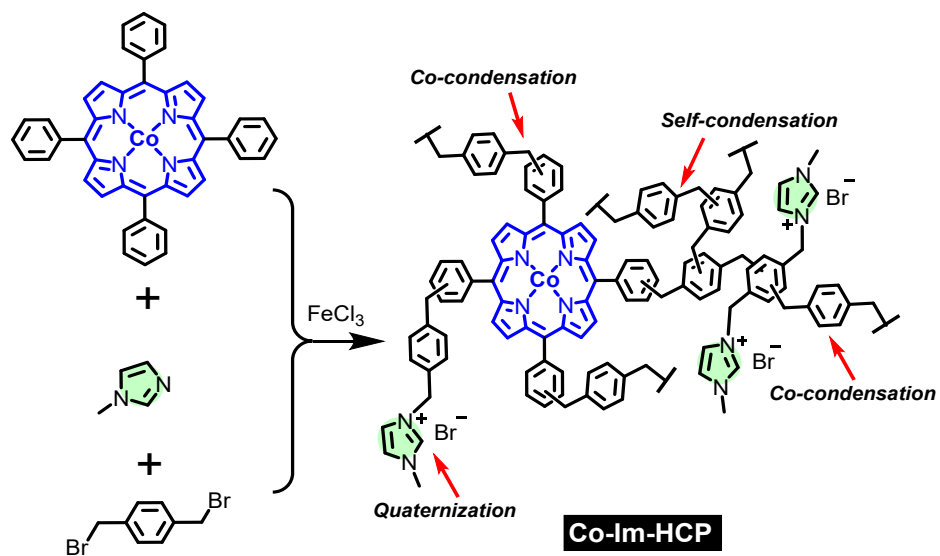
2.6 General procedure for the cycloaddition of CO₂ with epoxides

Epichlorohydrin (0.46 g, 5.0 mmol) and **CoPor-HIP** (10 mg, 0.01 mol%) were added into a pre-dried 10 mL autoclave. After pressurized with CO₂ to maintain the desired pressure, the autoclave was rapidly heated to the desired temperature. After stirring for the appropriate time, the autoclave was cooled quickly in an ice-water bath, and the remaining CO₂ was released slowly. The yields and selectivities of the products were determined by GC. The catalyst could be recycled and recovered as a solid by filtration, which was washed with methanol several times, dried under vacuum, and then used for the next run without further purification.

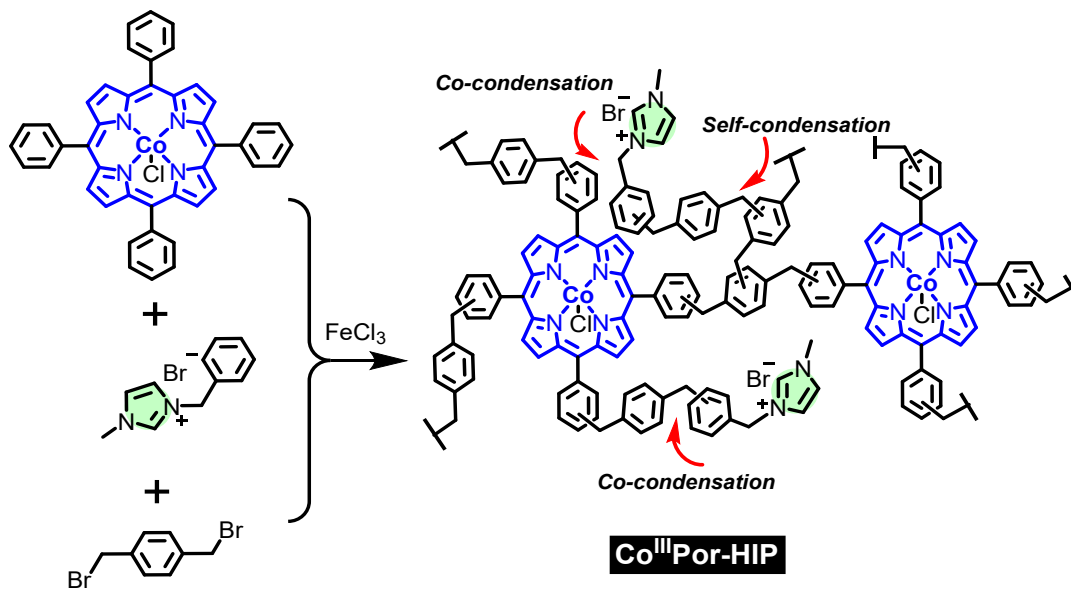
3. Figures and Tables



Scheme S1. Synthesis of AIPor-HIP



Scheme S2. Synthesis of Co-Im-HCP



Scheme S3. Synthesis of Co^{III} Por-HIP.

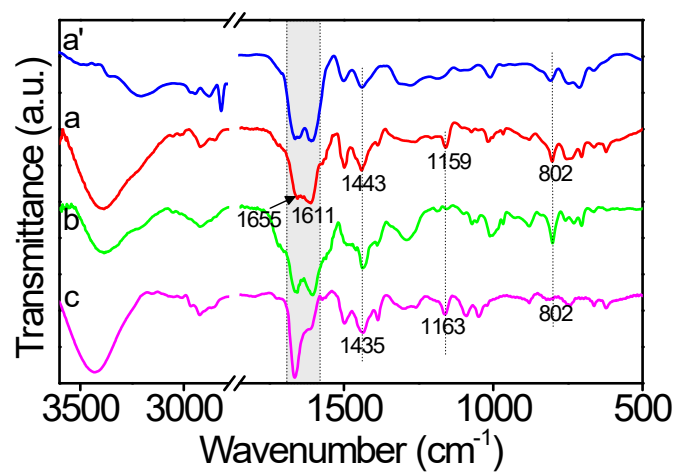


Figure S1. FT-IR spectra of (a)CoPor-HIP, (b)CoPor-HCP, (c)HIP and (a') reused catalyst

CoPor-HIP

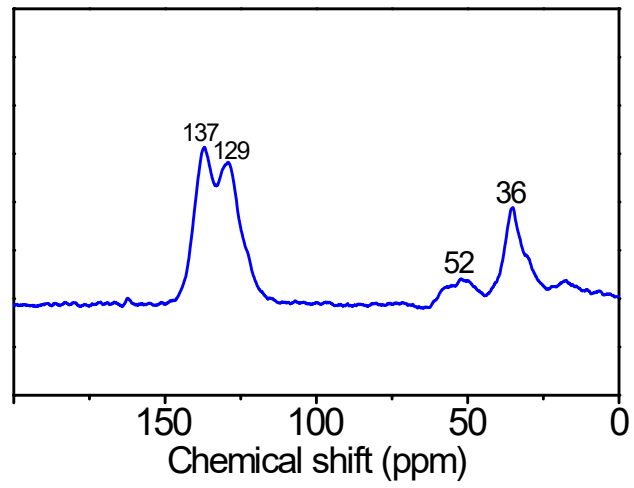


Figure S2. Solid-state ^{13}C MAR NMR spectrum of CoPor-HIP

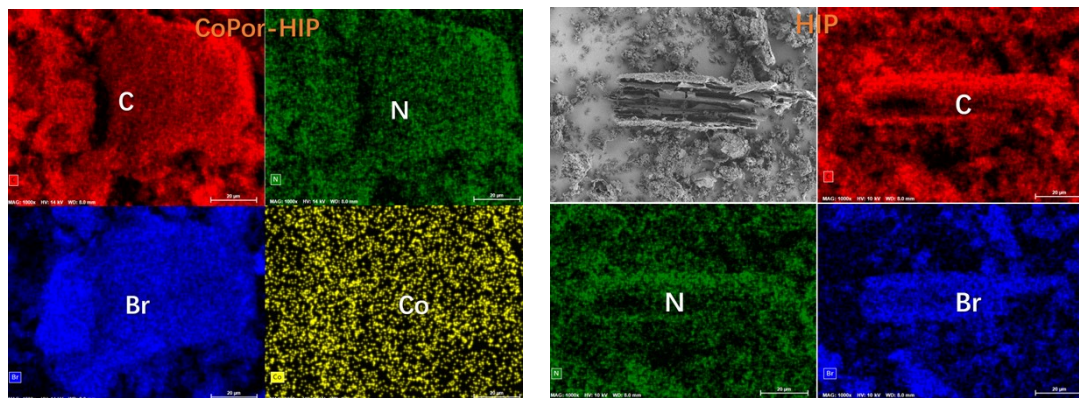


Figure S3. SEM images of CoPor-HIP (left) and HIP (right)

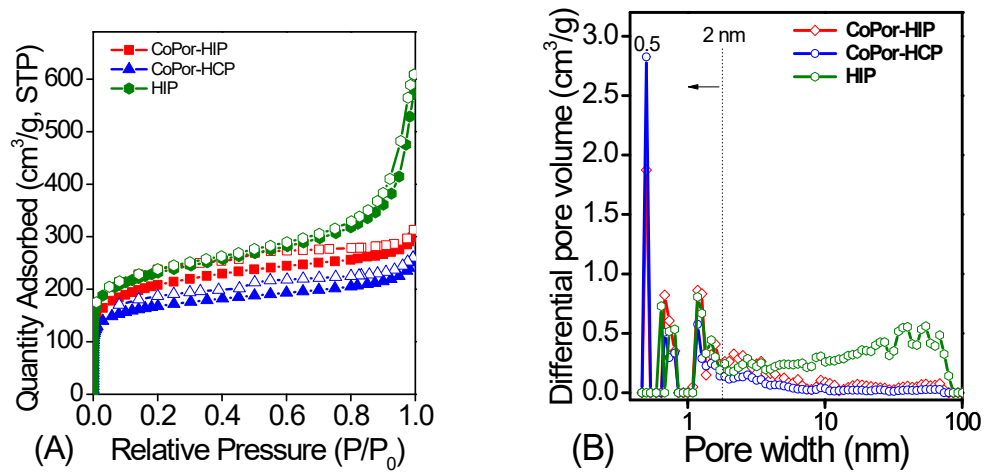


Figure S4. (A) N₂ sorption curves and (B) pore distributions of (a)CoPor-HIP, (b)CoPor-HCP and (c)HIP

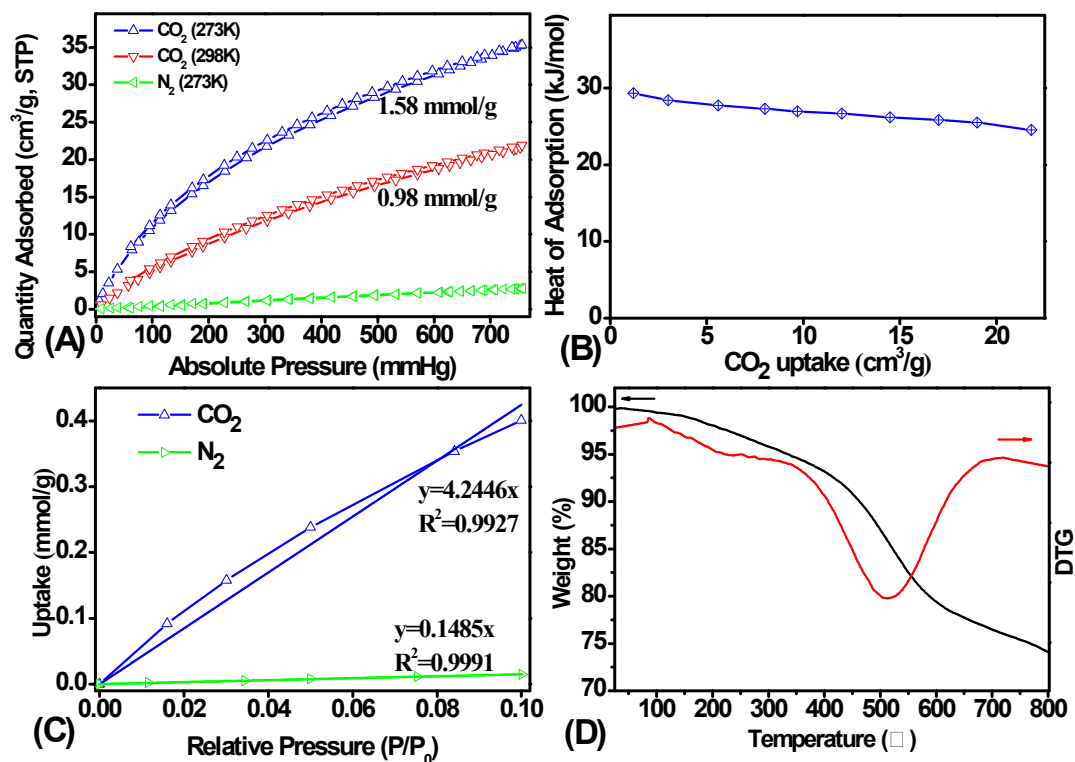


Figure S5. (A) CO₂ and N₂ adsorption and desorption isotherms for CoPor-HIP measured at 273 K and 298 K; (B) Isosteric heat of CO₂ adsorption of CoPor-HIP. (C) Selectivity of CO₂ over N₂ of CoPor-HIP from initial slope calculations of CO₂ and N₂ isotherms at 273 K; (D) TGA and DTG curves of CoPor-HIP.

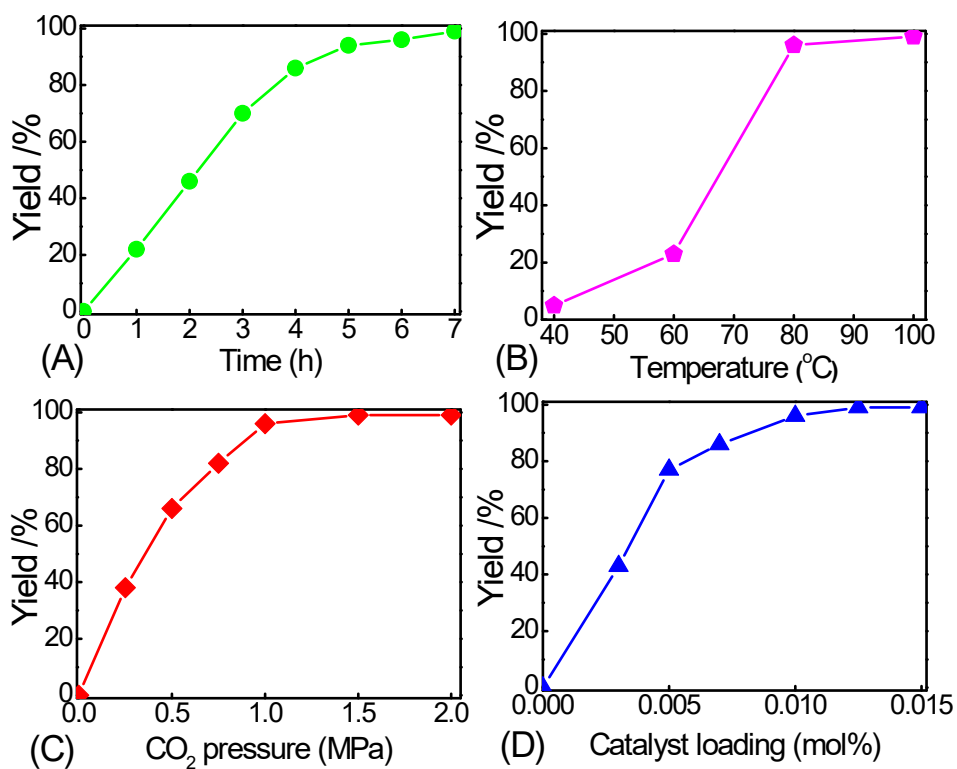


Figure S6. Investigate the effect of a single variable of the reaction. (A) reaction conditions: 80 °C, 6 h, catalyst loading 0.01 mol%; (B) reaction conditions: 80°C, catalyst loading 0.01 mol%, CO₂ pressure 10 bar; (C) reaction conditions: catalyst loading 0.01 mol%, 1 h, CO₂ pressure 10 bar; (D) reaction conditions: 80 °C, 6 h, CO₂ pressure 10 bar.

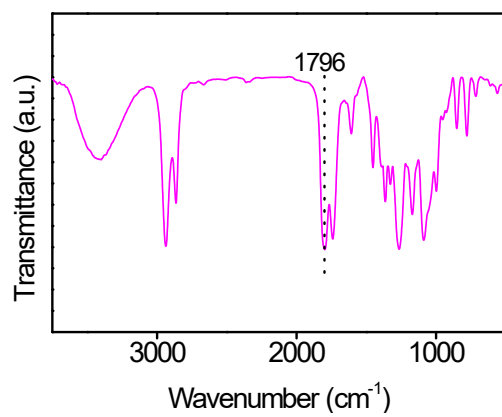


Figure S7. FT-IR spectrum of the *cis* isomer **2i**.

Table S1. Results of the contents of active sites over various catalysts.^a

Entry	Catalyst	Active sites	Metal	Br ⁻	M/Br ⁻	S _{BET} /m ² ·g ⁻¹
1	CoPor-HIP	Co ^{II} , Br ⁻	0.054	0.42	0.13	514
2	AlPor-HIP	Al, Br ⁻	0.21	0.086	2.44	256
3	Co-Im-HCP	Co ^{II} , Br ⁻	0.11	0.18	0.61	102
4	Co^{III}Por-HIP	Co ^{III} Br ⁻	n.d.	n.d.	–	602
5	CoPor-HCP	Co ^{II}	0.09	–	–	626
6	HIP	Br ⁻	–	0.61	–	824

^a n.d.=no detected. Because the catalytic activity of **Co^{III}Por-HIP** was inferior to that of **CoPor-HIP** under the same reaction conditions, we did not conduct relevant tests. When using 10 mg **Co^{III}Por-HIP** as catalyst, the reaction temperature was 80°C and the initial CO₂ pressure was 10 bar, a low yield of 23% was acquired after 6 h, while at this moment the yield of the product over **CoPor-HIP** reaches up to 96%.

Table S2. Results of the cycloaddition of CO₂ with ECH over typical metalloporphyrin-based iPOPs.^a

Entry	Catalyst /mol%	Metal loading ^b /mmol·g ⁻¹	S _{BET} /m ² ·g ⁻¹	CO ₂ uptake ^d /mmol·g ⁻¹	t /h	T /°C	P _{CO2} /bar	TOF ^e /h ⁻¹	Ref.
1	SYSU-Zn@IL2 (0.16)	0.40	21	1.36	12	80	10	52	1
2	ZnTPP/QA-azo-PIP (0.25)	0.53	181	2.1	12	80	10	33	2
3	PP-Br-Zn-0.09 (0.05)	0.09	12	0.7 ^f	2	100	15	940	3
4	Zn-CIF2-C₂H₄ (0.18)	0.40	577	n.d.	4	120	25	136	4
5	Mg-por/pho@POP (0.005)	0.16	558	n.d.	1	140	30	13400	5
6	AlPor-PIP-Br (0.02)	0.62	761	2.1	1	100	10	1200	6
7	AlPor-iPAF-3 (0.08)	0.12	719	1.8	2	100	10	625	7
8	Co-PCCTF₅ (0.08)	0.053	547	1.61	24	100	1	34	8
9	CoTPP-PIP-Br (0.2)	0.93	116	1.47	12	80	10	41	9
10	CoPor-HIP (0.01)	0.054	465	1.58	6	80	10	1600	This work
11	CoPor-HIP (0.01)	0.054	465	1.58	2	100	10	3450	This work
12	CoPor-HIP (0.01)	0.054	465	1.58	0.5	140	10	9000	This work

^a n.d.=not detected; ^b Determined by ICP-OES analysis; ^c Calculated from the molar ratio of metal and ionic sites; ^d Measured at 273 K and 1 atm CO₂; ^e Equal to the mole of product per mole of catalyst per hour.

Reference:

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