

## Electronic Supplementary Information

### **One-pot Synthesis of Pyridinium-based Ionic Porous Organic Polymers for Efficient CO<sub>2</sub> Catalytic Conversion**

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## **Section 1. Experimental and characterization details**

### **1.1 Reagents and materials**

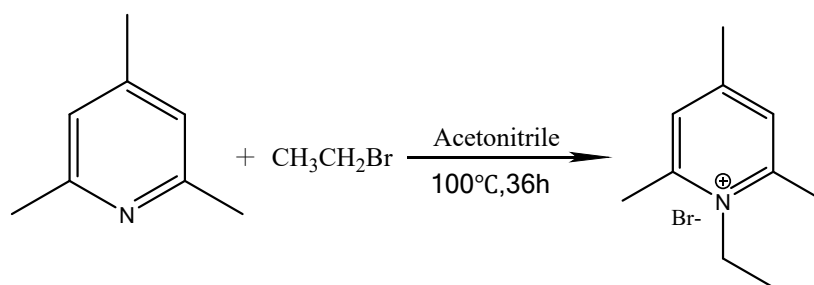
All chemicals and solvents, unless otherwise mentioned, are commercially available and used without further purification. All chemicals and reagents were used as received from commercial sources without further purification. Epichlorohydrin, butylene oxide, 1,2-epoxystyrene, glycidyl phenyl ether, mesitylene, N, N-dimethylformamide (DMF), *n*-BuOH (N-butanol), *o*-dichlorobenzene (*o*-DCB), Methanol (MeOH), dimethylamine were purchased from Aladdin industrial corporation, Shanghai, China. Dichloromethane, acetone, hydrochloric acid, sodium hydroxide, saturated sodium bicarbonate, anhydrous sodium sulfate, petroleum ether, ethanol, were purchased from Jiangtian chemical technology limited company, Tianjin, China.

### **1.2 Characterization techniques**

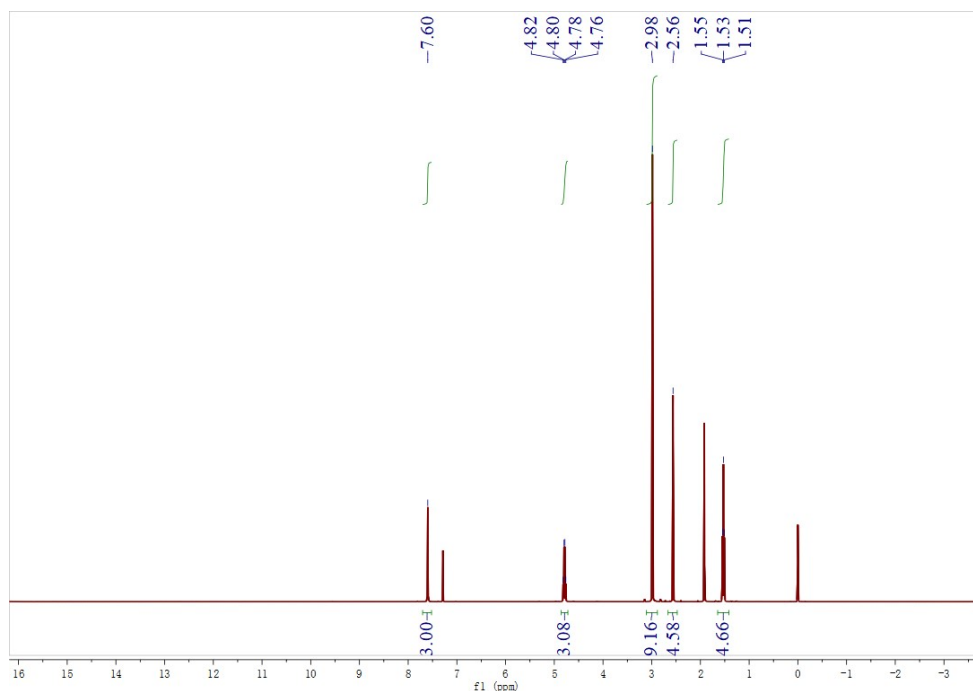
Liquid  $^1\text{H}$  NMR spectra of all monomers were recorded on a Bruker AVANCE IIIITM HD 400 MHz NanoBAY. The 600MHz solid  $^{13}\text{C}$  NMR spectra was obtained on Japan Electronics JEOL JNM ECZ600R. Powder X ray diffraction (PXRD) data were collected on Netherlands the Panalytical X'Pert Pro using Cu  $K\alpha$  radiation at 40 kV, 40 mA power, the scanning angle is from 3-30° and the scanning speed is 0.1°/s. Fourier-transform infrared (FTIR) spectra was measured on a Nicolet 6700 instrument (400-3500  $\text{cm}^{-1}$  region). Photoelectron spectrum datas were measured on an X-ray photoelectron spectrometer of Thermo Fisher ESCALAB-250Xi. Thermogravimetric analysis (TGA) was measured on Netzsch TG 209F3 with heat rate of 10°C in nitrogen atmosphere and the temperature measurement range is 30-800°C. The

Brunauer-Emmett-Teller (BET) surface areas was measured by nitrogen adsorption and desorption at 77 K using Autosorb-iQ2-MP and the samples were activated at 120 °C for 12 h under vacuum before analysis, the degassing temperature is 120°C and the degassing time is 6h. Field Emission Scanning Electron Microscopy (SEM) and energy dispersive spectroscopy (EDS) were measured on Hitachi S-4800, in order to avoid the influence of the C element on the carbon film, the sample was sonicated in petroleum ether and dropped onto the aluminum foil paper for EDS scanning. Transmission electron microscope (TEM) was measured on Japan Electronics JEM-2100F and JEM-F200.

### 1.3 Synthesis of N-ethyl-2,4,6-trimethylpyridinium bromide (ETMP-Br)

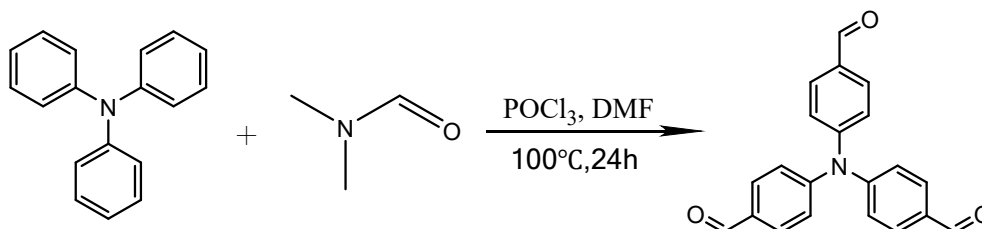


The synthetic route of ETMP-Br referred to the literature<sup>1</sup>. Bromoethane (6.02 mL, 80.0 mmol) was added dropwise to a solution of 2,4,6-trimethylpyridine (5 mL, 40.0 mmol) in acetonitrile (50 mL) at room temperature, which was also protected from light. After stirring at  $100^\circ\text{C}$  for 36 h, the solvent was evaporated to give a white solid, which was recrystallized in ethyl acetate to give 1.95 g product as white crystal with yield of 21.7 %.  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  1.55 (t, 3H), 2.56 (s, 3H), 2.98 (s, 6H), 4.78 (q, 2H), 7.60 (s, 2H).



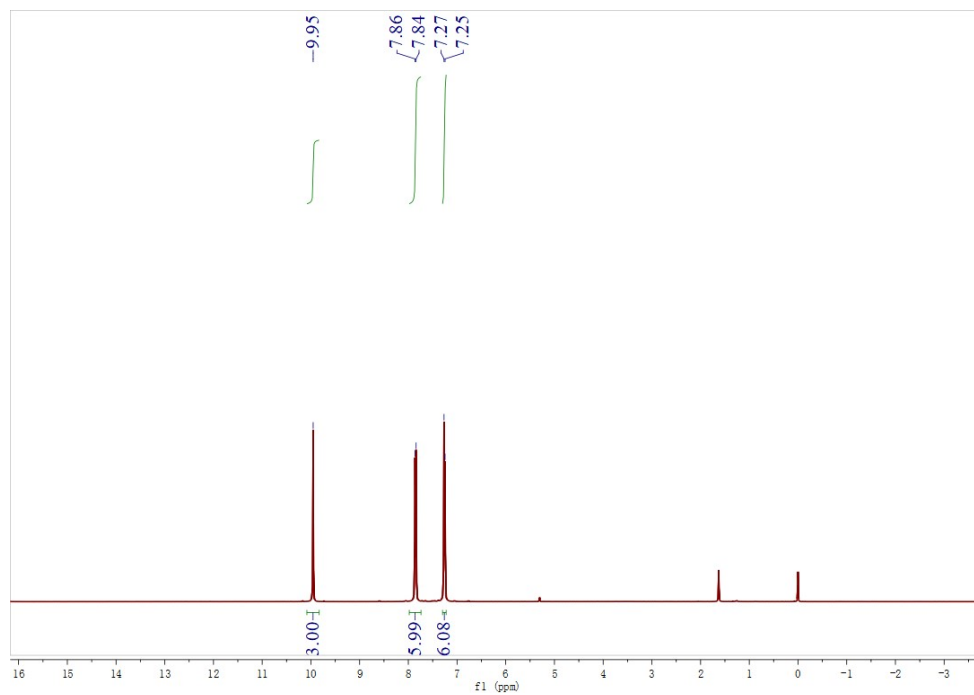
**Fig. S1.** The  $^1\text{H}$  NMR spectrum of ETMP-Br.

#### 1.4 Synthesis of Tris(4-formylphenyl)-amine (TFPA)



The synthetic route of TFPA referred to the literature<sup>2</sup>. Triethylamine (4.8 g, 0.02 mol) was dissolved in 16 mL DMF (16 mL).  $\text{POCl}_3$  (20.0 mL, 100.0 mmol) was added dropwise to the mixture at  $0^\circ\text{C}$ . After mixing, the temperature was raised to room temperature, during which the color of the solution turned red. The reaction mixture was then heated to  $60^\circ\text{C}$  and stirred for an additional 24 h. The product mixture was poured into an ice-bath and neutralized with sodium hydroxide. After filtration, the residue was dried in a vacuum desiccator, and then purified by column

chromatography. The product is yellow solid with yield of 14.9%.  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  9.95 (s, 3H), 7.84 (d, 6H), 7.27 (d, 6H).



**Fig. S2.** The  $^1\text{H}$  NMR spectrum of TFPA.

## 1.5 Exploration of synthesis conditions of TE-POPs

**Table S1.** Exploring the synthesis conditions of TE-POPs.

Control variable	Entry	Solvent systems /mL	Temperature /°C	Results	Yield/%
Solvent systems	1	DMF:o-DCB 2M Dimethylamine=1:1:0.2	120	Amorphous polymer	67
	2	DMF: <i>n</i> -BuOH 2M Dimethylamine=1:1:0.2	120	Amorphous polymer	78
	3	o-DCB: <i>n</i> -BuOH 2M Dimethylamine=1:1:0.2	120	Amorphous polymer	80
	4	<i>n</i> -BuOH:Mesitylene: 2M Dimethylamine=1:1:0.2	120	Amorphous polymer	64
	5	1,4-Dioxane:o-DCB: 2M Dimethylamine=1:1:0.2	120	Amorphous polymer	70
	6	1,4-Dioxane: <i>n</i> -BuOH: 2M Dimethylamine=1:1:0.2	120	Amorphous polymer	68
The amount of catalyst	7	o-DCB: <i>n</i> -BuOH 2M Dimethylamine=1:1:0.1	120	Amorphous polymer	82
	8	o-DCB: <i>n</i> -BuOH 2M Dimethylamine=1:1:0.3	120	Amorphous polymer	74
Temperature	9	o-DCB: <i>n</i> -BuOH 2M Dimethylamine=1:1:0.1	150	Amorphous polymer	80
	10	o-DCB: <i>n</i> -BuOH 2M Dimethylamine=1:1:0.1	180	Amorphous polymer	62
Different catalyst	11	o-DCB: <i>n</i> -BuOH 2M NaOH=1:1:0.1	120	Unreacted	-
	12	o-DCB: <i>n</i> -BuOH 2M DBU=1:1:0.1	120	Unreacted	-

The results obtained in Table S1 suggested that no crystalline materials could be obtained from the reaction. There were two reasons that might lead to this result. 1) the planarity of triarylamines was relatively poor; 2) this reaction was irreversible.

## Section 2. PXRD of TE-POPs

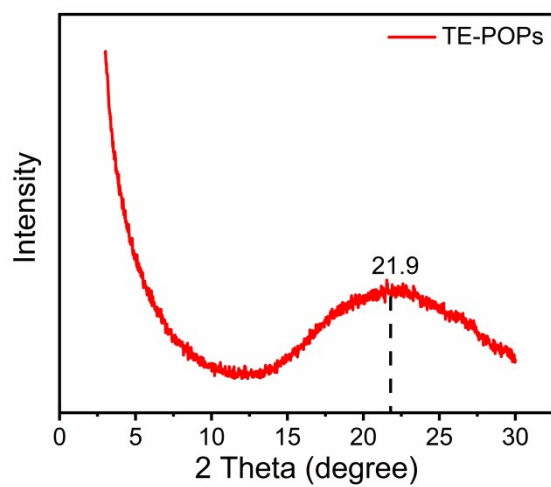


Fig. S3. PXRD spectrum of TE-POPs.

## Section 3. Zeta potential of TE-POPs

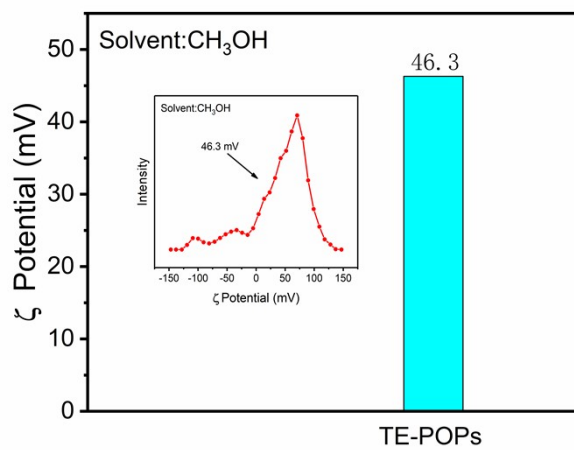


Fig. S4. Zeta potential of TE-POPs.



#### Section 4. TGA curve of TE-POPs.

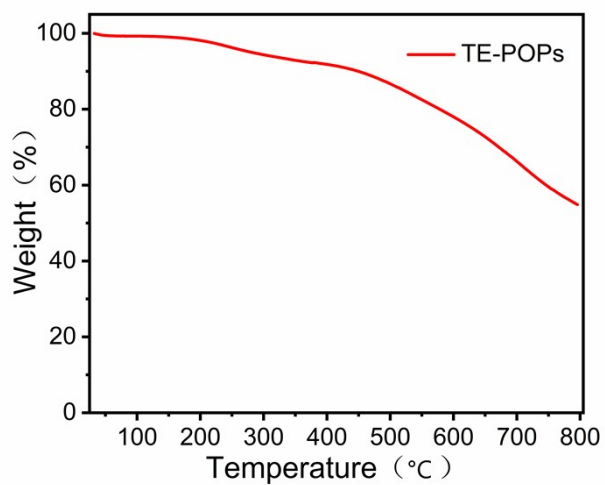


Fig. S5. The thermogravimetric analysis (TGA) curve of TE-POPs.

#### Section 5. Chemical stability test of TE-POPs.

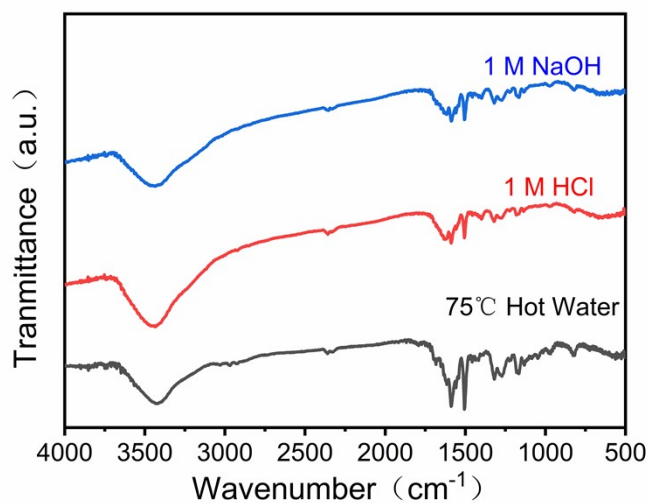
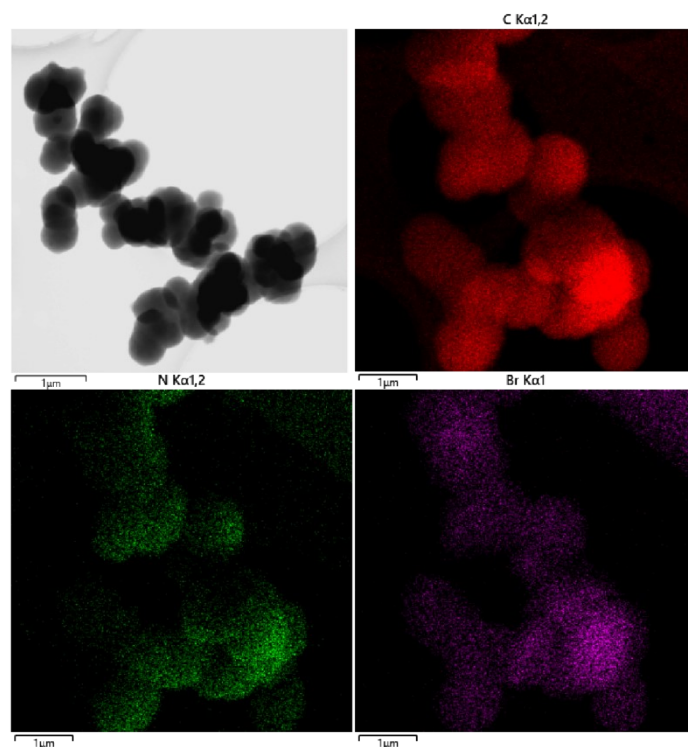


Fig. S6. Chemical stability test of TE-POPs.

## Section 6. EDS of TE-POPs



**Fig. S7.** EDS images of TE-POPs. Red, green and purple respectively represent the three elements of C, N, Br.

## Section 7. Summary of studies of CO<sub>2</sub> adsorption

**Table S2.** Comparison with the previous catalytic systems.

Entry	Catalyst	CO <sub>2</sub> uptake	Ref.
1	AMIMBr@H <sub>2</sub> P-DHPhCOF	31.9	3
2	Py-iPOP-1	18.37	4
3	ZPOF-450-30	56	5
4	PEAMC1	19.04	6
5	TE-POPs	32.32	this work

## Section 8. Structure and morphological characterization after catalysis

Table S3. Recycling performance of TE-POPs.

Cycle	Temperature/°C	Residual Weight/mg	Time/h	Yield
1	90	20.0	20	96
2	90	19.9	20	96
3	90	19.8	20	94
4	90	19.8	20	96
6	90	19.6	20	93

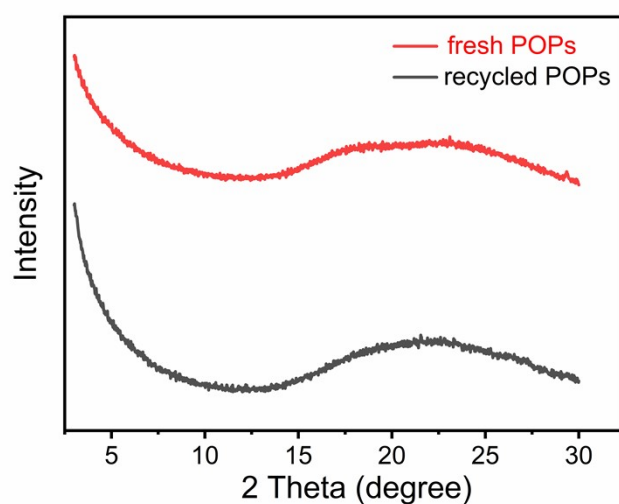


Fig. S8. PXRD spectrum before and after after cycloaddition of TE-POPs.

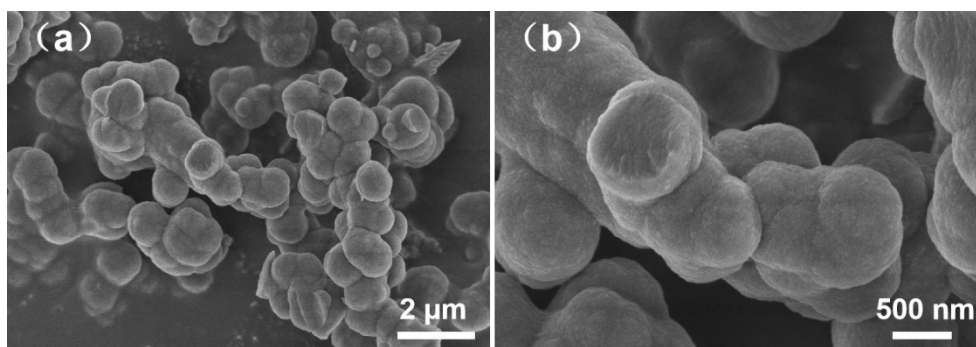
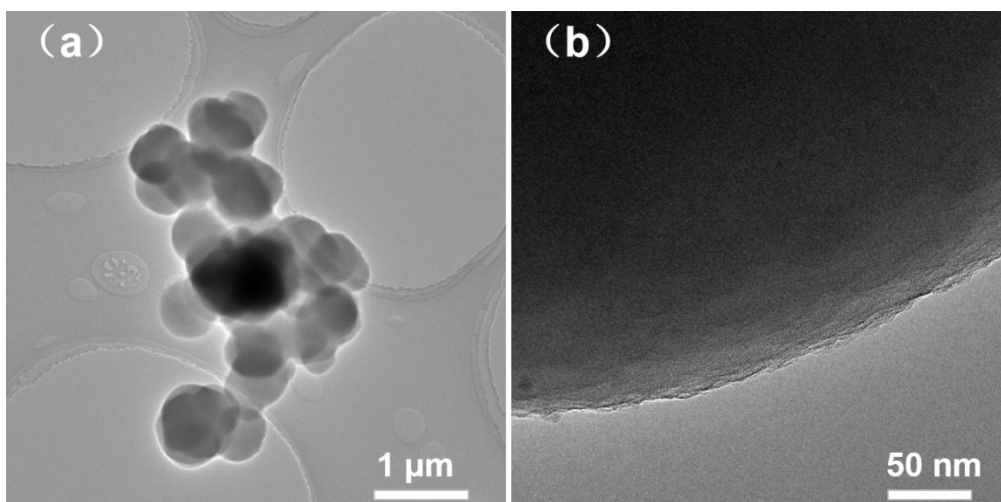
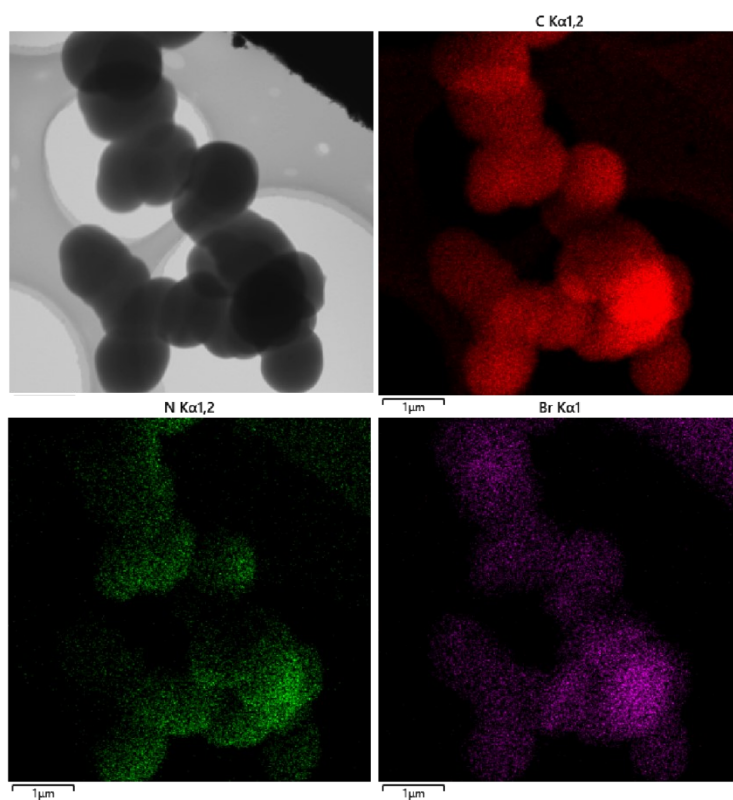


Fig. S9. (a, b) SEM images of TE-POPs after cycloaddition.

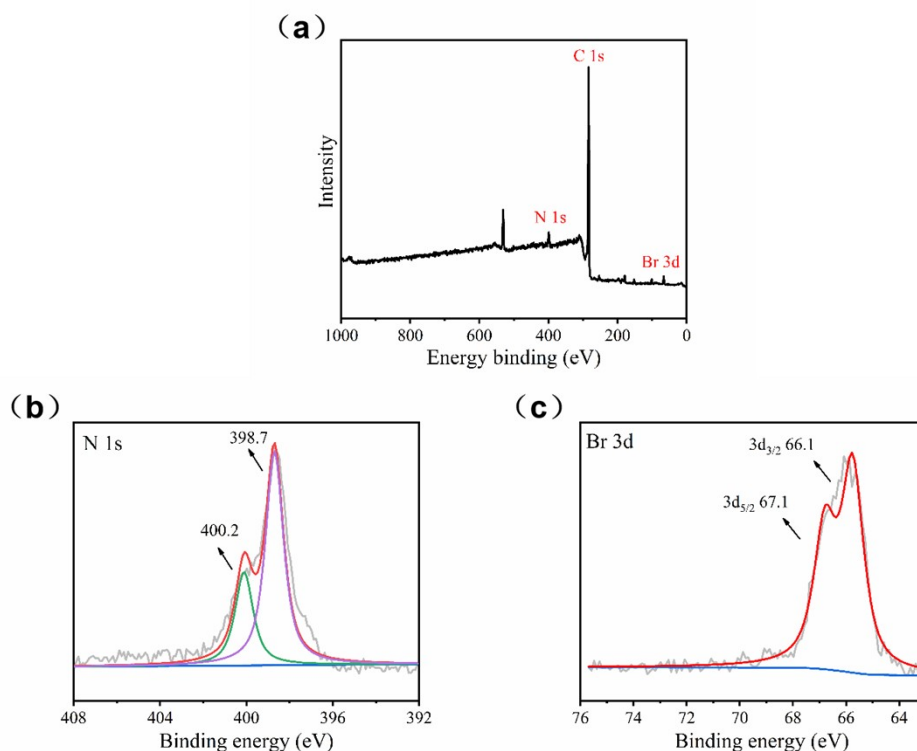


**Fig. S10.** (a, b) TEM images of TE-POPs after cycloaddition.



**Fig. S11.** EDS images after cycloaddition of TE-POPs. Red, green, purple respectively represent the elements of C, N, Br.

## Section 9. XPS of TE-POPs after cycloaddition



**Fig. S12.** The (a) N 1s XPS spectrum and (b) Br 3d XPS spectrum of TE-POPs after cycloaddition.

## Section 10. Summary of studies on CO<sub>2</sub> cycloaddition

The results obtained from this work were compared to some other reported heterogeneous catalysts such as porous organic polymers (POPs),<sup>4,5,7-11</sup> covalent organic frameworks (COFs),<sup>3,12,13</sup> metal organic frameworks (MOFs)<sup>14,15</sup> and covalent triazine frameworks (CTFs)<sup>16,17</sup> for the same reaction (Table S4). According to the data listed in Table S4, it was noted that this reaction could be carried out under relatively mild conditions and without the presence of any additives. Therefore, we could reach the conclusion that the TE-POPs could be regarded as a type of potential catalyst for CO<sub>2</sub> chemical fixation.

**Table S4.** Comparison with various catalysts in the performance of the coupling of epichlorohydrin and CO<sub>2</sub>.

Entry	Catalyst	Loading	Cocatalyst	t/h	T/°C	P <sub>CO2</sub> /MPa	Yield/%	Ref
1	Py-iPOP-1	40 mg	-----	72	40	0.1	80	4
2	ZPOF-450-30	3.5 mmol%	TBAI	2	70	2.0	99	5
3	ZnTPP/QA-azo-PiP1	0.25 mol%	-----	12	80	1.0	99	7
4	ImTPOF-400-15	3.5 mmol%	TBAB	5	90	2.0	99	8
5	CorPOP-1(Mn)	10.8 mg	TBAB	12	40	1 bar	97	9
6	Py-HCP-Br	400 mg	-----	8	120	2	99	10
7	PIMBr-COOH	1 mol%	-----	4	100	1	94	11
8	COF1/ZnBr <sub>2</sub>	0.1 mol% (Zn)	TBAB	12	80	0.1	99	12
9	AMIMBr@H <sub>2</sub> P-DHPhCOF	50 mg	-----	24	120	1.0	91	3
10	Zn/TPA-TCIF(BD)	50 mg	TBAB	10	40	0.5	99	13
11	PIL-COOH@MIL-101	200 mg	-----	2.5	70	1.0	93	14
12	Zn <sub>9</sub> O <sub>2</sub> (OH) <sub>2</sub> (pyz) <sub>12</sub>	0.5 mol%	TBAB	24	80	7 bar	96	15
13	CTF-0-400-40-1	100 mg	-----	4	130	0.69	99	16
14	CTF-1-HSA	6 mol%	TBAB	4	130	0.7	96	17
15	TE-POPs	20 mg	-----	20	90	1 bar	96	this work

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