Supporting Information for

# An Imidazolium-functionalized mesoporous cationic metalorganic framework for cooperative CO<sub>2</sub> fixation into cyclic carbonates

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#### **Experimental section:**

# 1. Materials and characterization

2-(Imidazol-1-yl)terephthalic acid was synthesized according to previous report.<sup>1</sup> MOFs including MIL-101,<sup>2</sup> HKUST-1, MOF-5<sup>3</sup> ZIF-8,<sup>4</sup> UiO-66 and NH<sub>2</sub>-UiO-66<sup>5</sup> were synthesized and characterized according to references and activated before catalysis tests. All solvents and reagents were commercially available and used without further purification. N<sub>2</sub> and CO<sub>2</sub> sorption isotherms for MOFs were measured by using a Micrometrics ASAP 2020 instrument at 77 K and 273 K, 298 K, respectively. Before the measurement, the samples were evacuated and activated at 423 K in vacuum for 12 hours. Powder X-ray diffraction patterns (PXRD) were recorded on a Rigaku Dmax 2500 diffractometer equipped with Cu-K $\alpha$  radiation ( $\lambda$ = 1.54056 Å) over the 20 range of 4-40° with a scan speed of 3° min<sup>-1</sup> at room temperature. Infrared (IR) spectra were recorded using KBr pellets on a PerkinElmer Spectrum One in the range of 400-4000 cm<sup>-1</sup>. Elemental analyses of C, H, and N were carried out on an Elementar Vario EL III analyzer. The <sup>1</sup>H NMR was performed at AVANCE III Bruker Biospin spectrometer, operating at 400 MHz. The morphologies of MOFs were studied using a FEIT 20 transmission electron microscope (TEM) working at 200 kV and scanning electron microscope (SEM) working at 10 KV. The gas chromatography (GC) measurements were performed on a G7890A-GC equipped with a HP-5 column, FID detector and autosampler. The gas chromatography-mass spectrometry (GC-MS) measurements were performed on a Varian 450-GC/240-MS.

#### 2. Synthesis of ligand (Br<sup>-</sup>)Etim-H<sub>2</sub>BDC



Scheme S1 The synthesis process of (Br<sup>-</sup>)Etim-H<sub>2</sub>BDC.

# Synthesis of (Br<sup>-</sup>)Etim-H<sub>2</sub>BDC

Thionyl chloride (60 mmol, 4.4 mL) was added dropwise to a stirred suspension of 2-(imidazol-1-yl)terephthalic acid (12 mmol, 3.21 g) and DMF (2 drops) in ethanol (40 mL). The mixture was refluxed at 80 °C for 48 hours before cooling down to room temperature. The solvent was removed and the residue was dissolved in 25 mL water. The pH was adjusted to above 9 with 2 M aq. KOH. The solution was extracted with EtOAc (45 mL) four times. The combined extracts were dried and the solvent was removed to give white solid as diethyl 2-(imidazol-1-yl)terephthalate.

Each diethyl 2-(imidazol-1-yl)terephthalate (1 mmol, 0.288 g) was dissolved in 4 mL THF before bromoethane was added. The mixture was stirred in the Teflon-lined autoclave for half an hour before being sealed and heated at 100 °C for 24 hours. After cooling down to room temperature, the solvent was removed and the residue was dried under vacuo overnight.

Then, the obtained solid was dissolved in 20 mL 6 M HCl and the mixture was refluxed for 12 hours. The solvent was removed and the residue was dried fully under vacuo to give the smallest bi-topic straight imidazolium carboxylate ligand, (Br<sup>-</sup>)Etim-H<sub>2</sub>BDC. It should be noted that this ionic ligand could absorb water easily, thus

it should be kept in glove box under N<sub>2</sub> atmosphere for further use. <sup>1</sup>H NMR, (400 MHz, DMSO- $d_6$ , 25 °C):  $\delta$  (ppm) = 1.49 (t, 3H, CH<sub>3</sub>), 4.30 (q, 2H, -CH<sub>2</sub>-), 8.00 (s, 1H, N-CH-CH-N), 8.08 (s, 1H, N-CH-CH-N), 8.24-8.29 (br, 3H, Ar-H), 9.62 (s, H, N-CH-N), 13.89 (br, 2H, COOH). Mass (C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>, m/e): 261.09<sup>+</sup>. IR characteristics (KBr,  $v_{max}$ , cm<sup>-1</sup>): 3330 (w), 3090 (s), 2965 (w), 2864 (w), 1722 (s), 1575 (w), 1551 (s), 1450 (s), 1200 (m), 1102 (s), 755 (s).



**Fig. S1** <sup>1</sup>H NMR spectrum of (Br)Etim-H<sub>2</sub>BDC in DMSO- $d_6$  (r.t).



**Fig. S2** The mass spectra of (Br<sup>-</sup>)Etim-H<sub>2</sub>BDC in DMSO- $d_6$  (r.t).



3. Topology and synthesis of targeted mesoporous MOFs

**Fig. S3** (a) Super tetrahedron (ST) formed by linear dicarboxylic linkers and inorganic trimers. (b) Simplification of adjacent STs by sharing corner trimers. (c) and (d) Schematic 3D representation of Mobil Thirty-Nine (MTN) zeotype architecture with (e) medium (with 20 STs and pentagonal windows, in sky blue) cage and (e)

large (with 28 STs and hexagonal windows, in red) cages. Chromium octahedral, green; oxygen, red; chloride and carbon atoms, black, respectively.

# Synthesis of FJI-C10

A mixture of CrCl<sub>3</sub>·6H<sub>2</sub>O (0.3 mmol, 81 mg), (Br<sup>-</sup>)Etim-H<sub>2</sub>BDC (0.159 mmol, 54 mg), H<sub>2</sub>BDC (0.108 mmol, 18 mg) and H<sub>2</sub>O (1.8 mL) was sonicated for 5 minutes and then transferred into autoclaves. The tightly capped autoclave was kept in an oven at 180 °C for 24 h under static conditions before cooling slowly to room temperature. The pale green precipitates were isolated by centrifugation washed with 7 mL of  $H_2O$ two times and 7 mL DMF two times. Residual terephthalic acid and imidazolium linker in the as-synthesized can be effectively removed by subsequent solution treatments. The product was further dispersed in fresh DMF for twice in 48 hours before being dispersed in hot water at 80 °C for 6 hours and further being dispersed in ethanol at 80 °C for 10 hours two times, resulting the more purified product FJI-C10. Finally, FJI-C10 was precipitated from the solution by centrifugation and dried at 70 °C under vacuo for 12 hours before further use. Elemental analysis (%) found: C 37.86, H 13.14, N 2.45, Cr 13.11. FJI-C10 (calculated): {Cr<sub>3</sub>OCl(H<sub>2</sub>O)<sub>2</sub>(BDC)<sub>3</sub>[(X<sup>-</sup> )Etim-BDC].nH<sub>2</sub>O} (X= Br/Cl). IR characteristics (KBr,  $v_{max}$ , cm<sup>-1</sup>): 3416 (w), 3092 (w), 2960 (w), 2864 (w), 1626 (w), 1507 (s), 1401 (m), 1206 (s), 1120 (s), 1017 (s), 749 (m), 659 (s), 586 (s).



Fig. S4 Photographs of FJI-C10 (pale green) and MIL-101(green).

#### 5. Details of catalytic cycloaddition of epoxide and carbon dioxide.

The reaction kinetics were monitored by carefully withdrawing small amounts of the mixture after the reaction over certain time and the solid catalyst was separated from the mixture with a syringe filter after being diluted with ethyl acetate. When homogeneous catalyst [(Etim-H<sub>2</sub>BDC)<sup>+</sup>(Br)] was used, extraction processes were conducted with distilled water/ethyl acetate and a portion of the ethyl acetate mixture was diluted with ethyl acetate before GC analysis. The turnover number (TON) were calculated as follows:

TON = (No. of moles of cyclic carbonate formed/ No. of moles of imidazolium in the catalyst).

#### Typical procedures for chloropropene carbonate from epichlorohydrin and CO<sub>2</sub>:

In a typical procedure, FJI-C10 (20 mg, equal to 0.0175 mmol imidazolium moiety) and 5 mmol epichlorohydrin were placed in a 15 mL thick-walled reaction tube equipped with a magnetic stirrer. After being sealed, the tube was purged thrice with  $CO_2$ . The reaction was carried out at 80 °C for 12 h under constant 1 bar  $CO_2$ . The qualitative analysis of product was determined by GC-MS and quantitative analysis by GC.

**Recyclability test for FJI-C10:** The recyclability test was conducted as follows: after reaction, the catalyst was separated by centrifugation and washed by ethyl acetate twice and by dichloromethane, ether twice, respectively. After being dried at 150 °C for 12 hours in vacuum, the catalyst was used in the next catalytic reaction.

**Filtration test:** FJI-C10 (20 mg, equal to 0.0175 mmol imidazolium moiety) and 10 mmol epichlorohydrin were placed in a 15 mL thick-walled reaction tube equipped with a magnetic stirrer. After being sealed, the tube was purged thrice with CO<sub>2</sub>. The reaction was carried out at 80 °C for 2 h under constant 1 bar CO<sub>2</sub>. Then the suspension was withdrawn and filtered through a membrane filter to remove the catalyst away. The filtrate was put in a new reaction tube under the same conditions without further filtration. The quantitative analysis of product after further 10 h was determined by GC.



Fig. S5 The SEM (a) and TEM (b) images of as synthesized FJI-C10.



Fig. S6 The FT-IR spectra of (Br)Etim-H<sub>2</sub>BDC ligand and FJI-C10.



Fig. S7 The mass spectrum of digested FJI-C10.



**Fig. S8** The UV/Vis adsorption spectra of **FJI-C10** and **MIL-101**. It can be seen that the UV/Vis adsorption spectrum of **FJI-C10** was broader between 200 nm and 300 nm and the intensity was higher than that of **MIL-101** due to the incorporation of Etim-BDC linkers in **FJI-C10**.



Fig. S9 XPS images of representative elements in activated FJI-C10.



**Fig. S10** (a) TEM image; (b) HAADF-STEM; (c) EDX elemental mapping (C, N, O, Cr, Cl, Br) of a **FJI-C10** sample.



Fig. S11 PXRD patterns for FJI-C10 at variable temperatures.



Fig. S12 Thermo gravimetric curves of FJI-C10.



Fig. S13 The PXRD patterns for FJI-C10 after treatment with different aqueous solutions.

MOFs	Functionality type	-Q <sub>st</sub> (kJ/mol)	Ref.
Im-UiO-66(1)	imidazole	27.4	1
FJI-C10	imidazolium	20.9	this work
MAF-7		17.2	6
MAF-26		23.3	6
MAF-4		25.1	6
MAF-25		26.3	6
MAF-2		27	7
IFMC-1		30.7	8
MOF-5		34	7
UiO-66(Zr)-(COOH) <sub>2</sub>	carboxylic acid	34.8	9
HKUST-1	exposed cations	35	7
MOF-74-Ni		41.0	9
Cu-TDPAT		42.2	9
Bio-MOF-11		45.0	9
MOF-74-Mg	exposed cations	47	7
TBA@bio-MOF-1	amines	55	7

Table S1 Zero-Coverage Heat of  $CO_2$  adsorption in metal organic frameworks.

$\begin{array}{c} Cl \\ \hline \\ $							
Entry	Т	time	Catalyst	Conversion	Selectivity	Yield <sup>b</sup>	
	(°C)	(h)	(mg)	(%)	(%)		
1	100	24	20	100	57.1	57.1	
2	90	24	20	100	82.8	82.8	
3	80	24	20	100	88.5	88.5	
4	70	24	20	100	86.4	86.4	
5	60	24	20	99.7	88.2	87.9	
6	40	24	20	77.2	87.6	67.6	
7	25	24	20	27.3	60.7	16.6	

Table S2 Cycloaddition of  $CO_2$  with epichlorohydrin catalyzed by FJI-C10<sup>*a*</sup>

<sup>*a*</sup>Reaction conditions: 5 mmol of epichlorohydrin, 20 mg of **FJI-C10**, CO<sub>2</sub> (constant 1 bar), solvent-free. <sup>*b*</sup>Determined by GC-MS.

**Table S3** The effect of catalyst amount on the cycloaddition of  $CO_2$  with epichlorohydrin catalyzed by **FJI-C10**<sup>*a*</sup>

Entry	Catalyst	time	Conversion	Selectivity	Yield <sup>b</sup>	TON <sup>c</sup>	TOF
	(mg)	(h)	(%)	(%)			(h <sup>-1</sup> )
1	5	24	59	84.7	50	570	23.7
2	10	24	98.8	87.8	86.8	494	20.6
3	10	20	84.4	88.5	74.70	425	21.3
4	15	24	99.9	87.4	87.3	331	13.8
5	20	24	99.7	88.2	87.9	250	10.4
6	20	12	80.7	88.6	71.5	203	16.9
7 <sup>d</sup>	20	12	99.9	86.7	86.7	247	20.6
8	25	24	100	87.9	87.9	200	8.3

<sup>*a*</sup>Reaction conditions: solvent-free, 5 mmol of epichlorohydrin, CO<sub>2</sub> (constant 1 bar), temperature 60 °C. <sup>*b*</sup>Determined by GC-MS. <sup>*c*</sup>Turnover number (TON): number of moles of product per mole of catalyst. <sup>*d*</sup>Temperature 80 °C.



**Fig. S14** Time course of the production of chloropropene carbonate. Inset: leaching test (red line). Reaction conditions: solvent free, 5 mmol of epichlorohydrin, **FJI-C10** (0.35 mol% based on imidazolium),  $CO_2$  (constant 1 bar), temperature 80 °C, solvent-free, in a 15 ml glass tube. The solid catalyst of **FJI-C10** was filtrated from the reaction solution after 2 h, whereas the filtrate was transferred to a new glass tube and reaction was performed under the same conditions for an additional 10 h.

entry	y catalytic system	time (h)	conversion (%)	selectivity (%)	yield $(\%)^b$
1 °	MIL-101	12	41	29	12
2 <sup><i>d</i></sup>	[(Etim-H <sub>2</sub> BDC) <sup>+</sup> (Br)]	12	81	100	81
3 e	MIL-101				
	+	12	98	93	91
[(Eti	$m-H_2BDC)^+(Br^-)$ ]				

Table S4 The effect of catalyst on the cycloaddition of CO<sub>2</sub> with epichlorohydrin<sup>a</sup>

<sup>*a*</sup>Reaction conditions: solvent-free, 5 mmol of epichlorohydrin, CO<sub>2</sub> (constant 1 bar), temperature (80 °C). <sup>*b*</sup>Determined by GC-MS. <sup>*c*</sup>20 mg MIL-101. <sup>*d*</sup>0.35 mol % [(Etim-H<sub>2</sub>BDC)<sup>+</sup>(Br)] ligand. <sup>*e*</sup>14 mg MIL-101 and 0.35 mol % [(Etim-H<sub>2</sub>BDC)<sup>+</sup>(Br)] ligand.

entry	catalyst	conversion (%)	selectivity (%)	yield (%) <sup>b</sup>	
1	FJI-C10	100	87	87	
2	MIL-101	41	29	12	
3	HKUST-1	18	71	13	
4	ZIF-8	3	98	3	
5	UiO-66	trace	-	0	
6	NH <sub>2</sub> -UiO-66	trace	-	0	
7	MOF-5	trace	-	0	

Table S5 The effect of catalyst on the cycloaddition of CO<sub>2</sub> with epichlorohydrin<sup>a</sup>

<sup>*a*</sup>Reaction conditions: 5 mmol of epichlorohydrin, 20 mg of catalyst, CO<sub>2</sub> (constant 1 bar), solvent-free, temperature (80 °C), time (12 hours). <sup>*b*</sup>Determined by GC-MS.



Fig. S15 Catalytic recycled experiments of FJI-C10.



Fig. S16 a) Nitrogen sorption curves of FJI-C10 and regenerated FJI-C10 after catalysis (filled circles for adsorption, open circles for desorption). b) The pore size distribution of FJI-C10 and regenerated FJI-C10.

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