

## **Electronic Supporting Information**

### **Optimizing the mobility of active species in ionic liquid/MIL-101 composites for boosting carbon dioxide conversion**

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## S1 Characterization

The powder X-ray diffraction (XRD) patterns were obtained from Rigaku Ultima IV. Thermo Electron Nicolet-360 was applied to collect Fourier transform infrared spectra. X-ray photoelectron spectroscopy measurement of samples was carried out over an AXIS ultraDLD. Micromeritics TriStar 3020 automatic volumetric adsorption equipment was utilized to measure CO<sub>2</sub> and nitrogen (N<sub>2</sub>) sorption isotherms. The yield was determined with a gas chromatograph (HF-901A, Shandong Huifen Instrument Co., Ltd., China). Thermogravimetric analysis (TGA) was measured by a STA2500 Regulus with a ramp rate of 10 °C min<sup>-1</sup> in atmosphere of N<sub>2</sub>. AVANCE III 600 MHz spectrometer was employed to record <sup>1</sup>H spectra. The morphology of materials was observed using a scanning electron microscope (SEM) (Regulus 8100). Transmission electron microscopy (TEM) experiments were carried out on a transmission electron microscope (JEM 1400). Surface zeta potential of acetonitrile solution of catalyst was measured with Zetasizer Nano ZS (Malvern).

## S2 Experimental Section

**Materials:** Of note, all chemicals were utilized as received without any other treatment as follows: chromic nitrate nonahydrate (AR), ammonium fluoride (AR), acetonitrile (AR), ethyl acetate (EA, AR), DMF (AR) and ethanol (EtOH, AR) were provided from Sinopharm Chemical Reagent Co., Ltd. terephthalic acid (99.5%), 1-methylimidazole (99.5%), 1-vinylimidazole (99%), epichlorohydrin (ECH, 99.5%), epibromohydrin (99.5%), styrene oxide (99.5%) was obtained from Aladdin Industrial Inc. hydrofluoric acid (AR), silver nitrate (AgNO<sub>3</sub>, 99%) were provided by Nanjing Chemical Reagent Co., Ltd. 1,2-epoxybutane (99%), glycidyl phenyl ether (99%), 1,2-epoxyhexane (99%), cyclohexene oxide (99%) was provided by energy chemical.

1-bromobutane (AR) were obtained from Shanghai lingfeng chemical reagent co., Ltd. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%) was provided by Shanghai Mackin Biochemical Co., Ltd.

**Synthesis of IL@MIL-101:** MIL-101 was prepared according to reported literature.<sup>32</sup> MIL-101 (300 mg) was activated for 8 h under vacuum to eliminate the remaining organic matter in the pore, then a mixture of 1-methylimidazole (18 mmol) and activated MIL-101 was stirred at room temperature (RT) for 24 h. Afterwards, 1-bromobutane (20 mmol) was added to the above system. The mixed system was continually stirred for another 24 h at RT. After washing with ethanol three times, the resulting product was dried in an 80 °C vacuum overnight.

**Synthesis of polyILs@MIL-101:** MIL-101 (300 mg) was activated for 8 h under vacuum to eliminate the remaining organic matter in the pore. Then, 1-vinylimidazole (18 mmol) was added to a flask containing activated MIL-101 and the mixture was stirred at RT for 24 h. Follow this, 1-bromobutane (20 mmol) was added to the above system and continued to be stirred at RT for another 24 h. The resulting solid was dispersed with ethanol, separated using filtration and then thoroughly washed with EtOH several times. After that, the powder was activated under 120 °C vacuum for 8 h. A mixture of AIBN (0.067 mmol) and DMF (1 mL) were added to the above powder and the system was then stirred for 24 h at 70 °C under the N<sub>2</sub>. Finally, the green powder was thoroughly washed with EtOH, and dried overnight at 80 °C in vacuum.

**Preparation of [Bmim]Br:** Under N<sub>2</sub> atmosphere, the mixture of 1-methylimidazole (18 mmol) and 1-bromobutane (20 mmol) was stirred at RT for 24 h. Then, the product was washed by EA and EtOH three times and the residual EA and/or EtOH

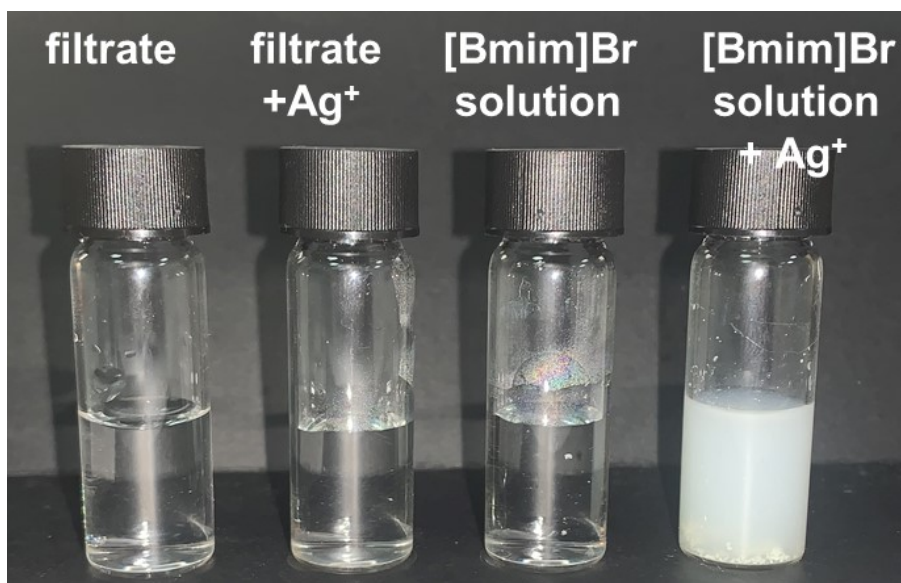
were removed with rotary evaporation.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 9.64 (s, 1H), 7.35 (s, 1H), 3.92 (t,  $J = 7.4$  Hz, 2H), 3.68 (s, 3H), 2.68 (s, 1H), 1.48–1.44 (m, 2H), 0.94 (dd,  $J = 15.1, 7.5$  Hz, 2H), 0.49 (t,  $J = 7.4$  Hz, 3H).

**Preparation of 1-vinyl-3-butylimidazolium bromide:** Under  $\text{N}_2$  atmosphere, the mixture of 1-vinylimidazole (18 mmol) and 1-bromobutane (20 mmol) was stirred at RT for 8 h. The product was then washed with EA three times and the residual EA was removed using rotary evaporation.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.62 (s, 1H), 8.19 (d,  $J = 21.3$  Hz, 1H), 7.86 (d,  $J = 16.0$  Hz, 1H), 7.46 (dd,  $J = 15.5, 8.7$  Hz, 1H), 6.09 (dt,  $J = 15.7, 3.5$  Hz, 1H), 5.30 (s, 1H), 4.40 (s, 2H), 1.90 (s, 2H), 1.31 (s, 2H), 0.85 (s, 3H).

**Cycloaddition of epoxides with  $\text{CO}_2$ :** Typically, the mixture of catalyst (50 mg), acetonitrile (2 mL) and epoxide (1 mmol) was charged into a flask connected to a flask filled with  $\text{CO}_2$  balloons. The system was then stirred at 70  $^\circ\text{C}$  and 600 rpm. After 24 h, the process was monitored by gas chromatography.

**Investigation of catalytic cycle performance of IL@MIL-101:** After the reaction was completed, IL@MIL-101 was recovered using centrifugation, washed with EtOH three times, and then dried overnight in a vacuum oven. To test the cycling stability of IL@MIL-101, the same process was carried out 5 times.

**Free bromine ion detection:** IL@MIL-101 (5 mg) and [Bmim]Br (1 mg) were separately dispersed into water (2 mL) and sonicated with a commercial ultrasonic cleaner for 10 min. Subsequently, both filtrates were collected by centrifugation. After that, added 15mM  $\text{AgNO}_3$  aqueous solution to the filtrate observed the precipitation.



**Fig. S1** Digital images of filtrate obtained by IL@MIL-101 and [Bmim]Br solution before and after adding silver nitrate solution.

**Table S1** The mass loading ratios of IL in three IL@MIL-101 samples.

|          | $M_{IL}$ (mg) | $M_{IL}/M_{IL@MIL-101}$ (wt%) |
|----------|---------------|-------------------------------|
| Sample 1 | 30.7          | 9.3                           |
| Sample 2 | 29.3          | 8.9                           |
| Sample 3 | 31.8          | 9.6                           |

**Table S2** The mass loading ratios of polyILs in three polyILs@MIL-101 samples.

|          | $M_{polyILs}$ (mg) | $M_{polyILs}/M_{polyILs@MIL-101}$ (wt%) |
|----------|--------------------|---|
| Sample 1 | 30.8               | 9.3                                     |
| Sample 2 | 32.6               | 9.8                                     |
| Sample 3 | 27.1               | 8.3                                     |

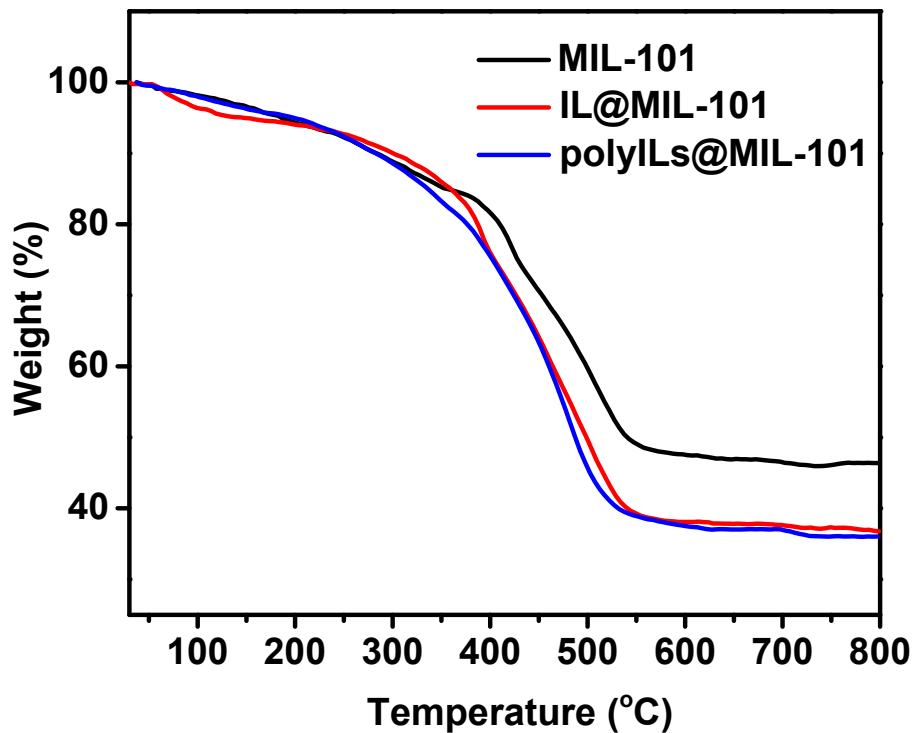


Fig. S2 TGA patterns of MIL-101, IL@MIL-101 and polyILs@MIL-101.

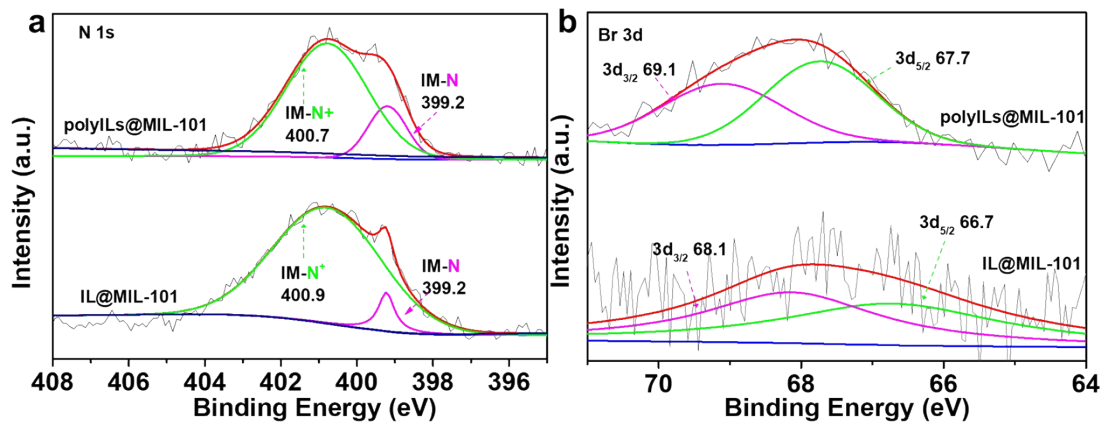
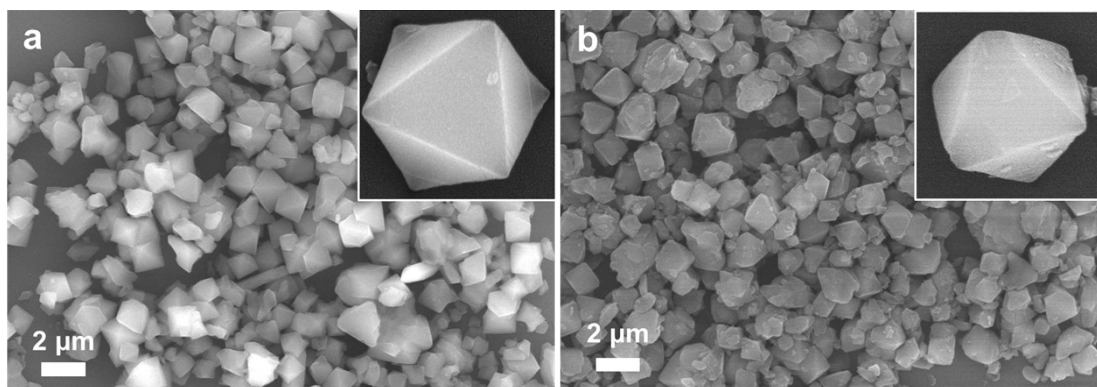
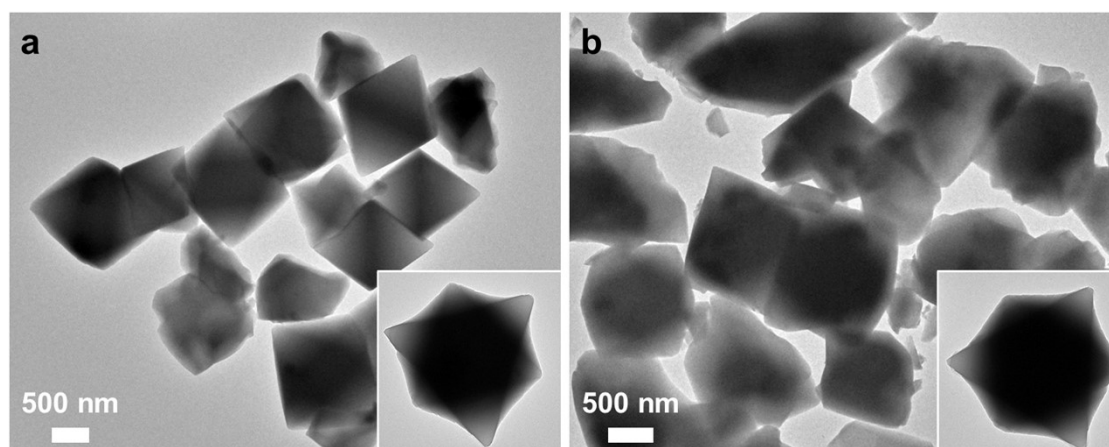


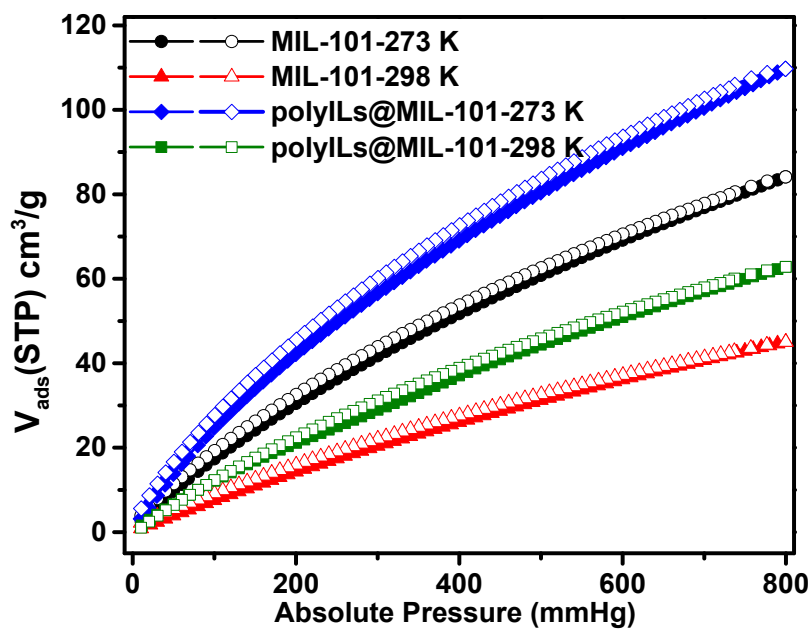
Fig. S3 The XPS spectra of (a) N 1s and (b) Br 3d for two composites.



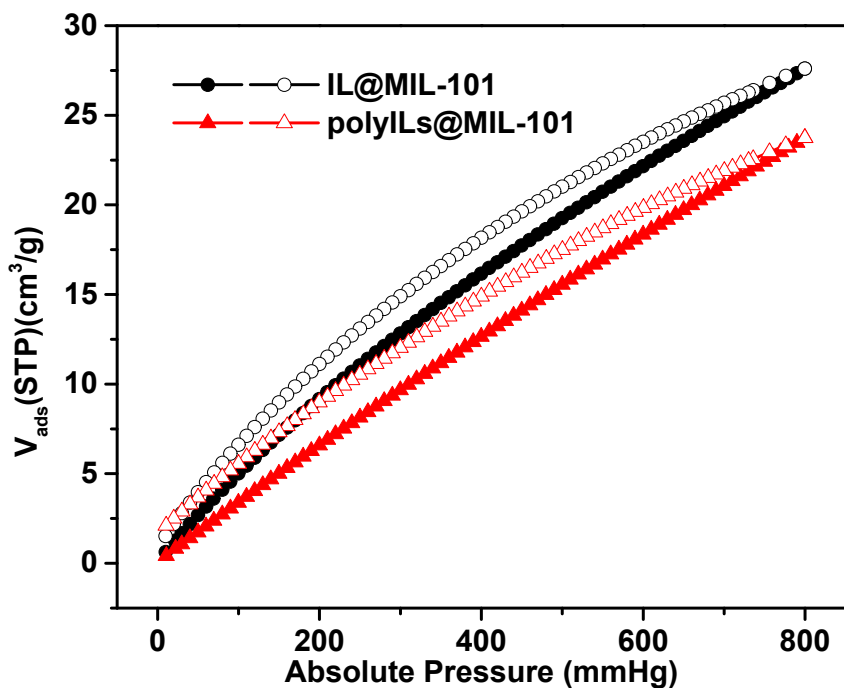
**Fig. S4** SEM images of (a) MIL-101 and (b) polyILs@MIL-101 (inset: enlarged images).



**Fig. S5** TEM images of (a) MIL-101 and (b) polyILs@MIL-101 (inset: enlarged images).

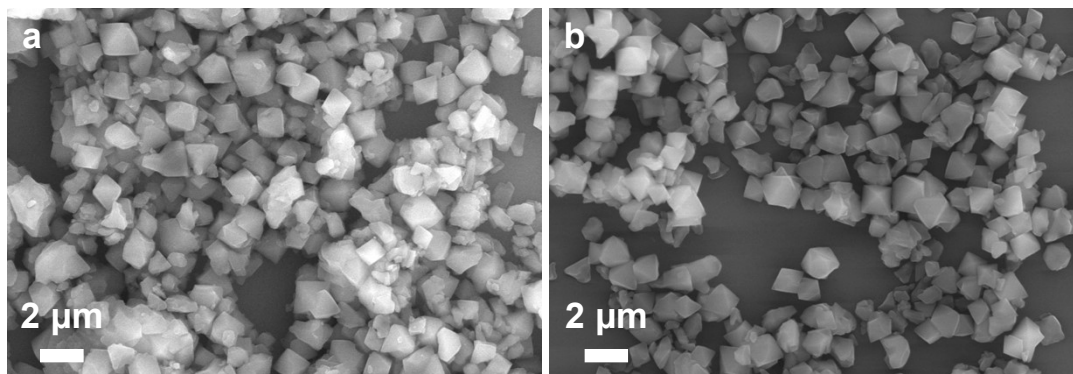


**Fig. S6**  $\text{CO}_2$  sorption isotherms of MIL-101 and polyILs@MIL-101 at different temperatures.

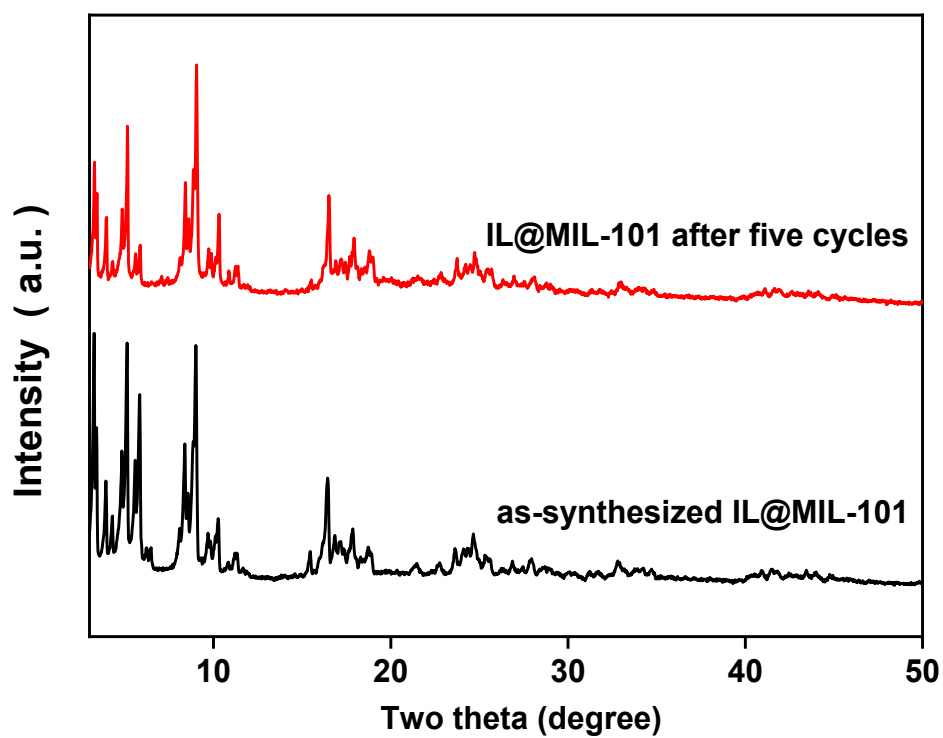


**Fig. S7**  $\text{CO}_2$  sorption isotherms of IL@MIL-101 and polyILs@MIL-101 at 70 °C.





**Fig. S8** SEM images of IL@MIL-101 (a) before and (b) after five catalytic cycles.



**Fig. S9** XRD patterns of as-synthesized IL@MIL-101 and IL@MIL-101 after five cycles.

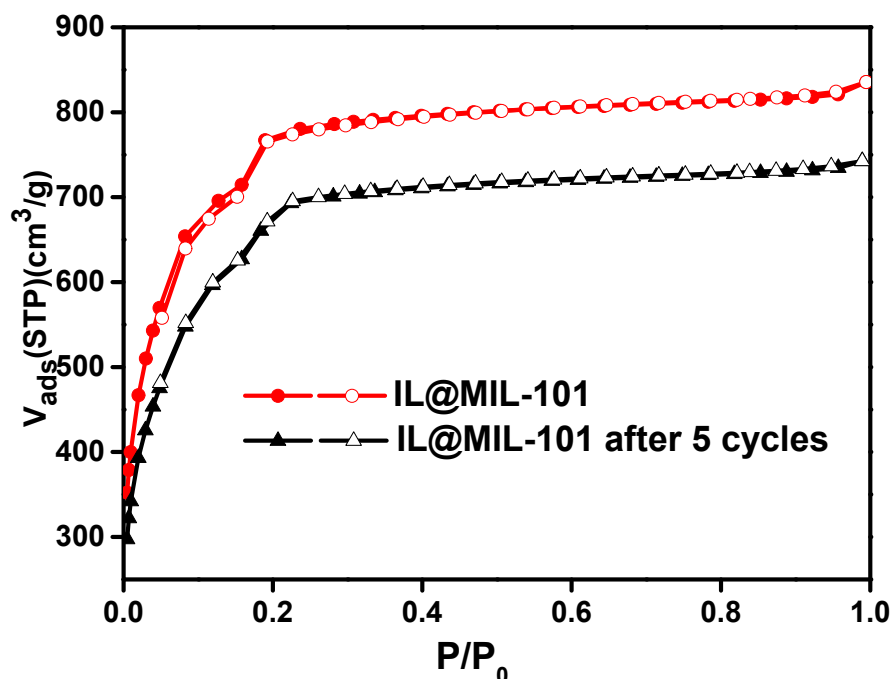



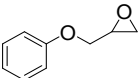
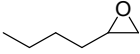



Fig. S10 N<sub>2</sub> sorption isotherms of IL@MIL-101 before and after five catalytic cycles.

Table S3 IL@MIL-101 catalyzed coupling of CO<sub>2</sub> and epoxides bearing different functional groups<sup>[a]</sup>

| Entry            | Epoxide   | Temp. [°C] | Time [h] | Yield <sup>[b]</sup> [%] |
|------------------|---|------------|----------|--------------------------|
| 1                |  | 55         | 24       | 94                       |
| 2                |  | 80         | 24       | 92                       |
| 3                |  | 80         | 24       | 89                       |
| 4 <sup>[c]</sup> |  | 70         | 24       | 88                       |
| 5                |  | 80         | 24       | 78                       |
| 6 <sup>[c]</sup> |  | 120        | 48       | 48                       |

<sup>[a]</sup> Reaction conditions: 100 mg of IL@MIL-101, 1 mmol of substrate, 2 mL of acetonitrile. <sup>[b]</sup> Determined by gas chromatograph analysis. <sup>[c]</sup> N,N-dimethylformamide (DMF).