Supplementary Information for

In situ rapid synthesis of ionic liquid/ionic covalent organic framework composites for CO_2 fixation

Zhifeng Xu[†a], Wenting Wang[†a], Bowei Chen[a], Haitao Zhou[a], Qiufang Yao[b], Xianjie Shen[a], Yuchen Pan[a], Dongxian Wu[a], Yongyong Cao[a], Zhangfeng Shen[a], Yanan Liu[a], Qineng Xia[a], Xi Li[a], Xiaoqin Zou[*c], Yangang Wang[*a] and Lingchang Jiang[*a]

[a] College of Biological, Chemical Science and Engineering, Jiaxing University, Jiaxing, Zhejiang 314001, China. E-mail: jianglingchang@zjxu.edu.cn

[b] College of Advanced Materials Engineering, Jiaxing Nanhu University, 572 Yuexiu Road, Jiaxing 314001, China

[c] Faculty of Chemistry, Northeast Normal University, No.5268, Renmin Street, Nanguan District, Changchun, Jilin 130024, China. E-mail: zouxq100@nenu.edu.cn

† These authors contributed equally.

Email: jianglingchang@zjxu.edu.cn; zouxq100@nenu.edu.cn

Experimental section

Reagents and Materials.

1,3,5-Triphenylbenzene (TP), dichloromethane (CH_2Cl_2), Ethidium Bromide (EB), 1-Butyl-3-Methylimidazolium Tetrafluoroborate, 1-Hexyl-3-Methylimidazolium Tetrafluoroborate, 1-Decyl-3-Methylimidazolium Tetrafluoroborate, tetrahydrofuran (THF) and methanol were purchased from Titan Technology (Shanghai) in 99.5% purity and ethanol was obtained from Sinopharm Chemical Reagent in 95% purity. All the reagents and reactants are used as received without any purification.

Synthesis of catalytic composites

Preparation of C_4-IL/ICOF: TP (10.5 mg, 0.01 mmol), EB (29.6 mg, 0.075 mmol) and 1-Butyl-3-Methylimidazolium (0.2 ml) were added into a 5 mL centrifuge tube. Then the mixture was rapidly stirred for 0.5 h under ambient conditions. The resulting product was firstly washed with adequate methanol, and ethanol, THF and CH_2Cl_2 were further used to purify the product by Soxhlet extraction. The final material was obtained as a red powder after drying under vacuum for 12 h at 80°C.

Preparation of C_6-IL/ICOF: The synthesis process of C_6-IL/ICOF was similar to that of C_4-IL/ICOF except that 1-Hexyl-3-Methylimidazolium Tetrafluoroborate was used instead of 1-Butyl-3-Methylimidazolium.

Preparation of C_{10}-IL/ICOF: The synthesis process of C_{10}-IL/ICOF was similar to that of C_4-IL/ICOF except that 1-Decyl-3-Methylimidazolium Tetrafluoroborate was used instead of 1-Butyl-3-Methylimidazolium.

Preparation of amorphous POP: TP (10.5 mg, 0.01 mmol), EB (29.6 mg, 0.075 mmol) and DMF (20 ml) were added into a 50 mL a round bottomed flask. Then the mixture was rapidly stirred and heated at 120°C for 24 h. The resulting product was firstly washed with adequate methanol, and ethanol, THF and CH_2Cl_2 were further used to purify the product by Soxhlet extraction. The final material was obtained as a red powder after drying under vacuum for 12 h at 80 °C.

Catalytic test

The cycloaddition reaction of CO_2 to epoxides into cyclic carbonate was carried at a 25 mL high-pressure stainless-steel reactor. 25 mg of IL/ICOF and epoxide (35 mmol) were charged into a reactor, which was pressurized with 0.5 MPa CO_2 for 3 times to purge the air. Then the reactor was stirred and reacted under different conditions (CO_2 pressure, temperature, time). After reaction, the reactor was cooled to room temperature and then the extra CO_2 was released slowly into the water. The catalyst and the product were separated by centrifugation. The yields were analyzed by a gas chromatograph (Agilent 7890B). The internal standard substance of n-dodecane was selected to quantificationally analyze the composition of the cycloaddition products. The stability of the catalyst was tested by a five-run test and the catalyst was washed by ethanol and deionized water to recycle for the next run.

Characterization

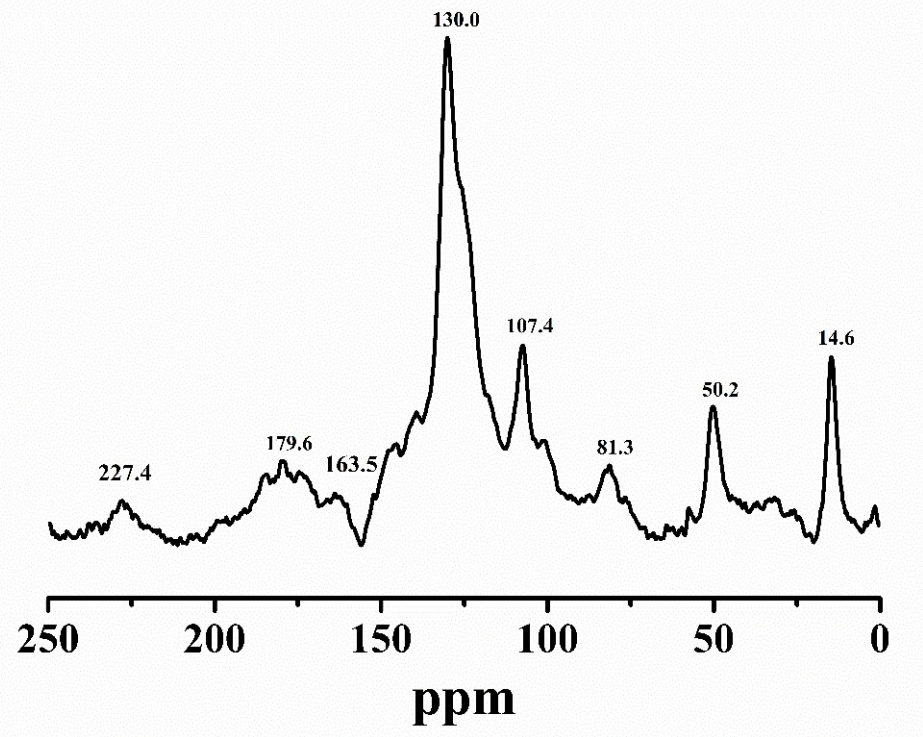


Fig. 1 ^{13}C CP/MAS NMR spectrum of C_4-IL/ICOF.

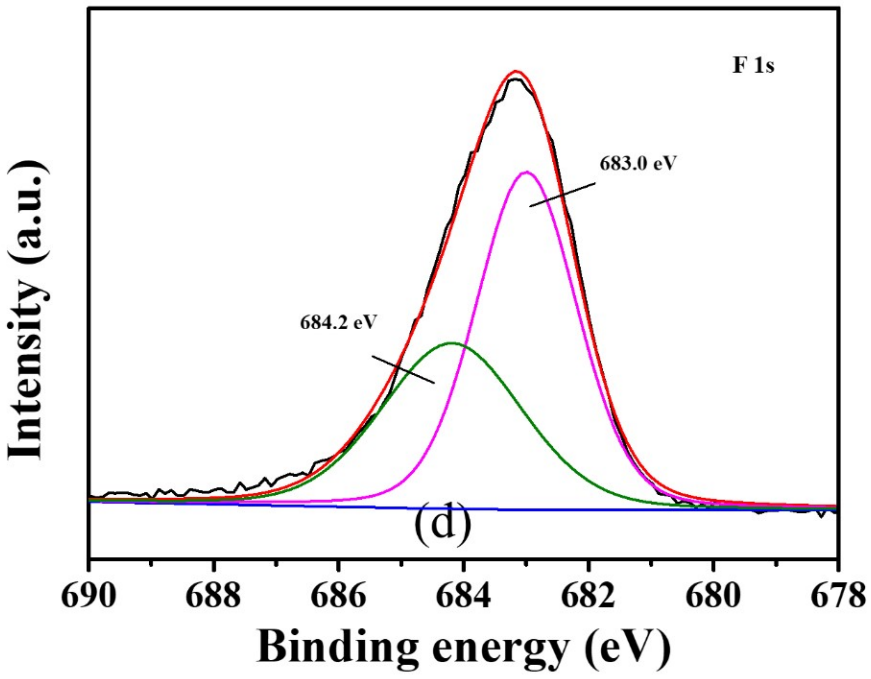


Fig. 2 F 1s XPS spectrum of C_4-IL/ICOF.

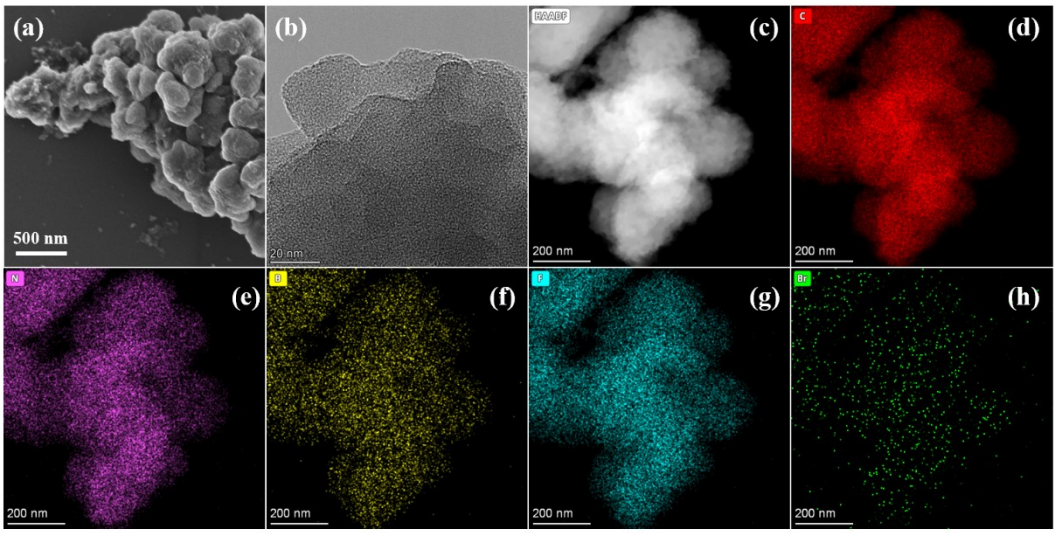


Fig. 3 (a) SEM image of C_4-IL/ICOF; (b) TEM image of C_4-IL/ICOF; (c-h) the EDS mapping images of C, N, O, B, F and Br of C_4-IL/ICOF.

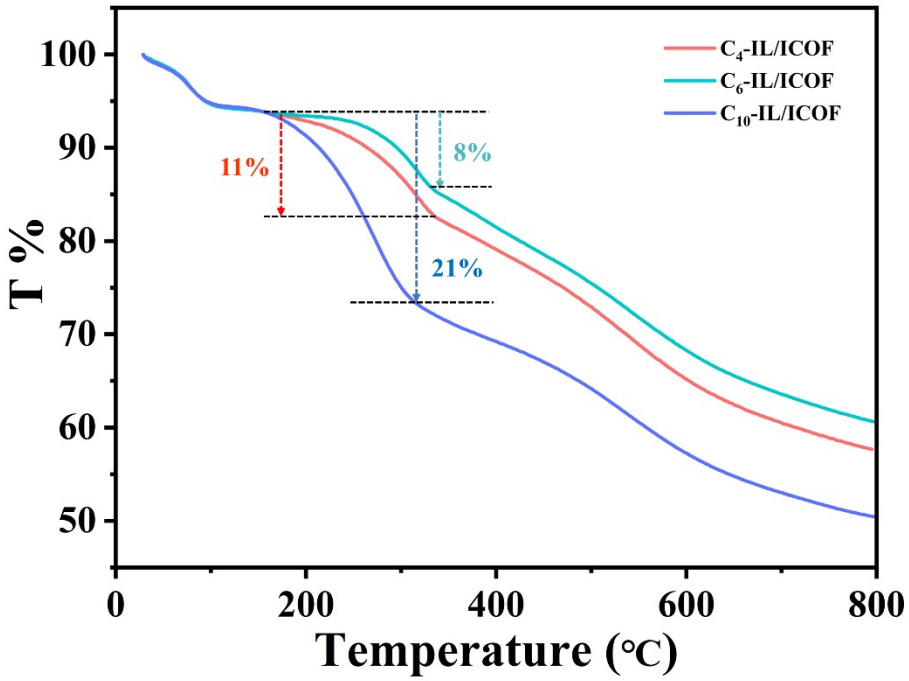


Fig. 4 TGA of C_4-IL/ICOF, C_6-IL/ICOF and C_{10}-IL/ICOF.

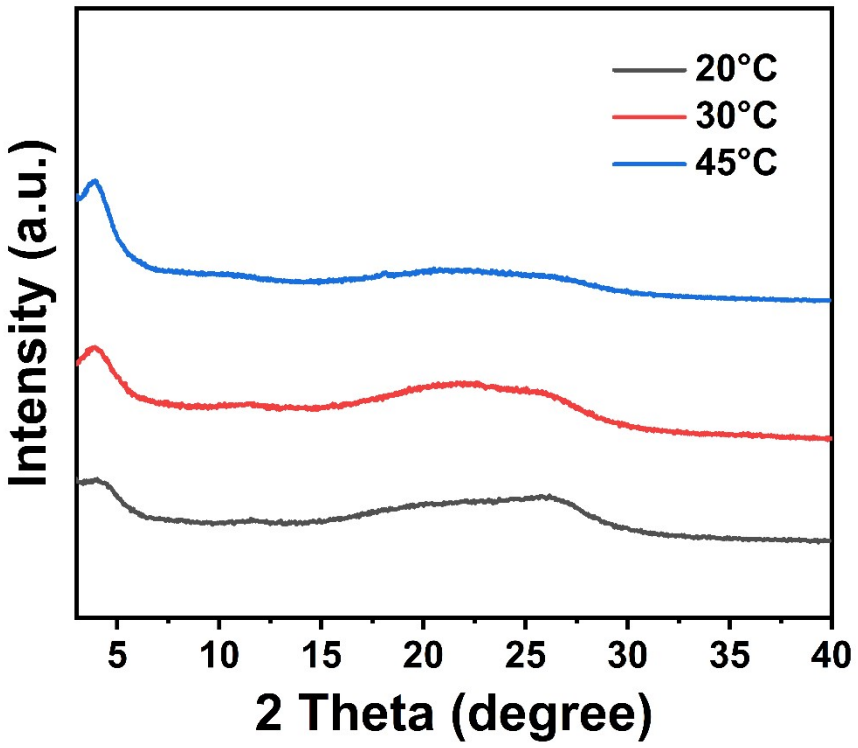


Fig. 5 PXRD patterns of C_4-IL/ICOF synthesized at 20, 30 and 45°C, respectively.

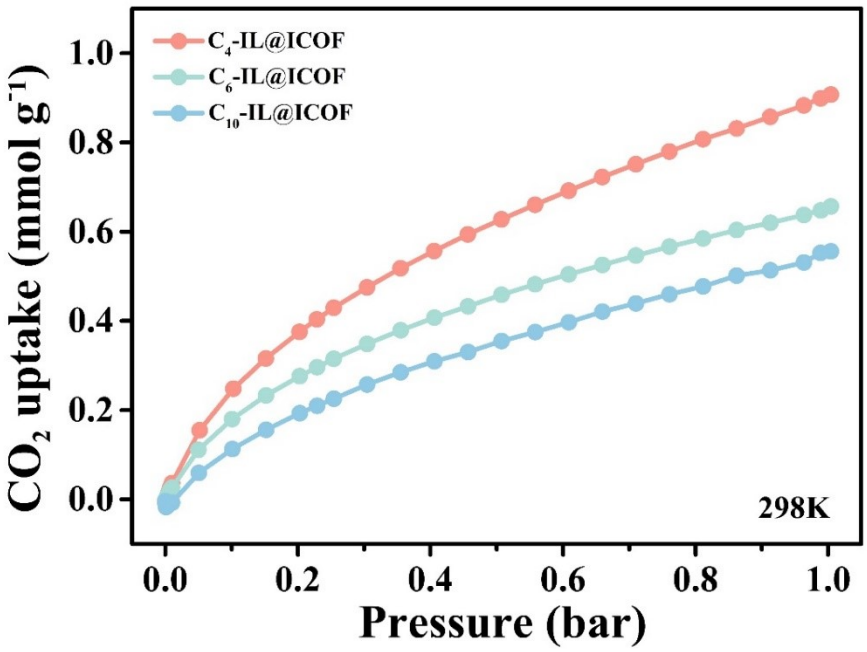


Fig. 6 CO_2 adsorption isotherms of C_n-IL/ICOF at 298 K (n = 4, 6, 10, respectively).

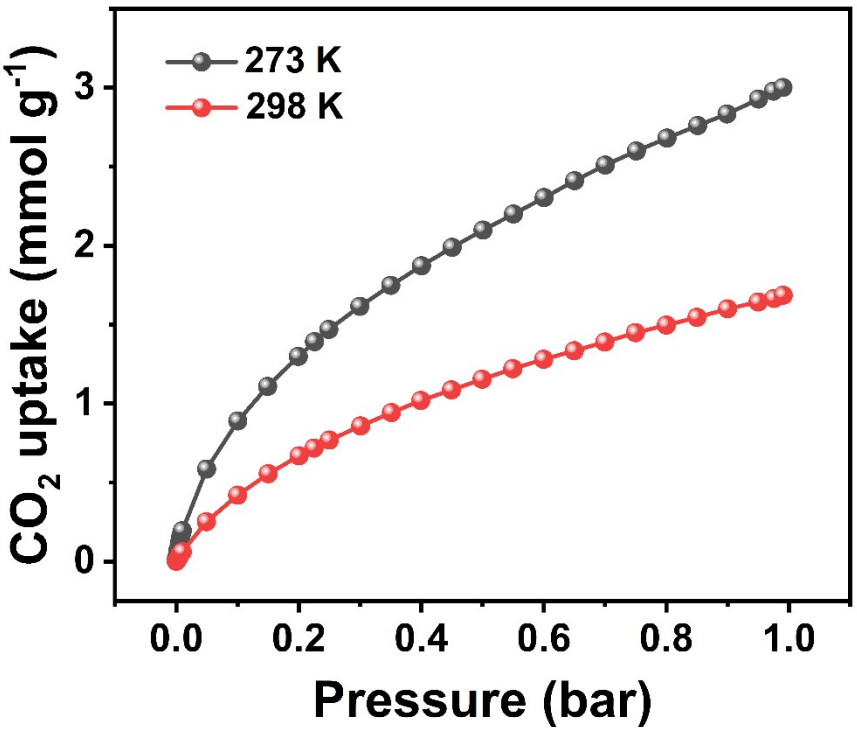


Fig. 7 CO_2 adsorption isotherms of EB-COF at 273 and 298 K.

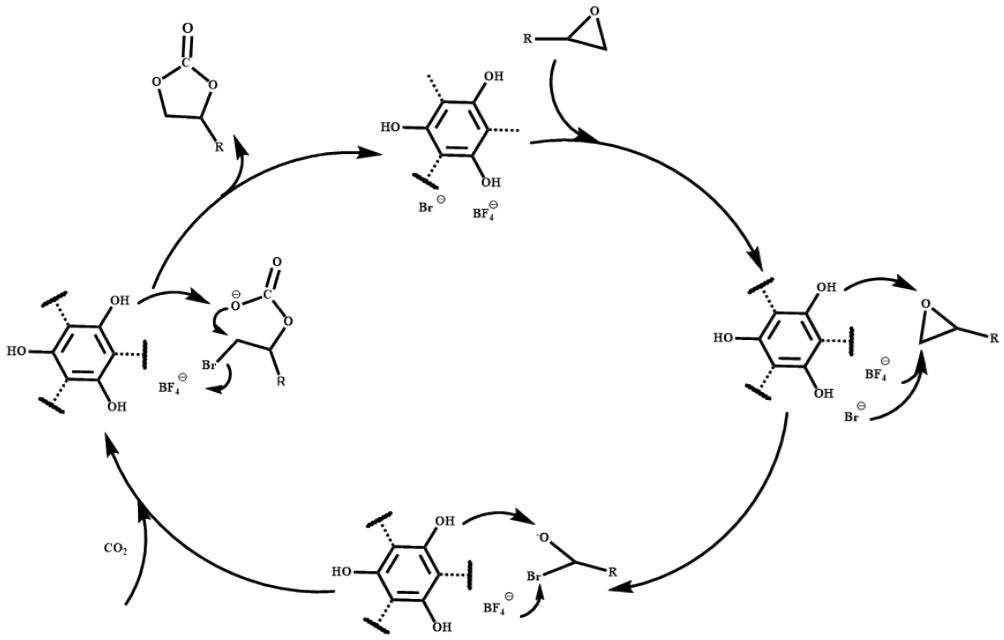
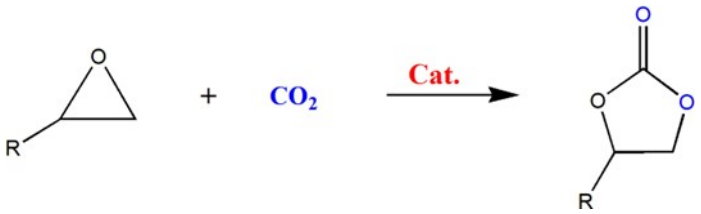


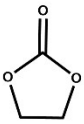
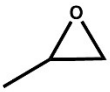
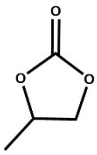
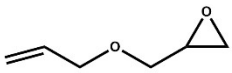
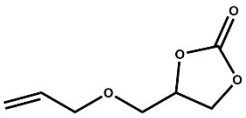
Fig. 8 A possible mechanism of cycloaddition of CO_2 with oxide over C_4-IL/ICOF.

Table 1 CO_2 adsorption performance of some typical materials at 273 and 298 K

Materials	S_{BET} (m^2/g)	CO_2 uptake (mmol/g)		Ref.
		273 K	298 K	
ZIF-8	1769	1.47	-	S1
POP-PBnCl-TPPMg-4	411	1.25	0.84	S2
POP-PA-COOH	754	1.89	1.09	S3
FJC-1	1726	2.86	1.84	S4
PAF-1	5640	2.07	-	S5
C_4-IL/ICOF	53	1.63	0.91	This work
C_6-IL/ICOF	103	1.41	0.66	This work
C_{10}-IL/ICOF	113	0.86	0.56	This work

Table 2 Cycloaddition of epoxides with CO_2 using C_n-IL/ICOF and the corresponding amorphous POP as catalysts



Entry	Epoxides	Product	Catalyst	Yield (%)
1			C_4-IL@ICOF	**14.0**
			C_6-IL@ICOF	**10.1**
			C_{10}-IL@ICOF	**11.5**
2			C_4-IL@ICOF	**93.8**
			C_6-IL@ICOF	**92.6**
			C_{10}-IL@ICOF	**95.4**
			POP	**49.8**
3			C_4-IL@ICOF	**99.8**
			C_6-IL@ICOF	**99.8**
			C_{10}-IL@ICOF	**99.8**

Reaction conditions: CO_2 pressure (1.8 MPa), reaction time (7 h), temperature (130°C)

Reference

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[2] Z.F. Dai, Y.Q. Tang, F. Zhang, Y.B. Xiong, S. Wang, Q. Sun, L. Wang, X.J. Meng, L.H. Zhao, and F.S. Xiao, *Chin. J. Catal.*, 2021, **42**, 618-626.

[3] Z.F. Dai, Y.F. Bao, J.D. Yuan, J.Z. Yao and Y.B. Xiong, *Chem Commun*, 2021, **57**, 9732-9735.

[4] M. R. Liebl and J. Senker, *Chem. Mater*, 2013, **25**, 970-980.

[5] M. G. Rabbani and H.M. El-Kaderi, *Chem. Mater.*, 2011, **23**, 1650-1653.