Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

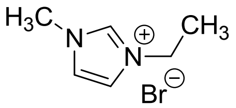
Highly ordered mesoporous polymer supported imidazolium-based ionic liquid: an efficient catalyst for cycloaddition of CO_2 with epoxide to produce cyclic carbonates

Wei Zhang, Qixiang Wang, Haihong Wu*, Peng Wu, Mingyuan He*

1. Compounds characterization data

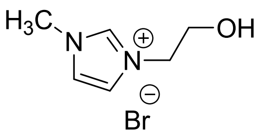
The products were identified by matching the ^{1}H NMR data with those reported in literature [1-4].

1-ethyl-3-methylimidazolium bromine (EMIMBr).



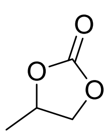
^{1}H NMR (400 MHz, DMSO-d_6) δ 1.42 (t, J = 7.3 Hz, 3H), 3.85 (s, 3H), 4.20 (q, J = 7.3 Hz, 2H), 7.72 (t, J = 1.7 Hz, 1H), 7.81 (t, J = 1.7 Hz, 1H), 9.20 (s, 1H).

3-(2-Hydroxyethyl)-1-methylimidazolium bromide (HEMIMBr).



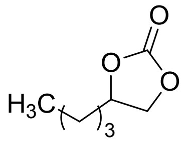
^{1}H NMR (500 MHz, DMSO-d_6): δ 3.67-3.73 (m, 2H), 3.85 (s, 3H), 4.16-4.23 (t, J = 5.0 Hz, 2H), 5.17 (s, 1H), 7.66-7.74 (m, 2H), 9.08 (s, 1H).

4-Methyl-1, 3-dioxolan-2-one.



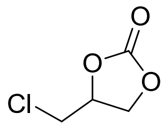
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (d, J = 6.3 Hz, 3H), 4.03 (dd, J = 7.2, 8.4 Hz, 1H), 4.56 (dd, J = 7.2, 8.4 Hz, 1H), 4.82-4.91(m, 1H).

4-butyl-1, 3-dioxolan-2-one.



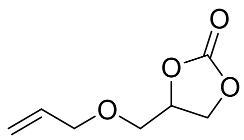
[1]H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.0 Hz, 3H), 1.33-1.49 (m, 4H), 1.62-1.72 (m, 1H), 1.74-1.85 (m, 1H), 4.05 (dd, *J* = 7.2, 8.4 Hz, 1H), 4.51 (t, *J* = 8.1 Hz, 1H), 4.69 (dq, *J* = 5.5, 7.5 Hz, 1H). 4.42 (dd, *J* = 8.9, 5.7 Hz, 1H).

4-(chloromethyl)-1, 3-dioxolan-2-one.



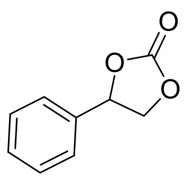
[1]H NMR (500 MHz, $CDCl_3$) δ 3.72-3.79 (m, 2H), 4.42 (dd, *J* = 5.7, 8.9 Hz, 1H), 4.59 (t, *J* = 8.5 Hz, 1H), 4.93-4.98 (m, 1H).

4-Allyloxymethyl-1, 3-dioxolan-2-one.



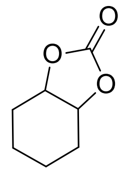
[1]H NMR (500 MHz, $CDCl_3$) δ 3.66 (ddd, *J* =7, 11.0, 39.7Hz, 2H), 4.03-4.10 (m, 2H), 4.40-4.42 (m, 1H), 4.51 (t, *J* = 8.4 Hz, 1H), 4.82-4.86 (m, 1H), 5.22-5.31(m, 2H), 5.84-5.91(m, 1H).

4-Phenyl-1, 3-dioxolan-2-one.



[1]H NMR (400 MHz, $CDCl_3$) δ 4.34 (t, *J* = 8.4Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 5.67 (t, *J* = 8.0 Hz, 1H), 7.32 – 7.47 (m, 5H).

Hexahydrobenzo[d] [1, 3] dioxol-2-one.



^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39-1.48 (m, 2H), 1.60-1.68 (m, 2H), 1.87-1.95 (m, 4H), 4.65-4.73 (m, 2H).

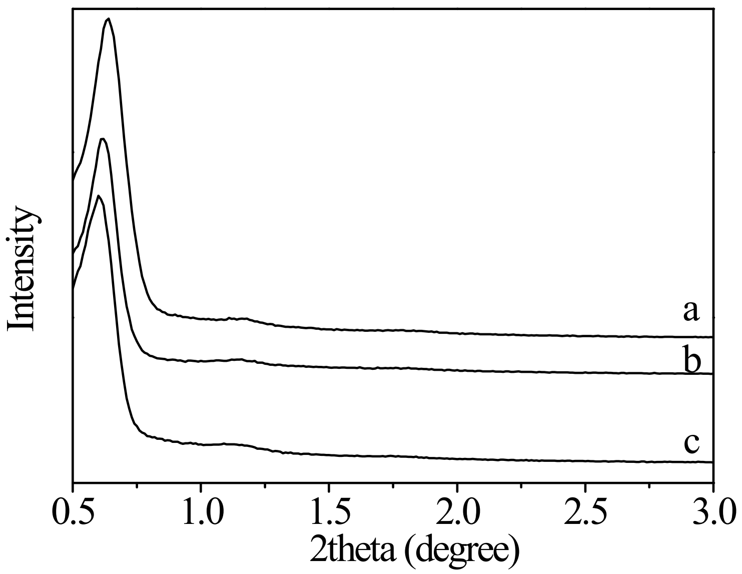


Fig.S1 Small angle XRD patterns of (a) FDU-DHPIMBr, (b) FDU-CMIMBr and (c) FDU-EIMBr

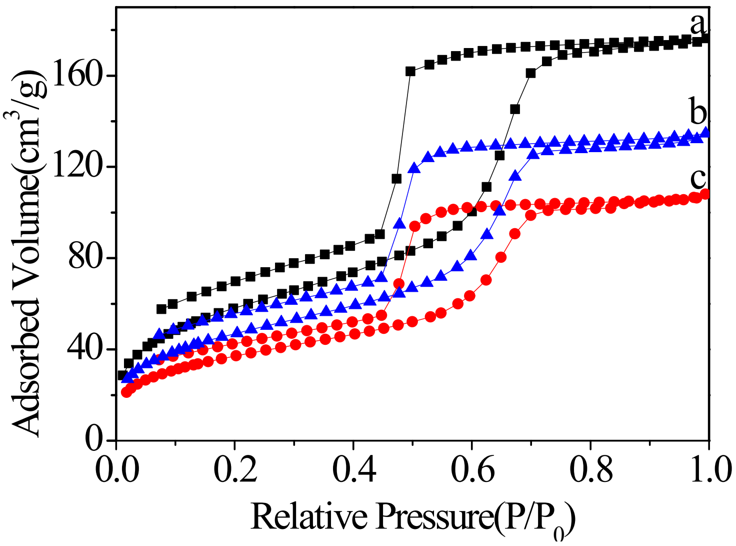


Fig. S2 The Nitrogen adsorption–desorption isotherms of (a) FDU-EIMBr, (b) FDU-DHPIMBr, and (c) FDU-CMIMBr.

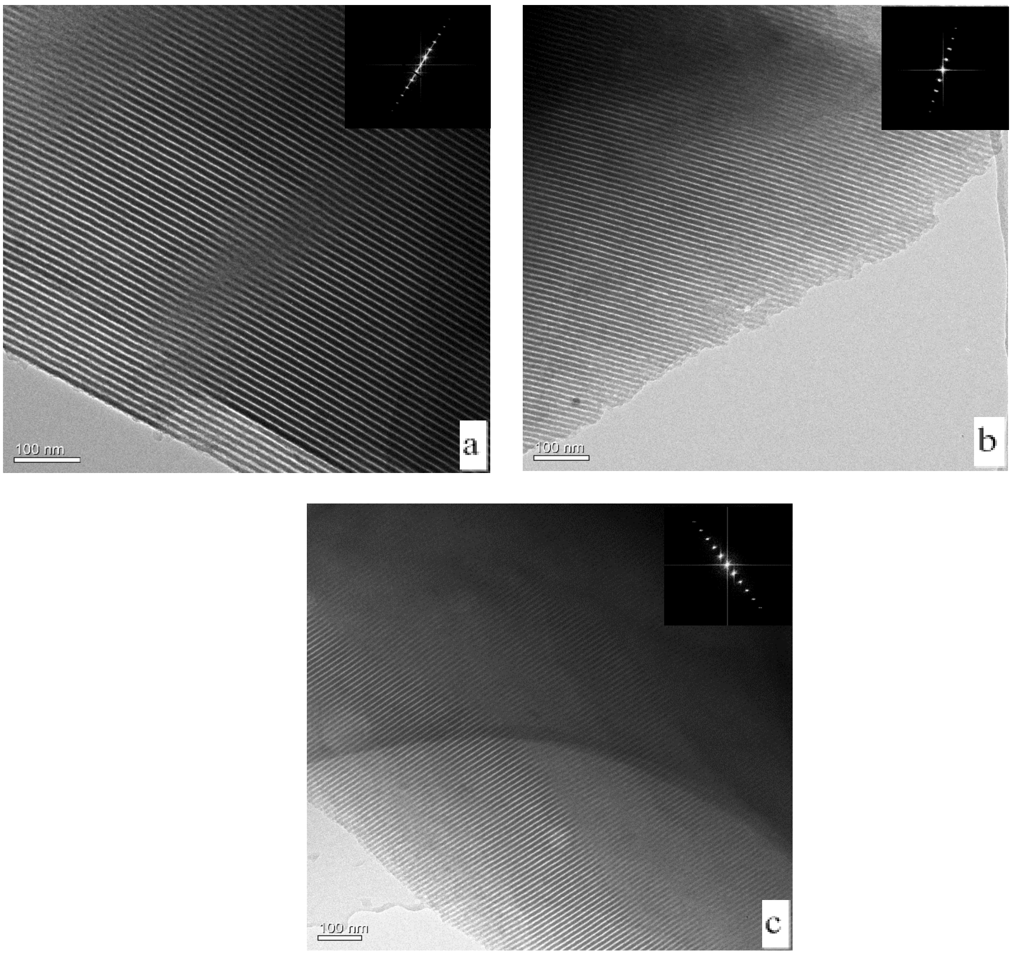


Fig. S3 TEM images of (a) FDU-EIMBr, (b) FDU-CMIMBr and (c) FDU-DHPIMBr.

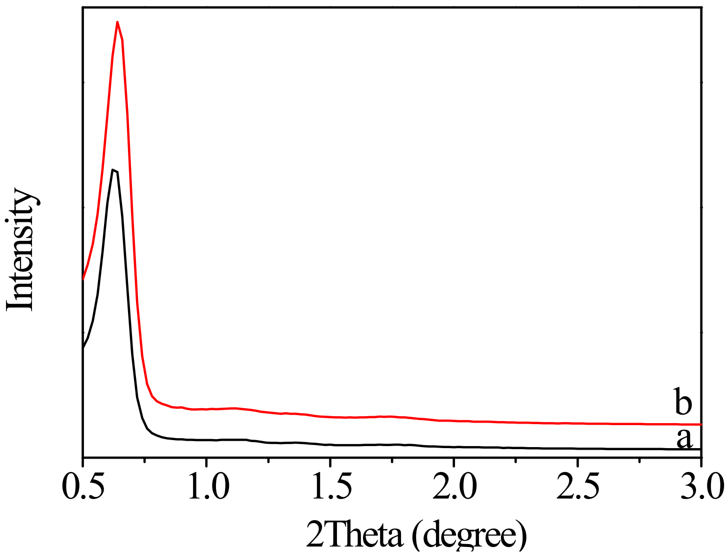


Fig. S4 Small angle XRD patterns of (a) fresh FDU-HEIMBr and (b) FDU-HEIMBr after five catalytic runs.

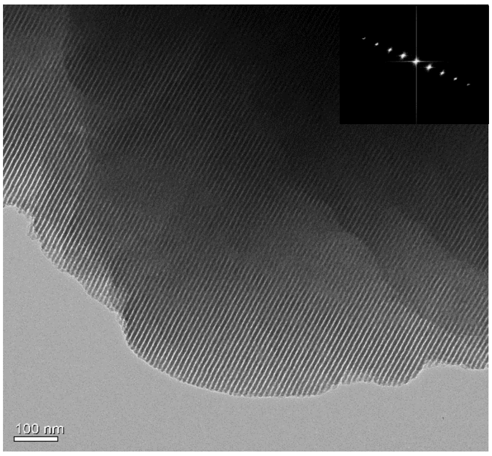


Fig. S5 TEM images of the FDU-HEIMBr after used five times.

Table S1 catalytic activity of analogous heterogeneous catalyst systems for cycloaddition of CO_2 to propylene oxide.

Entry	Reference	Catalyst	Reaction conditions	PC Yield (%)[b]	TON
1	Watile et al.2012[5]	PS supported supported 1-(2,3-di-hydroxyl-propyl)-imidazolium bromide (PS-DHPIMBr)	PO (25 mmol), catalyst (1.2 mol%), CO_2 (2.0 MPa), 130 ^oC, 3 h	97	81
2	Yang et al. 2012[6]	PEG supported 1,5,7-triazabicyclo[4.4.0]dec-5-enium bromide (BrTBDPEG150TBDBr)	PO (10 mmol), catalyst (1.0 mol%), CO_2 (1.0 MPa), 120 ^oC, 3h	99	99
3	Yang et al. 2014[7]	Fluoro-functionalized polymeric ionic liquids with imidazolium bromide (F-PIL-Br)	PO (10 mmol), catalyst (1.0 mol%), CO_2 (1.0 MPa), 120 ^oC, 9 h	94	94
4	Sun et al. 2012[8]	Chitosan supported 1-ethyl-3-methyl imidazolium bromide (CS-EMIMBr)	PO (1 mL, 25 ^oC), catalyst (1.0 mol%), CO_2 (1.0 MPa), 120 ^oC, 9 h	96	96
5	Roshan et al. 2012[9]	Carboxymethyl cellulose supported 1-Methyl-3-(3-triethoxysilylpropyl) imidazolium iodide (CMIL-4-I)	PO (42.8mmol), catalyst (1.2 mol%), CO_2 (1.8 MPa), 110 ^oC, 2 h	99	82
6	Roshan et al. 2013[10]	Microwave synthesized methyl iodide-quaternized cellulose (mQC-1.I)	PO (42.8mmol), catalyst (0.4 mol%), CO_2 (1.2 MPa), 120 ^oC, 3 h	97	242

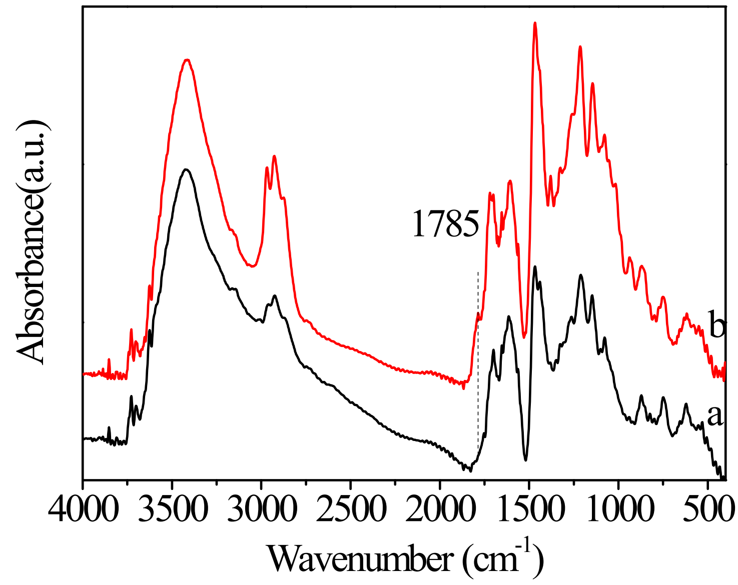


Fig. S6 FT-IR spectra of (a) fresh FDU-HEIMBr and (b) FDU-HEIMBr after five catalytic runs.

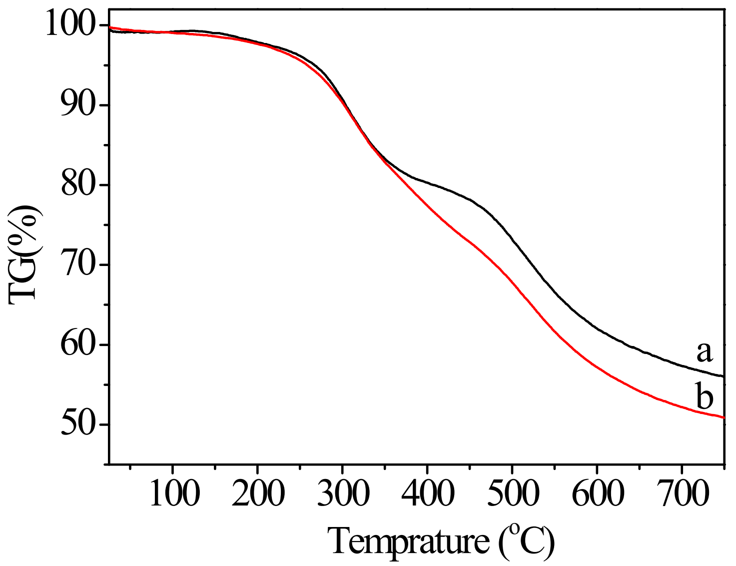


Fig. S7 Thermogravimetric curves of (a) fresh FDU-HEIMBr and (b) FDU-HEIMBr after five catalytic runs.

References

1 J. R. Harjani, J. Farrell, M. T. Garcia, R. D. Singer and P. J. Scammells, *Green Chem.*, 2009, **11**, 821.

2 T. Ema, Y. Miyazaki, S. Koyama, Y. Yano and T. Sakai, *Chem. Commun.*, 2012, **48**, 4489.

3 C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1228.

4 J. Gao, Q.-W. Song, L.-N. He, C. Liu, Z.-Z. Yang, X. Han, X.-D. Li and Q.-C. Song, *Tetrahedron*, 2012, **68**, 3835.

5 R. A. Watile, K. M. Deshmukh, K. P. Dhake and B. M. Bhanage, *Catalysis Science & Technology*, 2012, **2**, 1051.

6 Z.-Z. Yang, Y.-N. Zhao, L.-N. He, J. Gao and Z.-S. Yin, *Green Chemistry*, 2012, **14**, 519.

7 Z.-Z. Yang, Y. Zhao, G. Ji, H. Zhang, B. Yu, X. Gao and Z. Liu, Green Chemistry, 2014, **16**, 3724.

8 J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang and Y. She, *Green Chemistry*, 2012, **14**, 654.

9 K. R. Roshan, G. Mathai, J. Kim, J. Tharun, G.-A. Park and D.-W. Park, *Green Chemistry*, 2012, **14**, 2933.

10 K. R. Roshan, T. Jose, A. C. Kathalikkattil, D. W. Kim, B. Kim and D. W. Park, *Appl. Catal., A*, 2013, **467**, 17.