

## Supporting Information

# Sulfur-containing amino acid derived ionic liquid as halogen-free catalyst for CO<sub>2</sub> mild transformation into cyclic carbonates

Yanxi Gong,<sup>a</sup> Yifan Li,<sup>a</sup> Jiayin Hu,<sup>\*a</sup> Zheng Wang,<sup>a</sup> Tianlong Deng<sup>\*b</sup>

a. Tianjin Key Laboratory of Brine Chemical Engineering and Resource Eco-utilization, College of Chemical Engineering and Materials Science, Tianjin University of Science and Technology, Tianjin, China

b. College of Marine and Environmental Science, Tianjin University of Science and Technology, Tianjin, China

E-mail: [hujiayin@tust.edu.cn](mailto:hujiayin@tust.edu.cn); [tldeng@tust.edu.cn](mailto:tldeng@tust.edu.cn).

## Content

1. General information .....	2
2. Experimental section .....	3
3. NMR data of products .....	4
4. Table S1 .....	5

## 1. General information

CO<sub>2</sub> was supplied by Tianjin Feilin Gases Co., Ltd with a purity of 99.99%. 1,8-Diazabicyclo[5.4.0]undec-7-ene (98%) and Tetramethylguanidine (99%) were purchased by J&K Scientific Ltd. 1-Butyl-3-methylimidazolium acetate (99%) was supplied by Lanzhou Yulu Fine Chemical Co., Ltd. Epichlorohydrin (99%) and 3-Bromo-1,2-epoxypropane (97%) were purchased by Tokyo Chemical Inorganic Co., Ltd. N,N-Dimethylformamide (AR), Dimethyl sulfoxide (AR), 2-[(2-Methylphenoxy)methyl] oxirane (90%) and Cycloethane oxide (98%) were purchased by Shanghai Macklin Biochemical Co., Ltd. Dimethyl sulfoxide-d<sub>6</sub> (99.9%) was supplied by Cambridge Isotope Laboratories, Inc. Acetic acid (AR), Diethyl ether (99.5%), L-cysteine (BR) and glycidol were supplied by Sinopharm Chemical Reagent Co., Ltd.

The ILs 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) were supplied by Lanzhou Yulu Fine Chemical Co., LTD. The ILs were used without further purification.

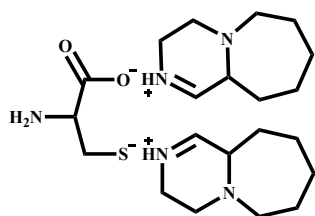
Standard column chromatography was performed on 20-40 μm silica gel using flash column chromatography. NMR spectra were recorded on a Bruker Fourier 400 MHz NMR spectrometer (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C).

## 2. Experimental section

### 2.1 The procedure for the synthesis of [DBUH]<sub>2</sub>[Cys]

The ILs were synthesized via neutralization. As an example, the procedure for the synthesis of [DBUH]<sub>2</sub>[Cys] is described, and those for other ILs were similar. In the experiment, methanol (10 mL), DBU (20 mmol, 3.0884 g) and Cys (10 mmol, 1.2116 g) were loaded into a 50 mL flask in a 30 °C water bath and the neutralization reaction was allowed to proceed for 24 h. Then, the solvent was removed by rotary evaporation under vacuum at 70 °C, and finally the IL was obtained. This IL was a colourless liquid at room temperature 99.2% yield.

#### 2.1.1 NMR data of IL system



[DBUH]<sub>2</sub>[Cys], Light yellow solution (Purity > 99%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 3.91 (s, 4H), 3.14 (d, *J* = 37.5 Hz, 12H), 2.30 (s, 4H), 1.60 (d, *J* = 60.6 Hz, 16H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 176.06, 163.62, 58.47, 55.96, 53.05, 48.14, 33.47, 29.12, 27.38, 24.96, 20.81.

### 2.2 Typical procedure for the synthesis of cyclic carbonates

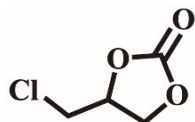
As an example, the procedure using epichlorohydrin as the substrate is described, and those for other substrates were similar. Epichlorohydrin (2 mmol, 0.2403 g) and [DBUH]<sub>2</sub>[Cys] (0.5 mmol, 0.1557 g) were loaded into a 22 mL stainless-steel batch reactor equipped with a magnetic stirrer. The air in the reactor was removed by blowing CO<sub>2</sub> into the reactor. Then the pressure of CO<sub>2</sub> was kept at 0.1 MPa using a balloon with CO<sub>2</sub>. The reactor was placed in a constant temperature and the reaction mixture was stirred for a desired time. After the reaction, the reactor was placed in ice water for 30 minutes and the reaction mixture was passed through a plug of silica gel. The crude mixture was purified via silica gel column chromatography (EtOAc:petroleum ether=1:15) to obtain the desired cyclic carbonate 4-chloromethyl-[1,3]dioxolan-2-one.

### 2.3 The procedures for reuse of the IL

Epichlorohydrin (2 mmol, 0.2403 g) and [DBUH]<sub>2</sub>[Cys] (0.5 mmol, 0.1557 g) were loaded into a 22 mL stainless-steel batch reactor equipped with a magnetic stirrer. The air in the reactor was removed

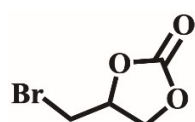
by blowing CO<sub>2</sub> into the reactor. Then the pressure of CO<sub>2</sub> was kept at 0.1 MPa using a balloon with CO<sub>2</sub>. The reaction was proceeded at 30 °C within 24 h. After the reaction, the product was extracted by diethyl ether (3 × 2 mL) and the yield was determined via <sup>1</sup>H NMR using DMF as the internal standard. The IL separated was used directly for the next run after being dried under vacuum at 70 °C for 12 h.

### 3. NMR data of products



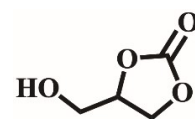
#### 4-Chloromethyl-[1,3]dioxolan-2-one

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 5.04 (d, *J* = 43.6 Hz, 1H), 4.57 (s, 1H), 4.25 (s, 1H), 3.96 (d, *J* = 3.3 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 154.96, 75.44, 67.36, 45.88.



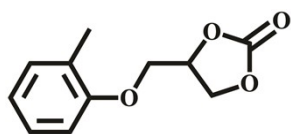
#### 4-Bromomethyl-[1,3]dioxolan-2-one

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 5.02 (d, *J* = 31.1 Hz, 1H), 4.56 (s, 1H), 4.17 (s, 1H), 3.81 (d, *J* = 14.9 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 154.83, 74.99, 68.44, 34.94.



#### 4-(hydroxymethyl)-1,3-dioxolan-2-one

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 5.12 (s, 1H), 4.76 (d, *J* = 3.0 Hz, 1H), 4.45 (t, *J* = 8.3 Hz, 1H), 4.31 – 4.23 (m, 1H), 3.61 (d, *J* = 9.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 155.67, 73.05, 66.37, 63.53.



#### 4-(*o*-tolylloxy)methyl-1,3-dioxolan-2-one

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 6.83 – 6.74 (m, 4H), 5.15 (s, 1H), 4.53 (d, *J* = 64.7 Hz, 2H), 4.20 (d, *J* = 41.5 Hz, 2H), 1.95 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 156.77, 156.36, 130.93, 127.43, 126.24, 121.03, 112.03, 75.27, 69.25, 66.74, 16.41.

#### 4. Table S1

Table S1 A comparison of the catalytic activity [DBUH]<sub>2</sub>[Cys] in this work and reported ILs.

Entry	Catalyst	T (°C)	P (MPa)	T (h)	Solvent	Yield (%)	Ref.
1	[DBUH][BO <sub>2</sub> ]	30	0.1	4	-	94	1
2	[P <sub>4444</sub> ][2-O]	30	0.1	20	-	90	2
3	[PAD][IDA]	65	1	12	-	95	3
4	[N <sub>4444</sub> ][His]	80	0.1	4.5	DMC	98	4
5	[Bmim][ASP]	130	0.1	12	-	98	5
6	[Bmim][Ala]	130	4	18	-	96	6
7	[DBUH][TA]	60	3	8	-	99	7
8	Ammonium betaine	100	1	24	-	99	8
9	[P <sub>8,8,8,1</sub> ][AcO]	100	0.1	23	-	75	9
10	[DMIm] <sub>2</sub> [(Me <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ]	100	3.5	1	-	94.4	10
11	Urea derivative based IL	130	1.5	2	-	97	11
12	[DBUH] <sub>3</sub> [NbO <sub>5</sub> ]	130	3	5	-	91.8	12
13	Betaine-based salt	140	0.8	8	-	96	13
14	[DBUH] <sub>2</sub> [Cys]	30	0.1	24	-	96	This work

#### References

1. Z. Wang, D. Li, S.Q. Chen, J. Y. Hu, Y. X. Gong, Y. F. Guo, T. L. Deng. *N. J. Chem.*, 2021, **45**, 4611;
2. G. Yuan, Y. Zhao, Y. Wu, R. Li, Y. Chen, D. Xu, Z. Liu. *Sci. China. Chem.*, 2017, **60**, 958;
3. Y. Zhou, W. Zhang, L. Ma, W. Jun. *Sustain. Chem. Eng.*, 2019, **7**, 938;
4. P. Kumar, M. Varyani, P. K. Khatri, S. Paul, S. L. Jain. *J. Ind. Eng. Chem.*, 2017, **49**, 152;
5. S. Yue, X. J. Hao, P. P. Wang, J. Li. *Mol. Catal.*, 2017, **433**, 420;
6. F. Wu, X. Y. Dou, L. N. He, C. X. Miao. *Lett. Org. Chem.*, 2010, **7**, 73;
7. C. Yang, M. Liu, J. Zhang, X. Wang, Y. Jiang, J. Sun. *Mol. Catal.*, 2018, **450**, 39;
8. M. Liu, L. Liang, X. Li, X. Gao, J. Sun. *Green Chem.*, 2016, **18**, 2851;
9. M. Galvan, M. Selva, A. Perosa, M. Noè. *J. Asian. Org. Chem.*, 2014, **3**, 504;
10. J. K. Lee, Y. J. Kim, Y. S. Choi, H. Lee, J. S. Lee, J. Hong, E. K. Jeong, H. S. Kim, M. Cheong. *Appl. Catal. B-Environ.*, 2012, **111-112**, 621;
11. (a) R. L. Vekariya, *J. Mol. Liquids*, 2017, **227**, 44; (b) X. Kang, X. Sun, B. Han, *Adv. Mater.*, 2016, **28**, 1011; (c) J. P. Hallett, T. Welton. *Chem. Rev.*, 2011, **111**, 3508;
12. A. Chen, C. Chen, Y. Xiu, X. Liu, J. Chen, L. Guo, R. Zhang, Z. Hou. *Green Chem.*, 2015, **17**, 1842;
13. M. Alvaro, C. Baleizao, D. Das, E. Carbonell, H. García. *Catal.*, 2004, **228**, 254.