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Tetracarboxyl-Functionalized Ionic Liquid: Synthesis and Catalytic Properties

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Novel tetracarboxyl-functionalized 2,2'-biimidazolium-based ionic liquids (ILs) with different anions were synthesized in two steps from readily available and sustainable starting materials including ammonium acetate, glyoxal, and halogenated propionic acid. The functionalized IL exhibited higher catalytic activity towards the cycloaddition of CO_2 to terminal epoxides. With propylene oxide as a substrate, the optimum yield of propylene carbonate reached 82.7% at an initial CO_2 pressure of 2.0 MPa for 4 h at 140°C. Moreover, the functionalized IL catalyst displayed a high stability and can be reused for at least five cycles without obvious loss of catalytic activity. The results provide a simple and economical way to synthesize multi-functionalized imidazolium-based ILs with versatile potential applications.

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Introduction

In recent years, ionic liquids (ILs) have stood out in many fields especially in electrochemistry, adsorption, as solvents, and for catalysis.^[1] The biggest advantages of ionic liquids lie not only in the exhibited excellent properties such as non-volatility, high stability, ease of handling, but also in their infinite versatility, functionality, and potential applications.^[2] Ionic liquids have tens of thousands of species in theory, but only a few have been synthesized and studied.^[3] In addition, ionic liquids are not a panacea and specified ionic liquids only work in limited applications.^[4] Therefore, more functionalized ionic liquids need to be synthesized and explored in an efficient and economical way.

A number of mono- or dual functionalized ionic liquids, for example, with hydroxyl, thiol, amino, or carboxyl functionalities have been synthesized and widely applied in the field of chemistry over the last decade.^[5] Alkylation of nitrogencontaining compounds is the most common strategy to decorate the cation with reactive functionalities.^[6] The number of nitrogen atoms in the starting compounds determines the maximum number of introduced reactive groups. However, more functional groups often means higher activity and lower usage for various applications.^[7] Sun et al. reported dual carboxyl functionalized ionic liquids showed higher catalytic properties in the cycloaddition of CO₂ to epoxides.^[8] On the other hand, diquaternized 2,2'-biimidazole molecules have recently been efficiently synthesized, which provided an opportunity to synthesize tetra-functionalized ionic liquids.^[9] However, biimidazolium-based multifunctional ILs have been relatively rarely studied for their potential versatility, such as as a catalyst, as

media, or as an organic ligand.^[10] Therefore we explored the synthesis of tetracarboxyl-functionalized biimidazolium-based ILs and tested its catalytic properties in this work.

Herein, tetracarboxyl-functionalized biimidazolium-based ILs with different anions have been synthesized and their catalytic properties tested for the synthesis of cyclic carbonates from CO_2 and epoxides. The influence of the catalyst's structure and reaction conditions (temperature, reaction time, pressure, amount of catalyst) on the catalyst performance were systematically studied. A possible reaction mechanism was proposed.

Results and Discussion

Two tetracarboxyl-functionalized 2,2'-biimidazolium-based ILs with different anions have been synthesized in this study, which is outlined in Scheme 1. 2,2'-Biimidazole was first synthesized in one step in high yield using cheap substrates such as ammonium acetate and glyoxal. The 2,2'-biimidazole was then alkylated with halogenated propionic acid in the presence of KOH. The key to successful synthesis of two tetracarboxylfunctionalized 2,2'-biimidazolium dihalide was achieved by precisely controlling the pH during the synthesis. The structures of the compounds were confirmed by ¹H NMR spectroscopy and electrospray ionization-mass spectrometry (ESI-MS). The tetracarboxyl-functionalized 2,2'-biimidazolium dihalides were then tested as acidic catalysts for the coupling reaction of CO₂ and epoxide. The propylene carbonate yields were 80.8 and 82.7% for the tetracarboxyl-functionalized 2,2'-biimidazolium ILs with Cl⁻ and Br⁻ anions respectively, which is in agreement



Scheme 1. Synthesis of 1,3,1',3'-tetracarboxyl-2,2'-biimidazolium dihalide.



Fig. 1. Effect of initial CO₂ pressure on PC yield. Reaction conditions: PO (14.3 mmol), TCBM-Br (1.19 mol-%), 140°C, 4 h.

with the nucleophilicity of these anions tethered by the imidazolium cation. $\ensuremath{^{[11]}}$

The catalytic activity of 1,3,1',3'-tetracarboxyl-2,2'biimidazolium dibromide (TCBM-Br) for the cycloaddition of CO₂ and propylene oxide (PO) was further investigated. The effects of several important reaction parameters, such as temperature, pressure, reaction time, and catalyst loading on the yield of the propylene carbonates (PC) were studied by designing a series of single factor experiments.

Effect of Pressure

The effect of initial CO₂ pressure on the yield of propylene carbonates was carried out at 140°C with 14.3 mmol of PO and 1.19 mol-% catalyst loading of TCBM-Br for 4 h. The results are shown in Fig. 1. The yield of propylene carbonates first increased according with increasing CO₂ pressure from 1 to 2 MPa and then decreased at pressures greater than 2 MPa. The maximum yield obtained was 82.7 %, at 2 MPa. The existence of optimum CO_2 pressure can be explained from the coupling mechanism of CO_2 and epoxide,^[12] as shown in Scheme 2. After the formation of PO-IL hydrogen bonding complexes, the Br^{-} anion attacks the less sterically hindered β -carbon atom of the epoxide to afford an alkoxide anion. CO₂ insertion of the alkoxide anion intermediate and subsequent dehalogenation gives PC and regenerates the TCBM-Br catalyst. As shown in the reported reaction mechanism, the interaction between PO, CO₂, and catalyst all have an effect on the yield of the PC. Increasing the pressure over 2 MPa resulted in decreased catalyst activity.



Scheme 2. Proposed reaction mechanism for cycloaddition of epoxide and CO₂ catalyzed by TCBM-X.



Fig. 2. Effect of reaction time on PC yield. Reaction conditions: PO (14.3 mmol), TCBM-Br (1.19 mol-%), 140°C, 2 MPa.

Effect of Reaction Time

The effect of reaction time on the carbonate yield was examined at 2 MPa with a catalyst loading of 1.19 mol-% at 140°C (Fig. 2). As reaction time is increased from 1 to 4 h, the yield of the propylene carbonate increased from 68.3 to 82.7%. The PC yield improved to 83.6% when the reaction time was further prolonged to 5 h. Therefore, the optimal reaction time was 4 h from a practical standpoint.



Fig. 3. Effect of temperature on PC yield. Reaction conditions: PO (14.3 mmol), TCBM-Br (1.19 mol-%), 2 MPa, 4 h.



Fig. 4. Effect of catalyst loading on PC yield. Reaction conditions: PO (14.3 mmol), 2 MPa, 140°C, 4 h.

Effect of Temperature

The influence of temperature on the PC yield is shown in Fig. 3. It is noted that temperature has a greater influence on the catalytic activity of TCBM-Br. When the reaction temperature is increased from 100 to 140°C, the yield of PC increased from 55.0 to 82.7%. When the temperature is increased to 160°C, the PC yield reached 89.2%. However, characterization of the products via ESI-MS demonstrated that after completion of the reaction, the catalyst may have changed into an acid anhydride. Thus, 140°C was chosen as the most suitable temperature.

Effect of Catalyst Loading

The experimental result of catalyst usage demonstrated that the tetracarboxyl-functionalized ILs TCBM-Br can efficiently catalyze PC production from CO_2 and PO at low catalyst loading (0.47 mol-%). As catalyst usage increases, the PC yield first increased slowly and reached the optimum in the range of 1.19 to 2.4 mol-% catalyst loading. There was little change in PC yield with a 1.19 to 2.4 mol-% catalyst was the most suitable catalyst loading (Fig. 4). Therefore, 1.19 mol-% of catalyst was the most suitable catalyst loading in terms of turnover number. The PC yield decreased



Fig. 5. Recycling test of TCBM-Br. Reaction conditions: PO (14.3 mmol), TCBM-Br (0.1 g), initial CO₂ pressure 2 MPa, 140° C, 4 h.

sharply when the catalyst loading is greater than 2.4 mol-%, possibly due to additional side effects.

Reusability of the Catalyst

Stability and recyclability of TCBM-Br were examined by recycle experiments at 140°C, 2.0 MPa for 4 h. Typically, the catalyst was recycled by distilling out the PC product and directly reused for the next cycle. The results are displayed in Fig. 5. There was only a slight decrease in its catalytic activity, after five consecutive cycles, which showed that TCBM-Br exhibited good stability.

Coupling Carbon Dioxide and Other Epoxides

In order to explore the potential applications of the ILs, various epoxides were coupled with CO_2 using TCBM-Br catalyst under the optimized reaction conditions. The results are summarized in Table 1. It can be seen that the TCBM-Br catalyst exhibited a high activity towards a variety of aliphatic and aromatic epoxides (entries 1 to 5). The glycidyl phenyl ether was the most preferred substrate due to its good electron-withdrawing capability as the carbon atoms on the epoxide ring can be easily attacked by the halide. Very low yield of *cis*-hexahydrobenzo [1,3]-dioxolan-2-one^[8] was obtained for the cyclohexene oxide (entry 5) due to its higher hindrance originating from the two fused rings.^[13]

Conclusions

Tetracarboxyl-functionalized 2,2'-biimidazolium-based ILs with different anions were synthesized and used as catalysts for the cycloaddition of CO₂ to epoxides without the use of a co-catalyst and solvent. TCBM-Br exhibited high catalytic activities towards a variety of terminal epoxides. With PO as a substrate, PC yield of 89.2 % was obtained (1.19 mol-% catalyst at initial CO₂ pressure of 2.0 MPa for 4 h at 160°C), and 78.7 % yield was achieved with 0.47 mol-% catalyst at 140°C. Compared with the reported carboxyl-functionalized imidazolium-based ILs, our tetracarboxyl-functionalized ILs showed relatively lower catalytic activities at high loading but high activity at low catalyst loadings for the cycloaddition of CO₂ to epoxide. In addition, the TCBM-Br catalyst showed good stability without obvious loss in catalytic activity after five cycles.

 Table 1. Coupling of CO2 and various epoxides with TCBM-Br

 Reaction conditions: epoxide (14.3 mmol), catalyst (TCBM-Br, 0.1 g), 140°C, 2 MPa, 4 h.

Entry	Epoxide	Product	Yield [%]
1	°>		82.7
2		CH ₂ CI	73.0
3	O ↓>──Ph	0 0 Ph	87.7
4			90.5
5	$\bigcirc \circ$		11.3

Our findings provide a simple and cheap way to synthesize multi-functionalized ionic liquids with potential applications as catalysts, media, and organic ligands amongst others.

Experimental

Materials

CO₂ was supplied by Beijing Bei Temperature Gas Factory with a purity of 99.99%. Ammonium acetate, glyoxal, chloropropionic acid, and bromopropionic acid were obtained from Sinopharm Chemical Reagent Co., Ltd. Other reagents and solvents were bought from Beijing Chemical Works. All the above reagents were used as received unless otherwise noted. NMR spectra were recorded on a JEOL ECA-600 spectrometer. ESI-MS analyses were performed on a Bruker micro TOF-QII spectrometer.

Synthesis of 1,3,1',3'-Tetracarboxyl-2,2'-biimidazolium dihalide (in Scheme 1)

2,2'-Biimidazole

2,2'-Biimidazole was synthesized according to a reported procedure.^[9] In a typical reaction, aqueous glyoxal (23.0 mL, 40 wt-%) was added dropwise to a vigorously stirred solution of ammonium acetate (70.0 g) and H₂O (13.0 mL) at 40°C over a period of 4 h. After completion of the reaction, the crude product (4.44 g, 54.15%) was filtered and washed several times with water and acetone. The product was then further purified by liquid anti-solvent crystallization and dried overnight under vacuum before use and analysis. $\delta_{\rm H}$ ([D₆]DMSO) 7.08 (d, 4H), 12.65 (s, 2H). *m/z* (ESI-MS) 135.0751; calcd for C₆H₇N₄⁺, 135.0609 [M]⁺.

1,3,1',3'-Tetracarboxyl-2,2'-biimidazolium dichloride (TCBM-Cl)

2,2'-Biimidazole (0.4 g, 3 mmol) was added to a 100 mL three-necked flask charged with 3-chloropropionic acid (1.3 g, 12 mmol), KOH (0.336 g, 6 mmol), and water (10 mL) at room temperature. The reaction mixture was adjusted to a pH level of 10 to 12 with a 5 M aqueous solution of KOH and the reaction mixture was heated slowly to reflux for 8 h. The product mixture was acidified to pH = 2-3 with hydrochloric acid (1 M), and then concentrated under reduced pressure. The concentrated mixture was diluted with ethanol and filtered to remove the undissolved salt. The final filtrate was concentrated to give a brown viscous liquid (85.1 % yield). The product was dried overnight under vacuum before use and analysis. $\delta_{\rm H}$ (D₂O) 2.51 (t, *J* 6.0, 8H), 3.74 (t, *J* 6.0, 8H), 7.40 (s, 4H). *m/z* (ESI-MS, +ve mode) 423.1565 [M – H]⁺; calcd for C₁₈H₂₄N₄O²⁺₈, 424.1589.

1,3,1',3'-Tetracarboxyl-2,2'-biimidazolium dibromide (TCBM-Br)

1,3,1',3'-Tetracarboxyl-2,2'-biimidazolium dibromide was prepared in a similar process to TCBM-Cl. Brown viscous liquid was obtained (88.2 % yield). $\delta_{\rm H}$ (D₂O) 2.37 (t, *J* 6.0, 8H), 3.62 (t, *J* 6.0, 8H), 7.28 (s, 4H). *m/z* (ESI-MS, +ve mode) 423.1389 [M - H]⁺; calcd for C₁₈H₂₄N₄O₈²⁺, 424.1589. *m/z* (ESI-MS, -ve mode) 80.9157; calcd for Br⁻, 80.92.

Procedure for Cycloaddition of CO₂ and Epoxides

The catalytic properties of tetracarboxyl-functionalized 2,2'biimidazolium-based ILs for the cycloaddition of CO_2 and epoxides were investigated in a 15 mL stainless steel autoclave equipped with a magnetic stirrer. In a typical procedure, 1.19 mol-% catalyst (0.1 g), epoxide (1.0 mL), and an appropriate amount of biphenyl (as an internal standard for gas chromatography analysis) were successively charged into the reactor. The reactor was filled with a given initial CO_2 pressure and was heated to the desired temperature. After the reaction was complete, the reactor was cooled to 0°C in an ice-water bath, and de-pressurized by slowly releasing the remaining CO_2 . The products were quantitatively analyzed by a GC-SP6890 (Rainbow Chemical Instrument Co., Ltd, Shandong Lunan) equipped with a DB-wax column. More details are shown in our group's previous work.^[14]

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References

- [1] (a) M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* 2009, *8*, 621. doi:10.1038/NMAT2448
 (b) D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem. Int. Ed.* 2010, *49*, 6058. doi:10.1002/ANIE.201000431
 (c) R. Sheldon, *Chem. Commun.* 2001, 2399. doi:10.1039/B107270F
 (d) T. Welton, *Chem. Rev.* 1999, *99*, 2071. doi:10.1021/CR980032T
 (e) Z.-Z. Yang, Y.-N. Zhao, L.-N. He, *RSC Adv.* 2011, *1*, 545. doi:10.1039/C1RA00307K
- [2] Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, Angew. Chem. Int. Ed. 2007, 46, 7255. doi:10.1002/ANIE.200701467

- [3] G. A. Baker, S. N. Baker, S. Pandey, F. V. Bright, *Analyst* 2005, 130, 800. doi:10.1039/B500865B
- [4] Y. L. Gu, Q. H. Zhang, Z. Y. Duan, J. Zhang, S. G. Zhang, Y. Q. Deng, J. Org. Chem. 2005, 70, 7376. doi:10.1021/JO0508021
- [5] (a) K. S. Kim, D. Demberelnyamba, H. Lee, *Langmuir* 2004, 20, 556. doi:10.1021/LA0355848
 (b) X.-L. Meng, Y. Nie, J. Sun, W.-G. Cheng, J.-Q. Wang, H.-Y. He, S.-J. Zhang, *Green Chem.* 2014, 16, 2771. doi:10.1039/C3GC42331J
 (c) J. Sun, S. Zhang, W. Cheng, J. Ren, *Tetrahedron Lett.* 2008, 49, 3588. doi:10.1016/J.TETLET.2008.04.022
 (d) L.-F. Xiao, D.-W. Lv, D. Su, W. Wu, H.-F. Li, *J. Clean. Prod.* 2014, 67, 285. doi:10.1016/J.JCLEPRO.2013.12.031
- [6] H. Xue, Y. Gao, B. Twamley, J. M. Shreeve, *Chem. Mater.* 2005, 17, 191. doi:10.1021/CM048864X
- [7] W. Wu, X. Sheng, Y. Qin, L. Qiao, Y. Miao, X. Wang, F. Wang, J. Polym. Sci., Part A: Polym. Chem. 2014, 52, 2346. doi:10.1002/POLA. 27247
- [8] J. Sun, L.-J. Han, W.-G. Cheng, J.-Q. Wang, X.-P. Zhang, S.-J. Zhang, *ChemSusChem* 2011, 4, 502. doi:10.1002/CSSC.201000305

- J. C. Xiao, J. M. Shreeve, J. Org. Chem. 2005, 70, 3072. doi:10.1021/ JO0501083
- [10] (a) Z. Fei, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* 2006, *45*, 6331. doi:10.1021/IC060297N
 (b) W. Shen, L.-M. Wang, H. Tian, J. Tang, J.-J. Yu, *J. Fluor. Chem.* 2009, *130*, 522. doi:10.1016/J.JFLUCHEM.2009.02.014
- [11] J. Sun, L. Wang, S. Zhang, Z. Li, X. Zhang, W. Dai, R. Mori, J. Mol. Catal. A: Chem. 2006, 256, 295. doi:10.1016/J.MOLCATA.2006.05.004
- [12] (a) T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, *Chem. Commun.* 2006, 1664. doi:10.1039/B517140G
 (b) L. Han, H.-J. Choi, S.-J. Choi, B. Liu, D.-W. Park, *Green Chem.* 2011, *13*, 1023. doi:10.1039/C0GC00612B
- [13] Y. Zhou, S. Hu, X. Ma, S. Liang, T. Jiang, B. Han, J. Mol. Catal. A: Chem. 2008, 284, 52. doi:10.1016/J.MOLCATA.2008.01.010
- [14] X.-L. Meng, Y. Nie, J. Sun, W.-G. Cheng, J.-Q. Wang, H.-Y. He, S.-J. Zhang, *Green Chem.* 2014, 16, 2771.