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Efficient fixation of CO₂ into organic carbonates catalyzed by 2-hydroxymethyl-functionalized ionic liquids[†]

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Several novel 2-hydroxymethyl-functionalized ILs act as the catalysts for synthesis of cyclic carbonates from CO_2 and epoxides without the use of any co-catalysts or organic solvent. Moreover, the 2-hydroxymethyl-functionalized ILs were compatible with base, which combined with K_2CO_3 were used as effective catalytic system for green synthesis of dimethyl carbonate from CO_2 *via* ethylene carbonate without catalyst separation. Additionally, the mechanistic details of the fixation of CO_2 into cyclic carbonate catalyzed by 2-hydroxymethyl-functionalized ILs were also elucidated by density functional theory. The process reported here represents a simple, ecologically safer, cost-effective and energy-saving route to organic carbonates from CO_2 .

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1. Introduction

Carbon dioxide fixation, which is universally defined as conversion of this greenhouse gas into value-added chemicals, is presently receiving enormous and increasing attention from the chemical community.^{1,2} In particular, the chemical fixation of CO_2 into cyclic carbonates has attracted extensive attention in both academia and industry (Scheme 1),^{2,3} These carbonates have wide applications as polar aprotic solvents, electrolytic



Scheme 1 Fixation of CO_2 with epoxides by OH-functionalized ionic liquids.

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† Electronic supplementary information (ESI) available: General experimental and DFT computational methods, ESI figures, characterization of cyclic carbonates, and also cartesian coordinates for the optimized geometries of all intermediates and transition states. See DOI: 10.1039/c3ra45918g elements in lithium secondary batteries, intermediates for organic synthesis and ingredients for fine chemicals.⁴

HEMISTRY

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Various homogeneous catalysts have been used for the production of cyclic carbonates from CO₂ and epoxides including metal oxides,5 alkali metal salts,6 quaternary onium salts,7 ionic liquids (ILs),8 transition metal complexes9 and functional organic polymers.10 Among these, ILs are demonstrated as effective and environmental benign catalysts for fixation of CO2 with epoxides.11 Recently, 1-hydroxyl and carboxyl-functionalized ILs are observed more efficient than conventional ones.12 These newly prepared catalysts involving the hydroxyl or carboxyl-functionalized groups located at nitrogen of imidazolium rings are generally thought not very stable especially in the presence of base because of the reactive C(2)-H in imidazolium.13 The products of cyclic carbonates are generally used to produce glycols and dialkyl carbonates, which commonly catalyzed by base. The two processes are not compatible. Therefore, the investigation and developing basestable ILs used for two-step is highly desirable. Additionally, as far as we known, the mechanism details and the role of hydrogen bond for hydroxyl-functionalized ionic liquids as catalysts for fixation of CO₂ with epoxides are not very clear.

As a point of the framework of our continuous efforts on utilization of hydrogen bond-functionalized ionic liquids as catalysts for the conversion of CO_2 into organic carbonates,^{12d,e,13,14} In this work, we synthesized a series of novel base-stable 2-hydroxymethyl-functionalized ILs by introducing hydroxymethyl group to the reactive C(2)–H of imidazolium and investigated their catalytic behaviour in the synthesis of cyclic carbonates from CO_2 and epoxides without any co-catalyst or organic solvent (Scheme 2). The mechanistic details of the fixation of CO_2 with epoxide catalyzed by 2-hydroxymethyl-functionalized ILs were elucidated



by DFT. Moreover, the functionalized ILs combined with K_2CO_3 were effective for two-step green synthesis of dimethyl carbonate (DMC) from CO_2 , ethylene oxide (EO) and methanol without catalyst separation.

2. Results and discussion

2.1 Effect of catalysts

The reaction of propylene oxide (PO) with CO_2 to produce propylene carbonate (PC) was chosen as the model to test the catalytic activities of various 2-hydroxymethyl-functionalized ILs (Scheme 2), and the results were summarized in Table 1. It can be seen that 2-hydroxymethyl-functionalized ILs employed exhibited high activity and selectivity (Table 1, entries 1–7), especially the IL5 (entry 5). In addition, the catalytic efficiency decreased in the order of $Br^- > Cl^-$ in the case of the same cation (entry 1 *vs.* 2, 4 *vs.* 5), and the alkyl length of cation of ILs had a little influence on catalytic activity (entries 2, 3, 5–7). In addition, the similar activity can be found for 1-hydroxyethyl-3methyl imidazolium bromide (IL8) (entry 8 *vs.* 3), which indicated that the position of hydroxyl group has little effect on catalytic activity. The traditional ionic liquids (BmimCl, BmimBr, EmimBr, BmimBF₄ and BmimPF₆) were not efficient

Table 1	2-Hydroxymethyl-functionalized I	Ls screening for fixation CO2ª
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Entry	Cat	PO Conv $(\%)^b$	PC vield $(\%)^{l}$
Enery	Out.	10 0011. (70)	1 0 yield (70)
1	IL1	83	83
2	IL2	86	86
3	IL3	91	90
4	IL4	84	84
5	IL5	92	92
6	IL6	90	90
7	IL7	90	89
8	IL8	91	90
9	BmimCl	59	59
10	BmimBr	74	73
11	EmimBr	70	70
12	$BmimBF_4$	Trace	/
13	BmimBF ₆	Trace	/

^{*a*} Reaction condition: PO (14.3 mmol), IL (1.0 mol %), CO₂ pressure (2.0 MPa), reaction time (1 h), temperature (110 °C). ^{*b*} Yield and conversion were determined by GC using biphenyl as the internal standard. Every experiment was repeated 3 times.

for the synthesis of cyclic carbonate under the same condition (entries 9–13), although they have been observed activity with high temperature or long reaction time.

2.2 Reaction mechanism

We next studied the mechanism details of fixation of CO_2 with epoxide by 2-hydroxymethyl-functionalized ionic liquids and the role of hydrogen bond through DFT study, and all calculations were carried out by use of the B3PW91 functional with the 6-311++G (d, p) basis set as implemented in Gaussian 09 program package. For comparing the positive function of hydroxymethyl group, we investigated the mechanisms for fixation of CO_2 with EO catalyzed by 1-ethyl-3-methylimidazolium bromide (EmimBr) and IL3 respectively (Fig. 1 and 2). The results demonstrated that the hydrogen bond between 2-hydroxymethyl-functionalized ILs and EO indeed played an important role in all the intermediates and transition states, which possibly promoted the reaction (Fig. 3).

In the case of EmimBr, the reactive C(2)–H in imidazolium was critical for the activity through the weak hydrogen bond interaction with the reactant and intermediates (Fig. 1). The fixation of CO_2 with EO proceeded catalyzed by 2-hydroxymethyl-1-methyl-3-ethylimidazole bromide (IL3) with much less barrier compared to EmimBr-catalyzed process (Fig. 2) because of stronger hydrogen bond interaction (Table 2). The notable activity for IL3 possibly originated from the cooperative actions of hydrogen bond and Br⁻, which helped to activate and open the rings of epoxides (Fig. 2, TS_{f-g}), and also more easily stabilize



Fig. 1 Optimized geometries for the intermediates and transition states for fixation of CO₂ with EO catalyzed by 1-ethyl-3-methyl-imidazolium bromide. H: white, C: gray, N: blue, O: red, Br: dark red. Bond lengths and distances in Å. See the ESI† for computational details.



Fig. 2 Optimized geometries for the intermediates and transition states. H: white, C: gray, N: blue, O: red, Br: dark red. Bond lengths and distances in Å. See the ESI† for computational details.



Fig. 3 Relative energies for activation of CO₂ by the values refer to relative energies at the B3PW91/6-311++G (d, p) level.

Table 2 Hydrogen bond distances (Å) between EmimBr or IL3 and EO

ILs	a/f	Ts_{a-b}/Ts_{f-g}	b/g	$\mathrm{Ts}_{c-d}/\mathrm{Ts}_{h-i}$	d/i	Ts _{d-e} /Ts _{i-j}
EmimBr TS3	2.049 1.792	1.741 1.564	1.929 1.551	1.438 1.268	1.648 1.570	1.781 1.706

the intermediates (Fig. 2, f–g) and transition states (Fig. 2, TS_{f-g} , TS_{h-i} , TS_{i-j}). In addition, the different chain length had little influence on the relative activation energy of the rate-determining step (Fig. S1 and S2†), it is found that the barrier of each elementary step slightly decreased with enlarging the chain length (Table S1†).



Scheme 3 The proposed mechanism for fixation of CO $_2$ with EO into EC catalyzed by 2-hydroxymethyl-1-methyl-3-ethylimidazole bromide.

Based on the published reports^{11,14b,15} and the results in this work, an anion–cation cooperative catalysis mechanism for conversion of CO₂ with EO was proposed (Scheme 3 and Fig. 2). First, the epoxide was activated by hydrogen bond interaction (f), which made the ring opening easier. Subsequently, the ring of the epoxide opened *via* nucleophilic attack by Br⁻ through TS_{f-g} , and then CO₂ inserted through TS_{h-i} (h). Consequent cyclization *via* an intermolecular nucleophilic attack through TS_{i-g} led to the EC and the regeneration of the catalyst. The hydrogen bond in this process helped to stabilize the intermediates and transition states, which promoted the fixation of CO₂ with epoxide.

2.3 Effect of other reaction parameters

We investigated influence of the reaction parameters on fixation of CO_2 with PO into PC using IL5 as the catalyst. The reaction temperature had a remarkable effect on the catalytic activity of this catalyst. The yield of PC significantly increased with enhancement of reaction temperature (Fig. 4). The yield of PC



Fig. 4 Dependence of the PC yield and selectivity on reaction temperature. *Reaction condition*: PO (14.3 mmol), Catalyst (IL5, 1.0 mol %), reaction time (1 h), pressure (2 MPa).



Fig. 5 Dependence of the PC yield and selectivity on reaction pressure. *Reaction condition*: PO (14.3 mmol), catalyst (IL5, 1.0 mol %), reaction time (1 h), temperature (120 $^{\circ}$ C).

was 10% at 60 $^\circ \rm C,$ and increased to near 100% at 150 $^\circ \rm C,$ whereas the selectivity was almost invariable.

The effect of CO_2 pressure on the yield of PC in the presence of catalyst IL5 was also studied. As depicted in Fig. 5, the pressure had a significant effect on the yield of PC upon variation of the CO_2 pressure from 0.5 to 2.0 MPa, whereas the yield changed only slightly in the range 2.0–3.5 MPa. This could be explained by the pressure effect on the concentrations of CO_2 and epoxides in the two phases.¹⁶ Since PO was in its liquid form under the adopted reaction conditions, and when the reaction was carried out in a low-pressure region of 0.5–2.0 MPa, higher CO_2 pressure enhanced PC yield due to the higher CO_2 concentration in the liquid phase of the reaction system.

Additionally, the influence of the reaction time on the reaction was investigated under identical reaction conditions. Fig. 6 showed the dependence of the PC yield on reaction time at 130 °C and 2.0 MPa CO_2 . It can be seen that the yield of PC increased rapidly with the reaction time and that nearly all the PO could be converted within 2.5 h with near 100% selectivity of PC.



Fig. 6 Dependence of the PC yield and selectivity on reaction time. *Reaction condition*: PO (14.3 mmol), Catalyst (IL5, 1.0 mol %), pressure (2 MPa), temperature (120 °C).



Fig. 7 Catalyst recycling of IL5 for cycloaddition reaction. *Reaction condition*: PO (14.3 mmol), Catalyst (IL5, 1.0 mol %), pressure (2 MPa), temperature (120 °C), time (1 h).

2.4 Catalyst recycling

A series of catalytic recycles were run to investigate the reusability of the catalyst under the optimized conditions. In each cycle, the catalysts were recovered by distillation and reused for subsequent reactions. As shown in Fig. 7, the yields and selectivities of the products obtained from the second to fifth runs were similar to those obtained with the fresh catalyst. After fivetimes reuse, a 97% PO conversion with 99% PC selectivity could also be obtained using this optimal catalyst, indicating its stable activity. The thermo-gravimetric analysis of also proved that the IL5 was thermally stable up to 250 °C before and after fifth runs in the reaction (Fig. S3†).

2.5 Catalytic activity towards other epoxides

Consequently, we investigate the scope and activity of substrates, and the fixation of CO_2 with other epoxides were performed in the presence of 1 mol% IL5. As shown in Table 3, the catalytic system was found to be effective for a variety of terminal epoxides (entries 1–8). Moreover, the activity of epoxides decreased as the alkyl length increasing (entries 1–4). The styrene oxide was observed relative lower substrate activity, and needs longer reaction time to achieve high yield (entries 6). To further exemplify the catalytic potential of 2-hydroxymethyl-functionalized ionic liquids, disubstituted epoxide was also tested (entry 8). Cyclohexene oxide and showed lower activity, and long reaction time was needed, which may have resulted from the steric hindrance and electronic effects.

2.6 Two-steps synthesis of dimethyl carbonate from EO and CO₂ and methanol

We previously found the binary catalysts of imidazolium-type ILs and alkali metals (KOH or K_2CO_3) were shown low activity for two-steps synthesis of dimethyl carbonate even much lower than single alkali metal because the reactive C(2)–H in imidazolium decreased the basicity of alkali metal and influenced catalytic acivity.^{13a} we reasoned that the 2-hydroxymethyl-functionalized ILs combined with K_2CO_3 would be active for

Table 3 Substrate scope^a



^{*a*} *Reaction condition*: epoxides (14.3 mmol), catalyst (IL5, 1.0 mol%), CO₂ pressure (2.0 MPa), temperature (120 °C). ^{*b*} Yield and conversion were determined by GC, Every experiment was repeated 3 times.

two-steps synthesis of dimethyl carbonate, and create a powerful catalytic system with high potential for conversion of CO_2 into dimethly carbonate. As expected, the 2-hydroxymethylfunctionalized ILs combined with K_2CO_3 were observed high activity for synthesis of dimethyl carbonate from CO_2 and ethylene oxide and methanol without catalyst separation (Scheme 4). 99.9% yield of EC was obtained for the cycloaddition reaction (Step 1), and the transesterification reaction was observed 90% conversion of EC and 100% selectivity of DMC without catalyst separation (Step 2). In the transesterification process, the K_2CO_3 was the active catalyst.^{13a}

Subsequently, a series of catalytic cycles were conducted to study the constancy of the catalysts activity and recycle for the two-step synthesis of dimethyl carbonate from CO_2 *via* EC. In





Fig. 8 Catalyst recycling for fixation of CO₂ with EO. Reaction condition: EO (25 mmol), catalyst ($IL5/K_2CO_3$, 1.0/0.5 mol%), CO₂ pressure (2.0 MPa), temperature (120 °C), time (1 h).

each cycle, the reaction of fixation of CO_2 with epoxide was first carried out in the presence of $IL5/K_2CO_3$, when the reaction finished, the CH_3OH was added to the reaction mixture for transesterification reaction without separation of catalysts. After the two-step process, the catalysts were recovered *via* distillation, and then used for next cycle. The results illustrated in Fig. 8 and 9 showed that the catalysts could be reusable for at least up to 6 times without loss in activity, while the yield of the product remained the same. Therefore, the recyclability of the



Fig. 9 Catalyst recycling for transesterification reaction. Reaction condition: CH_3OH (250 mol), temperature (60 °C), time (60 min).

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catalysts indicated the 2-hydroxymethyl-functionalized ILs were compatible with base. The water content of IL5 was below 50 ppm and the presence of the OH group on the side chain of the ionic liquid makes the presence of water not necessary, which made the process economically and potentially viable for commercial applications.

3. Experimental section

3.1 Materials

Carbon dioxide with a purity of 99.99% was provided by a commercial source. Paraformaldehyde was purchased from Shanghai Chemical Reagent Company. Halogenated hydrocarbons and epoxides were brought from Aladdin Reagent Co. and other organic and inorganic reagents were purchased from J&KCHEMICA without further purification.

3.2 Synthesis of imidazolium-based ILs

Synthesis of 2-hydroxymethyl-1-methylimidazole: *N*-methylimidazole (10.0 g, 0.12 mol) and paraformaldehyde (10.0 g, 0.33 mol) were refluxed at 160 °C for 1 h. The brown solution was dissolved in methanol (20 mL) and cooled to -18 °C in refrigerator and triturated to precipitate a brown solid that was filtered off. The product was recrystallized from methanol/petrol ether to give 2-hydroxymethyl-1-methylimidazole (8.10 g, 0.07 mol, 58%) as a light brown solid. The NMR data are as follow: ¹H NMR (DMSO-d₆) δ (ppm): 3.64 (s, 3H), 4.46 (s, 2H), 5.35 (br s, 1H), 6.75 (s, 1H), 7.06 (s, 1H); ¹³C NMR (DMSO-d₆) δ (ppm): 147.8, 126.6, 123.4, 56.1, 32.9.

2-Hydroxymethyl-1-methylimidazole (3.40 g, 0.03 mol), n-butyl bromide (8.22 g, 0.06 mol) and THF (30 mL) were added to a 100 mL three-necked flask equipped with a magnetic stirrer. The mixture was heated at reflux for 24 h in an oil bath at 70 °C with stirring. Then, the reaction mixture was cooled down to room temperature. The top phase was poured out, and the light yellow liquid was washed three times with ethyl acetate and then dried at 60 °C for 12 h under vacuum. Finally, yellow liquid 2-hydroxymethyl-1-methyl-3-n-buthylimidazole bromide (5.03 g, 0.02 mol, 67%) was obtained. The synthesis of the other 2-hydroxymethyl-functionalized ionic liquids was similar with this procedure. The NMR data are as follow: 2-hydroxymethyl-1methylimidazole hydrochloride (IL1), ¹H NMR (DMSO-d₆) δ(ppm): 3.79 (s, 3H), 4.82 (s, 2H), 6.15 (br s, 1H), 7.59 (s, 1H), 7.70 (s, 1H) 14.01 (br s, 1H); 13 C NMR (DMSO-d₆) δ (ppm): 147.6, 125.5, 122.9, 56.2, 32.8. Anal. calcd: C, 40.42; H, 6.10; N, 18.85. Found: C, 40.40; H, 6.09; N, 18.80%. 2-Hydroxymethyl-1-methylimidazole hydrobromide (IL2), ¹H NMR (DMSO-d₆) δ (ppm): 3.80 (s, 3H), 4.79 (s, 2H), 6.17 (br s, 1H), 7.60 (s, 1H), 7.68 (s, 1H) 14.21(br s, 1H); ¹³C NMR (DMSO-d₆) δ (ppm): 147.9, 125.7, 123.6, 56.4, 32.3. Anal. calcd: C, 31.11; H, 4.70; N, 14.51. Found: C, 30.06; H, 4.66; N, 14.48%. 2-Hydroxymethyl-1-methyl-3-ethylimidazole bromide (IL3), ¹H NMR (DMSO-d₆) δ (ppm): 1.40 (t, 3H), 4.27 (q, 2H), 3.87 (s, 3H), 4.78 (d, 2H), 6.01 (br s, 1H), 7.74 (s, 1H), 7.80 (s, 1H); 13 C-NMR (DMSO-d₆) δ (ppm): 145.3, 123.7, 121.6, 50.9, 43.7, 35.5, 16.0. Anal. calcd: C, 38.03; H, 5.93; N, 12.67%. Found: C, 38.00; H, 5.89; N, 12.66. 2-Hydroxymethyl-

1-methyl-3-n-buthylimidazole chloride (IL4), ¹H-NMR (DMSOd₆) δ(ppm): 0.90 (t, 3H), 1.30 (m, 2H), 1.73 (m, 2H), 3.92 (s, 3H), 4.21 (t, 2H), 4.78 (d, 2H), 6.00 (br s, 1H), 7.73 (s, 1H), 7.79 (s, 1H); ¹³C-NMR (DMSO-d₆) δ(ppm): 145.3, 123.4, 122.0, 50.0, 48.2, 35.6, 32.4, 19.6, 13.8. Anal. calcd: C, 52.81; H, 8.37; N, 13.69%. Found: C, 52.76; H, 8.33; N, 13.62. 2-Hydroxymethyl-1-methyl-3*n*-buthylimidazole bromide (**IL5**), ¹H-NMR (DMSO-d₆) δ (ppm): 0.91 (t, 3H), 1.30 (m, 2H), 1.75 (m, 2H), 3.90 (s, 3H), 4.22 (t, 2H), 4.78 (d, 2H), 6.01 (br s, 1H), 7.75 (s, 1H), 7.80 (s, 1H); ¹³C-NMR $(DMSO-d_6) \delta$ (ppm): 145.5, 123.5, 122.1, 50.8, 48.1, 35.6, 32.3, 19.5, 13.9. Anal. calcd: C, 43.39; H, 6.88; N, 11.24%. Found: C, 43.35; H, 6.84; N, 11.20%. 2-Hydroxymethyl-1-methyl-3-n-hexylimidazole bromide (IL6), ¹H-NMR (DMSO-d₆) δ (ppm): 0.80 (t, 3H), 1.21 (m, 10H), 1.70 (m, 2H), 3.84 (s, 3H), 4.21 (t, 2H), 4.73 (d, 2H), 6.00 (br s, 1H), 7.76 (s, 1H), 7.81 (s, 1H); ¹³C-NMR $(DMSO-d_6) \delta$ (ppm): 145.5, 123.6, 122.1, 50.9, 48.3, 33.0, 31.2, 30.2, 25.8, 22.4, 14.3. Anal. calcd: C, 47.66; H, 7.64; N, 10.11%. Found: C, 47.62; H, 7.61; N, 10.08%. 2-Hydroxymethyl-1-methyl-3-*n*-octylimidazole bromide (**IL7**), ¹H-NMR (DMSO-d₆) δ (ppm): 0.80 (t, 3H),1.21 (m, 10H), 1.71 (m, 2H), 3.86 (s, 3H), 4.20 (t, 2H), 4.73 (d, 2H), 5.98 (br s, 1H), 7.74 (s, 1H), 7.79 (s, 1H); ¹³C-NMR (DMSO-d₆) δ (ppm): 145.5, 123.6, 122.1, 50.9, 48.3, 35.6, 33.1, 31.7, 30.3, 29.0, 26.2, 22.6, 14.4. Anal. calcd: C, 51.15; H, 8.25; N%, 9.18. Found: C, 51.13; H, 8.20; N, 9.14%.

3.3 Cycloaddition reaction procedure

All the coupling reactions were conducted in a 25 mL stainless steel reactor equipped with a magnetic stirrer and an automatic temperature control system. A typical reaction was carried out as follows: CO_2 (1.0 MPa) was added to a mixture of PO (1.0 mL, 14.3 mmol), and catalyst (1 mol%) at room temperature. Then, the temperature was raised to 120 °C with the addition of CO_2 from a reservoir tank to maintain a constant pressure (2.0 MPa). After the reaction had proceeded for 1.0 h, the reactor was cooled to an ambient temperature, The products were analyzed by GC using biphenyl as the internal standard and identified by GC-MS by comparing retention times and fragmentation patterns with authentic samples. The catalyst was recycled by vacuum distillation and dried under vacuum for the reused experiments.

3.4 Two-step synthesis of dimethyl carbonate from EO and CO₂ and methanol

The cycloaddition reaction of CO_2 with EO (Step 1) was conducted in a 25 mL stainless steel reactor equipped with a magnetic stirrer and automatic temperature control system. Typically, a typical reaction was carried out as follows: CO_2 (1.0 MPa) was added to a mixture of EO (25 mmol), IL5 (1 mol%) and K_2CO_3 (0.5%) at room temperature. Then, the temperature was raised to 120 °C with the addition of CO_2 from a reservoir tank to maintain a constant pressure (2.0 MPa). After the reaction had proceeded for 1.5 h, the reactor was cooled to 273 K in an ice water bath, and the remaining CO_2 was removed slowly. After the volatile organic products and starting materials were removed from the catalyst by distillation, the products were analyzed by GC. After that, 8 g CH₃OH was added to mixture and

transferred to a 50 mL flask equipped with a magnetic stirrer and automatic temperature control system for transesterification reaction (Step 2), then reacted at 60 °C for another 60 min. After the vessel was then cooled to room temperature, the catalysts were distilled from the mixture, and the products were analyzed by GC.

4. Conclusions

We have developed a series of novel base-stable 2-hydroxymethyl-functionalized ILs as catalysts for the synthesis of cyclic carbonates from CO2 and epoxides without the use of any co-catalyst or organic solvent. The effects of the types of cation and anion of 2-hydroxymethyl-functionalized ILs, and other reaction parameters on the reaction are investigated. In addition, the catalyst can be easily recovered by a distillation and reused over six times without obvious loss of its catalytic activity. The mechanistic details of the fixation of CO₂ with epoxide into cyclic carbonate catalyzed by 2-hydroxymethylfunctionalized ILs are elucidated by density functional theory. The results demonstrate the fixation of CO₂ catalyzed by 2hydroxymethyl-functionalized ILs with less barrier compared to process catalyzed by corresponding ILs without hydroxymethyl group. Moreover, the 2-hydroxymethyl-functionalized ILs combined with K₂CO₃ are effective for green synthesis of dimethyl carbonate from CO2, ethylene oxide and methanol without catalyst separation. The process reported here represents a simple, ecologically safer, cost-effective and energysaving route to organic carbonates from CO₂.

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