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Novel urea derivative based ionic liquids with dual-functions: CO₂ capture and conversion under metal- and solvent-free conditions

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Abstract: Several urea derivative based ionic liquids (UDILs) with superior thermal stability were facilely synthesized, structurally analyzed, and applied for CO₂ capture and conversion under mild conditions. These UDILs may reversibly capture CO₂ with double molar CO₂ absorption and exhibit outstanding catalytic activity for the conversion of CO₂ and various epoxides to cyclic carbonates under metal- and solvent-free conditions. The effects of reaction parameters on the catalytic activity for propylene carbonate (PC) synthesis from propylene oxide (PO) and CO₂ were investigated thoroughly. Since water is inevitably contained in real gases to be treated, the influence of water on CO₂ capture and conversion was also studied. Furthermore, the reaction kinetic studies were also made and a cation-anion synergistic catalytic mechanism was proposed. The single-component, metal-free, dual functional, stable, easily recyclable ionic liquids reported herein are interesting materials, displaying good performance for both CO₂ capture and conversion.

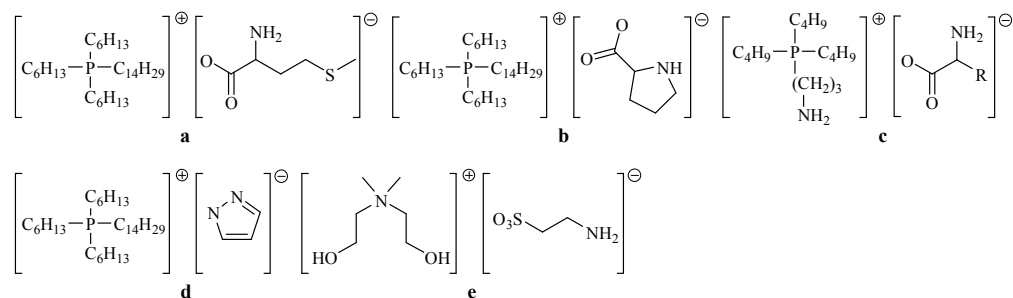
Keywords: Urea derivative ionic liquids; Carbon dioxide; Capture; Conversion; Cyclic carbonates

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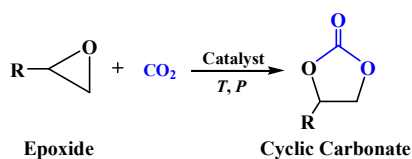
Introduction

Annually exceeding 13 gigatonnes carbon dioxide, generated from the combustion of fossil fuels for the production of heat and electricity, is a major contributor to climate change and ocean acidification.¹ It has been predicted by the International Panel for Climate Change (IPCC) that by the year 2100, the mean global temperature could rise by as much as 1.9 °C.² Therefore, a reduction of the greenhouse gas emissions that promote climate change is severely urgent globally. One protocol towards reducing CO₂ emissions is carbon capture and storage (CCS) which has the potential to reduce future world emissions from energy by 20%.³ However, one of the main problems associated with CCS is the requirement of a certain amount of energy consumption, which leads to further emission of CO₂.⁴ In 2002, Davis et al.⁵ first reported that the ionic liquid (IL) featuring a primary amine tethered to an imidazolium cation ([NH₂p-bim][BF₄]) could chemically react with CO₂ and reversibly captured 1 mol CO₂ per 2 mol of IL. Inspired by the concept of Davis, Hanioka et al.⁶ and Myers et al.⁷ investigated the capture of CO₂ from gas mixtures using supported IL membranes that contained amine functionality appended to the imidazolium cation. However, the synthesis of amine-functionalized ILs required more steps, including the complex removal of protecting group. Meanwhile, the resultant IL was extremely viscous at ambient temperature and became almost difficultly treated after reaction with CO₂. Brennecke et al.,⁸ Zhang,⁹ Dai,¹⁰ and Maier¹¹ developed the anion-functionalized ionic liquids (Scheme 1) for CO₂ capture. Although the CO₂ adsorption capacity by anion-functionalized ILs was significantly improved, the complex synthesis for the functionalized ILs and CO₂ capacity were not satisfactory.



Scheme 1 Typical structures of the anion-functionalized ILs.

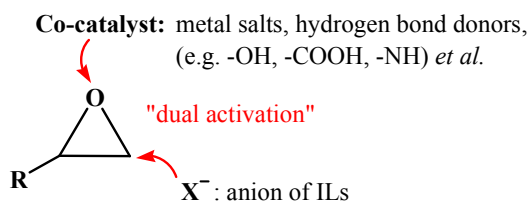
For another, CO₂ is the most environmentally abundant renewable C1 feedstock, and the chemical conversion of captured CO₂ into desirable, economically competitive products via carbon capture and utilization (CCU) technology is of great significance from viewpoints of both environmental protection and sustainable chemistry.^{12,13} One prominent product is the cyclic carbonate formed by 100% atom-economical coupling of CO₂ and epoxides (Scheme 2), which has wide potential applications ranging from the pharmaceutical to fine chemical industries.¹⁴



Scheme 2 Fixation of CO₂ with epoxides into cyclic carbonates.

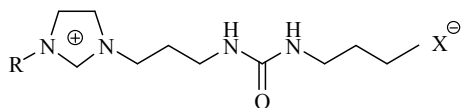
In the past few decades, a plethora of homogeneous and heterogeneous catalysts for this transformation have been developed successfully, such as metal oxides,¹⁵ alkali metal salts,¹⁶ metal-salen complexes,¹⁷ metal organic frameworks,¹⁸ ionic liquids (ILs)¹⁹ and functional polymers²⁰ etc. Among these, ILs are regarded as one of the most attractive alternative for the CO₂ cycloaddition reaction and CO₂ capture due to their unique properties and high CO₂ solubility. However, the neat ILs could not give the satisfactory adsorption capacity and catalytic activity under mild reactions,^{19d} the cocatalyst such as transition metal halides,²¹ hydrogen bond donors^{16b,22} is necessary to activate epoxide for facile epoxy-ring open thus improving their catalytic activity (Scheme 3). Alternatively, the ILs are functioned by active moieties of hydroxyl groups²³ or metal complexes^{17b,24} with dual activations for enhanced catalytic performance. To the best of our knowledge, most of the reported IL catalysts suffer from necessary existence of toxic metal, the need of the organic solvent, loss of cocatalyst during the recycling, and inexhaustive separation from the products. Hence, the development of metal- and/or cocatalyst- free, solvent absent and

easy-to-separation ILs with superior activity, is still highly desirable.



Scheme 3 The dual activations of epoxide with the IL/cocatalyst binary catalytic systems.

Taking this into account, we designed single-component urea derivative based ionic liquids (UDILs) catalysts with multi-secondary amine groups which have comparable hydrogen-bond donor capability and reactivity, and halide anion would nucleophilically attack the activated epoxide to open the epoxy-ring facilely (Scheme 4). The designed UDILs were theoretically to stimulate the above IL/cocatalyst binary catalysts and would be anticipated to exhibit the satisfactory activity for the CO₂ cycloaddition reaction. Moreover, the developed urea derivative based ionic liquids showed reversibly CO₂ capture ability with double molar CO₂ absorption, and outstanding catalytic activity for the CO₂ conversion to various cyclic carbonates under metal-, cocatalyst-, and solvent-free conditions was simultaneously gained. Furthermore, based on the kinetic studies and experimental results, the plausible reaction mechanism derived from the synergetic effects of hydrogen-bond donor cations and halide anions was proposed. Attractively, the UDILs could be easily recycled by simple extraction with diethyl ether, and avoided the complex distillation process which had a negative effect on the carbon footprint. Also the developed novel highly efficient and environmentally benign catalysts prevented the pollutions caused by toxic transition metal ions and organic solvents, providing green and promising alternative for practically effective CO₂ treatment.



UDIL-1: R = H; X = Cl, Br, I, HSO₄, NO₃, CH₃COO

UDIL-2: R = CH₂CH₂CH₂CH₃; X = Cl, Br, I

Scheme 4 Chemical structures of UDILs developed in this work.

Results and discussion

CO₂ absorption capacity

The effect of different UDILs on the capture of CO₂ was evaluated (Table 1). Most of these UDILs showed good to excellent CO₂ captures under 50 °C and 0.5 MPa CO₂ (entries 1-9). It was clear that the influence of different anions on CO₂ absorption was significant. For example, 1.42 mmol of CO₂ capture could be achieved over per mmol UDIL-1-Cl absorbent and UDIL-1-CH₃COO showed a higher CO₂ capacity of 1.81 mmol due to the relative lower viscosity caused by anion.²⁵ Hydrogen bonding of the Cl⁻ anion with the cation might increase the viscosity of UDIL-Cl and reduce the CO₂ physical solubility. According to the literature^{8b,26} as well as our results, with the same anion, increasing the alkyl chain length of cations resulted in a decrease in viscosity due to weaker hydrogen bonding with the anion and also in an increase of molar free volumes defined by Rebelo et al.^{26a}, which was favorable to the solubility of CO₂ species in the ILs. As increasing alkyl chain length in imidazolium cation ring, UDIL-2 possessed lower viscosity than UDIL-1, which thus enhanced the absorption of CO₂ on UDIL-2. Also the state of the IL after the CO₂ absorption was different between UDIL-1 and UDIL-2, which was liquid for the latter but gel for the former. Hence, UDIL-2 showed much higher capacity for CO₂ capture than UDIL-1 with the same anion (entry 7 vs. 1, entry 8 vs. 2, entry 9 vs. 3). The results were in good consistent with the previous other ILs reported by Peters et al.²⁷ and Gomes et al.²⁸ The ¹³C NMR was adopted to verify the CO₂ absorption state (Fig. 1); besides the peaks of pure UDIL-1-I, there appeared new peaks ascribed to the formation of new species in the presence of CO₂.²⁸ The C chemical shifts in the UDIL-1-I before and

after CO₂ absorption almost unchanged, indicating that the high CO₂ absorption is the consequence of the chemisorption and physical solubility of CO₂ in the UDIL, leading to the formation of the new chemical species. Furthermore, FT-IR spectra were employed to identify the possible intermediate during CO₂ absorption (Fig. 2A), the bands at 3300 cm⁻¹~3500 cm⁻¹ were ascribed to the stretching vibrations of N-H groups in the cation of UDILs, but with CO₂ captured, the band at ca. 3439 cm⁻¹ was weakened or vanished, and there appeared a new band at ca. 1787 cm⁻¹, corresponded to the new asymmetric C=O vibration of carbamate salt ^{21b}, which was resulted from activated CO₂ by N-H groups of UDILs, and similar activation pattern was also obtained by Lu et al. using nitrogen-doped porous carbon monolith for CO₂ capture.²⁹ Comparatively, the traditional unfunctionalized ILs gave the CO₂ capture capacities lower than 1 mmol per mmol ILs (entries 10-12), as well, the previous reported CO₂ absorbents such as [bmim][Tf₂N]/DBU,³⁰ potassium phthalimide³¹ and trihexyl (tetradecyl) phosphonium proline ([P₆₆₆₁₄][Pro]),^{8a} could interact with CO₂ in a molar ratio of one CO₂ per one absorbent (1:1 stoichiometry). Taking [P₆₆₆₁₄][Pro] as an example, the interaction with CO₂ was shown in Scheme 5. There also reported that the trapping of CO₂ in a stoichiometry of one mmol CO₂ molecule per two mmol the absorbents, such as dihydroxyethylmethylammonium taurinate,¹¹ phosphonium ILs with β-Alanine ([P(C₄)₄][β-Ala]) (Scheme 6).³² Additionally, Rogers³³ and Heldebrant et al.³⁴ respectively demonstrated the proton at C(2) position of the imidazolium ring and diamines containing two secondary amines could react with CO₂ as the absorption sites. Based on the above results and pioneering works,²⁹⁻³⁵ a plausible double stoichiometry mechanism for CO₂ absorption by UDILs was proposed in Scheme 7. It was worth mentioning that, UDIL-2 showed a higher CO₂ absorption capacity at more than 2.0 mmol per mmol absorbent, which was possibly ascribe to the additional dissolved CO₂. To our delight, the captured CO₂ could be easily stripped by heating at 80 °C for 4 h under vacuum (Fig. 2B), the stretching vibration of N-H groups at ca. 3439 cm⁻¹ was re-emerged and the new appeared band at ca. 1787 cm⁻¹ ascribed to C=O of formed carbamate was re-vanished. The stripping result was also verified by TGA (Fig. 2C), UDIL-1-I with absorbed CO₂ appeared an

obvious weight loss in the temperature range of 70 °C to 180 °C, indicating that the CO₂ capture process over UDILs was reversible. Also, the recovered UDIL could be repeatedly recycled for CO₂ uptake with no obvious loss of absorption capacity (entries 13-15), exhibiting the appealing alternative absorbent for CO₂ capture.

In addition, water is inevitable in real postcombustion flue gases and some amount of water would be absorbed by the UDIL depending on its hydrophilicity.^{8b} The effect of water on the absorption of CO₂ in the UDIL-1-I was investigated (entries 16-18). The addition of water has a small effect on the viscosity of the CO₂-UDIL system at low water contents. But, when the water content was increased to about 5 wt%, the viscosity was suddenly dropped and the absorption state changed from gel to liquid. This is because the water should begin to interfere with the UDIL-CO₂ hydrogen bonded network.^{8b} The CO₂ absorption capacity was not affected remarkably in the presence of moderate amounts of water. But, at 10 wt% of water, the CO₂ absorption capacity of UDIL-1-I was reduced by approximately 0.12 mmol of CO₂. It was suggested that water seemed to substantially influence the UDILs absorption capability towards CO₂ only when a large quantity of H₂O was present. This trend was consistent with the absorption to CO₂ over amine-functionalized anion-tethered IL trihexyl (tetradecyl) phosphonium methioninate [P₆₆₆₁₄][Met].^{8b}

Table 1 CO₂ absorption by different UDILs ^a

Entry	IL	time (min) ^b	CO ₂ absorption ^c (mmol)	state
1	1-Cl	45	1.42	liquid
2	1-Br	45	1.68	gel
3	1-I	45	1.72	gel
4	1-HSO ₄	30	1.39	gel
5	1-NO ₃	30	1.45	liquid
6	1-CH ₃ COO	30	1.81	liquid
7	2-Cl	60	2.09	liquid

8	2-Br	60	2.17	liquid
9	2-I	60	2.62	liquid
10	[Bmim]Br ^d	30	0.32	gel
11	[Bmim]I ^e	30	0.47	liquid
12	[Hmim]I ^f	30	0.31	gel
13 ^g	1-Br	45	1.65	gel
14 ^h	1-Br	45	1.63	gel
15 ⁱ	1-Br	45	1.58	gel
16 ^j	1-I	45	1.73	gel
17 ^k	1-I	45	1.75	liquid
18 ^l	1-I	45	1.60	liquid

^a Conditions: ionic liquid (1 mmol), 50 °C, 0.5 MPa CO₂. ^b Time required to reach absorption equilibrium. ^c Moles of CO₂ captured per mole of ionic liquid. ^d [Bmim]Br represents 1-butyl-3-methylimidazolium bromide. ^e [Bmim]I represents 1-butyl-3-methylimidazolium iodide. ^f [Hmim]I represents 1-methylimidazolium iodide. ^g The 2nd-absorption. ^h The 3rd-absorption. ⁱ The 4th-absorption. ^j The presence of 2 wt% water to UDIL-1-I. ^k The presence of 5 wt% water to UDIL-1-I. ^l The presence of 10 wt% water to UDIL-1-I.

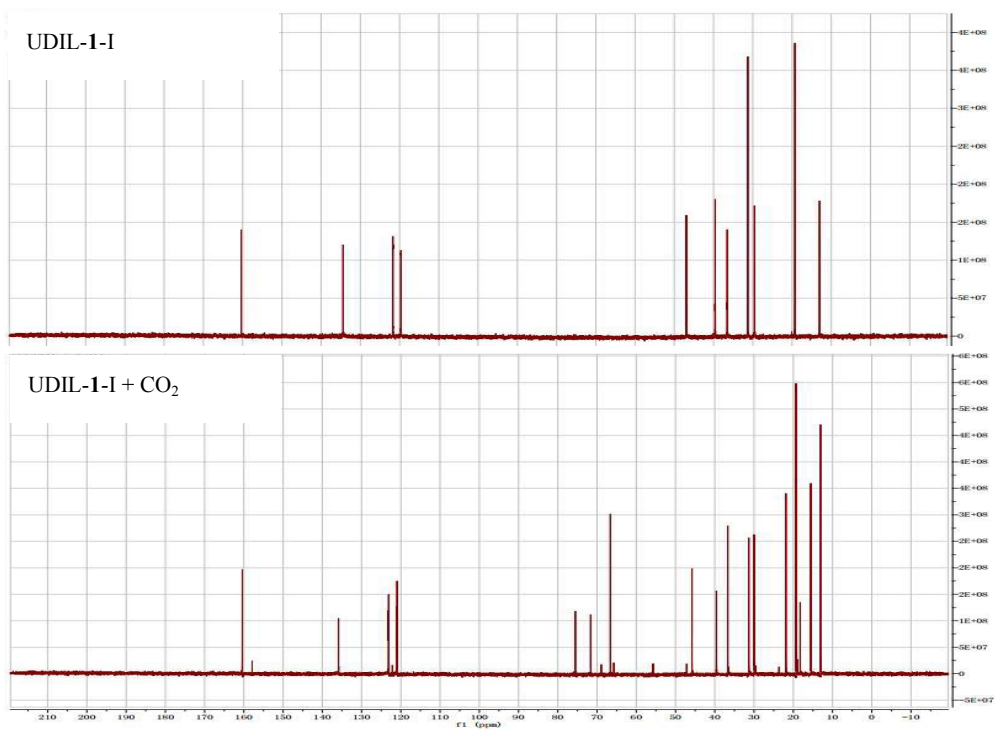
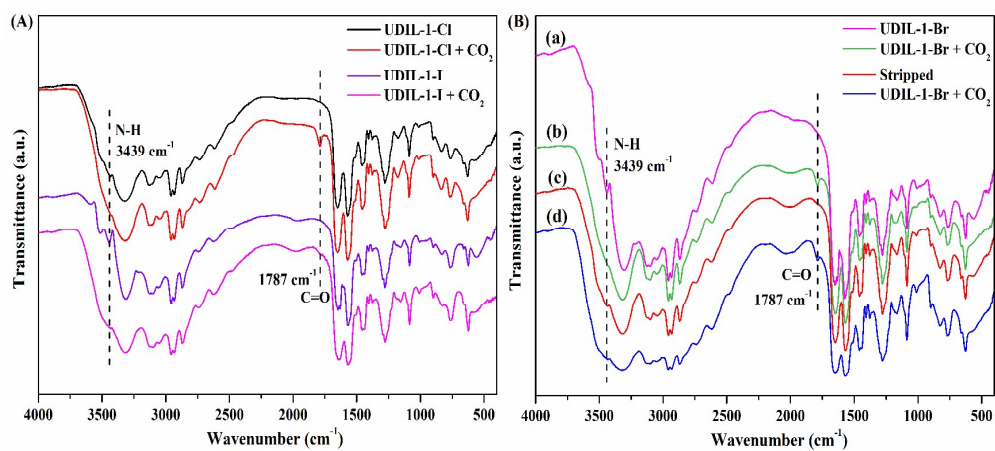


Fig. 1 ^{13}C NMR spectra of UDIL-1-I and after adsorption of CO₂.



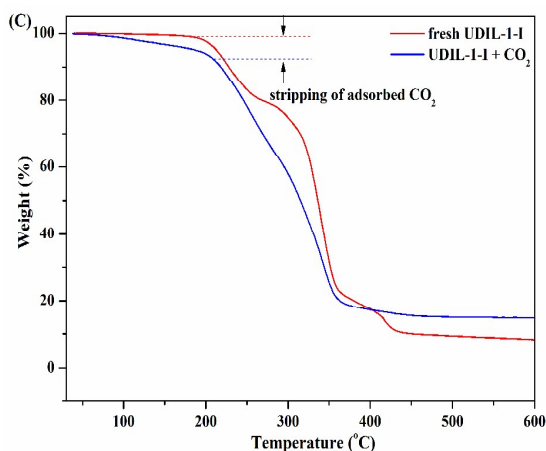
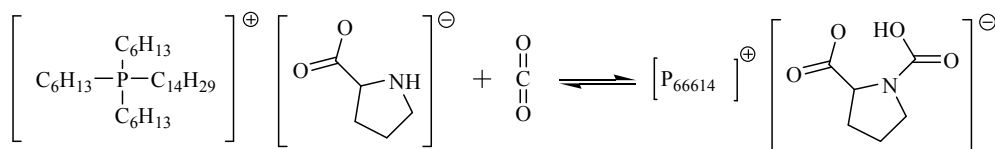
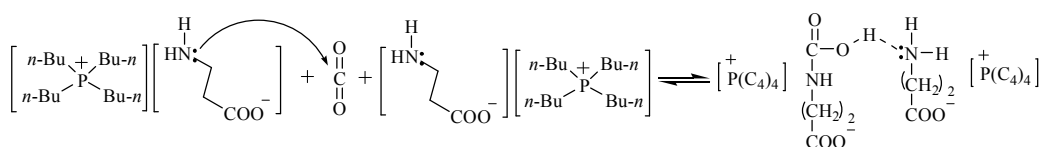


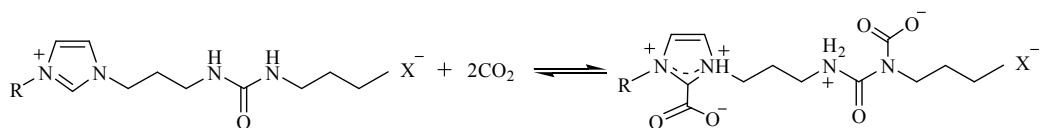
Fig. 2 (A) FT-IR spectra of CO₂ absorption by various UDILs at 50 °C; (B) The two recycles of absorption and release of CO₂ by UDIL-1-Br. (a) fresh UDIL-1-Br, (b) after CO₂ absorption, (c) after stripping at 80 °C under vacuum, (d) re-absorption of CO₂ over the stripped UDIL-1-Br. (C) TGA curves for the decomposition of fresh and spent UDIL-1-I after absorption of CO₂.



Scheme 5 Interaction schematic of CO₂ with [P₆₆₆₁₄][Pro].²¹



Scheme 6 Interaction schematic of CO₂ with [P(C₄)₄][β-Ala].²³



Scheme 7 Plausible CO₂ absorption mechanism over UDILs.

Catalyst screening for the cycloaddition of CO₂ to PO

With excellent CO₂ absorption capacity and superior thermal stability (Fig. S1), UDILs were anticipated to use for the catalytic reaction for CO₂ cycloaddition to

epoxides. From Table 2, it can be observed that no product was detected in the absence of catalyst under the applied reaction conditions (entry 1). Also UDILs with HSO_4^- , NO_3^- and CH_3COO^- anions had no activities to the CO_2 cycloaddition (entries 5–7) because the weak nucleophilicity of anions led to the difficulty of epoxy-ring open.^{13b,24} Gratifyingly, UDILs with halide anion exhibited pronounced catalytic activities and anion had great influence on activity, following the catalytic order of $\text{UDIL-I} > \text{UDIL-Br} > \text{UDIL-Cl}$ (entries 2–4, 8–10). The enhanced activity was possibly resulted from the synergetic effects of CO_2 activation as well as hydrogen bond donor groups of $-\text{NH}_2$, $-\text{NH}$ and $\text{C}(2)\text{-H}$ in cation, cooperated with the strong nucleophilic anion, which synergetic promoted the reaction.²² For the same anion, the steric hindrance caused by UDIL-2 cation resulted in the reduced activity compared with UDIL-1. Comparatively, UDIL-1 exhibited superior activity than traditional imidazole-based ILs (entries 11-13). To our delight, the selectivity to PC remained 99% in all examined cases. Comprehensively, UDIL-1-I was chosen as the efficient catalyst for the further examinations, and an appreciable 97% PC yield was obtained under metal-, cocatalyst- and solvent-free conditions of 130 °C and 1.5 MPa CO_2 for 3.0 h (entry 14). Also 90% yield of PC was obtained under even milder temperature of 90 °C but at the expense of longer reaction time (entry 15). Recyclability is an important and essential feature of any catalyst to be considered for practical applications. More interestingly, UDIL-1-I could be easily recovered and reused by adding diethyl ether after each run, and no significant loss of catalytic activity was resulted even in the four recycles, the yield of PC remained above 90% (entries 16-18). On the addition of 5 wt% additional fresh catalyst after the 4th-reuse, the initial catalytic activity was then restored completely (entry 19). FT-IR spectra indicated that after recycles, the structure of spent UDIL-1-I catalyst had no significant change except for N-H groups disappearance (Fig 3A), possibly attributed to the incomplete stripping of absorbed CO_2 which has been demonstrated in Fig. 2. Additionally, Fig 3B suggested the recycled UDIL-1-I catalyst still exhibited excellent stability and slight decrease of decomposition rate in the temperature range of 206 °C to 274 °C compared with the fresh catalyst, which was mainly caused by the

high-boiling PC product residue. UDIL with halide anion showed good candidate for further developments and applications in sustainable processes concerned with CO₂ fixation.

Table 2 Catalyst screening for CO₂ cycloaddition to PO^a

Entry	Catalyst	Temperature (°C)	Time (h)	Reaction results ^b	
				Y _{PC} (%)	S _{PC} (%)
1	none	130	6.0	trace	–
2	1 -Cl	130	2.0	35	99
3	1 -Br	130	2.0	62	99
4	1 -I	130	2.0	84	99
5	1 -HSO ₄	130	2.0	trace	–
6	1 -NO ₃	130	2.0	trace	–
7	1 -CH ₃ COO	130	2.0	trace	–
8	2 -Cl	130	2.0	30	99
9	2 -Br	130	2.0	45	99
10	2 -I	130	2.0	63	99
11	[Bmim]Br ^c	130	2.0	53	99
12	[Bmim]I ^d	130	2.0	67	99
13	[Hmim]I ^e	130	2.0	74	99
14	1 -I	130	3.0	97	99
15	1 -I	90	18.0	90	99
16 ^f	1 -I	130	3.0	95	99
17 ^g	1 -I	130	3.0	94	99
18 ^h	1 -I	130	3.0	91	99
19 ⁱ	1 -I	130	3.0	96	99

^a Reaction conditions: PO (34.5 mmol), catalyst (0.4 mmol), 1.5 MPa CO₂. ^b Y_{PC}: PC yield; S_{PC}: PC selectivity; all based on GC analysis. ^c [Bmim]Br represents 1-butyl-3-methylimidazolium bromide. ^d [Bmim]I represents 1-butyl-3-methylimidazolium iodide. ^e [Hmim]I represents

1-methylimidazolium iodide. ^f 2nd-reuse. ^g 3rd-reuse. ^h 4th-reuse. ⁱ Supplementing additional 5 wt% of fresh catalyst after 4th-reuse.

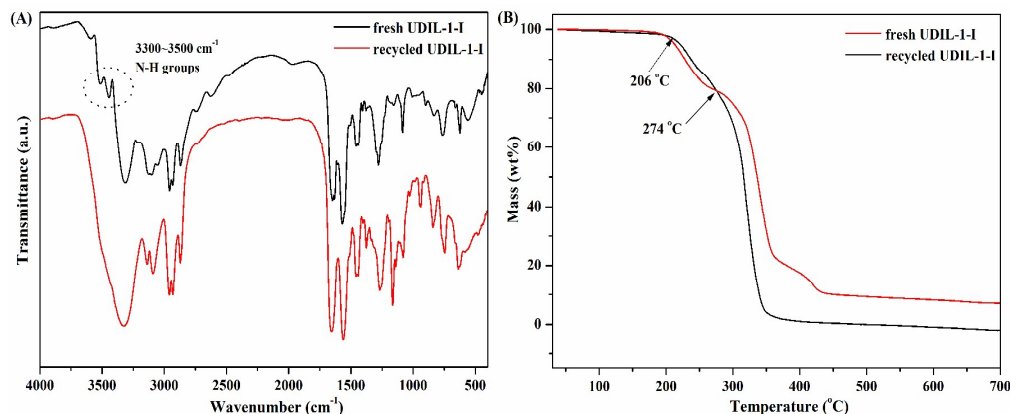


Fig. 3 (A) FT-IR spectra and (B) TGA curves of UDIL-1-I catalyst.

Effects of catalytic reaction parameters

In order to optimize the reaction conditions, the effects of various reaction parameters such as reaction temperature, CO₂ pressure, catalyst loading and reaction time were investigated in Fig. 4. The temperature had a pronounced positive effect on the coupling reaction, the catalytic activity increased with elevated temperature, which was ascribed to the enhanced more effective collisions between the active species of catalyst and the substrates at high temperature.³⁶ From the viewpoint of practical application, as the CO₂ cycloaddition reaction is highly exothermic, thus, effective heat removal is fundamental to save energy. Besides, in order to recover the reaction heat as steam, the reaction temperature around 130 °C is desirable, because temperature lower than 100 °C will result in a low heat exchange efficiency.³⁷

Remarkably, the product yield was very sensitive to the CO₂ pressure below 1.0 MPa shown in Fig. 4B, PC yield increased smoothly as a result of the enhancement of CO₂ concentration in the liquid reactive phase. Whereas, CO₂ pressure during 1.0–2.5 MPa had little effects on PC yield and selectivity, which were resulted from the concentration variations of reactants PO and CO₂ in CO₂-rich gas phase and PO-rich liquid phase.³⁸ The CO₂ influence of the catalytic system was also consistent with

bifunctional porphyrin catalyst system, which was verified by the phase observations for CO₂ fixation to PO.³⁹

As depicted in Fig. 4C, the catalytic activity of UDIL-1-I strongly depended on the catalyst loading. PC yield significantly improved with the increase of the catalyst loading from 0.3 to 1.2 mol%. When the amount of catalyst was further enhanced up to 1.5 mol%, the PC yield was unchanged obviously as the high viscosity caused by the excess catalyst to some extent enhanced the mass transfer resistances.

In addition, the effect of reaction time on PC yield and selectivity under identical conditions was presented in Fig. 4D. The PC yield increased rapidly with the reaction time and 3.0 h was necessary for the completion of the reaction. Again, the selectivity to PC stayed above 99 % throughout.

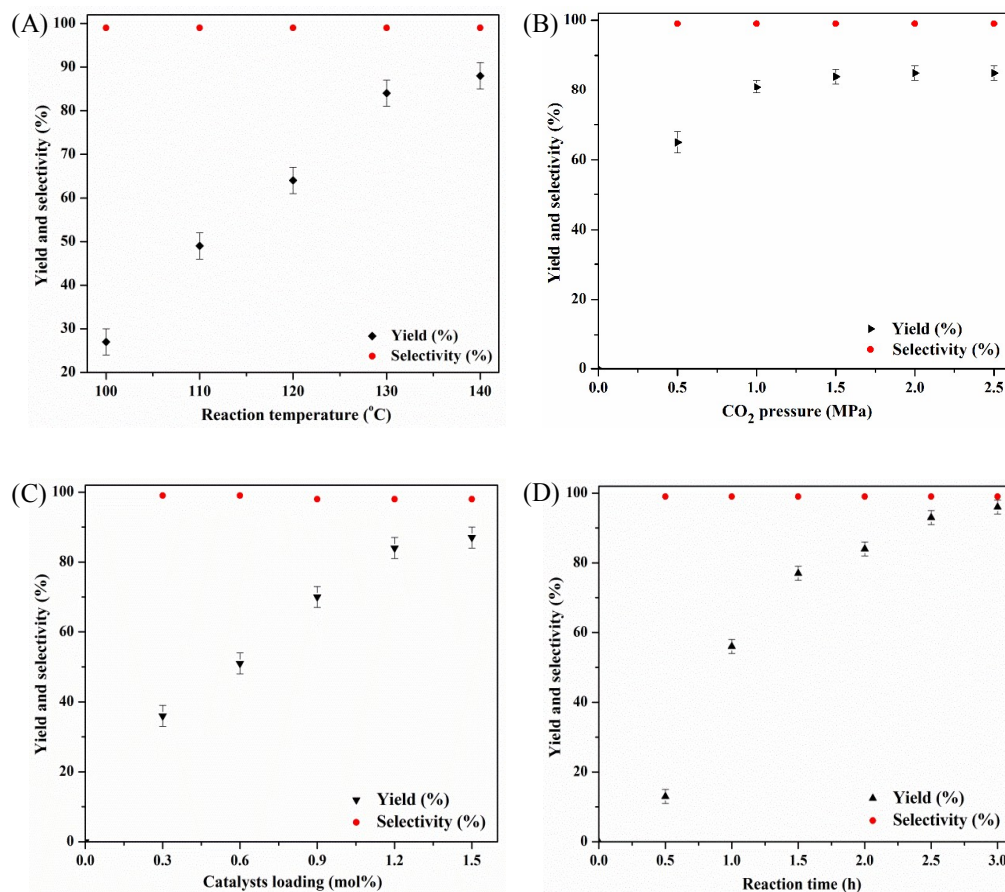


Fig. 4 Effects of different reaction parameters on PC synthesis over UDIL-1-I catalyst. (A) Effects of reaction temperature, conditions: PO 34.5 mmol, catalyst 0.4 mmol, 1.5 MPa, 2.0 h. (B) Effects

of CO₂ pressure, conditions: PO 34.5 mmol, catalyst 0.4 mmol, 130 °C, 2.0 h. (C) Effects of catalyst loading, conditions: PO 34.5 mmol, 130 °C, 1.5 MPa, 2.0 h. (D) Effects of reaction time, conditions: PO 34.5 mmol, catalyst 0.4 mmol, 130 °C, 1.5 MPa.

Effects of water

As mentioned above, water would be present in real postcombustion flue gases and the effect of water on PC synthesis was further studied over UDIL-1-I catalyst by changing H₂O/PO molar ratio from 0 to 1.0 (Fig. 5). With UDIL-1-I alone in the absence of water, 84 % PC yield was obtained with 99% selectivity. In the presence of water, the PC yield increased smoothly in the H₂O/PO ratio range of 0 to 0.6, because water reduced the viscosity of UDIL-1-I and increased the relative homogeneity of the reaction system at a fixed reaction temperature. Meanwhile, H₂O as the hydrogen bond donor assisted the smooth ring-opening of epoxide by forming hydrogen bonds with the oxygen atom of PO.²² While, further increase in H₂O/PO molar ratio to 1.0 caused a decrease in PC yield and selectivity, and a possible reason was the occurrence of PO hydrolysis to produce corresponding 1,2-propylene glycol.⁴⁰

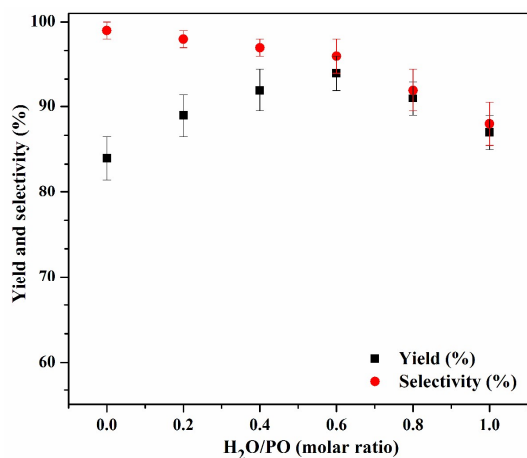



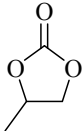
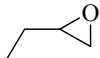
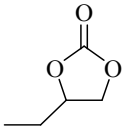
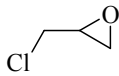
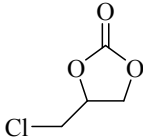
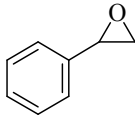
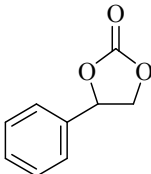
Fig. 5 Effect of the water amount on PC synthesis over UDIL-1-I catalyst. Conditions: PO (34.5 mmol), catalyst (0.4 mmol), 130 °C, 1.5 MPa, 2.0 h.

Catalytic activity towards other epoxides

In order to show the potential and general applicability of urea derivative based ionic

liquids, the chemical fixation of CO₂ to various epoxides were investigated over UDIL-1-I catalyst, as shown in Table 3. All examined terminal epoxides were smoothly converted to the corresponding cyclic carbonates with high yields and excellent selectivities under metal-, cocatalyst- and solvent- all free conditions (entries 1-4). The activity of epoxides decreased as the alkyl length increasing (entry 1 vs. entry 2). And the excellent activity of epichlorohydrin (entry 3) could be explained by the electron-withdrawing effect of its substituent, which also helped to facilitate the nucleophilic attack to the carbon atom of epoxide ring.^{13b} However, the catalytic activity was impeded by steric hindrance from side chain substituent of epoxide ring (entry 5). In the case of cycloaddition to cyclohexene oxide, the higher hindrance originated from the two rings of substrate obstructed the nucleophilic attack of I⁻ and caused the decrease of ring-opening rate, thus, harsh reaction conditions of improving the reaction temperature and CO₂ pressure, prolonging reaction time were necessary to achieve the satisfactory cyclohexene carbonate yield.

Table 3 Coupling reactions of CO₂ with various epoxides catalyzed by UDIL-1-I catalyst ^a

Entry	Epoxide	Product	T (°C)	t (h)	Reaction results ^b	
					Y (%)	S (%)
1			130	3.0	97	99
2			130	3.0	92	99
3			130	3.0	99	98
4			130	3.0	90	98

5 ^c			140	9.0	43	96
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^a Reaction conditions: epoxide 34.5 mmol, catalyst 0.4 mmol, 1.5 MPa CO₂. ^b Y: product yield; S: product selectivity; all based on GC analysis. ^c 3.0 MPa CO₂.

Catalytic kinetics study and mechanistic investigation

In order to provide useful evidences for the interpretation of reaction mechanism, a study of the reaction kinetics catalyzed by UDIL-1-I was undertaken for the model reaction of CO₂ cycloaddition to PO, and the general form of rate equation for this process was depicted in eq. (1):

$$r = k[PO]^a [Cat.]^b [CO_2]^c \quad (1)$$

in which k represents the rate constant, $[PO]$, $[CO_2]$ and $[Cat.]$ represent the PO, CO₂ and the catalyst concentrations respectively; a , b and c represent the orders of reactants. For the synthesis of cyclic carbonates, the pioneering works have shown that the reaction is first order with respect to CO₂.^{20b,41} In the present catalytic system, assuming that reaction is also first order for CO₂ and the concentration of catalyst does not change significantly during the reaction, eq. (1) can be rewritten as eq. (2) or eq. (3):

$$r = k_{obs} [PO]^a \quad k_{obs} = k [Cat.]^b [CO_2] \quad (2)$$

$$r = -d[PO]/dt = k_{obs} [PO] \quad (3)$$

where, k_{obs} is the observed pseudo-first-order rate constant for PO conversion.

Integrating eq. 3 yields eq. 4:

$$\ln[PO] = -k_{obs} t \quad (4)$$

To determine the reaction order of PO, experiments were carried out at three different PO concentrations in Fig. 6. All the kinetic experiments showed good fits to the first order kinetics, implying that the reaction is first order for PO (eq. 5).

$$r = k_{obs} [PO] \quad (5)$$

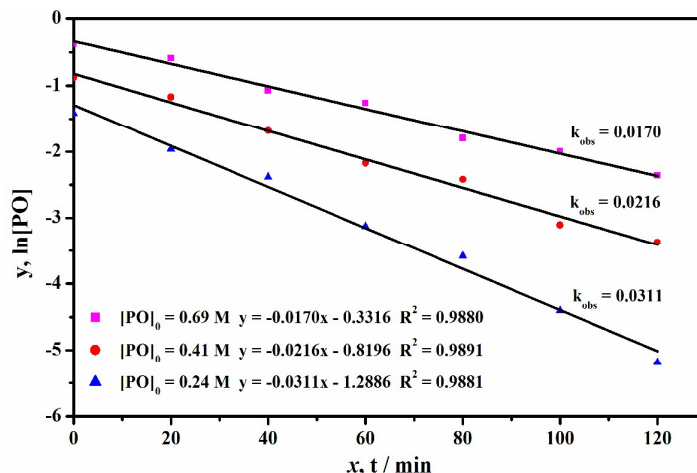


Fig. 6 Pseudo-first order kinetics plots for the natural logarithm of different PO concentrations versus time catalyzed by UDIL-1-I catalyst (0.4 mmol) at 130 °C and 1.5 MPa CO₂.

The same method was used to determine the order with respect to the catalyst (eq. 6), reactions were carried out at four different contents of UDIL-1-I (Fig. 7). Four equations were fitted according to the $(-\ln[PO])$ - t curves, and the slopes represent the reaction rates (η_{obs}) at the corresponding concentrations of UDIL-1-I (Fig. 7A). Fig. 7B gives a linear correlation of η_{obs} to the catalyst concentration, indicating that the reaction order for UDIL-1-I catalyst is also 1. The double logarithmic plot (eq. 7) had a slope of 1.09, further suggesting that the reaction was first order for UDIL-1-I catalyst (inset in Fig. 7C). The kinetics studies showed that the synthesis of PC catalyzed by UDIL-1-I obeys the following rate shown in eq. (8):

$$r = \eta_{obs}[Cat.]^b \quad (6)$$

$$\ln r = \ln \eta_{obs} + b \ln [Cat.] \quad (7)$$

$$r = k[PO][Cat.][CO_2] \quad (8)$$

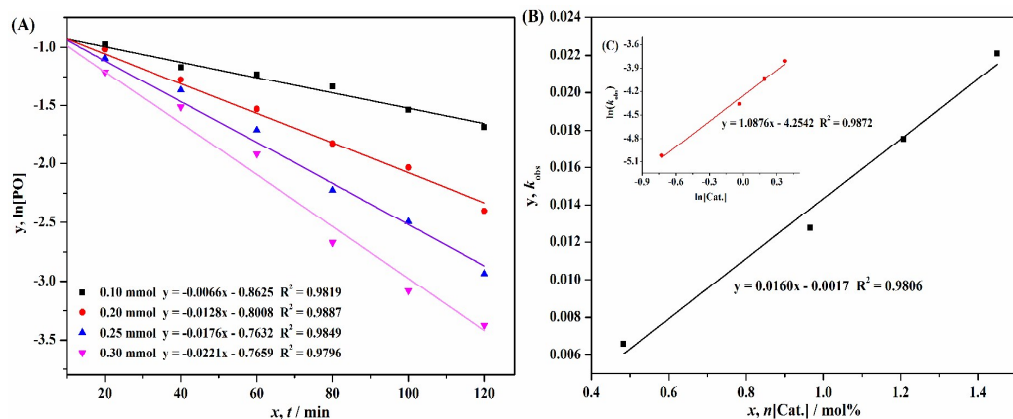


Fig. 7 (A) First-order kinetics plots for the conversion of PO at four different contents of UDIL-1-I catalyst. Reaction conditions: PO 20.7 mmol, 130 °C, 1.5 MPa CO₂; (B) Kinetic plots of k_{obs} versus molar content of catalyst. (C) The fitting curve of $\ln k_{\text{obs}}$ versus $\ln[\text{Cat.}]$.

Additionally, FT-IR spectra were employed to track the change and reaction process for PC synthesis (Fig. 8). The absorption peak at 1790 cm^{-1} was ascribed to the carbonyl group of PC product,^{23c} and the peak was intensified gradually along with the reaction time, proving the efficient proceeding of the cycloaddition reaction of PO and CO₂. Based on the kinetics studies and the cycloaddition reaction results, a possible acid-base synergetic catalytic mechanism catalyzed by UDIL was proposed in Scheme 8. As theoretical studies have suggested that the ring opening of epoxide was the rate-determining step,⁴² thus, it is of the utmost importance to activate epoxide for the subsequent CO₂ cycloaddition to the opened epoxide. Pioneering work⁴³ has calculated the two adjacent secondary amine N-H groups in imidazolium branched-chain as hydrogen bond donors were more inclined to form hydrogen bonding to activate epoxide compared with the quaternary amine N-R (R = H) and C(2)-H groups in imidazole ring. Hence, step (I): the epoxide was firstly activated through hydrogen bonding of the adjacent N-H groups in imidazolium branched-chain. Then C-O bond was weakened and facilitated the nucleophilic attack by the basic X⁻ anion, resulting in the ring-opening of epoxide. Step (II): the oxyanion species was stabilized by the hydrogen-bond donors and simultaneously CO₂ species were activated by N-R and C(2)-H groups in imidazole ring demonstrated in Scheme 7.

Thereafter, step (III): the oxyanion intermediate made nucleophilic attack on activated CO_2 species then by following intramolecular cyclic step to produce the new alkyl carbonate compound. With the subsequent intramolecular ring-closure step (step IV), the cyclic carbonate was formed and the catalyst regenerated.

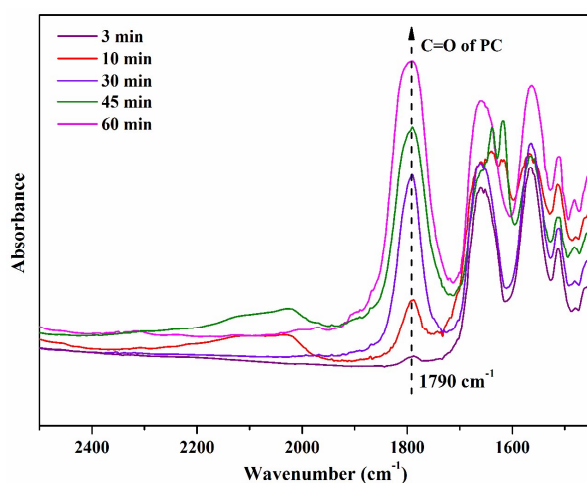
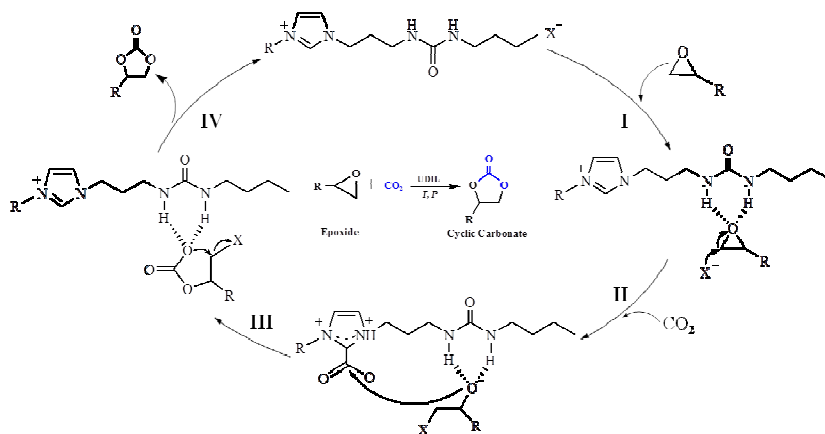


Fig. 8 FT-IR monitor for the PC synthesis at various reaction time, reaction conditions: PO 34.5 mmol, Cat. 0.25 mol%, 1.5 MPa, 130°C .



Scheme 8 Plausible mechanism for the CO_2 cycloaddition to epoxide catalyzed by UDIL.

Experimental

General Information

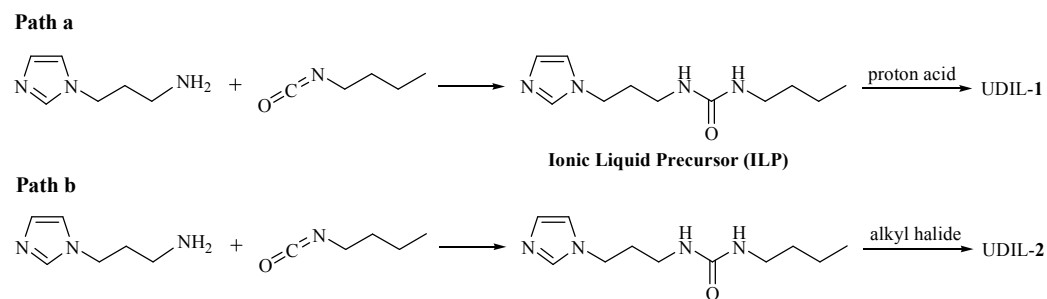
Carbon dioxide with 99.99% purity was purchased from Harbin Qinghua Industrial

gases Co. Ltd.. Isocyanic acid butyl ester (98%), 1-iodobutane (98%), 1,2-epoxypropane (99%) were purchased from Adamas Reagent Co., Ltd.. 1-(3'-aminopropyl) imidazole (98%) was purchased from Alfa Aesar Chemical Co., Ltd.. *N*-methylimidazole (99%), *n*-butyl chloride, *n*-butyl bromide ($\geq 99\%$) and other epoxides were purchased from Aladdin Chemical Co.. Hydrochloric acid (36-38%), hydrobromic acid (40%), hydroiodic acid (45%) were purchased from Sinopharm Chemical Reagent Co. Ltd.. All other chemicals were provided by Tianjin Kemiou Chemical Reagent Co. Ltd. with analytical purity and used without further purification.

^1H and ^{13}C NMR data were acquired on Bruker AV-400 MHz spectrometer. FT-IR spectra were measured on a PerkinElmer Spectrum 100 FT-IR spectrometer. GC analyses were performed on Agilent GC-7890A equipped with a capillary column (Agilent 19091J-413) using flame ionization detector. Thermogravimetric analysis (TGA) was carried out using NETZSCH STA 449F3 simultaneous thermogravimetric analyzer under N_2 atmosphere in the temperature range from room temperature to $800\text{ }^\circ\text{C}$ with the heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Catalyst preparation and characterization

The typical preparation process provided in Scheme 9 and characterizations (see Supporting Information) of the urea derivative based ILs were described as follows.



Scheme 9 Synthesis process for urea derivative based task-specific ILs.

Synthesis of ionic liquid precursor (ILP). The synthesis procedure was carried out

according to the literature.⁴⁴ 1-(3'-aminopropyl) imidazole (6.0 g, 47.9 mmol) was mixed with 20 mL acetonitrile under an atmosphere of dry nitrogen. To the stirring solution was added the mixture of equimolar isocyanic acid butyl ester pre-dissolved in 10 mL acetonitrile in a dropwise fashion. The above solution was stirred overnight followed by removing the solvent *via* rotary evaporation. The residue was then dried at 60 °C under vacuum overnight to obtain yellow-brownish oil. Yield: 90%. ¹H NMR and FT-IR spectroscopy confirmed the structure of the product as being the desired urea-appended imidazole.

¹H NMR (400 MHz, D₂O): $\delta_{\text{H}} = 7.07$ (s, 1H), 6.93 (s, 1H), 3.99-3.96 (t, $J = 6.0$ Hz, 2H), 3.01-2.95 (m, 4H), 1.91-1.84 (m, 2H), 1.38-1.31 (m, 2H), 1.26-1.17 (m, 2H), 0.82-0.78 (t, $J = 8.0$ Hz, 3H). FT-IR (KBr), $\gamma_{\text{max}}/\text{cm}^{-1}$: 3311, 3110, 2957-2930, 2868, 1654, 1562, 1512, 1456, 1375, 1250, 1112-1080, 916, 825, 733, 661, 621, 445.

Synthesis of urea derivative based ILs 1 (UDIL-1). Different UDIL-1 were prepared by protonating ILP with the corresponding protonic acid (e.g. HCl, HBr, HI, et. al.). Typically, HI aqueous solution (20 mL, 0.5 M) was slowly dripped into ILP (2.24 g, 10 mmol) and stirred for 12 h at ambient temperature with light avoided by black paper. The reaction mixture was reduced *via* rotary evaporation, and designated UDIL-1-I was dried under vacuum overnight to give red-brown oil. Yield: 95%. The methods were similar when hydrobromic acid, hydrochloric acid, acetic acid, nitric acid and sulphuric acid as the protonating agents used.

UDIL-1-I: ¹H NMR (400 MHz, D₂O): $\delta_{\text{H}} = 8.69$ (s, 1H), 7.48 (s, 1H), 7.42 (s, 1H), 4.25-4.22 (t, $J = 6.0$ Hz, 2H), 3.13-3.10 (t, $J = 6.0$ Hz, 2H), 3.02-2.98 (t, $J = 8.0$ Hz, 2H), 2.07-2.00 (m, 2H), 1.41-1.33 (m, 2H), 1.28-1.19 (m, 2H), 0.84-0.80 (t, $J = 8.0$ Hz, 3H). FT-IR (KBr), $\gamma_{\text{max}}/\text{cm}^{-1}$: 3500-3317, 3117, 2960-2932, 2866, 2732, 2613, 1650, 1568, 1456, 1368, 1277, 1158, 1090, 838, 759, 622, 557, 445.

UDIL-1-Cl: ¹H NMR (400 MHz, D₂O): $\delta_{\text{H}} = 8.67$ (s, 1H), 7.46 (s, 1H), 7.41 (s, 1H), 4.24-4.20 (t, $J = 8.0$ Hz, 2H), 3.11-3.08 (t, $J = 6.0$ Hz, 2H), 3.00-2.97 (t, $J = 6.0$ Hz, 2H), 2.05-1.98 (m, 2H), 1.39-1.32 (m, 2H), 1.25-1.20 (m, 2H), 0.83-0.79 (t, $J = 8.0$ Hz, 3H). ¹³C NMR (400 MHz, D₂O): $\delta_{\text{C}} = 160.46$, 134.42, 121.69, 119.67, 46.91, 39.55, 36.48, 31.29, 29.57, 19.26, 12.97. FT-IR (KBr), $\gamma_{\text{max}}/\text{cm}^{-1}$: 3500-3317, 3117,

2960-2932, 2866, 2732, 2613, 1650, 1568, 1456, 1368, 1277, 1158, 1090, 838, 759, 622, 557, 445.

UDIL-1-NO₃: ¹H NMR (400 MHz, D₂O): δ_H = 8.66 (s, 1H), 7.45 (s, 1H), 7.40 (s, 1H), 4.23-4.20 (t, *J* = 6.0 Hz, 2H), 3.11-3.08 (t, *J* = 6.0 Hz, 2H), 3.00-2.97 (t, *J* = 6.0 Hz, 2H), 2.05-1.98 (m, 2H), 1.39-1.32 (m, 2H), 1.27-1.18 (m, 2H), 0.83-0.79 (t, *J* = 8.0 Hz, 3H). FT-IR (KBr), γ_{max}/cm⁻¹: 3500-3334, 3127, 2957-2937, 2871, 2740, 2626, 1650, 1571, 1355, 1276, 1175, 1087, 831, 759, 628, 559, 445.

UDIL-1-HSO₄: ¹H NMR (400 MHz, D₂O): δ_H = 8.64 (s, 1H), 7.43 (s, 1H), 7.38 (s, 1H), 4.21-4.18 (t, *J* = 6.0 Hz, 2H), 3.09-3.06 (t, *J* = 6.0 Hz, 2H), 2.98-2.95 (t, *J* = 6.0 Hz, 2H), 2.03-1.96 (m, 2H), 1.37-1.30 (m, 2H), 1.25-1.16 (m, 2H), 0.80-0.77 (t, *J* = 6.0 Hz, 3H). FT-IR (KBr), γ_{max}/cm⁻¹: 3500-3334, 3127, 2957-2937, 2871, 2740, 2626, 1650, 1571, 1460, 1283, 1179, 1041, 857, 768, 628, 580, 445.

Synthesis of urea derivative based ILs-2 (UDIL-2). Different UDIL-2 were prepared by nucleophilic addition ILP with the corresponding alkyl halides (e.g. 1-iodobutane, *n*-butyl bromide and *n*-butyl chloride). Typically, a mixture of ILP (2.24 g, 10 mmol), 1-iodobutane (2.21 g, 12 mmol) and acetonitrile (25 mL) was charged into 100 mL round bottom flask, and heated gently at 70 °C with continuous stirring for 12 h, the remained acetonitrile was then removed *via* rotary evaporation, leaving a sticky residue. The designated UDIL-2-I residue was washed repeatedly with ethyl acetate (3×10 mL) and dried at 60 °C for 12 h under vacuum. Yield: 92%.

UDIL-2-Br: ¹H NMR (400 MHz, D₂O): δ_H = 7.43 (s, 2H), 4.19-4.02 (m, 4H), 3.08-2.97 (m, 4H), 2.01-1.76 (m, 4H), 1.38-1.20 (m, 6H), 0.87-0.79 (m, 6H). FT-IR (KBr), γ_{max}/cm⁻¹: 3437-3314, 3137, 3084, 2957-2930, 2865, 2740, 1656, 1564, 1453, 1375, 1257, 1165, 1112, 1080, 916, 837, 752, 634.

UDIL-2-I: ¹H NMR (400 MHz, D₂O): δ_H = 7.45 (s, 2H), 4.20-4.12 (m, 4H), 3.12-3.08 (t, *J* = 8.0 Hz, 2H), 3.03-2.98 (m, 2H), 2.04-1.98 (m, 2H), 1.83-1.76 (m, 2H), 1.40-1.33 (m, 2H), 1.29-1.18 (m, 4H), 0.88-0.80 (m, 6H). FT-IR (KBr), γ_{max}/cm⁻¹: 3437-3314, 3137, 3084, 2957-2930, 2865, 2740, 1656, 1564, 1453, 1375, 1257, 1165, 1112, 1080, 916, 837, 752, 634.

Absorption of CO₂

In a typical absorption of CO₂, a certain amounts of vacuum drying UDIL were loaded in a 50 mL high pressure stainless-steel autoclave that equipped with magnetic stirring bar. The reactor was firstly purged with CO₂ to evacuate the remaining air, then immersed in an oil bath to 50 °C and simultaneously CO₂ was introduced into the autoclave to 0.5 MPa then stirred until absorption equilibrium. The amount of CO₂ absorbed was determined at regular intervals by an electronic balance with an accuracy of ± 0.1 mg. The UDIL was regenerated by heating at 80 °C for 4 h under vacuum for reuse.

Catalytic cycloaddition reaction of CO₂ with epoxides

All the cycloaddition reactions were carried out in a 50 mL high pressure stainless-steel autoclave that equipped with magnetic stirring bar. For a typical catalytic reaction, the reactor was firstly purged with CO₂ to evacuate the remaining air, then IL catalyst (0.40 mmol, 1.2 mol% of PO) and PO (34.5 mmol) were added successively. The autoclave was heated to the required temperature, thereafter, CO₂ was introduced into the autoclave to a constant pressure (e.g. 1.5 MPa). After a designated period of time, the autoclave was cooled to 0 °C in an ice-water bath, and the remaining CO₂ was released slowly. The products were extracted by easily recyclable, low-boiling point diethyl ether and analyzed on GC. UDIL catalyst could be separated by centrifugalization, washed with diethyl ether (3 × 5 mL), dried under vacuum (60 °C, 8 h) then reused directly for another run under the same conditions.

Conclusions

In this work, the novel single-component urea derivative based ionic liquids with superior thermal stability and bi-functionalities have been successfully synthesized and structurally characterized. Notably, UDILs were proven to be highly and reversibly capture CO₂ with double molar CO₂ per molar UDIL, which was superior to the most reported absorbents with 0.5 or 1.0 stoichiometry of CO₂ uptake capacity.

Moreover, the UDILs can efficiently convert CO₂ with various epoxides to yield the corresponding cyclic carbonates under metal- and cocatalyst-free conditions without organic solvent, which solved the seriously concerned issues of environmental burdens. The kinetic studies combined with the experimental results help to propose a plausible catalytic reaction mechanism, where the urea-functionalized cations simultaneously activated epoxide and CO₂, the basic anion as nucleophile facilitated the ring-opening of epoxide, the synergetic effects in single-component catalyst promoted the reaction smoothly. Also, the inevitable water in real postcombustion flue gases at a moderate amount was permissible for CO₂ capture and catalytic conversion. The urea derivative based ionic liquids reported herein were metal-free, stable, easily recyclable and environmentally benign, and possessed characteristics of both CO₂ capture and conversion, which have great guiding significance to achieve CO₂ capture and conversion integration. Anyway, this development is of great interest in the view of ecological and economical points and will help to minimize the carbon footprint of the ecology.

Acknowledgements

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