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Lewis Basic Ionic Liquids-Catalyzed Conversion of Carbon Dioxide to Cyclic Carbonates

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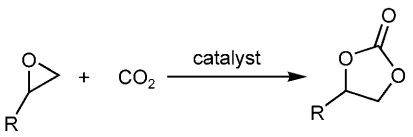
Abstract: A series of easily prepared Lewis basic ionic liquids were developed for cyclic carbonate synthesis from epoxide and carbon dioxide at low pressure without utilization of any organic solvents or additives. Notably, quantitative yields together with excellent selectivity were attained when 1,8-diazabicyclo[5.4.0]undec-7-enium chloride ([HDBU]Cl) was used as a catalyst. Furthermore, the catalyst could be recycled over five times without appreciable loss of catalytic activity. The effects of the catalyst structure and various reaction parameters on the catalytic performance were investigated in detail. This protocol was found to be applicable to a variety of epoxides producing the corresponding cyclic carbonates in high yields and selectivity. Therefore, this solvent-free process thus represents an environmentally friendly example for the catalytic conversion of carbon dioxide into value-added chemicals by employing Lewis basic ionic liquids as catalyst. A possible catalytic cycle for the hydrogen bond-assisted ring-opening of epoxide and activation of carbon dioxide induced by the nucleophilic tertiary nitrogen of the ionic liquid was also proposed.

Keywords: carbon dioxide fixation; cycloaddition; green chemistry; homogeneous catalysis; ionic liquids

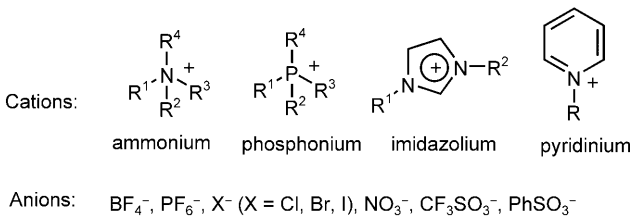
Introduction

Carbon dioxide (CO_2) is an easily available renewable carbon resource, which has the advantages of being non-toxic, abundant, and economical.[1–4] One of the few commercial routes using CO_2 as a raw material is the insertion of CO_2 into epoxides to afford the 5-membered cyclic carbonates (Scheme 1), which can serve as electrolytes in secondary batteries, valuable monomers of polycarbonates and polyurethanes, aprotic polar solvents, and raw materials in a wide range of chemical reactions.[5–9]

In the past decades, numerous heterogeneous catalysts have been proposed for this reaction, such as metal oxides,[10] oxychlorides,[11] Cs-loaded zeolite and alumina,[12] active species supported by natural or synthesized polymers,[13] silica,[14] zeolite[15] and other materials.[16] In addition, the cycloaddition reaction also proceeded smoothly using homogeneous catalysts including amines and phosphines,[17] alkali metal halides and onium salts,[18] organometallic compounds,[19] CO_2 adducts of N-heterocyclic carbenes[20] and especially ionic liquids (ILs) which possess specific features such as good solvating ability, negligible vapor pressure, variable polarity and ease of work-up.[4,9,21] To the best of our knowledge, most of the ILs used in the cycloaddition of CO_2 to epoxides are quaternary ammonium-, phosphonium-, imidazolium- or pyridinium-based cations with inorganic counter anions (Scheme 2). Although significant advances have been made, most of the IL catalysts suffer from low catalyst activity,[21a] water or air sensitivity,[21e,f] or the requirement for high CO_2 pressure[21c,i] or expensive transition metal additives.[21b,d–g] Therefore, the development of a low cost, easily prepared, thermal stable



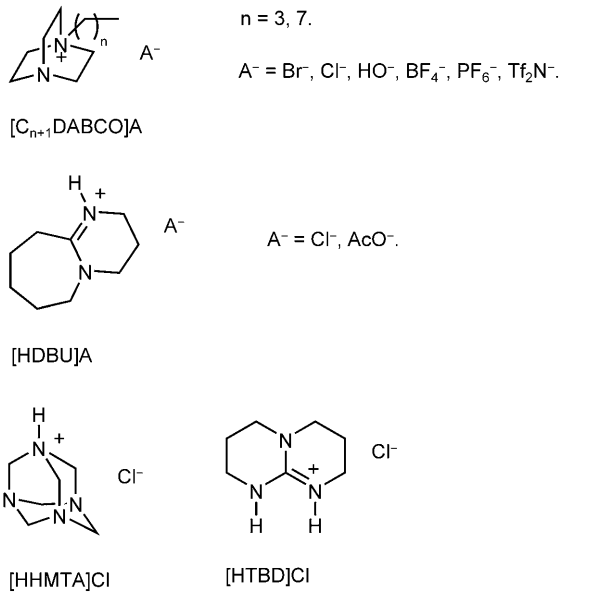
Scheme 1. Cycloaddition of CO_2 to epoxide.



Scheme 2. Ionic liquids used in the synthesis of cyclic carbonate.

and efficient single component catalyst for the conversion of CO_2 to cyclic carbonate is still highly required.

In this work, a series of Lewis basic ILs derived from 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and hexamethylenetetramine (HMTA) (Scheme 3) are considered to catalyze the cycloaddition reaction of propylene oxide (PO) and CO_2. Interest in these salts stems from their facile preparation from commercially available and relatively inexpensive starting materials, gratifyingly thermal behaviour, air/water stability. More importantly, the presence of the tertiary nitrogen in the cation has the potential to form the carbamate species with CO_2, which can be considered as an activated form of CO_2.[22,23] On the other hand, epoxide activation could be attained by a hydrogen bond formed *in situ* between the oxygen of the epoxide and the proton attached to the ammonium nitrogen atom of the IL. Indeed, the ionic liquid [HDBU]Cl displayed high catalytic activity for conversion of CO_2 and almost quantitative yield together with excellent selectivity were obtained in the absence of any additional organic solvent or additive.



Scheme 3. Lewis basic ionic liquids used in this study.

Results and Discussion

The synthesis of propylene carbonate (PC) from CO_2 and PO was carried out in the presence of a series of ILs based on C_4DABCO^+, C_8DABCO^+, $HDBU^+$, $HTBD^+$ or $HHMTA^+$ cation and OH^-, Cl^-, Br^-, BF_4^-, PF_6^-, Tf_2N^- or AcO^- anion under identical reaction conditions. For comparison, imidazolium- and pyridinium-based ILs were also tested in this study. Obviously, no reaction occurred without any catalyst (entry 1, Table 1). DBU was also found to be inactive probably due to loss of a nucleophilic species to run ring-opening of the epoxide although it could active CO_2 to form the carbamate salt (entry 2 *vs.* 10 and 11). As a result, both the cations and anions of the investigated ILs have strong impacts on the catalytic activities (entries 3–19). The results revealed that catalytic efficiency decreased in the order of $HDBU^+ > HTBD^+ \sim OMIm^+ > C_4DABCO^+ \sim C_8DABCO^+ > BMIm^+ > HHMTA^+$ (entries 4–6, 11–15). This is understandable because stabilization of the ring-opened structure of epoxide (as an intermediate, see the proposed mechanism in Scheme 5) is crucial for performing the reaction particularly at low CO_2 pressure,[14h,24] and those cations which can help stabilize the inter-

Table 1. PC synthesis catalyzed by Lewis basic ionic liquids.[a]

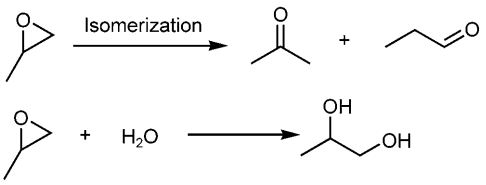
Entry	Catalyst	Yield [%][b]	Selectivity [%][b]
1	No catalyst	0	0
2	DBU	2	3
3	$[C_4DABCO]OH$	88	97
4	$[C_4DABCO]Cl$	81	96
5	$[C_4DABCO]Br$	79	>99
6	$[C_8DABCO]Br$	78	98
7	$[C_8DABCO]NTf_2$	9	50
8	$[C_8DABCO]PF_6$	4	9
9	$[C_8DABCO]BF_4$	2	6
10	[HDBU]OAc	86	90
11	[HDBU]Cl	97	>99
12	[HTBD]Cl	86	93
13	[HHMTA]Cl	33	48
14	[BMIm]Br[c]	54	70
15	[OMIm]Br[c]	85	91
16	$[BMIm]BF_4$[c]	7	29
17	$[OMIm]BF_4$[c]	1	5
18	[HMIm]Cl[c]	83	90
19	[HPy]Cl[c]	59	87

[a] *Reaction conditions:* PO (0.7 mL, 10 mmol), catalyst (1 mol%, relative to PO), CO_2 (1 MPa), 140 °C, 2 h.
[b] Determined by GC using an internal standard technique.
[c] [HMIm]Cl: 3-methylimidazolium chloride; [HPy]Cl: pyridium chloride; [BMIm]Br: 1-butyl-3-bromide; $[BMIm]BF_4$: 1-butyl-3-methylimidazolium tetrafluoroborate; [OMIm]Br: 1-octyl-3-methylimidazolium bromide; $[OMIm]BF_4$: 1-octyl-3-methylimidazolium tetrafluoroborate.

mediate could thus show higher activity. In this context, the delocalized cations showed better performance than $C_{n+1}DABCO^+$ (entries 11 and 12 *vs.* 4). Furthermore, the positive charge density would account for the catalytic activity decreasing in the order of $HDBU^+ > HTBD^+ > HMIm^+ > HPy^+$ (entries 11 and 12, 18 and 19). The lower activity of $HHMTA^+$ would presumably be due to its steric hindrance (entry 13). Whereas the alkyl length of the cation has a negligible effect on the reaction in the case of $[C_{n+1}DABCO]A$ as a catalyst (entry 5 *vs.* 6), which is quite different from the imidazolium salt-based ILs (entry 14 *vs.* 15).

The anion effect of ILs with different anions (OH^-, Cl^-, Br^-, BF_4^-, PF_6^-, Tf_2N^-, AcO^-) on the reaction was also investigated (entries 3–19). Interestingly, the IL with OH^-, which can easily react with CO_2, showed excellent performance (entry 3). And halide anions Cl^-, Br^- also gave good results probably thanks to their good leaving ability and nucleophilicity. Besides, the acetate anion with strong Lewis basicity in the case of $HDBU^+$ as a cation also showed comparable catalytic activity with the chloride (entry 10); but its thermal stability was not optimal.[23c] Notably, Tf_2N^-, PF_6^- and BF_4^- were found to be inefficacious (entries 7–9, 16 and 17). Therefore, [HDBU]Cl was identified as the most effective IL catalyst with excellent thermal stability, and was thus chosen as the model catalyst for further investigation.

Subsequently, the influence of catalyst loading on PC synthesis was investigated under identical reaction conditions (Figure 1). The yield and selectivity of PC reached a maximum as the catalyst loading was increased up to 1 mol%. Notably, the selectivity remained almost constant when the catalyst loading was reduced to 0.5 mol%. A >99% yield and selectivity of PC could be obtained by prolonging the reaction time to 5 h. However, the selectivity decreased when the catalyst loading was decreased to 0.1 mol%. This may be due to possible side reactions such as isomerization and hydrolysis of PO (Scheme 4). In this context, the catalyst amount is an important factor to



Scheme 4. Possible side reactions.

retard side reactions in this process.[13c] So, 1 mol% catalyst loading would be appropriate for the reaction.

Furthermore, we found that PC yield and selectivity were strongly affected by the reaction temperature. As shown in Figure 2, both yield and selectivity of PC were increased with temperature and optimal performances were achieved at 140 °C. The lower selectivity could possibly be due to by-products easily formed at lower temperature. In addition, the high catalytic activity can be maintained when the temperature was further increased to 160 °C, which also could experimentally prove the excellent thermal stability of this kind of Lewis basic IL like [HDBU]Cl. On the other hand, a reaction temperature around 150 °C would be desirable from a practical viewpoint because the cycloaddition is highly exothermic and the temperature below 100 °C could result in low heat exchange efficiencies and produce nearly useless warm water.[4,8] Conclusively, 140 °C could be the optimal temperature for PC synthesis.

Generally, a significant drawback associated with using CO_2 as a reactant and a reaction medium in organic synthesis is the potential dangers of operating at high pressure. Figure 3 shows the effect of CO_2 pressure on the reaction for the catalyst [HDBU]Cl. As can easily be seen, an almost quantitative yield together with excellent selectivity could be retained at a low CO_2 pressure of 1 MPa, demonstrating the preferential effect of the Lewis basic structure of the cation for promoting the reactivity of CO_2. Moreover, even when CO_2 pressure was further lowered to 0.5 MPa, 98% yield and >99% selectivity of PC could also be attained by prolonging the reaction time to 3 h. Be-

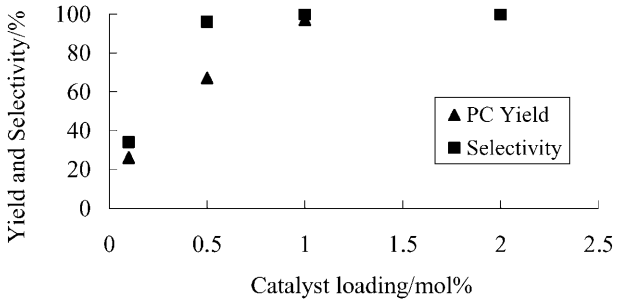


Figure 1. Effect of catalyst loading on PC synthesis. *Reaction conditions:* PO (0.7 mL, 10 mmol), catalyst ([HDBU]Cl), CO_2 (1 MPa), 140 °C, 2 h.

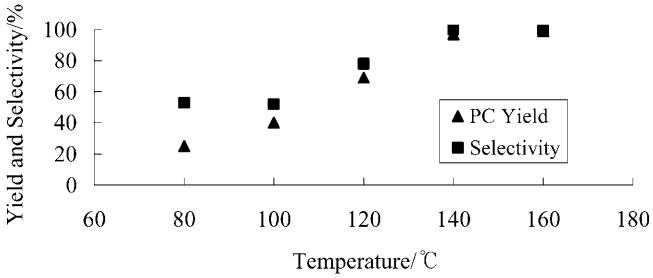


Figure 2. Influence of temperature on PC yield and selectivity. *Reaction conditions:* PO (0.7 mL, 10 mmol), [HDBU]Cl (1 mol%), CO_2 (1 MPa), 2 h.

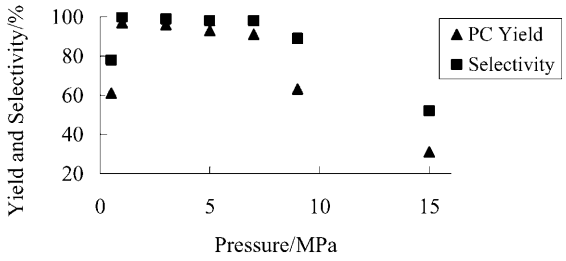


Figure 3. Dependence of PC yield and selectivity on CO_2 pressure. *Reaction conditions:* PO (0.7 mL, 10 mmol), [HDBU]Cl (1 mol%), 140 °C, 2 h.

sides, there was no obvious change of the outcome in the range of 1–7 MPa. However, too high a CO_2 pressure of over 9 MPa might retard the interaction between epoxide and the catalyst,[21a,c] and might cause a low concentration of epoxide in the vicinity of the catalyst, thus resulting in a low yield. Therefore, the suitable CO_2 pressure would be *ca.* 1 MPa.

The influence of reaction time on the PC synthesis is given in Figure 4. The reaction proceeded rapidly within the first 2 h, and almost quantitative yield could be achieved with >99% selectivity. In other words, a reaction time of 2 h is needed for complete PO conversion, and [HDBU]Cl could be an effective catalyst for converting CO_2 into cyclic carbonate. Interestingly, the selectivity of the reaction increased with reaction time, being probably attributed to the *in situ* formation of polycarbonates and depolymerization into PC during the reaction at elevated temperature and low CO_2 pressure, as reported in the literature.[25]

It is well-known that the stability and reusability of a catalyst system are the two key factors that identify whether it finds potentially practical application in industry. To test catalyst reusability, the reaction was carried out in the presence of a catalytic amount of [HDBU]Cl under the optimal conditions. The catalyst was recovered after separation of PC from the reaction mixture by distillation under reduced pressure and then used for the next run under the same conditions. The results as shown in Figure 5 indicated that the isolated yield of PC was almost consistent after five successive recycles. In addition, the catalyst also showed excellent recyclability even with a shortened reaction time (1 h).

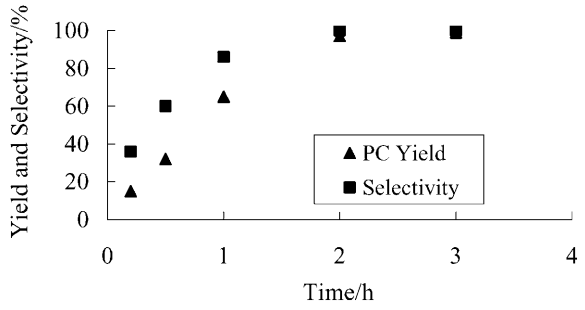


Figure 4. Reaction time dependence of PC yield and selectivity for [HDBU]Cl. *Reaction conditions:* PO (0.7 mL, 10 mmol), [HDBU]Cl (1 mol%), CO_2 (1 MPa), 140 °C.

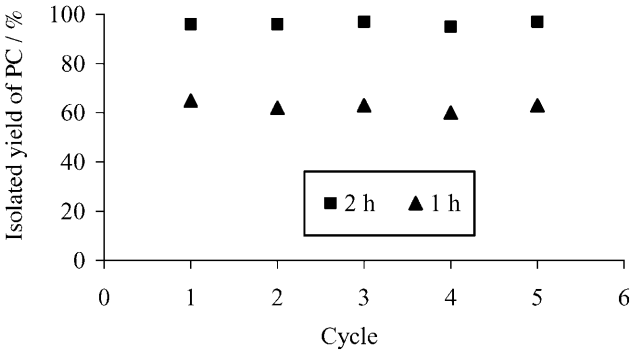


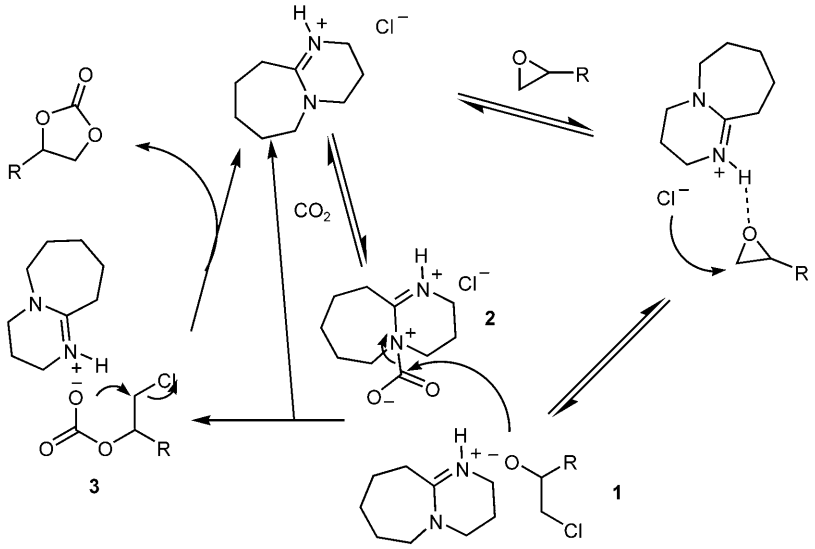
Figure 5. Recyclability of the catalyst. *Reaction conditions:* PO (0.7 mL, 10 mmol), [HDBU]Cl (1 mol%), 140 °C, CO_2 (1 MPa), 2 h or 1 h.

The utility and generality of [HDBU]Cl catalyst was also examined. And the results are summarized in Table 2. Both terminal and internal epoxides could be transformed to the corresponding cyclic carbo-

Table 2. Various carbonates synthesis using [HDBU]Cl as a homogeneous catalyst.[a]

Entry	Substrate	Product	Yield [%]	Selectivity [%]
1	**1a**	**2a**	97	>99
2	**1b**	**2b**	>99	>99
3	**1c**	**2c**	94	98
4	**1d**	**2d**	81	>99
5	**1e**	**2e**	19[b]	79

[a] *Reaction conditions:* epoxide (10 mmol), [HDBU]Cl (1 mol%), CO_2 (1 MPa), 140 °C, 2 h.
[b] 10 h.



Scheme 5. The proposed mechanism.

nates. Fortunately, high selectivity and almost quantitative yield were achieved within 2 h for the terminal epoxides. It is worth mentioning that **1d** with a phenyl group gave **2d** in 81% yield. On the other hand, internal cyclohexene oxide showed poor reactivity and just 19% of the corresponding cyclic carbonate was obtained even after prolonging the reaction time to 10 h, presumably due to the steric effect of cyclohexene oxide (entry 5). Generally, epoxides with an electron-withdrawing group are able to stablize the ring-opened structure of epoxides (**1**, Scheme 5), thus showing higher activity (**1b** > **1c** > **1d**).

Based on previous reports[14a,21h,22e] and the obtained results, a probable catalytic cycle was proposed for the cycloaddition of CO_2 to epoxides using [HDBU]Cl as a catalyst, as depicted in Scheme 5. Firstly, the proton is coordinated with the oxygen of the epoxide through a hydrogen bond, resulting in activation of an epoxide, and simultaneously, the nucleophilic attack of chloride anion on the less sterically hindered β-carbon atom of the epoxide furnishes the ring-opened intermediate **1**. In parallel, the tertiary nitrogen atom of the catalyst coordinates reversibly with CO_2 to afford the carbamate salt **2**, which would be an activated form of CO_2. Then, nucleophilic attack of the intermediate **1** on the carbamate salt **2** produces the alkyl carbonate anion **3**. Finally, the cyclic carbonate is formed by subsequent intramolecular ring-closure and the catalyst is regenerated.

Conclusions

In summary, a type of Lewis basic ILs such as [HDBU]Cl and [C_4DABCO]OH proved to be highly efficient and recyclable catalysts for the cycloaddition of CO_2 to epoxides under solvent-free conditions. The ILs used in this study represent air stable, high temperature tolerable, easily synthesized, cheap, extremely robust and environmentally benign catalysts. Therefore, this protocol could have great potential application for the catalytic conversion of CO_2 into valuable compounds and materials. Further applicability of the Lewis basic ILs to other reactions and organic synthesis is currently under investigation in our laboratory.

Experimental Section

General Information

The products were analyzed on a gas chromatograph (Shimadzu 2014 chromatographer) equipped with a RTX-5 capillary column (30 m × 0.25 μm) using a flame ionization detector (FID). NMR spectra were recorded on a Bruker 300 or 400 spectrometer in $CDCl_3$ or D_2O. ^1H and ^{13}C NMR chemical shifts (δ) in ppm are downfield from tetramethylsilane ($CDCl_3$: $\delta_C = 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H = 7.26$ ppm). ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in the ESI mode with a spray voltage of 4.8 kV. High-resolution mass spectrometry was conducted using an Ionspec 7.0 T spectrometer by means of the ESI-FT-ICR technique. Carbon dioxide of 99.99% purity was commercially available and epoxides were supplied from Aldrich Company. Other reagents were of analytical grade and were used as received.

Catalysts Preparation and Characterization

Ionic liquids based on 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), hexamethylenetetramine(HMTA), 1-*n*-butyl-3-methylimidazolium (BMIm), 1-*n*-octyl-3-methylimidazolium (OMIm) and pyridium (Py)

with different anions such as OH^-, AcO^-, Cl^-, Br^-, BF_4^-, PF_6^- or Tf_2N^- were prepared according to the procedures reported previously.[23,26] General procedures for the preparation of [C_4DABCO]Br, [C_4DABCO]Cl, [C_8DABCO]Br, [C_8DABCO]BF_4, [C_8DABCO]PF_6, [C_8DABCO]NTf_2, [BMIm]Br, [BMIm]BF_4, [OMIm]Br and [OMIm]BF_4 were available in the Supporting Information.

[C_4DABCO]Br: White glassy solid; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.65$ (t, $^3J_{H,H}=7.2$ Hz, 6H), 3.47 (t, $^3J_{H,H}=8.4$ Hz, 2H), 3.22 (t, $^3J_{H,H}=6.6$ Hz, 6H), 1.70–1.75 (m, 2H), 1.36–1.40 (m, 2H), 0.94 (t, $^3J_{H,H}=7.2$ Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta=64.3$, 52.4, 45.4, 23.9, 19.7, 13.6; ESI-MS (4.8 kV): m/z (%)=169.38 (100) $[M-Br]^+$, 79.02 (100) $[M-C_{10}H_{21}N_2]^-$.

[C_4DABCO]OH: Solid potassium hydroxide (0.112 g, 2 mmol) was added to a solution of [C_4DABCO]Br (0.4984 g, 2 mmol) in dry methylene chloride (2 mL), and the mixture was stirred vigorously at room temperature for 10 h. The precipitated KBr was filtered off, and the filtrate was evaporated to leave the crude [C_4DABCO]OH as a white solid that was washed with ether (2×2 mL) and dried at 90 °C for 10 h to give 1-butyl-4-aza-1-azaniabicyclo-[2.2.2]octane hydroxide. ^{1}H NMR (400 MHz, D_2O): $\delta=3.39$ (t, $^3J_{H,H}=7.6$ Hz, 6H), 3.25 (t, $^3J_{H,H}=8.8$ Hz, 2H), 3.19 (t, $^3J_{H,H}=7.2$ Hz, 6H), 1.74 (quintet, $^3J_{H,H}=8$ Hz, 2H), 1.33–1.42 (m, 2H), 0.94 (t, $^3J_{H,H}=7.6$ Hz, 3H); ^{13}C{^{1}H} NMR (100.6 MHz, D_2O): $\delta=64.4$, 52.0, 44.1, 23.1, 19.1, 12.7; ESI-MS (4.8 kV): m/z (%)=169.3 (100) $[M-OH]^+$, bromide was not detected under the negative ion mode.

[C_4DABCO]Cl: White glassy solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.67$ (t, $^3J_{H,H}=7.2$ Hz, 6H), 3.54 (t, $^3J_{H,H}=8.4$ Hz, 2H), 3.25 (t, $^3J_{H,H}=7.2$ Hz, 6H), 1.69–1.77 (m, 2H), 1.36–1.45 (m, 2H), 0.97 (t, $^3J_{H,H}=7.2$ Hz, 3H); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta=64.3$, 52.4, 45.4, 23.9, 19.7, 13.7; ESI-MS (4.8 kV): m/z (%)=169.44 (100) $[M-Cl]^+$.

[C_8DABCO]Br: Yellow glassy solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.49$ (t, $^3J_{H,H}=7.6$ Hz, 6H), 3.27 (t, $^3J_{H,H}=8.4$ Hz, 2H), 3.08 (t, $^3J_{H,H}=7.2$ Hz, 6H) , 1.59 (s, 2H), 1.06–1.15 (m, 10H), 0.68 (t, $^3J_{H,H}=7.2$ Hz, 3H); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta=64.1$, 52.0, 45.0, 31.1, 28.6, 28.5, 25.9,22.1, 21.6, 13.6; ESI-MS (4.8 kV): m/z (%)=225.46 (100) $[M-Br]^+$, 79.03 (100) $[M-C_{14}H_{29}N_2]^-$.

[C_8DABCO]BF_4: Clear colourless liquid; ^{1}H NMR (400 MHz,$CDCl_3$): $\delta=3.28$ (t, $^3J_{H,H}=7.6$ Hz, 6H), 3.10–3.16 (m, 8H), 1.66 (s, 2H), 1.20–1.27 (m, 10H), 0.81 (t, $^3J_{H,H}=7.2$ Hz, 3H); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta=64.5$, 52.0, 44.9, 31.3, 28.7, 26.0, 22.2, 21.4, 13.7; ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): $\delta=-151.10$, -151.15; ESI-MS (4.8 kV): m/z (%)=225.45 (100) $[M-BF_4]^+$, 87.1 (100) $[M-C_{14}H_{29}N_2]^-$.

[C_8DABCO]NTf_2: Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.17$ (t, $^3J_{H,H}=6.4$ Hz, 6H), 2.98–3.07 (m, 8H), 1.58 (s, 2H), 1.16–1.21 (m, 10H), 0.76 (t, $^3J_{H,H}=6.8$ Hz, 3H); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta=117.2$ (q, $J_{C,F}=321$ Hz), 62.4, 49.9, 42.5, 28.9, 26.3, 26.2, 23.5, 19.9, 19.0, 11.4; ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): $\delta=-81.60$; ESI-MS (4.8 kV): m/z (%)=225.43 (100) $[M-C_2F_6NO_4S_2]^+$, 280.10 (100) $[M-C_{14}H_{29}N_2]^-$.

[C_8DABCO]PF_6: White solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.27$–3.30 (m, 6H), 3.13–3.22 (m, 8H), 1.70 (s, 2H), 1.26–1.33 (m, 10H), 0.87 (t, $^3J_{H,H}=7.2$ Hz, 3H); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta=65.0$, 52.5, 45.2, 31.6, 28.94, 28.92, 26.2, 22.5, 21.7, 14.0; ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): $\delta=-71.02$, -72.91; ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$): $\delta=-144.33$ (septet, $J_{P,F}=712$ Hz); ESI-MS (4.8 kV): m/z (%)=225.43 (100) $[M-PF_6]^+$, 145.20 (100) $[M-C_{14}H_{29}N_2]^-$.

[HDBU]Cl: NH_4Cl (0.1605 g, 3 mmol) was introduced into a 25-mL stirred reactor fitted with nitrogen inlet and suspended in 2 mL of methanol. Over the course of 30 min, DBU (0.448 mL, 3 mmol) was added. The mixture was stirred for a further 3 h and then the solvent was evaporated. And the remaining solid was dried under vacuum at 60 °C for 24 h to afford 1,8-diazabicyclo[5.4.0]undec-7-enium chloride as a white glassy solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.57$–3.60 (m, 2H), 3.54 (t, $^3J_{H,H}=6$ Hz, 2H), 3.33 (t, $^3J_{H,H}=5.6$ Hz, 2H), 2.63–2.65 (m, 2H), 2.02 (quintet, $^3J_{H,H}=5.6$ Hz, 2H), 1.69–1.74 (m, 6H); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta=165.9$, 54.2, 48.5, 37.7, 31.9, 28.7, 26.5, 23.7, 19.2; HR-MS (ESI): $m/z=153.1386$, calcd. for $C_9H_{17}N_2$ ($M-Cl^+$): 153.1383; ESI-MS (4.8 kV): m/z (%)=153.41 (100) $[M-C_2H_3O_2]^+$.

[HDBU]OAc: To a 50-mL three-necked flask was added DBU (0.9134 g, 6 mmol). Acetic acid (0.3603 g, 6 mmol) was then added dropwise at the temperature of <5 °C cooled by ice bath. After addition, the ice bath was removed and the reaction mixture was stirred at room temperature for 24 h. The oil residue was dried under vacuum at 60 °C for 24 h to afford 1,8-diazabicyclo[5.4.0]undec-7-enium acetate as a colourless, viscous liquid. ^{1}H NMR (400 MHz, D_2O): $\delta=3.53$–3.59 (m, 4H), 3.33 (t, $^3J_{H,H}=5.2$ Hz, 2H), 2.65–2.67 (m, 2H), 2.02 (t, $^3J_{H,H}=6$ Hz, 2H), 1.97 (s, 2H), 1.70–1.73 (m, 7H); ^{13}C{^{1}H} NMR (100.6 MHz, D_2O): $\delta=179.0$, 165.9, 54.2, 48.3, 38.0, 32.8, 28.5, 26.0, 23.4, 22.4, 19.0; ESI-MS (4.8 kV): m/z (%)=153.41 (100) $[M-Cl]^+$.

[HHMTA]Cl: According to the synthetic procedure of [HDBU]Cl, 1,3,5,7-tetraazatricyclo[1.1.1.1.1.1]dec-1-anium chloride was obtained as a white solid. ^{1}H NMR (400 MHz, D_2O): $\delta=4.75$ (s, 6H), 4.74 (s, 6H); ^{13}C{^{1}H} NMR (100.6 MHz, D_2O): $\delta=71.7$; HR-MS (ESI): $m/z=141.1135$, calcd. for $C_6H_{13}N_4$ ($M-Cl^+$): 141.1131, 317.1963, calcd. for $C_{12}H_{26}N_8$ Cl ($2M-Cl^+$): 317.1971; ESI-MS (4.8 kV): m/z (%)=141.4 (100) $[M-Cl]^+$.

[HTBD]Cl: Similarly, 1,5,7-triazabicyclo[4.4.0]dec-5-enium chloride was obtained as a white solid. ^{1}H NMR (400 MHz, D_2O): $\delta=3.36$ (t, $^3J_{H,H}=6$ Hz, 4H), 3.28 (t, $^3J_{H,H}=5.6$ Hz, 4H), 2.00 (quintet, $^3J_{H,H}=6$ Hz, 4H); ^{13}C{^{1}H} NMR (100.6 MHz, D_2O): $\delta=151.0$, 46.5, 37.8, 20.2; HR-MS (ESI): $m/z=140.1182$, calcd. for $C_7H_{14}N_3$ ($M-Cl^+$): 140.1177, 315.2057, calcd. for $C_{14}H_{28}N_6Cl$ ($2M-Cl^+$): 315.2059; ESI-MS (4.8 kV): m/z (%)=140.40 (100) $[M-Cl]^+$.

[BMIm]Br: White solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.27$ (s, 1H), 7.60 (t, $^3J_{H,H}=1.6$ Hz, 1H), 7.47 (t, $^3J_{H,H}=1.6$ Hz, 1H), 4.28 (t, $^3J_{H,H}=7.2$ Hz, 2H), 4.07 (s, 3H), 1.85 (quintet, $^3J_{H,H}=7.6$ Hz, 2H), 1.32 (sextet, $^3J_{H,H}=7.6$ Hz, 2H), 0.89 (t, $^3J_{H,H}=7.6$ Hz, 3H); ^{13}C{^{1}H} NMR (100.6 MHz, D_2O): $\delta=135.8$, 123.2, 122.2, 49.3, 35.7, 31.3, 18.7, 12.6; ESI-MS (4.8 kV): m/z (%)=139.32 (100) $[M-Br]^+$, 79.03 (100) $[M-C_8H_{15}N_2]^-$.

[BMIm]BF_4: Light yellow liquid; ^{1}H NMR (400 MHz, D_2O): $\delta=8.71$ (s, 1H), 7.51 (s, 1H), 7.47 (s, 1H), 4.22–4.23 (m, 2H), 3.94 (s, 3H), 1.87–1.89 (m, 2H), 1.35–1.37 (m, 2H), 0.96 (t, $^3J_{H,H}=7.6$ Hz, 3H); ^{13}C{^{1}H} NMR (100.6 MHz,

D_2O): $\delta = 135.9$, 123.5, 122.2, 49.3, 35.6, 31.3, 18.8, 12.7; $^{19}F\{^1H\}$ NMR (377 MHz, $CDCl_3$): $\delta = -150.12$, -150.30; ESI-MS (4.8 kV): m/z (%) = 139.32 (100) $[M-BF_4]^+$, 87.11 (100) $[M-C_8H_{15}N_2]^-$.

[OMIm]Br: Colourless liquid; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 10.06$ (s, 1H), 7.59 (s, 1H), 7.40 (s, 1H), 4.17 (t, $^3J_{H,H} = 6.8$ Hz, 2H), 3.99 (s, 3H), 1.76–1.77 (m, 2H), 1.09–1.17 (m, 10H), 0.70 (t, $^3J_{H,H} = 6.4$ Hz, 3H); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 136.0$, 123.1, 121.4, 49.2, 35.9, 30.7, 29.4, 28.1, 28.0, 25.3, 21.6, 13.2; ESI-MS (4.8 kV): m/z (%) = 195.46 (100) $[M-Br]^+$, 79.03 (100) $[M-C_{12}H_{23}N_2]^-$.

[OMIm]BF_4: Light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.70$ (s, 1H), 7.38 (s, 1H), 7.32 (s, 1H), 4.12 (t, $^3J_{H,H} = 7.2$ Hz, 2H), 3.89 (s, 3H), 1.82 (t, $^3J_{H,H} = 6.8$ Hz, 2H), 1.20–1.26 (m, 10H), 0.81 (t, $^3J_{H,H} = 6.8$ Hz, 3H); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 136.0$, 123.7, 122.1, 49.9, 36.0, 31.5, 29.9, 28.9, 28.7, 26.0, 22.4, 13.9; $^{19}F\{^1H\}$ NMR (377 MHz, $CDCl_3$): $\delta = -150.99$, -151.05; ESI-MS (4.8 kV): m/z (%) = 195.39 (100) $[M-BF_4]^+$, 87.10 (100) $[M-C_{12}H_{23}N_2]^-$.

[HMIm]Cl: To a 50-mL round-bottom flask were added 1-methylimidazole (0.2663 g, 3 mmol) and concentrated hydrochloric acid (0.3 mL, 3 mmol). The reaction mixture was stirred at room temperature for 24 h. The oil residue was dried under vacuum at 65 °C for 24 h to afford 1-hydro-3-methylimidazolium chloride as a colourless, viscous liquid. ^1H NMR (400 MHz, D_2O): $\delta = 8.70$ (s, 1H), 7.47 (s, 2H), 3.95 (s, 3H); $^{13}C\{^1H\}$ NMR (100.6 MHz, D_2O): $\delta = 135.0$, 123.0, 119.5, 35.5; ESI-MS (4.8 kV): m/z (%) = 83.16 (100) $[M-Cl]^+$.

[HPy]Cl: According to the synthetic procedure of [HMIm]Cl, pyridinium chloride was prepared as a colourless solid. ^1H NMR (400 MHz, D_2O): $\delta = 8.78$ (d, $^3J_{H,H} = 5.6$ Hz, 2H), 8.62 (t, $^3J_{H,H} = 8$ Hz, 1H), 8.07 (t, $^3J_{H,H} = 6.4$ Hz, 2H); $^{13}C\{^1H\}$ NMR (100.6 MHz, D_2O): $\delta = 147.2$, 141.0, 127.4; ESI-MS (4.8 kV): m/z (%) = 80.11 (100) $[M-Cl]^+$.

Typical Procedures for PC Synthesis from PO and CO_2

A stainless steel autoclave (25 mL inner volume) was purged with CO_2 to evacuate air, and then [HDBU]Cl (0.0189 g, 1 mol%), biphenyl (0.05 g, internal standard of GC) and propylene oxide (0.7 mL, 10 mmol) were added successively. CO_2 was charged in the reactor and the pressure was adjusted to 1 MPa at 140 °C. The autoclave was heated at that temperature for 2 h, and the pressure was kept constant during the reaction. After reaction, the autoclave was allowed to be cooled, and then the excess of CO_2 was vented. The product yields were determined by GC with a flame ionization detector and were further identified using GC-MS by comparing retention times and fragmentation patterns with authentic samples. The products structures were also identified by ESI-mass and NMR spectra as previously reported.[14c]

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