

# Quaternary Ammonium Ionic Liquids as Bi-functional Catalysts for One-step Synthesis of Dimethyl Carbonate from Ethylene Oxide, Carbon Dioxide and Methanol

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**Abstract** One kind of novel ionic liquids (ILs) with a tertiary amino moiety and a quaternary ammonium group were synthesized and identified by FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The elemental chemical state and basicity of ILs were determined by XPS and Hammett indicator method, respectively. Then the catalytic performance of these bi-functional catalysts was investigated in one-step synthesis of dimethyl carbonate (DMC) from ethylene oxide (EO), carbon dioxide and methanol. The best catalytic performance with 99% EO conversion and a maximum of 74% DMC selectivity was obtained using  $[\text{N}_{111,6}\text{N}_{11}]I$  as catalyst under optimized reaction conditions. And the catalyst could be reused for several times. Normally, stronger basicity could be obtained by altering the anions with different nucleophilicity in ILs and a better catalytic activity could be achieved correspondingly. A mechanism that both the ring opening of epoxide through nucleophilic attacks and the transesterification play an important role in the reaction was proposed based on experimental results.

**Keywords** Ionic liquid · Bi-functional · One-step synthesis · Dimethyl carbonate · Carbon dioxide

## 1 Introduction

Dimethyl carbonate (DMC) is considered to be a safe, non-corrosive and environmentally benign chemicals and industrial intermediate. It is extensively used as building-block to replace toxic phosgene in the production of polycarbonates/polyurethane, and in stead of dimethyl sulfate in the synthesis of agrochemicals and pharmaceuticals [1–3]. Additionally, DMC also can be used as solvent due to its low toxicity and good solubility, as additive in fuel oil owing to its high oxygen content, high octane number, and as electrolyte in lithium batteries due to its low viscosity and good solubility for lithium salts [4–6].

Up to now, several routes have been developed for DMC synthesis, i.e., the phosgene process [7], the oxidative carbonylation of methanol [8], the transesterification process [9–12], the alcoholysis of urea process [13], and the direct synthesis method via  $\text{CO}_2$  [14]. Among them, the transesterification process can be divided into a one-step and a two-step method. The two-step method is one of the commercialized routes for massive production of DMC and considered to be an environmentally friendly process owing to the utilization of  $\text{CO}_2$ , which may be one of the most valuable and promising routes for large-scale utilization of  $\text{CO}_2$  besides urea production [15, 16]. It contains the cycloaddition reaction of ethylene oxide (EO) with  $\text{CO}_2$  and subsequently the transesterification reaction of ethyl carbonate (EC) with methanol. This route has advantages such as mild reaction conditions, high selectivity, and low equipment investment. However, the cycloaddition reaction is strong exothermic and EO is explosive under solvent-free conditions. And the complicated operation process is one of the main drawbacks for this route due to the separation of intermediates of cyclic carbonates. To eliminate this drawback, one-step synthesis of DMC

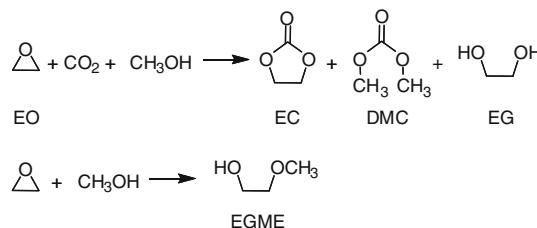
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from epoxides,  $\text{CO}_2$  and methanol is extensively studied (Scheme 1). Several catalysts, such as inorganic bases [17], Mg containing smectite [18],  $\text{KI}/\text{K}_2\text{CO}_3$  or supported  $\text{KI}/\text{K}_2\text{CO}_3$  [19–22], amines [23],  $\text{KOH}/4\text{A}$  molecular sieve [24],  $n\text{-Bu}_4\text{NBr}/n\text{-Bu}_3\text{N}$  [25], and choline hydroxide/MgO [26], etc., have been employed. Unfortunately, catalysts for the one-step synthesis of DMC are normally double components and the occurrence of the side reactions is usually unavoidable. Furthermore, most of these catalysts are difficult to be recycled and rigorous reaction conditions are required.

Ionic liquids (ILs) have attracted considerable attentions as versatile media and materials because of their peculiar physicochemical properties, such as extremely low volatility, high thermal stability, wide liquid-temperature range, and strong solvating power for various substances [27–29]. Therefore, ILs can be considered to be alternatives for volatile organics in chemical processes. Moreover, ILs have been used widely in catalysis for its “designer” and “task-specific” characteristics [30]. Among them, amino-functionalized ILs exhibit good catalytic activity in some base catalyzed reactions [31, 32]. However, till now, no amino-functionalized ILs as catalyst for the one-step synthesis of DMC from EO,  $\text{CO}_2$  and methanol has been reported.

As mentioned in the literature [25], quaternary ammonium salts were active for the cycloaddition of epoxide with  $\text{CO}_2$ , tertiary amines could promote the transesterification reaction. And  $n\text{-Bu}_4\text{NBr}/n\text{-Bu}_3\text{N}$  was one of the most effective catalyst systems for the one-step synthesis of DMC. Inspired by this work, herein, we synthesized one kind of novel quaternary ammonium ILs with a tertiary amino moiety and a quaternary ammonium group (Scheme 2), which are usually more stable than corresponding organics. These ILs are viscous liquid or waxy solid at room temperature and its purities were characterized by FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR. Then they are used for the one-pot synthesis of DMC from EO,  $\text{CO}_2$  and methanol under mild conditions. Compared with  $\text{KI}/\text{K}_2\text{CO}_3$  and  $n\text{-Bu}_4\text{NBr}/n\text{-Bu}_3\text{N}$ , these bi-functional ILs catalysts,  $[\text{N}_{114,6}\text{N}_{11}]X$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ), exhibited higher catalytic



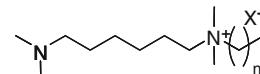
**Scheme 1** One-step synthesis of DMC and corresponding side reaction

performance in terms of turnover number (TON). These catalysts were nonvolatile, stable and can be reused for several times. Moreover, the bi-functional ILs can solely catalyze the reaction. And the catalytic performance of the bi-functional ILs could be regulated by altering the anions or the alkyl chain lengths.

## 2 Experimental

### 2.1 General

*N,N,N',N'*-Tetramethyl-1,6-hexanediamine (TMHDA) was purchased from TCI. Epoxides were purchased from Sigma-Aldrich or Alfa Aesar. These chemicals were used as received. Other chemicals were of analytical grade and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer, and the chemical shifts are reported relative to TMS. The water content was measured by means of a Karl-Fischer titration, using a Metrohm 831 KF Coulometer. IR spectra of catalysts were recorded on a thermo Nicolet 5700 FTIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed with a VG ESCALAB 210 instrument with  $\text{Mg K}\alpha$  source at pass energy of 150 eV, and calibrated versus the Au 4f<sub>7/2</sub> peak at 83.8 eV that arising from gold substrate. Qualitatively and quantitatively analysis were carried out with GC-MS (HP 6890/5973) and GC-FID (Agilent 6820, *n*-octane was used an internal standard). The UV-Visible spectra were recorded on an Agilent 8453 diode array spectrophotometer. Standard 1 cm cells were housed. Methyl red (MR) + bromothymol blue (BTB) was used as an indicator (0.2 w% + 0.5 w% methanol solution), ILs concentrations in methanol was 20 mmol/L, and 50  $\mu\text{L}$  indicator for 2 mL methanol solutions of ILs was used.

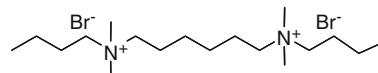


$n = 1, X = \text{Br}, [\text{N}_{112,6}\text{N}_{11}]\text{Br}; n = 3, X = \text{Br}, [\text{N}_{114,6}\text{N}_{11}]\text{Br};$

$n = 5, X = \text{Br}, [\text{N}_{116,6}\text{N}_{11}]\text{Br}; n = 3, X = \text{Cl}, [\text{N}_{112,6}\text{N}_{11}]\text{Cl};$

$n = 3, X = \text{I}, [\text{N}_{112,6}\text{N}_{11}]\text{I}; n = 3, X = \text{BF}_4^-, [\text{N}_{112,6}\text{N}_{11}]\text{BF}_4^-;$

$n = 3, X = \text{NTf}_2^-, [\text{N}_{112,6}\text{N}_{11}]\text{NTf}_2^-$



$[\text{N}_{114}\text{C}_6\text{N}_{114}]\text{Br}_2$

**Scheme 2** Structural formula and abbreviations of quaternary ammonium ILs

## 2.2 Preparation and Characterization of the Quaternary Ammonium ILs

Inspired by the synthesis of 6-(*N,N'*-dimethylamino)-1-(*N,N,N*-trimethylammonium)hexane iodide ([N<sub>111,6N11</sub>]I) mentioned in the literature [33, 34], [N<sub>112,6N11</sub>]Br was synthesized as follows: TMHDA (40 mmol), bromoethane (20 mmol) and ethanol (50 mL) were charged into a sealed reactor with magnetic stirring and reacted at room temperature for 48 h. Then, the ethanol was removed with rot-vap and 30 mL acetone was added, and the bi-quaternary ammonium salt as a white precipitate formed immediately. After filtration, diethyl ether was added to the filtrate to precipitate the product of [N<sub>112,6N11</sub>]Br. The product was purified by recrystallization from acetone/diethyl ether (1:2) and a white hygroscopic powder was obtained.

[N<sub>114,6N11</sub>]Br, [N<sub>114,6N11</sub>]I, [N<sub>116,6N11</sub>]Br was prepared with a similar procedure but processed at 60 °C for 12 h. [N<sub>114,6N11</sub>]Br and [N<sub>114,6N11</sub>]I as white hygroscopic powder were obtained. [N<sub>116,6N11</sub>]Br was a viscous liquid. [N<sub>114</sub>–C<sub>6</sub>–N<sub>114</sub>]Br<sub>2</sub> was a white powder and obtained as the byproduct of [N<sub>114,6N11</sub>]Br.

[N<sub>114,6N11</sub>]Cl was a viscous liquid and also prepared with a similar procedure but processed at 120 °C for 24 h.

For the synthesis of [N<sub>114,6N11</sub>]BF<sub>4</sub> [35], the silver tetrafluoroborate solution was titrated with [N<sub>114,6N11</sub>]Br solution in water against a silver wire electrode. Precipitated silver bromide was removed by filtration and water was removed at 70 °C under reduced pressure. [N<sub>114,6N11</sub>]BF<sub>4</sub> was checked for residual bromide using aqueous AgNO<sub>3</sub>, and no AgBr precipitate was detectable.

For the synthesis of [N<sub>114,6N11</sub>]NTf<sub>2</sub> [36], the CH<sub>2</sub>Cl<sub>2</sub> solution of [N<sub>114,6N11</sub>]Br is reacted with 1.1 equivalence of lithium bis(trifluoromethylsulfonyl)imide (LiNTf<sub>2</sub>) overnight and the organic layer was repeatedly washed with water to remove bromide. CH<sub>2</sub>Cl<sub>2</sub> and water are removed under vacuum and [N<sub>114,6N11</sub>]NTf<sub>2</sub> was obtained.

Before each physicochemical property test, the prepared ILs were dried at 85 °C and 10<sup>-2</sup>–10<sup>-3</sup> mbar for 12 h. And the water content for all the ILs was lower than 200 ppm.

[N<sub>112,6N11</sub>]Br, <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz) δ = 1.32–1.39 (m, 7H), 1.47–1.51 (m, 2H), 1.74–1.78 (m, 2H), 2.19 (s, 6H), 2.32–2.36 (t, J = 7.4, 2H), 3.03 (s, 6H), 3.25–3.29 (m, 2H), 3.35–3.40 ppm (q, J = 7.4, 2H). <sup>13</sup>C NMR (D<sub>2</sub>O, 400 MHz) δ = 8.05, 22.32, 25.97, 26.56, 26.72, 44.33, 50.50, 58.84, 60.12, 64.07 ppm. IR (KBr): 2941, 2861, 2823, 2778, 1487, 1467, 1397, 1259, 1172, 1099, 1039, 1023, 928, 843, 815, 513 cm<sup>-1</sup>.

[N<sub>114,6N11</sub>]Br, <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz) δ = 0.94–0.98 (t, J = 7.4, 3H), 1.36–1.41 (m, 6H), 1.48–1.52 (m, 2H), 1.71–1.77 (m, 4H), 2.19 (s, 6H), 2.33–2.36 (t, J = 7.6, 2H),

3.05 (s, 6H), 3.26–3.30 ppm (t, J = 8.4, 4H). <sup>13</sup>C NMR (D<sub>2</sub>O, 400 MHz) δ = 13.37, 19.64, 22.33, 24.44, 25.93, 26.50, 26.65, 44.32, 51.10, 58.83, 64.39, 64.51 ppm. IR (KBr): 2940, 2863, 2822, 2778, 1487, 1468, 1382, 1260, 1171, 1100, 1040, 1006, 910, 843, 737, 536 cm<sup>-1</sup>.

[N<sub>116,6N11</sub>]Br, <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, 400 MHz): δ = 0.88–0.91 (t, J = 6.8, 3H), 1.34–1.54 (m, 12H), 2.17 (s, 6H), 2.25–2.28 (t, J = 6.8, 2H), 3.41 (s, 6H), 3.67–3.74 ppm (m, 4H). <sup>13</sup>C NMR (D<sub>2</sub>O, 400 MHz) δ = 13.72, 22.27, 25.63, 25.85, 26.31, 26.55, 30.91, 44.19, 51.07, 58.72, 64.35, 64.51 ppm. IR (KBr): 2933, 2860, 2821, 2778, 1487, 1467, 1379, 1260, 1160, 1100, 1041, 1011, 931, 844, 729, 535 cm<sup>-1</sup>.

[N<sub>114,6N11</sub>]Cl, <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz): δ = 0.97–1.01 (t, J = 7.6, 3H), 1.41–1.49 (m, 8H), 1.78–1.86 (m, J = 7.8, 4H), 2.16 (s, 6H), 2.24–2.27 (t, J = 7.0, 2H), 3.45 (s, 6H), 3.71–3.77 ppm (m, J = 6.3, 4H). <sup>13</sup>C NMR (D<sub>2</sub>O, 400 MHz) δ = 13.37, 19.64, 22.33, 24.43, 25.92, 26.49, 26.66, 44.30, 51.07, 58.81, 64.40, 64.52 ppm. IR (KBr): 2940, 2863, 2822, 2778, 1487, 1468, 1383, 1261, 1160, 1100, 1040, 1005, 910, 843 cm<sup>-1</sup>.

[N<sub>114,6N11</sub>]I, <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, 400 MHz): δ = 0.98–1.01 (t, J = 7.2, 3H), 1.41–1.49 (m, 8H), 2.12 (s, 6H), 2.18–2.22 (t, J = 6.8, 2H), 3.37 (s, 6H), 3.63–3.69 ppm (m, 4H). <sup>13</sup>C NMR (D<sub>2</sub>O, 400 MHz) δ = 13.40, 19.64, 22.34, 24.44, 25.90, 26.51, 26.67, 44.32, 51.14, 58.79, 64.41, 64.53 ppm. IR (KBr): 2939, 2862, 2820, 2778, 1482, 1466, 1380, 1260, 1157, 1099, 1039, 1008, 904, 843, 733 cm<sup>-1</sup>.

[N<sub>114,6N11</sub>]BF<sub>4</sub>, <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz): δ = 0.96–1.00 (t, J = 7.4, 3H), 1.40–1.49 (m, 8H), 1.80–1.88 (m, 4H), 2.15 (s, 6H), 2.21–2.25 (t, J = 6.8, 2H), 3.25 (s, 6H), 3.47–3.51 ppm (t, J = 8.6, 4H). <sup>13</sup>C NMR (D<sub>2</sub>O, 400 MHz) δ = 13.35, 19.66, 22.30, 24.31, 24.44, 25.65, 25.74, 43.16, 51.08, 58.14, 64.38, 64.49 ppm. IR (KBr): 2939, 2863, 2821, 2778, 1635, 1468, 1383, 1115, 1038, 843, 739, 533, 483 cm<sup>-1</sup>.

[N<sub>114,6N11</sub>]NTf<sub>2</sub>, <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, 400 MHz): δ = 0.97–1.01 (t, J = 7.4, 3H), 1.41–1.48 (m, 8H), 1.85–1.93 (m, 4H), 2.15 (s, 6H), 2.21–2.25 (t, J = 6.8, 2H), 3.29 (s, 6H), 3.49–3.54 ppm (t, J = 8.6, 4H). <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>, 400 MHz) δ = 13.76, 20.27, 23.12, 25.08, 26.82, 27.40, 27.98, 45.57, 51.31, 59.99, 64.93, 65.12, 120.89, 206.12 ppm. IR (KBr): 2942, 2866, 2818, 2779, 1486, 1470, 1352, 1331, 1226, 1194, 1138, 1057, 789, 740, 654, 617, 571, 514 cm<sup>-1</sup>.

[N<sub>114</sub>–C<sub>6</sub>–N<sub>114</sub>]Br<sub>2</sub>, <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz): δ = 0.94–0.98 (t, J = 7.4, 6H), 1.36–1.43 (m, 8H), 1.72–1.78 (m, 8H), 3.06 (s, 12H), 3.28–3.32 ppm (t, J = 8.2, 8H). <sup>13</sup>C NMR (D<sub>2</sub>O, 400 MHz) δ = 13.43, 19.69, 22.42, 24.51, 25.76, 51.16, 64.39, 64.54 ppm. IR (KBr): 3011, 2960, 2865, 1487, 1465, 1251, 1164, 1067, 965, 935, 910, 809, 737 cm<sup>-1</sup>.

### 2.3 General Procedure for Synthesis of DMC from EO, CO<sub>2</sub> and Methanol

Typically, 0.6 mmol catalyst, 45 mmol EO and 560 mmol methanol were charged into a 90 mL autoclave with magnetic stirring. Then 2 MPa CO<sub>2</sub> was introduced. The reaction was processed at 150 °C for 4–8 h with reaction pressure of 4–5 MPa. After reaction, it was cooled to r.t., and the CO<sub>2</sub> was released. The products were analyzed by GC and GC-MS.

### 2.4 Recycling of the Catalyst

The methanol, DMC, EGME and EG are removed by rotavap under vacuum at 110 °C. Then, fresh EO and methanol were added for next run.

## 3 Results and Discussion

The catalyst screening results for the one-step synthesis of DMC from EO, CO<sub>2</sub> and methanol are listed in Table 1. TMHDA exhibited obvious catalytic activity for this reaction and 36% DMC selectivity was obtained. For tested ILs, 43–74% selectivities for DMC and 3–30% selectivities for byproduct EGME were observed. An catalytic activity sequence of [N<sub>116,6N11</sub>]Br > [N<sub>114,6N11</sub>]Br > [N<sub>112,6N11</sub>]Br was obtained with different alkyl chain length, which maybe due to the different solubility of ILs in reaction systems [37]. Further on, the increasing of alkyl chain length forces the Br<sup>-</sup> away from the cation, and this less electrostatic interaction would render Br<sup>-</sup> more nucleophilic [38]. The order of the activity of ILs with different anions was found to be [N<sub>114,6N11</sub>]I > [N<sub>114,6N11</sub>]Br > [N<sub>114,6N11</sub>]Cl > [N<sub>114,6N11</sub>]BF<sub>4</sub> > [N<sub>114,6N11</sub>]NTf<sub>2</sub>, which is consistent with the order of the nucleophilicity of the anions [27, 39, 40]. Furthermore, the leaving ability of anions has great influence on the catalytic activity. And the leaving ability of the halide anions is I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>, which is consistent with the order of the nucleophilicity of these anions [41]. The best results with 74% DMC yield and only 3% EGME are achieved using [N<sub>114,6N11</sub>]I as catalyst, which displays better catalytic activity in term of TON than other typical catalysts (KI/K<sub>2</sub>CO<sub>3</sub>: 28, DBU: 20, n-Bu<sub>4</sub>NBr/n-Bu<sub>3</sub>N: 34) [19, 23, 25]. This may because of the intramolecular synergistic effect of tertiary amino moiety and quaternary ammonium salt group [11, 42]. Bis-quaternary ammonium salt [N<sub>114-C<sub>6</sub>-N11</sub>]Br<sub>2</sub> were also tested in this reaction. Much lower DMC yields and higher EC yields than that using [N<sub>114,6N11</sub>]I are observed. All these results suggest that both a quaternary ammonium salt group and a tertiary amino moiety are needed for this reaction.

**Table 1** Catalysts screening for the one-pot synthesis of DMC

Catalyst	EO Con. (%) <sup>a</sup>	Sel. (%) <sup>a</sup>				TON <sup>b</sup>
		DMC	EG	EC	EGME	
TMHDA	97	36	35	35	21	29
[N <sub>112,6N11</sub> ]Br	98	62	58	27	10	46
[N <sub>114,6N11</sub> ]Br	99	69	69	25	5	52
[N <sub>116,6N11</sub> ]Br	99	71	68	22	6	53
[N <sub>114,6N11</sub> ]Cl	98	63	62	22	14	47
[N <sub>114,6N11</sub> ]I	99	74	72	22	3	56
[N <sub>114,6N11</sub> ]BF <sub>4</sub>	99	48	49	21	30	36
[N <sub>114,6N11</sub> ]NTf <sub>2</sub>	99	43	43	33	23	32
[N <sub>114-C<sub>6</sub>-N11</sub> ]Br <sub>2</sub>	99	19	14	71	12	12
KI/K <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	100	73	70	23	3	28

Reaction conditions: EO 45 mmol, catalyst 0.6 mmol (1.33 mol% of EO), methanol 560 mmol, initial CO<sub>2</sub> pressure 2 MPa, 150 °C, 8 h

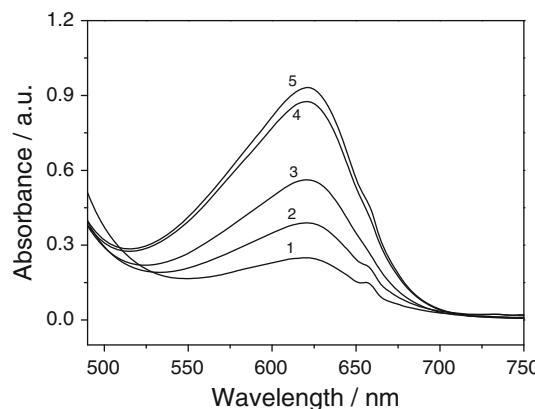
<sup>a</sup> Determined by GC using an internal standard technique

<sup>b</sup> Mol of DMC per mol of catalyst

<sup>c</sup> The TON is calculated based on the amount of KI in Ref. [19]

It has been reported that the Brønsted acidity of ILs can be evaluated by UV–Visible spectroscopy in the presence of Hammett indicator [43–45]. Based on the same theory, we attempted to investigate the base strength of catalysts using MR + BTB as the indicator and a reasonable result was obtained. Figure 1 show the absorbance of indicator in the presence of various ILs. Firstly, several salts such as NaNO<sub>3</sub>, NaOAc, Na<sub>2</sub>HPO<sub>4</sub> and NaOH, which basicity increase gradually, are used as a model system. For these salts, the absorbance of protonated form of BTB at 620 nm increased corresponding, which indicates that this method can be used for the comparison of basicity. As to the catalysts used in this work, the sequences were obtained as follows: [N<sub>112,6N11</sub>]Br > [N<sub>114,6N11</sub>]Br > [N<sub>116,6N11</sub>]Br and [N<sub>114,6N11</sub>]I > [N<sub>114,6N11</sub>]Br > [N<sub>114,6N11</sub>]Cl > [N<sub>114,6N11</sub>]NTf<sub>2</sub> > [N<sub>114,6N11</sub>]BF<sub>4</sub>, indicating that the base strength sequence was not entirely consistent with the catalytic activity order. Normally, better catalytic efficiency could be obtained using quaternary ammonium ILs with stronger base strength by altering anions. However, ILs with longer alkyl chain length, which exhibit lower basicity, have better catalytic efficiency for this reaction, this should be due to the increase in anion activation ability with longer distance between quaternary cation and the anion.

To gain insight into the elemental chemical states of catalyst, [N<sub>114,6N11</sub>]Br was also characterized by XPS. Only C, N, Br elements were observed in XP full spectra analysis, indicating that no other elements were introduced in the IL. As shown in Fig. 2a, the N 1s can be deconvoluted by two pronounced lines at 399.8 and 402.8 eV, which agrees with the nitrogen in tertiary amino moiety

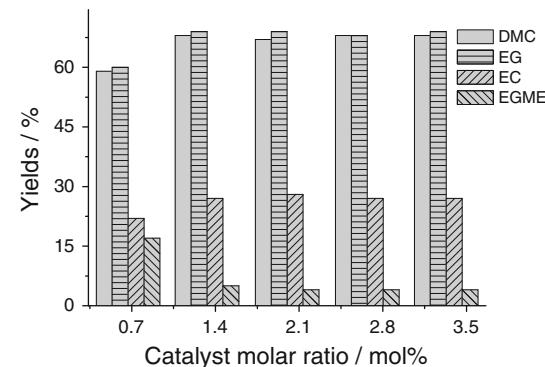


**Fig. 1** Absorption spectra of BTB + MR in methanol solutions of various ILs: 1  $[N_{114,6}N_{11}]BF_4$ , 2  $[N_{114,6}N_{11}]NTf_2$ , 3  $[N_{114,6}N_{11}]Cl$ , 4  $[N_{114,6}N_{11}]Br$ , 5  $[N_{114,6}N_{11}]I$

and quaternary ammonium group, respectively. An exactly 1:1 peak area ratio for these two kinds nitrogen was obtained and it is full accord with the theoretical proportion. As to Br 3d spectrum shown in Fig. 2b, only one kind of bromine was obtained and it can be divided into two peaks at 67.7 and 68.8 eV, this two peaks were assigned to  $3d_{5/2}$  and  $3d_{3/2}$  of  $Br^-$ . The XP analysis also indicated that an intended and pure IL was obtained.

Considering that  $[N_{114,6}N_{11}]Br$  is more stable than  $[N_{114,6}N_{11}]I$ .  $[N_{114,6}N_{11}]Br$  is used to investigate various reaction parameters. The effect of catalyst molar ratio is examined and the results are shown in Fig. 3. If  $[N_{114,6}N_{11}]Br$  was increased from 0.67 to 3.32 mol% (based on EO), DMC, EG and EC yields increased initially and then keep stable. To our delight, the EGME yields decreases from 17 to 4% gradually. Therefore, 1.33 mol% of  $[N_{114,6}N_{11}]Br$  was enough for this reaction with 68% DMC, 69% EG, 25% EC and 5% EGME yields.

In order to investigate the influence of reaction temperatures, the experiments were carried out in the range of 130–170 °C, Fig. 4. At 130 °C, high EC yield but low DMC and EG yield are obtained, which indicates that EC is not efficiently converted into DMC under this reaction temperature. If increasing the reaction temperature from



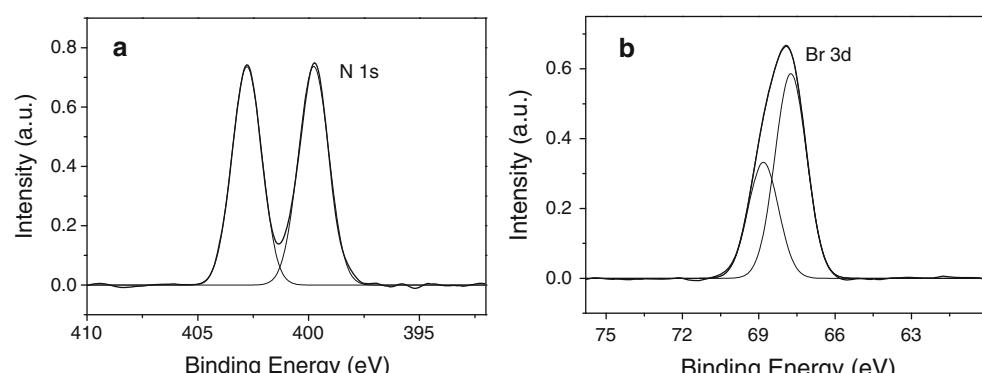
**Fig. 3** Effect of catalyst molar ratio on the one-step synthesis of DMC. Reaction conditions EO 45 mmol, methanol 560 mmol, initial  $CO_2$  pressure 2 MPa, 150 °C, 8 h

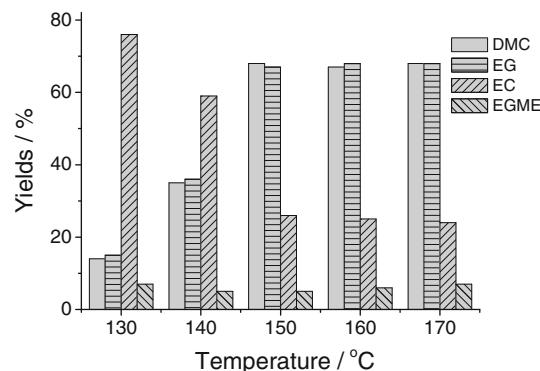
130 to 150 °C, the DMC yield increases gradually and reaches to 69%. Simultaneously, the EC yield decreases from 76 to 24%. Further raising the temperature to 170 °C, the yields for DMC, EG and EC remain constant. All these results illustrate that  $[N_{114,6}N_{11}]Br$  has good catalytic activity and stability in the temperature region of 150–170 °C.

The dependence of yields of DMC, EG, EC and EGME on reaction time is illustrated in Fig. 5. When the reaction processed for 2 h, EO has been converted almost completely and 31% DMC, 32% EG, 61% EC and 4% EGME yields are obtained. And prolonging the reaction time to 4 h, an obvious increase to DMC yield and decrease to EC yield are observed. No increase for DMC yield was observed further prolonging the reaction time to 10 h, which suggested that 4 h is proper for this reaction.

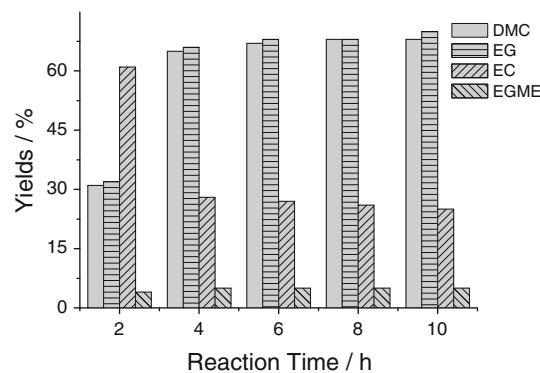
The Influence of reaction pressure on the synthesis of DMC is investigated and the results are shown in Fig. 6. When the pressure increases from 1 to 2 MPa, which provides a pressure between 2.5 and 5 MPa during the reaction, the DMC yields increase from 61 to 69%. If further increasing the pressure to 5 MPa, which provide total 15 MPa pressure during reaction, the DMC yield holds invariable. The results indicate that 2 MPa of initial

**Fig. 2** Deconvoluted **a** N 1s and **b** Br 3d spectra of  $[N_{114,6}N_{11}]Br$





**Fig. 4** Influence of reaction temperature on the one-step synthesis of DMC. *Reaction conditions* EO 45 mmol, methanol 560 mmol, initial CO<sub>2</sub> pressure 2 MPa, [N<sub>114,6N11</sub>]Br 0.6 mmol, 8 h



**Fig. 5** Effect of reaction time on the one-step synthesis of DMC. *Reaction conditions* EO 45 mmol, methanol 560 mmol, initial CO<sub>2</sub> pressure 2 MPa, [N<sub>114,6N11</sub>]Br 0.6 mmol, 150 °C

CO<sub>2</sub> pressure is suitable for this reaction, but higher pressure can reduce the side reactions slightly.

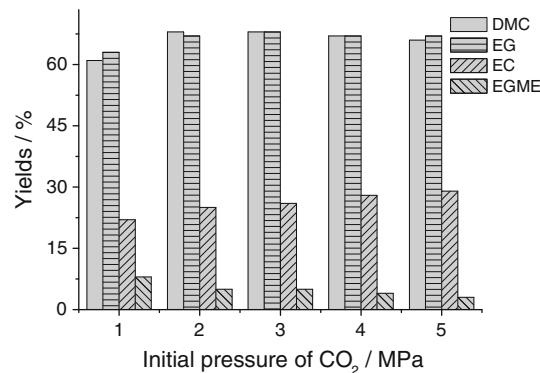
If the methanol/EO molar ratio increases from 3 to 12, the DMC yield increases from 41 to 69%, as shown in Fig. 7. And DMC yield decreases to 64% if further increasing the molar ratio to 18. And a similar result was

obtained for EG. As to EC and EGME, EC yield decreases gradually from 54 to 23% with the increasing of the methanol/EO molar ratio and EGME yield increases from 3 to 9%. Therefore, the appropriate methanol/EO molar ratio is 12, and higher methanol/EO molar ratio is unfavorable to this reaction.

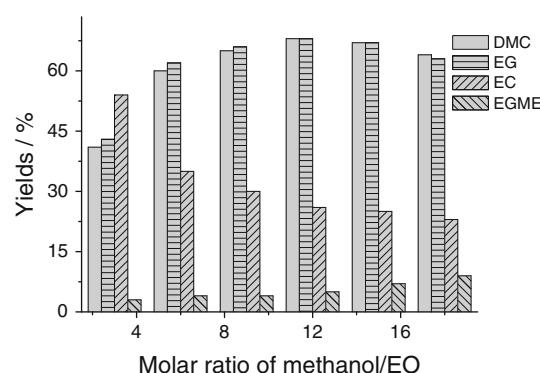
The reusability of the catalyst was also examined using EO as the substrate under the optimized reaction conditions and the results are shown in Fig. 8. The catalyst could be used for six times with a slight decrease of DMC yield. However, an obvious decrease for DMC yield from 63 to 35% was observed when the catalyst was used at the seventh time. The deactivated catalyst was characterized by <sup>1</sup>H NMR, we found that most of tertiary amine moiety of the catalyst, which is the effective component for transesterification reaction, has been alkylated possibly. This should be the reason for the deactivation.

To survey the universality of [N<sub>114,6N11</sub>]Br to other epoxides for the one-step synthesis of DMC, reactions employing propylene oxide (**a**), 1,2-epoxyhexane (**b**), styrene oxide (**c**), glycidyl isopropyl ether (**d**), allyl glycidyl ether (**e**), glycidyl phenyl ether (**f**), and cyclohexene oxide (**g**) were proceeded. The results are summarized in Table 2. At 150 °C, by using 1.5 mol% [N<sub>114,6N11</sub>]Br as catalyst, 90–99% epoxides were transformed to the product and corresponding by-product, monomethyl ether. The DMC selectivity from different epoxides varied obviously and an activity sequence was found to be **f** > **e** > **d** > **c** > **g** > **a** > **b**. In comparison with **a**, a lower DMC yield was obtained for **b** due to the steric hindrance effect of *n*-butyl. If increasing the reaction temperature to 170 °C using **a** and **b**, the DMC yields increased correspondingly, while a slight increase for monomethyl ether was also observed.

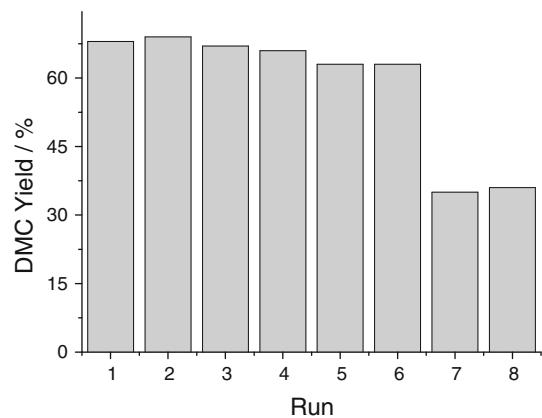
It is accepted that the transesterification reaction is a reversible process and would be the yield-determined step for whole process. However, as to the ILs catalysts, the experimental results showed that the DMC selectivity



**Fig. 6** Influence of initial CO<sub>2</sub> pressure on the one-step synthesis of DMC. *Reaction conditions* EO 22 mmol, methanol 280 mmol, [N<sub>114,6N11</sub>]Br 0.3 mmol, 150 °C, 8 h



**Fig. 7** Effect of methanol/EO molar ratio on the one-step synthesis of DMC. *Reaction conditions* EO 45 mmol, initial CO<sub>2</sub> pressure 2 MPa, [N<sub>114,6N11</sub>]Br 0.6 mmol, 150 °C, 8 h



**Fig. 8** Reuse of the catalyst. *Reaction conditions*: EO 45 mmol, methanol 560 mmol, initial CO<sub>2</sub> pressure 2 MPa, [N<sub>114,6N11</sub>]Br 1 mmol, 150 °C, 8 h

**Table 2** DMC synthesis from various epoxides via one-step method catalyzed by [N<sub>114,6N11</sub>]Br

Substrate	Con. (%) <sup>a</sup>	Sel. (%) <sup>a</sup>		
		DMC	Cyclic carbonate	Monomethyl ether
	99 99 <sup>b</sup>	35 43	59 48	5 8
	98 99 <sup>b</sup>	22 37	75 59	2 3
	95	57	33	9
	97	63	31	5 <sup>c</sup>
	98	66	28	5 <sup>c</sup>
	98	72	23	4 <sup>c</sup>
	90	43	32	23 <sup>c</sup>

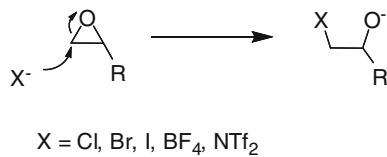
Reaction conditions: epoxide 20 mmol, [N<sub>114,6N11</sub>]Br 0.3 mmol (1.5 mol% of epoxide), methanol 240 mmol, initial CO<sub>2</sub> pressure 2 MPa, 150 °C, 8 h

<sup>a</sup> Determined by GC using an internal standard technique

<sup>b</sup> Reaction temperature 170 °C

<sup>c</sup> Obtained from peak area ratio of monomethyl ether/1,2-diols

could be improved with the increase of the nucleophilicity of anion in ILs. So the ring opening of epoxide through nucleophilic attacks of X<sup>-</sup> also plays an important role in the reaction (Scheme 3). Therefore, higher DMC selectivity was obtained using ILs with nucleophilic anions (such



**Scheme 3** The ring opening of epoxide by nucleophilic attacks

as Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) than less nucleophilic anions (such as BF<sub>4</sub><sup>-</sup> and NTf<sub>2</sub><sup>-</sup>).

#### 4 Conclusion

In conclusion, one kind of novel quaternary ammonium ILs with a tertiary amino moiety and a quaternary ammonium group are synthesized and for the first time used in the one-step synthesis of DMC from EO, CO<sub>2</sub> and methanol. Normally, better catalytic efficiency could be obtained using these ILs with stronger basicity by altering anions. Up to 99% EO conversion and 74% DMC selectivity are obtained using [N<sub>111,6N11</sub>]I as catalyst under relatively mild reaction conditions. These catalysts can be recovered and reused for several times without significant loss in activity.

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