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## Glycerol functionalized imidazolium tri-cationic room temperature ionic liquids: Synthesis, properties and catalytic performance for 2-azidoalcohol synthesis from epoxide



### Avinash A. Chaugule, Ashif H. Tamboli, Faheem A. Sheikh, Wook-Jin Chung, Hern Kim\*

Department of Energy Science and Technology, Energy and Environment Fusion Technology Center, Myongji University, Yongin, Gyeonggi-do 449-728, Republic of Korea

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#### ABSTRACT

Imidazolium based tri-cationic room temperature ionic liquid (RTILs) were synthesized and characterized, and their physicochemical properties such as thermal stability, viscosities and solubility were investigated. These ionic liquids exhibited excellent catalytic activity for 2-azidoalcohol synthesis from epoxide and sodium azide. The present tri-cationic RTILs/water catalytic systems showed better catalytic performance than their mono-cationic counterparts. Among all prepared ionic liquids, [GLY(mim)<sub>3</sub>][OMs] gave best results with up to 96% yield of 2-azidoalcohol. The reusability test of glycerol-tri (3-methylimidazolium) trimesylate [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> were studied for five consecutive cycles presenting the highest yield without loss in their catalytic activity. Hence, the experimental results demonstrated that structural variation of synthesized tri-cationic RTILs can dictate their physicochemical and catalytic activities.

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#### 1. Introduction

Recently, ionic liquid (IL) have attracted much attention towards academic and industrial research since they have shown intense advantages in the context of green chemistry and therefore have great promising potential [1]. Ionic materials are used as a substitute for volatile solvents in organic synthesis. This class of solvent often combines attractive features of considerable thermal stability and low vapor pressure in a single solvent system [2]. ILs are mainly composed of symmetrical and of bulky organic cation paired with anion that can be either organic or inorganic in nature. Moreover, it is well known that physical and chemical properties of an IL are determined by structure of constituent cation and anion. Thus one can systematically tailor an IL with specific properties. This structural flexibility has made ILs most popular among several disciplines of science such as electrochemistry [4,5], biology [6] bio-materials science [7,8] and chemistry [4,5]. These molten salts are extensively persuaded as solvents for chemical reactions, lubricants, modifiers for column chromatography, catalyst and/or catalyst carrier for wide verity of organic reactions [9,10].

In addition, the ILs are frequently used in acid catalysis reaction for synthetic and industrial chemistry [11]. Over the past several decades, halogenated ILs have been looked as a promising candidate for substituting mineral and solid acid catalysts due to their desirable acidic

\* Corresponding author. *E-mail address:* hernkim@mju.ac.kr (H. Kim). and high soluble properties [12]. However, the halogenated ILs are very sensitive to hydrolysis because a trace amount of moisture can change the composition of salt and concentration of protons. Therefore, the development of moisture stable and efficient non-halogenated acidic ILs are advantageous [13,14]. In this regard, various types of non-halogenated room temperature acidic ILs have been reported; such as SO<sub>3</sub>H functionalized IL and 1-butyl-3-methylimidazolium hydrogen sulfate, which are prepared by ion exchange between [BMIm] Cl and H<sub>2</sub>SO<sub>4</sub> [15,16].

Multi-cationic ILs such as di-cationic and tri-cationic ILs have emerged as a new class of ILs that presents improved thermal stability, broader liquid range, higher viscosity and biological activity [17,18]. Diatonic ILs, especially those based on imidazolium or pyridinium cation have shown various pharmaceutical applications [19,20]. Tricationic ILs on the other hand have a rigid geometry. Due to the presence of three charges carrying moieties in very close proximity with each other renders them high apparent polarity. Hence, multi-cationic and tri-cationic ILs have the highest probability of forming room temperature ionic liquids (RTILs) [21]. Current method for synthesis of tricationic ILs involves passing of HCl gas in the mixture of formaldehyde and glycerol followed by reaction with tertiary amine [22]. Resultant ILs were quite efficient for separation of aromatics, alcohols and thiophene from aliphatic hydrocarbon. However, their synthetic method involved the use of highly toxic and corrosive reagents such as HCl gas. Previously, our research group has successfully synthesized a short oligo functioned imidazolium diatonic ILs from ethylene glycol, which shows high thermal stability and catalytic activity [23–25]. From the above analysis, we believe that synthesis of tri-cationic ILs from glycerol would be an eco-friendly procedure.

In the present study, we report synthesis and application of tricationic room temperature ionic liquid (RTILs) in organic reaction. It is reported that glycerol is a non-toxic, biodegradable liquid and can impart different advantages when combined with ILs. These advantages make it ideal for use as a solvent and/or catalyst in organic synthesis. Herein, we introduced imidazolium based tri-cationic RTILs functionalized with glycerol chain. Further, three different types of tri-cationic RTILs using metathesis by changing the ion chemistry were synthesized. We expected such ILs to have excellent physicochemical properties than parent glycerol [26,27]. Furthermore, catalytical activities of these new tri-cationic RTILs in probe of acid catalyzed reaction to 2-azidoalcohol synthesis from epoxide were also investigated.

#### 2. Experimental section

#### 2.1. Material

3-methyl imidazole (99% pure), methane sulfonyl chloride (99% pure), trimethyl amine (99% pure), glycerol (99% pure), potassium bromide (99% pure), bis(trifluoromethanesulfonyl)imide lithium salt (99.95%), potassium hexafluorophosphate (99% pure), sodium sulfate (99%) and all substrates used for azidoalcohol synthesis from epoxide reaction were purchased form Sigma Aldrich, USA with (99%) purity and were used as received. TLC analysis was performed on silica-gel (SIL G/UV 254) plates to monitor the reaction.

#### 2.2. Characterization and measurements

The products were characterized by comparison of their spectroscopic data (<sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR analysis) with physical properties to those reported in the literature. NMR spectra were recorded in DMSO- $d_6$  on 400 MHz spectrometers using TMS as an internal standard. The FTIR spectra of samples were obtained by pelletizing the dried samples with potassium bromide (KBr) and recorded using Varian 2000 (Scimitar series) spectrophotometer. A spectrum was recorded from 4000 to 500 cm<sup>-1</sup> maintaining a resolution of 4 cm<sup>-1</sup> with 32 scans in transmittance mode. Mass spectra for samples were obtained using Waters Micromass ZO LC/MS 2000 (Scimitar series) spectrophotometer. Thermogravimetric analysis (TGA, model SETARAM-92-16-18) was used to check the thermal stability of samples. The heating of samples were carried out at room temperature to 600 °C, with a heating rate of 10 °C/min under a continuous purge of nitrogen (50 mL/min), and spectra were collected using Q600 Software (TA Instruments). Differential scanning calorimetry (DSC) data were obtained in sealed aluminum pan with cooling and heating rate of 10 °C/min on Mettler DSC822, under the continuous purge of nitrogen (50 mL/min). Viscosity measurements were performed using a Brook-field model DV-II+ programmable viscometer connected with temperature controlled heating bath. All yields refer to isolated products.

#### 2.3. Typical procedure for synthesis of tri-cationic RTILs

#### 2.3.1. Typical procedure for synthesis of trimesylate precursors<sup>a</sup>

Scheme 1 illustrates the procedure for synthesis of trimesylate precursors. Initially, 1.0 mmol of glycerol and 3.5 mmol of trimethylamine were added in a round bottom flask with excess of dichloromethane. Then, the reaction mixture was cooled to 0 °C in ice bath, and subsequently stirred to have proper mixing. To this solution, 3.5 mmol of methane sulfonyl chloride was added in a dropwise manner within a period of 10 to 15 min. This reaction mixture was further subjected continuous stirring at room temperature for 12 h. Meanwhile, the completion of the reaction was monitored by TLC using (30% ethyl acetate: hexane). After the completion of reaction, the reaction mixture was extracted with water and dichloromethane. The organic layer was washed with water three times, dried over sodium sulfate and concentrated by rotary evaporator. Resultant pre-precursor product appeared orange in color which was kept at room temperature for 24 h to obtain afforded solid as trimesylate precursor (yield 89%).

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ): $\partial$  3.25 (s, 9H), 4.45 (d, 4H), 5.15 (m, 1H). FT-IR (500–4000 cm<sup>-1</sup>): 768 cm<sup>-1</sup> (S–O), 1113, 1380 cm<sup>-1</sup> (S = O), 2866, 2985 cm<sup>-1</sup> (C–H). <sup>13</sup>C NMR (125 MHz): 14, 15, 45, 53. HR-MS m/z [M-OMs]<sup>+</sup>: 138.19. Calcd (%): C 22.08, H 4.32, O 44.12, S 29.47; Found: C 21.07, H 4.31, O 44.12, S 29.46.

# 2.3.2. Synthesis of glycerol-tri (3-methylimidazolium) trimesylate [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub>

In this typical procedure, trimesylate precursor (1.0 mmol) and 3-methylimidazolium (3.0 mmol) was refluxed in acetonitrile at 75 °C for 28 h. After completion of the reaction, obtained mixture was cooled down at room temperature and excess solvents were removed by using a rotary evaporator. The remaining mixture was washed three times with ethyl acetate to remove un-reacted starting material. And, the afforded product resulted in formation of glycerol-tri(3-methylimidazolium) trimesylate IL. (yield 91.25%)

[GLY(mim)<sub>3</sub>][OMs]<sub>3</sub>, Thick liquid: <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ): $\partial$  2.41 (m, 3 × 3H), 3.47 (s, 3 × 3H), 3.66 (m, 5H), 9.24 (s, 3 × 1H), 7.59–7.67 (m, 3 × 2H); FT-IR (500–4000 cm<sup>-1</sup>): 1198, 1210 cm<sup>-1</sup> (S = O), 1398, 1465 cm<sup>-1</sup> (C = C), 1623 cm<sup>-1</sup> (C = N), 3095 cm<sup>-1</sup> (Ar-H), 2912 cm<sup>-1</sup>, 2870 cm<sup>-1</sup> (C-H). <sup>13</sup>C NMR (125 MHz): 33.26, 39.4, 45.44, 48.5, 118, 120.34, 125.96, 136.90. HR-MS m/z [M-OMs]<sup>+</sup>: 382.18. Analysis: C<sub>21</sub>H<sub>41</sub>N<sub>6</sub>O<sub>9</sub>S<sub>3</sub>, Calcd (%): C 40.83, H 6.69, N 13.60, O 23.31, S 15.56; Found: C 40.80, H 6.66, N 13.61, O 22.98, S 15.6.

### 2.3.3. Synthesis of glycerol-tri (3-methylimidazolium)

 $bis(trifluoromethanesufonyl)imide [GLY(mim)_3][NTf_2]_3$ 

In round bottom flask, as aforementioned procedure the prepared glycerol-tri (3-methylimidazolium)trimesylate (0.17 mol) and bis(trifluoromethanesulfonyl)imide lithium salt (0.52 mol) reacted in acetone at room temperature for 28 h. Then, the reaction mixture was filtered and washed three times with acetone for complete removal of salts formed during reaction. The [GLY(mim)<sub>3</sub>][NTf<sub>2</sub>]<sub>3</sub> was afforded by evaporating the acetone under vacuum. (yield 91.96%).

 $[GLY(mim)_3][NTf_2]_3$ , Thick liquid: <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ): $\partial$  3.65 (s, 3 × 3H), 3.80 (m, 5H), 8.78 (s, 3 × 1H), 7.8 (m, 3 × 2H). FT-IR



Scheme 1. Synthesis of glycerol-tri (3-methylimidazolium) trimesylatetricationic RTILs.

 $(500-4000\ cm^{-1}): 1055\ cm^{-1}\ (C-F), 1198\ cm^{-1}, 1210\ cm^{-1}\ (S=O), 1346\ cm^{-1}, 1441\ cm^{-1}\ (C=C), 1623\ cm^{-1}\ (C=N), 3095\ cm^{-1}\ (Ar-H), 2912\ cm^{-1}, 2870\ cm^{-1}\ (C-H). ^{13}C\ NMR\ (125\ MHz): 33.86, 36.18, 46.88, 49.46, 117.92, 121.11\ (C-N), 126.15, 137.\ HR-MS\ m/z\ [M-OMs]^+: 567.11.\ Analysis: C_{24}H_{32}F_{18}N_9O_{12}S_6, Calcd\ (\%): C\ 24.58, H\ 2.75, N\ 10.76, O\ 16.37, S\ 16.40\ Found: C\ 24.50, H\ 2.78, N\ 10.76, O\ 16.30, S\ 16.38.$ 

# 2.3.4. Synthesis of glycerol-tri (3-methylimidazolium) hexafluorophosphate [GLY(mim)<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub>

Glycerol-tri (3-methylimidazolium) hexafluorophosphate IL was synthesized with the same procedure as described for  $[GLY(mim)_3][NTf_2]_3IL$ using glycerol-tri(3-methylimidazolium)trimesylate (0.17 mol) and potassium hexafluorophosphate (0.52 mol) to obtain  $[GLY(mim)_3][PF_6]_3$ IL. The crude salts in reaction were removed by filtration and  $[GLY(mim)_3][PF_6]_3$  IL was collected by evaporating acetone under reduced pressure. (Yield 93.12%)

[GLY(mim)<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub>, Thick liquid: <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): $\partial$ 3.63 (s, 3 × 3H), 3.51–3.71 (m, 5H), 9.21 (s, 3 × 1H), 7.76–7.80 (m, 3 × 2H). FT-IR (500–4000 cm<sup>-1</sup>): 1198 cm<sup>-1</sup>, 1210 cm<sup>-1</sup> (S–O), 1364 cm<sup>-1</sup>, 1441 cm<sup>-1</sup> (C = C), 1623 cm<sup>-1</sup> (C = N), 3095 cm<sup>-1</sup>(Ar– H), 2912, 2870 cm<sup>-1</sup>(C–H). <sup>13</sup>C NMR (125 MHz): 33.90, 39.58, 46.12, 50.28, 120, 128, 137. HR-MS *m/z* [M-OMs]<sup>+</sup>: 432.29. Analysis: C<sub>18</sub>H<sub>32</sub>F<sub>18</sub>N<sub>6</sub>P<sub>3</sub>, Calcd (%): C 28.17, H 4.20, N 10.95; Found: C 28.17, H 4.18, N 10.92.

#### 2.3.5. Glycerol-tri (3-methylimidazolium) bromide [GLY(mim)<sub>3</sub>][Br]<sub>3</sub>

Glycerol-tri(3-methylimidazolium) bromide IL was also synthesized by the same strategy as was done in the case of  $[GLY(mim)_3][NTf_2]_3$ using glycerol-tri(3-methylimidazolium)trimesylate (0.17 mol) and potassium bromide (0.52 mol) to form  $GLY(mim)_3][Br]_3$ . The crude salts in reaction mixture were removed by filtration and  $[GLY(mim)_3][Br]_3$  IL was obtained by evaporating acetone under a reduced pressure. (yield 92.50%). [GLY (mim)<sub>3</sub>][Br]<sub>3</sub> Thick liquid: <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ): $\partial$ 3.51 (s, 3 × 3H), 3.83 (m, 5H), 8.80 (s, 3 × 1H), 7.71–7.80 (m, 3 × 2H). FT-IR (500–4000 cm<sup>-1</sup>): 1198 cm<sup>-1</sup>, 1210 cm<sup>-1</sup> (S = 0), 1364 cm<sup>-1</sup>, 1441 cm<sup>-1</sup> (C = C), 1623 cm<sup>-1</sup> (C = N), 3095 cm<sup>-1</sup>(Ar-H), 2912 cm<sup>-1</sup>, 2870 cm<sup>-1</sup>(C-H). <sup>13</sup>C NMR (125 MHz): 33.96, 39.58, 46.12, 50.25, 120.79, 128.55, 137.16. HR-MS *m*/*z* [M-OMs]<sup>+</sup>: 367.25. Analysis: C<sub>18</sub>H<sub>32</sub>Br<sub>3</sub>N<sub>6</sub>. Calcd (%): C 37.73, H 5.64, Br 41.89, N 14.69; Found: C 37.70, H 5.61, Br 41.91, N 14.65.

#### 2.4. General procedure of 2-azidoalcohol formation from epoxides

The procedure to synthesize 2-azidoalcohol was carried our using previously reported conditions [23]. In brief, epoxides (0.83 mol) and sodium azide (1.24 mol) was taken in a 50 ml round bottom flask. Then 0.15 mol of corresponding tri-cationic ILs/water (IL/H<sub>2</sub>O (2:1)) was used as catalyst/solvent in reaction media. The reaction mixture was heated at 60 °C for 60 to 180 min for different catalysts prepared in this study. Reaction progress was monitored by TLC using (5% ethyl acetate: hexane). After the completion of reaction, the obtained mixture was extracted three times with ether, dried in sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and associated ether solvent was removed under reduced pressure. The resulting 2-azidoalcohol product was purified by column chromatography.

Table 3 A: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>); $\partial$  1.2–1.80 (8H, m), 3.11(1H, td, J = 6.0 Hz), 3.35(1H, td, J = 7.1 Hz), 4.05(1H, brs); FI-IR (500–4000 cm<sup>-1</sup>):2100 cm<sup>-1</sup>, 3400 cm<sup>-1</sup>. <sup>13</sup>CNMR (125 MHz): 24.5, 24.6, 30, 33, 67, 74.

Table 3 B: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>);  $\partial$  1.96 (1H, brs, OH), 3.70 (2H, d, J = 6.1 Hz, CH<sub>2</sub>OH), 4.8 (1H,t, J = 6.3, 4.4 Hz), 7.23–7.48 (5H, m, AH), <sup>13</sup>C NMR (125 MHz): 55, 78, 126,128, 128.5, 139; FI-IR (500–4000 cm<sup>-1</sup>): 2100 cm<sup>-1</sup>, 3400 cm<sup>-1</sup>.

Table 3 C: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>); $\partial$  1.2 (1H, dd, J = 8.0 Hz, 12 Hz, CH<sup>a</sup>N3), 3.3 (1H, dd, J = 4.1 Hz, 8.1 Hz, CH<sup>b</sup>N3), 3.8 (1H, m, CHOH), 3.75 (1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, CH<sup>a</sup>Cl), 4.0 (1H, s, OH), 4.05(1H, dd, J = 7.9 Hz, 12 Hz, 1



[GLY(mim)<sub>3</sub>][NTf<sub>2</sub>]<sub>3</sub>

 $[GLY(mim)_3][PF_6]_3$ 

[GLY(mim)<sub>3</sub>][Br]<sub>3</sub>

#### Scheme 2. Synthesis of tri-cationic RTILs using metathesis of glycerol-tri (3-methylimidazolium) trimesylate IL.



Fig. 1. Thermogravimetric analysis of synthesized tri-cationic RTILs.

4.1 Hz, 8.0 Hz, CH<sup>b</sup>Cl); FT-IR (500–4000 cm<sup>-1</sup>): 3326 cm<sup>-1</sup>, 2113 cm<sup>-1</sup>. <sup>13</sup>C NMR (125 MHz); 54.5, 78, 65.

Table 3 D: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>); 0.98 (3H, t, J = 7.0, 4.0 Hz, CH<sub>3</sub>), 1.42–1.66 (2H, m, CH<sub>2</sub>), 1.94 (1H, s, OH), 3.16–3.50 (m, 2H, CH<sub>2</sub>N<sub>3</sub>), 3.56–3.76 (m, 1H, CHOH). FT-IR (500–4000 cm<sup>-1</sup>): 3326 cm<sup>-1</sup>, 2113 cm<sup>-1</sup>. <sup>13</sup>C NMR (125 MHz); 54.5, 78, 30.2, 11.9.

Table 3 E: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>); 1.6 (1H, dd, J = 8.0 Hz, 12 Hz, CH<sup>a</sup>N3), 3.5 (1H, dd, J = 4.1 Hz, 8.1 Hz, CH<sup>b</sup>N3), 3.7 (1H, m, CHOH), 3.80 (1H, dd, J = 7.6 Hz, 12 Hz, CH<sup>a</sup>OH), 4.0–4.2 (2H, s, OH), 4.05 (1H, dd, J = 4.5 Hz, 7.8 Hz, CH<sup>b</sup>Cl); FT-IR (500–4000 cm<sup>-1</sup>): 3326, 2113 cm<sup>-1</sup>. <sup>13</sup>C NMR (125 MHz); 53.5, 75.8, 65.2.

Table 3 F: <sup>1</sup>H NMR (400 MHz, CDCl3); 1.26 (brs, 1H, OH), 1.48–2.37 (m, 6H, CH2), 3.64–3.72 (q, 1H, CHN3), 4.08–4.28 (q, 1H, CHOH). FT-IR (500–4000 cm<sup>-1</sup>): 3289 cm<sup>-1</sup>, 2213 cm<sup>-1</sup>. 13C NMR (125 MHz); 24.3, 30.1, 33.2, 78.6, 65.1.

#### 2.5. Separation of tri-cationic RTILs

After the completion of reaction, the reaming excess of NaN<sub>3</sub> and NaOH containing tri-cationic RTILs was transferred to round bottom flask. This mixture was diluted with acetonitrile and stirred for 20 min. The actonitrile containing layer was separated out by simple decantation and dried over sodium sulfate. Finally, the acetonitrile was evaporated under reduced pressure to obtain the tri-cationic RTILs as a thick liquid.

#### 3. Results and discussion

#### 3.1. Preparation and characterization of tri-cationic RTILs

Scheme 1 illustrates the synthetic route for preparation of tricationic RTILs and synthesized materials were characterized using various techniques. Initially the preliminary trimesylate precursor was prepared from protecting hydroxyl groups of glycerol by methanesulfonyl

Fable 1	
Solubility and thermal stability properties of synthesized tri-cationic RTI	Ls.

	Tri-cationic ILs	Solvent	Solvent								
		H <sub>2</sub> 0	MeOH	Acetone	EtOAc	CHCl <sub>3</sub>	Toluene	CH <sub>3</sub> CN	$C_{6}H_{12}$	Td	
1	[GLY(mim) <sub>3</sub> ][OMs] <sub>3</sub>	М	М	М	IM	М	IM	М	IM	343	
2	[GLY(mim) <sub>3</sub> ][NTF <sub>2</sub> ] <sub>3</sub>	IM	М	М	IM	Μ	IM	Μ	IM	301	
3	[GLY(mim) <sub>3</sub> ][PF <sub>6</sub> ] <sub>3</sub>	IM	М	М	IM	Μ	IM	Μ	IM	321	
4	[GLY(mim) <sub>3</sub> ][Br] <sub>3</sub>	М	Μ	Μ	IM	М	IM	Μ	IM	202	

M = miscible, IM = immiscible, Td = thermal decomposition temperature.

chloride. Further, protected glycerol compound was used for the synthesis of four *N*-methylimidazolium based ILs. The ILs were afforded by reacting *N*-methylimidazolium and various anions salts such as  $^{-}$ OMs,  $^{-}$ NTf<sub>2</sub>,  $^{-}$ PF<sub>6</sub>, and  $^{-}$ Br (Scheme 2). The *N*-methylimidazolium was preferred because of its compatibility with acid, easy availability as well as low cost. The detailed synthetic procedure is described in the aforementioned experimental sections. The obtained RTILs were characterized by <sup>1</sup>HNMR, FT-IR and elemental analysis. We used glycerol as starting reactant to develop trimesylate precursor which was further converted to a tri-cationic IL. The [OMs]<sup>-</sup> and [NTf<sub>2</sub>]<sup>-</sup> types of anions in between the three imidazolium cation were discovered efficient to develop physicochemical properties and catalytic activity in organic reaction.

#### 3.2. Thermal properties of tri-cationic ionic liquid

#### 3.2.1. TGA and DSC analyses

Thermal decomposition (Td) temperatures of all synthesized tricationic RTILs were measured by thermogravimetric analyzer (TGA) under nitrogen atmosphere with heating rate of 10 °C/min. The TGA curve obtained for synthesized tri-cationic RTILs are shown in Fig. 1 and the Td values are presented in Table 1. It was observed that the thermal behavior of all tri-cationic RTILs presented a higher stability and thermal decomposition was observed in the range of 202 to 343 °C. TGA curves for  $GLY(mim)_3$  [OMs]<sub>3</sub> and  $GLY(mim)_3$  [PF<sub>6</sub>]<sub>3</sub> clearly shows thermal decomposition occurring at 343 °C and 321 °C. Subsequently, TGA curve for GLY(mim)<sub>3</sub>][Br]<sub>3</sub> IL shows thermal decomposition start at 170 °C in the first step. Finally, the 90% weight loss was observed at 383 °C. For GLY(mim)<sub>3</sub>][NTf<sub>2</sub>]<sub>3</sub> IL, 20% weight loss occurred at 243 °C and further 90% weight loss was observed at 387 °C. As compared all values of T<sub>d</sub> for tri-cationic RTILs exhibited to be more thermally stable than commonly used traditional mono-cationic ILs [28,29]. This implies that TGA curves for all tri-cationic IL is strongly affected by presence of anions. The [OMs]<sup>-</sup> anion presented the higher thermal stability, whereas [Br]<sup>-</sup> anion has showed a lower thermal stability. The high thermal stability of [OMs]<sup>-</sup> anionic tri-cationic RTIL was due to the presence of three imidazolium ring. From the above observation it can be concluded that the presence of three imidazolium cation moieties can significantly increase the thermal stability of ILs.

Fig. 2 shows the results of differential scanning calorimetry (DSC) analysis for prepared tri-cationic RTILs. The DSC curve for all tricationic ILs was observed in two cycles that was 200 °C to -30 °C and -30 °C to 200 °C. The 200 °C to -30 °C cycles for [OMs]<sup>-</sup>, [NTf<sub>2</sub>]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup> and [Br]<sup>-</sup> anionic tri-cationic ILs did not show any crystallization effect on cooling, and -30 °C to 200 °C cycles shows well stability of ILs on heating. However, DSC analysis estimated the higher stability of tricationic RTILs and even at -30 °C all tri-cationic ILs were in a liquid state. This indicates that these ILs have wide liquid range coupled with higher thermal stability. Therefore, these ILs can offer a wide variety of application.

#### 3.3. The viscosity and solubility of prepared tri-cationic RTILs

Viscosity of the ILs is of enormous importance for its use as a solvent, catalyst in chemical reactions and its diffusion rate in various



Fig. 2. Differential scanning colorimetry analysis of synthesized tri-cationic RTILs.

reactions [3,12,17]. Fig. 3 shows the viscosity of all prepared tri-cationic RTILs at temperature ranging from 25 °C to 80 °C. Before measuring viscosity, the ILs were dried at 60-80 °C for 3 h under vacuum. The results show that all four different anions containing ILs shows different viscosity at 25, 40, 60 and 80 °C. Preliminary at 25 °C (i.e., room temperature), viscosity of all ILs were observed nearly in the range of 1396 cP, 1203 cP, 610 cP and 400 cP for  $[PF_6]^-$ ,  $[OMs]^-$ ,  $[NTf_2]^-$ ,  $[Br]^-$  anions, respectively, containing tri-cationic ILs. From these values it clearly demonstrates that viscosity of  $[PF_6]^-$  and  $[OMs]^-$  containing IL was significantly higher than [NTf<sub>2</sub>]<sup>-</sup> and [Br]<sup>-</sup> containing ILs. Furthermore, when we increase the temperature from 40 to 60 °C, it was found that viscosity of all ILs decreased in the range of 100-202 cP and 400-180 cP, respectively. At last, when temperature was further increased from 60 to 80 °C, we observed a strong decrease in viscosity in the range of 120-80 cP for all ILs. In all prepared tri-cationic RTILs cation and anion moieties play an important role for high range of viscosity. According to observed viscosity (Fig. 3) IL containing  $[PF_6]^-$  and  $[OMs]^-$  anion were more viscous compared to others. The tri-imidazolium symmetric moieties with  $[OMs]^-$  and  $[PF_6]^-$  anions are mainly responsible for hydrogen bonding and Van der waals interaction which create a positive effect on viscosity of RTILs. Hence, we can conclude that the synthesized RTILs show a high range of viscosity which is strongly dependent on cation and anion com-



Fig. 3. Viscosity of synthesized tri-cationic RTILs at different temperatures.

bination. Moreover, the higher viscosity tri-cationic ILs are reported for various applications such as stationary phase in liquid chromatography for solving separation of organic compounds [15].

Solubility of the synthesized tri-cationic RTILs was determined in different solvents at room temperature and results are summarized in Table 1. As mentioned earlier, RTILs are amphiphilic in nature which strongly depend on it constituent cation and anions. The [OMs] and [Br] anionic tri-cationic IL was soluble in polar solvent and insoluble in non-polar solvents. This property may be attributed due to the hydrogen bonding strength of imidazolium cation with polar solvents. The  $[NTf_2]^-$  and  $[PF_6]^-$  anionic tri-cationic IL was sinsoluble in water and non-polar solvents. The solubility behavior of  $[OMs]^-$ ,  $[Br]^-$ ,  $[PF_6]^-$  and  $[NTf_2]^-$  anionic tri-cationic ILs was similar to previously reported di-cationic ILs [30].

#### 3.4. Determination of acidity for tri-cationic RTILs

To determine the acidity of ILs is challenging and moderately a new subject. Therefore, various methods have been reported to investigate the phenomenon; such methods include determination of Lewis acidity by IR spectroscopic method and bronsted acidity using UV-vis spectroscopy [31]. Yang and Kou et al. determined Lewis and bronsted acidity of IL by monitoring the shift of IR absorption bands at 1450  $\text{cm}^{-1}$  and 1540 cm<sup>-1</sup> for pyridine. This method implies that the presence of band occurring at 1437  $\text{cm}^{-1}$  for pure pyridine is shifted near 1450 cm<sup>-1</sup> that indicates pyridine is coordinated to Lewis acid sites. Moreover, the band that shifted near 1540 cm<sup>-1</sup> is an indication of pyridinium ions resulting from the presence of Brønsted acidic sites. Similarly we used IR spectroscopic methods for determination of Lewis acidity of tri-cationic ILs. In this regard, Fig. 4 shows the shifting of IR bands for pyridine mixed ILs near the band position of 1450 cm<sup>-1</sup>. The characteristic band of pure pyridine was observed at 1435  $\text{cm}^{-1}$ . Therefore, the pure pyridine was added to the ILs and shifting of characteristic band of pyridine was observed. When pyridine was mixed with GLY(mim)<sub>3</sub>][Br]<sub>3</sub> IL, no shift of 1435 cm<sup>-1</sup> band occurred that indicates the neutral behavior. However, for  $GLY(mim)_3$  [OMs]<sub>3</sub> shifting of 1435 cm<sup>-1</sup> to 1442 cm<sup>-1</sup> was observed that indicates the presence of Lewis acidity. Correspondingly, for GLY(mim)<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub> and GLY(mim)<sub>3</sub>][NTF<sub>2</sub>]<sub>3</sub> ILs the shift in pyridine band was observed at  $1439 \text{ cm}^{-1}$  and  $1437 \text{ cm}^{-1}$  that confirm the presence of Lewis acidic sides. Hence, the above results showed that all synthesized tri-cationic ILs do not belong to Brønsted acidic sites. However, we can conclude that except [Br] containing ILs, [NTF<sub>2</sub>], [PF<sub>6</sub>] and [OMs]



**Fig. 4.** FT-IR spectra of (A) pure pyridine; (B) pyridine +  $GLY(mim)_3][Br]_3(1:5)$ ; (C) pyridine +  $GLY(mim)_3][NTf_2]_3(1:5)$ ; (D) pyridine +  $GLY(mim)_3][PF_6]_3$  (1:5); (E) pyridine +  $GLY(mim)_3][OMs]_3$  (1:5).

Table 2	
Catalytic activity for synthesized RTILs for 2-azidoalcohol from epo	oxide reaction. <sup>a</sup>

Entry	Catalyst/reagent	Time (min)	Temperature	Catalyst amount (equiv.)	Conversion (%)	Yield (%)	Refs.
1	[GLY(mim) <sub>3</sub> ][OMs] <sub>3</sub>	60	60	0.15	100	96	In this study
2	[GLY(mim) <sub>3</sub> ][NTFs] <sub>3</sub>	90	60	0.15	100	85	In this study
3	$[GLY(mim)_3][PF_6]_3$	100	60	0.15	100	78	In this study
4	[GLY(mim) <sub>3</sub> ][Br] <sub>3</sub>	100	60	0.15	100	50	In this study
5	[Bmim]PF <sub>6</sub>	180	65	0.3	85	95	[32]
6	MPTC	30	Reflux	0.5	77	85	[33]
7	Er(OTf) <sub>3</sub>	400	r.t.	2 to 1.5	93	85	[34]
8	NaN <sub>3</sub> /H <sub>2</sub> O	180	60	0	40	25	In the study

<sup>a</sup> All reactions were carried out on a 1.0 mmol scale of substrate and NaN<sub>3</sub> with 0.15 equivalent of RTILs/H<sub>2</sub>O (2:1).

anion containing imidazolium tri-cationic ILs were Lewis acidic in nature.

#### 3.5. Catalytic activity test for synthesized tri-cationic RTILs

The prepared tri-cationic ILs possess Lewis acidity therefore, we used these ILs for acid catalyzed reaction. The epoxide opening reaction by azide addition is a typical acid-catalyzed reaction; therefore, various acidic catalysts have been examined [32]. We studied the ILs catalyst loading effect on reaction yield by varying the quantity of [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> IL (i.e., 0.05, 0.10, 0.15 and 0.2 mmol/1 mmol of cyclohexene oxide). It was observed that 0.15 mmol of GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> IL shows high yield of 2azidoalcohol. Therefore, 0.15 mmol of catalyst amount was selected for further ILs catalytic reactions.

The effect of reaction time and product yield for 2-azidoalcohol formation catalyzed by tri-cationic RTILs were estimated and compared with different reported catalysts summarized in Table 2. We performed the 2-azidoalcohol formation reaction on cyclohexene oxide with sodium azide using RTILs/H<sub>2</sub>O (2:1) system at 60 °C (Scheme 3). Initially, in the absence of RTILs the reaction gives only 25% of yield for 2azidoalcohol product from cyclohexene oxide. While as, in presence of tri-cationic ILs the yield of 2-azidoalcohol was considerably increased more than 25%. Hence, the above results describe the role of tri-cationic RTILs as an efficient catalyst.

Furthermore, all synthesized tri-cationic ILs efficiently revealed the conversion for cyclohexene oxide to 2-azidoalcohol in appreciable time. Especially, the [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> IL was giving the 100% conversion and 96% yield in short time than the other ILs. The  $[GLY(mim)_3][NTf_2]_3$ . [GLY(mim)<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub> and [GLY(mim)<sub>3</sub>][Br]<sub>3</sub> ILs also provided higher vields and conversion efficiency. Addition of RTILs significantly improve the reaction rate and yields. This is probably due to activation of the epoxide ring by acidic hydrogen of the imidazole moieties and rapid nucleophilic attack of azide on epoxide. Hence, the combination of IL and water as catalyst/solvent system were found to be a valuable reaction media for the conversion of epoxides. The cleavage of the epoxide with sodium azide was performed in both hydrophobic and hydrophilic RTILs. However, the [GLY(mim)<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub> and [GLY(mim)<sub>3</sub>][Br]<sub>3</sub> ILs showed less yield of azidoalcohol than [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> IL. This is because of the mass transfer issue of hydrophobic IL during the reaction. The [GLY(mim)<sub>3</sub>][Br]<sub>3</sub> IL was observed to be of neutral behavior and presented a relatively acceptable yield of 50% (Table 2).

To compare the catalyst activity of reported mono-cationic IL and MPTC [32,33] with prepared tri-cationic ILs (Table 2 entries 5 and 6). We performed the 2-azidoalcohol formation reaction on cyclohexene oxide epoxide using 0.15 equivalent [Bmim]PF<sub>6</sub> IL and MPTC at 60 °C. The [Bmim]PF<sub>6</sub> IL presented 80% conversion and 76% yield of 2azidoalcohol in 180 min, while, MPTC catalyst provides 81% conversion and 77% yield. From these observations it can be concluded that by using 0.15 equivalent of tri-cationic ILs catalyst amount shows the higher catalytic activity than [Bmim]PF<sub>6</sub> and MPTC ILs.

In addition to that, we have also tested structurally varied epoxide with different functional groups for title reactions with using catalytic amount of [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> IL. Table 3 summarizes the yield of azide addition product for different derivatives of epoxide. Through cyclic epoxide, the complete ring opening took place by transstereospecific pathway and obtained trans isomers as a major product (Table 3 entries A, F). In the case of styrene oxide, due to formation of the stabilized benzylic cation through the reaction, ring opening with NaN<sub>3</sub> resulted in 2-azido-2-phenylethanol as the major product with selectively (Table 3 entry B). This reaction was completed in 100 min with 85% yield of 2-azido-2-phenylethanol using a [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> IL. In order to investigate the effect of polar electron withdrawing groups adjacent to the epoxide ring, the reaction of 3-chloro-1,2epoxypropane with azide was performed to obtained the 1-azido and 2-azido product with 91% and 9% yield in [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> IL (Table 3 entry C). With acyclic terminal olefin the major product acquired from the attack of nucleophile at the less hindered carbon of the epoxides. Therefore, all terminal epoxide gives the highly selective 1,2 azidoalcohol product with good and excellent yields. Moreover, 3azidopropane-1, 2-diol was obtained as a major product from cyclopropylmethanol (Table 3 entries D & E).

#### 3.6. Reusability of tri-cationic RTILs

The catalytic reusability and stability are very significant factors in catalyzed organic reactions. The reusability of [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> was selected to verify the precise recyclability for 2-azidoalcohol synthesis from cyclohexene oxide. Fig. 5 shows the yield of 2-azidohexanol synthesized from cyclohexene oxide for five cycles. The results clearly demonstrate that GLY(mim)<sub>3</sub>[[OMs]<sub>3</sub> IL provide above 92% yield until five consecutive cycles. This indicates a high stability and nearly no loss of activity. However, the slight decrease in activity was observed serially



2-azidocyclohexanol

Scheme 3. Conversion of cyclohexene oxide to 2-azidocyclohexanol in various synthesized tricationic RTILs.

#### Table 3

Conversion for various epoxides to 2-azidoalcohol using synthesized tri-cationic RTILs<sup>a</sup>.

Entry	Substrate	Product	Time (min)	Yield (%) a'	IR range (cm <sup>-1</sup> )
A	<b>○</b>	OH ,,,Na	100	96	1740, 2201
В	Å	OH N <sub>3</sub>	120	85	1734, 2098
С	CI		100	91	1736, 2108
D	$\Delta$	OH Na.	100	90	1734, 2087
E	О	OH N <sub>3</sub> OH	100	95	1741, 2104
F	0	ОН	120	94	1738, 2204

 $a' = [GLY(mim)_3][OMs]_3$ 

<sup>a</sup> All reactions were carried out on 1.0 mmol scale of substrate and NaN<sub>3</sub> with 0.15 equivalent of tri-cationic RTILs/H<sub>2</sub>O (2:1).

until the last cycle. Overall, it can be concluded that synthesized tricationic RTIL [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> is able to be reused for synthesis of 2-azidoalcohol from epoxide. Currently, development and modification of synthesized tri-cationic RTIL is continuing in our laboratory to improve the catalytic activity of tri-cationic RTIL for fine chemical synthesis.

#### 4. Conclusion

In conclusion, four new imidazolium based tri-cationic RTILs were synthesized from glycerol. We investigated physical properties including viscosity, thermal stability and Lewis acidity of these synthesized tri-cationic RTILs. The prepared ILs showed excellent catalytic activity





for 2-azidoalcohol synthesis from epoxide opening reactions by azide addition. The physical properties and Lewis acidity of RTILs plays a critical role in catalytic activity of prepared ILs. The overall study reveals that the synthesized RTIL [GLY(mim)<sub>3</sub>][OMs]<sub>3</sub> showed excellent performance in catalytic activity as well as physicochemical properties.

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#### Appendix A. Supplementary data

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#### References

- [1] L. Zhou, C. Gao, W.J. Xu, ACS Appl. Mater. Interfaces 5 (2010) 1483-1491.
- [2] R.J. Yogesh, Y.C. Dae Yoon, Ionic liquids: an environmentally friendly media for nucleophilic substitution reactions, Bull. Korean Chem. Soc. 27 (2006) 345–353.
- [3] J.L. Anderson, R. Ding, A. Ellern, D.W. Armstrong, Structure and properties of high stability germinal dicationic ionic liquids, J. Am. Chem. Soc. 127 (2005) 593–604.
- [4] A.H. Tamboli, A.A. Chaugule, F.A. Sheikh, W.J. Chung, H. Kim, Synthesis, characterization, and application of silica supported ionic liquid as catalyst for reductive amination of cyclohexanone with formic acid and triethyl amine as hydrogen source, Chin. J. Catal. (2015) http://dx.doi.org/10.1016/S1872-2067(15)60848-8.
- [5] K. Ghandi, A review of ionic liquids, their limits and applications, Green Sustainable Chem. 4 (2014) 44–53.
- [6] M. Moniruzzaman, K. Nakashima, N. Kamiya, M. Goto, Recent advances of enzymatic reactions in ionic liquids, Biochem. Eng. J. 48 (2010) 295–314.
- [7] J. Pernak, A. Skrzypczak, G. Lota, E. Frackowiak, Synthesis and properties of trigeminal tricationic ionic liquids, Chem. Eur. J. 13 (2007) 3106–3112.
- [8] W.L. Hough, R.D. Rogers, Ionic liquid then and now; from solvents to materials to active pharmaceutical ingredients, Bull. Chem. Soc. J. 80 (2007) 2262–2269.
- [9] C.H. Jin, Y. Polyakova, K.H. Row, Effect of concentration of ionic liquids on resolution of nucleotides in reversed-phase liquid chromatography, Bull. Korean Chem. Soc. 28 (2007) 601–606.

- [10] Y. Polyakova, K.H. Row, Retention behaviour of N-Cbz-D-phenylalanine and Dtryptophan: effect of ionic liquid as mobile-phase modifier, Acta Chromatogr. 17 (2006) 210–221.
- [11] C.C. Amanda, L.J. Jessica, N.I. Oanna, L.T. Kim, J.W. Kristin, C.F. David, H.D. James, Novel Brønsted acidic ionic liquids and their use as dual solvent–catalysts, J. Am. Chem. Soc. 124 (2002) 5962–5963.
- [12] C.M. Gordon, New development in catalysis using ionic liquid, Appl. Catal. A Gen. 222 (2001) 101–117.
- [13] H. Olivier-Bourbigou, L. Magna, Ionic liquid perspectives for organic acid catalytic reactions, J. Mol. Catal. A Chem. 182–183 (2002) 419–437.
- [14] K.R. Sheldon, Catalytic reaction in ionic liquid, Chem. Commun. 2001 (2001) 2399–2407.
- [15] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weave, D.C. Forbes, J.H. Davis, Novel Brønsted acidic ionic liquids and their use as dual solvent-catalysts, J. Am. Chem. Soc. 124 (2002) 5962–5963.
- [16] J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J.P. Bazureau, J. Hamelin, Catalyse esterifications in room temperature ionic liquids with acidic counteranion as recyclable reaction media, Catal. Commun. 3 (2002) 185–190.
- [17] M.I. Hossain, M. El-Harbawi, Y.A. Noaman, M.A. Bustam, N.B.M. Alitheen, N.A. Affandi, G. Hefter, C.Y. Yin, Synthesis and antimicrobial activity of hydroxyl ammonium ionic liquids, Chemosphere 84 (2011) 101–104.
- [18] T. Walton, Room-temperature ionic liquids: solvents for synthesis and catalysis, Chem. Rev. 99 (1999) 2071–2084.
- [19] T. Payagala, J. Huang, S.B. Zachary, S.S. Pritesh, W.A. Daniel, Unsymmetrical dicationic ionic liquids: manipulation of physicochemical properties using specific structural architectures, Chem. Mater. 19 (2007) 5848–5850.
- [20] P.S. Sharma, T. Payagala, E. Wanigasekara, A.B. Wijeratne, J. Huang, D.W. Armstrong, Trigonal tricationic ionic liquids: molecular engineering of trications to control physicochemical properties, Chem. Mater. 20 (2008) 4182–4184.
- [21] T. Payagala, Y. Zhang, E. Wanigasekara, K. Huang, Z.S. Breitbach, P.S. Sharma, L.M. Sidisky, D.W. Armstrong, Trigonal tricationic ionic liquids: a generation of gas chromatographic stationary phases, Anal. Chem. 81 (2009) 161–173.
- [22] F. Mutelet, J.C. Moise, Evaluation of the performance of trigeminal tricationic ionic liquids for separation problems, J. Chem. Eng. Data 57 (2012) 918–927.
- [23] A.H. Jadhav, H. Kim, Short oligo (ethylene glycol) functionalized imidazolium dicationic room temperature ionic liquids: synthesis, properties, and catalytic activity in azidation, Chem. Eng. J. 200–202 (2012) 264–274.
- [24] T.J. Dickerson, N.N. Reed, K.D. Janda, Soluble polymers as scaffolds for recoverable reagents and catalysis, Chem. Rev. 102 (2002) 3325–3344.

- [25] V.H. Jadhav, H.J. Jeong, S.T. Lim, M.H. Sohn, D.W. Kim, Polymer-supported pentaethylene glycol as a facile heterogeneous catalyst for nucleophilic fluorination, Org. Lett. 12 (2010) 3740–3743.
- [26] Y. Gu, F. Jerome, Glycerol as a sustainable solvent for green chemistry, Green Chem. 12 (2010) 1127–1138.
- [27] K.P. Nandre, J.K. Salunke, J.P. Nandre, V.S. Patila, A.U. Borseb, S.V. Bhosale, Glycerol mediated synthesis of 5-substituted 1H-tetrazole under catalyst free conditions, Chin. Chem. Lett. 23 (2012) 161–164.
- [28] S. Chowdhury, R.S. Mohan, J.L. Scott, Reactivity of ionic liquids, Tetrahedron 63 (2007) 2363–2389.
- [29] J.P. Hallett, T. Walton, Room-temperature ionic liquids: solvents for synthesis and catalysis, Chem. Rev. 111 (2011) 3508–3576.
- [30] Z. Zeng, B.S. Phillips, J. Xiao, J.M. Shreeve, Polyfluoroalkyl, polyethylene glycol, 1,4bismethylenebenzene or 1,4-bismethylene-2,3,5,6-tetrafluorobenzene bridged functionalized dicationic ionic liquids: synthesis and properties as high temperature lubricants, Chem. Mater. 20 (2008) 2719–2726.
- [31] Y. Yang, K. Yuan, Determination of the Lewis acidity of ionic liquids by means of an IR spectroscopic probe, Chem. Commun. 2004 (2004) 226–227.
- [32] J.S. Yadav, B.V.S. Reddy, B. Jyothirmai, M.S.R. Murty, Ionic liquids/H<sub>2</sub>O systems for the reaction of epoxides with NaN<sub>3</sub>: a new protocol for the synthesis of 2azidoalcohols, Tetrahedron Lett. 46 (2005) 6559–6562.
- [33] A.R. Kiasat, R. Mirzajani, H. Shalbaf, T. Tabatabaei, M. Fallah-Mehrjardi, Green regioselective azidolysis of epoxides catalyzed by multi-site phase-transfer catalyst, J. Chin. Chem. Soc. 56 (2009) 594–599.
- [34] A. Procopio, P. Costanzo, R. Dalpozzo, L. Maiuolo, M. Nardi, M. Oliverio, Efficient ring opening of epoxides with trimethylsilylazide and cyanide catalyzed by erbium(III) triflate, Tetrahedron Lett. 51 (2010) 5150–5153.