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# Synthesis and thermophysical characterization of novel azide functionalized imidazolium based ionic liquids

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#### 6 Abstract

7 Several new monocationic and unsymmetrical dicationic azide functionalized ionic liquids (ILs) 8 were synthesized. FT-IR, <sup>1</sup>HNMR, <sup>13</sup>CNMR and elemental analyses were applied to identify the 9 molecular structure of these compounds. The density of these ionic liquids was measured too. 10 Unsymmetrical dicationic ionic liquids had higher density than monocationic analogues. The 11 shear viscosity of a dicationic ionic liquid (1-(2-azido-3-methyl-3H-imidazole-1-ium) propyl)-3-12 vinyl-3H-imidazole-1-ium di-dicyanamide) and its corresponding monocationic analogue were 13 also measured. Further thermal behavior and heat capacity of this dicationic ionic liquid were 14 investigated by TGA and DSC techniques. TGA analysis suggested that the decomposition 15 temperature increases with increasing the heating rate and unsymmetrical dicationic ionic liquid 16 has good thermal stability (up to 502.4 – 533.6 K) and heat capacity (298 to 343 K).

18 Keywords: Thermal properties; Unsymmetrical dicationic ionic liquids; Dicyanamide; Heat 19 capacity.

20

#### 21 **1. Introduction**

22 Ionic liquids have attracted substantial interest in recent years. They are liquid at or near the 23 room temperature. They can also be considered organic salts. ILs are composed solely of cations 24 and anions. They exhibit several unique properties, such as extremely low vapor pressure, non-25 flammability, and high thermal stability [1, 2]. Moreover, the physical and chemical properties of 26 ILs can be adjusted or tuned by controlling the nature and functionality of the cations and anions 27 [3]. Therefore, ILs have been considered for many applications, including the replacement of 28 organic solvents [4, 5], electrochemistry [6], enzyme catalyzed reactions [7], separation [8], 29 electrolyte [9], dye-sensitized solar cells (DSSC) [10], absorption of  $CO_2$  [11] and stationary 30 phases in gas chromatography [12]. 31 Recently, dicationic ILs, in which two monocations are combined into a dication have been

32 reported [13, 14]. These ILs are solids or melts near room temperature. So they could afford new

33 supramolecular IL architectures with potential applications ranging from lubrication [15] to

34 organic synthesis [16]. Dicationic ILs have been classified to geminal (the two monocations that

35 form the dication are the same) and unsymmetrical (the monocations are different). Thermal

36 stability measurements of 39 mono and dicationic imidazolium and pyrrolidium based ILs

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37 showed that dicationic ILs have higher thermal stabilities than monocationic ones [14]. Some 38 researchers reported that thermal stabilities of unsymmetrical dicationic ILs are higher than 39 monocationic and geminal dicationic ones [17-19]. Another research on some germinal 40 dicationic ILs showed that these ILs have higher densities, viscosities and longer liquid ranges

41 than monocationic ones [14, 16, 20, 21].

42 ILs based on dicyanamide (DCA) anion have been synthesized and characterized. DCA has 43 afforded highly fluid and conductive ILs made by combining heterocyclic cations such as 1,3-

44 dimethylimidazolium [22], and 1-ethyl-3-methylimidazolium [22, 23] as well as

45 diethylmethylsulfonium [24], and thereby have been utilized as components of electrolyte for

46 high performance dye-sensitized solar cell [25]. The DCA-based ILs exhibit lower viscosity than

47 their bis (trifluoromethanesulfonyl)imide (TFSI) counterparts [26].

48 Many works on the preparation of interesting energy-rich compounds containing organic azide 49 groups [27] have been reported recently. Several energetic azide based ionic liquids such as 50 methylated hydrazinium azides [28] and 1, 5-diamino-4-methyl-tetrazolium azide [29], have 51 been synthesized and characterized [30]. Schneider et al reported synthesis and characterization 52 of imidazolium cation azide based energetic ILS [31]. The importance of azide containing ILs, is 53 in their potential applications as liquid fuels in bipropellant systems. These ILs are thermally 54 stable and have significantly reduced sensitivity and toxicity characteristics because of their 55 negligible vapor pressure. Among different liquid propellants, hydrazine and its derivatives, such 56 as monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), have been 57 widely used. Although they have high performance characteristics, they are also carcinogens. For 58 these reasons, it is desirable to replace hydrazine derivatives with ionic liquids which have 59 become species of green chemistry [32]. It seems that, azide containing ILs would be good 60 candidates to replace hydrazine and its derivatives in certain liquid fuel applications.

61 Although imidazolium based ILs and azide based ILs have desirable properties such as high 62 thermal stabilities, there have been no reports on the synthesis of dicationic azide functionalized 63 imidazolium based ILs. We report here, the synthesis, characterization and thermal properties of 64 the dicationic ionic liquid with dicyanamide, in which the unsymmetrical dications contain azide 65 functional group. In order to synthesize this dicationic IL, some monocationic ILs with or 66 without azide functional group were synthesized too. The reaction steps for the synthesis of azide 67 functionalized imidazolium based ILs are shown in scheme 1. In this research six novel azide 68 functionalized ILs were synthesized; two unsymmetrical dicationic ILs (ILs 4, 7) and four 69 monocationic ILs (ILs 2, 3, 5, 6). Characterization of synthesized ILs was carried out by use of 70 FT-IR and NMR spectroscopies as well as CHN analysis. The viscosity and the density of 71 dicationic ILs were also measured. Furthermore, the thermal stability and heat capacity of IL-7 72 was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter 73 (DSC).

- 74
- 75
- 76

<Scheme 1.>

#### 77 **2.** Experimental

#### 78 2.1. Reagents and instruments

79 All of the solvents and chemicals were purchased from Sigma-Aldrich chemical company and 80 were used without further purification. <sup>1</sup>H and <sup>13</sup>CNMR spectra were recorded on a Brucker 81 Avance DRX – 500 MHz spectrometer, in CDCl<sub>3</sub> and D<sub>2</sub>O. TMS was used as an internal 82 standard. FT-IR spectra were recorded on a Nicolet 800 instrument. Elemental analyses were 83 conducted using Heraeous CHN analyzer (Germany) instrument. Thermo gravimetric analysis 84 (TGA) was conducted using a thermal analysis instrument Perkin Elmer (Pyris Diamond model) 85 in a nitrogen atmosphere. In this method, the temperature range was between 298 and 1173 K at 86 a heating rate of 5, 10 and 20 K.min<sup>-1</sup>. Runs were carried out in 40  $\mu$ L alumina pans and under an 87 inert atmosphere of nitrogen. Nitrogen flow was 20 mL.min<sup>-1</sup>. Initial mass introduced in to the 88 pan was set to  $(10\pm1)$  mg. The melting point of synthesized ILs and the heat capacity of the 89 unsymmetrical dicationic IL were measured using a differential scanning calorimeter (DSC) in a 90 Perkin Elmer instrument (Pyris 6 DSC model) in a nitrogen atmosphere with a temperature rate 91 of 20 K.min<sup>-1</sup>. The measurements were carried out using  $(10\pm1)$  mg of sample. The melting 92 transition (T=429.31 K, 3.296 kg.mol<sup>-1</sup>) of standard indium sample was used in order to calibrate 93 temperature and energy. The zero-heat flow producer described by TA instruments was flowed 94 for heat capacity measurements using a synthetic sapphire sample as the reference compound. 95 All these experiments allowed estimating an overall uncertainty of  $\pm 0.1$  K in temperature and 96  $\pm$  3% in the heat capacities. Water content was eliminated in a treatment before each experiment 97 that consisted of isothermal heating at 378 K for 0.5 h. This was found to be the optimal 98 condition for removing all water presented in the ILs matrix. The experiments were performed at 99 298 to 373 K, with a 20 K.min<sup>-1</sup> heating rate. Density was measured at room temperature using a 100 Micromeritics Accupyc 1330 gas pycnometer, whereas viscosities,  $\eta$ , were analyzed using Anton 101 Paar MCR 300 rheometer with a cp 25-2 fixture (25 mm diameter, 2° cone angle). Density and 102 viscosity measurements were carried out at atmospheric pressure and temperature range of 298 103 to 373 K. The estimated uncertainty of measured densities is  $\pm 5 \times 10^{-3}$  g.cm<sup>-3</sup>. The relative 104 uncertainty in the dynamic viscosity was  $\pm 1.1\%$ , whereas the uncertainty in temperature was 105 within  $\pm 0.1$  K.

106

#### 107 2.2. Synthesis of ILs (1-7)

108 2.2.1. Synthesis of 1-allyl-3-methylimidazolium bromide [IL-1]

109 A mixture of 1-methylimidazole (10 mmol, 0.82 g) and allyl bromide (10 mmol, 0.86 mL), was

- 110 stirred at 353K for 24 h. The viscous product was washed three times using *n*-hexane to remove
- 111 any unreacted reactants. After drying the product under vacuum at 333K for 3h, brown, slightly
- 112 viscous liquid was obtained (Scheme 1, reaction 1).
- 113 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.08 (s, 3H; CH<sub>3</sub>), 4.97 (d, 2H; CH<sub>2</sub>), 5.42 (d, 1H; CH<sub>2</sub>), 5.45
- 114 (d, 1H; CH<sub>2</sub>), 5.91-6.05 (m, 1H; CH), 7.39 (s, 1H; CH), 7.55 (s, 1H; CH), 10.33 (s, 1H; CH)
- 115 ppm;  ${}^{13}$ C NMR (125 MHz, D<sub>2</sub>O):  $\delta$  = 36.7, 51.6, 122.0, 122.1, 123.8, 130.2, 136.4 ppm. IR

116 (KBr, v/cm<sup>-1</sup>): 3084.1, 2857.3, 1625.2, 1448.0, 1312.8, 948.0, 761.2, 1167.0, 1573.2, 1423.6,

- 117 843.2, 760.3. Anal. Calcd. for  $C_7H_{11}N_2Br$ : C, 41.40; H, 5.46; N, 13.79%; found: C, 41.38; H, 118 5.41; N, 13.68%.
- 119

#### 120 2.2.2. Synthesis of 1-(2-Azido-3-bromo-propyl)-3-methyl-3H-imidazol-1-ium bromide [IL-121 2]

- Bromine (10 mmol, 0.80 g) was added to an ice-cooled mixture of sodium azide (50 mmol, 3.25 g), dichloromethane (10 mL) and 30% HCl (2.5 mL). The mixture was stirred for 1 h. The organic layer containing the bromine azide was decanted. Then sodium sulfate (1 spatula) was added. The mixture was stirred for additional 30 minutes and then filtered. 1-allyl-3-126 methylimidazolium bromide [IL-1] (10 mmol, 1.89 g) in nitromethane (10 mL) was added to round-bottomed flask containing bromine azide solution at 293K and the mixture was stirred for 128 24h. The solvent was removed by a rotary evaporator and the product washed three times using *n*-hexane and ethyl acetate. After drying the product under vacuum at 333K for 3h, light brown viscous liquid was obtained (Scheme 1, reaction 2).
- 131 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.09 (s, 3H; CH<sub>3</sub>), 4.98 (d, 2H; CH<sub>2</sub>), 5.44 (d, 1H; CH<sub>2</sub>), 5.46
- 132 (d, 1H; CH<sub>2</sub>), 5.98-6.04 (m, 1H; CH), 7.32 (s, 1H; CH), 7.42 (s, 1H; CH), 10.27 (s, 1H; CH)
- 133 ppm;  $^{13}\text{C}$  NMR (125 MHz, D2O):  $\delta$  = 37.6, 54.5, 120.1, 124.0, 124.9, 131.4, 138.1 ppm. IR
- 134 (KBr, v/cm<sup>-1</sup>): 757.2, 840.2, 949.8, 1164.3, 1312.6, 1339.2, 1424.5, 1460.8, 1573.3, 1648.0,
- 135 2107.1, 2798.9, 3073.1. Anal. Calcd. for C<sub>7</sub>H<sub>11</sub>N<sub>5</sub>Br<sub>2</sub>: C, 25.87; H, 3.41; N, 21.55%; found: C,

136 25.60; H, 3.38; N, 21.58%.

137

#### 138 2.2.3. Synthesis of 1-(3-Azido-2-bromo-propyl)-3-methyl-3H-imidazol-1-ium bromide [IL-139 3]

- H40 Bromine (10 mmol, 0.80 g) was added to an ice-cooled mixture of sodium azide (50 mmol, 3.25 141 g), dichloromethane (10 mL) and 30% HCl (2.5 mL). The mixture was stirred for 1 h. The 142 organic layer containing the bromine azide was decanted. Then sodium sulfate (1 spatula) was 143 added. The mixture was stirred for additional 30 minutes and then filtered. 1-allyl-3-144 methylimidazolium bromide [IL-1] (10 mmol, 1.89 g) in pentane (10 mL) was added to round-145 bottomed flask containing bromine azide solution, under nitrogen atmosphere at 293K and the 146 mixture was stirred for 24h. The solvent was removed by a rotary evaporator and the product 147 washed three times using *n*-hexane and ethyl acetate. After drying the product under vacuum at 148 333K for 3h, light brown viscous liquid was obtained (Scheme 1, reaction 3).
- 149 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.03 (s, 3H; CH<sub>3</sub>), 4.94 (d, 2H; CH<sub>2</sub>), 5.35 (d, 1H; CH<sub>2</sub>), 5.39
- 150 (d, 1H; CH<sub>2</sub>), 5.92-5.97 (m, 1H; CH), 7.44 (s, 1H; CH), 7.61 (s, 1H; CH), 10.06 (s, 1H; CH) 151 ppm; <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O):  $\delta$  = 37.3, 52.5, 122.5, 123.3, 124.8, 131.7, 137.2 ppm. IR
- 151 ppin, C NMR (125 M12,  $D_2O$ ). 0 = 57.3, 52.3, 122.3, 123.3, 124.0, 131.7, 137.2 ppin. IK152 (KBr, v/cm<sup>-1</sup>): 758.8, 841.6, 948.0, 1166.9, 1312.7, 1340.7, 1423.2, 1455.8, 1575.0, 1646.1,
- 153 2110.1, 2800.2, 3069.9. Anal. Calcd. for  $C_7H_{11}N_5Br_2$ : C, 25.87; H, 3.41; N, 21.55%; found: C,
- 153 2110.1, 2800.2, 5009.9. Anal. Calcu. for  $C_7 H_{11} N_5 B_{12}$ : C, 25.87, H, 5.41, N, 21.55%; found 154 25.77; H, 3.40; N, 21.51%.

#### 156 2.2.4. Synthesis of 1-(2-azido-3-methyl-3H-imidazole-1-ium) propyl)-3-vinyl-3H-imidazole-157 1-ium dibromide [IL-4]

158 1-vinylimidazole (12 mmol, 1.13 g) was slowly added into the 1-(2-Azido-3-bromo-propyl)-3-

159 methyl-3H-imidazol-1-ium bromide [IL-2] (10 mmol, 3.25 g) under solvent free condition. The

160 reaction mixture was stirred for 48h at 353K to form IL-4. After that, the reaction mixture was

161 cooled to room temperature, and then washed three times using ethyl acetate and toluene to

162 remove any unreacted reactants. After drying the product under vacuum at 333K for 3h, dark

163 brown and very viscous liquid was obtained (Scheme 1, reaction 4).

164 <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O):  $\delta$  = 4.12 (s, 3H; CH<sub>3</sub>), 5.01 (d, 2H; CH<sub>2</sub>), 5.08 (d, 2H; CH<sub>2</sub>), 5.09 (d,

165 2H; CH<sub>2</sub>), 5.44-5.47 (dd, 2H; CH<sub>2</sub>), 5.99-6.02 (m, 1H, CH), 7.20 (t, 1H; CH), 7.30 (s, 1H; CH),

166 7.38 (s, 1H; CH), 7.48 (s, 1H; CH), 7.64 (s, 1H; CH), 8.58 (s, 1H; CH), 10.20 (s, 1H; CH), ppm;

167 <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O):  $\delta$  = 37.2, 52.4, 110.7, 120.2, 120.7, 122.2, 123.1, 123.9, 124.6,

168 128.7, 129.1, 136.9 ppm. IR (KBr, v/cm<sup>-1</sup>): 750.3, 825.4, 998.3, 1089.4, 1224.4, 1342.3, 1423.9,

169 1495.9, 1575.6, 1648.7, 2292.6, 3099.0, 3148.6, 3406.6. Anal. Calcd. for  $C_{12}H_{17}N_7Br_2$ : C, 34.39;

170 H, 4.09; N, 23.39%; found: C, 34.26; H, 3.97; N, 23.31%.

171

#### 172 2.2.5. General procedure for anion exchange reaction

173 To a solution of IL (10 mmol) in distilled water (20 mL), was added silver dicyanamide (10 174 mmol, 1.74g for IL-1, IL-2, IL3, and 20 mmol, 3.48 g for IL-4). The reaction mixture was stirred 175 for 24 h at 313K. A green precipitate of silver bromide was formed. After that, the reaction 176 mixture was cooled to room temperature and filtered to remove any precipitate of silver bromide. 177 Water was removed by a rotary evaporator and the produced dicyanamide based IL finally dried, 178 under vacuum at 333K for 3h (Scheme 1, reactions 5-7).

179

180 **1-(2-Azido-3-bromo-propyl)-3-methyl-3H-imidazol-1-ium dicyanamide** [**IL-5**]: <sup>1</sup>H NMR 181 (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.05 (s, 3H; CH<sub>3</sub>), 4.91 (d, 2H; CH<sub>2</sub>), 4.95 (d, 1H; CH<sub>2</sub>), 5.41 (d, 1H; 182 CH<sub>2</sub>), 5.82-6.02 (m, 1H; CH), 7.30 (s, 1H; CH), 7.38 (s, 1H; CH), 9.85 (s, 1H; CH) ppm; <sup>13</sup>C 183 NMR (125 MHz, D<sub>2</sub>O):  $\delta$  = 37.8, 54.1, 119.3, 123.6, 125.4, 130.1, 138.9 ppm. IR (KBr, v/cm<sup>-1</sup>): 184 761.5, 841.2, 943.1, 1167.3, 1312.0, 1332.8, 1429.5, 1456.2, 1572.8, 1637.6, 2108.3, 2135.0, 185 2194.9, 2233.6, 2658.2, 3084, 3431.4. Anal. Calcd. for C<sub>9</sub>H<sub>11</sub>N<sub>8</sub>Br: C, 34.74; H, 3.56; N, 186 36.01%; found: C, 34.59; H, 3.47; N, 36.09%.

187

188 1-(3-Azido-2-bromo-propyl)-3-methyl-3H-imidazol-1-ium dicyanamide [IL-6]:

189 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.80 (s, 3H; CH<sub>3</sub>), 4.90 (d, 2H; CH<sub>2</sub>), 5.28 (d, 1H; CH<sub>2</sub>), 5.31

190 (d, 1H; CH<sub>2</sub>), 5.46-5.54 (m, 1H; CH), 7.30 (s, 1H; CH), 7.47 (s, 1H; CH), 9.89 (s, 1H; CH) ppm;

191 <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O):  $\delta$  = 37.7, 51.8, 121.6, 123.5, 122.1, 130.9, 137.3 ppm. IR (KBr, 192 v/cm<sup>-1</sup>): 760.5, 840.4, 946.1, 1166.2, 1312.4, 1333.9, 1425.7, 1454.7, 1574.6, 1645.4, 2118.3,

193 2133.5, 2190.7, 2236.2, 2649.2, 3081, 3427.4. Anal. Calcd. for  $C_9H_{11}N_8Br$ : C, 34.74; H, 3.56; N,

194 36.01%; found: C, 34.68; H, 3.51; N, 36.05%.

196 1-(2-azido-3-methyl-3H-imidazole-1-ium) propyl)-3-vinyl-3H-imidazole-1-ium di-

#### 197 dicyanamide [IL-7]

198  $^{1}$ H NMR (500 MHz, D<sub>2</sub>O):  $\delta$  = 3.87 (s, 3H; CH<sub>3</sub>), 4.61 (d, 2H; CH<sub>2</sub>), 4.74 (d, 2H; CH<sub>2</sub>), 5.05 (d, 2

199 2H; CH<sub>2</sub>), 5.29-5.39 (dd, 2H; CH<sub>2</sub>), 5.77-5.83 (m, 1H, CH), 7.02 (t, 1H; CH), 7.25 (s, 1H; CH),

200 7.39 (s, 1H; CH), 7.44 (s, 1H; CH), 7.59 (s, 1H; CH), 8.64 (s, 1H; CH), 9.99 (s, 1H; CH), ppm;

201  $^{13}\text{C}$  NMR (125 MHz, D2O):  $\delta$  = 36.6, 52.2, 108.3, 120.2, 121.3, 121.9, 122.9, 123.5, 124.3,

202 128.8, 131.0, 136.6 ppm. IR (KBr, v/cm<sup>-1</sup>): 750.9, 825.1, 993.4, 1086.3, 1228.0, 1344.3, 1419.8,

203 1511.2, 1573.0, 1647.9, 2134.9, 2194.1, 2239.4, 2292.6, 3095.7, 3144.3, 3414.4. Anal. Calcd. for

 $204 \ C_{14}H_{17}N_{10}: C, 51.66; H, 5.27; N, 43.07\%; found: C, 51.60; H, 5.21; N, 43.09\%.$ 

#### 205 **3. Results and discussion**

206

#### 207 **3.1.** The density and melting point of synthesized ILs

208 Density is governed by molecular structures. Some properties such as high density make ILs 209 likely candidates for energetic applications. In Table 1, density values for synthesized ILs in this 210 study are compared with density of similar ILs reported in the literatures.

211

212

#### 213

### <Table 1. >

214 It is clear from Table 1 that the density for the dicationic ILs is consistently higher than that for

215 the monocationic ILs with the same anions.  $V_{VDW}/V$  ( $V_{VDW}$  = van der Waals volume, V = molar

216 volume) in the dicationic ILs is larger than in monocationic ILs with the same anions, which

217 implies that the interionic interactions of the dicationic ILs are stronger than that in the 218 monocationic ILs [35].

219 As Table 1 shows, imidazolium based ILs which were synthesized in this study, showed higher

220 densities than ammonium based ILs (Table 1). Usually in ILs, the density decreases as the size of

221 the cation increases but there are exceptions, the density of the functionalized ILs is higher than

222 the density of the respective non-functionalized ILs (Table 1, entries 1, 5). The densities of ILs

223 are also affected by the identity of the organic anion; so that for ILs containing the same cation

224 species, increasing the anion mass corresponds to increasing the IL density. For this reason, the

density of ILs with bromide anion (Table 1, entries 3, 4, 7) is higher than corresponding ILs with

dicyanamide anion (Table 1 entries 5, 6, 8).

227 Table 1 also shows the melting points  $(T_m)$  of the synthesized ILs. All of mono and dicationic

228 ILs are liquid at room temperature. We also found that  $T_m$  of the dicationic ILs are substantially

229 higher than that of the monocationic ILs.

230

#### 231 **3.2.** The viscosity of 1-(2-azido-3-methyl-3H-imidazole-1-ium) propyl)-3-vinyl-3H-232 imidazole-1-ium di-dicyanamide [IL-7] and its corresponding mono cationic analogue

233 Viscosity is an important property of ILs because it strongly influences diffusion of species that

234 are dissolved or dispersed within ILs. IL viscosity is ordinarily influenced by the cation, anion

235 interactions, hydrogen bonding and the symmetry of the ions [36]. An increase in temperature

236 will substantially decrease the hydrogen bonding interactions, and therefore the viscosity will

237 decrease. The viscosity ( $\eta$ ) of [IL-7] and its corresponding monocationic analogue, [IL-5], were

238 measured at several temperatures in the range 298–358 K. Viscosity – temperature dependence

239 for these ILs are shown in Figure 1. As expected, the viscosity of both [IL-5] and [IL-7]

### ED)

240 decreased with increase in temperature. In addition, the viscosity of the dicationic IL is larger 241 than that of the corresponding monocationic one.

242

243 244

#### <Figure 1.>

#### 245 3.3. Thermal property of [IL-7]

246 The thermal stability of [IL-7] was investigated using TGA. Dynamic runs of [IL-7] were carried

247 out at three different heating rates (5, 10, 20 K.min<sup>-1</sup>). The thermogravimetric (TG) and the 248 differential thermogravimetric (DTG) curves of this IL are shown in Figure 2.

249 250

#### <Figure 2.>

251

252 As shown in Figure 2, there are two steps where the mass gently decreases as temperature 253 increases. According to the weight percent of each ion in the IL, it is possible to determine which 254 ion decomposes first. For this reason, the weight percent of dicyanamide anion was calculated.

255 This was 20% for [IL-7]. So the first decomposition step (502 to 683 K), involves approximately 256 20% weight loss, can be attributed to the decomposition of dicyanamide anion. Decomposition

257 of the cation occurs from 623 to 843 K. It is important to highlight that the anion could modify 258 the beginning of the cation decomposition. At range 843 to 903 K little mass lost is observed.

259 This mass lost is related to inorganic compounds formed in the decomposition processes. This 260 constant pattern behavior occurs for all heating rates attributed to the presence of a similar 261 reaction mechanism. These data are in agreement with the literature [37, 38].

262 The decomposition temperatures (Tonset, Tpeak, T50%) at each heating rate are summarized in Table 263 2. As can be seen in Table 2, the lowest decomposition temperature was occurred at 5 K/min 264 heating rate. Thermal stability is closely dependent on time. Thus, thermal stability parameters 265 decrease when experimental time increase, the decomposition temperatures increase with the 266 heating rate. T<sub>peak</sub> could be increased by 65K when the heating rate goes up from 5 to 20 K/min. 267 However, the results confirm that the decomposition temperatures depend on the heating rate, 268 and they are in agreement with the literature [39, 40].

269

#### 270

271

272 In order to compare the thermal stability of [IL-7] with other ILs,  $T_{50\%}$  for [IL-7] and several ILs 273 reported in the literatures are listed in Table 3.

<Table 2.>

<Table 3.>

- 274
- 275
- 276

277 As it can be observed in Table 3, thermal stability of IL-7 is higher than [emim]DCA and 278 [bmim]DCA. Generally, in ILs with the same anion, thermal stabilities of dicationic ILs are significantly higher than their monocationic analogues, due to their higher harge, higher 279 280 molecular weight and greater intermolecular interactions [14].

281

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285 3.4. Heat capacity of 1-(2-azido-3-methyl-3H-imidazole-1-ium) propyl)-3-vinyl-3H 286 -imidazole-1-ium di-dicyanamide [IL-7] 287 The heat capacity of the IL-7 was tested in the range 298–343 K. Figure 3 shows the variation of 288 heat capacity with temperature. 289 290 <Figure 3. > 291 292 As Figure 3 shows the variation in the heat capacity of [IL-7] with temperature is weak. For this 293 ionic liquid, a second order polynomial model was used to correlate the heat capacity (Cp) 294 against temperature (T) [42]. 295 296 The heat capacity of several imidazolium based ILs with the dicyanamide anion have been 297 reported in literature, and is provided in Table 4. 298 299 <Table 4.> 300 301 Generally, energy can be stored in translational, vibrational, and rotational modes of freedom. 302 Therefore, one would expect that a molecule containing more atoms would have more energy 303 storage modes and thus a higher heat capacity. As shown in Table 4, for ILs with the same anion, 304 the higher the atom number, the higher the heat capacity. 305 306 4. Conclusion 307 Novel azide functionalized imidazolium based ionic liquids with the dicyanamide anion were 308 synthesized and characterized by NMR, IR spectroscopies as well as elemental analysis. The 309 densities and melting points of all synthesized ILs were measured. Among dicyanamide based 310 ILs 1-(2-azido-1-(2-azido-3-methyl-3H-imidazole-1-ium) propyl)-3-vinyl-3H-imidazole-1-ium 311 di-dicyanamide [IL-7] had the highest density. The viscosity of this IL at several temperatures 312 was compared with its corresponding monocationic analogue. Most common dicationic ILs have

- 313 high melting point and viscosity, but we found that [IL-7] has low viscosity and melting point, so 314 it is liquid at room temperature. For this reason, [IL-7] could be a suitable candidate for energetic
- 315 applications. Other thermophysical properties, heat capacity and thermal behavior were
- 316 investigated for this ionic liquid. Heat capacities of [IL-7] were measured from 298 to 373 K.
- 317 The obtained data show that this IL has a good heat storage capability; hence, it would also be
- 318 able to replace harmful heat transfer fluids. The thermal stability of [IL-7] was evaluated using 319 TGA at three different heating rates (5, 10 and 20 K.min<sup>-1</sup>). [IL-7] with one unsaturated
- 320 substituent and azide functionality had good thermal stability.
- 321 Based on the above results, it seems that the new synthesized dicationic ionic liquid with good
- 322 thermophysical properties could be used as an energetic material in propellant systems.
- 323

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- 472 Figure caption:
- 473 Scheme 1. Synthesis of new azide functionalized imidazolium based ILs.
- 474 Figure 1. Viscosity measurement of [IL-5] and [IL-7] as a function of temperature.
- 475 Shear Rate: d(gamma)/dt = 500 1/s, Motor Correction Factor = 1.
- 476 Uncertainty in the dynamic viscosity and temperature was  $\pm 1.1\%$  and  $\pm 0.1$  K, respectively.
- 477 Figure 2. The effect of the heating rate on the course of TG and DTG scans for [IL-7].
- 478 **Figure 3.** Heat capacity of [IL-7] at the rate of 20 K/min.
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#### 571 Table caption:

**Table 1.** Comparison the densities and melting points of the synthesized mono and dicationic ILs

573 and some reported ones.

574 Table 2. Dynamic TGA characteristic parameters for [IL-7].

**Table 3.** Comparison of  $T_{50\%}$  values between [IL-7] and dicyanamide based ILs reported in 576 literature.

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**Table 4.** Comparison of heat capacity of imidazolium based ILs with the dicyanamide anion.

| <ul> <li>589</li> <li>590</li> <li>591</li> <li>592</li> <li>593</li> <li>594</li> <li>595</li> <li>596</li> <li>597</li> <li>598</li> <li>599</li> <li>600</li> <li>601</li> <li>602</li> <li>603</li> <li>604</li> <li>605</li> <li>606</li> <li>607</li> <li>608</li> </ul> |       |   |                    |                                  |            |
|--|-------|---|--------------------|----------------------------------|------------|
| 609<br>610   |       |   |                    |                                  |            |
| 010  | Entry | Structure   | T <sub>m</sub> (K) | $\rho^{a}$ (g.cm <sup>-3</sup> ) | reference  |
| -  | 1     | <sup>O</sup> N(CN) <sub>2</sub><br><sup>N</sup> N<br>N<br>CH <sub>3</sub> | 263                | 1.06                             | [22],[33]  |
|  | 2     | $ \begin{array}{c}                                     $                  | 282                | 1.15                             | [34]       |
|  | 3     | Br Br Br  | 283                | 1.36                             | This study |
|  | 4     | BI<br>W<br>N<br>N<br>CH <sub>3</sub><br>Br                                | 290                | 1.34                             | This study |
|  | 5     | $ \begin{array}{c}                                     $                  | 271                | 1.31                             | This study |

|     | 6  | $ \begin{array}{c}  Br \\  & \swarrow \\  & N \\  & \Theta \\  & N(CN)_2 \end{array} $ | 279              | 1.28 | This study     |
|-----|--|--|------------------|------|----------------|
|     | 7 N  | N<br>N<br>2Br<br>N<br>N<br>CH <sub>3</sub>   | 296              | 1.56 | This study     |
|     | 8 N  | $N \oplus N_3 \oplus N_1$<br>$N \oplus N \to N$<br>$2N(CN)_2$ $N \oplus CH_3$          | 292              | 1.49 | This study     |
| 611 | <sup>a</sup> Densities measured at 298K              |  |                  |      |                |
| 612 | Table 1.   |  |                  |      |                |
| 613 |  |  |                  |      |                |
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| 621 |  |  |                  |      |                |
| 622 |  |  |                  |      |                |
| 623 |  |  |                  |      |                |
|     | Heating rate (K.min <sup>-1</sup> )                  | 5  | 10               |      | 20             |
|     | $I_{onset}$ (K)<br>T (V) <sup>a</sup>                | 502.4  | 513.3            |      | 533.0<br>612 5 |
|     | $T_{\text{peak}}$ (K)<br>$T_{50\%}$ (K) <sup>b</sup> | 793.8  | 509.2<br>796.8   |      | 874.0          |
| 624 | <sup>a</sup> The maximum weight loss to              | emperature in the first range that the m   | ass decreases    |      | 047.0          |
| 625 | <sup>b</sup> The temperature at which th             | e mass loss equals to 50% of the initia  | l mass introduce | ed   |                |
| 626 | Table 2.   |  |                  |      |                |
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|   |                                     | Ionic liquid             |                          |        |  |
|---|-------------------------------------|--------------------------|--------------------------|--------|--|
|   | Heating rate (K.min <sup>-1</sup> ) | [emim][DCA] <sup>a</sup> | [bmim][DCA] <sup>b</sup> | [IL-7] |  |
| - | 5                                   | 614.6                    | 591.0                    | 793.8  |  |
|   | 10                                  | 638.0                    | 617.8                    | 796.8  |  |
|   | 20                                  | 647.9                    | 625.3                    | 824.0  |  |

<sup>663 &</sup>lt;sup>a</sup> Ethylmethylimidazolium dicyanamide [41].
664 <sup>b</sup> Butylmethylimidazolium dicyanamide [41].
665 Table 3.

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| Entry | Compound   | T (K) | Method | $C_p(J/\text{mol.K})$ | Reference  |
|-------|--|-------|--------|-----------------------|------------|
| 1     | $[C_2 mim]N(CN)_2^a$                                   | 303   | DSC    | 328                   | [43]       |
| 2     | [C <sub>3</sub> CNmmim]N(CN) <sub>2</sub> <sup>b</sup> | 298   | DSC    | 389.8                 | [44]       |
| 3     | $[C_4 mim]N(CN)_2^c$                                   | 323   | DSC    | 375.7                 | [42]       |
| 4     | [IL-7]   | 298   | DSC    | 400                   | This study |
| 5     | [IL-7]   | 303   | DSC    | 409.7                 | This study |
| 6     | [IL-7]   | 323   | DSC    | 452                   | This study |

688 <sup>a</sup>1-Ethyl-3-methyl-1*H*-imidazolium 689 <sup>b</sup>3-(3-Cyanopropyl)-1,2-dimethyl-1*H*-imidazolium 690 <sup>c</sup>1-Butyl-3-methyl-1H-imidazolium.

691 Table 4.

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| 698 |        |   |
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| 699 |        |   |
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| 701 | Highli | ghts  |
| 702 | •      | We synthesized new mono and asymmetric dicationic azide functionalized ionic liquids. |
| 703 | •      | We measured the density of synthesized ILs at room temperature.                       |
| 704 | •      | Asymmetric dicationic ILs have higher densities.                                      |
| 705 | •      | Thermal behavior of asymmetric dicationic IL with dicyanamide was investigated.       |
| 706 | •      | Dicationic IL with dicyanamide has good thermal stability and heat capacity.          |
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