

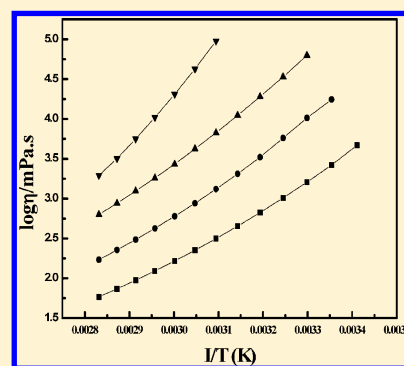
## Thermophysical Properties of Dual Functionalized Imidazolium-Based Ionic Liquids

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**S** Supporting Information

**ABSTRACT:** In this work, some new dual functionalized imidazolium-based ionic liquids 3-(3-butyl-1*H*-imidazol-3-ium-1-yl)propanenitrile chloride [C<sub>2</sub>CNBim]Cl, 3-(3-allyl-1*H*-imidazol-3-ium-1-yl)propanenitrile chloride [C<sub>2</sub>CNAim]Cl, 3-[3-(2-hydroxyethyl)-1*H*-imidazol-3-ium-1-yl]propanenitrile chloride [C<sub>2</sub>CNHEim]Cl, and 3-(3-benzyl-1*H*-imidazol-3-ium-1-yl)propanenitrile chloride [C<sub>2</sub>CNBzim]Cl have been synthesized and characterized by <sup>1</sup>H NMR, FTIR, and elemental analysis. Their thermophysical properties such as viscosity and density were measured for a temperature range of (293.15 to 353.15) K at atmospheric pressure, and their refractive indices were measured in the range of (293.15 to 333.15) K. The effect of functionalized side chains on their thermophysical properties was studied. The thermal expansion coefficient values were calculated using experimental density values. Thermal behavior of these ionic liquids was investigated using a thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC).



### INTRODUCTION

Ionic liquids are organic salts with melting point less than 100 °C. Ionic liquids are considered to be relatively green solvents due to their inherent characteristics such as negligible vapor pressure, nonflammable, nonexplosive, electrochemically stable, thermally stable, and highly conductive; in addition, they can be easily recycled.<sup>1,2</sup> Since ionic liquids mainly consist of an organic cation, and either an inorganic or organic anion, there is a great possibility to design and tune their properties for various applications, like separation,<sup>3</sup> tribology,<sup>4</sup> biomass processing,<sup>5</sup> etc. Currently, task-specific ionic liquids take great intention in the field of ionic liquid research.<sup>6,7</sup> It has been achieved by the incorporation of different functional groups (such as sulfonic acid, ether, alcohol, carboxylic, and nitrile, etc.)<sup>8–12</sup> into the alkyl side chains on the cationic part of ionic liquid, to impart its additional specific properties. Among these, nitrile-based ionic liquids are receiving more consideration due to their more advantageous properties; they act as a suitable reaction media and ligands for catalytic reactions,<sup>12</sup> as electrolyte in lithium battery, as dye-sensitized solar cells,<sup>13</sup> as solvent for extraction of metals,<sup>6</sup> and as a solvent for dissolution of cellulose;<sup>14</sup> and they are also observed to have better tribological properties.<sup>4</sup>

To date, the thermophysical properties of nitrile-based ionic liquids have been studied with respect to the length of the alkyl chain unit linking the imidazolium ring and the nitrile group and also the effect of alkyl chain length in the third position with a fixed propyronitrile side chain in the first position of the imidazolium ring.<sup>4,15</sup> In this work, some new ionic liquids, i.e., [C<sub>2</sub>CNBim]Cl, [C<sub>2</sub>CNAim]Cl, [C<sub>2</sub>CNHEim]Cl, and [C<sub>2</sub>CNBzim]Cl, are synthesized and characterized. Their structural

formulas are depicted in Figure 1. These ionic liquids are synthesized with a fixed propyronitrile side chain in the first position, and another functionalized side chain (butyl, allyl, ethoxyl, and benzyl) is incorporated in the third position of the imidazolium-based cation with fixed chloride anion. These synthesized ionic liquids, having these functionalized side chains, were suggested to have useful applications in the field of electrochemistry, biomass process, solubility of gases, etc. The structures of the products are verified by <sup>1</sup>H NMR, FTIR, and elemental analysis. An attempt was made to measure some of their thermophysical properties (such as density, viscosity, and refractive index) at atmospheric pressure and different temperatures. The values of the thermal expansion coefficient were determined from the results of density values as a function of temperature. Their thermal behaviors were studied using TGA and DSC analysis.

### EXPERIMENTAL SECTION

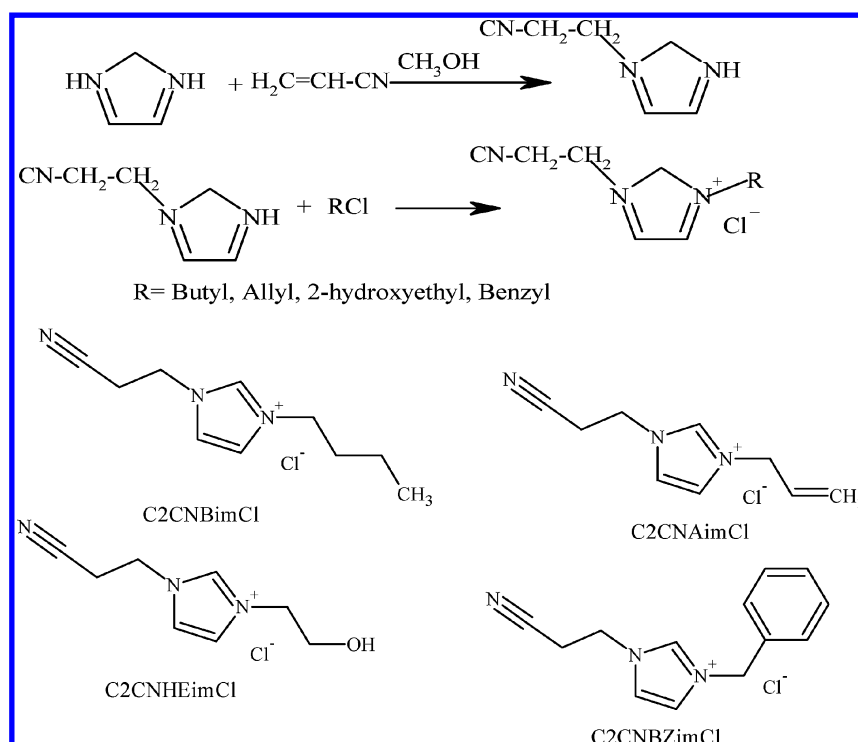
**Materials.** All the starting materials used were of analytical grade. These include imidazole (Merck), acrylonitrile (Sigma), methanol (Merck), 1-chlorobutane, allyl chloride (Sigma), 2-chloroethanol, benzyl chloride (Merck), diethyl ether (Fisher), and Millipore grade water.

**Synthesis of RTILs.** The ionic liquids [C<sub>2</sub>CNBim]Cl, [C<sub>2</sub>CNAim]Cl, [C<sub>2</sub>CNHEim]Cl, and [C<sub>2</sub>CNBzim]Cl were synthesized by using the following procedure. In the first step,

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**Figure 1.** General route for the synthesis and structure of the present ionic liquids.

imidazole (0.2 mol) and methanol were charged into a three-necked flask and stirred until the imidazole completely dissolved. Acrylonitrile (0.23 mol) was added dropwise, and the system was heated at 55 °C for 16 h under nitrogen flow with continuous stirring of 300 rpm. The methanol solvent and unreacted acrylonitrile were removed by using vacuum rotary at 70 °C. In the second step, the resultant 1-propyronitrile imidazole was again charged separately into a three-necked flask, and the other reactants, i.e., 1-chlorobutane (0.4 mol), allyl chloride (0.5 mol), chloroethanol (0.4 mol), and benzyl chloride (0.5 mol), were added under cooling with continuous stirring for synthesis of  $[\text{C}_2\text{CNBim}]\text{Cl}$ ,  $[\text{C}_2\text{CNAim}]\text{Cl}$ ,  $[\text{C}_2\text{CNHEim}]\text{Cl}$ , and  $[\text{C}_2\text{CN Bzim}]\text{Cl}$  ionic liquids, respectively. Then the mixture was heated at the desired temperature for a known period of time, under a nitrogen atmosphere. The resultant viscous product was washed three times with diethyl ether, and the remaining solvent was removed by vacuum rotary at 80 °C for 6 h, followed by a vacuum oven at 80 °C for 48 h.

**Characterization.**  $^1\text{H}$  NMR spectra were taken in  $\text{CDCl}_3/\text{DMSO}-d_6$  solvent and recorded on a Bruker Avance 300 spectrometer. FTIR spectra for the samples were taken by using SHIMADZU 8400S in wavenumber range of 400–4000  $\text{cm}^{-1}$ , and CHNS-932 (LECO instruments) was used for elemental analysis.

All of the synthesized ionic liquids, before measuring their properties, were purified under low pressure by keeping in a vacuum oven for 4 h at 80 °C. A coulometric Karl Fischer titrator, DL 39 (Mettler Toledo), was used to determine water content of the above synthesized ILs, using Hydranal coulomat AG reagent (Riedel-de Haen). The measurement for each IL was made in triplicate, and the average values are reported in Table 1.

**Properties Measurement.** Millipore grade water with known viscosity, density, and refractive index was used for

**Table 1.** Mass Fraction of Water  $w$  and Estimated Purities of Synthesized Ionic Liquids

	$[\text{C}_2\text{CNBim}]\text{Cl}$	$[\text{C}_2\text{CNAim}]\text{Cl}$	$[\text{C}_2\text{CNHEim}]\text{Cl}$	$[\text{C}_2\text{CN Bzim}]\text{Cl}$
$w_{\text{H}_2\text{O}}$ ( $10^6 w$ )	356	215	386	327
estimated purities (%)	97.3	98.5	97.9	98.4

calibration of instruments. The instruments were also calibrated with ionic liquids, namely, 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide,  $[\text{C}_6\text{Mim}]\text{TF}_2\text{N}$ , 1-butylpyridinium bromide,  $[\text{C}_4\text{py}]\text{Br}$ , and 1-propyronitrile-3-butylimidazolium bromide,  $[\text{C}_2\text{CN Bim}]\text{Br}$ , for which the data have been established by our research group.<sup>15,16</sup>

**Density and Viscosity Measurements.** An Anton Paar viscometer (model SVM3000) and Anton Paar densitometer (DMA5000) were used for measurement of viscosity and density, respectively, at a temperature range of (293.15 to 353.15) K. The temperature was controlled to within  $\pm 0.01$  °C. The uncertainty of measurements was  $\pm 0.32$  % and  $\pm 5 \cdot 10^{-6} \text{ g}\cdot\text{cm}^{-3}$  for viscosity and density, respectively.<sup>15,17</sup>

**Refractive Index Measurements.** The refractive indices of all samples were determined using an ATAGO programmable digital refractometer (RX-5000 $\alpha$ ), with a measuring uncertainty of  $\pm 4 \cdot 10^{-5}$  at a temperature range of (293.15 to 333.15) K with control accuracy of  $\pm 0.05$  K. The apparatus was calibrated before each series of measurements and was checked using pure organic solvents with known refractive indices.<sup>17</sup>

**Thermal Decomposition.** A Perkin-Elmer, Pyris V-3.81 thermal gravimetric analyzer was used to measure the onset temperature and thermal decomposition temperature for the synthesized ionic liquids. The samples were placed in an aluminum pan under a nitrogen atmosphere at a heating rate of 10 °C $\cdot\text{min}^{-1}$  with temperature accuracy better than  $\pm 3$  K.

**Differential Scanning Calorimetry.** The thermal measurements were performed using a Perkin-Elmer (model Pyris 1). The samples were kept in sealed Al pans and heated from room temperature to 120 °C. Then the samples were cooled (10 °C·min<sup>-1</sup>) to -40.75 °C and, then, heated (10 °C·min<sup>-1</sup>) to 120 °C and again cooled to -40.75 °C. The onset and glass transition temperatures were measured with temperature uncertainty of ± 2 K.

## RESULTS AND DISCUSSION

These ionic liquids can be synthesized using cheap materials, and the yields of reactions were also high; however, it consumed too much time for synthesis. The estimated purities of the synthesized ionic liquids, namely, [C<sub>2</sub>CNBim]Cl, [C<sub>2</sub>CNAim]Cl, [C<sub>2</sub>CNHEim]Cl, and [C<sub>2</sub>CN Bzim]Cl, are 97.3 %, 98.5 %, 97.9 %, and 98.4 %, respectively (Table 1). The results acquired by NMR, elemental analysis, and FTIR for the synthesized ionic liquids confirmed their structures.

[C<sub>2</sub>CNBim]Cl. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.90 (3H, t), 1.38 (2H, m), 1.85, (2H, m), 3.20 (2H, t), 4.25 (2H, t), 4.59 (2H, t), 4.70 (1H, s), 7.75 (1H, s), 9.25 (1H, s).

Elemental Analysis (%). Calcd: C, 56.20; H, 7.54; N, 19.66. Found: C, 56.05; H, 7.71; and N, 19.54.

[C<sub>2</sub>CNAim]Cl. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ = 3.22 (2H, t), 4.53 (2H, t), 4.89 (2H, d), 5.33 (2H, d), 6.05 (1H, m), 7.78 (1H, s), 7.87 (1H, s), 9.30 (1H, s).

Elemental Analysis (%). Calcd: C, 54.68; H, 6.11; N, 21.25. Found: C, 54.49; H, 6.34; and N, 21.12.

[C<sub>2</sub>CNHEim]Cl. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ = 3.28 (2H, t), 3.73 (2H, t), 4.28 (2H, t), 5.33 (2H, d), 4.55 (2H, t), 5.43 (1H, t), 7.85 (1H, s), 7.91 (1H, s), 9.40 (1H, s).

Elemental Analysis (%). Calcd: C, 47.64; H, 5.99; N, 20.83. Found: C, 47.39; H, 6.18; and N, 20.71.

[C<sub>2</sub>CN Bzim]Cl. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ = 3.29 (2H, t), 4.55 (2H, t), 5.47 (2H, s), 7.44 (5H, m), 7.89 (1H, s), 7.93 (1H, s), 9.62 (1H, s).

Elemental Analysis (%), Calcd: C, 63.02, H, 5.69; N, 16.83. Found: C, 62.95; H, 5.83; and N, 16.74.

From FTIR analysis (Figure 2) it is observed that in all spectra a characteristic peak appeared at 2248.84 cm<sup>-1</sup>, which is assigned to the C≡N functional group and also for C=N at (1550 to 1570) cm<sup>-1</sup>. The C-H symmetric and asymmetric stretching is observed between (2852 and 3134) cm<sup>-1</sup>, possibly due to formation of hydrogen bonds with the anion.<sup>4,12</sup> In the spectrum of [C<sub>2</sub>CN AIm]Cl, the unsaturation of the allyl side chain appeared at 1645.17 cm<sup>-1</sup>, and in the [C<sub>2</sub>CN HEim]Cl spectrum, the alcoholic OH group stretching vibration is observed at 3236.33 cm<sup>-1</sup>. While in the spectrum of [C<sub>2</sub>CN Bzim]Cl, C-H out of plane bending (in benzene structure) is observed at 713.16 cm<sup>-1</sup>.

**Viscosity.** Table 2 shows the effect of temperature and functionalized side chain on viscosity of nitrile containing an imidazole cation with fixed Cl anion ionic liquids. It is observed that the viscosity increases in the order of [C<sub>2</sub>CNBim]Cl < [C<sub>2</sub>CNAim]Cl < [C<sub>2</sub>CNHEim]Cl < [C<sub>2</sub>CN Bzim]Cl. These differences in viscosities might be due to the different strength of intermolecular forces (hydrogen bonding, π-π interaction, van der Waals interactions, etc.) in each ionic liquid molecule and the size of the functionalized side chain. Regarding the structure moiety of each ionic liquid, the strength of intermolecular forces (hydrogen bonding, π-π interaction, van der Waals interactions, and size of functionalized side chain) is found to increase in the order of [C<sub>2</sub>CNBim]Cl <

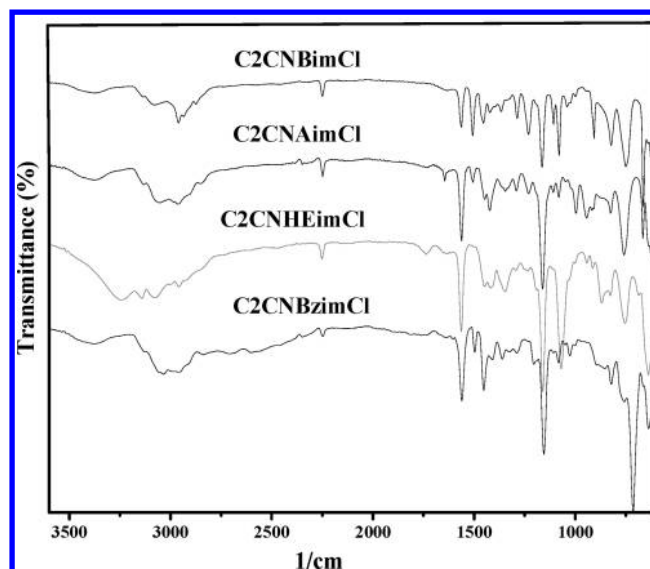


Figure 2. FTIR spectrum of [C<sub>2</sub>CNBim]Cl, [C<sub>2</sub>CNAim]Cl, [C<sub>2</sub>CNHEim]Cl, and [C<sub>2</sub>CN Bzim]Cl from upper to lower, respectively.

Table 2. Experimental Dynamic Viscosities  $\eta$  for [C<sub>2</sub>CNRim]Cl as a Function of Temperature

T/K	$\eta$ /(mPa·s)			
	[C <sub>2</sub> CNBim]Cl	[C <sub>2</sub> CNAim]Cl	[C <sub>2</sub> CNHEim]Cl	[C <sub>2</sub> CN Bzim]Cl
293.15	4707	-	-	-
298.15	2637	17544	-	-
303.15	1612	10294	62813	-
308.15	1020	5761	33772	-
313.15	668	3316	19046	-
318.15	451	2046	11119	-
323.15	314	1314	6721	95152
328.15	224	873	4213	42665
333.15	164	599	2708	20463
338.15	123	423	1817	10434
343.15	94	306	1245	5635
348.15	73	226	873	3190
353.15	58	171	632	1958

[C<sub>2</sub>CNAim]Cl < [C<sub>2</sub>CNHEim]Cl < [C<sub>2</sub>CN Bzim]Cl, while temperature has an inverse effect on viscosity as shown in Figure 3.

**Density.** Table 3 shows the densities of nitrile-containing ILs with different functional side chains in the temperature range from (293.15 to 353.15) K. The densities are found in the same range of reported values for nitrile-containing ionic liquids<sup>4</sup> instead of [C<sub>2</sub>CN HEim]Cl, possibly having compact structure due to more hydrogen bonding. It is observed that density increases in the order [C<sub>2</sub>CN Bim]Cl < [C<sub>2</sub>CN AIm]Cl < [C<sub>2</sub>CN Bzim]Cl < [C<sub>2</sub>CN HEim]Cl. No possible correlation was observed among the densities of the above synthesized ionic liquids, which might be due to different internal arrangement of the cation and anion in each ionic liquid. Similar to viscosity, temperature is observed to have an inverse effect on density as shown in Figure 4. The densities of this series of ILs were estimated using the Ye and Shreeve method.<sup>18</sup> The calculated density values are (1.1408, 1.1558, 1.2112, and 1.1990) g·cm<sup>-3</sup>, which show good agreement with the experimental results.

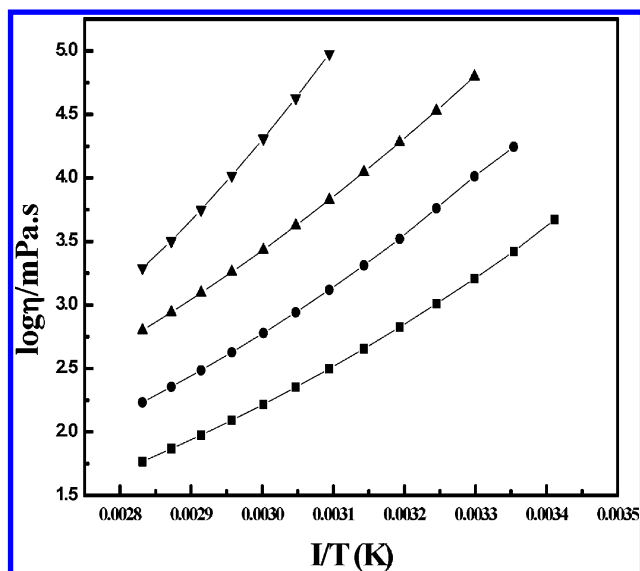


Figure 3. Viscosities as a function of temperature for (■), [C<sub>2</sub>CNBim]Cl; (●), [C<sub>2</sub>CNAim]Cl; (▲), [C<sub>2</sub>CNHEim]Cl; and (▼), [C<sub>2</sub>CNBzim]Cl.

Table 3. Experimental Densities  $\rho$  for [C<sub>2</sub>CNRim]Cl as a Function of Temperature

T/K	$\rho/(g\cdot cm^{-3})$			
	[C <sub>2</sub> CNBim]Cl	[C <sub>2</sub> CNAim]Cl	[C <sub>2</sub> CNHEim]Cl	[C <sub>2</sub> CNBzim]Cl
293.15	1.132547	1.173792	1.257900	-
298.15	1.129354	1.170785	1.255047	1.202672
303.15	1.126147	1.167788	1.252201	1.200284
308.15	1.122934	1.164804	1.249381	1.197331
313.15	1.119665	1.161837	1.246584	1.194370
318.15	1.116488	1.15888	1.243807	1.191425
323.15	1.113338	1.155932	1.241052	1.188500
328.15	1.110185	1.152911	1.238316	1.185587
333.15	1.107027	1.150012	1.23559	1.182688
338.15	1.103869	1.147108	1.232862	1.179797
343.15	1.100717	1.144221	1.230134	1.176881
348.15	1.097574	1.141323	1.227412	1.174006
353.15	1.094436	1.138419	1.224567	1.171158

**Molar Volume.** Molar volume is the volume ( $V_m$ ) occupied by one mole of a substance at a particular temperature and pressure.  $V_m$  was calculated for the synthesized ionic liquids at room temperature and atmospheric pressure using the following equation

$$V_m = M/\rho \quad (1)$$

where  $M$  is the molecular weight in  $g\cdot mol^{-1}$ ;  $\rho$  is the density in  $g\cdot cm^{-3}$ ; and  $V_m$  is molar volume in  $cm^3\cdot mol^{-1}$ . The values of  $V_m$  calculated for the ionic liquids are listed in Table 4. Table 4 shows that there is no specific correlation among the values of molar volume, viscosities, and densities.

**Refractive Index.** Table 5 presents the refractive index of the synthesized ionic liquids. It is observed that the refractive index values are high in comparison to other reported nitrile-containing ionic liquids.<sup>4</sup> This could be due to extra electron mobility around the functionalized side chain as compared to the alkyl side chain on the cation part of the ionic liquid. The refractive index is observed to be linearly decreasing with an increase in temperature as shown in Figure 5.

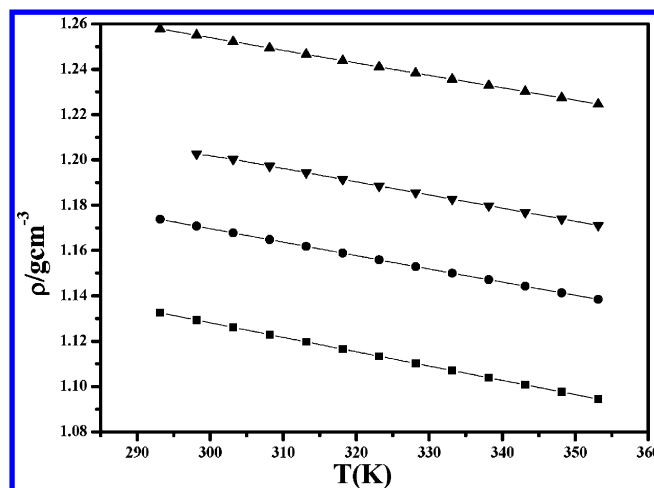


Figure 4. Densities as a function of temperature for (■), [C<sub>2</sub>CNBim]Cl; (●), [C<sub>2</sub>CNAim]Cl; (▲), [C<sub>2</sub>CNHEim]Cl; and (▼), [C<sub>2</sub>CNBzim]Cl.

Table 4. Molar Volume  $V_m$  of the Present Ionic Liquids at 298.15 K and Atmospheric Pressure

ionic liquids	$V_m (cm^3\cdot mol^{-1})$
[C <sub>2</sub> CNBim]Cl	189.23
[C <sub>2</sub> CNAim]Cl	168.82
[C <sub>2</sub> CNHEim]Cl	160.67
[C <sub>2</sub> CNBzim]Cl	205.97

Table 5. Experimental Refractive Indices  $n_D$  for [C<sub>2</sub>CNRim]Cl as a Function of Temperature

T/K	$n_D$		
	[C <sub>2</sub> CNBim]Cl	[C <sub>2</sub> CNAim]Cl	[C <sub>2</sub> CNHEim]Cl
293.15	1.5257	1.5473	1.5499
298.15	1.5243	1.5460	1.5484
303.15	1.5228	1.5447	1.5469
308.15	1.5213	1.5433	1.5455
313.15	1.5199	1.5420	1.5441
318.15	1.5184	1.5407	1.5427
323.15	1.5170	1.5394	1.5413
328.15	1.5156	1.5381	1.5398
333.15	1.5141	1.5368	1.5384

The experimental viscosity  $\eta$ , density  $\rho$ , and refractive index  $n_D$  were fitted by the least-squares method using the following reported equations<sup>15–17</sup>

$$\log \eta/(mPa\cdot s) = A_0 + (A_1/T) \quad (2)$$

$$\rho/(g\cdot cm^{-3}) = A_2 + A_3T \quad (3)$$

$$n_D = A_4 + A_5T \quad (4)$$

where  $\eta$ ,  $\rho$ , and  $n_D$  denote the viscosity, density, and refractive index of the synthesized ionic liquids, respectively.  $A_0$ ,  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$ , and  $A_5$  are correlation coefficients.  $T$  is temperature in Kelvin. The correlation coefficients were estimated by a least-squares fitting method using eqs 2, 3, and 4. The estimated values of correlation coefficients are presented together with standard deviation values (SD) in Tables 6, 7, and 8. The



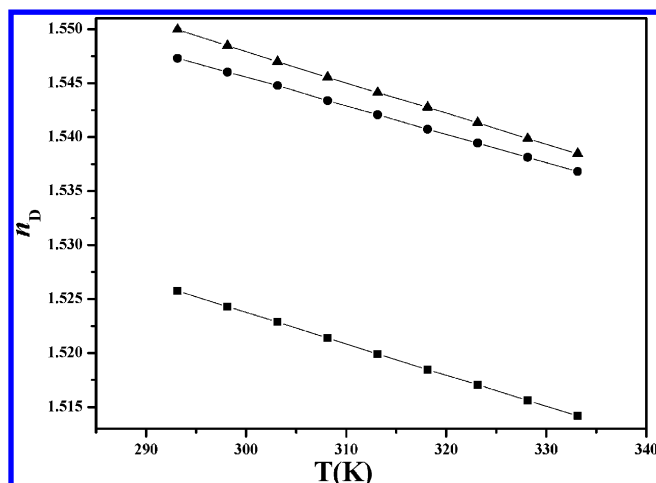


Figure 5. Refractive index as a function of temperature: (■), [C<sub>2</sub>CN Bim]Cl; (●), [C<sub>2</sub>CN Aim]Cl; and (▲), [C<sub>2</sub>CN HEim]Cl.

Table 6. Fitting Parameter Values (Viscosities) of Equation 2 and the Standard Deviations (SDs) Using Equation 5

ionic liquids	A <sub>0</sub>	A <sub>1</sub>	SD	R <sup>2</sup>
[C <sub>2</sub> CNBim]Cl	-7.52	3253.30	5.04·10 <sup>-2</sup>	0.9969
[C <sub>2</sub> CNAim]Cl	-8.78	3864.72	5.05·10 <sup>-2</sup>	0.9974
[C <sub>2</sub> CNHEim]Cl	-9.35	4271.52	3.88·10 <sup>-2</sup>	0.9985
[C <sub>2</sub> CN Bzim]Cl	-14.95	6428.77	3.63·10 <sup>-2</sup>	0.9985

Table 7. Fitting Parameter Values (Densities) of Equation 3 and the Standard Deviations (SDs) Using Equation 5

ionic liquids	A <sub>2</sub>	A <sub>3</sub>	SD	R <sup>2</sup>
[C <sub>2</sub> CNBim]Cl	1.31	-6.35·10 <sup>-4</sup>	6.61·10 <sup>-5</sup>	0.9999
[C <sub>2</sub> CNAim]Cl	1.34	-5.89·10 <sup>-4</sup>	8.01·10 <sup>-5</sup>	0.9999
[C <sub>2</sub> CNHEim]Cl	1.41	-5.531·10 <sup>-4</sup>	8.50·10 <sup>-5</sup>	0.9999
[C <sub>2</sub> CN Bzim]Cl	1.37568	-5.79227·10 <sup>-4</sup>	1.28553·10 <sup>-4</sup>	0.9999

Table 8. Fitting Parameter Values (Refractive Indices) of Equation 4 and the Standard Deviations (SDs) Using Equation 5

ionic liquids	A <sub>4</sub>	A <sub>5</sub>	SD	R <sup>2</sup>
[C <sub>2</sub> CNBim]Cl	1.61	-2.89·10 <sup>-4</sup>	2.43·10 <sup>-5</sup>	0.9999
[C <sub>2</sub> CNAim]Cl	1.62	-2.63·10 <sup>-4</sup>	3.22·10 <sup>-5</sup>	0.9998
[C <sub>2</sub> CNHEim]Cl	1.63	-2.86·10 <sup>-4</sup>	4.62·10 <sup>-5</sup>	0.9999

standard deviation values were calculated by using the following eq 5<sup>15</sup>

$$SD = \sqrt{\frac{\sum_i^{n_{\text{DAT}}} (Z_{\text{exp}} - Z_{\text{cal}})^2}{n_{\text{DAT}}}} \quad (5)$$

where SDs,  $n_{\text{DAT}}$ ,  $Z_{\text{exp}}$ , and  $Z_{\text{cal}}$  are the standard deviations, number of experimental points, and experimental and calculated data values, respectively.

The calculated density for the synthesized ionic liquids was used to calculate another thermophysical property, i.e., thermal expansion coefficient ( $\alpha$ ) (Table 9), by using the following eq 6<sup>15</sup>

$$\alpha_p = -\frac{1}{\rho} \left( \frac{\delta \rho}{\delta T} \right)_p = -\frac{A_3}{A_2 + A_3 T} \quad (6)$$

Table 9. Thermal Expansion Coefficient Values of Presented Ionic Liquids As a Function of Temperature Using Equation 6

T/K	$\alpha \cdot 10^4 / (\text{K}^{-1})$			
	[C <sub>2</sub> CNBim]Cl	[C <sub>2</sub> CNAim]Cl	[C <sub>2</sub> CNHEim]Cl	[C <sub>2</sub> CN Bzim]Cl
293.15	5.60	5.02	4.39	4.80
298.15	5.62	5.03	4.40	4.81
303.15	5.64	5.04	4.41	4.82
308.15	5.65	5.06	4.42	4.83
313.15	5.67	5.07	4.43	4.85
318.15	5.68	5.08	4.44	4.86
323.15	5.70	5.10	4.45	4.87
328.15	5.72	5.11	4.46	4.88
333.15	5.73	5.12	4.47	4.89
338.15	5.75	5.14	4.48	4.90
343.15	5.77	5.15	4.49	4.92
348.15	5.78	5.16	4.50	4.93
353.15	5.80	5.18	4.51	4.94

where  $A_2$  and  $A_3$  are the fitting parameters of eq 3 and  $\alpha_p$ ,  $\rho$ , and  $T$  are the thermal expansion coefficient, density, and absolute temperature, respectively. The thermal expansion coefficient ( $\alpha_p$ ) is also known as volume expansivity. It can be observed from Table 9 that the coefficients of thermal expansion of the synthesized ionic liquids do not change appreciably with respect to temperature and show its independency on temperature. The sequence of the ionic liquids with respect to thermal expansion coefficients is [C<sub>2</sub>CNHEim]Cl < [C<sub>2</sub>CN Bzim]Cl < [C<sub>2</sub>CNAim]Cl < [C<sub>2</sub>CNBim]Cl. The values of thermal expansion coefficient tabulated in Table 9 are similar to those reported for imidazolium, pyridinium, phosphonium, and ammonium-based ILs, (4.8·10<sup>-4</sup> to 6.5·10<sup>-4</sup>) K<sup>-1</sup>.<sup>19,20</sup>

Thermal decomposition values of the synthesized ionic liquids are reported in terms of onset temperature and thermal decomposition temperature  $T_d$  as shown in Table 10. It is clear

Table 10. Onset  $T_s$  and Decomposition  $T_d$  Temperatures for [C<sub>2</sub>CNRim]Cl

property	[C <sub>2</sub> CNBim]Cl	[C <sub>2</sub> CNAim]Cl	[C <sub>2</sub> CNHEim]Cl	[C <sub>2</sub> CN Bzim]Cl
$T_s$ /K	473	491	494	504
$T_d$ /K	514	526	560	529

that the thermal decomposition temperatures of [C<sub>2</sub>CNBim]Cl, [C<sub>2</sub>CNAim]Cl, and [C<sub>2</sub>CN Bzim]Cl are in the same range, while [C<sub>2</sub>CNHEim]Cl has a higher  $T_d$  than the rest, which might be due to the presence of more hydrogen bonding, thereby giving more thermal stability. The thermal decomposition temperature values are in the same range as reported for other nitrile-containing ionic liquids ([C<sub>2</sub>CNBim]Br, 524 K; [C<sub>3</sub>CNIm]Cl, 528 K).<sup>4,15</sup> However, the thermal decomposition temperature  $T_d$  of the synthesized ionic liquids is less compared with the corresponding ionic liquids without a CN group ( $T_d$  of [C<sub>4</sub>mim]Cl, [Amim]Cl are (528, 546) K, respectively).<sup>21,22</sup> It seems that the incorporation of the CN group decreases the thermal stability of the corresponding ionic liquids.

The onset and glass transition temperatures were measured as the inflection point of change in the DSC trace, and the values are tabulated in Table 11. The onset temperature was

**Table 11. Onset  $T_s$  and Glass Temperatures  $T_g$ : Midpoint for  $[C_2CN \text{ Rim}]Cl$** 

property	$[C_2CNBim]Cl$	$[C_2CNAim]Cl$	$[C_2CNHEim]Cl$	$[C_2CN \text{ Bzim}]Cl$
$T_s/K$	263.82	268.06	282.42	284.16
$T_g/K$	267.92	271.67	287.65	289.36

measured from cooling side, and  $T_g$  was measured as the midpoint in the small change of DSC trace. All the synthesized ionic liquids were room temperature. The ionic liquids in the order of increasing  $T_g$  are  $[C_2CNBim]Cl < [C_2CNAim]Cl < [C_2CNHEim]Cl < [C_2CN \text{ Bzim}]Cl$ . Lower values of  $T_g$  are reported for other nitrile-functionalized ionic liquids, which might be due to different side chains attached to the imidazole ring.<sup>4</sup>

## CONCLUSIONS

Some new types of dual functionalized imidazolium-based ionic liquids, namely, of  $[C_2CNBim]Cl$ ,  $[C_2CNAim]Cl$ ,  $[C_2CNHEim]Cl$ , and  $[C_2CNBzim]Cl$ , have been synthesized, and their thermophysical properties, viscosity, density, and refractive indices, were measured. Different viscosities are observed for each type of ionic liquid which is attributed to different strengths of intermolecular interactions (hydrogen bonding, pi–pi interaction, van der Waals interactions, etc.) in each ionic liquid molecule. The viscosity increases in the order of  $[C_2CNBim]Cl < [C_2CNAim]Cl < [C_2CNHEim]Cl < [C_2CNBzim]Cl$ . The densities of three ionic liquids, namely,  $[C_2CNBim]Cl$ ,  $[C_2CNAim]Cl$ , and  $[C_2CNBzim]Cl$ , are in the range of reported values for nitrile-containing ionic liquids; however, the density for  $[C_2CNHEim]Cl$  is higher. They also exhibit higher refractive index compared to other reported nitrile-containing ionic liquids. In general, their thermophysical properties of viscosity, density, and refractive index decrease as temperature increases. The coefficient of thermal expansion is considered to be independent of temperature in the range of (293.15 to 353.15) K, as no appreciable change was observed with an increase of temperature. The high thermal decomposition temperature of  $[C_2CNHEim]Cl$  is attributed to more high hydrogen bonding. The  $T_g$  values observed for these ionic liquids are higher compared to those reported for nitrile-based ionic liquids.

## ASSOCIATED CONTENT

### Supporting Information

Additional Figures 1 and 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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