Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPLEMENTARY INFORMATION

Studies on Radical Polymerization of Monomeric Ionic Liquids – Nanostructure Ordering as a Key Factor Controlling Reaction and Properties of Nascent Polymer.

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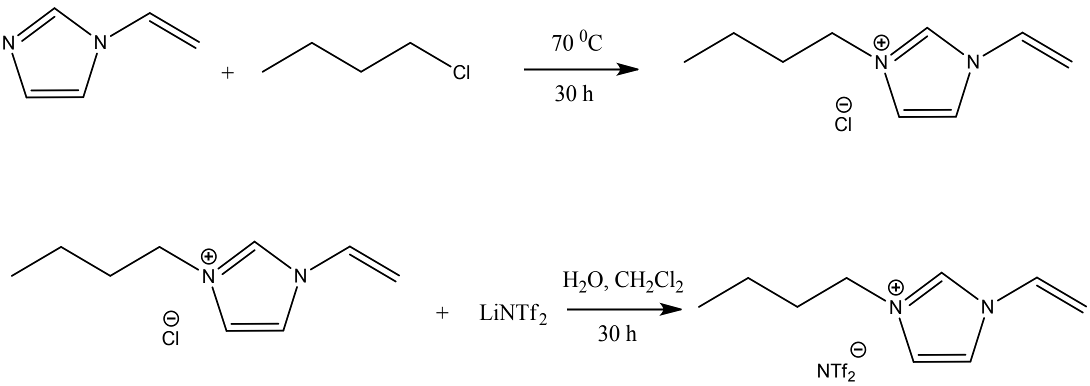
1. Monomer method synthesis and NMR analysis

^{1}H and ^{13}C NMR spectra of ionic liquids were recorded at 600 MHz using Varian spectrometer with TMS as internal standard. High resolution mass spectrometry analyses were performed on a Waters Xevo G2 Q-TOF mass spectrometer (Waters Corporation) equipped with an ESI source operating in positive and negative ion modes. Full-scan MS data were collected from 100 to 1000 Da in both ion modes with scan time of 0.1 s. To ensure accurate mass measurements, data were collected in centroid mode and mass was corrected during acquisition using leucine enkephalin solution as an external reference (Lock-Spray TM), which generated reference ion at m/z 556.2771 Da ($[M^{+}H]^{+}$) in positive and m/z 554.2615 Da ($[M^{-}H]^{-}$) negative ESI mode. The accurate mass and composition for the molecular ion adducts were calculated using the MassLynx software (Waters) incorporated with the instrument.

***Synthesis of 1-butyl-3-vinylimidazolium chloride [bvim][Cl]*:**

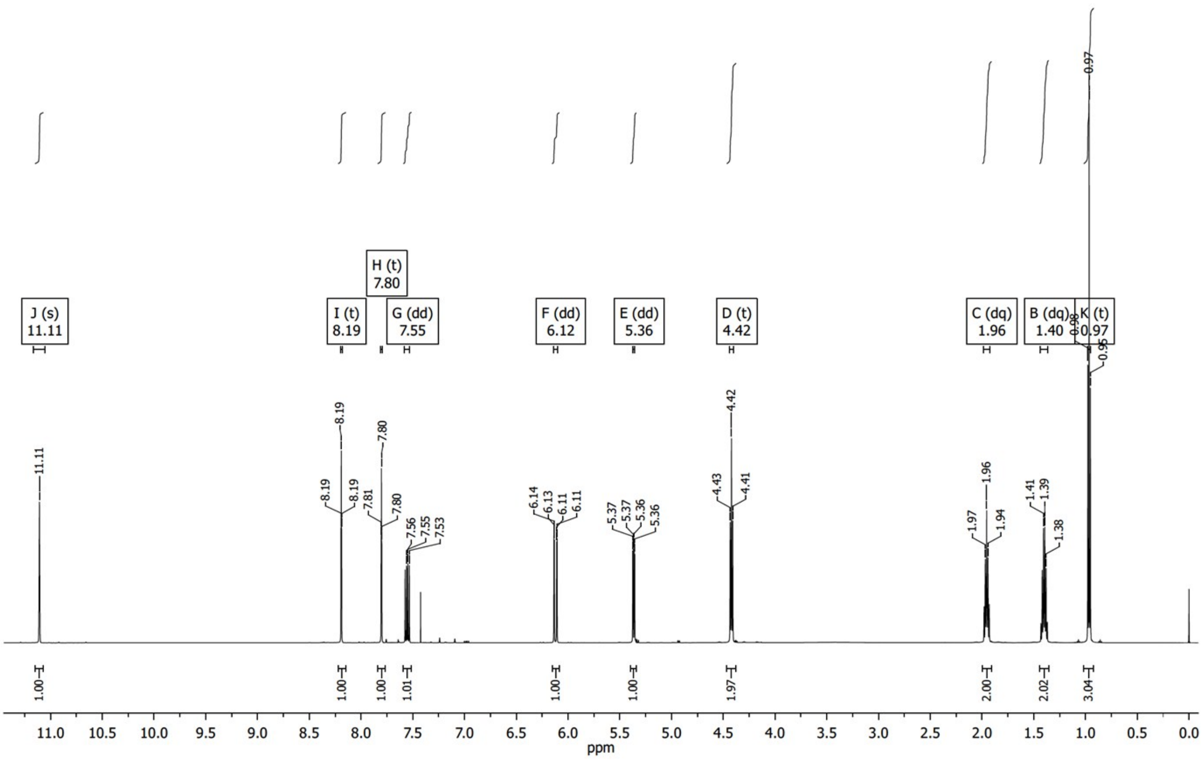
1-vinylimidazole (10.0 g, 106 mmol) and butyl chloride (37.0 g, 400 mmol) were stirred vigorously at 70 °C for 30 h under argon atmosphere. Next, the reaction mixture was cooled to 0 °C, and then the upper liquid layer was removed by decantation, then the residue was washed with ethyl acetate (3×30 ml) and dried under vacuum. As a result, a pale-yellow solid of [bvim][Cl] (14.4 g) was obtained with 73% yield. The monomer synthesis path is presented in the Scheme 1.



Scheme 1. The synthesis path of [bvim][NTf_2].

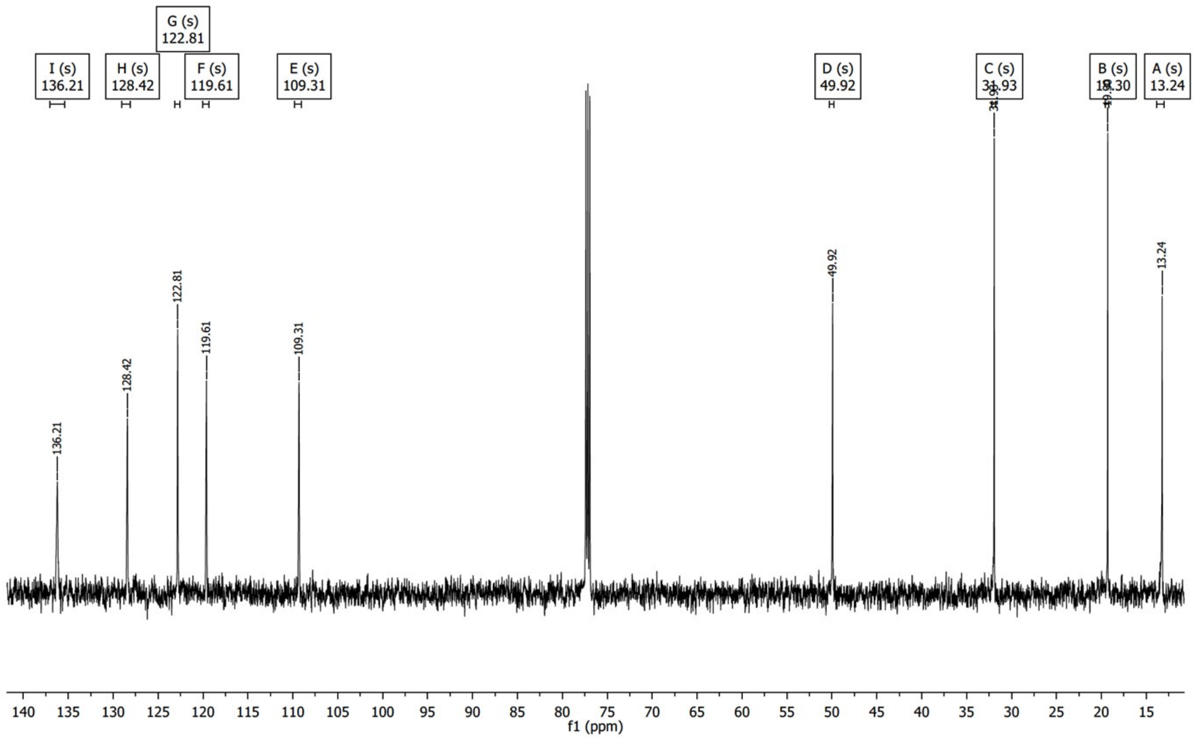
^{1}H NMR δ (600 MHz, $CDCl_3$): δ 11.11 (s, 1H), 8.19 (t, J = 1.9 Hz, 1H), 7.80 (t, J = 1.8 Hz, 1H), 7.55 (dd, J = 15.7, 8.8 Hz, 1H), 6.12 (dd, J = 15.7, 2.9 Hz, 1H), 5.36 (dd, J = 8.8, 3.0 Hz, 1H), 4.42 (t, J = 7.4 Hz, 1H), 1.96 (dq, J = 12.8, 7.6 Hz, 1H), 1.40 (dq, J = 14.9, 7.4 Hz, 1H), 0.97 (t, J = 7.4 Hz, 1H) ppm.

^{1}H NMR (600 MHz, cdcl$_3$) δ 11.11 (s, 1H), 8.19 (t, J = 1.9 Hz, 1H), 7.80 (t, J = 1.8 Hz, 1H), 7.55 (dd, J = 15.7, 8.8 Hz, 1H), 6.12 (dd, J = 15.7, 2.9 Hz, 1H), 5.36 (dd, J = 8.8, 3.0 Hz, 1H), 4.42 (t, J = 7.4 Hz, 1H), 1.96 (dq, J = 12.8, 7.6 Hz, 1H), 1.40 (dq, J = 14.9, 7.4 Hz, 1H), 0.97 (t, J = 7.4 Hz, 1H).



^{13}C NMR δ (150 MHz, $CDCl_3$): 136.21, 128.42, 122.81, 119.61, 109.31, 49.92, 31.93, 19.30, 13.24 ppm.

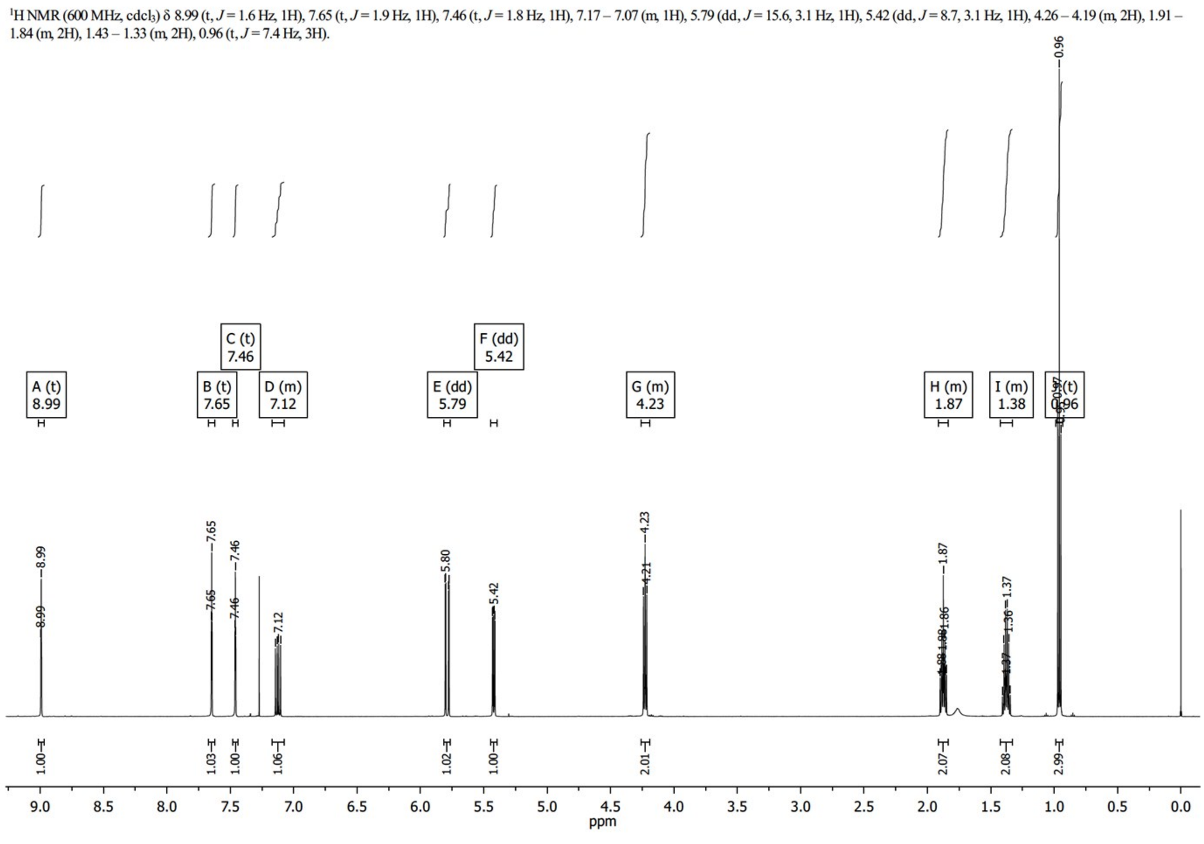
^{13}C NMR (151 MHz, cdcl$_3$) δ 136.21 (s), 128.42 (s), 122.81 (s), 119.61 (s), 109.31 (s), 49.92 (s), 31.93 (s), 19.30 (s), 13.24 (s).



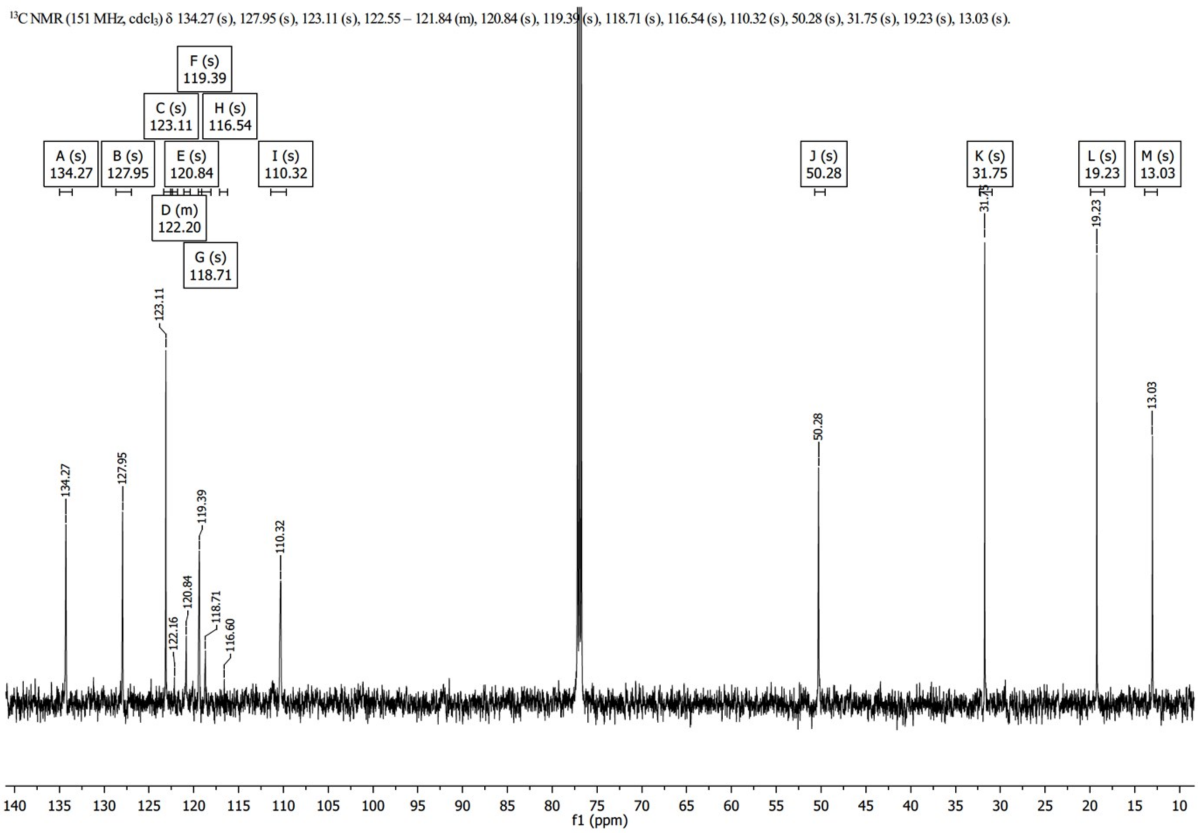
Synthesis of 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide [bvim][NTf$_2$]:

LiNTf$_2$ (24.0 g, 84 mmol) dissolved in deionized water (10 ml) was added in portions into the vigorously stirred [bvim][Cl] (14.4 g, 77 mmol) dissolved in CH_2Cl_2 (10 ml). After 24 h, the layers were separated. Organic layer was washed once with deionized water (10 ml) and water layer was extracted with CH_2Cl_2 (2x10 ml). The combined organic layers were dried under vacuum to obtained liquid product [bvim][NTf$_2$] (28.9 g) with 87% yield.

^{1}H NMR (600 MHz, cdcl3) δ 8.99 (t, J = 1.6 Hz, 1H), 7.65 (t, J = 1.9 Hz, 1H), 7.46 (t, J = 1.8 Hz, 1H), 7.17 – 7.07 (m, 1H), 5.79 (dd, J = 15.6, 3.1 Hz, 1H), 5.42 (dd, J = 8.7, 3.1 Hz, 1H), 4.26 – 4.19 (m, 2H), 1.91 – 1.84 (m, 2H), 1.43 – 1.33 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H).



^{13}C NMR (150 MHz, cdcl3) δ 134.27, 127.95, 123.11, 122.55, 120.84, 119.39, 118.71, 116.54, 110.32, 50.28, 31.75, 19.23, 13.03.



ESI-MS:

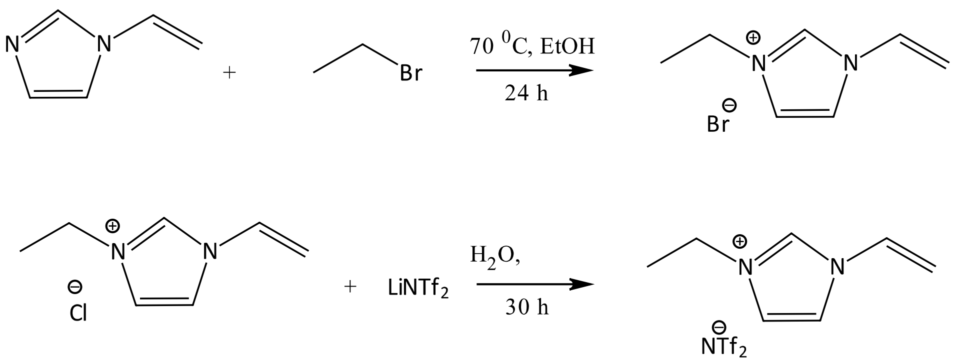
$[M + H]^+$ calcd: 151.23, found: 123.0945.

$[M - H]^-$ calcd: 280.15, found: 279.9169.

Synthesis of 1-ethyl-3-vinylimidazolium bromide [evim][Br[1]:

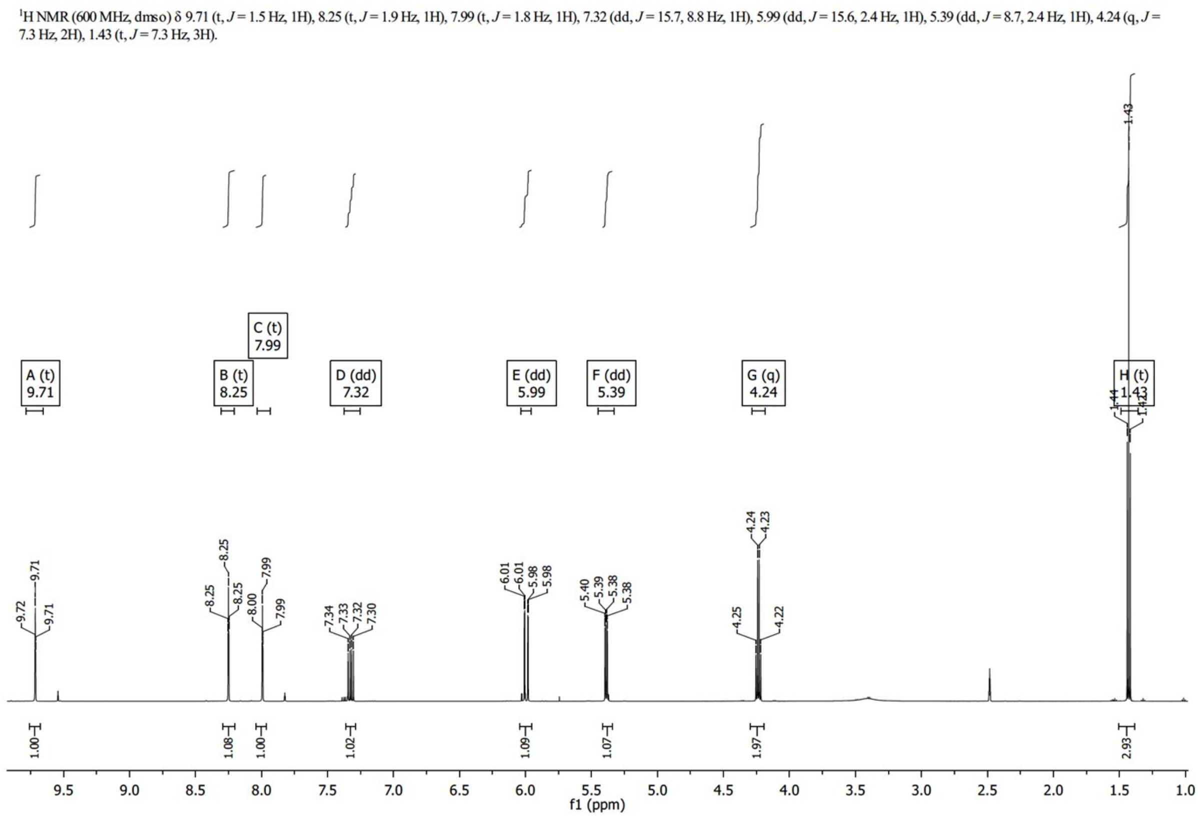
1-vinylimidazole (10.0 g, 106 mmol) and absolute ethanol (30 ml) were placed in a round bottom flask and hated to 70 °C under the argon atmosphere. A mixture of ethyl bromide (21.8 g, 200 mmol) in absolute ethanol (20 ml) was dropped into the flask. Reaction were stirred vigorously at 70 °C for 24 h. Next, the reaction mixture was cooled down and the unreacted starting materials were removed under vacuum. As a result, a yellow solid of [evim][Cl] (17.0 g) was obtained with 78% yield. The monomer synthesis path is presented in Scheme 2.

[1] B. Zhang, L. Zhang, Q. Wu, Q. Wang, B. Song, W. Wu, B. Lu and T. Ren; *RSC Adv.*, 2014, 4, 20506.



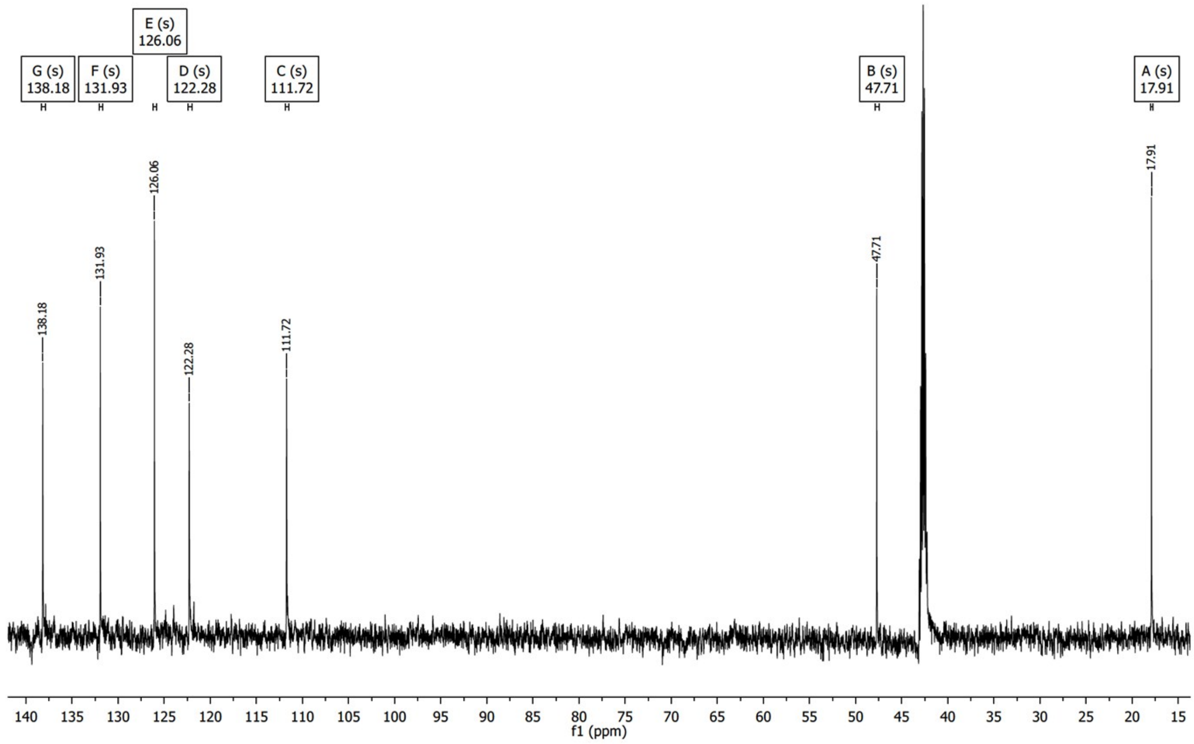
Scheme 2. The synthesis path of [evim][NTf_2].

[1]H NMR (600 MHz, dmso) δ 9.71 (t, J = 1.5 Hz, 1H), 8.25 (t, J = 1.9 Hz, 1H), 7.99 (t, J = 1.8 Hz, 1H), 7.32 (dd, J = 15.7, 8.8 Hz, 1H), 5.99 (dd, J = 15.6, 2.4 Hz, 1H), 5.39 (dd, J = 8.7, 2.4 Hz, 1H), 4.24 (q, J = 7.3 Hz, 2H), 1.43 (t, J = 7.3 Hz, 3H) ppm.



[13]C NMR (150 MHz, dmso) δ 138.18, 131.93, 126.06, 122.28, 111.72, 47.71, 17.91 ppm.

^{13}C NMR (151 MHz, dmso) δ 138.18 (s), 131.93 (s), 126.06 (s), 122.28 (s), 111.72 (s), 47.71 (s), 17.91 (s).

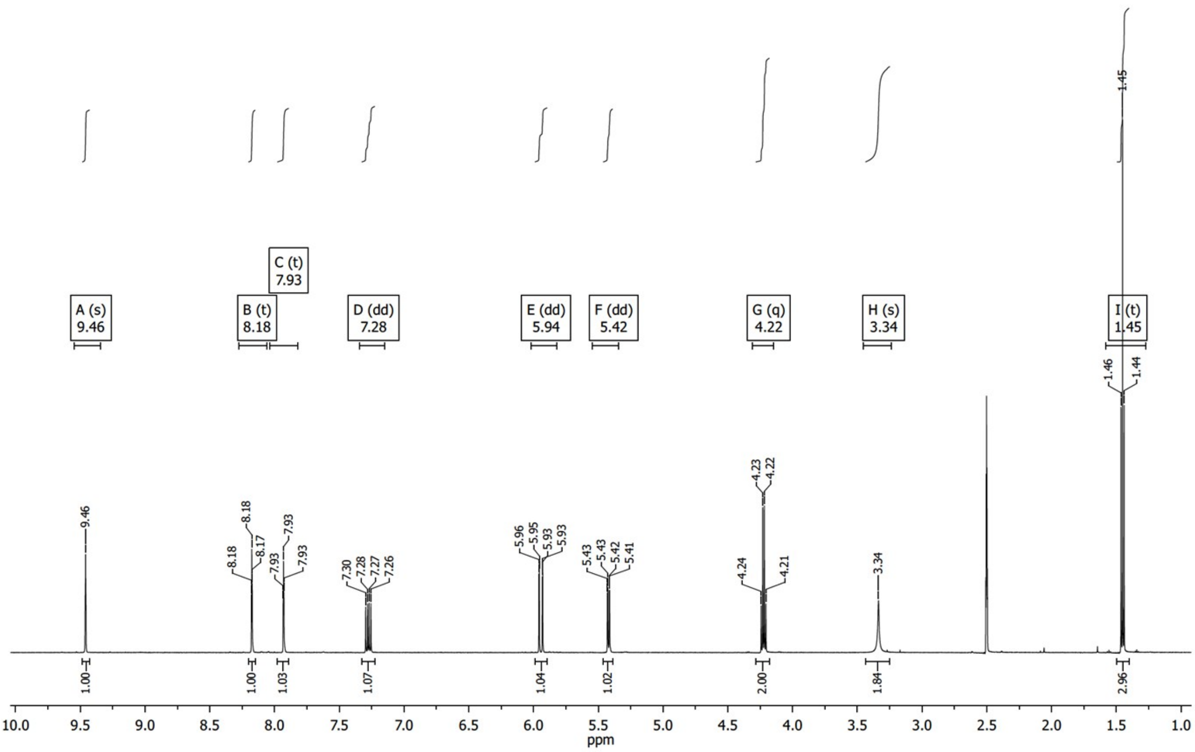


Synthesis of 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide [evim][NTf$_2$]:

$LiNTf_2$ (16.0 g, 56 mmol) dissolved in deionized water (10 ml) was added in portions into the vigorously stirred [evim][Cl] (10 g, 49 mmol) dissolved in CH_2Cl_2 (10 ml). After 24 h, the layers were separated. Organic layer was washed once with deionized water (10ml) and water layer was extracted with CH_2Cl_2 (2x10 ml). The combined organic layers were dried under vacuum to obtained liquid product [evim][NTf$_2$] (28.9 g) with 97% yield.

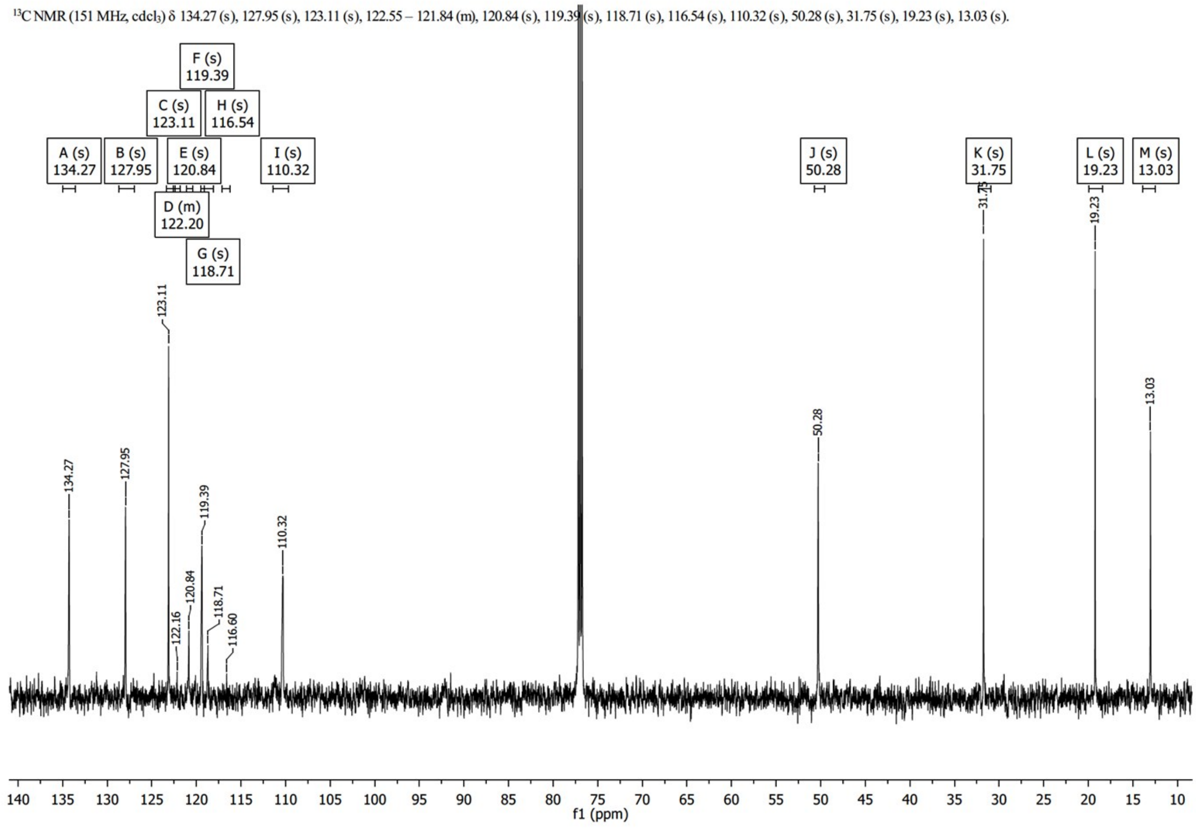
^{1}H NMR (600 MHz, dmso) δ 9.46 (s, 1H), 8.18 (t, J = 1.9 Hz, 1H), 7.93 (t, J = 1.8 Hz, 1H), 7.28 (dd, J = 15.7, 8.8 Hz, 1H), 5.94 (dd, J = 15.6, 2.4 Hz, 1H), 5.42 (dd, J = 8.7, 2.4 Hz, 1H), 4.22 (q, J = 7.3 Hz, 2H), 1.45 (t, J = 7.3 Hz, 3H).

[1]H NMR (600 MHz, dmso) δ 9.46 (s, 1H), 8.18 (t, J = 1.9 Hz, 1H), 7.93 (t, J = 1.8 Hz, 1H), 7.28 (dd, J = 15.7, 8.8 Hz, 1H), 5.94 (dd, J = 15.6, 2.4 Hz, 1H), 5.42 (dd, J = 8.7, 2.4 Hz, 1H), 4.22 (q, J = 7.3 Hz, 2H), 3.34 (s, 2H), 1.45 (t, J = 7.3 Hz, 3H).



^{13}C NMR (150 MHz, dmso) δ 135.48, 129.29, 123.36, 123.13, 120.99, 119.56, 118.86, 116.7, 109.03, 45.06, 15.07 ppm.

^{13}C NMR (151 MHz, cdcl$_3$) δ 134.27 (s), 127.95 (s), 123.11 (s), 122.55 – 121.84 (m), 120.84 (s), 119.39 (s), 118.71 (s), 116.54 (s), 110.32 (s), 50.28 (s), 31.75 (s), 19.23 (s), 13.03 (s).



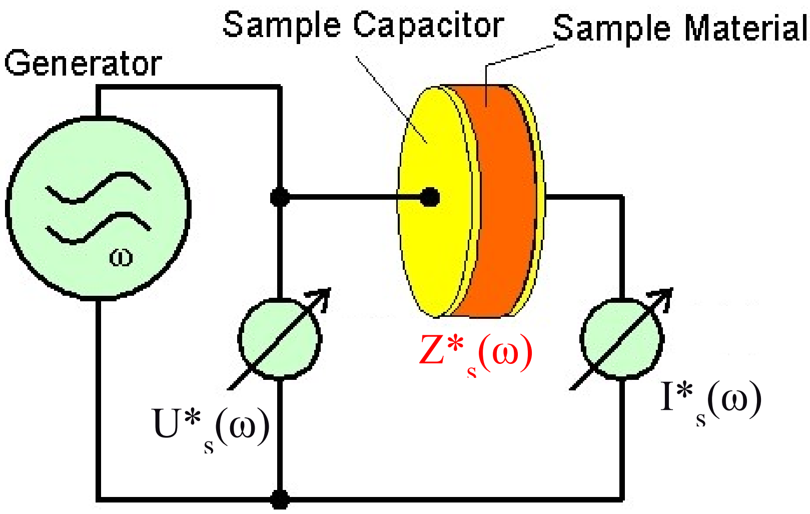
ESI-MS:

$[M + H]^+$ calcd: 123.18, found: 123.0945.

$[M - H]^-$ calcd: 280.15, found: 279.9169.

2. Broadband Dielectric Spectroscopy (BDS)[2]

Broadband Dielectric Spectroscopy is a powerful experimental tool probing the charge transport of the conductive materials, i.e. ionic liquids (IL).



Scheme 3. Setup of dielectric measurements.

During the dielectric measurement, the sample is placed between two stainless steel electrodes of capacitors. Scheme of dielectric measurements setup is presented in Scheme 3. When, we know voltage, *U**, applied to the capacitor filled with the sample and current, *I**, passed through the capacitor we can estimate impedance of the sample, *Z**:

$$Z_S^* = \frac{U_S^*}{I_S^*}$$

The capacitive impedance, *Z**, of sample and the complex permittivity, *ε**, are related as follow:

[2] F. Kremer, A. Schonhals, *Dielectric Relaxation Spectroscopy; Fundamentals and Applications*, Springer, Berlin, 2003

$$\varepsilon^* = -\frac{i}{\omega Z_S^* C_0} = \varepsilon' - i\varepsilon''$$

where real (*ε*') and imaginary (*ε''*) parts of *ε** can be calculated from these equation :

$$\varepsilon' = \frac{C}{C_0} \text{ and } \varepsilon'' = \frac{1}{\omega R C_0}$$

C_0, and C are capacity of empty and filled capacitor respectively, *R* – resistance, *ε'* and *ε''* are real and imaginary part of permittivity, respectively, and *ω* is an angular frequency ($\omega = 2\pi f$). Thus, the complex permittivity *ε** can be obtained from measuring *Z**, and capacity of empty capacitor, C_0.

For the majority of the glass formers, dielectric spectra are shown in susceptibility or permittivity, *ε**, representation. However for strongly conducting samples (such as ionic liquids), dielectric data are usually presented in terms of the complex conductivity $\sigma^* = i\omega\varepsilon_0\varepsilon^*$ or the complex electrical modulus $M^* = 1/\varepsilon^*$.