## **Supplementary Materials**

## Characterization of Local Structures of Confined Imidazolium Ionic Liquids in PVdF-co-HFP Matrices by High Pressure Infrared Spectroscopy

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Figure S1. IR spectra of the [HMIM][NTF<sub>2</sub>]/PVdF-co-HFP mixture featuring 10 wt% of [HMIM][NTf<sub>2</sub>] obtained at (a) ambient pressure and (b) 0.4, (c) 0.7, (d) 1.1, (e) 1.5, (f) 1.8, and (g) 2.5 GPa.

Figure S2. IR spectra of the [EMIM][NTF<sub>2</sub>]/PVdF-co-HFP mixture featuring 10 wt% of [EMIM][NTf<sub>2</sub>] obtained at (a) ambient pressure and (b) 0.4, (c) 0.7, (d) 1.1, (e) 1.5, (f) 1.8, and (g) 2.5 GPa.

Figure S3. IR spectra of the [HMIM][NTF<sub>2</sub>]/PVdF-co-HFP mixture featuring 50 wt% of [HMIM][NTf<sub>2</sub>] obtained at (a) ambient pressure, (b) 2.5 GPa, and (c) cycle back to ambient pressure.

Figure S4. IR spectra of pure  $[EMIM][NTf_2]$  obtained at the time of (a) 5 min (100 scans), (b) 1 hr (1000 scans), (c) 2 hr (1000 scans), and (d) 3 hr (1000 scans) after the compression under the pressure of 0.7 GPa.

Figure S5. IR spectra of pure  $[EMIM][NTf_2]$  (pre-heated to 155<sup>0</sup>C) obtained at (a) ambient pressure and (b) 0.4, (c) 0.7, (d) 1.1, (e) 1.5, (f) 1.8, and (g) 2.5 GPa at 25<sup>0</sup>C.



Figure S1. IR spectra of the [HMIM][NTF<sub>2</sub>]/PVdF-co-HFP mixture featuring 10 wt% of [HMIM][NTf<sub>2</sub>] obtained at (a) ambient pressure and (b) 0.4, (c) 0.7, (d) 1.1, (e) 1.5, (f) 1.8, and (g) 2.5 GPa.



Figure S2. IR spectra of the [EMIM][NTF<sub>2</sub>]/PVdF-co-HFP mixture featuring 10 wt% of [EMIM][NTf<sub>2</sub>] obtained at (a) ambient pressure and (b) 0.4, (c) 0.7, (d) 1.1, (e) 1.5, (f) 1.8, and (g) 2.5 GPa.



Figure S3. IR spectra of the [HMIM][NTF<sub>2</sub>]/PVdF-co-HFP mixture featuring 50 wt% of [HMIM][NTf<sub>2</sub>] obtained at (a) ambient pressure (in air), (b) 2.5 GPa (in DAC), and (c) cycle back to ambient pressure (in DAC).



Figure S4. IR spectra of pure  $[EMIM][NTf_2]$  obtained at the time of (a) 5 min (100 scans), (b) 1 hr (1000 scans), (c) 2 hr (1000 scans), and (d) 3 hr (1000 scans) after the compression under the pressure of 0.7 GPa.



Figure S5. IR spectra of pure  $[EMIM][NTf_2]$  (pre-heated to  $155^{0}C$ ) obtained at (a) ambient pressure and (b) 0.4, (c) 0.7, (d) 1.1, (e) 1.5, (f) 1.8, and (g) 2.5 GPa at  $25^{0}C$ .