

## Electronic Supplementary Information:

How Does the Flexibility of Pyrrolidinium Cations Affect the Phase Behaviour of 1-Alkyl-1-methylpyrrolidinium Bis(trifluoromethanesulfonyl)imide Homologues under Stressful Conditions?

Yoshihiro Koyama<sup>a</sup>, Kiyoto Matsuishi<sup>a</sup>, Takahiro Takekiyo<sup>b</sup>, Hiroshi Abe<sup>c</sup>, Yukihiro Yoshimura<sup>b\*</sup>

<sup>a</sup>*Graduate School of Pure and Applied Science, University of Tsukuba, Ibaraki 305-8537, Japan*

<sup>b</sup>*Department of Applied Chemistry, National Defense Academy, 1-10-20, Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan*

<sup>c</sup>*Department of Materials Science and Engineering, National Defense Academy, 1-10-20, Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan*

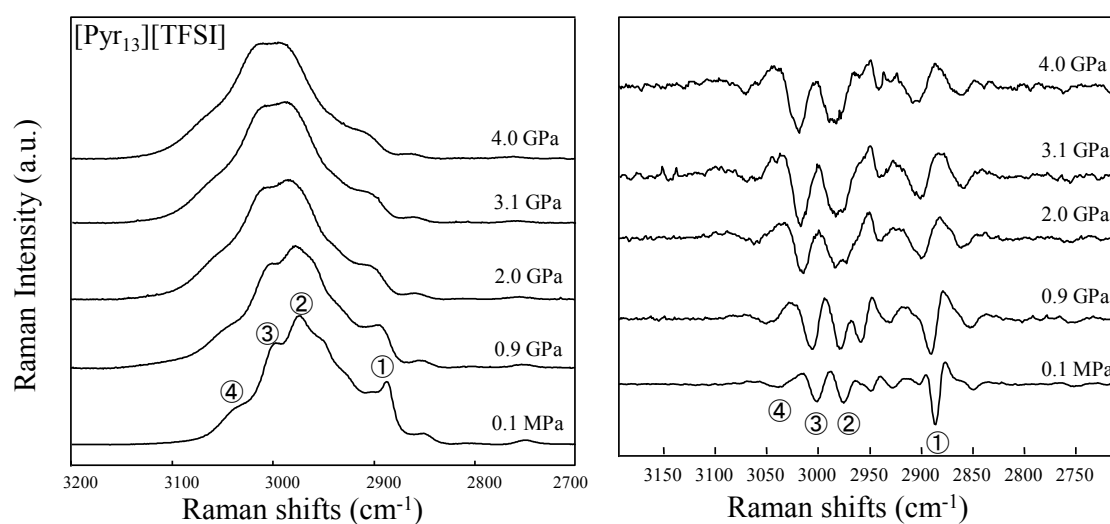


Figure S1. Typical Raman (left) and its second derivative (right) spectra in the CH stretching region of [Pyr<sub>13</sub>][TFSI] at several pressures (① 2850 cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the alkyl-chain (symmetric), ②  $\sim 2974$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the pyrrolidinium ring + alkyl chain, ③  $\sim 3000$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the pyrrolidinium ring, ④  $\sim 3040$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of CH<sub>3</sub>(N)).

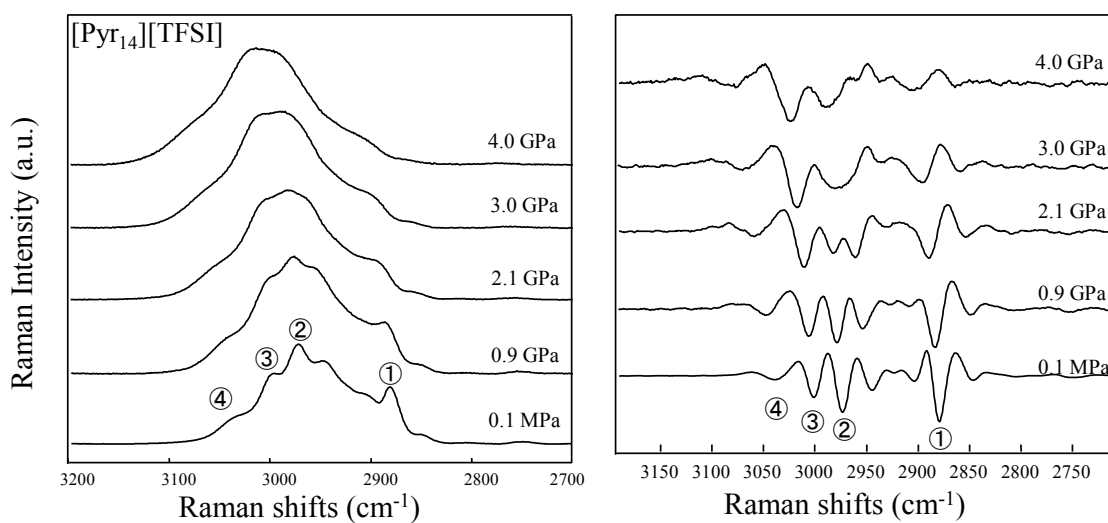


Figure S2. Typical Raman (left) and its second derivative (right) spectra in the CH stretching region of [Pyr<sub>14</sub>][TFSI] at several pressures (① 2850 cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the alkyl-chain (symmetric), ②  $\sim 2974$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the pyrrolidinium ring + alkyl chain, ③  $\sim 3000$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the pyrrolidinium ring, ④  $\sim 3040$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of CH<sub>3</sub>(N).

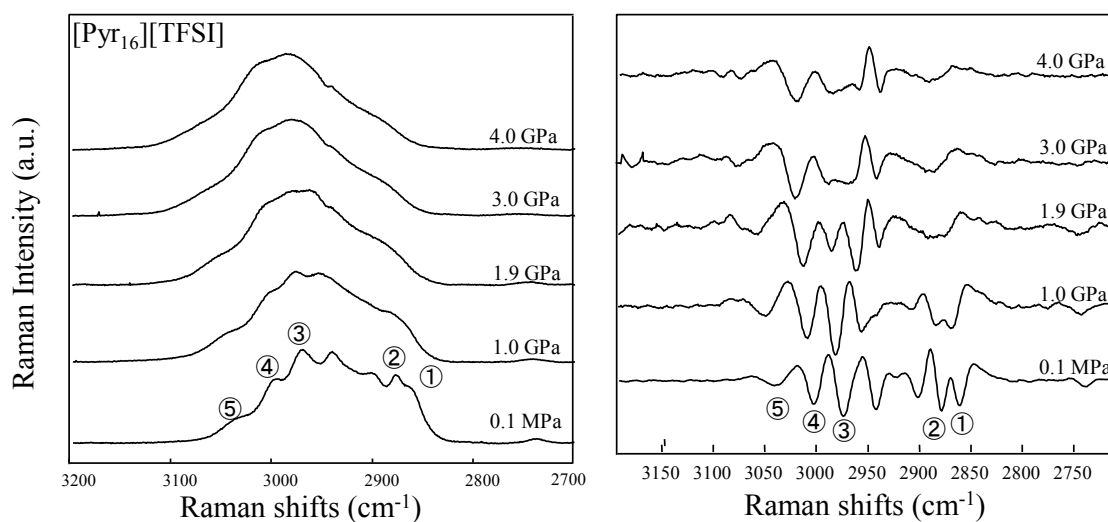


Figure S3. Typical Raman (left) and its second derivative (right) spectra in the CH stretching region of [Pyr<sub>16</sub>][TFSI] at several pressures pressures (① 2850 cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the alkyl-chain (symmetric), ②  $\sim 2880$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the alkyl-chain (symmetric), ③  $\sim 2974$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the pyrrolidinium ring + alkyl chain, ④  $\sim 3000$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the pyrrolidinium ring, ⑤  $\sim 3040$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of CH<sub>3</sub>(N).

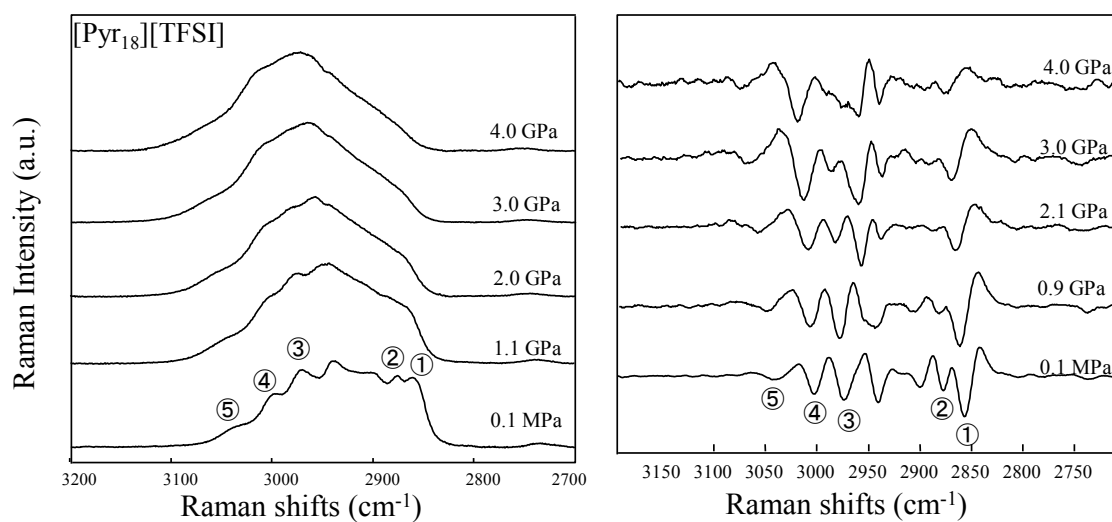


Figure S4. Typical Raman (left) and its second derivative (right) spectra in the CH stretching region of [Pyr<sub>18</sub>][TFSI] at several pressures pressures (① 2850 cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the alkyl-chain (symmetric), ②  $\sim 2880$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the alkyl-chain (symmetric), ③  $\sim 2974$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the pyrrolidinium ring + alkyl chain, ④  $\sim 3000$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of the pyrrolidinium ring, ⑤  $\sim 3040$  cm<sup>-1</sup> :  $\nu_{\text{CH}}$  of CH<sub>3</sub>(N).