Supplemental Information

Halide anion dependence on 1-*n*-butyl-3-methylimidazolium conformational isomerism in the ionic liquids

Yasuhiro Umebayashi[a*], Hiroshi Hamano[a], Seiji Tsuzuki[b*], José N. Canongia Lopes[c], Agilio A. H. Pádua[d], Yasuo Kameda[e], Shinji Kohara[f], Taishi Yamaguchi[a], Kenta Fujii[g], Shin-ichi Ishiguro[a]

[a] Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.
[b] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Center 5, Tsukuba, Ibaraki 305-8565, Japan.
[c] Centro de Química Estrutural, Instituto Superior Técnico, 1049 001 Lisboa, and Instituto de Tecnologia Química e Biológica, UNL, Av. República Ap. 127, 2780 901 Oeiras, Portugal.
[d] Laboratoire Thermodynamique et Interactions Moléculaires, Université Blaise Pascal Clermont-Ferrand/CNRS FRE3099, France.
[e] Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Kojirakawa-machi 1-4-12, Yamagata 990-8560, Japan.
[f] Japan Synchrotron Radiation Research Institute (JASRI), Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan.
[g] Neutron Science Labolatory, Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan.

To whom the correspondence should be addressed: yumeb@chem.kyushu-univ.jp (YU), TEL&FAX: +81-92-642-2582 and s.tsuzuki@aist.go.jp (ST)

Y. Umebayashi et al.

Figure S1

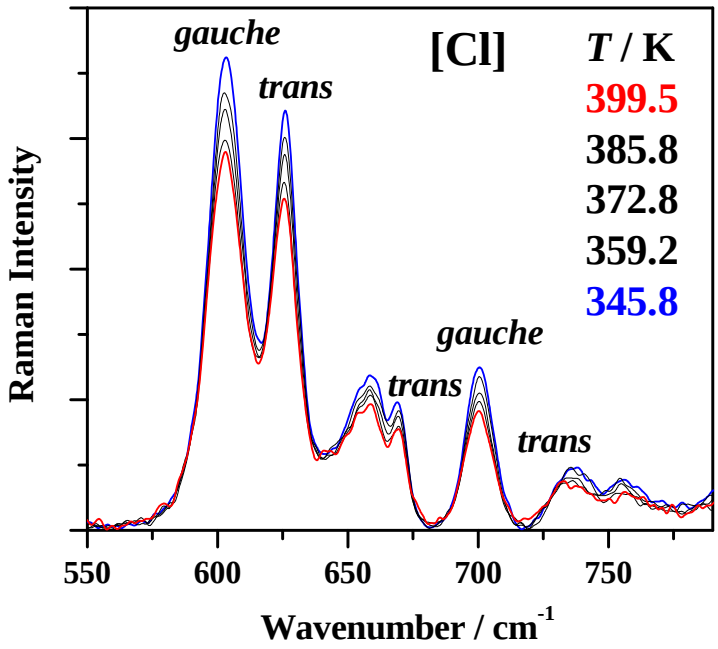

Figure S1 Temperature dependence of Raman spectra for [C_4mim][Cl] ionic liquid in the frequency range of 550–790 cm^{-1}. Temperatures are shown in the figure.

Y. Umebayashi et al.

Figure S2

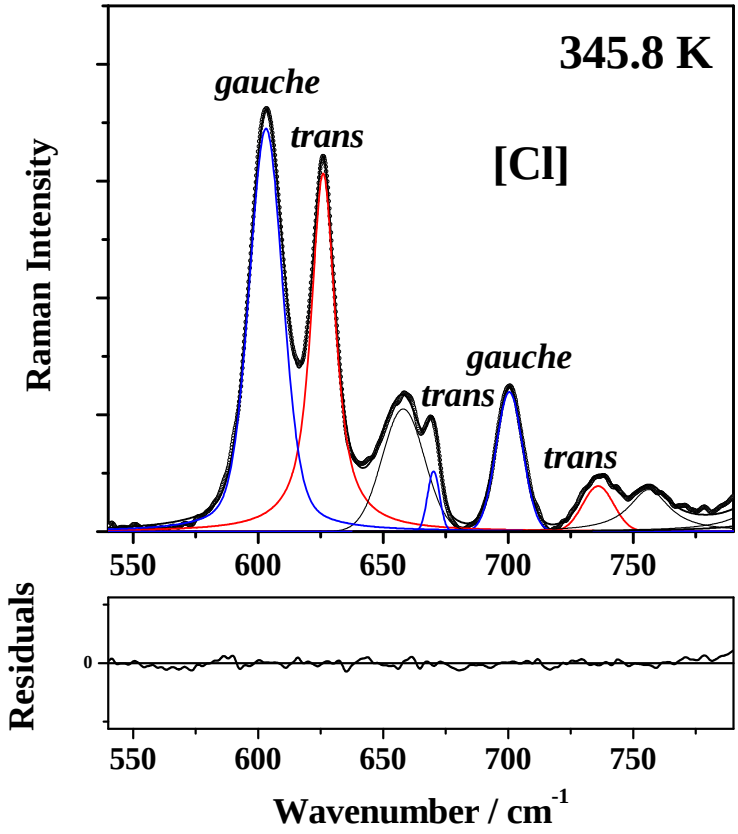

Figure S2 Typical extracted single Raman bands at the frequency range of 540–790 cm^{-1} for [C_4mim][Cl]. (upper panel) Residuals for the fitting are also shown. (lower panel)

Y. Umebayashi et al.

Figure S3

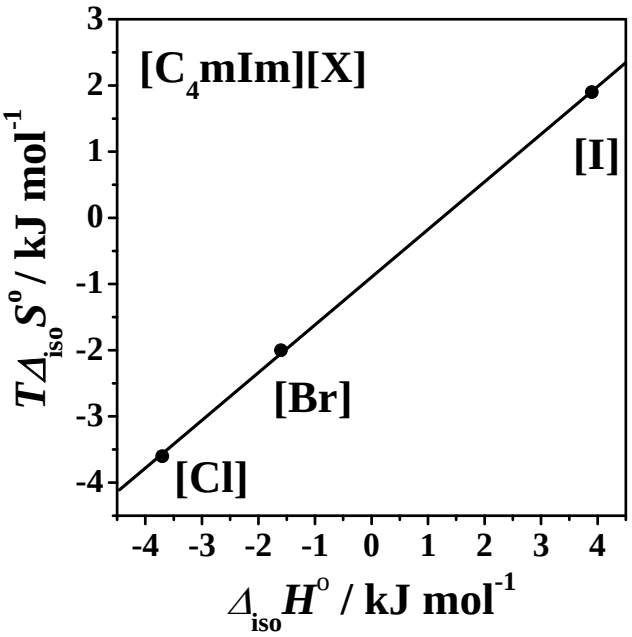

Figure S3 $\Delta_{iso}H^o$ and $T\Delta_{iso}S^o$ correlation for the conformational isomerism of [C_4mim] from trans to cis isomers in the halide based ionic liquids.

Y. Umebayashi et al.

Figure S4

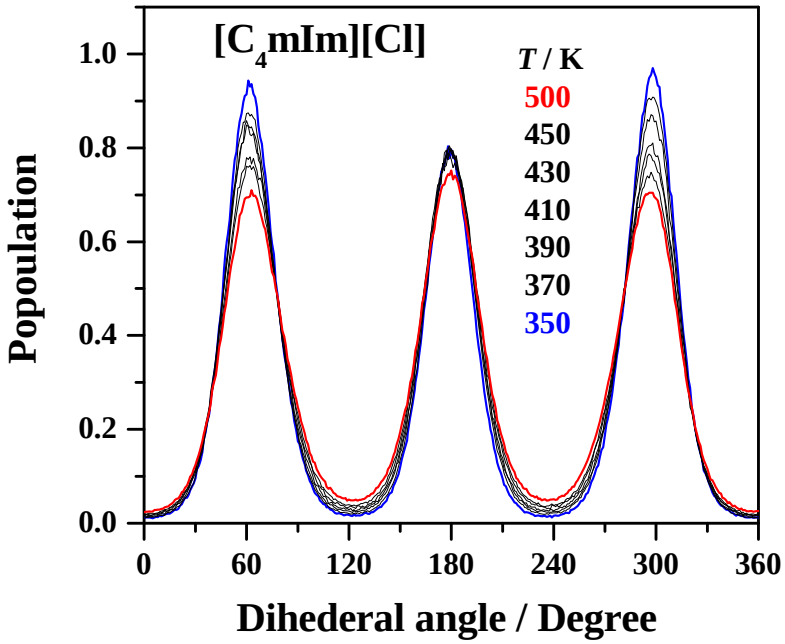

Figure S4 Temperature dependence of the dihedral angle distribution for the N1–C7–C8–C9 of C_4mim^+ in [C_4mim][Cl] in the temperature range of 350–500 K.

Y. Umebayashi et al.

Figure S5

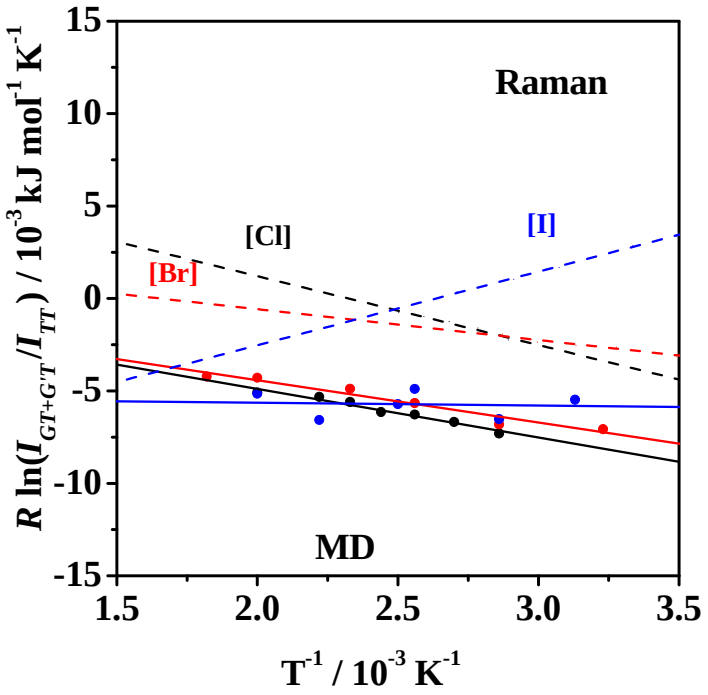

Figure S5 van't Hoff plots of the conformational isomerism of [C_4mim] from *trans* to *gauche* isomers with respect to the N1–C7–C8–C9 dihedral angle of C_4mim^+ in chloride, bromide and iodide ionic liquids, respectively, derived from MD simulations. Experimental data were also shown as broken lines for comparison.