Supplementary information

Improved Thermal Stability of Ionic Liquid through Hydrogen Bond Donor as an Electrolyte for Fluoride-Ion Battery

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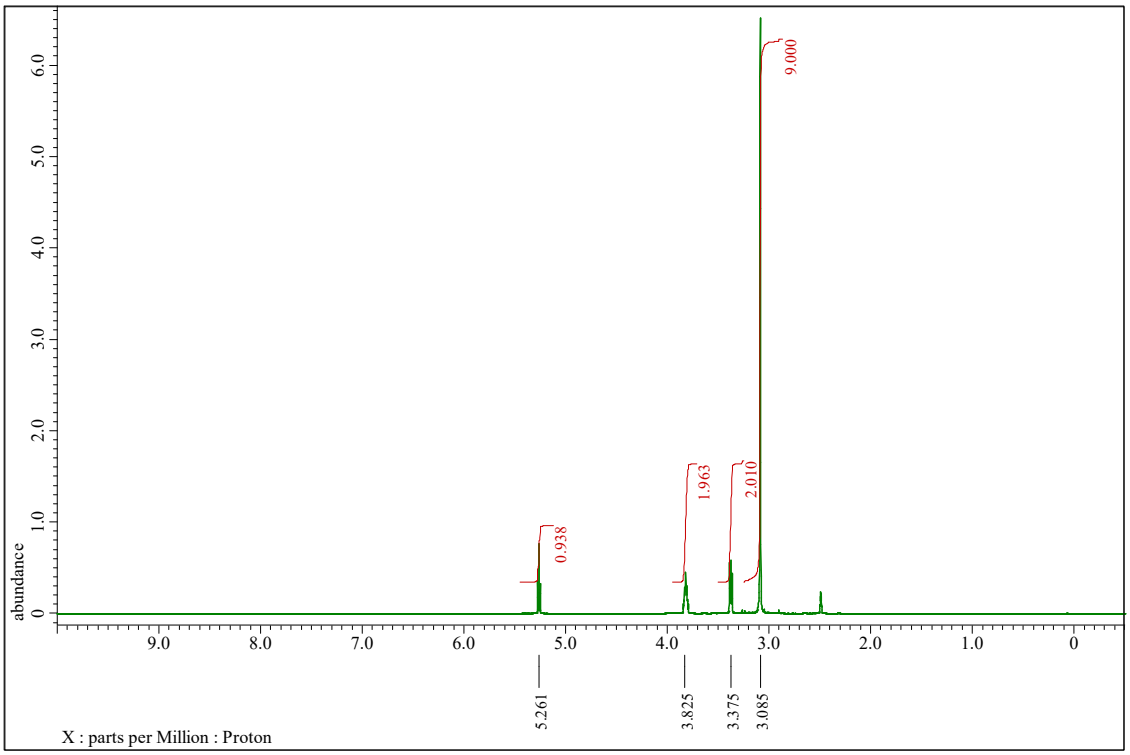

Figure S1. ^{1}H NMR spectrum of the synthesized $N_{111(2OH)}$TFSA in DMSO-d_6.

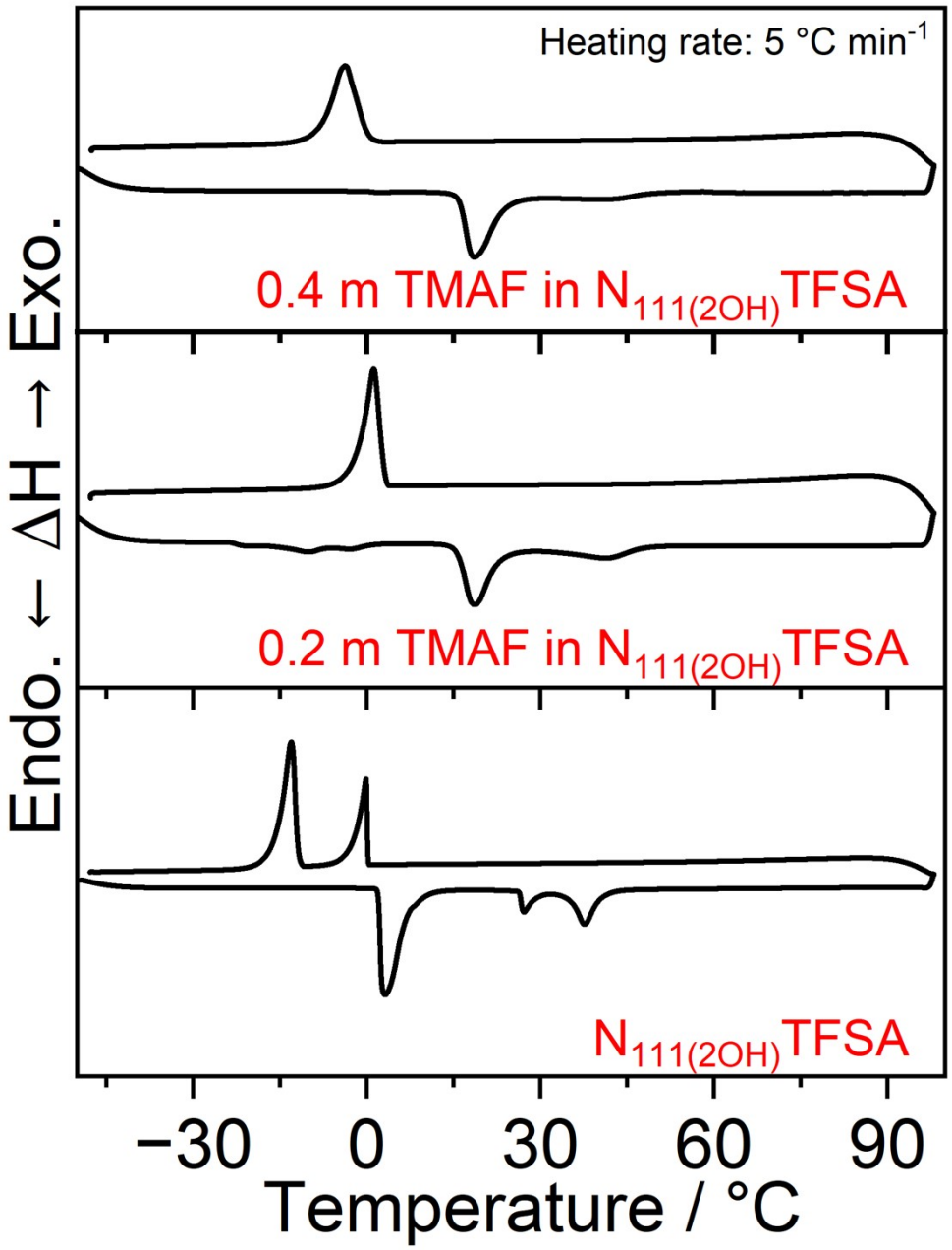

Figure S2. Full-range DSC curves of $N_{111(2OH)}$TFSA with different concentrations of TMAF (0, 0.2, and 0.4 m) at a heating rate of 5 ºC min^{-1}, corresponding to the data shown in Figure 2.

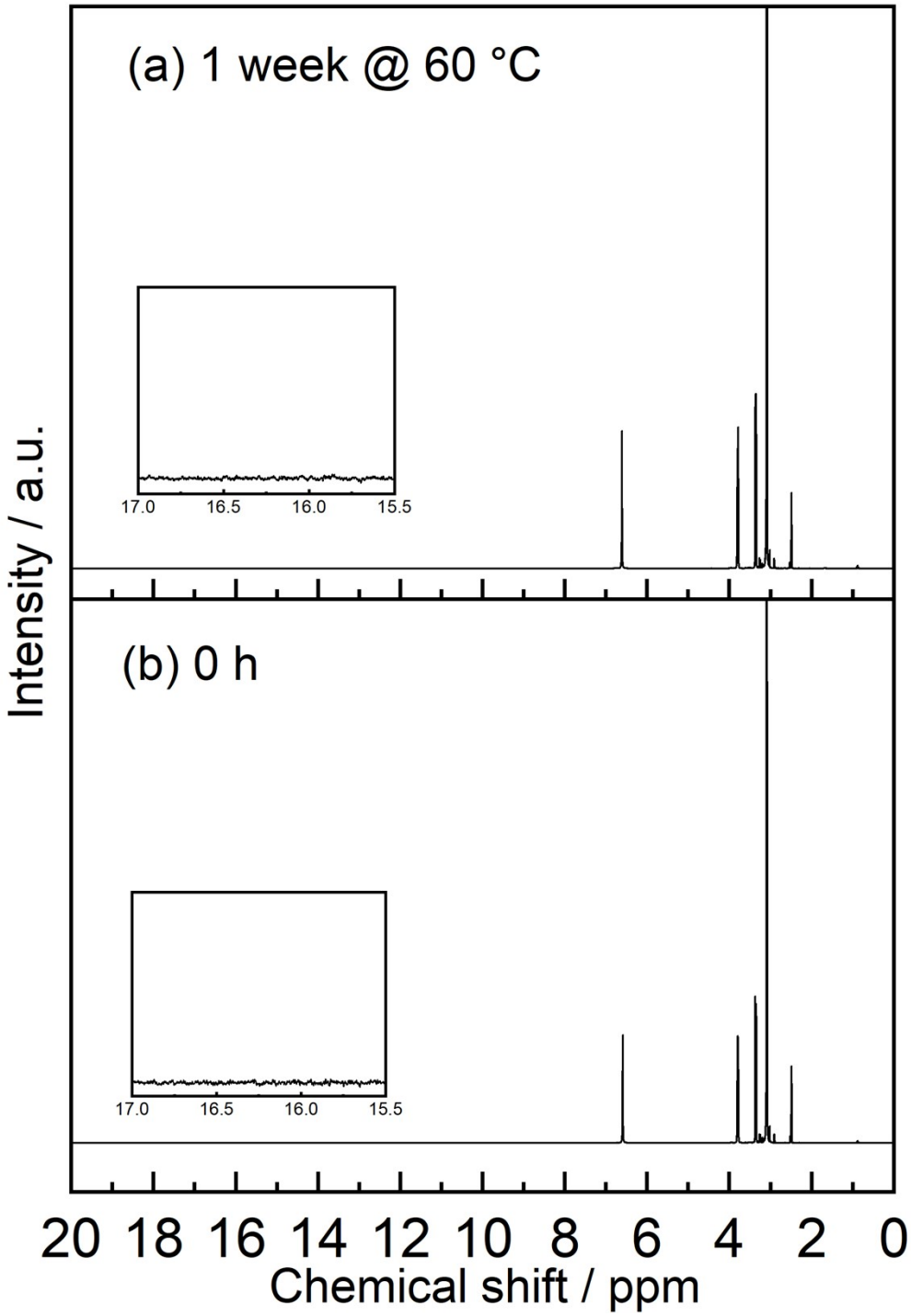

Figure S3. ^{1}H NMR spectra of 0.4 m TMAF in $N_{111(2OH)}$TFSA after (a) and before (b) stirring at 60 °C for one week.

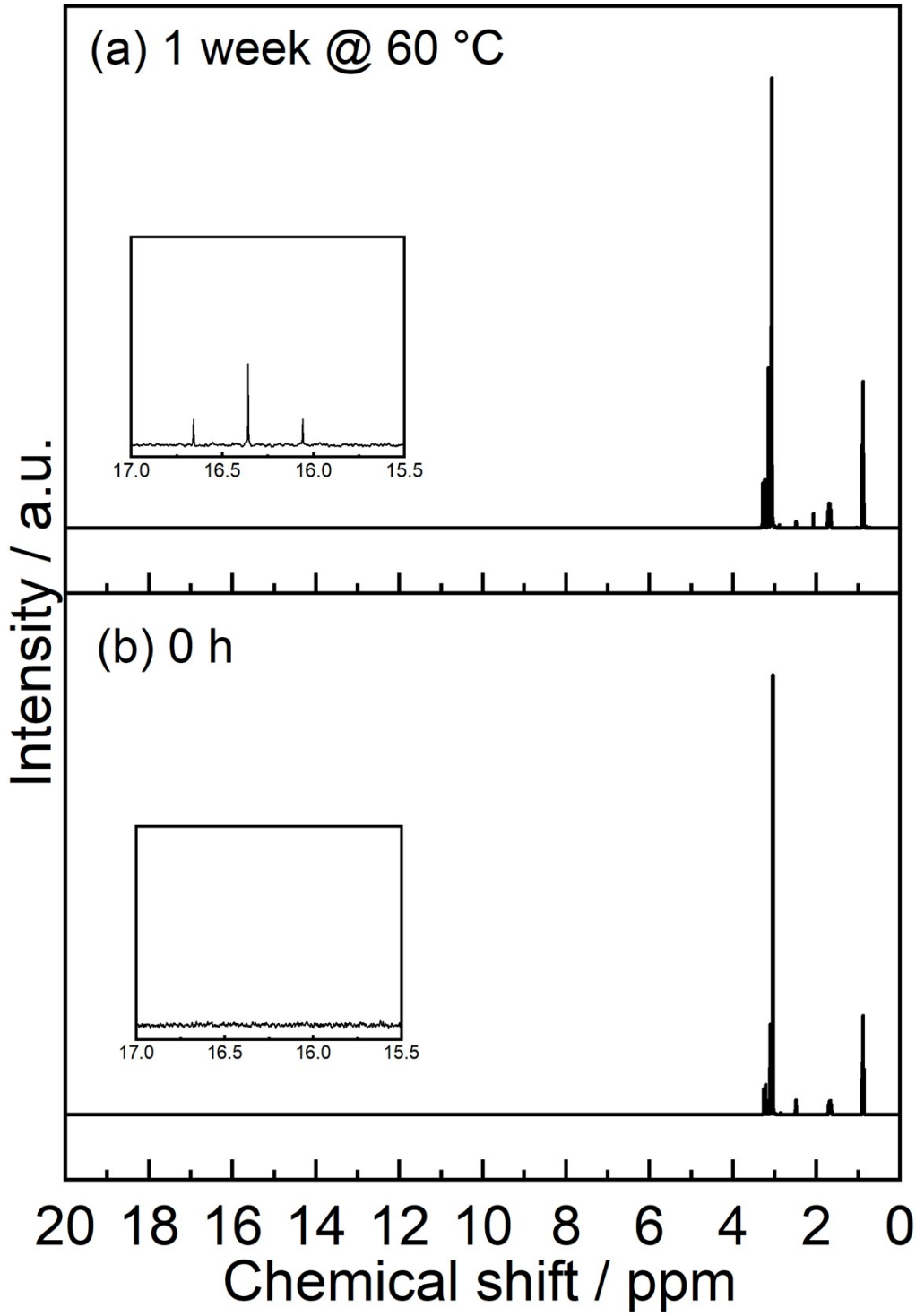

Figure S4. ^{1}H NMR spectra of 0.4 m TMAF in N_{1113}TFSA after (a) and before (b) stirring at 60 °C for one week.

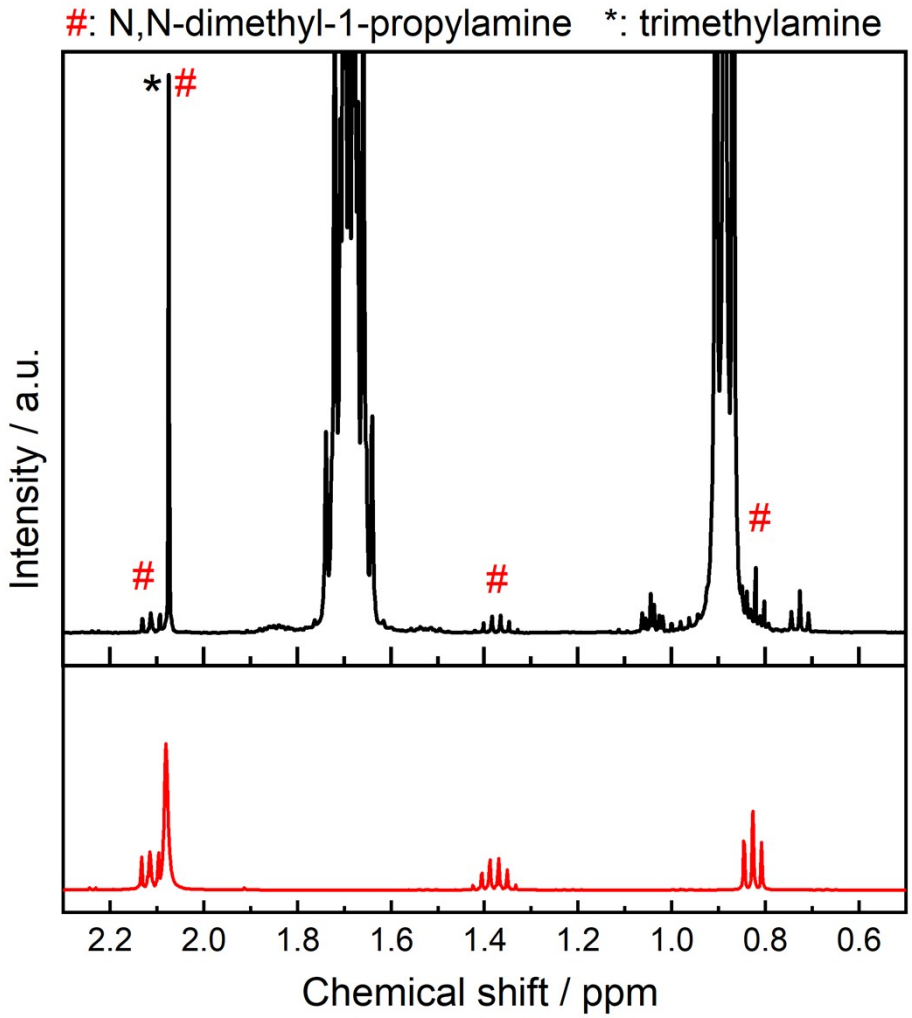

Figure S5. ^{1}H NMR spectra of 0.4 m TMAF in N_{1113}TFSA after stirring at 60 °C for one week (top) and *N*,*N*-dimethyl-1-propylamine in DMSO-d_6 (bottom).

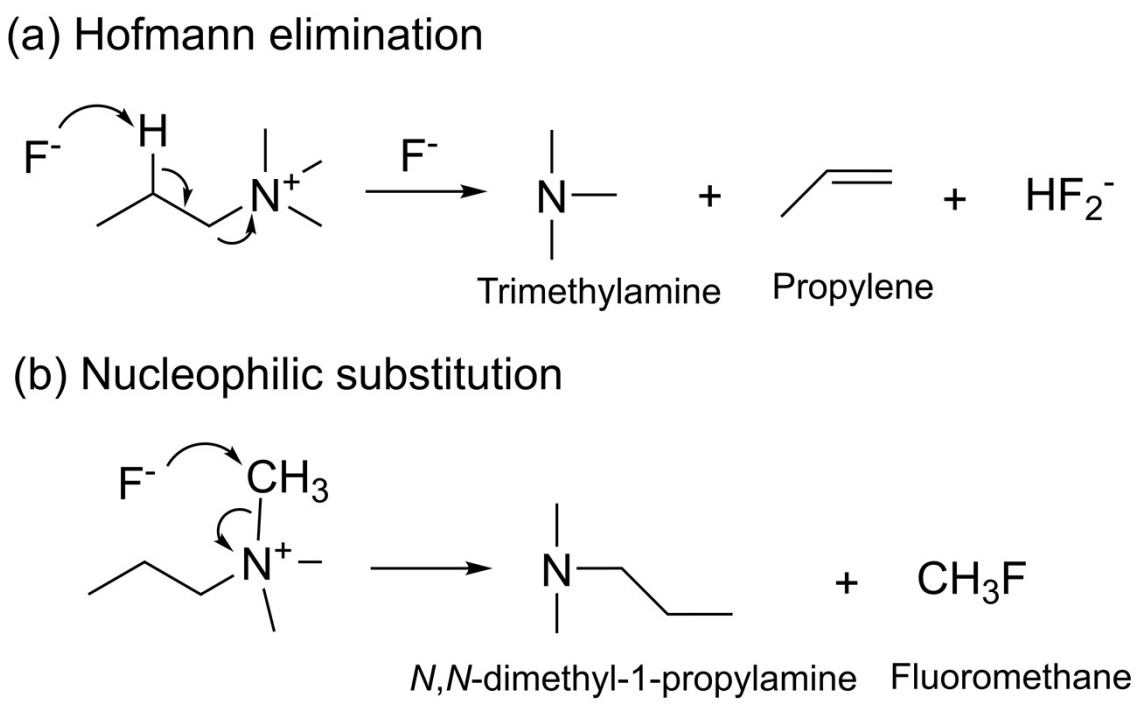

Figure S6. Possible decomposition reaction of N_{1113}^{+} cation with F^{-} ion: (a) Hofmann elimination (b) Nucleophilic substitution.

Table S1. Diffusion coefficient values of $N_{111(2OH)}TFSA$ electrolytes at various concentrations of TMAF at 60 ºC. Diffusion coefficients were measured using the stimulated echo pulse sequence with the gradient pulse duration δ of 3 ms, the diffusion time Δ of 20 ms, and a maximum gradient strength of 10 T/m. Transport numbers for ions i were calculated by $t_i = \frac{N_i D_i}{N_{N111(2OH)^+} D_{N111(2OH)^+} + N_{TMA^+} D_{TMA^+} + N_{TFSA^-} D_{TFSA^-} + N_{F^-} D_{F^-}}$, where D and N denote the diffusion coefficient and the number density of ions, respectively. Since we could not separate the chemical shifts of $N_{111(2OH)}^+$ and TMA^+, we assumed that D_{TMA^+} equals $D_{N111(2OH)^+}$.

Sample	$N_{111(2OH)}^+$ ($x10^{-11}$ m^2 s^{-1})	$TFSA^-$ ($x10^{-11}$ m^2 s^{-1})	F^- ($x10^{-11}$ m^2 s^{-1})
$N_{111(2OH)}TFSA$	6.52	4.33	-
0.1 m TMAF in $N_{111(2OH)}TFSA$	3.93	3.6	3.16
0.25 m TMAF in $N_{111(2OH)}TFSA$	3.28	3.05	2.34
0.4 m TMAF in $N_{111(2OH)}TFSA$	2.62	2.53	1.88