Supporting Information

Fluoride Superionic Conduction in TlF with the New Anti-α-CuBr Structure Containing Intrinsic F Vacancies

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Contents

Computational Methods; MD data to conductivity

Mean square displacements (MSDs) shown in Fig. 4(a) were calculated as

$$\mathrm{MSD}(t) = \frac{1}{N}\sum_{i=1}^{N} |\boldsymbol{r_i}(t) - \boldsymbol{r_i}(0)|^2 \qquad (1)$$

where $\boldsymbol{r_i}\ (t)$ is the position vector of the i-th mobile ion at time t, and N is the total number of the mobile ions. To calculate diffusion coefficient D, we adopted the time-averaging form [1] as

$$D(\Delta t) = \frac{1}{6N\Delta t}\sum_{i=1}^{N} \langle |\boldsymbol{r_i}(t+\Delta t) - \boldsymbol{r_i}(t)|^2 \rangle_t \qquad (2)$$

where the bracket represents averaging over t, which is intended for a good statistics. We calculate $D(\Delta t)$ in terms of Δt and obtain a well converged D that is almost insensitive to Δt as shown in Fig. 4(b). The ionic conductivity, σ, can be calculated using Nernst-Einstein relationship as

$$\sigma = \frac{nq^2}{k_B T} D \qquad (3)$$

where n is the number of mobile ions per MD cell and q is the ionic charge.

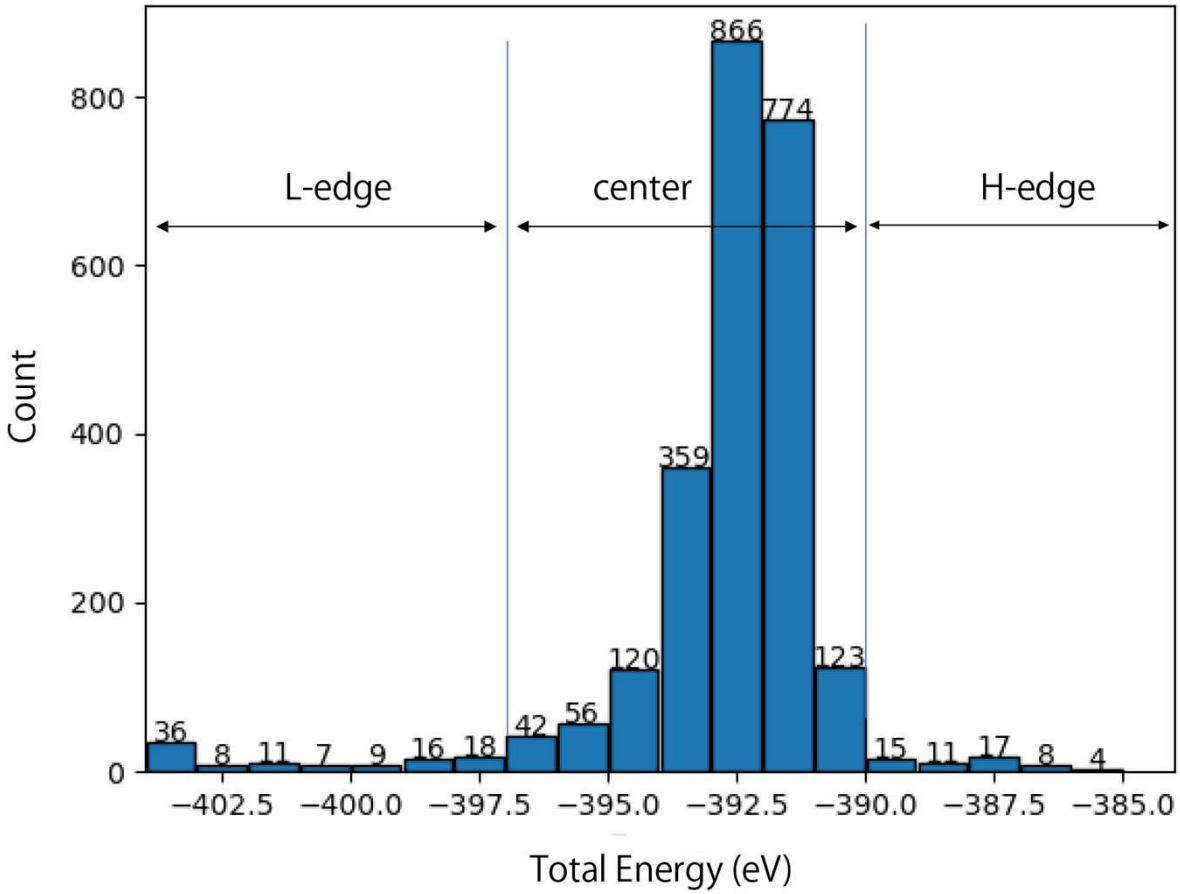

Figure S1. Example of the total energy histogram of an MD trajectory divided into three regions as left-edge, center, and right-edge. The left- and right-edges correspond to rare structures and the center major structures.

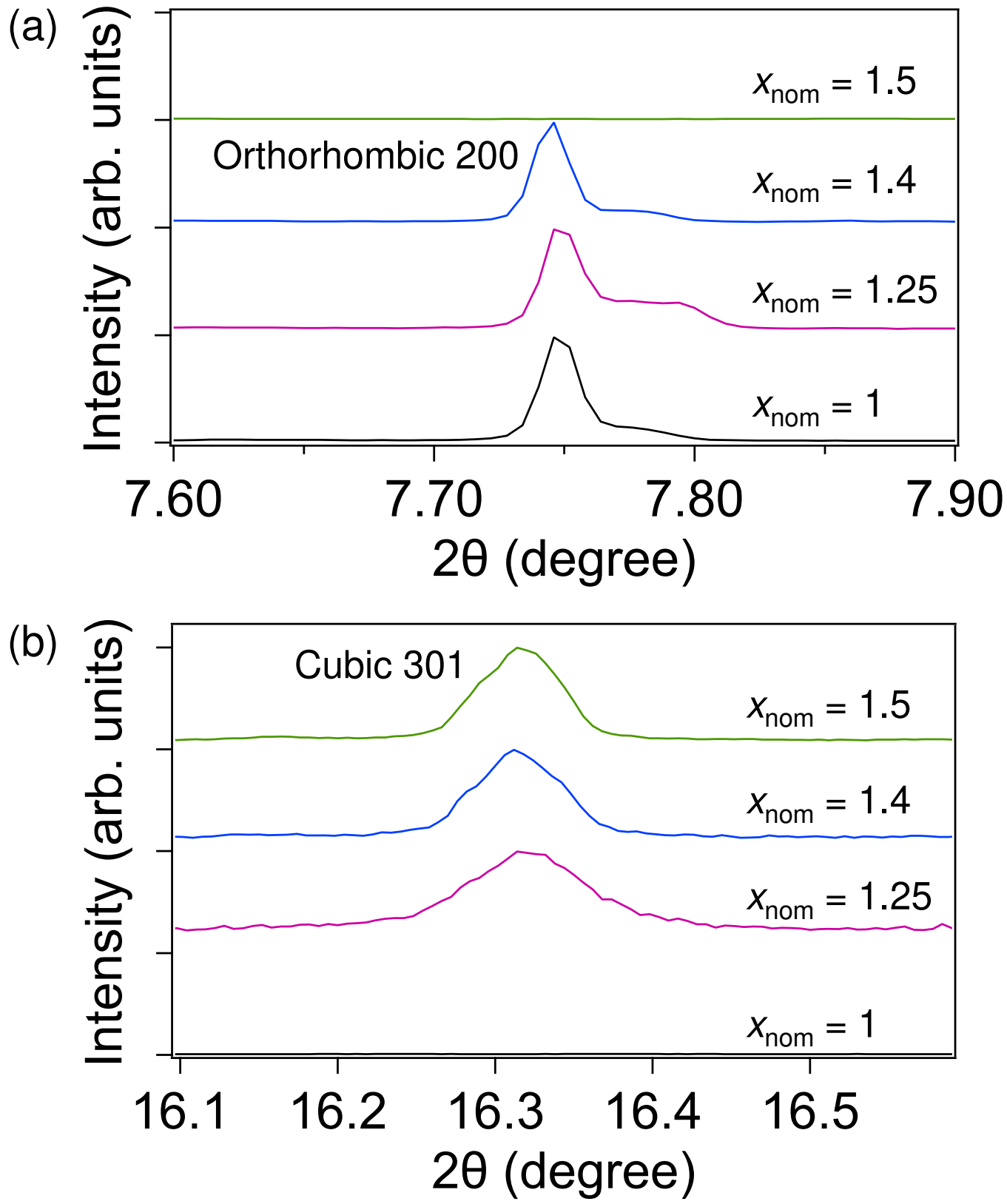

Figure S2. XRD patterns for (a) 200 peak for orthorhombic TlF and (b) 301 peak for cubic TlF.

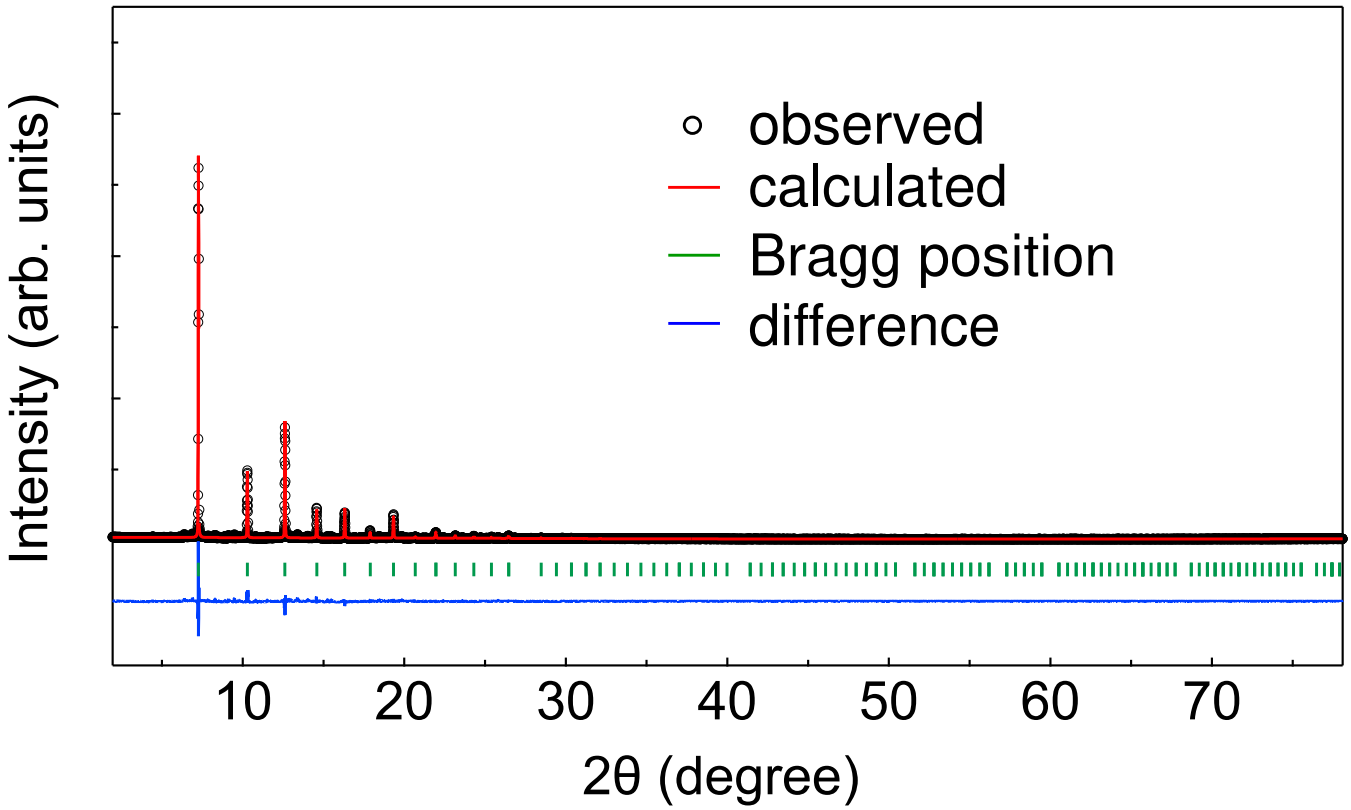

Figure S3. Rietveld refinement on synchrotron XRD pattern of cubic TlF.

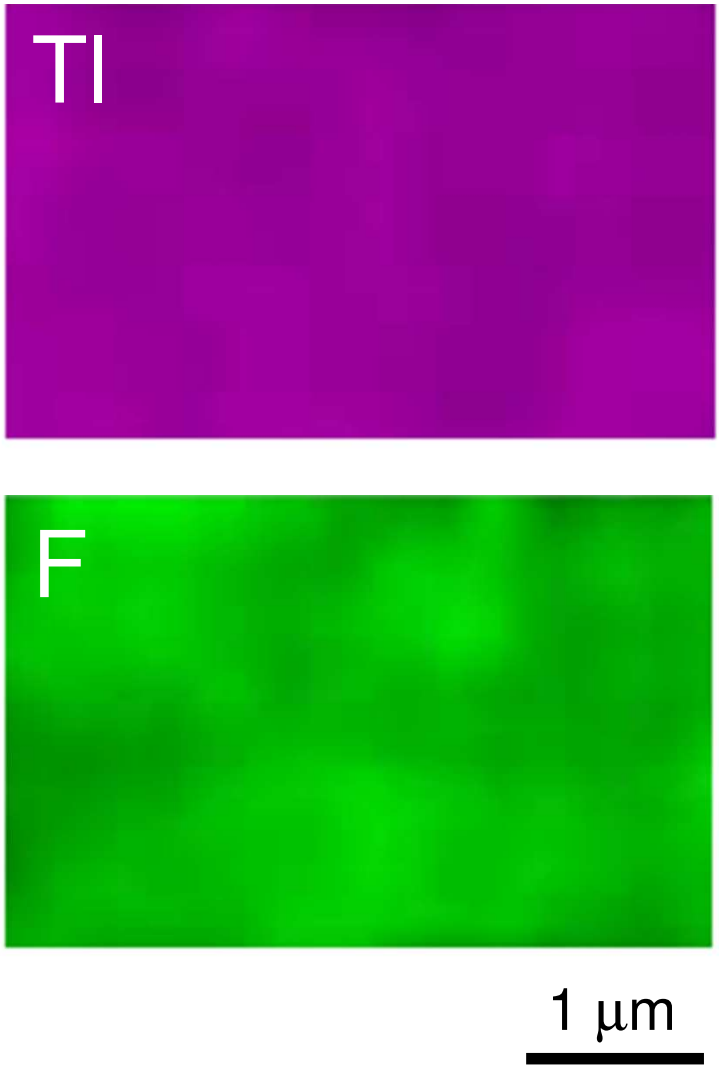

Figure S4. SEM-EDX mapping images of cubic TlF. Scale bar: 1 µm.

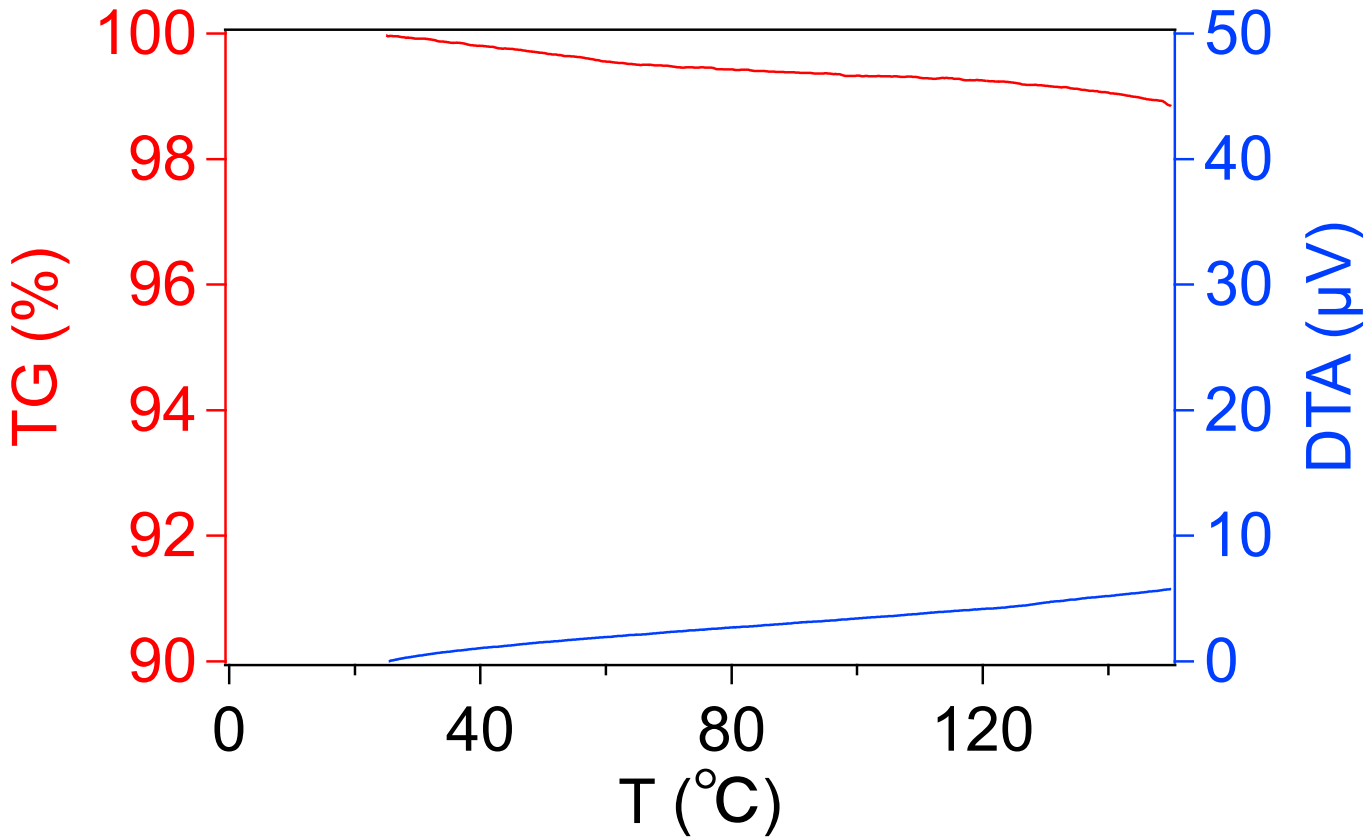

Figure S5. TG-DTA curves for cubic TlF.

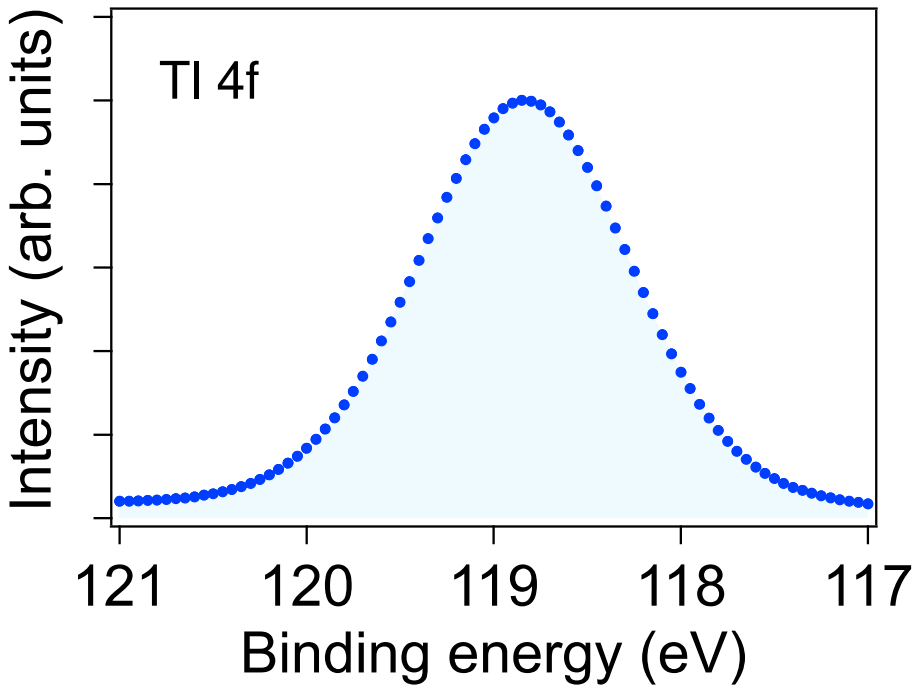

Figure S6. Tl $4f_{7/2}$ XPS spectrum at room temperature for cubic TlF. The symbols and filled area show the experimental data and the fitted results, respectively.

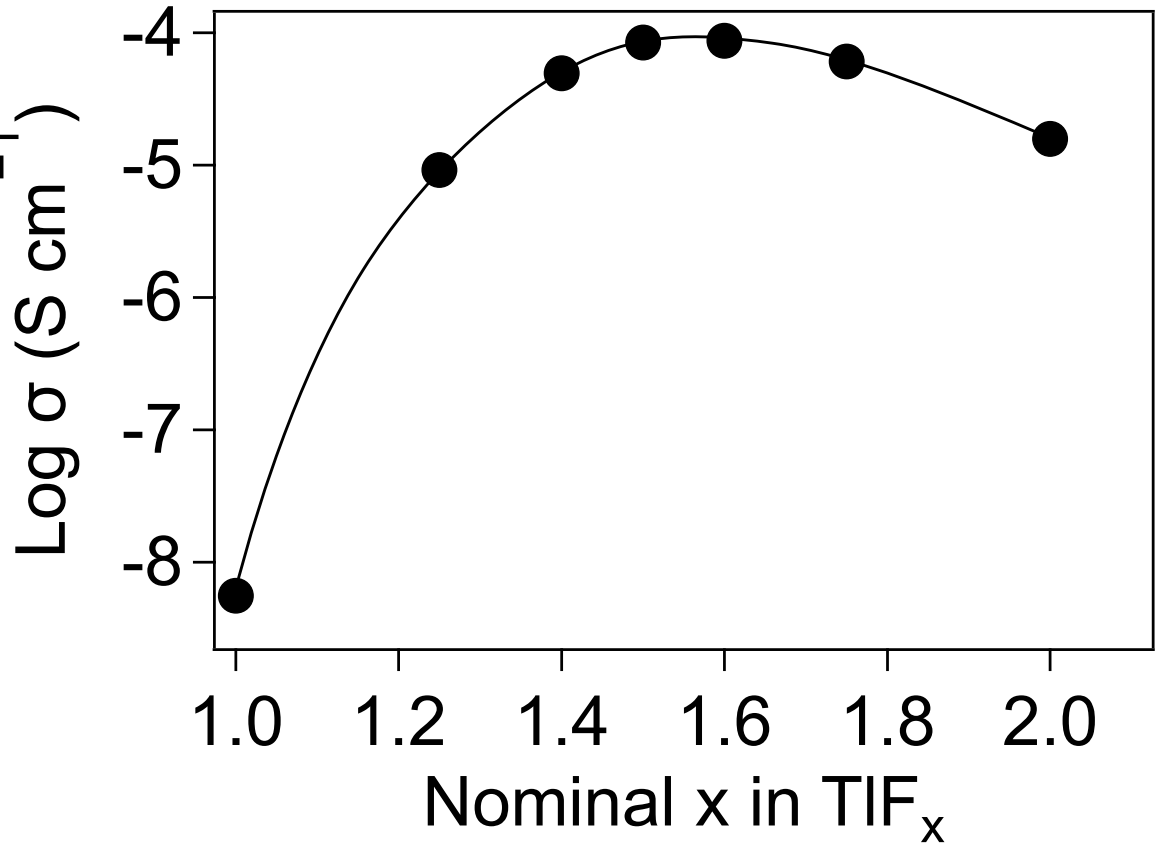

Figure S7. Room-temperature electrical conductivity as a function of nominal x of TlF_x. The solid line is the guide to the eyes.

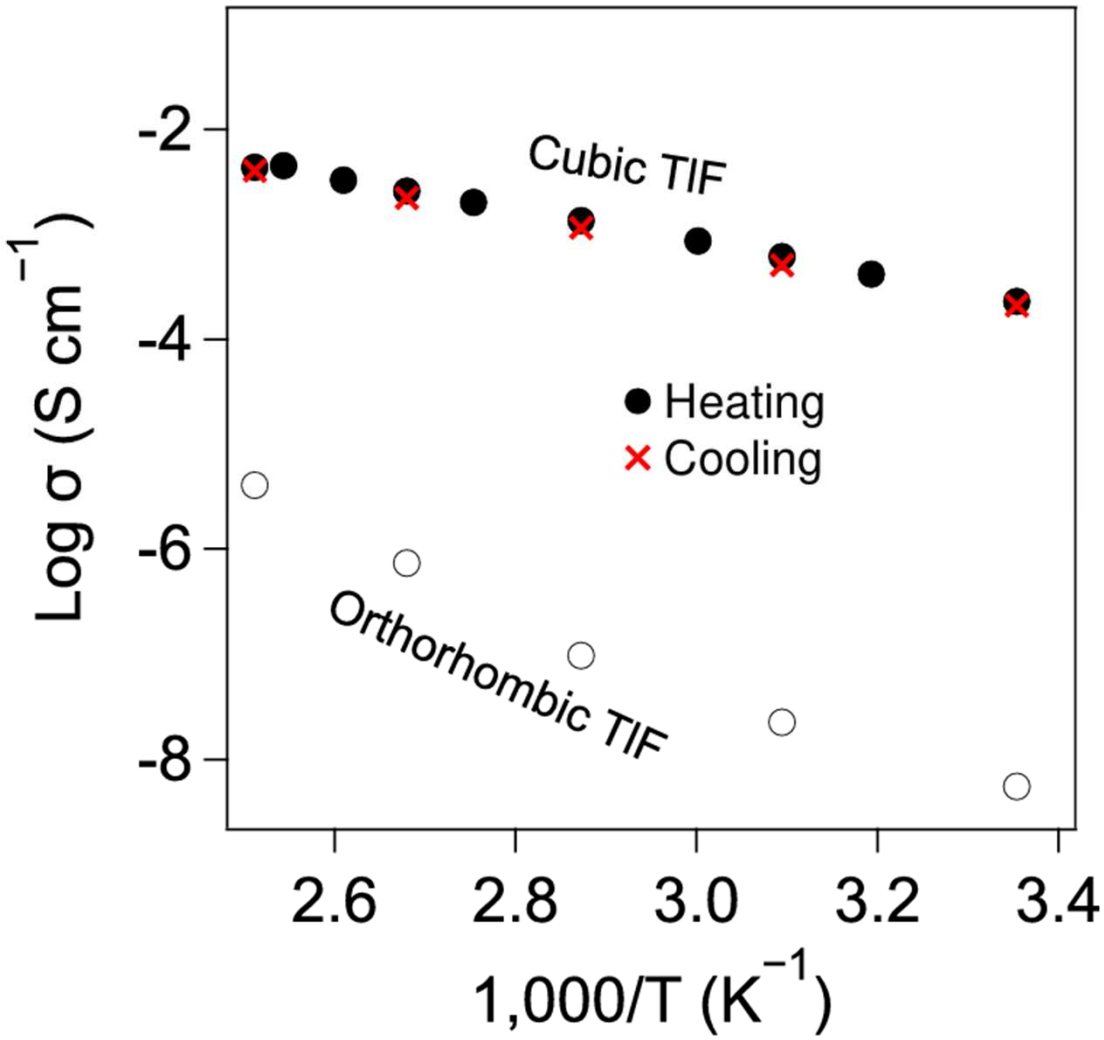

Figure S8. Fluoride-ion conductivity of cubic TlF upon heating and cooling, and orthorhombic TlF upon heating.

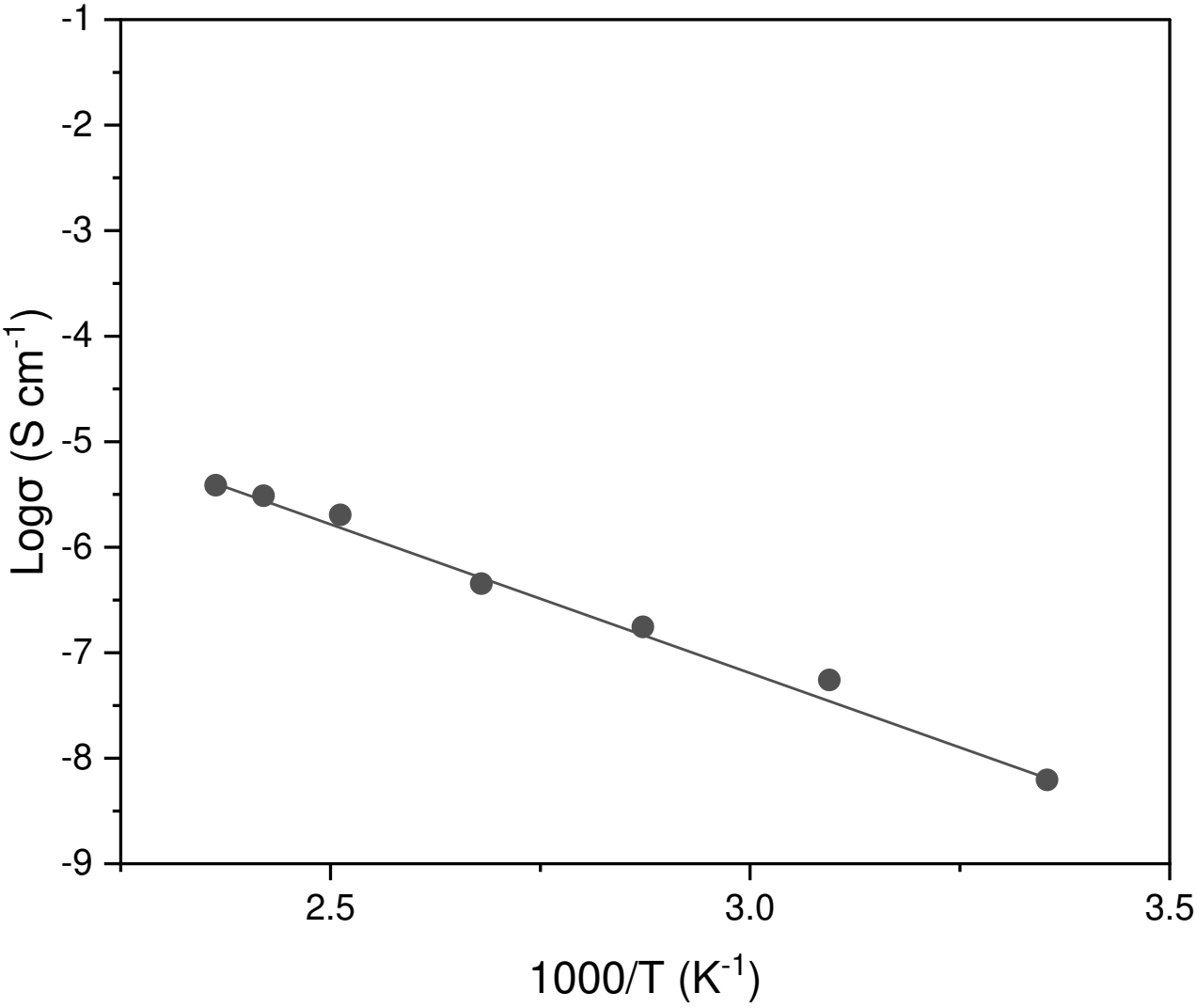

Figure S9. Arrhenius plot of the electronic conductivity for cubic TlF.

Figure S10. Photograph of the cubic TlF powder after the chemical fluorination using XeF_2.

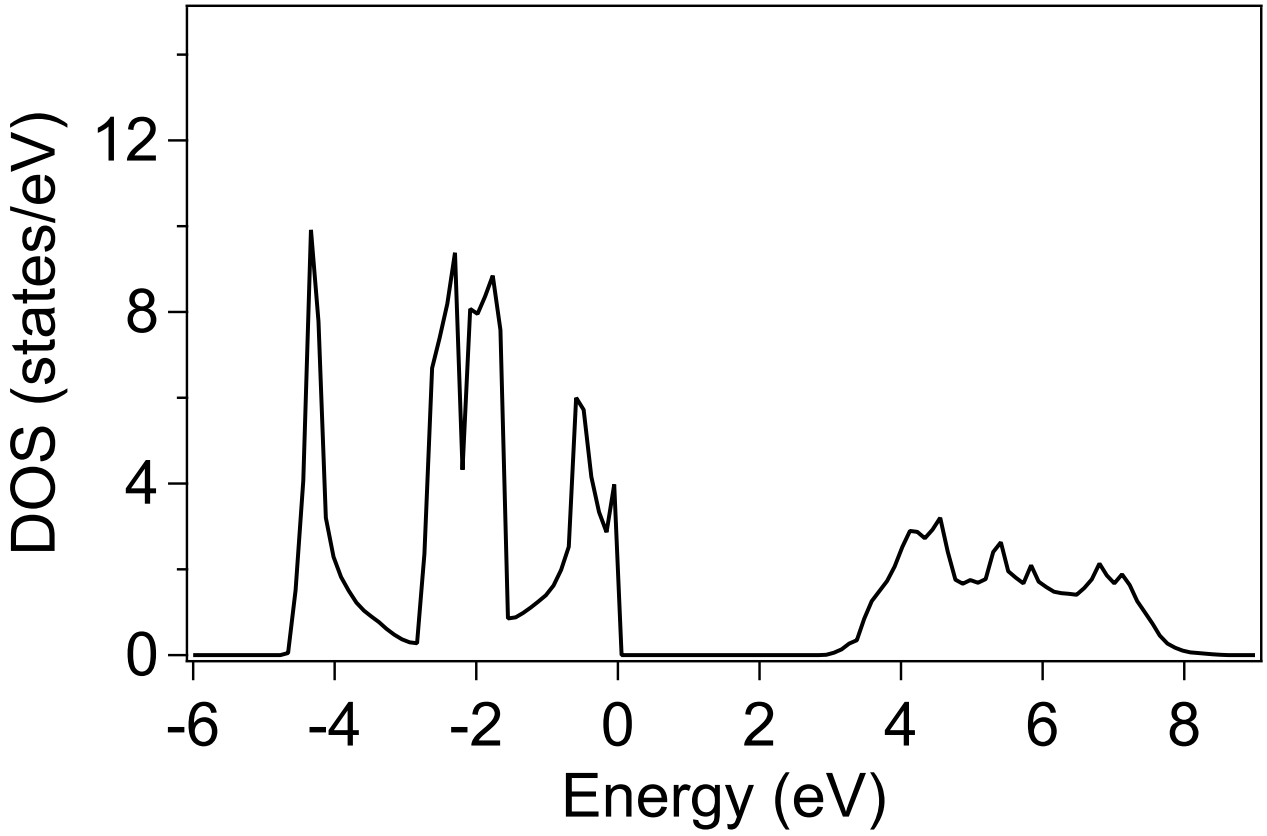

Figure S11. Electronic density of states of cubic TlF. The Fermi level corresponds to 0 eV.

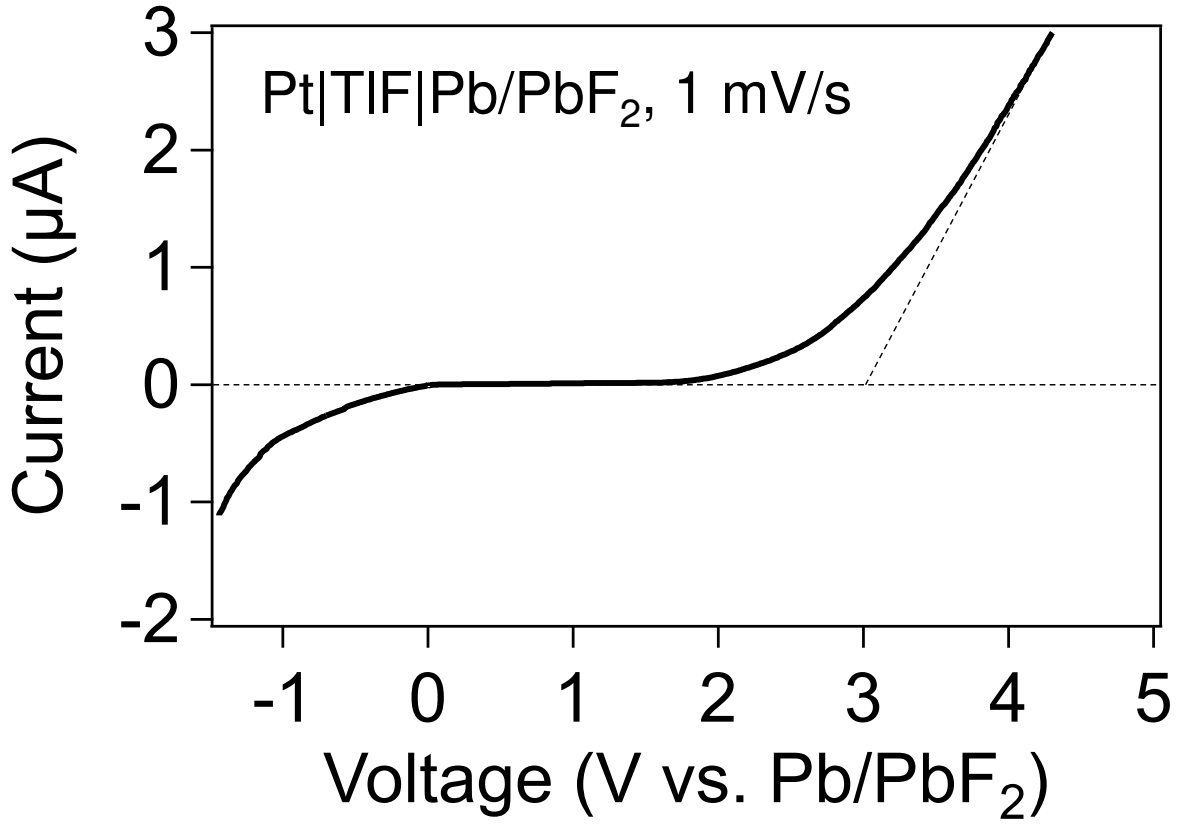

Figure S12. Electrochemical stability window of cubic TlF. The estimated stability limit is approximately 3.0 V at room temperature.

Table S1. Refined crystal parameters, space group, lattice parameters, reliability factors and agreement factor for cubic TlF at room temperature. *g*, occupancy; *B*, atomic displacement parameter. Here, the reliability factors R_{WP} and R_I are the weighted profile and integrated intensities, respectively.

Atom	Site	*g*	*x*	*y*	*z*	*B* (Å^2)
Tl	2*a*	1	0	0	0	0.322
F	12*d*	0.167(1)	1/4	0	1/2	5.195

Unit cell: Cubic $Im\bar{3}m$,
$a = b = c = 4.6024(3)$ Å,
$R_{WP} = 5.75\%$, $R_I = 3.94\%$, $S = 1.46$.

References

[1] X. He, Y. Zhu, Y. Mo. *Nat. Commun.* 2017, **8**, 15893.