Supplementary Information

Table S1. Anisotropic displacement parameters (Å^2) for HP-$Na_2Co[PO_4]F$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11}+...+2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na1	0.0191(15)	0.0191(15)	0.021(3)	0.0096(8)	0	0
Na2	0.0230(15)	0.0206(15)	0.0150(15)	0.0125(13)	0	0
Na3	0.0169(11)	0.0169(11)	0.0202(20)	0.0084(5)	0	0
Co	0.0123(5)	0.0102(5)	0.0086(4)	0.0065(4)	0.0007(3)	0.0001(3)
P	0.0079(8)	0.0096(8)	0.0082(8)	0.0036(7)	0	0
O1	0.007(2)	0.017(2)	0.015(3)	0.0042(18)	0	0
O2	0.0139(16)	0.0133(16)	0.0097(16)	0.0044(13)	0.0005(13)	0.0004(13)
O3	0.018(2)	0.018(3)	0.022(3)	0.012(2)	0	0
F	0.0113(18)	0.015(2)	0.0095(19)	0.0045(15)	0	0

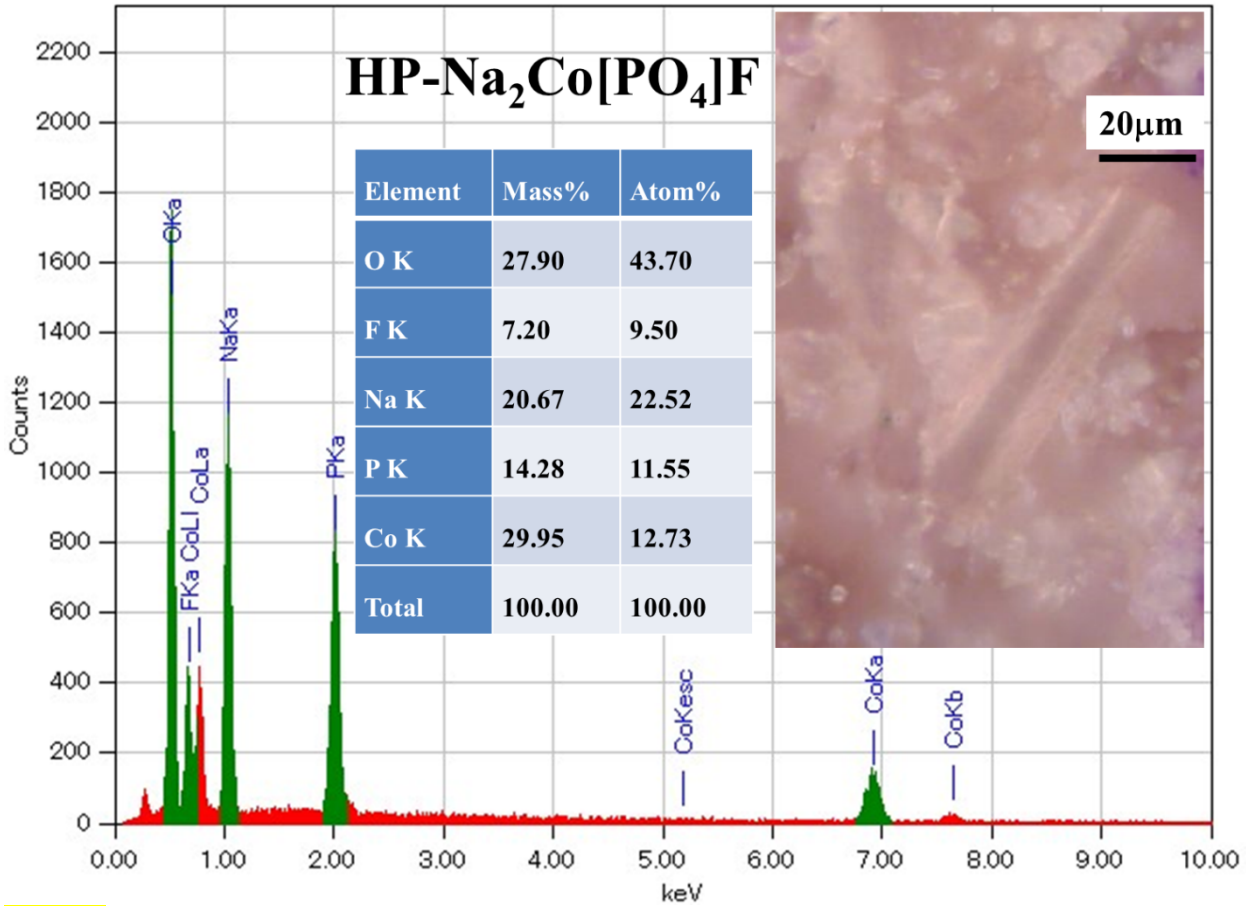


Fig. S1. Image and EDX analyses of the HP-$Na_2Co[PO_4]F$ single crystal used for the data collection.

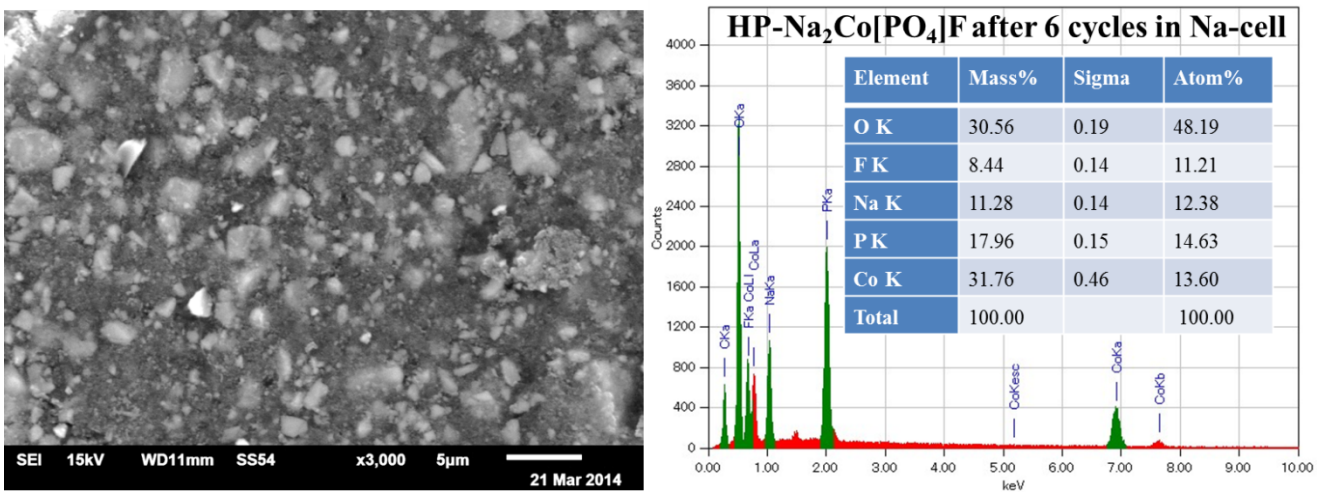


Fig. S2. Image and EDX analyses of the HP-$Na_2Co[PO_4]F$ phase (embedded in PTFE) after six cycles in Na-cell.

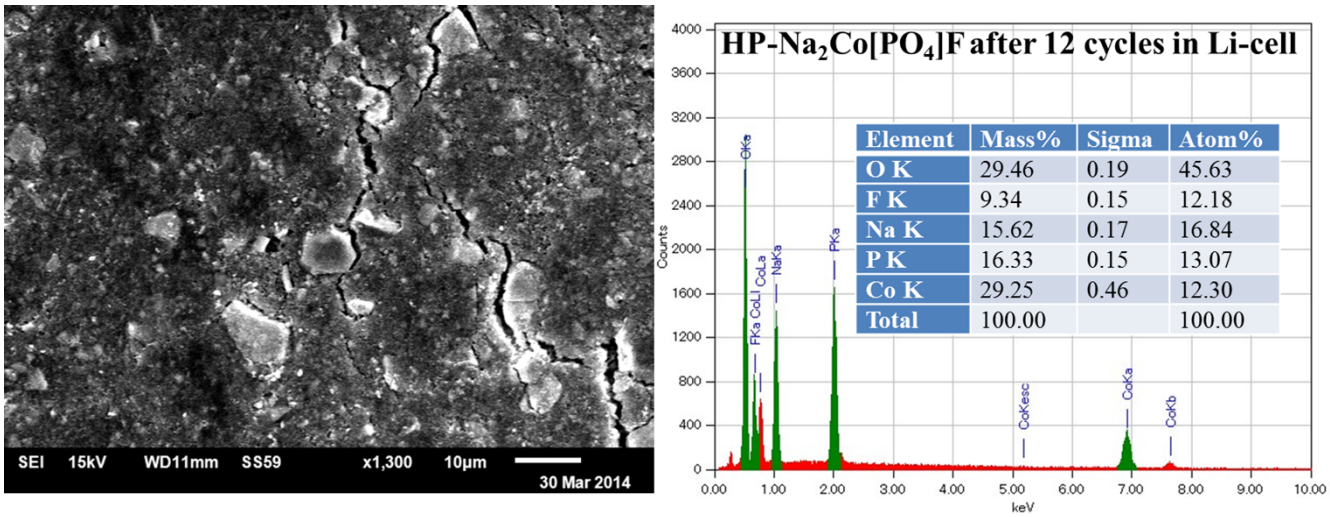
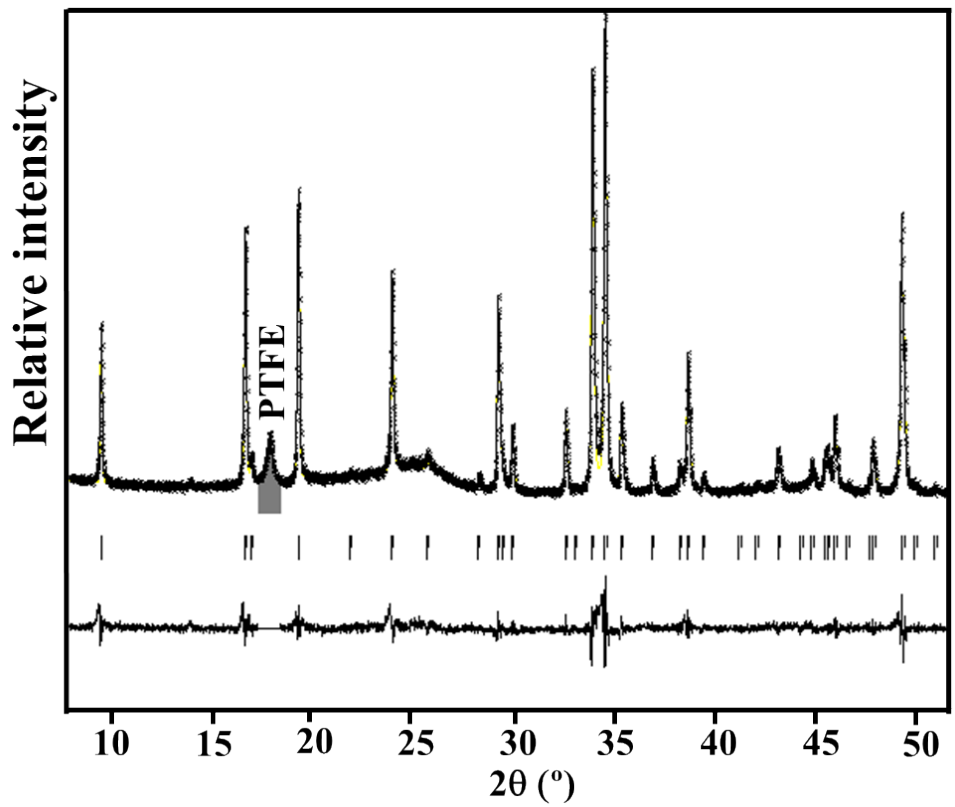


Fig. S3. Image and EDX analyses of the HP-$Na_2Co[PO_4]F$ phase (embedded in PTFE) after twelve cycles in Li-cell.



5 Fig. S4. Final observed, calculated and difference plots for powder XRD (Cu*Kα*) refinement of HP-$Na_2Co[PO_4]F$ after twelve cycles in Li-cell. The identified impurity corresponds to (PTFE).

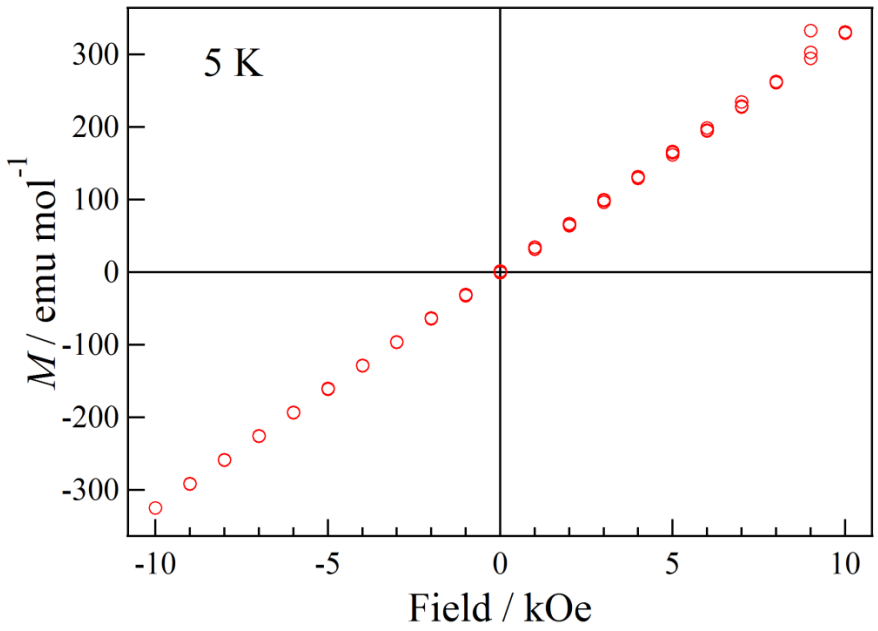


Fig. S5. Magnetization curve of HP-$Na_2Co[PO_4]F$ at 5 K.

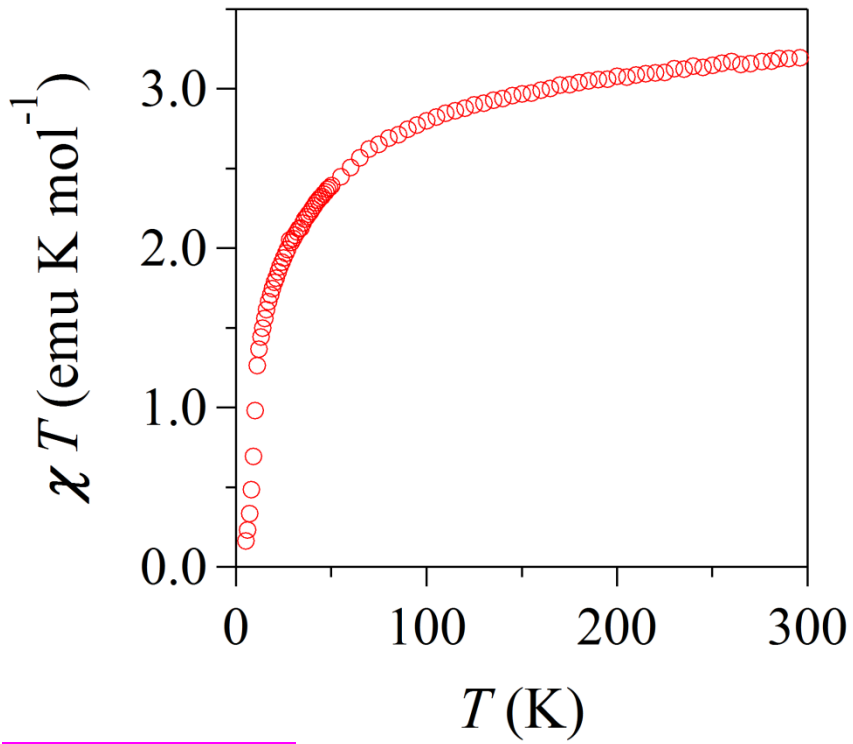


Fig. S6. χT vs T curve.