Supporting Information: A New Disordering Mode for $TFSI^-$ Anions - The Nonequilibrium, Plastic Crystalline Structure of Et_4NTFSI

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Salt Preparation: Et_4NTFSI was prepared using a metathesis reaction by mixing Et_4NCl and LiTFSI in deionized water. The resulting white Et_4NTFSI salt was washed several times by melting and recrystallizing in deionized water.

Single Crystal Preparation: Single crystals of the salt were obtained from these recrystallization steps. A crystal (approximate dimensions 0.45 x 0.30 x 0.12 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer.[1]

XRD Structural Analysis: The structure has Z' = 4 with both twinning and disorder issues. Half of the anions and cations are disordered. The bond distance and anisotropic displacement restraints, and constraints for the latter, were applied where deemed appropriate, respectively. 1859 restraints were applied altogether involving only disordered species; no paradigm non-disordered species were used as templates. C37/F13/F14/F15 were not modeled as disordered species as suggested by SHELXTL since this motion was considered a less severe translational displacement. The specimen was found to be a non-merohedral twin with the program Cell_Now.[2] 131 reflections were indexed exclusively to two twin components in the triclinic crystal system with the twin law by rows [1 –0.143 –0.084 / 0-1 0 / 0 0 –1], which is a 180º rotation about [100] in reciprocal space. Final cell constants were calculated from 2425 strong reflections from the actual data collection after integration (SAINT).[3] The intensity data were corrected for absorption and decay (TWINABS).[4] Redundant reflections were removed from the HKLF 5 data with Strip_Redundant V1.3.[5] The structure was solved using Bruker SHELXTL[16] and refined using Bruker SHELXTL.[6] The space group P_1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The

structures were drawn using Ortep-3. Crystal data: formula $C_{10}H_{20}F_6N_2O_4S_2$, M = 410.40, triclinic, a = 13.467(2), b = 16.968(3), c = 17.082(3) Å, α = 65.669(3), β = 84.842(3), γ = 83.572(3)°, V = 3530.0(11) Å^3, T = 100(2) K, space group P_1, Z = 8, μ(Mo-Kα) = 0.378 mm^{-1}, R_1 = 0.0621, wR_2 = 0.1606 [$I > 2\sigma(I)$].

References

(1) SMART V5.054, Bruker Analytical X-ray Systems, Madison, WI, 2001.
(2) Cell_Now, G. Sheldrick, 2003.
(3) SAINT+ V6.45, Bruker Analytical X-Ray Systems, Madison, WI, 2003.
(4) An empirical correction for absorption anisotropy, Blessing, R. *Acta Crystallogr. Sect. A* **1995**, *51*, 33.
(5) Strip_Redundant V1.3, Brennessel, W.; Young, Jr., V. G. 2003.
(6) SHELXTL V6.14, Bruker Analytical X-Ray Systems, Madison, WI, 2000.