Supplementary Information

Spatial confinement — Rapid 2D $F^{\scriptscriptstyle -}$ diffusion in micro- and nanocrystalline $RbSn_2F_5$

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In Fig. S1 scanning electron microscopy images of $RbSn_2F_5$ are shown which were recorded after different annealing steps of the fluoride in Ar atmosphere. At elevated annealing temperatures we clearly see that the sample decompose. Metallic spots (needles) seen in light microscopy indicate Sn^0 . SEM reveals that microcrystalline $RbSn_2F_5$ is composed of small particles and rectangular tubes (or needles). Some of the tubes reach lengths in the order of 20 μ m.



Fig. S1 a) RbSnF₅ annealed at 265 °C. left: image obtained via light microscopy (Olympus BX60) under 20 fold magnification; right: SEM picture (VEGA3 TESCAN electron microscope, 20 kV) under 2500 fold magnification. b) RbSnF₅ annealed at 225 °C. left: image obtained via light microscopy under 20 fold magnification; right: SEM picture under 2000 fold magnification. Annealing at 200 °C does not reveal any spots of metallic Sn.

In Fig. S2 the electrical permittivity spectra of microcrystalline $RbSn_2F_5$ are shown. They also reveal a two-step behaviour that mirrors electrical responses due to bulk and g.b. regions.



Fig. S2 Permittivity spectra of RbSn₂F₅ annealed at 473 K. The solid lines are to guide the eye; they help identify the bulk and g.b. responses (as indicated). Temperatures varied from 173 K to 473 K (in steps of 20 K).