

Electronic supplementary information:

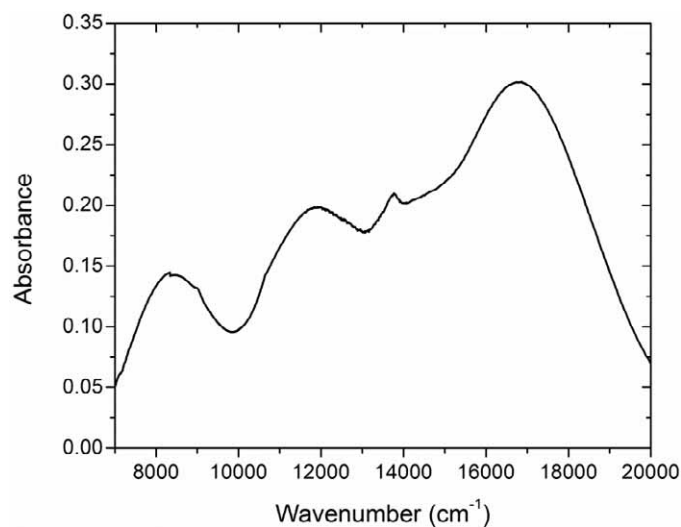


Figure S1. Solid state UV-Vis spectrum of β -[Ni(HF₂)(pyz)₂]PF₆ obtained at 295 K.

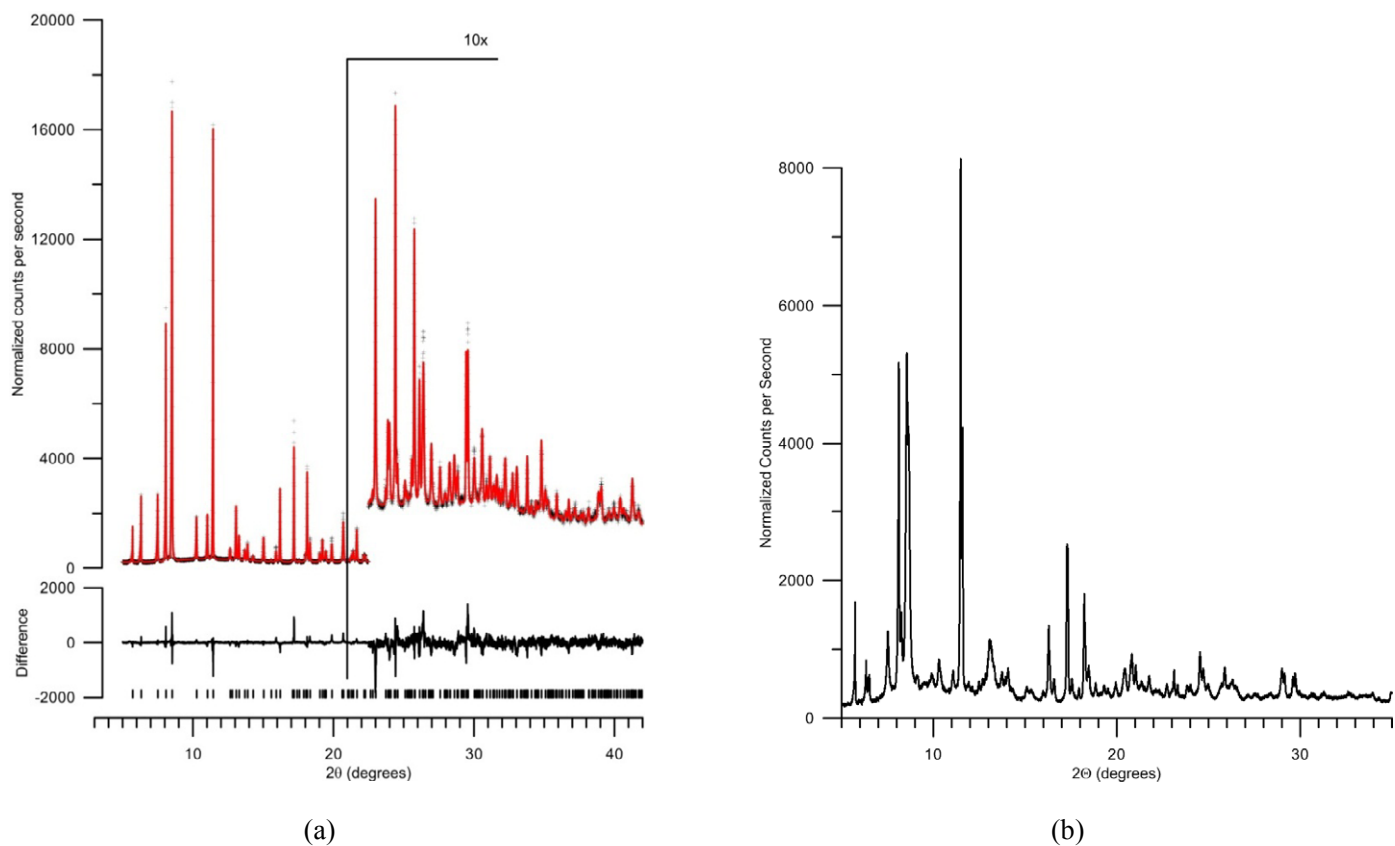


Figure S2. (a) Room temperature synchrotron X-ray powder diffraction data (+), Rietveld refinement (red) and difference curve (bottom) for β -[Ni(HF₂)(pyz)₂]PF₆. (b) For comparison, the powder pattern of the same material at 80 K.

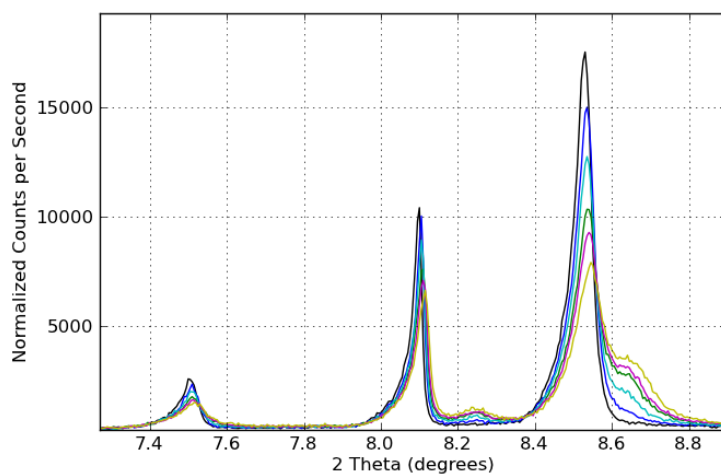


Figure S3. X-ray powder diffraction patterns obtained at different temperatures: 295K (Black), 245 K (Blue), 215K (Green), 180K (Cyan), 140K (Magenta), 90K (Yellow). The sample reverted back to the 295K pattern upon warming.

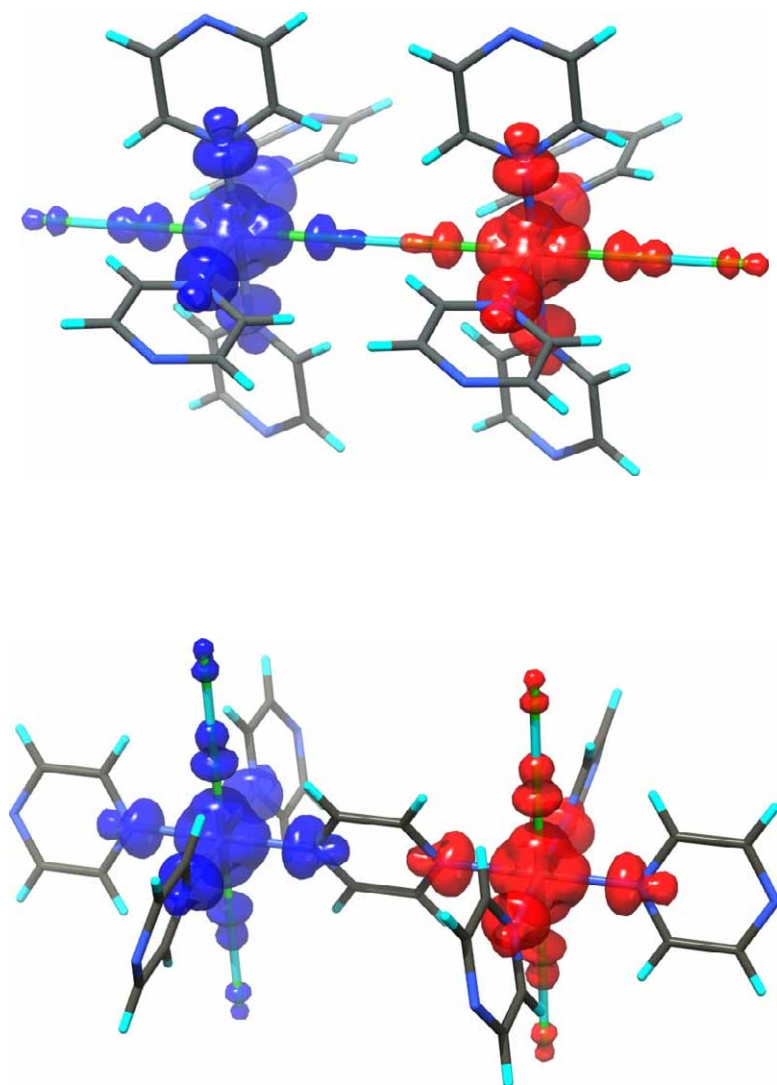


Figure S4. Spin densities for the broken-symmetry (BS) states of {Ni-FHF-Ni} (top) and {Ni-pyz-Ni} (bottom) fragments. The isosurface value is ± 0.002 for both plots. The two-fold symmetry of the former fragment prevents any spin density on the central hydrogen of the bifluoride bridge in the BS-state.