crystals

Supplementary Materials: Packing of Helices: Is Chirality the Highest Crystallographic Symmetry?

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Experimental Details

Synthesis. Hydrofluoric acid is toxic and corrosive! It must be handled with extreme caution and the appropriate protective gear [1–3].

The compounds were synthesized by hydrothermal method with similar amount of starting materials. A mixture of M_2O_5 (M = Nb^{5+} or Ta^{5+}) (0.75 mmol, Aldrich 99.99%), ZnO (1.67 mmol, Alpha Aesar 99.99%), 2,2′-bipyridine (2.56 mmol, Aldrich 99%), deionized water (5.5 mmol) and 48% aqueous HF (27.8 mmol, Aldrich) was placed in a Teflon pouch.[4] The pouches were placed into a 125 mL Parr autoclave with a backfill of 45 mL distilled water. The autoclave was heated to 150°C for 24 h and slowly cooled to room temperature at 6 °C/h. Single-crystals were recovered by vacuum filtration.

X-Ray diffraction. Single crystal diffraction experiments were conducted at 100K using a Bruker-APEX II CCD diffractometer with monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal-to-detector distance was 60 mm and data integrations were made using SAINT-PLUS program [5]. Absorption corrections have been processed using SADABS [6]. The structures were determined by means of direct methods and completed by Fourier difference syntheses using SIR97 [7] and then refined using SHELXL-97 [8]. Additional symmetry elements were checked using the program PLATON [9]. Anisotropic displacement parameters were refined using SHELXL-97. Hydrogen atoms of 2,2′-bipyridine molecules were constrained to ride at distances of 0.93 Å from the associated C atoms with $U_{iso}(H) = 1.5U_{eq}(C)$. Crystallographic data are reported in Table S1. A twinning which was identified to not be racemic was considered with the twin law **R** = (-1-10, 010, 00-1). The two materials $(Zn(2,2'\text{-bipy})_3](NbF_6)_2$ and $Zn(2,2'\text{-bipy})_3](TaF_6)_2$ are isostructural and each of them crystallize into two enantiomers: $P3_1$ and $P3_2$.

In compounds **I-II**, the helices do not exhibit any perpendicular 2-axis and are, consequently, polar (Additional symmetry elements of helices were checked with the program PLATON). The two polar structures result from the alignment of the polar helices along the *c* axis. The polarity in the structures can be visualized by the alignment of net dipole moment induced by the slight distortion of $[MF_6]^-$ octahedra (Figure S1).

Table S1. Crystal data and summary of data collections, structure solutions and refinements for compounds $[Zn(2,2'\text{-bpy})_3]$ $(NbF_6)_2$ (space-group $P3_1$) (I) and $[Zn(2,2'\text{-bpy})_3](TaF_6)_2$ (space-group $P3_1$) (II).

	$[Zn(2,2'\text{-bpy})_3](NbF_6)_2$	**$[Zn(2,2'\text{-bpy})_3](TaF_6)_2$**
Space group	$P3_1$	$P3_1$
a (Å)	10.4782(4)	10.4872(3)
c (Å)	26.5334(10)	26.5498(8)
V (Å^3)	2522.88(17)	2528.78(13)
T (°K)	100	100
Z	3	3
Maximum θ	36.4°	30.8°
λMo Kα (Å)	0.71073	0.71073
$\varrho P_{calc.}$ (g.cm^{-3})	1.871	2.214
Rint	0.019	0.032
R_1	0.022	0.034
wR_2	0.053	0.048
Goodness-of-fit	1.04	1.02
Flack parameter	0.020(8)	0.054(8)

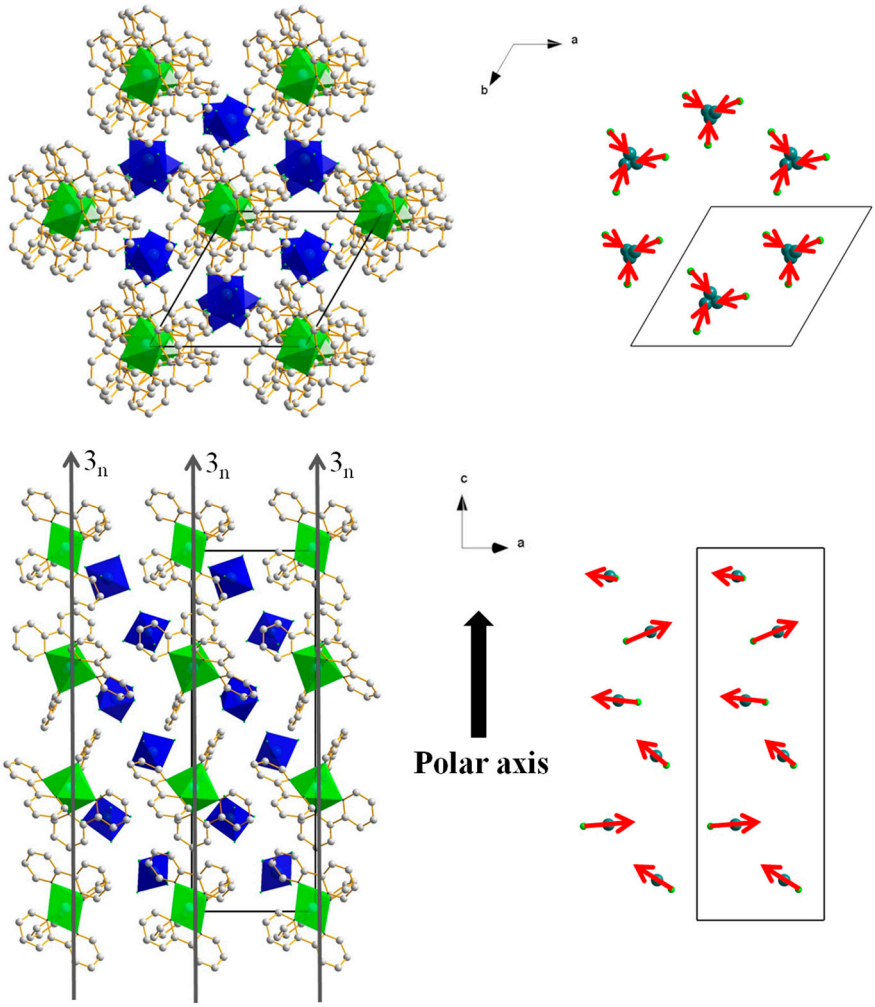

Figure S1. View along *c* and *b* of the structure with the relative orientation of the distortion represented by the shortest Nb-F bond. Along *a* and *b* axes, the individual dipole moments are canceled by the 3_n screw axis along *c*. The alignment of the individual polarizations is collinear to the polar axis of the structure.

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