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From Solution to the Solid State: Control of Niobium Oxide−Fluoride $[NbO_xF_y]^{n-}$ Species

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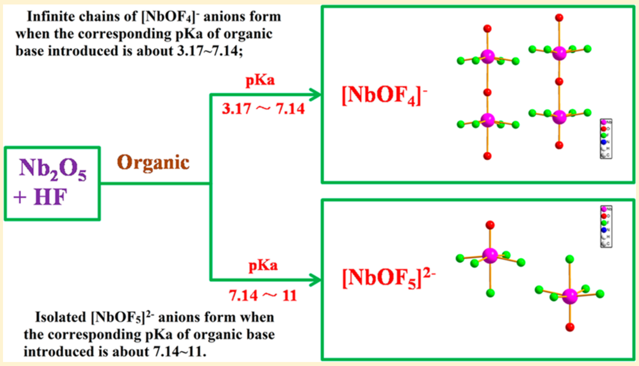
Supporting Information

ABSTRACT: In this study, we describe the crystallization of specific niobium oxide−fluoride anions (either $[NbOF_4]^-$ or $[NbOF_5]^{2-}$) by increasing the fluoride concentration with the appropriate use of organic bases with varied corresponding pK_a values to create suitable equilibria for the formation of each anion. $HpyNbOF_4$ (**I**; py = pyridine) contains the $[NbOF_4]^-$ anion, while $[H_2(4,4'\text{-bpy})]NbOF_5$ (**II**; 4,4′-bpy = 4,4′-bipyridyl) contains the $[NbOF_5]^{2-}$ anion; their identity is correlated with reagent ratios. The increase of basic species (proton acceptors) results in an increase in the fluoride concentration and high fluoride-containing anions. The crystallization of $[NbOF_4]^-$ in $[NbO_{2/2}F_4]_\infty$ chains in **I** was controlled with the use of weak base pyridine (pK_a = 5.23), while isolated $[NbOF_5]^{2-}$ crystallized in **II** with strong base 4,4′-bipyridyl (pK_a = 10.5). This approach can be broadly applied to target-specific basic building units for fundamentally new and potentially functional solid-state materials.



INTRODUCTION

Early-transition-metal oxide−fluorides have been extensively investigated as basic building units (BBUs) to target remarkable properties and applications, such as piezoelectricity, ferroelectricity, nonlinear optical activity, and battery materials.[1−6] For niobium oxide−fluorides, the $[NbOF_4]^-$, $[NbOF_5]^{2-}$, and $[NbF_6]^-$ octahedral anions have been previously used as BBUs to make functional materials.[7−14] Early transition metals of d^0 electronic configurations (such as Nb^{5+}) are prone to undergoing second-order Jahn−Teller distortions; these distortions are responsible for the high efficiency of $LiNbO_3$ as a piezoelectric and a second-harmonic-generation (SHG)-active material.[15,16] These BBUs can crystallize as (i) 0D frameworks with isolated $[NbOF_5]^{2-}$[7,17] or $[NbF_6]^-$[18,19] octahedra, (ii) 1D frameworks with chains of $[NbO_{2/2}F_4]^-$ octahedra,[7,20] (iii) 2D frameworks with layers of $NbOF_3$,[21] or (iv) 3D frameworks such as NbO_2F.[22] Each type of BBU can be implemented in different functional materials, where the specific identity of the $[NbO_xF_y]^{n-}$ BBU is integral to target-specific applications.

In solution at room temperature, the equilibria of niobium oxide−fluoride species have been previously identified under different aqueous conditions by NMR, Raman, or IR spectroscopy.[23−26] The corresponding methods, however, to guide their crystallization have not been studied. In this study, we present two new structures: $HpyNbOF_4$ (**I**; py = pyridine) with $[NbO_{2/2}F_4]^-$ chains and $[H_2(4,4'\text{-bpy})]NbOF_5$ (**II**; 4,4′-bpy = 4,4′-bipyridyl) with isolated $[NbOF_5]^{2-}$, which demonstrate that the addition of bases in the presence of HF(aq) results in crystallization of the three main soluble niobium oxide−fluoride anionic species: $[NbOF_4]^-$, $[NbOF_5]^{2-}$, and $[NbF_6]^-$. They crystallize from solution successively with increasing corresponding pK_a of the organic amines. Each pK_a mentioned for introduced organic base in this study refers to the corresponding pK_a of the protonated organic acid.

EXPERIMENTAL SECTION

***Caution!** Hydrofluoric acid is toxic and corrosive! It must be handled with extreme caution and the appropriate protective gear.*[27−29]

Materials. Niobium oxide (Nb_2O_5; 99.9%, Alfa Aesar), pyridine (C_5H_5N; 99%, Aldrich), 4,4′-bipyridyl ($C_{10}H_8N_2$; 98%, Aldrich), and aqueous hydrofluoric acid (48% HF by weight, Aldrich) were used as received.

Synthesis. Single crystals of compounds **I** and **II** have been synthesized by hydrothermal methodologies. Colorless single crystals of **I** were synthesized by adding 0.400 g (1.51×10^{-3} mol) of Nb_2O_5, 0.1 mL (1.23×10^{-3} mol) of py, and 0.8 mL (2.21×10^{-2} mol) of 48% aqueous HF to a Teflon [fluoro(ethylenepropylene), FEP] pouch made as described previously;[30−32] brown single crystals of **II** were synthesized by adding 0.400 g (1.51×10^{-3} mol) of Nb_2O_5, 0.400 g (2.56×10^{-3} mol) of 4,4′-bpy, and 0.8 mL (2.21×10^{-2} mol) of 48%

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aqueous HF to a Teflon pouch. All reagents were sealed with an impulse sealer in Teflon pouches and placed into a 125 mL Parr autoclave with a backfill of 45 mL of deionized water. The autoclave was quickly heated to 200 °C, held at this temperature for 24 h, and cooled to ambient temperature at a rate of 0.1 °C/min. The single crystals were recovered in air after vacuum filtration. The yields of **I** and **II** were 18.9% and 52.4% (based on Nb_2O_5), respectively. The same phases were obtained with different reagent ratios in the syntheses of both compounds.

Crystallographic Determination. Single-crystal X-ray diffraction experiments were conducted at 100 K on a Bruker APEX II CCD diffractometer with monochromatic Mo Kα radiation (λ = 0.71069 Å). The crystal-to-detector distance was 60 mm, and data integrations were made using *SAINT*, version 7.23A.[33] Multiscan absorption corrections were applied with *SADABS*.[34] The structures were determined by direct methods, completed by Fourier difference syntheses with *SIR97*,[35] and refined using *SHELXL-97*.[36] No higher symmetry or unit cells were found by examination with *PLATON*.[37] Hydrogen atoms of organic molecules were included in the refinement model as riding atoms in idealized positions [C−H = 0.93 Å, N−H = 0.86 Å, and U_{iso}(H) = $1.5U_{eq}$(C,N)]. Crystallographic data are reported in Table 1.

Table 1. Crystal Data, Structure Solutions, and Refinements for Compounds I and II

	1	2
cryst syst	monoclinic	orthorhombic
space group	$P2_1/m$	*Pbcn*
a (Å)	3.9511(4)	11.9786(5)
b (Å)	14.0715(17)	6.7669(3)
c (Å)	7.0890(9)	14.1792(7)
α (deg)	90	90
β (deg)	93.464(5)	90
γ (deg)	90	90
V (Å^3)	393.41(8)	1150.20(8)
Z	2	4
T (K)	100(2)	100(2)
θ_{max} (deg)	30.0	25.1
λ(Mo Kα) (Å)	0.71069	0.71069
ρ_{calcd} (g/cm^3)	2.237	2.091
R1	0.049	0.020
wR2	0.075	0.052
GOF	0.97	1.02

Fourier Transform Infrared (FTIR) Spectroscopy. The FTIR spectra of both compounds were collected on a Bruker 37 Tensor FTIR instrument. A total of 64 scans were recorded at 4 cm^{-1} resolution and averaged from 400 to 4000 cm^{-1}, and a background spectrum was subtracted.

Thermogravimetric Analysis (TGA). The TGA measurements for both compounds were performed on a TGA Q50 analyzer with a standard furnace under an argon atmosphere with a heating rate of 1 °C/min from ambient temperature to 900 °C. The materials were held at this temperature for 12 h and then cooled to room temperature at a rate of 1 °C/min.

■ RESULT AND DISCUSSION

Structural Descriptions. Compounds **I** and **II** contain niobium oxide−fluoride anions and organic cations (Figures 1 and 2). Electrostatic interactions exist between protonated $[Hpy]^+$ cations and $[NbOF_4]^-$ anions in **I** and between protonated $[H_2(4,4'\text{-bpy})]^{2+}$ cations and $[NbOF_5]^{2-}$ anions in **II**. These hydrogen-bonding and electrostatic interactions influence the supramolecular network and stabilize the crystal structure of both compounds **I** and **II**.

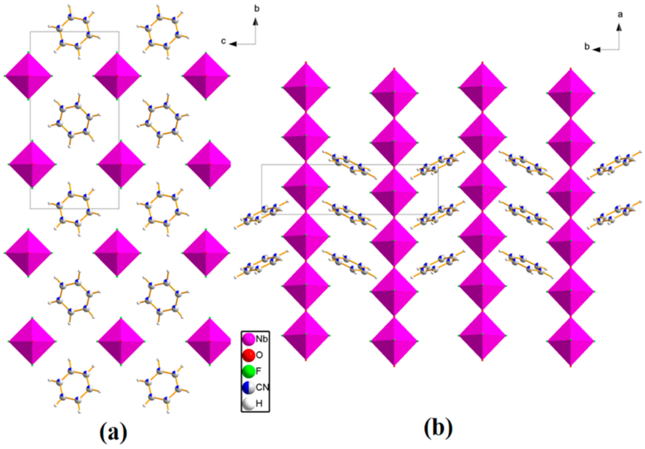

Figure 1. Perspective view of **I**: (a) along axis *a*; (b) along axis *c*.

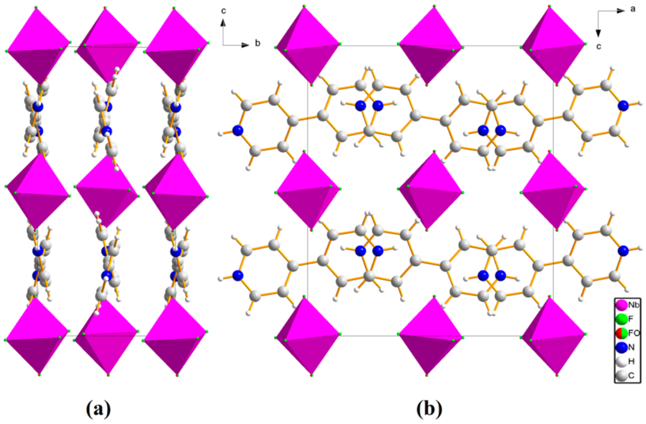

Figure 2. Perspective view of **II**: (a) along axis *a*; (b) along axis *b*.

$HpyNbOF_4$ (I). **I** crystallizes in the space group $P2_1/m$ and consists of infinite chains of $[NbOF_4]^-$ anions linked by oxygen sited in the shared-vertices position. The spaces between the chains are occupied by the $[Hpy]^+$ cations, as shown in Figure 1. The $[NbOF_4]^-$ anions form parallel infinite chains along the *a* axis through bridging oxygen anions. The anions as expected exhibit a strong second-order Jahn−Teller distortion.[38,39] Each distorted niobium octahedron is composed of four equatorial Nb−F bonds and two bridging O−Nb−O bonds: one long Nb−O bond and one short Nb−O bond. The equatorial Nb−F bond distances range from 1.898(4) to 1.902(3) Å; the short Nb═O and long Nb−O bonds are 1.729(4) and 2.222(4) Å in length, respectively (Table 2). These distances are in agreement with previously reported 1D chains of $[NbOF_4]^-$.[1,7,40] Individual chains align in an antiparallel configuration with neighboring chains. The planar $[Hpy]^+$ molecules lie on two

Table 2. Selected Bond Length R_i for I and II

I		II	
bond	R_i, Å	bond	R_i, Å
Nb1−O1	1.729(4)	Nb1−F3	1.923(1)
Nb1−F4	1.898(4)	Nb1−F3	1.923(1)
Nb1−F3	1.899(4)	Nb1−F2	1.924(1)
Nb1−F1	1.902(3)	Nb1−F2	1.924(1)
Nb1−F1	1.902(3)	Nb1−F1|O1	1.939(1)
Nb1−O1	2.222(4)	Nb1−F1|O1	1.939(1)

planes that are at an angle of 45.5° with each other. Nitrogen and carbon atoms are modeled to be equally disordered among the six positions within aromatic rings owing to no classic strong hydrogen bonding observed in **I**.[41]

[H_2(4,4′-bpy)]$NbOF_5$ (II). Anions of $[NbOF_5]^{2-}$ are isolated in a hydrogen-bond network created by $[H_2(4,4'\text{-bpy})]^{2+}$ cations in the space group *Pbcn* in **II** (see Figure 2). For these niobium-centered octahedra, the six Nb−F or Nb−F/O bond distances range from 1.923(1) to 1.939(1) Å (see Table 2). It is difficult to distinguish oxide anion from fluoride anion using X-ray diffraction, particularly for disordered species; the similar bond distances indicate that the O^{2-}/F^- anions may be disordered among the six frequent positions. However, owing to no observation of strong hydrogen-bonding interactions to the four equatorial ions, disorder over two orientations is more likely in the structure of **II**. F_2, F_2^i, F_3, and F_3^i are fully ordered fluorides, and *trans*-O_1/F_1 and *trans*-O_1^i/F_1^i are disordered oxide−fluoride sites. This disordered $[NbOF_5]^{2-}$ has been observed previously in the structures of $[C_{10}H_9N_3]_2[NbOF_5]\cdot 2H_2O$[7] and $[C_9H_8NO]_2[NbOF_5]\cdot H_2O$.[42]

FTIR. As mentioned, owing to their similar polarizability and ionic radii, it is difficult to definitively distinguish oxide and fluoride anions with X-ray crystallography.[43−45] To validate that the oxide−fluoride BBUs in **I** and **II** are $[NbOF_4]^-$ and $[NbOF_5]^{2-}$, respectively, we employed FTIR spectroscopy. The IR spectrum of **I** (Figure 3a) show two strong characteristic bands for $[NbOF_4]^-$ at ν_s(Nb−O−Nb) = 809 cm^{-1}[17,31,40,46] and ν_s(Nb−F) = 587 cm^{-1},[47−49] respectively. The remaining vibrations may be assigned to py (see Figure S1 in the SI). The vibration ν_s(Nb−O−Nb) at 809 cm^{-1} in the spectrum of **I** indicates that bridging niobium oxide bonds (Nb−O−Nb) exist in **I**, consistent with our crystallographic model. The IR spectrum of **II** (Figure 3b) shows two strong characteristic bands for $[NbOF_5]^{2-}$ at ν_s(Nb═O) = 876 cm^{-1}[17,50,51] and ν_s(Nb−F) = 548 cm^{-1},[47−49] respectively. The remaining vibrations may be assigned to 4,4′-bpy (see Figure S1b in the SI). The vibration ν_s(Nb═O) at 876 cm^{-1} in the spectrum of **II** indicates that terminal niobium oxide bonds (Nb═O) exist in **II**. The strong ν_s(Nb−O−Nb) or ν_s(Nb═O) peaks show that niobium oxide bonds are present in both structures, bridging niobium oxide bonds (Nb−O−Nb) in **I** and terminal niobium oxide bonds (Nb═O) in **II**.

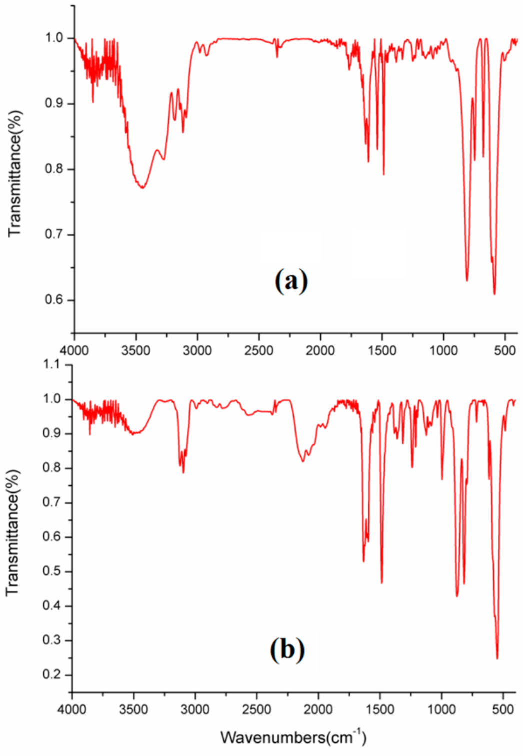

Figure 3. FTIR spectra of compounds (a) **I** and (b) **II**.

Thermal Analysis. To further verify the structures and contents of **I** and **II**, TGA was performed. The TGA curves of **I** and **II** showed weight losses of **I** (61.1%) and **II** (68.4%), which mainly corresponded to losses of their relevant organic molecules. The calculated loss of **I** (58.9%) and **II** (69.9%) corresponded to niobium monoxide (NbO; Figure 4). After cooling of **I** and **II** to room temperature from 900 °C and exposure to air, a white polycrystalline sample remained. For both **I** and **II**, the polycrystalline sample was identified as Nb_2O_5 by powder X-ray diffraction (JCPDS PDF no. 37-1468). The presence of Nb_2O_5 can be explained by oxidation of NbO in air at ambient conditions as previously reported.[7]

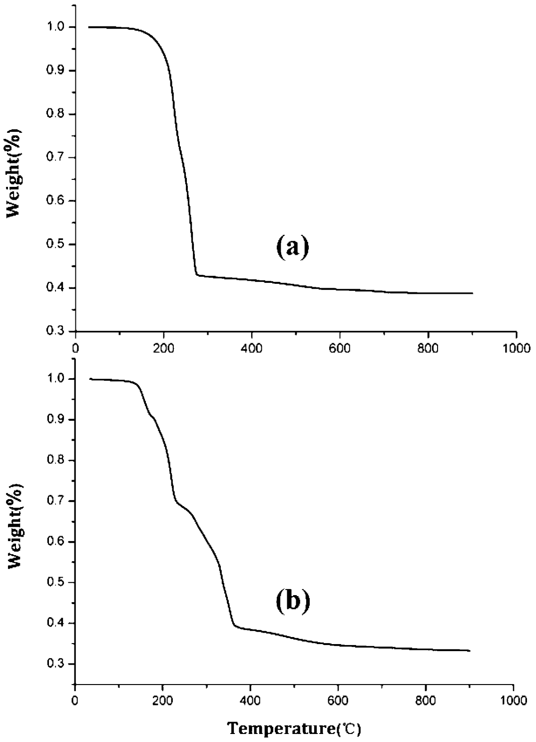

Figure 4. TGA measurements of compounds (a) **I** and (b) **II**.

Control of Niobium Oxide−Fluoride Anions $[NbOF_4]^-$ and $[NbOF_5]^{2-}$. We have previously demonstrated control of the niobium oxide−fluoride species in hydrothermal syntheses with hydrofluoric acid.[7] The two niobium oxide−fluoride species of $[NbOF_4]^-$ and $[NbOF_5]^{2-}$ can be isolated in solid-state structures by adjusting the *amount* of a neutral reagent organic molecule, 2,2′-dipyridylamine (dpa; pK_a = 7.14),[7,52] While in this study, infinite chains of $[NbOF_4]^-$ anions or isolated $[NbOF_5]^{2-}$ anions are obtained with modulation of the basicity of the organic reagent. Compound **I** is formed with chains of $[NbOF_4]^-$ when py with a corresponding pK_a of 5.23[53] is introduced to an aqueous hydrofluoric solution with niobium oxide. In contrast, compound **II** is formed with

Table 3. List of Niobium Anions with Different pK_a Values of Organic Ligands in Various Niobium Oxide–Fluoride Hybrid Structures

organics	pK_a	$[NbO_xF_y]^{n-}$	hybrid compounds
tetraethylammonium	11[61]	$[NbF_6]^-$	$[(C_2H_5)_4N]NbF_6$[62]
4,4′-dipyridyl	10.5[54]	$[NbOF_5]^{2-}$	$[H_2(4,4'\text{-bpy})]NbOF_5$
β-alanine	10.19[66]	$[NbOF_5]^{2-}$	$(C_3H_8NO_2)_2[NbOF_5]\cdot 2H_2O$[65]
8-hydroxyquinoline	9.89[68]	$[NbOF_5]^{2-}$	$(C_9H_8NO)_2[NbOF_5]\cdot 2H_2O$[42]
piperazine	9.82[59]	$[NbOF_5]^{2-}$	$[H_2N(C_2H_4)_2NH_2][NbOF_5]$[17]
DL-valine	9.62[66]	$[NbOF_5]^{2-}$	$(C_5H_{12}NO_2)_2NbOF_5$[67]
glycine	7.4[64]	$[NbOF_5]^{2-}$	$(C_2H_6NO_2)_2[NbOF_5]$[65]
2,2′-dipyridylamine (more)	7.14[52]	$[NbOF_5]^{2-}$	$[Hdpa]_2NbOF_5$[7]
2,2′-dipyridylamine (less)	7.14[52]	$[NbOF_4]^-$	$HdpaNbOF_4$[7]
pyridine	5.23[53]	$[NbOF_4]^-$	$HpyNbOF_4$
1,10-phenanthroline	4.27[53]	$[NbOF_4]^-$	$[Hphen][NbOF_4]\cdot H_2O$[20]

isolated $[NbOF_5]^{2-}$ anions when 4,4′-bpy with a corresponding pK_a of 10.5[54] is introduced. No other solid-state niobium oxide–fluoride species could be observed with other molar ratios of the reactants Nb_2O_5, py/4,4′-bpy, and HF(aq).

Varied equilibria exist in the aqueous hydrofluoric solution with niobium species.[25,55] In a HF(aq) solution at room temperature, various species have been identified by NMR, Raman, and IR analysis as a function of the F/Nb mole ratio and/or fluoride ligand F^- concentration.[23−25] Il'in et al.[23,26] reported that *trans*-$[NbOF_4\cdot H_2O]^-$ is observed in situ at a molar ratio of F/Nb ≤ 5 and $[NbOF_5]^{2-}$ is observed following basic hydrolysis by further increasing the alkalinity. Kasamatsu et al. reported that $[NbOF_4]^-$ is present at $[F^-] = 2.0 \times 10^{-4}$ and 3.0×10^{-3} M; $[NbOF_5]^{2-}$ is the dominant species at $[F^-] = 8.9 \times 10^{-3}$–$1.9 \times 10^{-2}$ M.[24] Monroy-Guzman et al. also reported that $[NbOF_5]^{2-}$ exists in the solution with [HF] < 11 M and $[NbF_6]^-$ and $[NbF_7]^{2-}$ are observed when [HF] > 11 M.[25] Throughout these concentrations ranges, $[NbOF_5]^{2-}$ is stable and will coexist with the other niobium species.[7,24] Thus, $[NbOF_4\cdot H_2O]^-$, $[NbOF_5]^{2-}$, and $[NbF_6]^-$ successively form by increasing the fluoride concentration in a HF(aq) solution, as expressed by the reactions (1)–(5):[56−58]

$$Nb_2O_5 + 2HF(aq) \rightleftharpoons 2NbO_2F + H_2O \tag{1}$$

$$NbO_2F + 2H^+ + 3F^- \rightleftharpoons [NbOF_4\cdot H_2O]^- \tag{2}$$

$$[NbOF_4]^- + F^- \rightleftharpoons [NbOF_5]^{2-} \tag{3}$$

$$[NbOF_5]^{2-} + 2H^+ + F^- \rightleftharpoons [NbF_6]^- + H_2O \tag{4}$$

$$[NbF_6]^- + F^- \rightleftharpoons [NbF_7]^{2-} \tag{5}$$

Hydrofluoric acid, a moderately weak acid with pK_a of 3.17,[59] exists in the presence of HF, F^-, and HF_2^- species in solution according to the chemical equilibriums (6) and (7).[24,60] After being introduced into a HF(aq) solution, organic bases (py, dpa, 4,4′-bpy, etc.) with higher corresponding pK_a values than that of hydrofluoric acid are protonated according to reaction (8) (L = organic ligand). This protonation of organic bases contributes to dissociation of hydrofluoric acid and increases the fluoride concentration in solution. Organic bases with higher corresponding pK_a values, or stronger basicities, are more readily protonated by hydrofluoric acid. This increases the fluoride concentration in the solution, whereas weak bases less readily are protonated by hydrofluoric acid, and the resulting fluoride concentration is decreased. Thus, when py (pK_a = 5.23) is introduced into a solution, infinite chains of $[NbOF_4]^-$ anions will crystallize in **I** owing to weakly basic solutions (*low* fluoride concentration), while when 4,4′-bpy (pK_a = 10.5) is introduced into a solution, isolated $[NbOF_5]^{2-}$ anions crystallize in **II** owing to strong basic solutions (*high* fluoride concentration).[7] The $[NbF_6]^-$ anion was reported to crystallize with tetraethylammonium (pK_a = 11[61]) in the structure of $[(C_2H_5)_4N]NbF_6$.[62] When an organic base is introduced with a corresponding pK_a lower than the pK_a of hydrofluoric acid (pK_a = 3.17) such as pyrazine and quinoxaline in our experiments, no crystals were obtained, probably because the weak acid HF does not protonate the very weak organic bases. The effect of the temperature can be neglected because the pK_a of organic acids had been reported to decrease only slightly with increasing temperature.[63]

$$HF \rightleftharpoons H^+ + F^- \tag{6}$$

$$HF + F^- \rightleftharpoons HF_2^- \tag{7}$$

$$L + H^+ \rightleftharpoons HL^+ \tag{8}$$

These results are in agreement with the previously reported niobium oxide–fluoride structures with organic cations; see Table 3. Infinite chains of $[NbOF_4]^-$ anions were formed with 1,10-phenanthroline (Phen; pK_a = 4.27[53]) in the crystal structure of $[Hphen][NbOF_4]\cdot H_2O$;[20] isolated $[NbOF_5]^{2-}$ anions are formed with (i) glycine (pK_a = 7.4[64]) in $(C_2H_6NO_2)_2$ $[NbOF_5]$,[65] (ii) DL-valine (pK_a = 9.62[66]) in $(C_5H_{12}NO_2)_2NbOF_5$,[67] (iii) piperazine (pK_a = 9.82[59]) in $[H_2N(C_2H_4)_2NH_2]NbOF_5$,[17] (iv) 8-hydroxyquinoline (pK_a = 9.89[68]) in $(C_9H_8NO)_2[NbOF_5]\cdot 2H_2O$,[42] and (v) β-alanine (pK_a = 10.19[66]) in $(C_3H_8NO_2)_2$ $[NbOF_5]\cdot 2H_2O$.[65] We also note that the isolated $[NbOF_4\cdot H_2O]^-$ anion has been reported with triethylamine (Net$_3$; pK_a = 10.75[69]) in $[HNet_3][NbOF_4\cdot H_2O]$.[70] To the best of our knowledge, all $[NbOF_4]^-$ anions in the solid state form infinite chains except for $[HNet_3][NbOF_4\cdot H_2O]$. Because a detailed synthesis was not given, the formation of the unusual isolated $[NbOF_4\cdot H_2O]^-$ anion in $[HNet_3][NbOF_4\cdot H_2O]$ warrants further investigation.

■ CONCLUSION

In this study, two niobium oxide–fluoride species in solid-state structures were formed by adjusting the acidity of the solution. The use of organic bases with varied corresponding pK_a values allow tunability of the fluoride concentration, which, in turn, results in the crystallization of specific $[NbO_xF_y]^{n-}$ species. According to this study and previous reports, the $[NbOF_4]^-$, $[NbOF_5]^{2-}$, and $[NbF_6]^-$ anions can be successively targeted in crystal structures by increasing the corresponding pK_a of the organic reagent. Infinite chains of $[NbOF_4]^-$ anions form when the corresponding pK_a of the organic base introduced ranges approximately between 3.17 and 7.14. In contrast, isolated $[NbOF_5]^{2-}$ anions form when the corresponding pK_a of the organic base introduced is approximately between 7.14 and 11, and $[NbF_6]^-$ forms when the corresponding pK_a of the organic molecule is above 11. This control is promising for the future design of new functional materials based on other early-transition-metal oxide−fluoride BBUs.

■ ASSOCIATED CONTENT

Supporting Information

Listings of crystallographic data for compounds **I** and **II** (CCDC 965519 and 965520) and FTIR spectra for py and 4,4′-bpy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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