



Bi[NC₅H₃(CO₂)₂](OH₂)_xF (x = 1 and 2): New one-dimensional Bi-coordination materials—Reversible hydration and topotactic decomposition to α-Bi₂O₃

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ABSTRACT

Two one-dimensional bismuth-coordination materials, Bi[NC₅H₃(CO₂)₂](OH₂)_xF (x = 1 and 2), have been synthesized by hydrothermal reactions using Bi₂O₃, 2,6-NC₅H₃(CO₂H)₂, HF, and water at 180 °C. Structures of the two materials were determined by single-crystal X-ray diffraction. Although they have different crystal structures, both Bi-organic materials shared a common structural motif, a one-dimensional chain structure consisting of Bi³⁺ cations and pyridine dicarboxylate linkers. Detailed structural analyses include infrared spectroscopy, thermogravimetric analysis, and reversible hydration reactions for the coordinated water molecules were reported. Also, thermal decomposition of the rod-shaped Bi[NC₅H₃(CO₂)₂](OH₂)F single crystals at 800 °C led to α-Bi₂O₃ that maintained the same morphology of the original crystals.

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1. Introduction

Coordination polymers or metal-organic frameworks are an extraordinary class of materials that have attracted enormous attentions attributable to their technologically important applications in gas storage, isolation and absorption of major radioactive metal cations through ion-exchange, separation, sensing, membranes, and selective catalysis [1–7]. Although a huge number of coordination polymers have been extensively synthesized from the combination of various metal cations and organic linkers, it remains an ongoing challenge to explore materials further with new insights, which include understanding of the formation processes, morphology controls, and functionalization of the materials [8–11]. One of the most effective preparation methods for novel coordination polymers with structural versatilities and functional properties is hydrothermal synthesis reaction, in which mineralizers and templates are rudimentarily used in order to improve the solubility of the reagents and to control the morphologies, respectively [12–14].

Thus far, a wide variety of main group, transition, rare-earth, lanthanide, actinide, alkali, and alkali earth metal cations have been combined with diverse organic linker molecules to form novel structural networks [15–20]. Of the many metal cations, Bi³⁺ cation has been a very important node in the building of interesting functional materials, since Bi³⁺ can exhibit variable

coordination numbers, framework flexibilities, and diverse structural characteristics [21–23]. Also, Bi³⁺ cation inherently possesses an asymmetric structural geometry attributed to the lone pair. It has been well known that materials containing lone pair cations tend to exhibit local asymmetric coordination environments [24,25]. In fact, several materials on the basis of bismuth-carboxylates have been reported, and most of them are exhibiting two- or three-dimensional framework structures [26–32]. We have used hydrothermal reaction techniques to create new types of materials by introducing both Bi³⁺ cation with a variable coordination environment and an organic linker molecule, pdc (pdc = 2,6-pyridine dicarboxylate). Besides, we used hydrofluoric acid as mineralizer. Herein, we report the synthesis, crystal structures, and characterization of two one-dimensional bismuth-coordination materials, Bi[NC₅H₃(CO₂)₂](OH₂)_xF (x = 1 (CAUMOF-9) and x = 2 (CAUMOF-10)). With the Bi[NC₅H₃(CO₂)₂](OH₂)F, detailed dehydration–rehydration reactions and topotactic decomposition to metal oxide will be discussed.

2. Experimental

Bi₂O₃ (Aldrich, 99.9%), 2,6-NC₅H₃(CO₂H)₂ (Alfa Aesar, 98%), N(CH₃)₄Cl (Aldrich, 97%), and HF (J.T. Baker, 49.1%) were used as received. Bi[NC₅H₃(CO₂)₂](OH₂)F was synthesized by a hydrothermal reaction method, with 0.466 g (1.00 mmol) of Bi₂O₃, 0.167 g (1.00 mmol) of 2,6-NC₅H₃(CO₂H)₂, 0.5 mL of HF, and 13 mL of deionized water. The reaction mixture was transferred to a Teflon lined stainless steel autoclave. The autoclave was

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subsequently sealed and heated to 180 °C, held for 3 day, and cooled down to room temperature at a rate of 6 °C h⁻¹. After cooling, the product was recovered by filtration and washed with water. Colorless rod crystals were Bi[NC₅H₃(CO₂)₂](OH₂)F in 79% yield based on Bi₂O₃.

Bi[NC₅H₃(CO₂)₂](OH₂)₂F was synthesized similarly, with 0.466 g (1.00 mmol) of Bi₂O₃, 0.167 g (1.00 mmol) of 2,6-NC₅H₃(CO₂H)₂, 0.110 g (1.00 mmol) of N(CH₃)₄Cl, 2.0 mL of HF, and 10 mL of deionized water. Colorless rod crystals of Bi[NC₅H₃(CO₂)₂](OH₂)₂F were recovered in 10% yield based on Bi₂O₃ along with BiF₃. Although several attempts have been made, it was not possible to obtain phase pure Bi[NC₅H₃(CO₂)₂](OH₂)₂F. Detailed structural description of Bi[NC₅H₃(CO₂)₂](OH₂)₂F was deposited to the Supporting Information.

Crystal structures of the Bi[NC₅H₃(CO₂)₂](OH₂)_xF were determined by using a standard crystallographic method. A colorless rod crystal (0.10 × 0.14 × 0.33 mm³) of Bi[NC₅H₃(CO₂)₂](OH₂)F and a colorless rod crystal (0.10 × 0.12 × 0.25 mm³) of Bi[NC₅H₃(CO₂)₂](OH₂)₂F were used for single-crystal data analyses. The data were collected by using a Bruker SMART APEX diffractometer equipped with a 1 K CCD area detector using graphite monochromated Mo K α radiation at 200 K at the Korea Basic Science Institute. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in omega, and an exposure time of 5 s/frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was < 1%. The data were integrated using the SAINT program [33], with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. A semiempirical

absorption correction was made on the hemisphere of data with the SADABS program [34]. The data were solved and refined using SHELXS-97 and SHELXL-97, respectively [35,36]. All of the atoms except for hydrogen were refined with anisotropic displacement parameters and converged for $I > 2\sigma(I)$. All calculations were performed using the WinGX-98 crystallographic software package [37]. Crystallographic data and selected bond distances of the Bi[NC₅H₃(CO₂)₂](OH₂)_xF are given in Tables 1 and 2.

Powder XRD pattern was collected by using a Bruker D8-Advance diffractometer using Cu K α radiation at room temperature with 40 kV and 40 mA. The polycrystalline sample of Bi[NC₅H₃(CO₂)₂](OH₂)F was scanned in the 2 θ range 5–70° with a step size of 0.02° and a step time of 0.2 s. The powder XRD pattern of the synthesized material is in good agreement with the calculated pattern from the single-crystal data (see the Supporting Information).

Infrared spectrum was recorded by using a Varian 1000 FT-IR spectrometer over 400–4000 cm⁻¹, with the sample embedded in KBr matrix.

Thermogravimetric analysis was performed by using a Setaram LABSYS TG-DTA/DSC Thermogravimetric Analyzer. The polycrystalline sample of Bi[NC₅H₃(CO₂)₂](OH₂)F was heated at a rate of 10 °C min⁻¹ from room temperature to 800 °C under flowing argon.

Scanning Electron Microscope/Energy Dispersive Analysis by X-ray (SEM/EDAX) analysis was performed by using a Hitachi S-3400N/Horiba Energy EX-250 instruments.

Dehydration/rehydration reactions of the coordinated water molecules were performed by heating ca. 100 mg of Bi[NC₅H₃(CO₂)₂](OH₂)F at 250 °C for 3 h in vacuum. Then the sample was immersed in water and heated to 70 °C for 10 h. After that, the

Table 1
Crystallographic data for Bi[NC₅H₃(CO₂)₂](OH₂)F and Bi[NC₅H₃(CO₂)₂](OH₂)₂.

Empirical formula	Bi ₇ H ₇ FNO ₅	Bi ₇ H ₇ FNO ₆
Formula weight	411.09	429.01
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1 (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>Z</i>	2	4
<i>a</i> (Å)	6.2532(13)	11.744(2)
<i>b</i> (Å)	11.841(2)	13.223(3)
<i>c</i> (Å)	13.328(3)	6.2279(12)
α (deg.)	110.76(3)	90
β (deg.)	94.47(3)	103.44(3)
γ (deg.)	104.37(3)	90
Volume (Å ³)	878.8(3)	940.7(3)
Temperature (K)	200.0(2)	200.0(2)
ρ_{calcd} (g cm ⁻³)	3.092	3.029
μ (mm ⁻¹)	20.080	18.777
Crystal color	Colorless	Colorless
Crystal habit	Rod	Rod
Crystal size (mm ³)	0.10 × 0.14 × 0.33	0.10 × 0.12 × 0.25
Reflections collected	4856	5275
Independent reflections	2893	1643
<i>R</i> (int)	0.0423	0.0248
<i>T</i> _{min} , <i>T</i> _{max}	0.05, 0.13	0.08, 0.15
No. of parameters	271	146
Goodness-of-fit on <i>F</i> ²	1.064	1.218
X-ray radiation (λ , Å)		Mo K α (0.71073)
θ range (deg.)	1.66–24.50	1.78–24.97
Limiting indices	–7 ≤ <i>h</i> ≤ 7 –13 ≤ <i>k</i> ≤ 13 –15 ≤ <i>l</i> ≤ 15	–13 ≤ <i>h</i> ≤ 13 –12 ≤ <i>k</i> ≤ 15 –7 ≤ <i>l</i> ≤ 7
Refinement method	Full-matrix least-squares on <i>F</i> ² [SHELXL-97]	
Final <i>R</i> ^a , <i>b</i> indices [$I > 2\sigma(I)$]	<i>R</i> (<i>F</i>) = 0.0301, <i>R</i> _w (<i>F</i> _o ²) = 0.0760	<i>R</i> (<i>F</i>) = 0.0236, <i>R</i> _w (<i>F</i> _o ²) = 0.0584
<i>R</i> indices (all data)	<i>R</i> (<i>F</i>) = 0.0369, <i>R</i> _w (<i>F</i> _o ²) = 0.0912	<i>R</i> (<i>F</i>) = 0.0284, <i>R</i> _w (<i>F</i> _o ²) = 0.0755
Largest diff. peak and hole (e Å ⁻³)	1.875 and –1.735	1.607 and –1.342

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

Table 2Selected bond distances (Å) for $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$.

Bi(1)–O(1)	2.472(6)	N(1)–C(1)	1.350(12)	C(1)–C(2)	1.362(14)
Bi(1)–O(1)	2.722(6)	N(1)–C(5)	1.337(11)	C(1)–C(6)	1.532(12)
Bi(1)–O(3)	2.255(6)	N(2)–C(8)	1.333(11)	C(2)–C(3)	1.377(14)
Bi(1)–OW(1)	2.427(6)	N(2)–C(12)	1.343(13)	C(3)–C(4)	1.372(15)
Bi(1)–N(1)	2.374(8)	C(6)–O(1)	1.265(12)	C(4)–C(5)	1.393(14)
Bi(1)–F(1)	2.490(6)	C(6)–O(2)	1.246(12)	C(5)–C(7)	1.484(14)
Bi(1)–F(2)	2.284(6)	C(7)–O(3)	1.286(12)	C(8)–C(9)	1.376(14)
Bi(1)–F(2)	2.489(5)	C(7)–O(4)	1.240(11)	C(8)–C(13)	1.472(13)
Bi(2)–O(2)	2.609(6)	C(13)–O(5)	1.287(11)	C(9)–C(10)	1.363(16)
Bi(2)–O(5)	2.314(6)	C(13)–O(6)	1.283(11)	C(10)–C(11)	1.400(14)
Bi(2)–O(7)	2.387(7)	C(14)–O(7)	1.285(12)	C(11)–C(12)	1.346(14)
Bi(2)–OW(2)	2.576(7)	C(14)–O(8)	1.223(13)	C(12)–C(14)	1.526(14)
Bi(2)–N(2)	2.348(8)				
Bi(2)–F(1)	2.096(5)				
Bi(2)–F(2)	2.552(6)				

products were recovered by filtration, washed with excess H_2O , and dried in air for 1 d.

3. Results and discussion

3.1. Structure

$\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ has a triclinic space group $P-1$ (No. 2). Bi^{3+} cations and 2,6-pyridine dicarboxylate linkers are connected through oxygen and nitrogen atoms. There are two unique Bi^{3+} cations, in six- and seven-coordinate environments. The ORTEP drawings of the structure are given in Fig. 1 with dashed lines indicating long atom contacts. As seen in Fig. 1, the $\text{Bi}(1)^{3+}$ cation exhibits a six-coordinate environment with two oxygen, one nitrogen, and three fluorine atoms. Two longer contacts between the $\text{Bi}(1)^{3+}$ and oxygen atoms are observed as well. The $\text{Bi}(2)^{3+}$ cation shows a seven-coordinate moiety with four oxygen, one nitrogen, and two fluorine atoms. Both Bi^{3+} cations are in asymmetric coordination environments, attributable to their nonbonded electron pairs. The bond distances of Bi–O, Bi–F, and Bi–N are 2.255(6)–2.722(6), 2.096(5)–2.490(6), and 2.348(8)–2.374(8) Å, respectively (see Table 2). The bond distances are consistent with those reported materials [23,26–32]. Bond valence calculations [38,39] on the $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ resulted in a value of 2.89–2.93 for the Bi^{3+} cations. The assignment of the coordinated atoms to the Bi center was straightforward: the bond type of the organic ligand, subsequent crystallographic refinements, and complete chemical and spectroscopic analyses were used for the assignment. First, the atoms directly coordinated to Bi^{3+} from 2,6-pyridine dicarboxylate ligands could be easily assigned to oxygen. Second, the assignment of fluoride anions was based on the bond valence calculation. Moreover, several refinements with an oxygen atom for the fluorine position or with a fluorine atom for the oxygen position all resulted in slightly worse final R values, which confirmed our model. Finally, Infrared spectrum, charge balance, and thermal analysis data all consistently confirm the presence of the coordinated water molecule and fluoride anions. The carboxylate groups of the 2,6-pyridine dicarboxylate are bound to the bismuth cations through oxygen and nitrogen atoms. The C–O and C–N bond distances within the organic linker are 1.223(13)–1.287(11) Å and 1.333(11)–1.350(12) Å, respectively. As can be seen in Fig. 2, hydrogen bonds between the coordinated water molecules $[\text{OW}(2)\cdots\text{OW}(2)$ 3.07(7) Å] are observed. Also, interestingly, all the 2,6-pyridine dicarboxylate ligands are attached to the Bi^{3+} cations as left-handed propeller along the [100] direction. It is interesting to note that the one-dimensional zig-zag chain is completely encompassed by the 2,6-pyridine

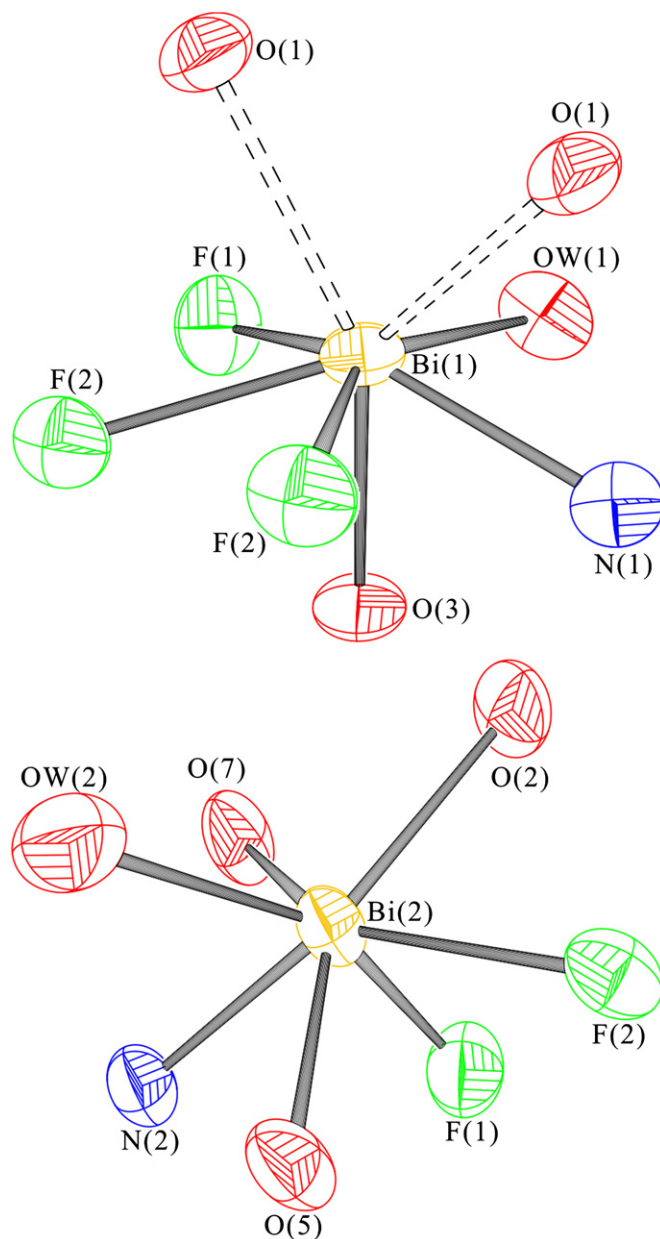


Fig. 1. ORTEP representations (50% probability ellipsoids) of Bi^{3+} moieties in $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$.

dicarboxylate groups. The $\text{Bi}(1)\text{O}_4\text{NF}_3$ groups share their edges through oxygen [O(1)] and fluorine [F(2)] atoms and form a one-dimensional zig-zag chain along the a -direction. Also, the $\text{Bi}(2)\text{O}_4\text{NF}_2$ groups share their edges through fluorine atoms, F(1) and F(2) on both sides of the chain along the c -direction. Finally, the 2,6-pyridine dicarboxylate groups link to the $\text{Bi}(1)\text{O}_4\text{NF}_3$ and $\text{Bi}(2)\text{O}_4\text{NF}_2$ groups and complete a novel bismuth-organic chain structure (see Fig. 3). The powder XRD pattern of the polycrystalline $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ is in a good agreement with the calculated pattern from the single-crystal model (see Supporting Information).

3.2. Infrared spectroscopy

The infrared spectrum of $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ shows C–H and C=C stretches of the pyridine ring at ca. 3069–3094 and 1675 cm^{-1} , respectively. The characteristic vibrations at around 1567–1629 and 1382–1433 cm^{-1} can be assigned to the

antisymmetric CO_2 and symmetric CO_2 stretches, respectively. The vibrations for the coordinated water molecules are observed at around 3412 cm^{-1} . The intense bands at 427 and 588 cm^{-1} correspond to the Bi–F and Bi–O stretching vibrations, respectively. The assignments are consistent with those previously reported [40–43]. Also, all these spectroscopic evidences are consistent to our structural model. The IR spectrum of $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ has been deposited to the Supporting Information.

3.3. Thermogravimetric analysis

A weight loss of 3.72% is observed between 210 and $270\text{ }^\circ\text{C}$, which is attributed to the release of the coordinated water molecule (calc. 4.38%). The framework of the material seems to be stable up to $310\text{ }^\circ\text{C}$. Above $310\text{ }^\circ\text{C}$, a sharp weight loss is observed and the framework collapses by $800\text{ }^\circ\text{C}$ which is due to

the decomposition of the organic linkers. Thermal decomposition at $800\text{ }^\circ\text{C}$ in air for $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ resulted in $\alpha\text{-Bi}_2\text{O}_3$ [44] as shown by powder XRD measurement (see the Supporting Information).

3.4. Dehydration/rehydration reactions

Initially, approximately 100 mg of the $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ was evacuated at $250\text{ }^\circ\text{C}$ in order to remove the coordinated water molecules. Once the coordinated waters are removed, the resulting material exhibits a light brown color. The powder XRD pattern of the water free material revealed a non-crystalline phase. However, the loss of coordinated water from the material is fully reversible. If the activated materials were immersed in water at $70\text{ }^\circ\text{C}$ for 10 h , their color changed back to white. Complete re-coordination of water molecules occurred, which was confirmed by the powder XRD patterns. Even the activated water free materials were allowed to stand in atmospheric air, re-coordination of water occurred within a day.

3.5. Topotactic decomposition reaction

One-dimensional structured metal oxides, such as nano- and/or microsized rods or wires, are of great interest, attributable to their essential applications, such as photocatalysis, gas sensors, optics, supercapacitor, and imaging [45–51]. One-dimensional structured Bi_2O_3 have been prepared by hydrothermal, electrodeposition, metal vapor transport deposition, and pulsed laser ablation methods. Recently, a couple of iron oxides nanorods have been selectively prepared by controlling the calcination conditions of rod shaped MOFs [52]. We tried to calcine the rod shaped $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ at $800\text{ }^\circ\text{C}$ to produce Bi_2O_3 , as confirmed by EDAX spectrum (see Fig. 4(a)–(c)). XRD pattern revealed that the resulting product is $\alpha\text{-Bi}_2\text{O}_3$ (Fig. 4(d)).

4. Conclusions

Two one-dimensional bismuth-coordination polymer materials, $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)_x\text{F}$ ($x=1$ and 2), were synthesized through a hydrothermal reaction method. The materials have

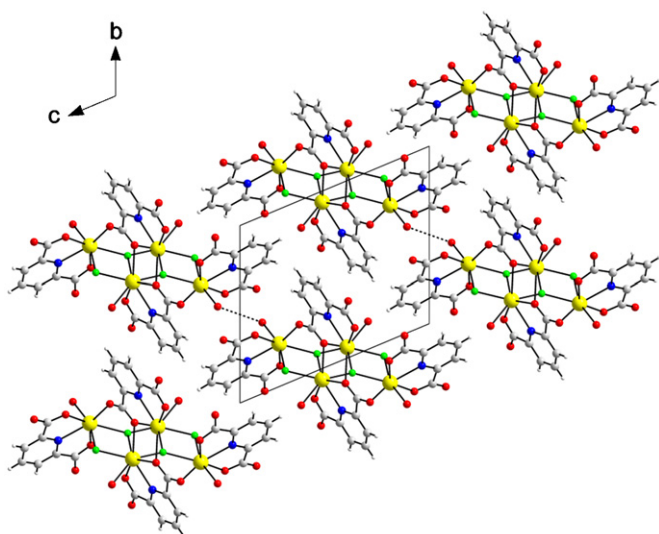


Fig. 2. Ball-and-stick model of $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ in the bc -plane (yellow, Bi; blue, N; green, F; red, O; gray, C; white, H). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

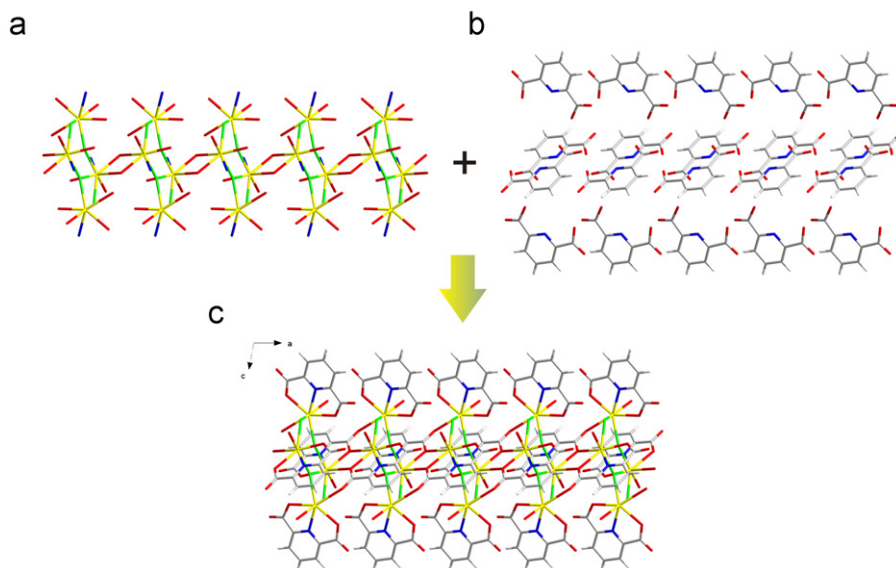


Fig. 3. Wire diagrams representing (a) a chain of edge-sharing $\text{Bi}(1)\text{O}_4\text{NF}_3$ and $\text{Bi}(2)\text{O}_4\text{NF}_2$ polyhedra, (b) 2,6-pyridine dicarboxylate groups, and (c) the “linking” to form a one-dimensional structure of $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ in the ac -plane (yellow, Bi; blue, N; green, F; red, O; gray, C; white, H). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

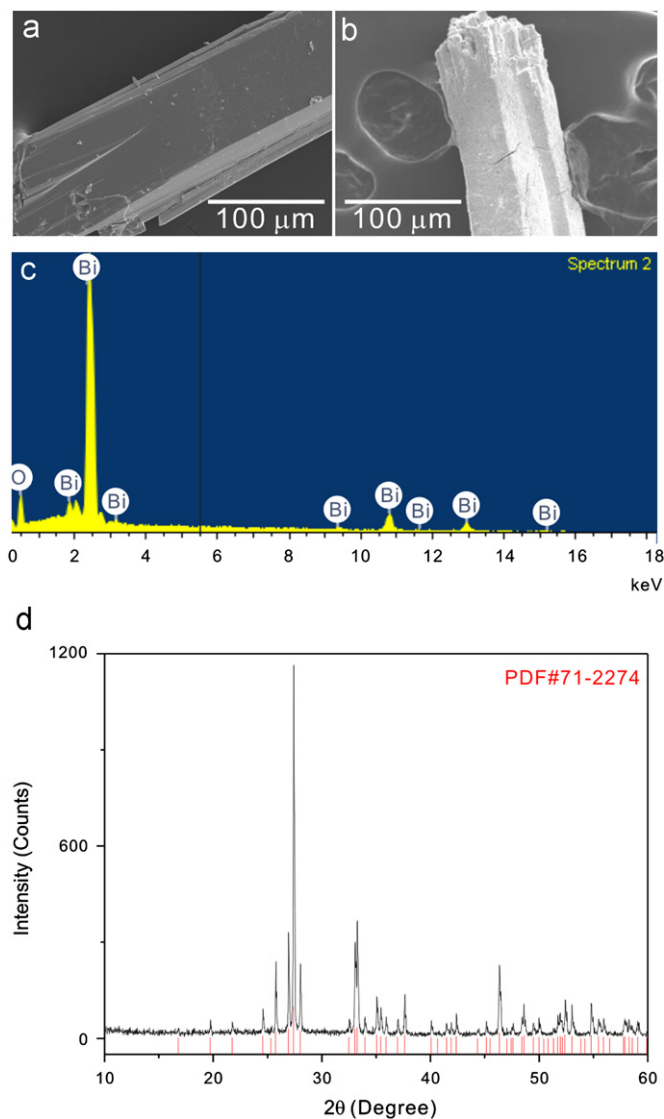


Fig. 4. SEM images of a rod-shaped (a) $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ crystal and (b) calcined product, and (c) EDAX spectrum and (d) powder XRD pattern of the decomposed product at 800 °C.

been structurally characterized by single-crystal X-ray diffraction. Although the two materials shared a common structural motif, a one-dimensional chain structure with Bi^{3+} cations and pyridine dicarboxylate linkers, they exhibited different crystal structures. The coordinated water molecules are reversibly dehydrated and rehydrated. Interestingly, the material decomposed topotactically at 800 °C and resulted in rod-shaped $\alpha\text{-Bi}_2\text{O}_3$.

5. Supporting information

Experimental and calculated powder X-ray diffraction patterns, infrared spectrum, and thermogravimetric analysis diagram of the $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$, powder XRD pattern for the thermal decomposition product, and detailed structural description of the $\text{Bi}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)_2\text{F}$ are available (PDF). CCDC 837820 and CCDC 842430 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44(0)1223 336033.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.12.044.

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