



# In[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>](OH<sub>2</sub>)F: A new layered indium-organic framework material (NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>=2,6-pyridinedicarboxylate)

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## ABSTRACT

A new layered indium-organic framework material, In[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>](OH<sub>2</sub>)F has been synthesized by a hydrothermal reaction using In<sub>2</sub>O<sub>3</sub>, NH<sub>4</sub>F, 2,6-NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>H)<sub>2</sub> (2,6-pyridinedicarboxylic acid), HF, and water at 200 °C. Single-crystal X-ray diffraction was used to determine the structure of the reported material. In[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>](OH<sub>2</sub>)F has a novel layered structure consisting of InO<sub>5</sub>NF polyhedra and the pyridinedicarboxylate organic linker. Detailed structural analyses with full characterization including infrared spectrum, thermogravimetric analysis, elemental analysis, exchange reactions for the coordinated water molecule, and gas adsorption experiments are reported.

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## 1. Introduction

Recently, a huge number of new metal-organic framework (MOF) materials are reported 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]. Chemists have been deliberately trying to tailor the structural geometries and framework flexibilities by tuning the polyhedral units of the metal cations and organic linkers [8–10]. Currently, a variety of further extraordinary characteristics and/or new insight into formation processes including the morphology and pore size control of given materials are actively pursued [11–13]. One very effective method for the preparation of novel MOFs with structural variations and functional properties is hydrothermal synthesis reactions [14–16], where mineralizers and structure-directing agents are routinely used to facilitate the solubility of the reagents and to control the framework morphologies, respectively. So far, a wide variety of main group, transition, rare-earth, lanthanide, actinide, and alkali metal cations have been combined with diverse organic linker molecules to form novel structural networks [7,17–22]. Among the candidate framework metal cations, many p-elements were introduced to the new MOF in order to mimic the open nature of zeolites (aluminosilicates), which can exhibit the defining characteristics through

the large channels or pores within the structural architecture. The selection of framework cations has been extended to indium, since In<sup>3+</sup> can exhibit variable coordination numbers: thus, many zeolite-like microporous indium-organic hybrid framework structures with diverse structural characteristics were reported [23–26]. With their unique fundamental structural units, interesting features such as gas sorption, separation, drying, etc., were also observed. In contrast, however, relatively few examples of *indium-organic framework materials exhibiting layered structures* have been reported. In fact, only a few indium-organic framework materials such as [In(HBTC)<sub>2</sub>(4,4'-bpy)](4,4'-Hbpy)(H<sub>2</sub>O)<sub>0.5</sub> (BTC=1,3,5-benzenetricarboxylate, 4,4'-bpy=4,4'-bipyridine) [27], [In<sub>2</sub>(BTC)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> · 2nH<sub>2</sub>O [28], In<sub>2</sub>(OH)<sub>2</sub>(BDC)<sub>2</sub>(phen)<sub>2</sub> (BDC=1,4-benzenedicarboxylate, phen=*o*-Phenanthroline) [29], In(H<sub>2</sub>O)(BTC)(bpy) · (H<sub>2</sub>O)<sub>0.25</sub> [29], In(H<sub>2</sub>O)(BTC)(phen) [29], and [In(OH)(hfipbb)] (hfipbb=4,4'-(hexafluoroisopropylidene)bis(benzoate)) [30] were demonstrating diverse *layered* architectures with some catalytic properties. In these reported materials, the observed coordination numbers for In<sup>3+</sup> cations are six, seven, and eight, which result in a variety of structural geometries. However, the use of organic linkers has been rather limited to BTC, BDC, and hfipbb. Thus, we tried to combine both of the In<sup>3+</sup> cation with a variable coordination environment and the new organic linker molecule, pdc (pdc=2,6-pyridine dicarboxylate) to create a new type of indium-organic framework. Furthermore, when we initially designed the hydrothermal synthesis reaction, we decided to introduce a hydrofluoric acid as a mineralizer. Herein, we report the phase pure synthesis, crystal structure, and characterization of a new layered indium-organic framework material, In[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>](OH<sub>2</sub>)F.

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## 2. Experimental

### 2.1. Synthesis

**Caution!** HF is toxic and corrosive!

$\text{In}_2\text{O}_3$  (99.9%, Alfa Aesar), 2,6- $\text{NC}_5\text{H}_3(\text{CO}_2\text{H})_2$  (99+%, Aldrich),  $\text{NH}_4\text{F}$  (95%, Shinyo), and HF (49.1%, J.C. Baker) were used as received.  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  was synthesized by a hydrothermal reaction method. 0.833 g (3.00 mmol) of  $\text{In}_2\text{O}_3$ , 0.250 g (1.50 mmol) of 2,6- $\text{NC}_5\text{H}_3(\text{CO}_2\text{H})_2$ , 0.111 g (3.00 mmol) of  $\text{NH}_4\text{F}$ , 6 mL of HF, and 5 mL of deionized water were combined. The reaction mixture was transferred to a Teflon lined stainless steel autoclave. The autoclave was subsequently sealed and heated to 200 °C, held for 3 days, and cooled down to room temperature at a rate of 6 °C h<sup>-1</sup>. After cooling, the autoclave was opened and the product was recovered by filtration and washed with water. Colorless rhombus crystals that are the only reaction product were recovered for  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  in 23% yield based on  $\text{In}_2\text{O}_3$ .

### 2.2. Single crystal X-ray diffraction

The crystal structure of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  was determined by a standard crystallographic method. A colorless rhombus crystal of dimension 0.12 × 0.12 × 0.22 mm<sup>3</sup> was used for structural determination. The data were collected on a Bruker SMART APEX CCD X-ray diffractometer at the Korea Basic Science institute at room temperature using graphite monochromated MoK $\alpha$  radiation. 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 per 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 [31], with the intensities corrected for Lorentz, 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 [32]. The structures were solved by direct methods using SHELXS-97 [33] and refined using SHELXL-97 [34]. All atoms except for hydrogen atoms were refined with anisotropic displacement parameters and converged for  $I > 2\sigma(I)$ . All calculations were performed using the WinGX-98 crystallographic software package [35]. Crystallographic data and selected bond distances for  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  are given in Tables 1 and 2.

### 2.3. Powder X-ray diffraction

The powder XRD pattern was collected on a SCINTAG XDS2000 diffractometer using CuK $\alpha$  radiation at room temperature with 35 kV and 30 mA. The polycrystalline sample of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  was mounted on a glass sample holder and scanned in the 2 $\theta$  range 5–70° with a step size of 0.02° and a step time of 1 s. The powder X-ray diffraction pattern on the synthesized material is in good agreement with the calculated pattern from the single-crystal data (see the Supporting Information).

### 2.4. Infrared spectroscopy

Infrared spectrum was recorded on a Varian 1000 FT-IR spectrometer in the 400–4000 cm<sup>-1</sup> range, with the sample intimately pressed between two KBr pellets. IR (KBr, cm<sup>-1</sup>): 3395 m, 3105 m, 2998 m, 2920 m, 1648 s, 1618 s, 1597 s, 1579 m, 1476 w, 1457 s, 1406 s, 1370 s, 1284 s, 1191 m, 1084 m, 1032 w, 995 m, 925 m, 884 w, 822 w, 804 w, 767 s, 738 s, 689 m, 672 m, 610 w, 553 w, 493 m, 476 m, 460 w, 437 s.

**Table 1**  
Crystallographic data for  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ .

Empirical formula	$\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$
Formula weight	316.93
Crystal system	Monoclinic
space group	$I2/a$ (no. 15)
Z	8
a (Å)	12.929(3)
b (Å)	7.8554(16)
c (Å)	17.740(4)
$\beta$ (deg)	100.66(3)
Volume (Å <sup>3</sup> )	1770.6(6)
Temperature (K)	298.0(2)
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	2.498
$\mu$ (mm <sup>-1</sup> )	2.702
Crystal color	Colorless
Crystal habit	Rhombus
Crystal size (mm <sup>3</sup> )	0.12 × 0.12 × 0.22
Reflections collected	5702
Independent reflections	1961
R (int)	0.0194
$T_{\text{min}}, T_{\text{max}}$	0.680, 0.760
No. of parameters	137
Goodness-of-fit on $F^2$	1.316
X-ray radiation ( $\lambda$ , Å)	MoK $\alpha$ (0.71073)
$\theta$ range (deg)	2.34–27.49
Limiting indices	$-14 \leq h \leq 16, -8 \leq k \leq 10,$ $-23 \leq l \leq 18$
Refinement method	Full-matrix least-squares on $F^2$ [SHELXL-97]
Final $R^a, b$ indices [ $I > 2\sigma(I)$ ]	$R(F)=0.0319, R_w(F_o^2)=0.0635$
R indices (all data)	$R(F)=0.0455, R_w(F_o^2)=0.1109$
Largest diff. peak and hole (e Å <sup>-3</sup> )	1.330 and -1.473

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

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

**Table 2**

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

In(1)–O(1)	2.352(5)	N(1)–C(2)	1.325(9)	C(2)–C(8)	1.513(9)
In(1)–O(1)	2.354(5)	N(1)–C(6)	1.331(9)	C(6)–C(7)	1.510(10)
In(1)–O(2)	2.125(5)	C(2)–C(3)	1.395(10)	C(7)–O(1)	1.285(8)
In(1)–O(3)	2.339(5)	C(3)–C(4)	1.390(11)	C(7)–O(4)	1.215(9)
In(1)–OW(1)	2.156(5)	C(4)–C(5)	1.383(11)	C(8)–O(2)	1.262(8)
In(1)–N(1)	2.254(6)	C(5)–C(6)	1.404(10)	C(8)–O(3)	1.234(9)
In(1)–F(1)	2.033(4)				

### 2.5. Thermogravimetric analysis

Thermogravimetric analysis was performed on a Setaram LABSYS TG-DTA/DSC thermogravimetric analyzer. The polycrystalline sample of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  was contained within an alumina crucible and heated at a rate of 10 °C min<sup>-1</sup> from room temperature to 800 °C under flowing argon.

### 2.6. Elemental analysis

Elemental analysis was carried out by a Carlo Erba EA1108 CHNS-O analyzer at Organic Chemistry Research Center, Sogang University. Elemental microanalysis for  $\text{C}_7\text{H}_3\text{NInO}_4\text{F}(\text{H}_2\text{O})$  obsd. (calcd.): C, 26.48% (26.53%); H, 1.64% (1.59%); N, 4.32% (4.42%).

### 2.7. Scanning electron microscope/energy dispersive analysis by X-ray (SEM/EDAX)

SEM/EDAX analysis has been performed using a Hitachi S-3400N/Horiba Energy EX-250 instruments.

## 2.8. BET analyses

The surface area measurement of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  was performed by a Quantachrome NOVA 1200e surface area analyzer. The sample was evacuated at 180 °C for 2 h before being analyzed. The gas adsorption isotherms were obtained at 77 K using  $\text{N}_2$  and  $\text{H}_2$ , and at 195 K using  $\text{CO}_2$ . The surface area was calculated from a linear five-point BET plot obtained from the analysis at 77 K using  $\text{N}_2$  gas.

## 2.9. Exchange experiments

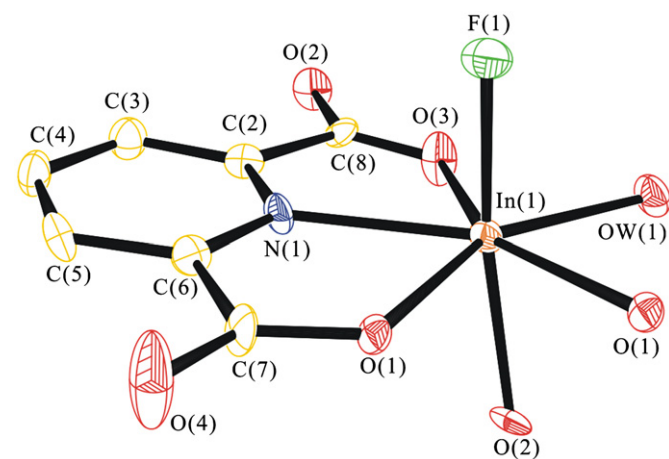
Exchange reactions for the coordinated water molecule were performed by stirring ca. 100 mg of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  sample in 2 mL of water, trimethyl amine, and triethyl amine. The reactions were performed at room temperature or at 150 °C for 12 h. The reaction products were recovered by filtration, washed with excess  $\text{H}_2\text{O}$ , and dried in air for 1 d.

## 3. Results and discussion

### 3.1. Structure

$\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  has been synthesized under a hydrothermal reaction condition by the reaction of  $\text{In}_2\text{O}_3$ , 2,6-pyridine dicarboxylic acid,  $\text{NH}_4\text{F}$ , HF, and water at 200 °C for 3 days. Colorless rhombus crystals have been isolated in phase pure form.  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  is crystallizing in a monoclinic space group  $I2/a$  (no. 15). The structure contains layers consisting of seven-coordinate  $\text{InO}_5\text{NF}$  polyhedra and pyridine dicarboxylate groups that are connected through oxygen and nitrogen atoms (see Fig. 1).

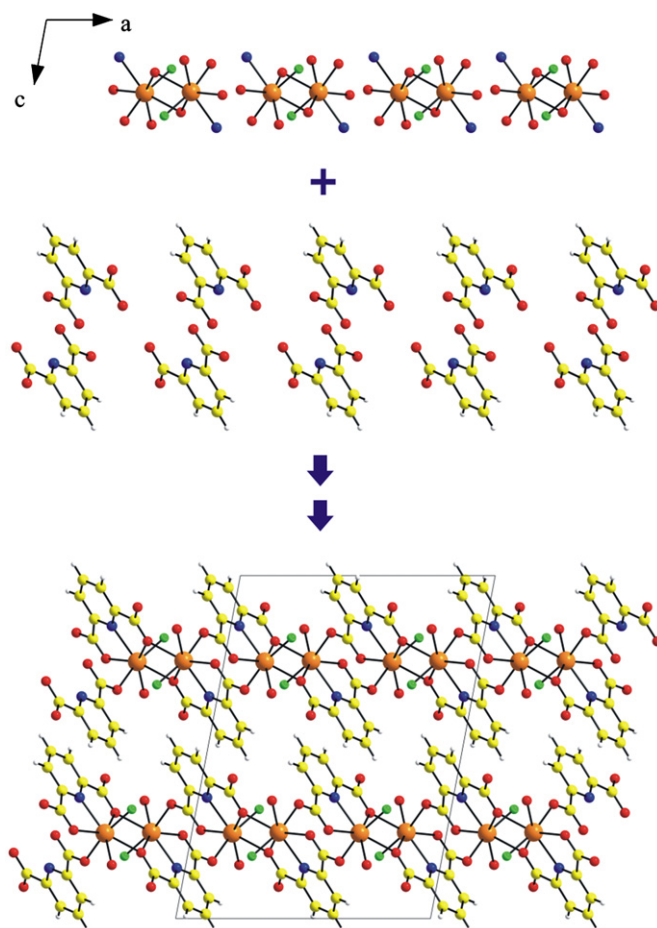
The unique  $\text{In}^{3+}$  cation exhibits a seven-coordinate pentagonal bipyramidal environment with five oxygen, one nitrogen, and one fluorine atoms. The five equatorial ligands are composed of three oxygen atoms from the carboxylates, one nitrogen atom from the pyridine moiety, and one oxygen atom from the water molecule. Also, the pentagonal bipyramid around In center contains one axial oxygen and one axial fluorine. The bond distances for In–O, In–F, and In–N are 2.125(5)–2.354(5), 2.033(4), and 2.254(6) Å, respectively (see Table 2). The bond distances are consistent with those reported earlier [27–30,36]. Bond valence calculations [37,38] on the  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  resulted in a value of 3.02 for the  $\text{In}^{3+}$  cation. The geometry around In center including an assignment of



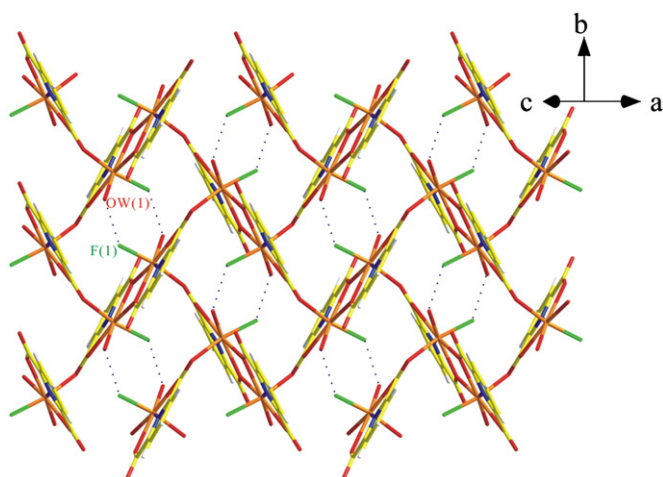
**Fig. 1.** ORTEP (50% probability ellipsoids) drawing of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ . Hydrogen atoms have been omitted for clarity.

the fluoride anion was mainly on the basis of the bond type of the organic ligand, subsequent crystallographic refinements, and complete chemical and spectroscopic analyses. The coordinated oxygen atoms from the 2,6-pyridine dicarboxylate ligands could be easily assigned. Furthermore, several refinements with an oxygen atom for the fluorine position or with a fluorine atom for the oxygen position all result in slightly worse final  $R$  values, which confirms our model. Finally, as we will discuss later in detail, elemental analysis, Infrared spectrum, and thermal analysis data all consistently confirm the presence of the coordinated water molecule. The carboxylate groups of the 2,6-pyridine dicarboxylate linkers are bound to the indium cations through oxygen and nitrogen atoms. While the C–O bond lengths range from 1.215(9) to 1.285(8) Å, the C–N distances range from 1.325(9) to 1.331(9) Å within the organic linker.

The  $\text{InO}_5\text{NF}$  pentagonal bipyramidal groups share their edges through the equatorial oxygen atoms [O(1)] and form the edge-sharing  $\text{In}_2\text{O}_8\text{N}_2\text{F}_2$  dimers. Then the 2,6-pyridine dicarboxylate groups link to the  $\text{In}_2\text{O}_8\text{N}_2\text{F}_2$  dimers on both sides, above and below along the approximate  $c$ -direction and complete a novel indium-organic layer structure (see Fig. 2). Within the layer rectangular rings consisting of the four  $\text{In}_2\text{O}_8\text{N}_2\text{F}_2$  dimers and four organic linkers are observed. The dimensions of the rings in the layer are approximately  $2.6 \text{ \AA} \times 9.1 \text{ \AA}$ . As can be seen in Fig. 3, strong hydrogen bonds between the coordinated fluorines



**Fig. 2.** Ball-and-stick diagram of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$ . The 2,6-pyridine dicarboxylate groups link to the edge-sharing  $\text{In}_2\text{O}_8\text{N}_2\text{F}_2$  dimers on both sides, above and below along the approximate  $c$ -direction to create a novel 2-D indium-organic layered structure (orange, In; yellow, C; red, O; green, F; blue, N; white, H). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



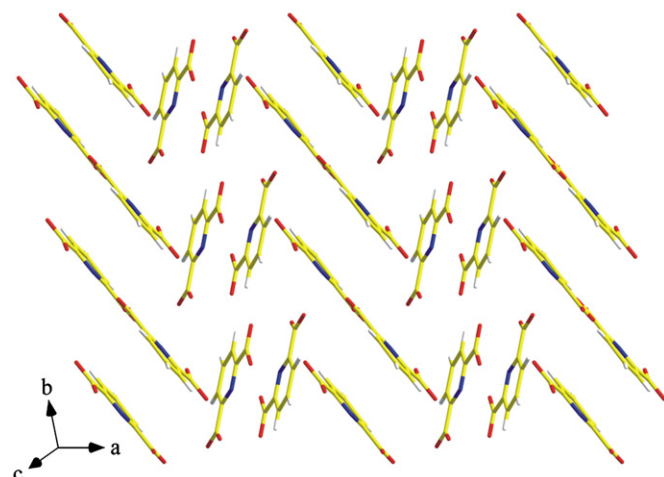
**Fig. 3.** Wire representation for the one indium-organic layer of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  in the [101] direction. Rectangular rings are observed within the layer. Note there are strong hydrogen bonds between the coordinated F and water molecules (orange, In; yellow, C; red, O; green, F; blue, N; white, H). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and the coordinated water molecules [ $\text{F}(1)\cdots\text{OW}(1)$  2.557(3) Å] are observed. Although  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  shows a novel indium-organic framework structure with rings in the 2-D layers, no solvent accessible volume has been calculated from the CALC SOLV command in PLATON [39], which might be attributable to the van der Waals radii of the constituent atoms as well as the strong hydrogen bond interactions. The nonporous nature of the material was confirmed by several adsorption isotherms obtained with  $\text{N}_2$  and  $\text{H}_2$  at 77 K, and with  $\text{CO}_2$  at 195 K (see the Supporting Information). The  $\text{N}_2$  adsorption isotherm for  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  at 77 K shows features resulting from multilayer adsorption. The adsorption capacity of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  for  $\text{CO}_2$  or  $\text{H}_2$  is much less than that of  $\text{N}_2$ . This observation may be attributable to the stronger interaction of the  $\text{N}_2$  molecules which have considerable quadrupole interactions with the electrostatic field gradients near the framework surface. Analysis of the experimental data based on the  $\text{N}_2$  adsorption yields 6.85  $\text{m}^2/\text{g}$  for the specific surface area. Although the material is nonporous as shown on gas adsorption experiments, however, it might be applied to heterogeneous catalysis or proton conductivity.

An interesting structural feature of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  is that the organic linker 2,6-pyridine dicarboxylate groups are aligned parallel to each other approximately along the *a*- and *c*-axis (see Fig. 4). The distance between the two consecutive pyridine rings is approximately 3.6 Å. The close contacts suggest that there are significant parallel  $\pi$ - $\pi$  stacking interactions, even though the parallel pyridine rings are slightly slipped. Although there is some preferred orientation attributable to the layered nature of the material, the powder X-ray diffraction pattern of the polycrystalline sample of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  is in a good agreement with the calculated pattern on the basis of the single-crystal model (see the Supporting Information).

### 3.2. Infrared spectroscopy

The infrared spectrum of the material shows the C–H and C=C stretches of the pyridine ring at ca. 2920–3000 and 1579–1648  $\text{cm}^{-1}$ , respectively. The characteristic vibrations around 1597–1618 and 1370–1406  $\text{cm}^{-1}$  can be assigned to the antisymmetric  $\text{CO}_2$  and symmetric  $\text{CO}_2$  stretches, respectively.



**Fig. 4.** Wire representation exhibiting 2,6-pyridinedicarboxylate groups that are packed parallel attributable to the  $\pi$ - $\pi$  stacking interactions (yellow, C; red, O; blue, N; white, H). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The vibrations for the coordinated water molecules are observed around 3395  $\text{cm}^{-1}$ . The assignments are consistent with those previously reported [27,28].

### 3.3. Thermogravimetric analysis

The thermal behavior of  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  was investigated using thermogravimetric analysis.  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  is stable up to 210 °C. Then, a weight loss of 5.20% was observed between 210 and 280 °C, that is attributed to the coordinated water molecule from the material (calc. 5.68%). The framework of the material seems to be stable up to 370 °C. Above the temperature, the material starts decomposing and the framework collapses by 800 °C. Thermal decomposition product at 800 °C in air for  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  resulted in  $\text{In}_2\text{O}_3$  [40] as shown by powder X-ray diffraction measurement (see the Supporting Information).

### 3.4. Exchange experiments

Attempts have been made to exchange the coordinated water molecule for *N,N*-dimethylformamide (DMF) or some amine molecules. Initially, approximately 100 mg of the  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  was evacuated at 200 °C in order to remove the coordinated water molecules. The powder X-ray diffraction pattern for the resulting material revealed a highly crystalline phase (see the Supporting Information). The water free material has a slightly larger inter-layer distance of  $d \sim 19.3$  Å, which was calculated from the (002) peak. The slight increase of inter-layer distance may be attributed to the change of coordination environment around  $\text{In}^{3+}$  cation and a subsequent distortion of the overall layer framework. However, we found that once the structural change occurs by removing the coordinated water molecules, the re-coordination of incoming solvent molecules to the indium cation is difficult. Although the activated water free material has been immersed in DMF at 50 °C for 24 h, no structural change has been observed at all based on the powder X-ray diffraction. Meanwhile, approximately 100 mg of the  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  was stirred in  $\text{Me}_3\text{N}$  (aq) or  $\text{Et}_3\text{N}$  (aq) at 150 °C without removing the coordinated water molecules. Now  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  completely decomposed to  $\text{In}(\text{OH})_3$ . In other words, the deprotonation from the coordinated water by excess amine rather than the substitution of the incoming amine for the coordinated water has been facilitated at higher temperature, which subsequently induced the decomposition

of the framework. The formation of  $\text{In}(\text{OH})_3$  has been confirmed by the powder X-ray diffraction on the resulting powder sample. Thus, exchanging the coordinated water in  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  is irreversible.

#### 4. Conclusions

We have successfully synthesized a novel layered indium-organic framework material,  $\text{In}[\text{NC}_5\text{H}_3(\text{CO}_2)_2](\text{OH}_2)\text{F}$  through a hydrothermal reaction. The material has been structurally characterized by single-crystal X-ray diffraction. Within the layer, the material exhibits rectangular rings with strong hydrogen bonds. The reported compound has been fully characterized by infrared spectrum, thermogravimetric analysis, elemental analysis, and exchange reactions. We continue to extend this work to other systems with different organic linkers and will report them shortly.

#### 5. Supporting information available

Experimental and calculated powder X-ray diffraction patterns, thermogravimetric analysis diagram, Infrared spectrum, ORTEP drawing, and  $\text{N}_2$  gas adsorption isotherm are available (PDF).

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2010.08.016](https://doi.org/10.1016/j.jssc.2010.08.016).

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