# Exploring the Ruddlesden-Popper Layered Organic-Inorganic Hybrid Semiconducting Perovskite for Visible-Blind Ultraviolet Photodetection 

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## Experimental section

## Synthesis of 1.

For the chemical synthesis of $\mathbf{1}$, stoichiometric $\mathrm{Pb}\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2} \cdot 3\left(\mathrm{H}_{2} \mathrm{O}\right)$ ( $0.01 \mathrm{~mol}, 3.79 \mathrm{~g}$ ) and 4-Fluorophenethylamine ( $0.02 \mathrm{~mol}, 2.78 \mathrm{~g}$ ) were slowly dissolved in the hydrobromic acid ( 60 mL ) by heating to boiling, which forms a clearly-white solution. Firstly, the $\mathrm{PbCl}_{2}$ was synthesized by the reaction of $\mathrm{Pb}\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2} \cdot 3\left(\mathrm{H}_{2} \mathrm{O}\right)(0.01 \mathrm{~mol}, 3.79 \mathrm{~g})$ with excessive hydrochloric acid in a bath. Secondly, an appropriate amount of 4-Fluorophenethylamine $(0.02 \mathrm{~mol}$, 2.78 g ) was added into the above solution (the stoichiometric molar ratio of 4Fluorophenethylamine and lead (II) with a 2:1 molar ratio) after heating and stirring for 50 minutes until the precipitate dissolved completely at $100^{\circ} \mathrm{C}$. In addition, the mixture was placed in a $100^{\circ} \mathrm{C}$ oven for 2 days. Then we put it in the oven to cool down and grow the crystals, and the temperature drop is 0.5 ${ }^{\circ} \mathrm{C} /$ day, large size white crystals were grown in the above clarified solution.

## Device fabrication based on the crystal of 1.

Actually, the substrate is the glass and the crystals were fabricated after polished by using dried silk. Then, the crystal surface was covered by conductive paste to do photoelectricity tests. Moreover, the electrode spacing is $400 \mu \mathrm{~m}$ and electrode length is about 2.5 mm .

## Materials and methods.

X-ray diffraction experiments were performed out at 302 K on a Bruker D8 Quesr/Venture diffractometer with Mo K $\alpha$ radiation $(\lambda=0.77 \AA$ ). Crystal
structure was resolved by direct methods and confirmed by the full-matrix method based on $\mathrm{F}^{2}$ using the SHELXTL software packing. PXRD measurement was performed on a Rigaku MiniFlex II diffractometer and the experimental data is in good accordance with the simulated data (Figure S1), indicating the high phase purity of $\mathbf{1}$. UV-Vis diffuse-reflectance spectrometry was performed on a PerkinElmer Lambda 950 UV-vis-IR Spectrophotometer. The instrument model is FLS 920 of Edinburgh Instruments, and the laser instrument is Vibrant 355 II of OPOTEK. Photoelectrical measurements were investigated on a Keithley 6517 B source meter. The $I-V$ test was performed on a voltage scanning manner with a scan rate of $10 \mathrm{~V} / \mathrm{s}$. Responding time was achieved by the high-speed Tektronix MDO3014 Oscilloscope.

## Figures



Figure S1. The optical image of the crystal of $\mathbf{1}$.


Figure S2. Powder X-ray Diffraction (PXRD) patterns of experimental data and the calculated data.


Figure S3. TG curves for 1.

Table S1. Crystal data and structure refinement for $\mathbf{1 .}$

| Empirical formula | $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{~F}_{2} \mathrm{~N}_{2} \mathrm{PbBr}_{4}$ |
| :---: | :---: |
| Formula weight | 807.19 |
| Temperature/K | 173.15 |
| Crystal system | monoclinic |
| Space group | C2/c |
| $\mathrm{a} / \AA, \mathrm{b} / \AA, \mathrm{c} / \AA$ | 32.7746(6), 8.10520(10), 8.3503(2) |
| $\alpha /{ }^{\circ}, \beta /{ }^{\circ}, \gamma^{\circ}$ | 90, 95.503(2), 90 |
| Volume/ $\AA^{3}$ | 2207.99(7) |
| Z | 4 |
| $\rho_{\text {calc }} \mathrm{g} / \mathrm{cm}^{3}$ | 2.4280 |
| $\mathrm{m} / \mathrm{mm}^{-1}$ | 23.512 |
| F(000) | 1465.1481 |
| Theta range for data collection | 2.71 to $75.78^{\circ}$ |
| Index ranges | $-41 \leqslant \mathrm{~h} \leqslant 40,-10 \leqslant \mathrm{k} \leqslant 9,-9 \leqslant 1$ |
| Reflections collected | 18537 |
| Independent reflections | $2226\left[\mathrm{R}_{\text {int }}=0.0877\right]$ |
| Data/restraints/parameters | 2226/0/116 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.9960 |
| Final R indexes [ $\mathrm{I}>2 \sigma$ ( I ] | $\mathrm{R}_{1}=0.0796, \mathrm{wR}_{2}=0.1819$ |
| $\underline{\text { Largest diff. peak/hole / e } \AA^{-3}}$ | 8.0032/-1.4966 |

Table S2. Bond Lengths for 1.

| Atom | Atom | Length/ $\AA$ | Atom | Atom | Length/ $\AA$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Pb 1 | Br 2 | $2.9893(6)$ | C 8 | C 7 | $1.516(13)$ |
| Pb 1 | Br 2 | $2.9845(6)$ | C 6 | C 1 | $1.379(12)$ |
| Pb 1 | Br 2 | $2.9845(6)$ | C 6 | C 5 | $1.385(13)$ |
| Pb 1 | Br 2 | $2.9893(6)$ | C 2 | C 3 | $1.388(13)$ |
| Pb 1 | Br 1 | $3.0048(10)$ | C 3 | C 2 | $1.378(12)$ |
| Pb 1 | Br 1 | $3.0048(10)$ | C 2 | C 1 | $1.399(11)$ |
| F 1 | C 1 | $1.365(14)$ | C 5 | C 4 | $1.400(12)$ |
| N 1 | C 8 | $1.506(9)$ | C 4 | C 7 | $1.504(16)$ |

[^0]Table S3. Bond Angles for 1.

| Atom | Atom | Atom | Angle ${ }^{\circ}$ | Atom | Atom | Atom | Angle ${ }^{\circ}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Br2 | Pb1 | Br2 | 91.685(6) | C6 | C1 | F1 | 118.5(7) |
| Br2 | Pb1 | Br2 | 91.685(6) | C2 | C1 | F1 | 118.5(7) |
| Br2 | Pb1 | Br 2 | 180.0 | C2 | C1 | C6 | 123.0(11) |
| Br2 | Pb1 | Br2 | 180.0 | C1 | C2 | C3 | 118.1(9) |
| Br1 | Pb1 | Br2 | 85.35(2) | C5 | C6 | C1 | 118.2(9) |
| Brl | Br1 | Br1 | 94.65(2) | C5 | C4 | C3 | 118.6(10) |
| Br1 | Pb1 | Br2 | 94.65(2) | C4 | C3 | C 2 | 121.0(9) |
| Br1 | Pb1 | Br2 | 90.30(2) | C4 | C5 | C6 | 121.1(8) |
| Br1 | Pb1 | Br2 | 89.70(2) | C4 | C7 | C8 | 113.3(8) |
| Br1 | Pb1 | Br2 | 90.30(2) | C7 | C8 | N1 | 110.5(6) |
| Brl | Pb1 | Br2 | 89.70(2) | C7 | C4 | C3 | 120.7(7) |
| Brl | Pb1 | Br2 | 85.35(2) | C7 | C4 | C5 | 120.7(6) |
| Brl | Pb1 | Brl | 180.0 |  |  |  |  |


[^0]:    ${ }^{1} 2-X, 1 / 2+Y, 3 / 2-Z ;{ }^{2}+X, 1 / 2-Y, 1 / 2+Z$

