Electronic Supplementary Information

Organic–inorganic Hybrid (CH$_3$NH$_3$)$_2$FeCuI$_4$Cl$_2$ and (CH$_3$NH$_3$)$_2$InCuI$_6$ for Ultraviolet Light Photodetector

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1. Experimental Section
Preparation of solution: The MA$_2$FeCuI$_4$Cl$_2$ solution was prepared as follows. The molar ratio of FeCl$_3$:CuI [Alfaesa (China) Chemistry Co., Ltd.]: MAI (Yingkou OPV Tech New Energy Co. Ltd) was 1:1:5. Firstly, 162.20 mg FeCl$_3$ was dissolved in 1 mL DMF. Subsequently, 190.45 mg CuI was added into above solution. The mixed solution is dissolved well. Finally, 794.5 mg MAI was added into the mixed solution. The MA$_2$FeCuI$_4$Cl$_2$ solution was prepared successfully. In the preparation of the MA$_2$InCuI$_6$ solution, the molar ratio of InI$_3$:CuI:MAI was 1:1:2, and the other preparation steps were the same as that of MA$_2$FeCuI$_4$Cl$_2$.

Fabrication of photodetector device based on MA$_2$FeCuI$_4$Cl$_2$ and MA$_2$InCuI$_6$: Briefly, 15 Ωsq$^{-1}$ FTO-coated glass substrates were cleaned sequentially in a washing liquid, deionized water, and ethanol. In an argon-filled glove box, FTO-coated glass substrates with a sheet resistance of 15 Ω sq$^{-1}$ were covered with a TiO$_2$ compact layer by spin-coating the TiO$_2$ organic sol at 3000 r.p.m. for 30s, tracked by drying at 450°C for 60 min (following our earlier literature). The M-TiO$_2$ layer was coated with a commercial TiO$_2$ paste (18NR-T) diluted in ethanol (1:3.5, weight
ratio) by spin coating at 5000 r.p.m for 30 s, followed by gradually heating to 500 °C and maintained at this temperature for 30 min. After the drying was completed, the solution of \( \text{MA}_2\text{FeCuI}_4\text{Cl}_2 \) was spin-coated by a two-step spin coating method. The parameter settings are 1000 r.p.m for 5 s and 6000 r.p.m for 20 s, then heated at 45 °C for 30 min on the hot plate. Gold electrodes were then deposited by evaporation under high vacuum of \( 1.2 \times 10^{-4} \text{ Pa} \).

**Characterization:** Nanostructures of the films and photodetector devices were analyzed by scanning electron microscopy (Thermo Fisher Scientific SEM GX4). The photocurrent density–time performance at different wavelengths and electrochemical impedance of photodetector device were carried out by an electrochemical workstation system (ZAHNER CIMPS-2 pro, Germany). The electrochemical impedance is carried out from 1 MHz to 0.05Hz. The photocurrent of devices was measured under the bias voltage of 0.00 V. The physical property of \( \text{MA}_2\text{InCuI}_6 \) compounds were measured by Hall effect measurement system (MMR technologies. Inc. USA). The test parameters are as follows: (magnetic field intensity: 0.5 T, thickness of \( \text{MA}_2\text{InCuI}_6 \) film: 500 nm, area: \( 1 \times 1 \text{ cm} \)). UV–vis absorption spectra were recorded using a UV–vis–NIR spectrometer (PerkinElmer, \( \lambda \), 750S).

2. Results

![Figure S1 X-ray diffraction patterns of \( \text{MA}_2\text{FeCuI}_4\text{Cl}_2 \) and \( \text{MA}_2\text{InCuI}_6 \) film](image)

Figure S1 X-ray diffraction patterns of \( \text{MA}_2\text{FeCuI}_4\text{Cl}_2 \) and \( \text{MA}_2\text{InCuI}_6 \) film
The XRD patterns of MA$_2$FeCuI$_4$Cl$_2$ and MA$_2$InCuI$_6$ are shown in the Figure S1. The diffraction peaks of MA$_2$FeCuI$_4$Cl$_2$ appear at 10.51, 32.01 and 43.01 degrees. According to Bragg law $2d\sin\theta=n\lambda$ (where $d$, interplanar distance, $\lambda$, wavelength of the incident X-ray beam, $\theta$, diffraction angle), the interplanar distance of 10.51 degrees is about 8.3 Å. The large interplanar distance indicates that MA$_2$FeCuI$_4$Cl$_2$ is layered structure. We speculate that the corresponding crystal planar of diffraction peaks at 10.51, 32.01 and 43.01 degrees should be (001), (003) and (004), respectively. The position of the diffraction peak at the minimum diffraction angle for MA$_2$InCuI$_6$ is 13.35 degrees. The results show that the interplanar distance of MA$_2$InCuI$_6$ is smaller than that of MA$_2$FeCuI$_4$Cl$_2$. Thus, MA$_2$InCuI$_6$ is a three-dimensional-like perovskite structure. This may be the reason for its better photoelectric performance than that of MA$_2$FeCuI$_4$Cl$_2$.

Table S1 Physical properties of MA$_2$InCuI$_6$ at 300.0 K

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (ohm*cm)</td>
<td>+1.9303E+04</td>
</tr>
<tr>
<td>Mobility (cm$^2$/Vs)</td>
<td>-1.0860E+04</td>
</tr>
<tr>
<td>Density (cm$^3$)</td>
<td>-2.9774E+10</td>
</tr>
<tr>
<td>Hall Coeff. (cm$^3$/Coul)</td>
<td>-2.0965E+08</td>
</tr>
<tr>
<td>Sheet Res. (ohm/cm$^2$)</td>
<td>+1.9303E+08</td>
</tr>
<tr>
<td>Type of Carriers</td>
<td>Electrons</td>
</tr>
</tbody>
</table>

Figure S2 The absorption spectra of MA$_2$FeCuI$_4$Cl$_2$ and MA$_2$InCuI$_6$
The charge transfer resistance ($R_{ct1}$) and constant phase element ($CPE_1$) come from the charge transfer between organic-inorganic hybrid materials and TiO$_2$. The charge transfer resistance ($R_{ct2}$) and constant phase element ($CPE_2$) come from the charge transfer between organic-inorganic hybrid materials and Au electrode.