**Supporting Information For**

# (3-Phenylpyridin-1-ium)$SbI_4$: Coulomb Interaction-Assembled Lead-free Hybrid Perovskite-like Semiconductor

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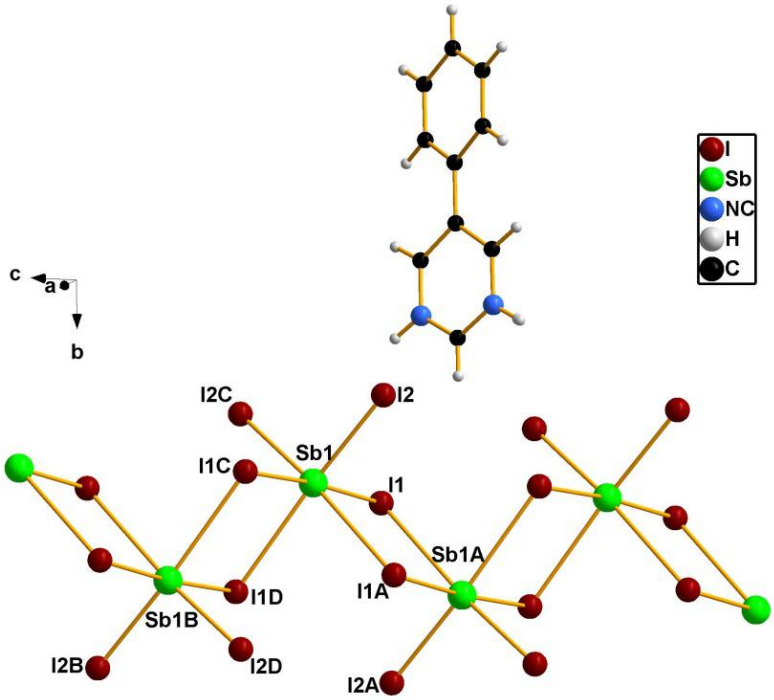


**Figure S1.** The molecular structure of **3ppi-SbI$_4$**. Symmetry codes: A 1-x, 2-y, 1-z; B 1-x, 2-y, 2-z; C 1-x, y, 1.5-z; D x, 2-y, 1/2-+z.

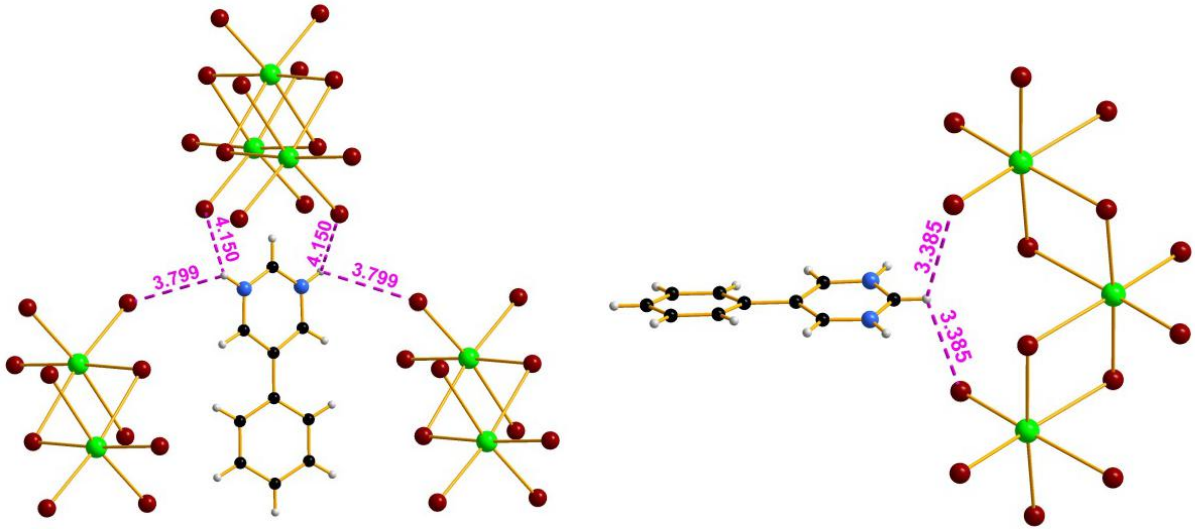


**Figure S2.** The shortest distances between I and H atoms between the organic and inorganic moieties, which exceeds the sum of the relevant van der Waals radii of 3.08 Å.

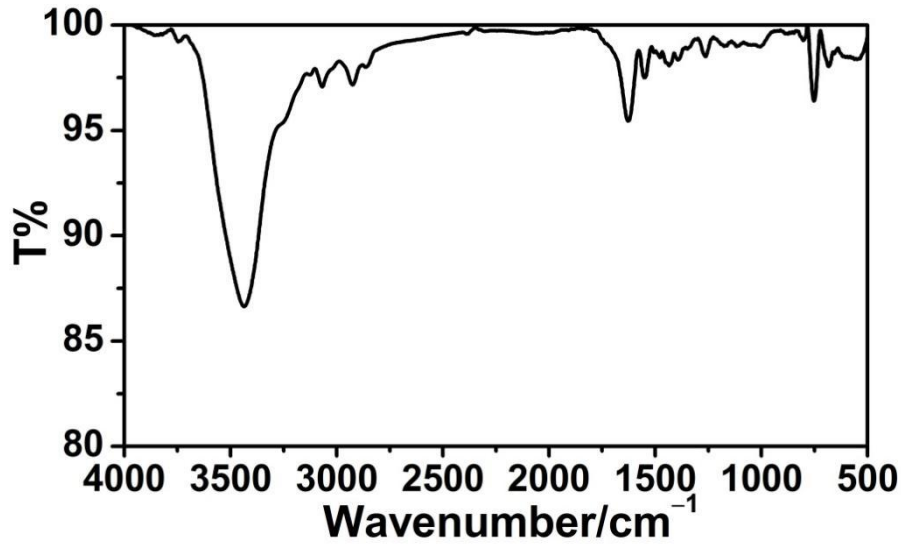


**Figure S3.** IR spectrum of **3ppi-SbI$_4$**.

**IR analysis:** The relatively weak bands in the region of 3100–3050 cm$^{-1}$ correspond to the C–H vibrations of the aromatic ring hydrogen atoms, ν(=C–H). The bands of ring vibrations of the conjugated ligand (ν(C=C) and ν(C=N)) are observed at 1650–1400 cm$^{-1}$, suggesting the presence of **3ppi** cation. The existence of protonated pyridine-N atom can also be confirmed by their IR spectra. The IR bands at 2950–2840 cm$^{-1}$ are attributed to the N–H$^+$ stretching vibrations of ≡NH$^+$.[1] The strong band at ~ 3440 cm$^{-1}$ is assigned to the stretching of trace water since the measurements were conducted in air. In brief, the above results are all in agreement with the single crystal X-ray diffraction studies.

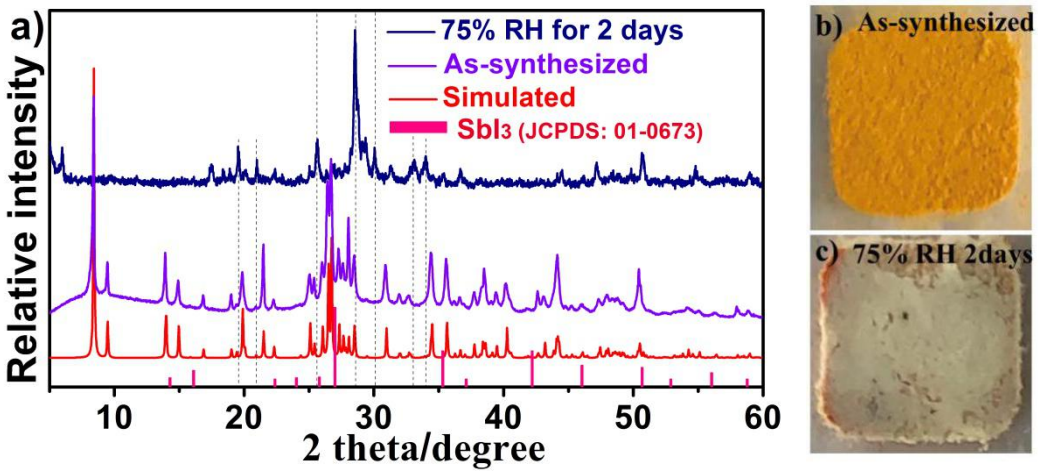


**Figure S4.** (a) The PXRD pattern of **3ppi-SbI$_4$** after two days 75% RH treatment. (b, c) The photographs of the related powdery samples before and after moisture stability experiments.

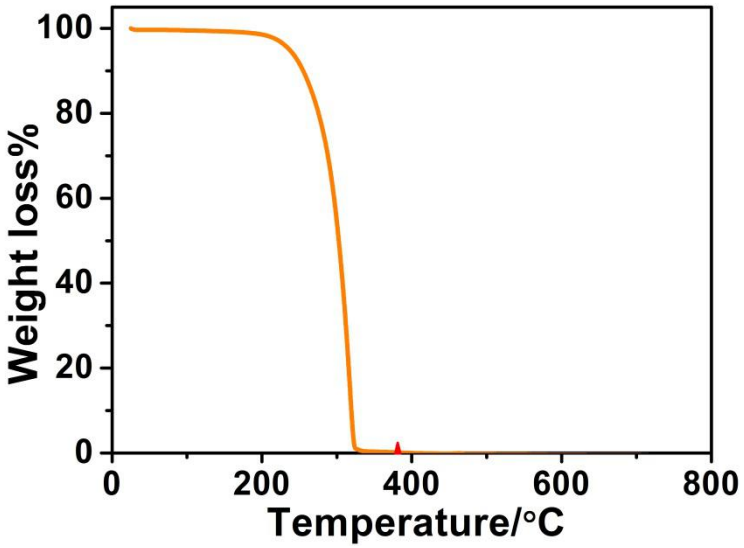


**Figure S5.** The TGA curve for **3ppi-SbI$_4$**.

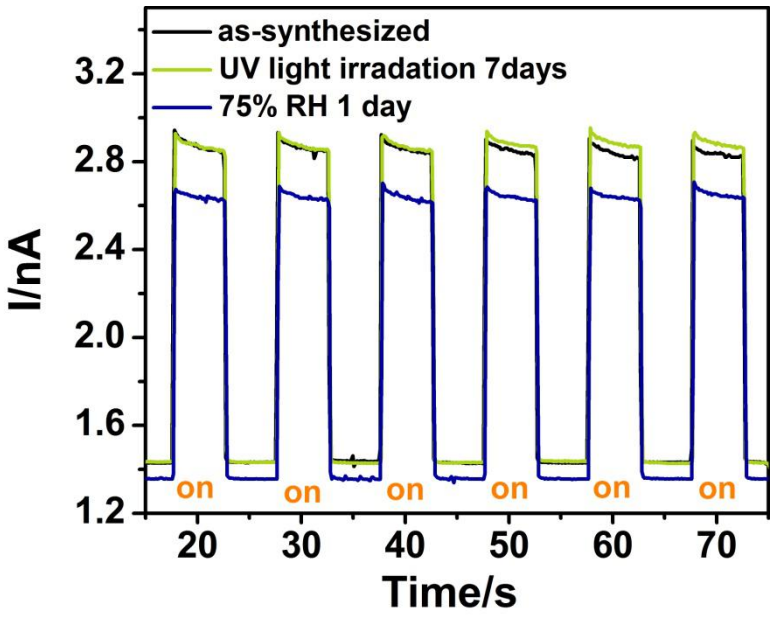


**Figure S6.** The I-T curves for **3ppi-SbI$_4$**.

**Table S1. Selected Bond Distances (Å) and Angles (°) for 3ppi-SbI$_4$.**

| **3ppi-SbI$_4$** | | | |
|---|---|---|---|
| Bond | (Å) | Bond | (Å) |
| I(1)-Sb(1) | 3.0230(2) | C(3)-C(4) | 1.393(3) |
| I(2)-Sb(1) | 2.8500(2) | C(4)-C(3)#2 | 1.393(3) |

| | | | |
|---|---|---|---|
| Sb(1)-I(1)#1 | 3.02299(18) | C(4)-C(5) | 1.474(5) |
| Sb(1)-I(2)#1 | 2.8500(2) | C(5)-C(6)#2 | 1.383(4) |
| N(1)-C(6) | 1.350(4) | C(5)-C(6) | 1.383(4) |
| N(1)-C(8) | 1.319(4) | C(6)-C(7) | 1.350(4) |
| C(1)-C(2)#2 | 1.390(4) | C(7)-C(8) | 1.319(4) |
| C(1)-C(2) | 1.390(4) | C(8)-N(1)#2 | 1.319(4) |
| C(2)-C(3) | 1.356(4) | C(8)-C(7)#2 | 1.319(4) |
| | | | |
| Angle | (°) | Angle | (°) |
| I(1)#1-Sb(1)-I(1) | 175.965(9) | C(3)#2-C(4)-C(5) | 121.13(18) |
| I(2)-Sb(1)-I(1)#1 | 89.111(6) | C(3)-C(4)-C(5) | 121.12(18) |
| I(2)#1-Sb(1)-I(1)#1 | 93.589(6) | C(6)-C(5)-C(4) | 123.75(18) |
| I(2)#1-Sb(1)-I(1) | 89.111(6) | C(6)#2-C(5)-C(4) | 123.75(18) |
| I(2)-Sb(1)-I(1) | 93.590(6) | C(6)#2-C(5)-C(6) | 112.5(4) |
| I(2)-Sb(1)-I(2)#1 | 96.044(9) | C(2)-C(1)-C(2)#2 | 119.0(4) |
| C(8)-N(1)-C(6) | 121.1(3) | C(7)-C(6)-C(5) | 123.1(3) |
| N(1)-C(6)-C(5) | 123.1(3) | C(8)-C(7)-C(6) | 121.1(3) |
| N(1)-C(8)-N(1)#2 | 118.9(4) | C(3)-C(2)-C(1) | 120.3(3) |
| C(3)-C(4)-C(3)#2 | 117.8(4) | C(7)-C(8)-C(7)#2 | 118.9(4) |

Symmetry transformations used to generate equivalent atoms: #1 -x+1, y, -z+3/2; #2 -x+1, y, -z+1/2.

**Reference**

1. G. N. Liu, J. R. Shi, X. J. Han, X. Zhang, K. Li, J. Li, T. Zhang, Q. S. Liu, Z. W. Zhang, C. C. Li, *Dalton Trans.,* **2015,** *44*, 12561-12575.