Supplementary Information

Inch-sized single crystal of radiation-sensitive copper-based hybrid perovskite for direct X-ray detection

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Experiment

Synthesis and crystal growth

$CuCO_3 \cdot Cu(OH)_2$ (0.22 g, 1 mmol) was dissolved in a 38% w/w aqueous HCl solution (5 mL) by heating under constant stirring. Subsequently, 2,2-difluoroethanamine (0.167 g, 2 mmol) was added to form $(2FEA)_2CuCl_4$ microcrystals in the solution. This solution was heated until the initial microcrystalline was completely dissolved. Large crystals grew in a closed temperature-controlled oven. The temperature decreased at the rate of 1 K day^{-1}. A few days later, a size of 30 × 28 × 0.5 mm^3 single crystal was acquired.

Single crystal and powder X-ray diffraction

We utilized Mo Ka radiation at 200 K on a Super Nova diffractometer to obtain single crystal X-ray diffraction (SC-XRD) data for $(2FEA)_2CuCl_4$. Our crystal structure was solved through the direct method and refined by full-matrix least-squares method refinements on F2 using the SHELXLTL software. Using the difference Fourier transform, we determined the non-hydrogen atoms and hydrogenated the hydrogen atoms according to our knowledge of structural chemistry. **Table S1** outlines the crystal data and structural refinement of $(2FEA)_2CuCl_4$. We also performed powder X-ray diffraction of $(2FEA)_2CuCl_4$ on a Rigaku by MiniFlex 600 diffractometer at room temperature, collecting diffractograms at a scan speed of 7.0 degrees per minute over a 2θ range from 5° to 40°.

Optical measurement

UV-visible diffuse reflectance spectroscopy was carried out at ambient temperature, with the scanning wavelength ranging from 200 to 800 nm, using a Lambda 950 spectrometer. The reference material with a reflectivity of 100% was $BaSO_4$.

Fabrication and measurement of X-ray detector

The vertical-type detectors have been engineered to stand perpendicular to the surface of $(2FEA)_2CuCl_4$ single crystals. Silver (Ag) electrodes were evenly applied across the opposing faces of the crystal, which measures 0.7 mm in thickness, covering an electrode area of 5.2 mm^2. We conducted the photoconductive assessments in the presence of X-ray radiation, set at an energy level of 80 keV. The rate of radiation dose was precisely calibrated using a standard commercial dosimeter.

Degree of octahedral distortion

The average octahedral elongation, Δd, is calculated as:

$$\Delta d = \sum_{i=1}^{6} \frac{(d_i - d_0)^2}{6}$$

where d_i represents the individual Cu-Cl bond lengths and is the average Cu-Cl bond length. Calculated according to **Table S2**, Δd is 0.01454.

The bond angle variance, σ^2, is calculated as:

$$\sigma_\theta^2 = \sum_{i=1}^{12} \frac{(\theta_i - 90°)^2}{11}$$

where θ_i represents the individual Cl-Cu-Cl bond angles. Calculated according to **Table S3**, σ^2 is 0.46.

Table S1 Crystal data and structure refinement for $(2FEA)_2CuCl_4$.

Identification code	$(2FEA)_2CuCl_4$
Empirical formula	$C_4H_{12}Cl_4CuF_4N_2$
Formula weight	369.50
Temperature/K	300.16
Crystal system	monoclinic
Space group	*C*2/*c*
a/Å	22.958(5)
b/Å	7.4311(13)
c/Å	7.3162(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1248.2(4)
Z	4
ρ_{calc}g/cm^3	1.966
μ/mm^{-1}	2.625
F(000)	732.0
Crystal size/mm^3	30 × 28 × 0.5
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.762 to 55.002
Index ranges	$-29 \le h \le 28$, $-9 \le k \le 8$, $-9 \le l \le 8$
Reflections collected	3437
Independent reflections	1421 [R_{int} = 0.0776, R_{sigma} = 0.0828]
Data/restraints/parameters	1421/49/72
Goodness-of-fit on F^2	1.149
Final *R* indexes [I>=2σ (I)]	R_1 = 0.1419, wR_2 = 0.3735
Final *R* indexes [all data]	R_1 = 0.1549, wR_2 = 0.3849
Largest diff. peak/hole / e Å^{-3}	1.56/-1.07

Table S2 Bond Lengths for $(2FEA)_2CuCl_4$.

Atom	Atom	Length/Å
Cu (01)	Cl (02)1	2.303(3)
Cu (01)	Cl (02)	2.303(3)
Cu (01)	Cl (02)2	2.925(3)
Cu (01)	Cl (03)	2.269(4)
Cu (01)	Cl (03)1	2.269(4)
N (1)	C (5)	1.48(5)
C (5)	C (8)	1.406(19)
C (8)	F (1)	1.347(14)
C (8)	F (2)	1.355(14)

Table S3 Bond Angle for $(2FEA)_2CuCl_4$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl02	Cu01	$Cl02^1$	180.0	$Cl03^1$	Cu01	$Cl02^2$	89.90(16)
Cl02	Cu01	$Cl02^2$	90.95(3)	Cl03	Cu01	$Cl02^3$	89.90(16)
Cl02	Cu01	$Cl02^3$	89.05(3)	$Cl03^1$	Cu01	$Cl02^3$	90.10(16)
$Cl02^3$	Cu01	$Cl02^2$	180.0	Cl03	Cu01	$Cl02^2$	90.10(16)
$Cl02^1$	Cu01	$Cl02^2$	89.05(3)	$Cl03^1$	Cu01	Cl03	180.00(2)
$Cl02^1$	Cu01	$Cl02^3$	90.95(3)	C8	C5	N1	114(3)
Cl03	Cu01	Cl02	90.52(18)	F1	C8	C5	119(5)
$Cl03^1$	Cu01	Cl02	89.48(18)	F1	C8	F2	96(4)
$Cl03^1$	Cu01	$Cl02^1$	90.52(18)	F2	C8	C5	119(3)
Cl03	Cu01	$Cl02^1$	89.48(18)				

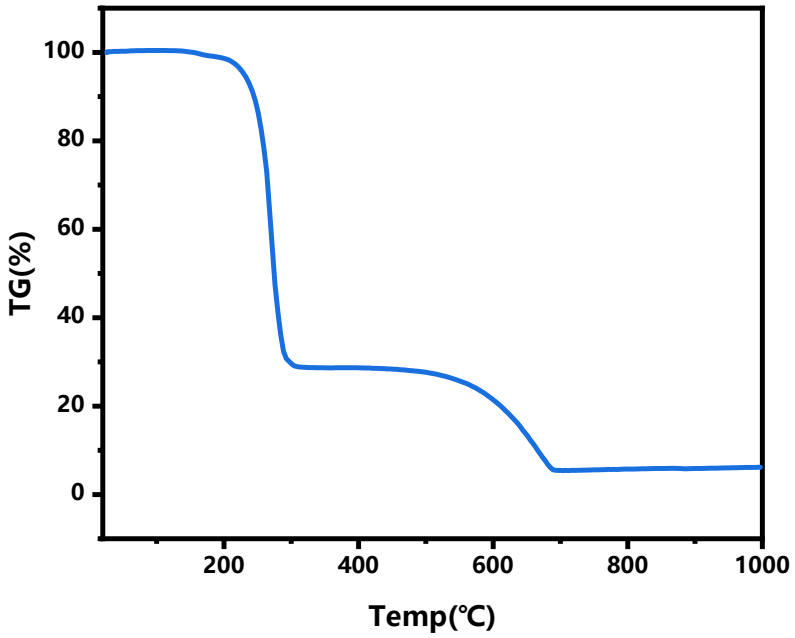

Figure S1 The TG curve of $(2FEA)_2CuCl_4$.

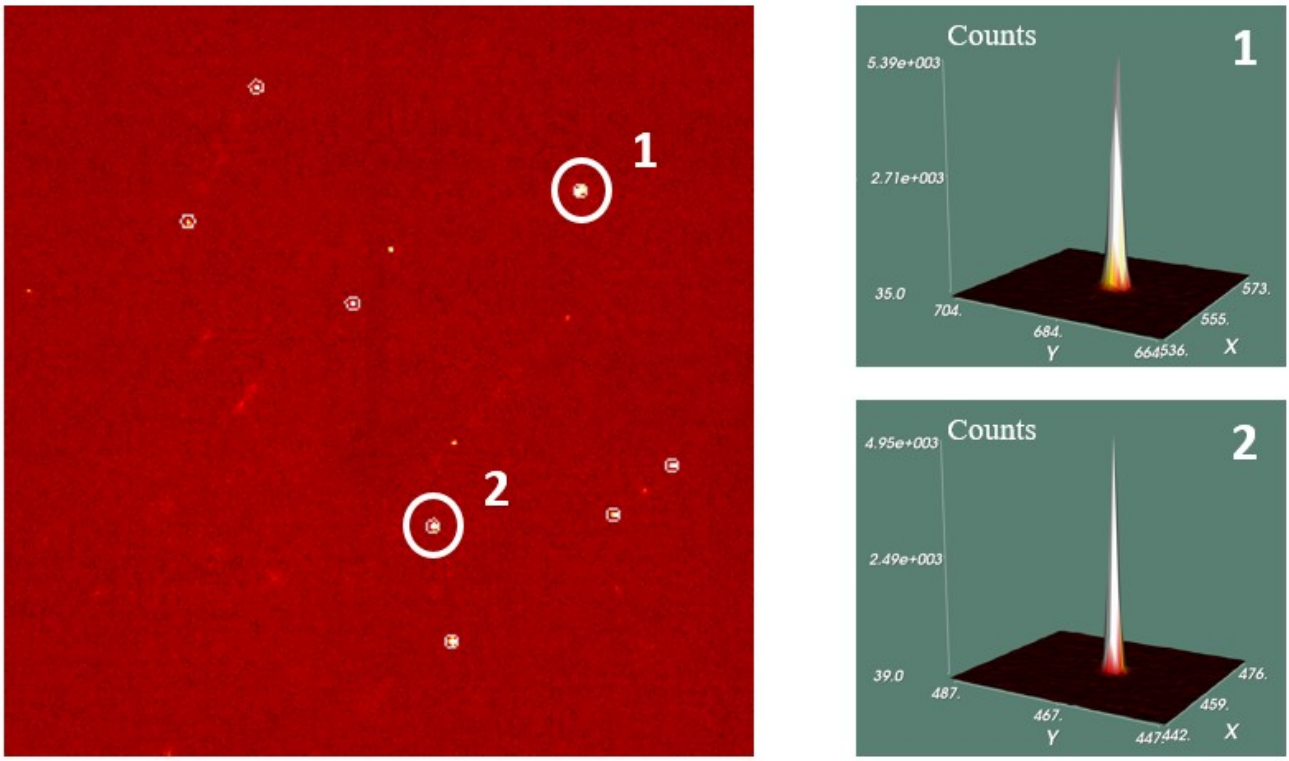

Figure S2 SCXRD diffraction spots of $(2FEA)_2CuCl_4$.

Table S4 Performances of some reported halide perovskite X-ray SC detectors.

Compound	Dimensionality	μτ ($cm^2 V^{-1}$)	LoD ($\mu Gy s^{-1}$)	Sensitivity ($\mu C Gy^{-1} cm^{-2}$)	Refs.
$(3AP)PbCl_4$	2D	2.74×10^{-3}	1.54	791.8	1
$(3AP)PbBr_4$	2D	2.38×10^{-3}	3.04	348.6	1
$(3AP)PbI_4$	2D	2.61×10^{-3}	3.483	124.9	1
$(BDA)PbI_4$	2D	4.43×10^{-4}	0.34	242	2
$MAPbBr_3$	3D	1.2×10^{-2}	0.5	80	3
$(R\text{-}MPA)_4AgBiI_8$	2D	2.2×10^{-5}	0.547	949.6	4
$(2FEA)_2CuCl_4$	2D	5.06×10^{-4}	0.130	1106.44	This work

Reference

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