

Supporting Information

**Ferroelasticity, thermochromism, semi-conductivity,
and ferromagnetism in a new layered perovskite:
(4-fluorophenethylaminium)₂[CuCl₄]**

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Table S1. Crystal data and structure refinement parameters for **1** at RTP, ITP, and HTP.

Compound	1		
Formula	(FPEA) ₂ [CuCl ₄]		
<i>T</i> /K	298(1)	365(1)	415(1)
Phases	RTP	ITP	HTP
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>A</i> 2/ <i>m</i>	<i>Cmce</i>
<i>a</i> /Å	20.0414(5)	20.4140(9)	40.211(5)
<i>b</i> /Å	7.3061(2)	7.3636(3)	7.3967(3)
<i>c</i> /Å	7.3103(2)	7.3256(2)	7.3999(4)
β /°	96.732(2)	100.344(3)	90
<i>V</i> /Å ³	1063.03(5)	1083.29(7)	2201.0(3)
<i>Z</i>	2	2	4
ρ_{calc} /g cm ⁻³	1.517	1.489	1.466
μ /mm ⁻¹	6.251	6.134	6.038
Reflections collected	3816	3423	5878
Independent reflections	2077	1183	1045
$R_1^a/wR_2^b [I \geq 2\sigma(I)]$	0.0449,0.1234	0.0414,0.1112	0.0978,0.2765
R_1^a/wR_2^b (all data)	0.0481,0.1285	0.0426,0.1138	0.1262,0.3325
GOF	1.045	1.120	1.082
CCDC number	2130391	2130394	2130395

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2 \}^{1/2}$$

Table S2. Selected bond lengths (Å) and bond angles (°) for **1** at RTP, ITP, and HTP.

(FPEA) ₂ [CuCl ₄]				
RTP	Cu1–Cl1	2.2866(6)	Cu1–Cl1C	2.8963(6)
	Cu1–Cl1A	2.2866(6)	Cu1–Cl2	2.2978(7)
	Cu1–Cl2A	2.2977(7)	Cl1–Cu1B	2.8963(6)
	∠Cl1–Cu1–Cl1A	180	∠Cl1A–Cu1–Cl1B	89.931(5)
	∠Cl1–Cu1–Cl1B	90.068(5)	∠Cl1A–Cu1–Cl1C	90.069(5)
	∠Cl1C–Cu1–Cl1B	180	∠Cl1–Cu1–Cl1C	89.932(5)
	∠Cl1–Cu1–Cl2A	90.10(3)	∠Cl2A–Cu1–Cl1C	88.36(2)
	∠Cl2A–Cu1–Cl1B	91.64(2)	∠Cl2–Cu1–Cl1C	91.64(2)
	∠Cl2–Cu1–Cl1B	88.36(2)	∠Cl1A–Cu1–Cl2	90.10(3)
	∠Cl2A–Cu1–Cl2	180		
	A) 1–x, 1–y, –z; B) 1–x, –1/2+y, 1/2–z;; C) +x, 3/2–y, –1/2+z			
ITP	Cu1–Cl2A	2.2870(9)	Cu1–Cl2	2.2870(8)
	Cu1–Cl1B	2.2839(7)	Cu1–Cl1C	2.2839(7)
	Cu1–Cl1D	2.910(2)	Cu1–Cl1E	2.910(2)
	∠Cl2A–Cu1–Cl2	180	∠Cl1D–Cu1–Cl2A	89.83(1)
	∠Cl1E–Cu1–Cl2	89.83(1)	∠Cl1–Cu1–Cl2	90.43(17)
	∠Cl1–Cu1–Cl2A	89.57(17)	∠Cl1E–Cu1–Cl2A	90.17(1)
	∠Cl1D–Cu1–Cl2	90.17(1)	∠Cl1A–Cu1–Cl2A	90.43(17)
	∠Cl1A–Cu1–Cl2	89.57(17)	∠Cl1D–Cu1–Cl1	90.25(4)
	∠Cl1A–Cu1–Cl1	180	∠Cl1E–Cu1–Cl1A	90.25(4)
	∠Cl1D–Cu1–Cl1A	89.75(4)	∠Cl1D–Cu1–Cl1E	180
	∠Cl1E–Cu1–Cl1	89.75(4)		
	A) 1–x, 1–y, 1–z; B) 1–x, +y, 1–z; C) +x, 1–y, +z; D) 1–x, 1/2+y, 3/2–z; E) 1–x, 1/2–y, –1/2+z.			
HTP	Cu1–Cl2	2.283(4)	Cu1–Cl2A	2.283(4)
	Cu1–Cl1B	2.953(2)	Cu1–Cl1	2.278(2)
	Cu1–Cl1A	2.278(2)	Cl1–Cu1C	2.953(2)
	∠Cl2A–Cu1–Cl2	180	∠Cl1A–Cu1–Cl2A	90
	∠Cl1A–Cu1–Cl2	90	∠Cl1–Cu1–Cl2A	90
	∠Cl1–Cu1–Cl2	90	∠Cl1–Cu1–Cl1A	180
	A) 1–x, 1–y, 1–z; B) +x, –1/2+y, 1/2–z; C) +x, 3/2–y, –1/2+z.			

Table S3. N–H···Cl hydrogen bonds of **1** at RTP, ITP, and HTP.

	D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	< DHA	<i>d</i> (D···A)
RTP	N1–H1A···Cl1	0.89	2.39	170.4	3.273(3)
	N1–H1B···Cl2A	0.89	2.50	165.9	3.370(3)
	N1–H1C···Cl1B	0.89	2.65	133.0	3.317(3)
	N1–H1C···Cl2C	0.89	2.80	142.4	3.548(3)
	A) 1– <i>x</i> , –1/2+ <i>y</i> , 1/2– <i>z</i> ; B) + <i>x</i> , 3/2– <i>y</i> , 1/2+ <i>z</i> ; C) 1– <i>x</i> , 1– <i>y</i> , 1– <i>z</i> .				
ITP	N1–H1A···Cl1A	0.89	2.64	133.5	3.313(12)
	N1–H1A···Cl1B	0.89	2.76	123.3	3.330(12)
	N1–H1B···Cl1C	0.89	2.51	172.7	3.394(15)
	N1–H1B···Cl2D	0.89	2.53	168.7	3.407(16)
	N1A–H1C···Cl1E	0.89	2.77	129.8	3.414(14)
	A) + <i>x</i> , 1– <i>y</i> , –1+ <i>z</i> ; B) 1– <i>x</i> , 1/2+ <i>y</i> , 1/2– <i>z</i> ; C) 1– <i>x</i> , 1– <i>y</i> , 1– <i>z</i> ; D) + <i>x</i> , 1/2+ <i>y</i> , –1/2+ <i>z</i> ; E) + <i>x</i> , 1/2– <i>y</i> , –1/2+ <i>z</i> .				
HTP	N1–H1A···Cl1	0.89	2.89	113.96	3.356
	N1–H1A···Cl1A	0.89	2.89	119.01	3.414
	N1–H1B···Cl1B	0.89	2.53	147.28	3.315
	A) <i>x</i> , <i>y</i> +1/2, – <i>z</i> +1/2; B) – <i>x</i> +1, – <i>y</i> +3/2, <i>z</i> +1/2				

Table S4. The state energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of **1**.

<i>k</i>-point	L-CB	H-VB
Z (0.000, 0.000, 0.500)	2.21975	−0.30798
G (0.000, 0.000, 0.000)	2.39111	−0.00032
Y (0.000, 0.500, 0.000)	2.24141	−0.27762
A (−0.500, 0.500, 0.000)	2.24146	−0.27749
B (−0.500, 0.000, 0.000)	2.39114	0
D (−0.500, 0.000, 0.500)	2.21968	−0.30906
E (−0.500, 0.500, 0.500)	2.37831	−0.10966
C (0.000, 0.500, 0.500)	2.37829	−0.10965

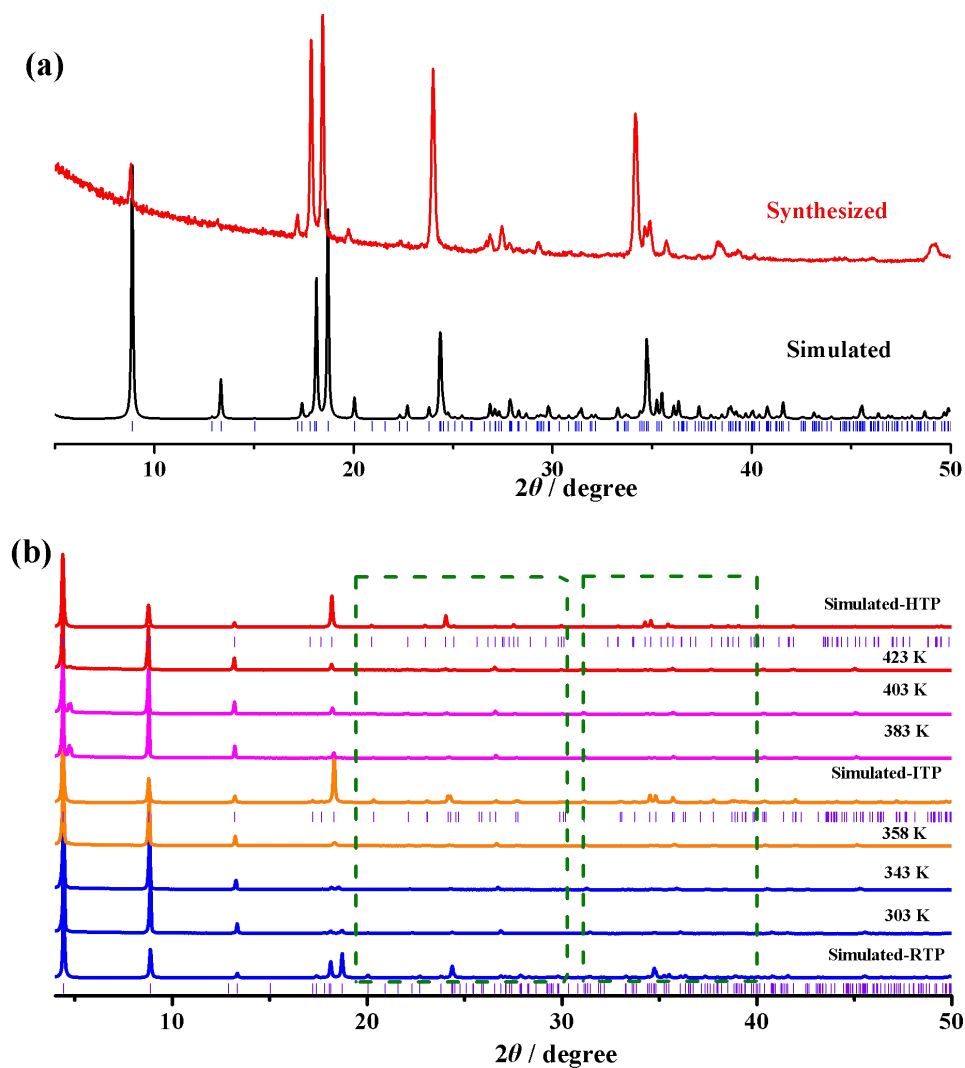


Figure S1. The experimental PXRD pattern of the as-synthesized powder sample (red) and the simulated PXRD pattern (black) based on the single-crystal structure at room-temperature; (b) Variable-temperature PXRD patterns of **1**.

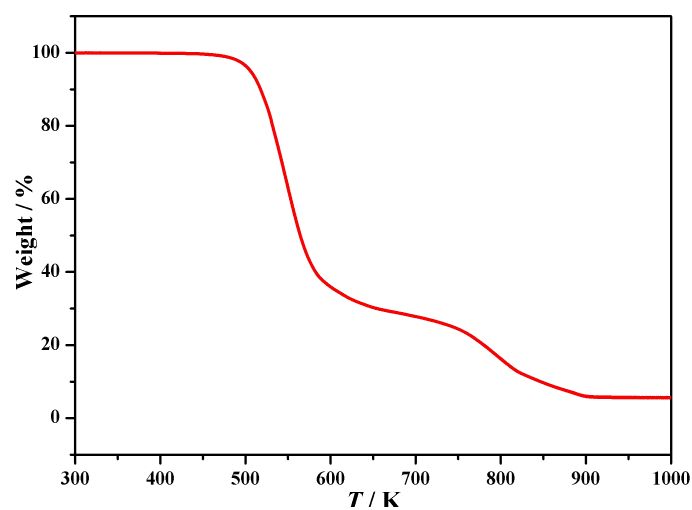


Figure S2. Thermogravimetric analysis (TGA) curve of **1**.

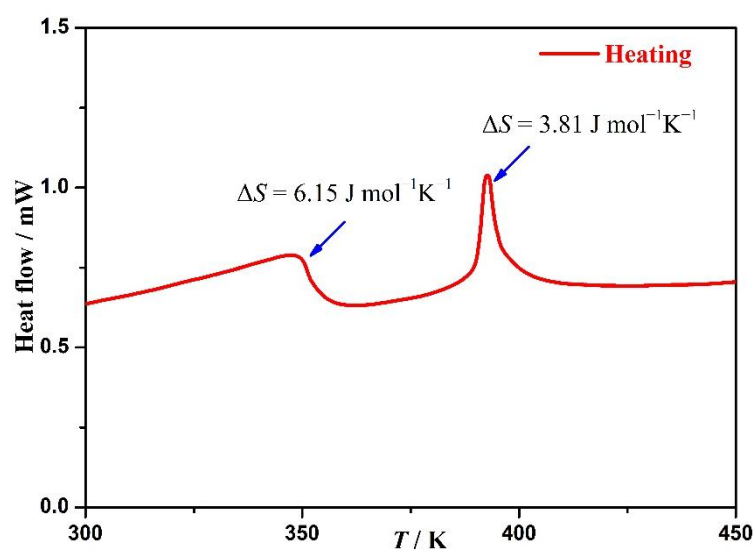


Figure S3. The total entropy changes (ΔS) of phase transitions in the heating process.

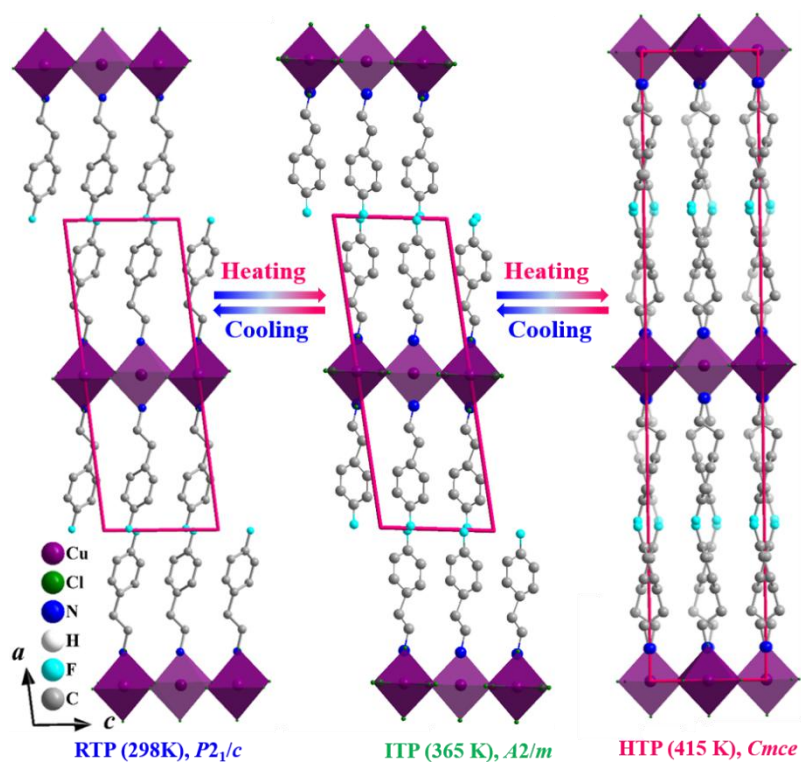


Figure S4. The structures of **1** in RTP, ITP, and HTP viewed along the b axis.

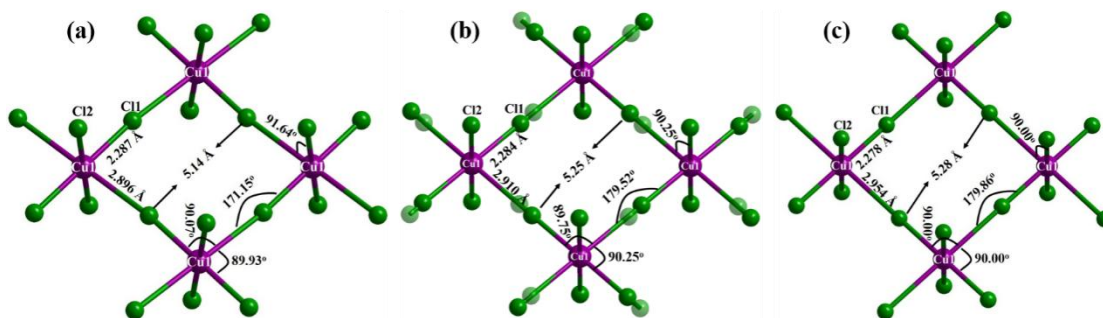


Figure S5. The structural parameters of inorganic layers in RTP, ITP, and HTP.

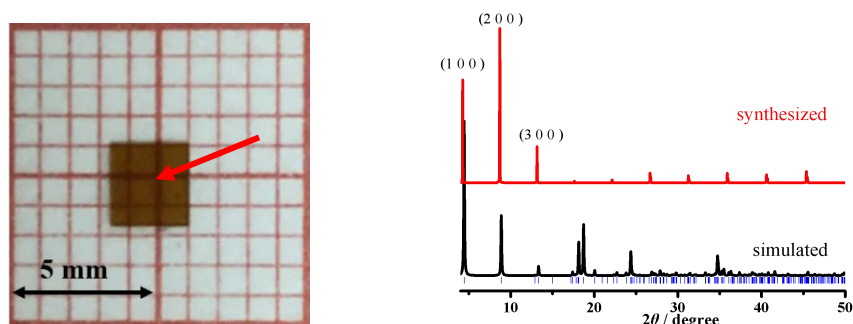


Figure S6. Morphology of a single crystal and its measured PXRD pattern showing that the normal of the largest exposed crystal plane is the a axis.

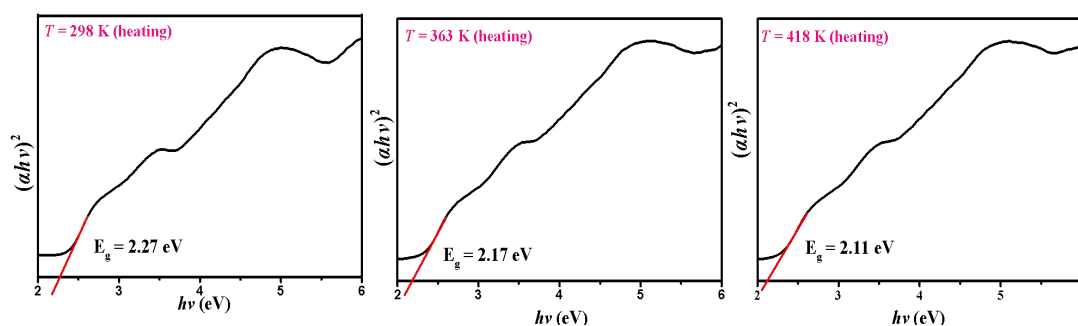


Figure S7. The extrapolated optical band gaps for RTP, ITP, and HTP.

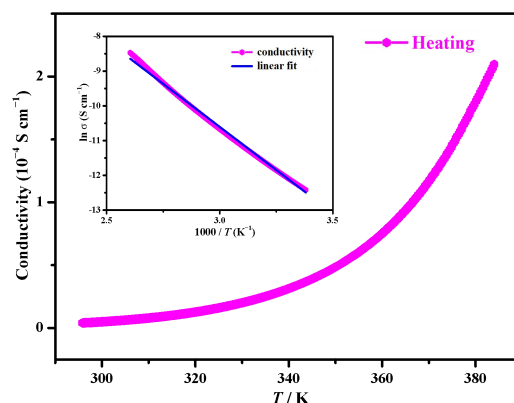


Figure S8. Temperature-dependent conductivity of $(\text{PEA})_2[\text{CuCl}_4]$. Inset: blue line indicates fitting of the data to the Arrhenius equation, yielding an average value for E_a of 0.428 eV.

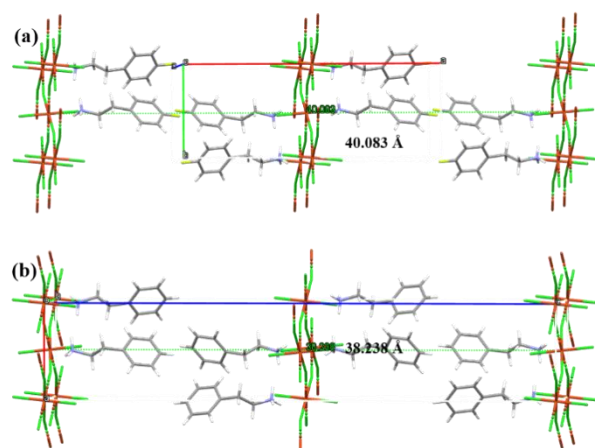


Figure S9. Distance between adjacent inorganic layers of **1** (a) and (PEA)₂[CuCl₄] (b).

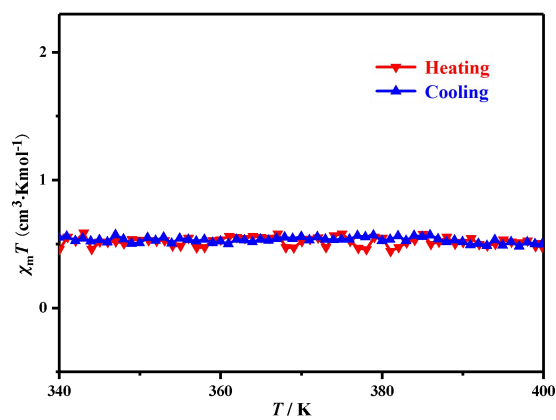


Figure S10. Temperature dependence of $\chi_m T$ measured in a heating-cooling cycle during 340-400 K.

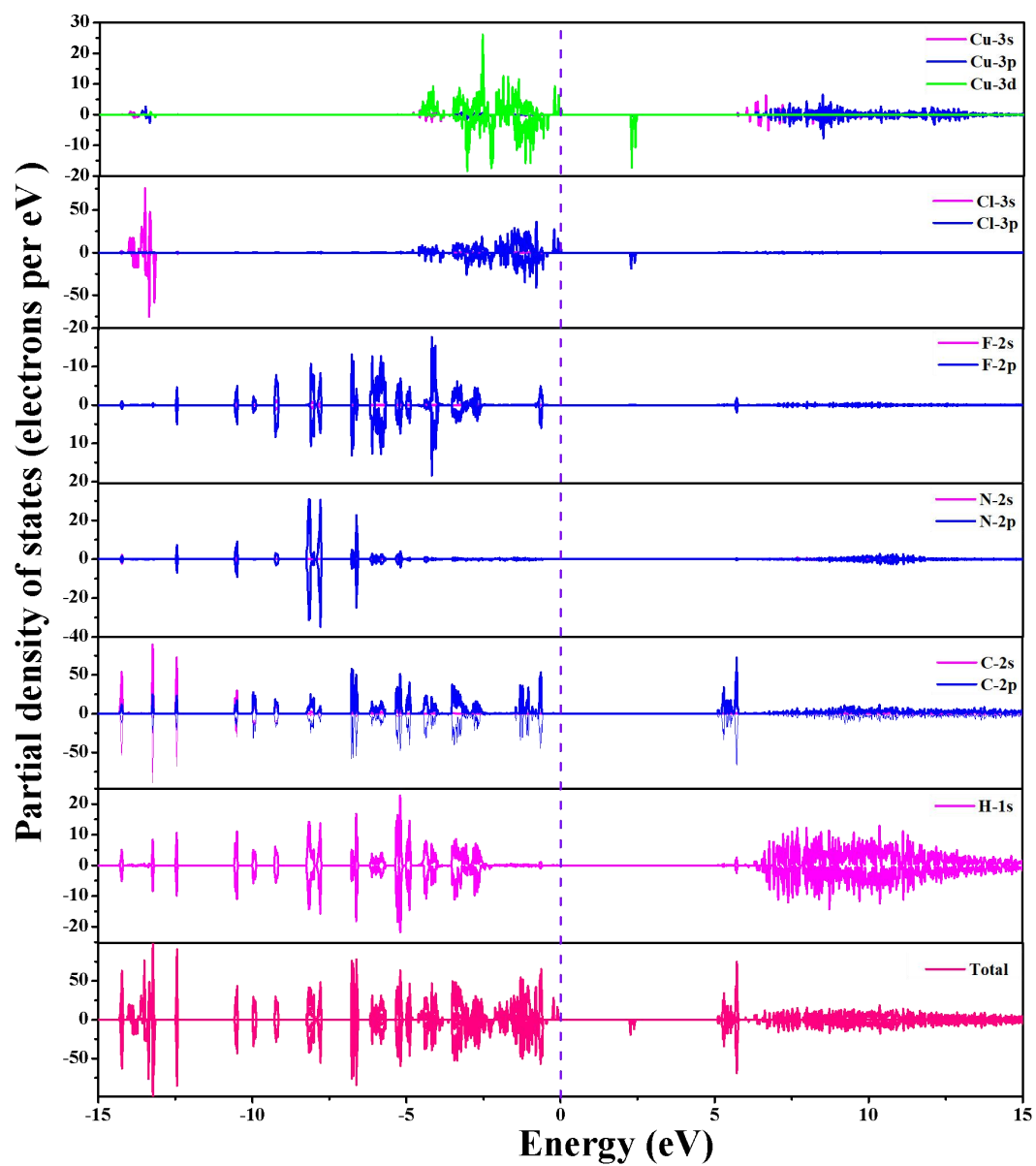


Figure S11. The partial and total density of states of 1.

Computational Method

The single-crystal structure of (FPEA)₂[CuCl₄] at 298 K was used for the theoretical calculations. The electron structure calculations and optical properties were performed on the CASTEP code in the Material Studio package,^{S1-S2} a total energy package based on plane-wave pseudopotential method using density functional theory (DFT). The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof for solids (PBEsol) was used for the exchange-correlation energy.^{S3-S4} The following valence-electron configurations were considered in the computation: Cu-3d¹⁰4s¹, Cl-3s²3p⁵, F-2s²2p⁵, C-2s²2p², N-2s²2p³, H-1s¹. The numbers of plane waves include in the basis sets were determined by a cut-off energy of 850 eV. The numerical integration of the Brillouin zone was performed using a Monkhorst-Pack *k*-point sampling of 1 × 2 × 2.

The calculation of the spontaneous strain

For the present *mmm*F2/*m* species of 1,^{S5} as the cell setting of orthorhombic lattice is different from the monoclinic one, a necessary conversion matrix, (0.5 0 −0.5 0 1 0 0 0 1), was applied for the cell of HTP to match with the monoclinic cell of ITP, giving a converted cell parameters for HTP: $a_0 = 20.443 \text{ \AA}$, $b_0 = 7.397 \text{ \AA}$, $c_0 = 7.400 \text{ \AA}$, $\beta_0 = 100.43^\circ$. Based on geometric relationship, new monoclinic lattice should be:

$$a_0 = \sqrt{\left(\frac{1}{2}a\right)^2 + \left(\frac{1}{2}c\right)^2}$$

$$b_0 = b$$

$$c_0 = c$$

Then the spontaneous strain tensor is give as:⁶

$$\varepsilon_{ij} = \begin{bmatrix} 1 - \frac{a \sin \beta}{a_0 \sin \beta_0} & 0 & \frac{1}{2} \left(\frac{c \cos \beta}{c_0 \sin \beta_0} - \frac{a \cos \beta}{a \sin \beta_0} \right) \\ 0 & 1 - \frac{b}{b_0} & 0 \\ \frac{1}{2} \left(\frac{c \cos \beta}{c_0 \sin \beta_0} - \frac{a \cos \beta}{a \sin \beta_0} \right) & 0 & 1 - \frac{c}{c_0} \end{bmatrix}$$

$$\varepsilon_{ss} = \sqrt{\sum_{i,j} \varepsilon_{ij}^2} = 0.011$$

In the equation, a , b , c and β refer to the cell parameters of low-symmetry form ITP, and a_0 , b_0 and c_0 are the converted triclinic cell parameters of high-symmetry form HTP.

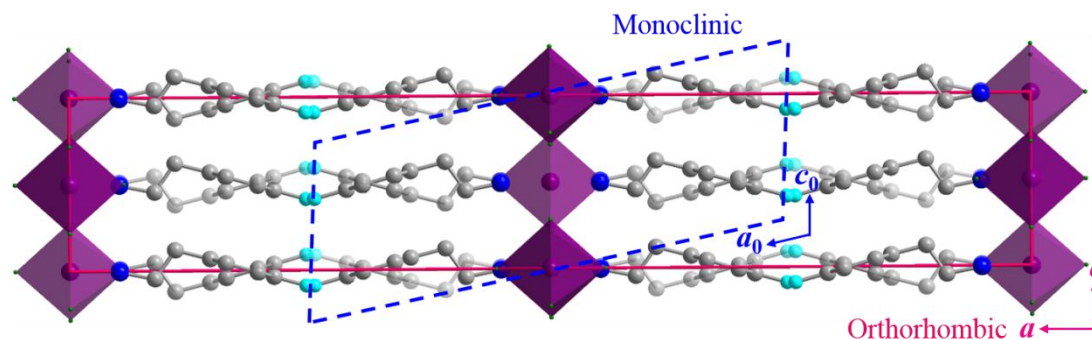


Figure S12. The orthorhombic cell (red) of HTP converted to monoclinic cell (blue) for comparison with the monoclinic unit cell of ITP.

References

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