

Supporting information

$K_4Cu_3(C_3N_3O_3)_2X$ ($X = Cl, Br$): strong anisotropic layered semiconductors containing mixed p - p and d - p conjugated π -bonds

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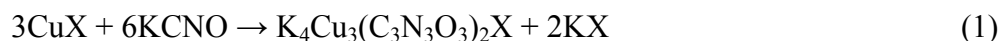
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1. Experimental methods

Solid state reaction. The analytical pure starting reagents CuCl, CuBr and KCNO were directly purchased from Aladdin Co., Ltd and all the manipulations were performed in an Ar-filled glove box with H₂O and O₂ contents less than 0.1 ppm.

Polycrystalline samples of K₄Cu₃(C₃N₃O₃)₂Cl or K₄Cu₃(C₃N₃O₃)₂Br were obtained by traditional solid state reaction in a stoichiometric mixture of CuX (X = Cl or Br) and KCNO according to the equation (1).



The raw materials with appropriate KOCN as a flux were loaded into fused-silica tubes and then, the ampoules were flame-sealed under a high vacuum of 10⁻³ Pa. The tubes were then placed in a computer-controlled furnace and heated to 773 K within 8 h and left for 48 h. After that, the furnace was slowly cooled at a rate of 3 K/h to room temperature. Block samples with a little copper at the bottom were obtained in the tubes. The copper was removed directly. Finally, the products were washed by methanol to remove the chloride.

Single crystal growth. Single crystals of K₄Cu₃(C₃N₃O₃)₂Cl and K₄Cu₃(C₃N₃O₃)₂Br were obtained by spontaneous crystallization. A mixture of CuCl (CuBr) and KCNO with a molar ratio of 1:4 was ground and loaded into a fused-silica tube. The tube was then flame-sealed under a high vacuum of 10⁻³ Pa and heated to 773 K in 8h, left for 48h, cooled to 473 K at a rate of 3 K/h, and finally, the furnace was cooled to room temperature by switching off the furnace. Pale crystals with prismatic-shape and chunk-shape were obtained.

Structure determination. Single-crystal X-ray diffraction data for $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Cl}$ and $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Br}$ were collected at 273K on a Rigaku XtaLAB Synergy four-circle diffractometer equipped with a HyPix-6000HE area detector using Mo $K\alpha$ (PhotonJet-S Mo 50w Microfocus) radiation source, with a frame time of 4 s, a frame width of 0.5° , and a detector distance of 32 mm. Data extraction and integration were carried out with use of the CrysAlisPro software. Structure solution and refinement were carried out with use of the SHELXTL (version 6.12) program package.¹ Initial atomic positions were located by direct methods and refinements proceeded in a straightforward fashion. All atomic sites were confirmed to be fully occupied and exhibited reasonable displacement parameters. No additional symmetry was revealed by the ADDSYM routine in the PLATON suite programs.²

Powder X-ray diffraction. The powder X-ray diffraction pattern of the as-obtained polycrystalline powder was performed at room temperature on a Dandong DX-2700 diffractometer with Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The scanning step width of 0.5° and a fixed counting time 3 s/step were applied to record the patterns in the 2θ range of $10\text{-}60^\circ$. The measured XRD powder pattern matched well with the calculated one generated using the CIF of the refined structure, which verified the purity of the as-synthesized samples.

UV-vis-IR diffuse reflectance spectrum. The spectrum was measured from 200 nm (6.2 eV) to 2000 nm (0.62 eV) on a Cary 7000 UV-vis-NIR spectrophotometer equipped with a diffuse reflectance accessory. A compacted pellet of BaSO_4 was used as a 100% reflectance standard. The bandgaps were obtained according to the Kubelka

- Munk equation: $\alpha/S = (1-R)^2/2R$. Where α , S and R is the absorption, scattering and reflectance coefficients, respectively.

Infrared spectrum. Infrared (IR) spectroscopy was collected on a Varian Excalibur 3100 spectrometer in the 400 – 1800 cm^{-1} range. KBr and samples with mass ratio about 100:1 were mixed thoroughly.

Photocurrent measurement. The transient photocurrent measurement was carried out on an electrochemical workstation (CHI-660E, Chenhua Instruments Co., Ltd) with a standard three-electrode system. The platinum wire and saturated calomel electrode were used as the counter electrode and the reference electrode, respectively. The samples films on indium-tin oxide (ITO) glass prepared by a drip-coating method were applied as the working electrodes. The light source is a 300 W Xe lamp and 0.1 M Na_2SO_4 solution serves as the electrolyte. The applied voltage is 0.0 V.

2. Computational methods.

The first-principles calculations of title $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{X}$ ($\text{X}=\text{Cl}, \text{Br}$) were performed with CASTEP package³ based on plane-wave pseudo-potential methods. All of simulations were modeled on basis of experimental lattices with the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBEsol) functional,⁴ and the optimized norm-conserving pseudopotentials⁵ (K 5s, Cu 3d¹⁰4s, C 2s²2p², N 2s²2p³, O 2s²2p⁴, Cl 3s²3p⁵, Br 4s²4p⁵) were utilized to simulate ion-electron interactions. A kinetic energy cutoff of 850 eV was chosen with dense k -point meshes (8×8×3) in the first Brillouin zone.⁶ An additional charge of +2 was adopted owing to partially occupied ratio 2/3 of K atom in pseudo chemical formula $\text{K}_6\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{X}$. The

choice of these computational parameters is good enough to ensure the accuracy of the present purpose.⁷ The molecular orbitals were plotted band-by-band for *p-p* π -bond in [C₃N₃] ring and *d-p* π -bond in N-Cu-N line. Moreover, the refractive indices and absorption coefficients were simulated by scissor-operator corrected band structure.

Table S1. Crystal data and structure refinements for $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Cl}$ and $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Br}$.

Empirical formula	$\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Cl}$	$\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Br}$
Formula weight	634.59	679.05
Crystal system	Trigonal	Trigonal
Space group	$P\bar{3}m1$	$P\bar{3}m1$
$a/\text{\AA}$	11.1833(9)	11.2089(8)
$c/\text{\AA}$	3.6304(4)	3.7195(4)
Volume/ \AA^3	393.21(6)	404.71(6)
Z	3	3
$\rho_{\text{calc}}/\text{g/cm}^3$	2.680	2.786
μ/mm^{-1}	5.290	7.443
F(000)	306.0	324.0
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
Index ranges	$-13 \leq h \leq 13, -13 \leq k \leq 13, -4 \leq l \leq 4$	$-13 \leq h \leq 11, -14 \leq k \leq 14, -4 \leq l \leq 4$
Reflections collected	3866	4134
Goodness-of-fit on F^2	1.091	1.119
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0335,$ $wR_2 = 0.0893$	$R_1 = 0.0563,$ $wR_2 = 0.1641$
Final R indexes [all data]	$R_1 = 0.0391,$ $wR_2 = 0.0934$	$R_1 = 0.0653,$ $wR_2 = 0.1733$

Table S2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Cl}$.

Atom	S.O.F	x	y	z	Ueq
Cu1	1	0.0000	0.5000	0.0000	0.0446 (4)
K1	2/3	0.0000	0.76381 (16)	0.5000	0.0806 (8)
Cl1	1	0.0000	1.0000	0.0000	0.0443 (6)
C1	1	0.2637 (2)	0.7363 (2)	-0.0002 (11)	0.0458 (11)
O1	1	0.19916 (18)	0.80084 (18)	-0.0002 (11)	0.0632 (10)
N1	1	-0.1921 (4)	0.40394 (18)	-0.0001 (10)	0.0420 (8)

Table S3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Br}$.

Atom	S.O.F	x	y	z	Ueq
Cu1	1	0.0000	0.5000	0.0000	0.0362 (7)
K1	2/3	0.0000	0.7549 (4)	0.5000	0.091 (2)
Br1	1	0.0000	1.0000	0.0000	0.0444 (9)
C1	1	0.2635 (6)	0.7365 (6)	0.000 (2)	0.043 (3)
O1	1	0.1992 (4)	0.8008 (4)	-0.002 (3)	0.057 (2)
N1	1	-0.1936 (8)	0.4032 (4)	0.000 (2)	0.0377 (19)

Table S4. Bond lengths (Å) and angles (degree) for $K_4Cu_3(C_3N_3O_3)_2Cl$.

Cu1—N1 ⁱ	1.861 (3)	Cl1—K1 ⁱⁱ	3.2050 (15)
Cu1—N1	1.861 (3)	Cl1—K1 ^{xi}	3.2050 (15)
K1—O1 ^v	2.739 (3)	Cl1—K1 ^{xii}	3.2050 (15)
K1—O1 ^{vi}	2.739 (3)	Cl1—K1 ^{xv}	3.2050 (15)
K1—O1	2.740 (3)	Cl1—K1 ^{iv}	3.2050 (15)
K1—O1 ^{iv}	2.740 (3)	C1—O1	1.251 (6)
K1—Cl1 ^{vi}	3.2050 (15)	C1—N1 ^{xi}	1.358 (3)
K1—Cl1	3.2050 (15)	C1—N1 ⁱ	1.358 (3)
Cl1—K1 ^{vii}	3.2050 (15)	O1—K1 ⁱⁱ	2.739 (3)
Cl1—K1 ^v	3.2050 (15)	O1—K1 ^{xi}	2.739 (3)
Cl1—K1 ⁱⁱⁱ	3.2050 (15)	O1—K1 ⁱⁱⁱ	2.740 (3)
Cl1—K1 ^{viii}	3.2050 (15)	N1—C1 ^v	1.358 (3)
Cl1—K1 ^{ix}	3.2050 (15)	N1—C1 ⁱ	1.358 (3)
Cl1—K1 ^x	3.2050 (15)		
O1—C1—N1 ^{xi}	119.3 (2)	N1 ^{xi} —C1—N1 ⁱ	121.4 (4)
O1—C1—N1 ⁱ	119.3 (2)	C1 ^v —N1—C1 ⁱ	118.6 (4)

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $x, y, z-1$; (iii) $x-y+1, x+1, -z+1$; (iv) $y-1, -x+y, -z+1$; (v) $y-1, -x+y, -z$; (vi) $x, y, z+1$; (vii) $-y+1, x-y+2, z$; (viii) $-x, -y+2, -z+1$; (ix) $-x+y-1, -x+1, z-1$; (x) $-y+1, x-y+2, z-1$; (xi) $x-y+1, x+1, -z$; (xii) $-x, -y+2, -z$.

Table S5. Bond lengths (Å) and angles (degree) for $K_4Cu_3(C_3N_3O_3)_2Br$.

Cu1—N1 ⁱ	1.879 (8)	Br1—K1 ^x	3.318 (4)
Cu1—N1	1.879 (8)	Br1—K1 ^{xi}	3.318 (4)
K1—O1 ⁱⁱⁱ	2.746 (8)	Br1—K1 ^{vi}	3.318 (4)
K1—O1 ^{iv}	2.746 (8)	Br1—K1 ^{xii}	3.318 (4)
K1—O1 ^{vi}	2.754 (8)	Br1—K1 ^{xiii}	3.318 (4)
K1—O1	2.754 (8)	C1—O1	1.247 (12)
K1—Br1 ^{iv}	3.318 (4)	C1—N1 ^{xiii}	1.357 (7)
K1—Br1	3.318 (4)	C1—N1 ⁱ	1.357 (7)
Br1—K1 ^{vii}	3.318 (4)	O1—K1 ⁱⁱ	2.746 (8)
Br1—K1 ⁱⁱⁱ	3.318 (4)	O1—K1 ^{xiii}	2.746 (8)
Br1—K1 ^v	3.318 (4)	O1—K1 ^v	2.754 (8)
Br1—K1 ^{viii}	3.318 (4)	N1—C1 ⁱⁱⁱ	1.357 (7)
Br1—K1 ^{ix}	3.318 (4)	N1—C1 ⁱ	1.357 (7)
Br1—K1 ⁱⁱ	3.318 (4)		
O1—C1—N1 ^{xiii}	120.0 (5)	N1 ^{xiii} —C1—N1 ⁱ	120.0 (10)
O1—C1—N1 ⁱ	120.0 (5)	C1 ⁱⁱⁱ —N1—C1 ⁱ	120.0 (10)

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $x, y, z-1$; (iii) $-x, -y+1, -z+1$; (iii) $y-1, -x+y, -z$; (iv) $x, y, z+1$; (v) $x-y+1, x+1, -z+1$; (vi) $y-1, -x+y, -z+1$; (vii) $-y+1, x-y+2, z$; (viii) $-x, -y+2, -z+1$; (ix) $-x+y-1, -x+1, z-1$; (x) $-x+y-1, -x+1, z$; (xi) $-y+1, x-y+2, z-1$; (xii) $-x, -y+2, -z$; (xiii) $x-y+1, x+1, -z$.

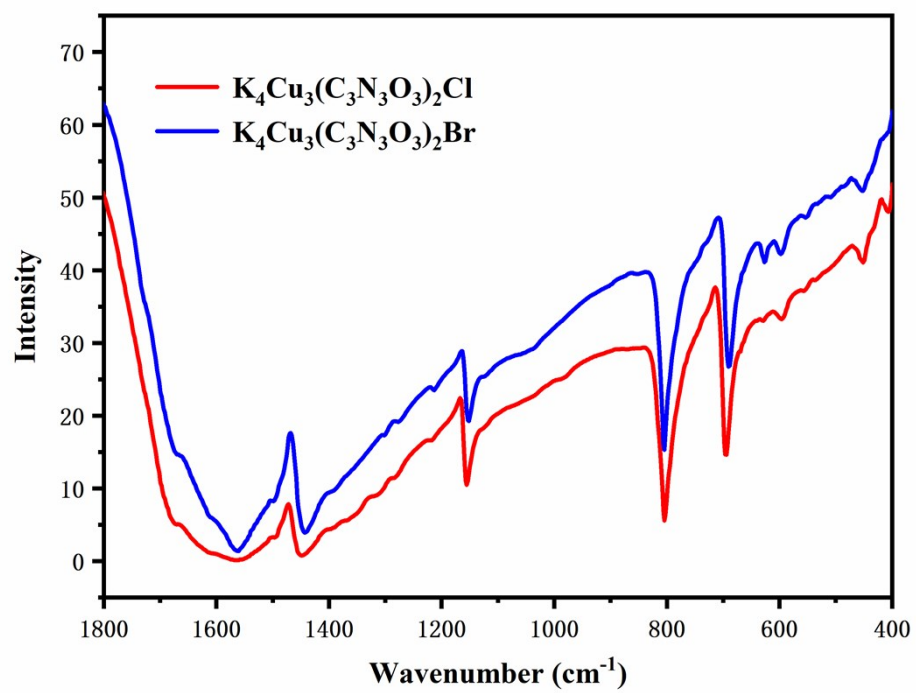


Figure S1. IR spectra of $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Cl}$ and $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Br}$.

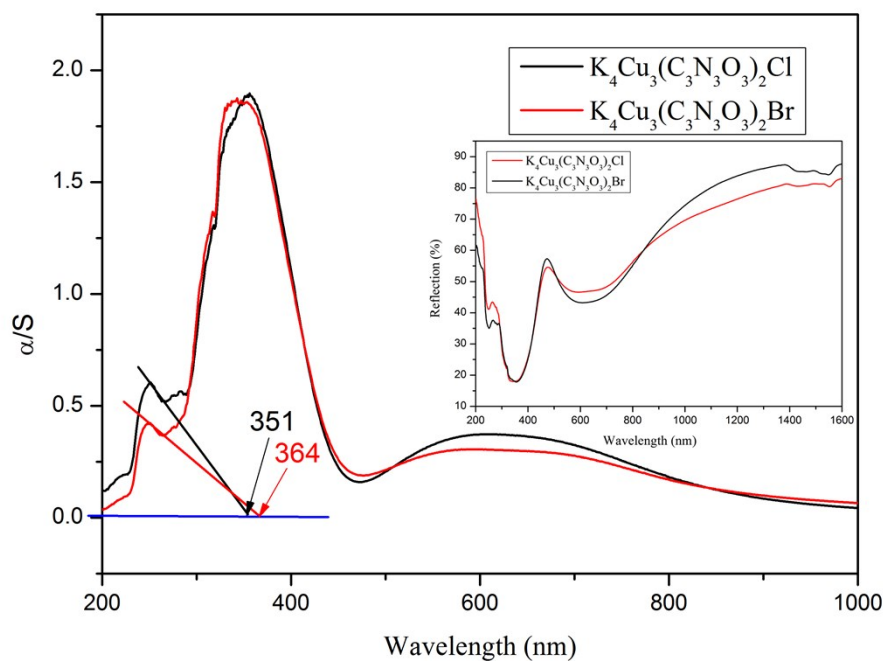


Figure S2. The Kubelka–Munk curves of $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Cl}$ and $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Br}$. Inset shows the reflectance spectra of them.

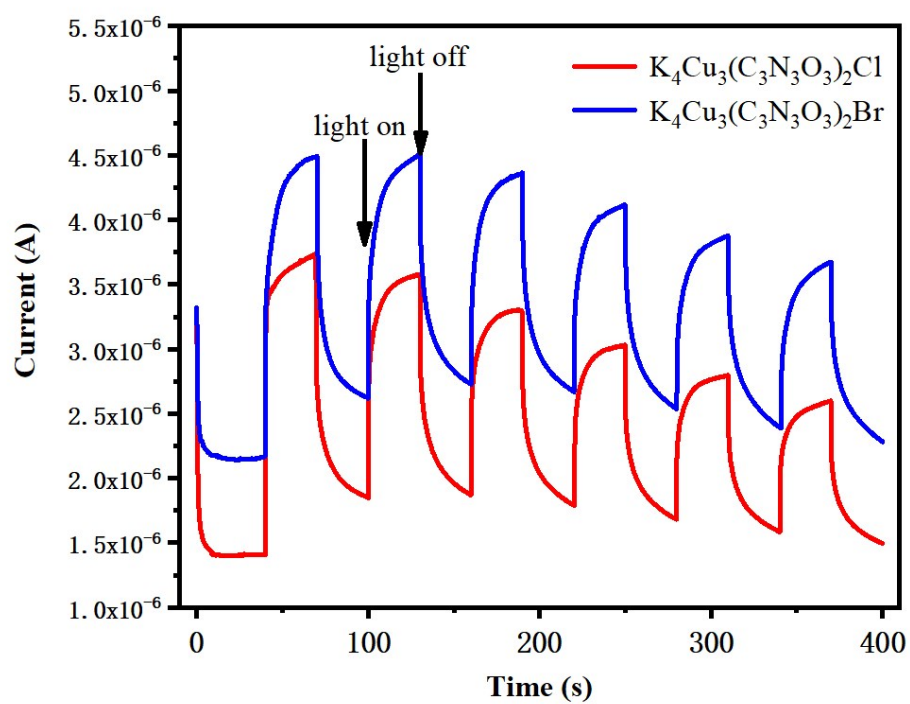


Figure S3. The photocurrent data of $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Cl}$ and $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Br}$.

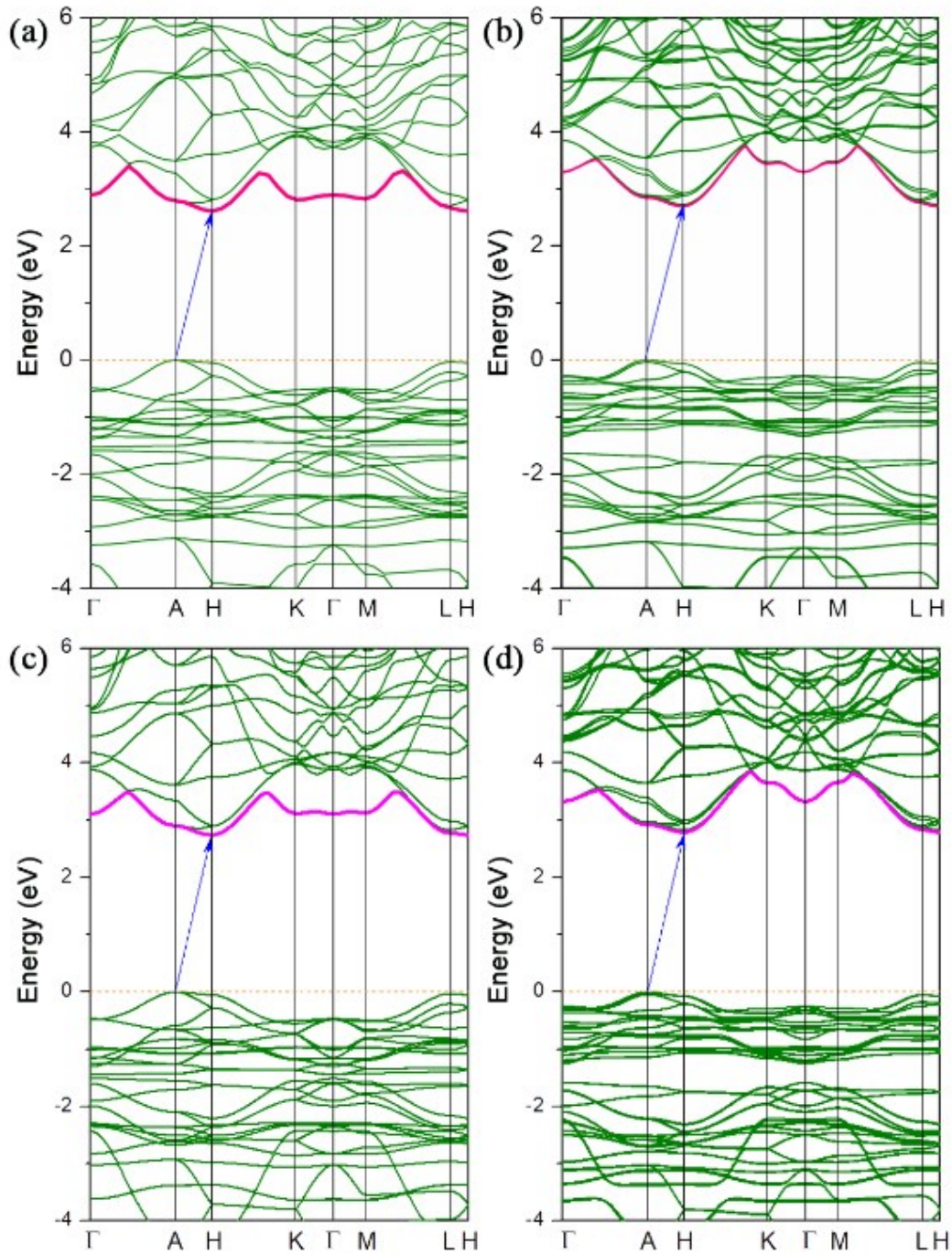


Figure S4. (a and b) Calculated band structures of $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Cl}$ without SOC and with SOC; (c and d) calculated band structures of $\text{K}_4\text{Cu}_3(\text{C}_3\text{N}_3\text{O}_3)_2\text{Br}$ without SOC and with SOC.

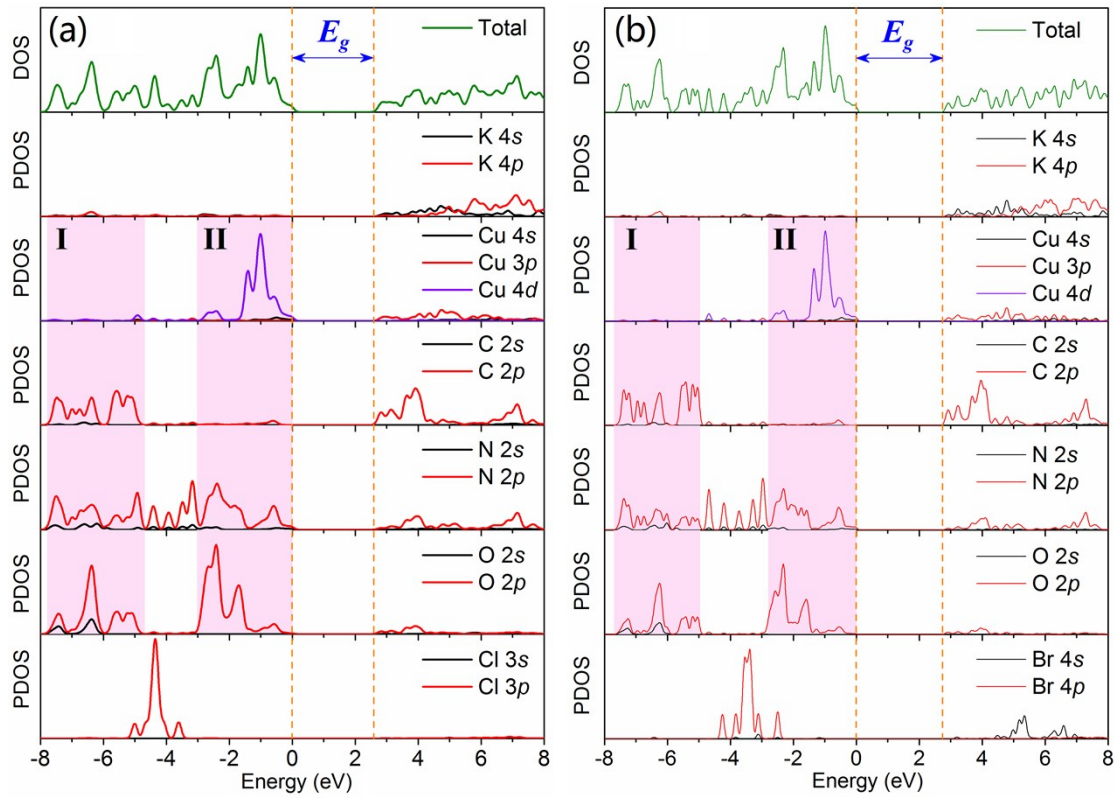


Figure S5. Density of states of (a) $K_4Cu_3(C_3N_3O_3)_2Cl$ and (b) $K_4Cu_3(C_3N_3O_3)_2Br$.

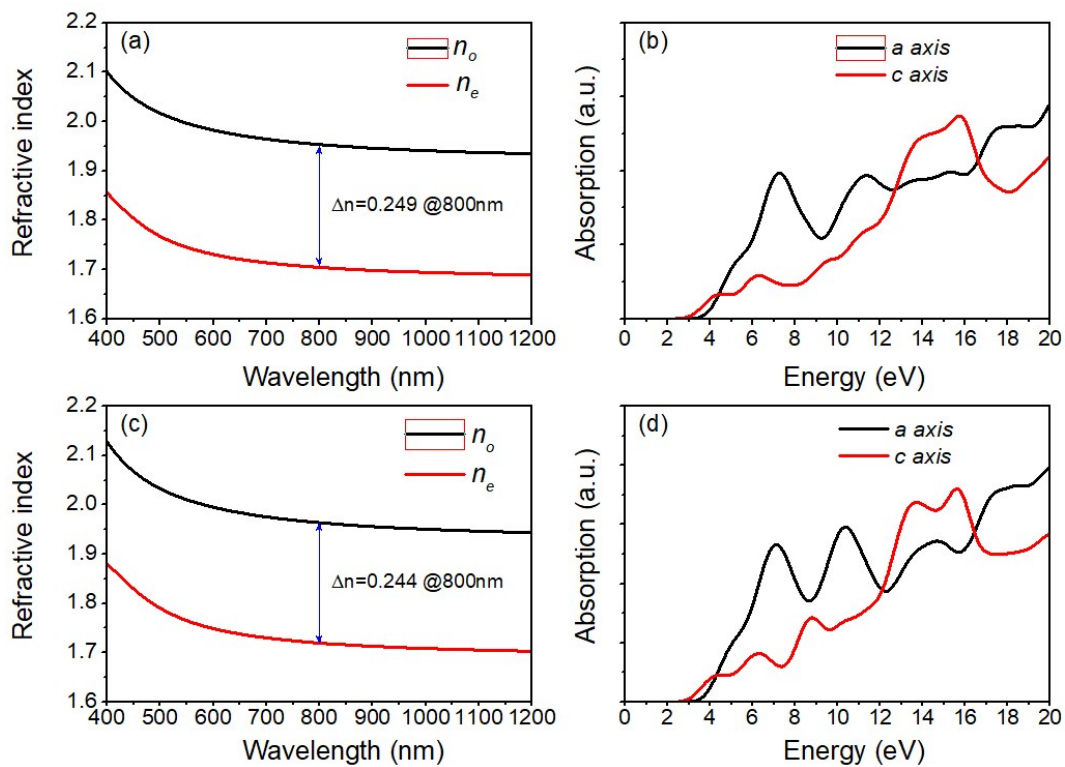


Figure S6. The simulated refractive indices and absorption coefficients of along different axis of (a, b) $K_4Cu_3(C_3N_3O_3)_2Cl$ and (c, d) $K_4Cu_3(C_3N_3O_3)_2Br$.

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