Electronic Supporting Information (ESI)

A semiconductive copper iodobismuthate hybrid: Structure, optical property and photocurrent response

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1. Selected bond lengths and bond angles

Table S1 Selected bond lengths (Å) and bond angles (°) for compound **1**.

Bi(1)−I(6)	2.9288(16)	I(1)−Cu(1)#1	2.700(4)
Bi(1)−I(2)	2.9460(16)	I(4)−Cu(1)#1	2.666(4)
Bi(1)−I(3)	2.9698(15)	I(5)−Cu(1)#1	2.682(4)
Bi(1)−I(4)	3.1721(16)	Cu(1)−I(4)#1	2.666(4)
Bi(1)−I(5)	3.2798(16)	Cu(1)−I(5)#1	2.682(4)
Bi(1)−I(1)	3.3066(16)	Cu(1)−I(1)#1	2.700(4)
I(1)−Cu(1)	2.560(3)	Cu(1)−Cu(1)#1	2.597(8)
I(6)−Bi(1)−I(2)	91.83(5)	I(4)−Bi(1)−I(1)	82.69(4)
I(6)−Bi(1)−I(3)	90.41(4)	I(5)−Bi(1)−I(1)	77.04(4)
I(2)−Bi(1)−I(3)	92.70(5)	Cu(1)−I(1)−Cu(1)#1	59.10(15)
I(6)−Bi(1)−I(4)	91.68(5)	Cu(1)−I(1)−Bi(1)	124.07(10)
I(2)−Bi(1)−I(4)	94.55(5)	Cu(1)#1−I(1)−Bi(1)	65.15(8)
I(3)−Bi(1)−I(4)	172.39(5)	Cu(1)#1−I(4)−Bi(1)	67.59(8)
I(6)−Bi(1)−I(5)	99.88(4)	Cu(1)#1−I(5)−Bi(1)	65.73(8)
I(2)−Bi(1)−I(5)	168.05(5)	I(1)−Cu(1)−I(4)#1	107.08(13)
I(3)−Bi(1)−I(5)	89.60(4)	I(1)−Cu(1)−I(5)#1	116.58(14)
I(4)−Bi(1)−I(5)	82.83(4)	I(4)#1−Cu(1)−I(5)#1	105.91(14)
I(6)−Bi(1)−I(1)	173.85(4)	I(1)−Cu(1)−I(1)#1	120.85(15)
I(2)−Bi(1)−I(1)	91.08(4)	I(4)#1−Cu(1)−I(1)#1	105.84(13)
I(3)−Bi(1)−I(1)	94.87(4)	I(5)#1−Cu(1)−I(1)#1	99.30(12)

Symmetry codes: #1 −*x*+1, *y*, −*z*+1/2.

Table S2 Hydrogen bonds (Å) and angles (º) for compound **1**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
C(1)−H(1C)···I(2)#4	0.96	3.31	3.98(2)	128.8
C(1)−H(1C)···I(6)#4	0.96	3.25	3.71(2)	111.5
C(3)−H(3A)···I(6)#3	0.97	3.06	3.984(18)	159.5
C(3)−H(3B)···I(5)#2	0.97	3.16	3.93(2)	137.6

C(5)−H(5B)···I(2)#5	0.97	3.02	3.91(2)	152.6
C(6)−H(6A)···I(1)#5	0.97	3.32	3.948(19)	124.1
C(6)−H(6A)···I(2)#5	0.97	3.09	3.95(2)	147.5

Symmetry transformations used to generate equivalent atoms: #2 *x*, *y*, *z*+1; #3 *x*, *y*−1, *z*+1; #4 −*x*+1/2, −*y*+3/2, −*z*+1; #5 *x*, −*y*+2, *z*+1/2.

2. Crystal structure

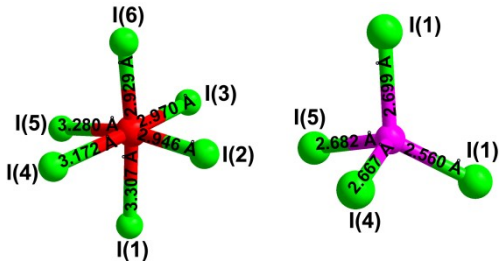

Fig. S1 The primary building units of BiI_6 (left) and CuI_4 (right) in compound **1**.

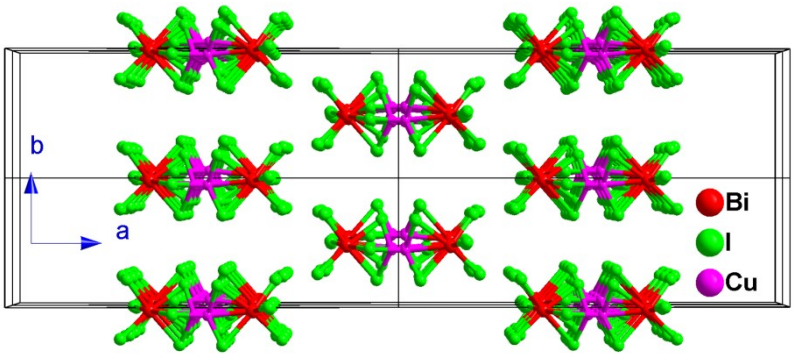

Fig. S2 Perspective view of compound **1** viewed along the *c*-axis.

3. Hirshfeld surface

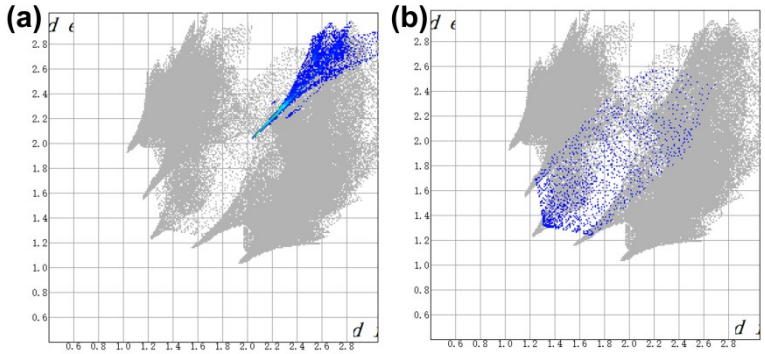

Fig. S3 Fingerprint plots: resolved into I···I (a) and Cu···Cu (b) contacts for compound **1**.

4. Physical measurements

4a). EDX

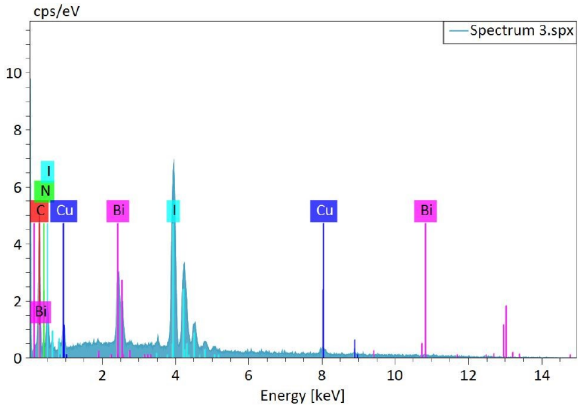

Fig. S4 EDX spectrum of compound **1**.

4b). XPS

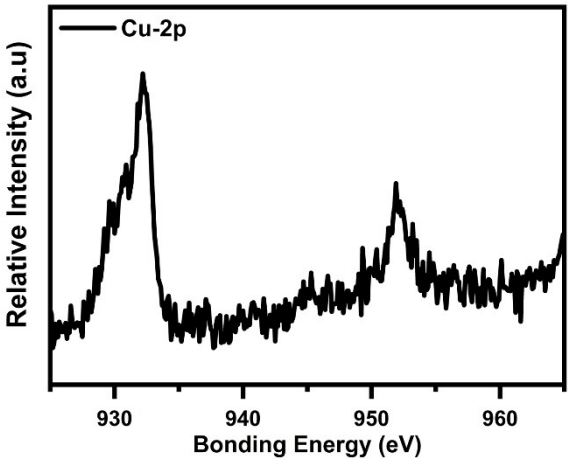

Fig. S5 High-resolution Cu-2p spectrum of compound **1**.

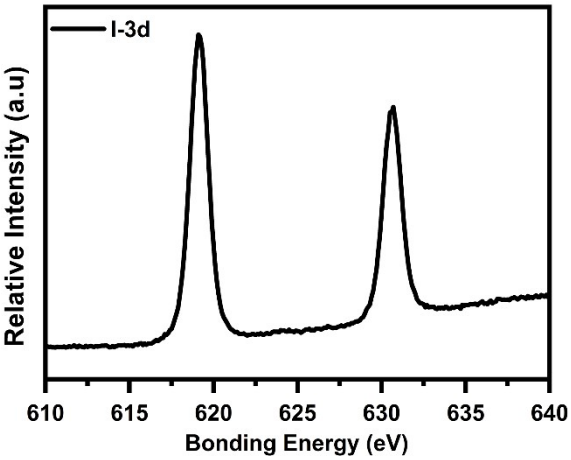

Fig. S6 High-resolution I-3d spectrum of compound **1**.

5. DFT calculations

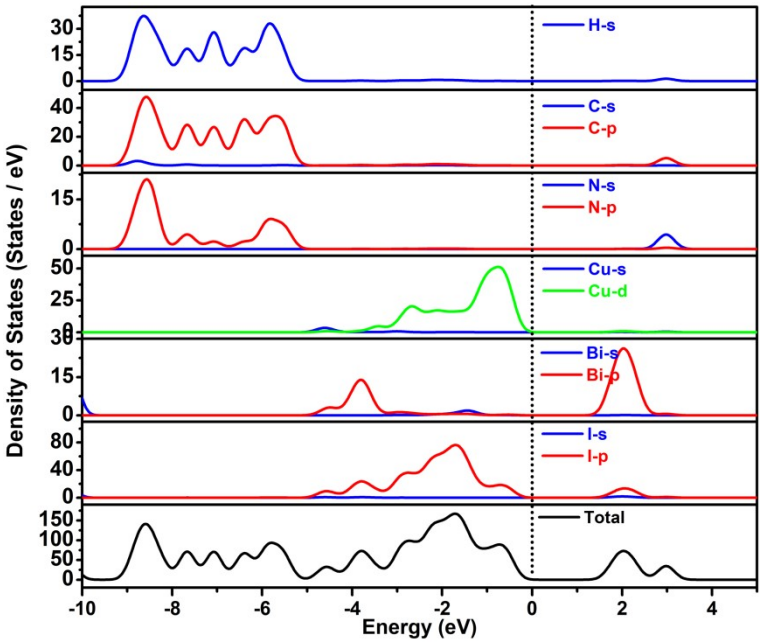

Fig. S7 The total density of states and partial density of states of compound **1**. The valence-band maximum (VBM) is set at 0 eV.

Table S3 Summary of band gaps of representative halobismuthates in the literature.

Compound	**Space group**	**Band gap (eV)**	**Reference**
$[Et_4N]_2Ag_2Bi_2I_{10}$	$P\bar{1}$	2.05	[1]
$[Et_4N]_2Ag_2Bi_4I_{16}$	$P2_1/c$	1.93	[1]
$[SMe_3]_2Ag_2Bi_2I_{10}$	$P2_1/n$	1.82	[2]
$[Bu_4N]_2[(PPh_3)_2Bi_2Cu_2I_{10}]$	$P2_1/c$	NA	[3]
$[Fe(bipy)_3]AgBiI_6$	$P2_1/c$	1.92	[4]
$[Fe(bipy)_3]AgBiBr_6$	$C2/c$	1.82	[4]
$[(C_8H_{17}N_2)]_2Cu_2Bi_2I_{10}$	$P2_1/n$	1.82	[5]
$[(C_6H_{13}N_2)_2BiCu_2I_7]\cdot C_2H_5OH$	$P2_1/c$	1.91	[5]
$[Et_4N]_2Cu_2Bi_2I_{10}$	$P\bar{1}$	1.89	[6]
$[Cu(CH_3CN)_4]_2Cu_2Bi_2I_{10}$	$P\bar{1}$	1.80	[6]
$[PPh_4]_4Cu_2Bi_2I_{12}$	$Pbca$	1.80	[7]
$[PPh_4]_4Ag_2Bi_2I_{12}$	$Pbca$	2.10	[7]
$[Et_4N]_4Hg_2Bi_4I_{20}$	$P1$	2.08	[8]
$[4FPEA]_4AgBiI_8$	$P\bar{1}$	2.16	[9]
$[4FPEA]_4AgBiBr_8$	$P\bar{1}$	2.80	[9]
$[4FPEA]_4AgBiCl_8$	$P\bar{1}$	3.30	[9]
$[C_3H_9NCl]_4AgBiBr_8$	Pc	2.69	[10]
$[C_3H_9NI]_4AgBiI_8$	$P\bar{1}$	1.87	[11]
$[CH_3NH_3]_2AgBiBr_6$	$Fm\bar{3}m$	2.02	[12]
$[C_6H_{16}N_2]_2CuBiI_8\cdot 0.5H_2O$	$P2_1/c$	1.68	[13]
$[C_8H_{20}N_2]_2AgBiBr_8$	$P\bar{1}$	2.70	[14]
$[H_2EPZ]_2AgBiBr_8$	$P2_1/c$	2.77	[15]
$[H_2MPA]_2AgBiBr_8$	$P2_1/n$	2.84	[15]

$[AMP]_4[AgBiI_8]_2 \cdot H_2O$	*C*2/*c*	2.07	[16]
$[APP]_4[AgBiI_8] \cdot H_2O$	*C*2/*c*	2.12	[16]
$[C_6H_{16}N_2]_2AgBiI_8 \cdot H_2O$	$P2_1/n$	1.93	[17]
$[C_6H_{16}N_2]_2CuBiI_8 \cdot 0.5H_2O$	$P2_1/n$	1.68	[17]
$[La(DMSO)_8]Bi_2I_9$	$P\bar{1}$	2.21	[18]
$[Bi(DMSO)_8]Bi_2I_9$	$P\bar{1}$	2.17	[18]
[AmV]BiI_5	NA	1.54	[19]
$[PiC_2]_2Bi_2I_{10}$	$P2_1/n$	2.08	[20]
PiC_5BiI_5	*I*222	1.73	[20]
$[PiC_5]_2Bi_4I_{16}$	$P2_1/n$	2.10	[20]
$[HpipeH_2]_2Bi_2I_{10} \cdot 2H_2O$	$P\bar{1}$	1.80	[21]
$LiBiI_4 \cdot 5H_2O$	*C*2/*c*	1.70	[22]
$KBiI_4 \cdot H_2O$	$P2_1/n$	1.76	[22]
$[(Me)_2$-(DABCO)]$CuBiI_6$	*C*2/*c*	1.80	This work

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