Supporting Information for

Two-dimensional semiconducting Cs(I)/Bi(III) bimetallic iodide hybrids for light detection

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1. Experimental Section

1.1. General remarks

Single crystal X-ray diffraction data of **CsBiI-1** and **CsBiI-2** were collected on a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo-k radiation (λ = 0.71073 Å) by using the θ - ω scan technique at 150K. PXRD intensities were measured at ambient temperature (298 K) on a Rigaku D/max-IIIA diffractometer (Cu-k λ , λ =1.54056 Å). The crystalline powder samples were prepared by grinding the single-crystals and collected in the 2 θ range of 5°–50° with a step size of 10°/min. Scanning electron microscopy (SEM) was performed using KYKY-EM3200, 25 KV instrument. Solid-state UV-Vis diffusion reflectance spectra of pressed powder and films samples were measured on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer using BaSO₄ powder as the reflectance reference. All density-functional theory (DFT) calculations were carried out within CASTEP using Materials Studio. The Photo response measurement of **CsBiI-1** and **CsBiI-2** was calculated using a combination of picoammeter (Keithley 6485) with a source meter (Keithley 2400) to detect the small current in this test. A 350 W solar-simulating Xenon lamp was used as light source.

2. Materials and Sample Preparation

2.1. Materials

Chemicals listed were used as purchased and without further purification: (i) cyclohexane-1,4-diamine, 98%, Alfa Aesar; (ii) 2-Piperidinoethylamine, 98%, sigma Aldrich; (iii) hydroiodic acid, 57% w/w, sigma Aldrich; (iv) bismuth iodide, 99.9 %, sigma Aldrich; (v) Cesium iodide, 99.99%, sigma Aldrich.

2.2. Preparation of CsBiI-1 and CsBiI-2 Single crystals

Crystals of **CsBiI-1** were synthesized from heating a reaction mixture containing cyclohexane-1,4-diamine (0.216 g, 2 mmol), BiI_3 (1.178 g, 2 mmol) and CsI (0.777 g, 3 mmol) in 15 mL of hydrogeniodide acid (HI, 57%) at 160 °C for 6 hours in a PTFE reaction kettle. Single crystals of **CsBiI-1** were grown by programmed cooling down to room temperature for 24 hours. The crystals of **CsBiI-1** were suction filtered with diethyl ether and dried in vacuum (Yield: *ca*. 71% based on Bi). XRD indicates the phase purity (**Figure S2a**).

Red crystals of **CsBiI-2** were obtained from a similar method. A mixture of 2-Piperidinoethylamine (0.256 g, 2 mmol), BiI₃ (0.589 g, 1 mmol) and CsI (0.259 g, 1 mmol) were added to a 15 mL of HI (57%), then the reaction was heated at 160 °C for 6 hours. The system was allowed to cool to room temperature at the rate of 5 °C/h. The crystals of **CsBiI-2** were washed with diethyl ether and dried in vacuum (Yield: *ca.* 72% based on Bi). XRD indicates the phase purity (**Figure S2b**).

2.3. Fabrication of CsBiI-1 and CsBiI-2 Thin Films

CsBiI-1 and **CsBiI-2** organic-inorganic hybrid compounds (0.4 g for each compound) were dissolved in 1 mL of DMF solution and were coated onto ITO glass substrate (ITO glass or ordinary glass was washed with detergent, and then ultrasonically bathed in deionized water, acetone and isopropyl alcohol for 15 minutes each) by spin coating method at 1000 rpm for 60 second. To evaporate the residual solvent, the obtained film was followed by annealing on a hot plate at 75 °C for 10 minutes, obvious color change from light red to dark red can be observed.

3. Characterization methods and Simulation details

3.1. Characterization methods

X-ray Crystallographic Study

Single-crystal X-ray diffraction data collections for CsBiI-1 and CsBiI-2 were conducted on a Bruker SMART APEX II CCD diffractometer (Mo, $\lambda = 0.71073$ Å) by using the θ - ω scan technique at 150 K. The structures were solved by direct methods and refined with a full-matrix least-squares technique within the SHELXTL program package and Olex.^{1, 2} All non-hydrogen atoms were refined anisotropically. The crystallographic details are provided in Table S1-S5 Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre. The crystallographic data for above compounds can be found in the Supporting Information or can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. CCDC Numbers: 1900560 (CsBiI-1), 2034154 (CsBiI-2).

Optical absorption measurement. Solid-state UV-Vis diffusion reflectance spectra were measured at room temperature on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer using BaSO₄ powder as the reflectance reference. The absorption spectra were calculated

from reflectance spectra by the Kubelka-Munk function: $F(R) = \alpha/S = (1-R)^2/2R$, where *R*, α , and *S* are the coefficients for the reflection, the absorption and the scattering, respectively.

Photo response measurement. Pellets of pressed powder were prepared by grinding 50-100 mg polycrystalline samples of **CsBiI-1** and **CsBiI-2** into a homogeneous powder. To test the photo-response, the positive and negative poles were attached to the same side of pellets using conductive silver paste. It's worthy to note that we left one narrow strip like area without paint which can receive light from the lamp. A 350 W solar-simulating Xenon lamp was used as light source and we used a bias voltage of 11 V. For every 40 s we passed or blocked the light and detected the current change.

The on/off ratio of the photodetector is calculated using equation 1.

ON /OFF = $I_{\text{light}}/I_{\text{dark}}$ (1)

Where I_{light} is the photocurrent (21.51 nA for CsBiI-1 and 17.21 nA for CsBiI-2 and I_{dark} is the dark current (4.81 nA and 1.71 nA for CsBiI-1 and CsBiI-2 respectively).



Sheme S1. Scheme of photo-response test device.

Stability studies. Freshly prepared powder samples and films of **CsBiI-1** and **CsBiI-2** were stored either in the dark to minimize light exposure and the relative humidity was maintained at ~55% humidity for 30 days.

3.2. Simulation details Computational methods. All density-functional theory (DFT) calculations were carried out within the Materials Studio software. ^{3, 4} The crystallographic data of compound **CsBiI-2** obtained from Single Crystal XRD tests was used to calculate the electronic band structures and the densities of the states (DOSs). The ab initio calculations of the band structure and partial DOS (PDOS) were performed using the CASTEP. Before the calculation, geometric optimization was carried out until the energy fluctuation below 2×10^{-6} 5 eV/atom and residual forces on the nuclei were below 0.05 eV/Å in magnitude. The exchange-correlation energy was calculated using Perdew-Burke-Ernzerhof (PBE) modification to the generalized gradient approximation (GGA).⁵ The convergence threshold for the self-consistent field was 2×10^{-6} eV/atom. The pseudopotential form was OTFG ultrasoft mode and the energy cutoff was 489.8 eV. The Brillouin zone has been sampled with a highly-converged.

4. Supporting Tables and Figures

	CsBil(1)	CsBiI(2)
Empirical formula	$C_{12}H_{30}BiCs_{3}I_{8}N_{4}$	C ₁₄ H ₃₅ Bi Cs I ₇ N ₄
Formula weight	1853.31	1487.63
Crystal dimensions (mm)	0.12*0.2*0.14	0.13*0.18*0.11
Crystal system	Orthorhombic	Monoclinic
Space group	I b a m	$P2_1/c$
a/Å	11.007(2)	17.005(3)
<i>b</i> /Å	13.875(3)	15.424(3)
$c/\text{\AA}$	23.483(12)	14.317(3)
α/°	90	90
β/°	90	114.493(2)
γ/°	90	90
Volume/Å ³	3586(2)	3417.2(11)
Ζ	4	4
ρ calcg/cm ³	3.432	2.895
μ /mm ⁻¹	14.813	12.543
F(000)	3208.0	2624.0
Index ranges	-15<=h<=15, -18<=k<=18, - 32<=l<=32	-21<=h<=21, -19<=k<=19, - 17<=l<=17
Reflections measured	6118	34332
Data Completeness	100%	99.9%
Data/restraints/parameters	2392/0/70	7077/0/251
Goodness-of-fit on F2	1.14	1.07
	$w = 1/[\sigma 2(Fo2) + (0.070P)^{2} + 10.225P]$	$w = 1/[\sigma_2(Fo_2) + (0.0342P)^2 + 43.162P]$
Weight	$2Fc^2)/3$	where $P = (Fo2 + 2Fc^2)/3$
$R=\sum Fo-Fc /\sum Fo , wR_2$	$R_1 = 0.041, wR_2 = 0.113$	$R_1 = 0.0338, wR_2 = 0.103$

 Table S1 Summary of crystal data and structural refinements of CsBiI-1 and CsBiI-2

R1 = Σ ||F0| - |Fc||/ Σ |F0|, wR₂= [Σ w(Fo² -Fc²)² / Σ w(Fo²)²]^{1/2}

Bond	Lengths/Å	Bond pair	Angles / °
Bi1-I2	3.0654 (6)	I2-Bi1-I2 ⁱ	180.0
Bi1-I2 ⁱ	3.0654 (6)	I3 ⁱⁱ -Bi1-I2	90.738 (12)
Bi1-I3	3.0550 (8)	I3 ⁱⁱⁱ -Bi1-I2 ⁱ	90.739 (12)
Bi1-I3 ⁱⁱ	3.0550 (8)	I3 ⁱ -Bi1-I2 ⁱ	90.739 (12)
Bi1-I3 ⁱ	3.0550 (9)	I3 ⁱⁱⁱ -Bi1-I2	89.262 (12)
Bi1-I3 ⁱⁱⁱ	3.0550 (8)	I3-Bi1-I2 ⁱ	89.261 (12)
Cs1-I1	3.8613 (14)	I3 ⁱ -Bi1-I2	89.262 (12)
Cs1-I1 ^v	3.8613 (14)	I3 ⁱⁱ -Bi1-I2 ⁱ	89.261 (12)
Cs1-I2	4.4273 (12)	I3-Bi1-I2	90.739 (12)
Cs1-I2 ^v	4.4273 (12)	I3 ⁱⁱ -Bi1-I3 ⁱ	92.03 (3)
Cs2-I3 ^{iv}	4.346 (17)	I3 ⁱⁱⁱ -Bi1-I3 ⁱ	87.97 (3)
Cs2-I3 ^{vii}	4.346 (17)	I3-Bi1-I3 ⁱ	180.0
Cs2-I3	4.346 (17)	I3 ⁱⁱ -Bi1-I3	87.97 (3)
Cs1 ^v -I1	3.8613 (14)	I1-Cs1-I2	56.58 (2)
Cs1 ^v -I2	4.4273 (12)	I1 ^v -Cs1-I2	55.65 (2)
C1-C2	1.535 (6)	I3-Cs2-I3 ^{vii}	126.74 (2)
C1-C3	1.524 (6)	I3-Cs2-I3 ^{iv}	152.888 (14)
C2-C3 ^{viii}	1.528 (6)	I3 ^{iv} -Cs2-I3 ^{vii}	60.77 (3)
C3-C2 ^{viii}	1.529 (6)	I3 ^{iv} -Cs2-I3 ⁱⁱⁱ	126.74 (2)
С3-НЗА	0.9700	Bi1-I2-Cs1	113.494 (13)
N1-H1B	0.9000	N1-C1-C2	109.6 (4)
N1-H1C	0.9000	N1-C1-C3	109.3 (3)
		C3-C1-C2	112.1 (4)
		C3 ^{viii} -C1-C2	110.1 (4)
		C1-C3-C2 ^{viii}	110.7 (4)

Table S2 Summary of selected bond lengths (Å) and bond angles (°) of CsBiI-1

Symmetry codes: (i) -*x*, -*y*, -*z*; (ii) *x*, *y*, -*z*; (iii) -*x*, -*y*, *z*; (iv) *x*, -*y*, -*z*+1/2; (v) -*x*+1, -*y*, -*z*; (vi) -*x*+1, -*y*, *z*; (vii) -*x*, *y*, -*z*+1/2; (viii) -*x*+1/2, -*y*+1/2, -*z*+1/2.

Bond	Lengths/Å	Bond pair	Angles / °	Bond pair	Angles / °
Bi1-I2	3.1070 (8)	I6—Bi1—I3	178.83 (2)	C13—N2—C8	113.1 (7)
Bi1-I3	3.0920 (8)	I6—Bi1—I2	91.07 (2)	C12—N2—C8	111.0 (7)
Bi1-I4	3.1239 (8)	I6—Bi1—I5	90.86 (2)	C12—N2—C13	114.6 (8)
Bi1-I5	3.0511 (8)	I6—Bi1—I1	88.05 (2)	C6—N4—C5	112.2 (8)
Bi1-I6	3.0467 (9)	I3—Bi1—I4	90.08 (2)	C6—N4—C1	112.7 (8)
Cs1-I4	4.4801 (12)	I3—Bi1—I2	90.05 (2)	C1—N4—C5	112.7 (9)
Cs1 ⁱ -I6	4.1662 (11)	I2—Bi1—I4	89.86 (2)	N1—C7—C6	108.9 (8)
Cs1-I6 ⁱⁱⁱ	4.1662 (11)	I5—Bi1—I3	88.03 (2)	N4—C6—C7	113.2 (8)
Cs1-I6 ^{iv}	4.2342 (11)	I5—Bi1—I2	178.04 (2)	N4—C5—C4	109.6 (9)
Cs1-I7	3.4008 (11)	I1—Bi1—I4	175.95 (2)	N4—C1—C2	110.1 (10)
N3-C14	1.496 (12)	I1—Bi1—I2	86.90 (2)		
N2-C8	1.521 (12)	I1—Bi1—I5	93.53 (2)		
N2-C13	1.502 (12)	Bi1—I4—Cs1	142.44 (2)		
N2-C12	1.501 (13)	Bi1—I6—Cs1 ⁱⁱ	136.75 (2)		
N4-C6	1.480 (13)	Bi1—I6—Cs1 ⁱ	168.10 (2)		
N4-C5	1.505 (13)	Cs1 ⁱ —I6—Cs1 ⁱⁱ	38.849 (19)		
N4-C1	1.497 (13)	I6 ⁱⁱⁱ —Cs1—I4	117.033 (19)		
N1-C7	1.493 (13)	I6 ^{iv} —Cs1—I4	64.067 (16)		
C7-C6	1.520 (13)	I6 ⁱⁱⁱ —Cs1—I6 ^{iv}	141.151 (19)		
C3-C4	1.51 (2)	Cs1 ^v —Cs1—I4	90.86 (3)		
C8-C9	1.522 (14)	$Cs1^v$ — $Cs1$ — $I6^{iv}$	69.26 (3)		
C14-C13	1.550 (13)	Cs1 ^v —Cs1—I6 ⁱⁱⁱ	71.89 (3)		
C9-C10	1.543 (14)	Cs1 ^v —Cs1—I7	175.19 (4)		
C11-C12	1.522 (14)	Cs1 ^v —Cs1—N1	120.13 (14)		
C4-C5	1.519 (16)	I7—Cs1—I4	84.36 (2)		
C1-C2	1.534 (16)	I7—Cs1—I6 ^{iv}	108.86 (3)		
C2-C3	1.51 (2)	I7—Cs1—I6 ⁱⁱⁱ	109.87 (3)		

Table S3 Summary of selected bond lengths (Å) and bond angles (°) of CsBiI-2

Symmetry codes: (i) -x+1, y-1/2, -z+1/2; (ii) x, -y+3/2, z+1/2; (iii) -x+1, y+1/2, -z+1/2; (iv) x, -y+3/2, z-1/2; (v) -x+1, -y+2, -z

 Table S4 Potential hydrogen bonding data of compound CsBiI-1

D-H	d(D-H)	d(HA)	<dha< th=""><th>d(DA)</th><th>Α</th></dha<>	d(DA)	Α
N1-H1A	0.900	3.151	142.22	3.901	I2

Table S5 Potential hydrogen data of compound CsBiI-2

D-H	d(D-H)	d(HA)	<dha< th=""><th>d(DA)</th><th>Α</th></dha<>	d(DA)	Α	
N3-H3A	0.890	2.680	151.60	3.485	I8	
N3-H3B	0.890	2.70	160.7	3.548	I2	
N3-H3C	0.890	3.07	126.6	3.673	I4(a)	
N3-H3C	0.890	3.04	138.3	3.751	I5(a)	
N2-H2	0.980	2.92	136.8	3.693	I6(b)	
N4-H4	0.980	2.83	133.5	3.580	I3(c)	
N4-H4	0.980	3.24	124.7	3.884	I1(c)	
C7-H7A	0.970	3.11	123.9	3.743	I2(d)	
C8-H8A	0.970	3.11	126.8	3.774	I5(b)	
C8-H8B	0.970	3.23	167.2	4.177	I6	
C14-H14A	0.970	3.20	117.7	3.753	I4(a)	
C14-H14A	0.970	3.26	150.6	4.137	I6	
C14-H14B	0.970	3.17	151.4	4.050	I4(a)	
C13-H13A	0.970	3.19	136.3	3.951	I5(a)	
C12-H12A	0.970	3.27	138.7	4.049	I4	
C6-H6B	0.970	3.31	118.6	3.867	I3(c)	
C6-H5A	0.970	3.13	125.8	3.784	I1(c)	
С5-Н5В	0.970	3.01	165.3	3.956	13	
C1-H1C	0.970	3.00	162.4	3.940	I2	
C1-H1D	0.970	3.22	117.1	3.761	I3(c)	
N1-H1A	0.850	3.24	117	3.710	I2(d)	
N1-H1A	0.85	3.01	153	3.790	I1(d)	
N1-H1B	0.61	3.16	131	3.584	I4	
N1-H1B	0.61	3.23	135	3.689	I6(d)	
Symmetry transformations used to generate equivalent atoms : (a) [x, $3/2 - y$, $z + 1/2$]; (b) [1 -x, $\frac{1}{2} + y$,						
$1/2-z]; (c) [2-x, \frac{1}{2}+y, \frac{1}{2}-z]; (d) [x, \frac{3}{2}-y, -\frac{1}{2}+z]$						



Figure S1. (a) Assymetric unit of CsBiI-1. (b) Assymetric unit of CsBiI-2



Figure S2. (a) Powder XRD patterns of CsBiI-1. (b) Powder XRD patterns of CsBiI-2.



CsBiI-1



Figure S3. Hirshfeld surfaces mapped with dnorm **CsBiI-1** (a) and (b) **CsBiI-2** (color coding: white, distance d equals VDW distance; blue, d exceeds VDW distance, red, d, smaller than VDW distance).



Figure S4. The Tauc Plot for a direct band gap (a) and for indirect band gap (b) semiconductor of CsBiI-1 and CsBiI-2.



Figure S5. (a-d) Partial density of states (PDOS) of compound CsBiI-2 (organic part, Bi-s, Bi-p and Bi-d, I-s, I-p, Cs-s, Cs-p).



Figure S6. Stability of **CsBiI-1** and **CsBiI-2** towards humidity showing XRD of **CsBiI-1** and **CsBiI-2** thin films before and after exposure to 55% relative humidity and 25 °C at different times



Figure S7. Stability of **CsBiI-1** and **CsBiI-2** towards humidity showing PXRD of **CsBiI-1** and **CsBiI-2** before and after exposure to 55% relative humidity and 25 °C at different times

2Θ(°)

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