Supporting Information

A Lead-free Halide Hybrid Perovskite (TMHD)$BiCl_5$ for the Ultraviolet Photodetection

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Experimental Section

Synthesis. All the chemical reagents were purchased as high purity (AR grade) and used without any further purification. The compound of (TMHD)$BiCl_5$ has been synthesized in aqueous solution of Bi_2O_3 and TMHD in a ratio of 2:1 in concentrated HCl.

Single-crystal structure determination. Single-crystal X-ray diffractions for **1** were performed on a Bruker 8 diffractometer with the Mo Kα radiation at 300K. The data were processed by the Crystalclear software package. The structures of **1** were solved by direct methods and then refined by the full-matrix least-squares refinements on F^2 using SHELXLTL software package. Crystallographic data and structure refinements for **1** at different temperatures are given in Table S1.

The optical ultraviolet-visible absorption spectrum measurements. The UV absorptions in solid state were measured at room temperature on a PE Lambda 900 UV-Visible spectrophotometer.

Computational description. Single-crystal structure data of **1** at 300 K was used for the theoretical calculations. Band structure and partial density of states (PDOS) were performed by the DFT method within the total-energy code CASTEP. The exchange and correlation effects were treated by Perdew-Burke-Ernzerh in the generalized gradient approximation. The core-electrons interactions between the ionic cores and the electrons were described by the norm-conserving pseudo potential.

Fabrication and Measurements of Detectors: The surface of crystal **1** was cleaned with nitrogen flow before device fabrication. The vertical-type detectors were fabricated based on single crystals of **1**, with an electrode length of about 1 mm and gold electrode spacing of about 300 μm. The photoresponse experiments were performed by using a Keithley 6517B source meter at room temperature under 266 nm illumination.

Figures

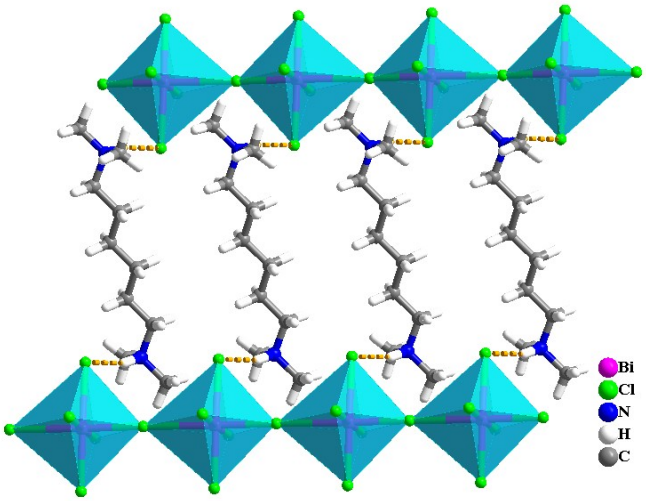

Figure S1. N-H•••Cl hydrogen bonds generated from the N atom of organic cation and Cl atom of inorganic skeleton.

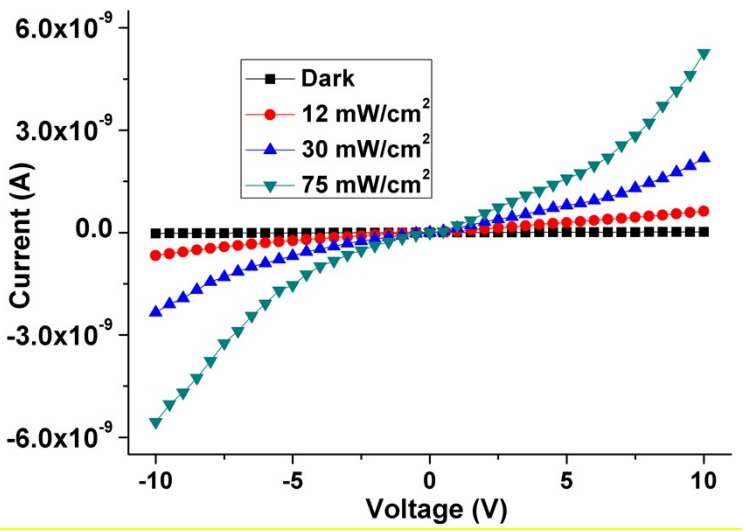

Figure S2. I–V curves of (TMHD)$BiCl_5$ under 405 nm light illumination with different power density.

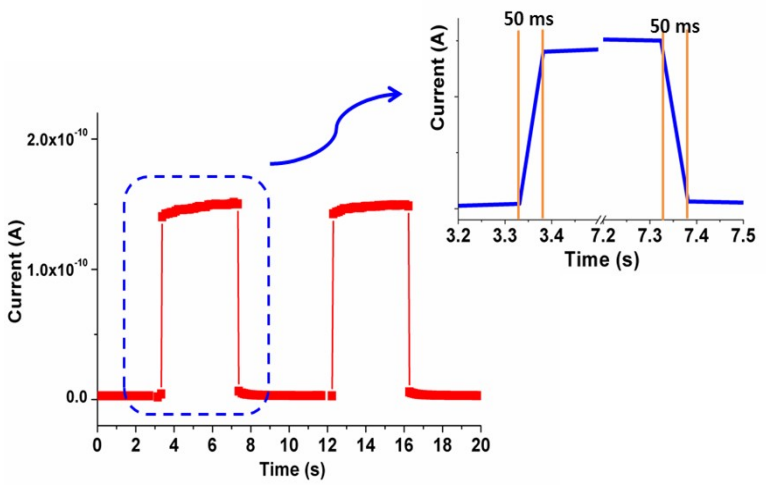

Figure S3. I–t curves of (TMHD)$BiCl_5$ and the photoresponse time.

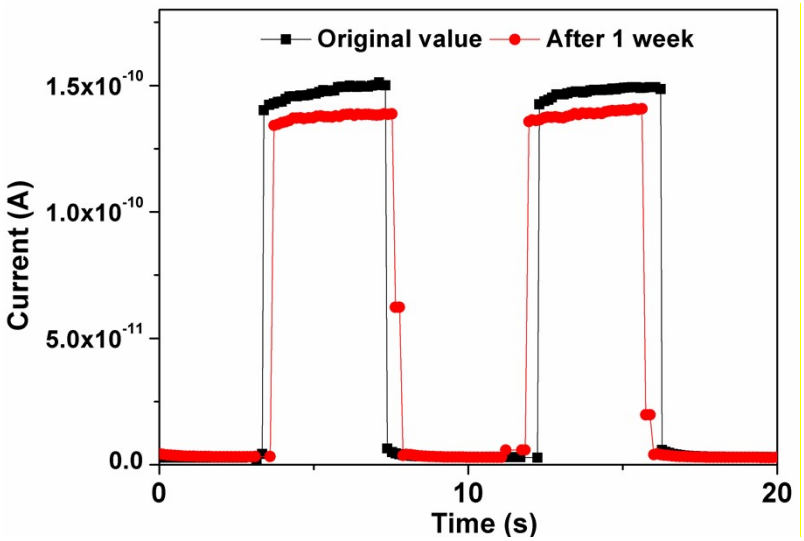

Figure S4. Variation in the photocurrent of (TMHD)$BiCl_5$ with exposure time in air. After exposure to the air for 1 week, the photocurrent of the device maintained > 95.0% of its initial state.

Tables

Table S1. Crystal Data and Structure Refinement

Empirical formula	$C_{10}H_{26}Bi_7Cl_5N_2$
Formula weight	560.56
Temperature/K	173(2)
Space group	$P2_1/c$
a/Å	5.565000(10)
b/Å	18.5529(5)
c/Å	18.7630(5)
α/°	90.00
β/°	97.124(2)
γ/°	90.00
Volume/ Å^3	1922.27(8)
Z	4
ρ_{calc}g/cm^3	1.937
μ/mm^{-1}	9.855
F(000)	1072.0
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.92 to 52.74
Index ranges	$-6 \le h \le 6$, $-20 \le k \le 23$, $-22 \le l \le 23$
Reflections collected	11859
Independent reflections	3903 [R_{int} = 0.0394, R_{sigma} = N/A]
Data/restraints/parameters	3903/0/167
Goodness-of-fit on F^2	1.131
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.0928
Largest diff. peak/hole / e Å^{-3}	1.16/-3.54

Table S2. The bond lengths

Bond	(Å)	Bond	(Å)
Bi(1) - Cl(5)	2.5466(18)	C(8) - C(9)	1.512(9)
Bi(1) - Cl(3)	2.5973(16)	C(9) - C(10)	1.511(10)
Bi(1) - Cl(2)	2.6052(17)	C(10) - C(10)^3	1.507(13)
Bi(1) - Cl(4)	2.7614(16)	N(1) - C(1)	1.475(9)
Bi(1) - Cl(1)	2.8061(16)	N(1) - C(2)	1.485(9)
Bi(1) - Cl(5)^1	3.0191(18)	N(1) - C(3)	1.501(8)
Cl(5) – Bi(1)^2	3.0191(18)	C(4) - C(3)	1.501(10)
N(2) – C(7)	1.478(8)	C(4) - C(5)	1.543(10)
N(2) – C(6)	1.492(8)	C(5) - C(5)^4	1.481(14)
N(2) – C(8)	1.495(8)		

^{1}-1+X,+Y,+Z; ^{2}1+X,+Y,+Z; ^{3}1-X,1-Y,1-Z; ^{4}-1-X,1-Y,-Z

Table S3. The bond angles

Bond	Angle/°	Bond	Angle/°
Cl(5) - Bi(1) – Cl(3)	90.45(6)	Cl(2) - Bi(1) – Cl(1)	88.19(5)
Cl(5) - Bi(1) – Cl(2)	91.60(6)	Cl(4) - Bi(1) – Cl(1)	87.33(5)
Cl(3) - Bi(1) – Cl(2)	93.83(6)	Cl(5) - Bi(1) – Cl(5)[1]	178.21(9)
Cl(5) - Bi(1) – Cl(4)	87.79(6)	Cl(3) - Bi(1) –Cl(5)[1]	87.89(5)
Cl(3) - Bi(1) – Cl(4)	90.67(5)	Cl(2) - Bi(1) –Cl(5)[1]	89.18(6)
Cl(2) - Bi(1) – Cl(4)	175.47(5)	Cl(4) - Bi(1) –Cl(5)[1]	91.56(5)
Cl(5) - Bi(1) – Cl(1)	90.54(5)	Cl(1) - Bi(1) –Cl(5)[1]	91.09(5)
Cl(3) - Bi(1) – Cl(1)	177.73(5)	Bi(1) - Cl(5) – Bi(1)[2]	178.21(9)

[1]-1+X,+Y,+Z; [2]1+X,+Y,+Z; [3]1-X,1-Y,1-Z; [4]-1-X,1-Y,-Z