Supporting Information

Reduced-dimensional polar hybrid perovskite for self-powered broad-spectrum photodetection

Dong Li,[a, b] Wentao Wu,[a, b] Shiguo Han,[a, b, c] Xitao Liu,[a, b, c] Yu Peng,[a, b] Xiaoqi Li,[a, b] Lina Li,*[a, b, c] Maochun Hong,[a, b, c] Junhua Luo[a, b, c]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China
[b] Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108, P. R. China
[c] University of Chinese Academy of Sciences, Beijing, 100049, China

*To whom correspondence should be addressed.
lilina@fjirsm.ac.cn

Experimental Section

Materials: $Pb(Ac)_2$ (99%, Aladdin), methylamine (MA, 29%, Aladdin), hydroiodic acid (HI, 48%, Aladdin), Aminobutanol (99%, Aladdin). All the chemicals were bought and used without further purification.

Synthesis. $Pb(Ac)_2$ (2.27 g, 6 mmol) was dissolved in 48% aqueous HI solution (15 mL) by heating to boil under constant magnetic stirring to give a yellowish solution. Subsequent addition of Aminobutanol (0.36 g, 4 mmol) and MA (0.45 g, 4 mmol) to the hot solution formed yellowish precipitation, which were dissolved under stirring to afford a red solution. Finally, dark-red crystals were obtained after the solution cooling to room temperature.

Powder X-ray diffraction. Powder X-ray diffractions (PXRD) were performed on a Rigaku MiniFlex 600 diffractometer at room temperature. The diffraction patterns were collected in the 2θ range of 5°−50° with a step size of 0.5 °/min. The experimental PXRD patterns match fairly well with the simulated data based on the single-crystal structure, which confirm the pure phase of **IMP**.

Second harmonic generation (SHG) measurement. SHG experiments of **IMP** were performed on powder samples using the fundamental laser beam with a low divergence (pulsed Nd:YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate). The numerical values of the nonlinear optical coefficients for SHG have been determined by comparison with a KH_2PO_4 reference.

Single-crystal structure determination. Single-crystal X-ray diffractions for **IMP** were performed on a BRUKER D8 with the Mo Kα radiation. The data were processed by the Crystalclear software package. The structures of **IMP** were solved by direct methods and then refined by the full-matrix least-squares refinements on F^2 using SHELXLTL software package. All the non-hydrogen atoms were located from the trial structure and refined anisotropically with SHELXTL using the full-matrix least-squares procedure.

Optical property measurements. The UV absorptions in solid state were measured at room temperature on a PE Lambda 900 UV-Visible spectrophotometer.

Detector performance measurement. The current-voltage and current-time curves were measured using KEITHLEY in an electromagnetically shielded probe station. The light was generated from LEDs with wavelength of 405 nm, 520 nm, 637 nm (THORLABS, ITC4001).

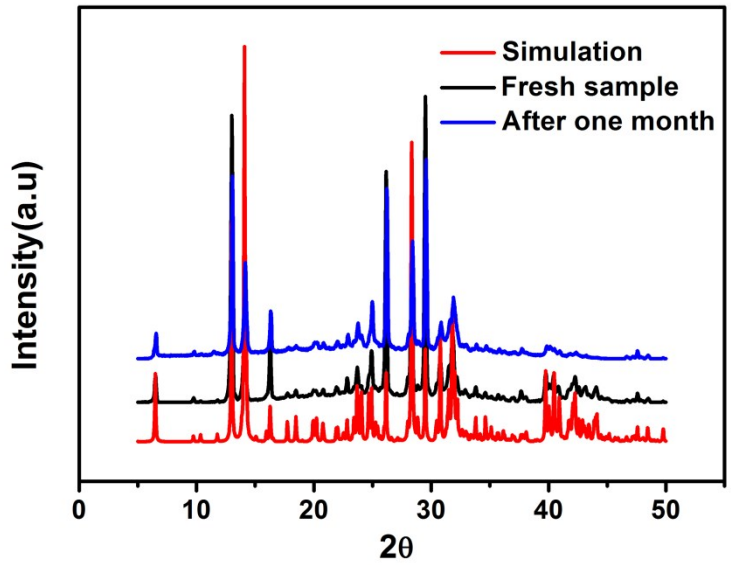

Figure S1. X-ray diffraction patterns for **IMP**

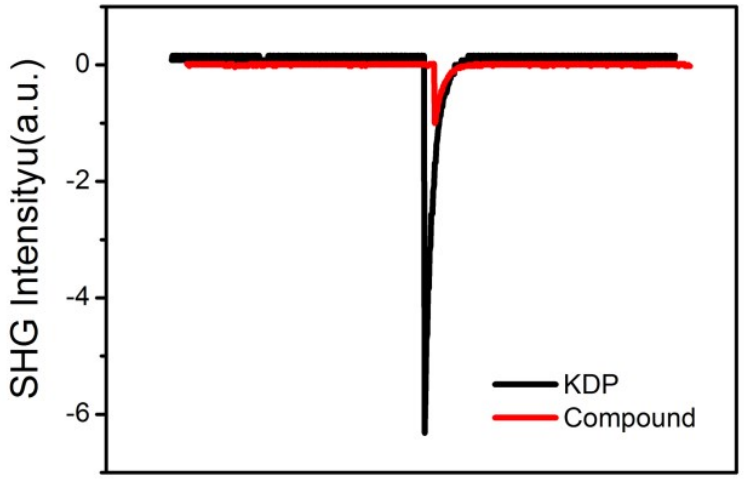

Figure S2. The SHG signals for the KDP standard and polycrystalline sample of **IMP** at room temperature.

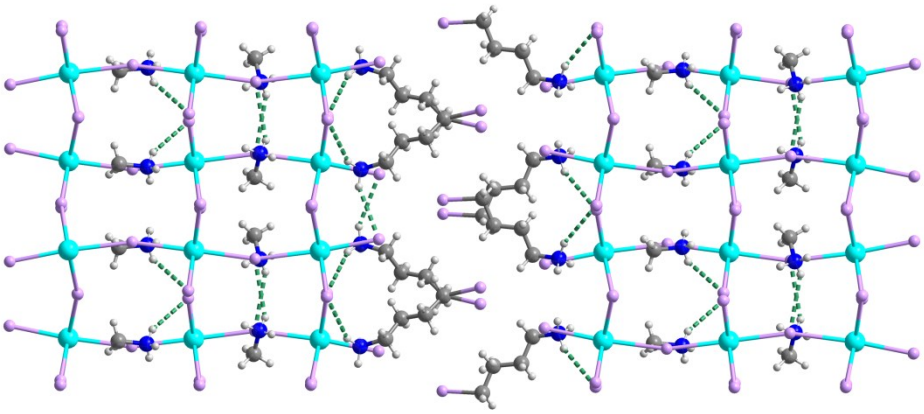

Figure S3. Hydrogen bonds in the compound **IMP** (In order to clearly express the hydrogen bond, some hydrogen atoms are removed).

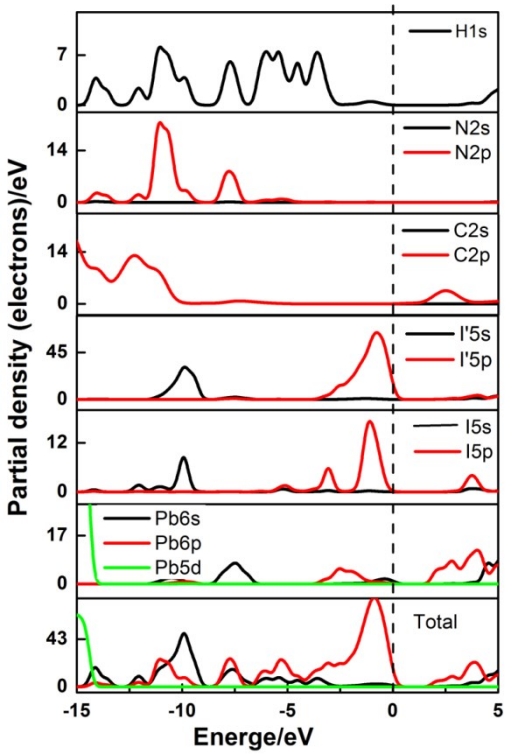

Figure S4. Partial density of states of **IMP**.

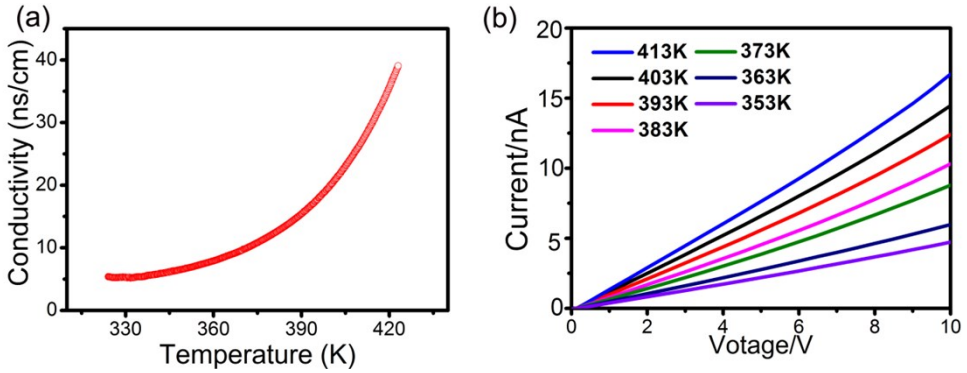

Figure S5. (a) Temperature-dependent conductivity. (b) The current-voltage (*I*–*V*) measurement at various temperatures.

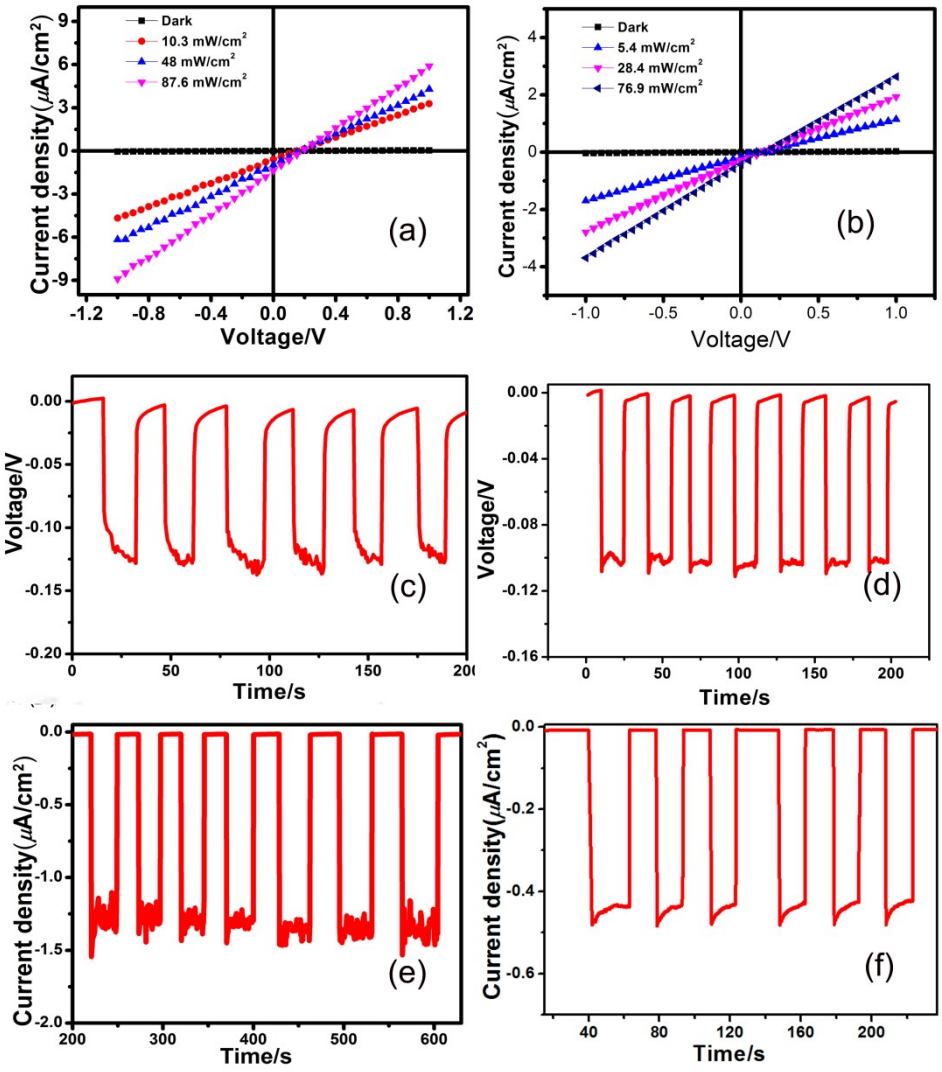

Figure S6. (a, b) *I*–*V* characteristics along *c*-axis of **IMP** at 520 and 405 nm laser, respectively. (c, d) Reproducible bulk photovoltaic on/off switches of 520 and 405 nm laser. (e, f) Reproducible photocurrent on/off switches of 520 and 405 nm laser at zero bias.

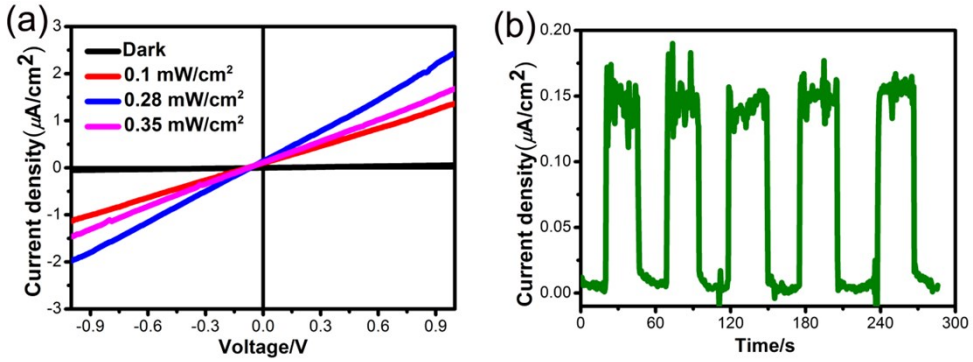

Figure S7. (a) *I*–*V* characteristics along *c*-axis for **IMP** at 700 nm. (b) Reproducible photocurrent on/off switches of 700 nm.

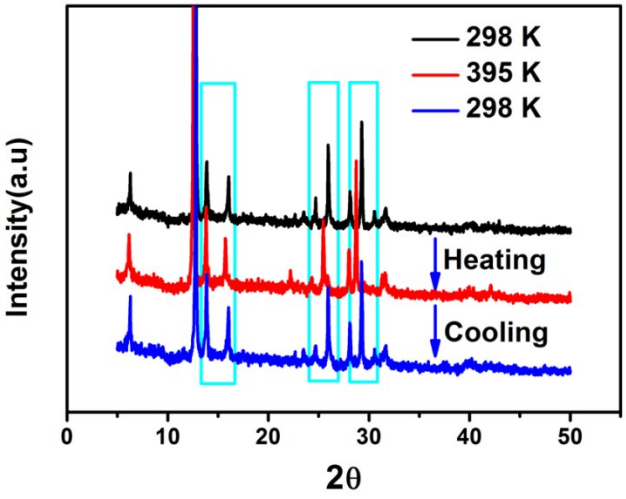

Figure S8. PXRD at different temperatures with some changes labelled.

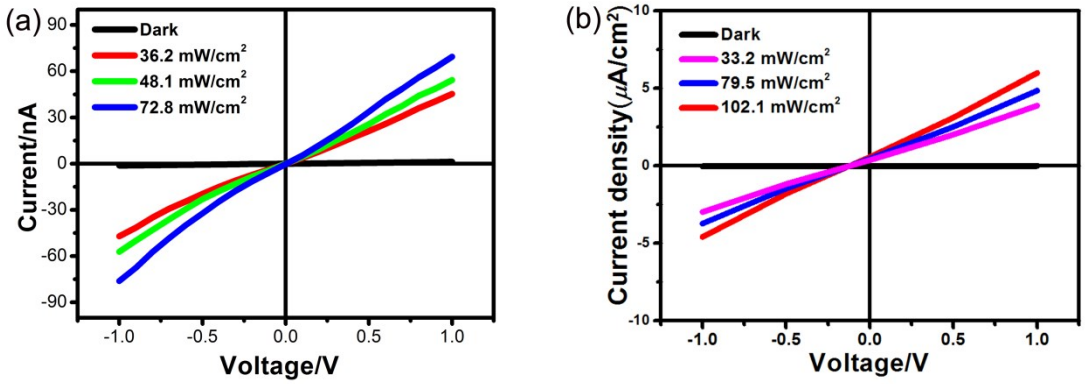

Figure S9. (a) *I*–*V* characteristics for *b*-axis of **IMP** with different incident powers. (b) *I*–*V* characteristics for *a*-axis of **IMP** with different incident powers (637 nm laser).

Table S1. Crystal data for **IMP**

Temperature (K)	290 K	385 K
Empirical formula	$C_{10}H_{34}I_{12}N_4Pb_3$	$C_{10}H_{34}I_{12}N_4Pb_3$
Formula weight	2354.78	2354.78
Temperature/K	290.0	385.0
Crystal system	monoclinic	monoclinic
Space group	*Pc*	*C*2/*m*
a/Å	27.3848 (12)	8.909 (2)
b/Å	9.0015 (4)	9.012 (3)
c/Å	8.8216 (3)	27.896 (8)
α/°	90	90
β/°	95.9990 (10)	92.832 (10)
γ/°	90	90
Volume/Å^3	2162.65 (15)	2237.1 (11)
Z	2	2
*ρ*calcg/cm^3	3.616	3.496
μ/mm^{-1}	20.223	19.550
F(000)	2008.0	2008.0
Radiation	Mo K*α* (λ = 0.71073)	Mo K*α* (λ = 0.71073)
Theta range (°)	4.486 to 52.84	4.386 to 49.982
Index ranges	-33 ≤ h ≤ 34, -11 ≤ k ≤ 11, -11 ≤ l ≤ 9	-10 ≤ h ≤ 9, -10 ≤ k ≤ 10, -33 ≤ l ≤ 33
Reflections collected	36105	17421
Independent reflections	8192 [R_{int} = 0.0546, R_{sigma} = 0.0520]	2111 [R_{int} = 0.0814, R_{sigma} = 0.0495]
Data/restraints/parameters	8192/102/269	2111/62/98
GOF	1.038	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0627, wR_2 = 0.1686	R_1 = 0.0948, wR_2 = 0.2620
Final R indexes [all data]	R_1 = 0.0783, wR_2 = 0.1832	R_1 = 0.1099, wR_2 = 0.2731

Table S2. Bond angles for **IMP**.

Bond	Angle	Bond	Angle
I(1)-Pb(1)-I(3)$^{[\#1]}$	87.32 (3)	I(5)$^{[\#3]}$-Pb(2)-I(6)$^{[\#4]}$	88.97(4)
I(1)-Pb(1)-I(3)	93.07(3)	I(5)-Pb(2)-I(6)	94.33(4)
I(1)-Pb(1)-I(2)	94.06(3)	I(6)-Pb(2)-I(4)	90.53(5)
I(1)-Pb(1)-I(2)$^{[\#2]}$	88.97(3)	I(6)-Pb(2)-I(5)$^{[\#3]}$	177.22(4)
I(1)-Pb(1)-I(4)	173.45(3)	I(6)-Pb(2)-I(6)$^{[\#4]}$	88.305(18)
I(3)$^{[\#1]}$-Pb(1)-I(3)	87.789(11)	I(10)-Pb(3)-I(9)	93.79(3)
I(3)$^{[\#1]}$-Pb(1)-I(2)$^{[\#2]}$	94.89(3)	I(10)-Pb(3)-I(9)$^{[\#4]}$	89.85(3)

I(3)[#1]-Pb(1)-I(2)	176.96(3)	I(10)-Pb(3)-I(7)	174.65(3)
I(3)-Pb(1)-I(4)	87.26(3)	I(10)-Pb(3)-I(8)[#3]	87.56(3)
I(3)[#1]-Pb(1)-I(4)	86.16(3)	I(10)-Pb(3)-I(8)	92.56(3)
I(2)[#2]-Pb(1)-I(3)	176.71(3)	I(9)-Pb(3)-I(9)[#4]	87.998(11)
I(2)-Pb(1)-I(3)	89.43(3)	I(9)[#4]-Pb(3)-I(7)	90.68(3)
I(2)[#2]-Pb(1)-I(2)	87.844(11)	I(9)-Pb(3)-I(7)	91.54(3)
I(2)-Pb(1)-I(4)	92.48(4)	I(9)-Pb(3)-I(8)[#3]	176.54(3)
I(2)[#2]-Pb(1)-I(4)	91.01(4)	I(9)[#4]-Pb(3)-I(8)[#3]	95.19(2)
I(7)-Pb(2)-I(4)	179.41(5)	I(8)-Pb(3)-I(9)[#4]	176.13(3)
I(7)-Pb(2)-I(5)[#3]	89.91(4)	I(8)-Pb(3)-I(9)	88.82(2)
I(7)-Pb(2)-I(5)	89.98(4)	I(8)[#3]-Pb(3)-I(7)	87.09(3)
I(7)-Pb(2)-I(6)	89.52(5)	I(8)-Pb(3)-I(7)	87.20(3)
I(7)-Pb(2)-I(6)[#4]	89.90(5)	I(8)-Pb(3)-I(8)[#3]	87.939(11)
I(4)-Pb(2)-I(6)[#4]	89.51(5)	Pb(1)[#4]-I(3)-Pb(1)	163.00(4)
I(5)-Pb(2)-I(4)	90.60(4)	Pb(3)-I(9)-Pb(3)[#1]	166.78(5)
I(5)[#3]-Pb(2)-I(4)	90.01(4)	Pb(2)-I(7)-Pb(3)	165.10(5)
I(5)-Pb(2)-I(5)[#3]	88.392(18)	Pb(3)-I(8)-Pb(3)[#2]	163.66(5)
I(5)-Pb(2)-I(6)[#4]	177.36(4)	Pb(1)[#3]-I(2)-Pb(1)	164.78(5)
Pb(2)-I(4)-Pb(1)	165.45(6)	Pb(2)-I(5)-Pb(2)[#2]	167.92(6)
Pb(2)-I(6)-Pb(2)[#1]	165.37(6)		

[#1] = +X, 1-Y, 1/2+Z; [#2] = +X, 2-Y, 1/2+Z; [#3] = +X, 2-Y, -1/2+Z; [#4] = +X, 1-Y, -1/2+Z.

Table S3. Bond lengths for **IMP**.

Bond	(Å)	Bond	(Å)	Bond	(Å)
Pb(1)-I(1)	3.0634(10)	Pb(2)-I(5)[#3]	3.1746(13)	Pb(3)-I(8)[#3]	3.2019(9)
Pb(1)-I(3)[#1]	3.1668(10)	Pb(2)-I(5)	3.1592(13)	Pb(3)-I(8)	3.1541(10)
Pb(1)-I(3)	3.1952(10)	Pb(2)-I(6)[#4]	3.1867(14)	I(3)-Pb (1)[#4]	3.1668(10)
Pb(1)-I(2)	3.1924(11)	Pb(2)-I(6)	3.1968(14)	I(9)-Pb(3)[#1]	3.1905(10)
Pb(1)-I(2)[#2]	3.1749(11)	Pb(3)-I(10)	3.0490(10)	I(8)-Pb(3)[#2]	3.2019(9)
Pb(1)-I(4)	3.2623(11)	Pb(3)-I(9)	3.1639(9)	I(2)-Pb (1)[#3]	3.1749(11)
Pb(2)-I(7)	3.1434(14)	Pb(3)-I(9)[#4]	3.1904(10)	I(5)-Pb (2)[#2]	3.1747(13)
Pb(2)-I(4)	3.1780(14)	Pb(3)-I(7)	3.3334(10)	I(6)-Pb (2)[#1]	3.1867(14)

[#1] = +X, 1-Y, 1/2+Z; [#2] = +X, 2-Y, 1/2+Z; [#3] = +X, 2-Y, -1/2+Z; [#4] = +X, 1-Y, -1/2+Z.

Calculation of polarization of **IMP** according to a point charge model:

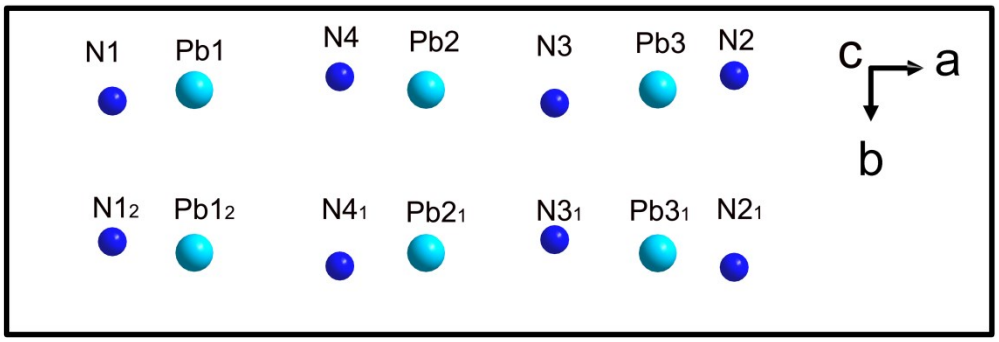

Figure S10. Point-charge model for calculating the polarization of **IMP** at 290 K. Hydrogen atoms are omitted for clarity.

Atom coordinates for cell of **IMP** (290 K).

Atoms	Atoms coordinate		Coordinate of charge center
Pb	Pb1(0.19055, 0.25067, 0.95588) Pb2 (0.42572, 0.24994, 0.03430) Pb3 (0.66095, 0.24915, 0.11329)	$Pb1_2$ (0.19055, 0.74933, 0.45588) $Pb2_1$ (0.42572, 0.75006, 0.53430) $Pb3_1$ (0.66095, 0.75085, 0.61329)	(0.42574, 0.5, 0.45115)
N	N1 (0.1073, 0.28448, 0.3671) N2 (0.73853, 0.2063, 0.6413) N3 (0.55627, 0.29089, 0.538) N4 (0.33825, 0.21002, 0.5366)	$N1_2$ (0.1073, 0.71552, 0.8671) $N2_1$ (0.73853, 0.7937, 0.1413) N b2 (0.55627, 0.70911, 0.038) N b4(0.33825, 0.77899, 0.0366)	(0.43509, 0.5, 0.39575)

$P_{s\ a\text{-axis}} = [(-e \times 0.42574) \times 6 \times 4/3 + (e \times 0.43509) \times 8] \times a / V$
$= [0.0748 \times 1.6 \times 10^{-19} \times 27.3848 \times 10^{-10}\ C\ m]/V$
$= 3.28 \times 10^{-29}\ C\ m / (2162.65 \times 10^{-30}\ m^3)$
$= 1.51 \times 10^{-2}\ C\ m^{-2}$
$|P_s| = 1.51 \times 10^{-2}\ C\ m^{-2} = 1.51\ \mu C\ cm^2$

$P_{s\ c\text{-axis}} = [(-e \times 0.45115) \times 8 + (e \times 0.39557) \times 8] \times c / V$
$= [0.5558 \times 1.6 \times 10^{-19} \times 8.8216 \times 10^{-10}\ C\ m]/V$
$= 7.84 \times 10^{-29}\ C\ m / (2162.65 \times 10^{-30}\ m^3)$
$= 3.62 \times 10^{-2}\ C\ m^{-2}$
$|P_s| = 3.62 \times 10^{-2}\ C\ m^{-2} = 3.62\ \mu C\ cm^2$