Pyridinium lead tribromide and pyridinium lead triiodide: quasi-one-dimensional perovskites with optically active aromatic π-system

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Supplementary information

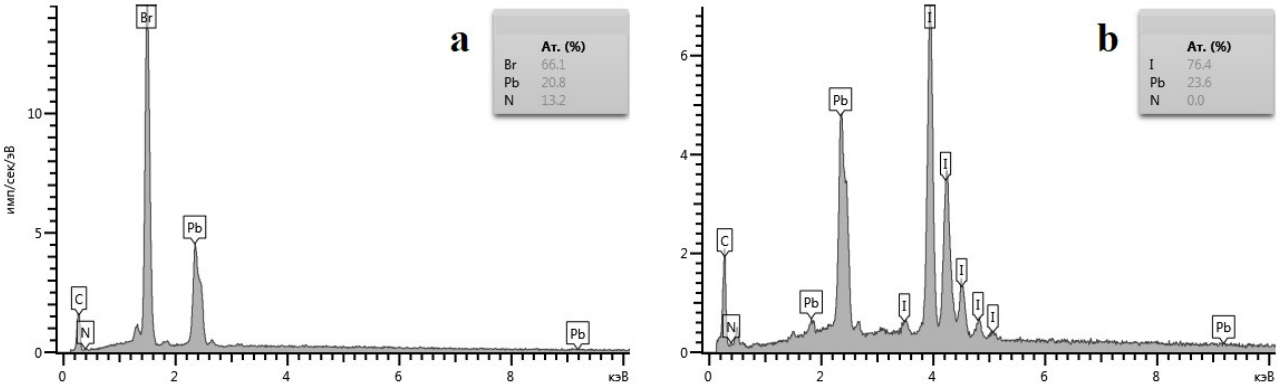


Figure S1. EDX-spectra of $PyPbBr_3$ (a) and $PyPbI_3$ (b).

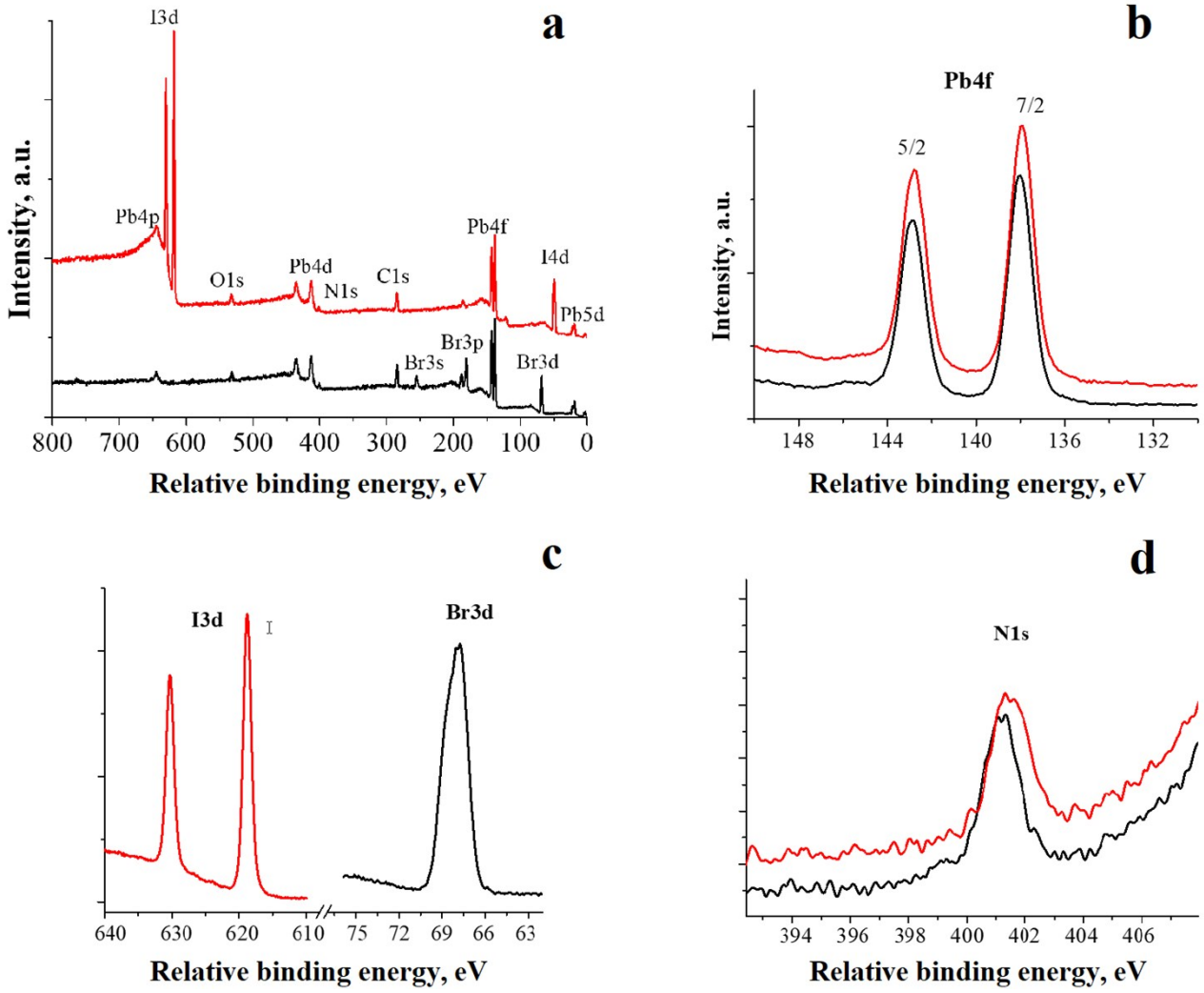


Figure S2. XPS survey spectrum (a) and the high-resolution XPS of Pb 4f (b); Br 3d, I 3d (c); N 1S (d) states of the powdered $PyPbBr_3$ (black) and $PyPbI_3$ (red) perovskites.

The full energy range (0.0-800.0 eV) X-ray photoelectron spectra (XPS) of both compounds as well as the high-resolution XPS of Pb 4f, Br 3d, I 3d, and N 1S states are presented in Figure S2 (see supplementary information). Presumably, the O 1S peaks present in Figure S2a originate from a molecular oxygen adsorbed on a surface of the perovskite samples.

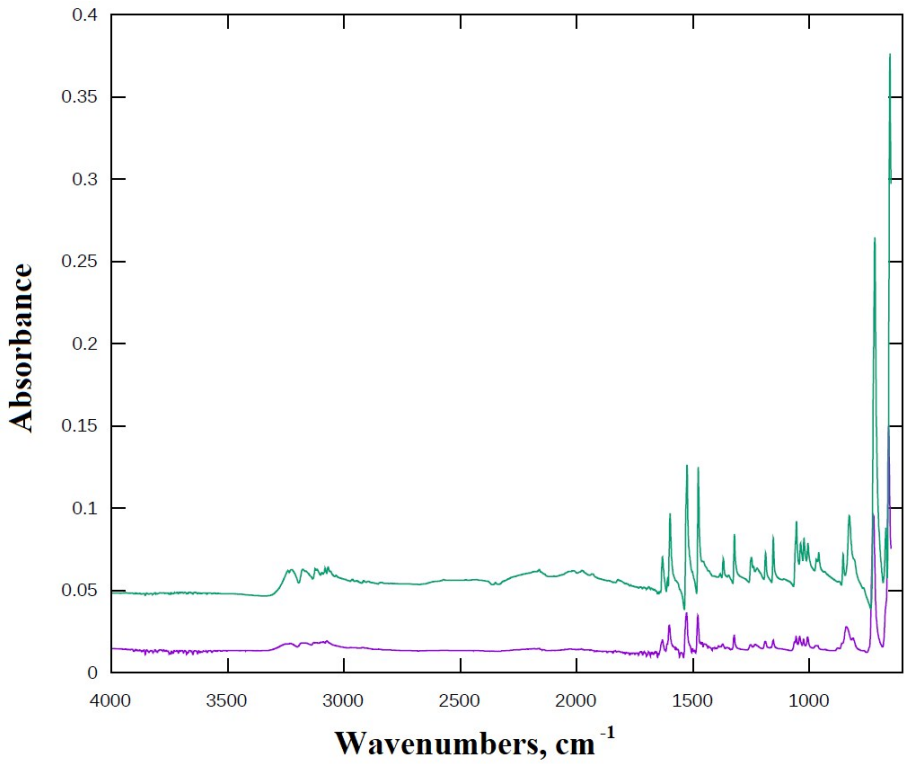


Figure S3. IR spectra of the powdered $PyPbBr_3$ (violet) and $PyPbI_3$ (green) perovskites. The figure shows the N^+-H stretching in the range ~3300-3200 cm^{-1}, pyridinium ring vibrations around 1500 cm^{-1}, and C-H deformation vibrations in the range ~1300-1100 cm^{-1}.

The IR spectra of the studied substances were recorded with a Nicolet FTIR iS50 spectrometer with 4 cm^{-1} resolution using iTR ATR accessory. For each spectrum, 60 scans were accumulated. The spectra were recorded at room temperature.

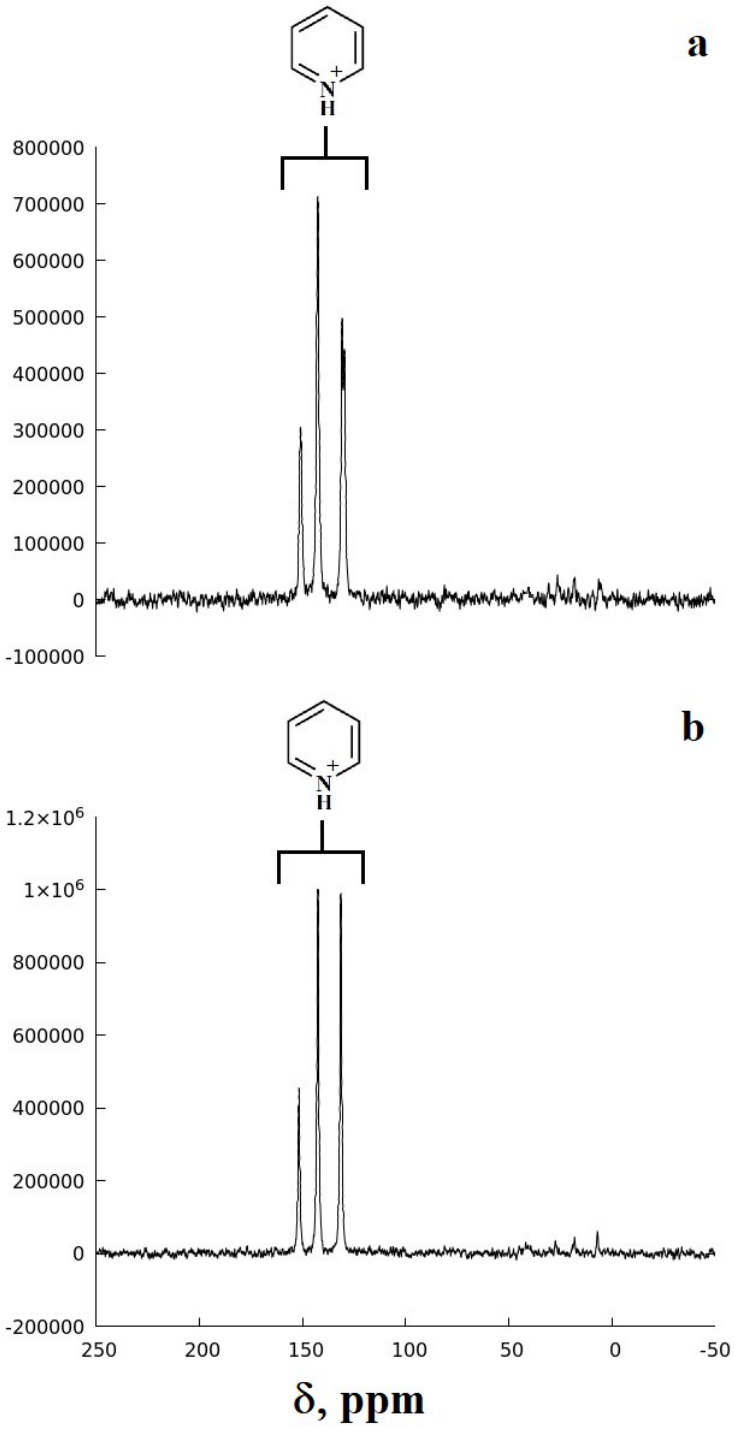


Figure S4. ^{13}C NMR spectra of the powdered $PyPbBr_3$ (a) and $PyPbI_3$ (b) perovskites.

The ^{13}C NMR characterization of the samples was performed with Bruker Avance III 400 WB spectrometer (working frequency was 100.64 MHz). The samples were placed into a zirconia rotor with the external diameter of 4 мм and were rotated with the frequency of 12.5 kHz at a magic angle spinning. The measurements were performed at 30 C. For a signal registration from ^{13}C nucleus the cross-polarization sequence of the exciting pulses (CP/MAS method) was used. The contact time for

CP/MAS was 2 ms, the relaxation time delay was 2 c and the accumulation number was 2000. Tetramethyl silane was used as a reference sample.

The NMR spectra presented in Figure S4 correspond to a pyridinium cation and confirm its incorporation into the perovskite crystal structure.

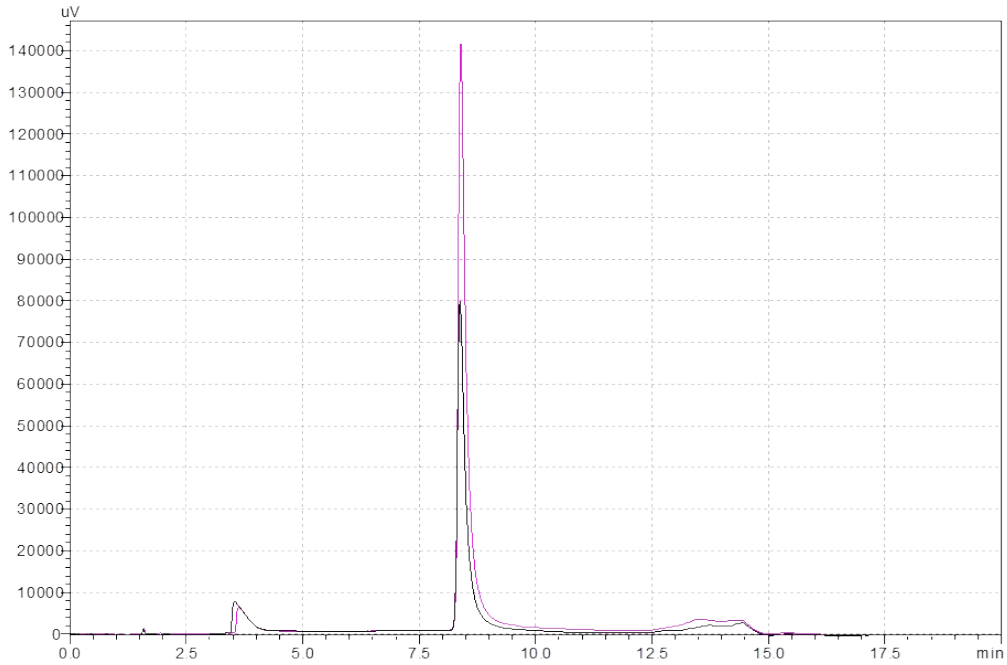


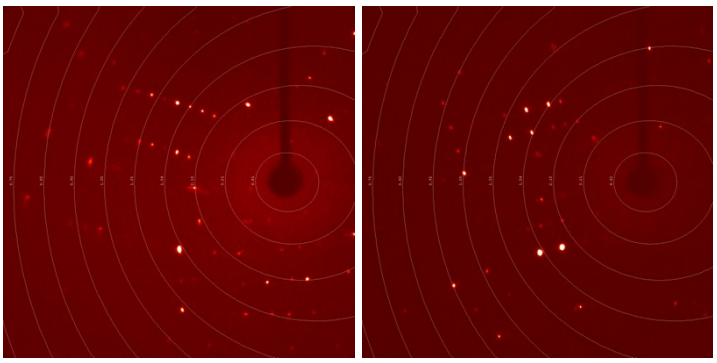
Figure S5. Chromatograms of the dissolved $PyPbBr_3$ perovskite (after the separation of the $PbBr_2$ sediment) (black line) and pyridine hydrobromide solution (pink line).

The chromatographic analysis was performed using the inverse phase HPLC method with LC-20 Prominence (Shimadzu) chromatograph (column Luna C18(2) 150×4,6 mm) equipped with DAD SPD-M20A. The detection wavelength was 254 nm. The mobile phase consisted of water and methanol was used in a gradient regime. The synthesized samples (1 mg) were dissolved in 100 µl of DMFA and 400 µl of water. An addition of 200 µl of methanol results in a formation of a precipitate. The residual solution was centrifugated and filtered in order to remove the sediment. The analyzed sample volume was 5 µl.

The comparison of the obtained chromatograms (Figure S5) of the sample and pyridine hydrobromide solution confirms the presence of pyridinium in the synthesized perovskite materials.

Table S1. XPS perovskite's composition analysis.

Element	Start BE	Peak BE	End BE	FWHM eV	Atomic %
$PyPbBr_3$					
C1s	297.90	284.42	277.10	2.16	51.44
Br3d	75.90	68.00	62.10	2.00	27.26
Pb4f	149.90	138.01	130.10	1.26	7.61
N1s	409.90	401.12	392.10	1.42	6.03
$PyPbI_3$					
C1s	297.90	284.58	277.10	2.68	50.72
I3d	639.90	618.77	610.10	1.41	26.35
Pb4f	149.90	137.92	130.10	1.25	7.45
N1s	409.90	401.39	392.10	1.50	5.31



a **b**

Figure S6. Experimental lauegrams obtained for $PyPbBr_3$ (a) and $PyPbI_3$ (b) single crystals.

Table S2. The characteristic data of the perovskite single crystals obtained by XRD.

Identification code	PbBr3	PbI3
Empirical formula	$C_5H_6Br_3NPb$	$C_5H_6I_3NPb$
Formula weight	527.03	668.00
Temperature/K	100(2)	100(2)
Crystal system	orthorhombic	orthorhombic
Space group	Pnma	Pnma
a/Å	14.0045(6)	14.9049(4)
b/Å	7.7690(4)	8.0660(2)
c/Å	9.1780(5)	9.5902(3)
α/°	90	90
β/°	90	90
γ/°	90	90

Volume/Å^3	998.57(8)	1152.96(6)
Z	4	4
ρ_{calc}g/cm^3	3.506	3.848
μ/mm^{-1}	28.834	22.610
F(000)	920.0	1136.0
Crystal size/mm^3	0.2 × 0.2 × 0.2	0.2 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.306 to 54.994	5.466 to 54.99
Index ranges	-18 ≤ h ≤ 18, -10 ≤ k ≤ 10, -11 ≤ l ≤ 11	-19 ≤ h ≤ 15, -10 ≤ k ≤ 10, -12 ≤ l ≤ 10
Reflections collected	15722	5028
Independent reflections	1231 [R_{int} = 0.1080, R_{sigma} = 0.0406]	1417 [R_{int} = 0.0347, R_{sigma} = 0.0311]
Data/restraints/parameters	1231/0/52	1417/0/52
Goodness-of-fit on F^2	1.171	1.136
Final R indexes [I>=2σ (I)]	R_1 = 0.0579, wR_2 = 0.1350	R_1 = 0.0306, wR_2 = 0.0717
Final R indexes [all data]	R_1 = 0.0696, wR_2 = 0.1420	R_1 = 0.0337, wR_2 = 0.0732
Largest diff. peak/hole / e Å^{-3}	4.56/-2.69	1.78/-3.30

Table S3a. Cartesian coordinates of the perovskite $PyPbBr_3$. The first three lines are the crystal lattice vectors. The data is given in Angstroms.

14.00450	0.00000	0.00000
0.00000	7.76900	0.00000
0.00000	0.00000	9.17800

Pb	4.9999999934E-07	3.8845005000E+00	4.5889985000E+00
Pb	4.9999999934E-07	4.9999999999E-07	4.5889995000E+00
Pb	7.0022505000E+00	3.8845005000E+00	-5.0000000010E-07
Pb	7.0022505000E+00	4.9999999999E-07	-1.5000000001E-06
Br	7.5652025000E-01	5.8267502500E+00	6.8449490000E+00
Br	2.2645307500E+00	1.9422502500E+00	4.9955887500E+00
Br	1.5186505000E+00	5.8267505000E+00	2.8515985000E+00
Br	4.7377202500E+00	5.8267502500E+00	4.0658875000E-01
Br	6.2457307500E+00	1.9422502500E+00	2.2559490000E+00
Br	8.5209005000E+00	5.8267505000E+00	1.7373995000E+00
Br	5.4836005000E+00	1.9422505000E+00	7.4405985000E+00
Br	1.3247980750E+01	1.9422502500E+00	2.3330490000E+00
Br	9.2667807500E+00	1.9422502500E+00	8.7714092500E+00
Br	1.1739970250E+01	5.8267502500E+00	4.1824092500E+00
Br	7.7587702500E+00	5.8267502500E+00	6.9220490000E+00
Br	1.2485850500E+01	1.9422505000E+00	6.3263995000E+00
C	5.5597902500E+00	6.4855605000E+00	3.8942292500E+00
C	4.8959700000E+00	7.1940905000E+00	4.8542395000E+00
C	4.1943500000E+00	6.4793502500E+00	5.8436290000E+00
C	4.1943500000E+00	5.1741502500E+00	5.8436290000E+00
C	4.8959700000E+00	4.4594105000E+00	4.8542390000E+00
C	2.8079010000E+00	1.2896502500E+00	1.2546290000E+00

C	2.1062810000E+00	5.7491050000E-01	2.6523900000E-01
C	1.4424607500E+00	2.6010605000E+00	-6.9477075000E-01
C	2.1062810000E+00	3.3095905000E+00	2.6523950000E-01
C	2.8079010000E+00	2.5948502500E+00	1.2546290000E+00
C	9.1085310000E+00	3.3095905000E+00	4.3237585000E+00
C	8.4447107500E+00	2.6010605000E+00	5.2837687500E+00
C	9.1085310000E+00	5.7491050000E-01	4.3237590000E+00
C	9.8101510000E+00	1.2896502500E+00	3.3343690000E+00
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C	1.1898220000E+01	4.4594105000E+00	8.9127590000E+00
C	1.1196600000E+01	5.1741502500E+00	7.9233690000E+00
C	1.1196600000E+01	6.4793502500E+00	7.9233690000E+00
C	1.1898220000E+01	7.1940905000E+00	8.9127585000E+00
C	1.2562040250E+01	6.4855605000E+00	9.8727687500E+00
N	5.5597902500E+00	5.1679405000E+00	3.8942290000E+00
N	1.4424607500E+00	1.2834405000E+00	-6.9477100000E-01
N	8.4447107500E+00	1.2834405000E+00	5.2837690000E+00
N	1.2562040250E+01	5.1679405000E+00	9.8727690000E+00
H	7.9422367500E+00	8.0084000000E-01	6.0011365000E+00
H	1.3064514250E+01	4.6853400000E+00	1.0590136500E+01
H	6.0622642500E+00	4.6853400000E+00	3.1768615000E+00
H	9.3998675000E-01	8.0084000000E-01	-1.4121385000E+00
H	3.3103750000E+00	3.0774515000E+00	1.9719967500E+00
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H	1.0694123500E+01	4.6915570000E+00	7.2059985000E+00
H	1.1898215250E+01	8.1940905000E+00	8.9127512500E+00
H	1.1898220000E+01	3.4594105000E+00	8.9127590000E+00
H	1.3064511750E+01	6.9681692500E+00	1.0590132750E+01
H	1.0312625000E+01	3.0774515000E+00	2.6170012500E+00
H	9.1085357500E+00	4.3095905000E+00	4.3237512500E+00
H	1.0312627500E+01	8.0705700000E-01	2.6169985000E+00
H	9.1085310000E+00	-4.2508950000E-01	4.3237590000E+00
H	7.9422392500E+00	3.0836692500E+00	6.0011327500E+00
H	4.8959700000E+00	3.4594105000E+00	4.8542390000E+00
H	4.8959652500E+00	8.1940905000E+00	4.8542467500E+00
H	3.6918735000E+00	4.6915570000E+00	6.5609995000E+00
H	3.6918760000E+00	6.9619515000E+00	6.5609967500E+00
H	6.0622617500E+00	6.9681692500E+00	3.1768652500E+00

Table S3b. Cartesian coordinates of the perovskite $PyPbI_3$. The first three lines are the crystal lattice vectors. The data is given in Angstroms.

14.91410	0.000000	0.000000
0.00000	8.045300	0.000000
0.00000	0.000000	9.593300

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Pb	5.3247527676E-07	5.1778221123E-07	4.7966494774E+00
Pb	7.4570505325E+00	4.0226505178E+00	-5.2262475495E-07
Pb	7.4570505325E+00	5.1778221123E-07	-1.5678742646E-06
I	8.0565665754E-01	6.0339752589E+00	7.1546795862E+00
I	2.4116132713E+00	2.0113252589E+00	5.2216366916E+00
I	1.6172876877E+00	6.0339755178E+00	2.9806319340E+00
I	5.0454377936E+00	6.0339752589E+00	4.2498669159E-01
I	6.6513944074E+00	2.0113252589E+00	2.3580295862E+00
I	9.0743376877E+00	6.0339755178E+00	1.8160159755E+00
I	5.8397633773E+00	2.0113255178E+00	7.7772819340E+00
I	1.4108444407E+01	2.0113252589E+00	2.4386183233E+00
I	9.8686632713E+00	2.0113252589E+00	9.1683112179E+00
I	1.2502487794E+01	6.0339752589E+00	4.3716612179E+00
I	8.2627066575E+00	6.0339752589E+00	7.2352683233E+00
I	1.3296813377E+01	2.0113255178E+00	6.6126659755E+00
C	5.9209016936E+00	6.7162157151E+00	4.0704412142E+00
C	5.2139659522E+00	7.4499441755E+00	5.0738914573E+00
C	4.4667753461E+00	6.7097846011E+00	6.1080503471E+00
C	4.4667753461E+00	5.3581659166E+00	6.1080503471E+00
C	5.2139659522E+00	4.6180068600E+00	5.0738909347E+00
C	2.9902757188E+00	1.3355159166E+00	1.3114003471E+00
C	2.2430851128E+00	5.9535686004E-01	2.7724093470E-01
C	1.5361493714E+00	2.6935657151E+00	-7.2620878579E-01
C	2.2430851128E+00	3.4272941755E+00	2.7724145733E-01
C	2.9902757188E+00	2.6871346011E+00	1.3114003471E+00
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C	1.2671015952E+01	4.6180068600E+00	9.3160569748E+00
C	1.1923825346E+01	5.3581659166E+00	8.2818975624E+00
C	1.1923825346E+01	6.7097846011E+00	8.2818975624E+00
C	1.2671015952E+01	7.4499441755E+00	9.3160564522E+00
C	1.3377951694E+01	6.7162157151E+00	1.0319506695E+01
N	5.9209016936E+00	5.3517353205E+00	4.0704409529E+00
N	1.5361493714E+00	1.3290853205E+00	-7.2620904710E-01
N	8.9931993714E+00	1.3290853205E+00	5.5228569566E+00
N	1.3377951694E+01	5.3517353205E+00	1.0319506957E+01
H	8.4580894079E+00	8.2932141228E-01	6.2726849843E+00
H	1.3913061657E+01	4.8519714123E+00	1.1069334984E+01
H	6.4560116570E+00	4.8519714123E+00	3.3206129253E+00
H	1.0010394079E+00	8.2932141228E-01	-1.4760370747E+00
H	3.5253856823E+00	3.1868992860E+00	2.0612286361E+00
H	3.5253883447E+00	8.3575951630E-01	2.0612315105E+00
H	2.2430851128E+00	-4.4020756267E-01	2.7724093470E-01
H	2.2430901713E+00	4.4628585982E+00	2.7724903539E-01
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H	1.1388712720E+01	4.8584095163E+00	7.5320663990E+00

H	1.2671010894E+01	8.4855085982E+00	9.3160488741E+00
H	1.2671015952E+01	3.5824424373E+00	9.3160569748E+00
H	1.3913058995E+01	7.2159881667E+00	1.1069331065E+01
H	1.0982435682E+01	3.1868992860E+00	2.7354192734E+00
H	9.7001401713E+00	4.4628585982E+00	4.5193988741E+00
H	1.0982438345E+01	8.3575951630E-01	2.7354163990E+00
H	9.7001351128E+00	-4.4020756267E-01	4.5194069748E+00
H	8.4580920703E+00	3.1933381667E+00	6.2726810646E+00
H	5.2139659522E+00	3.5824424373E+00	5.0738909347E+00
H	5.2139608936E+00	8.4855085982E+00	5.0738990354E+00
H	3.9316627203E+00	4.8584095163E+00	6.8578815105E+00
H	3.9316653827E+00	7.2095492860E+00	6.8578786361E+00
H	6.4560089947E+00	7.2159881667E+00	3.3206168449E+00

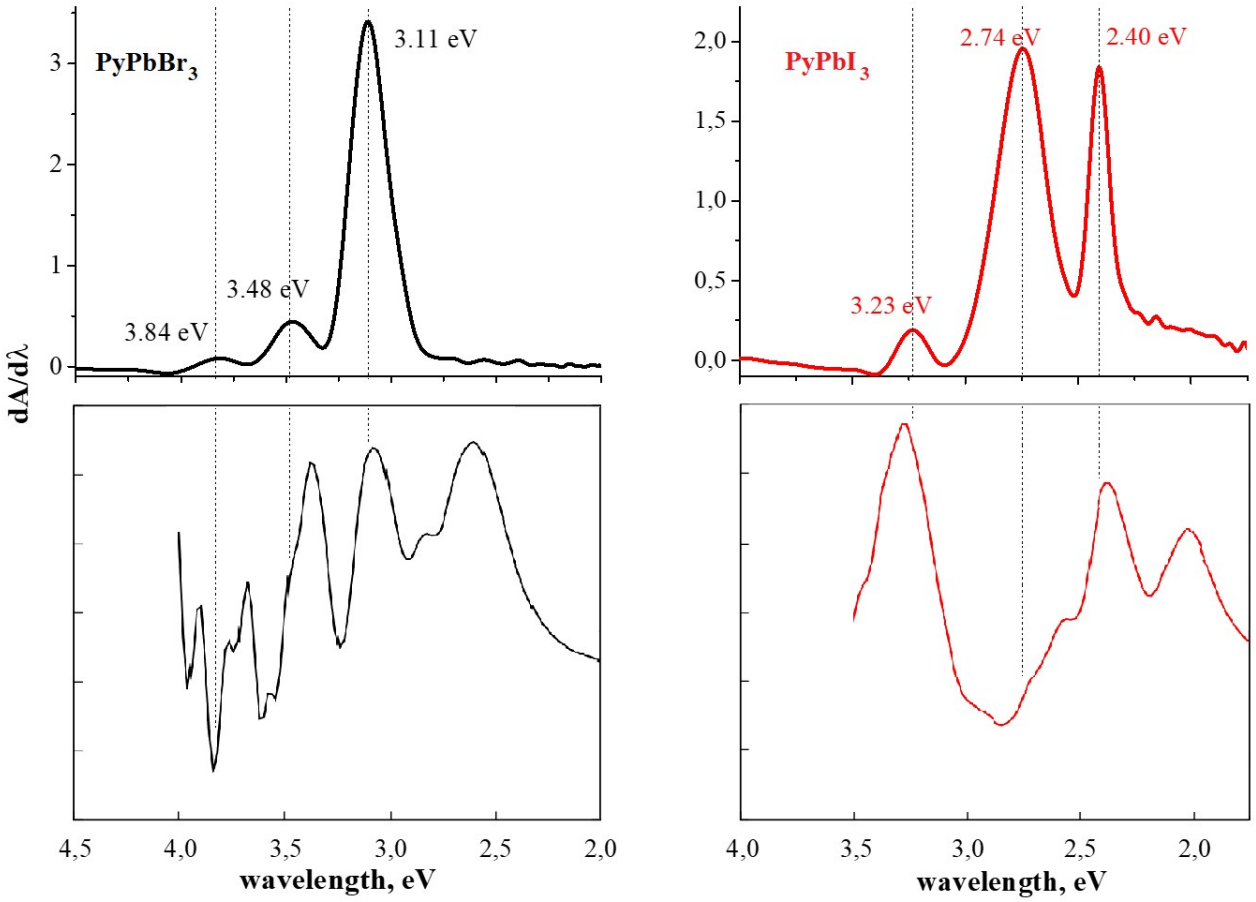

Figure S7. First derivative of the experimental (top) and computed (bottom) absorption dA/dλ for $PyPbBr_3$ and $PyPbI_3$. Given the narrow spectral range, dA/dλ of an experimental absorption spectrum serves a mean of estimation of the energy of electronic transition.

We shall note that first derivative of absorption spectra dA/dλ is only a mathematical treatment that helps to estimate the energies of the spectral features and does not have true physical meaning that can provide the mechanism of the light absorption by solids.