Mechanochemical synthesis of one-dimensional (1D) hybrid perovskites incorporating polycyclic aromatic spacers: highly fluorescent cation-based materials

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Experimental Section

Materials & Methods. $PbBr_2$ (Sigma-Aldrich, 99.999 %), 2-aminofluorene (Sigma-Aldrich, 98 %), 2-aminoanthracene (Sigma-Aldrich, 96 %), 2,7-diaminofluorene (Sigma-Aldrich, >97 %), HBr (Sigma-Aldrich, 48 wt. % in H_2O, ≥99.99 %) and dimethylformamide (Sigma-Aldrich, anhydrous, 99.8 %) were commercially available and used as received without further purification.

Synthesis of (AF)Br, (AA)Br and (DAF)Br_2. 1 mmol 2-aminofluorene, 2-aminoanthracene or 2,7-diaminofluorene was dissolved in ethanol with a slight heating. While heating and stirring, an excess of HBr was added dropwise. The reaction mixture was stirred for 15-20 min at ca. 60 ºC, and after that, the solvent was evaporated in an oven at 100 ºC.

Mechanochemical synthesis of the perovskite powders. The perovskite powders were synthesized by grinding the corresponding organic cation bromide ((AF)Br, (AA)Br and (DAF)Br_2) and $PbBr_2$ in a Retsch Emax electric ball mill for 30 min at 900 rpm, employing two 125 mL reaction chambers and 10 mm stainless steel balls. The total mass of the precursors in each reaction chamber was 1 g, with a molar ratio of 1:2 for the (AF)Br and (AA)Br cations and 1:1 for the (DAF)Br_2 cation.

Perovskite thin films preparation. The precursors were dissolved in DMF to form a solution with the same molar ratios than above. The concentration of the organic cations was 0.1 M in all cases. The concentration of $PbBr_2$ was 0.05 M when mixing it with (AF)Br and (AA)Br, and 0.1 M with (DAF)Br_2. The solutions were deposited as thin films via the spin-coating method for 30 s at 2000 rpm using a hydrophobic quartz as substrate.

Characterization. X-ray diffraction (XRD) data of perovskites as both powder and thin film were collected at room temperature on a Bruker D8 Discover diffractometer operating at 40 kV and 40 mA and using Cu-K_α radiation (1.54059 Å).

Absorption spectra of perovskites as thin film were recorded with a Cary 100 Bio UV-Visible spectrometer putting the substrates with the thin film perovskite directly into the receptacle for trays. A clean glass substrate was used as reference.

Steady-state photoluminescence spectra of perovskites as thin film were recorded with a FLS980 (Edinburgh Instruments) fluorescence spectrometer using a 450 W Xe1 xenon arc lamp and a R298P photomultiplier as detector.

X-ray photoelectron spectroscopy (XPS) measurements of perovskite powders were carried out in a PHOIBOS 150 MCD (SPECS) spectrometer with a non-monochromatic X-ray source (Aluminum K_α line of 1486.6 eV energy and 300 W), placed perpendicular to the analyzer axis. All measurements were made in an ultra-high vacuum (UHV) chamber.

Diffuse-reflectance spectra of perovskites as powder were performed using a Cary 5000 spectrometer with a Pb Smart NIR detector for extended photometric range (200 to 1000 nm). $BaSO_4$ was used as non-absorbing reflectance reference.

Thermal analysis of the powders was performed by simultaneous TG-DSC measurements using a System Setaram Setsys 12 TGA instrument. Samples were heated at a rate of 5 ºC min^{-1} in N_2 (40 mL min^{-1}) at the temperature range 30-800 ºC.

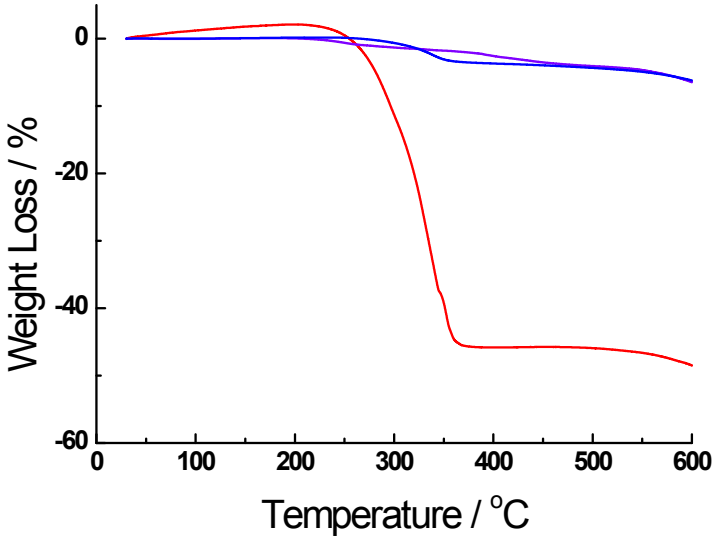

Figure S1. Thermogravimetric analysis (TGA) curves of the synthesized powders with AF (red line), AA (violet line) and DAF (blue line).

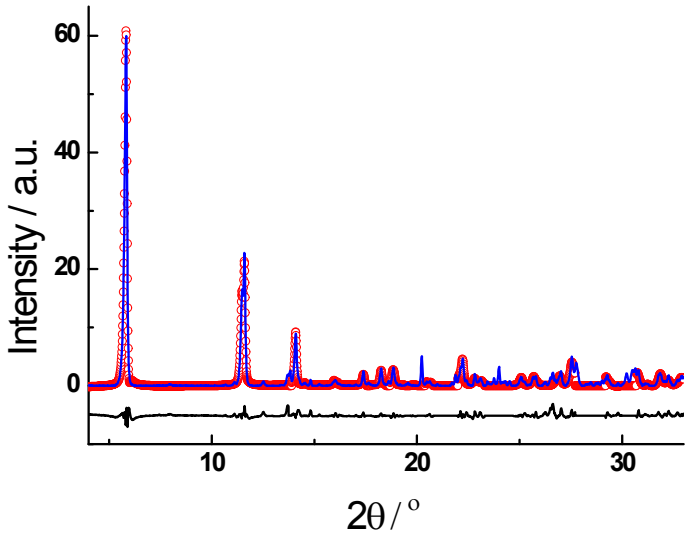

Figure S2. Rietveld refinement of the XRD pattern of $(AF)_2PbBr_4$.

Table S1. Crystal data and structure refinement of $(AF)_2PbBr_4$ at 298 K.

Chemical formula Wavelength	$PbBr_4C_{26}H_{24}N_2$ 1.5405262 Å	
Crystallographic system	Monoclinic	
Space group	I1C1	
Unit-cell dimensions	a = 12.16 ± 0.03 Å b = 8.20 ±0.02 Å c = 31.38 ± 0.08 Å	α = 90º β = 90.84 ±0.01º γ = 90º
Density	1.893 g/cm^3	
Z	4	
Absorption coefficient		
2θ range for data collection	4 – 33.5 deg	
Time per step/sec.	288	
Refinement method	Rietveld	
R_{wp}	0.064	
R_{wb}	0.07	
R_p	0.16	

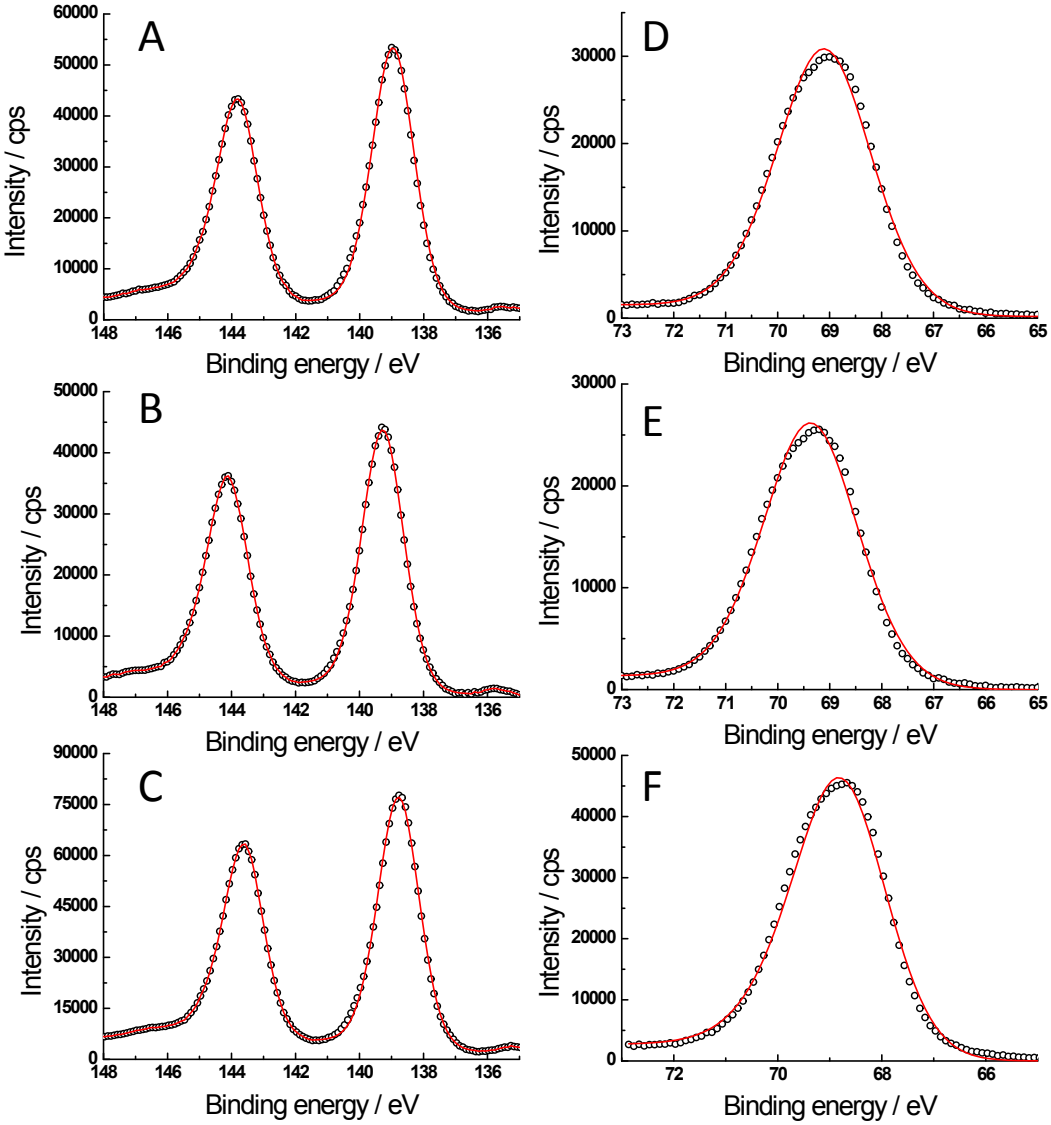

Figure S3. XPS spectra of Pb 4f (A-C) and Br 3d (D-F) of the synthesized powders with 2-ammonium fluorene (A and D), 2-ammonium anthracene (B and E), and 2,7-diammonium fluorene (C and F) cations.

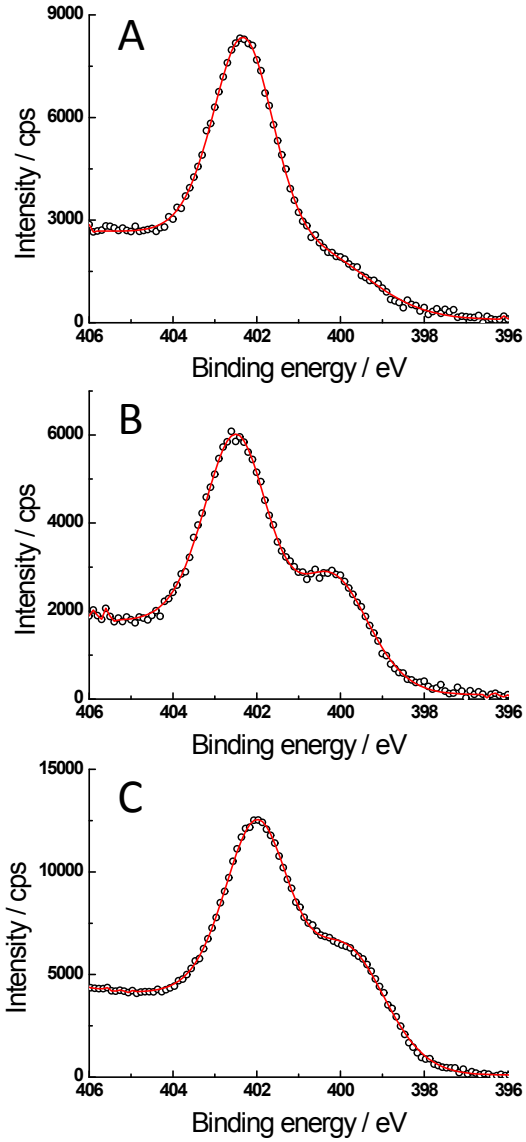

Figure S4. XPS spectra of N 1s of the synthesized powders with 2-ammonium fluorene (A), 2-ammonium anthracene (B), and 2,7-diammonium fluorene (C) cations.

XPS measurements of the protonated organic compounds.

We have performed XPS experiments for the as-prepared (AF)Br, (AA)Br and (DAF)Br2 compounds after protonation. Figure S5 displays the N 1s photoemission peaks attributed to NH_3^+ groups (402.5 eV) and non-protonated NH_2 groups (400.0 eV) for the three organic compounds. The percentage of the non-protonated species that can be considered as impurity since do not participate in the formation of the perovskite material can be calculated from the relative area between the two peaks. Thus, the percentage of the non-prononated form is 15% in the case of the AF and around 30% for the AA and DAF compounds.

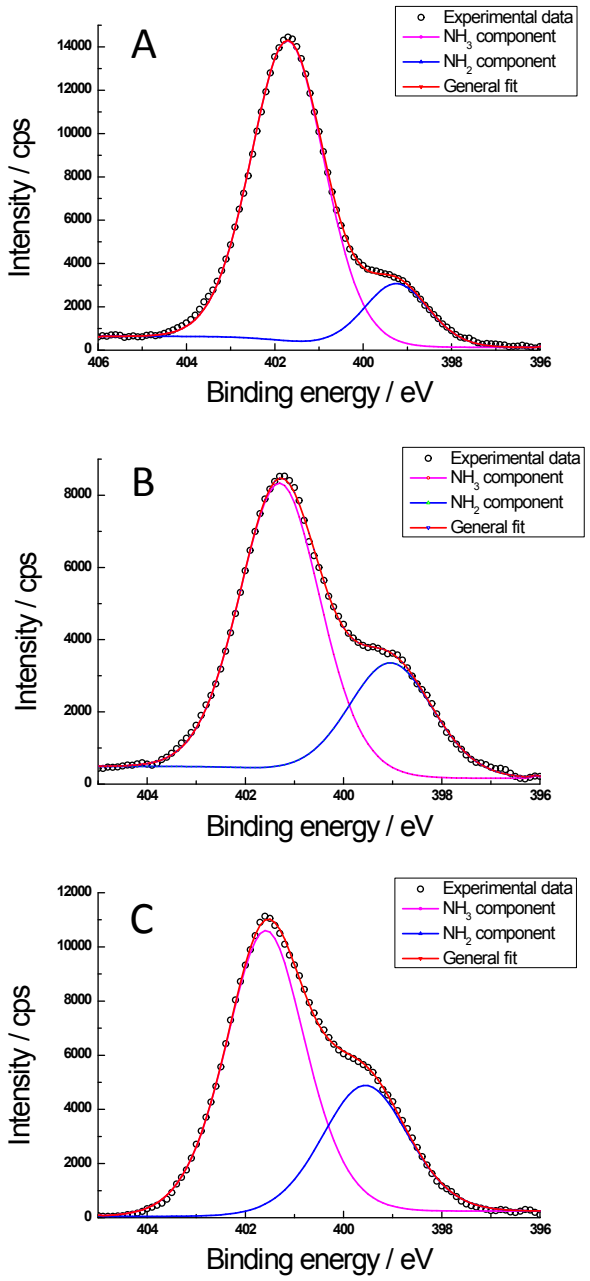

Figure S5. XPS spectra of N 1s of the 2-ammonium fluorene (A), 2-ammonium anthracene (B), and 2,7-diammonium fluorene (C) compounds after protonation with HBr.

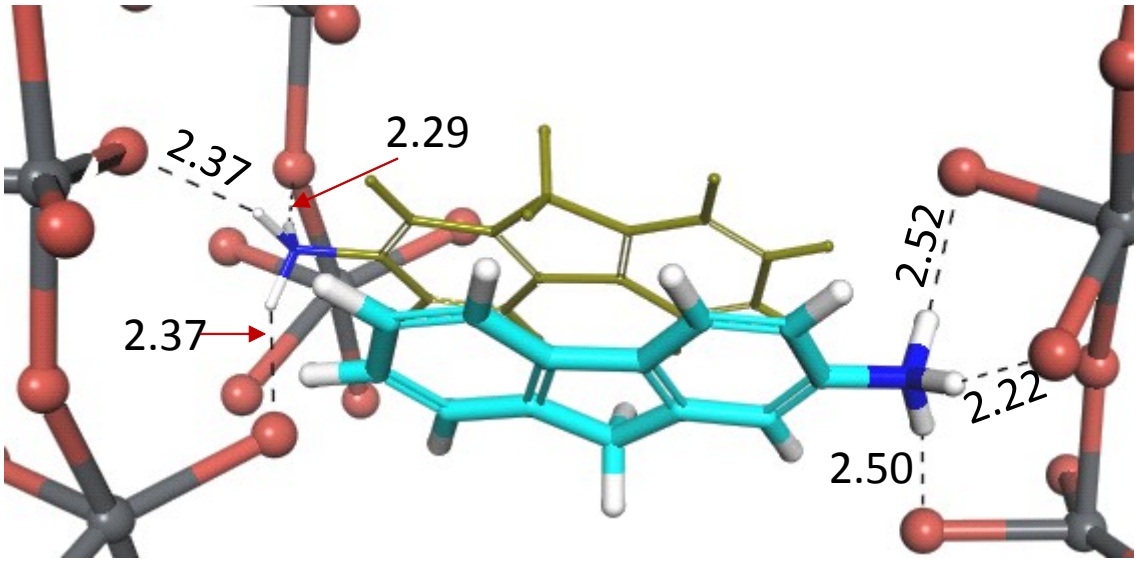

Figure S6. Partial view of the crystal structure of $(AF)_2PbBr_4$ showing the Br-H distances that allow the formation of H-bonds.

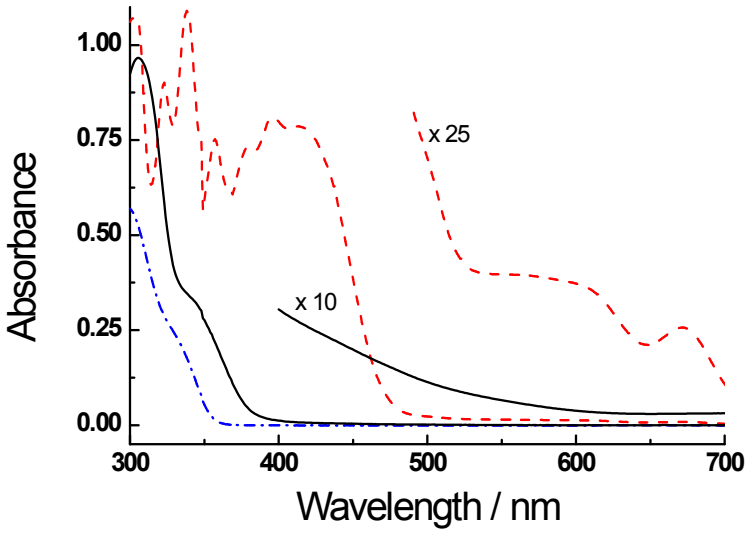

Figure S7. Absorption spectra of the AF (dashed-dotted blue line), AA (dashed red line) and DAF (solid black line) cations in water solution.

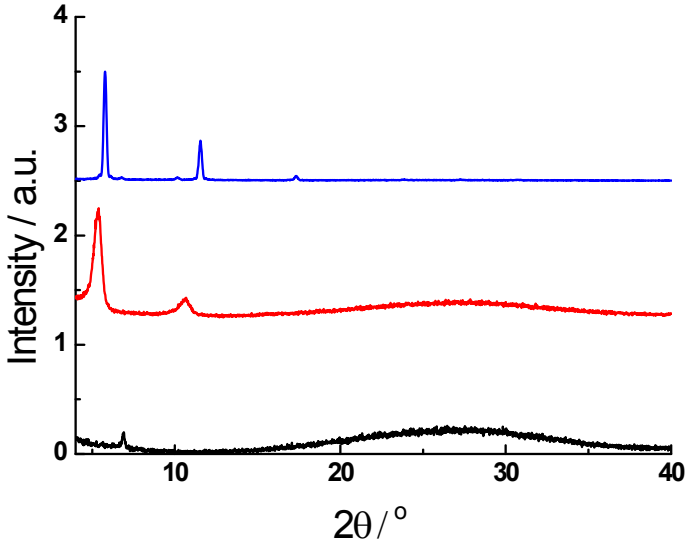

Figure S8. X-ray powder diffraction (XRD) data of the films synthesized with the AF (blue line), AA (red line) and DAF (black line) cations.

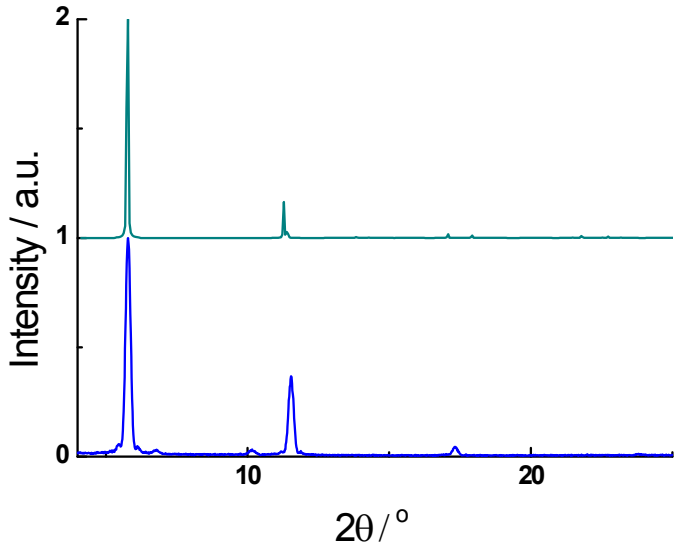

Figure S9. Experimental (blue line) and theoretical with preferential orientation along the <100> direction (green line) X-ray diffractograms of the AF_2PbBr_4 structure in the thin films.

Table S2. Refined atomic position for $(AF)_2PbBr_4$ crystal structure at 298 K.

Atom	x	y	z
Pb	0.2785(0)	0.2783(0)	0.5376(5)
Br1	0.0832(0)	0.1952(0)	0.5220(5)
Br2	0.3282(0)	0.340(3)	0.4585(8)
Br3	0.3081(0)	0.0062(0)	0.5776(0)
Br4	0.1965(0)	0.506(0)	0.5833(0)
N1	0.068(4)	0.8587(0)	0.6064(3)
C	0.054(4)	0.877(2)	0.6513(6)

C	0.129(3)	0.810(1)	0.6807(0)
C	0.107(3)	0.819(1)	0.7245(0)
C	0.178(3)	0.7690(6)	0.7610(0)
C	0.113(3)	0.8138(0)	0.7987(0)
C	0.145(3)	0.8053(4)	0.8416(5)
C	0.081(3)	0.8811(0)	0.8723(8)
C	-0.018(3)	0.9546(0)	0.8602(7)
C	-0.049(3)	0.9608(0)	0.8169(4)
C	0.020(3)	0.8943(0)	0.7862(0)
C	0.016(3)	0.8973(9)	0.739(5)
C	-0.057(4)	0.968(2)	0.7101(7)
C	-0.037(3)	0.961(1)	0.6663(8)
N2	0.060(2)	0.4503(0)	0.9418(0)
C	0.076(2)	0.4222(0)	0.8973(5)
C	0.172(2)	0.3473(0)	0.8839(0)
C	0.185(1)	0.3061(0)	0.8410(0)
C	0.1039(6)	0.3454(0)	0.8111(0)
C	0.0981(8)	0.3266(0)	0.7642(2)
C	0.1714(3)	0.2639(0)	0.7348(3)
C	0.1494(3)	0.2784(0)	0.6909(2=
C	0.053(1)	0.3558(0)	0.6770(3)
C	-0.022(1)	0.408(0)	0.7067(0)
C	0.0014(6)	0.3926(0)	0.7502(1)
C	-0.058(1)	0.4665(0)	0.7862(2)
C	0.0107(1)	0.4220(0)	0.8240(3)
C	-0.0045(2)	0.4650(0)	0.8668(2)

Table S3. Anisotropic atomic displacement parameters ($Å^2$) $(AF)_2PbBr_4$ crystal structure at 298 K.

Name	**U_{eq}**	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{23}**	**U_{13}**
Pb	25.87529 ± *0.00549*	14.06006 ± *0.00000*	25.28907 ± *0.00000*	37.96693 ± *0.00000*	15.75096 ± *0.00000*	-19.67543 ± *0.18469*	-10.15347 ± *0.18787*
Br1	14.68207 ± *0.00000*	3.65426 ± *0.00000*	11.02698 ± *0.00000*	29.44301 ± *0.00000*	-2.31574 ± *0.00000*	-12.24200 ± *0.00000*	2.89775 ± *0.00000*
Br2	7.63229 ± *0.39496*	4.69217 ± *0.15045*	4.61357 ± *0.00000*	13.66356 ± *0.03274*	-2.39132 ± *0.06962*	-1.85032 ± *0.07788*	2.59807 ± *0.12778*
Br3	88.39648 ± *0.00000*	48.70863 ± *0.00000*	65.54611 ± *0.00000*	153.10199 ± *0.00000*	-52.83840 ± *0.00000*	-81.79434 ± *0.00000*	75.18953 ± *0.00000*
B4	15.75764 ± *1.23288*	3.49646 ± *0.00000*	34.64651 ± *0.48062*	9.09707 ± *0.00000*	0.90464 ± *0.38725*	-14.24729 ± *0.00000*	-1.02511 ± *0.32019*
N	6.51300 ± *1.62704*	6.43514 ± *0.57943*	9.67970 ± *0.22721*	3.51558 ± *0.12229*	2.56828 ± *0.00000*	0.81136 ± *0.15130*	3.18186 ± *0.26941*

C	28.11273 ± *4.86329*	24.60078 ± *0.00000*	4.11029 ± *0.00000*	56.55812 ± *1.89547*	-0.77659 ± *0.37570*	-3.11747 ± *0.00000*	32.25853 ± *0.00000*
C	5.07646 ± *1.36237*	4.73327 ± *0.49050*	3.36758 ± *0.00000*	7.13438 ± *0.20364*	-2.37214 ± *0.16484*	-1.66327 ± *0.00000*	0.28631 ± *0.00000*
C	10.71960 ± *2.59340*	8.81717 ± *0.81712*	7.41098 ± *0.00000*	15.64670 ± *0.59523*	-6.35942 ± *0.30999*	3.66284 ± *0.00000*	-9.47706 ± *0.44720*
C	12.27075 ± *4.69280*	18.06380 ± *1.82796*	1.64204 ± *0.07457*	17.34680 ± *0.00000*	-3.84023 ± *0.00000*	0.07837 ± *0.00000*	8.43524 ± *0.00000*
C	113.08900 ± *63.40757*	8.60315 ± *0.00000*	1.72145 ± *0.13121*	329.64327 ± *24.71247*	-3.13134 ± *0.00000*	-12.04809 ± *0.00000*	26.32167 ± *12.04043*
C	9.56462 ± *1.78233*	6.30341 ± *0.20549*	18.33877 ± *0.66375*	4.03083 ± *0.00000*	1.02239 ± *0.61890*	-8.34352 ± *0.22389*	-0.63288 ± *0.33503*
C	58.27204 ± *1.36385*	2.90393 ± *0.53154*	2.16809 ± *0.00000*	169.71731 ± *0.00000*	-1.13936 ± *0.24370*	-14.37242 ± *0.00000*	0.35778 ± *1.14692*
C	12.32061 ± *0.61877*	4.32531 ± *0.24117*	5.53410 ± *0.00000*	26.82970 ± *0.00000*	1.85312 ± *0.16762*	0.32954 ± *0.04996*	-9.04551 ± *0.48044*
C	6.22087 ± *3.88971*	12.47732 ± *1.50458*	1.91738 ± *0.04169*	4.10742 ± *0.18413*	1.92818 ± *0.20290*	-1.30670 ± *0.15161*	-5.33622 ± *0.54777*
C	9.18337 ± *0.11218*	11.93876 ± *0.00000*	1.94283 ± *0.04373*	13.50738 ± *0.00000*	-0.85818 ± *0.00000*	1.09396 ± *0.16808*	-5.29332 ± *0.00000*
C	14.14033 ± *0.00000*	19.62173 ± *0.00000*	18.82889 ± *0.00000*	4.21120 ± *0.00000*	-18.30570 ± *0.00000*	-8.79266 ± *0.00000*	8.36545 ± *0.00000*
C	8.02627 ± *4.74181*	15.82937 ± *1.83589*	3.18265 ± *0.00000*	5.23520 ± *0.21626*	-3.86207 ± *0.34382*	-1.28463 ± *0.00000*	5.88190 ± *0.18389*
C	18.47874 ± *4.45382*	5.14208 ± *0.53850*	8.53183 ± *0.30390*	41.93737 ± *1.62208*	1.64831 ± *0.22488*	-13.88436 ± *0.44322*	6.29895 ± *0.00000*
N	6.51300 ± *1.62704*	6.43514 ± *0.57943*	9.67970 ± *0.22721*	3.51558 ± *0.12229*	2.56828 ± *0.00000*	0.81136 ± *0.15130*	3.18186 ± *0.26941*
C	11.88119 ± *0.00000*	8.94867 ± *0.00000*	9.51474 ± *0.00000*	17.50313 ± *0.00000*	6.56805 ± *0.00000*	4.98894 ± *0.00000*	11.17834 ± *0.00000*
C	6.87891 ± *0.01114*	2.81604 ± *0.00000*	9.17306 ± *0.00000*	8.62336 ± *0.00000*	0.30065 ± *1.50166*	-1.55593 ± *0.40065*	-0.74148 ± *0.38091*
C	11.89058 ± *5.55692*	2.68042 ± *0.00000*	6.35914 ± *0.84447*	26.55446 ± *1.99449*	-2.64369 ± *0.00000*	3.78035 ± *1.53815*	-2.42890 ± *0.00000*
C	13.83688 ± *1.44505*	10.30216 ± *0.00000*	24.39582 ± *0.56335*	6.92581 ± *0.00000*	-11.09592 ± *0.64110*	-12.34949 ± *0.00000*	3.97547 ± *0.00000*
C	13.84785 ± *4.58471*	13.96535 ± *0.71851*	5.92495 ± *0.24661*	22.10840 ± *1.61744*	-8.04401 ± *0.33905*	-7.69731 ± *0.29258*	15.74433 ± *0.85094*
C	5.35119 ± *1.34656*	4.44494 ± *0.43944*	8.16283 ± *0.28716*	3.36871 ± *0.00000*	5.09972 ± *0.27537*	-2.87136 ± *0.17529*	-2.56368 ± *0.15933*
C	15.94391 ± *2.57407*	3.69013 ± *0.50417*	13.50244 ± *0.23024*	30.69793 ± *0.83634*	0.00874 ± *0.00000*	17.22121 ± *0.06517*	2.25154 ± *0.00000*
C	8.87098 ± *9.02669*	21.94603 ± *3.51548*	1.33492 ± *0.00000*	3.42851 ± *0.15828*	0.78229 ± *0.02072*	0.58978 ± *0.03441*	3.46937 ± *0.21961*
C	18.68069 ± *2.45748*	23.88242 ± *0.00000*	1.77376 ± *0.08050*	31.05490 ± *0.95442*	2.21910 ± *0.00000*	-0.50211 ± *0.13899*	23.15597 ± *0.00000*
C	22.05197 ± *140.03487*	50.72157 ± *54.59103*	1.50965 ± *0.03655*	13.91464 ± *0.38143*	-0.33147 ± *0.00000*	0.72993 ± *0.00000*	0.13318 ± *0.00000*
C	76.96171 ± *22.66931*	26.28411 ± *3.90105*	2.49517 ± *0.32930*	199.97509 ± *7.92075*	3.68296 ± *0.13420*	-13.67784 ± *0.78780*	-70.80140 ± *7.36518*
C	7.76167 ± *0.93247*	0.72473 ± *0.04397*	13.87990 ± *0.14750*	8.65146 ± *0.32925*	0.72440 ± *0.00000*	-9.57618 ± *0.25406*	-0.91480 ± *0.00000*
C	49.83114 ± *9.52617*	5.01664 ± *0.63387*	3.35185 ± *0.00000*	141.63016 ± *3.65836*	1.83884 ± *0.20704*	-6.68800 ± *0.65311*	18.25945 ± *0.00000*