Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Exciton band tuning induced by the cross-sectional size of the cation in 2D Lead Iodide Perovskite Hybrids

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Supporting Information

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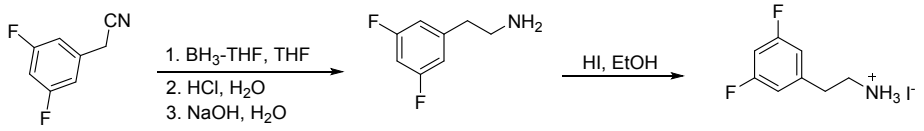
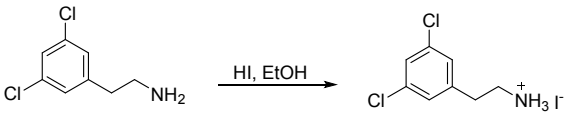
1. Experimental Procedures

Synthesis.



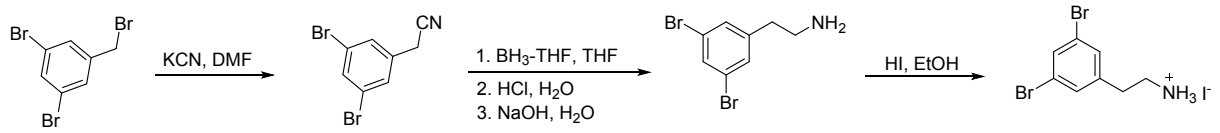
dF-PEA-I

1,3-Difluorophenylethylammonium iodide (dF-PEA-I): To a solution of 1,3-difluorophenylacetonitrile (1.5 g, 10 mmol) in THF (5 mL) was added BH_3•THF (25 mL of a 1 M solution in THF, 26 mmol) at room temperature was slowly added over 10 min under nitrogen. The mixture was heated under reflux and the reaction was followed by TLC. After 3 h, the reaction mixture was cooled in an ice bath and distilled water (20 mL) was added cautiously; this was followed by addition of concentrated aqueous hydrochloric acid (20 mL) over a period of 5 min. The mixture was brought up to reflux for 1 h and was then cooled in an ice bath and poured into water (20 mL) and brought to pH 12 with a 40% aqueous sodium hydroxide solution and extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried over sodium sulfate and then filtered; the solvent was removed using a rotary evaporator, while keeping the solution below 40 °C, to yield a colorless oil. The crude oil was dissolved in ethanol (2 mL) and cooled down to 0 °C. Hydroiodic acid (57 wt% aqueous solution) was added and the mixture was stirred for 1 h at 0 °C. The solid was filtered and washed with diethyl ether to yield dF-PEA-I as a white powder (1.4 g, 49%). ^{1}H NMR (DMSO-d_6, 500 MHz): 7.09 (td, J = 9.6, 4.8 Hz, 1H), 7.06 – 7.02 (m, 2H), 3.11 (t, J = 7.6 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H) ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): δ 163.78, 142.18, 112.64, 102.71, 39.73, 32.91. HRMS-ESI (*m/z*): calcd for $C_8H_{10}NF_2$ $(M–I)^+$, 158.0772; found, 158.0776. Anal. Calcd for $C_8H_{10}NF_2I$: C, 33.71; H, 3.54; N, 4.91. Found: C, 33.96; H, 3.56; N, 4.90.



dCl-PEA-I

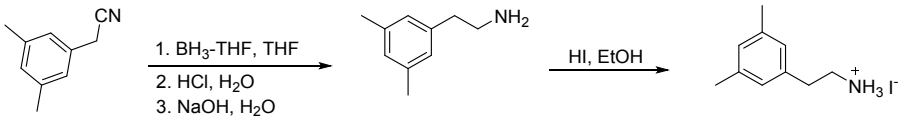
1,3-Dichlorophenylethylammonium iodide (dCl-PEA-I): 1,3-dichlorophenylethylamine (1 g, 5.26 mmol) was dissolved in ethanol (2 mL) and cooled down to 0 °C. Hydroiodic acid (57 wt% aqueous solution) was added and the mixture was stirred for 1 h at 0 °C. The solid was filtered and washed with diethyl ether to yield dCl-PEA-I as a white powder (1.3 g, 78%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.75 (br, 3H), 7.51 (s, 1H), 7.39 (s, 2H), 2.37 (br, 2H), 2.88 (t, J = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): δ 141.99, 134.51, 128.27, 126.97, 32.65. HRMS-ESI (*m/z*): calcd for $C_8H_{10}NCl_2$ $(M–I)^+$, 190.0182; found, 190.0185. Anal. Calcd for $C_8H_{10}NCl_2I$: C, 30.22; H, 3.17; N, 4.41. Found: C, 30.51; H, 3.10; N, 4.23.



dBr-PACN **dBr-PEA-I**

2-(3,5-dibromophenyl)acetonitrile (dBr-PACN): To a stirred solution of 3,5-Dibromobenzyl bromide (4 g, 12 mmol) in a mixture of EtOH (63 mL) and H_2O (16 mL) was added NaCN (0.73 g, 15 mmol). The mixture was stirred under reflux until completion of the reaction. Then the EtOH was removed under reduced pressure and the residue was extracted with EtOAc, dried over Na_2SO_4 and filtered. The filtrate was evaporated under reduced pressure and the resulting residue was purified by flash column chromatography (1:9 Ethyl acetate/Hexanes) to obtain a white powder (2.49 g, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.68 (s, 1H), 7.47 (s, 2H), 3.75 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 134.1, 133.4, 129.8, 123.7, 116.5, 22.9. HRMS-ESI (m/z): calcd for $C_8H_5NBr_2$ $(M+H)^+$, 272.8783; found, 272.8784. Anal. Calcd for $C_8H_5NBr_2$: C, 34.95; H, 1.83; N, 5.09. Found: C, 35.13; H, 1.67; N, 4.98.

2-(3,5-dibromophenyl)ethan-1-amine (dBr-PEA-I): 2-(3,5-dibromophenyl)acetonitrile (1.0 g, 3.63 mmol) in anhydrous tetrahydrofuran (2 mL) was added to 1M solution of BH_3-THF (9 mL, 9.1 mmol) over 10 min at room temperature. Following the addition, the mixture was heated under reflux and under argon. The reaction was cooled, water was added and the mixture was extracted with dichloromethane. The organic layer was washed with brine (4.5 mL), dried over sodium sulfate and evaporated at reduced pressure to yield transparent oil (1.02g, 100%). The product was used without further purification. HI solution (0.91 mL, 5 mmol) was added dropwise to a cold (0 °C), stirred solution of 2-(3,5-dibromophenyl)ethan-1-amine (1.02 g, 3.7 mmol) in ethanol (0.6 mL). The solution was stirred for 30 minutes and the solvent was evaporated. The resulting solids were filtered through paper and washed repeatedly with diethyl ether to afford a yellow powder. The product was precipitated in ether from ethanol to afford a white powder (0.79 g, 53%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.75 (t, J=1.8Hz, 1H), 7.73 (br, 3H), 7.55 (d, J=1.8Hz, 2H), 3.10 (q, J=7.0 Hz, 2H), 2.86 (t, J=7.5Hz, 2H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 125 MHz): δ 142.6, 132.3, 131.5, 123.0, 32.6. HRMS-ESI (m/z): calcd for $C_8H_{10}NBr_2$ $(M+H)^+$, 277.9175; found, 277.9175. Anal. Calcd for $C_8H_{10}NBr_2I$: C, 23.62; H, 2.48; N, 3.44. Found: C, 23.48; H, 2.66; N, 3.30.



dMe-PEA-I

1,3-Dimethylphenylethylammonium iodide (dMe-PEA-I): To a solution of 1,3-dimethylphenylacetonitrile (1.7 g, 12 mmol) in THF (5 mL) was added BH_3•THF (25 mL of a 1 M solution in THF, 30 mmol) at room temperature was slowly added over 10 min under nitrogen. The mixture was heated under reflux and the reaction was followed by TLC. After 3 h, the reaction mixture was cooled in an ice bath and distilled water (20 mL) was added cautiously; this was followed by addition of concentrated aqueous

hydrochloric acid (20 mL) over a period of 5 min. The mixture was brought up to reflux for 1 h and was then cooled in an ice bath and poured into water (20 mL) and brought to pH 12 with a 40% aqueous sodium hydroxide solution and extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried over sodium sulfate and then filtered; the solvent was removed using a rotary evaporator, while keeping the solution below 40 °C, to yield a colorless oil. The crude oil was dissolved in ethanol (2 mL) and cooled down to 0 °C. Hydroiodic acid (57 wt% aqueous solution) was added and the mixture was stirred for 1 h at 0 °C. The solid was filtered and washed with diethyl ether to yield dMe-PEA-I as a white powder (0.7 g, 22%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.74 (br, 3H), 6.89 (s, 1H), 6.86 (s, 2H), 3.02 (t, J = 7.9 Hz, 2H), 2.77 (t, J = 7.9 Hz, 2H), 2.25 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): δ 138.03, 137.43, 128.63, 126.87, 40.45, 33.36, 21.36. HRMS-ESI (*m/z*): calcd for $C_{10}H_{16}N$ $(M–I)^+$, 150.1274; found, 150.1277. Anal. Calcd for $C_{10}H_{16}NI$: C, 43.34; H, 5.82; N, 5.05. Found: C, 43.22; H, 5.95; N, 4.94.

General synthesis of bulk crystals. PbI_2 (1 eq) was dissolved in HI (57 wt% aqueous solution) and stirred at 100 °C for 2 min. A solution of dY-PEA-I (2 eq) in HI and MeOH was added to the hot PbI_2 solution and the resultant mixture was stirred at 130 °C for 2 min. The solution was then allowed to crystallize at room temperature for 12 h. The solids were filtered and dried under high vacuum.

Bis(3,5-difluorophenylethylammonium) tetraiodoplumbate ($(dF\text{-}PEA)_2PbI_4$). PbI_2 (510 mg, 0.1 mmol) in HI (10 mL). dF-PEA-I (580 mg, 0.2 mmol) in MeOH (10 mL) gave pale orange crystals (560 mg, 54%). Anal. Calcd. for $(C_8H_{10}NF_2)_2PbI_4$: C, 18.64%; H, 1.96%; N, 2.72%. Found: C, 18.80%; H 1.85%; N, 2.76%.

Bis(3,5-dichlorophenylethylammonium) tetraiodoplumbate ($(dCl\text{-}PEA)_2PbI_4$). PbI_2 (50 mg, 0.1 mmol) in HI (4 mL). dCl-PEA-I (68 mg, 0.2 mmol) in HI (4 mL) and MeOH (2 mL) gave dark orange crystals (90 mg, 81%). Anal. Calcd. for $(C_8H_{10}NCl_2)_2PbI_4$: C, 17.52%; H, 1.84%; N, 2.55%. Found: C, 17.56%; H 1.71%; N, 2.50%.

Bis(3,5-dibromophenylethylammonium) tetraiodoplumbate ($(dBr\text{-}PEA)_2PbI_4$). PbI_2 (46 mg, 0.1 mmol) in HI (0.5 mL). dBr-PEA-I (64 mg, 0.2 mmol) in MeOH (2.5 mL) gave dark orange crystals (68 mg, 53%). Anal. Calcd. for $(C_8H_{10}NBr_2)_2PbI_4$: C, 15.08%; H, 1.58%; N, 2.20%. Found: C, 15.36%; H 1.55%; N, 2.22%.

Bis(3,5-dimethylphenylethylammonium) tetraiodoplumbate ($(dMe\text{-}PEA)_2PbI_4$). PbI_2 (46 mg, 0.1 mmol) in HI (0.5 mL). dMe-PEA-I (94 mg, 0.2 mmol) in MeOH (2 mL) gave dark orange crystals (68 mg, 64%). Anal. Calcd. for $(C_9H_{16}N)_2PbI_4$: C, 21.79%; H, 3.25%; N, 2.83%. Found: C, 21.87%; H 2.71%; N, 2.56%.

Bis(3-chlorophenylethylammonium) tetraiodoplumbate ($(3Cl\text{-}PEA)_2PbI_4$). PbI_2 (460 mg, 1 mmol) in HI (10 mL). 3Cl-PEA (310 mg, 2 mmol) in HI (0.2 mL) and MeOH (5 mL) gave orange crystals (706 mg, 69%). Anal. Calcd. for $(C_8H_{11}NCl)_2PbI_4$: C, 18.69%; H, 2.16%; N, 2.72%. Found: C, 18.84%; H 2.00%; N, 2.72%.

Bis(3-bromophenylethylammonium) tetraiodoplumbate ($(3Br\text{-}PEA)_2PbI_4$). PbI_2 (461 mg, 1 mmol) in HI (10 mL). 3Br-PEA (400 mg, 2 mmol) in HI (0.2 mL) and MeOH (2.5 mL) gave orange crystals (685 mg, 66%).

Bis(3-methylphenylethylammonium) tetraiodoplumbate ($(3Me\text{-}PEA)_2PbI_4$). PbI_2 (460 mg, 1 mmol) in HI (10 mL). 3Me-PEA (270 mg, 2 mmol) in HI (0.2 mL) and MeOH (5 mL) gave orange crystals (620 mg, 63%). Anal. Calcd. for $(C_9H_{14}N)_2PbI_4$: C, 21.90%; H, 2.86%; N, 2.84%. Found: C, 22.03%; H 2.88%; N, 2.87%.

General synthesis of single crystals. A solution of PbI_2 in HI (1 mL of a 25 mg mL^{-1} solution) was added to a vial. 2 mL of MeOH was added on top. The cation was dissolved in a minimum of MeOH and added in the vial slowly. Crystals started appearing at the interface between the HI and MeOH after 24 h.

Single-crystal X-ray diffraction. Suitable crystals were selected from the reaction mixtures obtained using the general procedure above and were mounted on a loop with paratone oil on a XtaLAB Synergy-S, Dualflex, HyPix diffractometer. The crystals were cooled at the temperature indicated in Table S1 during data collection. Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using least squares minimization. Details of the crystals, data collection, and data refinements are summarized in Tables S1 and S2, while data may be obtained in CIF format from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk); the deposition numbers for the structures are CCDC 1986784-1986789 and 1987208. Simulated powder patterns were calculated by Mercury software[4] using the CIF from the single-crystal X-ray experiment.

Powder X-ray diffraction (PXRD). PXRD patterns were acquired on a Panalytical XPert PRO Alpha-1 XRD Diffractometer using Cu K X-ray tube radiation at a voltage of 45 kV and 40 mA, with an incident beam Johannsson monochromator and an X'Celerator solid-state detector. The diffraction pattern was scanned over the angular range of 3-40° with a step size of 0.016°, at room temperature.

Thermal gravimetric analysis (TGA). TGA was performed using Mettler Toledo Instrument (TGA/ DSC 3+ Star e system) with a scan rate set to 10 $^oC\ min^{-1}$, under a nitrogen gas flow of 80 mL min^{-1}.

Absorbance. Absorbance and diffuse reflectance were measured on a Cary 5000 UV-vis/NIR.

Photoluminescence. Photoluminescence were measured on a Horiba FL3-2i Fluorometer with an excitation at 350 nm.

Table S1. Single-crystal data and structure refinement data.

	$(dF\text{-}PEA)_2PbI_4$ $C_{32}H_{41}F_8N_4Pb_2I_8$	**$(dCl\text{-}PEA)_2PbI_4$** $C_{16}H_{20}Cl_4N_2PbI_4$	**$(dBr\text{-}PEA)_2PbI_4$** $C_{16}H_{20}Br_4N_2PbI_4$	**$(dMe\text{-}PEA)_2PbI_4$** $C_{10}H_{16}NPbI_4$
Formula weight (g mol^{-1})	2063.27	1096.93	1274.77	1015.26
Temperature (K)	109(4)	106(2)	106(9)	100(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)
***a* (Å)**	12.21680(19)	18.0323(4)	18.1147(7)	18.0933(15)
***b* (Å)**	12.27147(16)	8.64280(10)	8.7853(3)	8.7451(7)
***c* (Å)**	16.8535(3)	8.8430(2)	8.8694(3)	8.9006(7)
α (°)	100.4107(13)	90	90	90
β (°)	95.9(10)	100.226(2)	95.314(4)	98.823(3)
γ (°)	90.0024(12)	90	90	90
Volume (Å^3)	2471(4)	1356.29(5)	1403.42(9)	1391.66(19)
Z	2	2	2	2
Z'	1	0.5	0.5	0.5
ρ_{calc} (g cm^{-3})	2.773	2.686	3.012	2.423
μ (mm^{-1})	11.858	11.173	16.088	10.524
***F*(000)**	1842.0	984	1128	920
Crystal size (mm^3)	0.195 × 0.107 × 0.073	0.539 × 0.191 × 0.063	0.30×0.16×0.02	0.213×0.182×0.147
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection (°)	3.35 to 66.28 (0.65 Å)	4.59 to 72.63 (0.60 Å)	4.52 to 51.35 (0.82 Å)	4.56 to 76.15 (0.58 Å)
Index ranges	-18 ≤ h ≤ 18 -18 ≤ k ≤ 18 -25 ≤ l ≤ 25	-30 ≤ h ≤ 30 -14 ≤ k ≤ 14 -14 ≤ l ≤ 14	-21 ≤ h ≤ 21 -10 ≤ k ≤ 10 -10 ≤ l ≤ 10	-30 ≤ h ≤ 30 -15 ≤ k ≤ 14 -14 ≤ l ≤ 15
Reflections collected	66819	41439	16074	43561
Independent reflections	18736 R_{int} = 0.0480 R_{sigma} = 0.0430	6585 R_{int} = 0.1089 R_{sigma} = 0.0572	4218 R_{int} = 0.0584 R_{sigma} = 0.0734	7239 R_{int} = 0.0454 R_{sigma} = 0.0239
Data/restraints/parameters	18736/328/528	6585/0/125	4218/69/126	7239/63/173
Goodness-of-fit on F^2	1.031	1.00	1.063	1.116
Final *R* indexes [I>=2σ(I)]	R_1 = 0.0326 wR_2 = 0.0782	R_1 = 0.0556 wR_2 = 0.1416	R_1 = 0.0654 wR_2 = 0.1835	R_1 = 0.0202 wR_2 = 0.0459
Final *R* indexes [all data]	R_1 = 0.0450 wR_2 = 0.0819	R_1 = 0.0657 wR_2 = 0.1472	R_1 = 0.0690 wR_2 = 0.1880	R_1 = 0.0223 wR_2 = 0.0464
Largest diff. peak/hole (e Å^{-3})	2.29/-3.04	10.94/-3.98	5.38/-1.91	1.76/-1.12

Table S2. Single-crystal data and structure refinement data.

	$(3Cl\text{-}PEA)_2PbI_4$ $C_{32}H_{44}Cl_4N_4Pb_2I_8$	**$(3Br\text{-}PEA)_2PbI_4$** $C_{32}H_{44}Br_4N_4Pb_2I_8$	**$(3Me\text{-}PEA)_2PbI_4$** $C_{18}H_{28}N_2PbI_4$
Formula weight (g mol^{-1})	2056.09	1116.96	988.16
Temperature (K)	99.9(5)	100(2)	104(7)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	Cc (9)	$P1$ (1)	$P\bar{1}$ (2)
***a* (Å)**	34.0099(5)	8.65320(10)	12.32860(10)
***b* (Å)**	8.54985(11)	8.65570(10)	19.0688(2)
***c* (Å)**	8.82458(12)	17.9336(2)	24.3751(2)
α (°)	90	86.6110(10)	67.7520(10)
β (°)	94.8655(14)	79.4250(10)	89.9860(10)
γ (°)	90	89.7100(10)	80.6850(10)
Volume (Å^3)	2556.76(6)	1318.07(3)	5222.14(9)
Z	2	2	8
Z'	0.5	2	4
ρ_{calc} (g cm^{-3})	2.671	2.814	2.514
μ (mm^{-1})	11.645	14.120	11.205
***F*(000)**	1840	992	3555
Crystal size (mm^3)	0.324×0.19×0.092	0.219×0.181×0.07	0.347×0.119×0.084
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection (°)	4.808 to 72.630(0.60 Å)	4.71 to 62.96 (0.68 Å)	2.35 to 56.56 (0.75 Å)
Index ranges	-56 ≤ h ≤ 56 -14 ≤ k ≤ 14 -14 ≤ l ≤ 14	-12 ≤ h ≤ 12 -12 ≤ k ≤ 12 -23 ≤ l ≤ 26	-16 ≤ h ≤ 16 -25 ≤ k ≤ 25 -31 ≤ l ≤ 32
Reflections collected	42345	24825	69618
Independent reflections	12144	11923 R_{int} = 0.0306 R_{sigma} = 0.0372	25770 R_{int} = 0.0784 R_{sigma} = 0.0774
Data/restraints/parameters	12144/162/240	15453/387/459	25770/924/958
Goodness-of-fit on F^2	1.032	1.169	1.023
Final *R* indexes [I>=2σ(I)]	R_1 = 0.0291 wR_2 = 0.0708	R_1 = 0.0391 wR_2 = 0.1106	R_1 = 0.0434 wR_2 = 0.1097
Final *R* indexes [all data]	R_1 = 0.0307 wR_2 = 0.0714	R_1 = 0.0426 wR_2 = 0.1146	R_1 = 0.0504 wR_2 = 0.1144
Largest diff. peak/hole (e Å^{-3})	1.57/-1.86	2.11/-3.06	2.37/-1.89

2. Additional Comparison of X-Ray Crystallographic Data

Table S3. Calculated offset of the inorganic layers for the different analogues (dY-PEA)$_2$PbI$_4$ (Y = F, Cl, Br, Me), along with the offset for the previously reported (PEA)$_2$PbI$_4$.[4]

Cation	Offset
dF-PEA	0.30
PEA	0.37
dCl-PEA	0.37/0.36
dBr-PEA	0.19
dMe-PEA	0.31/0.32

Table S4. Comparison of key structural parameters between the different analogues (dY-PEA)$_2$PbI$_4$ (Y = F, Cl, Br, Me), along with the distortion parameters for the previously reported (PEA)$_2$PbI$_4$.[4] The distortion parameters are calculated using Vesta software.

	(PEA)$_2$PbI$_4$	(dF-PEA)$_2$PbI$_4$	(dCl-PEA)$_2$PbI$_4$	(dBr-PEA)$_2$PbI$_4$	(dMe-PEA)$_2$PbI$_4$
Distortion index	0.00569	0.02235	0.00654	0.00429	0.00513
Quadratic elongation	1.0011	1.0055	1.0019	1.0025	1.0024
Bond angle variance	3.6988	15.5784	6.3297	8.7720	8.4389
Pb-I-Pb (°)	152.83	149.75	155.62	158.25	158.41

3. Additional Figures

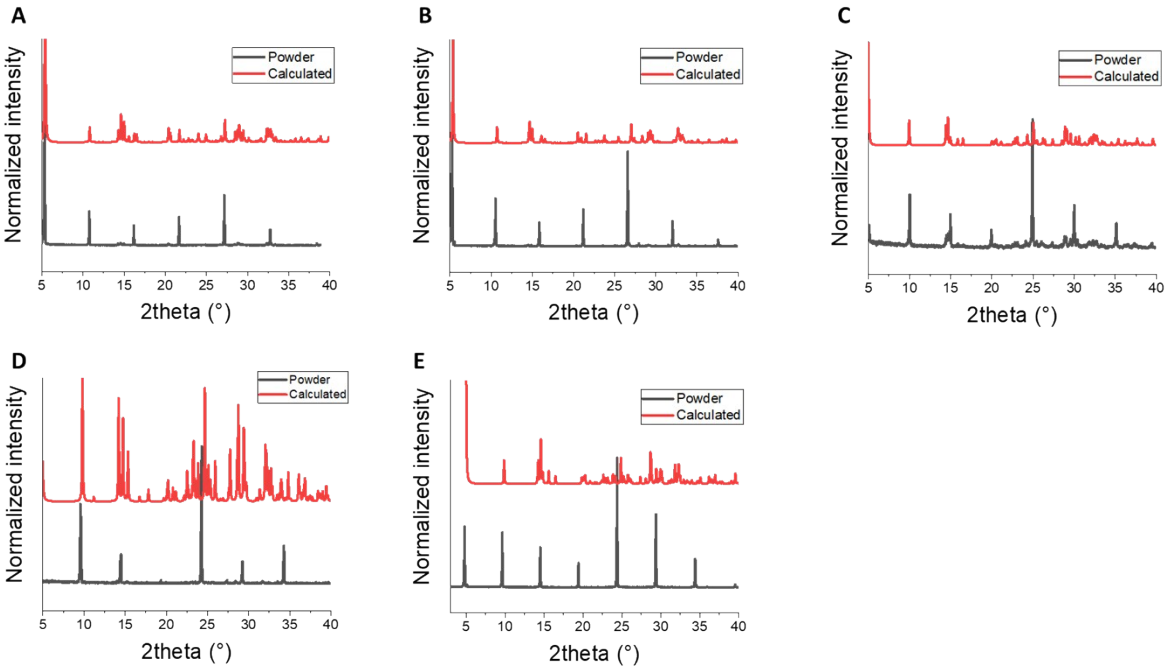


Figure S1. Comparison of the powder X-ray diffraction patterns for (A) $(dF\text{-}PEA)_2PbI_4$, (B) $(PEA)_2PbI_4$, (C) $(dCl\text{-}PEA)_2PbI_4$ and (D) $(dBr\text{-}PEA)_2PbI_4$ and $(dMe\text{-}PEA)_2PbI_4$ powder (gray) with a pattern calculated (red) using the single-crystal data.

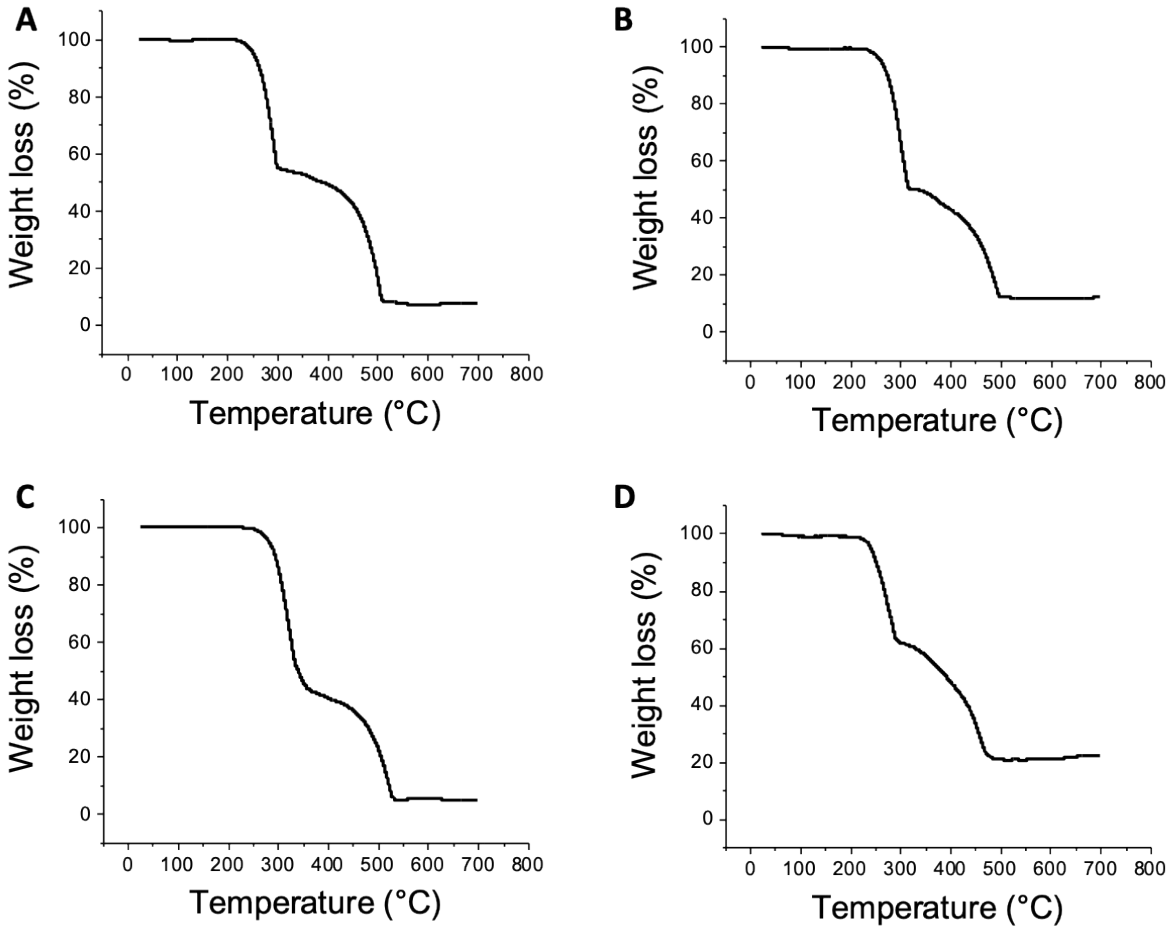


Figure S2. Thermogravimetric analysis of (A) $(dF\text{-}PEA)_2PbI_4$, (B) $(dCl\text{-}PEA)_2PbI_4$, (C) $(dBr\text{-}PEA)_2PbI_4$ and (D) $(dMe\text{-}PEA)_2PbI_4$ from 25 to 700 °C (5 °C min^{-1}). Weight loss for these two HOIPs begins at ca. 280 °C. This initial weight lost is likely due to the organic cation decomposition and loss, while the second period of weight loss is presumably due to the sublimation of the lead halide.

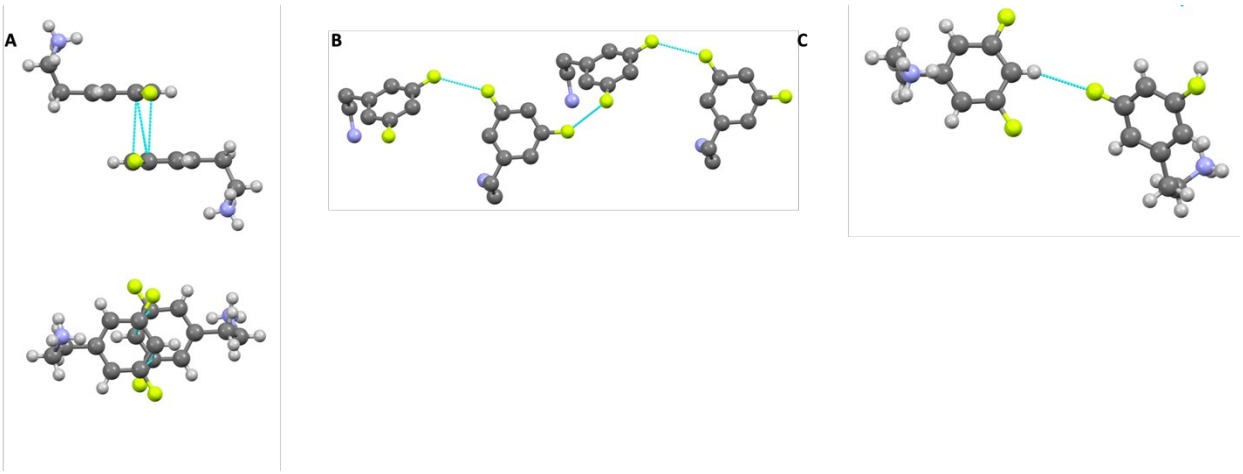


Figure S3. Cation-cation interactions present in the different analogues $(dF\text{-}PEA)_2PbI_4$: (A) pi-pi stacking (3.390 A), (B) F-F interaction (2.930 A), (C) CH_{arom}-F interaction (2.631 A).

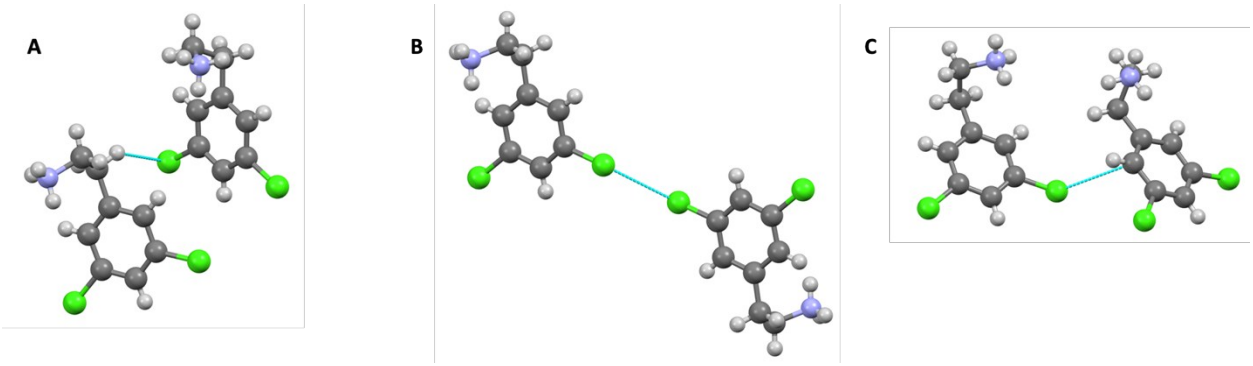


Figure S4. Cation-cation interactions present in the different analogues $(dCl\text{-}PEA)_2PbI_4$: (A) CH_{alkyl}-Cl interaction (2.895 A), (B) Cl-Cl interaction (3.389 A) Cl-CH_{arom} (3.390 A).

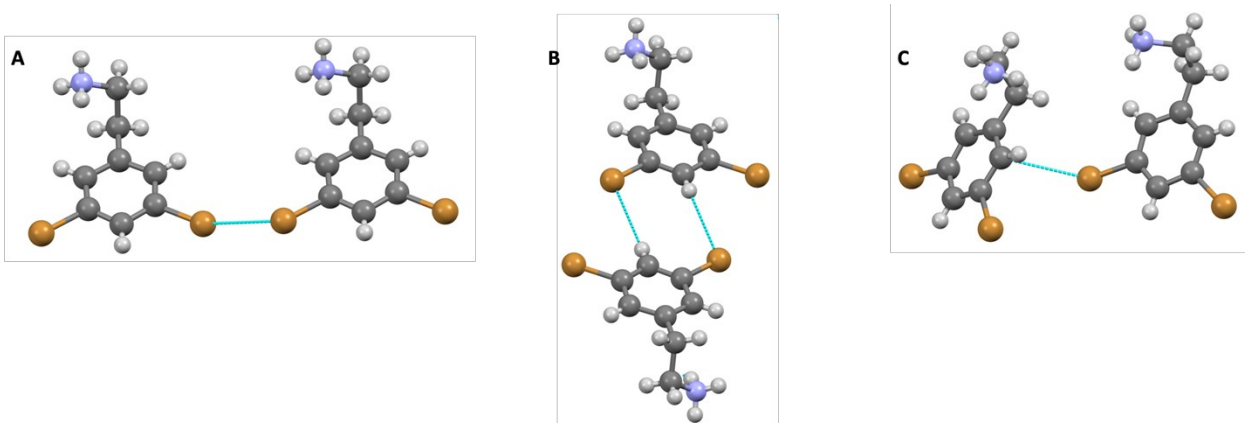


Figure S5. Cation-cation interactions present in the different analogues $(dBr\text{-}PEA)_2PbI_4$: (A) Br-Br interaction (3.587 A), (B) CH_{arom}-Br interaction (2.970 A), pi-Br interaction (3.386 A).

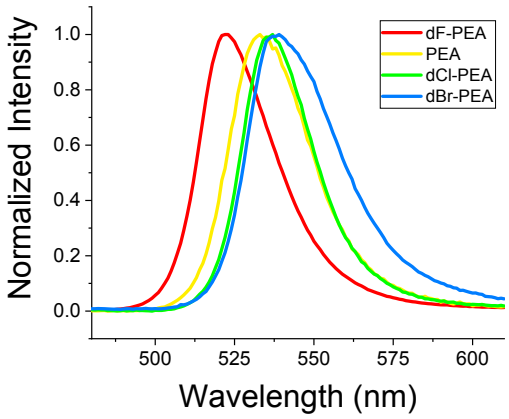


Figure S5. PL spectra of the different analogues $(dY\text{-}PEA)_2PbI_4$ (Y= F, H, Cl, Br) powder (excitation wavelength 400 nm).

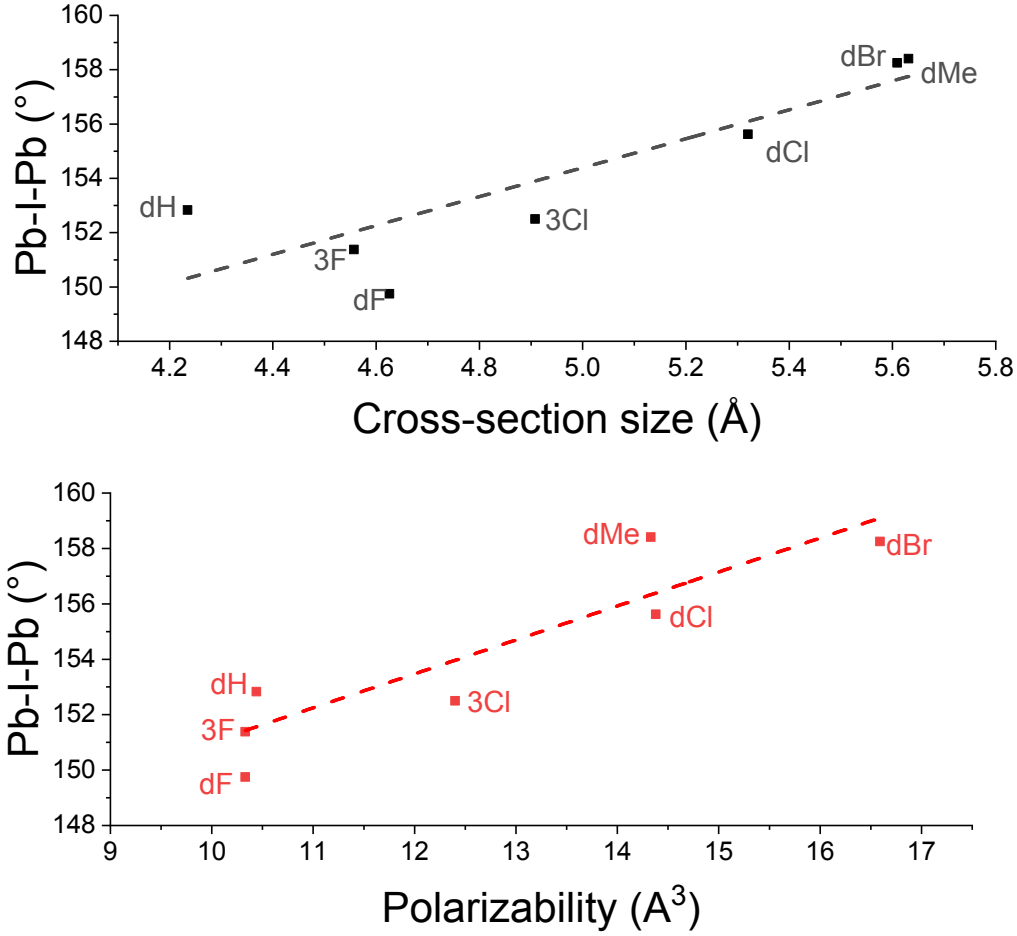


Figure S6. Relationship between the Pb-I-Pb bond angle of the inorganic and structural indicators: (top) cross-section size, (bottom) polarizability.

4. References

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