Supplementary Information for:

Towards Fluorinated Ruddlesden-Popper Perovskites with Enhanced Physical Properties: A Study on $(3\text{-}FC_6H_4CH_2CH_2NH_3)_2PbI_4$ Single Crystals

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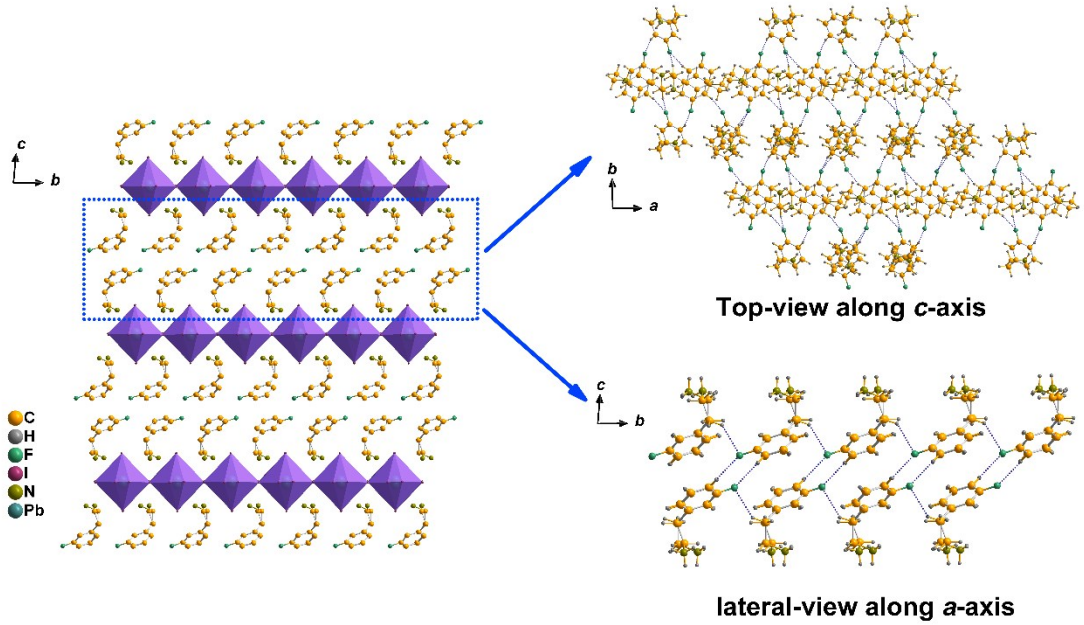

Figure S1. Two-dimensional C-F···H-C hydrogen bond network. Clearly, the spacer cations interact with each other by weak hydrogen bonds, forming an interconnected cationic bilayer and improving the stability of the materials. Parts of H atoms are omitted for clarity.

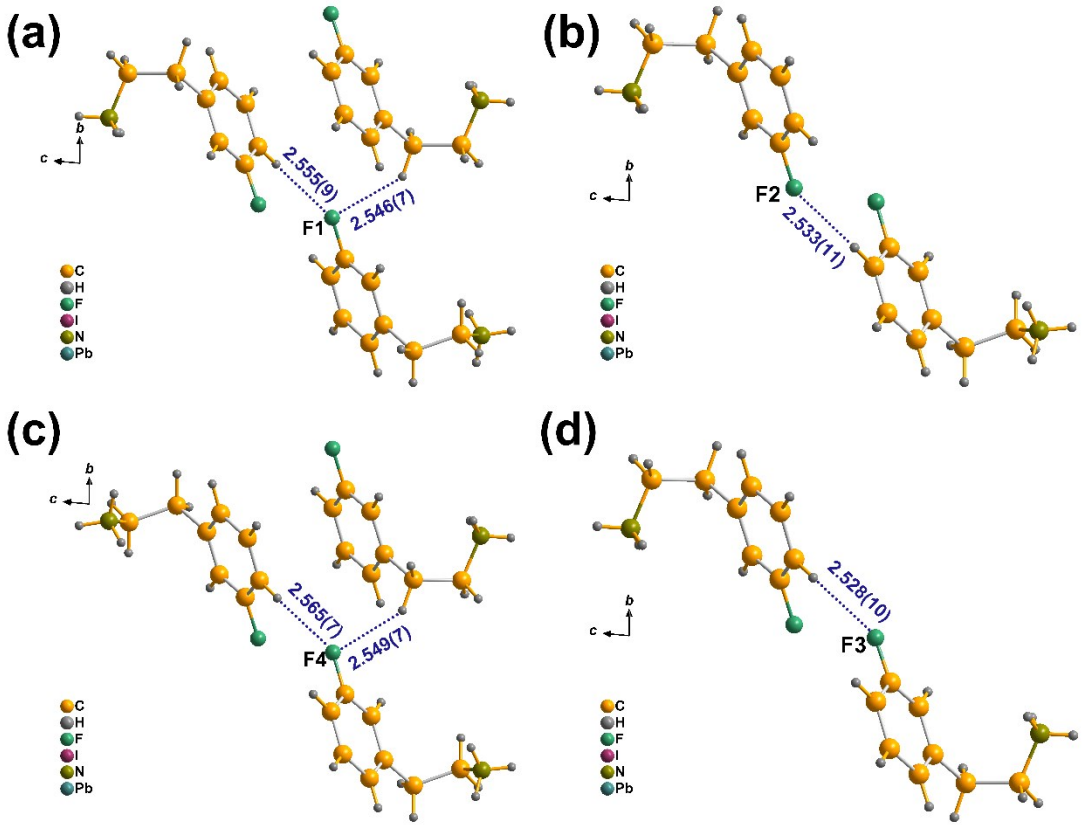

Figure S2. The C-F···H-C hydrogen bonding interactions within the spacer cation slabs. (a)~(d) presents the ball-and-stick representations around the F1, F2, F4, and F3, respectively, where F1and F4 are related to two adjacent 3-fluorophenethylamine cations by forming hydrogen bonding interactions with one hydrogen atom on the C of the benzene ring and the other on the ethylamine branch, respectively, while F2 and F4 forms hydrogen bonding interactions with only one H atom on the C of the benzene ring.

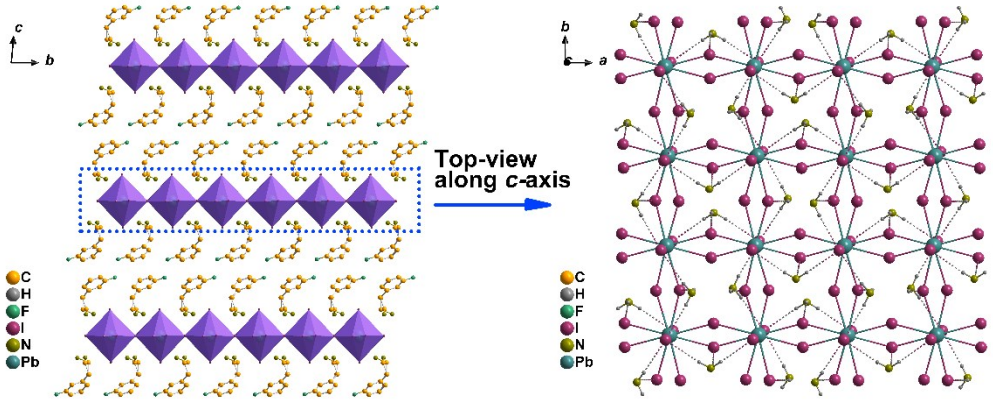

Figure S3. The weak N-H···I hydrogen bonding interacrtions (dashed lines) between the organic and inorganic layers in $(3\text{-FPEA})_2PbI_4$. Parts of H atoms are omitted for clarity.

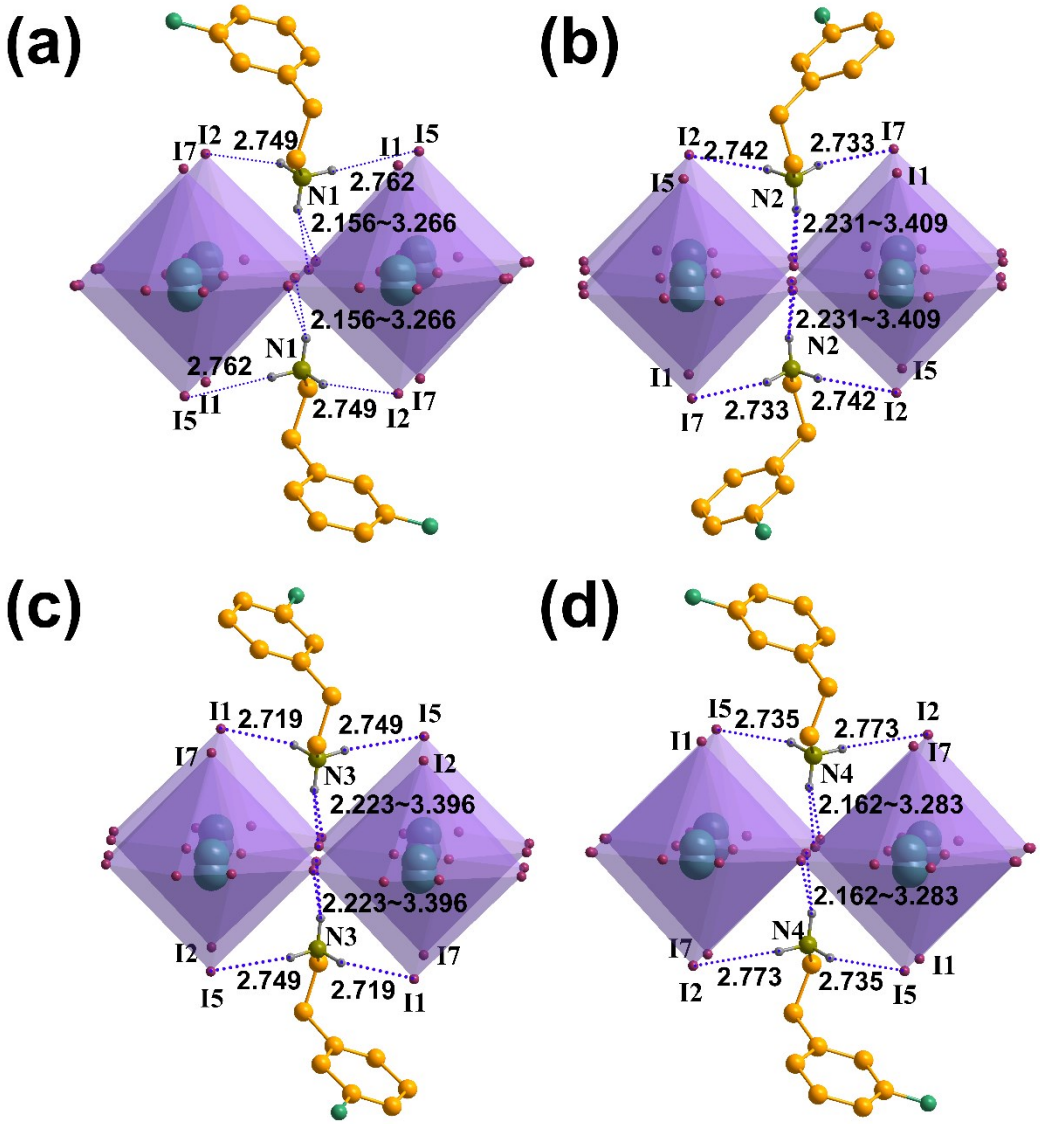

Figure S4. The weak N-H···I hydrogen bonding interactions between the organic cations and the inorganic layers in $(3\text{-FPEA})_2PbI_4$. Parts of H atoms are omitted for clarity.

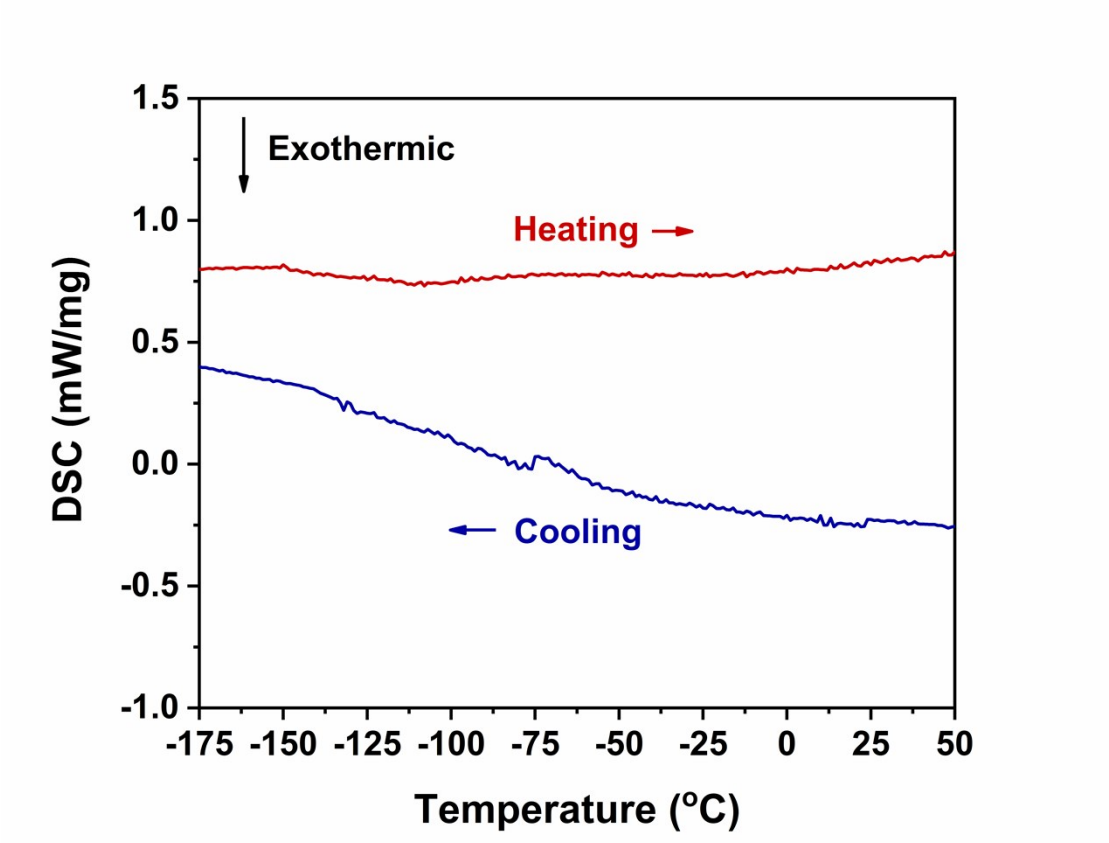

Figure S5. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) plots of $(3\text{-FPEA})_2PbI_4$ crystals within the temperature range of -175 ~ 50 °C.

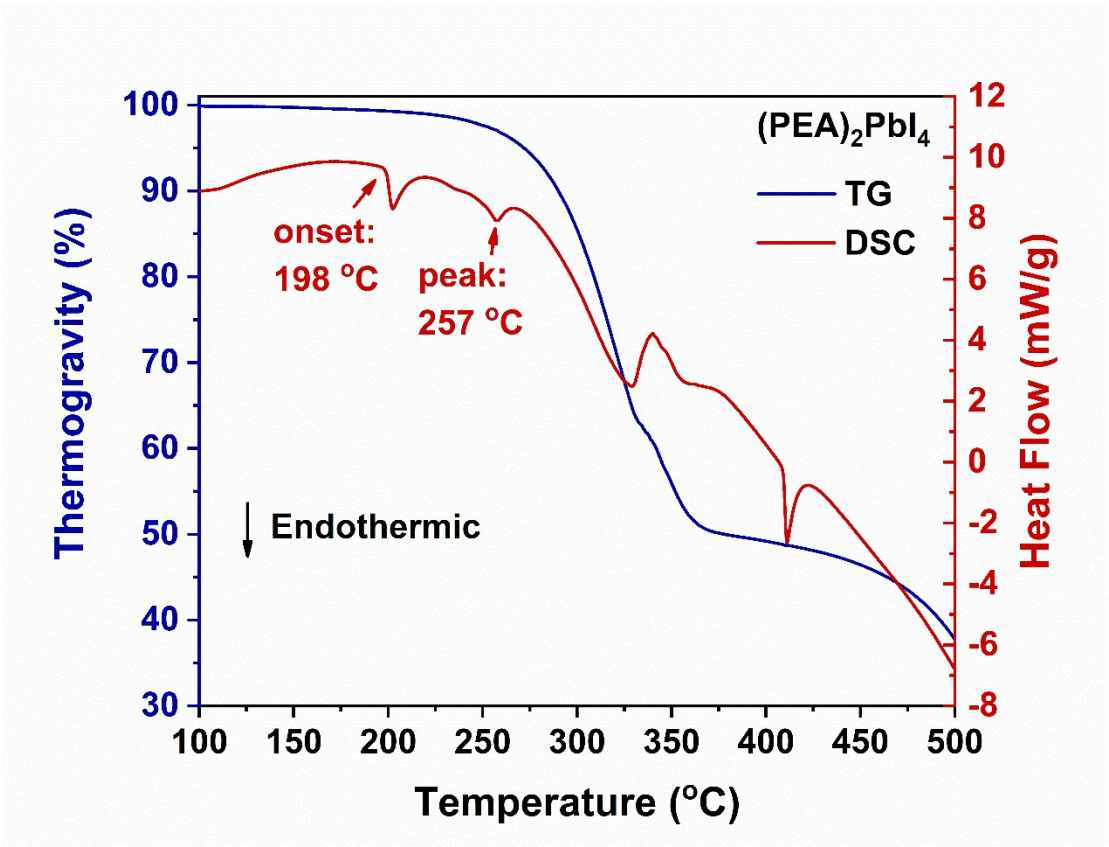

Figure S6. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) plots of $(PEA)_2PbI_4$.

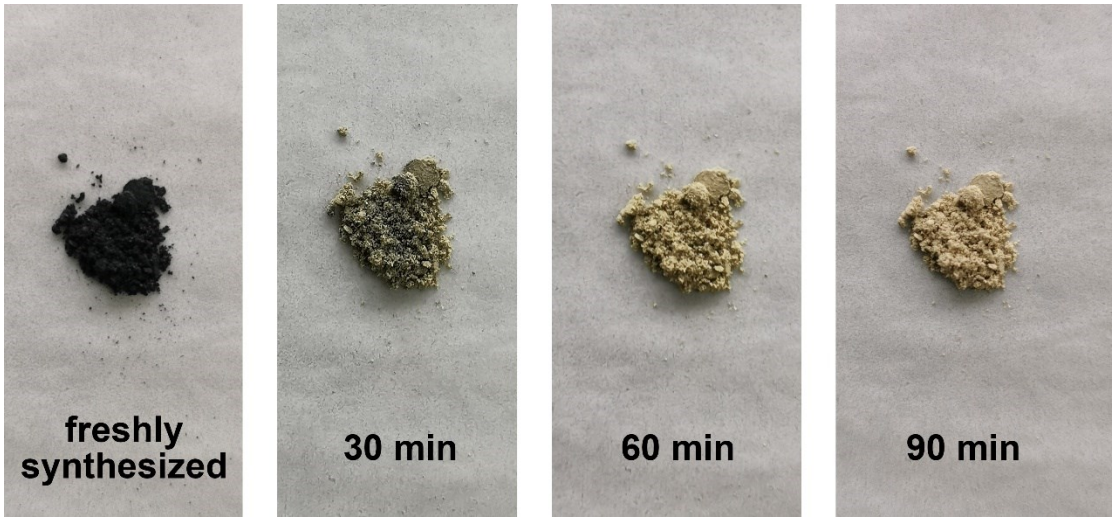

Figure S7. Images of four $MAPbI_3$ perovskite powders when placed under humidity for different time.

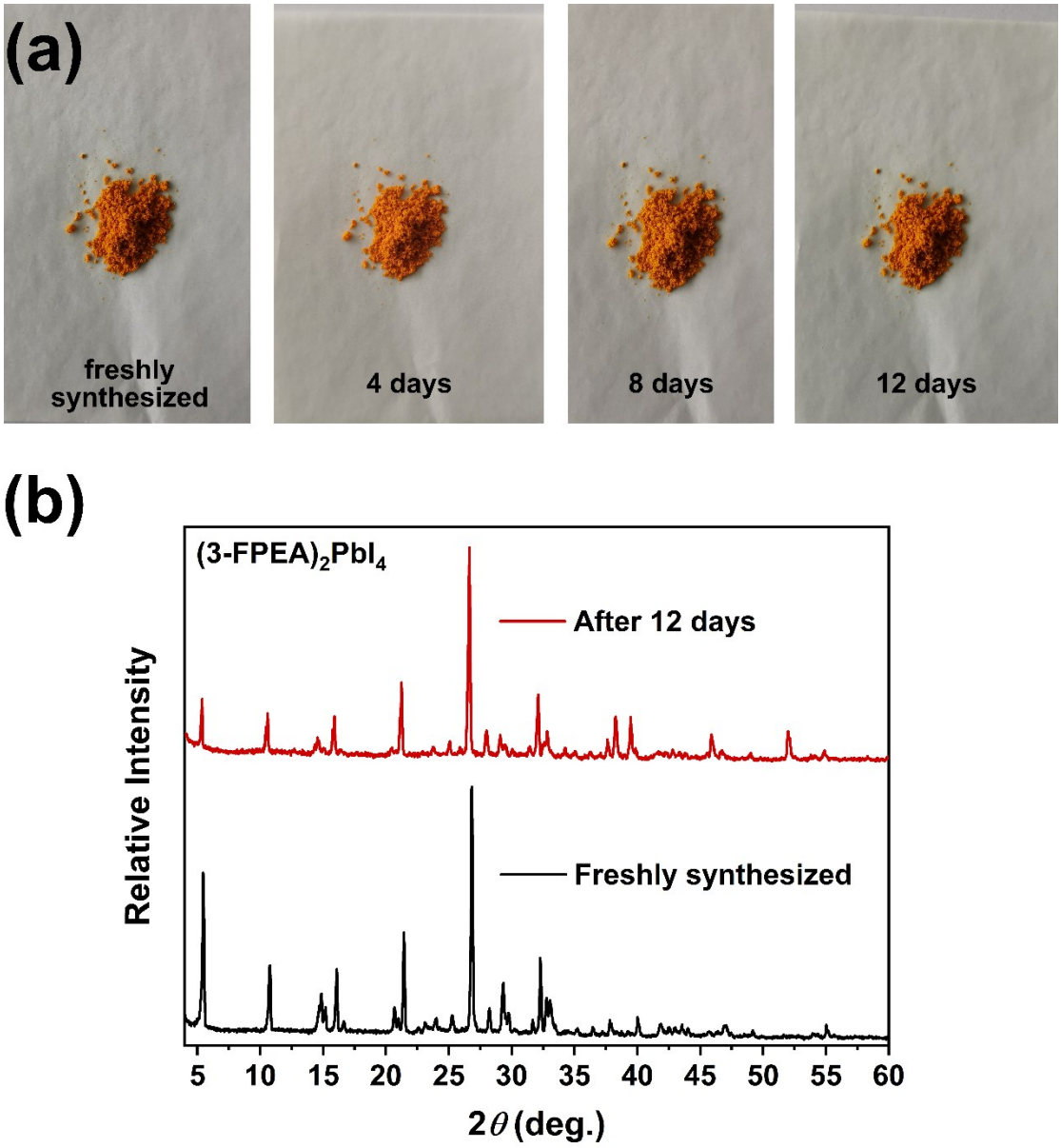

Figure S8. (a) Images of $(3\text{-FPEA})_2PbI_4$ powders after being placed in humidity for different time. (b) PXRD patterns of the freshly synthesized and aged (12 days) $(3\text{-FPEA})_2PbI_4$ powders.

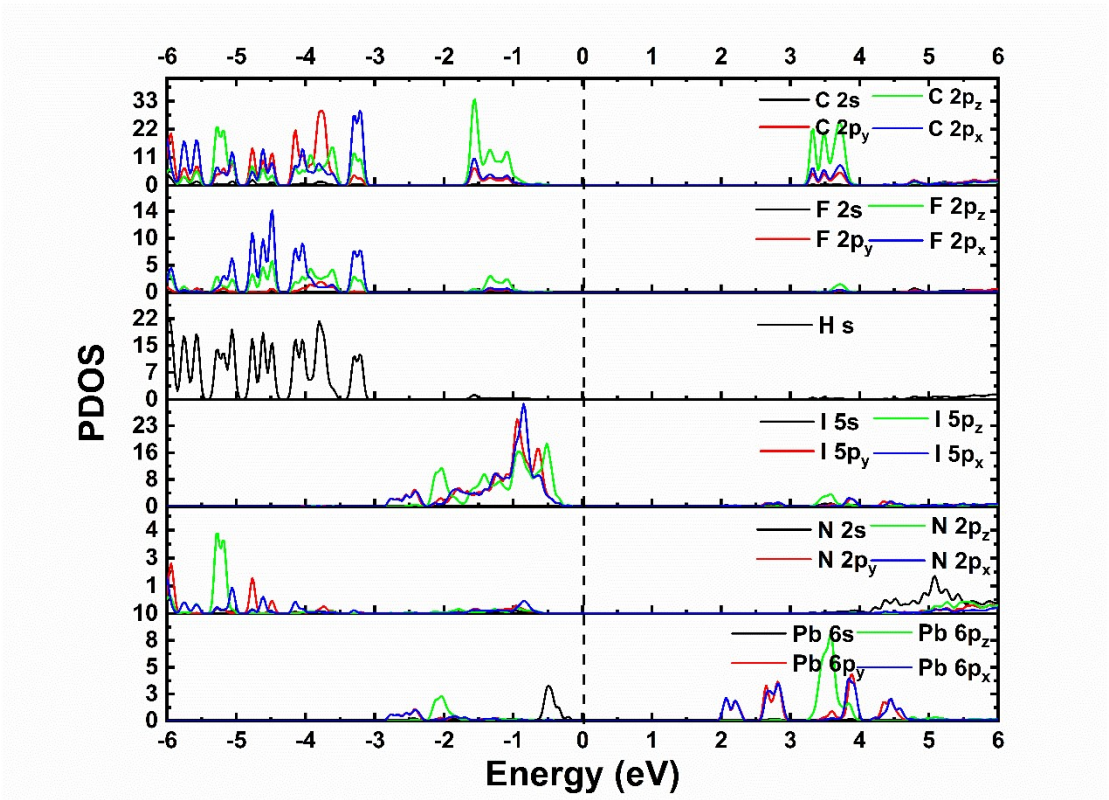

Figure S9. The partial density of states of $(3\text{-FPEA})_2PbI_4$.

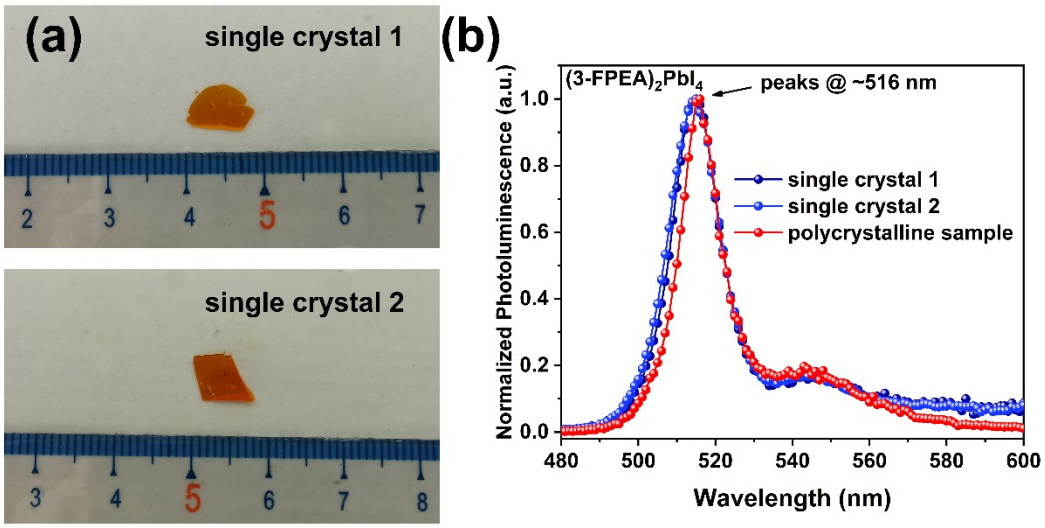

Figure S10. Photoluminescence spectra of $(3\text{-FPEA})_2PbI_4$ based on single crystal and polycrystalline samples, respectively. (a) Single crystals employed in the spectrum recoding. (b) The corresponding photoluminescence spectra.

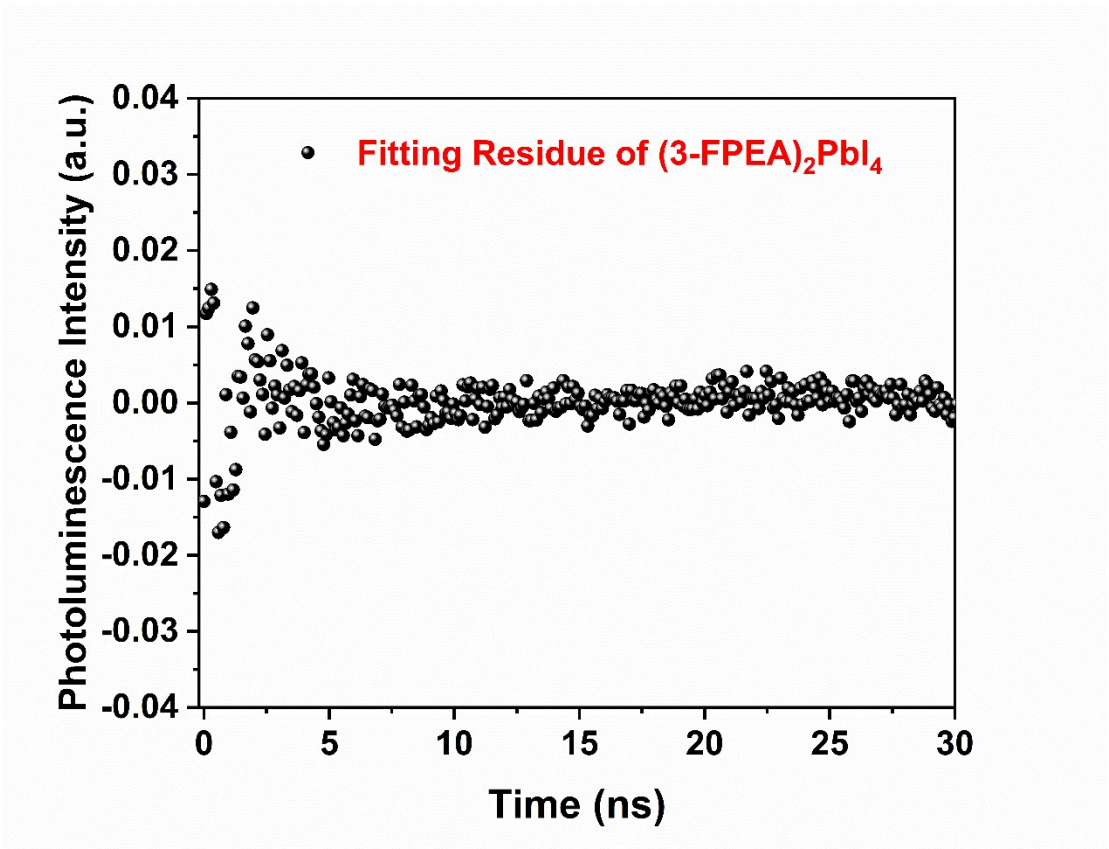

Figure S11. Residues for the lifetime decay fittings of $(3\text{-FPEA})_2PbI_4$.

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(3\text{-FPEA})_2PbI_4$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U_{(eq)}$
C(1)	2508(8)	4408(8)	8641(5)	44(2)
C(2)	1624(9)	4958(10)	9130(6)	53(2)
C(3)	1861(9)	5973(9)	9346(6)	53(2)
C(4)	2912(10)	6420(9)	9092(6)	54(2)
C(5)	3740(9)	5915(8)	8620(6)	46(2)
C(6)	3540(8)	4888(7)	8384(5)	39(2)
C(7)	4434(8)	4305(8)	7841(5)	44(2)
C(8)	4663(7)	4821(8)	6972(5)	42(2)
C(9)	4359(9)	977(8)	8623(5)	47(2)
C(10)	5018(10)	1462(10)	9092(6)	59(2)
C(11)	5923(10)	1006(10)	9330(6)	58(2)
C(12)	6284(10)	-13(10)	9098(6)	59(2)
C(13)	5610(8)	-525(9)	8623(5)	44(2)
C(14)	4674(7)	-57(8)	8389(5)	40(2)
C(15)	4028(8)	-621(8)	7845(5)	45(2)
C(16)	4575(8)	-516(7)	6965(5)	42(2)
C(17)	689(8)	-605(8)	8647(5)	44(2)
C(18)	1326(8)	-73(9)	9131(6)	50(2)
C(19)	998(8)	948(9)	9349(5)	48(2)
C(20)	78(9)	1408(9)	9092(5)	50(2)
C(21)	-529(8)	928(8)	8614(5)	43(2)
C(22)	-220(7)	-124(8)	8387(5)	40(2)
C(23)	-858(8)	-688(8)	7846(5)	46(2)
C(24)	-655(7)	-180(8)	6991(5)	43(2)
C(25)	2095(11)	3547(10)	913(6)	57(2)
C(26)	3127(10)	4026(10)	682(6)	59(2)
C(27)	3325(10)	5054(10)	909(6)	56(2)
C(28)	2419(8)	5558(9)	1385(5)	47(2)
C(29)	1370(8)	5051(7)	1622(5)	38(2)
C(30)	1218(9)	4023(8)	1372(5)	48(2)
C(31)	451(8)	5610(8)	2153(5)	46(2)
C(32)	548(8)	5522(8)	3030(5)	44(2)
F(1)	3087(8)	7409(7)	9322(5)	96(3)
F(2)	1944(10)	2561(9)	680(6)	130(3)
F(3)	4711(10)	2436(8)	9339(6)	134(4)
F(4)	-198(7)	2414(6)	9314(5)	91(2)
I(1)	2987(1)	7782(1)	3032(1)	30(1)

I(2)	1902(1)	7199(1)	6941(1)	27(1)
I(5)	2126(1)	2202(1)	6940(1)	27(1)
I(3)	1828(1)	4977(1)	5035(1)	25(1)
I(4)	5051(1)	3162(1)	5020(1)	26(1)
I(6)	60(1)	1837(1)	4979(1)	26(1)
I(8)	3154(1)	-24(1)	5036(1)	25(1)
I(7)	2997(1)	2780(1)	3032(1)	30(1)
N(1)	3658(6)	4839(6)	6603(4)	37(2)
N(2)	488(5)	4381(6)	3377(4)	36(2)
N(3)	4685(5)	626(6)	6625(4)	36(2)
N(4)	534(6)	-161(6)	6604(4)	37(2)
Pb(1)	2466(1)	7504(1)	4877(1)	19(1)
Pb(2)	2592(1)	2503(1)	4892(1)	24(1)
I(3')	3173(4)	5017(4)	4972(3)	29(1)
I(4')	5058(4)	1836(4)	4982(3)	29(1)
I(6')	52(4)	3167(4)	5020(3)	29(1)
I(8')	1847(4)	17(4)	4975(3)	29(1)
Pb(1')	2395(6)	7477(6)	5143(3)	20(1)

Table S2. Bond lengths [Å] and angles [º] for $(3\text{-FPEA})_2PbI_4$ single crystal.

C(1)-C(6)	1.368(13)
C(1)-C(2)	1.440(13)
C(1)-H(1)	0.95
C(2)-C(3)	1.367(15)
C(2)-H(2)	0.95
C(3)-C(4)	1.373(15)
C(3)-H(3)	0.95
C(4)-F(1)	1.329(12)
C(4)-C(5)	1.353(14)
C(5)-C(6)	1.383(12)
C(5)-H(5)	0.95
C(6)-C(7)	1.513(12)
C(7)-C(8)	1.522(12)
C(7)-H(7A)	0.99
C(7)-H(7B)	0.99
C(8)-N(1)	1.472(10)
C(8)-H(8A)	0.99
C(8)-H(8B)	0.99
C(9)-C(14)	1.389(13)
C(9)-C(10)	1.391(14)
C(9)-H(9)	0.95
C(10)-C(11)	1.346(16)
C(10)-F(3)	1.327(13)
C(11)-C(12)	1.385(16)
C(11)-H(11)	0.95
C(12)-C(13)	1.426(14)
C(12)-H(12)	0.95
C(13)-C(14)	1.383(13)
C(13)-H(13)	0.95
C(14)-C(15)	1.520(12)
C(15)-C(16)	1.509(12)
C(15)-H(15A)	0.99
C(15)-H(15B)	0.99
C(16)-N(3)	1.456(11)
C(16)-H(16A)	0.99
C(16)-H(16B)	0.99
C(17)-C(22)	1.379(13)
C(17)-C(18)	1.420(13)
C(17)-H(17)	0.95
C(18)-C(19)	1.371(14)
C(18)-H(18)	0.95

C(19)-C(20)	1.379(15)
C(19)-H(19)	0.95
C(20)-F(4)	1.341(11)
C(20)-C(21)	1.356(13)
C(21)-C(22)	1.405(12)
C(21)-H(21)	0.95
C(22)-C(23)	1.510(12)
C(23)-C(24)	1.498(13)
C(23)-H(23A)	0.99
C(23)-H(23B)	0.99
C(24)-N(4)	1.479(10)
C(24)-H(24A)	0.99
C(24)-H(24B)	0.99
C(25)-F(2)	1.321(14)
C(25)-C(26)	1.364(16)
C(25)-C(30)	1.365(14)
C(26)-C(27)	1.377(16)
C(26)-H(26)	0.95
C(27)-C(28)	1.420(14)
C(27)-H(27)	0.95
C(28)-C(29)	1.397(13)
C(28)-H(28)	0.95
C(29)-C(30)	1.380(13)
C(29)-C(31)	1.507(12)
C(30)-H(30)	0.95
C(31)-C(32)	1.501(12)
C(31)-H(31A)	0.99
C(31)-H(31B)	0.99
C(32)-N(2)	1.459(11)
C(32)-H(32A)	0.99
C(32)-H(32B)	0.99
I(1)-Pb(1)	3.0537(7)
I(2)-Pb(1')	2.975(5)
I(2)-Pb(1)	3.4142(7)
I(5)-Pb(2)	3.3888(6)
I(3)-Pb(1)	3.1575(11)
I(3)-Pb(2)	3.1783(6)
I(4)-Pb(2)	3.1543(6)
I(4)-Pb(1)#1	3.1699(11)
I(6)-Pb(1)#2	3.1579(11)
I(6)-Pb(2)	3.1682(6)
I(8)-Pb(2)	3.1578(6)
I(8)-Pb(1)#3	3.1790(11)

I(7)-Pb(2)	3.0769(6)
N(1)-H(1A)	0.91
N(1)-H(1B)	0.91
N(1)-H(1C)	0.91
N(2)-H(2A)	0.91
N(2)-H(2B)	0.91
N(2)-H(2C)	0.91
N(3)-H(3A)	0.91
N(3)-H(3B)	0.91
N(3)-H(3C)	0.91
N(4)-H(4A)	0.91
N(4)-H(4B)	0.91
N(4)-H(4C)	0.91
Pb(2)-I(4')	3.144(4)
Pb(2)-I(8')	3.151(5)
Pb(2)-I(3')	3.169(5)
Pb(2)-I(6')	3.179(4)
I(3')-Pb(1')	3.173(9)
I(4')-Pb(1')#1	3.183(9)
I(6')-Pb(1')#2	3.153(9)
I(8')-Pb(1')#3	3.171(9)
C(6)-C(1)-C(2)	121.7(9)
C(6)-C(1)-H(1)	119.2
C(2)-C(1)-H(1)	119.2
C(3)-C(2)-C(1)	117.3(10)
C(3)-C(2)-H(2)	121.3
C(1)-C(2)-H(2)	121.3
C(4)-C(3)-C(2)	119.4(10)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
F(1)-C(4)-C(5)	120.2(11)
F(1)-C(4)-C(3)	116.4(10)
C(5)-C(4)-C(3)	123.4(10)
C(4)-C(5)-C(6)	119.3(10)
C(4)-C(5)-H(5)	120.3
C(6)-C(5)-H(5)	120.3
C(1)-C(6)-C(5)	118.8(9)
C(1)-C(6)-C(7)	120.1(8)
C(5)-C(6)-C(7)	121.1(9)
C(6)-C(7)-C(8)	113.2(7)
C(6)-C(7)-H(7A)	108.9
C(8)-C(7)-H(7A)	108.9

C(6)-C(7)-H(7B)	108.9
C(8)-C(7)-H(7B)	108.9
H(7A)-C(7)-H(7B)	107.8
N(1)-C(8)-C(7)	112.1(7)
N(1)-C(8)-H(8A)	109.2
C(7)-C(8)-H(8A)	109.2
N(1)-C(8)-H(8B)	109.2
C(7)-C(8)-H(8B)	109.2
H(8A)-C(8)-H(8B)	107.9
C(14)-C(9)-C(10)	116.5(10)
C(14)-C(9)-H(9)	121.8
C(10)-C(9)-H(9)	121.8
C(11)-C(10)-F(3)	117.8(11)
C(11)-C(10)-C(9)	125.0(11)
F(3)-C(10)-C(9)	117.2(12)
C(10)-C(11)-C(12)	120.7(10)
C(10)-C(11)-H(11)	119.7
C(12)-C(11)-H(11)	119.7
C(11)-C(12)-C(13)	114.9(11)
C(11)-C(12)-H(12)	122.6
C(13)-C(12)-H(12)	122.6
C(14)-C(13)-C(12)	124.1(10)
C(14)-C(13)-H(13)	118
C(12)-C(13)-H(13)	118
C(9)-C(14)-C(13)	118.8(9)
C(9)-C(14)-C(15)	119.7(9)
C(13)-C(14)-C(15)	121.4(9)
C(16)-C(15)-C(14)	113.9(7)
C(16)-C(15)-H(15A)	108.8
C(14)-C(15)-H(15A)	108.8
C(16)-C(15)-H(15B)	108.8
C(14)-C(15)-H(15B)	108.8
H(15A)-C(15)-H(15B)	107.7
N(3)-C(16)-C(15)	112.1(8)
N(3)-C(16)-H(16A)	109.2
C(15)-C(16)-H(16A)	109.2
N(3)-C(16)-H(16B)	109.2
C(15)-C(16)-H(16B)	109.2
H(16A)-C(16)-H(16B)	107.9
C(22)-C(17)-C(18)	122.3(9)
C(22)-C(17)-H(17)	118.8
C(18)-C(17)-H(17)	118.8
C(19)-C(18)-C(17)	117.6(10)

C(19)-C(18)-H(18)	121.2
C(17)-C(18)-H(18)	121.2
C(20)-C(19)-C(18)	119.0(9)
C(20)-C(19)-H(19)	120.5
C(18)-C(19)-H(19)	120.5
F(4)-C(20)-C(21)	119.0(10)
F(4)-C(20)-C(19)	116.6(9)
C(21)-C(20)-C(19)	124.4(10)
C(20)-C(21)-C(22)	117.8(10)
C(20)-C(21)-H(21)	121.1
C(22)-C(21)-H(21)	121.1
C(17)-C(22)-C(21)	118.7(9)
C(17)-C(22)-C(23)	121.3(9)
C(21)-C(22)-C(23)	119.9(9)
C(24)-C(23)-C(22)	113.4(8)
C(24)-C(23)-H(23A)	108.9
C(22)-C(23)-H(23A)	108.9
C(24)-C(23)-H(23B)	108.9
C(22)-C(23)-H(23B)	108.9
H(23A)-C(23)-H(23B)	107.7
N(4)-C(24)-C(23)	113.1(8)
N(4)-C(24)-H(24A)	109
C(23)-C(24)-H(24A)	109
N(4)-C(24)-H(24B)	109
C(23)-C(24)-H(24B)	109
H(24A)-C(24)-H(24B)	107.8
F(2)-C(25)-C(26)	117.6(11)
F(2)-C(25)-C(30)	118.5(12)
C(26)-C(25)-C(30)	123.9(11)
C(25)-C(26)-C(27)	119.8(10)
C(25)-C(26)-H(26)	120.1
C(27)-C(26)-H(26)	120.1
C(26)-C(27)-C(28)	116.8(11)
C(26)-C(27)-H(27)	121.6
C(28)-C(27)-H(27)	121.6
C(29)-C(28)-C(27)	122.6(10)
C(29)-C(28)-H(28)	118.7
C(27)-C(28)-H(28)	118.7
C(30)-C(29)-C(28)	118.0(9)
C(30)-C(29)-C(31)	121.8(9)
C(28)-C(29)-C(31)	120.2(9)
C(25)-C(30)-C(29)	118.9(10)
C(25)-C(30)-H(30)	120.6

C(29)-C(30)-H(30)	120.6
C(32)-C(31)-C(29)	114.0(7)
C(32)-C(31)-H(31A)	108.7
C(29)-C(31)-H(31A)	108.7
C(32)-C(31)-H(31B)	108.7
C(29)-C(31)-H(31B)	108.7
H(31A)-C(31)-H(31B)	107.6
N(2)-C(32)-C(31)	111.8(8)
N(2)-C(32)-H(32A)	109.3
C(31)-C(32)-H(32A)	109.3
N(2)-C(32)-H(32B)	109.3
C(31)-C(32)-H(32B)	109.3
H(32A)-C(32)-H(32B)	107.9
Pb(1)-I(3)-Pb(2)	149.01(2)
Pb(2)-I(4)-Pb(1)#1	150.28(3)
Pb(1)#2-I(6)-Pb(2)	150.18(3)
Pb(2)-I(8)-Pb(1)#3	148.99(2)
C(8)-N(1)-H(1A)	109.5
C(8)-N(1)-H(1B)	109.5
H(1A)-N(1)-H(1B)	109.5
C(8)-N(1)-H(1C)	109.5
H(1A)-N(1)-H(1C)	109.5
H(1B)-N(1)-H(1C)	109.5
C(32)-N(2)-H(2A)	109.5
C(32)-N(2)-H(2B)	109.5
H(2A)-N(2)-H(2B)	109.5
C(32)-N(2)-H(2C)	109.5
H(2A)-N(2)-H(2C)	109.5
H(2B)-N(2)-H(2C)	109.5
C(16)-N(3)-H(3A)	109.5
C(16)-N(3)-H(3B)	109.5
H(3A)-N(3)-H(3B)	109.5
C(16)-N(3)-H(3C)	109.5
H(3A)-N(3)-H(3C)	109.5
H(3B)-N(3)-H(3C)	109.5
C(24)-N(4)-H(4A)	109.5
C(24)-N(4)-H(4B)	109.5
H(4A)-N(4)-H(4B)	109.5
C(24)-N(4)-H(4C)	109.5
H(4A)-N(4)-H(4C)	109.5
H(4B)-N(4)-H(4C)	109.5
I(1)-Pb(1)-I(6)#2	95.30(3)
I(1)-Pb(1)-I(3)	96.27(2)

I(6)#2-Pb(1)-I(3)	91.49(3)
I(1)-Pb(1)-I(4)#1	92.09(2)
I(6)#2-Pb(1)-I(4)#1	172.57(2)
I(3)-Pb(1)-I(4)#1	88.49(3)
I(1)-Pb(1)-I(8)#4	93.17(3)
I(6)#2-Pb(1)-I(8)#4	90.67(3)
I(3)-Pb(1)-I(8)#4	170.07(2)
I(4)#1-Pb(1)-I(8)#4	88.12(3)
I(1)-Pb(1)-I(2)	179.57(4)
I(6)#2-Pb(1)-I(2)	85.06(2)
I(3)-Pb(1)-I(2)	83.95(2)
I(4)#1-Pb(1)-I(2)	87.55(2)
I(8)#4-Pb(1)-I(2)	86.58(2)
I(7)-Pb(2)-I(4')	94.36(9)
I(7)-Pb(2)-I(4)	94.885(16)
I(7)-Pb(2)-I(8')	93.26(9)
I(4')-Pb(2)-I(8')	91.36(13)
I(7)-Pb(2)-I(8)	95.815(16)
I(4)-Pb(2)-I(8)	91.420(15)
I(7)-Pb(2)-I(3')	91.56(9)
I(4')-Pb(2)-I(3')	91.33(13)
I(8')-Pb(2)-I(3')	174.29(12)
I(7)-Pb(2)-I(6)	91.562(16)
I(4)-Pb(2)-I(6)	173.514(17)
I(8)-Pb(2)-I(6)	88.631(15)
I(7)-Pb(2)-I(3)	92.750(16)
I(4)-Pb(2)-I(3)	90.871(15)
I(8)-Pb(2)-I(3)	170.913(17)
I(6)-Pb(2)-I(3)	88.103(15)
I(7)-Pb(2)-I(6')	92.16(9)
I(4')-Pb(2)-I(6')	173.46(13)
I(8')-Pb(2)-I(6')	88.77(13)
I(3')-Pb(2)-I(6')	87.98(13)
I(7)-Pb(2)-I(5)	179.553(15)
I(4')-Pb(2)-I(5)	86.08(9)
I(4)-Pb(2)-I(5)	85.508(14)
I(8')-Pb(2)-I(5)	86.72(9)
I(8)-Pb(2)-I(5)	84.386(15)
I(3')-Pb(2)-I(5)	88.44(9)
I(6)-Pb(2)-I(5)	88.042(15)
I(3)-Pb(2)-I(5)	87.029(15)
I(6')-Pb(2)-I(5)	87.39(9)
Pb(1')-I(3')-Pb(2)	150.1(2)

Pb(2)-I(4')-Pb(1')#1	149.6(2)
Pb(1')#2-I(6')-Pb(2)	148.7(2)
Pb(2)-I(8')-Pb(1')#3	150.5(2)
I(2)-Pb(1')-I(3')	94.1(2)
I(2)-Pb(1')-I(4')#1	95.0(2)
I(2)-Pb(1')-I(6')#2	93.6(2)
I(2)-Pb(1')-I(8')#4	96.1(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+1 #3 x,y-1,z #4 x,y+1,z

Table S3. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $(3\text{-FPEA})_2PbI_4$ single crystal.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	57(5)	50(5)	30(4)	-7(3)	-18(4)	1(4)
C(2)	55(5)	70(5)	39(4)	-2(4)	-25(4)	12(4)
C(3)	65(5)	61(5)	35(4)	-7(4)	-14(4)	23(4)
C(4)	80(5)	46(5)	37(4)	-9(4)	-13(4)	7(4)
C(5)	61(5)	43(4)	36(4)	-2(3)	-14(4)	1(4)
C(6)	53(4)	39(4)	27(3)	-4(3)	-17(3)	7(3)
C(7)	47(4)	50(5)	38(4)	-4(4)	-20(4)	15(4)
C(8)	34(4)	61(5)	34(4)	-11(4)	-9(3)	6(4)
C(9)	57(5)	46(5)	32(4)	4(3)	3(4)	-3(4)
C(10)	87(6)	51(5)	36(4)	-9(4)	5(4)	-9(4)
C(11)	68(5)	78(6)	29(4)	-3(4)	-11(4)	-26(5)
C(12)	62(5)	78(6)	30(4)	-1(4)	7(4)	-18(5)
C(13)	47(4)	54(5)	28(4)	-2(3)	2(3)	-4(4)
C(14)	43(4)	45(4)	29(3)	0(3)	1(3)	-9(3)
C(15)	48(4)	46(5)	37(4)	5(4)	-4(4)	-15(4)
C(16)	50(5)	36(4)	41(4)	0(3)	-13(4)	-4(4)
C(17)	49(4)	50(5)	29(4)	-6(3)	4(3)	-4(4)
C(18)	42(4)	67(5)	35(4)	1(4)	4(4)	-8(4)
C(19)	58(5)	56(5)	30(4)	-6(4)	-4(4)	-20(4)
C(20)	71(5)	46(5)	30(4)	-13(3)	3(4)	-5(4)
C(21)	55(4)	43(4)	26(4)	-5(3)	6(3)	-3(4)
C(22)	44(4)	43(4)	27(3)	-3(3)	9(3)	-8(3)
C(23)	44(4)	52(5)	38(4)	-6(4)	5(4)	-14(4)
C(24)	35(4)	58(5)	39(4)	-11(4)	-10(4)	-4(4)
C(25)	90(6)	55(5)	29(4)	-7(4)	-17(4)	13(5)
C(26)	71(5)	71(6)	34(4)	-1(4)	-11(4)	26(5)
C(27)	66(5)	71(6)	35(4)	-4(4)	-22(4)	13(5)
C(28)	52(4)	56(5)	33(4)	-3(4)	-10(4)	3(4)
C(29)	50(4)	40(4)	27(3)	3(3)	-17(3)	6(3)
C(30)	66(5)	51(5)	30(4)	3(3)	-15(4)	2(4)
C(31)	51(4)	47(5)	37(4)	7(4)	-11(4)	14(4)
C(32)	50(5)	40(5)	39(4)	-1(4)	3(4)	2(4)
F(1)	152(7)	60(5)	73(5)	-14(4)	-9(5)	-4(5)
F(2)	198(10)	93(7)	98(7)	-17(6)	-23(7)	-1(7)
F(3)	197(10)	87(7)	112(8)	-17(6)	-6(7)	8(7)
F(4)	144(7)	57(5)	71(5)	-16(4)	-9(5)	13(4)
I(1)	32(1)	34(1)	26(1)	-3(1)	-5(1)	-5(1)
I(2)	31(1)	24(1)	27(1)	-3(1)	-7(1)	3(1)

I(5)	29(1)	24(1)	27(1)	-3(1)	-3(1)	-3(1)
I(3)	29(1)	14(1)	33(1)	-4(1)	-10(1)	1(1)
I(4)	14(1)	28(1)	36(1)	1(1)	-6(1)	-1(1)
I(6)	15(1)	28(1)	36(1)	1(1)	-8(1)	0(1)
I(8)	26(1)	15(1)	33(1)	-4(1)	-3(1)	0(1)
I(7)	32(1)	34(1)	25(1)	-3(1)	-5(1)	6(1)
N(1)	43(4)	35(4)	32(4)	1(3)	-6(3)	2(3)
N(2)	32(3)	40(4)	34(4)	-2(3)	-3(3)	1(3)
N(3)	34(3)	36(4)	38(4)	-5(3)	-6(3)	-2(3)
N(4)	39(4)	41(4)	32(4)	-1(3)	-8(3)	-2(3)
Pb(1)	17(1)	17(1)	23(1)	-1(1)	-4(1)	0(1)
Pb(2)	18(1)	17(1)	36(1)	-2(1)	-8(1)	0(1)
I(3')	33(2)	19(2)	36(3)	-6(2)	-9(2)	0(2)
I(4')	17(2)	35(3)	35(2)	5(2)	-7(2)	0(2)
I(6')	19(2)	33(3)	35(2)	1(2)	-8(2)	2(2)
I(8')	30(2)	21(2)	36(3)	-6(2)	-2(2)	1(2)
Pb(1')	12(2)	12(2)	36(3)	0(3)	-7(3)	1(1)

Table S4. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3 for $(3\text{-FPEA})_2PbI_4$ single crystal.

	x	y	z	$U_{(eq)}$
H(1)	2372	3695	8492	53
H(2)	904	4628	9296	63
H(3)	1304	6365	9670	63
H(5)	4451	6263	8453	55
H(7A)	4202	3527	7845	52
H(7B)	5132	4316	8062	52
H(8A)	4948	5583	6962	51
H(8B)	5248	4400	6649	51
H(9)	3728	1334	8471	56
H(11)	6318	1387	9661	70
H(12)	6931	-345	9244	71
H(13)	5816	-1231	8458	53
H(15A)	3937	-1411	8037	54
H(15B)	3275	-303	7895	54
H(16A)	5324	-845	6909	51
H(16B)	4127	-932	6655	51
H(17)	896	-1319	8497	53
H(18)	1958	-412	9297	60
H(19)	1399	1334	9674	58
H(21)	-1144	1291	8440	52
H(23A)	-645	-1471	7848	55
H(23B)	-1665	-664	8070	55
H(24A)	-1088	-597	6672	52
H(24B)	-930	583	6984	52
H(26)	3707	3652	364	71
H(27)	4035	5408	754	67
H(28)	2530	6268	1550	56
H(30)	515	3654	1518	58
H(31A)	452	6397	1955	55
H(31B)	-273	5283	2103	55
H(32A)	1265	5858	3087	53
H(32B)	-61	5938	3334	53
H(1A)	3336	4157	6677	55
H(1B)	3850	5046	6064	55
H(1C)	3168	5327	6839	55
H(2A)	-96	4030	3236	54
H(2B)	392	4363	3925	54
H(2C)	1132	4039	3186	54

H(3A)	4026	970	6766	54
H(3B)	4868	650	6077	54
H(3C)	5228	970	6821	54
H(4A)	901	381	6793	56
H(4B)	592	-32	6059	56
H(4C)	839	-822	6722	56