Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

On the crystal structure thermal evolution of formamidinium lead tribromide, $CH(NH_2)_2PbBr_3$

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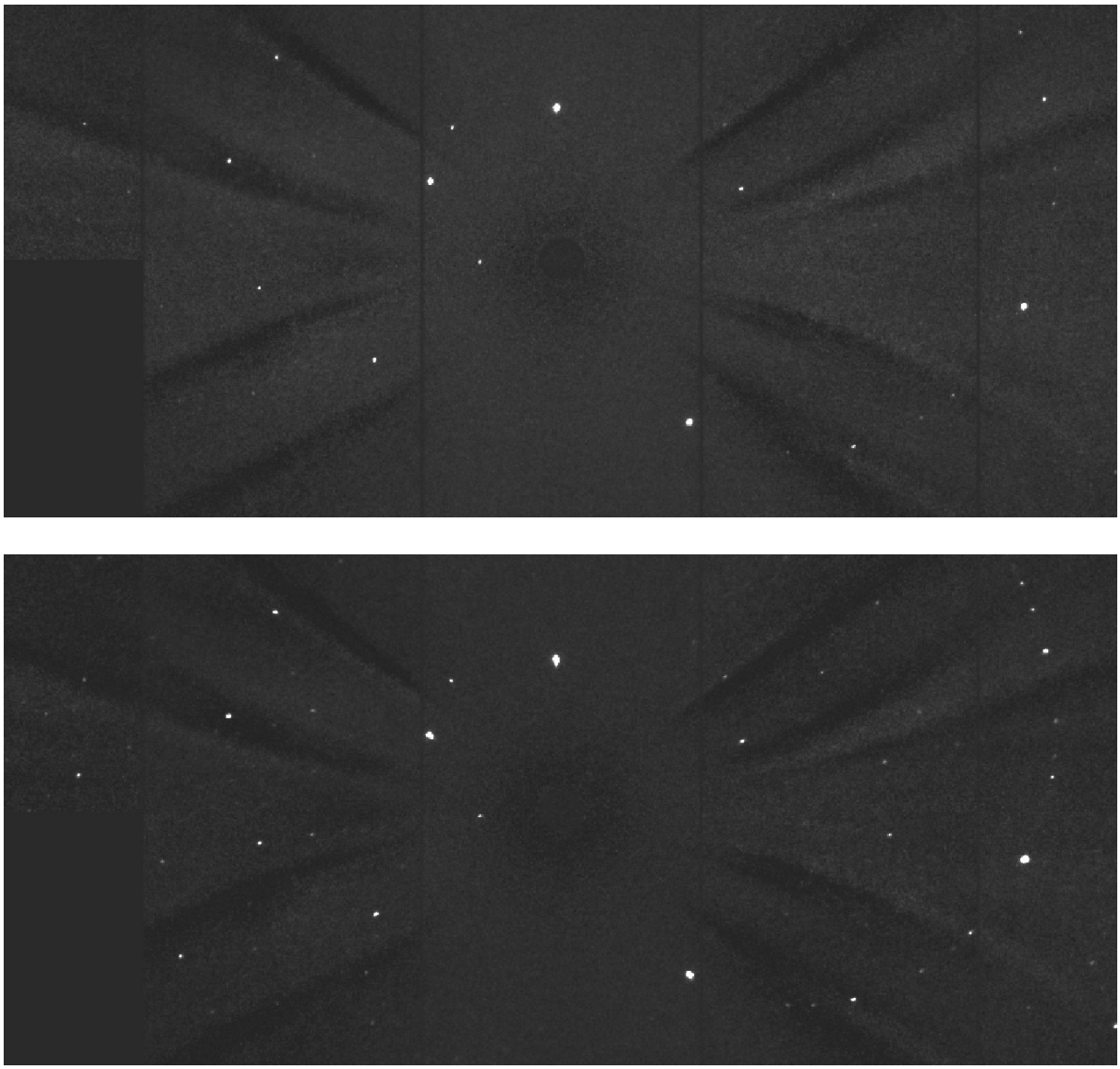

Figure S1: Comparative Laue diffraction pattern at 300 K (top) and 90K (bottom) where the differences in the number of reflections reveals the crystal has gone through a phase transition; data collected in the single crystal Laue diffractometer CYCLOPS, ILL.

Table S1: Crystallographic data for $FAPbBr_3$ from the SXRD data at room temperature.

System: Cubic, Space group: $Pm\bar{3}m$, Z = 1. Unit-cell parameters: a = 5.99248(3) Å, and V = 215.19(1) Å^3.

Atom		**x**	**Y**	**z**	**U_{iso}*/U_{eq}**	**Occ**
Pb	1*a*	0	0	0	0.0356(4)	1
Br	3*d*	0.5	0	0	0.080(1)	1
C	6*f*	0.5	0.580(2)	0.5	0.02(2)*	0.166
N	24*l*	0.69662	0.490(2)	0.5	0.021(6)*	0.083
Anisotropic displacement parameters (Å^2)						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.0356(4)	0.0356(4)	0.0356(4)	0	0	0
C/N	0.024(2)	0.107(1)	0.107(1)	0	0	0
R_p: 8.37%; R_{wp}: 11. 80%; R_{exp}: 4.57%; χ^2: 6.6; R_{Bragg}: 4.06%						

Table S2: Crystallographic data for $FAPbBr_3$ from NPD data at room temperature.

System: Cubic, Space group: $Pm\bar{3}m$, Z = 1. Unit-cell parameters: a = 5.9987(4)Å, and V = 215.86(3) Å^3.

Atom		**x**	**y**	**z**	**U_{iso}*/U_{eq}**	**Occ**
Pb	1*a*	0	0	0	0.037(2)	1
Br	3*d*	0.5	0	0	0.099(5)	1
C	6*f*	0.5	0.567(2)	0.5	0.137(4)*	0.166
N	24*l*	0.69041	0.467(2)	0.5	0.137(4)*	0.083
H1	6*f*	0.5	0.748(2)	0.5	0.137(4)*	0.166
H2	24*l*	0.83073	0.557(2)	0.5	0.137(4)*	0.083
H3	24*l*	0.70060	0.300(2)	0.5	0.137(4)*	0.083
Anisotropic displacement parameters (Å^2)						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.037(2)	0.037(2)	0.037(2)	0	0	0
Br	0.037(5)	0.130(5)	0.130(5)	0	0	0
R_p: 1.46%; R_{wp}: 1.88%; R_{exp}: 1.67%; χ^2: 1.27; R_{Bragg}: 11.4%						

Table S3: Position of FA and reliability factors using rigid body formalism for single crystal ND data at RT.

		FA fixed along [100] direction	FA free
Position of FA			
H location*	x	0.240(1)	0.279(4)
	y	0.5	0.473(4)
	z	0.5	0.603(6)
$H \rightarrow CN_2H_4$ Direction**	Θ	0°	24.4(3)
	Φ	0°	35.0(5)
	X	0°	-14.3(7)
Reliability factors			
RF^2 =		21.2	20.6
RF^2_w =		25.5	25.3
RF =		19.7	21.8
χ^2 =		20.1	20.2

* H bonded to C

** In respect to [100] direction in Euler angles

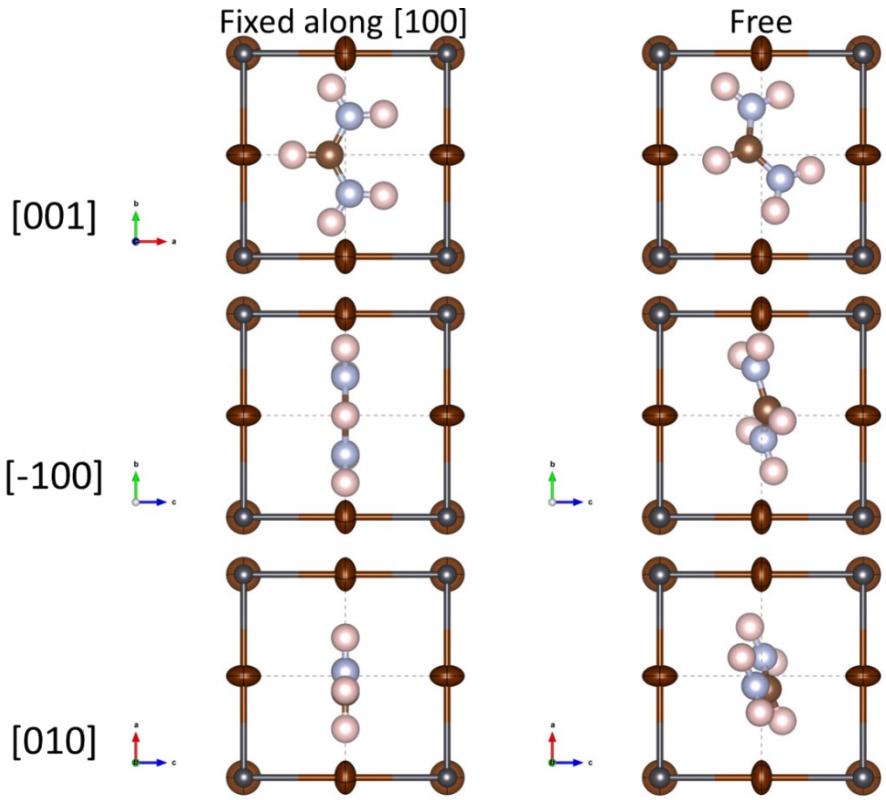

Figure S2: Different views of the refined crystallographic models of $FAPbBr_3$ at room temperature from SCND data. The first model was obtained by fixing the organic molecule FA along the [100] direction, while in the second one the FA unit remains free.

Table S4: Crystallographic results obtained from single crystal ND measurements at room temperature, including a full anisotropic refinement for all atoms.

System: Cubic, Space group: $Pm\bar{3}m$, Z = 1. Unit-cell parameters: a = 6.05033 Å, and V = 221.48 Å^3.						
Atom		**x**	**Y**	**z**	**U_{eq}**	**Occ**
Pb	1*a*	0	0	0	0.045(1)	1
Br	3*d*	0.5	0	0	0.091(2)	1
C	6*f*	0.5	0.56267(2)	0.5	0.078(2)	0.166
N	24*l*	0.69038(3)	0.46312(2)	0.5	0.116(5)	0.083
H1	6*f*	0.5	0.74448(2)	0.5	0.0777(2)	0.166
H2	24*l*	0.83069(4)	0.55355(2)	0.5	0.28(1)	0.083
H3	24*l*	0.7004(6)	0.29650(2)	0.5	0.19(1)	0.083
Anisotropic displacement parameters (Å^2)						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.045(1)	0.045(1)	0.045(1)	0	0	0
Br	0.044(2)	0.115(2)	0.115(2)	0	0	0
C	0.089(1)	0.054(2)	0.089(1)	0	0	0
N	0.129(3)	0.109(6)	0.109(4)	0.083(5)	0	0
H1	0.089(1)	0.054(2)	0.089(1)	0	0	0
H2	0.116(6)	0.069(6)	0.64(2)	0.061(5)	0	0
H3	0.19(2)	0.12(1)	0.25(1)	0.128(8)	0	0
RF^2 = 11.1%; RF^2w = 13.3%; χ^2 = 5.92						

Table S5: Crystallographic results obtained from synchrotron XRD at 220 K.

System: Tetragonal, Space group: *P*4/*mbm*, Z = 2. Unit-cell parameters: a = 8.43785(5) Å, c = 5.96330(4) Å and V = 424.57(1) Å^3.						
Atom		**x**	**y**	**y**	**U_{iso}*/U_{eq}**	**Occ**
Pb	2*a*	0	0	0	0.030(2)	1
Br1	2*b*	0	0	0.5	0.069(7)	1
Br2	4*g*	0.2677(4)	0.7677(4)	0	0.065(5)	1
C	4*f*	0.5	0	0.58(1)	0.01(2)*	0.5
N	8*k*	0.40126	0.09874	0.49(1)	0.04(1)*	0.5
Anisotropic displacement parameters (Å^2)						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.010(1)	0.010(1)	0.071(3)	0	0	0
Br1	0.080(6)	0.080(6)	0.049(9)	0		
Br2	0.045(4)	0.045(4)	0.105(9)	0.039(4)	0	0
R_p: 7.30%; R_{wp}: 10.5%; R_{exp}: 4.58%; χ^2: 5.25; R_{bragg}: 3.92%						

Table S6: Crystallographic results obtained from synchrotron XRD at 170 K.

System: Orthorhombic, Space group: *Pnma*, Z = 4. Unit-cell parameters: a = 8.40844(6) Å, b = 11.89642(4) Å, c = 8.41693(6) Å and V = 841.95(1) Å^3.

Atom		**x**	**y**	**y**	**U_{iso}*/U_{eq}**	**Occ**
Pb	4*b*	0	0	0.5	0.0201(3)*	1
Br1	4*c*	−0.012(1)	0.25	0.502(3)	0.07(1)	1
Br2	8*d*	0.7704(9)	0.0030(1)	0.2257(7)	0.054(6)	1
C	8*d*	0.5	0.290(1)	0.5	0.019*	0.5
N	8*d*	0.600(1)	0.240(3)	0.401(1)	0.025*	0.5
N	8*d*	0.401(1)	0.240(3)	0.600(1)	0.025*	0.5
Anisotropic displacement parameters (Å^2)						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.11(2)	0.003(9)	0.09(1)	0	−0.04(1)	0
Br2	0.053(6)	0.071(8)	0.038(5)	−0.002(8)	−0.029(3)	−0.019(6)
R_p: 8.16%; R_{wp}: 11.0%; R_{exp}: 4.60%; χ^2: 5.73; R_{bragg}: 4.61%						

Table S7: Crystallographic results obtained from synchrotron XRD at 155 K.

System: Orthorhombic, Space group: *Pnma*, Z = 4. Unit-cell parameters: a = 8.40287(5) Å, b = 11.88992(4) Å, c = 8.41310(6) Å and V = 840.55(1) Å^3.

Atom		**x**	**y**	**y**	**U_{iso}*/U_{eq}**	**Occ**
Pb	4*b*	0	0	0.5	0.0183(3)*	1
Br1	4*c*	−0.013(1)	0.25	0.501(3)	0.068(9)	1
Br2	8*d*	0.7746(7)	0.002(1)	0.2303(8)	0.052(6)	1
C	8*d*	0.5	0.288(1)	0.5	0.019*	0.5
N	8*d*	0.599(1)	0.238(2)	0.401(1)	0.025*	0.5
N	8*d*	0.401(1)	0.238(2)	0.599(1)	0.025*	0.5
Anisotropic displacement parameters (Å^2)						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.10(1)	0.003(9)	0.097(1)	0	0.03(1)	0
Br2	0.04(4)	0.075(8)	0.040(5)	−0.007(7)	−0.028(3)	−0.022(6)
R_p: 7.88%; R_{wp}: 10.7%; R_{exp}: 4.59%; χ^2: 5.43; R_{Bragg}: 4.34%						

Table S8: Crystallographic results obtained from synchrotron XRD at 120 K.

System: Orthorhombic, Space group: *Pnma*, Z = 4. Unit-cell parameters: a = 8.38791(4) Å, b = 11.87367(3) Å, c = 8.38035(4) Å and V = 834.64(1) Å^3.

Atom		**x**	**y**	**y**	**U_{iso}*/U_{eq}**	**Occ**
Pb	4*b*	0	0	0.5	0.0131(3)*	1
Br1	4*c*	−0.0163(9)	0.25	0.501(3)	0.064(8)	1
Br2	8*d*	0.7770(5)	0.0029(8)	0.241(1)	0.062(4)	1
C	8*d*	0.5	0.292(1)	0.5	0.019*	0.5
N	8*d*	0.599(1)	0.240(3)	0.401(1)	0.025*	0.5
N	8*d*	0.401(1)	0.240(3)	0.599(1)	0.025*	0.5
Anisotropic displacement parameters (Å^2)						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.06(1)	0.003(9)	0.13(1)	0	0.024(8)	0
Br2	0.016(3)	0.122(5)	0.049(5)	−0.019(5)	−0.031(4)	−0.015(6)

R_p: 8.02%; R_{wp}: 11.0%; R_{exp}: 4.61%; χ^2: 5.72; R_{bragg}: 4.54%

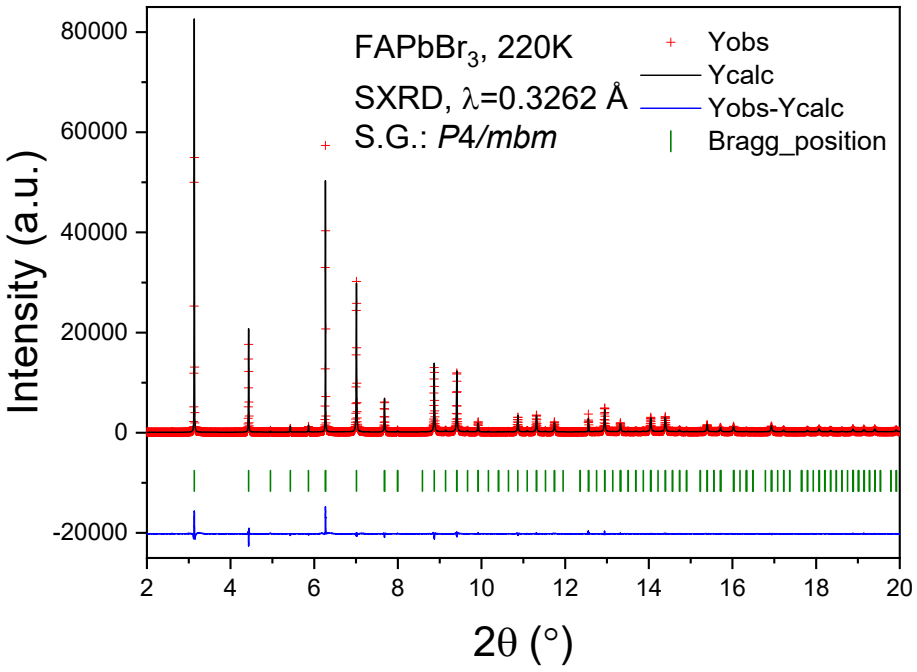

Figure S3. Observed (red crosses) calculated (back line) and difference (blue line) synchrotron X-ray diffraction profile after the Rietveld refinement at 220K.

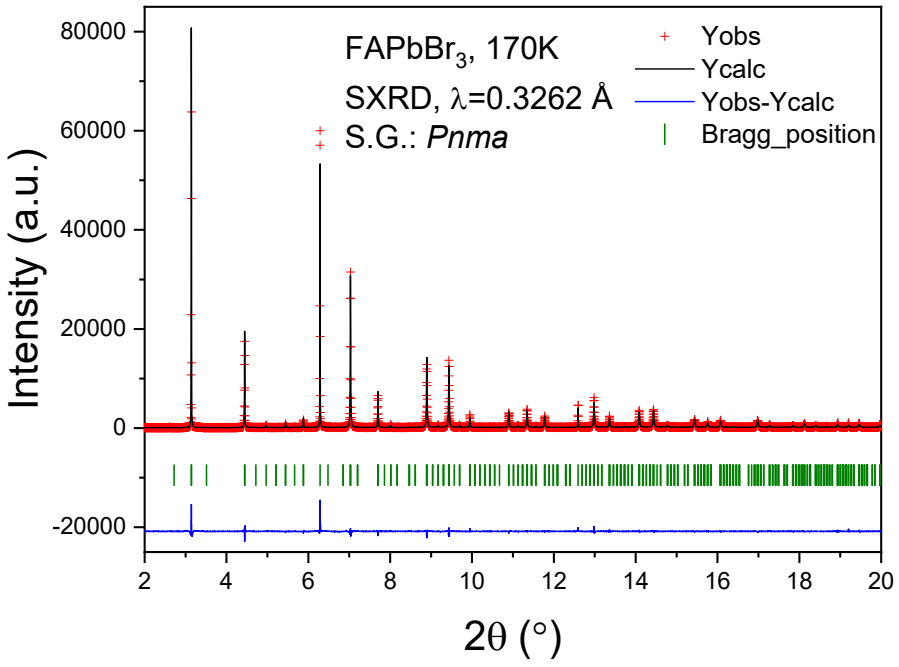

Figure S4. Observed (red crosses) calculated (back line) and difference (blue line) synchrotron X-ray diffraction profile after the Rietveld refinement at 170K.

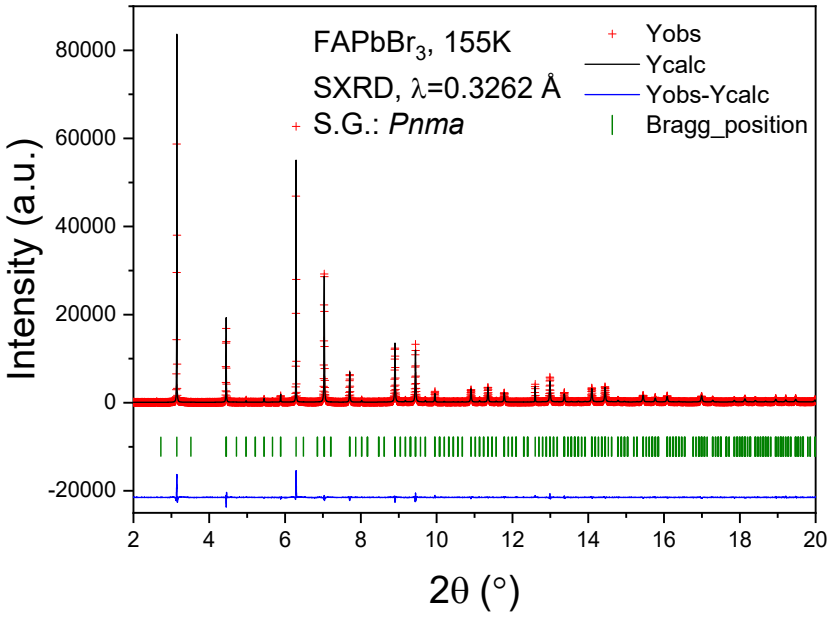

Figure S5. Observed (red crosses) calculated (back line) and difference (blue line) synchrotron X-ray diffraction profile after the Rietveld refinement at 155 K.

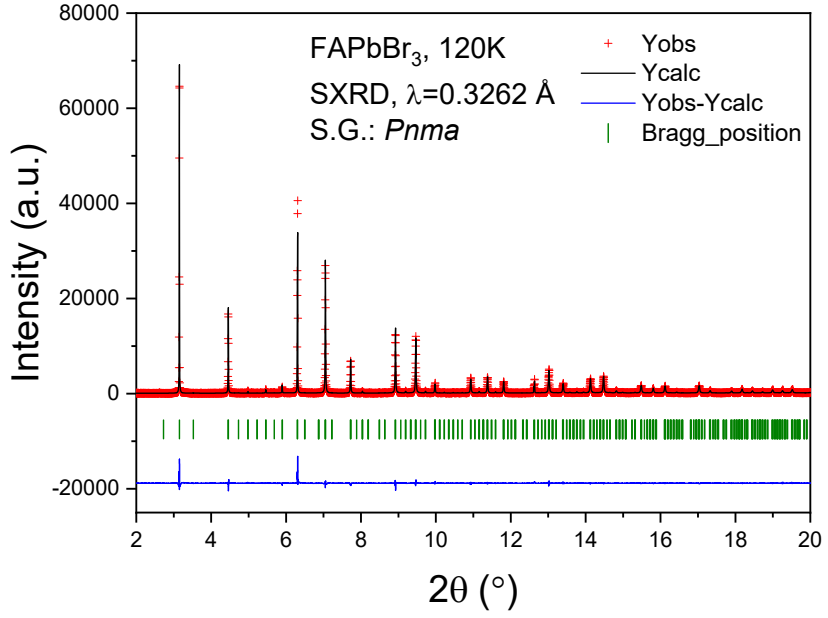

Figure S6. Observed (red crosses) calculated (back line) and difference (blue line) synchrotron X-ray diffraction profile after the Rietveld refinement at 120K.

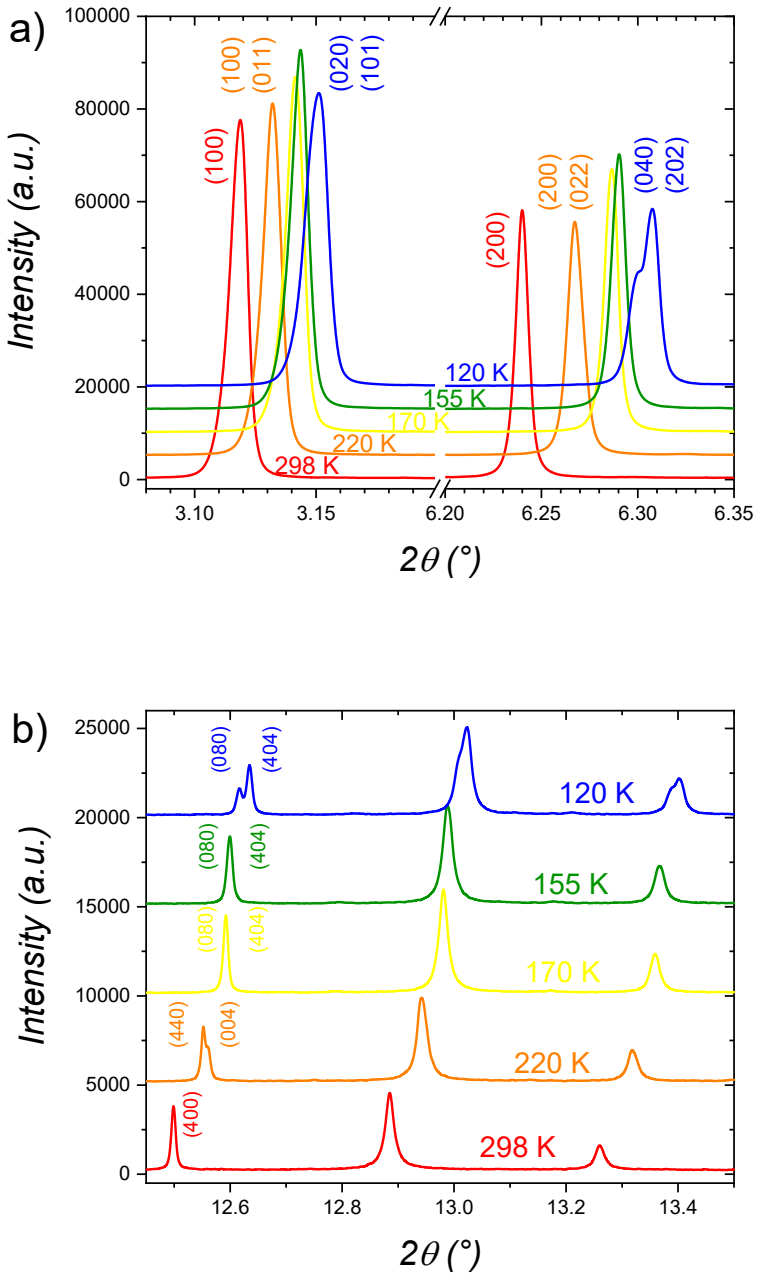

Figure S7. Thermal evolution of the diffraction patterns in selected angle ranges.

Table S9: Crystallographic data for $FAPbBr_3$ phase in tetragonal system (*P4/mbm)* from NPD at 200 K, *a* = 8.4303(12), *c* = 5.9620(14) Å and V = 423.72(13)Å^3

	x	*y*	*z*	U_{iso}	f_{occ}
Pb1	0	0	0	0.0141(15)	1
Br1	0	0	0.5	0.047(7)	1
Br2	0.2726(13)	0.7726(13)	0	0.052(4)	1
C1	0.51253	-0.0125	0.43078	0.019(6)	0.25
N1	0.40503	0.09497	0.46733	0.048(4)	0.25
N2	0.58889	-0.0889	0.58644	0.048(4)	0.25
H1	0.35143	0.14857	0.33614	0.118(11)	0.25
H2	0.37405	0.12595	0.62500	0.118(11)	0.25
H3	0.54097	-0.0410	0.25526	0.118(11)	0.25
H4	0.67077	-0.1708	0.54303	0.118(11)	0.25
H5	0.56775	-0.0677	0.75049	0.118(11)	0.25
R_p = 2.00%, R_{wp} = 2.54 %, χ^2 = 1.31, R_{Bragg} = 17.3%					

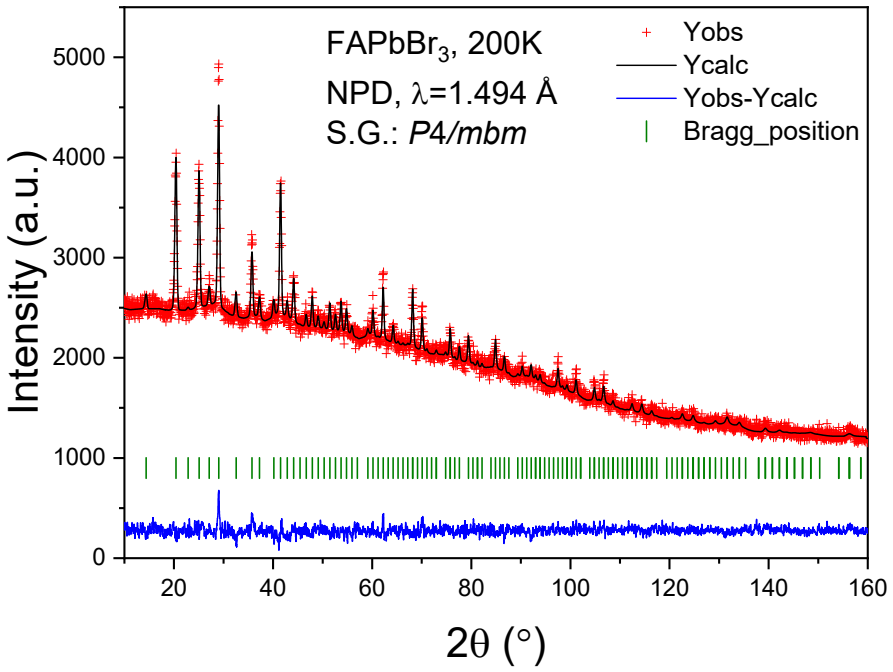

Figure S8. Observed (red crosses) calculated (back line) and difference (blue line) neutron diffraction profile after the Rietveld refinement at 200K.

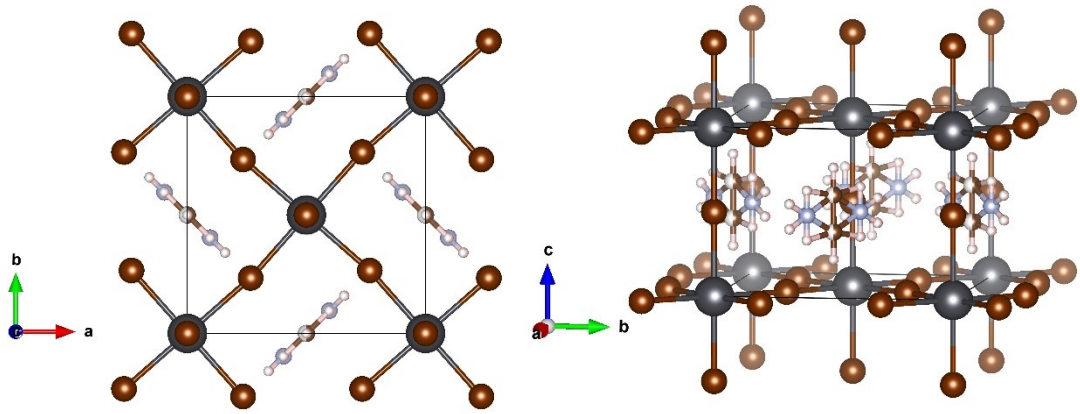

Figure S9: Different views of the refined crystallographic models of $FAPbBr_3$ at 220 K from SCND data.

Table S10: Crystallographic results obtained from single crystal ND measurements at 220 K.

System: Cubic, Space group: *P4/mbm,* Z = 2. Unit-cell parameters: a = 8.4287(13), c = 5.9584(15) Å and V = 423.30(14)Å^3						
Atom		**x**	**Y**	**z**	**U_{eq}**	**Occ**
Pb	2*a*	0	0	1	0.020(3)	1
Br1	8*i*	0.2659(12)	0.2341(12)	1	0.074(5)	1
Br2	2*b*	0	0	0.5	0.084(7)	1
C1	4*f*	0.5	0	0.3908(4)	0.17(3)	0.25
N	4*h*	0.5959(16)	0.0959(16)	0.5	0.163(8)	0.25
H1	4*f*	0.5	0	0.229654	0.1999	0.25
H2	8*k*	0.658862	0.158862	0.42625	0.1961	0.25
H3	8*k*	0.596299	0.096299	0.64601	0.1961	0.25
Anisotropic displacement parameters (Å^2)						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.026(3)	0.026(3)	0.009(7)	0	0	0
Br1	0.060(5)	0.060(5)	0.100(13)	-0.041(5)	0	0
Br2	0.122(13)	0.122(13)	0.007(14)	0	0	0
C	0.047(11)	0.047(11)	0.40(10)	-0.025(12)	0	0
N	0.123(10)	0.123(10)	0.24(2)	-0.028(12)	0	0
H1	0.056955	0.056955	0.485858	-0.030325	0	0
H2	0.14789	0.14789	0.292493	-0.033463	0	0
H3	0.14789	0.14789	0.292493	-0.033463	0	0
RF^2 = 19.3%; RF^2w = 28.5%; χ^2 = 4.42						

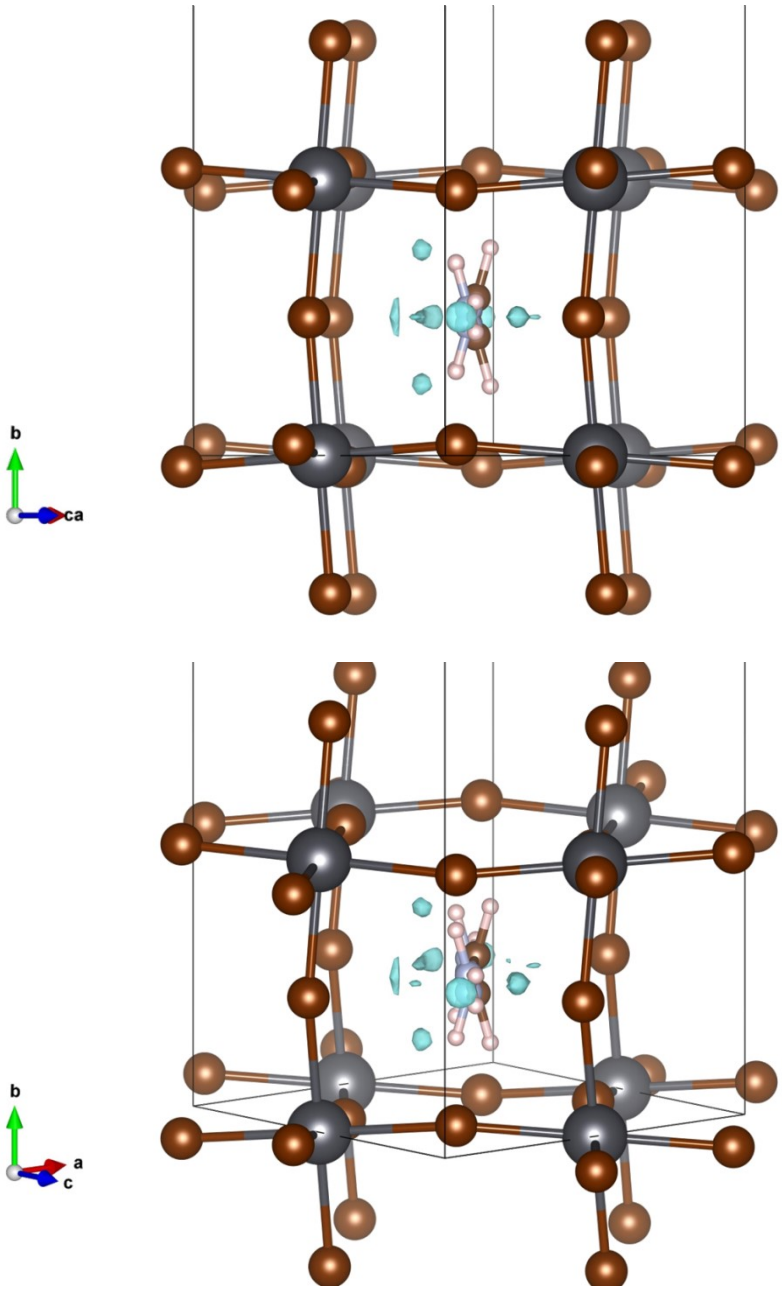

Figure S10. Views of the orthorhombic crystal structure of $FAPbBr_3$, showing negative areas (blue) in the Difference Fourier Maps, suggesting an additional FA molecule.

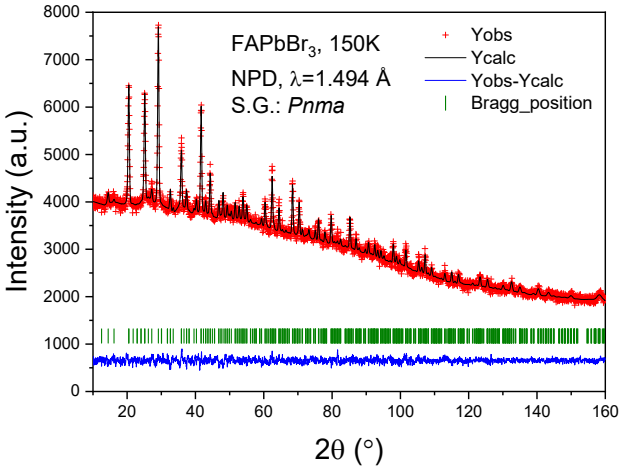

Figure S11. Observed (red crosses) calculated (back line) and difference (blue line) neutron diffraction profile after the Rietveld refinement at 150 K.

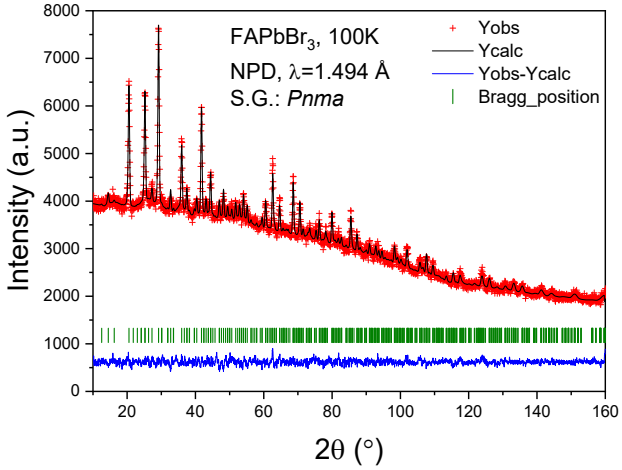

Figure S12. Observed (red crosses) calculated (back line) and difference (blue line) neutron diffraction profile after the Rietveld refinement at 100 K.

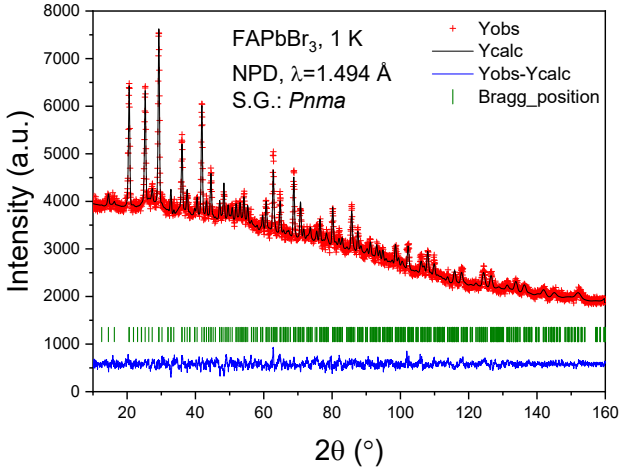

Figure S13. Observed (red crosses) calculated (back line) and difference (blue line) neutron diffraction profile after the Rietveld refinement at 1K.

Table S11: Crystallographic data for $FAPbBr_3$ phase in orthorhombic system (*Pnma)* from NPD at 150 K, *a* = 8.400(2) Å, *b* = 11.8784(16) Å, *c* = 8.4068(20) Å and V = 838.8(3)Å^3

	x	***y***	***z***	U_{iso}	f_{occ}
Pb1	0	0	0.5	0.0184(17)	1
Br1	-0.051(3)	0.25	0.511(7)	0.050(7)	1
Br2	0.769(3)	0.004(3)	0.231(3)	0.040(3)	1
C1	0.53881	0.28534	0.52617	0.019(6)	0.25
C2	0.48263	0.27743	0.49481	0.019(6)	0.25
N1	0.60767	0.21885	0.42442	0.048(4)	0.25
N2	0.40403	0.26459	0.59632	0.048(4)	0.25
N3	0.41839	0.21107	0.59970	0.048(4)	0.25
N4	0.59321	0.24788	0.39499	0.048(4)	0.25
H1	0.59900	0.36501	0.55504	0.052(8)	0.25
H2	0.71263	0.24163	0.37544	0.052(8)	0.25
H3	0.55795	0.14461	0.39337	0.052(8)	0.25
H4	0.35894	0.32106	0.67401	0.052(8)	0.25
H5	0.34342	0.19280	0.57447	0.052(8)	0.25
H6	0.44033	0.36501	0.49018	0.052(8)	0.25
H7	0.63658	0.30500	0.31726	0.052(8)	0.25
H8	0.63666	0.16860	0.39376	0.052(8)	0.25
H9	0.33293	0.24107	0.67282	0.052(8)	0.25
H10	0.45248	0.12983	0.60942	0.052(8)	0.25
R_p = 1.65%, R_{wp} = 2.07%, χ^2 = 1.39, R_{Bragg} = 10.9%					

Table S12: Crystallographic data for $FAPbBr_3$ phase in orthorhombic system (*Pnma)* from NPD at 100K, *a* = 8.384(2) Å, *b* = 11.8471(17) Å, *c* = 8.382(2) Å and V = 832.5(3) $Å^3$

	x	***y***	***z***	U_{iso}	f_{occ}
Pb1	0	0	0.5	0.0171(18)	1
Br1	-0.043(2)	0.25	0.506(6)	0.031(4)	1
Br2	0.769(3)	-0.0146(15)	0.230(4)	0.048(4)	1
C1	0.52733	0.28947	0.52793	0.014(5)	0.25
C2	0.49015	0.27981	0.48886	0.014(5)	0.25
N1	0.58794	0.22691	0.41585	0.043(5)	0.25
N2	0.40071	0.26425	0.61006	0.043(5)	0.25
N3	0.41699	0.21769	0.59370	0.043(5)	0.25
N4	0.59898	0.24356	0.39098	0.043(5)	0.25
H1	0.58762	0.36964	0.55528	0.057(8)	0.25
H2	0.68691	0.25303	0.35790	0.057(8)	0.25
H3	0.53770	0.15244	0.38559	0.057(8)	0.25
H4	0.36172	0.31788	0.69522	0.057(8)	0.25
H5	0.34045	0.19178	0.59019	0.057(8)	0.25
H6	0.45757	0.36964	0.48251	0.057(8)	0.25
H7	0.64982	0.29778	0.31312	0.057(8)	0.25
H8	0.63370	0.16193	0.39137	0.057(8)	0.25
H9	0.33374	0.25284	0.66524	0.057(8)	0.25
H10	0.44198	0.13467	0.60495	0.057(8)	0.25
R_p = 1.70%, R_{wp} = 2.14%, χ^2 = 1.45, R_{Bragg} = 13.2%					

Table S13: Crystallographic data for $FAPbBr_3$ phase in orthorhombic system (*Pnma)* from NPD at 1 K, a = 8.3633(16) Å, b = 11.8204(16) Å, c = 8.3663(17) Å and V = 827.1(3) Å^3

	x	y	z	U_{iso}	f_{occ}
Pb1	0	0	0.5	0.0108(18)	1
Br1	-0.052(2)	0.25	0.499(5)	0.020(3)	1
Br2	0.769(3)	-0.0108(16)	0.232(3)	0.035(3)	1
C1	0.52370	0.28490	0.52505	0.002(4)	0.25
C2	0.49201	0.28239	0.49079	0.002(4)	0.25
N1	0.59364	0.22601	0.41399	0.026(4)	0.25
N2	0.40832	0.24822	0.61534	0.026(4)	0.25
N3	0.59942	0.24935	0.38862	0.026(4)	0.25
N4	0.42238	0.21709	0.59466	0.026(4)	0.25
H1	0.56521	0.37218	0.54401	0.044(7)	0.25
H2	0.68257	0.26124	0.34923	0.044(7)	0.25
H3	0.56057	0.14543	0.39122	0.044(7)	0.25
H4	0.36067	0.29981	0.69896	0.044(7)	0.25
H5	0.36532	0.16882	0.60335	0.044(7)	0.25
H6	0.45751	0.37218	0.48922	0.044(7)	0.25
H7	0.64749	0.30589	0.31193	0.044(7)	0.25
H8	0.63578	0.16792	0.38454	0.044(7)	0.25
H9	0.33999	0.24987	0.66980	0.044(7)	0.25
H10	0.44926	0.13394	0.60161	0.044(7)	0.25
R_p = 1.83%, R_{wp} = 2.35%, χ^2 = 1.77, R_{Bragg} = 16.1%					

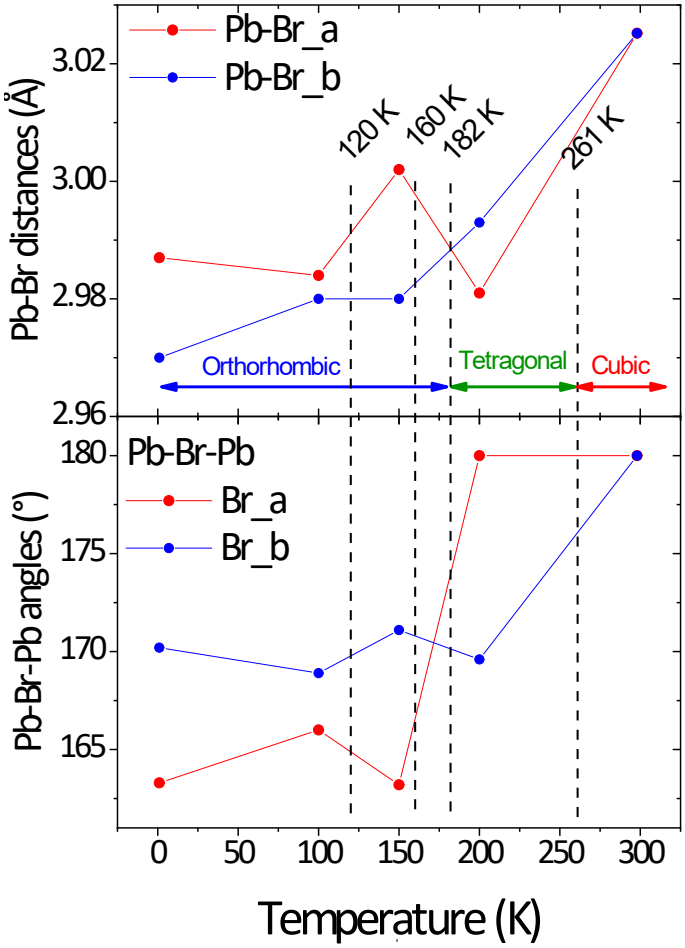

Figure S14. Thermal evolution of Pb–Br distances and Br–Pb–Br angles. Dashed lines indicate the events observed in DSC.

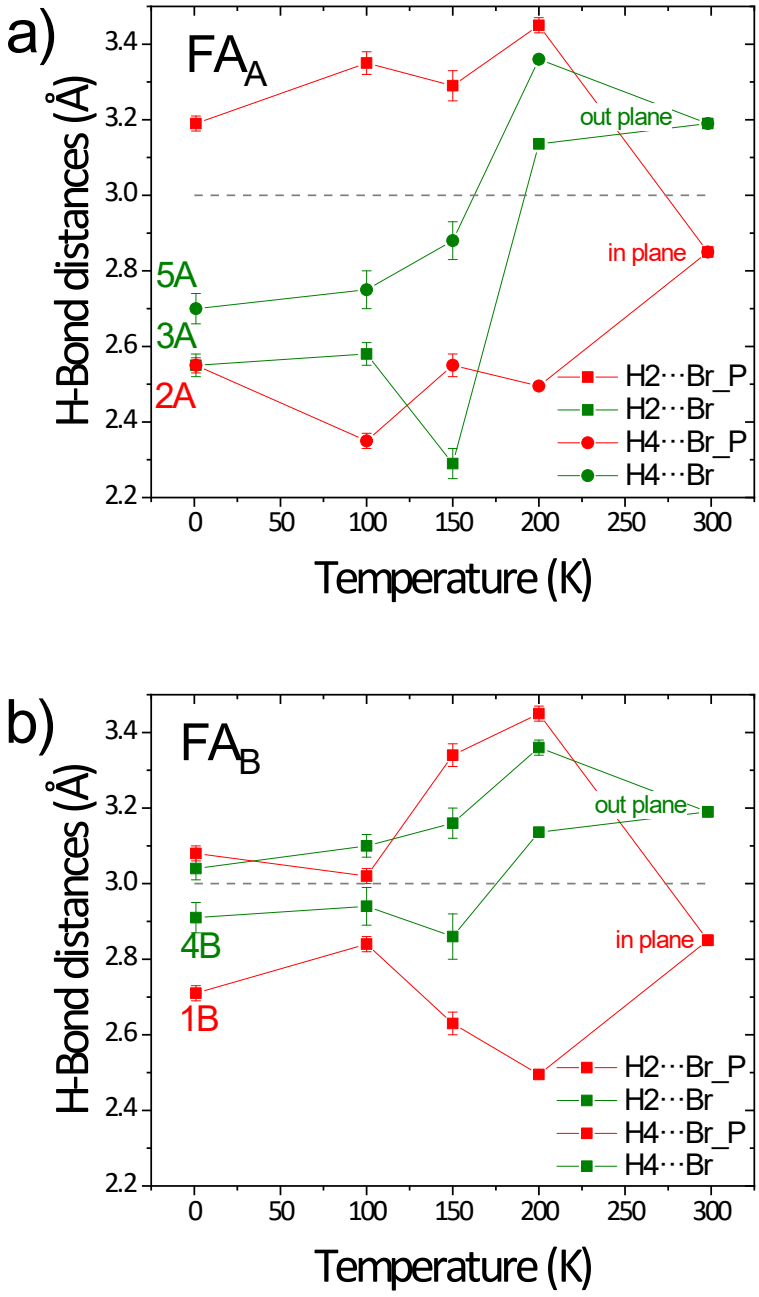

Figure S15: Thermal evolution of the H-bond distances of the atom H2 and H4 from 1 K to 300K, obtained from NPD data.

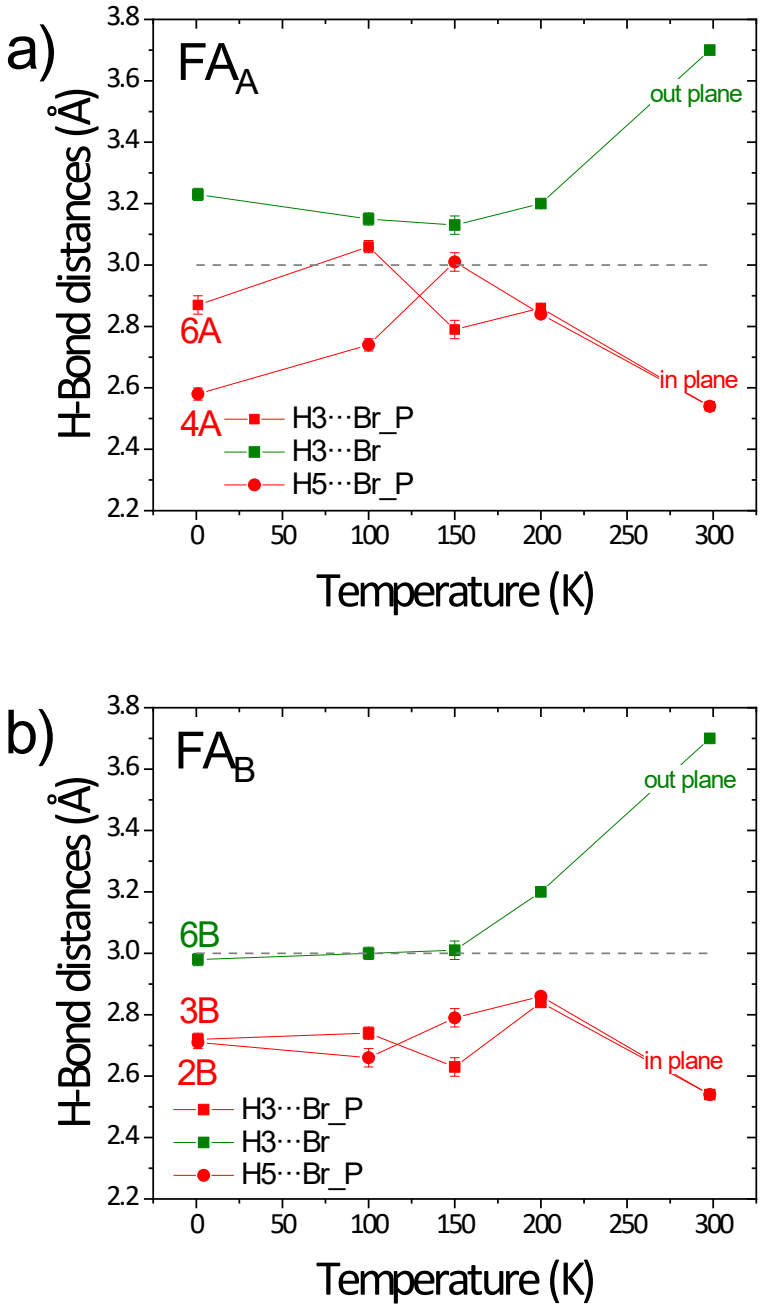

Figure S16: Thermal evolution of the H-bond distances of the atom H3 and H5 from 1 K to 300K, obtained from NPD data.