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

Supporting Information

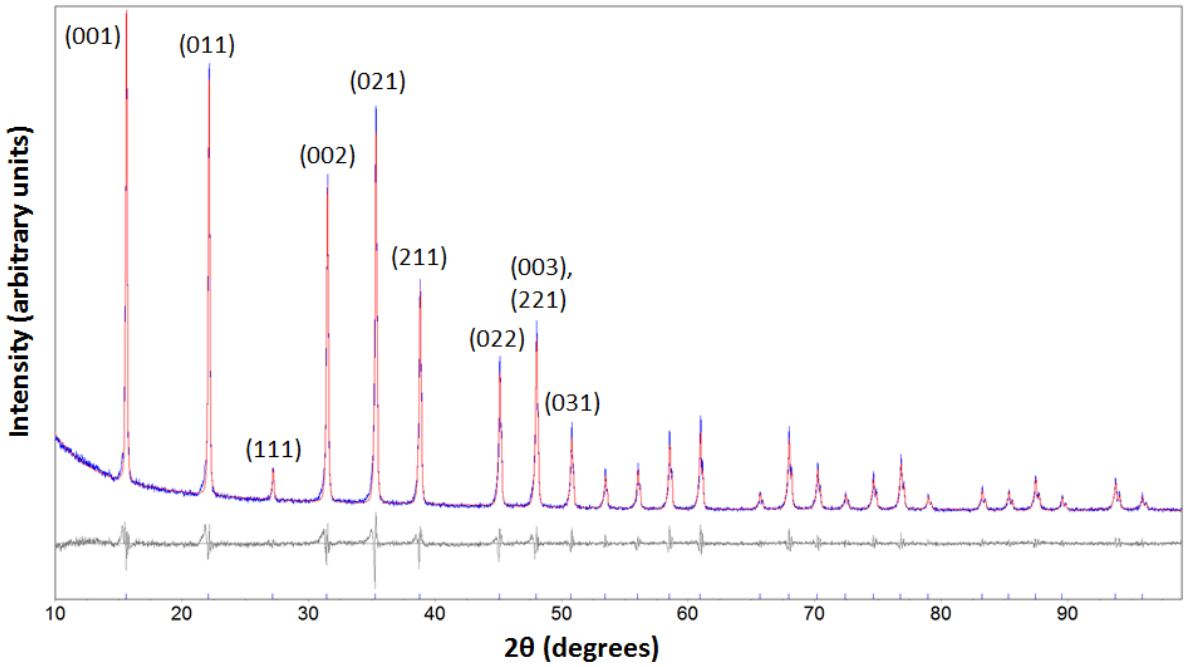

Figure S1. Powder X-ray diffraction pattern of *MA*$PbCl_3$, which has been indexed assuming cubic symmetry (*Pm*-3*m*). Pattern obtained when HCl added in excess which prevents the conformation of $PbCl_2$.

Table S1. Experimental parameters for solid-state MAS NMR experiments performed on a Bruker Avance III spectrometer.

Isotope	Sample	MAS rate (Hz)	D1 (s)	Scans	Mass (mg)	LB (Hz)
^{1}H	*MA*$PbBr_3$	10000	30	142	231.7	1
^{1}H	*MA*PbI_3	8000	25	4	238.5	1
^{13}C	*MA*$PbBr_3$	10000	40	32	231.7	10
^{13}C	*MA*$PbBr_3$	10000	25	32	231.7	10
^{13}C	*MA*PbI_3	8000	40	32	238.5	10

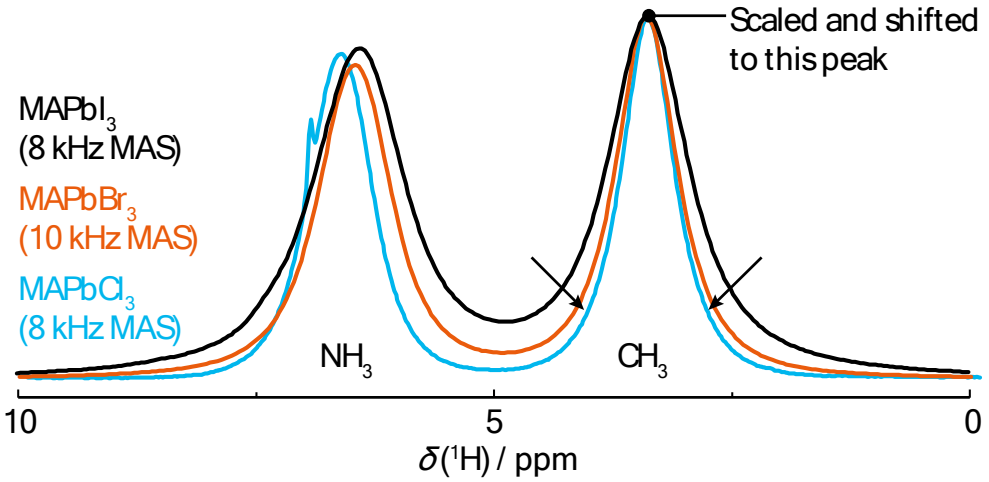

Figure S2. Overlaid ^{1}H spectra for the *MA*PbX$_3$ (X = Cl, Br and I) indicating a progressive line narrowing.

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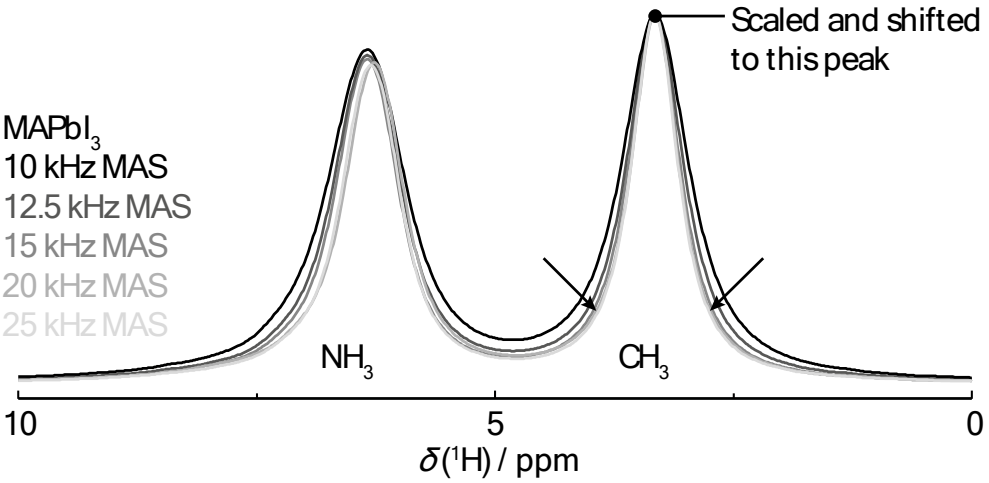


Figure S3. ^{1}H spectra for *MA*PbI$_3$ collected at different magic angle spinning rates, indicating that the lines become narrower with faster spinning rates up to a point.

Table S2. FWHM from the ^{1}H spectra for *MA*PbX$_3$ (X = Cl, Br and I)

	^{1}H NH$_3$ FWHM (ppm)	**^{1}H CH$_3$ FWHM (ppm)**
***MA*PbI$_3$**	1.14	1.01
***MA*PbBr$_3$**	0.91	0.77
***MA*PbCl$_3$**	0.81	0.68

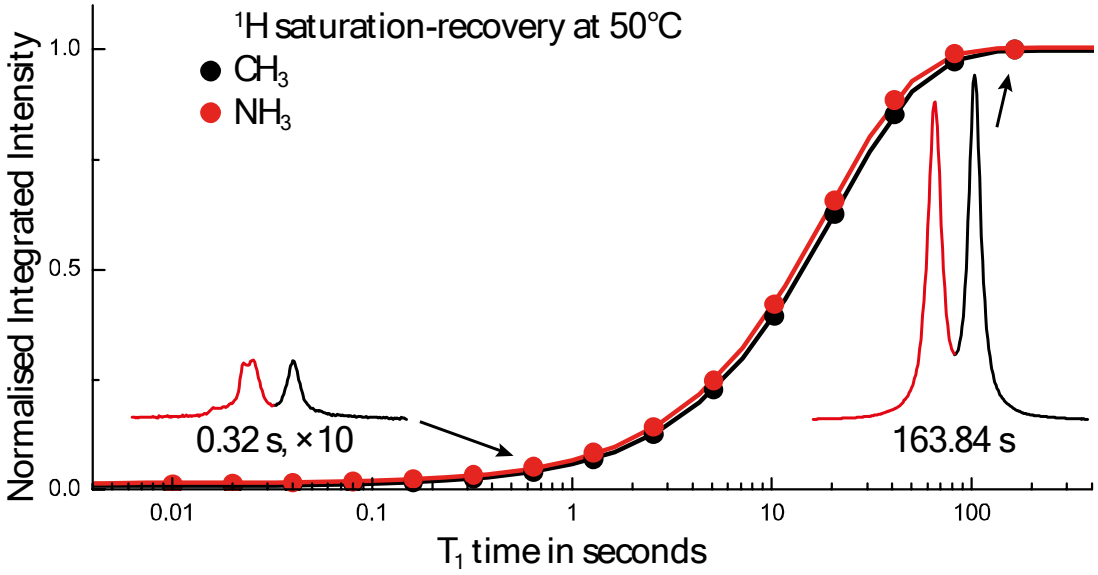


Figure S4. ^{1}H solid-state MAS NMR saturation-recovery data at 50°C for *MA*PbI$_3$. Two spectra are shown for short (scaled 10 times) and long relaxation times.

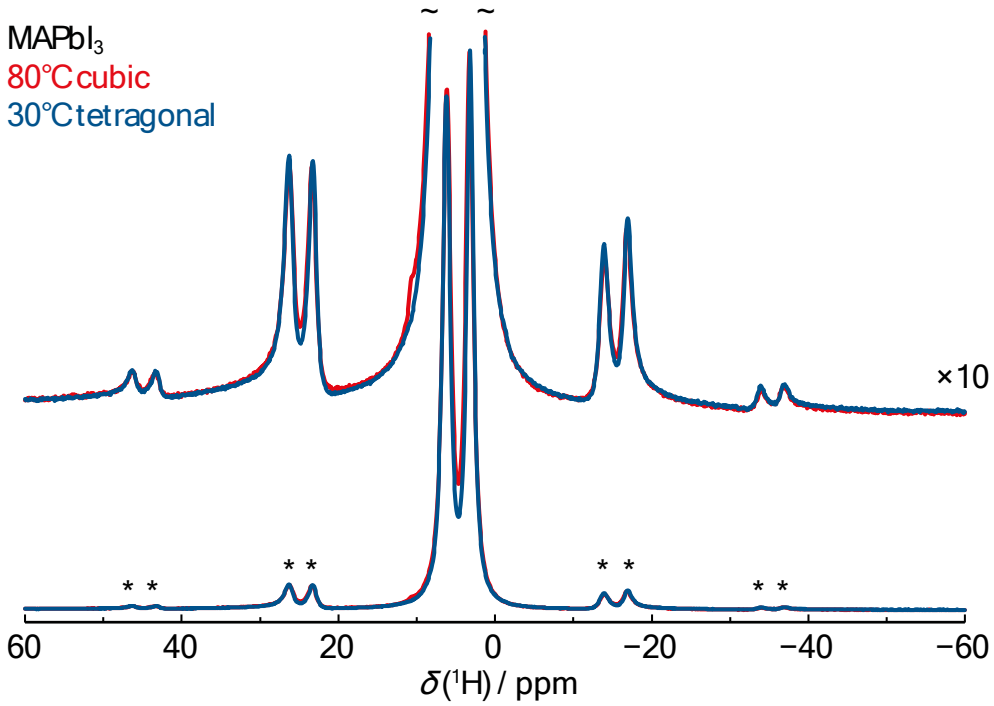


Figure S5. ^{1}H solid-state MAS NMR spectra of *MA*PbI$_3$ above and below the high temperature phase transitions. The asterisks indicate the spinning sidebands.

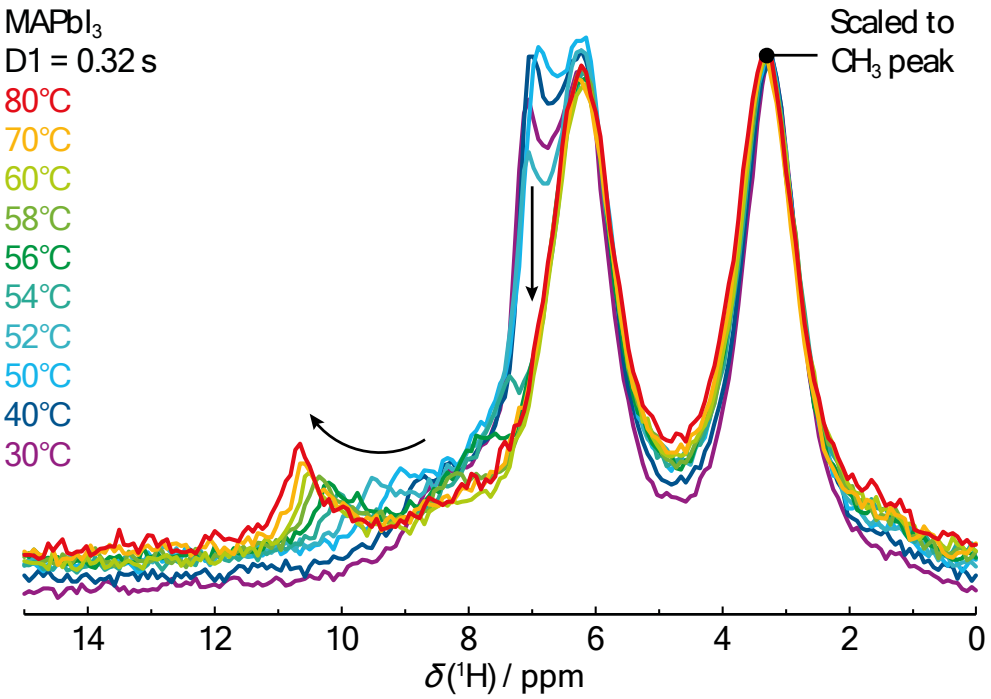


Figure S6. Scaled ^{1}H solid-state MAS NMR spectra of *MA*PbI$_3$ at short relaxation time.

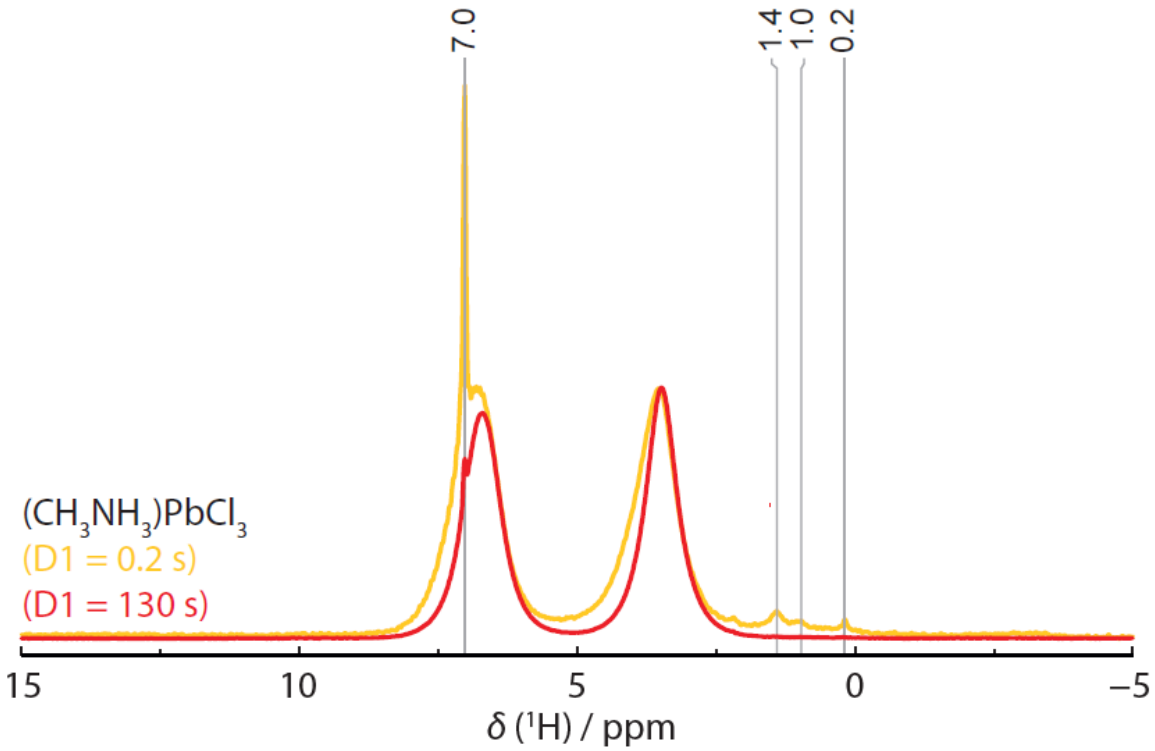


Figure S7. ^{1}H solid-state MAS NMR spectra of *MA*PbCl$_3$, comparing short and long D1 pulse delay values to highlight sharp features. Scaled to the CH$_3$ peak.

Impedance Spectra

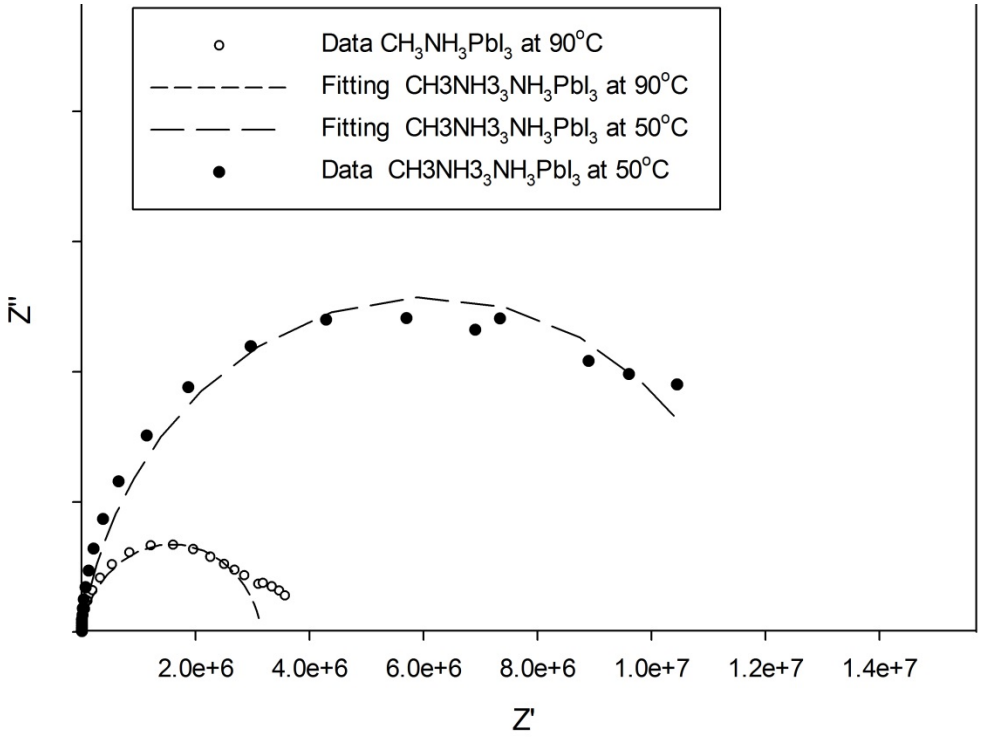


Figure S8. Representative impedance spectra for $MAPbI_3$.

Single Crystal X-ray Diffraction Data

Table S3. Parameter of the single crystal X-ray diffraction data of *MA*PbI_3 performed in the tetragonal space groups *P*4*mm*.

Crystal size	0.05 × 0.036 × 0.015 mm
Crystal system	Tetragonal
Temperature	400*K*
Space Group	*P*4*mm*
Unit cell dimensions	
a (Å)	6.3180(5)
c (Å)	6.3249(5)
V (Å^3)	252.47(3)
Z	1
μ (cm^{-1})	51.572
Radiation Mo *Kα* (Å)	0.71069

Collection limits (θ, deg)	3.22 – 32.49
Data measured	3070
Unique reflections	596
Reflections with I≥3σ(I)	517
R	0.0340
R_W	0.0482
GOF	2.72
D residual ($eÅ^{-3}$)	
+	2.15
-	1.25

Table S4. Atomic positions and atomic displacement parameters from the single crystal X-ray diffraction data of $MAPbI_3$ refined in the tetragonal space group *P*4*mm*.

s.g	*P*4*mm*	*a* = 6.3180(5) Å	*c* = 6.3249(5) Å	
Site	***x***	***y***	***z***	$\boldsymbol{U_{Iso}}$
Pb	0	0	0.95563(19)	0.04292(19)
I1	-0.5	0	0.9556(9)	0.1283(8)
I2	0	0	0.4560(8)	0.1277(8)

	$\boldsymbol{U_{11}}$	$\boldsymbol{U_{22}}$	$\boldsymbol{U_{33}}$	$\boldsymbol{U_{12}}$	$\boldsymbol{U_{13}}$	$\boldsymbol{U_{23}}$
Pb	0.0426(3)	0.0426(3)	0.0436(4)	0	0	0
I1	0.0317(5)	0.1758(16)	0.1775(16)	0	0	0
I2	0.1752(15)	0.1752(15)	0.0327(8)	0	0	0

Bond Lengths

Bond	**Distance**
Pb – I1	3.1590(5)
Pb – I2	3.160(5), 3.165(5)

Table S5. Parameters of the single crystal X-ray diffraction data of *MA*PbI_3 performed in the hexagonal space groups *R*-3*m and R*3*m*.

Crystal size	0.05 × 0.036 × 0.015 mm
Crystal system	Hexagonal
Temperature	400*K*
Space Group	*R*-3*m* (No.166) *R*3*m* (No.160)
Unit cell dimensions	
a (Å)	8.9427(5)
c (Å)	10.9465(4)
V ($Å^3$)	758.13(9)

Z	1	
μ (cm^{-1})	8.586	
Radiation Mo $K\alpha$ (Å)	0.71069	
Collection limits (θ, deg)	3.22 – 32.49	
Data measured	9849	
Unique reflections	367	723
Reflections with I≥3σ(I)	323	627
R	0.0301	0.0292
R_W	0.0457	0.0498
GOF	2.62	2.50
D residual (eÅ^{-3})		
+	2.25	2.34
-	1.60	1.27

Table S6. Atomic positions, atomic displacement parameters and selected bond lengths from the single crystal X-ray diffraction data of *MA*PbI$_3$, refined in the hexagonal space group space group *R*-3*m*.

s.g	*R*-3*m*	a = 8.9427(5) Å	c = 10.9465(4) Å	
Site	***x***	***y***	***z***	U_{Iso}
Pb	1/3	2/3	1/6	0.0429(3)
I	0.5	0	0	0.1281(8)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.0429(3)	0.0429(3)	0.0429(3)	0.02143(17)	0	0
I	0.1522(12)	0.0801(9)	0.1280(12)	0.0400(5)	0.0340(4)	0.0680(9)

Bond	**Distance**
Pb – I	3.1611(4), 3.16115(18)

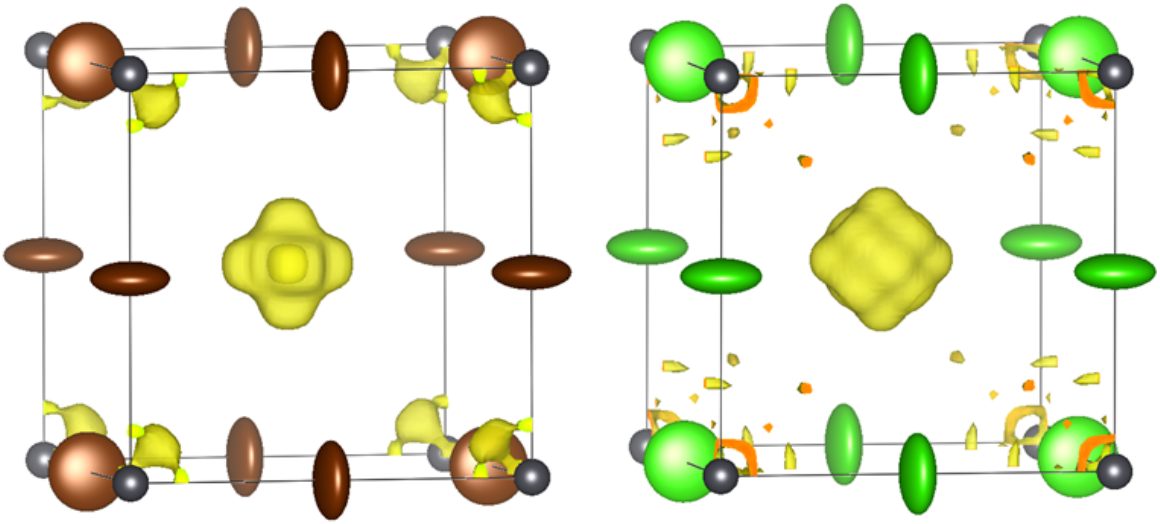
Table S7. Atomic positions, atomic displacement parameters and selected bond lengths from the single crystal X-ray diffraction data of *MA*PbI$_3$, refined in the hexagonal space group space group *R*3*m*.

s.g	*R*3*m*	a = 8.9427(5) Å	c = 10.9465(4) Å	
Site	***x***	***y***	***z***	U_{Iso}
Pb	1/3	2/3	0.29065(8)	0.0419(2)
I	0.4999(3)	-0.0002(6)	0.12380(19)	0.1273(7)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.0418(3)	0.0418(3)	0.0419(3)	0.02091(13)	0	0
I	0.1517(10)	0.0790(7)	0.1271(10)	0.0395(4)	0.0338(4)	0.0677(7)

Bond	Distance
Pb – I	3.161(4)

Figure S9. Difference Fourier maps from single crystal XRD data for *MA*$PbBr_3$ (left) and *MA*$PbCl_3$ (right) when considering the Pb (0,0,0) and halogen (0.5,0,0) positions in the cubic space group *Pm*-3*m*. Electron density > 1electron.



Single Crystal Laue Neutron Diffraction Data

Table S8. Refined atomic positions and atomic displacement parameters derived from the single crystal neutron diffraction data of *MA*PbI_3 collected at 70°C.

Site	*x*	*y*	*z*	U_{Iso}
Pb	0	0	0	0.0372(4)
I1	0.5	0	0	0.1226(15)
C/N	0.5	0.447(4)	0.399(2)	0.140(8)
H1	0.5	0.415(3)	0.255(3)	0.087(7)
H2	0.3456(18)	0.3456(18)	0.435(2)	0.124(7)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.0372(6)	0.0372(6)	0.0372(6)	0	0	0
I	0.0299(13)	0.169(3)	0.169(3)	0	0	0

Reflections with I≥3σ(I)	57
R	0.0326
R_W	0.0298
GOF	1.81
D residual (eÅ^{-3})	
+	0.70
-	0.33

Table S9. Refined atomic positions and atomic displacement parameters derived from the single crystal neutron diffraction data of *MA*$PbBr_3$ collected at 25°C.

Site	***x***	***y***	***z***	U_{Iso}
Pb	0	0	0	0.0258(4)
Br1	0.5	0	0	0.1001(11)
C/N	0.5	0.4374(15)	0.3910(11)	0.081(4)
H1	0.5	0.414(2)	0.252(4)	0.063(5)
H2	0.3325(14)	0.3325(14)	0.4324(18)	0.095(5)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.0258(6)	0.0258(6)	0.0258(6)	0	0	0
Br	0.0258(11)	0.137(2)	0.137(2)	0	0	0

Reflections with I≥3σ(I)	71
R	0.0591
R_W	0.0695
GOF	2.04
D residual (eÅ^{-3})	
+	1.17
-	0.43

Table S10. Refined atomic positions and atomic displacement parameters derived from the single crystal neutron diffraction data of *MA*$PbCl_3$ collected at 25°C.

Site	***x***	***y***	***z***	U_{Iso}
Pb	0	0	0	0.0233(4)
Cl1	0.5	0	0	0.0904(14)
C/N	0.5	0.4336(19)	0.3878(16)	0.065(5)
H1	0.5	0.414(3)	0.241(4)	0.050(6)
H2	0.323(2)	0.323(2)	0.431(3)	0.091(7)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.0233(8)	0.0233(8)	0.0233(8)	0	0	0
Cl	0.0277(14)	0.124(3)	0.124(3)	0	0	0

Reflections with I≥3σ(I)	62
R	0.0748
R_W	0.0455
GOF	2.21
D residual (eÅ^{-3})	
+	2.66
-	-1.00

Figure S10. Structural representations of the *MA*PbI_3 (left) *MA*$PbBr_3$ (centre) and *MA*$PbCl_3$ (right) series derived from single crystal neutron diffraction in the space group *Pm*-3*m*. The large white spheres represent the large isotropic displacement parameters of the H ions and indicate a disordered arrangement of the MA groups within the perovskite structure.