Supporting Information for

Examining year-long chemical degradation process and reaction kinetics in pristine and defect-passivated lead halide perovskites

Parth Raval,¹ Mohammad Ali Akhavan Kazemi,² Julie Ruellou,² Julien Trébosc,³ Olivier Lafon,¹ Laurent Delevoye,¹ Frédéric Sauvage,² and G. N. Manjunatha Reddy¹*

¹University of Lille, CNRS, Centrale Lille Institut, Univ. Artois, UMR 8181–UCCS– Unité de Catalyse et Chimie du Solide, F-59000, Lille, France

²Laboratoire de Réactivité et Chimie des Solides (LRCS), UMR CNRS 7314 - Institut de Chimie de Picardie FR 3085, Université de Picardie Jules Verne, 33 rue Saint Leu, FR-80039 Amiens Cedex, France.

³Université de Lille, CNRS, INRAE, Centrale Lille, Univ. Artois, FR 2638 - IMEC - Institut Michel-Eugène Chevreul, F-59000 Lille, France

*Corresponding author: gnm.reddy@univ-lille.fr

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1. Solid-state NMR experimental details

All the 1D ¹H and ¹³³Cs MAS NMR spectra were acquired using a single pulse experiment. All the 2D ¹H-¹H double-quantum (DQ)-single-quantum (SQ) NMR spectrum was acquired using a Back-to-Back (BaBa) sequence.^{1–3} The DQ coherences were excited using a rotor-synchronized recoupling time. The 2D ¹H-¹H spin-diffusion NMR spectrum was acquired using a three-pulse noesy-like sequence.⁴

Exposure time	NMR experiment	Probe diameter (mm)	$v_{\rm R}$ $({\rm kHz})^a$	τ ₉₀ (μs) ^b	NS ^c	t_1^d	$ au_{ m mix}/ au_{ m rec}{}^e$	Figure
0	1D H	1.3	50	1.3	8	-	-	1b
	2D ¹ H- ¹ H DQ-SQ	1.3	50	2.2	16	128	40 µs	4b, S3a
	2D ¹ H- ¹ H SD	1.3	50	2.0	4	300	200 ms	4a, S3b, S5a
	1D H	1.3	50	1.3	8	-	-	1b
17 h	2D ¹ H- ¹ H DQ-SQ	1.3	50	2.2	16	128	40 µs	S3b
	2D ¹ H- ¹ H SD	1.3	35	2.0	1	500	200 ms	S3a, S5b
24 h	1D H	1.3	35	1.3	8	-	-	1b
34 n	2D ¹ H- ¹ H SD	1.3	35	2.0	4	400	500 ms	S5c
	1D H	1.3	55	1.3	8	-	-	1b
45 h	2D ¹ H- ¹ H DQ-SQ	1.3	35	2.2	32	128	57 µs	4d
0 17 h 34 h 45 h	2D ¹ H- ¹ H SD	1.3	35	2.0	4	400	500 ms	4c, S5d

Table S1. Experimental parameters used for the NMR data acquisition of aged MAPbI₃ (85% RH).

^{*a*} The MAS frequency is denoted by v_R , ^{*b*} Duration of the 90° pulse (τ_{90}). ^{*c*} Number of co-added transients (scans, NS). ^{*d*} t_1 -increments to construct the indirect dimension ^{*e*} Duration of the mixing time (τ_{mix}) used for ¹H-¹H SD experiments and recoupling time (τ_{rec}) used for the ¹H-¹H DQ excitation.

Exposure time	NMR experiment	Probe diameter (mm)	v _R (kHz) ^a	τ ₉₀ (μs) ^b	NS ^c	t_1^{d}	$ au_{mix}/ au_{rec}^{e}$	Figure
1 month	1D ¹ H	1.3	50	1.3	16	-	-	3
3 months	1 D H	1.6	35	2.9	32	-	-	3
6 months	1 D H	1.3	50	1.2	48	-	-	3
9 months	1 D H	1.3	35	1.3	60	-	-	3
	1D H	1.6	35	2.9	16	-	-	3
12 months	2D ¹ H- ¹ H DQ-SQ	1.3	30	2.2	16	80	67 µs	4f
	2D ¹ H- ¹ H SD	1.6	30	2.9	1	256	500 ms	4e

Table S2. Experimental parameters used for the NMR data acquisition of aged MAPbI₃ (40% RH).

^{*a*} The MAS frequency is denoted by v_{R} , ^{*b*} Duration of the 90° pulse (τ_{90}). ^{*c*} Number of co-added transients (scans, NS). ^{*d*} t_1 -increments to construct the indirect dimension ^{*e*} Duration of the mixing time (τ_{mix}) used for ¹H-¹H SD experiments and recoupling time (τ_{rec}) used for the ¹H-¹H DQ excitation.

Table	S3.	Experimental	parameters	used	for	the	NMR	data	acquisition	of	fresh	and	aged
MAPb	I3.TF	PA(4%) (85% I	RH).										

Exposure time	NMR experiment	Probe diameter (mm)	v _R (kHz) ^a	$ au_{90} \ (\mu s)^b$	NS^{c}	t_1^{d}	Figure
0 h	1D H	2.5	25	3.0	8	-	5b
	2D ¹ H- ¹ H DQ- SQ	2.5	25	3.0	16	160	бb
	2D ¹ H- ¹ H SD	2.5	25	3.0	2	400	6a, S10a
15 h	1D H	2.5	25	3.0	32	-	5b
	2D ¹ H- ¹ H SD	2.5	25	3.0	2	400	S10b
22 h	1D ¹ H	2.5	25	3.0	32	-	5b
48 h	1D ¹ H	2.5	25	3.0	32	-	5b
	2D ¹ H- ¹ H SD	2.5	25	3.0	8	256	S10c
	1D ¹ H	2.5	25	3.0	16	-	5b
72 h	2D ¹ H- ¹ H DQ- SQ	2.5	25	3.0	32	102	6d
	2D ¹ H- ¹ H SD	2.5	25	3.0	8	256	6c, S10d

^{*a*} The MAS frequency is denoted by v_R , ^{*b*} Duration of the 90° pulse (τ_{90}). ^{*c*} Number of co-added transients (scans, NS). ^{*d*} t_1 -increments to construct the indirect dimension ^{*e*} Duration of the mixing time (τ_{mix}) used for ¹H-¹H SD experiments and recoupling time (τ_{rec}) used for the ¹H-¹H DQ excitation.

Exposure time	NMR experiment	Probe diameter (mm)	v _R (kHz) ^a	τ ₉₀ (μs) ^b	NS ^c	t_1^{d}	$ au_{ m mix}/ \ au_{ m rec}{}^{ m e}$	Figure
3 months	1D ¹ H	1.3	50	1.3	8	-	-	5c
6 months	1D ¹ H	1.3	50	1.2	4	-	-	5c
9 months	1D ¹ H	1.3	40	1.3	64	-	-	5c
	1D H	1.6	35	2.9	32	-	-	5c
12 months	2D ¹ H- ¹ H DQ-SQ	1.3	40	2.2	32	128	50 µs	6f
	2D ¹ H- ¹ H SD	1.6	30	2.9	4	55	500 ms	6e

Table S4. Experimental parameters used for the ¹H MAS NMR data acquisition of aged MAPbI₃.TPA(4%) (40% RH).

^{*a*} The MAS frequency is denoted by v_R , ^{*b*} Duration of the 90° pulse (τ_{90}). ^{*c*} Number of co-added transients (scans, NS). ^{*d*} t_1 -increments to construct the indirect dimension ^{*e*} Duration of the mixing time (τ_{mix}) used for ¹H-¹H SD experiments and recoupling time (τ_{rec}) used for the ¹H-¹H DQ excitation.

Table S5. Experimental parameters used for the acquisition of ¹H and ¹³³Cs NMR spectra of CsMAFA exposed to 85% RH.

Exposure time	NMR experiment	Probe diameter (mm)	$v_{R} (kHz)^{a}$	$ au_{90} \ (\mu s)^b$	NS^c	t1 ^d	Figure
0 h	1D ¹³³ Cs	1.3	50	3.6	192	-	7a
	1D H	1.3	50	1.3	16	-	7b
	$2D H^{-1}H SD$	1.3	50	1.3	2	400	8a
17 h	1D ¹³³ Cs	1.3	50	3.6	512	-	7a
1/11	1D H	1.3	50	1.3	16	-	6b
	1D ¹³³ Cs	1.3	50	3.6	3072	-	7a
167 h (7 days)	1D ¹ H	1.3	50	1.3	16	-	7b
(, auys)	2D ¹ H ⁻¹ H SD	1.3	40	1.3	8	160	8b

^{*a*} The MAS frequency is denoted by v_{R} , ^{*b*} Duration of the 90° pulse (τ_{90}). ^{*c*} Number of co-added transients (scans, NS). ^{*d*} t_1 -increments to construct the indirect dimension ^{*e*} Duration of the mixing time (τ_{mix}) used for ¹H-¹H SD experiments.

Exposure time	NMR experiment	Probe diameter (mm)	ν _R (kHz) ^a	τ ₉₀ (μs) ^b	NS ^c	t_1^{d}	t _{mix} e	Figure
9	1D ¹³³ Cs	1.3 mm	50	3.6	672	-	-	7c
8 months	1D H	1.3 mm	50	1.3	16	-	-	7d
	1D ¹³³ Cs	1.3 mm	50	3.6	1024	-	-	7c
12 months	1D H	1.3 mm	50	1.3	16	-	-	7d
	2D ¹ H- ¹ H SD	1.3 mm	50	1.3	4	160	500 ms	8c

Table S6. Experimental parameters used for the acquisition of NMR spectra of CsMAFA exposedto 40% RH.

^{*a*} The MAS frequency is denoted by v_{R} , ^{*b*} Duration of the 90° pulse (τ_{90}). ^{*c*} Number of co-added transients (scans, NS). ^{*d*} t_1 -increments to construct the indirect dimension ^{*e*} Duration of the mixing time (τ_{mix}) used for ¹H-¹H SD experiments.

Table S7. Experimental parameters used for the acquisition of 1D 133 Cs MAS NMR spectra of CsPb₂Br_xI_{5-x} (x= 1-5), CsPbBr₃, δ -CsPbI₃, and CsI

Material	Probe	$\nu_{R} (kHz)^{a}$	$ au_{90}$ (µs) ^b	NS ^c	Figure
CsBr:2PbBr ₂	3.2 mm	20	2.0	32	S 13
CsI:2PbBr ₂	3.2 mm	20	2.0	32	S 13
CsBr:PbBr ₂ :PbI ₂	3.2 mm	20	2.0	32	S 13
CsI:PbBr ₂ :PbI ₂	3.2 mm	20	2.0	32	S 13
CsBr:2PbI ₂	3.2 mm	20	2.0	32	S 13
CsPbBr ₃	3.2 mm	20	2.0	32	S 13
δ-CsPbI ₃	3.2 mm	20	2.0	32	S 13
CsI	3.2 mm	20	2.0	32	S 13

^{*a*} The MAS frequency denoted by the symbol, v_R . ^{*b*} Duration of the 90° pulse, τ_{90} . ^{*c*} Number of scans (NS).

2. SEM images of MAPbI₃ and MAPbI₃.TPA (4%)



Figure S1. SEM images of (a) MAPbI₃ thin film examined from top (left) and cross-section (right) views, (b) MAPbI₃ thin films passivated by TPAI examined from (left) and cross-sectional (right), demonstrating the favorable morphology with grain sizes in the sub-micron to micron lengths, which is typical for the high efficiency perovskite photovoltaic devices. Passivation by TPA molecules improves the surface ad bulk the morphology, as evidenced from the SEM images.

3. Powder XRD patterns of fresh and aged MAPbI₃ and the degradation products

Figure S2a.b presents powder X-ray diffractograms of fresh and moisture treated MAPbI₃ (72 hours under 85% R.H) with the peak fitting and refinement and the simulated patterns of the byproducts are presented in **Figure S2c**. These results, together with the SEM analysis, demonstrate that the phase purity of the pristine MAPbI₃ sample. In addition, the moisture aged MAPbI₃ film shows consistently peak indexing and refinement for three phases such as MAPbI₃ (MAPI, blue), MAPbI₃.H₂O (MAPI.H₂O, green) and PbI₂ (red), supporting our initial assessment of degradation pathways and byproducts. However, the XRD patterns of MAI are not detected, due the lack of long-range order or due to the low concentration of this compound or both. For pristine MAPbI₃ (MAPI) and the different degradation products, the refined lattice cell parameters for these phases are:

MAPbI₃ aged: Space group = I4/mcm; a = b = 8.8549(4) Å, c = 12.596(3) Å PbI₂: Space group = P6₃mc; a = b = 4.6439(11) Å, c = 13.881(5) Å MAPbI₃.H₂O: Space group P₂₁/m; a = 10.461(2) Å, b = 4.6350(4) Å, c = 11.1037(12) Å



Figure S2. Experimental powder XRD patterns with lineshape fitting analysis for (a) pristine and (b) moisture aged MAPbI₃ with peak indexing of different degradation products. (c) Experimental and simulated patterns MAPbI₃ (MAPI), MAPbI₃.H₂O (MAPI.H₂O) and PbI₂ compounds, in comparison with the moisture aged MAPbI₃ material.





Figure S3. Solid-state (a) 2D 1 H- 1 H DQ-SQ and (b) 2D 1 H- 1 H spin diffusion spectra of fresh MAPbI₃ (blue) and exposed to moisture (red) during 17 h at 85% RH acquired at 18.8 T. All 2D spectra were acquired with a powder obtained by scratching the MAPbI₃ thin films deposited on glass substrates. (a) is adopted from ref. 5.

5. Solid-state 1D ¹H MAS NMR spectrum of methylammonium iodide powder (MAI)



Figure S4. Solid-state 1D 1 H (800 MHz, 18.8 T) MAS NMR spectrum of MAI powder acquired with MAS frequency of 25 kHz and at room temperature.

6. 2D ¹H-¹H spin-diffusion spectra of MAPbI₃ before and after exposure to moisture



Figure S5. 2D 1 H- 1 H spin-diffusion spectra of MAPbI₃: (a) before (fresh) and after exposure to moisture at 85% RH for (b) 17h, (c) 34h and (d) 45h. All spectra were acquired at 18.8 T and more acquisition details are presented in Section 1.

7. Powder XRD patterns of the MAPbI₃.TPA and the degradation products

For the moisture aged MAPbI₃.TPA thin films, Figure S6 presents the PXRD patterns with the peak indexing analysis for the different byproducts. While the MAPbI₃ thin film is passivated with TPAI enhanced the moisture stability, one can observe that the XRD patterns originating from three phases (MAPbI₃, MAPI.H₂O and PbI₂) after exposure to moisture at 85% RH, though with much lower intensities than the aged $MAPbI_3$ (i.e., without passivation). In addition, two diffraction peaks attributed to the low-dimensional TPAPb₄I₉ are observed, consistently with the literature.⁶ Although the crystallographic data including space group and lattice parameters therefore cannot be completely refined, due to of lack of 3D structure of this low dimensional phase, however, the diffraction peaks labelled in green are family of plane based on their d(hkl) positions. It is noteworthy, the formation of MAPbI₃.H₂O and PbI₂ are exhibiting strong preferential orientation, as expected since the pristine film is already high oriented along (110) direction, as reported in our previous study.⁵ These results and analyses confirm that the defect passivation via TPAI increased the longevity of the MAPbI₃ thin films. The refined lattice cell parameters presented for MAPbI₃ with and without passivation depends on the MAPbI₃ stoichiometry. The lattice cell parameters refined in our study are consistent with the two values reported in literature.^{7,8}

MAPbI₃ aged: Space group = I4/mcm; a = b = 8.8695(10) Å, c = 12.578(3) Å PbI₂: Space group = 63mc; a = b = 4.6383(3) Å, c = 13.9260(11) Å MAPbI₃.H₂O: Space group = P₂₁/m; a = 10.441(2) Å, b = 4.6450(8) Å, c = 11.1237(18) Å, β =101.28(2)°



Figure S6. Experimental powder XRD patterns of moisture aged MAPbI₃.TPA (72 h at 85% RH) with the peak patterns indexed to MAPbI₃ (MAPI), MAPbI₃.H₂O, TPAPb₄I₉, and PbI₂ materials.

8. Solid-state 1D ¹H MAS NMR spectra of tetrapropylammonium iodide (TPAI) powder



Figure S7. Solid-state 1D ¹H (800.1 MHz, 18.8 T) NMR spectra of TPAI acquired with a MAS frequency of 58 kHz. Spectrum was acquired using a neat TPAI powder.

9. Solid-state 1D ¹H NMR spectra of MAPbI₃.TPA(4mol.%) exposed to 85% RH



Figure S8. Solid-state 1D ¹H (800 MHz, 18.8 T) NMR spectra of MAPbI₃.TPA (4 mol.%) exposed to 85% RH as a function of time. The magnified inset displays the intensity build-up of $-NH_3^+$ protons of MAI.

10. Analysis of 2D ¹H-¹H spin-diffusion spectra of fresh and aged MAPbI₃.TPA(4%)

Insight into the molecular-level mixing of TPA⁺ cations and MAPbI₃ can be obtained by analyzing 2D ¹H-¹H spin-diffusion NMR spectra of TPA_xMA_{1-x}PbI₃ 4% acquired with different mixing times. **Figure S9** presents 2D ¹H-¹H SD spectra acquired with 100 ms and 500 ms mixing times. When 100 ms is used (Figure S9a), the off-diagonal peaks (i.e. magnetization exchange between the various proton sites occurs during this time) corresponding to the through-space proximities between the CH₃ groups of MA and -CH₂-CH₃ groups of TPA cations (red circles) are detected. In addition, the through-space proximities between the CH₃ and NH₃ groups of MA (orange circles) are detected. When 500 ms of mixing time is used, the off-diagonal peaks between all MA proton sties and the TPA sites are detected, which evidence the exchange of magnetization between different proton sites via ¹H-¹H spin diffusion. For the same material after exposure to moisture at 85% RH for 72 h, the on- and off-diagonal peaks associated with the MA and TPA cations are detected with weak intensities (broken red circles), indicating the subtleties in the intermolecular interactions.



Figure S9. Top: solid-state 2D 1 H- 1 H spin-diffusion spectra of pristine MAPbI₃.TPA (4 mol.%) acquired with (a) 100 ms and (b) 500 ms of spin diffusion time. Bottom: the same spectra acquired after exposure to 85% RH for 72 h with mixing time of (c) 50 and (d) 500 ms. All spectra were acquired at 18.8 T and at room temperature.

11. 2D ¹H-¹H spin-diffusion spectra of fresh and moisture aged MAPbI₃.TPA(4%)

Figure S10 presents the 2D ¹H-¹H spin-diffusion spectra of MAPbI₃.TPA(4%) as a function of moisture (85% RH) exposure time, in which the weak intensity off-diagonal peaks corresponding to the MA and TPA cations are detected. While greater than 90% of MAPbI₃ transformed into byproducts such as PbI₂ and MAI within 45h of exposure to moisture at 85% RH (Figure 2, main manuscript), the defect passivated MAPbI₃ via TPA decelerates the degradation kinetics and very low concentration of MAI is formed (<5%) even after exposure to 72h at the same condition. Enhanced longevity of defect passivated material is due to the intermolecular interactions between the passivating ligand and perovskite, which leads to low ingression of water molecules, although the presence of surface adsorbed water molecules in the moisture ages material cannot be completely ignored. The though-space intermolecular interactions between TPA and MAPbI3 are detected after the exposure to moisture at 85% RH for 72h.



Figure S10. Solid-state 2D 1 H- 1 H spin-diffusion spectrum of MAPbI₃.TPA (4 mol.%): (a) fresh , (b-d) exposed to 85% RH for (b) 15 h, (c) 48 h and (d) 72 h. All the spectra were acquired at 18.8 T. For more acquisition details, refer to Section 1.

12. Analysis of 2D ¹H-¹H DQ-SQ spectra of MAPbI₃.TPA(4%)

Insight into the through-space proximities and intermolecular interactions between TPA⁺ cations and MAPbI₃ in fresh and aged thin films can be obtained by analysing 2D NMR spectra. In 2D ¹H-¹H DQ-SQ NMR spectrum of fresh MAPbI₃.TPA (4 mol.%) presented in Figure 5a, the autocorrelation peaks at 0.9 + 0.9 = 1.8 ppm, 1.3 + 1.3 = 2.6 ppm and 4.9 + 4.9 = 9.8 ppm, stems from the short proximities between protons within methyl, $C^{\beta}H_2$ and $-NC^{\alpha}H_2$ groups of TPA⁺, respectively. No cross-peak between $C^{\beta}H_2$ and $-NC^{\alpha}H_2$ groups is detected owing to the low concentration of TPA⁺ as well as the weaker dipolar interactions between vicinal protons compared to those between geminal ones. Furthermore, the BaBa recoupling is affected by dipolar truncation and the intensity of cross-peaks between remote protons is attenuated by the dipolar coupling with the nearest protons.⁹ The autocorrelation peaks at 3.5 + 3.5 = 7.0 ppm and 6.5 + 6.5 = 13.0 ppm stem from proximities within the methyl and ammonium groups of MA⁺ cations. Cross-peaks between protons of these groups are also observed. For the same material, the 2D ¹H-¹H SD spectrum acquired with 500 ms mixing time (Figure 5b) displays off-diagonal peaks due to intramolecular ¹H-¹H dipolar interactions between methyl and ammonium proton of MA⁺ cations (black shaded rectangle) as well as intermolecular ¹H-¹H dipolar interactions between MA⁺ protons and TPA⁺ protons (green shaded rectangle), corroborating the molecular-level mixing of the TPA⁺ and MAPbI₃.



13. Powder XRD patterns of precursors, CsPb₂Br₅, CsPb₂Br_xI_{5-x} (x= 1-5) and CsMAFA

Figure S11. (a) Powder XRD patterns of precursor compounds (PbI₂, PbBr, CsBr, and CsI) and final products with different molar stoichiometry of precursors in order to obtain $CsPb_2Br_xI_{5-x}$ obtained at room temperature. XRD patterns of precursor compounds are compared with the final products, as indicated by the vertical dashed lines. (b) Experimental and calculated XRD patterns of CsPb₂Br₅ shown for a comparison. (b) is adapted from ref. 10.



Figure S12. XRD patterns of with peak refinements for the CsMAFA film (a) before and (b) after exposure to moisture at 85% RH for 17 h. Spectral patterns of CsMAFA, PbI₂ and CsPb₂Br₅ moieties are color coded as depicted in the inset. Figure adapted from ref. 11. Bragg positions associated with the CsPb₂I₅ and CsI presented on top of the (b) are obtained from ref. 16.

14. 1D¹³³Cs ssNMR spectra of CsPb₂Br_xI_{5-x} (x= 1-5), CsI, CsPbI₃, CsPbBr₃, and CsMAFA

The different byproducts formed during the moisture induced degradation reactions are further corroborated by synthesis and characterization of CsPb₂Br_xI_{5-x} (x= 1-5) phases and precursors.^{11–} ¹⁶ For these compounds, 1D ¹³³Cs MAS NMR spectra were acquired and compared with the aged CsMAFA (**Figure S13**). Notably, ¹³³Cs MAS NMR spectra of precursor compounds enabled the peaks associated with the CsI, δ -CsPbI₃, CsPbBr₃ to be identified and distinguished. The ¹³³Cs peaks at ~240 ppm (δ -CsPbI₃), ~120 ppm (CsPbBr₃), ~300 ppm (CsI) and ~260 (CsBr).Our attempt to synthesize CsPb₂I₅ using halide exchange process may lead to poor formation of this phase. Although ssNMR characterization of CsPb₂I₅ has not been previously reported, the ¹³³Cs MAS NMR spectra of thermodynamically stable CsPbI₃ and Cs₄PbI₆ are reported in the previous studies.^{17,18,19,20} A peak at ~220 ppm is attributable to the trigonal Cs₄PbBr₆ phase and CsBr salt produces a peak at ~250 ppm, as corroborated by the literature studies.^{16,17} The reference CsI:2PbBr₂ contain CsPbBr₃, and the CsBr:2PbBr₂ compound exhibits Cs₄PbBr₆, δ -CsPbI₃ and low concentration of ¹³³Cs signal (220–250 ppm) is expected to originate from the different local chemical environments of Cs⁺ ions in these inorganic materials, or the precursors thereof.^{17,20}



Figure S13. Solid-state 1D ¹³³Cs MAS NMR (104.9 MHz, 18.8 T with 50 kHz MAS at room temperature) spectra of different Cs lead halides as indicated. All spectra were acquired on polycrystalline powders. *denotes the spinning sidebands. [#]adapted from ref. 17.

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