Layer-by-layer structural identification of 2D Ruddlesden-Popper hybrid lead iodide perovskites by solid-state NMR spectroscopy

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Abstract: Application of two-dimensional (2D) organic-inorganic hybrid halide perovskites for optoelectronic devices requires detailed understanding of the local structural features including the Pb-I bonding in the 2D layers and the capping ligand-perovskite interaction. In this study, we show that ^1H and ^{207}Pb solid-state Nuclear Magnetic Resonance (NMR) spectroscopy can serve as a non-invasive and complementary technique to quantify the composition and to probe the local structural features of 2D Ruddlesden-Popper phase $\text{BA}_2\text{MA}_{n-1}\text{Pb}_{n/3n+1}\text{I}_{3n+1}$ ($n=1-4$) with butylammonium (BA) spacers. ^{207}Pb echo and ^1H -detected $^{207}\text{Pb} \rightarrow ^1\text{H}$ heteronuclear correlation (HETCOR) experiments enables layer-by-layer structural detection of 2D halide perovskites. We show that the observed correlation between ^{207}Pb NMR shifts and mean Pb-I bond lengths around each Pb site allows us to probe the local bonding environment of Pb via its ^{207}Pb NMR shift. We envisage that this technique will be vital for better understanding the materials properties as determined by the local atomistic environments in multi-dimensional halide perovskites.

Introduction

Since the discovery of metal-halide perovskites (MHPs) as active materials for high-efficiency photovoltaic cells, their outstanding photophysical properties and solution-processability have been further exploited in various optoelectronic and electronic device applications.^[1-8] One of the most established MHPs is methylammonium lead iodide (MAPbI_3) perovskite, the poor stability of which has urged the field to search for a more stable formulation in the vast chemical composition space.

In particular, addition of bulky cations have resulted in formation of layered perovskites in Ruddlesden-Popper (RP) phase with $\text{A}'_2\text{A}_{n-1}\text{M}_n\text{X}_{3n+1}$, where A' is an extra aliphatic or aromatic alkylammonium cation (e.g. butylammonium, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$), which comprises spacer layers that separate the two-dimensional networks comprising n layers of inorganic perovskite polyhedra.^[9-11] A significantly improved chemical and photo-stability^[12-14] of two-dimensional (2D) RP perovskites have indeed been demonstrated and a wealth of room for potential discoveries remain in better understanding their highly tunable physical properties coupled to their structures at both atomic and micro-scale levels.^[14,15] Thus, it is essential to develop an experimental toolkit for accurately determining and decomposing the structural components of 2D RP perovskites, which is also relevant for understanding the role of various n

compositions of compositionally non-pure quasi-2D RP perovskite (i.e. $n>1$) films used in light emitting diodes.^[15,16]

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful non-invasive tool for examining the bulk and surface structures of functional materials. Whereas spectroscopic or structural techniques utilizing high-energy X-ray or electrons often suffer from significant beam damage over time,^[17] NMR only involves low-energy radiofrequency pulses to excite a given nucleus and thus is a more benign technique to probe 'softly' bonded halide systems. Multinuclear NMR spectroscopy can distinguish chemically inequivalent atomic sites, which have been proven useful for structural investigations of halide perovskites and other Pb-containing systems.^[18-22] Extension of this methodology to 2D RP perovskites, however, has not been reported to date. As the physio-chemical properties of these 2D perovskites are mainly determined by the structural building blocks (e.g. anion coordination of Pb, phonon modes), determination of the ^{207}Pb NMR parameters of the individual Pb layers and their spatial information relative to the capping ligands is crucial. As evidenced by a conceptually similar study on individual oxygen layers near the surface in CeO_2 nanocrystals,^[23] this layer-by-layer detection approach would allow us to identify and characterize the structure and dynamics of Pb layers in 2D RP perovskites.

Here, we show that a combined ^{207}Pb and ^1H multidimensional solid-state NMR can be useful for determining the composition and local structural features of 2D RP lead-iodide perovskites ($n=1-4$). 1D NMR spectra could be used to identify each Pb and H sites present in the crystal structure. ^{207}Pb - ^1H 2D heteronuclear correlation (HETCOR) experiments show the spatial proximities between each Pb and H sites, thus allowing us to reveal the nature of perovskite-ligand interactions in 2D RP perovskites.

Results and Discussion

X-ray Diffraction. We performed powder X-ray diffraction (XRD) measurements for pulverized single crystals of both 2D RP lead-iodide samples, $\text{BA}_2\text{MA}_{n-1}\text{Pb}_{n/3n+1}\text{I}_{3n+1}$ ($n=1-4$) and 3D MAPbI_3 (see Figure 1a for schematics) synthesized as reported by K. Leng et al.^[24,25] (see Supporting Information for more details). As denoted in Figure 1b, all the samples show diffraction peaks which match well with previously reported reflections.^[14,24,26]

Figure 1. (a) Schematic structures of the 2D Ruddlesden-Popper BA₂MA_{n-1}PbI_{3n+1} ($n=1-4$) and 3D MAPbI₃ perovskites considered in this study. (b) Powder X-ray diffraction data for the prepared crystalline phases with labelled Miller indices for each reflection.^[24,25]

Figure 2. Solid-state MAS NMR spectra of 2D BA₂MA_{n-1}PbI_{3n+1} and 3D MAPbI₃ perovskites. (a) Quantitative single-pulse ¹H spectra, taken at 50 kHz MAS. Each H site in the BA molecule is color-coded. (b) ²⁰⁷Pb Hahn-echo spectra, taken at 62.5 kHz MAS. Dotted line is a guide for the eye indicating the evolution of outer layers. Spinning sidebands are marked by asterisks (*).

¹H NMR. We start by presenting the ¹H solid-state NMR spectra of these 2D hybrid perovskites in Figure 2a. For the parent 3D MAPbI₃ and 2D layered structures ($n=2-4$), the peaks arising from the MA (6.36 and 3.43 ppm) and BA (6.84, 3.84, 2.19, 1.69, and 1.17 ppm) cations can be assigned.^[10,27]

Upon further reduction in the perovskite layer thickness to the $n=1$ sample (BA₂PbI₄), the MA peaks disappear altogether as expected. At the same time, however, the BA peaks broaden significantly and the amino resonance (-NH₃⁺) shifts towards higher frequency (7.18 ppm). This broadening is a direct evidence for the disordered alkyl chain arrangement in the $n=1$ sample, as discussed in detail in the SI.

Finally, the quantitative nature of solid-state NMR allows us to determine the MA:BA ratio from peak intensities. This allows a direct confirmation of the structural formula for these 2D hybrid perovskites under crystalline conditions, whereas previous study by Soe et al. have relied on solution-state NMR with dissolved samples in NMR solvents.^[10]

²⁰⁷Pb NMR. Direct polarization ²⁰⁷Pb Hahn-echo spectra of the 2D and 3D samples are presented in Figure 2b. Observed isotropic shifts for each Pb site are summarized in Table 1. Peak assignments for the 3D and $n=1$ cases are straightforward as only a single crystallographically distinct Pb site exists for these structures.^[11] The observed shift of 1443 ppm for the 3D structure is in good agreement with the literature value of 1445 ppm.^[28] For the $n=3$ structure, the ‘outer’ and ‘inner’ sites could be identified from the approximately 2:1 peak intensities for the 1543 and 1330 ppm resonances. As the $n=3$ structure consists of one ‘inner’ Pb layer sandwiched between the two ‘outer’ Pb layers,^[10] the 1543 ppm should correspond to the ‘outer’ Pb site. For the $n=2$ sample, only a single peak is observed, signifying that the two inequivalent Pb sites on the XRD timescale is made equivalent on the NMR timescale; the broad feature of the ‘outer’ Pb site of the $n=4$ sample signifies this motional equivalence is made much slower upon approaching the 3D structure (see SI).

For the 2D perovskites ($n=1$ to $n=4$), a general trend of increasing shifts for the ‘outer’ Pb sites are observed (dotted line, Figure 2b) whereas the ‘inner’ Pb sites retain similar shifts to the 3D MAPbI₃ case. This similar shift clearly shows the ‘bulk’ or 3D-like nature of the ‘inner’ Pb sites relative to the ‘outer’ Pb sites subject to the BA encapsulation. This allows us to clearly distinguish between the ‘surface’ and ‘bulk’ Pb sites in 2D

perovskites through directly exciting and observing the ^{207}Pb nuclei. The ability to distinguish the inner 'bulk-like' and the outer 'surface-like' chemical environments shows a potential for extracting information on the surface states such as edge states which have been shown to play important roles in providing a fast route for exciton dissociation and carrier conduction in 2D RP perovskites.^[29–31]

Finally, the absence of spinning sidebands in the $n=1$ and $n=4$ samples is thought to originate from the smaller ^{207}Pb chemical shift anisotropy of these structures compared to the others. This can be approximately correlated to the 'span' of the local Pb-I bonds (defined as the range between the shortest and longest Pb-I bond lengths)^[32] as shown in Table 1; for further discussion see SI.

Table 1. Summary of observed ^{207}Pb shifts for 2D $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ and 3D MAPbI_3 perovskites. The average Pb-I distances as well as information on each crystallographic site are presented. Errors in ^{207}Pb shifts are estimated from the fitting of spectra. Span refers to the range of Pb-I distances for each site (i.e. differences between the longest and shortest Pb-I distances).^[9,10] SSB refers to the presence of spinning sidebands.

Site		Nature	Average $d_{\text{Pb-I}}$ / Å	^{207}Pb shift / ppm	Span / Å	SSB?
$n=1$		-	3.189	1100	0.052	No
$n=2$	Pb1	MA-CH3	3.165	1361±10	0.168	Yes
	Pb2	MA-NH3	3.173	1361±10	0.203	Yes
$n=3$	Pb1	Inner	3.157	1330±20	0.184	Yes
	Pb2	Outer	3.142	1543±20	0.132	Yes
$n=4$	Pb1&2	Inner	3.161	1467±50	0.14	Yes
	Pb3&4	Outer	3.169	1607±50	0.32	Yes
3D	3D	-	3.161	1443	0.071	No

$^{207}\text{Pb} \rightarrow ^1\text{H}$ HETCOR. In order to aid the assignment of the overlapping peaks for the $n=3$ and $n=4$ samples, ^1H -detected $^{207}\text{Pb} \rightarrow ^1\text{H}$ heteronuclear correlation (HETCOR) experiments were performed on these samples.

Figure 3a shows the $^{207}\text{Pb} \rightarrow ^1\text{H}$ HETCOR spectra for the $n=3$ sample. The correlation between the BA $-\text{CH}_2\text{CH}_2\text{CH}_3$ alkyl chain (marked as grey on plot) and the 1543 ppm resonance clearly demonstrates that this peak corresponds to the 'outer' Pb site. The presence of this correlation is also consistent with the fitted result of the ^{207}Pb spin echo spectrum, where the 1543 ppm resonance was assigned to the 'outer' Pb based on the intensity argument. Interestingly, the ^1H detected ^{207}Pb spectrum (black line on top of Figure 3a) shows a significantly reduced intensity for the 'outer' Pb resonance when compared to the ^{207}Pb direct spin echo spectrum (red line). As ^1H detected HETCOR experiments exclusively measure the polarization transferred from the nearby Pb spins, this indicates that more efficient CP transfer occurs to the MA protons than BA protons. The major

factor which could contribute to this lower efficiency is the significantly longer BA-Pb distances compared to MA-Pb distances. (Figure S2) Hence, this discrepancy in two ^{207}Pb spectra arises from the difference in the local structure of Pb atoms: the 'inner' Pb is sandwiched between two MA layers whereas the 'outer' Pb is surrounded by one MA and one BA layer. Finally, less efficient CP transfer could also be evidenced from the reduced intensity of BA protons on the ^1H HETCOR projection compared to the direct excitation spectrum.

Figure 3. ^1H -detected $^{207}\text{Pb} \rightarrow ^1\text{H}$ spectra for (a) $n=3$ $\text{BA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ and (b) $n=4$ $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ samples. Both experiments were conducted under 62.5 kHz MAS. Overlaid are ^{207}Pb and ^1H direct polarization spectra taken from Figure 2.

Similar results are observed for the $n=4$ sample (Figure 3b), but only a very weak correlation is observed between the 'outer' Pb (~1607 ppm) and the $-\text{CH}_3$ protons on the BA. This correlation arises from the spatial proximity (~6 Å) between the end-chain $-\text{CH}_3$ and 'outer' Pb on the nearby Pb layer.^[9] At this distance, the resulting ^1H polarization is expected to be reduced by approximately half relative to the $-\text{NH}_3/\text{CH}_3$ group (Figure S2). The significantly reduced ^1H intensity is potentially due to the reduced CP efficiency arising from the larger ^{207}Pb CSA of the 'outer' Pb sites. However, the strong correlation of the ~1467 ppm (lower frequency) peak to the MA protons signify that this resonance comes from the 'inner' Pb, in line with the trend of $n=3$ sample.

Trends in ^{207}Pb isotropic shifts for pseudo-octahedral PbI_6^{4-} systems. Figure 4 shows the plot of ^{207}Pb isotropic shift against the average Pb-I bond distance (obtained from previous single crystal X-ray diffraction studies^[9,10]) in 2D and 3D perovskites as obtained in this study. A clear negative trend exists in the linear fit; strikingly the trend extends well to solid PbI_2 , where the structure could be described as stacked 2D sheets of edge-sharing PbI_6^{4-} octahedra.^[33,34] A similar negative correlation was previously observed between mean Pb-O bond length and Pb isotropic shifts,^[35] indicating this trend is general and could be extended to other systems. A detailed discussion on the origin of this relationship based on the Ramsey theory is presented in the SI.

Figure 4. Plot of ^{207}Pb isotropic shift versus average Pb-I distance of 3D and 2D ($n=1,2,3$) perovskites in this study. The $n=4$ sample was omitted in the fit as only a broad distinction between the 'inner' and 'outer' site could be made. For PbI_2 , the shift was taken from Taylor et al., where a slower spinning of 15 kHz was used; the discrepancy in shift due to frictional heating is expected to be small and positive (approx. 30 ppm).^[33] The reported structure was determined from a single-crystal XRD of the 2H polytype.^[34]

Linear correlations between chemical shifts and bond distances have been well established in many other systems; examples include ionically bonded $^{23}\text{Na}-\text{O}$,^[36,37] covalently bonded $^{29}\text{Si}-\text{O}$ and $^{13}\text{C}-\text{I}$,^[38,39] hydrogen bonded $\text{O}-^1\text{H}\dots\text{O}$,^[40] and halogen bonded $\text{P}=\text{Se}\dots\text{I}$.^[41] Our result suggests that this correlation could be extended to match the Pb-I system with good agreements. As many structural and functional properties such as band structures depend on the nature of local Pb-I bonding, this result provides us with a tool to probe the local chemical

environment of Pb via its ^{207}Pb NMR shift. As NMR is a non-invasive technique which works equally well in an absence of structural periodicity, the present relationship could be useful, for instance, for identifying and rationalizing ^{207}Pb NMR shifts in novel and/or disordered systems.^[42] Further extensions of this correlation to other halides with different halide anion components (e.g. $\text{Pb}-\text{X}$ where $\text{X}=\text{Cl}^-$, Br^-) and other metal cation components (e.g. $\text{M}-\text{X}$, where $\text{M}=\text{Sn}^{2+}$) would also be possible. Application to other 2D hybrid perovskite phases adopting Dion-Jacobson, Aurivillius and alternating cation perovskite structures could also be envisaged.^[43,44]

Conclusion

Through the combined solid-state NMR methodology of ^{207}Pb and ^1H nuclei, layer-by-layer detection and quantification of individual Pb layers in 2D Ruddlesden-Popper hybrid lead iodide perovskites are enabled. $^{207}\text{Pb} \rightarrow ^1\text{H}$ HETCOR allows distinction of the bulk-like and surface-like Pb sites in the 2D perovskite layer through spatial correlation between the MA/BA protons and Pb spins. This allows us to probe the nature of ligand-surface interaction, providing insights into the local atomistic structure and dynamics in these systems. This methodology also enables us to extract the linear dependence of ^{207}Pb isotropic shift and mean Pb-I distance. We believe the methodology and understanding presented in this work can potentially be extended to provide insights towards understanding the relationships between highly tuneable local structures and properties of other 2D perovskite systems; our work also sheds light on a new opportunity to probe structural changes upon surface-initiated degradation or local creation of novel phases in layered perovskites.

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Layer-by-layer structural identification of 2D Ruddlesden-Popper hybrid lead iodide perovskites by solid-state NMR spectroscopy

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S1. Discussion on Alkyl Disorder in the $n=1$ Sample

Supporting our NMR evidence for the alkyl chain disorder in the $n=1$ sample, a relatively larger organic layer spacing (here defined as the Pb-Pb distance between the adjacent $\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ layers, as determined from the previously reported single crystal structures^[1–3]) of 13.8 Å has been reported for the $n=1$ structure compared to the other 2D perovskites ($n=2$, 13.2 Å, $n=3\&4$, 13.1 Å). In line with this observation, Mitzi has also reported relatively large thermal displacement parameters for the C atoms in the $n=1$ crystal together with several anomalously short C-C distances for singly bonded carbon atoms,^[1] which is consistent with the disorder or thermal motion of the alkyl chains as shown with ^1H NMR. Kind et al. also have shown significant liquid-like motion of the *n*-decylammonium (DA) chains in an isostructural $n=1$ compound DA_2CdCl_4 above room temperature.^[4] Faster spinning in this case does not give any significant improvement in resolution of the methylene ($-\text{CH}_2-$) protons (Figure S1), which further supports the case for the disordered chains.

S2. Discussion on Relaxation and Line Broadening Mechanism in ^{207}Pb Spectra

Apart from the obvious overall broadening due to the presence of multiple Pb sites, the individual Pb resonances are also broadened to tens of kHz, as evidenced from the 3D and $n=1$ cases. Previous studies on MAPbX_3 ($\text{X}=\text{halogens}$) have ascribed this phenomenon to a combined effect of scalar ^{207}Pb - ^{127}I J -coupling (estimated to be 4.9 kHz for PbI_2) and coupling to fast-relaxing quadrupolar ^{127}I nuclei.^[5–7] ^{207}Pb spin-lattice relaxation rate (T_1) in MAPbI_3 was shown to decrease upon faster MAS spinning and $T_1 < 0.1$ s was measured under 50 kHz MAS. Thus, a fast MAS of 62.5 kHz was necessary to allow sideband separation away from the isotropic centerband. Fast relaxation of Pb atoms under this fast MAS, as shown elegantly by Hanrahan et al., also allows an efficient ^1H detection through $^{207}\text{Pb} \rightarrow ^1\text{H}$ HETCOR experiments.^[5] This experiment exploits the fast spin-lattice or T_1 -relaxation of ^{207}Pb nuclei and the high sensitivity of ^1H detection due to the nearly 5-fold higher Larmor frequency of protons. We note this method has previously been reported to yield 4-fold gain in sensitivity over direct ^{207}Pb spin echo in MAPbBr_3 ; however, its performance in MAPbI_3 was only comparable to the direct spin echo in MAPbI_3 due to the concomitant reduction in the ^{207}Pb T_1 -relaxation in the rotating frame ($T_{1\rho}$).^[5] Despite the comparable efficiencies, $^{207}\text{Pb} \rightarrow ^1\text{H}$

HETCOR could provide us with the valuable information on the distances between the Pb-H spins, which could aid in the assignment of the 'inner' and 'outer' Pb sites in these 2D perovskites.

S3. Discussion on the ^{207}Pb NMR of $n=2$ and $n=4$ Samples

Previous single crystal X-ray diffraction, combined with *ab initio* calculations, has identified non-centrosymmetric space groups for the $n=2$ and $n=4$ samples;^[2,3] however, only a single Pb resonance is observed for the $n=2$ sample at 1361 ppm with a similar peak width to the 3D MAPbI_3 with a single Pb site. As NMR can only probe structures on ms to μs timescale, this discrepancy could arise from the NMR probing the time-averaged structure of MA group reorientation and/or PbI_6 octahedral motion happening at a much faster timescale than the NMR timescale.^[8]

Assuming this averaging happens for the $n=4$ sample, we would then expect to observe two Pb resonances of equal intensity arising from the 'inner' and 'outer' Pb sites. Contrary to this expectation, however, the observed $n=4$ spectrum only shows a broadened hump for the 'outer' Pb shift region. Thus, we speculate that the MA reorientation dynamics is much slower in the $n=4$ sample, resulting in the four Pb sites made inequivalent on the NMR measurement timescale.

This NMR result is also in line with the conclusion by Stoumpos et al. that the $n=4$ structure bears a non-centrosymmetric $Cc2m$ space group in which four crystallographically distinct Pb sites could be identified.^[2] These sites, broadly classified as 'inner' (Pb1,2) and 'outer' (Pb3,4) Pb sites, are assigned based on $^{207}\text{Pb} \rightarrow ^1\text{H}$ HETCOR experiments (*vide infra*). Under the centrosymmetric $Ccmm$ space group, only two distinct 'inner' and 'outer' sites are present by the MA ions aligning parallel to the layer direction (a), whereas the sites undergo a symmetry-lowering transition in the non-centrosymmetric $Cc2m$ space group by the MA ions aligning perpendicular to the layer direction (c). Despite the lack of resolution between the Pb3 and Pb4 shifts due to the significantly broadened peaks, the observed broad resonance for the outer Pb3 and Pb4 peaks clearly indicates the local environments for these Pb ions are subtly different, thereby supporting the non-centrosymmetric $Cc2m$ space group.

S4. Discussion on ^{207}Pb Chemical Shift Trends

Whereas a full theoretical rationalization of the correlation of ^{207}Pb chemical shift against the mean Pb-I bond length is trend is beyond the scope of this paper, a qualitative explanation could be given in terms of the Ramsey theory of chemical shielding:^[9,10] in this framework, the total chemical shielding σ is expressed in terms of diamagnetic term σ_d , paramagnetic term σ_p , and spin-orbit term σ_{so} , where the observed chemical shift δ is negatively related to σ . The dominant paramagnetic shielding term σ_p , which arises from a mixing of ground and excited states by application of an external magnetic field, is known to be inversely proportional to the mean distance to electric charge density r^3 , $\sigma_p \propto -1/r^3$. Under this theory, shrinking of the Pb-I bond would result in decreased (more negative) paramagnetic shielding and increased (more positive) chemical shift. Although the spin-orbit contribution, σ_{so} , is expected to be significant for heavy atoms such as Pb, estimation of σ_{so} is not trivial; moreover, the magnitude of σ_{so} is typically small relative to σ_p and we have neglected this in our evaluation.

S5. Discussion on ^{207}Pb Chemical Shift Anisotropy

As the anisotropy of the bond lengths directly influences the electron distribution around the Pb atoms, the magnitude of ^{207}Pb chemical shift anisotropy (CSA) is likely to be proportional to this span. This correlation of local symmetry and ^{207}Pb CSA has also been evidenced for a series of oxides by Zhao et al.^[11] A full determination of the ^{207}Pb CSA was not possible in this study arising from hardware limitations to the maximum spinning frequency and rf power; experiments at lower field utilizing fast spinning and/or frequency-stepped acquisition is likely to alleviate this problem.^[11]

S6. Materials and Methods

Materials synthesis. The chemicals used for the single crystal syntheses were purchased as the following: PbO (>99.9 %) from Sigma-Aldrich, n-butylammonium iodide (BAI, > 99.5 %) and methylammonium iodide (MAI, > 99%) from Greatcellsolar, hypophosphorous acid (H₃PO₂, 50 % w/w aq. soln.) from Thermo Fisher Scientific and hydroiodic acid (HI, 57% in water). For the crystal synthesis of BA_{2n}MA_{n-1}Pb_nI_{3n+1} (n=1-4), PbO, BAI and MAI were dissolved in mixed acid solutions of HI and H₃PO₂ according to the recipes provided by Li et al.^[12] For the synthesis of MAPbI₃ we mixed an equimolar ratio of MAI (1.90 g) and PbO (2.66 g) in a mixed acid solution of HI (18 ml) and H₃PO₂ (2 ml). The solutions were heated to 130 °C until all the precursors were dissolved. The solutions were then cooled down to room temperature to precipitate single crystals. All the crystals were isolated by filtration and dried in vacuo. Structures of the prepared crystals were analyzed by powder X-ray diffraction (Rigaku SmartLab).

Solid-state NMR spectroscopy. NMR spectra were collected on a 14.1 T Bruker Avance III spectrometer with Bruker 1.3mm MAS probes with spinning speeds of 50 and 62.5 kHz. ¹H shifts were referenced to solid adamantane (1.87 ppm) and ²⁰⁷Pb shifts were referenced to solid Pb(NO₃)₂ (-3474 ppm). For direct excitation experiments, ¹H and ²⁰⁷Pb radiofrequency (rf) amplitudes of 200 kHz and 175 kHz were employed, respectively. For direct detection experiments, simple pulse-acquire and rotor-synchronized spin echo experiments were performed for ¹H and ²⁰⁷Pb, respectively. For ¹H-detected ²⁰⁷Pb→¹H HETCOR experiments, Hartmann-Hahn conditions were experimentally optimized with ²⁰⁷Pb rf amplitude fixed to 100 kHz and a fixed contact time of 6 ms was employed. Experimental details of each data set are reported in Table S1. CP transfer efficiency was simulated with the SIMPSON code by varying the ¹H-²⁰⁷Pb dipolar coupling under identical rf and MAS conditions to the experiment. We note that the presence of residual ¹H-¹H dipolar coupling and ²⁰⁷Pb chemical shift anisotropy would result in a significantly lower transfer efficiency, but this was not included in the simulation. Spectral fitting was performed with the SOLA code as included in the Topspin software.

S6. Supporting Figures and Tables

Figure S1. Evolution of the ^1H spectra as a function of MAS frequency for the n=1 sample. Identical number of transients were acquired for each spectrum.

Figure S2. Efficiency of polarization transfer from ^{207}Pb to ^1H spins under varying Pb-H distance. Color-coded bars indicate the approximate range of distances between different proton environments in the structure.

Figure S3. Fitting of the experimental ^{207}Pb direct excitation spectra for the n=3 sample. Legend: black (experimental), red (fitted), and green (individual sites).

	^1H Pulse-acquire (50 kHz MAS)	^{207}Pb Spin echo (62.5 kHz MAS)	$^{207}\text{Pb} \rightarrow ^1\text{H}$ HETCOR (62.5 kHz MAS)
BA ₂ PbI ₄ (n=1)			
Recycle delay / s	60	0.1	-
Number of scans	8	55360	-
BA ₂ MAPb ₂ I ₇ (n=2)			
Recycle delay / s	60	0.1	-
Number of scans	8	518848	-
BA ₂ MAPb ₃ I ₉ (n=3)			
Recycle delay / s	60	0.1	0.5
Number of scans	8	631728	5120*28
BA ₂ MAPb ₄ I ₁₃ (n=4)			
Recycle delay / s	60	0.1	0.5
Number of scans	8	622432	2560*28
MAPbI ₃ (3D)			
Recycle delay / s	60	0.1	-
Number of scans	8	117904	-

Table S1. Acquisition parameters for the NMR spectra collected in this study. For two-dimensional spectra, the number of scans for each t_1 -slice is multiplied by the number of t_1 -slices.

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