Spectacular Enhancement of the Thermal and Photochemical Stability of MAPbI$_3$ Perovskite Films Using Functionalized Tetraazaadamantane as a Molecular Modifier

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Abstract: Perovskite solar cells represent a highly promising third-generation photovoltaic technology. However, their practical implementation is hindered by low device operational stability, mostly related to facile degradation of the absorber materials under exposure to light and elevated temperatures. Improving the intrinsic stability of complex lead halides is a big scientific challenge, which might be addressed using various “molecular modifiers”. These modifiers are usually represented by some additives undergoing strong interactions with the perovskite absorber material, resulting in enhanced solar cell efficiency and/or operational stability. Herein, we present a derivative of 1,4,6,10-tetraazaadamantane, NAdCl, as a promising molecular modifier for lead halide perovskites. NAdCl spectacularly improved both the thermal and photochemical stability of methylammonium lead iodide (MAPbI$_3$) films and, most importantly, prevented the formation of metallic lead Pb$_0$ as a photolysis product. NAdCl improves the electronic quality of perovskite films by healing the traps for charge carriers. Furthermore, it strongly interacts with the perovskite framework and most likely stabilizes undercoordinated Pb$^{2+}$ ions, which are responsible for Pb$_0$ formation under light exposure. The obtained results feature 1,4,6,10-tetraazaadamantane derivatives as highly promising molecular modifiers that might help to improve the operational lifetime of perovskite solar cells and facilitate the practical implementation of this photovoltaic technology.

Keywords: perovskite solar cells; complex lead halides; photostability; thermal stability; molecular additives; molecular modifiers

1. Introduction

Perovskite solar cells have recently attracted tremendous attention among academic and industry research communities due to their impressive efficiency records, surpassing 25.5% and coming close to the performance of the best laboratory samples of crystalline silicon solar cells [1]. Some efforts have been made to commercialize perovskite photovoltaics,
particularly using high-efficiency monolithic perovskite–silicon tandem devices [2]. Unfortunately, the commercial potential of this technology is severely restricted by the low operational stability of perovskite solar cells [3]. The stability issues are related, in particular, to facile degradation of perovskite-type absorber materials induced by ambient species (moisture, oxygen, CO$_2$) [4–8], as well as elevated temperatures [9–11] and light [12–14].

Several molecular and supramolecular chemistry approaches were developed in order to overcome the low intrinsic stability of complex lead halides [15–21]. In particular, the ambient stability of perovskite films can be boosted by coating them with thin layers of strongly hydrophobic reagents comprising long alkyl chains and/or aromatic fragments, often loaded with fluorine substituents, which are known to be moisture-repellent [22–25]. Furthermore, the truly 3D perovskite structure can be converted to a large variety of 2D or 2D/3D architectures by introducing additional amounts of ammonium salts, usually with bulky organic cations [26–28]. It has been reported in a number of studies that decreasing the dimensionality of the perovskite lattice improves the ambient stability of the absorber materials, as well as the operational stability of perovskite solar cells [29–31].

Using adamantane and, especially, adamantylammonium salts as reagents to modify perovskite films has delivered quite impressive results. In particular, loading perovskite films with either pristine adamantane or 1-adamantylamine resulted in passivation of the surface defects at the grain boundaries and improvements in the solar cell open-circuit voltage (V$_{OC}$) and power conversion efficiency (PCE) [32]. This modification also substantially increased the hydrophobicity of perovskite films and improved their ambient stability. Furthermore, perovskite solar cells comprising adamantane and, in particular, adamantylamine showed enhanced operational stability under 1-sun illumination as compared to reference cells based on non-modified perovskite.

The incorporation of adamantylammonium salts in the hole-transport layer of 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) was reported to improve the interface with the perovskite absorber, thus resulting in enhanced device V$_{OC}$ and PCE [33]. Passivation of the interfacial trap states also boosted the operational stability of perovskite solar cells: virtually no decay in the efficiency was observed within 500 h under 1-sun illumination for devices incorporating adamantylammonium iodide, whereas the reference cells showed considerable degradation under the same conditions. Adamantylammonium chloride in combination with formamidinium chloride was applied as a molecular modulator to control the perovskite crystallization, leading to improved device performance and stability [34].

Adamantylammonium and adamantylmethylammonium iodides were also used as building blocks to design layered 2D Ruddlesden–Popper perovskite-like phases, which were thoroughly investigated using a series of complementary techniques [35]. The optimal A$_2$FA$_2$Pb$_3$I$_{10}$ (FA-formamidinium cation) material formulations delivered efficiencies exceeding 7% in mesoscopic device architectures without any additional treatment or use of antisolvents, which was an important improvement compared to other reported state-of-the-art FA-based 2D perovskites. The designed 2D absorber materials exhibited good operational stability and excellent resistance to moisture due to the presence of bulky hydrophobic adamantane fragments in their structure. Adamantylammonium salts were also used as passivation reagents for perovskite quantum dots, leading to enhanced luminescence and improved stability [36].

The presented literature overview clearly shows that adamantane and its functional derivatives represent a promising family of molecular modifiers that can be used to control the structure and properties of perovskite films. While the positive effect of such modification on the ambient and operational stability of perovskite solar cells is well documented, the impact of adamantane derivatives on the intrinsic thermal and photochemical stability of the absorber films has not been studied so far. Furthermore, among the vast diversity of known nitrogen-substituted aza-analogs of adamantane, only 1,3,5,7-tetraazaadamantane or urotropin was investigated as a reagent to passivate defects at the grain boundaries in perovskite films [37].
Herein, we explored for the first time 4,6,10-trihydroxy-1,4,6,10-tetraazaadamantane hydrochloride (NAdCl) as a molecular modifier for methylammonium lead iodide (MAPbI$_3$) perovskite films. We show that this reagent passivates trap states in MAPbI$_3$, improves the electronic quality of this material, and spectacularly enhances the intrinsic photochemical and thermal stability of the perovskite films.

2. Results

The presence of multiple nitrogen atoms capable of coordinating lead cations inaza-derivatives of adamantane makes them highly promising molecular modifications for perovskite absorber films. In this work, we investigated NAdCl, which was synthesized from readily available chloroacetone (Scheme 1) using a modified two-step literature method [38]. The details on the synthesis and spectroscopic characterization of this material are provided in Section 4 below. It is worth mentioning that NAdCl represents just an individual exemplary compound from a large family of relevant azaadamantane derivatives that were previously used to design water-soluble phthalocyanines [39], boronate-based covalent organic frameworks [40], and high-valence manganese complexes with interesting magnetic properties [41], among other things.

![Scheme 1. Synthesis of NAdCl from chloroacetone.](image)

It should be emphasized that NAdCl also comprises three hydroxyl groups in its structure, which might enable additional supramolecular interactions such as hydrogen bonding [38] or N–O–M covalent bond formation [41]. Since NAdCl represents an ammonium salt, we incorporated it in MAPbI$_3$ perovskite precursor solution to obtain the quasi-2D perovskite formulation NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$, following previous reports where other AX ammonium salts were used to design “A$_2$MA$_{39}$Pb$_{40}$X$_{121}” frameworks in a straightforward manner [42–44]. While it is often assumed that A$_2$MA$_{39}$Pb$_{40}$X$_{121}$ compounds have a homogeneous distribution of A cations within the crystal structure, there are multiple indications of the accumulation of bulky A$^+$ cations mostly on the surface of the perovskite grains and at the grain boundaries, thus providing the desired grain covering coupled with the passivation of defects [45]. Therefore, we consider NAdCl, used in this work, as a molecular modifier of the perovskite films, leaving beyond the scope of the discussion the structural aspects of this modification.

Following our standard approach, the reference MAPbI$_3$ and NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ films (thickness 450–500 nm) were prepared by spin coating inside a nitrogen-filled glove box. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) showed that the introduction of NAdCl drastically changed the film morphology. The MAPbI$_3$ films had a typical morphology with distinct and rather large grains (200–600 nm) with well-defined grain boundaries (Figure 1a,c). On the contrary, NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ films were composed mostly of tiny fused grains (<20 nm) and had some pores that appeared presumably due to the evaporation of the solvent (DMF) strongly interacting with NAdCl, e.g., via hydrogen bonding. Furthermore, the NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ films were considerably smoother than the MAPbI$_3$ reference films, as concluded from the AFM topography images. The obtained results demonstrate the effect of compositional engineering on the structure of the absorber material films.
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Figure 1. (a,b) SEM and (c,d) AFM images of (a,c) MAPbI3 and (b,d) NAd2MA39Pb40I119Cl2 films.

The spin-coated MAPbI3 and NAd2MA39Pb40I119Cl2 films were transferred to another glove box with integrated aging setups without any contact with ambient oxygen and moisture. The samples were subjected to continuous light soaking using LED-generated white light with a power of ~100 mW/cm² under a pure nitrogen atmosphere (O2 and H2O levels of <1 ppm). Half of each sample was protected by black and chemically inert plastic, so heat became the main stress factor for the shaded parts of the samples. The stabilized temperature on the surface of the samples in the aging chamber was 40 ± 4 °C. A more detailed description of the experimental setup can be found in our previous reports [46,47].

The degradation behavior of the samples was monitored by taking periodic measurements of their UV–vis absorption spectra using a fiber spectrometer integrated into the glove box. Figure 2 shows the evolution of the absorption profiles of the samples during the heat- or light-induced aging. The reference MAPbI3 films underwent substantial heat-induced degradation, as can be concluded from the decay in the intensity of the perovskite absorption band at 600–800 nm after 1150 h of aging (Figure 2a). On the contrary, the modified NAd2MA39Pb40I119Cl2 films showed no signs of thermal degradation under the same conditions (Figure 2b). This result indicates that the introduction of NAdCl remarkably improved the thermal stability of the MAPbI3 films, which might be explained by the surface covering of the perovskite grains suppressing the loss of volatile perovskite decomposition products and facilitating their recombination and defect healing [46].
Most importantly, the NAd\textsubscript{2}MA\textsubscript{39}Pb\textsubscript{40}I\textsubscript{119}Cl\textsubscript{2} films demonstrated remarkably enhanced photostability: the absorption spectrum evolved mostly due to the appearance of a “scattering tail” at 800–1050 nm, which might be associated with the light-induced crystallization of the material [48]. On the contrary, the reference MAPbI\textsubscript{3} films underwent almost complete photobleaching at 600–800 nm after 1150 h of light exposure, suggesting that the perovskite phase severely degraded. A comparison of the degradation dynamics of the MAPbI\textsubscript{3} and NAd\textsubscript{2}MA\textsubscript{39}Pb\textsubscript{40}I\textsubscript{119}Cl\textsubscript{2} films is given in Figure 2e by plotting the evolution of the relative absorbance of the films (A\textsubscript{t}/A\textsubscript{0}) at 700 nm as a function of the aging time. It can be seen from the figure that NAd\textsubscript{2}MA\textsubscript{39}Pb\textsubscript{40}I\textsubscript{119}Cl\textsubscript{2} films did not significantly change their absorbance at the characteristic perovskite absorption wavelength, in contrast to MAPbI\textsubscript{3} films, which underwent severe heat- and light-induced bleaching. Thus, the obtained results reveal NAdCl as a highly promising molecular modifier strongly improving both the intrinsic thermal and photochemical stability of the MAPbI\textsubscript{3} perovskite films.

The optical spectroscopy data were supplemented by analysis of the X-ray diffraction (XRD) patterns of pristine samples and the films subjected to heat- and light-induced aging.

Figure 2. The behavior of the UV–vis spectra of (a,c) MAPbI\textsubscript{3} and (b,d) NAd\textsubscript{2}MA\textsubscript{39}Pb\textsubscript{40}I\textsubscript{119}Cl\textsubscript{2} films in the course of (a,b) heat-induced and (c,d) light-induced aging. (e) The comparison of the degradation dynamics of the samples is based on the evolution of the relative absorbance of the films (A\textsubscript{t}/A\textsubscript{0}) at 700 nm as a function of the aging time.
for ~1400 h (Figure 3). The reference MAPbI$_3$ films showed virtually complete heat-induced decomposition with the formation of PbI$_2$ as a sole product.

However, the light-induced aging of MAPbI$_3$ produced PbI$_2$ and metallic lead Pb$^0$ appearing with comparable diffraction peak intensities on the XRD pattern (Figure 3a). These results are fully consistent with the previously established thermal and photochemical decomposition pathways of MAPbI$_3$ [10–13,46]. The XRD patterns of NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ films (Figure 3b) revealed almost no heat-induced degradation (only a minor peak of PbI$_2$ appeared). The light soaking of NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ resulted in a pronounced amorphization of the films and a change of their texture, as can be concluded from the suppressed intensity of the diffraction peak at 14.3$^\circ$ and enhanced 28.7$^\circ$ peak. The light-induced aging of NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ produced PbI$_2$, as can be concluded from a broad peak at 12.8$^\circ$, while metallic lead was not formed, which is an important finding.

The XRD data are fully consistent with the visual appearance of the aged samples. The photographs (Figure 3c) show that the reference MAPbI$_3$ films became yellow in the shaded part (PbI$_2$ formation) and grey in the part exposed to light (due to metallic lead Pb$^0$ formation). On the contrary, the NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ films stayed black in the shadow (the perovskite survived thermal aging) and became inhomogeneously yellowish upon light exposure (perovskite was partially converted to PbI$_2$). The obtained results indicate

![Figure 3](image-url)
that the introduction of NAdCl not only improved the perovskite film stability but also altered the film’s light-induced degradation pathways, which is a crucially important finding potentially helping to improve the operational lifetime of perovskite photovoltaics.

The degradation behavior of the studied perovskite formulations was additionally assessed using X-ray photoelectron spectroscopy (XPS). The XPS Pb 4f\(_{7/2}\) spectra of the reference MAPbI\(_3\) films showed strong high-energy shifts after the heat-induced and, in particular, the light-induced aging, which is consistent with the accumulation of PbI\(_2\) as the main aging product (Figure 4a).

The formation of PbI\(_2\) is also consistent with the behavior of the XPS I 3d\(_{5/2}\) band, which underwent a high-energy shift upon thermal or photochemical aging of the samples (Figure 4c). Interestingly, we observed only a small contribution of Pb\(^0\) to the XPS Pb 4f\(_{7/2}\) spectra of the MAPbI\(_3\) films exposed to light, whereas XRD revealed the formation of substantial amounts of metallic lead. This apparent contradiction can be explained by the formation of metallic lead mostly in the bulk of the films rather than on the film surface, which was selectively probed by XPS. The XPS spectra of the NAd\(_2\)MA\(_{39}\)Pb\(_{40}\)I\(_{119}\)Cl\(_2\) films showed no high-energy shifts due to PbI\(_2\) formation (Figure 4b,d), which matches the UV–vis and XRD data revealing the superior stability of this perovskite formulation.

The UV–vis spectroscopy, XRD, and XPS data presented above unambiguously prove that introduction of the NAdCl modifier strongly enhanced the intrinsic thermal and photochemical stability of the MAPbI\(_3\) perovskite films. The observed stabilization effect might be related to the passivation of defects localized mostly at the grain boundaries. It is known from the literature that such defects can behave as traps for, e.g., positive charge carriers, which degrade the material with the formation of molecular iodine (I\(_2\)) or triiodide (I\(_3^-\)) [49]. The concentration of defects strongly affects the recombination of charge carriers. However, the predominant charge carrier recombination pathway can be

![Figure 4](image-url)
deduced by considering the dependence of the photoluminescence (PL) intensity on the power of the excitation beam [50]. We performed such experiments (Figure 5) and showed that both the MAPbI$_3$ and NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ films had good electronic quality.

Still, the introduction of NAdCl modifier decreased the slope (S) of the log($I_{PL}$) vs. log$(P_{ex})$ dependence from 1.25 to 1.13, which is consistent with a significant reduction in the concentration of traps. It should be emphasized that the bimolecular charge recombination pathway strongly dominates over trap-assisted recombination for the perovskite films with S = 1.13. Suppressed trap-assisted recombination in the perovskite films directly translates to enhanced photostability, as we have shown recently [51].

A particularly important finding is the fact that NAdCl modifier prevented the formation of metallic lead as a product of light-induced degradation of perovskite films. The mechanism behind this effect is not clear at the moment. We hypothesize that NAd$^+$ cations interact efficiently with the surrounding ions in the perovskite framework, involving efficient coordination and hydrogen bonding. This hypothesis is supported by the fact that the XPS N 1s band of the pristine NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ sample became considerably broader and underwent a low-energy shift by ~0.3 eV as compared to the spectrum of the freshly deposited reference MAPbI$_3$ film (Figure 6a).

Similar electronic effects were observed in XPS spectra and were reported previously [52,53] as signatures of strong electronic interactions between the introduced molecular modifier and the entire perovskite framework. We believe that these interactions induce a strong stabilization effect on Pb$^{2+}$ cations (particularly the ones with an unsaturated coordination environment), which suppresses their reduction to Pb$^0$ via electron trapping. Indeed, the XPS Pb 4f$_{7/2}$ band also shifted by ~0.1 eV to higher energy, which supports the existence of some electronic interactions of Pb$^{2+}$ with NAd$^+$ (Figure 6b). Similar observations were reported recently for MAPbI$_3$ films passivated using pentaerythritol tetras(3-mercaptopropionate) as a molecular modifier [52].
interactions of corresponding solar cells to be extended. This effect most likely originates from strong interactions of ITO/SnO$_2$/PCBA/perovskite/PTAA/MoO$_3$/Ag (ITO is indium-tin oxide; PCBA is phenyl-C$_6$-butyric acid; PTAA is poly[bis(4-phenyl)(2,5,6-trimethylphenyl)amine] following a procedure reported previously [34] and with the optimal loading of NAdCl, showed decent photovoltaic characteristics: open-circuit voltage ($V_{OC}$) of 1045 mV, short-circuit current density ($J_{SC}$) of 23.1 mA/cm$^2$, fill factor (FF) of 63.4%, and power conversion efficiency (PCE) of 15.5% as extracted from the reverse scan of the current–voltage characteristics. The forward scan pro-

![Figure 6. XPS (a) N 1s and (b) Pb 4f$_{7/2}$ spectra of pristine films of MAPbI$_3$ and NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$.](image-url)

3. Discussion

We introduced herein the 1,4,6,10-tetraazaadamantane derivative NAdCl as a promising molecular modifier for MAPbI$_3$ films. The incorporation of NAdCl dramatically improved the thermal and photochemical stability of the perovskite films, as revealed using a set of complementary analytical techniques. The observed effects are consistent with the hypothesis that bulky NAd$^+$ cations are mostly localized at the surface of the perovskite grains and grain boundaries, thus providing an efficient surface covering suppressing the loss of volatile perovskite decomposition products. Furthermore, the introduction of NAdCl improved the electronic quality of the perovskite films and suppressed trap-assisted recombination of charge carriers, which is a major pathway leading to material degradation (trapping holes or electrons launches a series of parasitic redox reactions). Most importantly, NAdCl prevented the formation of metallic lead as the perovskite photodegradation product, which might allow the lifetime of perovskite absorber materials and the corresponding solar cells to be extended. This effect most likely originates from strong interactions of NAd$^+$ cations with undercoordinated Pb$^{2+}$ ions at the grain surface, which results in healing of the traps for electrons and suppression of the parasitic redox reaction Pb$^{2+}$ + 2e $\rightarrow$ Pb$^0$.

Importantly, the perovskite solar cells assembled in the n–i–p configuration ITO/SnO$_2$/PCBA/perovskite/PTAA/MoO$_3$/Ag (ITO is indium-tin oxide; PCBA is phenyl-C$_6$-butyric acid; PTAA is poly[bis(4-phenyl)(2,5,6-trimethylphenyl)amine] following a procedure reported previously [34] and with the optimal loading of NAdCl, showed decent photovoltaic characteristics: open-circuit voltage ($V_{OC}$) of 1045 mV, short-circuit current density ($J_{SC}$) of 23.1 mA/cm$^2$, fill factor (FF) of 63.4%, and power conversion efficiency (PCE) of 15.5% as extracted from the reverse scan of the current–voltage characteristics. The forward scan pro-
vided very similar parameters: $V_{OC} = 1047 \text{ mV}$, $J_{SC} = 23.3 \text{ mA/cm}^2$, FF = 60.8%, and PCE = 14.8%. These results also indicate small hysteresis in the current–voltage characteristics, as shown in Figure 7.

![Figure 7](image-url)

**Figure 7.** The current–voltage characteristics of the ITO/SnO$_2$/PCBA/perovskite/PTAA/MoO$_3$/Ag perovskite solar cell, where the perovskite is represented by MAPbI$_3$ loaded with 0.025% of NAdCl.

The overall set of obtained results features 1,4,6,10-tetraazaadamantane derivatives as a highly promising family of molecular modifiers for perovskite-type absorber materials, deserving of further systematic exploration.

4. Materials and Methods

4.1. Materials

Lead iodide (PbI$_2$, 99.99%) and methylammonium iodide (MAI, 99.9%) were purchased from FOMaterials Ltd. (Chernogolovka, Russia). Anhydrous dimethylformamide (DMF) and chlorobenzene were purchased from Sigma-Aldrich and used as received inside nitrogen glove boxes. Glass slides (25 × 25 mm) were cut from standard objective borosilicate glass purchased from Isolab GmbH.

4.2. Synthesis and Characterization of 4,6,10-Trihydroxy-3,5,7-Trimethyl-1,4,6,10-Tetraazaadamantan-1-Ium Chloride (NAdCl)

The title compound was synthesized using a two-step literature method [38], which was modified for gram-scale preparation.

Step 1. Concentrated ammonia solution (ca. 25% in water, 25 mL, 316 mmol) was added to a solution of hydroxylamine hydrochloride (4.38 g, 63 mmol) in water (25 mL) at 0 °C. To the resulting solution, chloroacetone (5.0 mL, 62 mmol) was slowly added upon intensive stirring (the reaction is exothermic). The cooling bath was removed and the reaction mixture was stirred for 1 h at room temperature. The white precipitate of 1,1',1”-nitrilotris(propan-2-one) trioxime (TRISOXH3) was collected by filtration, washed with water and diethyl ether, and dried in vacuum. Yield: 1.4 g (30%).

Step 2. Glacial acetic acid (0.9 mL, 15.8 mmol) was added to a suspension of TRISOXH3 (1.15 g, 5 mmol) in methanol (20 mL) at room temperature. The mixture was stirred overnight until the complete conversion of TRISOXH3 was observed (controlled by thin-layer chromatography). The resulting solution was carefully treated with concentrated hydrochloric acid (ca. 36% in water, 0.45 mL, 5.2 mmol) at room temperature (precipitation of NAdCl takes place) and kept in a fridge (0–5 °C) for several hours. The precipitate of NAdCl was collected, rinsed with a small amount of methanol, and dried in vacuum until constant weight. Yield: 1.05 g (79% from TRISOXH3). White crystalline solid. Mp 181–
184 °C (with decomp.) (lit. [38] 181–183 °C). $^1$H NMR (300 MHz, D$_2$O, 24 °C): δ 1.25 (singlet, 9H, 3 CH$_3$), 3.41–3.53 (broad singlet, 6H, 3 CH$_2$), 3 NOH and NH were not observed due to the proton–deuterium exchange process. The NMR spectrum was in agreement with literature data [38].

4.3. Preparation of the MAPbI$_3$ and NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ Films

MAPbI$_3$ precursor solution with a final concentration of 1.35 M was obtained by dissolving together equimolar amounts of MAI and PbI$_2$ in anhydrous DMF by continuous stirring at 70 °C. The NAd$_2$MA$_{39}$Pb$_{40}$I$_{119}$Cl$_2$ precursor solution was obtained by dissolving 18.4 mg of NAdCl, 214.6 mg of MAI, and 638.4 mg of PbI$_2$ in 1 mL of DMF by continuous stirring at 70 °C. Both prepared solutions were filtered through 0.45 µm PTFE syringe filters before spin coating, though they were transparent and showed no signs of undissolved solids before the filtration. A 55 µL aliquot of the corresponding precursor solution was dropped on a glass substrate rotating at 3000 rpm and then quenched after 8–9 s by dripping 120 µL of anhydrous chlorobenzene. The sample was kept at 3000 rpm for an additional 40 s and then annealed at 100 °C on a hot plate for 5 min. All aforementioned operations were performed in an inert atmosphere inside nitrogen-filled MBraun glove boxes. A few samples from every batch of the prepared films were characterized by XRD to confirm their phase purity before starting the aging experiments.

4.4. Aging Experiments

Aging experiments were performed in a pure nitrogen atmosphere inside an MBraun glove box (O$_2$ and H$_2$O levels below 1 ppm) using a specially designed white light chamber [39]. An LED array provided light flux of 100 ± 5 mW/cm$^2$. Half of each sample was exposed to light, whereas the other half was shaded by a chemically inert plastic holder. Such an experimental design allowed us to investigate both heat-induced and light-induced aging pathways on the same glass slide. The samples loaded in the aging chamber were cooled by multiple fans fixed at the back of the sample holder, which provided an equilibrium temperature of 40 ± 4 °C as measured by a thermocouple and non-contact IR thermometer on the sample surface. The samples were periodically characterized by taking UV–vis spectroscopy measurements in the same glove box without exposure to the ambient atmosphere.

4.5. Characterization Techniques

Steady-state PL spectra were measured under a nitrogen atmosphere using a Horiba spectrometer and a 532 nm laser as the excitation source. UV–vis spectra, XRD patterns, and XPS spectra were obtained using an AvaSpec-2048-2UV-VIS fiber spectrometer, Bruker D8 instrument with a Cu Ka source, and PHI 5000 Versa Probe spectrometer (ULVAC-Physical Electronics, Chanhassen, USA), respectively, following previously reported procedures [40]. The samples for XRD characterization were coated with polystyrene films inside the glove box to protect them from aging under ambient conditions during the measurement (5–7 min). The samples for XPS measurements were sealed in airtight Al-coated plastic foil envelopes during transportation. Opening the envelopes and loading the samples in the spectrometer chamber was done within 1–3 min to minimize the samples’ exposure to air.

Author Contributions: P.A.T. and S.M.A. conceptualized and designed the performed experiments. V.V.O. performed a major part of the work related to sample preparation and aging experiments. I.S.Z. and E.Z.K. performed XPS studies. A.B. performed and interpreted PL measurements. N.N.D. performed SEM measurements. G.V.S. organized XRD studies and participated in analysis of the data. N.A.E. performed AFM studies. A.Y.S. provided the NAdCl modifier for this study. L.A.F. and P.A.T. participated in the supervision of the work. All authors contributed to the discussion and writing the original draft of the paper. All authors have read and agreed to the published version of the manuscript.
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