Exploring the Steric Hindrance of Alkylammonium Cations in the Structural Reconfiguration of Quasi-2D Perovskite Materials Using a High-throughput Experimental Platform

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Reduced-dimensional (2D or quasi-2D) perovskites have recently attracted considerable interest due to their superior long-term stability. The nature of the intercalating cations plays a key role in determining the physicochemical properties and stability of the quasi-2D perovskites. Here, the thermal stability of a series of 2D Ruddlesden–Popper (RP) perovskites is studied using seven types of intercalating cations with increasing linear carbon-chain length from ethylammonium (EA) to n-dodecylammonium (DA) through a high-throughput platform. The results show that long-chain cations in quasi-2D perovskite films lead to strong steric hindrance between adjacent perovskite domains, thus suppressing Ostwald ripening during the thermal-aging process. For short-chain cations, increased-dimensional phase redistribution during the aging period is observed, which can benefit a concomitant regeneration of the 3D/3D-like perovskite phases. The impact of steric hindrance on structural reconfiguration and the subsequent phase redistribution in quasi-2D perovskites are systematically characterized by UV–vis absorption spectra, photoluminescence spectra, and X-ray diffraction patterns. Due to the steric hindrance effect, an optimal chain length is found to maximize film stability by balancing the water/oxygen resistance and increased-dimensional phase redistribution. This study provides new insight into the thermal stability of quasi-2D perovskites.

1. Introduction

Hybrid organohalide lead perovskite is a potential game-changer for photovoltaics (PV) and recently achieved over 25% power conversion efficiency (PCE). However, 3D perovskite solar cells (PSCs) are frequently reported to suffer from intrinsic environmental instability and degradation that greatly obstructs their practical commercialization.[4–6] Improving the long-term operational stability of lead-halide perovskite semiconductors, therefore became a tremendous priority.[7,8] Reduced-dimensional (2D or quasi-2D) perovskites,[9–11] represented by the Ruddlesden–Popper (RP) type, recently attracted considerable interest as a means to address the long-term stability issue.[12–15] The pure-phase RP perovskites are generally described as L2A n−1B n X 3n+1, where L/A/B/X denote long-chain organic ammonium cation, monovalent cation, divalent metallic cation, and halide anion, respectively, and the n value indicates the layer number of inorganic [PbI4]− framework in a single well. In this report, we use <n> to denote the nominal number of perovskite layers based on the stoichiometry of the precursor to distinguish from the layer number of n in a single well. For example, a film processed from a precursor with <n> = 4 may contain a mixture of n = 1, n = 2, n = 3, 3D etc.[16]

The RP-2D perovskite exhibits superior structural diversity, and its optoelectronic properties can be modulated effectively...
by the steric configuration of intercalating cations.\cite{17-19} For example, the deformation of each octahedron (deviation from the perfect octahedron), as well as the distortion of the in-plane B–X–B bond angles, can be affected by the intercalating cations.\cite{20,21} the exciton binding energy of the 2D perovskite can also be tailored by the dielectric constant of the intercalating cations.\cite{22-23} Notably, the stability of the materials can also be improved by regulating the hydrophobicity of the cations as a protective layer to increase moisture tolerance with suppressed ion migration.\cite{24,25} Recently, extensive studies on RP-PSCs have made great progress through molecular engineering of the intercalating cations.\cite{26-29} The structural flexibility of the intercalating cations provides a large scope to investigate the role of the L-site cations in the optoelectronic properties and stability performance of quasi-2D perovskite materials.\cite{30-32} However, most studies on 2D-based perovskites are based on small datasets for one or two intercalating cations, lacking a global view of the feature of different intercalating cations.\cite{20} On the other hand, the stumbling block for a systematic stability evaluation is the huge time-consuming and high-labor-intensity, also demand for fabricating and measuring hundred of samples with excellent reproducibility and reliability.\cite{33} To achieve a global understanding, automated high-throughput synthesis and characterization technique has been used to accelerate the exploration.\cite{34,35} In our previous high-throughput experiments, we revealed a stability-bowing effect in 2D/3D perovskites by studying the stability of a full range of quasi-2D $L\text{X}_{n-1}\text{B}_n\text{X}_{3n+1}$ perovskites with the same intercalating cation.\cite{36} Therefore, more discoveries are expected if we can fully explore the quasi-2D $L\text{X}_{n-1}\text{B}_n\text{X}_{3n+1}$ perovskites with a series of intercalating cations and $<n>$ values.

In this work, we utilized a high-throughput platform to systematically study the thermal stability of quasi-2D perovskites based on seven kinds of intercalating alkylammonium cations from ethylammonium (EA, two carbons) to n-dodecylammonium (DA, twelve carbons) with various $<n>$ values. Over 500 samples were fabricated via the drop-casting method and characterized to illustrate the structural evolution of quasi-2D perovskite films during the degradation process. We find that the longer chain the cations has (e.g., HA/OA vs EA/PA), the stronger steric hindrance is observed in quasi-2D perovskite films, which is evidenced by UV–vis absorption spectra, photoluminescence spectra, and XRD spectral evolution during the thermal-aging process. This steric hindrance effect contributes to the stability of samples but also inhibits the increased-dimensional phase redistribution during the aging period, which benefits the film stability. A shorter cation does not provide better resistance against gas release from the inside and water/oxygen adsorption from the outside, while it favors the increased-dimensional perovskite-phase redistribution compared to longer cations; therefore, an optimal carbon-chain length should be adopted to maximize the film stability of quasi-2D perovskites.

2. Results and Discussion

Based on the unit of “$R$–NH$_3$”*, eight linear alkyl ammoniums with various carbon chain-lengths (methylammonium (CH$_3$NH$_3^+$, abbreviated as MA), ethylammonium (C$_2$H$_5$NH$_3^+$, EA), n-propylammonium (C$_3$H$_7$NH$_3^+$, PA), n-butyllammonium (C$_4$H$_9$NH$_3^+$, BA), n-pentylammonium (C$_5$H$_{11}$NH$_3^+$, AA), n-hexylammonium (C$_6$H$_{13}$NH$_3^+$, HA), and n-octylammonium (C$_8$H$_{17}$NH$_3^+$, OA), n-dodecylammonium (C$_{12}$H$_{25}$NH$_3^+$, DA)) were employed as intercalating cations to construct quasi-2D perovskites with different $<n>$ value (Figure 1a,b). The samples were fabricated through a high-throughput robotic platform combined with automatic optical characterization, including UV–vis absorption spectrum, steady-state PL spectrum, and time-resolved PL spectrum.\cite{36-39} Here the drop-casting technique that is highly compatible with our high-throughput robotic platform is adopted to fabricate high-quality perovskite films with excellent reproducibility and reliability.\cite{38} Specifically, 1.5 µL precursor solution (Figure S1, Supporting Information) was drop cast onto common glass substrates, as shown in Figure 1c. The perovskite solution spreads spontaneously from the central position to the outer edge of the substrate, then the dry circular films were formed.\cite{40} Eventually, a post thermal annealing step at 100 °C for 10 min was performed in an N$_2$-filled glove box for better crystallization. The samples were then characterized intermittently during the subsequent thermal-aging process. The snapshot (Figure 1d) of a series of samples (L$_2$MA$_{n-1}$PbI$_{3n+1}$; $<n>$ = 1 to 7, oo) shows a decreasing spot size for the longer intercalating cations, indicating reduced wettability for the longer-chain cations (e.g., OA/DA).

Figure 2a and Figure S2 (Supporting Information) show the UV–vis absorption spectra of various quasi-2D perovskite thin films with $<n>$ = 4. With longer cations, the excitonic absorption becomes more pronounced for the low-dimension perovskites (i.e., 575, 610, and 645 nm). In normalized PL spectra excited from the air side of the films (Figure 2b), the emission from 3D or quasi-3D perovskites (~770 nm) dominates the spectra, which is consistent with previous reports that 3D perovskites tend to be distributed at the top while 2D perovskites tend to be formed at the bottom.\cite{41-43} We also notice that the exciton emission from quasi-2D phases becomes more distinct as the chain length of cations increases (e.g., HA/OA/DA), indicating that
the length of the intercalating cations can affect the distribution of 2D and 3D phases in quasi-2D perovskites. This effect is further manifested in XRD patterns, as shown in Figure 2c. The XRD peaks are mainly attributed to 3D MAPbI$_3$ for most samples of $\langle n \rangle = 4$, except for OA and DA-based samples. This phenomenon is further confirmed by the XRD patterns of quasi-2D $\text{L}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ perovskite thin films with different $\langle n \rangle$ values (Figure S3, Supporting Information). We, therefore, conclude that increasing the cations’ length could favor the formation of low-dimensional perovskites.

Moreover, we find that only PA/BA/AA formed homogeneous and shiny films through the drop-casting method while either a shorter chain or longer chain leads to poor morphology and macroscopic aggregates (Figure 2d,e; Figure S4, Supporting Information).[44] Micrometer-scale phase segregation appears once the chain length increases over six carbons (HA) (Figure 2f), well evidenced by the rough surface for HA/OA/DA-based samples. The evolution of microstructure and morphology can be explained by classic and non-classic crystallization theories for perovskite formation with different $\langle n \rangle$ values and intercalating cation.[45,46] With $\langle n \rangle$ value increases, the growth will transform from classic layer growth (Frank-van der Merwe) to island growth (Volmer–Weber) due to less 2D perovskite moiety. The same mechanism also applies to the shortening of intercalating cations in perovskite films, such as MA. However, overlong cation also makes a rough film morphology with macroscopic phase separation, which might be related to the broadening of colloids in perovskite precursor solution and phase mixture character, corresponding to a non-classic crystallization process.[47,48] The spatial phase segregation of EA/HA/OA/DA-based samples is also evidenced by PL mapping with excitation at $\lambda_{ex} = 405$ nm. Three representative wavelengths are labeled by red (at 760 nm), green (at 575/610 nm), and blue (900 nm), respectively. The mapping signal from 900 nm is used as background. For HA/OA/DA-based film, the stripe-like crystals in SEM images correspond to red or yellow regions in PL mapping. We also note the coexistence of red/yellow and green colors, indicating micro-scale phase inhomogeneity. Considering the massive impact of the intercalating cation’s alkyl chain length on the film morphology and phase formation, we could expect a similarly strong effect on the film stability of quasi-2D perovskites.

First, we examined the hydrophobicity of various quasi-2D perovskite films by measuring contact angles (CA) with...
water droplets (Figure 2g). With longer cations, a larger CA is observed and the surface energy with the longer cations is comparable to purely aliphatic surfaces like PE (96°) or PP (102.1°). For instance, the CA is 30.8° for EA cation, whereas it is increased to 102.7° for DA cation, indicating a stronger hydrophobic surface. We further move on to test the thermal stability of these films by tracking the UV–vis absorption spectra over time. Without any encapsulation, all samples were aged at 85 °C in an N₂-filled glovebox and characterized intermittently. Figure 3a–c show the ageing time-dependent absorption spectra for perovskite films with <n> = 4. We find a large difference in the spectral evolution between different samples. With shorter-chain cations (e.g., EA/PA), we can observe a significant increase in the absorption at ≈750 nm (quasi-3D perovskites) initially; in stark contrast, the increased absorption at ≈750 nm gradually disappears when the cation becomes longer than BA. This trend is also confirmed by tracking the aging time-dependent absorption spectra of
films with longer intercalating cations (Figure S5, Supporting Information).

To better visualize the change of absorption spectra during thermal degradation, we further extracted the relative difference in absorbance ($\Delta$Abs) and the change rate of absorbance spectra (Figure 3 d–i).\(^{[50]}\)

$$\Delta$Abs($t$) = Abs($t$) − Abs(0) \quad (1)$$

$$\text{Absorbance change rate} (t) = \Delta$Abs($t$)$ \times t^{-1} \quad (2)$$

in which Abs($t$) is the absorption value of a sample at $t$ h, Abs(0) is the initial absorption value. Perovskite films with shorter-chain cations (e.g., EA/PA) show absorption loss at quasi-2D phase regions with a concomitant absorption increase at $\approx$750 nm (3D phase), implying a typical Ostwald ripening process from low-dimensional perovskite crystals to 3D perovskite crystals\(^{[51-53]}\). This structural reconfiguration induces an increased-dimensional phase redistribution that stabilizes the 3D perovskite phase in the quasi-2D perovskite films for the short-chain intercalating cations. In contrast, for long-chain cations, the film shows a global decrease in absorption spectrum without implying a clear structural reconfiguration or phase redistribution. Besides $<n>$ = 4, the films with other $<n>$ values were also investigated (Figures S6 and S7, Supporting Information). For $<n>$ = 1 without MA, a pure 2D RD phase is observed for most intercalating cations accompanied by a continuous decrease in absorption spectrum during thermal degradation. Ostwald’s ripening process is not possible due to the absence of MA. For $<n>$ = 3/5, the phenomenon is similar to $<n>$ = 4 regarding the change in absorption spectra, which shows a clear increased-dimensional phase redistribution for

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**Figure 3.** Evolution of time-dependent a–c) absorption, d–f) relative difference in absorption ($\Delta$Abs) spectra of EA, PA, and BA-cation-based perovskite thin films ($<n>$ = 4), respectively. g–i) Spectra of time-dependent absorbance change rate at 750 nm of EA/PA/BA-based perovskite samples ($L_2MA_{2-n-1}$Pb$_n$I$_{3n-1}$, $<n>$ = 2 to 7, $\infty$). The unsealed films were aged at 85 °C in a N$_2$-filled glovebox, the arrow orientation stands for an increase in the aging time (0 to 1035 h).
shorter-chain cations (e.g., PA) while it becomes negligible for longer-chain cations (e.g., HA/OA).

To further promote our understanding, we plot the rate of absorbance change over aging time at 750 nm for EA/PA/BA-based samples with various \(<n>\) values from 2 to 7 (Figure 3g–i). With shorter cation length, a larger positive rate of change is observed for \(<n>\) below 6, indicating an increase in the 3D perovskite phase. Without 2D perovskite phase, the pure 3D perovskite film presents a negative rate during the entire aging period. The Ostwald ripening phenomenon is also manifested by the time-dependent XRD patterns (Figure S8, Supporting Information) and normalized steady-state PL spectra (Figure S9, Supporting Information). XRD patterns of films with short-chain cations (e.g., EA/PA) show a decrease of 2D phases and a simultaneous increase of 3D phases during the thermal-aging process, implying a clear increased-dimensional structural reconfiguration or phase redistribution. In contrast, perovskite films with long-chain cations (e.g., BA/AA/HA) do not show such behavior. PL spectra show redshift in EA/PA/BA-based films during the thermal-aging process. The gradual shift in the emission peaks implies an Ostwald ripening from low-dimensional perovskite to 3D/3D-like perovskites. In contrast, AA/HA-based samples, as well as MAPbI₃, do not show this phase reconfiguration (Figure S10, Supporting Information).

To explain the above phenomenon, we propose a model based on steric hindrance and phase redistribution. As shown in Figure 4a,b and Figure S11 (Supporting Information), the \(d\)-spacing calculated by Bragg law increases linearly with longer carbon chains, from 1.14 nm (EA, 2 carbons) to 2.46 nm (DA, 12 carbons). This result indicates that the length of intercalating cations is proportional to the interlayer distance in 2D perovskites.\(^{[54]}\) Considering the alkyl chain towards the outside, a larger interlayer distance makes the perovskite surface less polar, which explains the improved hydrophobicity against the water with longer intercalating cations,\(^{[55]}\) as shown in Figure 2 g. A larger interlayer distance also induces a stronger steric hindrance due to an increased barrier to the movement of intercalating cations inside perovskite films.\(^{[56]}\) This strong steric hindrance could effectively slow down two adjacent crystals from fusion, thus suppressing the increased-dimensional 2D/3D phase redistribution during the thermal-aging process, as illustrated in Figure 4c.\(^{[57]}\) For shorter-chain cations such as EA/PA, the steric hindrance effect is too weak to prevent the

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**Figure 4.** a) XRD patterns of L₂PbI₄ (<\(n>\) = 1) films based on seven cations. b) Relationship between different cations (carbon numbers) and \(d\)-spacing values of (004)-orientation crystal of samples. c) Schematic visualization of thermally assisted structural reconfiguration and steric hindrance effects for perovskite films with differently long alkyl cations.
fusion of two adjacent pieces of crystallites during the thermal-aging process. The structural reconfiguration in EA/PA/BA-based film is helpful to increase the $T_{80}$ lifetime of 3D perovskite phase in 2D/3D ensemble, thanks to a gradual fusion of crystallites during the aging process. As shown in Figure 5, we selected several characteristic absorption peaks ($n = 1, 2, 3, 4$ and $\infty$) that dominate the UV–vis absorption spectra of each sample to assess their real $T_{80}$ lifetimes (80% value of the initial absorbance). For 3D perovskite phase in these films, the real $T_{80}$ lifetimes become shorter with longer cations due to inefficient Ostwald ripening to regenerate 3D perovskite. Besides, we also observe a decreasing trend of $T_{80}$ lifetime for low-dimensional or 2D perovskite phase with longer cations. For example, at the wavelength of 744 nm, unsealed PA$_2$MA$_3$Pb$_4$I$_{13}$ film shows the longest $T_{80}$ lifetime of 1030 h at 85 °C in N$_2$ atmosphere.

3. Conclusions

This work shows that the length of intercalating cation has a great impact on the physicochemical properties, phase distribution, redistribution, and thermal stability of quasi-2D perovskite films. The longer chain the cation has (e.g., HA/OA vs EA/PA), the more 2D phase is formed and the stronger steric hindrance is observed in the resulting perovskite film. This steric hindrance contributes to the stability of samples but also inhibits the increased-dimensional phase redistribution during a thermal-aging process. The increased-dimensional phase redistribution is accompanied by regeneration or the Ostwald ripening of the 3D/quasi-3D perovskite phases only in short-chain-based perovskites. This work highlights the complex effect of the steric hindrance of the intercalating cation on perovskite stability performance. We expect that fine-tuning the incorporating concentration and steric structure of the intercalating cation will confer both high stability and high crystallinity in quasi-2D perovskites in the future. This finding sheds light on the composition–stability relationships in the quasi-2D perovskite films, which would guide compositional engineering to further improve the crystal quality and stability of quasi-2D perovskite films.

4. Experimental Section

Materials: Methylammonium iodide (MAI, 99%), anhydrous N,N-Dimethylformamide (DMF, anhydrous, 99.8%) were purchased from Sigma Aldrich. Ethylammonium iodide (EAI, 99.5%), n-propylammonium iodide (PAI, 99.5%), n-butylammonium iodide (BAI, 99.5%), n-pentylammonium iodide (AAI, 99.5%), n-hexylammonium iodide (HAI, 99.5%) were bought from Xi’an Polymer Light Technology Crop. N-octylammonium iodide (OAI, 99%), n-dodecylammonium iodide (DAI, 99%) were purchased from Greatcell Solar Ltd. Lead iodide (PbI$_2$, 99.99%) was purchased from TCI CO., LTD. All reagents were used as received without further purification and additional treatment.

Preparation of Perovskite Precursor Solutions: Stock solution of 0.3 M MAPb$_1$ and L$_2$Pb$_4$ perovskite precursors ($L$ represents different long-chain organic cations) were prepared by dissolving 0.3 m PbI$_2$ and 0.6 m corresponding organic cations iodide in DMF and stirred at 60 °C for 60 min, and then filtered by a polytetrafluoroethylene (PTFE, 0.2 μm) filter in an N$_2$-filled glove box. L$_2$MA$_{n-1}$Pb$_n$I$_{3n+1}$ perovskite precursors were acquired by blending 3D (MAPb$_1$) and 2D (L$_2$Pb$_4$) perovskite precursor solutions with a specific volume ratio ($v/v$) via HT-Robot pipetting system in ambient air.

Film Fabrication via Drop Casting assisted by HT Automatic Platform: Through the automated liquid-handling-robot setup [Freedom Evo 100; Tecan Group AG, Switzerland], the mixed perovskite precursor solutions were acquired by blending the above-mentioned mother solutions with specific stoichiometric ratios ($v/v$). The blended solutions contained in 96-well polypropylene plates were thermal-hermetically sealed with special aluminum foil, followed by continuous high-frequency (300 rpm s$^{-1}$) shaking for 15 min. Meanwhile, the common glass substrate ($125$ mm $\times$ $85$ mm $\times$ $2$ mm) treated with UV–Ozone for 15 min was placed on a 65 °C hot plate. To guarantee complete intermixing,
an aspirate-dispense process was repeating for ten times (40 μL each time) before dropping 1.5 μL prepared solution onto the glass substrate via four pipettes of the HT-Robot. Subsequently, the films were dried completely at 65 °C for another 2–3 min. The aforementioned film-fabrication processes were carried out in ambient air. Eventually, a post thermal annealing step at 100 °C for 10 min was performed in an N2-filled glove box for better crystallization.

**High-Throughput Automatic In Situ Optical Characterization:** The high-throughput in-situ steady-state PL and UV–vis absorption spectra measurements were performed with TECAN infinite 200 Pro in the air. The PL data were collected from the central position of perovskite films from 500 to 850 nm with a 5 nm scanning step (Δex = 450 nm). The absorbance signals were gathered from 450 to 850 nm with a 3 nm scanning step. For thermal stability testing, the unsealed films on a large common substrate were placed on a hot plate kept at 85 °C in an N2-filled glove box, the substrates were transferred back and forth between the analytical setup and hot plate. A standard program and calibration process before stability tests to make sure that each sample could be measured at the same spot every time. The high-throughput data were processed by the MATLAB/VBA codes, which are provided in the Supporting Information.

**Individual Film Characterization:** Crystallographic information of the thin films was obtained by X-ray diffraction characterization utilizing a Panalytical X'pert powder diffractometer (Cu-Kα radiation, λ = 0.154 nm) and an X'Celerator solid-state stripe detector under conditions of 40 kV and 30 mA. The morphology and microstructure of the films were characterized by field emission scanning electron microscope (SEM, HITACHI S4800) and a digital microscope (VHX-2000, Keyence, Osaka, Japan). AFM was performed using a Veeco Dimension 3100 microscope (tapping mode) to observe the surface morphology of samples. Photoluminescence maps imaging was measured using a wide-field, hyperspectral imaging microscope (Photon, etc. IMA VIS) setup. The excitation source was a 405 nm continuous-wave, power-tunable laser as the PL excitation source. The sample was positioned on an X–Y piezo stage of the microscope. The photoluminescence signal was collected in reflection mode with the 50× objective and detected using a spectrometer fitted with a CCD (charge-coupled device) detector. The map was obtained by collecting the PL intensity from the air side of samples at a PL peak of 575, 610, and 750 nm, respectively. The background mapping is emission signals collected from 900 nm. The contact angles (CA) were tested on a Dataphysics OCA20 contact-angle system at room temperature. 5.0 µL prepared solution onto the glass substrate for the next generations of PV technologies” (No. 44–6521a/20/4) by the Bavarian State Government.

**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

The study was conceptualized by J.Z., Y.Z. and C.J.B. J.Z. designed and performed whole high-throughput experiments. J.Z. analyzed the stability data. J.Z. and J.W. characterized the contact angle. B.Z. carried out AFM test. Z.X and A.B. performed SEM measurement. J.Z. and H.A.A carried out PL mapping test. J.A.H., Y.Z., and C.J.B. supervised the project. J.Z. made the figures and wrote the manuscript, Y.Z. and C.J.B. contributed mainly to the revision of the manuscript. All authors contributed to the discussion of experimental results and the manuscript.

**Data Availability Statement**

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords**

2D perovskite materials, high-throughput platforms, steric structure, structural reconfiguration, steric hindrance, stability performance

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

J.Z., B.Z., Z.X., W.M., K.Z., and C.L gratefully acknowledge financial support from the China Scholarship Council (CSC). Y.Z. acknowledges the Alexander von Humboldt Foundation for supporting his scientific research during the postdoctoral period (Grant No. 11996004). J.W. and J.L. are grateful for financial support from the Sino-German Postdoc Scholarship Program (CSC-DAAD). H.A.A. is funded by a full scholarship from the Ministry of Higher Education of the Arab Republic of Egypt. C.J.B. gratefully acknowledges financial support through the “Aufbruch Bayern” initiative of the state of Bavaria (EnCN and “Solar Factory of the Future”), the Bavarian Initiative “Solar Technologies go Hybrid” (SoTech), and the German Research Foundation (DFG) SFB 953—No. 182849149. J.A.H., Y.Z., and C.J.B. gratefully acknowledge the grants “ELF-PV-Design and development of solution-processed functional materials for the next generations of PV technologies” (No. 44–6521a/20/4) by the Bavarian State Government.

Open access funding enabled and organized by Projekt DEAL.

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