# Emergence of Light-Transforming Layered Hybrid Halide Perovskites

*Ghewa AlSabeh and Jovana V. Milić**

Dedicated to Prof. Michael Graetzel on the occasion of his 81st birthday

**Layered hybrid halide perovskites (LHPs) have attracted considerable attention in optoelectronics. They are based on tailored organic spacer cations templating halide perovskite slabs, featuring improved stabilities compared to their 3D halide perovskite analogs. This has been especially relevant under functional optoelectronic device operating conditions, such as upon light irradiation, which has been associated with reduced ion migration that is responsible for material and device instabilities. The versatility of LHPs structures provides the opportunity to further enhance their functionality through light-induced transformations in hybrid materials and optoelectronic devices, setting the basis for multifunctional systems. The emerging class of such light-transforming layered hybrid halide perovskite materials is reviewed, outlining the challenges and perspectives for further development toward their application in (multi)functional opto(electro)ionic devices in the future.**

## 1. Introduction

Layered (2D) halide perovskite materials (LHPs) have emerged as promising semiconductors in optoelectronics in recent years.[1–3] They are soft mixed ionic-electronic conductors[4–7] based on the $S_xA_{n-1}M_nX_{3n+1}$ formula, defining the $\{AMX_3\}$ perovskite structure (**Figure 1a**). This involves the central A cations (e.g., methylammonium (MA), formamidinium (FA), and Cs) within the octahedral corner-sharing $\{MX_6\}$ metal-halide framework ($M$ = Pb, Sn; $X$ = I, Br, Cl) templated by organic spacer ($S$) cations (with $x = 2$ for mono and $x = 1$ for divalent cations, respectively).[1–3] LHPs are often classified by the number of inorganic layers ($n$ = 1, 2, 3, etc.) and the alignment between the adjacent inorganic slabs, defining the most common Ruddlesden–Popper (RP) and Dion–Jacobson (DJ) 2D perovskite phases (Figure 1b).[1–3,8] While RP phases feature a half-unit-cell offset between the adjacent inorganic slabs,[9] which are commonly based on monovalent ($x = 2$) organic spacer cations forming a bilayer, the DJ systems involve minimal to no offset between the slabs and are typically based on divalent ($x = 1$) organic spacer.[3,10] The characteristics of 2D phases are highly dependent on the organic spacer (Figure 1c).

LHPs display higher operational stabilities than their 3D $AMX_3$ perovskite analogs due to increased hydrophobicity and reduced ion migration, which is associated with superior device stability under operating conditions of voltage bias, light, and temperature changes.[11–14] They also feature inferior performance in optoelectronics, such as solar-to-electric power conversion in photovoltaics, which is often attributed to the inhibition of charge transport. Specifically, electronically insulating organic spacer layers lead to the behavior of 2D perovskites as quantum wells (QW), with charges confined within the inorganic framework (Figure 1c).[11,14] This also results in larger exciton binding energies and wider bandgaps.[11,13,14] The versatility of this material class, however, enables tailoring of their properties through modification of the compositional elements, as well as the spacer layer, which can alter the QW structure (Figure 1c), such as by introducing functionalized organic moieties[11,13,14] and their electroactive,[13,15–17] photoactive,[18–24] or chiral[25–31] derivatives. For instance, semiconducting cations have been effectively employed in perovskite optoelectronics to advance device performance.[13,16,32–36] So far, this has rarely involved light-induced structural transformations relevant to dynamic device operating conditions. Light-responsive organic spacers can undergo substantial structural changes upon irradiation, leading to unique optoelectronic characteristics.[11,13,14] For instance, this can include light-triggered photopolymerization,[18–20,24,37] or photoisomerization.[38] Other relevant photoredox-active systems

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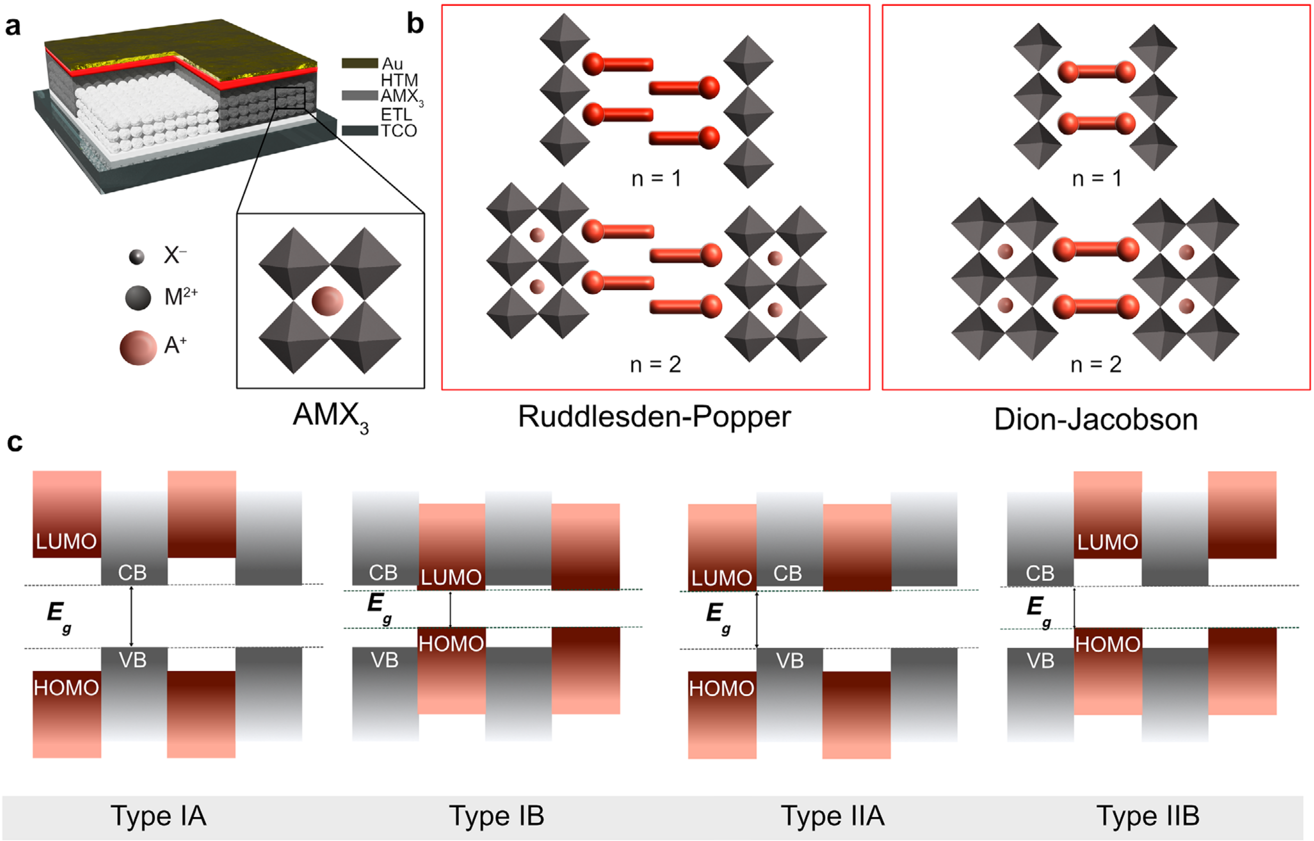

**Figure 1.** Layered hybrid halide perovskite materials. a) Schematic of a perovskite device (based on perovskite solar cell and the corresponding layers) with the structure of 3D hybrid perovskites with the AMX$_3$ formula (b, black box) and 2D perovskites (b, red boxes) based on $S_xA_{n-1}M_nX_{3n+1}$ composition ($n$ = 1, 2, 3, etc. while $x$ = 1 for bi- and $x$ = 2 for monofunctional spacer ($S$) cations as red rods). Organic or inorganic cations occupy position A (red), whereas metal cations and halides occupy the M (gray) and X (purple) positions, respectively. c) Schematic of the quantum-well (QW) electronic structures based on the energy level alignments of conduction band (CB) minima, valence band (VB) maxima, highest occupied (HOMO) and lowest unoccupied (LUMO) frontier molecular orbitals. Adapted from ref. [11,12]. Copyright 2022, Royal Society of Chemistry.

have been demonstrated, whereby semiconductive spacer cations can influence the electronic structure of the perovskite framework, such as by utilizing oligothiophene organic moieties.[39] These early studies revealed the potential of using aromatic spacer moieties to modulate optoelectronic properties, sparking the development of a wide range of multifunctional systems incorporating phenyl, thiophene, and polymer-based units.[13] Other examples include carbazole, pyrene, perylene, quaterthiophene, and benzothienobenzothiophene derivatives, enhancing the resulting optoelectronic properties of perovskite materials and devices.[39] In addition, the photoredox-active moieties can also stabilize the perovskite lattice, enhancing chemical and thermal stability.[11] These hybrid materials demonstrate promise in photovoltaics, light-emitting diodes, and field-effect transistors, owing to their structural modularity and ability to stabilize perovskite frameworks while introducing new functionalities, yet without transforming the composition or structure upon irradiation.[11] Such dynamic light-induced transformations can provide a versatile tool to advance material functionality while reducing exciton binding energy, enabling effective charge transport, modulating the band structure, and altering the QW structure of the material. This potentially paves the way to advanced functionalities, such as in multifunctional self-powered devices, neuromorphic computing, and self-healing, which can set the basis for smart materials that can adapt to their operating conditions.[2,11,40–45] The integration of light-transforming LHPs, however, remains limited and requires further investigation to fully realize their potential.

Here, we review the emerging class of light-transforming layered perovskites that change their structural and optoelectronic characteristics in response to light. This involves a range of light-induced transformations, from photopolymerization to photoisomerization or photoswitching, offering a unique tool for dynamic tailoring of the optoelectronic characteristics in perovskite materials and devices, revealing challenges and opportunities toward smart materials.

## 2. Phototransforming Layered Hybrid Perovskites

Functional light-responsive organic molecules can alter the performance of LHPs in optoelectronic devices through changes in structural and optoelectronic characteristics of perovskite frameworks upon irradiation, allowing dynamic control under operating conditions.[11,41] Depending on their design, this can involve (ir)reversible structural and optoelectronic transformations, which can influence bandgap and charge

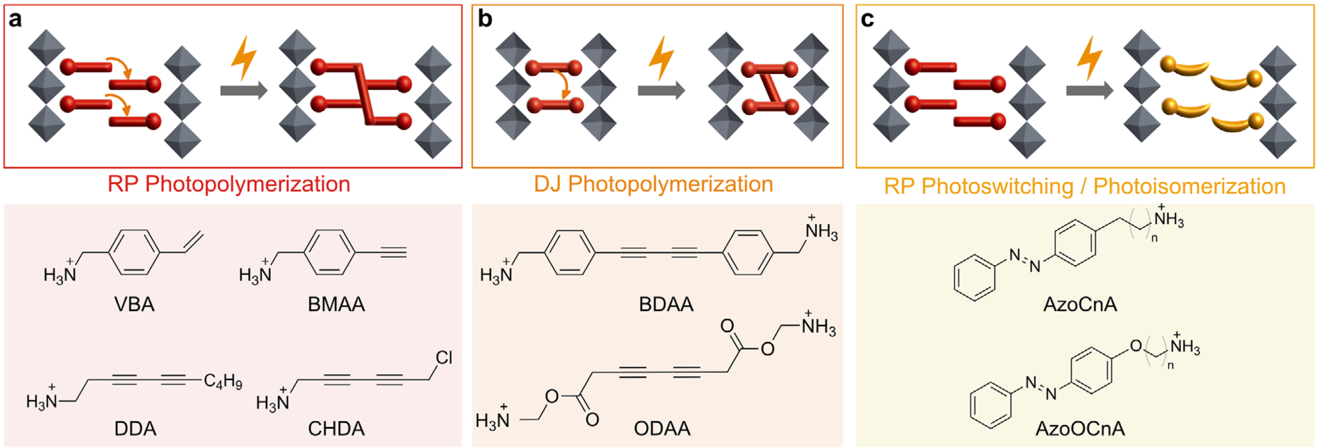

**Figure 2.** Phototransforming layered hybrid perovskites. Schematic representation of a,b) photopolymerizing and c) photoswitching or photoisomerization strategies in LHPs for RP (a,c) and DJ (b) phases with the corresponding spacer cations. VBA = 4-vinylbenzylammonium; BMAA = (4-ethynylphenyl)methylammonium; DDA = deca-2,4-diyn-1-ammonium; CHDA = 6-chlorohexa-2,4-diyn-1-ammonium; BDAA = buta-1,3-diyne-1,4-diylbis(4,1-phenylene)dimethylammonium; ODAA = ((octa-3,5-diynedioyl)bis(oxy))dimethylammonium; AzoCnA and AzoOCnA = azobenzene (Azo)-alkylammonium derivatives (with *n* = 1–5).

transport for various applications. Recent advances in LHPs have demonstrated relevant light-transforming strategies, such as through *photopolymerization*[18–20,24,37] and *photoisomerization or photoswitching*[21,22,38] within layered perovskite frameworks (**Figure 2**). *Photopolymerization* enables the formation of cross-linked polymer networks within the organic spacer layer (Figure 2a,b), enhancing charge transfer between the inorganic slabs and altering the QW structure (Figure 1c). On the other hand, *photoswitching* could offer another gauge for tunable optoelectronic properties through light-induced conformational or other structural changes, including reversible photoisomerization or photocyclization (Figure 2c). Such emerging strategies offer opportunities for the next-generation optoelectronics, and we discuss them from the perspective of recent examples, as well as those that reveal challenges for realizing their potential through integration within LHPs.

### 2.1. Photopolymerizing LHPs

Reactive functional groups within the organic spacer layers can act as monomers that undergo photopolymerization, creating crosslinked networks within the layered perovskite framework (**Figures** 2a,b and 3). This can be relevant to their performance in solar cells, for instance, as operated under constant illumination, thus enabling continuous improvement in optoelectronic properties and operational stability. To date, a few pioneering studies have shown photopolymerization in LHPs by using olefin and acetylene-based spacers (Figure 3).[18–20,24,37]

The early work of Day and Tieke et al. indicated that LHPs with photoactive unsaturated spacers can undergo photochemical polymerization.[20,37] This pioneering investigation in the 1980s relied on cadmium chloride perovskites, which feature large bandgaps unsuitable for optoelectronics. In particular, the solid-state photopolymerization of unsaturated organic cations was explored based on tetrachlorocadmate ($\mathrm{CdCl_4}^{2-}$) salts with chlorinated amino-diacetylene (CHDA, Figure 2a) cations.[20] Upon ultraviolet (UV) and X-ray irradiation, polymerization was detected in monofunctional $(\mathrm{R^1NH_3})_2\mathrm{CdCl_4}$ perovskite frameworks, leading to the formation of a deep red product with infrared (IR) bands indicative of a polydiacetylene backbone. However, another structurally similar bifunctional diacetylene (ODAA, Figure 2b) salt (represented as $(\mathrm{H_2NR^2NH_3})\mathrm{CdCl_4}$) showed only a light color change with no changes in the infrared (IR) spectra, suggesting that the spacer functionality and their intermolecular orientation play a critical role in the polymerization. The authors hypothesized that the better structural flexibility of the monofunctional spacers (associated with the corresponding RP phases, Figure 2a) improved their photoreactivity. In contrast, the lack of flexibility and unfavorable packing of bifunctional systems (associated with DJ phases) limited their photopolymerization capacity. Moreover, this work explored the potential of LHPs as templates for synthesizing oriented conjugated polymers, though further optimization is required to realize this.

The early findings stimulated a systematic investigation by Tieke et al. of the solid-state polymerization of various unsaturated organic cations embedded within the LHPs.[37] They demonstrated that the primary amines with butadiene and butadiyne functional groups can effectively undergo UV- or high-energy irradiation-induced polymerization, resulting in ordered polyelectrolytes. The structural limitations of incorporating functional spacers within the perovskite framework with a certain molecular packing resulted in 1,4-addition polymerization in some cases.[37] However, unsaturated amines containing isolated double and triple bonds or cinnamic acid units were photochemically inactive, likely due to unfavorable intermolecular distances (higher than 5 Å between the adjacent monomers) preventing effective polymerization. The intermolecular distances were ideal for solid-state reactions of butadiene and butadiyne spacer cations due to favorable packing, but exceeded the required threshold for effective reactions of other derivatives. The investigations on how different metal-halide compositions affect reactivity provided further insights into the tunability of photopolymerization reactions within hybrid perovskite frameworks, with

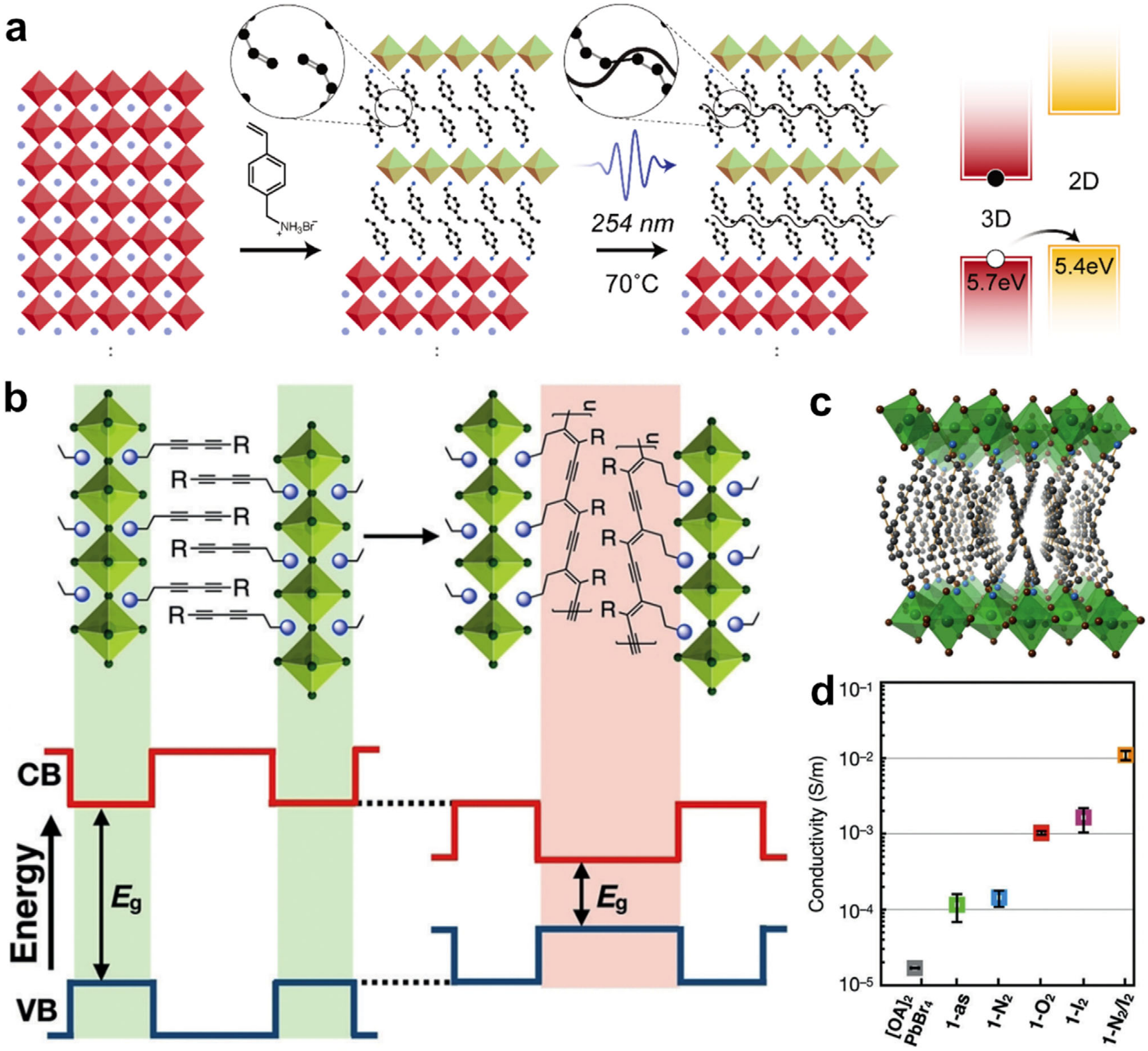

**Figure 3.** Representative LHPs based on (photo)polymerizing olefin and acetylene spacers. a) Schematic representation of the photopolymerization of 4-vinylbenzylammonium (VBA) bromide-based 2D/3D perovskites after irradiation at 254 nm and 70 °C (left) with the energy level diagram of their 2D/3D interface (right). Images adapted from ref. [19]. Copyright 2018, American Chemical Society and ref. [11]. Copyright 2021 Royal Society of Chemistry. b) Schematic of diacetylene-based LHPs (left) and the corresponding polymerized polydiacetylenes (right) with their energy levels and bandgaps ($E_g$). c) X-ray crystal structure of deca-3,5-diyn-1-ammonium (DDA) based $(DDA)_2PbBr_4$ LHPs and d) average values (with standard uncertainties) for the in-plane conductivity (at 423 K) of reference *n*-octylammonium (OA) based $(OA)_2PbBr_4$ and comparison with the $(DDA)_2PbBr_4$ LHPs (1-as) and their polydiacetylenes prepared by thermal annealing for 24 h at 160 °C under inert $N_2$ atmosphere (1-$N_2$), after exposure to air (1-$O_2$), to iodine (1-$I_2$), and to iodine after preparation in an inert $N_2$ atmosphere (1-$N_2/I_2$). Images adapted from ref. [18]. Copyright 2018, John Wiley and Sons.

Cd- and Mn-based perovskites displaying higher polymerization efficiency compared to Cu analogs. X-ray diffraction (XRD) evidenced structural changes post-polymerization, whereas thermal analysis indicated improved thermal stability of polymerized products. This work highlighted LHPs as potential templates for highly ordered conjugated polymers, opening a new avenue for hybrid photo-responsive materials in recent years.

Proppe et al. explored the irradiation in 2D/3D perovskite heterostructures with olefin spacers in 2018 (Figure 3a).[19] They focused on photochemical cross-linking of olefin-based spacers to enhance stability and efficiency in photovoltaics by applying LHPs as protective overlayers to 3D perovskite active layers, a common approach to using 2D perovskites in optoelectronics. These systems relied on 4-vinylbenzyl-ammonium (VBA) bromide derivatives containing a vinyl group that undergoes UV-induced cross-linking when exposed to 254 nm light, forming new covalent bonds among perovskite quantum wells (PQWs). This was evidenced by Fourier-transform infrared spectroscopy

(FTIR), which confirmed the disappearance of vinyl C═C bonds upon UV irradiation as an indication of cross-linking. In addition, XRD and UV–vis absorption spectroscopy showed that, while PQWs structures remained unchanged, there were apparent transformations, including shifts in the bandgap and changes in inter-well distances, suggesting the formation of new networks. The cross-linked perovskite solar cell devices exhibited higher stability, maintaining 90% of their efficiency after 2300 h of aging in the dark in air, compared to only 20% retention for the control 3D perovskites, signifying greater resistance to moisture and thermal degradation.[19] Furthermore, UV treatment improved open-circuit voltages and reduced device hysteresis, implying that the UV exposure stabilized the structure and improved charge transport. This showcased UV-induced cross-linking as an effective method to strengthen PQWs interfaces and enhance the lifetime and efficiency of perovskite solar cells.

Ortiz-Cervantes et al. incorporated other functionalized conjugated diynes into 2D LHPs in 2018 (Figure 3b)[18] using deca-3,5-diyn-1-ammonium (DDA) spacers (Figures 2a and 3c). The materials were characterized by IR and UV–vis absorption spectroscopy, single-crystal analysis, and thin film XRD. Inspired by earlier studies on light-triggered polymerization in LHPs, the authors irradiated hybrid perovskite films with UV light (250 and 354 nm) to induce polymerization. However, no measurable spectral or structural changes were observed after prolonged irradiation, suggesting the absence of photopolymerization. This lack of reactivity was ascribed to the high UV absorption coefficients of the lead halide perovskite layers, which likely inhibited sufficient light penetration to activate the polymerization process. The materials were thereafter thermally treated at 160 °C under an inert atmosphere instead, leading to thermochemical polymerization of the diynes into polydiacetylene chains within the perovskite framework. As a result, structural analysis revealed increased interlayer spacing, along with spectral transformations indicating the polymer formation. In addition, treating these perovskites thermally in an oxygen atmosphere or under iodine vapor led to partially oxidizing the polydiacetylene backbone, producing stable organic radicals. This process led to a dramatic shrinkage in the optical bandgap, from 3.0 to 1.4 eV (Figure 3c), significantly enhancing light absorption into the near-infrared (NIR) region, which is favorable for photovoltaic applications. Furthermore, electrical measurements on single-crystal devices revealed that oxygen- and iodine-doped perovskite samples exhibited a conductivity increase of up to three orders of magnitude compared to the undoped material (Figure 3d). The highest conductivity values reported in this study were comparable to those of 3D methylammonium lead iodide ($MAPbI_3$), making this one of the most conductive 2D perovskites ($n = 1$) ever reported.[18] As a result, this study presented a case for improving charge transfer in LHPs by incorporating conducting polymer networks into the perovskite materials. Unlike previous strategies based on UV or $\gamma$-ray-induced polymerization, thermal polymerization was used as an alternative to overcome the limitations of photoinduced transformations while providing a method feasible for real-world applications that sets the basis for future photopolymerization strategies. Furthermore, the ability to tune conductivity and optical characteristics through controlled oxidation processes suggests potential not only in photovoltaics but also in light-emitting diodes, sensors, and other optoelectronic devices.

Recently, AlSabeh et al. expanded the use of aryl-acetylenes in LHPs in photovoltaics.[24] Previous studies have shown that alkyl-acetylene or vinyl-aryl-based spacer derivatives can undergo polymerization within perovskite structures, improving the electronic conductivity and device performance. However, this approach has focused primarily on RP phases, leaving the more optoelectronically attractive DJ systems and their corresponding aryl-acetylene spacers unexplored, despite their potential, as in photovoltaics. AlSabeh et al. investigated the potential for photopolymerization in *aryl-acetylene-based* LHPs, incorporating the monofunctional (4-ethynylphenyl)methylammonium (BMAA) spacer as RP and the bifunctional buta-1,3-diyne-1,4-diylbis(4,1-phenylene)dimethylammonium (BDAA) spacer as DJ representative (**Figure 4a**).[24] The optoelectronic properties of these materials were examined in LHPs films of $n = 1$ ($(BMAA)_2PbI_4$ and $(BDAA)PbI_4$) compositions under UV irradiation. However, irradiating the material showed no significant changes in their UV–vis absorption spectra, suggesting the absence of bulk polymerization (Figure 4b). In situ grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed to observe structural variations under prolonged UV irradiation. Although minor changes were observed in $(BDAA)PbI_4$ after irradiation, these alterations were insufficient to indicate bulk photopolymerization (Figure 4b). The impact of UV exposure of $(BDAA)PbI_4$ on their electrical properties was explored through direct-current (DC) galvanostatic polarization and alternating-current (AC) impedance spectroscopy, before and after irradiation with a UV lamp, revealing mixed ionic-electronic conductivity with minor changes upon irradiation. Specifically, activation energy calculations for ionic carriers revealed no significant differences between irradiated and non-irradiated samples (0.73 ± 0.02 eV vs 0.75 ± 0.02 eV), further corroborating that the UV exposure did not induce bulk photoinduced ionic or electronic changes but rather a potential local photopolymerization.[24] The inability to undergo bulk photopolymerization was attributed to geometric constraints dominating the reaction (Figure 4a). An effective 1,4-addition polymerization required a maximum distance of 4.9 Å, a C─C contact distance of 3.5 Å, and a tilt angle of 45° between reacting units, whereas density functional theory calculations revealed that the BDAA spacer layer was tilted 55.7° away from the axis perpendicular to the perovskite layer, with a distance between stacked acetylene groups that is larger than 4.5 Å, making polymerization unfavorable (Figure 4a, inset). Similarly, in the BMAA-based system, even though the intermolecular C─C distance was smaller, the large tilting of the BMAA spacer and the relative orientation at a ≈90° angle between the layers still prevented effective polymerization. Nonetheless, both materials demonstrated competitive photovoltaic performances in 2D/3D perovskite heterostructures with power conversion efficiencies (PCE) up to 23% for BDAA-based devices, as compared to 21.8% for BMAA-based and 21.5% for the control champion devices (Figure 4c), which was accompanied by enhanced operational stabilities (Figure 4d).[24] These findings point to the need for further molecular (re)design considerations or alternative approaches in the future that may be necessary to optimize spacer packing and facilitate polymerization.

In summary, photoinduced polymerization in LHPs is a powerful tool for advancing optoelectronic properties of

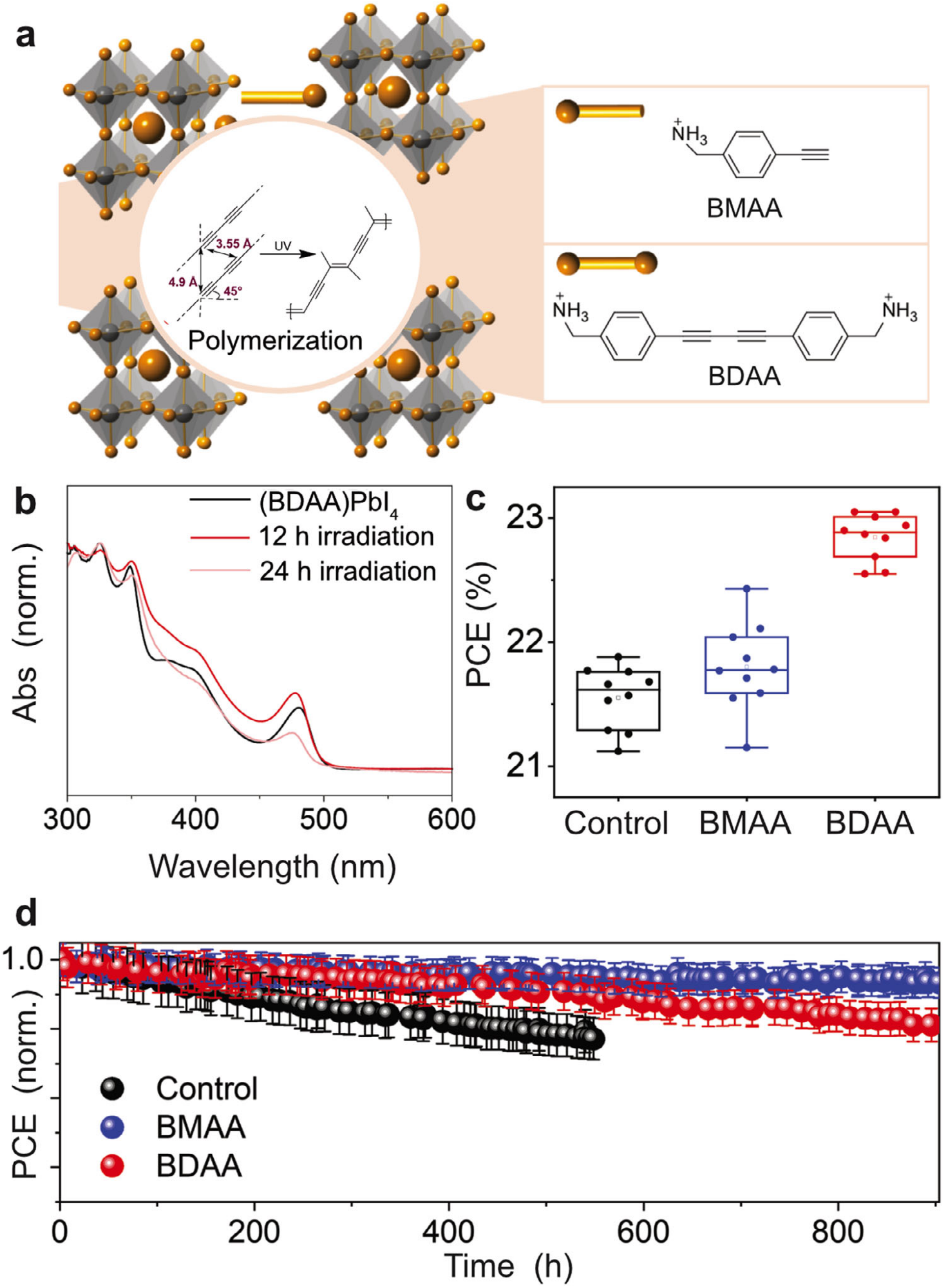

**Figure 4.** Photopolymerizing aryl-acetylene LHPs and their application in photovoltaics. a) Structural representation of BMAA and BDAA aryl-acetylene spacer cations and their corresponding LHPs, with the geometric constraints for photopolymerization shown in the inset. b) UV–vis absorption spectra of (BDAA)PbI$_4$ upon irradiation. c) Photovoltaic performance (power conversion efficiency, PCE) of the perovskite solar cell devices incorporating BMAA and BDAA in 2D/3D perovskite heterostructures and their d) operational stabilities. Adapted from ref. [24]. Copyright 2025, John Wiley and Sons.

materials and controlling their performance and stability during operation in functional devices, such as solar cells. Early reports have demonstrated the potential to achieve effective photopolymerization, improving optical properties, including conductivities and charge transport, which has involved a limited range of effective transformations. This results from the process being obstructed by either optical or geometric constraints. Specifically, in the case of lead halide perovskites, high UV absorption of the inorganic perovskite framework can limit light penetration,[18] which requires careful compositional tailoring to benefit from the light-induced transformation. On the other hand, strict geometric constraints have posed substantial challenges to achieving photopolymerization within the organic spacer layer due to intermolecular misalignments, which have been more pronounced for bifunctional organic spacers and DJ architectures as compared to monofunctional analogs or

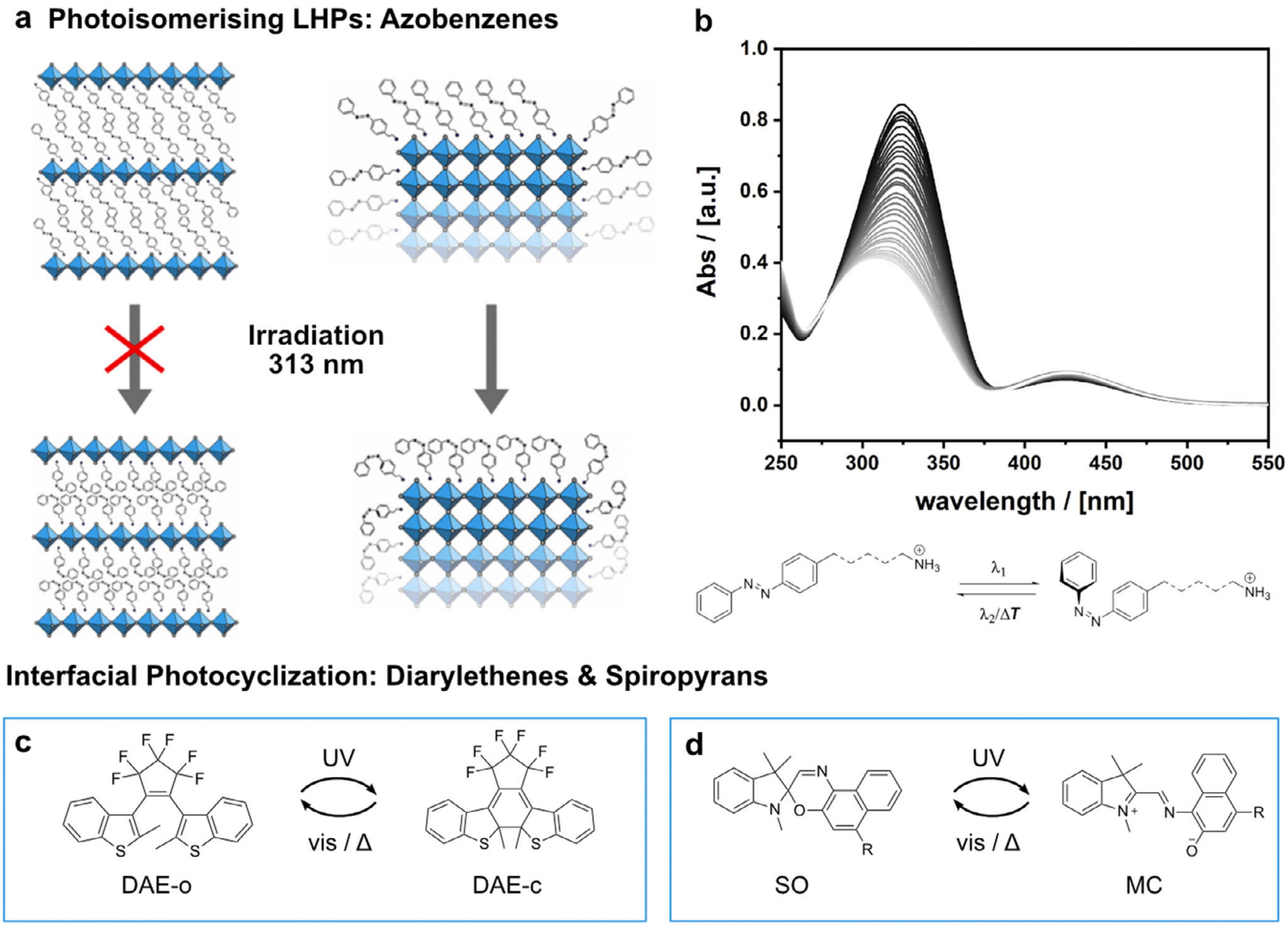

**Figure 5.** Photoisomerizing LHPs and interfacial photocyclization perspectives. a) Schematic of photoisomerizable LHPs based on azobenzenes (left) and their 2D/3D heterostructures containing azobenzene molecules on the surface (right). b) Photoswitching of derivatized azobenzene spacers (bottom) and the changes in their UV–vis absorption spectra upon irradiation with 313 nm light (top). The black line marks the beginning of the reaction, whereas the light gray lines mark the ending of the reaction. Images adapted from ref. [22] and ref. [11] under CC-BY license. c,d) Representative interfacial photocyclization applied to 3D hybrid halide perovskites and the corresponding solar cells to date, with LHP integration potential,[42–44] including diarylethenes (DAEs), shown in open (o) and closed (c) forms, and spiro-naphthoxazines shown in the closed (SO) and open (merocyanine, MC) forms.

RP phases.[24] To overcome some of these challenges, alternative strategies for inducing photopolymerization can be considered, such as using derivatization of the aromatic components to enable beneficial molecular packing for effective photoreactivity. Moreover, pressure-induced photopolymerization or post-synthetic modifications can facilitate the process, such as by applying external pressure to overcome steric limitations or introducing reactive species into the composition, as via intercalation, to overcome geometric constraints. To this end, intercalation could be a viable alternative to the reactivity of organic spacers, as small polymerizable monomers can be inserted between perovskite layers to enable beneficial alignment or initiate the polymerization reaction. These methods should allow for controlled polymerization under light irradiation, facilitating polymer network formation while maintaining the structural integrity of the perovskite framework. Integrating these approaches could enable photo polymerization in LHPs to achieve its potential while stimulating alternative strategies to rely on light-mediated transformation in advancing hybrid materials.

### 2.2. Photoswitching LHPs

To control LHPs in response to light, photoinduced conformational changes can provide another powerful gauge.[38] For instance, this can be achieved by using functionalized photoswitches, such as azobenzenes (**Figure 5**),[21,22] which can undergo trans-cis photoisomerization upon irradiation by UV light and be reverted with visible light.[38] Such reversible photoinduced transformations would be of interest to switchable devices, such as memory elements, as well as for stabilization under day-night cycling conditions. The process is challenging to achieve in the solid-state due to the limited free volume for such conformational changes.[11,41] However, soft yet crystalline perovskite structure can potentially provide a suitable framework for hosting such dynamic transformations,[11,41] which can be translated into the changes in the optoelectronic properties. There are a few representative examples showcasing this in LHPs, while others display interfacial photoswitching with potential for integration within LHP materials and devices.

Sasai et al. attempted to incorporate azobenzenes into LHPs to control their properties.[21] Upon irradiation with 350 nm UV light, the 350 nm *trans*-azobenzene absorption band decreased, while the 450 nm *cis*-azobenzene band increased (Figure 5a).[22] These changes were originally ascribed to the photoisomerization. However, Fillafer et al. studied the photoswitching of azobenzene-alkylammonium spacers in solution and the solid-state, as surface-coordinated or integrated within LHPs. In solution, upon 313 nm irradiation, photoisomerization of these ligands was observed (Figure 5b, bottom), accompanied by the changes in the UV–vis absorption maximum at 325 nm (assigned to the $S_0 \rightarrow S_2$ molecular orbital transition) that gradually fades. In return, the signal at 425 nm (of the $S_0 \rightarrow S_1$ transition of the *trans*-isomer) shows much weaker absorption, which steadily intensifies (Figure 5b, top). Once implemented into LHPs, these photoswitches feature steric hindrance that could prohibit the photoswitching of the corresponding LHPs.[22] Instead, they analyzed azobenzene-alkylammonium spacers with different alkyl group lengths that were found to interact with the surface of 3D perovskite (Figure 5a, left), resulting in observable photochromism. The effects were distance-dependent, and they were found to be more effective for shorter alkyl chains. As a result, this was ascribed to the energy transfer between the azobenzene spacer moieties and 3D perovskite surface,[11,22] which provides an illustration of the complexity of photoisomerization or photoswitching in LHPs.

Other recent examples show potential interfacial photoisomerization in halide perovskites with potential for LHP integration.[42–45] This includes the use of reversible photocyclization strategies of representative photoswitches. For instance, diarylethenes (DAEs) were applied as interfacial modulators enabling reversible photoluminescence switching under alternating UV (365 nm) and visible (561 nm) light (Figure 5c), simultaneously improving the UV stability of perovskite nanocrystals and films.[43,44] UV light excites the open-ring form and a new C—C bond forms to yield the closed isomer. Visible light or heating drives the reverse reaction to regenerate the open form. Similarly, spiropyrane (SP) derivatives were applied to enhance photostability, suggesting interfacial photoswitching.[42] In particular, SP treatment showed PCE over 22%, while also enhancing hydrophobicity, UV resistance, and biocompatibility of films.[42] Finally, such phenomena have been used to enhance operational stabilities of perovskite solar cells through spironaphthoxazine (SINO) derivatives at the interface of 3D perovskite and hole transport layer (Figure 5d). SINO was found to anchor to the perovskite surface through hydrogen bonding and metal coordination.[45] The UV light phototransforms the closed SINO to an open merocyanine (MC) form, which has a larger dipole that binds to the perovskite surface and reduces ion migration. In the dark, the MC thermally cyclizes back to SINO, allowing the recovery of some of the ion migration without affecting the perovskite lattice. In addition, incorporating SINO improved solar cell performance while reducing hysteresis. Moreover, this enabled the perovskite stabilization in response to simulated day-night cycles, setting the stage for stable LHPs with enhanced functionality. Despite their potential, these early photoactive organic moieties have not been integrated within LHPs and related optoelectronics, which remain to be exploited in the near future.

In summary, photoisomerization or photocyclization of various photoswitches has demonstrated potential in hybrid perovskite materials and optoelectronic devices, such as solar cells. However, this has primarily involved interfacial photoswitching, and the demonstration of their photoinduced transformation within the layered perovskite framework remains to be realized. One of the pressing challenges is the high steric demand, which necessitates careful molecular design and consideration of geometric compatibilities. Early examples of interfacial photoswitching using molecular moieties reveal promising perspectives toward their derivatization and stimulate further investigations to enable their application in LHPs toward other multifunctional photochromic materials and smart optoelectronic devices.

## 3. Conclusion

There has been an emergence of layered hybrid perovskites (LHPs) that can be transformed in response to light. This has involved a range of functionalized organic spacer cations based on styrene, aryl-acetylene, and other derivatives that are photoresponsive. While the potential of these systems to change structural and optoelectronic characteristics has already been demonstrated, they remain underexploited in functional devices.

Light-induced transformations of the organic spacer layer, such as via photopolymerization, provided a versatile tool to enhance functionality, operational stability, and performance of perovskite optoelectronics. Similarly, photoswitches, which reversibly photoisomerize or photocyclize upon irradiation, could further advance perovskite materials and devices, such as by enabling adaptation to light irradiation and photochromism. This would require advancing molecular design and the integration of photoactive moieties within layered perovskite frameworks, followed by the in-operando investigation to provide a better understanding and further advancements.

While challenges remain to fully implementing phototransforming organic moieties into layered perovskite frameworks, chemical modification of the organic spacer cations offers a platform for further tuning and optimizing the properties through (supra)molecular engineering. This could also provide a tool for post-synthetic transformations through interactions in the spacer layers, which can enhance their optoelectronic properties and stability during operation. It is desirable to introduce additional functionalities that can enhance charge transport and reduce exciton binding energies upon light irradiation. This approach would permit further enhancing the stability of devices without compromising their performance, while opening the perspective for multifunctional and self-powered optoelectronics. Furthermore, self-assembling such light-transforming layered hybrid perovskite frameworks would provide a unique platform for photo transformations of interest in organic electronics. This can set the stage for light-adaptive perovskite materials that heal, tune their band alignment on demand, and ultimately operate within self-powered optoelectronics. It could also extend further beyond photovoltaics and light-emitting diodes, to enable new devices for energy storage, memories, and spintronics, as well as optoionics that combines ionic motion with photon management. The recent developments in this research field promise advancements toward smart materials, stimulating further investigation.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

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