Host-guest complexation in hybrid perovskite optoelectronics

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Abstract

Hybrid halide perovskites have become one of the leading materials in the new generation photovoltaics. While their performances are rapidly increasing, the stability under operating conditions remains a limiting factor to their application. There is an ongoing effort to overcome the performance and stability limitations by designing new perovskite materials as well as modifying their structure through various molecular modulators that affect their crystal structure, defect chemistry, and optoelectronic properties. It is desirable to control the properties of materials and devices without compromising their stabilities, and host-guest complexation has recently provided a powerful strategy to achieve that goal. This article provides an overview of the host-guest complexation strategies and their utility in hybrid perovskite optoelectronics, along with the emerging perspectives for future applications.

1. Introduction

Hybrid perovskites are proven extraordinary materials for various optoelectronic applications, in particular solar-to-electric energy conversion in photovoltaics [1–4]. These materials are based on a hybrid organic-inorganic AMX3 composition (figure 1(a)) defined by the inorganic metal-halide [MX6] corner-sharing octahedral framework based on divalent metals M (mostly Pb2+ and Sn2+) and halide anions X (I–, Br–, or Cl–) hosting a central A cation (such as inorganic Cs+ or organic methylammonium (MA) or formamidinium (FA)) [3, 5]. The major obstacle to their practical deployment is their limited environmental stability (e.g. exposure to oxygen and moisture) and intrinsic instabilities under device operating conditions (e.g. voltage bias, light, and temperature changes) [6, 7]. This is particularly related to ionic (e.g. A cation or X halide) migration in the applied electric field, which can be detrimental for the resulting performance and long-term stability [8–12]. There has been an effort to overcome this limitation by using various compositional, interface, and device engineering approaches, such as by employing molecular modulators or low-dimensional perovskites based on larger organic moieties [13–17]. A particularly versatile strategy that has recently emerged relies on host-guest (HG) complexation (figure 1(b)) employing various macrocyclic host molecules that can selectively bind and deliver smaller guest molecules [18–22], such as various ions in the perovskite composition. This could provide a unique approach to controlling the perovskite crystal structure, defect chemistry, and the resulting optoelectronic properties of materials and devices toward increasing their long-term stability [23–30].

Herein, we provide an overview of the recent developments in the use of HG complexation strategies for controlling hybrid perovskite materials. This emerging approach benefiting from the synergistic effects of the host, the guest, and the HG complexes enables controlling the chemistry of the perovskite precursors and the resulting material structure as well as the resulting device performances and stabilities. We illustrate the potential of the approach and provide perspectives for future applications in optoelectronics.

2. The basic principles of HG chemistry

HG complexation describes the formation of supramolecular complexes composed of two or more molecules or ions via noncovalent interactions (figure 1(b)) [18–21]. The host (H) selectively binds a guest (G) to create
a HG complex through various noncovalent interactions, such as hydrogen bonds, ionic forces, van der Waals interactions and others [31–35]. In the design of HG systems, the principles of complementarity and preorganization play critical roles in defining the binding affinity [34, 35]. The principle of complementarity refers to the size and shape of the binding sites of the host and the guest molecules, which should be in contact without generating internal strain or unfavorable repulsive interactions, thereby contributing to favorable enthalpies of HG formation [34, 35]. It is an important factor for the HG complex formation and HG interactions are dependent on it, determining the binding strength [36]. Likewise, the principle of preorganization considers that the resulting complexes will be more stable for those hosts and guests that are more pre-organized for binding prior to their complexation, which is often associated with the entropic factors of the process [33, 35–38]. This particularly refers to the structural preorganization based on the use of macrocyclic hosts or the use of acyclic hosts which are pre-organized for binding specific guest molecules. Accordingly, the supramolecular systems formed by HG interaction with macrocyclic hosts, such as crown ethers [25, 26, 28, 39], cyclodextrins (CDs) [23, 27, 40, 41], cucurbiturils [42], and others (figure 2), represent the most promising category of supramolecular materials for various applications [32, 43–45]. Their preorganization, which includes both enthalpic and entropic contributors to the thermodynamics of the HG complex formation, is an essential determinant of binding ability. However, it is important to note that solvation also has a significant effect on the degree of preorganization and the presence of solvents could introduce competing interactions in the complexation process. The use of macrocyclic hosts thus increases preorganization by enhancing the binding ability while also reducing the solvation effects [37].

Supramolecular HG interactions have demonstrated numerous advantages in modifying physicochemical properties of materials and optoelectronic devices [46–55]. The noncovalent nature of HG complexes makes them suitable for tuning the molecular properties of materials through competitive binding and other stimuli, such as light, temperature etc [46]. It has attracted considerable attention due to its potential in different applications, including sensors, drug delivery, and optoelectronics [25, 26, 46]. This is particularly the case for macrocycle-based HG interactions, which exhibit extraordinary properties and significant potential for practical applications. They can be prepared under different conditions, such as organic or aqueous solution-processing, in gel- and solid-state, which further facilitates their application [49, 56–59].

Crown-ethers and CDs are two commonly used macrocyclic hosts that have dominated supramolecular chemistry over the past 50 years (figure 2) [60]. Crown-ether-based molecular recognition has been studied in organic solvents and water (figure 2(a)), and CD-based interactions are typically studied in aqueous media (figure 2(b)). Complexes in gels and in the solid-state are widely used for these macrocyclic hosts [56]. CDs are a family of macrocyclic oligosaccharides consisting glucopyranose units attached by α,1,4-linkages (figure 2(b)). They consist of six, seven or eight glucopyranose units, named α-, β-, and γ-CD, respectively, which contain hydroxyl groups on the outside and a hydrophobic environment inside of the cavity. Therefore, they are able to capture hydrophobic guests in aqueous media, and they can be further functionalized through active hydroxyl groups [60]. The approximate cavity diameter of CDs is in the 4.9–8.0 Å range (i.e. α-CD: 4.9 Å; β-CD: 6.2 Å; γ-CD: 8.0 Å) [60]. Generally, native CDs are non-toxic and commercially available reagents, and they can form supramolecular HG complexes in aqueous media [60–62].

Crown ethers present another category of well-known cyclic host molecules comprising ether groups that result in a remarkable selectivity to different cations, based on the highly electronegative cavity. The selectivity is dependent on the size of the macrocycle [25, 26]. They can be used in both aqueous and organic media due to the presence of amphiphilic ethylene oxide moieties as repeating units. Their functionalization can be achieved by various organic reactions. The formation of HG complexes between crown ethers and organic ammonium cations and the high solubility and functionality of crown ethers in organic solvents facilitates the synthesis of molecular machines, such as molecular shuttles [60, 63, 64]. The complexation of metal cations by crown ethers could help increase the solubility of metal cations in organic solvents and, in
this manner, the reactivity of counter anions. Thus, crown ethers can be used as phase-transfer catalysts [25, 60].

There is an emergence of the use of these common macrocyclic hosts to create supramolecular HG complexes with metal halide perovskites for application in optoelectronic devices, such as solar cells and light-emitting diodes (LEDs) [23–30]. This has involved their utility in solubilizing hybrid perovskite precursors and controlling their morphology, passivating the defects, as well as stabilizing the materials and devices during operation. We provide a brief account of these applications of HG complexes in hybrid perovskite optoelectronics and the effects on solubility, morphology, and defect chemistry at surfaces and grain boundaries of hybrid perovskites, while outlining challenges and perspectives in the future.

3. HG complexation in hybrid optoelectronics

3.1. HG chemistry of perovskite precursors

HG complexation is commonly used to control the solubility, such as in phase-transfer catalysis via crown-ether complexes that solubilize metal cations in organic solvents [25, 26]. This strategy has been effectively employed to control the perovskite precursor solutions chemistry in the preparation of perovskite thin-films and quantum dots (QDs) [26].

In particular, one of the barriers for the development of Cs-based perovskites has been that cesium iodide (CsI) is the only cesium halide soluble in common organic solvents, in which other salts, such as CsBr and CsCl, are poorly soluble. This challenge has limited the progress in compositional engineering of inorganic halide perovskite materials and the preparation of high-quality thin films for optoelectronic applications. For instance, CsPbBr$_3$ nanocrystals have shown high structural stability, near-unity photoluminescence quantum yields, narrow emission widths, and versatility [26]. However, the low solubility of Cs ions in polar solvents has severely limited their usage. Typically, the synthesis of these QDs is performed by using high temperatures, stringent conditions, large quantities of surface ligands, and judicious purification steps [65–72].

Veldhuis et al demonstrated the synthesis of CsPbBr$_3$ nanocrystals at low temperatures by employing crown ethers [26]. As a result, these systems could be applied in optoelectronic devices, such as LEDs, despite the otherwise low solubility of Cs precursor salts in polar media. In their study, Veldhuis et al demonstrated a general strategy to overcome the low solubility of Cs precursors in polar solvents by forming HG complexes between dibenzo-21-crown-7 (DB21C7) and Cs (figure 3(a)) [26]. This enabled the synthesis of core–shell QDs at low temperatures. The use of crown ethers facilitated the dissolution of CsBr in N,N-dimethylformamide (DMF) by increasing the solubility of these materials four times compared to the reported solubility without the addition of crown ethers [73]. The complexation was verified by $^1$H nuclear magnetic resonance (NMR; figure 3(b)). Moreover, high-resolution transmission electron microscopy (HRTEM) images showed high degree of crystallinity and formation of core/shell structures (figure 3(c)). The formation of a complex with DB21C7 was confirmed by Fourier transform infrared (IR) spectra (figure 3(d)). Based on these observations, the authors propose several consecutive steps for the preparation of CsPbBr$_3$ nanocrystals (NCs, figure 3(e)). In the first step, Cs cations are strongly bound to the crown ether

![Figure 2. Chemical structures of (a) crown ether $⊃$ metal complexes and (b) cyclodextrins with (c) representative x-ray crystal structures (CCDC no. 911558 and 1978630) [60].](image-url)
Figure 3. (a) Structure of dibenzo-21-crown-7 (DB21C7; top) and representation of its complex with Cs cations. (b) $^1$H NMR spectra of DB21C7 in dimethylformamide-d$_7$ (DMF-d$_7$) (red) and CsBr dissolved in a mixture of DB21C7/DMF (blue). A weak chemical shift $\Delta \delta$ of 0.01–0.05 ppm is observed for all signals upon HG complexation with Cs cations. The peak numbers correspond to the protons in (a). (c) HRTEM image of a small ensemble of CsPbBr$_3$ QDs, which display high crystallinity, with visible shells on the outside of the crystal that are marked by white arrows. (d) Fourier-transform IR spectra of DB21C7 (black) and spin-coated thin film of CsPbBr$_3$ nanocrystals (NCs) on glass (blue). (e) Schematic of the QD and shell formation steps. Adapted with permission from [26]. Copyright (2018) American Chemical Society.

in the precursor solutions. Next, during the injection into the non-coordinating solvent, the precipitation of CsPbBr$_3$ occurs immediately. It is assumed that the crown ether-perovskite complex forms a stable seed particle through the interaction between crown ether and CsPbBr$_3$, which imparts repulsive forces between the ligands and the seeds. This directs the ligands on the outer side of the crown ether cavity where $\pi-\pi$ stacking of the phenyl groups of the crown ether puts the seeds into close contact. As a result, the process enables NC growth and ligand reorganization, leading to the formation of core–shell crown ether-perovskite NCs capped with appropriate ligands [26].

Vashishtha et al have also employed the DB21C7 to incorporate Cs cations from solid CsBr into a mixed-cation perovskite composition [28]. They reported the synthesis of novel triple cation perovskite nanocrystals with nominal stoichiometries Cs$_x$(FA$_{0.83}$MA$_{0.17}$)$_{1-x}$PbBr$_3$ ($x = 0–0.15$) using the room-temperature ligand-assisted reprecipitation method. The crown ether played an effective role in dissolving the Cs$^+$ salts in DMF, resolving the main limitation in employing CsBr in mixed-cation perovskites. As a result, the development of a high-performance Cs-containing triple-cation perovskite nanocrystals was possible for applications in optoelectronics. The authors further indicated that this new system is able to deliver high photoluminescence quantum yield and excellent photostability under continuous ultraviolet illumination [28], which is relevant for various applications.

Another investigation by Masi et al focused on using HG complexation to overcome inhomogeneous crystal growth that originates from non-negligible differences in the solubility of perovskite precursors [27]. The solubilities of PbI$_2$ and methylammonium iodide (MAI) are different, which leads to a high defect density in deposited film and thereby non-optimal optoelectronic properties as well as instability in photovoltaic operation [27]. The supramolecular HG approach was thus explored based on the use of CDs to tailor the availability of precursors in solution. The $\beta$-CDs enabled a more than two-fold enhancement of the precursor solubility in the reaction media. In addition, it was shown that $\beta$-CDs form a complex with organic cations and simultaneously dissociate PbI$_2$ aggregates through intercalation between PbI$_2$ layers,
which provides soluble species and intermolecular space that can accommodate a framework of organic components (figure 4). In addition, they showed that β-CDs do not interfere with the perovskite crystal structure, which is released from the crystalline phase during the solvent evaporation step. Instead, it only promotes the reaction between the precursors, thus positively affecting film formation. Therefore, β-CDs have an important role both in solution and in perovskite film formation through a solubilizing effect, resulting in an improved nucleation process of the perovskite materials and thus in high crystallinity, moisture stability, and excellent optical properties. This effect has been applied to enhance the performances and stabilities of MAPbI\(_2\) perovskite solar cells, demonstrating an increase in power conversion efficiencies from 12%–4% to 14.1% accompanied by reduced hysteresis [27].

### 3.2. HG complexation in crystal engineering

Apart from affecting the solubility of the precursors, the presence of host moieties in the precursor solution could greatly affect the crystallization conditions and thereby the structure and morphology of the resulting materials.

Chen et al have recently shown that the interaction between the crown ether (18-crown-6) and metal cations (Cs\(^+\) and Pb\(^{2+}\)) has a significant effect on the formation of thin perovskite films by providing uniform crystal growth, which contributed to suppressing the effect of moisture during the crystallization of α-FACsPbI\(_3\) (FA, CH(NH\(_2\))\(_2\)\(^+\)) phase [29]. The crown ether was introduced into the FACsPbI\(_3\) precursor solution and perovskite films were prepared through solvent evaporation by either spin-coating or vacuum-flash-assisted blade coating [29]. The nucleation and growth of perovskite crystals within the films was shown to be affected by the interactions between the crown ether and metal ions (figure 5(a)). The beneficial effect of the crown ether was studied by several methods, including scanning electron microscopy (SEM), suggesting that it improves the crystallinity and overall quality of perovskite films (figures 5(b) and (c)) by simultaneously suppressing the non-perovskite δ- and the PbI\(_3\) phases (figure 5(d)). This could partly be the result of the increased hydrophobicity of the surface upon treatment, as shown by water contact-angle measurements (figure 5(e)) [29]. To better understand the underlying mechanisms, the interaction of the crown ether and perovskite precursors was also examined in solution by \(^1\)H NMR to suggest that there is a stronger interaction between the crown ether and Cs\(^+\) compared to the Pb\(^{2+}\), which was supported by comparing their calculated binding energies. The authors concluded that crystal growth is affected by the HG interaction between the crown ether and Cs\(^+\) ions, which could slow down the crystallization process of FACsPbI\(_3\) and suppress its transition into the non-perovskite phase. As a result, they fabricated perovskite solar cell modules with the total area of 16 and 100 cm\(^2\) showing respective champion device solar-to-electric power conversion efficiencies of 16.69% and 13.84%, with an excellent storage stability over 1000 h (figures 5(f) and (g)) [29].

In another work, Huang et al successfully employed β-CD as a host molecule to prepare core/shell-structured CH\(_3\)NH\(_3\)PbBr\(_3\) nanocrystals (MAPbBr\(_3\) NCs) via HG complexation (figure 6(a)) [23]. The aim was to synthesize MAPbBr\(_3\) NCs with a narrow size distribution and uniform geometry, while improving their stability when exposed to heat, UV light, oxygen, and moisture. The core/shell-structured MAPbBr\(_3/β\)-CD nanodots were successfully formed through HG interactions between the β-CD and the aliphatic chain of the capping ligand, n-hexylamine, by using a one-step reprecipitation method [23]. The morphology of the resulting material, synthesized with an optimized amount of hexylamine, was studied by transmission electron microscopy (TEM; figures 6(b) and (c)). The results revealed a well-defined core/shell nanostructure of MAPbBr\(_3\) nanodots, showing good crystallinity. It was also found that, by increasing the amount of n-hexylamine as a capping ligand in the precursor solution, the average size of MAPbBr\(_3\) nanodots...
decreased, which was related to the fast nucleation of MAPbBr$_3$ that are fully capped by n-hexylamine in the solution, limiting further growth. In addition, it was demonstrated that the further increase of hexylamine concentration caused the disappearance of the core/shell structure. Therefore, the size of nanodots can be tuned by the amount of capping ligand even in the presence of the HG complex with β-CD. The phase purity of MAPbBr$_3$/β-CD nanodots was confirmed by x-ray diffraction (XRD; figure 6(d)). To establish the use of MAPbBr$_3$/β-CD nanodots in optoelectronic devices, green-light emitting LEDs were fabricated, showing that the use of β-CD improves the stability of the nanodots when exposed to heat, UV light and water (figures 6(e)–(g)). The ease of preparation, good crystallinity, and high stability make MAPbBr$_3$/β-CD nanodots particularly promising candidates for various applications in optoelectronic devices [23].

Similarly, Li et al used graphdiyne (GD) as a host material in the MAPbI$_3$ layer of a perovskite solar cell (figures 7(a) and (b)) [24]. They demonstrated that GD improves perovskite crystallinity, film morphology, and optoelectronic properties, including charge carrier transport efficiency in the active perovskite layer. The SEM images revealed that the presence of a certain amount of GD results in a change in film morphology stemming from a uniform crystal growth (figures 7(c) and (d)). Furthermore, to understand the improvement in crystallinity, the interaction between GD and perovskite was studied by x-ray photoelectron spectroscopy, which revealed that the coordination between Pb$^{2+}$ and GD takes place. This interaction is associated with the resulting improvement of crystal quality and stability [24]. Moreover, the power-conversion efficiency of MAPbI$_3$-based devices was shown to increase from 16.69% to 21.01% by the introduction of GD, which was accompanied with a negligible current–voltage hysteresis and a significant stability improvement in perovskite solar cells. It was thereby shown that applying GD as a host material...
Figure 6. (a) Schematic of the MAPbBr$_3$/β-CD core/shell nanodots formation through HG supramolecular assembly. (b) TEM images of MAPbBr$_3$/β-CD nanodots prepared in the presence of 0.45 mmol l$^{-1}$ hexylamine. Inset: HRTEM image of a MAPbBr$_3$ nanodot core. (c) Size distribution histogram of MAPbBr$_3$ nanodots obtained from the TEM image. (d) XRD patterns and (e)–(f) PL spectra of MAPbBr$_3$/β-CD nanodots at 70 °C (e) or under 365 nm UV light (f). (g) Evolution of the stability of MAPbBr$_3$/β-CD nanodots when exposed to water. [23] John Wiley & Sons. © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

presents a promising strategy to improve the crystallinity of the active perovskite layer, enhancing the performance and stability of the corresponding solar cells.

3.3. HG complexation for controlling stability

The presence of host moieties in the perovskite composition could be relevant to controlling their defect chemistry, particularly in the cases where HG complexation could contribute to suppressing the defects (i.e. passivating) in perovskite materials. These defects can, for instance, involve anion vacancies or undercoordinated metal cations, which can form at the surface and grain boundaries of the perovskite films, affecting the resulting device performances and operational stabilities [74–77].

Chen et al have recently developed a strategy that relies on 18-crown-6 to passivate high-quality α-CsPbI$_3$ perovskite phases (figures 8(a) and (b)) [30]. They also showed that this passivation strategy could contribute to the stabilization of α-CsPbI$_3$ perovskite phase (figures 8(b) and (c)) and the fabrication of high quality perovskite films (figure 8(d)). Apart from stabilizing the perovskite phase, the crown ether also prevented the penetration of moisture (figure 8(e)), suppressing phase transformations under ambient conditions. This is the result of the inner cavity of the crown ether selectively binding Cs ions, hence passivating surface defects and inhibiting defect migration (figure 8(b)), which is relevant for the improvement of optoelectronic properties (figure 8(f)), photovoltaic performances (figure 8(g)), and operational stability (figure 8(h)) of CsPbI$_3$ perovskite solar cells [30].

To understand the mechanism responsible for these effects, the interaction between the crown ether and CsPbI$_3$ was studied by solution $^1$H NMR spectroscopy (figure 8(c)), which confirmed the interaction between the crown ether and Cs$^+$ ions [30]. Furthermore, the defect passivation effect on the perovskite film was investigated via space-charge-limited current measurements to evaluate the trap-state densities in perovskite film [30]. The results showed a significant reduction in defect density for crown-ether-treated CsPbI$_3$ films, indicating that the crown ether passivation effect effectively suppressed the non-radiative charge recombination, which is in agreement with the enhanced PL emission (figure 8(f)). Finally, a
Figure 7. (a) Schematic representation of a perovskite solar cell treated with graphdiyne (GD). (b) Schematic illustration of the adduct between GD as a host and PbI$_2$ as a guest. (c) Cross-sectional and (d) top-view SEM images of the perovskite active layer treated with GD. Adapted with permission from [24]. Copyright (2018) American Chemical Society.

Figure 8. (a) Schematic illustration of a crown ether (18-crown-6) passivating the surface of α-CsPbI$_3$ and suppressing the phase transformation from α-CsPbI$_3$ to γ-CsPbI$_3$. (b) A model of a crystal structure of CsPbI$_3$-18-crown-6 (Cs red, Pb dark green, I purple, C black, O light blue) interacting with the perovskite surface (CCDC no. 1978630). (c) $^1$H NMR spectra of CsPbI$_3$-crown complexes dissolved in DMSO-d$_6$ with the crown-ether and its complex with CsI as reference. (d) Top-view SEM images of the CsPbI$_3$-crown-ether films. (e) Water contact angle measurements of the CsPbI$_3$-crown-ether films. (f) Steady-state PL spectra of films deposited on glass substrates using 377 nm excitation wavelength. (g) J–V curves of the champion perovskite solar cell devices. (h) Performance evolution of perovskite solar cell devices under operating conditions (AM 1.5 G) at RH 45 ± 5%. (i) Storage stability of unencapsulated devices in a chamber with controlled temperature and humidity (RH 20%). The error bars in (h,i) represent the standard error. Adapted from [30] with permission of The Royal Society of Chemistry.

significant enhancement in the long-term stability was obtained, which was ascribed to the suppression of the defect migration through interaction with the crown ether (figures 8(h) and (i)). Consequently, a champion efficiency of 16.9% was achieved and a perovskite module with a larger area (16 cm$^2$) was fabricated, which resulted in efficiency over 11.8% and considerable operational stability (figures 8(g)–(i)).
In another recent study, Su et al [25] reported a crown-ether-based modulation in PSCs, which resulted in the reduction of defect densities at the surface and grain boundaries of a formamidinium-based perovskite (FAPbI$_3$). Two crown ethers with comparable cavities were examined, which were either aliphatic, i.e. 18-crown-6 ether (18C6), or benzannulated, i.e. dibenzo-18-crown-6 (DB18C6; figure 9(a)). DB18C6-treated devices showed a better photovoltaic performance and hydrophobicity and were thus selected for further analysis. It has been shown that DB18C6 has higher hydrophobicity compared to 18C6 [78], which is relevant for the prevention of moisture invasion. The crown ether enabled HG complexation through interaction with the cations at the surface of perovskite, including FA$^+$ and Pb$^{2+}$ (figure 9(b)). This resulted in surface electronic defect reduction and suppression of nonradiative charge recombination, accompanied by improved device stability under air and operation conditions [25]. In addition, to explore the effect of the crown ether, solid-state NMR (figure 9(c)) and density functional theory (DFT) calculations (figure 9(d)) were used to provide evidence for the coordination of the crown-ether to the metal and the organic cations, thereby passivating the uncoordinated Pb$^{2+}$ defects and FA$^+$ ions on the surface of the perovskite films. The crown ether treatment ultimately resulted in an improved operational stability, with power conversion efficiencies exceeding 23% and lower hysteresis (figures 9(e) and (f)) [25]. This approach has been recently extended to form 2D/3D perovskite heterostructures [79]. Moreover, the competitive binding with FA-cations and Pb$^{2+}$ was employed to selectively deliver Cs$^+$ cations into FAPbI$_3$-rich perovskite compositions, further stabilizing them and reaching solar cell performances that exceed 24% with enhanced operational stabilities [79]. It was also demonstrated that the approach could contribute to
Table 1. Summary of the HG complexation strategies in hybrid perovskite optoelectronics reported to date.

| Strategy                                      | Perovskite composition | Effects                                                                 | Reference |
|-----------------------------------------------|------------------------|------------------------------------------------------------------------|-----------|
| HG complexation of perovskite precursors: using dibenzo-21-crown-7 to dissolve CsBr in DMF | CsPbBr$_3$ quantum dots | Enabling CsPbBr$_3$ inks and resulting in LEDs with current efficiency and external quantum efficiency of 9.22 cd A$^{-1}$ and 2.64%, respectively | Veldhuis et al [26] |
| HG complexation of perovskite precursors: using dibenzo-21-crown-7 to incorporate CsBr into mixed-cation perovskites | Cs$_x$(FA$_{0.83}$MA$_{0.17}$)$_{1-x}$PbBr$_3$ ($x = 0–0.15$) nanocrystals | Max. PLQY of $\sim$93% that in LEDs delivers max. EQE of 7.4% (30 cd A$^{-1}$) with improvements compared to CsPbBr$_3$ reference (max. PLQY $\sim$50%, EQE 2.5% (7.2 cd A$^{-1}$)). | Vashishtha et al [28] |
| HG complexation of perovskite precursors: using $\beta$-CDs to increase solubility of precursors | MAPbI$_3$ thin films | Improved crystallinity and moisture stability, with solar cell PCE increase from 12.4% to 14.1% with no hysteresis and stabilized MPP | Masi et al [27] |
| HG complexation in crystal engineering: using 18-crown-6 complex with metal cations (Pb$^{2+}$ and Cs$^{+}$) in the formation of perovskite thin films | $\alpha$-FACsPbI$_3$ thin films | Improved crystallinity by suppressing non-perovskite $\delta$- and PbI$_2$ phases, leading to champion device PCEs of 16.69% and 13.84% for modules of 16 and 100 cm$^2$ area, respectively, and storage stability for over 1000 h | Chen et al [29] |
| HG complexation in crystal engineering: using $\beta$-CD to prepare core/shell nanocrystals | MAPbBr$_3$ nanocrystals | Good crystallinity and higher stability with PLQY of 89.7% in solution and 38% in solid-state (as compared to 1% for reference samples without $\beta$-CD) | Huang et al [23] |
| HG complexation in crystal engineering: using GD in the MAPbI$_3$ thin film preparation | MAPbI$_3$ thin films | Improving crystallinity and charge carrier transport, resulting in the increase of champion solar cell PCEs from 16.69% to 21.01%, negligible hysteresis, and higher stability | Li et al [24] |
| HG complexation in controlling stability: using 18-crown-6 to passivate CsPbI$_3$ thin films | CsPbI$_3$ thin films | Passivation and stabilization of $\alpha$-CsPbI$_3$ phase, resulting in champion solar cell PCEs of 16.9% and over 11.8% for a 16 cm$^2$ module, as well operational stability during 2000 h | Chen et al [30] |
| HG complexation in controlling stability: using aliphatic (18-crown-6) or benzannulated (dibenzo-18-crown-6) crown ethers to passivate perovskite films | FAPbI$_3$-rich thin films | Reduction of defect densities at the surface and grain boundaries to reach PCEs increased from around 19% to over 23% with lower hysteresis and improved operational stability for over 300 h period using dibenzo-18-crown-6 | Su et al [25] |
| HG complexation in controlling stability: using 15-crown-5 to passivate thin films | FA$_{0.85}$MA$_{0.15}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$ thin films | Passivation and stabilization through 2D-layer formation to reach PCEs up to 21.5% in solar cells with enhanced operational stabilities during 1000 h | Gao et al [79] |

(Continued.)
Table 1. (Continued.)

| Strategy                                      | Perovskite composition         | Effects                                                                 | Reference       |
|-----------------------------------------------|--------------------------------|-------------------------------------------------------------------------|-----------------|
| **HG complexation in controlling stability:** using | **FAPbI₃-rich thin films**     | Stabilization of α-FAPbI₃ to reach solar cell PCEs from about 20% to over 24% with enhanced operational stabilities for over 500 h and reduced Pb leakage upon immersion in water | **Zhang et al [80]** |

HG = host-guest; DMF = N,N-dimethylformamide; MA = methylammonium; FA = formamidinium; LED = light emitting diode; PLQY = photoluminescence quantum yield; EQE = external quantum efficiency; CD = cyclodextrin; GD = graphdiyne; PCE = power conversion efficiency; MPP = maximum power point.

reducing the environmental impact of Pb, which provides a complementary perspective [80]. These reports (summarized in table 1) demonstrate the versatility of this supramolecular approach, promising to advance hybrid perovskite optoelectronics in the future.

4. Summary and perspective

HG complexation presents a versatile strategy for controlling structural and physicochemical properties of various materials through noncovalent interactions between the host and guest moieties. It has recently gained attention in controlling the properties of metal halide perovskites, from structural and optoelectronic properties to their device performances and stabilities, in particular for perovskite solar cells and LEDs. For this purpose, two common macrocyclic hosts have so far been particularly relevant, namely crown ethers and cyclodextrins, which can interact with various cation species within the hybrid perovskite phases, resulting in changes of their structural and electronic properties. This involved improving the solubility of poorly soluble metal precursors, such as Cs-halides, as well as the ability to control the crystallization process and stabilize the desired perovskite phases, which is critical for their long-term stability. Furthermore, HG complexes were effectively used to coordinate and passivate surface defects, reducing their concentration at the surface and grain boundaries, hence improving the resulting optoelectronic properties. Similarly, the capacity to bind various ions while increasing the hydrophobicity of the surface of perovskite thin-films was found to achieve improved extrinsic and operational stabilities of the resulting materials and devices.

These early reports illustrate the synergistic effects of the host, the guest, and the HG complexes in perovskite optoelectronics, which open a new path to develop high-performing perovskite-based devices for a wide range of applications. For instance, the challenges related to controlling the ion migration during operation of perovskite devices could be addressed by relying on selective binding of specific ions through HG chemistry. This is particularly relevant for the suppression of ion migration through selective complexation across the interfaces with charge-extraction layers that are critical for long-term stabilities. In addition, competitive HG complexation strategies could be utilized to controllably deliver specific guest moieties (e.g. ions) into various perovskite compositions of interest to their stabilization and performances. Finally, such selective and competitive complexation strategies are of interest to addressing the environmental impact of lead that presents another major obstacle to large-scale deployment. For this purpose, it is vital to develop rigorous structural assessment methodologies, especially in perovskite devices during operation, which could provide a better understanding of the underlying mechanisms and guide advanced material design. We envisage that these versatile and scalable complexation strategies will play an important role in addressing some of the critical challenges associated with hybrid perovskite materials and devices, especially those related to their long-term stability and the environmental impact of toxic components.

Data availability statement

No new data were created or analysed in this study.

Author contributions

All authors have contributed to the manuscript.
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