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Supramolecular engineering in hybrid perovskite optoelectronics†

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This review explores the emerging field of supramolecular engineering in hybrid organic–inorganic perovskite optoelectronics. The incorporation of supramolecular agents has shown transformative effects on the crystallization, morphology, stability, and performance of perovskite-based materials and devices. We systematically review the types of supramolecular interactions, mechanisms of supramolecular engineering crystallization, synthesis of perovskite quantum dots, and interface engineering advancements for device stability. This comprehensive evaluation discusses the latest progress, challenges, and promising future directions, highlighting supramolecular engineering's potential in advancing hybrid organic–inorganic perovskite optoelectronic technologies.

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1. Introduction

Hybrid organic–inorganic perovskites typically represented by the formula ABX₃ (where “A” is a cation, “B” is a metal cation, and “X” is a halogen anion) have gained tremendous attention in optoelectronic applications due to their remarkable electronic and optical properties such as high optical absorption coefficients,^{1,2} tunable bandgaps,^{3,4} and excellent charge-carrier mobilities.^{5–7} These characteristics have positioned them as promising candidates for solar cells,⁸ light-emitting diodes (LEDs),^{9,10} photodetectors,^{11,12} lasers,^{13,14} and transistors.^{15,16}

The popularity of perovskite materials in optoelectronics emerged from their success in perovskite solar cells (PSCs). Since the first PSCs with a modest power conversion efficiency (PCE) of 3.8% were reported in 2009,¹⁷ efficiencies have rapidly advanced to exceed 26%,¹⁸ nearly rivaling traditional silicon-based solar cells. The key advantages of hybrid organic–inorganic

perovskites include solution-processed fabrication^{19,20} and compatibility with flexible substrates,^{21,22} which promises low-cost and large-scale production.^{23–25}

In addition to PSCs, hybrid organic–inorganic perovskites have also been studied for use in LEDs due to their efficient radiative recombination and narrow emission line widths.^{26,27} By adjusting the halide composition, researchers can tune the emission color across the visible spectrum, making perovskites viable candidates for display technologies²⁸ and solid-state lighting.²⁹ Furthermore, photodetectors benefit from perovskites' high carrier mobility and response speed,³⁰ while lasers made with perovskite materials can achieve low threshold energies due to high optical gain.³¹

While hybrid organic–inorganic perovskite-based optoelectronic devices exhibit impressive performance and these advances, they face several challenges that hinder their long-term stability and efficiency.³² Hybrid organic–inorganic perovskite materials are environmentally unstable and highly sensitive to moisture,^{33,34} oxygen,^{35,36} and UV light,³⁷ all of which cause material degradation and device failure. It has been proved that perovskite-based optoelectronic devices exposed to moisture lead to the rapid decomposition of perovskites into lead halide and other by-products,^{38,39} compromising both the structural and optoelectronic properties. Ion migration within hybrid organic–inorganic perovskite materials is another significant issue that affects device efficiency and operational stability.⁴⁰ Ions such as halides and metal cations can move within the perovskite lattice under an electric field or due to temperature gradients, leading to hysteresis in current–voltage measurements, performance degradation, and even phase segregation in mixed-halide perovskites.⁴¹ This ion migration not only reduces the device's lifespan but also poses challenges in

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maintaining consistent performance metrics.⁴² In addition, the grain boundaries within perovskite films are prone to trapping charge carriers, which results in non-radiative recombination losses.⁴³ These grain boundaries can also act as pathways for moisture ingress, accelerating degradation.⁴⁴ Therefore, achieving large, defect-free grains is essential for minimizing charge-trapping sites and enhancing device efficiency. Scalability is yet another challenge, as the solution-processing methods commonly used in research may not easily transfer to industrial-scale production. Issues such as solvent toxicity,⁴⁵ processing reproducibility, and compatibility with large-area substrates must be addressed before perovskites can achieve commercial viability.⁴⁶ Addressing these stability and efficiency challenges is crucial to the future of perovskite-based devices. Researchers are investigating various approaches, including surface passivation,^{47,48} additive

engineering,^{49,50} and encapsulation,^{51–54} to enhance device robustness. Particularly, supramolecular chemistry offers a promising avenue by providing tools to control molecular interactions, stabilize structures, and passivate defects, all of which can lead to improved material and device stability.^{55–57} It is often described as “chemistry beyond the molecule”, which studies the interactions and assemblies formed through non-covalent interactions such as hydrogen bonding,⁵⁸ van der Waals forces,⁵⁹ π - π interactions,⁶⁰ and host-guest chemistry.⁶¹ Unlike traditional covalent chemistry, which relies on fixed bonds, supramolecular interactions are dynamic, reversible, and often stimuli-responsive. This flexibility enables the design of materials with tunable properties that respond to external factors like light, temperature, and electric fields.⁶² The principles of supramolecular chemistry have led to significant advances in materials science, allowing



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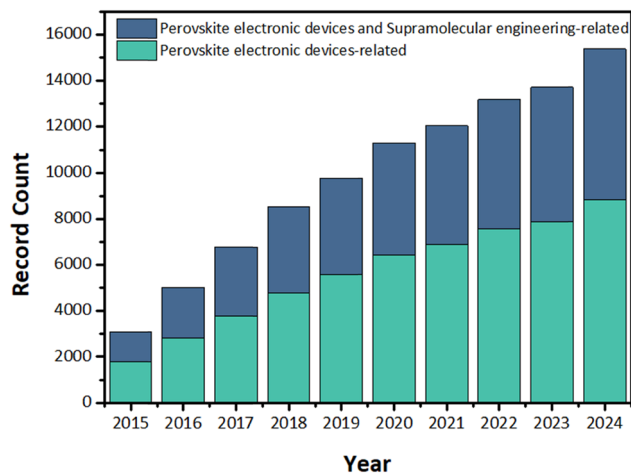


Fig. 1 Counts of recent 10-year publications related to perovskite electronic devices, and related to perovskite electronic devices and supramolecular engineering (statistics from Web of Science).

researchers to create complex assemblies that mimic natural processes and structures. In hybrid organic–inorganic perovskite research, supramolecular engineering can be utilized to stabilize the perovskite material by introducing agents that interact with perovskite components at the molecular level. This can lead to enhanced crystallinity, reduced defect density, and improved resistance to environmental factors such as moisture and temperature.⁶³ Supramolecular agents, including small organic molecules, polymers, and macrocyclic compounds,⁶² can be introduced during perovskite synthesis⁶⁴ or as post-treatment additives.⁶⁵ These agents can passivate surface defects, control crystal growth, and improve film morphology. Moreover, supramolecular chemistry can improve interfaces within perovskite devices. By engineering interfaces at the molecular level, researchers can enhance charge-carrier transport, minimize recombination losses, and create stable junctions between perovskites and other

device components.⁶⁴ Thus, supramolecular engineering offers a versatile toolkit for addressing the complex challenges associated with hybrid organic–inorganic perovskites. During the developmental course of hybrid organic–inorganic perovskite electronic devices, effective supramolecular engineering has been developed aiming at solving those inherent problems to boost the device performance. More and more publications related to supramolecular engineering on perovskite electronic devices in recent 10 years reveal that this strategy has become a key step for performance enhancement as shown in Fig. 1. This review explores how supramolecular interactions can be incorporated into hybrid organic–inorganic perovskites and be leveraged to improve these identified challenges including morphology, stability, and efficiency of optoelectronic applications.

2. Strategies for incorporating supramolecular into perovskites

Supramolecular interactions, such as hydrogen bonding, π – π interactions, and host–guest chemistry, have revolutionized the development of hybrid perovskite optoelectronics. These interactions are enabled by organic molecules, ionic liquids, and self-assembled monolayers, which are versatile, readily available, and compatible with commonly used perovskite solvents. Especially, some molecules are typically liquid, cost-effective, and dissolve easily in polar solvents, including water and perovskite precursor formulations.⁴⁹ Their adaptability allows them to serve not only as additives but also as integral components that directly influence perovskite film formation and device performance. Strategies for incorporating these supramolecular interactions into perovskites involve various methods such as direct addition into precursor formulations, surface post-treatments, and vapor-assisted treatments (Fig. 2). For instance, the direct inclusion of organic molecules in the perovskite precursor solution can fine-tune the crystal growth and structural properties during film formation.⁶⁶ Meanwhile, surface post-treatments involve the application of organic molecules to passivate defects, protect the films from moisture, and enhance charge transport properties.⁴⁷ Additionally, vapor-assisted treatments and ligand anchoring exploit the volatility and reactivity of organic molecules to heal defects and create protective surface layers.⁶⁷ These strategies leverage the unique structural and chemical properties of small molecules, providing a multifaceted approach to optimizing perovskite-based devices and extending their applicability in fields like photovoltaics, LEDs, and photodetectors.

2.1. Additive engineering via supramolecular interactions

Incorporating organic molecules as additives in perovskite formulations has emerged as a pivotal strategy for improving film quality and device performance. Organic molecules with sulfate or amino groups act as Lewis bases due to their electron donor capability, forming coordination bonds with Pb^{2+} , a methylammonium ion (MA^+), or a formamidinium ion (FA^+) in the perovskite lattice. This interaction slows the crystallization process, enabling the growth of uniform and highly



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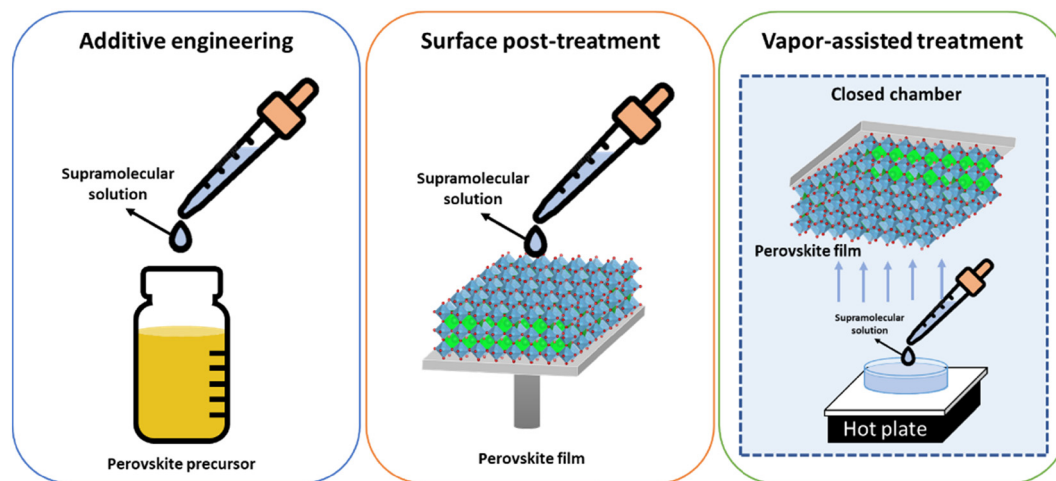


Fig. 2 Scheme of strategies to incorporate supramolecules into perovskites.

crystalline films with improved orientation and surface smoothness.⁶⁶ Short-chain molecules can integrate directly into the three-dimensional perovskite matrix, residing within grain boundaries or acting as organic spacers that facilitate the formation of two-dimensional or quasi-two-dimensional structures. These low-dimensional perovskite layers improve the stability and optoelectronic properties of the films, creating favorable heterostructures. On the other hand, long-chain molecules tend to localize at grain surfaces, where they play a crucial role in passivating surface defects. This passivation reduces charge recombination losses and enhances the overall efficiency of the device.⁶⁸ Furthermore, studies have shown that certain volatile molecules can be retained in perovskite films after the annealing process due to strong chemical interactions with the perovskite components. For example, urea, which has a boiling point of 130 °C, and thiourea, with a boiling point of 180 °C, can remain in the perovskite film during annealing and actively regulate its crystallization.^{69,70} In contrast, TAA, which is volatile at 100 °C, does not remain in the perovskite film after annealing.⁷¹ The dual role of supramolecules, as both crystal growth modulators and defect passivators, makes them indispensable in the pursuit of high-performance, durable perovskite films.⁷² Additionally, their molecular design flexibility enables tailored interactions with perovskites, allowing researchers to address specific challenges in film formation and device stability.

2.2. Surface post-treatment using supramolecular approaches

Surface post-treatment using supramolecular interactions offers a robust solution to address the inherent challenges in perovskite film stability and performance. Hybrid organic-inorganic perovskites are particularly prone to degradation due to their sensitivity to moisture and high density of surface defects, such as uncoordinated ions and halide vacancies. Applying a thin layer of molecules onto the perovskite surface helps mitigate these issues through multiple mechanisms. Hydrogen bonding, π - π interactions, and host-guest chemistry from molecules form a protective layer that shields perovskite grains from environmental moisture and reduces water

absorption energy.⁷³ This treatment also passivates under-coordinated ions and fills halide vacancies, suppressing non-radiative charge recombination pathways and stabilizing the operational performance of devices.⁷⁴ Furthermore, the organic molecule layer can induce the formation of low-dimensional perovskites, which act as insulating barriers to prevent ion diffusion and phase segregation. This is particularly beneficial in suppressing interactions between the perovskite layer and metal electrodes, which can otherwise lead to device degradation.⁷⁵ Molecular post-treatments also stabilize black-phase perovskites through π - π stacking-induced strain management, enhancing their structural integrity under operational conditions.⁷⁶ Another advantage is the improvement in interfacial energy-level alignment at the perovskite/charge transport layer interface, which facilitates more efficient charge extraction and transport.⁷⁷ Additionally, this approach can stimulate secondary crystal growth, heal pinholes, and optimize grain structures for better film quality. However, careful control of the amine layer thickness is crucial to avoid excessive interfacial resistance that could hinder charge transport. By addressing both surface defects and stability challenges, supramolecular surface post-treatment has become an essential tool in advancing the reliability and efficiency of perovskite optoelectronic devices.

2.3. Vapor-assisted supramolecular functionalization

Vapor-assisted treatment represents an innovative approach to harnessing supramolecular interactions for enhancing perovskite film quality and device performance. In this method, the volatility of organic molecules, such as methylamine (MA), *n*-butylamine (*n*-BA), acetic acid, *etc.* is utilized to treat perovskite films through vapor-phase exposure.^{78,79} This process eliminates pinholes, heals defects, and achieves highly uniform films with full surface coverage. By reacting with the perovskite surface during vapor annealing, these volatile molecules facilitate the self-assembly of low-dimensional perovskites or robust passivation layers. These layers play a dual role: they enhance the moisture resistance of the films by blocking pathways for

water ingress and suppress ion migration at critical interfaces, thereby improving the stability of the devices under operational conditions. The vapor-assisted approach is particularly advantageous for fabricating large-area perovskite films, which require high uniformity and defect-free surfaces for optimal performance.⁷⁹ Additionally, supramolecular interactions during the vapor treatment enhance film crystallinity and grain orientation, further improving the optoelectronic properties of the material.⁶⁷ The resulting perovskite films exhibit reduced non-radiative recombination, higher charge carrier mobility, and improved energy-level alignment at interfaces. Moreover, these treatments are versatile and can be adapted to different perovskite compositions, including FAPbI₃ and CsPbX₃ (X = I or Br).^{80,81} By leveraging the self-assembly and anchoring capabilities of specific ligands, this method offers a scalable and effective solution for producing high-performance, stable perovskite devices, addressing critical challenges in the commercialization of perovskite-based technologies.

3. Molecular interactions between perovskites and supramolecular agents

Supramolecular engineering is a powerful approach to enhancing the properties of hybrid organic–inorganic perovskites by introducing molecular agents that interact with perovskite components through non-covalent forces. These interactions can improve film morphology, stabilize structures, and influence charge carrier dynamics. This section delves into key supramolecular interactions including hydrogen bonding,^{58,82,83} π – π interactions,^{60,84,85} and host–guest chemistry^{86–88} (Fig. 3), and advanced tools for investigating interactions.

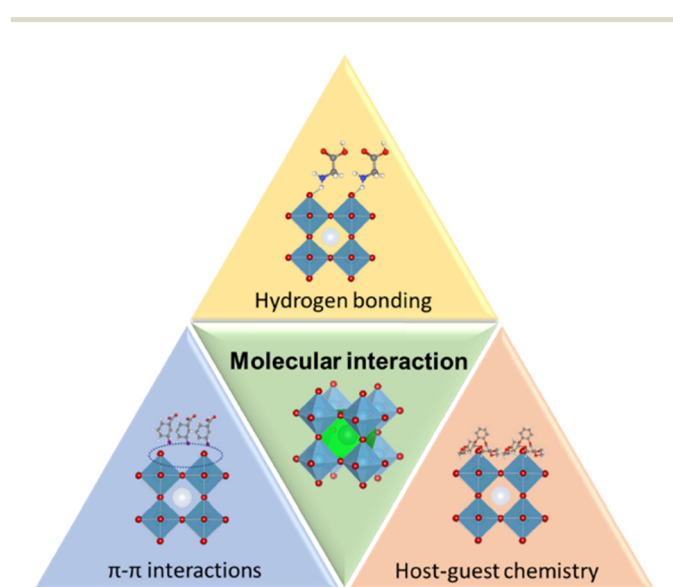


Fig. 3 The key types of supramolecular interactions between molecules and perovskites.

3.1. Hydrogen bonding effects on perovskite film formation

Hydrogen bonding is one of the most prominent and effective supramolecular interactions used to influence perovskite film formation and stability. In hybrid organic–inorganic perovskite materials, hydrogen bonds can form between organic cations (such as MA⁺ or FA⁺) and halide anions (I[−], Br[−], or Cl[−]).⁸⁹ Supramolecular agents with hydrogen-donating or -accepting functional groups can be introduced to enhance these bonds, impacting film crystallization and defect passivation. Bi *et al.* demonstrated a scalable and stable perovskite solar cell design using a multifunctional bifunctional 3-(5-mercapto-1H-tetrazol-1-yl)benzenaminium iodide (SN) (Fig. 4a), which passivates surface defects and directs the formation of large, high-quality grains in formamidinium-cesium mixed perovskites, achieving efficiency over 20% for large-area devices with remarkable ambient stability.⁸² Li *et al.* proposed a multifunctional fluorinated additive that enhances the crystallization and stability of mixed-halide perovskite films by suppressing intermediate phases, forming a hydrogen-bonded network (Fig. 4c), and providing hydrophobic protection, enabling unencapsulated solar cells to achieve 24.10% efficiency and prolonged durability under sunlight and humid conditions.⁹⁰ By encouraging large-grain morphology through hydrogen bonding, supramolecular agents help reduce non-radiative recombination pathways and increase charge-carrier mobility. Li *et al.* reported a multifunctional, non-volatile additive that enhances perovskite film quality by leveraging hydrogen-bond-bridged intermediate phases to promote large-grain growth, significantly boosting device efficiency (24.8%) and thermal stability while reducing non-radiative recombination and energy loss.⁹¹ Normally, amines help control the crystallization process, resulting in films with large grain sizes and fewer defects, while ammonium salts can passivate charged defects⁹² (Fig. 4d). Alanazi *et al.* also noted that the bifunctional molecule 5-ammonium valeric acid iodide (AVAI) stabilizes the α -phase of FAPbI₃ perovskites by forming hydrogen bonds *via* its NH₃⁺ group and dynamic hydrogen bonding *via* its COOH group (Fig. 4b), improving film morphology, prolonging charge carrier lifetimes, and achieving a PCE of 18.94% with high stability under continuous illumination for over 300 hours.⁵⁸ Overall, hydrogen bonding is a valuable mechanism to influence film morphology by affecting nucleation and growth processes during film formation leading to uniform films with fewer pinholes and defects, resulting in improved film quality and stability under ambient conditions.

3.2. π – π interactions in molecular assembly and film growth

π – π interactions, or stacking interactions between aromatic rings, are another type of non-covalent force that can influence the assembly and performance of perovskite films. Although perovskites themselves are not inherently aromatic, organic components or supramolecular additives with aromatic rings such as phenyl-based compounds,^{93–95} polythiophenes,⁹⁶ or porphyrins⁹⁷ can introduce π – π stacking into the system, creating ordered networks that improve film stability and charge transport.⁹⁸ π – π interactions have been shown to facilitate charge transport pathways, especially in layered perovskite

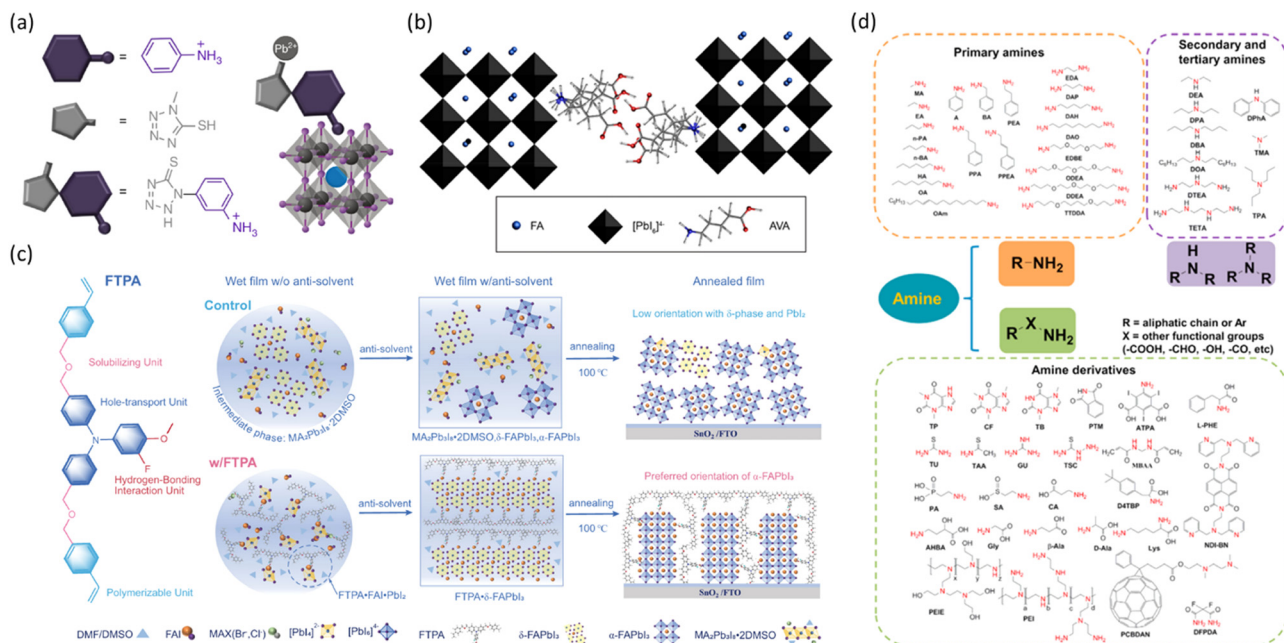


Fig. 4 Chemical structures of (a) 3-(5-mercapto-1H-tetrazol-1-yl)benzenaminium iodide. Reproduced with permission.⁸² Copyright 2018, Springer Nature; (b) 5-ammonium valeric acid iodide. Reproduced with permission.⁵⁸ Copyright 2019, American Chemical Society; (c) 3-fluoro-4-methoxy 4',4''-bis(4-vinyl benzyl ether) methyl triphenylamine and (d) amines and its interaction with perovskite. Reproduced with permission.^{90,92} Copyright 2023, Springer Nature and Copyright 2021, Elsevier Inc.

structures, where organic spacers enhance stability without compromising charge carrier mobility.⁹⁹ Hope *et al.* reported a mixed-spacer model using 2-phenylethylammonium (PEA⁺) and 2-(perfluorophenyl)ethylammonium (FEA⁺) in layered hybrid perovskites, which reveals nanoscale segregation, where π - π interactions within the hydrophobic spacer layer enhance crystallinity (Fig. 5a), leading to PSCs with over 21% efficiency and superior stability, outperforming systems using either spacer individually.¹⁰⁰ In particular, π - π interactions can aid in aligning organic cations within the perovskite matrix or assembling supramolecular agents at the perovskite interface to improve the thermal and environmental stability of perovskite films. Chen *et al.* incorporated a molecular bridging strategy using 2,4,6-tris(4-aminophenyl)-s-triazine (TAPT), which enhances perovskite solar cell efficiency and stability by leveraging π -interactions to tightly bind PTAA and the perovskite layer, passivate Pb²⁺ defects, reduce interfacial recombination, and create a pinhole-free interface (Fig. 5c), achieving a champion efficiency of 24.57% with remarkable thermal and operational stability.⁸⁴ Quiceno *et al.* reported that FAPbI₃ passivation with benzylamine provides superior moisture resistance and photovoltaic performance, while increasing the dipole of phenethylamine derivatives by fluorination enhances device efficiency.⁸⁵ Moreover, Kim *et al.* reported that a novel co-assembly process was developed, integrating chiral 2D perovskites with helical supramolecular structures formed from sulfonated porphyrins and stabilized by chiral ligands (R/S-MBA⁺). This approach leverages strong π - π interactions and ligand compatibility to create seamless perovskite-supramolecular assemblies. The co-assembly process promotes lattice distortion and transfers structural chirality from the helical supramolecular

assemblies to the perovskites, resulting in a multilevel amplification of chirality (Fig. 5b). This hierarchical interaction enhanced the anisotropy factor (g_{CD}) by 2.7-fold to 1.0×10^{-3} without spectral distortions.¹⁰¹ This work will hasten the development of sophisticated perovskite spin optoelectronics and offer a new tool for controlling the chiroptical behavior in perovskites. Recently, Fang *et al.* explored the integration of a redox-active supramolecular assembly of nickel octaethylporphyrin (NiOP) into perovskite films, in which supramolecular assembly serves dual functions: it acts as an immobilizer for volatile iodine produced by iodide oxidation and as a redox shuttle that regenerates impurities such as elemental lead and iodine. The modification of NiOP with ethyl groups distorts its π ring, enhancing the axial ligand adsorption capacity of the central metal ion and reducing intermolecular interactions. The adsorbed iodine transfers more electrons to the Ni ions, weakening the interactions within the I-I bond and promoting the generation of iodide ions. This structural modification facilitates iodine adsorption, achieving a maximum uptake of 3.83 mg mg⁻¹, while promoting the selective reduction of iodine and the oxidation of metallic lead defects to Pb²⁺. The NiOP supramolecule also improves hole transport across perovskite grain boundaries, leading to a champion device efficiency of 25.37%, surpassing the efficiency of the control device of 23.96%. Importantly, the modified devices exhibit significantly enhanced stability, maintaining over 90% of their initial performance after 1000 hours of continuous 1-sun illumination at 65 °C. These findings highlight the potential of NiOP integration in improving both the efficiency and the structural integrity of perovskite photovoltaics by mitigating defects, enhancing iodine adsorption, and facilitating defect repair *via* redox processes.¹⁰²

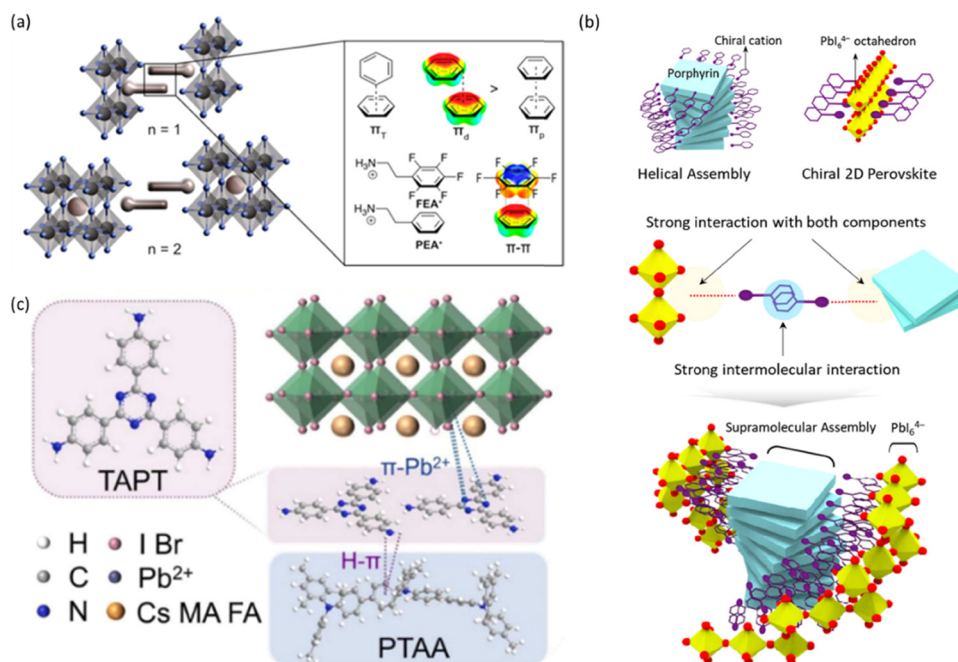


Fig. 5 Chemical structures and their interaction with perovskites of (a) 3-(5-mercapto-1H-tetrazol-1-yl)-2-phenylethylammonium (PEA⁺) and 2-(perfluorophenyl)ethylammonium (FEA⁺) benzenaminium iodide. Reproduced with permission.¹⁰⁰ Copyright 2021, American Chemical Society; (b) achiral sulfonated porphyrin (4,4',4'',4'''-(porphine-5,10,15,20-tetrayl)tetrakis(benzenesulfonic acid)). Reproduced with permission.¹⁰¹ Copyright 2024, American Chemical Society; and (c) 2,4,6-tris(4-aminophenyl)-s-triazine. Reproduced with permission.⁸⁴ Copyright 2023, Elsevier Ltd.

By forming a stable, ordered network at the molecular level, π - π interactions prevent undesirable molecular rearrangements that can lead to degradation under external stress. Thus, incorporating π - π interactions *via* supramolecular engineering enhances both the efficiency and resilience of hybrid perovskite-based optoelectronic devices.

3.3. Host-guest interactions for structural stability in perovskites

Host-guest chemistry, involving macrocyclic molecules like cyclodextrins,¹⁰³ cucurbiturils⁸⁷ and crown ethers,^{104,105} plays a unique role in stabilizing perovskite structures by encapsulating perovskite components or binding with specific ions. These host molecules possess a hollow, cage-like structure that can enclose “guest” molecules or ions through non-covalent interactions, thereby protecting them from environmental exposure.

Cyclodextrins are cyclic oligosaccharides with a hydrophobic interior and a hydrophilic exterior which are added to perovskite solutions to encapsulate organic cations such as methylammonium or formamidinium ions, stabilizing them against moisture and preventing them from interacting with oxygen or water molecules. Ferdowsi *et al.* introduced β -cyclodextrin (β -CD) (Fig. 6a) into triple cation perovskites to enhance crystal uniformity, passivate Pb²⁺ defects, prevent residual PbI₂ and manipulate crystallization, achieving a PCE of 21.36% and exceptional stability against thermal stress and humidity, significantly outperforming β -CD-free controls.¹⁰⁶ In addition, a supramolecular mercapto- β -cyclodextrin (SH- β -CD) (Fig. 6a) functionalization strategy was developed to systematically tune the optical properties of CsPbBr₃

nanocrystals, achieving fluorescence adjustable between 405 and 510 nm with quantum yields of 50–90%, driven by synergistic effects of the SH- β -CD cavities and hydrosulfuryl groups causing a blue shift, reversible in the presence of guest molecules.¹⁰⁷

Cucurbiturils form strong host-guest complexes with specific ions¹⁰⁸ and can be used to trap perovskite components within their cavities (Fig. 6b). These interactions not only prevent ion migration within the perovskite lattice but also reduce the likelihood of phase segregation in mixed-halide perovskites. Liu *et al.* proposed a multifunctional cucurbituril additive that enhances perovskite film quality by coordinating with dangling Pb²⁺ ions and creating an electric dipole field to suppress halide segregation, achieving a CsPbI₂Br solar cell efficiency of 15.59% with improved environmental stability.⁸⁷

Crown ethers form selective complexes with cations, such as Pb²⁺ or Cs⁺ (Fig. 6c), which regulate ion availability during crystallization, promoting uniform nucleation and growth, resulting in enhanced film morphology with larger grains and fewer defects.^{63,109,110} Additionally, crown ethers effectively passivate surface defects by coordinating with unbound ions, thereby reducing non-radiative recombination and improving the optoelectronic properties of the perovskite films.⁶⁵ Yang *et al.* proved that 1-aza-15-crown-5 (A15C5) with stronger interaction with Pb²⁺ exhibited improved morphology, reduced defect densities, and better energy-level alignment of perovskites compared to those using native crown ethers.⁸⁸ The strong affinity of B18C6 as an additive to enhance the crystallization process of wide-bandgap perovskites for metal cations like Cs⁺ and Pb²⁺ delays the precipitation of cesium salts, leading to

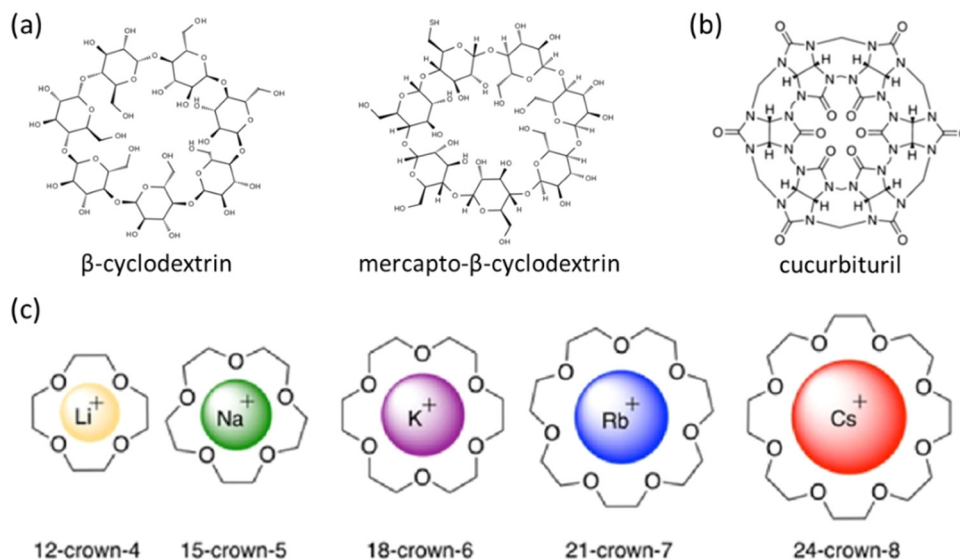


Fig. 6 Chemical structures of (a) cyclodextrins, (b) cucurbiturils and (c) crown ethers with metal complexes. Reproduced with permission.⁸⁶ Copyright 2021, IOP Publishing Ltd.

controlled crystallization, enlarged grain sizes, and elimination of lateral grain boundaries. Additionally, B18C6 induces a pronounced (110) crystal orientation, improving conductivity and carrier mobility.¹¹¹ Their ability to form protective layers also imparts resistance to environmental stressors like moisture and oxygen, contributing to the long-term stability of perovskite-based devices. This makes crown ethers valuable additives in applications such as solar cells,^{63,105,112,113} LEDs,¹¹⁴ and sensing devices,¹¹⁵ where they enhance efficiency and operational durability.

Overall, host-guest interactions *via* cyclodextrins, cucurbiturils, and crown ethers offer a promising approach for enhancing the structural stability and chemical robustness of perovskite materials, facilitating their application in demanding environments.

These supramolecular agents demonstrate that strategic molecular interactions can lead to more robust and efficient perovskite-based devices. The versatility of supramolecular chemistry provides a range of solutions for addressing stability, efficiency, and environmental resilience, pushing perovskite optoelectronics closer to practical applications. These reports (summarized in Table 1) demonstrate the versatility of this supramolecular approach, promising the advancement of hybrid perovskite optoelectronics in the future.

3.4. Computational insights into supramolecular engineering

Density functional theory (DFT) simulations are widely used to theoretically investigate the influence of supramolecular engineering on the properties and performance of hybrid perovskite materials in optoelectronic applications. DFT allows for a detailed understanding of the electronic structure, charge distribution, and intermolecular interactions within perovskite systems, providing valuable insights into how supramolecular interactions can modify their optoelectronic behavior. For instance, when considering the incorporation of organic molecules or ligands into the perovskite structure, DFT can predict how these

molecules interact with the perovskite's inorganic framework through non-covalent forces, such as hydrogen bonding, van der Waals interactions, or π - π stacking. These interactions can stabilize the perovskite structure, enhance charge transfer, and reduce defects at the interfaces. Gao *et al.* conducted first-principles DFT calculations to analyze the interaction of 15-crown-5 ether (15C5) with perovskite surfaces, focusing on specific lattice planes, defect passivation, and energy stabilization. Using a simplified $FAPbI_3$ perovskite model, the binding energies of 15C5 on both Pb-terminated and FA-terminated surfaces were evaluated. The results showed that 15C5 strongly binds to Pb-terminated surfaces (2.05–1.87 eV) *via* metal-organic coordination, while hydrogen bonding interactions with FA-terminated surfaces were much weaker (0.16–0.11 eV). Additionally, the role of 15C5 in defect passivation was investigated by calculating the formation energies of key defects, including iodine vacancies (V_I), Pb-I antisites (PbI), FA-I antisites (FAI), and FA vacancies (V_{FA}). Upon 15C5 adsorption, defect formation energies significantly increased from 0.39, 1.34, 1.38, and 2.73 eV to 13.09, 3.24, 1.50, and 5.99 eV, respectively, indicating a much lower probability of defect formation. These results suggest that 15C5 effectively passivates surface and grain boundary defects through supramolecular interactions, including metal-organic coordination and hydrogen bonding.⁶³

Through DFT, one can also evaluate how the presence of supramolecular units alters the electronic band structure, charge carrier mobility, and recombination dynamics within the material. For example, the introduction of specific organic ligands can influence the alignment of the perovskite's valence and conduction bands, improving charge injection and reducing energy loss at the interface between the perovskite and transport layers. Sui *et al.* elucidated the passivation mechanism of various 18-crown-6 (18C6) derivatives on $FAPbI_3(001)$ perovskite surfaces by DFT calculations. The binding energies follow the trend: *t*-bu-DB18C6@ $FAPbI_3$ (2.1 eV) > DB18C6@ $FAPbI_3$ (1.8 eV) > N-B18C6@ $FAPbI_3$ (1.6 eV) > 18C6@ $FAPbI_3$ (0.9 eV), indicating

Table 1 Summary of the supramolecular interactions in hybrid perovskite optoelectronics reported to date

Supramolecular interaction	Supramolecular agents	Perovskite composition	Strategy & effects	Ref.
Hydrogen bonding	Guaninium (G)	FAPbI ₃	A dimensional hybrid perovskite material comprising guaninium (G) 83 organic spacer layers that act as stabilizers of the three-dimensional α -FAPbI ₃ phase.	
	5-Ammonium valeric acid iodide (AVAI)	FAPbI ₃	AVAI stabilizes FAPbI ₃ against the detrimental α -to- δ phase transition 58 <i>via</i> hydrogen bonding on the atomic level, yielding crystalline films with large grains and improved charge-carrier lifetimes.	
	Ammonium-group (-NH ₃ ⁺)-containing modulator N + thiol- functionalized (-SH) modulator S	FA _{0.9} Cs _{0.1} PbI ₃	A bifunctional modulator SN passivates surface defects and directly 82 induces the formation of large and high-quality grain crystals in thermally stable FA _{0.9} Cs _{0.1} PbI ₃ perovskites.	
	-CN, -OH, or -COOH moiety	(CN-EA) ₂ (MA) ₃ Pb ₄ I ₁₃	Bifunctional ligands that are capable of making strong hydrogen 116 bonds within the organic bilayer enhance Pb-I-Pb angle stability, reduce band gap, boost in-plane mobility, and improve 2D hybrid perovskite.	
	3-Fluoro-4-methoxy 4',4''-bis((4-vinyl benzyl ether) methyl) triphenylamine (FTPA)	FA _{0.95} MA _{0.05} Pb(I _{0.95} Br _{0.05}) ₃	Fluorinated additive promotes α -FAPbI ₃ crystallization and stabilizes 90 the phase with a polymerized hydrogen-bonding network, achieving a prominent efficiency improvement and excellent water and humidity stability in unencapsulated devices.	
	π - π interactions 2, 4, 6-Tris(4-aminophenyl)-s-triazine (TAPT)	(FA _{0.98} MA _{0.02}) _{0.95} Cs _{0.05} Pb(I _{0.95} Br _{0.05}) ₃	TAPT produces H- π bond with the benzene ring in PTAA, enhances 84 binding, passivates Pb ²⁺ defects by forming π -Pb ²⁺ bonds, fixes fractures, and improves carrier transport, reducing nonradiative recombination.	
	Monoamine porphyrins (MPs, M = Co, Ni, Cu, Zn and H)	Cs _{0.05} Rb _{0.05} (FA _{0.83} MA _{0.17}) _{0.90} Pb(I _{0.95} Br _{0.05}) ₃	MPs self-assemble at grain boundaries, forming supramolecular 97 ammonium porphyrins that passivate defects, enhance hole transport, and boost PSC efficiency and stability.	
	Alkylthiophene-substituted-polythiophenes (PT4T-0F and PT4T-2F)	FA _{0.83} Cs _{0.17} Pb(I _{0.7} Br _{0.3}) ₃	Fluorinated PT4T-2F provided F...S intramolecular interactions that 96 enhances perovskite (100) orientation, passivates defects, and boosts hole mobility, achieving 19.20% efficiency and improved stability in WBG PSCs.	
	2-Phenylethylammonium (PEA ⁺) and 2-(perfluorophenyl)ethylammonium (FEA ⁺) moieties	(Cs _{0.05} FA _{0.9} MA _{0.1})(PbI ₃) _{1.05}	NMR crystallography reveals that PEA ⁺ and FEA ⁺ moieties enable 100 nanoscale phase segregation in mixed-spacer layered perovskites, achieving > 21% efficiency and improved stability in PSCs.	
	Phenylmethylethylammonium iodide (PMAI), phenethylammonium iodide (PEAI), phenylpropylammonium iodide (PPAI), and phenylbutylammonium iodide (PBAI)	FA _{0.83} Cs _{0.17} PbI ₃	Phenylalkylammonium iodides varying the alkyl chain length, especially PPAI, stabilize perovskite films by suppressing iodide migration, 94 achieving 17.5% EQE and record T50 of 130 hours.	
	<i>ortho</i> -, <i>meta</i> - and <i>para</i> -isomers of (phenylene)di(ethylammonium) iodide (PDEAI ₂)	Cs ₃ FA ₃ MA _{1-x-y} PbI ₂ Br _{3-z}	Sterically hindered <i>o</i> -PDEAI ₂ prevents 2D perovskite formation and 93 enhances defect passivation, achieving 23.9% PSC efficiency and > 1000 h stability.	

Table 1 (continued)

Supramolecular interaction	Supramolecular agents	Perovskite composition	Strategy & effects	Ref.
Host-guest interactions	Beta-cyclodextrin (β -CD)	$\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$	β -CD into perovskite prevents the crystallization of residual PbI_2 , resulting in uniform crystal growth and the passivation of under-coordinated Pb^{2+} defects. The treated device shows an improved PCE of 21.36%, surpassing the control, and enhanced stability against aggressive thermal stress and high humidity (85% RH).	106
	Protectant-mediated mercapto- β -cyclodextrin (SH- β -CD)	CsPbBr_3	SH- β -CD enables host-guest interaction with CsPbBr_3 NCs, tuning fluorescence (405–510 nm) at 50–90% QY, enhancing optical stability for advanced optoelectronics.	107
	15-Crown-5 (15C5)	$\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$	Crown ether supramolecular interactions form a 2D crystalline capping layer, passivating defects and enhancing PSC efficiency (21.5%) and stability against moisture, UV, and heat.	63
	2-Methoxyethanol and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6)	FACsPbI_3	Crown ether tailoring stabilizes FACsPbI_3 films, prevents phase transition, enhances moisture resistance, and enables scalable PSCs with 20.48% efficiency and robust stability.	109
	Dibenzo-21-crown-7 (DB21C7)	$\text{FA}_{0.97}\text{MA}_{0.03}\text{PbI}_{2.97}\text{Br}_{0.03}$	Crown ether modulation reduces the trap state density at the absorber/hole transporting material interface, thus greatly suppressing solar cell performance losses due to nonradiative recombination by 40% and the PCE of devices increases from around 19% to over 23% with lower hysteresis.	65
	Dibenzo-21-crown-7 (DB21C7)	FAPbI_3	Cs^+ is delivered into FAPbI_3 perovskites using DB21C7 to stabilize the α - FAPbI_3 , increase the PCE from roughly 20% to over 24%, improve operational stabilities for more than 500 hours, and decrease Pb leakage when submerged in water.	117
	Dibenzo-21-crown-7 (DB21C7)	MAPbBr_3	DB21C7 forms a host-guest complexation with MAPbBr_3 to control interfacial ion migration, resulting in a PCE of up to 5.9% with a V_{oc} as high as 1.5 V, which is accompanied by stability over 300 h at 85 °C under N_2 .	110

that the presence of benzene rings enhances Pb–O coordination, strengthening the molecular interaction. Edge-on adsorption was found to be the dominant configuration. While *t*-bu-DB18C6 exhibits the highest binding energy, DB18C6 provides the best defect passivation, as *t*-bu-DB18C6 introduces trap states in the bandgap. Electronic structure calculations reveal that DB18C6 passivation increases the perovskite bandgap from 1.31 eV to 1.40 eV, reducing shallow trap states and improving charge transport. In contrast, N-B18C6 and *t*-bu-DB18C6 lower the bandgap to 0.61 eV and 1.25 eV, respectively, due to their higher HOMO levels. Notably, DB18C6 enhances interfacial electronic transport by facilitating the delocalization of the valence band maximum (VBM) and hybridizing with the perovskite electronic states. Furthermore, DB18C6 significantly suppresses ion migration by increasing the activation energy barriers (ΔE_a) for Pb and FA migration from 0.95 eV to 1.31 eV (Pb) and 0.68 eV to 0.87 eV (FA). This stabilization effect reduces ion migration, aligning with experimental findings. Overall, DB18C6 emerges as the optimal passivating agent for perovskite/ETL interfaces, owing to its strong Pb–O coordination, defect suppression, and enhanced charge transport properties.¹⁰⁵

Additionally, DFT simulations can be used to assess the stability of hybrid perovskites under various environmental conditions, such as moisture, temperature, and UV exposure, by modeling how supramolecular interactions shield the perovskite from degradation. Wang *et al.* employed DFT simulations to elucidate the interfacial role of halide-terminated polar silanes, specifically chloropropyltrimethoxysilane (CPTMS), in defect passivation and energy-level alignment in perovskite materials. DFT calculations reveal that CPTMS introduces a strong molecular dipole at the perovskite interface, effectively modulating the surface potential and aligning energy levels for improved charge carrier transport. Additionally, the simulations demonstrate that the halide-terminated functional groups interact with under-coordinated Pb²⁺ ions, reducing deep-level trap states and suppressing non-radiative recombination. The theoretical insights support experimental findings, confirming that CPTMS plays a crucial role in defect passivation, thereby enhancing both device efficiency and operational stability.¹¹⁸

Thus, DFT-based calculations play a crucial role in predicting and designing the optimal supramolecular modifications needed to advance the performance and reliability of hybrid perovskite optoelectronics.

3.5. Advanced characterization techniques in supramolecular engineering

Understanding the complex supramolecular interactions within perovskite films requires advanced characterization techniques that can probe molecular-level details. One of the most insightful methods for investigating these interactions is solid-state Nuclear Magnetic Resonance (NMR) spectroscopy, which provides information about the local chemical environments within the material. Solid-state NMR offers a unique advantage in identifying and characterizing the types of bonding interactions that occur between supramolecular agents and perovskite materials.^{119–121} For example, solid-state NMR can reveal hydrogen-bonding interactions by analyzing chemical shifts

in proton (¹H)¹²² and nitrogen (¹⁴N)¹²³ spectra, which are sensitive to the electronic environments of bonded atoms. When supramolecular agents form hydrogen bonds with perovskite precursors, characteristic shifts in the NMR spectra indicate the strength and geometry of these interactions which influences crystallization rates, allowing for controlled growth of larger, well-ordered perovskite grains. Alanazi *et al.* explored the structural and dynamic characteristics of AVAI and its interaction with PbI₂ and α -FAPbI₃, revealing complex formation and significant impacts on perovskite properties. NMR analysis shows that AVAI forms distinct carbonyl environments and reacts fully with PbI₂, indicating the potential for forming recombinant polytypes rather than a simple Ruddlesden–Popper phase. In α -FAPbI₃ doped with AVAI, AVAI alters the cuboctahedral symmetry towards a more cubic structure, as evidenced by ¹⁴N MAS NMR. Dynamic atomic-level interactions between AVAI and FA are confirmed through ¹H–¹H spin diffusion NMR, excluding hollow perovskite formation due to an unchanged band gap. Structural dynamics, including AVAI reorientations, influence hydrogen bonding and perovskite stabilization, highlighting AVAI's role in tailoring the perovskite microstructure and symmetry. Computational simulations complement these findings by modeling hydrogen bonding and AVAI's integration into the inorganic sublattice, emphasizing its structural and electronic effects (Fig. 7a).⁵⁸

Additionally, solid-state NMR can differentiate between weak π – π interactions and stronger coordination bonds by analyzing variations in carbon (¹³C)¹²⁴ and lead (²⁰⁷Pb)^{125,126} spectra, respectively. The π – π interactions between aromatic supramolecular agents and perovskite layers improve film uniformity and enhance carrier mobility by creating ordered pathways for charge transport. Hope *et al.* reported that using solid-state NMR spectroscopy, complemented by MD simulations and DFT calculations, was used for the analysis of PEA⁺ and FEA⁺ moieties in layered hybrid perovskites, which reveals that these spacers exhibit nanoscale phase segregation due to their preferences for twisted (PEA⁺) and parallel (FEA⁺) π -stacking, with chemical shifts in NMR confirming the segregated structural model, which aligns closely with experimental data and enhances material properties. NMR crystallography reveals the nanoscale phase segregation in layered hybrid perovskites with mixed spacers (PEA⁺ and FEA⁺), highlighting the critical role of π – π interactions in achieving over 21% efficiency and enhanced stability in PSCs (Fig. 7b).¹⁰⁰

Solid-state NMR is also instrumental in studying host–guest chemistry, such as the encapsulation of perovskite quantum dots by cyclodextrins or cucurbiturils, as it enables researchers to observe changes in spectral patterns when host molecules interact with perovskite ions. Veldhuis *et al.* demonstrated the use of dibenzo-21-crown-[7] (DB21C7) to synthesize CsPbBr₃ nanocrystals at low temperatures, addressing the poor solubility of Cs precursor salts in polar solvents. The study employed host–guest complexation between DB21C7 and Cs ions to overcome this solubility limitation, facilitating the dissolution of CsBr in *N,N*-dimethylformamide (DMF) and enabling the synthesis of core–shell quantum dots at reduced temperatures. The inclusion of DB21C7 increased the solubility of CsBr by a

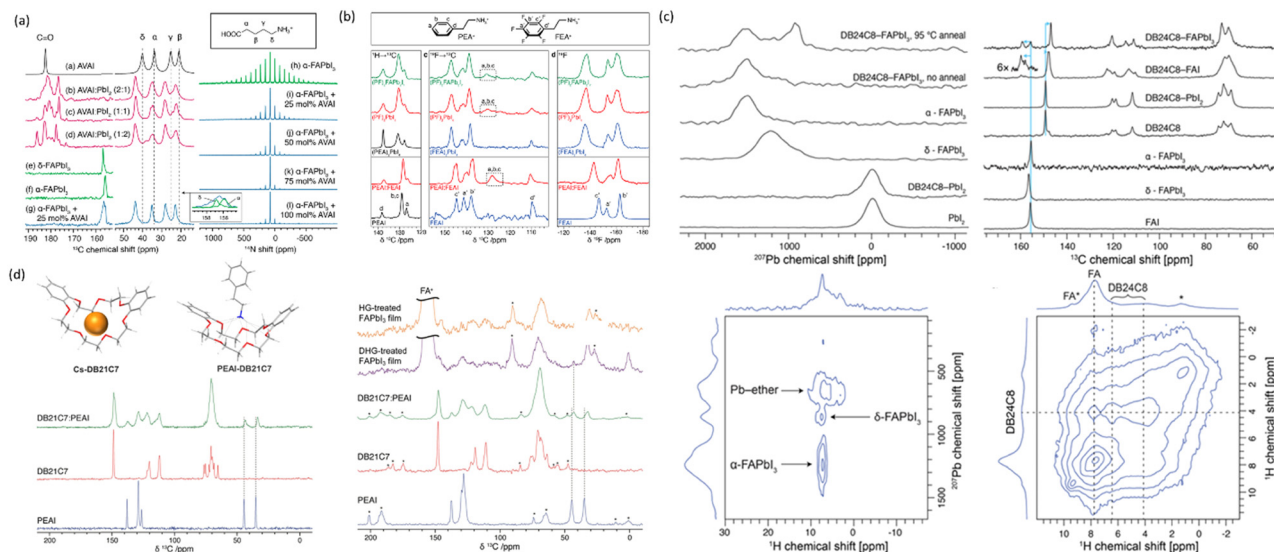


Fig. 7 Solid-state NMR characterization of the bulk mechanochemical materials. (a) FAPbI_3 and different ratio of $\text{AVAI}:\text{PbI}_2$ in ^1H - ^{13}C CP spectra at 21.1 T, 298 K, and 20 kHz AVAI and 14N NMR spectra at 21.1 T, 298 K, and 5 kHz. Reproduced with permission.⁵⁸ Copyright 2019, American Chemical Society. (b) Structures of PEA^+ and FEA^+ cations with the corresponding ^{13}C and ^{19}F sites labeled, $^1\text{H} \rightarrow ^{13}\text{C}$ CP, $^{19}\text{F} \rightarrow ^{13}\text{C}$ CP, and direct ^{19}F NMR spectra. Reproduced with permission.¹⁰⁰ Copyright 2021, American Chemical Society. (c) ^{207}Pb echo and $^1\text{H} \rightarrow ^{13}\text{C}$ CP NMR spectra of FAI , PbI_2 , and FAPbI_3 , with and without ball-milling with DB24C8 crown ether, recorded at 15 kHz MAS; $^{207}\text{Pb} \rightarrow ^1\text{H}$ HETCOR spectrum of DB24C8-FAPbI_3 recorded at 113 K and 30 kHz MAS; and ^1H - ^1H spin diffusion spectrum of DB24C8-FAPbI_3 , recorded at 40 kHz MAS with a mixing time of 10 ms. Reproduced with permission.⁶⁵ Copyright 2020, American Chemical Society. (d) The spatial interaction between the host molecule (DB21C7) and guest I (Cs^+) or guest II (PEA^+); $^1\text{H} \rightarrow ^{13}\text{C}$ NMR spectra of PEAI , DB21C7 , and a ball-milled 1:1 mixture of the two, as well as scraped thin films of FAPbI_3 with host-guest treatment, or dual host-guest treatment; spectra recorded at room temperature and 22 kHz MAS, and at 100 K and 8 kHz MAS. Reproduced with permission.⁵⁵ Copyright 2024, Springer Nature.

factor of four compared to systems without them. The formation of the DB21C7-Cs complex was confirmed through ^1H NMR spectroscopy, underscoring the potential of this approach for optoelectronic applications, such as LEDs.¹²⁷ For host-guest chemistry in perovskite films, Su *et al.* investigated the interactions of dibenzo-24-crown-8 (DB24C8) with FA^+ and Pb^{2+} in perovskites, demonstrating the formation of a DB24C8-FAI complex, as evidenced by NMR and X-ray diffraction (XRD) analyses, while DB24C8 does not complex with PbI_2 due to its high lattice energy. Interaction with FAPbI_3 reveals the formation of a mixed perovskite- DB24C8 phase, supported by atomic proximity between FA^+ , Pb^{2+} (Fig. 7c), and the crown ether, alongside structural modifications and polymorphic variations observed in XRD patterns.⁶⁵ Zhao *et al.* investigated the interaction between PEA^+ and DB21C7 in perovskite systems using solid-state NMR and XRD techniques. Solid-state NMR reveals broadening and shifts in ^{13}C resonances, indicating PEA^+ -ether interactions and reduced crystallinity in DB21C7:PEAI mixtures, with evidence of PEA^+ complexation in dual host-guest-treated FAPbI_3 films (Fig. 7d). XRD analysis confirms the preservation of the 3D perovskite's α -phase across all treatments, with host-guest and dual host-guest films showing enhanced crystallinity and slight lattice contraction due to Cs^+ doping. These findings suggest that DB21C7 mediates cooperative supramolecular interactions, modifying ammonium salt environments and promoting secondary crystal growth, which enhances the structural and optoelectronic properties of treated perovskite films.⁵⁵

The data obtained from solid-state NMR and other advanced techniques, such as XRD and scanning electron microscopy

(SEM), help elucidate the role of supramolecular interactions in modifying the optoelectronic properties of perovskite films. Layered Dion-Jacobson hybrid perovskites assembled with arene (PDMA) and perfluoroarene (F-PDMA) spacers exhibit nanoscale phase segregation and enhanced stability in humid environments, as confirmed by X-ray diffraction, UV-vis, photoluminescence, and solid-state NMR, highlighting their potential for advanced applications.¹²⁸

Additionally, supramolecular interactions facilitate defect passivation by binding to unsaturated lead or halide sites, effectively reducing non-radiative recombination centers that hinder device efficiency. The resulting improvements in film morphology, reduced defect density, and enhanced environmental resilience underscore the significant impact of supramolecular engineering on the performance and durability of optoelectronic devices. Supramolecular engineering, complemented by advanced characterization methods like solid-state NMR, is pivotal in advancing perovskite optoelectronics. These tools offer a molecular-level understanding of how tailored interactions can improve stability, efficiency, and longevity, providing valuable insights for the development of next-generation devices.

4. Supramolecular engineering in perovskite crystallization and film formation

Crystallization is a pivotal process in the formation of high-quality perovskite films, as it directly impacts the film

morphology, defect density, and ultimately, device efficiency and stability.^{129,130} Supramolecular engineering provides an approach to control crystallization at the molecular level by introducing agents that modify crystal growth rates, grain size, and orientation.¹³¹ Here, we explore how supramolecular agents influence the crystallization mechanisms of perovskite films and highlight the key analytical techniques.

4.1. Influence of supramolecular agents on crystallization kinetics

Supramolecular agents influence crystallization kinetics by modulating nucleation and crystal growth rates, which are crucial in determining the final structure and quality of perovskite films. These agents interact with perovskite precursors through non-covalent forces such as hydrogen bonding,^{82,90} van der Waals forces,¹³² π - π interactions^{93–96} and host-guest interactions^{85,107} that either promote or inhibit crystal formation. By carefully selecting the type and concentration of supramolecular agents, researchers can control the growth process to achieve uniform films with large and well-oriented crystals. In perovskite film formation, the rate of nucleation and growth often competes; high nucleation rates lead to smaller, polycrystalline grains, while slower nucleation can yield larger grains with fewer grain boundaries.^{133–135} These controlled crystallization kinetics are essential because they determine not only the film's microstructure but also its stability and optoelectronic properties.

By optimizing crystallization kinetics, supramolecular agents help mitigate the formation of defect sites that serve as traps for charge carriers, leading to improved device efficiency.¹³⁶

Supramolecular agents such as urea derivatives, thiols, and other hydrogen-bonding molecules interact with the ions in the precursor solution to modulate these rates, thereby influencing the kinetics of the crystallization process by slowing down crystal growth.¹³⁷ This slow growth process allows for the formation of larger, more ordered grains with fewer grain boundaries, which is beneficial for enhancing the efficiency and stability of perovskite-based devices. Yong *et al.* reported the effect of the 3-mercaptopbenzoic acid (3-MBA) additive on perovskite film morphology. The suppression of residual PbI_2 can be attributed to the slower crystallization rate induced by 3-MBA, allowing the grain crystals to more effectively consume adjacent PbI_2 during maturation (Fig. 8a).¹³⁸ In another study, the hydrogen-bonded polymer network formed by the fluorinated additive 3-fluoro-4-methoxy 4',4''-bis((4-vinyl benzyl ether) methyl) triphenylamine (FTPA) significantly influences the lattice arrangement of perovskite films. FTPA interacts with formamidinium (FA^+) ions and lead-halide (PbI_2) precursors through strong hydrogen bonding, stabilizing intermediate phases and facilitating the oriented growth of the α -FAPbI₃ phase. This interaction suppresses disordered nucleation and intermediate phases such as δ -FAPbI₃, allowing the controlled and directional crystallization of perovskite layers. As a result, the films exhibit high-quality, well-aligned

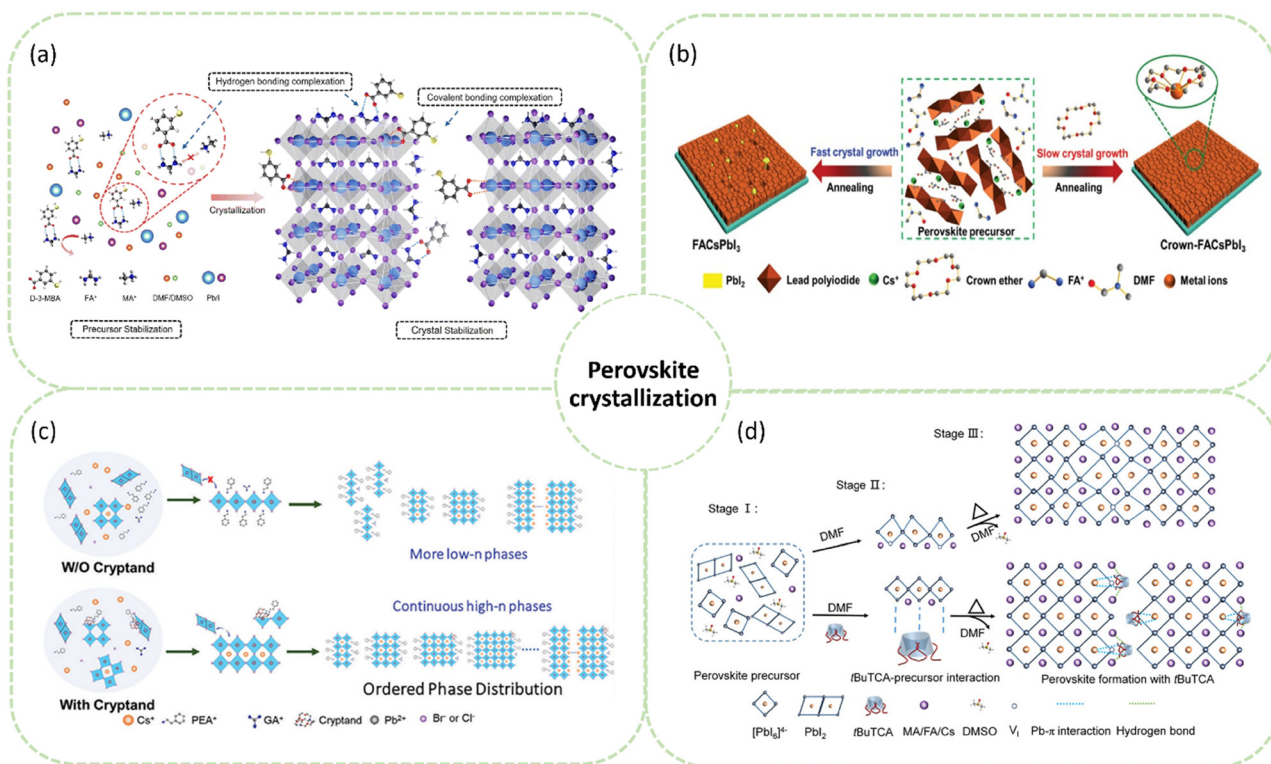


Fig. 8 Schematic illustration of the growth mechanism on perovskite formation. (a) D-3-MBA-mediated complexation. Reproduced with permission.¹³⁸ Copyright 2024, The Royal Society of Chemistry. (b) Without and with crown ether tailoring. Reproduced with permission.¹⁰⁹ Copyright 2020, Wiley-VCH GmbH. (c) Without and with cryptand additive. Reproduced with permission.¹⁴⁰ Copyright 2024, Wiley-VCH GmbH. (d) With tBuTCA additive. Reproduced with permission.¹⁴¹ Copyright 2023, Wiley-VCH GmbH.

crystal orientations, reduced defects, and improved stability, leading to enhanced optoelectronic properties.⁹⁰ The crystallization and lattice orientation of 2D perovskites, such as $(\text{PEA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ and $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, are strongly influenced by nucleation sites and growth conditions, with vertical stacking essential for efficient charge transport-favored under low supersaturation, heterogeneous nucleation at liquid-air interfaces, and controlled growth to prevent random orientations or horizontal alignment dominated by van der Waals interactions.¹³² The PEA^+ and FEA^+ moieties influence the lattice arrangement and crystallization of 2D perovskites by forming nanoscale phase-segregated domains due to their differing preferences for twisted (PEA^+) and parallel (FEA^+) aromatic stacking, enhancing material stability and photovoltaic performance through synergistic effects in mixed-spacer systems.¹⁰⁰ The β -diketone-based ligand tris(2-pyridylmethyl)-amine (TPMA) significantly influences the lattice arrangement and crystallization of Pb-Sn perovskite films. By coordinating with Pb^{2+} and Sn^{2+} ions, TPMA slows the crystallization rate, leading to uniform, pinhole-free films with reduced defect states. It effectively suppresses the migration of Pb^{2+} and prevents Sn^{2+} oxidation, minimizing the presence of detrimental Pb^0 and Sn^{4+} . These effects result in enhanced lattice stability, improved film quality, and reduced defect density, yielding PSCs with a high PCE of 20.68%, excellent long-term thermal stability, and enhanced durability under heat and storage conditions.¹³⁹ Perovskite formation could be regarded as the reaction between AX and BX_2 . Huang *et al.* also reported that hexafluorobenzene (HFB) as an F-containing additive regulates perovskite film growth by leveraging strong interactions with FAI to delay its reaction with PbI_2 (as the AX retardants), suppressing δ -FAPbI₃ formation and intermediate phases, while dual-site regulation through anion- π interactions improves phase purity and component uniformity in α -FAPbI₃.⁵⁷ By slowing down crystallization, hydrogen-bonding agents allow for better control over film morphology. Larger, well-ordered grains with reduced defect density enhance charge transport and reduce recombination losses, which are essential for improving the performance of perovskite optoelectronic devices.¹³⁷

In addition, macrocyclic compounds such as crown ethers and calixarenes have shown promising potential for directing crystal orientation and size in perovskite films. These compounds interact with specific ions in the perovskite precursor, influencing the orientation of crystal growth and enhancing film stability. 15-Crown-5 (15C5) influences perovskite lattice arrangement by coordinating with lead-halide octahedrons to form 1D frameworks *via* face-sharing, which subsequently combine with organic cations to create 2D assemblies through inorganic-organic bridges. These assemblies, stabilized by crown ether-hydrated proton interactions, evolve into layered 2D crystals *via* charge compensation. This process initiates controlled crystallization on 3D perovskite layers, optimizing their structural and electronic properties while suppressing defects, thus enhancing photovoltaic performance (PCE of 21.5%) and stability.⁶³ Moreover, it has been reported that 18-crown-6 ethers (18C6) were incorporated in the precursor to enhance the crystallization and prevent moisture invasion

during perovskite growth (Fig. 8b).^{109,142,143} Recently, Lin *et al.* employed benzo-18-crown-6 (B18C6) to regulate the crystallization process of wide-bandgap perovskites. The strong affinity of B18C6 for metal cations suppressed the rapid precipitation of cesium salts and delayed the crystallization process during perovskite deposition, eliminating large grains and transverse grain boundaries. Moreover, the B18C6-treated perovskite films exhibited a pronounced (110) orientation, resulting in higher conductivity and mobility. The improved charge transport performance within the perovskite significantly enhanced the FF of the fabricated PSCs by 3%. Combined with the passivation of non-coordinated Pb^{2+} defects, the champion wide-bandgap (1.68 eV) PSC with an n-i-p architecture achieved a high FF of 83%, a V_{OC} of 1.21 V, and a PCE of 20.6%. Simultaneously, the device exhibited enhanced long-term stability, retaining 99.6% of its initial PCE after 1080 hours of storage in the air without encapsulation. This work presents a novel strategy for further improving the performance of wide-bandgap perovskites and perovskite-based tandem devices.¹¹¹ The incorporation of D18C6 into lead-free CsCu_2I_3 films significantly impacts lattice arrangement and crystallization. D18C6 enhances crystal connectivity through strong complexation interactions with Cs^+ and Cu^+ cations, facilitated by complementary electrostatic interactions and π -cation conjugation. This reduces grain boundaries, eliminates cracks, and achieves a smoother, more uniform film with decreased root-mean-square roughness from 5.06 nm to 2.95 nm. D18C6 also passivates defects associated with uncoordinated cations, decreasing non-radiative recombination and increasing photoluminescence quantum yield (PLQY) and recombination lifetime. These effects lead to improved optoelectronic performance, including enhanced PeLED luminance (583 cd m^{-2}) and external quantum efficiency (0.662%). This demonstrates the potential of D18C6 in advancing Cu-based perovskite optoelectronics.¹¹⁴ Xiang *et al.* introduced 12-crown-4 ether (12C4) into quasi-2D perovskite $(\text{PEA}_2\text{Cs}_{n-1}\text{Pb}_n\text{Br}_{3n+1})$ effectively modulates the crystallization process, resulting in high-quality films with thicker PbBr_4 layers ($n \geq 4$) and improved device performance. The ether's oxygen atoms form hydrogen bonds with the ammonium group ($-\text{NH}_3^+$) of phenethylamine bromide (PEABr), weakening its bonding to the perovskite framework and slowing the crystal growth rate. This interaction suppresses the formation of low-dimensional small- n phases ($n = 1-3$) while enhancing the proportion of large- n phases. The slower crystallization produces films with lower trap densities, better carrier mobility, extended carrier diffusion lengths, and improved PLQY.¹⁴⁴ In addition, cryptand is also reported as an additive to regulate the phase distribution within quasi-2D perovskite films. Cryptand interacts strongly with Pb^{2+} and PEA^+ cations, forming a Pb^{2+} -cryptand- PEA^+ intermediate transition state. This interaction suppresses the formation of low- n phases by inhibiting PEA^+ aggregation and promoting the formation of continuous, graded intermediate phases with high- n values (Fig. 8c).¹⁴⁰

These are another type of macrocyclic compound that can host ions through their cavity structure. Calixarenes, like crown ethers, can selectively bind with perovskite components, thereby directing crystal growth. The 4-*tert*-butyl-1-(ethoxycarbonyl-

methoxy) thiacalix[4]arene (tBuTCA) as a host-type additive in perovskite films enhances crystallization by suppressing grain boundary defects and deep-level traps (Pb dimers/Pb⁰), improving valence band alignment and charge transport, which results in high-quality films with superior photovoltaic performance and long-term stability (Fig. 8d).¹⁴¹

The use of crown ethers and other macrocyclic compounds not only directs the crystal orientation but also enhances the structural stability of perovskite films. Films with optimized orientation and larger grain sizes exhibit superior charge transport and reduced non-radiative recombination, ultimately contributing to better device efficiency and extended operational lifetimes.

4.2. Analytical techniques for evaluating supramolecular-directed films

To analyze the impact of supramolecular agents on perovskite films such as their morphology, grain size, crystallinity, defects, interaction, *etc.*, a variety of microscopic and spectroscopic characterization techniques were employed, including SEM, XRD, atomic force microscopy (AFM), photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra, X-ray photoelectron spectroscopy (XPS), *etc.* These methods provide insights into crystal size, orientation, and defect density, which are essential for understanding the effects of supramolecular engineering on film quality and may aid in comprehending the efficacy of different approaches taken to maximize the material quality and device characteristics to create stable and reasonable device performance.¹⁴⁵ The basic functions of these tools have been individually displayed in Fig. 9. XRD is used to determine the crystal structure and orientation of perovskite films. By analyzing XRD patterns, researchers can identify changes in crystal orientation and phase purity caused by supramolecular agents. XRD also reveals the presence of any

preferred orientation (*e.g.*, vertical or horizontal) influenced by macrocycles like crown ethers.^{55,65} Such orientation data are crucial for optimizing charge transport in perovskite films. SEM provides high-resolution images of perovskite film morphology, allowing researchers to assess grain size, grain boundaries, and surface roughness.¹⁴⁶ A silane coupling agent 3-aminopropyltrimethoxysilane (APMS) not only forms a hydrogen bond with I (N–H...I), but also forms a coordinate bond with the uncoordinated Pb in the perovskite leading to an enhancement in grain size and uniformity are observable in SEM images.¹⁴⁷ At the interfaces of different layers, a smooth surface reduces the resistance and fault density.¹⁴⁸ The shape and crystallinity of the perovskite layer affect a number of variables, including defect density, charge diffusion length, and charge dissociation efficiency. AFM is used to measure surface roughness and film uniformity. By comparing AFM data before and after adding supramolecular agents, researchers can determine the degree of surface smoothing achieved through engineering crystallization.¹⁴⁷ The root-mean-square (RMS) values of the difficult functional group of 18C6 crown ether-treated perovskite films were lower than the control group exported from AFM images, indicating low surface roughness in passivated devices.¹⁰⁵ Smooth, defect-free films are essential for device performance, and AFM helps quantify these properties. PL spectroscopy assesses the quality of perovskite films by measuring non-radiative recombination rates. Films with fewer defects and larger, well-ordered grains typically exhibit stronger PL signals. By using PL spectroscopy, researchers can gauge the effectiveness of supramolecular agents in passivating defects and enhancing charge-carrier lifetime. PL and TRPL analyses reveal that crown ether treatments generally enhance perovskite optoelectronic properties by suppressing nonradiative recombination and improving carrier dynamics. Dibenzo-18-crown-6 (DB18C6) and 4'-4''-5''-Di-*tert*-dibenzo-18-crown-6 (*t*-bu-

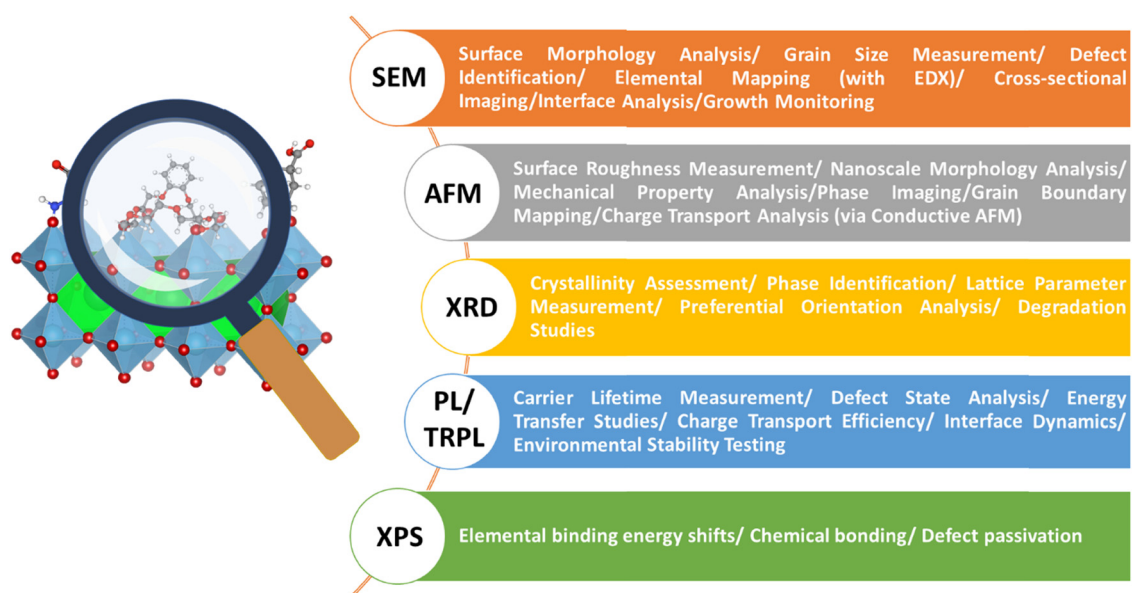


Fig. 9 Commonly used analytical techniques for supramolecular modified perovskite films.

DB18C6) treatment achieve the most significant improvements, as evidenced by enhanced PL intensity, blue-shifted PL peaks (reduced Urbach energy), prolonged carrier lifetimes, and efficient charge transport due to favorable band bending and reduced work function. In contrast, 4'-Aminobenzo-18-crown-6 (N-B18C6) treatment increases nonradiative recombination, lowers the Fermi level, and mismatches energy levels, hindering carrier transport and device performance.¹⁰⁵

Furthermore, XPS is another key tool for studying supramolecular interactions in hybrid perovskites by analyzing elemental binding energy shifts, chemical bonding, and defect passivation. It reveals how supramolecular agents influence charge redistribution, suppress defects, and modify surface dipoles, ultimately enhancing stability, energy alignment, and optoelectronic performance. For example, XPS analysis reveals significant changes in the Pb 4f and I 3d core energy levels of 4-amidinopyridine (4AP) adsorbed DB18C6 (DCAP)-treated perovskites. The I 3d peak shifts to lower binding energies, indicating interactions with DB18C6 or DCAP. Additionally, the Pb 4f_{5/2} and Pb 4f_{7/2} peaks shift downward by 0.19 eV and 0.23 eV, respectively. The Pb⁰ defect peaks (136.45 eV and 140.8 eV), associated with residual PbI₂ decomposition, disappear after DCAP or DB18C6 treatment, suggesting that the crown ether (DB18C6) passivates defects *via* Pb–O interactions. XPS fitting results of N 1s and C 1s further indicate a combined effect of crown ether passivation and surface electric field shielding. A slight shift of the I 3d peak toward higher binding energies suggests the screening of halide vacancies. The FA (N⁺=CH–N) peak in the C 1s spectrum shifts from 288.4 eV to 288.1 eV after DB18C6 deposition, indicating defect passivation. However, after introducing a surface dipole *via* 4AP, this peak shifts back to 288.6 eV, suggesting that the dipole-induced electric field reduces local charge density or defect-induced potential perturbations. This screening effect is also correlated with the reduced work function in DCAP-based films resulting in the enhancement of the interfacial charge transfer.¹⁴⁹ Another work also revealed significant shifts in the Pb 4f and I 3d core levels of crown ether-treated perovskites. Pb 4f peaks in DB18C6- and N-B18C6-treated samples showed lower binding energies by 0.30 and 0.15 eV, respectively, compared to the control. Pb⁰, present in the control due to PbI₂ decomposition, disappeared in DB18C6-treated perovskites, indicating oxidation to Pb²⁺. XPS also showed distinct C 1s and N 1s shifts, with a new O 1s peak at 533 eV resulting from the interaction between A-site cations and crown ethers.¹⁰⁵ These analytical techniques are critical for verifying the success of supramolecular engineering crystallization, offering quantitative insights into film morphology and crystallinity that directly correlate with device performance.

In summary, supramolecular engineering crystallization is a powerful approach for optimizing perovskite film quality. By controlling crystallization kinetics, morphology, and interaction, supramolecular agents help create high-performance, stable perovskite films that are essential for next-generation optoelectronic devices.

5. Supramolecular-controlled synthesis and functionalization of perovskite quantum dots

Perovskite quantum dots (PQDs) have gained significant attention due to their superior optical properties, such as high PLQY, tunable emission, and narrow emission linewidths.^{150–152} However, PQDs suffer stability challenges due to their moisture, oxygen, and light sensitivity. Supramolecular chemistry offers innovative solutions for synthesizing and stabilizing PQDs, allowing for more controlled and precise fabrication. Here, we discuss supramolecular control in PQD synthesis, exploring the techniques, types of ligands, host-guest chemistry, and applications.

5.1. Supramolecular approaches for PQD synthesis and stability enhancement

The synthesis of PQDs involves controlling the size, morphology, and surface chemistry to achieve the desired optical and electronic properties. Supramolecular approaches provide a way to manipulate these parameters by using non-covalent interactions to allow for the fine-tuning of quantum dot characteristics at the molecular level.¹⁵³ The hot injection method and ligand-assisted reprecipitation (LARP) are the most commonly used synthesis techniques for PQDs.¹⁵⁴ In the hot injection method, a precursor solution containing metal halides and organic halides is injected into a hot solution of a coordinating ligand, resulting in rapid nucleation and growth of PQDs. Supramolecular agents such as macrocyclic ligands or hydrogen-bond donors can be incorporated into the precursor or ligand solutions, allowing for better control over nucleation rates and crystal growth, which in turn affects PQD size and uniformity.^{155,156} In addition, LARP is a room-temperature synthesis technique that involves the addition of polar solvents to a nonpolar precursor solution, leading to precipitation and formation of PQDs. The presence of supramolecular ligands during the process can stabilize the crystal structure, reduce surface defects, and improve quantum yield. By carefully choosing supramolecular ligands that interact specifically with perovskite precursors, the LARP method can yield PQDs with controlled morphology and reduced defect density.¹⁵⁷ Li *et al.* demonstrated the *in situ* substitution of oleylamine, which reduces the spacing between neighboring nanocrystals, resulting in more tightly packed nanocrystal films (Fig. 10a).¹⁵⁸ After that, Li *et al.* also introduced *O*-tolylbiguanide (*O*-Tg) into CsPbI₃ quantum dots (QDs) system to passivate surface defects, achieving highly efficient and water-resistant perovskite LEDs. The biguanide group in *O*-Tg forms multiple hydrogen bonds with both terminal- and bridging-halogen defects on the QD surface, while also stabilizing the crystal structure by occupying A-site positions. Additionally, the hydrophobic benzene rings in *O*-Tg prevent the erosion of polar molecules, enhancing environmental stability.¹⁵⁹ The incorporation of dual-ligand molecules significantly enhances the long-range ordering and performance of perovskite QD films. An iodide-rich agent (aniline hydroiodide) facilitates anion exchange, while bromotrimethylsilane (TMSBr) generates a strong acid that dissolves smaller QDs

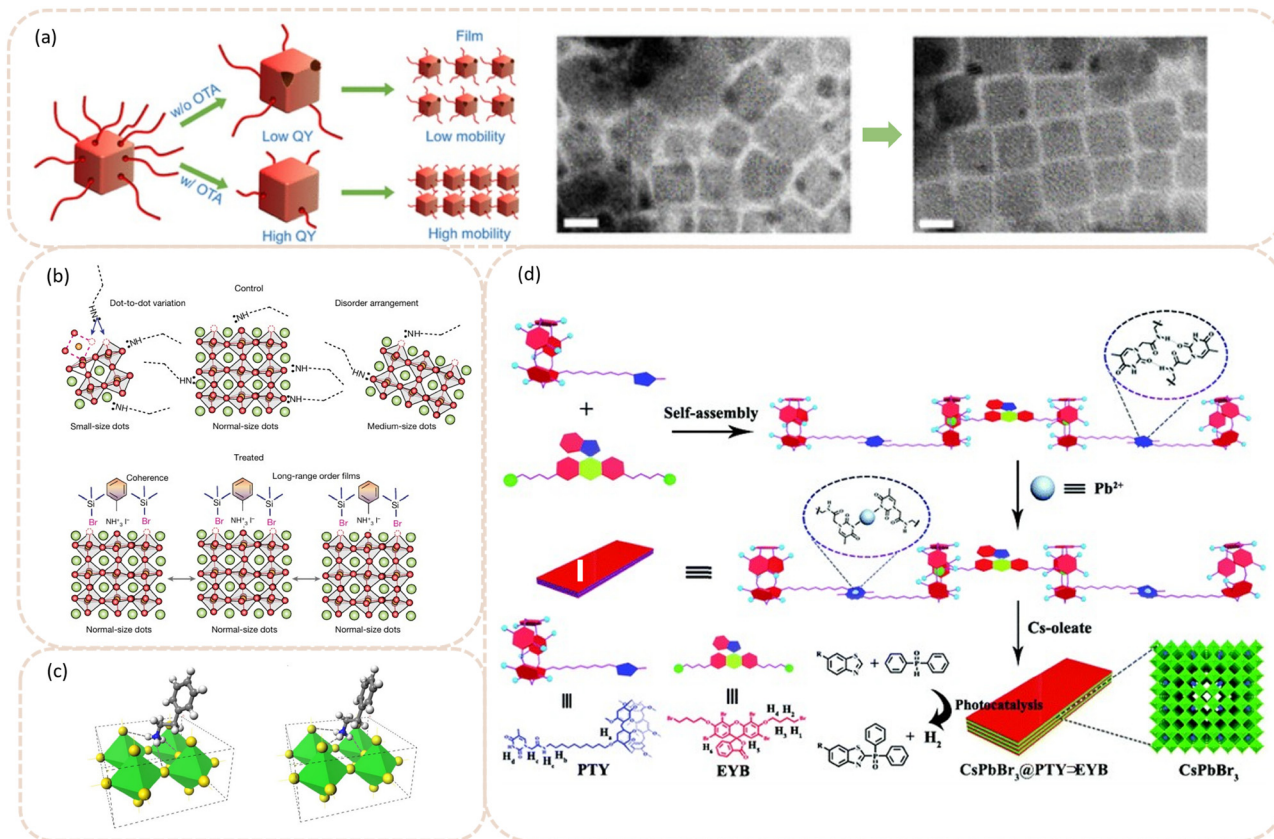


Fig. 10 The graphical depiction of (a) purification processes without and with OTA; TEM images of NCs: w/o OTA and w/OTA. The scale bar denotes 10 nm. Reproduced with permission.¹⁵⁸ Copyright 2022, American Chemical Society. (b) The long-range order control strategy of TMSBr on dot-to-dot coherence. Reproduced with permission.¹⁶⁰ Copyright 2022, Springer Nature. (c) Two hydrogen-bonding configurations for PEABr: (left) bridging halide configuration and (right) terminal halide configuration involving interactions between PEABr and the perovskite cubic structure. Reproduced with permission.¹⁶¹ Copyright 2018, Springer Nature. (d) The self-assembly process and photocatalytic hydrogen evolution mechanism of the supramolecular polymer $\text{CsPbBr}_3@PTY \supset EYB$. Reproduced with permission.¹⁶² Copyright 2021, The Royal Society of Chemistry.

and removes insulating oleate ligands (Fig. 10b), resulting in compact, defect-free films with improved conductivity. NMR analysis reveals that TMSBr effectively passivates QD surfaces by nearly eliminating signals from alkene hydrogens, indicating complete ligand removal and successful resurfacing. Fourier-transform infrared (FTIR) spectroscopy further supports these findings, showing reduced alkene signals and confirming the presence of methyl groups from TMSBr.¹⁶⁰

For the host-guest cases, Zhu *et al.* reported that crown ether-assisted supramolecular assembly approach enables the formation of highly emissive halide perovskite structures with tunable optoelectronic properties. By integrating tetravalent metal halide octahedra into (crown ether@A)₂MX₆ dumbbell units, this method achieves blue and green emissions with near-unity PLQYs. Specifically, (18C6@K)₂HfBr₆ exhibited blue emission with a remarkable PLQY of 96.2%, while (18C6@K)₂-ZrCl₄Br₂ demonstrated green emission with an 82.7% PLQY.¹⁶³ During synthesis, crown ethers coordinate strongly with Cs⁺ ions, forming stable precursor complexes that lead to the creation of core-shell QDs. The QD formation involves successive steps, including Cs⁺ coordination, rapid precipitation, and the assembly of micelle-like structures. The π - π stacking of

DB21C7's phenyl groups promotes proximity and coalescence of seeds, resulting in uniform core-shell QDs. This core-shell architecture, with CEs as the shell material, enhances surface passivation and optical properties, reducing charge injection barriers and leakage currents in optoelectronic devices. The electroluminescence spectra exhibit a narrow emission peak (519 nm) with minimal red-shift and improved temporal stability (luminance half-life of 555 seconds), underscoring the efficacy of this approach. Furthermore, the ability of CEs to selectively bind and stabilize halide perovskites introduces new opportunities to engineer diverse core-shell architectures. By modifying the synthesis conditions, such as introducing BuOH to disrupt CE binding temporarily, the QD morphology and ligand distribution can be further tailored, optimizing device performance. Despite some challenges, this strategy holds promise for advancing perovskite QD-based devices, particularly CsPbBr_3 QD LEDs, with enhanced stability, efficiency, and scalability for thin-film applications.¹²⁷ In another work, the incorporation of thymine-functionalized pillar[5]arene (PTY) and an eosin Y-based derivative (EYB) into a supramolecular assembly enables controlled growth and improved performance of CsPbBr_3 QDs. PTY and EYB form the host-guest assembly through hydrogen bonding

and π - π stacking interactions, with the thymine moieties of PTY coordinating Pb^{2+} ions to facilitate *in situ* crystallization of CsPbBr_3 QDs. This self-assembly process is confirmed by ^1H NMR and FTIR, showing significant shifts in proton and vibration peaks due to coordination and interaction. Confined growth of CsPbBr_3 QDs in the hydrophobic interlayers of PTY $\supset$ EYB suppresses self-quenching and enhances energy transfer efficiency to EYB, achieving 96.5% through Förster resonance energy transfer (FRET). The resulting system exhibits excellent photocatalytic performance, with hydrogen evolution product yields exceeding 2.5 times those obtained with eosin Y alone. This study demonstrates how molecular additives like PTY and EYB not only influence perovskite crystal growth but also optimize photophysical properties, enabling efficient artificial light-harvesting and energy conversion systems (Fig. 10c).¹⁶² These supramolecular assemblies, driven by strong electron-phonon coupling and microsecond PL lifetimes, minimize nonradiative recombination and maintain structural integrity. Zhang *et al.* demonstrated the application of supramolecular engineering in synthesizing uniform $\text{CsPbBr}_{3-x}\text{I}_x$ quantum dots (QDs) using an amphiphilic star-like diblock copolymer. This copolymer effectively controls QD size, composition, and surface passivation, leading to improved optoelectronic properties. The optimized QDs, when integrated into perovskite solar cells, exhibited enhanced charge transfer, reduced recombination losses, and higher power conversion efficiency, highlighting the effectiveness of the supramolecular approach in device performance enhancement.¹⁶⁴

Moreover, Ban *et al.* proposed crown-mediated crystallization also reduces non-radiative recombination, as evidenced by longer PL lifetimes (from 3 to 8 ns) and improved charge transport in thicker films (~ 50 nm). The inhibitory effect of phenylethylammonium bromide (PEABr) on perovskite crystal growth is attributed to the strong hydrogen bonding between the hydrogen atom of PEABr and the halide atom in PbBr_6 (Fig. 10d). Devices based on crown-additive films demonstrate enhanced stability, retaining performance longer under constant voltage or current compared to PEABr-only devices. This stability is attributed to improved thermal resistance against Joule heating.¹⁶¹ Moreover, compared to synthetic CsPbBr_3 nanocrystals, crown-additive films achieve higher charge transport efficiency while maintaining competitive PLQY and avoiding the insulating effects of long ligands.¹⁶¹ A dual-additive supramolecular strategy using 18C6 and sodium trifluoroacetate (STFA) effectively regulates the crystallization kinetics of perovskite emitters, significantly enhancing device performance. 18C6 coordinates with B-site cations (Pb^{2+}), while STFA interacts with A-site cations (FA^+) through coordination and hydrogen bonding. This dynamic coordination retards nucleation, enabling segmented crystallization and the formation of low-dimensional nanocrystals during the initial growth phase. Upon annealing, the supramolecular structure releases cations for secondary growth, resulting in larger, highly crystalline grains and a uniform nano-island morphology. This controlled crystallization process enhances film quality by narrowing the distribution of low-dimensional phases and passivating defects, leading to excellent photoluminescent quantum yields and efficient carrier injection.¹⁶⁵

6. Supramolecular interface engineering for perovskite optoelectronics

PSCs and PeLEDs have shown immense promise due to their remarkable optoelectronic properties and potential for cost-effective fabrication.¹⁶⁶ However, these devices often suffer from stability challenges, limiting their commercial viability. Supramolecular interface engineering offers a novel approach to enhance the stability of perovskite devices by introducing molecular interactions at interfaces, which reduce surface defects and improve the resilience of perovskite films to moisture, oxygen, thermal stress, and ion migration.⁷⁴ Supramolecular interface engineering aims to address these challenges and these approaches not only enhance stability but also improve the efficiency of perovskite devices by facilitating efficient charge transfer. Here, we explore supramolecular interface engineering strategies to address efficiency and stability issues in perovskite devices.

6.1. Energy-level alignment, defect passivation, and surface stabilization *via* supramolecular agents

Self-assembled monolayers (SAMs) provide a straightforward, efficient approach to enhancing interfacial properties in perovskite devices, enabling improved stability and performance.¹⁶⁷ Supramolecular chemistry plays a key role in designing SAM molecules with tailored functionalities that address specific challenges at perovskite interfaces.¹⁶⁸ By incorporating specific functional groups into SAMs and other supramolecular interfacial layers, researchers can design interfaces that address the unique stability challenges of perovskite devices. Li *et al.* demonstrated a co-adsorb (CA) strategy utilizing 2-chloro-5-(trifluoromethyl)isonicotinic acid (PyCA-3F) to improve SAMs at the buried interface of PSCs. By mitigating aggregation of [2-(9H-carbazol-9-yl)ethyl]phosphonic acid (2PACz), this approach enhances surface smoothness, increases work function, and forms a favorable heterointerface for perovskite layers. These enhancements lead to improved crystallinity, reduced trap states, and efficient hole extraction, achieving PCE of over 25% in p-i-n PSCs (certified at 24.68%). Stability tests confirm retention of $\sim 90\%$ of PCE after 1000-hour operation for encapsulated PSCs. This work presents a practical and effective method for advancing SAM performance, breaking efficiency records, and improving stability in PSC technologies.¹⁶⁹ Chiral helical assemblies, specifically P, M-(1-methylene-3-methylimidazolium)[6]helicene iodides, were utilized as interfacial modulators in hybrid metal halide PSCs to investigate their effects on crystal growth and stability. Despite comparable photovoltaic performance among enantiomers, racemic mixtures, and controls, the modulators enhanced operational stability by reducing residual PbI_2 and stabilizing the perovskite phase, as confirmed by XRD and SEM analyses. It shows enhanced surface defect passivation, particularly with racemic mixtures, as evidenced by higher PLQYs and suppression of metallic lead formation through $\text{Pb}(\text{ii})$ interaction. Additionally,

modulation increased surface hydrophobicity, mitigating moisture-induced degradation and extending device operational lifetimes beyond 1000 hours while maintaining over 80% efficiency. These findings underscore the modulators' stabilizing effects rather than direct contributions to photovoltaic performance, challenging the role of helical chirality and emphasizing the need for further exploration of interfacial engineering in perovskite photovoltaics.¹⁷⁰ Another study demonstrates that halide-terminated polar silanes, including CPTMS, effectively passivate defects in perovskite films by forming strong molecular dipoles at the interface. These dipoles facilitate defect passivation and energy-level alignment, improving charge transport and reducing non-radiative recombination. The effectiveness of CPTMS was validated through multiple characterization techniques, including XPS to confirm chemical bonding, PL and TRPL to assess defect passivation, UPS to analyze energy-level alignment, and AFM to evaluate film morphology. As a result, perovskite solar cells incorporating CPTMS exhibited enhanced PCE and improved stability compared to untreated devices.¹¹⁸

For the host-guest interactions, Chen *et al.* introduced A15C5 as a molecular modulator at the perovskite/hole transport layer interface significantly reduces electron trap density, forms 2D/3D heterojunctions to relieve residual strain, optimizes energy

level alignment, and achieves a PSC efficiency of 24.13% with excellent stability against humidity, light, and heat.¹⁷¹ Sui *et al.* introduced an ultrathin buffer layer of crown ethers between perovskite and electron transport layer (ETL) in NiO_x-based inverted p-i-n PSCs, including DB18C6, 18C6, 4'-4''-5'''-di-*tert*-dibenzo-18-crown-6 (*t*-bu-DB18C6), and 4'-aminobenzo-18-crown-6 (N-B18C6). It is noted that functionalized 18-crown-6 ethers modulate interfacial properties, while conventional 18C6 provides effective Lewis acid-base passivation *via* oxygen atoms. Derivatives like N-B18C6 enhance passivation with lower LUMO energy and milder acid-base behavior, DB18C6 improves charge transport and adhesion through benzene rings, and *t*-bu-DB18C6 targets grain boundary defects but struggles with shallow trap states, collectively influencing efficiency, voltage, and stability (Fig. 11a).¹⁰⁵ Moreover, the transformative role of benzo-18-crown-6-ether (B18C6) as a dual-functional additive at the perovskite-hole transport material (HTM) interface, leveraging their cyclic structures and electronegative cavities, not only capture and immobilize Pb²⁺ ions through host-guest complexation but also provide robust interfacial passivation. DFT calculations identified B18C6 as the optimal candidate, demonstrating high Pb²⁺ binding energy (−248.32 kcal mol^{−1}) and structural flexibility. Devices incorporating B18C6 achieved a PCE of 21.7%

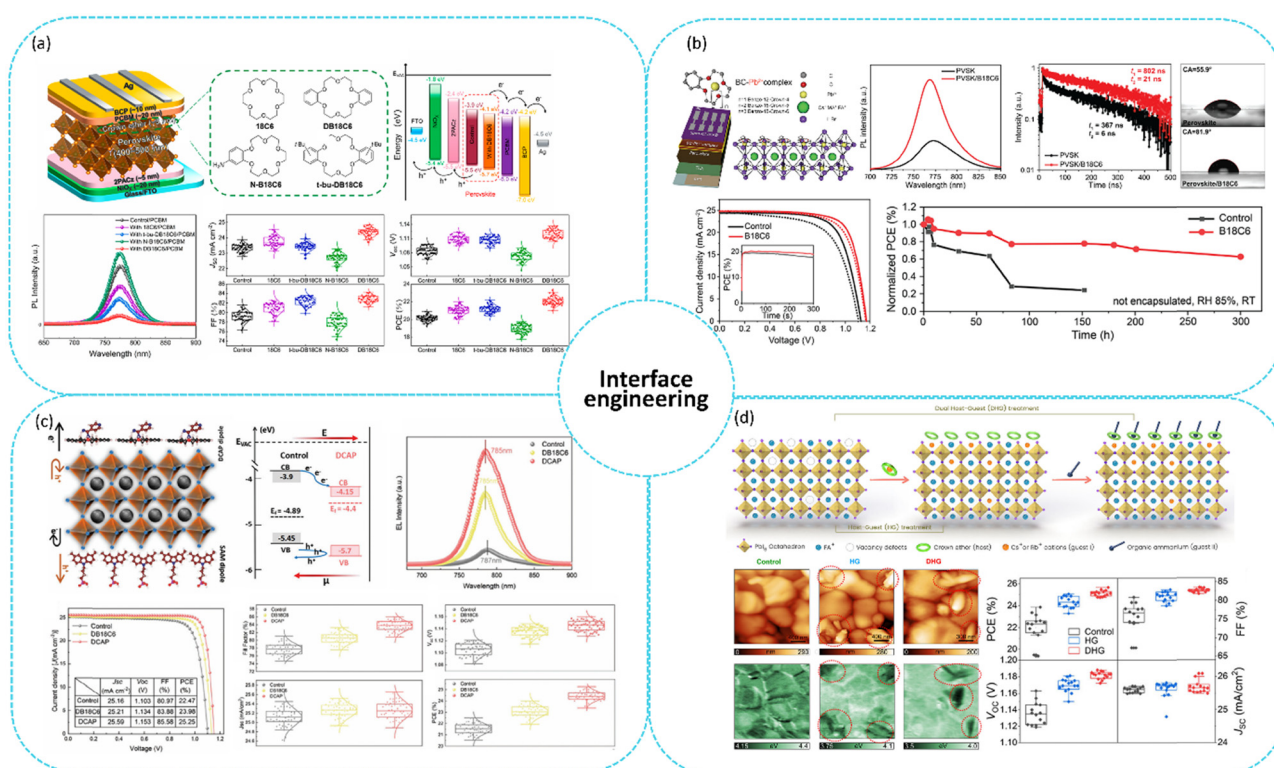


Fig. 11 (a) Device structure of inverted p-i-n PSCs; chemical structures of four crown ethers; band energy diagram and PL spectra of control and DB18C6-treated PSCs; performance of control and crown ether-treated devices. Reproduced with permission.¹⁰⁵ Copyright 2024, American Chemical Society. (b) Lead ion capture process in PSCs using B18C6; PL spectra and TRPL decay of pristine and B18C6-treated perovskites; *J*-*V* curve, maximum power point tracking (inset); contact angle of perovskite films with/without B18C6. Reproduced with permission.¹¹³ Copyright 2024, ELSEVIER B.V. and Science Press. (c) Dipole creation and charge transport at perovskite interfaces; EL spectra at 1.2 V; *J*-*V* curve under AM 1.5G sunlight; Average FF, *J*_{sc}, *V*_{oc}, and PCE from 24 devices. Reproduced with permission.¹⁴⁹ Copyright 2024, Wiley-VCH GmbH. (d) Supramolecular interface design; AFM topography and work function maps of control and host-guest treated films; Photovoltaic metrics of control, host-guest, and dual host-guest-treated devices. Reproduced with permission.⁵⁵ Copyright 2024, Springer Nature.

while exhibiting extended carrier lifetimes and suppressed non-radiative recombination, as confirmed by transient absorption spectroscopy (TAS), XPS, and ultraviolet photoelectron spectroscopy (UPS). Additionally, B18C6-treated films showed enhanced moisture resistance, as evidenced by increased water contact angles (81.9°) and stable crystal structures after 300 hours at 85% relative humidity. ToF-SIMS analysis further revealed mitigated Pb^{2+} migration under bias conditions, addressing environmental concerns related to lead leakage. By passivating surface defects and stabilizing the perovskite structure, B18C6 treatment significantly improved device performance and durability (Fig. 11b).¹¹³ The integration of 18C6 as an interface layer between the HTL, PEDOT:PSS and the thermally evaporated CsPbBr_3 emissive layer (EML) significantly improves PeLED performance. The 18C6 enhances HTL conductivity, passivates nonradiative defects, and suppresses the formation of the insulating Cs_4PbBr_6 phase. These effects lead to higher current density, brighter emission, and improved current efficiency. The optimized device demonstrates a turn-on voltage of 2.9 V, a maximum brightness of $15\,717\text{ cd m}^{-2}$, a current efficiency of 3.66 cd A^{-1} , and an external quantum efficiency of 1.02%. The working lifetime (T_{50} at 100 cd m^{-2}) is extended to 11.8 hours, over 30 times longer than control devices. This study highlights the importance of defect passivation and phase control for enhancing operational stability and efficiency in PeLEDs, with potential for further improvements using alternative passivation strategies.¹⁷² Another study on crown ether is DB21C7 which enables simultaneous modulation of surface and bulk properties in perovskite films by forming a Cs^+ -host-guest complex, which facilitates targeted Cs^+ infusion, passivates defects, stabilizes the α -phase, and enhances optoelectronic performance through synergistic surface gradient doping.¹¹⁷ Tang *et al.* focused on using amidopyridinium ions docked within DB12C6 cavities to regulate the top interface of inverted perovskite solar cells. They proposed a novel dual-molecule host-guest strategy, utilizing DB12C6 cavities as the host and ammonium ions as the guest. Through comprehensive experimental characterization and theoretical analysis, they thoroughly investigated the ion-docking phenomenon, providing strong confidence in the robustness of their findings. These results demonstrate that host-guest electrostatic interlocking induces electric dipoles on the perovskite surface, enhancing electron extraction and preventing hole recombination. As a result, the devices achieved a PCE of 25.25%, with significantly reduced photovoltage and non-radiative recombination losses. Additionally, the target devices exhibited excellent long-term stability under high humidity and high-temperature conditions (Fig. 11c).¹⁴⁹ Furthermore, DB21C7 forms host-guest complexes at the perovskite interface, reducing interfacial ion migration (e.g., Li and Au diffusion), altering morphology and hydrophobicity, and enhancing device stability and efficiency by improving charge transport and suppressing degradation.¹¹⁰ Zhao *et al.* went deeper into combining DB21C7 and PEAi synergistically to enhance perovskite solar cell performance by modulating interfacial properties through a dual host-guest complexation strategy (Fig. 11d), which passivates defects, reduces recombination, improves carrier transport, and achieves exceptional efficiency (25.89%) and stability ($>96.6\%$ retention after 1050 hours).⁵⁵

In the polymer family, Cao *et al.* proposed a 3D star-shaped PPP polymer that significantly enhances the crystallization and performance of perovskite films in inverted PSCs. The PPP polymer, composed of a polyhedral oligomeric silsesquioxane core with eight poly(trifluoroethyl methacrylate) and poly(methyl methacrylate) branches, incorporates multiple chemical anchor sites such as carbonyl ($\text{C}=\text{O}$) and $-\text{CF}_3$ groups. These sites interact strongly with perovskite components, passivating defects at grain boundaries and surfaces, reducing ion migration, and suppressing nonradiative recombination. XRD and PL analyses reveal improved crystallinity, reduced trap density, and enhanced carrier mobility, leading to optimized charge transport and reduced recombination losses. The PPP polymer also mitigates ion diffusion and stabilizes the perovskite structure through hydrogen bonding and chelation, significantly improving thermal and operational stability. As a result, PPP-modified PSCs achieve a high PCE of 22.1%, a near-record fill factor of 0.862, and outstanding stability, retaining over 93% efficiency after 6000 hours of exposure to ambient conditions. This work demonstrates the potential of multifunctional polymer modulators for advancing PSCs toward practical and durable applications.¹⁷³ Tian *et al.* investigated the role of the cage polyamine molecule 1,4-diazabicyclo[2.2.2]octane (DABCO) in modulating the interface between the ETL and perovskite layer in PSCs. By intercalating DABCO at the buried interface, significant improvements in defect passivation, crystal growth, lattice stress relief, and energy level alignment were achieved. This reduced trap-state density by 54%, improved carrier transport, and alleviated halide ion migration, resulting in enhanced material stability. The DABCO-modified PSC demonstrated a PCE increase from 20.5% to 23.6% and retained 87% of its initial efficiency after 1500 hours under standard conditions. This research highlights DABCO's potential as a molecular modulator to optimize PSC performance and environmental stability.¹⁷⁴

In addition, supramolecular dual interfacial positioning of ambipolar 2D black phosphorene (BP) effectively enhances carrier extraction by reducing interfacial recombination, facilitating charge separation, and improving energy level alignment. To validate its effectiveness, various characterization techniques were employed: PL and TRPL confirmed suppressed non-radiative recombination and extended carrier lifetime; UPS and XPS revealed optimized energy level alignment and interfacial chemical interactions; AFM and SEM showed improved surface morphology and film uniformity; and J - V characteristics and EQE highlighted the significant improvement in PCE and device stability. These findings underscore the crucial role of 2D black phosphorene in optimizing charge carrier dynamics and enhancing both the efficiency and operational stability of optoelectronic devices.¹⁷⁵

7. Supramolecular engineering for optoelectronic applications

Supramolecular engineering has been extensively explored in various hybrid perovskite optoelectronic applications. Since the research on supramolecular engineering in PSCs is extremely

extensive and we have also discussed it in other sections, the relevant detailed performance indicators are directly summarized in the supporting information of Table S1 for reference. This section focuses on the impact of supramolecular strategies on flexible solar cells, perovskite modules, LEDs and displays, and photodetectors.

7.1. Supramolecular-modified perovskite films for flexible solar cells

Flexible perovskite solar cells (F-PSCs) have garnered significant interest for applications in portable and wearable electronics, owing to their low cost and high power-to-weight ratio. However, challenges related to moisture resistance and mechanical stability remain key obstacles to their commercialization. More and more reports employing supramolecular engineering to enhance interface adhesion have emerged as an effective strategy to improve the mechanical durability of F-PSCs. A novel *in situ* passivation strategy using multifunctional fluorinated propylamine salts, 2,2,3,3,3-pentafluoropropylamine hydrochloride (PFPA) and 3,3,3-trifluoropropylamine hydrochloride (TFPACl), enhances the performance of perovskite films for flexible solar cell applications. These additives interact strongly with perovskite precursors,

forming supramolecular complexes with FAI, as revealed by NOESY NMR spectroscopy. The higher electronegativity of PFPA-Cl's fluoroalkyl tail results in stronger binding to A-site ion vacancies (V_{FA} defects) and improved defect passivation compared to TFPACl. Additionally, the Cl^- ions modulate perovskite crystallization, leading to films with reduced defect density, uniform coverage, and enhanced energy alignment with the hole transport layer. Incorporating PFPA improves the crystal quality and mechanical properties of the perovskite films, effectively releasing residual stress and ensuring a compact, homogeneous structure, beneficial to the device bending test. These enhancements result in flexible PSCs (FPSCs) with a remarkable PCE of 23.59%, excellent bending robustness (88% PCE retention after 2500 bending cycles, $R = 8$ mm), and impressive operational stability (89.8% PCE retention after 1000 hours under continuous illumination) (Fig. 12a).¹⁷⁶ Another symmetric polar small molecule, 2,2'-(2,5-dihydroxy-1,4-phenylene) bis (2-cyanoacetic acid), DPBCA, is used as an interfacial buffer layer to enhance the performance and stability of F-PSCs. DPBCA's strong polar functional groups ($-\text{C}=\text{O}$, $-\text{CN}$, and $-\text{OH}$) exhibit excellent adhesion at the electron transport layer (ETL)/perovskite interface, effectively reducing residual stresses and improving the mechanical

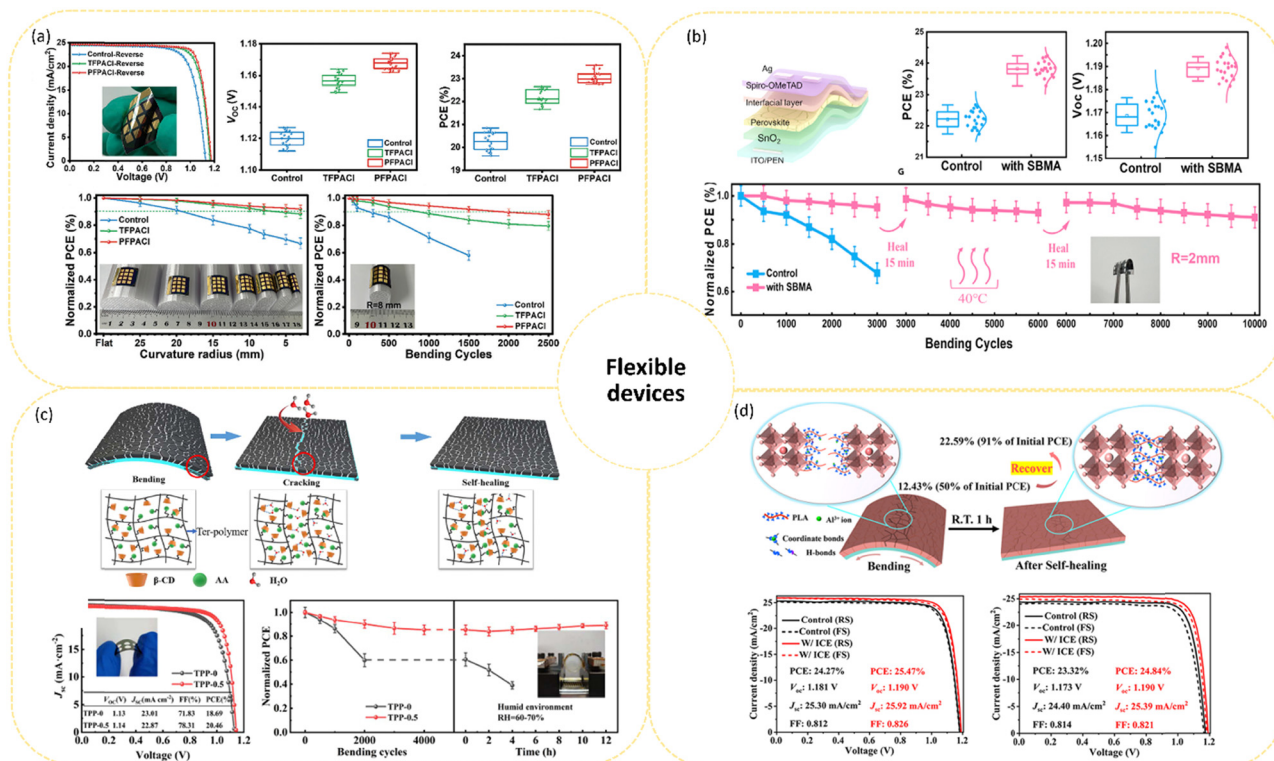


Fig. 12 (a) $J-V$ curves of control, FAPACl-treated, and PFPAI-treated FPSCs; inset shows a photograph of the FPSCs; statistical analysis of V_{OC} and PCE under different conditions; bending stability as a function of curvature, from flat to a radius of $R = 3$ mm; bending stability test for control, FAPACl-treated, and PFPAI-treated FPSCs ($R = 8$ mm, $\sim 35\%$ RH, ~ 298 K). Reproduced with permission.¹⁷⁶ Copyright 2024, Wiley-VCH GmbH. (b) Schematic of the F-PSC structure: PEN/ITO/ SnO_2 /perovskite/interfacial layer/spiro-OMeTAD/Ag; normal distribution of PCE for devices with and without SBMA; normal distribution of V_{OC} for devices with and without SBMA; normalized PCE of flexible devices as a function of bending cycles at a fixed radius of $r = 2$ mm for parallel bending. Reproduced with permission.¹⁸⁰ Copyright 2024, Elsevier Inc. (c) Schematic of the self-healing process via host-guest interactions; $J-V$ curves of the best F-PSCs for control TPP-0 and TPP-0.5; changes in PCE during bending cycles and self-healing (RH = 60–70%). Reproduced with permission.¹⁸¹ Copyright 2024, The Royal Society of Chemistry. (d) Diagram of the self-healing process for perovskite films with ICE; $J-V$ curves for rigid and flexible PSCs. Reproduced with permission.¹⁸² Copyright 2022, The Royal Society of Chemistry.

robustness of the buried interface. The symmetric structure of DPBCA amplifies its passivation capability, allowing it to synergistically interact with and passivate multisite defects, such as non-coordinated $\text{Pb}^{2+}/\text{Sn}^{4+}$ and iodine vacancies, through hydrogen bonding and other interactions. This defect passivation enhances the film quality, lowers defect density, and increases charge carrier lifetimes. DPBCA also facilitates *in situ* crystallization of the perovskite, reduces the stiffness of both the SnO_2 and perovskite films (as indicated by reduced Young's modulus), and significantly improves bending resistance. Devices incorporating DPBCA achieve a 33% improvement in PCE, reaching 23.05%, and retain over 81.3% of their initial PCE after 10 000 bending cycles, demonstrating superior mechanical and environmental stability compared to devices without DPBCA. These findings underscore the potential of multifunctional, symmetric small molecules like DPBCA to improve interface engineering for durable and efficient F-PSCs.¹⁷⁷ In addition, the supramolecular agents are also used as the self-healing additive in F-PSCs. A novel supramolecular adhesive, AD-23 synthesized through random copolymerization of acrylamide (AM) and *n*-butyl acrylate (BA), incorporates hydrogen-bond donors and receptors for effective defect passivation and stress buffering. The adhesive's amphiphilic nature and optimized glass transition temperature (T_g) enable it to improve the leveling of perovskite precursors, reduce trap density, and enhance carrier mobility. Its thermal self-healing property allows F-PSCs to recover mechanical damage at a low temperature of 70 °C, retaining 90% of their initial performance after 2000 bending cycles. Compared to devices without an adhesive, AD-23-modified F-PSCs exhibit superior stress tolerance and structural integrity due to the uniform redistribution of hydrogen bonds during thermal treatment. This innovative additive strategy achieves a PCE of 20.50% for flexible substrates and 21.99% for rigid substrates, demonstrating the feasibility of integrating buffering, passivation, and repair functions within a single material for advancing F-PSC applications in wearable technologies.¹⁷⁸ Another *in situ* crosslinking strategy using a functional monomer, bis((3-methyloxetan-3-yl)methyl) thiophene-2,5-dicarboxylate (OETC) enhances the growth and mechanical properties of perovskite films on flexible substrates. The OETC monomer effectively coordinates with PbI_2 to enlarge colloid sizes, reduce nucleation sites, and form a mesoporous PbI_2 scaffold that facilitates uniform cation penetration. During annealing, OETC undergoes a triggered crosslinking reaction that promotes the growth of large, (100)-oriented perovskite grains by consuming non-oriented small crystals. The resulting crosslinked polymer (COETC) fills grain boundaries, reducing defects, releasing mechanical stress, and lowering the Young's modulus. These structural improvements enable F-PSCs to achieve a record PCE of 23.4% (certified 22.9%), comparable to rigid devices, with robust mechanical durability. Notably, F-PSCs retain ~90% efficiency after 5000 bending cycles (5 mm radius) and exhibit excellent stability under extreme bending and moisture conditions. This strategy highlights how OETC-derived crosslinking enhances both the structural and functional performance of perovskite films, promoting their application in durable, high-efficiency flexible photovoltaics.¹⁷⁹ A zwitterionic

elastomer, known as 3-[[2-(methacryloyloxy)ethyl]dimethylammonio]propane-1-sulfonate (SBMA), used as a multifunctional additive for enhancing perovskite films and F-PSCs. SBMA coordinates with PbI_2 to form an intermediate SBMA- PbI_2 adduct, regulating nucleation and crystallization. The sulfur-end groups chemically passivate vacancies, suppress nonradiative recombination, and create a high-dielectric environment to screen carrier capture processes. During thermal annealing, SBMA undergoes *in situ* crosslinking, forming a flexible scaffold along grain boundaries, which alleviates mechanical and residual stresses. The zwitterionic interactions also enable self-healing capabilities under mild stimuli (e.g., 40 °C for 15 minutes). These enhancements result in a record-breaking PCE of 24.51% (certified 24.04%) for F-PSCs, with remarkable durability-retaining over 90% efficiency after 10 000 bending cycles. Compared to pristine films, SBMA-modified perovskite films show improved crystal size, preferential orientation, reduced defects, and higher mechanical robustness (Fig. 12b).¹⁸⁰ An ionic conductive elastomer (ICE) containing imidazolium-based ionic liquids significantly enhances the performance and durability of F-PSCs. The ICE effectively repairs grain boundary cracks at room temperature through dynamic covalent disulfide bonds, hydrogen bonds, and metal coordination bonds. Its incorporation into perovskite films passivates grain boundary defects, reduces potential differences between grains and grain boundaries, and promotes charge carrier extraction and transport. ICE-enabled F-PSCs achieve a record PCE of 24.84% and maintain over 90% of their efficiency after 5000 hours in an inert atmosphere. Furthermore, after 10 000 bending cycles at a 5 mm radius, device performance recovered from 50% (12.43%) to 91% (22.59%) of the initial PCE due to the self-healing mechanism (Fig. 12c).¹⁸¹ In the host-guest system, the interaction terpolymer was developed using glycidyl methacrylate-bonded β -cyclodextrin (GMA-CD) and *N*-adamantylacrylamide (*N*-AA), combined with methacrylguanidine hydrochloride (MAGH) to form a 2D/3D perovskite heterostructure. The additives significantly improved the perovskite's mechanical and moisture stability through hydrogen bonding with $[\text{PbI}_6]^{4-}$ octahedra, reducing deep energy level defects and enhancing passivation. Compared to control devices, the terpolymer-based F-PSCs achieved higher efficiencies (>20%) and retained over 85% of their initial efficiency after 4000 bending cycles. Furthermore, the host-guest interaction enabled self-healing of cracks, recovering up to 90% of the original efficiency (Fig. 12d).¹⁸² These strategies not only improve the mechanical and operational stability of F-PSCs but also paves the way for commercial applications in durable, high-efficiency wearable photovoltaic devices.

7.2. Supramolecular-engineered perovskite films for scalable and module applications

Introducing commonly used supramolecular agents in perovskite solar modules (PSMs), a novel 18C6 additive to enhance the quality and scalability of FA^+/Cs^+ mixed cation-based perovskite films. The 18C6 interacts strongly with Cs^+ and Pb^{2+} ions in the precursor solution, effectively regulating the nucleation and crystallization processes to produce uniform, high-quality films. During crystallization, the 18C6 assembles on the surface

and grain boundaries, stabilizing the α -phase FACsPbI_3 and improving moisture resistance by passivating surface defects. This approach also suppresses lateral iodide diffusion in module subcells, further enhancing stability. The optimized films achieved a champion efficiency of 20.48% with excellent storage stability over 1000 hours. Large-area modules fabricated using scalable blade-coating demonstrated efficiencies of 16.69% (16 cm^2) and 13.84% (100 cm^2), retaining 92% of their initial PCE after 1000 hours under ambient conditions (Fig. 13a).¹⁰⁹ Another work investigates the dipole moments of crown ethers, influenced by heteroatom substitution, determines their interaction strength with lead cations, which in turn enhances the coordination with perovskite surfaces. The A15C5 with a larger dipole moment showed improved coordination with lead ions, leading to better film morphology, reduced defect densities, and better energy-level alignment compared to native 15C5. These improvements resulted in PSCs with PCEs exceeding 25%, and PSMs with an active area of 14.0 cm^2 achieving a PCE of 21.5% (Fig. 13b). The findings

highlight that engineering the dipole moment of crown ethers can significantly improve the optoelectronic properties, stability, and efficiency of perovskite-based photovoltaics.⁸⁸ By using pseudohalides like trifluoroacetate (TFA) and aromatic cations like 3,3-diphenylpropylammonium (DPA+), the researchers develop a dual-ion passivation strategy that significantly improves perovskite performance. TFA forms strong non-covalent interactions with perovskite surfaces *via* hydrogen bonding and dispersion forces, while DPA+ enhances stability through hydrophobic interactions and prevents moisture penetration. This combination leads to superior passivation, better lattice orientation, and reduced defects, achieving a peak power conversion efficiency (PCE) of 25.63% in small-area PSCs and excellent stability under high-humidity conditions. Larger PSMs (area = 25 cm^2 and 64 cm^2) also demonstrated PCEs of 22.47% and 20.88%, respectively (Fig. 13c).¹⁸³ Furthermore, the high PCE of flexible modules is a dream application in the future life. A dynamic supramolecular ‘‘ligament’’ made of poly(dimethylsiloxane) polyurethane (DSSP-PPU) into the grain

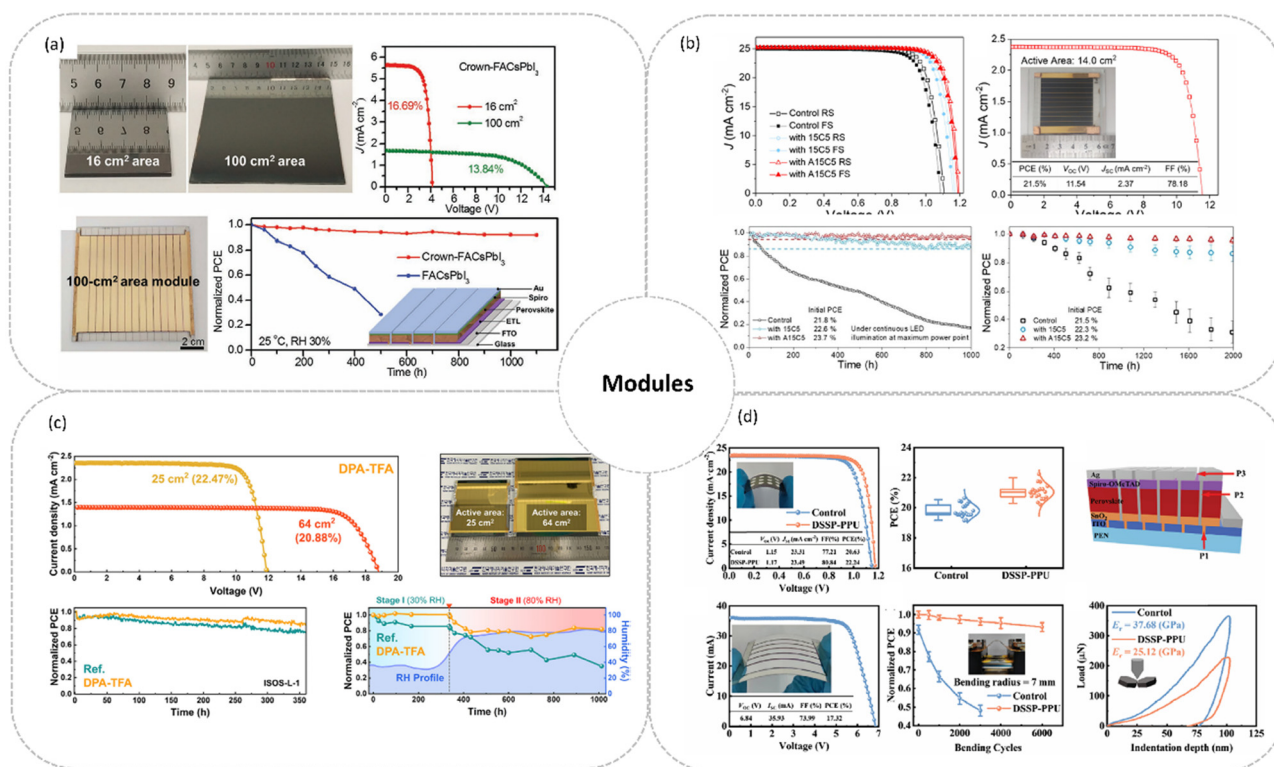


Fig. 13 (a) Digital images of crown-FACsPbI₃-based PSC films (16 cm^2 and 100 cm^2); J-V characteristics of 16 cm^2 and 100 cm^2 PSC modules; photograph of the 100 cm^2 PSC module; PCE evolution of unencapsulated PSCs (16 cm^2) of crown-FACsPbI₃ and FACsPbI₃ under storage conditions (25 °C, 30% RH). Inset: Schematic of module structure. Reproduced with permission.¹⁰⁹ Copyright 2020, Wiley-VCH GmbH. (b) J-V curves of PSCs with and without 15C5 and A15C5; J-V curves of perovskite solar modules using A15C5 as an additive. Inset: Photovoltaic parameters and device image; long-term stability of unencapsulated PSCs under continuous light at MPP in N₂ atmosphere at room temperature, and PCE evolution of unencapsulated devices (20 per condition) stored in dark and ambient conditions (40% RH) for 2000 hours. Error bars represent standard deviation. Reproduced with permission.⁸⁸ Copyright 2024, Wiley-VCH GmbH. (c) J-V curves and images of DPA-TFA PSC mini-modules (25 cm^2 and 64 cm^2); MPP tracking for encapsulated devices under continuous one-sun illumination; stability under high humidity (80% RH). Reproduced with permission.¹⁸³ Copyright 2024, Elsevier Inc. (d) J-V curves of best F-PSCs for control and DSSP-PPU-doped; PCE data of F-PSCs with and without DSSP-PPU; schematic of $5 \times 5\text{ cm}^2$ perovskite mini-modules; champion I-V curves of DSSP-PPU-doped flexible mini-modules; PCE evolution under bending cycles for control and DSSP-PPU-doped F-PSCs; loading/unloading force curves for control and DSSP-PPU-doped films. Inset: Measurement setup schematic. Reproduced with permission.¹⁸⁴ Copyright 2023, Wiley-VCH GmbH.

boundaries of perovskite films. This ligand helps release residual stress, soften grain boundaries, and enable room-temperature self-healing of cracks in the perovskite layer. As a result, F-PSCs achieved PCEs of 23.73% for rigid substrates, 22.24% for flexible substrates, and 17.32% for flexible mini-modules. Importantly, these devices maintained 77.25% of their initial efficiency after 8000 bending cycles and could recover nearly 90% of their efficiency through the self-healing process. This self-healing ability is attributed to the synergistic effects of dynamic disulfide bonds and hydrogen bonding, which improve flexibility, passivate grain boundary defects, and enhance device stability. These findings highlight the potential of the “ligament” strategy to significantly extend the lifetime and commercialization prospects of flexible modules by improving their mechanical and operational stability (Fig. 13d).¹⁸⁴ Overall, these strategies not only overcome challenges in phase stability and moisture resistance but also offer a pathway for industrial-scale production of highly efficient and stable perovskite modules, with potential applications in LEDs, photodetectors, and scintillators.

7.3. Supramolecular-engineered PQDs for application in LEDs and displays

PQDs have shown great potential in various optoelectronic applications, including LEDs, and displays, owing to their tunable emission properties and high PLQY. Supramolecular chemistry further enhances these properties, making PQDs more viable for commercial applications. Tri-coordinated trivalent P organic molecules (triphenylphosphine, TPP and 2-(diphenylphosphino)-biphenyl, DPB) anchor to CsPbI₃ perovskite nanocrystals surfaces, reducing V_i defects, stabilizing cubic symmetry, enhancing luminescence and material stability, while their short-chain ligands and benzene rings improve carrier transport and energy level balance, enabling top-emitting LEDs with 22.8% peak external quantum efficiency (EQE) and minimal efficiency roll-off (2.6% at 500 mA cm⁻²), offering a novel strategy for advanced perovskite nanocrystals optoelectronics.¹⁸⁵ Using a trace amount of octylamine (OTA) as an additive in the purification of CsPbI₃ nanocrystals (NCs) significantly enhances their optical and electronic properties, paving the way for high-performance LEDs. OTA regulates the dynamic balance between surface ligand adsorption and desorption, preserving nanocrystal integrity and reducing defects. This leads to improved photoluminescence stability, increased phase stability, and higher operational reliability of perovskite-based LEDs. Additionally, OTA enables *in situ* substitution of oleylamine, reducing the spacing between adjacent NCs and forming densely packed films with enhanced charge carrier transport. The additive also decreases ion migration by increasing activation energy, minimizing ion vacancy pathways. As a result, LEDs utilizing OTA-assisted Zn-doped CsPbI₃ NCs achieve a 4-fold increase in EQE and a 6-fold enhancement in operational lifetime, with peak EQE reaching 15.3%.¹⁵⁸ The O-Tg interacts with CsPbI₃ QD surfaces and bridges halogens through multiple hydrogen bonds, significantly improving optoelectronic properties and device stability. The biguanide functional group in O-Tg, effectively passivating surface defects while simultaneously stabilizing

the perovskite crystal structure by occupying the A-site. This strong binding affinity suppresses halogen and A-site vacancies, reduces ion migration, and lowers trap state density, increasing PLQYs from 75% to 96%. The hydrophobic benzene ring in O-Tg prevents degradation by polar molecules, rendering the QDs water-resistant, with films maintaining stability even after 30 hours of submersion. These features result in high-efficiency LEDs with EQEs exceeding 20%, achieving a peak T90 lifetime of 25 hours under a high current density of 50 mA cm⁻². Supported by first-principles calculations, this approach demonstrates the transformative potential of supramolecular interactions in defect passivation and stability enhancement, offering a robust strategy for advancing high-performance, durable perovskite LEDs (Fig. 14a).¹⁵⁹ The use of bidentate ligands to assemble halide perovskite nanocrystals (PNCs) into high-order supercrystals (SCs) offers precise control over their dielectric, electronic, and excitonic properties. Unlike monodentate ligand-based PNC assemblies, which are prone to mechanical deformation and exciton splitting, bidentate ligands such as eicosanedioic acid (EA) create mechanically stable, slipping-free SCs with long-range ordering. This interlocking mechanism leads to close-packed PNC lattices, overlapping electronic wave functions, and a higher dielectric constant, resulting in unique excitonic properties distinct from single PNCs or disordered PNC films. Structurally and excitonically ordered SCs exhibit several advantages: reduced spectral shifts (<35 meV) compared to PNC films or bulk crystals (>100 meV), excitation power-independent exciton lifetimes (<10 ns) in the single-exciton regime, and minimized non-geminate carrier recombination. These features are confirmed by fast Fourier transform (FFT) analyses, small-angle X-ray scattering (SAXS), and TRPL measurements, which demonstrate the superior structural stability and excitonic performance of SCs. The SCs retain the quantum confinement of individual PNCs while avoiding the delayed carrier recombination and prolonged PL lifetimes typical of PNC films. This bidentate ligand-assisted strategy not only enhances the mechanical and electronic stability of halide perovskite assemblies but also establishes a pathway to optimize their optoelectronic properties, offering significant potential for applications in high-performance perovskite-based devices.¹⁸⁶ The development of ultra-stable halide PNCs, particularly CsPbI₃ PNCs, has been achieved through the introduction of a novel multi-amine chelating ligand, *N'*-(2-aminoethyl)-*N'*-hexadecyl-ethane-1,2-diamine (AHDA). AHDA anchors to the PNC surface with a binding energy of 2.36 eV, significantly surpassing the 1.47 eV of conventional oleylammonium (OLA) ligands. This strong chelating interaction effectively suppresses dynamic ligand desorption, stabilizing the PNCs under various ambient stressors such as polar solvents, heat, light, and repeated purification (over 15 cycles). The enhanced stability of AHDA-CsPbI₃ PNCs is attributed to its dual amino groups, which provide multiple binding sites, ensuring robust lattice anchoring and minimizing morphological and structural disruptions. Unlike OLA, AHDA prevents ligand escape and dynamic surface binding, as evidenced by thermogravimetric analysis (TGA), enabling the retention of PL and quantum yield for over 110 days in air. AHDA's chelating effect also facilitates stable synthesis of other perovskite

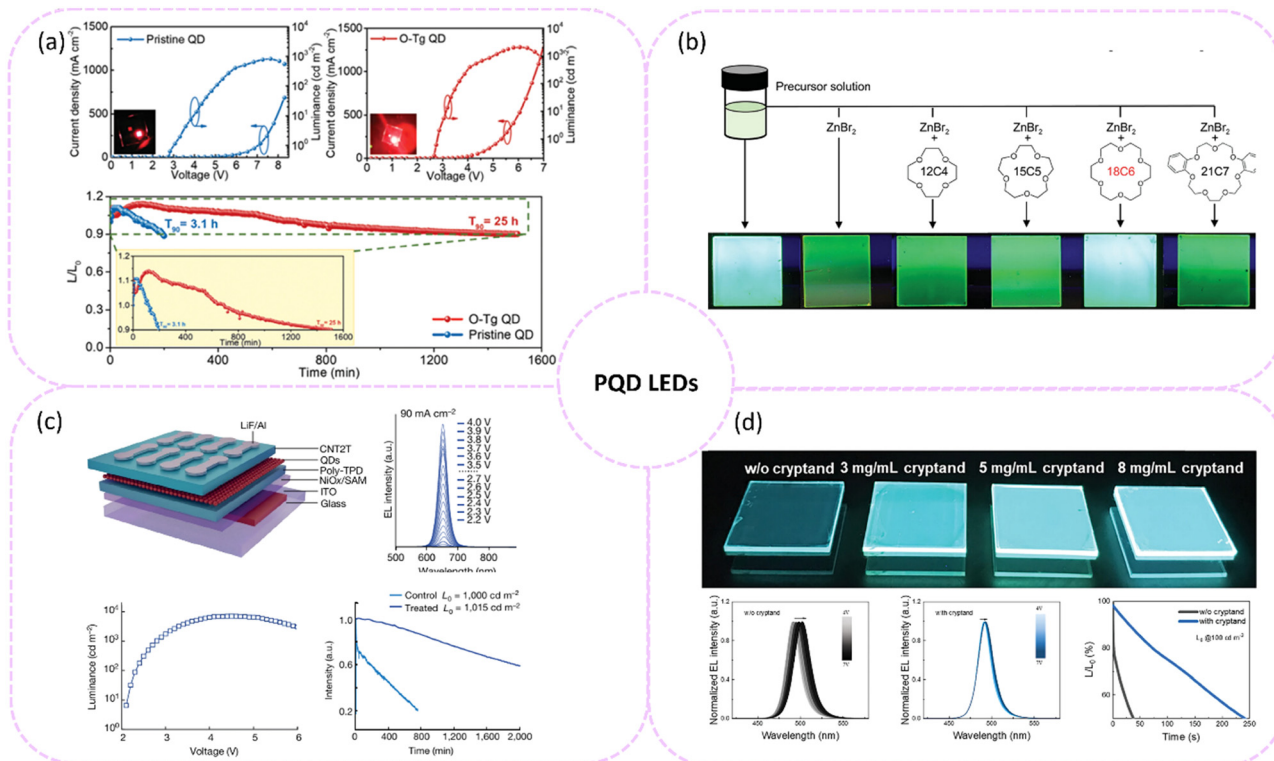


Fig. 14 (a) Current density–voltage–luminance curves and operational lifetime of LEDs with pristine and O-Tg QDs. Reproduced with permission.¹⁵⁹ Copyright 2024, Wiley-VCH GmbH. (b) Thin-film photoluminescence images under UV light ($\lambda = 365$ nm) showing the effect of crown ether cavity sizes. Reproduced with permission.¹⁸⁹ Copyright 2022, Wiley-VCH GmbH. (c) Device structure and materials of each layer; electroluminescence spectra at 2.2–4.0 V ($1\text{--}90\text{ mA cm}^{-2}$); EQE–luminance curve; operational stability of control and treated LEDs. Reproduced with permission.¹⁶⁰ Copyright 2024, Springer Nature. (d) PL image of perovskite film with varying cryptand concentrations under 365 nm UV light; EL spectra of original and cryptand-treated PeLEDs at different voltages; operational stability of PeLEDs with initial luminance $\approx 100\text{ cd m}^{-2}$. Reproduced with permission.¹⁴⁰ Copyright 2024, Wiley-VCH GmbH.

compositions (e.g., CsPbCl_3 , CsPbBr_3 , CsPbBrI_2 , and FAPbI_3) with consistent PL emission and enhanced robustness against environmental challenges. DFT calculations reveal that AHDA's larger binding energy arises from its ability to simultaneously bind multiple halide ions on the PNC surface, creating stronger surface passivation than mono-amine ligands. Furthermore, AHDA- CsPbI_3 PNCs exhibit lower surface ligand density, enhancing their efficiency in photocatalytic applications, such as stereoselective C–C oxidative coupling reactions. This innovative ligand strategy not only ensures the structural and optical stability of PNCs but also improves their catalytic and optoelectronic properties.¹⁸⁷ Furthermore, a low-temperature solution-based synthesis further enhances processability, allowing the creation of stable $(18\text{C6@K})_2\text{HfBr}_6$ inks in polystyrene (PS) and dichloromethane (DCM) retained PLQYs above 90% and facilitated the fabrication of uniform thin films and high-resolution emissive 3D-printed structures.¹⁶³ This strategy not only advances the development of halide perovskite emitters with ultrahigh PLQYs but also broadens their applications in displays, patterning, and functional material design.¹⁶³ The incorporation of crown ethers into the synthesis of all-inorganic cesium lead halide perovskite quantum dots (CsPbBr_3 QDs) offers a groundbreaking solution to overcome the low solubility of cesium precursors in polar media, enabling the production of QDs under ambient, low-temperature conditions. Quasi-2D perovskite ($\text{PEA}_2\text{Cs}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$) devices fabricated

with these 12C4 crown-ether assisted *in situ* grown (CAIG) perovskite crystals eliminate the need for multiple quantum wells (MQWs) while maintaining efficient exciton generation and slower exciton decay. This leads to a maximum brightness of $\sim 27\,562\text{ cd m}^{-2}$, an EQE of $\sim 16.1\%$, and exceptional ambient stability, with luminescence and EQE half-lifetimes exceeding 17 and 43 hours under 52% relative humidity. The findings highlight the crucial role of interfacial interactions in controlling the perovskite lattice, enabling more stable and efficient light-emitting devices.¹⁴⁴ The incorporation of the crown ether 2-hydroxymethyl-12-crown-4 (HM12C4) into PeLEDs demonstrates the transformative potential of supramolecular interactions in enhancing device performance. HM12C4 improves the nucleation process, forming smaller nanograins, and effectively passivates defects at grain boundaries, which are critical for achieving high efficiency. By suppressing PbBr_6 octahedron agglomeration in the precursor and enhancing wettability, HM12C4 facilitates the formation of smoother, denser perovskite films with superior morphology. The functional groups in HM12C4, such as $-\text{OH}$ and $\text{C}-\text{O}-\text{C}$, play vital roles by forming hydrogen bonds with halide atoms and weak chemical interactions with Pb^{2+} , as confirmed by FTIR analysis. However, the 12C4 lacks $-\text{OH}$ functional group couldn't show these beneficial behaviors. These interactions reduce non-radiative recombination and stabilize the perovskite structure,

significantly improving photophysical and electroluminescent properties. The optimized PeLEDs exhibit a low turn-on voltage of 2.3 V, high brightness of up to $27\,300\text{ cd m}^{-2}$, a current efficiency of 17.2 cd A^{-1} , and an external quantum efficiency of 4.52%.¹⁸⁸ Sim *et al.* highlighted the critical role of 18C6 in suppressing chemical reactions between metal oxides and hybrid perovskites in PeLEDs, significantly enhancing performance and stability without the need for traditional interlayers. Among crown ethers of varying cavity sizes, only 18C6 effectively prevents reaction-induced degradation, likely due to its selective formation of a $\text{ZnBr}_2(18\text{C}6)$ compound, as confirmed by XRD analysis. Smaller or larger crown ethers (*e.g.*, 12C4, 15C5, and 21C7) fail to achieve this effect, indicating that reaction inhibition depends on the precise cavity size rather than metal cation capture (Fig. 14b). The 18C6 additive not only suppresses detrimental reactions but also facilitates efficient charge injection, enabling an 82-fold longer device lifetime and a low operating voltage of 3.2 V at $10\,000\text{ cd m}^{-2}$. This dual-function approach establishes 18C6-treated PeLEDs as a superior alternative for high-performance, stable light-emitting applications.¹⁸⁹ Crown ethers, particularly dibenzo-21-crown-7 (DB21C7), facilitate complete dissolution of the CsBr precursor, overcoming traditional solubility limitations and making CsPbBr_3 QD inks practical for device fabrication. This strategy allowed for the fabrication of highly efficient LEDs with bright green emission, achieving a current efficiency of 9.22 cd A^{-1} and an EQE of 2.64%, marking the first room-temperature-synthesized CsPbBr_3 QD-based LEDs.¹²⁷ In addition, Wang *et al.* revealed TMSBr molecular modifications lead to PQD films with high PLQY, uniformity, and exceptional electrical transport properties. Consequently, red perovskite LEDs fabricated with these films achieve a record-low operating voltage of 2.8 V at 1000 cd m^{-2} luminance and exhibit 100 times greater stability than previous devices, marking a significant advancement toward practical, durable perovskite LED applications (Fig. 14c).¹⁶⁰

The synergism of two agents has been proven to enhance interaction between supramolecular and PQDs. Ban *et al.* reported the crystallization of PEABr incorporating crown is suppressed, leading to a more uniform domain size distribution, reduced phase segregation, and smaller perovskite crystallites (13.3 nm compared to 18.5 nm without crown). This results in improved PLQY of up to 70% and enhances the EQE of organometal halide perovskite LEDs to 15.5%. Molecular interactions between the ammonium head of PEABr and crown's oxygen atoms of crown ($\text{N-H}\cdots\text{O}$) (*via* hydrogen bonding) and between crown and Cs^+ or Pb^{2+} ions facilitate controlled nucleation and suppress aggregate formation.¹⁶¹ A green PeLEDs made by a dual-additive supramolecular strategy using 18C6 and sodium trifluoroacetate (STFA) achieve peak EQEs of 23.9%, with large-area (1 cm^2) devices reaching EQEs of 21.6%, and semi-transparent devices achieving a record EQE of 13.6%. These findings demonstrate the potential of supramolecular coordination strategies for advancing high-performance perovskite films suitable for large-area and transparent optoelectronic applications.¹⁶⁵ Another study using cryptand as an additive has been developed to regulate phase distribution in quasi-2D

perovskite films, significantly enhancing device performance. The resulting electronic structure enables efficient energy transfer from low-*n* to high-*n* phases, enhancing radiative recombination. Optimized blue PeLEDs treated with cryptand achieve an impressive EQE of 10.16% at 490 nm, a significant improvement over the reference device (2.33%). These devices also demonstrate exceptional spectral and operational stability, with only a minimal 2 nm shift in emission peak within a 4–7 V voltage range, and an operational lifetime extended by nearly eightfold (Fig. 14d). This work not only improves luminescent efficiency and stability but also provides a scalable method for precise phase distribution control, offering significant potential for the development of high-performance blue PeLEDs.¹⁴⁰ Supramolecular chemistry has thus enabled PQDs to move closer to practical applications by addressing critical challenges related to stability, efficiency, and device longevity.

7.4. Supramolecular interaction in perovskite photodetectors

One major challenge in perovskite photodetectors is mechanical stress-induced degradation, which can impact long-term stability and efficiency. Song *et al.* introduced fluorinated organic spacers (FPEA) to regulate interlayer interactions in 2D perovskites. The incorporation of fluorine atoms creates strong electrostatic interactions with benzene rings, effectively reducing microstrain and improving the overall flexibility of the material (Fig. 15a). This enhancement leads to improved photodetector stability, with a remarkable threefold increase in photocurrent recovery under mechanical stress. Additionally, the 60% microstrain can be released by compressive bending in $(\text{p-FPEA})_2\text{PbI}_4$ perovskite film., and the corresponding photocurrent response is recovered by about three times, demonstrating the effectiveness of supramolecular interactions in maintaining optoelectronic performance under mechanical deformation.¹⁹⁰ Another major limitation of perovskite photodetectors is their instability under continuous operation. Lu *et al.* introduced a short-chained fluorinated piperidinium (F-PIP) spacer to stabilize the perovskite structure and reduce defects. The fluorinated moiety enhances hydrophobicity, significantly improving moisture resistance. As a result, a high responsivity of 502 mA W^{-1} and a photoreactivity of $5.73 \times 10^{10}\text{ cm Hz}^{1/2}\text{ W}^{-1}$. Additionally, the device achieved fast response and recovery times of 42 ms and 46 ms, respectively, under 450 nm illumination at 20 V. Notably, the incorporation of the fluorinated short-chained segment into the organic spacer significantly enhanced the device's environmental stability, maintaining its performance for up to 49 days (Fig. 15b). These results highlight the potential of $(4\text{FH-PPH})_2\text{-PbI}_4$ HP as a promising candidate for next-generation optoelectronic devices, particularly in applications requiring high stability and efficiency.¹⁹¹ Environmental stability remains a critical challenge for perovskite photodetectors, as exposure to moisture and oxygen accelerates their degradation. To address this issue, researchers have introduced carbonized polymer dots (CPDs) as supramolecular stabilizers to suppress ion migration and enhance structural robustness. The strong polymer-perovskite interactions facilitate more efficient charge transport pathways, thereby extending the operational lifespan of the photodetector

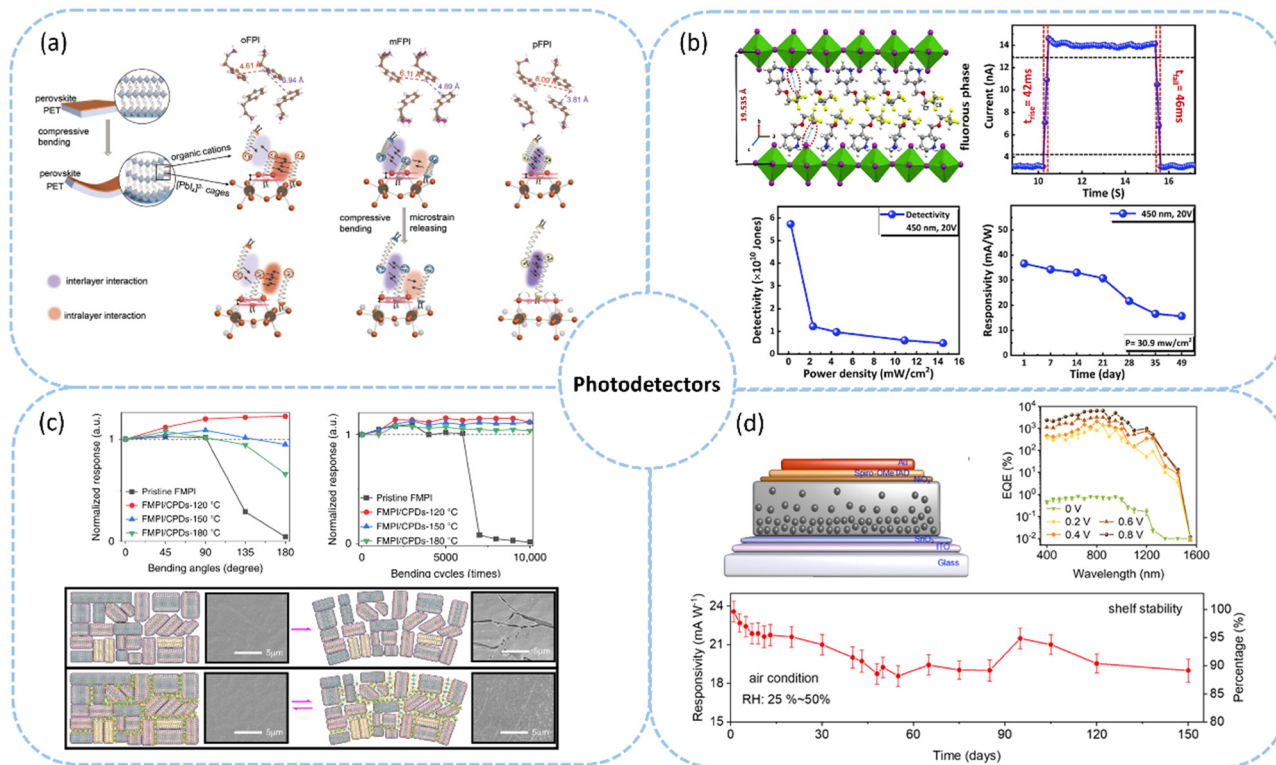


Fig. 15 (a) The scheme of perovskite organic cations packing structure and perovskite thin film microstrain changes with bending process. Reproduced with permission.¹⁹⁰ Copyright 2022, Wiley-VCH GmbH. (b) Single-crystal structure of $(4\text{FH-PPH})_2\text{PbI}_4$ displaying 2D layered packing with the unique fluorine phase; photodetection performance of a fluorinated short-chained $(4\text{FH-PPH})_2\text{PbI}_4$ HP device under 450 nm showing time-dependent photocurrent response under illumination of 30.9 mW cm^{-2} ; detectivity as a function of the power density and; stability of the device stored in air without any encapsulation for up to 49 days. Reproduced with permission.¹⁹¹ Copyright 2024, American Chemical Society. (c) The flexible stability of various bending angles and bending times; Schematic diagram of pristine perovskite and perovskite/CPDs thin films before and after bending process, with SEM images alongside. Reproduced with permission.¹⁹² Copyright 2022, Springer Nature. (d) The device structure of the photodetector, perovskite/F-PbS, was incorporated as an active layer; EQE of the photodetector varies with reverse bias voltage; Shelf stability of the unencapsulated photodetector with composed of quasi-2D perovskite and PbS CQDs. Reproduced with permission.¹⁹³ Copyright 2022, American Chemical Society.

under ambient conditions. Notably, devices incorporating CPDs exhibited no performance degradation after 10 000 bending cycles at a 90° angle. In contrast, pristine perovskite photodetectors experienced a rapid decline in response signal when the bending angle increased to 135° , with the response signal dropping to 30% of its initial amplitude. Furthermore, the coordinating CPDs effectively suppressed leakage current, significantly enhancing the detectivity of the photodetector. As a result, the device demonstrated the capability to resolve weak light signals as low as 10.1 pW cm^{-2} (Fig. 15c). These findings underscore the effectiveness of polymer-assisted stabilization in improving both the mechanical durability and optoelectronic performance of perovskite photodetectors.¹⁹² In addition, extending the spectral response of perovskite photodetectors to the near-infrared (NIR) region is essential for applications in telecommunications and biomedical imaging. Pan *et al.* utilized organic amine molecules to form supramolecular interactions between perovskite layers and PbS colloidal quantum dots (Fig. 15d). The amine-bridging effect improves interfacial charge transfer efficiency, leading to a significant enhancement in photodetector responsivity within the NIR spectrum. The optimized photodetector demonstrated an external quantum

efficiency of 1260% at 1200 nm, significantly outperforming conventional perovskite photodetectors. Additionally, the device retained 90% of its initial performance after 150 days of storage with relative humidity (RH) of 25–50%, highlighting the stability improvements achieved through supramolecular engineering.¹⁹³

Supramolecular engineering has demonstrated its versatility in improving various aspects of perovskite photodetectors, including mechanical flexibility, crystallinity, stability, and spectral response. By integrating supramolecular interactions through organic spacers, gel-assisted growth, polymer stabilization, and amine bridging, researchers have significantly enhanced the durability and performance of these photodetectors.

8. Conclusions and outlook

In conclusion, supramolecular engineering provides a powerful toolkit for advancing hybrid perovskite optoelectronics, addressing long-standing challenges related to stability, film quality, and device performance. Supramolecular interactions, including hydrogen bonding, van der Waals forces, and halide

bonding, play a vital role in the crystallization, morphology, stability, and properties of organic–inorganic hybrid perovskite materials. These interactions regulate nucleation and grain growth, leading to improved film uniformity, reduced defects, and enhanced charge transport. They also contribute to stability by mitigating moisture and thermal degradation while passivating defects. As a result, supramolecular engineering enhances the efficiency and longevity of perovskite-based devices, from solar cells to LEDs. Future research should focus on leveraging these interactions for scalable, durable, and high-performance perovskite technologies. By leveraging a variety of molecular interactions, researchers have achieved unprecedented control over perovskite crystallization, PQD synthesis, and interface stabilization. Continued exploration of supramolecular approaches has the potential to push the boundaries of what is achievable with perovskite-based devices, bringing us closer to the widespread commercial adoption of these promising materials in optoelectronic applications.

Supramolecular agents represent a versatile and transformative tool in perovskite engineering, offering significant potential to address key challenges in stability, defect passivation, and morphology control. By carefully designing supramolecular structures, researchers can create molecules that self-assemble on perovskite surfaces, reducing defect sites and creating hydrophobic barriers against moisture. Dual-functional agents combining thiol groups for defect passivation and hydrophobic chains for moisture resistance simultaneously address several issues that impact perovskite stability. This multifunctionality reduces the need for multiple additives, simplifying the material composition and making it more efficient for device fabrication. Additionally, the ability of supramolecular agents to guide crystal growth promotes enhanced morphology, improving charge transport and ultimately boosting device efficiency and stability.

The integration of computational methods, including machine learning (ML) and advanced molecular dynamics (MD) simulations, has become a transformative force in supramolecular engineering for perovskite systems. These tools provide unparalleled insight into the intricate interfacial chemistry and material stability that define these materials. By integrating crystallographic, spectroscopic, and device-performance data, ML models will predict the binding thermodynamics and kinetics of supramolecular agents with near-experimental fidelity. For instance, next-generation graph neural networks (GNNs) could incorporate the temporal evolution of local coordination environments, enabling dynamic predictions of how supramolecular ligands adapt to Pb^{2+} under-coordination or halide vacancies under light-soaking or thermal stress. This capability will be crucial for designing agents that not only passivate deep trap states (e.g., Pb° or I^- interstitials) but also actively mitigate fatigue in PSCs and PLEDs during prolonged operation. A key frontier lies in unraveling and controlling environment-dependent dynamics under increasingly complex conditions. MD simulations, enhanced by machine-learned interatomic potentials (e.g., neural network potentials trained on quantum mechanical data), will offer

near-DFT accuracy at a fraction of the computational cost, enabling real-time modeling of supramolecular reorganization in the presence of moisture, oxygen, or electric fields. These advances could elucidate how amphiphilic agents with flexible alkyl spacers or conjugated π -systems self-assemble into adaptive, protective networks at perovskite surfaces, potentially leading to “smart” passivation layers that respond dynamically to degradation triggers. For example, simulations could guide the synthesis of supramolecular agents with switchable functionalities—such as photoresponsive groups that modulate binding strength under illumination—offering a new paradigm for stabilizing perovskites under variable environmental stressors. Simultaneously, ML-driven generative models, including variational autoencoders and reinforcement learning frameworks, will push the boundaries of inverse design by proposing supramolecular architectures with unprecedented specificity. This could include trifunctional molecules combining Lewis-base anchors (e.g., $-\text{C}=\text{O}$, $-\text{NH}_2$ or $-\text{P}=\text{O}$) for defect passivation, hydrophobic barriers for moisture exclusion, and ionic bridges to suppress phase segregation. The future of these computational tools also lies in their ability to bridge multi-scale phenomena, connecting atomic-level interactions to macroscopic device performance with greater predictive power. ML algorithms trained on operando datasets—such as time-resolved photoluminescence, impedance spectroscopy, or transient absorption—could forecast how supramolecular binding influences charge recombination dynamics or ion migration over thousands of operational hours, directly informing strategies to maximize open-circuit voltages and fill factors in PSCs. Likewise, hybrid MD-Monte Carlo approaches will evolve to simulate agent diffusion and clustering within perovskite grain boundaries at industrially relevant scales, optimizing passivation strategies for advanced fabrication methods like slot-die coating or vapor deposition. A particularly exciting prospect is the development of closed-loop discovery platforms, where computational predictions feed directly into automated synthesis and testing workflows. Leveraging robotics and high-throughput characterization—such as XPS for coordination validation or GIWAXS for lattice analysis—these platforms could iteratively refine supramolecular designs in real time. As these computational frameworks mature, their synergy with experimental advances will eliminate inefficiencies in trial-and-error approaches, ushering in a new era of rational design in perovskite technologies. The goal is not merely incremental improvements but the realization of commercially viable, ultra-stable perovskite devices with tailored optoelectronic properties—such as PSCs exceeding 25% efficiency with lifetimes beyond 25 years or LEDs with external quantum efficiencies rivaling OLEDs.

The scalability of supramolecular-engineered hybrid perovskite optoelectronic devices—from laboratory prototypes to commercial products—depends critically on overcoming key manufacturing challenges. A primary hurdle is translating the precise molecular control offered by supramolecular engineering into industrially viable fabrication processes. Techniques like roll-to-roll printing, slot-die coating, and blade coating

have demonstrated success in depositing uniform perovskite thin films over large substrates. Adding supramolecular agents as additives in precursor inks requires minimal adjustments to this established solution-deposition infrastructure. This compatibility reduces economic and technical barriers, enabling manufacturers to incrementally adopt supramolecular strategies within mature workflows. Furthermore, the tunability of supramolecular interactions offers a versatile toolkit to tackle scale-up challenges, such as maintaining film homogeneity and device performance over large areas. By optimizing the concentration and molecular design of these agents, researchers can fine-tune perovskite nucleation and growth kinetics, ensuring that the efficiency and stability achieved in small-scale devices translate to industrial-scale formats. An alternative approach involves developing supramolecular motifs suitable for thermal evaporation, particularly for interface and surface passivation. Thermal evaporation, a well-established industrial process, allows for the deposition of highly uniform and ultrathin layers with precise thickness control, allowing the deposition of nanometer-scale passivation on meter-scale perovskite films to enhance uniformity and scalability further.

Additionally, as environmental sustainability gains prominence, developing eco-friendly synthesis routes for supramolecular agents and perovskite materials is increasingly vital. Traditional synthesis often relies on solvents and reagents with significant environmental footprints. To address this, researchers are exploring green chemistry approaches, such as using bio-based precursors and designing supramolecular agents soluble in non-toxic, green solvents. Another strategy involves leveraging renewable raw materials to synthesize organic ligands and macrocycles used in supramolecular engineering. These sustainable synthesis routes align supramolecular-engineered perovskite devices with environmental regulations, enhancing their appeal for widespread commercial adoption.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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