

Supramolecular Engineering of Hybrid Materials in Photovoltaics and Beyond

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Abstract: Solar-to-electric energy conversion has provided one of the most powerful renewable energy technologies. In particular, hybrid organic–inorganic halide perovskites have recently emerged as leading thin-film semiconductors for new generation photovoltaics. However, their instability under operating conditions remains an obstacle to their application. To address this, we relied on supramolecular engineering in the development of organic systems that can interact with the surface of hybrid perovskites through different noncovalent interactions and enhance their operational stabilities. Moreover, we have utilized the uniquely soft yet crystalline structure of hybrid perovskites and their mixed ionic–electronic conductivity to provide a platform to advance their functionality beyond photovoltaics. This account reviews our recent progress in supramolecular engineering of hybrid perovskites in photovoltaics and discusses their perspectives in the development of smart technologies.

Keywords: Hybrid perovskites · Photovoltaics · Smart materials · Supramolecular engineering



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1. Introduction

Smart technologies that can autonomously adapt to their operating conditions are increasingly required in modern optoelectronics.^[1–3] They can be realized by controlling material functions in response to external stimuli.^[4–7] Some of the most versatile strategies for accessing adaptive functional materials rely on supramolecular chemistry, which plays a critical role in natural systems and biological processes.^[5–8] However, the potential of stimuli-responsive (supra)molecular materials has not been fully realized in optoelectronics due to the challenges of transferring their function to the solid state in functional devices.^[8–10] This creates the need for ‘*amphidynamic*’ materials that are crystalline

yet capable of hosting dynamic and stimuli-responsive functionalities in the solid state (Fig. 1).^[8–12]

Hybrid organic–inorganic metal halide perovskites present a unique class of materials that display an untapped capacity to act as amphidynamic scaffolds (Fig. 2).^[11–13] These versatile and soft, yet crystalline, semiconductors that feature mixed ionic–electronic conductivities have recently attracted considerable attention due to their exceptional optoelectronic characteristics.^[14–19] In particular, they have demonstrated remarkable solar-to-electric power conversion in photovoltaics, despite routinely being prepared by solution-processing.^[18,19] However, they feature limited stabilities under atmospheric conditions of oxygen and moisture, as well as in response to voltage and light under operating conditions.^[20–25] This has stimulated extensive research on establishing the strategies to stabilize hybrid perovskite materials and optoelectronic devices.

In our work, we have relied on (supra)molecular engineering for the stabilization of hybrid halide perovskites by designing organic molecules that can interact with the perovskite interface through tailored noncovalent interactions. This has resulted in the enhancements of operational stabilities in perovskite solar cells without compromising their performances, while opening a path for enhancing their functionality. This account details some of the latest developments and future perspectives of supramolecular engineering in hybrid photovoltaics and beyond towards smart technologies.

2. Hybrid Halide Perovskites and their Supramolecular Control in Hybrid Photovoltaics

Hybrid organic–inorganic halide perovskites can be described by the AMX_3 formula (Fig. 2a–b), which defines the inorganic $\{MX_6\}$ -based corner-sharing octahedral framework (Fig. 2b) comprised of divalent metal ions ($M = Pb^{2+}, Sn^{2+}$), halide anions ($X = Cl^-, Br^-, I^-$), and central ‘A-cations’ (e.g. Cs^+ , methylammonium (MA), formamidinium (FA)).^[13] These solution-processed materials show excellent light absorption and long-living charge carriers with long diffusion lengths and high defect tolerance, which has stimulated their use in thin-film photovoltaics since 2009.^[13,26–31]

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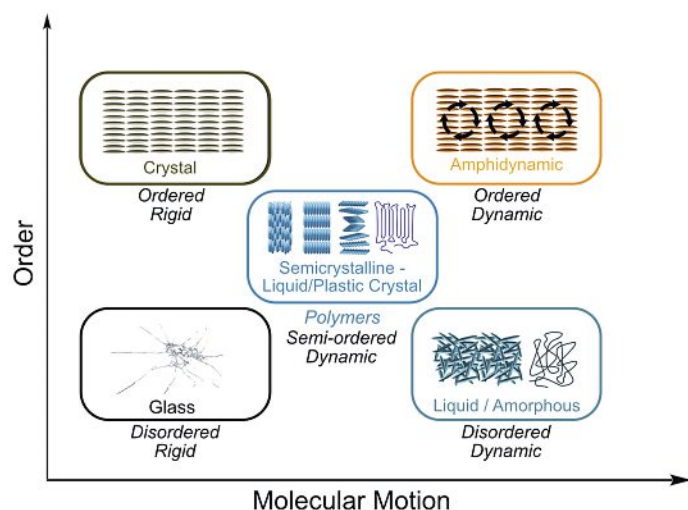


Fig. 1. Schematic representation of classes of condensed matter based on their order and molecular dynamics (*i.e.* molecular motion). Adapted based on ref. [10]

Moreover, they have been applied in light-emitting diodes,^[32] piezoelectrics,^[33] transistors and memory components,^[33,34] and they are of increasing interest in the emerging area of optoelectronics.^[14,16,17,35,36] The optoelectronic properties and energy bandgap (E_g) of hybrid perovskites are defined by the M–X interactions within the $\{MX_6\}$ octahedral framework (Fig. 2c), whereas organic components indirectly contribute to the structural integrity (*i.e.* octahedral connectivity) and thus optoelectronic properties (Fig. 2d).^[13,24,25] Hybrid perovskites are highly versatile and their properties can be tailored by compositional and interfacial engineering, as well as by applying organic modulators within perovskite materials and devices (Fig. 2b).^[24,25,37–39] The incorporation of organic components within the perovskite framework can result in the interfacial *molecular modulation* as well as the formation of *low-dimensional or layered (2D) perovskites* (Fig. 3a).^[24–26] These materials can be described by the $S_x A_{n-1} M_n X_{3n+1}$ formula,^[26–30] defining a layered structure of organic spacers (S) templating perovskite slabs comprised of $\{MX_6\}$ octahedra, gradually changing their properties, such as E_g (Fig. 3b–c), with the increasing number of slabs ($n = 1, 2, \text{etc.}$).^[26–31] The spacers, which are typically mono- ($x = 1$) or bifunctional ($x = 2$) ammonium cations, often form Ruddlesden-Popper (RP) and Dion Jacobson (DJ) phases (Fig. 3a).^[30,31] The commonly used spacers are based on alkyl or aryl ammonium groups, such as *n*-butylammonium (BA) or 2-phenylethylammonium (PEA), which can be further tailored to control their functionality (Fig. 3d).^[30] Most organic spacers have so far been electronically insulating, leading to the formation of natural quantum well (QW) structures with the E_g defined by the inorganic framework (Type IA, Fig. 3c).^[29,30] However, the octahedral connectivity (Fig. 2d) can also be controlled by the supramolecular assemblies of the organic spacer layers and their (opto)electronic properties (Fig. 3c).^[29,30,40]

We have relied on *supramolecular engineering* to design molecular modulators^[25,37–39] and layered hybrid perovskites (Fig. 3d)^[40–55] by using hydrogen bonding and metal coordination,^[37,49–51] van der Waals (vdW)^[41,42] and π interactions,^[43–48,54,55] halogen bonding^[52,53] and others, such as host–guest complexation.^[38,39] These materials have shown high operational stabilities and photovoltaic performances, enabled through the understanding of the atomic-level interactions.^[25,37–39,40,49–52,54–56]

We have demonstrated the utility of supramolecular engineering in the development of layered hybrid perovskites based on *vdW interactions* by using carbocyclic (1-adamantanyl)methanammo-

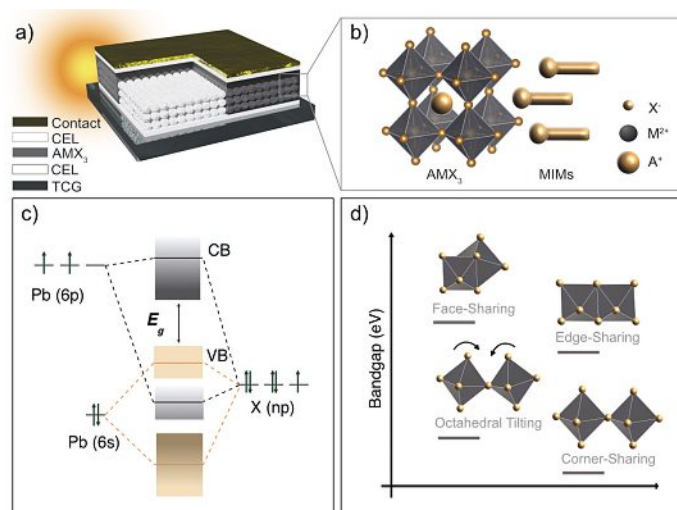


Fig. 2. Hybrid perovskite photovoltaics. (a) Schematic of perovskite solar cells and (b) the structure of modulated metal halide perovskites (AMX_3) with molecular modulators represented by orange rods. (c) Energy bandgap structure (E_g) of metal (M) halide (X) perovskites defined by the M–X orbital overlaps. Adapted based on ref. [35]. (d) Illustration of the dependence of the E_g on $\{MX_6\}$ octahedral connectivity in halide perovskites. CEL = charge-extraction layers; TCG = transparent conductive glass; CB/VB = conduction/valence band.

nium (ADAM) organic spacers (Fig. 3d).^[41,42] These materials were analyzed by a combination of techniques complemented by solid-state NMR spectroscopy to reveal atomic-level interactions in Ruddlesden-Popper phases. Adamantane is known to form ordered assemblies based on vdW interactions that were applied in functional materials, such as plastic crystals and molecular machines.^[41] The adamantane core was thereby functionalized with a methylammonium group and introduced into FA-based layered hybrid perovskites to provide a hydrophobic backbone through stronger vdW interactions as compared to conventional BA spacers.^[40] As a result, we obtained layered hybrid perovskites with power conversion efficiencies that exceed 7% in conventional perovskite solar cells.^[41] This was accompanied by long-term operational stability in one of the record-performing FA-based layered hybrid perovskite solar cells at the time.

This case study stimulated further efforts to advance hybrid perovskite materials by tailoring their supramolecular structures, such as by relying on π -based interactions.^[43–48,54,55] In fact, one of the most widely-employed organic spacers for layered perovskites, PEA, is assembled through π interactions, which are defined by the quadrupole moment of the aromatic ring and its relative orientation.^[54,55] Specifically, π -interactions between benzene rings are more favorable as T-shaped (π_T) and parallel-displaced (π_D) than parallel (π_P) orientations, which is due to their characteristic electronic density distribution (Fig. 4a, inset).^[54] On the contrary, fluoroarenes, such as 2-(perfluorophenyl)ethylammonium (FEA), have reversed quadrupole moments that favor parallel (π_P) interactions in benzene–perfluorobenzene systems (Fig. 4a, inset).^[54,55] Such alternating π interactions of arene–fluoroarene moieties could be used to template parallel π_P stacking of organic spacers in layered hybrid perovskites.^[48,54,55] Apart from controlling their structural and optoelectronic properties, this strategy can be relevant for the stabilization of materials since the presence of fluoroarene could increase the hydrophobicity and resilience to moisture, whereas anion– π interactions could potentially contribute to reducing halide ion migration.^[48,52,54] We analyzed the prospect of this π -templating approach in perovskite solar cells by using a layered hybrid perovskite based on a 1:1 mixture of PEA and FEA (labelled PF), demonstrating that the

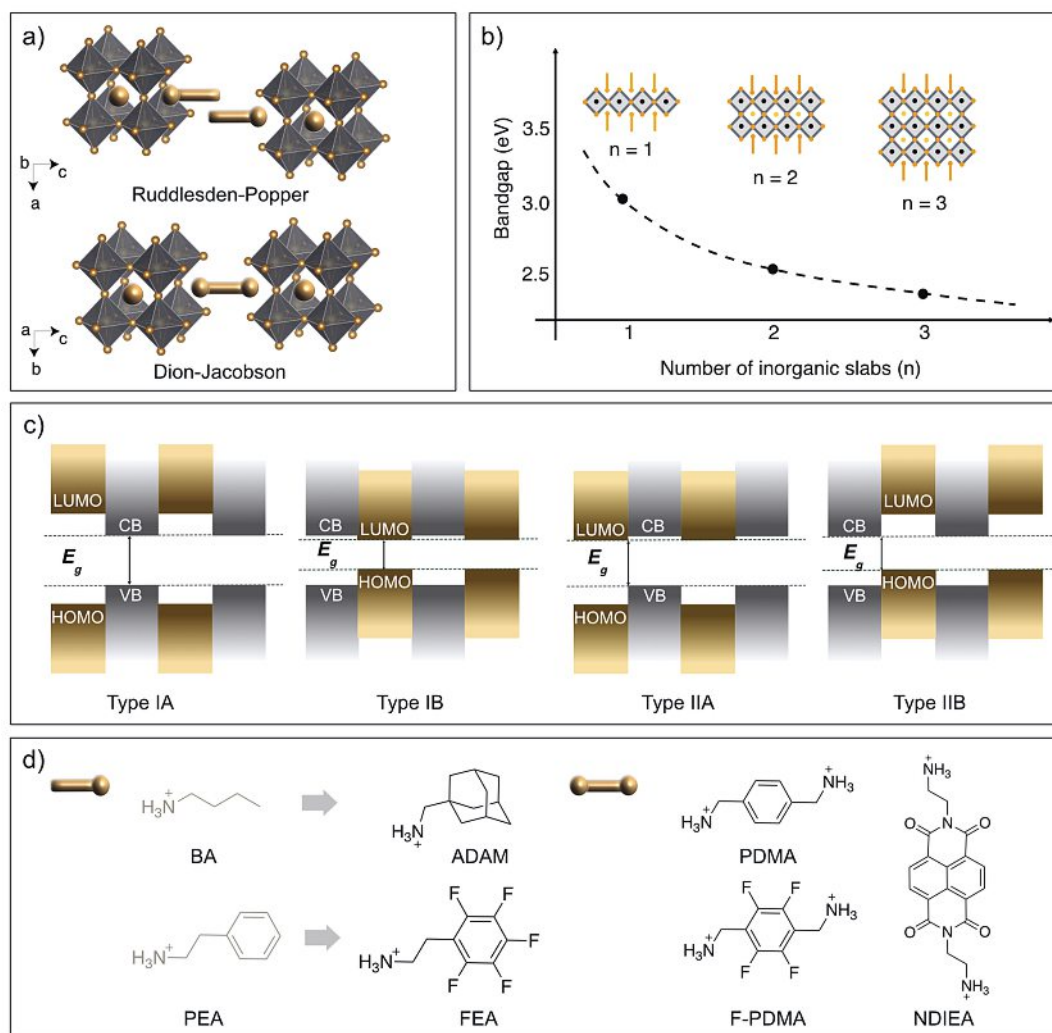


Fig. 3. Layered hybrid perovskites. Schematic of (a) layered hybrid perovskite architectures based on Ruddlesden-Popper (RP, top) and Dion-Jacobson (DJ, bottom) phases. (b) Illustration of the dependence of the bandgap (E_g) as a function of the number of inorganic slabs (n) in layered hybrid perovskites and (c) the representation of the Type I and Type II quantum-well electronic structures based on the energy level alignments of conduction band minima (CBM), valence band maxima (VBM), highest occupied (HOMO) and lowest unoccupied (LUMO) frontier molecular orbitals. Adapted based on ref. [35,36]. (d) Structures of representative organic spacers for layered hybrid perovskites, including archetypical *n*-butylammonium (BA) and 2-phenylethylammonium (PEA) organic spacers (in grey) and the representative analogues based on carbocyclic (ADAM = 1-adamantylmethylammonium) and perfluorinated (FEA = 2-(perfluorophenyl)ethylammonium) and spacers, along with the selected spacers that can form DJ phases, such as the 1,4-phenyldimethylammonium (PDMA) and its perfluorinated analogue (F-PDMA), as well as 2,2'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[Imn]) [3,8]phenanthroline-2,7-diyl) bis(ethylammonium) (NDIEA).

photovoltaic performances and operational stabilities are greater than for either of the spacers applied individually (Fig. 4a,b).^[54]

We used *NMR crystallography* to assess the atomic-level structure in a model comprising PEA and/or FEA spacers (S) in $S_2\text{PbI}_4$ ($n = 1$) layered perovskite compositions. $^{19}\text{F} \rightarrow ^{13}\text{C}$ cross polarization (CP) NMR spectra for mixtures of PEA and FEA spacer precursors and their layered perovskites showed atomic-level mixing between the two components (Fig. 4c), since CP relies on through-space dipole-dipole interactions at the sub-nanometer distance.^[54] However, layered perovskites based on a single type of spacer were found to exhibit similar spectral features to those with mixed spacers, suggesting the possibility of a nanoscale segregation. To scrutinize this, the chemical shifts were calculated using density functional theory (DFT) for different trial structures (Fig. 4d) that were generated by identifying low energy structures from molecular dynamics simulations of various assemblies, some of which were based on reported crystal structures optimized by DFT. The comparison of experimental and calculated ^{13}C and ^{19}F chemical shifts revealed the best agreement for a segregated model, indicating that the nonsegregated system matches the experimental data with 99.9% probability based on the Bayesian analysis (Fig. 4e-f).^[54] The generality of this observation was further confirmed in Dion-Jacobson layered perovskite analogues based on 1,4-phenylenedimethylammonium (PDMA) spacers and their perfluoroarene analogues (F-PDMA), which were also found to feature nanosegregation in thin films and mechanosynthetic powders.^[55] In contrast to

the previous reports, arene-fluoroarene interactions were thus not necessarily templating a uniform π -alternating structure in thin films and, instead, spacers form segregated domains, as revealed by the NMR crystallography. Nonetheless, the supramolecular assemblies with mixed-spacers could enhance the performances and stabilities of perovskite solar cells, suggesting the importance of nanoscale segregation in layered hybrid perovskites.

3. Enhanced Functionality of Hybrid Perovskites

While supramolecular control offers an effective strategy to control the properties of hybrid perovskite materials and their photovoltaic devices, it also provides a platform for enhancing their functionality.^[36] In particular, the assembly of organic spacer layers have so far been mostly used for templating layered hybrid perovskites and stabilizing them due to the increased hydrophobicity and suppression of ion migration. However, their structural versatility enables enhancing the functionality of hybrid perovskite assemblies towards multifunctional materials. This can be achieved through the incorporation of electro- and/or photoactive organic species, as well as chiral moieties (Fig. 5a) within the perovskite frameworks, tuning their optoelectronics and rendering them more responsive to various external stimuli.^[36]

The *electroactive spacers in layered perovskites* have been particularly relevant since the insulating character of organic spacer layer limits charge extraction, thereby leading to inferior performances of layered hybrid perovskites as compared to

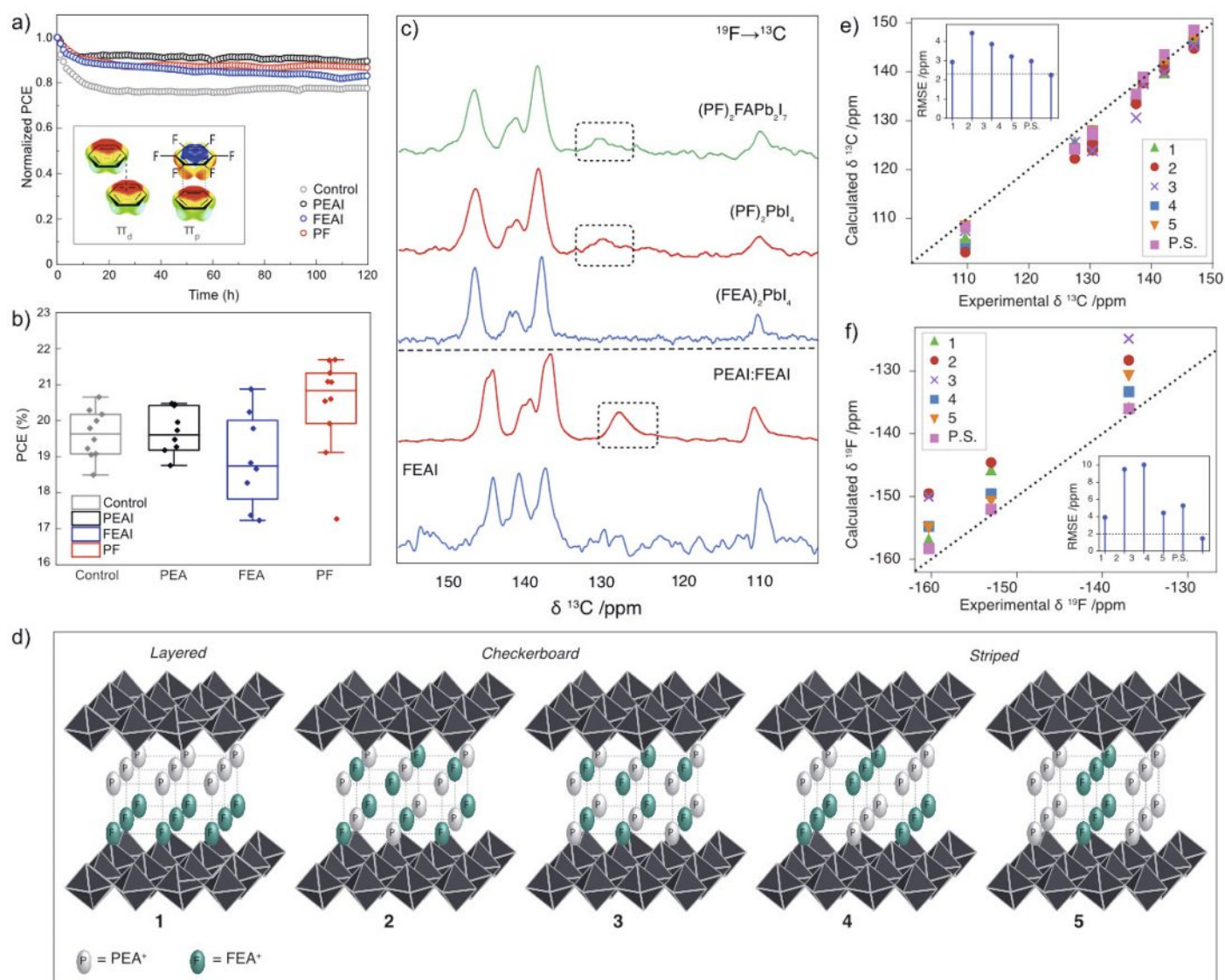


Fig. 4. Supramolecular π -templating in hybrid perovskite photovoltaics. (a) Evolution of power conversion efficiencies (PCE) over time and (b) PCE in a series of perovskite solar cells based on reference devices (control, grey) and those upon treatment of the perovskite interface by PEAI (black), FEAI (blue) and their 1:1 mixture (PF, red) to form 2D perovskite overlayers. The inset represents π - π interactions between the arene (left, π_a) and arene-perfluoroarene (right, π_p) systems. (c) $^{19}\text{F} \rightarrow ^{13}\text{C}$ cross-polarization (CP) magic angle spinning (MAS) NMR spectra. Top panels show the spectra of layered hybrid perovskites, whereas bottom ones show neat spacer precursors (FEAI) and their 1:1 mixture (PEAI:FEAI). Signals highlighted in dashed boxes arise from PEA in $^{19}\text{F} \rightarrow ^{13}\text{C}$ CP spectra. (d) Schematic of five trial structures (1–5) based on different alternating arrangements of arene (PEA) and perfluoroarene (FEA) spacers studied by NMR crystallography, including layered (1), checkerboard (2,3) and striped (4,5) models. (e–f) Calculated aromatic (e) ^{13}C and (f) ^{19}F NMR chemical shifts plotted with the experimental values for $(\text{PF})_2\text{PbI}_4$ model structures 1–5 (d) and a phase segregated (P.S.) model based on neat $(\text{PEA})_2\text{PbI}_4$ and $(\text{FEA})_2\text{PbI}_4$ phases. The diagonal lines indicate agreements, the insets show root mean square errors (RMSE) between the calculated and experimental chemical shifts for each structure, and the horizontal lines are expected error by RMSE. Adapted from ref. [54] under CC BY-NC-ND license. Copyright 2021 American Chemical Society.

their three-dimensional analogues.^[36] The use of electroactive spacers could thereby overcome this limitation by changing the electronic structure in hybrid materials (Fig. 5b). We recently applied a functionalized naphthalenediimide (NDI) based spacer, namely 2,2'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[*lmn*][3,8]phenanthroline-2,7-diyl)bis(ethylammonium) (NDIEA), in the formation of Dion-Jacobson perovskite phases.^[56] NDI materials are common electron acceptors used in organic electronics due to high electron affinity and charge carrier mobility, as well as thermal stability.^[56–58] An NDI-containing low-dimensional perovskite system has been previously described based on MA A-cation compositions.^[57] In general, the research on layered hybrid perovskites has been predominantly focused on MA-based systems while FA-based compositions remain underrep-

resented despite their attractive optoelectronic properties and higher thermal stability.^[40] This is partly since the photoactive α -FAPbI₃ perovskite phase is not thermodynamically stable at room temperature and stabilizing it remains an ongoing challenge. We have thereby studied NDI/FA-based low-dimensional hybrid perovskites by means of MD simulations and DFT, revealing the capacity to form layered hybrid perovskites featuring Type II QW structure in which spacer orbitals contribute to the band edge (Fig. 5b).^[56] This was evidenced experimentally in thin films and mechanochemically prepared powders by a combination of techniques, including solid-state NMR spectroscopy, X-ray diffraction (XRD), and transient absorption (TA) spectroscopy, complemented by time-resolved microwave conductivity (TRCM) measurements. XRD confirmed the formation of low-

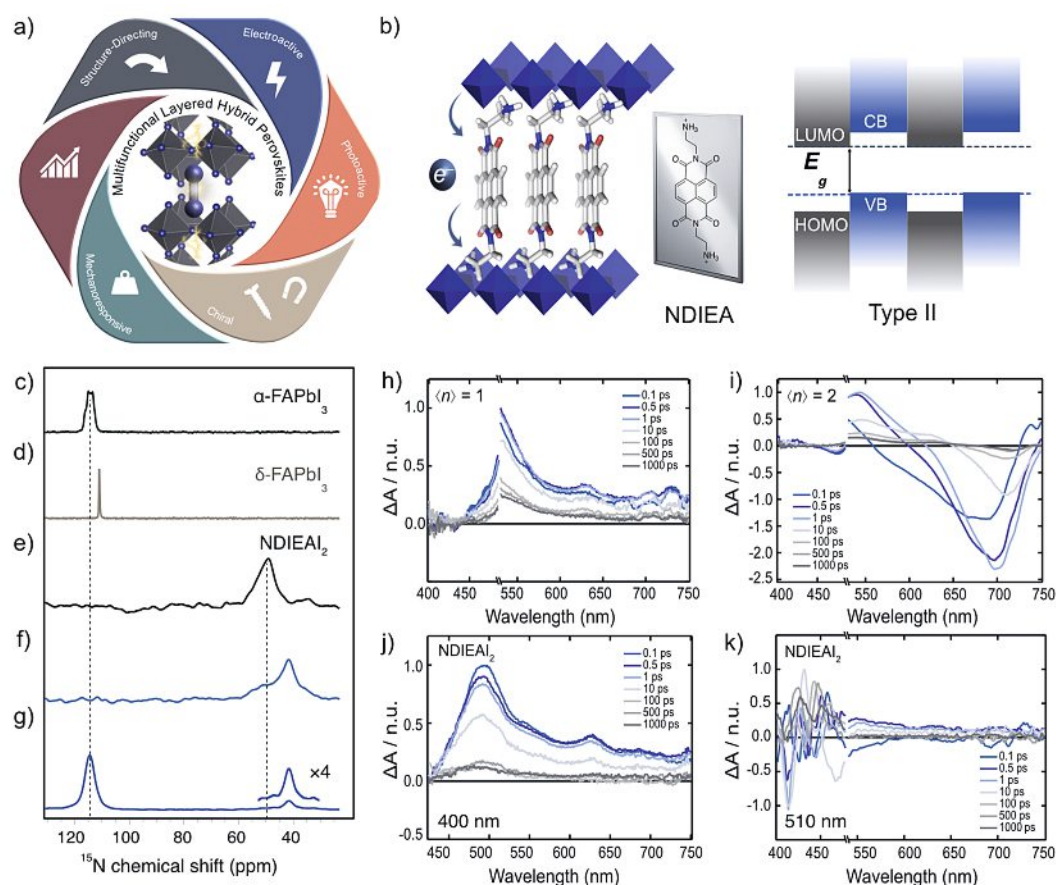


Fig. 5. Enhanced functionality of layered hybrid perovskites. (a) Schematic representation of emerging multifunctionalities associated with layered hybrid perovskites involving different functions of organic spacers, from their structure-directing roles, through electro- and photoactivity, to chirality and mechanoresponsiveness. Adapted with permission from ref. [36]. Copyright 2021 Royal Society of Chemistry. (b) Representative electroactive spacers applied in layered hybrid perovskites based on NDIEA moieties featuring Type II electronic structure. (c–g) ^{15}N solid-state NMR spectra at 21.1 T, 100 K, with 12.5 kHz magic angle spinning of (c) $\alpha\text{-FAPbI}_3$, (d) $\delta\text{-FAPbI}_3$, (e) neat NDIEAl_2 and (f–g) $(\text{NDIEA})\text{FA}_{n-1}\text{PbI}_{3n+1}$ ($n = 1, 3$) powders prepared mechano-synthetically. (h–k) Transient absorption spectra of (h–i) $(\text{NDIEA})\text{FA}_{n-1}\text{PbI}_{3n+1}$ composition and (j–k) NDIEAl_2 thin films upon excitation at 510 nm (h,i,k) and 400 nm (j). The spectral shape does not change over time and the generated species are long lived. Adapted with permission from ref. [56]. Copyright 2021 American Chemical Society.

dimensional perovskite phases, whereas solid-state NMR spectroscopy revealed that they contribute to stabilizing the $\alpha\text{-FAPbI}_3$ phase (Fig. 5c–g). Moreover, TA corroborated electron transfer between the NDI and the perovskite layers through the appearance of a positive feature in the spectra between 450–550 nm upon excitation at 510 nm of thin films (Fig. 5h–i), which was associated with the NDIEA-based radical anion.^[56] This was also apparent in the neat NDIEA spacer films excited at 400 nm (Fig. 5j) but not upon excitation at 510 nm (Fig. 5k), confirming that the spectral signatures originated from the electron transfer. This exchange did not take place in reference layered perovskite systems incorporating electronically inactive spacers, such as the PDMA.^[145,46] Moreover, the characteristic spectral shape did not change over time, suggesting the formation of long-lived radical anions in Type IIA QW structure predicted by DFT. However, TRCM revealed lower photoconductivity that could be attributed to the structural disorder in thin films and a highly localized nature of the bottom of the CB.^[56] This highlights the complexity and challenges in the development of multifunctional layered perovskites, which stimulates further investigations to enable their use in optoelectronics.

In the efforts to develop *multifunctional materials*, it would be of interest to control the properties of hybrid perovskites by relying on physical stimuli without changing their composition. This would open another path for their utility beyond photovoltaics, such as in flexible electronics and sensing.^[12] The characteristics of hybrid perovskites permit using mechanical stimuli for this purpose towards realizing *mechanoresponsive materials*.^[11,12] While there has been a number of studies on hybrid perovskites under pressure, this has so far not involved pressure

levels below 1 GPa that are compatible with practical applications. This pressure range is further of interest since the corresponding strain levels are comparable to those of intrinsic strain associated with polaron effects, conformational changes or lattice mismatches.^[12] The comparatively low bulk modulus of halide perovskites (of the order of 10s of GPa) with respect to their oxide analogues (>100 GPa) renders them more easily compressible across pressure ranges. This is even more pronounced in layered hybrid perovskites, although they remain underexplored in pressure-induced transformations (Fig. 6a).^[12] The optoelectronic properties of hybrid perovskites can be altered by affecting M–X interactions and octahedral connectivity under pressure, as well as the octahedral tilting and quantum confinement determined by the width of the potential barrier defined by the spacer in layered hybrid perovskites (Fig. 6a). The resulting changes in the optoelectronic properties in response to pressure would render these materials mechanochromic.^[12]

Towards this goal, we have relied on external pressure in the 0–0.35 GPa range in representative RP and DJ phases as model systems based on benzylammonium (BzA) and PDMA spacers, respectively.^[12] For a better understanding of their structure–property relationships, we have also investigated the role of halide anions in both iodide and bromide compositions. Pressure-dependent X-ray scattering evidenced that lattices of these perovskite materials monotonically shrink through compression, with a largest compression along the stacking direction (*a*-axis; Fig. 6b–c). Although it was expected that the additional degrees of freedom in RP phases would render them more compressible than DJ systems, with further differences for I- and Br-based compositions, the bulk moduli of RP and DJ phases were comparable under this pressure.^[12] Moreover, DJ-based phases

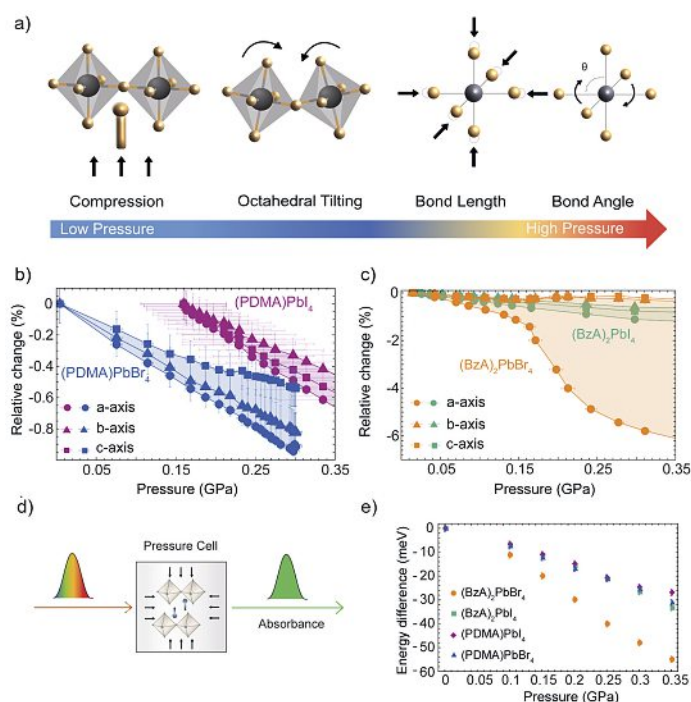


Fig. 6. Mechanochromism in layered perovskites. (a) Schematic representation of structural changes in hybrid perovskites in response to pressure across different ranges (for the medium pressure of about 5 GPa). At low pressure, the main change is reflected in the organic spacer reorientation and octahedral tilting, whereas at high pressures other effects are observed that impact the metal-halide bond lengths and angles. (b–c) Relative change of the lattice parameters as a function of pressure for (PDMA)PbX₄ (b) and (BzA)₂PbX₄ (c) compositions. (d) Schematic of the setup for pressure-dependent light absorbance measurements and (e) the energy difference of the excitonic peak energy as a function of pressure. Adapted from ref. [12] under CC BY-NC 4.0 license. Copyright 2022 John Wiley and Sons.

were not susceptible to major structural changes associated with the halide ion, which was presumably due to their higher geometric constraints. On the contrary, BzA-based RP phases featured larger structural rearrangements in Br-based compositions in contrast with their higher level of rigidity compared to I-based systems. This was more pronounced for (BzA)₂PbBr₄, with a compression in the stacking direction up to -6% relative

change, accompanied by an isostructural phase transition, which was associated with the non-centrosymmetric crystal structure featuring two distinct Pb–X–Pb angles.^[12] DFT calculations ascribed these structural changes to the interplay of interactions between the spacer layer and the inorganic slabs, suggesting that the isostructural transition can be related to a decrease in the distance between spacers, leading to an increased penetration depth into the inorganic lattice. We further assessed this effect by means of pressure-dependent UV-vis absorption and photoluminescence spectroscopy, revealing a mechanochromic response and a gradual red-shift with increasing pressure (Fig. 6d). (BzA)₂PbBr₄ showed the most significant shift of the optical absorption (-55 meV) as compared to the other compositions, featuring a rather comparable change (~ -30 meV; Fig. 6e).^[12] Unlike previous reports on pressure-induced changes in hybrid perovskites, these optical responses were fully reversible, which is critical for their practical application. The reversible mechanochromism of these materials has been associated with an interplay of interactions between the organic and inorganic layers in layered hybrid perovskite materials, which creates potential for perovskites as emerging mechanophores and amphidynamic platforms for smart materials.^[10–12]

4. Summary and Outlook

The use of supramolecular strategies in stabilizing hybrid organic–inorganic perovskites has shown potential for advancing hybrid materials and their application in renewable energy conversion in photovoltaics. In particular, the unique characteristics of hybrid perovskites as crystalline yet soft and solution-processable mixed (semi)conductors permitted tailoring their properties through molecular design of the organic components. These developments were further enabled by the use of NMR crystallography in assessing atomic-level interactions and determining their supramolecular structure. This has led to a new generation of layered hybrid perovskites as versatile platforms for enhancing the functionality of hybrid materials through the use of (photo)electroactive components. While this unlocks an attractive direction for opto(electro)ionics, the complexity of these systems requires an interdisciplinary approach for a better understanding of their structure–property relationships to guide advanced material design, which is the subject of our ongoing research (Fig. 7). This could set the stage for realizing the potential of hybrid multifunctional materials in smart and sustainable technologies in the future.

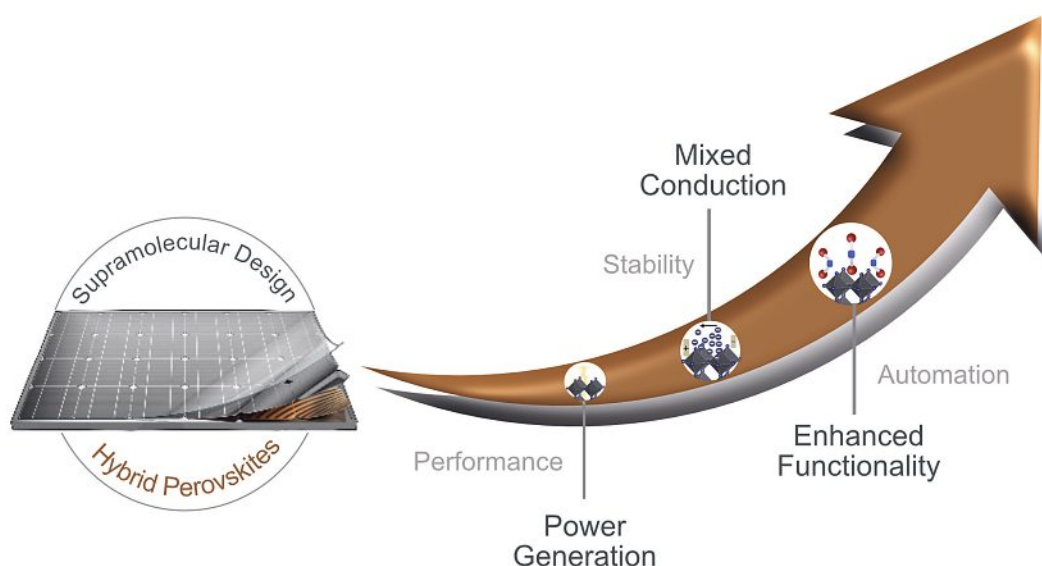


Fig. 7. Future perspectives for supramolecularly engineered hybrid perovskites. Schematic of the challenges and opportunities for the further development of hybrid perovskites through supramolecular design by exploiting their performance in renewable power generation, addressing their stability by controlling mixed conduction, and relying on their versatility and compatibility with flexible substrates for enhanced functionality towards smart and autonomous technologies. Device image adapted from @iaremenco/123rf.com

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