Two-Dimensional Organic–Inorganic Hybrid Perovskites: A New Platform for Optoelectronic Applications

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1. Introduction

Organic–inorganic hybrid halide perovskites (e.g., MAPbI3) have emerged as a new category of materials for a variety of optoelectronic applications.[1] The most explored perovskites are 3D and crystalline in nature, largely accounting for two unique properties: weak exciton binding energy and excellent charge transport, both of which are conducive to solar cells. Indeed, the power conversion efficiencies of solar cells based on these perovskites, e.g., band gap, are highly dependent on the thickness of the inorganic layers (i.e., the value of n).

Herein, 2D perovskites are arbitrarily divided into three classes, strict 2D (n = 1), quasi-2D (n = 2–5), and quasi-3D (n > 5), and research progress is summarized following this classification. The majority of existing 2D perovskites only employ very simple organic cations (e.g., butyl ammonium or phenylethyl ammonium), which merely function as the supporting layer/insulating barrier to achieve the 2D structure. Thus, a particularly important research question is: can functional organic cations be designed for these 2D perovskites, where these functional organic cations would play an important role in dictating the optoelectronic properties of these organic–inorganic hybrid materials, leading to unique device performance or applications?

2D perovskites are recently attracting a significant amount of attention, mainly due to their improved stability compared with their 3D counterpart, e.g., the archetypical MAPbI3. Interestingly, the first studies on 2D perovskites can be dated back to the 1980s. The most popular 2D perovskites have a general formula of \((RNH_3)_2MA_{n-1}MX_{3n+1}\), where \(n\) represents the number of metal halide octahedrons between the insulating organic cation layers. The optoelectronic properties of 2D perovskites, e.g., band gap, are highly dependent on the thickness of the inorganic layers (i.e., the value of \(n\)).

Among these low-dimensional perovskites, 0D, 1D and corrugated 2D perovskites (the sheets with twisted \([BX_6]^{4-}\) octahedrons along (110) plane in 3D perovskites), have been widely studied as white light phosphors due to their broad emission. Interested readers should look to recent work and reviews on these low-dimensional perovskites (0D, 1D and corrugated 2D).[3,5] In this research news, we will only focus on the research progress on 2D perovskites, especially the Ruddlesden–Popper phases (the sheets with planar \([BX_6]^{4-}\) octahedrons along (100) plane in 3D perovskites), and their optoelectronic applications including field-effect transistors (FETs), light-emitting diodes (LEDs), photodetectors, and photovoltaics (PV).

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The 3D perovskites are described through the general formula of ABX₃, where the small cation (A site, e.g., MA⁺, FA⁺ and Cs⁺) can fit into the body center of the cube formed by eight metal halide \([BX_6]^{4-}\) octahedrons. In the lower dimensional perovskites, there is at least one larger cation (typically organic based), which cannot fit in the cubic center, thus breaking the 3D lattice into sheets (2D), wires (1D) or individual \([BX_6]^{4-}\) dots (0D). Because of the insulating organic layers surrounding these sheets, wires or dots, low-dimensional perovskites exhibit quantum confined behaviors including quantum wells (2D), quantum wires (1D) or quantum dots (0D).[3] The general rule deciding the formation of low-dimensional perovskites follows Goldschmidt’s Tolerance Factor concept, which is described in Equation (1). Specifically, \(R_A\), \(R_B\), and \(R_X\) are the ionic radii for the organic cation, metal cation, and halide, respectively. When the tolerance factor \(t > 1\), lower dimensional perovskites will occur:[3]

\[
t = \frac{R_A + R_X}{2R_B} > 1
\]  

(1)

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PEA) and butyl ammonium (C₄H₉-NH₃⁺, BA). The optoelectronic properties of 2D perovskite (e.g., band gap and exciton binding energy) are highly dependent on the degree of quantum confinement, which is mainly dominated by the thickness of the inorganic layers (i.e., the value of \( n \)). For example, when the thickness (\( n \)) of the inorganic slab increases, the band gap of lead iodide-based 2D perovskites decreases from 2.43 eV (\( n = 1 \)) to 1.91 eV (\( n = 4 \)), with the color changing from orange to dark brown (Figure 1b). When the \( n \) reaches larger values (i.e., approaching infinity, \( \infty \)), the 2D perovskites essentially become 3D perovskites. Given the crucial role of \( n \), we arbitrarily divide 2D perovskites into three classes, strict 2D (\( n = 1 \)), quasi-2D (\( n = 2–5 \)), and quasi-3D (\( n > 5 \)), and summarize research progress on 2D perovskites following this classification. For each class, we will briefly introduce the historical background, and highlight the recent noteworthy discoveries.

2. Strict 2D (\( n = 1 \))

In the 1980s, Ishihara et al. first synthesized lead-based organic–inorganic hybrid halide perovskites with \( n = 1 \). Since then, many different organic cations and inorganic frameworks have been used to construct perovskite structures, mainly focused on \( n = 1 \) phase. Typically, the inorganic framework is mainly constructed with ions from group 14 (e.g., Pb²⁺ and Sn²⁺); however, in some cases, divalent ions like Ca²⁺, Eu²⁺, Yb²⁺, Cu²⁺, and Cd²⁺...
can also be employed.\[^{34,10}\] Besides these +2 cations, +1 and +3 cations with a 1:1 ratio (thereby having an average charge state of +2) can also be employed, for example, Ag\(^+\), Au\(^+\), and Tl\(^+\) mixed with Au\(^3+\), Bi\(^3+\), and Tl\(^3+\).\[^{3d,11}\] Herein, we will focus on the 2D perovskites based on group 14 (e.g., Pb\(^2+\) and Sn\(^2+\)), given that such materials have been actively investigated for optoelectronic applications. Similarly, most of the organic cations are organo-ammonium (RNH\(_3^+\)) based, where the R group can range from aliphatic, aromatic small molecules to conjugated oligomers, polymers, and fullerenes.\[^{3c,e,4a,12}\] Although there are studies showing that other types of cations such as tetraphiafulvalene\[^{[13]}\] and tropylium\[^{[14]}\] can be applied to lower dimensional perovskites including 0D, 1D, and corrugated 2D perovskites, such studies on 2D perovskite have not been reported, to our knowledge. This is likely because steric hindrance from these large cations would prevent them from fulfilling the required ratio of cation versus anion (e.g., 2:1 for butylammonium:PbI\(_4\), n = 1).

Early exploration of these 2D perovskites for optoelectronic application was mainly conducted by Mitzi, Tsutsui, and their coworkers. In 1999, Mitzi et al. reported a thin film field-effect transistor using (C\(_6\)H\(_5\)C\(_2\)H\(_4\)NH\(_3\))^2SnI\(_4\) (a sketch of the crystal structure is shown in Figure 2a) as the channel material, fabricated via a solution processing method (Figure 2b).\[^{[3e]}\] In addition, light emission from either inorganic framework\[^{[15]}\] or organic moiety\[^{[16]}\] in 2D perovskite LEDs was observed by tuning the alignment of band gaps and energy levels of the two parts (Figure 2c). More recently, hybrid perovskite materials have found new applications in spintronics due to strong spin orbital coupling (SOC) caused by heavy elements such as

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**Figure 2.** a) Structures of strict 2D perovskite as bulk form. b) Device structure of thin film FET based on PEA\(_2\)SnI\(_4\) 2D perovskite. b) Reproduced with permission.\[^{[3e]}\] Copyright 1999, The American Association for the Advancement of Science. c) Device structure and picture of 2D perovskite LED. Adapted with permission.\[^{[3d]}\] Copyright 2016, American Chemical Society. d) Optical image of mechanical exfoliated 2D perovskite. e) AFM image of mechanical exfoliated 2D perovskite. The thickness is about 2.4 nm. d,e) Reproduced with permission.\[^{[22b]}\] Copyright 2015, American Physical Society. f) Optical image of solution-grown 2D perovskite nanoplates. g) AFM image of solution-grown 2D perovskite nanoplates. The thickness is about 1.6 nm. h) Photoluminescence of solution-grown 2D perovskite nanoplate with different composition. (C\(_4\)H\(_9\)NH\(_3\))^2PbCl\(_4\) (I), (C\(_4\)H\(_9\)NH\(_3\))^2PbBr\(_4\) (II), (C\(_4\)H\(_9\)NH\(_3\))^2PbI\(_4\) (III), (C\(_4\)H\(_9\)NH\(_3\))^2PbCl\(_2\)Br\(_2\) (IV), (C\(_4\)H\(_9\)NH\(_3\))^2PbBr\(_2\)I\(_2\) (V), and (C\(_4\)H\(_9\)NH\(_3\))^2(CH\(_3\)NH\(_3\))^2PbI\(_6\) (VI). The corresponding optical PL images are shown in the inset. Scale bars, 2 \(\mu\)m for (I)–(V) and 10 \(\mu\)m for (VI). f–h) Reproduced with permission.\[^{[23]}\] Copyright 2015, The American Association for the Advancement of Science.
Pb or I.\cite{17} SOC can split the spin-degenerate bands in non-centrosymmetric compounds, generating the Rashba splitting, which could enhance the spin-to-charge conversion efficiency, such as in the spin-Hall effect or inverse spin-Hall effect.\cite{18} Rashba splitting may be enhanced in reduced dimensions, such as in 2D semiconductors, due to the presence of structural “inversion asymmetry”.\cite{19} In particular, 2D perovskites, having both the strong SOC and lacking inversion symmetry, would contribute to the Rashba splitting.\cite{20} For example, Zhai et al. found a 2D perovskite, PEA$_2$PbI$_4$, exhibited large Rashba splitting, a peculiar property that had been reserved to only a handful of materials.\cite{21}

As a layered material, 2D perovskites can be exfoliated or synthesized as single-layer or few-layer sheets, similar to graphene versus graphite. Mechanical exfoliation offers a general way to produce large flakes (with micrometer size in lateral) for study and applications of individual sheets (Figure 2d,e).\cite{22} However, the reproducibility of this exfoliation method is generally low, i.e., wide thickness/size distribution. The alternative method is to produce thin sheets of 2D perovskites via direct synthesis. Dou et al. developed a method to grow atomically thin nanoplates of 2D perovskites from solution (Figure 2f,g).\cite{23} This method can produce large-scale 2D sheets with thicknesses down to single layer of [BX$_6$]$^{2-}$ octahedrons with narrow thickness distributions. Excitingly, these nanoplates show tunable photoluminescence, indicating their potential application for LEDs (Figure 2h). In addition, high-performance photodetectors based on solution-grown (C$_4$H$_9$NH$_3$)$_2$MA$_2$Pb$_3$I$_{10}$ nanoplates have also been fabricated.\cite{24}

Besides the 2D nanoplates with well-defined crystal structures and quantum well thickness (n) from their layered counterparts, colloidal\cite{25} and chemical vapor deposition\cite{26} syntheses can also provide perovskite thin crystals with uniform thickness and lateral size. These nanocrystals can be used for various applications including LEDs, photodetectors, transistors, etc. For a more complete description of these low-dimensional perovskites, see recent research work and reviews.\cite{27}

3. Quasi-2D (n = 2–5)

In 1991, Calabrese et al. first pointed out that the stricit 2D (n = 1) and 3D perovskite are the two extremes of the Ruddlesden–Popper phase perovskite family, and this was proven for the first time as they synthesized quasi-2D lead perovskite (n = 2) crystals.\cite{28} By varying the thickness of the quantum well (n), the properties of 2D perovskite, such as band gap, can be widely tuned. The tunability of optoelectronic properties and the versatility of the structures (in particular, the possibility of incorporation of functional organics) make quasi-2D perovskites a unique class of materials for both fundamental studies and a variety of applications.\cite{6a,29} On the other hand, with larger n (>5), it becomes increasingly harder to synthesize pure crystals or films (e.g., with Sn- or Pb-based perovskites), because of the structural similarity between large n 2D perovskites and 3D perovskites.\cite{13c,8b,9a} In here, we will focus on the discussion on quasi-2D perovskite with n ≤ 5.

3.1. Quantum Confined Properties

As the transition between the strict 2D (n = 1) to (quasi) 3D perovskites, quasi-2D perovskites (n = 2–5) have rather unique properties when compared to these two extreme phases. One of the most important properties of quasi-2D perovskite is their tunable band gaps due to the increased degree of quantum confinement from large n to small n. For example, the Kanatzidis group recently reported a series of 2D lead iodide perovskite crystals and films, (C$_4$H$_9$NH$_3$)$_2$MA$_2$Pb$_3$I$_{10}$ (n = 1–5).\cite{20,9a} As shown in Figure 1b, the band gaps of these 2D lead iodide perovskite range from 2.43 eV (n = 1) to 1.83 eV (n = 5). When swapping out Pb with Sn in the same structure, the band gaps can be further tuned from 1.83 eV (n = 1) to 1.20 eV (n = ∞).\cite{20} Comparable tunability of band gaps has also been achieved for nanoplate form of 2D perovskite.\cite{10} This tunability allows for modification of the perovskite band gap to cover the majority of the visible light range, which renders 2D perovskite an attractive material for a variety of optoelectronic applications.

Moreover, the exciton binding energy (E$_{\text{B}}$) is also highly related to the thickness of the quantum well (i.e., the value of n). For example, in the case of lead iodide perovskites, the strict 2D perovskite (n = 1) has an E$_{\text{B}} = 360$ meV, whereas E$_{\text{B}}$ decreases to 260 meV (n = 2) and 150 meV (n = 3), as the thickness of the quantum well increases.\cite{9d,11} The E$_{\text{B}}$ eventually decreases to 20–60 meV for the 3D perovskites.\cite{9c,e,g} It is also important to note that for larger n phases (e.g., n ≥ 3), free carrier characters can already be observed due to the reduced quantum confinement.\cite{9b}

3.2. Phase Distribution and Crystal Orientation in Quasi-2D Perovskite Films

Although the pure crystals of quasi-2D perovskites can be synthesized, films deposited by solution methods appear to contain several phases with different values of n. For example, with a perovskite precursor solution that would lead to a pure quasi-2D perovskite of n = 4, the final film after the solution processing would contain n = 1–5 (maybe even larger n) and 3D perovskite phases, i.e., mixed phases. This assertion was supported by the multiple excitonic peaks in the UV–vis and photoluminescence (PL) spectra of the quasi-2D perovskite thin films, corresponding to the phases with different values of n (Figure 3a,b). Furthermore, the mixed phases were also observed in quasi-3D perovskite films (n > 5).\cite{29a,c,11} Thus, a question naturally arises: how would these different phases distribute across these perovskite thin films? Liu et al. pointed out that the phases with smaller n would dominate on the side of the substrate (where the film was deposited), while phases with higher n or 3D would appear more on the air side. Their claim was supported by the different photoluminescent and transient absorption (TA) responses between the perovskite film excited from the (glass) substrate and air side. When excited from the (glass) substrate side (i.e., back side), PL peaks and bleach peaks of phases with different n could be clearly observed; in contrast, when excited from the air side (i.e., front side), signals from 2D perovskites became much weaker and the peak of 3D perovskite was dominant (Figure 3b). TA further indicated there was...
an energy or charge transfer between different phases in the film, which could benefit the device performance of such quasi-2D perovskites-based solar cells.

Although it is clear that the n controls the band gap of these quasi-2D perovskites (i.e., n = 2 has larger band gap than n = 3), the relative position of the energy levels of these different phases remains ambiguous. For example, both Cao et al.\cite{8a} and Silver et al.\cite{32} measured the valence band position of BA2PbI4 through ultraviolet photoelectron spectroscopy and there is a huge difference (over 1.2 eV) between the results (4.55 versus 5.8 eV). Lacking agreed values on the energy levels of these different 2D phases makes it difficult to pinpoint the relative electronic configurations in these 2D phases; both type II (Figure 3c) and type I (Figure 3d) are possible. Both types could help explain the observed spectroscopic responses (PL and TA) through either energy, charge transfer or both, which were also proposed by others.\cite{29a,c} Though the exact mechanism is still under investigation, such energy or charge transfer can lead to a carrier funneling process and enhance the emitting of the lowest band gap light emitter in these quasi-2D perovskites. Thus, LEDs based on quasi-2D perovskites have been fabricated with increasing interest.\cite{29a,c,33} For example, Wang et al. demonstrated quasi-2D perovskite (n = 2) LEDs with low turn-on voltage of 1.3 V. They obtained an external quantum efficiency (EQE) of 11.7% at 2.6 V with a current density of 38 mA cm\(^{-2}\), and a high radiance of around 82 W sr\(^{-1}\) m\(^{-2}\) was achieved at 3.6 V. Similar high-performance LEDs were also achieved by Yuan et al. (e.g., n = 5, turn-on voltage as 3.8 V, EQE = 8.8%, and a radiance of 80 W sr\(^{-1}\) m\(^{-2}\)). Additionally, these LED devices were also quite stable under their working condition.\cite{29b,c} Furthermore, by modifying the composition of the films, such as adjusting the n value or changing the halide atoms, one can achieve tunable emission...
with blue, green, and red colors (Figure 3e,f).\textsuperscript{[30a,c,33a,d]} Although the quasi-2D perovskite LEDs have achieved a wide emission range, it is still relatively hard to achieve highly efficient emission at red or deep red. Recently, the Ma group reported high efficient (>6.23\%) red LEDs (emission peaked at 638, 664, 680, and 690 nm) by blending poly(ethylene oxide) into the perovskite layer.\textsuperscript{[38]} In addition to LEDs, quasi-2D perovskites have even recently been utilized to achieve room temperature amplified spontaneous emission and lasing, facilitated by population inversion from ultrafast energy transfer processes between quantum wells with different $n$ values (Figure 3g,h).\textsuperscript{[34a]}

Another significant difference between quasi-2D and 3D perovskites is the anisotropic charge transport in 2D perovskites. This is due to the large insulating organic cations separating inorganic metal halide layers, essentially preventing charge transport between the inorganic perovskite layers. Since the primary charge transport channels are within these inorganic layers, the crystal orientation of the 2D perovskite film becomes extremely important to the device performance. For example, a vertical alignment of these inorganic layers (i.e., perpendicular to the substrate) would be desirable for devices requiring charge transfer across the film (e.g., solar cells and LEDs). Unfortunately, the as-cast quasi-2D perovskites seem to often adopt a lateral alignment of these inorganic layers, which would account for the observed low current in the early work of using quasi-2D perovskites for solar cells.\textsuperscript{[8a]} A breakthrough came from Tsai et al. who applied a hot casting method to achieve much higher efficiency (>10\%) for quasi-2D perovskites-based solar cells (Figure 3j).\textsuperscript{[29]} Compared to the usual casting of these quasi-2D perovskites at room temperature, the new method of hot casting appeared to largely achieve the coveted vertical crystal orientation, thereby significantly improving the charge transport across the film, leading to the observed high current of the solar cells. The main evidence supporting this proclaimed vertical orientation came from the sharp, discrete Bragg spots in the Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) pattern of the hot cast film, in contrast to the room temperature film (Figure 3j,k), indicating (101) planes parallel to the substrate surface (i.e., the inorganic layer perpendicular to the substrate) in the hot-cast film (Figure 3l). However, due to the rather complex composition of these quasi-2D perovskites-based thin films (e.g., the mixed phases), it is still unclear which phases the patterns on GIWAXS can be assigned to. Many of these discrete Bragg diffraction spots, e.g., (111), (202), etc. can be observed from different quasi-2D phases and even 3D perovskites. Therefore, further study is needed to better understand the composition and the phase alignment in these quasi-2D perovskite films.

### 3.3. Advantages of Quasi-2D Perovskite in Optoelectronic Applications

These large organic cations in quasi-2D perovskites are believed to suppress defect formation, similar to the function of ligands in quantum dots.\textsuperscript{[14]} This passivation effect leads to a lower self-doping level and extraordinarily high light detectivity (10$^{13}$ Jones) of photodetectors based on these quasi-2D perovskites ($n = 1–3$).\textsuperscript{[34b]} On the other hand, Wu et al. showed increased excitonic traps in 2D perovskite crystals with smaller $n$ and the number of excitonic traps in 2D perovskites ($n = 1$ and 2) is much higher than that in 3D perovskites. Unlike common chemical defects that would typically serve as traps, these excitonic traps in quasi-2D perovskites originate from the self-trapping of band-edge excitons due to the stronger exciton-phonon interaction in low-dimensional crystals.\textsuperscript{[33]} In addition to the trap state, quasi-2D perovskites can also suppress ion migration which is believed to cause hysteresis and accelerated degradation in 3D perovskite-based solar cells.\textsuperscript{[34]} In short, though these large cations in quasi-2D perovskites have shown various advantageous properties (e.g., trap suppression), the exact mechanisms behind all these observations are still not clear and need to be addressed further.

Another noteworthy advantage of quasi-2D perovskites is the improved stability compared to the conventional 3D perovskites; this stability is particularly important for solar cells. In 2014, Smith et al. first reported that solar cells based on a layered quasi-2D perovskites ($n = 3$) with PEA as the large organic cation exhibited better stability than the archetypal MAPbI$_3$ solar cells.\textsuperscript{[24]} Soon thereafter, BA-based quasi-2D perovskites ($n = 1–4$) solar cells were also demonstrated to have enhanced stability.\textsuperscript{[8a]} Furthermore, the photovoltaic device efficiency values of quasi-2D perovskites have been improved to 12\% via different processing methods including hot casting and mixing with Cs\textsuperscript{[17]} or FA\textsuperscript{[14c]} cations. After testing the stability of solar cells based on quasi-2D perovskites with different $n$ and using density functional theory simulation to estimate the formation energy, Quan et al. proposed that the increased formation energy with these lower dimensional perovskites.\textsuperscript{[70]} A high formation energy would mean the formed materials are rather stable.

### 4. Quasi-3D ($n > 5$)

As stated earlier, when $n$ is larger than 5, it becomes extremely hard to synthesize pure 2D perovskites, either as crystals or as films. This is probably because the formation energy of 2D perovskites having large $n$ is very close to that of 3D perovskites. In most cases, the stoichiometric ratio of precursors can only represent the “nominal” $n$ phase, e.g., $n = 5, 10, 20, 40, \text{etc.}$ and the film mostly contains 3D perovskites and some 2D phases (illustrated as Figure 4a). Therefore, the properties of the final films are mainly dominated by the 3D perovskites and we thereby term these large $n$ 2D perovskites as quasi-3D perovskites.

The most noteworthy benefit of adding large cations into the 3D perovskite films is to passivate the defects and therefore, enhance the stability and efficiency of related solar cells. Quan et al. investigated the device performance and stability of the (PEA)$_x$(MA)$_{1-x}$PbI$_3$ perovskites with $n = 6–60$. As $n$ increases, the related solar cells show improved efficiency and decreased stability.\textsuperscript{[70]} In another report, Li et al. added a small amount of PEAI into 3D FAPbI$_3$ perovskites (FA,PEA)$_{1-x}$PbI$_3$ and discovered that with a small amount of PEAI (FA/PEA = 40), both high performance and improved stability could be achieved, ascribed to the defect passivation function of PEAI.\textsuperscript{[18]} Grancini et al. employed 3\% aminovaleric acid iodide (HOOC(CH$_2$)$_4$NH$_3$I) as a large cation into 3D perovskites, and these perovskite-based...
large solar modules (10 × 10 cm²) have been operating for one year without performance loss. Recently, Wang et al. added a small amount of BA in to (FA0.83Cs0.17)1−xPb(10.6Br0.4)x perovskite films with x = 0.09 (b) and x = 0.16 (c). The white arrows in the 2D-XRD images highlight diffraction from 2D perovskites. d) UV–vis absorption and PL spectra of film with x = 0 (black line) and x = 0.09 (red line). e) Time-resolved PL spectra for the same films. Longer carrier lifetime can be observed in quasi-3D perovskite film compared to 3D perovskite film. f) Proposed type-I heterojunction configuration of quasi-3D perovskite film. The 2D perovskite component passivates the 3D perovskite boundary. g) Stability test of quasi-3D perovskite devices without encapsulation and with encapsulation. a–g) Reproduced with permission. Copyright 2017, Nature Publishing Group.

5. Conclusions and Outlook

At this point, we hope the readers already have a fairly good understanding of these 2D perovskites, including historical background, the relationship with other types of perovskites (in particular, 3D perovskites), and some more recent developments in structures, properties, and applications. Perhaps the
most exciting aspect of these 2D perovskites, from a chemistry point of view, is the unprecedented opportunity to incorporate large organic cations into perovskites. However, the majority of existing 2D perovskites only employ very simple organic cations (e.g., BA or PEA), which serve no more than as the supporting layer/insulating barrier to achieve the 2D structure from the 3D perovskites. Can we design functional organicics and incorporate them into these 2D perovskites, where these functional organicics would play an important role in dictating the optoelectronic properties of these organic/inorganic hybrid materials, leading to unique device performance or applications? In fact, a variety of aromatic/conjugated ammoniums have been incorporated into 2D perovskites (n = 1), including oligothiophenes,[12c] acenes,[12f,41] fullerenes,[12c] among others, and light absorption or charge transfer between organic and inorganic moieties have been observed with these 2D perovskites.[12f,41,42] However, these cations do not provide more desirable and exciting functions such as charge transport, singlet/triplet manipulation, and spin selection; yet all these functions have been observed with organic materials.[43] Therefore, the challenge to achieve these novel functions with 2D perovskites should be the research priority; this includes both rationale design of the large organic cations and inorganic frameworks.

For quasi-2D perovskites (n = 2–5), in addition to the design challenge to achieve novel functions, other outstanding issues remain to be resolved. To begin with, how can the control of phase distribution and phase purity in the quasi-2D perovskite thin film be achieved? Appropriate phase distribution of the mixed phases can offer some benefits for charge transport,[11,44] however, the concomitant phase disorder would form traps at the lower energy levels. Proppe et al. recently reported that purer phases (i.e., a narrower distribution of different phases) could be obtained by using allylammonium as the large organic cation.[45] This narrow distribution of different phases (n) would generate a rather flat energy landscape with longer diffusion length for charge carriers, accounting for the improved solar cell performance. Thus, a complete understanding of how the judiciary choice of ligands would affect the phase purity and distribution is a significant future direction. In addition, there might be other external methods (e.g., solvent or thermal annealing) that could control the phase purity and distribution as well. Second, it is still unclear how the crystal domains are oriented to the substrate in the quasi-2D perovskites. GIWAXS can provide some information about this orientation; however, most of the diffraction peaks and patterns shown for a typical quasi-2D perovskite also exist in 3D perovskites.[46] More detailed studies on how to assign these unknown diffraction peaks and patterns are required for a better understanding of the orientation of crystal domains in respect to the substrate. A related question is how to control the orientation of crystal domains. For example, a vertical alignment of these inorganic layers would be preferred for solar cells, whereas a lateral alignment would be ideal for thin film FETs.

The most important research question for quasi-3D perovskites is how to improve the stability of such solar cells with the added 2D components while preserving the excellent efficiency from the 3D perovskite solar cells. Numerous studies have reported the improved stability and excellent device performance by introducing 2D components into 3D perovskite solar cells, yet further fundamental understanding is still needed to explore the mechanisms for such improvement of stability (without losing efficiency) and to provide further guidance for the selection of organic cations.

In summary, much progress has been made in exploring 2D perovskites’ structure, optoelectronic properties and applications. This is a truly multidisciplinary research field where chemists, physicists, materials scientists, and device engineers can work together to unravel new discoveries.

Acknowledgements
The authors are supported by the National Science Foundation (DMR-1728921) and UNC Research Opportunities Initiative (ROI).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
2D perovskites, optoelectronics, organic–inorganic hybrid perovskites

Received: March 30, 2018
Revised: June 20, 2018
Published online: September 10, 2018


