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Interplay between Morphology and Electronic Structure in Emergent Organic and π -d Conjugated Organometal Thin Film Materials

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ABSTRACT: The demand for multifunctional devices continues to drive the evolution and parametrization of technology. Simultaneously, the breadth of structural, morphological, and electronic information that can be used to study materials widens and grows in complexity. To keep up with the demand for superior technologies in disparate fields, such as energy, electronics, and biotechnology, an unparalleled amount of manpower and financial resources have been devoted to the development of materials that can integrate multiple functionalities, particularly functions that ostensibly exclude one another. To address different functionalities at once, materials have become highly complex and often exhibit multiple structural and morphological phases, hierarchical dependencies, and far-from-equilibrium dynamic structures with little to no long-range atomic ordering. A major area of study that is quickly



evolving deals with the quantitative characterization of structure–property–function relationships in complex materials based on π conjugated organic and organometal systems—particularly in thin film formulations. In this review, we discuss various research
avenues where cleverly engineered self-assembly protocols, as well as characterization methods for probing morphology and
electronic structure, are implemented to enable the fabrication of well-defined emergent materials.

INTRODUCTION

The electronic structure and morphology characterization landscapes of materials have radically changed from what was available during the formative years of organic and organometal materials research. The change in analytical methods and tools can be generally attributed to the growing complexity of organic and organometal materials as the demand for more efficient and faster devices drives technological advances. To close the gap between new and emerging organic/organometal materials and current silicon technologies, significant effort has been devoted to the development of new low-temperature synthesis and thin film fabrication techniques of complex materials with improved optoelectronic properties and welldefined electron transport pathways. While structural modifications to both organic and organometal semiconductors offer an avenue to easily tailor physical and chemical properties, the processing method (e.g., spin coating, dip coating, chemical vapor deposition) and processing conditions play substantial roles in their performance. It has been well documented that changes to morphological features such as crystallinity, structural alignment, defect formations, and microstructure affect the electronic properties of both organic and organometal semiconductors, although often in unforeseeable ways.¹⁻⁴ This has yielded difficulty in effective material

design and prediction of expectant charge transport properties. $^{5-8}$

This review discusses the role of morphology on the electronic structure of organic and organometal semiconductors that have emerged as key players in stretchable electronics, energy conversion and storage, and quantum electronics. First, we provide an introduction to modern characterization methods by which a material's electronic structure may be analyzed, followed by a discussion of the methods used to characterize a material's morphological characteristics. We then examine novel small molecule organic electronics, conductive polymers, coordination polymers, and organometal halide perovskite materials with an emphasis on how these are characterized and with specific attention paid to morphological features. Finally, we provide a basis for understanding how morphological control over these materials can provide

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avenues to understand and manipulate their electronic properties.

ELECTRONIC STRUCTURE OVERVIEW

Typical characterization methods employed for electronic structure characterization in organic materials differ drastically from those utilized for organometallic and metallic materials. The differences primarily stem from the behavior of amorphous and crystalline organic materials in comparison to their inorganic counterparts. While the electronic structures of inorganic materials do change in response to the degree of crystallinity, composition, morphology, grain size, and interfacial effects, organic materials are archetypally more complex in that they form discontinuous, amorphous, and semicrystalline microstructures whose electrical transport properties are best described by percolation theory.⁹ This is largely because π -conjugated organic materials (π -OMs) are monodisperse. They are composed of discrete molecular subunits made from low atomic weight species whose electronic properties, and by extension morphological features, are driven by the conjugation and configuration of discrete π orbitals within the individual monomers, as well as the degree of wave function overlap between neighboring subunits. The difference between amorphous and crystalline microstructural variations is visualized in Figure 1, which displays an amorphous structure (Figure 1A), a semicrystalline structure (Figure 1B), and a highly semicrystalline structure (Figure 1C).¹⁰ These images illustrate the broad range of regioregularity that can be observed in π -OMs, where the coexistence of order, disorder, and mixtures of the two in a films' microstructure will result in complex bimodal charge transport networks. Highly ordered regions are typically associated with more efficient charge transport. Differences in domain size, grain sizes, and distribution of these networks will generally dictate bulk transport properties (Figure 1D). Recent work by Kang and Snyder provides a foundation for understanding electronic transport through these domains, which is strongly influenced by the dynamic interplay between morphological ordering and the resultant electronic structure of a semiconducting material.9 When accounting for the inhomogeneous disorder prevalent in π -OMs, the transport model they present deviates from Mott's model and provides a more thorough description of the electronic structure in π -OMs. This is achieved by characterizing the transport function σ_E

$$\sigma_{E}(E, T) = \sigma_{E_{0}}(T) \times \left(\frac{E - E_{t}}{k_{B}T}\right)^{s} (E > E_{t})$$
$$= 0(E < E_{t})$$
(1)

Review

where the transport coefficient σ_{E_0} describes the magnitude of the conductivity, the transport parameter *s* is a shape factor describing the electron distribution allowed for the transport function, and the transport edge E_t describes the edge below which no electrons or holes contribute to the conductivity of a material. Here, σ_{E_0} can be determined through the relationship between a material's Seebeck coefficient (*S*) and its electrical conductivity (σ), as follows

$$S = \frac{1}{\sigma} \left(\frac{k_{\rm B}}{e} \right) \int \left(\frac{\mathbf{E} - E_F}{k_{\rm B}T} \right) \sigma_E \left(-\frac{\partial f}{\partial E} \right) dE \tag{2}$$

The role that E_t and *s* plays in describing the density of states can be visualized in Figure 2A, where E_t describes the



Figure 2. (A) Energy representation depicting the role that the transport edge (E_t) and shape factor (s) play on the electronic states used in conduction. (B) Energy depiction of the shape factor compared to a Mott mobility edge. Reproduced with permission from ref 9. Copyright 2016, Nature Publishing Group.⁹

threshold relative to the Fermi edge through which electrons or holes are available, and *s* describes the shape parameter of the transport function. Applying this model to some emergent π -conjugated conducting polymers in the literature such as PBTTT, PSBTBT, and PDPP3T reveal that they fit an *s* = 3 model. In contrast, the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) fits an s = 1 model and exhibits σ_{E_0} values a few orders of magnitude higher than the majority of other polymers. Differences in the transport function relative to the shape factor are depicted in Figure 2B, showing how a typical conjugated polymer differs from PEDOT and the shape profile assumed when using a Mott mobility edge. This suggests that conducting polymers can provide different transport parameters that can be used to understand their underlying electrical properties. Furthermore, different transport parameters can be used to establish structure–function relationships to help explain the complex electronic structure of π -OMs.

Contrastingly, charge transport in organometal materials has been expressly described in terms of traditional inorganic materials, although many organometallic materials exhibit both amorphous and crystalline domains.^{11,12} Indeed, the origin for the Kang–Snyder charge transport model can be tied to the seminal paper by Döhler et al. which discusses the relationship between conductivity and the Seebeck coefficient in amorphous semiconductors and suggests that both inorganic and organic materials exhibit a similar formulation of charge transport behavior, differentiating from one another according to their degree of crystallinity.¹³ Future work investigating charge transport behavior in organic and organometal materials will further improve upon this model by describing the precise role of structural orientation on electron percolation in amorphous, semicrystalline, and crystalline domains.

Modern materials have pressed the envelope of what is achievable by semiconducting and conducting materials. This has necessitated the ability to deconvolute the intrinsic morphological and electronic complexities in terms of ionic charge transport, where next to traditional electronic transport ions can also migrate under a bias.^{8,14} Ionic charge transport within materials can present advantageous or deleterious effects depending on the desired application.^{15,16} It has in these cases become crucial to identify ion migration effects within materials.

Ionic charge transport can be investigated using voltage/ current bias stress characterization methods. Application of a DC bias across a material creates a nonlinear transient effect typically in the form of an exponential decay or growth.¹⁶ This represents the migratory pattern of the ionic species, which upon saturation will exhibit an ohmic response. The reversibility of this response and the resultant response observed when turning the bias off provide valuable insight into the physical and chemical events occurring within a given material in terms of electronic and ionic transport.

MORPHOLOGICAL STRUCTURE OVERVIEW

Insight into thin film morphological features in emergent materials are necessary to deconvolute the various contributions of crystallite orientation, grain size, and grain boundaries from fabrication techniques for a given film. Each material can host a considerable variety of morphological structures, boundary interactions, and interfacial effects which depend upon the fabrication methodology and crystallization pathway. Foundational methods used to understand morphology such as electron microscopy, atomic force microscopy, powder X-ray diffraction, X-ray scattering, and X-ray absorption techniques allow for highly advanced morphological characterization.^{17–21} Grazing incidence wide-angle X-ray scattering (GIWAXS) is used to characterize Bragg reflections and their scattering orientation relative to the substrate, while grazing-incidence small-angle X-ray scattering (GISAXS) provides insight into the mesostructural size and shape of a material relative to the substrate. This can be coupled with near-edge X-ray absorption fine structure (NEXAFS) spectroscopy which provides complementary X-ray absorption data which provides the antibonding orbital structure relative to an atom-specific core.^{2,3,22,23} Moreover, the use of resonant soft X-ray scattering (RSoXS) has been quickly gaining traction as a fingerprint technique that can probe buried morphological features in materials. RSoXS is a hybrid technique that combines smallangle X-ray scattering (SAXS) with soft X-ray absorption spectroscopy (XAS) to yield a chemically sensitive tool that can be easily interfaced with in operando and in situ characterization tools to aid in the investigation of materials under dynamic and far-from-equilibrium conditions.^{20,24} Below, we provide a primer for each of these morphological characterization techniques.

GIWAXS is a powerful tool for morphological characterization of thin materials in which the X-ray source approaches the substrate at a grazing angle (Figure 3A).²⁵ GIWAXS often overcomes the very low X-ray scattering factors common in organic materials composed of low Z atoms. This is achieved by increasing the X-ray spot size on the sample. Depending on the grazing angle relative to the film's critical angle, the spot size can be further enlarged and isolated through evanescent wave enhancement. GIWAXS provides a 2D image of Bragg reflections which can provide orientational distribution information relative to the substrate. Cross-sectional linecuts of these distributions can be quantified using the mosaicity factor (MF), which can distinguish different orientations that can be observed for a single Bragg reflection, can compare their percent orientation, and can determine the orientational distribution for each reflection.²⁶ This is a powerful tool for comparative analysis of different thin films consisting of like materials. MF can be calculated using the following equation

$$\mathrm{MF}_{(hkl);\varphi}(\varphi) = \sum A_{w}(\varphi)S_{\varphi}(\varphi) = \frac{A_{\varphi}}{\sum A} \times \frac{45 - |\varphi_{s} - \varphi|}{45}$$
(3)

where φ_s is the azimuthal angle of interest, A_{ω} is the weighted amplitude of crystallographic signal intensity, and S_{φ_c} is a linear transformation that weighs values relative to φ_s . MF allows for the orientation of crystallites within a thin film to be compared on a linear scale from -1 to 1. As such, a Miller index reflection plane with an MF value of 1 corresponds to a crystal plane that is perfectly oriented along the q_z diffraction plane (φ = 0°) or out-of-plane with respect to the sample substrate, while a value of -1 corresponds to perfect orientation along (φ = 90°). A reflection with an MF value of 0 corresponds to randomly disordered crystallites with respect to the substrate.^{3,26} Care must be taken in curating the type of orientational information used as the scattering information on the 3D q-space object onto a 2D plane will not project the entire azimuthal data. This is due to the fact that the Ewald sphere does not project all of this information, especially at higher q values.^{27,28} This is visualized in Figure 3B, where the Ewald sphere cutoff shows the blind area on the 2D detector. To observe the full azimuthal specular reflections, constructing a complete pole figure of the orientational distributions of a particular set of crystallographic planes is required which will



Figure 3. (A) Visualization of GIWAXS/GISAXS setup showing an X-ray beam approaching a thin film sample at a grazing angle with the scattered beam collected by a 2D detector. Resolution in q space is controlled by adjusting the sample to detector distance dictating wide-angle vs small-angle data collection. Reproduced with permission from ref 17. Copyright 2019, Elsevier.¹⁷ (B) View of sample detector displaying how the Ewald sphere affects the observation of q-space objects at high grazing angles. Reproduced with permission from ref 28. Copyright 2019, IUCr Journals.²⁸

provide a full description of a material's morphology and texture when cast into thin films. $^{\rm 27}$

GIWAXS is able to provide scattering data from q spaces of 0.1–5 A⁻¹, while GISAXS offers insight into smaller q spacings ranging anywhere from 0.0001 up to 1 nm^{-1.29} In this range, GISAXS becomes a powerful tool for characterizing nano- and microstructural features. GISAXS can differentiate cylindrical, spherical-, and pyramidal-shaped parameters by fitting the scattering profile using a form factor equation.¹⁷ When GISAXS is used in concert with GIWAXS, it paints a complete morphological picture of crystalline orientation along with crystalline and noncrystalline shape parameters.

On the other hand, NEXAFS spectroscopy completes this morphological picture by characterizing unoccupied molecular orbitals, which are used to investigate crystalline and noncrystalline materials in unison.^{30,31} This has become a useful method for characterizing organic electronic materials because it can provide differences in both the energy and orientation of unfilled π -orbitals. This method can be accomplished by probing the absorption of soft X-rays by

core–shell electrons into unoccupied molecular orbitals. The most common NEXAFS studies for organic and organometallic materials are collected on the C 1s shell which can be excited into the π^* and σ^* orbitals.^{2,3,22,32} This becomes extremely valuable for organic electronics when investigating differences in orbital energies and the distributions of those energies.

Recent advancements in X-ray absorption and scattering experiments have envisioned a new method of characterizing orbital scattering resonance through the use of a 2D X-ray detector, resonant soft X-ray scattering (RSoXS).²¹ This is done by probing specific core X-ray energies observed in NEXAFS to map the spatial scattering of the resonant energy. The scattering profile of different π^* and σ^* orbitals can then be differentiated, allowing for a highly tailored map of how each orbital is oriented and how it relates to nearby related orbitals.

As the intricacy of state-of-the-art materials has become more advanced, it has also necessitated the development of characterization methods. When these morphological characterization techniques are utilized in harmony with electronic characterization, they become ever-more powerful tools for understanding the underlying role morphology plays in manipulating the electronic structure in both organic and organometallic materials. We can now investigate various emergent materials in order to understand how their morphologies affect their respective properties as these are assembled into functional devices.

\pi-CONJUGATED ORGANIC MATERIALS

Organic semiconductors are widely investigated for their prospect of low-cost modules whose electrical, optical, electrochemical, and morphological properties can be easily tuned via reproducible synthetic modifications. π -OMs may be generally subdivided into two primary categories: polymers and small molecules. Polymeric materials are typically composed of a series of electronically functional oligomers linked together into large domains. The chain length distribution, local and global morphological ordering, monomer architecture, and polymer microstructure are highly sensitive to small structural changes.³³ The properties of a given polymer's chemical structure and its thin film properties are thus highly sensitive to monomer selection.³⁴ Small molecules possess discrete sets of molecular orbitals, are monodisperse by nature, and have reproducible chemical structures.³⁵ Similar to polymers, the morphology and electronic structure of small molecules are highly sensitive to structural changes. Electron percolation through π -orbitals in a solid organic medium will strongly depend on the local and global ordering of the individual polymeric subunits or small molecules within the material. In percolation theory, the electrons will undergo site-to-site hopping between less ordered domains or band transport in domains with a large degree of π -orbital overlap.⁹ Indeed, the field-effect mobility and electrical conductivity of π -OMs can be remarkably high or negligible, being strongly influenced by their morphology.³

In terms of the functionality of π -OMs, the properties of either polymers or small molecules will depend upon the added complexity of effective electrical doping.³⁷ Doping methods within both types of materials involve either the addition of extrinsic dopants, where the semiconducting material is doped by the addition of whole molecules or self-dopants where the semiconductor is covalently attached to a moiety whose redox potential is favorably aligned to the

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Figure 4. (A) Conductivity vs dopant concentration of F4TCNQ doped P3HT. (B) q_z and (C) q_{xy} GIWAXS linecuts of P3HT with various concentrations of dopant. (D) Cartoon depiction of crystalline and amorphous domains of P3HT facilitated by ionized F4TCNQ. Reproduced with permission from ref 41. Copyright 2013, Elsevier.⁴¹

semiconductor's highest occupied or lowest unoccupied molecular orbital such that the pair undergo a ground-state charge transfer event.³⁸ In p-type doping, the lowest unoccupied molecular orbital (LUMO) should be slightly below that of the highest occupied molecular orbital (HOMO) of the polymer or small molecule semiconductor, while the reverse scenario characterizes n-type doping.⁸ The manner in which the dopant molecules disperse within the solid medium, as well as their relative orientations within said medium, may modulate the doping efficiency.^{38–40}

Illustrative work by Salleo et al. investigated the dispersive and morphological relationship between host and dopant in sequentially doped P3HT by F4TCNQ (p-type doping).⁴ Figure 4A depicts the electrical conductivity of P3HT films upon the addition of various F4TCNQ molar fractions and exhibits three separate conductivity regimes. Moreover, the conductivities observed for doped P3HT exhibited two different exponential relationships between lower and higher dopant concentrations: one from 0 to 0.012 and the other from 0.031 to 0.167. Above a 0.167 F4TCNQ molar fraction, the conductivity sharply decreased. Solution and thin-film absorption spectra of the 0 to 0.012 fractions revealed neutral F4TCNQ species, a finding which was further supported by q_z and q_{xy} GIWAXS linecuts for doped P3HT thin films whose lamellar spacing of 16.5 and 3.83 Å π -stacking distances were conserved across the low doping regime, commensurate with pure phase P3HT (Figure 4B, C). Within the 0.031 to 0.167 doping regime, sub-bandgap absorption features of the F4TCNQ radical anion appear and are accompanied by an increase in lamellar spacing by 2 Å up to 18.5 Å and now exhibit two discrete π -stacking distances of 3.85 and 3.59 Å. Above the 0.167 F4TCNQ molar fraction, an entirely new crystal phase of P3HT appears, and the conductivity suffers dramatically despite the increased dopant fraction. Work by Pingel et al. demonstrated that single F4TCNQ molecules form charge transfer complexes with quarterthiophene segments of the P3HT polymer chain when stacked face on. Therefore, the average maximum number of dopants that can bind to a polymer chain is approximately 19 F4TCNQ molecules per 100 thiophene substituents or a dopant fraction of ~0.16. Beyond this fraction, the P3HT chain becomes saturated with F4TCNQ anions, and neutral F4TCNQ begins to form single crystals within the P3HT matrix which disrupts the formation of morphologically oriented P3HT domains. Figure 4D offers a cartoon depiction of the relationship described above, where facile incorporation of F4TCNQ into morphologically ordered domains of P3HT results in charge transfer complexes and an increased intrachain distance, while neutral F4TCNQ remains in amorphous regions where the dopant is unable to interact with the quarterthiophene structures in the polymer backbone. Within this higher doping regime (0.031–0.167), the authors found that the doping efficiency was 2–3 orders of magnitude higher than that of the low doping regime (0–0.012).

We now turn our attention to two illustrative examples of how morphology may impact self-doping processes in π -OMs from our previous works. Self-doping presents several unique advantages over extrinsic doping, most notably that self-doped materials are monodisperse, negating the need for tailoring host/dopant miscibility or sequential doping studies. Modulation of self-doped systems is achieved by controlling the dopant architecture, judicious counterion selection, and morphology. Recently, we reported that dopants and polymerization protocols affect the electronic properties of polymeric systems. Specifically, we focused on PEDOT as a model system and the incorporation of counterion dopants such as chloride (Cl⁻) and tosylate (Tos⁻) into the polymer matrix. We then investigated the effects of thin film processing of PEDOT:Cl and PEDOT:Tos by chemical polymerization (CP) and vacuum vapor phase polymerization (VVPP) fabrication protocols.³ In our study, the doping method of the PEDOT scaffold, namely, via Cl⁻ or Tos⁻ incorporation, is held constant while the morphology is altered by the chosen processing method. Figure 5A shows GIWAXS linecuts of the (200) measured along the q_z axis, accompanied by the corresponding MF calculations for each processing method. For both materials, VVPP dramatically improves the alignment of both PEDOT derivatives, with PEDOT:Cl exhibiting an



Figure 5. (A) GIWAXS φ linecuts of the (200) reflection of the conductive polymer PEDOT under different processing conditions. The legend also displays the MF value for each film. (B) Conductivity vs Seebeck coefficient for PEDOT under different processing conditions. Reproduced with permission from ref 3. Copyright 2021, American Chemical Society.³

increase in MF of 0.52 and PEDOT: Tos showing an increase of 0.2. The improved morphological ordering results in

dramatic increases in electrical conductivity. As shown in Figure 5B, the conductivity of PEDOT:Cl increases from 6.7 to 107.8 S cm⁻¹, and PEDOT:Tos increases from 144.0 to 1027.3 S cm⁻¹ when employing VVPP in favor of CP. Raman spectroscopy and NEXAFS analysis of the various thin films allow us to further conclude that the more oriented VVPP films exhibit increased doping efficiencies and promote the formation of polarons.

Self-doping has also been investigated in a number of smallmolecule scaffolds, most notably in perylene diimide derivatives which have demonstrated great promise in many applications.^{3,43} By covalently attaching tertiary amines to the pervlene diimide scaffold, we found that these structures are effectively electrically doped by nitrogen, as confirmed by quantitative electron paramagnetic resonance (EPR).⁴ We demonstrated that the doping densities can be successfully controlled by introducing steric bulk about the doping structure, as shown in Figure 6A. We then investigated the thermodynamic landscape of liquid-solid and gas-solid phase transitions in self-doped perylene diimides and found that specific processing conditions allowed the materials to converge to their crystallized thermodynamic minimum rather than getting trapped in local disordered minima that represented metastable configurations. To do so, we evaluated simple drop-casting, ultrasonic spray coating (USP), and physical vapor deposition (PVD) as thin film fabrication methods. We compared the quantitative EPR results of these three thin films in Figure 6B and, surprisingly, did not observe a statistically significant change in doping density. This is especially interesting when considering the morphology characterized by the GIWAXS studies presented in Figure 6C of compound #1 processed with all three methods which demonstrate that the gas-solid transition employed by PVD allows the PDI structures to overcome the crystallization barrier present in the liquid-solid transition to form highly oriented thin films. We calculated the MF of the (001) peak



Figure 6. (A) EPR spectra for PDI with different end-group moieties. (B) EPR spectra for PDI prepared using drop-casting, USP, and PVD. (C) GIWAXS images for PDI prepared using drop-casting, spray coating, and PVD. Reproduced from ref 4 with permission from the Royal Society of Chemistry.⁴

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Review

for all three methods, finding that both methods employing the liquid–solid transition, namely, drop-casting and USP, yield comparable orientations while the MF for PVD films increases to 0.93. These two examples thus demonstrate that electrical doping can be strongly impacted by even modest changes to morphology and can also remain relatively unchanged even in systems with dramatically different morphological ordering. Care must thus be taken by researchers to fully characterize the impact of morphological ordering on doping processes that occur within their materials.

\pi-D ORGANOMETAL MOLECULAR HETEROSTRUCTURES

Organic-inorganic hybrid heterostructures provide a platform for property modulation through the selective control over the structural identity and composition of the inorganic and organic moieties. This has been realized in two dominant promising platforms: metal halide perovskites (MHPs) and metal-organic frameworks (MOFs). Both of these platforms are of interest for their synthetic modularity, wherein the structural composition can be adapted for a desired property. These properties can be tailored to a range of device applications from traditional diode and transistor stacks to photovoltaic and thermoelectric devices or even more recently topological insulating spintronic and magnonic materials.^{1,16,44-46} The broad range of applications befitting of MHPs and MOFs has inspired a growing interest to understand these materials. This section focuses on advances observed in each of these emerging materials and details the role of morphology on their resultant properties.

MOFs are a continuous coordination polymer (CP) with a metal-ligand (M-L) coordinated repeat chain.^{2,47-52} Their dimensionality is highly dependent on the types of coordination environments present in the material between the metal center and the type of ligation. Most MOFs exhibiting conducting behavior are 2D, taking advantage of continuous coordination of π and d orbitals to maintain a rigid aromatic structure. Examples of typical 2D MOF architectures are presented in Figure 7. Akin to organic conjugated polymers, polymer solubility significantly limits the formation of large crystalline repeat domains in 2D MOFs. A primary focus within the formation of conducting MOFs has been identifying methods to optimize their crystalline domain for scalability and crystalline purity.

There has been a significant disparity in the reported electronic properties of 2D MOFs in terms of computational predictions and values observed experimentally. The dominant theory as to why such discrepancies exist has been attributed to the dominance of morphological defects present in assynthesized 2D MOFs.^{2,7} As such, there has been a significant need for both understanding and overcoming limitations that drive such defects. Promising results have been found in synthetic optimizations of these materials which isolate larger grain boundaries and lead to more continuous materials. Continuous films are necessary for MOFs to be practically incorporated into functional devices, most significantly in applications relevant to quantum electronics.

2D MOFs can be accessed through numerous synthetic methods. These methods predominantly exploit interfacial interactions between two different material phases, either through vapor-liquid (Figure 8A), liquid-liquid (Figure 8B), vapor-vapor (Figure 8C), or solid-vapor interactions (Figure 8D). The chosen method typically employed in the literature



Figure 7. Structural representation of 2D MOFs as self-assembled CPs. These can be made with a number of metal salts and organic linker combinations.

depends on the metal-linker combination used. Conventional synthetic routes for the fabrication of 2D MOFs include liquid-air and liquid-liquid methodologies which allow for the interfacial formation of 2D structures upon the isolation of the metal salt and coordination ligands across a defined interface. This allows them to exclusively interact at either the liquid-liquid or liquid-air boundary. Naturally, research effort has been devoted to understanding how these materials form under different interfacial conditions, namely, vapor-vapor and solid-vapor phases, via chemical vapor deposition protocols.

Synthetic routes available for 2D MOFs are driven by the size and solubility of the organic ligand and also the redox requirements of the metal center for proper coordination. In liquid—liquid and liquid—air interfacial interactions, smaller organic molecular structures typically permit a range of solvent options, while larger linker structures limit solubility. This is also true for solid—vapor interactions and vapor—vapor interactions where larger linker coordination limits Brownian motion necessary for homogeneous metal—ligand coordination.

Computational studies on the impact of defects on the resultant electronic properties have shown that interfacial defects such as grain boundaries (Figure 9A), strike–slip faults (Figure 9B), and layer–layer displacements (Figure 9C) are dominant drivers for inhibiting the electronic properties of 2D MOFs.⁷ This has been investigated in Ni₃(2,3,6,7,10,11-hexaiminotriphenylene)₂ (Ni₃(HITP)₂), which like many 2D MOFs, is predicted to be metallic but has been experimentally verified to be a semiconductor. Ni₃(HITP)₂ is an interesting case study for discrepancies in computational and experimental observations. When characterized as a thermoelectric material, Ni₃(HITP)₂ is reported to be n-type from Seebeck coefficient measurements,⁵³ while field-effect transistor characterization has demonstrated that the material behaves as a p-type semiconductor.⁵⁴ This would suggest that the material is



Figure 8. Synthetic strategies for forming 2D MOFs: (A) vapor-liquid, (B) liquid-liquid, (C) vapor-vapor, (D) solid-vapor interfacial approaches. Reproduced with permission from ref 2. Copyright 2020, John Wiley and Sons.²



Figure 9. Examples of different interfacial defects that can affect the electronic structure of 2D MOFs: (A) grain boundaries, (B) strike–slip faults, and)C) layer–layer displacements. Reproduced with permission from ref 7. Copyright 2018, American Chemical Society.⁷

ambipolar, and p/n-type characteristics can be observed depending on the electrode's Fermi energy.⁷ When coupling the observable morphology features in $Ni_3(HITP)_2$ with computational modeling of various defect structures, it is found that grain boundaries, layer-layer displacements, and strike-slip faults all play a role in modulating the electronic structure resulting in a small bandgap. One other possible explanation for this discrepancy in metallic vs semiconducting behavior is that the electronic structure is molecular in nature and exhibits a HOMO-LUMO gap. This would then require thermal activation to attain more conductance. However, computational studies of oligomer stacking differences suggest that a molecule-like electronic structure will only appear for particles less than 20 Å in thickness (equivalent to six layers of $Ni_3(HITP)_2$). In regard to the electronic structure characterization of organic polymers, this would suggest that similar Seebeck coefficient vs electrical conductivity trends may be observed in defect prone coordination polymers which are charge hopping in nature. An interesting future research avenue is to identify how well traditional models of charge transport relate to 2D MOFs and further how we can modulate both the shape parameter s and transport coefficient σ_{E_s} .

The fabrication of 2D MOFs exhibiting metallic properties was recently observed in $Co_3(2,3,6,7,10,11$ -triphenylenehexathiolate)₂ (CoTHT) structures. This 2D MOF was synthesized using a liquid–liquid interfacial approach where pressed pellets of the material exhibited semiconducting

behavior at room temperature and metallic behavior at low temperatures which varied depending on the thickness of the pellet.⁵⁵ In this study, it was also shown that CoTHT thin films extracted from the liquid-liquid interface had a metallic transition that could be increased from 105 to 130 K by leaving the sample under vacuum for 2 h at 90 °C, which suggests that either the film undergoes orientational enhancement or desolvation, thereby directly affecting the electronic properties. The nonporous nature of MOF structures and stagnant crystalline structure would support the fact that solvent trapping can have a significant effect on the electronic properties of the resultant 2D MOF films. Room temperature metallic properties have also been observed recently in the 2D MOF copper benzenehexathiol (CuBHT) fabricated using a solid-vapor chemical vapor deposition (CVD) approach.² One major benefit of this technique is the lack of solvent during the self-assembly process. This method also showed the added benefit of forming continuous 2D MOF growth on a substrate. In the study by Ogle et al.,² the authors elegantly compared two different forms of CuBHT thin films prepared by CVD. Here, CuBHT films fabricated using a vapor-vapor interfacial CVD approach displayed semiconducting properties, whereas films fabricated using a solid-vapor synthesis exhibited metallic behavior. Both the vapor-vapor and solidvapor interfacial CVD methods yielded different morphologies and compositional structures. Using X-ray photoelectron spectroscopy (XPS) and NEXAFS, CuBHT thin films were shown to have different structural differences, where films prepared using a solid-vapor synthesis approach displayed a significant decrease in defect states. This is coupled with differences in the orientational distribution of CuBHT thin films observed via GIWAXS studies, where the vapor-vapor method yielded films with a lower orientational distribution as quantified by an $MF_{(001),0}$ of 0.54 for the (001) crystallographic plane for CuBHT. Conversely, the solid-vapor interfacial CVD approach yields thin films with a much higher orientational distribution as quantified by an MF(001):0 of 0.71. This would suggest that the effects observed from the lack of a liquid interface not only allow for the fabrication of

films with improved electrical properties but also promote the formation of well-defined structures where defects can be controlled. Further investigation of 2D MOFs prepared through CVD is warranted to understand mechanistically how different parametrization factors affect defect formation during self-assembly.

The final class of emergent semiconductors that we would like to discuss in this review is another organometal hybrid with a perovskite crystal structure, and here, we specifically focus on metal halide perovskites (MHP). A perovskite crystal structure is defined by a compound with an ABX₃ chemical formula with a network of corner-sharing BX_6 octahedra surrounding a larger A site cation as depicted in Figure 10A.



Figure 10. (A) Crystal structure of the 3D cubic MHP with A, B, and X sites labeled. (B) Distorted perovskite crystal lattice with size mismatch due to two different B site species. (C) Crystal structure of the 2D MHP with A, B, and X sites labeled. Modified from ref 58. Copyright 2020, American Chemical Society.⁵⁸

The cations, A and B sites, can vary largely depending on the application in which the MHP will be utilized, while the X site is commonly a halogen. The 3D cubic structure can be distorted due to size mismatch of the cations and anions, resulting in additional perovskite structures such as orthorhombic, tetragonal, and even 2D structures (Figure 10B).^{56,57} The electronic structure and the way charge transport occurs within the material is largely dependent on the resulting perovskite crystal structure. The role of crystallinity and morphology in MHPs is viewed as significant and instrumental toward the overall performance of these materials. For example, an MHP with a cubic structure would allow for isotropic charge transport which has proven beneficial when incorporated into a photovoltaic device that requires efficient charge separation.⁵⁸ Conversely, a 2D MHP structure has anisotropic charge transport that would occur along the metal halide octahedra sheets, as displayed in Figure 10C. So, the orientation of the octahedra sheets with respect to the substrate or electrode configuration would result in an available control of the charge transport directionality within the material. For instance, MHPs with anisotropic charge transport is more efficient when incorporated into devices that require lateral charge transport such as field-effect transistors.⁵

MHPs have drawn much attention in the past decade due to their tailorable properties and outstanding performance when incorporated into photovoltaic and transistor devices but have also shown promise in resistive memory devices, thermo-electric devices, and light-emitting diodes.⁶⁰⁻⁶² The bandgap tunability of MHPs contributes largely to this wide variety of applications and sets them apart from other thin-film semiconductors. The bandgap of MHPs used for photovoltaic applications usually ranges from 1.48 to 2.30 eV.63-65 However, this range can be further extended for other applications depending on structural variations, such as dimensionality, the composition of the inorganic framework, the choice of organic or inorganic cation, and stoichiometry.⁶⁶⁻⁶⁸ All of these factors can alter the bandgap. For example, the addition of large insulating components can drastically change the resulting morphology of the MHP film. When considering the benefits of how easily the electronic structure of MHPs can be influenced, it is no wonder that there has been a major focus within the field of perovskites to understand why certain alterations result in band structure changes and what underlying material properties cause them. In this review, we limit our focus to work that demonstrates how morphology alters the electronic structure of MHPs.

Different electronic characterizations including charge separation efficiency, charge mobility, and diffusion length of charge carriers are subjected to the crystallinity and morphology of the MHP films.⁶⁹ The morphology of MHPs has evolved systematically due to recent improvements for processing methods and various mixed compositions. Compositional engineering of MHPs is primarily done with A site cation mixtures, switching between Pb²⁺ and Sn²⁺ cations at the B site and X site anion mixtures or all simultaneously. It becomes hard to track what is causing the differences in material properties with certain MHP compositions due to subtle variations. Generally, however, when considering only halide substitution or mixing, as lighter halides are introduced into MHP structures, we observe an increase in their bandgap energy. 68,70 For example, one of the most common perovskite compositions in photovoltaic studies is methylammonium lead iodide (CH₃NH₃PbI₃) with a bandgap of 1.56 eV, but the addition of bromide causes the bandgap to increase as high as 2.23 eV.^{64,71} Altering the metal component at the B site can have the opposite effect on the bandgap. Sn²⁺ is the second most studied cation behind Pb²⁺ in MHPs. When incorporated, the perovskite becomes much more conducting due to the shrinking of the bandgap closer to 1.30 eV.⁷² Lastly the A site cation can alter the bandgap and other morphological properties. By the inclusion of cesium (Cs⁺) alongside methylammonium (MA⁺) and/or formamidinium (FA⁺), a black perovskite crystal structure is stabilized, suppressing the transition into a potential yellow phase.^{73,7} The combination of mixed cations and mixed halides to yield a MHP composition of $Cs_{0.1}(MA_{0.17}FA_{0.83})_{0.9}Pb(I_{0.83}Br_{0.17})_3$ has resulted in one of the highest performing perovskite solar devices, and this enhancement is primarily due to how all these components work together to influence the overall morphology and crystal structure of the MHP thin films. Another aspect of compositional engineering in the field of MHP that has been very influential in optimizing the electronic properties, besides the mixing of anions and cations, is the mixing of dimensions. Reducing the MHP dimensionality is done by the addition of large organic cations, commonly phenethylammonium or butylammonium. When these large insulating organic molecules are incorporated into the MHP material, the bandgap widens, the exciton binding energies



Figure 11. GIWAXS for the (A) mixed halide MHP and (B) triple cation MHP with labeled Miller indices crystallographic planes. (C) Azimuthal linecuts of the (110) crystallographic planes. Reproduced from ref 16 with permission from the Royal Society of Chemistry.¹⁶



Figure 12. (A) Cartoon depiction of the MHP structure displaying how the ions are understood to move along the (110) reflection or (100) reflection. (B) Mixed halide MHP and (C) triple cation MHP orientation relative to the substrate displaying the favorable migration pathway for the halide ions. Black arrows represent the proposed ion migration direction based on the crystallite orientation with respect to the substrate. Reproduced from ref 16 with permission from the Royal Society of Chemistry.¹⁶

increase compared to their 3D counterparts, and charge transport is hindered if the 2D sheets are not highly oriented.^{75,76} Although reducing the crystallographic dimensionality of MHPs limits their electronic properties, there is also a clear advantage in that these lower-dimensional structures are much more environmentally stable and do not degrade as easily in the presence of external factors such as humidity and oxygen. Research efforts have been devoted to developing 2D/3D multidimensional MHP structures where the long-term stability of 2D MHPs is married to the efficient charge transport of 3D MHPs. Due to the success in the synthesis of multidimensional MHP structures, there have been more recent studies on the incorporation of organic molecules at lower concentrations (<5%mol) which would preserve the 3D structure throughout the material but provide enhanced stability without deleteriously impacting charge transport.⁷² These organic molecule additives are commonly referred to as ligands or cross-linkers that include an amino group to anchor or link themselves to vacant A sites by hydrogen bonding to the I⁻ ions of the (PbI₆)^{4–} octahedra within the MHP crystal structure.^{72,77} When this occurs, it

results in defects passivation at the grain boundaries or surface of the MHP thin film by preventing water and oxygen intercalation. Moreover, the incorporation of cross-linkers within the MHP structure significantly reduces unwanted charge build-up at the lattice surfaces and grain boundaries.^{77,78}

The crystallization behavior and resulting film morphology of MHPs are also profoundly dependent on other processing parameters beyond the composition, such as surface structure and orientation. Recent processing advances for optimizing the surface structure and orientation of MHP thin films allow for control over the electronic structure by enhancing potential charge transport mechanisms and ion migration pathways within the material. An essential component of efficient charge transport in MHP thin films is to produce films of high quality. This requires tuning of the morphological properties including grain size, grain boundaries that are well passivated for better interfacial contact, continuity, and limited pinholes.^{69,79} Moreover, the addition of Cl⁻ ions has also been reported to induce larger grain sizes and preferred crystallite orientations within the MHP film.^{16,80} The crystallite orientation of MHP

thin films has recently been found to influence the possible ion migration pathways and therefore alter charge transport and electrical current stability within the MHP materials. Ion migration is the primary cause of bias stress effects in the form of internal current and voltage instabilities observed in MHPs. Although passivation techniques have been successful in mitigating certain types of ion migration, they also tend to have an insulating nature and affect charges that are transferred across grain boundaries between crystallites.^{72,78,79} It is, therefore, possible to control the crystallite orientation of MHPs without the addition of cross-linkers. By doing so, Flannery et al. were able to selectively control ion migration pathways in MHP thin films.¹⁶ Specifically, CH₃NH₃PbI_{3-x}Cl_x thin films can be fabricated where the (110) crystallographic plane is oriented along the q_{z_1} as displayed in the GIWAXS image in Figure 11A. This is the most common crystallite orientation within thin films for CH₃NH₃PbI₃ and other MHP compositions.¹ However, it is possible to orient the crystallites within an MHP thin film to about 45° with respect to the substrate (Figure 11B). The azimuthal linecuts of the (110) reflection shown in Figure 11C highlight the differences in crystallite orientation for MHP thin films. The black curve represents the (110) reflection for crystallites displaying a narrow distribution, while the red curve represents crystallites exhibiting a broad orientational distribution. It is well known that ion migration in MHPs is vacancy mediated.⁸ MHPs are predicted to have high vacancy concentrations on the order from 10^{17} to 10^{20} cm⁻³ even when assuming thermal equilibrium and noninteracting defects.^{81,82} The vacancymediated diffusion of ions through the conventional hopping mechanism between neighboring positions along the anion octahedral edge has been determined for oxide and inorganic halide MHPs.^{81–84} Theoretically, it is possible to predict how ions will migrate within an MHP crystal structure. Figure 12A shows a cartoon depiction of how ions migrate along the ABX₃ perovskite lattice (A = organic cation, B = Pb^{2+} or Sn^{2+} , X = halide).^{85–87} Here, the Pb²⁺ ions would move diagonally across the cubic unit cell or more specifically along the (110) crystallographic plane.⁸ The halide ions (X⁻) will move along the octahedron edge (i.e., along the (110) crystallographic plane) in a similar fashion as what would be expected for the Pb²⁺ ions. By knowing the directional path in which mobile ions move within the MHP lattice, as well as the ability to control crystallite orientation within thin films, we can effectively control ion directionality and ion accumulation at interfaces in MHP devices.^{8,87,88} For example, Figure 12B and C depict how different MHP lattice structures orient relative to the substrate when considering the independent (110) orientations as per the GIWAXS studies, respectively. Understanding how these MHP materials orient also informs what ionic contributions are favorable. The black arrows display how the halide ions migrate through the MHP layers along their respective (110) crystallographic planes. Figure 12B shows a schematic depiction for an MHP crystallographic arrangement where there is a more direct path for halide ion migration since the (110) reflection plane is perpendicular to the substrate. In a similar vein, Figure 12C shows a schematic depiction for a MHP crystallographic arrangement where there is a more direct path for cation migration since the (100) reflection plane is perpendicular to the substrate. Given the seminal work by Flannery et al., it becomes obvious that orientational control of crystallites within a MHP thin film could enable more efficient devices and could perhaps address the poor

device and environmental stability currently hindering the technological implementation of these materials.

CONCLUSION AND OUTLOOK

The growing complexity and interplay between structural morphology and electronic properties pose significant challenges in the development of emergent materials that can perform multiple functions at once. As improvements in device efficiency drive the field toward more complex architectures, novel devices continue to be engineered-particularly in the burgeoning field of quantum electronics. There is a mounting need for synthesis and characterization methods capable of identifying and controlling the means by which morphology affects electronic structure. To address this necessity, we have discussed many state-of-the-art methods of electronic and morphological characterization methods that together show great promise for understanding the fundamental properties of emergent organic and organometal systems. To continue to further investigate morphological and electronic properties, the experimental design of materials must be coupled with novel device characterization approaches that will enable the investigation of electrical processes occurring in heterogeneous, far-from-equilibrium environments. We invite the field to devise predictive tools, based on morphology and electronic structure descriptors, to tune both organic and organometal materials so as to enhance their compatibility with multiple device architectures and interfaces (i.e., substrates, electrodes, transport layers, dielectrics). In acknowledging modern advances in data science, we believe that the development of machine learning approaches and human-in-the-loop automated robotics would accelerate the coupling of predictive synthesis, morphological control, and composition tunability of emergent materials. Additionally, the development of novel in operando characterization approaches so as to establish an understanding of these materials under extreme and/or farfrom-equilibrium conditions will be revolutionary in the materials community.

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Notes

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Review

Biographies



Jonathan Ogle earned his B.S. degrees in engineering and chemistry at Fort Lewis College, before going on to pursue a Ph.D. from the Department of Chemistry at The University of Utah. His Ph.D. work focused on studying the relationship between morphology and electronic structure in novel materials and investigating new methods for fabricating two-dimensional coordination polymers.



Daniel Powell is a graduate research assistant and Ph.D. candidate in the Department of Chemistry at The University of Utah. His research focuses on developing and understanding novel electronic doping strategies in organic semiconductors. His research also involves developing novel characterization approaches of materials with an emphasis on automated robotics and machine learning approaches.



Laura Flannery is a Ph.D. candidate in the Department of Chemistry at the University of Utah. Her research investigates bias stress effects in semiconductor materials, with a focus on metal halide perovskites. Her research also involves understanding the interplay between individual material properties and the underlying effects of different device architectures on solar-to-electricity power conversion efficiencies.



Luisa Whittaker-Brooks is an Associate Professor of chemistry at the University of Utah. Her research centers on the design of well-defined hybrid materials with controlled morphology and interfaces that serve as conduits for deterministic and coherent energy and charge transfer for applications in energy conversion, storage, and electronics. She received her B.S. in chemistry from The University of Panama. Under a Fulbright Fellowship, she received her Ph.D. in chemistry from the University at Buffalo. She was a postdoctoral researcher at Princeton University under a L'Oréal for Women in Science Fellowship.

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