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## Introduction to molecular assembly of organic electronics

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Organic electronics are an exciting class of materials that feature conducting and semiconducting properties that originate from delocalized  $\pi$  electrons in hydrocarbons with extensive conjugation. The applications of organic electronic materials have expanded enormously over the past several decades to include “classic” devices such as organic thin film transistors (OTFTs), organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), and emerging devices such as organic electrochemical transistors (OECTs), organic thermoelectrics, and organic photocatalysts. In all of these devices, the application-relevant physical processes such as the transport of holes, electrons, or excitons occur across a three-dimensional material structure composed of many molecules. Transport among or between molecules is required, and therefore *molecular assembly* critically defines their ultimate performance. Organic conductors and semiconductors have several unique traits that make their assembly processes especially sensitive to molecular design. Their extensive conjugation gives rise to relatively rigid molecular conformation, often necessitating the attachment of

side groups to enhance solubility or broaden processing windows. The rich interplay between co-facial and/or edge-to-face  $\pi$  interactions involving planar conjugated moieties, coupled with the necessity to accommodate conformationally flexible solubilization groups having very different packing densities and crystallographic preferences in the same structure, leads to a staggering diversity of assembly motifs. This diversity is further extended by the continued emergence of novel devices and applications featuring multicomponent organic electronics systems, which often display complex and hierarchical assembly.

In this themed collection, we explore the application of molecular design principles to the assembly of organic electronics materials, through molecular conformation and packing, mesoscale domain size and orientation, and the formation of complex hierarchical structures. Articles in this collection address the fundamentals of crystallization, the interplay of those fundamentals in multicomponent systems, the role of molecular design as followed by *in situ* characterization of the assembly process, interactions between assembled structure and charge transport, and realization of these principles in emerging applications primarily focused on sensing. These themed collection articles collectively illustrate a rich molecular design space and provide

clear development vectors for future innovation in organic electronics.

The most fundamental aspect of assembly in organic electronics materials is *crystallization*; almost every organic semiconductor is liquid crystalline, semicrystalline, or crystalline, and crystals are the fundamental subunit of hierarchical structures. Thorley and co-authors (DOI: <https://doi.org/10.1039/D1ME00158B>) describe how molecular design principles affect the crystal unit cell of fluoroanthradithiophenes (F-ADTs), a storied family of solution-processable organic semiconductors featuring extremely high hole mobility. Two-dimensional brickwork packing is the key to unlocking the performance of F-ADT synthetic variants, and in this article the authors describe side-chain design rules that achieve this special packing motif. Crystal packing is also explored by Yang and co-authors (DOI: <https://doi.org/10.1039/D2ME00010E>), who purposefully induce mesoscale chirality in tetrathiafulvalene crystals, demonstrating that significant new optical activity can be gained by inducing chirality in a normally centrosymmetric system. Despite the distortion of the assembly process, the authors report no negative consequences for charge transport, and in fact some gains were observed. A correct representation of local structure is critically important for accurate computational simulations of organic

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semiconductors, and depicting this structure correctly is especially challenging for polymeric semiconductors (as it is for all semicrystalline polymers) because of their connectivity-constrained structural evolution and multiple anisotropic interactions. Reisjalali and co-authors (DOI: <https://doi.org/10.1039/D1ME00165E>) describe a new hybrid computational approach to address this challenge, that combines coarse-graining with atomistic information to yield a highly performant and accurate rendition of local structure in diketopyrrolopyrrole polymers.

Molecular design considerations become even more complex in multicomponent systems, which are often exploited to add spatially structured electronic or optical heterogeneity. An intriguing example of multicomponent hierarchical assembly is demonstrated by Palmer and co-authors (DOI: <https://doi.org/10.1039/D1ME00139F>), with a molecular light harvesting system based on conjugated polyelectrolyte complexes and a lipid vesicle scaffold. Molecular design rules for increasing the aqueous stability of these light harvesting ternary exciton funnels are proposed, including cues for desirable ordering extent, lipid melting point, and conjugated polymer electrolyte sidechain selection. A different type of multicomponent system is investigated by DiTusa and co-authors (DOI: <https://doi.org/10.1039/D1ME00192B>), who examine a model thermoelectric system in 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) vapor-doped poly(3-hexylthiophene) (P3HT). Strong correlations are reported between the conductivity of the F4TCNQ-doped P3HT and doping in crystalline domains, illustrating that molecular design principles must be applied to both polymer and dopant, not separately but together as a system to ensure facile access of the dopant to ordered polymer regions.

A powerful perspective on assembly and molecular design in organic electronics materials is provided through the lens of *in*

*situ* measurements. Although challenging, these measurements reveal the nonequilibrium structures and transient phases that occur throughout structural evolution and govern its outcomes, but which can be entirely missed by measuring only the assembly endpoints. Wan and co-authors (DOI: <https://doi.org/10.1039/D1ME00078K>) demonstrate the power of these methods with *in situ* X-ray scattering measurements describing the solidification of an asymmetric benzothieno-benzothiophene (BTBT) type small molecule organic semiconductor. A transient liquid crystal state is observed, with a surprisingly slow transformation over minutes or hours, to the stable crystalline phase by a nucleation process. Molecular design principles related to the asymmetry of the attached solubilization groups explain the complex structural evolution. Dynamic variations in crystal packing are also explored by Talmack and co-authors (DOI: <https://doi.org/10.1039/D1ME00153A>), who examine polymorphism in a dinaphthothienothiophene (DNNT) type small molecule organic semiconductor. This promising high hole mobility material must be processed at temperatures near a recently-discovered polymorphic phase transition, and the new crystal unit cell revealed by *in situ* methods is studied to understand thermal expansion and its implications for device performance. The authors find the DNNT polymorphism to be governed by side chain orientations, delivering molecular design cues for tailoring polymorphism behaviors by side chain engineering. In an unusual computational *in situ* study, Ryno and co-authors (DOI: <https://doi.org/10.1039/D1ME00157D>) demonstrate a combined molecular dynamics and graph characterization approach to the solidification of ADT type organic semiconductors. This novel combination of computational approaches explains differences in the structural evolution of the *syn*- and *anti*-isomers of ADT as they solidify from gas, to liquid, to solid. Dramatic

differences are observed in the smoothness of the assembly transitions and in the ultimate long axis ordering and final crystal morphology revealed by graph feature analysis. The results indicate a clear rationale for isomer separation and reinforce the expectation that isomerism matters in this widely used family of organic semiconductors.

Charge transport is a key physical process in almost every organic electronics device. Interrelationships between assembly and charge transport are explored by Pokuri and co-authors (DOI: <https://doi.org/10.1039/D1ME00163A>), who exploit all-atom simulations and graph theory characterization approaches to characterize the resilience of charge transport in PTB7, a model hole-transport material for OPVs. The authors study resiliency by selectively 'deactivating' monomers, ultimately demonstrating that the assembled PTB7 morphology is surprisingly resilient to the removal of parts of the morphology. The article provides a sophisticated advancement over simple percolation arguments by assessing atomistically realistic morphologies with highly performant modern abstraction algorithms. It suggests a convincing argument that charge transport in some systems may be governed by a minority of the assembled film structure, and it provides a powerful framework for designing resilient systems *in silico*.

Finally, a pair of minireview articles explore the themes of this collection from the perspective of emerging sensing applications in organic electronics. Interrelationships between assembled structure and chemical sensing are explored by Zhi and co-authors (DOI: <https://doi.org/10.1039/D2ME00020B>), with themes including morphology-dependent signal amplification and the effects of molecular stacking, film thickness, grain boundaries, molecular orientation, and mesoscale structure. Molecular design principles are reviewed including the interplay of hydrogen bonding and  $\pi$ -stacking interactions, heteroatom effects, and side chain selection. Meso- and macro-scale structure manipulation by processing,

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surface engineering, and nanoparticle inclusions are also discussed. A second minireview by Zhu and co-authors (DOI: <https://doi.org/10.1039/D1ME00134E>) focuses on the polymeric organic electrochemical transistors and their design principles, with valuable coverage of structural characterization methods and computational approaches, followed by discussion of morphology control strategies including the synthetic design of backbones and sidechains and approaches for formulation and processing. The engineering of the electrolyte–polymer interface is highlighted as a provocative emerging set of considerations that is quite unique to the organic electrochemical transistor device.

We thank the authors, reviewers, and the editorial staff at *Molecular Systems Design & Engineering* for contributing to this themed collection. Molecular design in organic electronics continues to evolve at a rapid pace, and this collection illustrates a trajectory of increasing sophistication in the prediction and manipulation of structures for optimization in specific applications. We anticipate an exciting future where molecular design demands driven by the increased complexity of multicomponent and hierarchically structured organic electronics materials, create a virtuous cycle of enhanced molecular design rules, processing rules, structural measurements, and advanced computational approaches that dramatically accelerate progress and expand the breadth of applications in years to come.



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