



# Crystal clear: the impact of crystal structure in the development of high-performance organic semiconductors

Callum J. McHugh\*

School of Computing, Engineering and Physical Sciences, University of the West of Scotland, Paisley Campus, Paisley PA1 2BE, United Kingdom. \*Correspondence e-mail: callum.mchugh@uws.ac.uk

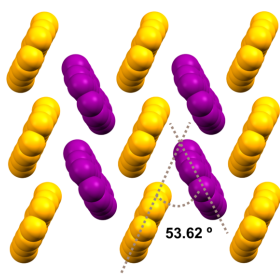
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Solid-state optical and electronic properties in  $\pi$ -conjugated small molecules are strongly influenced by molecular motions, packing and dimensionality (Ostroverkhova, 2016). Fine tuning of these regimes provides a powerful mechanism by which to inform and systematically establish guidelines in the design of superior materials (Schweicher *et al.*, 2014; Podzorov, 2013). In crystalline charge-mediating organic materials, control of molecular solid-state aggregation can exert a dramatic impact on intermolecular electronic properties which define delocalized band transport and localized thermally-activated hopping of charge carriers. Organic single crystals (OSCs) have been, and remain to be, crucial in realizing effective performance in optoelectronic devices bearing organic conjugated architectures, given their superior purity and long-range periodic order.

In their contribution to the 'Best practice in crystallography' series in *Acta Crystallographica Section C: Structural Chemistry*, Schweicher *et al.* (2024) present a compelling overview, describing the importance and influence of molecular structure, crystal packing and crystal lattice dynamics on both theoretical and experimental charge-transport behaviour in crystalline environments. The authors confront an historic challenge, of what limits the charge carrier mobility in these systems (Schweicher *et al.*, 2014), and rationalize the crucial role of crystal structure in the derivation of molecular and supramolecular design rules, to maximize optoelectronic performance.

Packing motifs in small-molecule organic semiconductors are crucial, and are typically represented by cofacial stacking, slipped-stacking, brick-wall and herringbone arrangements, where resultant intermolecular interactions strongly influence electronic behaviour. Electronic coupling, or charge-transfer integrals for hole and electron transport, describe the extent of wavefunction overlap and are related to the strength of the  $\pi$ - $\pi$  interactions between molecules and play a significant role in charge mobility. Inner-sphere reorganization energies for those charge carriers characterize the change in energy between charged and neutral molecular states, owing to geometrical relaxation of the localized molecular environment, and can be detrimental to transport behaviour when charge hopping is predominant. Large intermolecular interaction energies are highly desirable in organic semiconductors to preserve the integrity of crystalline intermolecular interactions involving  $\pi$ - $\pi$  stacking, and to perpetuate band structure. Thermally-induced slippage of  $\pi$ - $\pi$  stacking domains and electron-phonon dynamics, the so-called 'killer phonon', can result in considerable variation in transfer integrals, which can induce localization of charge carriers and be detrimental to carrier mobility (Schweicher *et al.*, 2019). In small-molecule semiconductors, high bulk dimensionality is advantageous, overcoming significant fabrication issues relating to structural defects and grain boundaries in devices. Most of the systems described by Schweicher and co-workers that are based on acene and thiophene molecular systems, and for which mobility has been reported to be high, pack in a herringbone manner, with this preferred supramolecular architecture exhibiting desirable electronic behaviour and higher dimensional charge-transport pathways.

Polymorphism is an elegant approach to examine the influence of supramolecular environment on a molecularly identical semiconductor scaffold (Pandey *et al.*, 2022; Izawa *et al.*, 2018; Wang *et al.*, 2018). This approach has also been extended to isotopically labelled materials (Schweicher *et al.*, 2024). Polymorphism at interfaces and surfaces are presented by Schweicher and co-workers as a unique opportunity to study differences in



semiconductor behaviour in their operating environment, which can be significantly different to the bulk crystalline state. This is crucial in understanding device performance in a range of applications that rely on the presentation of thin films at material boundaries. Phase changes can be induced through preferential interactions that occur between surfaces and the semiconductor unit-cell dimensions. The result can be manifested in a reduced interfacial tension between the charge-transport material and dielectric layer, leading to preferred orientation of the material, often in a metastable phase. Significant effort has been placed on the development of approaches to evaluate the role of substrate-induced phase transition, evoking a combination of experimental solid-state structure elucidation and theoretical modelling. This is of substantial interest in the fabrication of organic single-crystal arrays applied in flexible displays, smart wearable devices and biochemical sensors, *via* ink jet printing, solution and droplet patterning, guided crystallization, etching and solvent annealing (Zhao *et al.*, 2023).

*In-silico* design based upon intrinsic material behaviour represents a highly prized asset in the development of organic semiconductors, providing a tool to enable identification of superior materials by molecular argument. This approach has the potential to accelerate a paradigm shift from descriptive to predictive-based realization of organic semiconducting materials. Traditional computational approaches and theoretical modelling are now enhanced with artificial intelligence (AI), machine learning and data analytics, that rely on the curation and exploration of vast data sets. Accordingly, Nematiamram *et al.* (2020) have recently described a sophisticated approach to discover the largest possible mobility of molecular semiconductors. Using structural information available from the Cambridge Structural Database (CSD; Groom *et al.*, 2016), the authors were able to rank the importance of properties, such as molecular area, non-local electron–phonon coupling, two-dimensional transport, local electron–phonon coupling and transfer integral, on overall charge mobility. This new tool is proposed to provide an accurate evaluation of charge mobility from crystal structure data in a fully automated procedure that requires limited computing effort, the ultimate ambition being to realize bottom-up design parameters from top-performing architectures without the necessity for crystal structure prediction. In an alternative approach, Johnson *et al.* (2024) recently reported a machine learning strategy to predict the

thermal properties of OSCs. By screening almost half a million commercially available molecular candidates, they were able to select and experimentally validate a small number of systems most likely to crystallize in a platelet morphology, that has been identified as crucial in the fabrication of high-performing thin film devices.

In summary, small-molecule organic semiconductor evolution relies on a synergy of synthesis, crystal engineering, device fabrication, computational screening and material informatics. In their contribution, Schweicher and co-workers demonstrate that the successful development of the field is underpinned by a fundamental understanding of the key role that crystal structure exerts on charge mobility. The possibility to investigate controlling limits of charge and exciton transport in OSCs, by studying intrinsic structure–property relationships in the absence of grain boundaries, defects and impurities, has been, and will continue to be, transformative in realizing the next generation of optoelectronic materials and applications.

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