ACCEPTED VERSION

Belinda J Boehm, Huong TL Nguyen and David M Huang

The interplay of interfaces, supramolecular assembly, and electronics in organic semiconductors

Journal of Physics: Condensed Matter, 2019; 31(42):423001-1-423001-23

© 2019 IOP Publishing Ltd.

Originally published: http://dx.doi.org/10.1088/1361-648x/ab2ac2

This Accepted Manuscript is available for reuse under a CC BY-NC-ND licence after the 12 month embargo period provided that all the terms of the licence are adhered to.

PERMISSIONS

https://publishingsupport.iopscience.iop.org/accepted-manuscripts/

After acceptance, each Named Author of an article to be published/published on a subscription basis may:

Unless otherwise stated, any reference below to an Embargo Period is a reference to a period of 12 months from the Date of Publication.

3. Post the Accepted Manuscript to an institutional repository or subject repository (in both cases ONLY where non-commercial) after the Embargo Period under a CC BY-NC-ND licence, provided that all terms of the licence are adhered to, and any copyright notice and any cover sheet applied by IOP is not deleted or modified. *The above should satisfy the requirements of research funders for 'green open access', such as the Chinese Academy of Sciences, US National Institutes of Health, NASA, NSF, US Department of Energy, NIST, National Research Council of Canada and Austrian Science Fund, to deposit the outputs of research funded by them in a repository.*

4. Post the Accepted Manuscript to an institutional repository or a subject repository (in both cases ONLY where non-commercial) where necessary to comply with the requirements of the HEFCE REF 2021 open access policy. HEFCE's requirements are as follows:

- For articles with a Date of Acceptance between 1 April 2016 and 31 March 2018 inclusive, the Named Authors may make a Closed Deposit of the Accepted Manuscript to the non-commercial repository within three months of the Date of Publication of the article; or
- For articles with a Date of Acceptance on or after 1 April 2018, the Named Authors may make a Closed Deposit of the Accepted Manuscript to the non-commercial repository within three months of the Date of Acceptance of the article.

In both the above cases, after the Embargo Period, the full text of the Accepted Manuscript may be made available on the non-commercial repository for anyone with an internet connection to read and download. After the Embargo Period a CC BY-NC-ND licence applies to the Accepted Manuscript, in which case it may then only be posted under that CC BY-NC-ND licence provided that all the terms of the licence are adhered to, and any copyright notice and any cover sheet applied by IOP is not deleted or modified.

You may indicate that the CC BY-NC-ND licence applies after the Embargo Period by including the following wording on the Accepted Manuscript, "This Accepted Manuscript is available for reuse under a CC BY-NC-ND licence after the 12 month embargo period provided that all the terms of the licence are adhered to" (unless there is a cover sheet applied to it by IOP which already states this).

29 March 2021

http://hdl.handle.net/2440/121177

Topical Review

The interplay of interfaces, supramolecular assembly, and electronics in organic semiconductors

Belinda J Boehm, Huong TL Nguyen and David M Huang

Department of Chemistry, School of Physical Sciences, The University of Adelaide, SA 5005, Australia

E-mail: `david.huang@adelaide.edu.au`

Abstract. Organic semiconductors, which include a diverse range of carbon-based small molecules and polymers with interesting optoelectronic properties, offer many advantages over conventional inorganic semiconductors such as silicon and are growing in importance in electronic applications. Although these materials are now the basis of a lucrative industry in electronic displays, many promising applications such as photovoltaics remain largely untapped. One major impediment to more rapid development and widespread adoption of organic semiconductor technologies is that device performance is not easily predicted from the chemical structure of the constituent molecules. Fundamentally, this is because organic semiconductor molecules, unlike inorganic materials, interact by weak non-covalent forces, resulting in significant structural disorder that can strongly impact electronic properties. Nevertheless, directional forces between generally anisotropic organic-semiconductor molecules, combined with translational symmetry breaking at interfaces, can be exploited to control supramolecular order and consequent electronic properties in these materials. This review surveys recent advances in understanding of supramolecular assembly at organic-semiconductor interfaces and its impact on device properties in a number of applications, including transistors, light-emitting diodes, and photovoltaics. Recent progress and challenges in computer simulations of supramolecular assembly and orientational anisotropy at these interfaces is also addressed.

Keywords: soft condensed matter, organic electronics, molecular anisotropy, computer simulation, coarse graining, multiscale modelling

1. Introduction

Semiconductors underpin much of the technology that drives modern society, from computers to mobile phones and solar panels. Although this technology is dominated by inorganic materials such as silicon, organic semiconductors comprising carbon-based molecules and polymers are rapidly growing in importance, and are now the basis of a lucrative industry, particularly for electronic device displays. Organic semiconductors offer many advantages over conventional inorganic materials: they can be processed from solution by energy-efficient methods and only thin films are needed to produce functional devices, saving on material requirements and costs, and making them compatible with high-throughput printing processes and flexible substrates [1]. They can also potentially enhance inorganic semiconductor device performance, e.g. as singlet-fission or triplet-annihilation layers to improve light harvesting in silicon solar cells [2]. Nevertheless, many promising applications of organic semiconductors remain largely untapped, such as photovoltaics and energy-efficient lighting.

One of the main impediments to more rapid development and widespread adoption of organic semiconductor technologies is that device performance cannot easily be predicted from the chemical structure of the constituent molecules. Fundamentally, this is because molecules in organic semiconductor materials are held together by relatively weak non-covalent forces, resulting in significant structural disorder that can impact device properties in ways that are hard to predict. In addition, organic semiconductor thin films are generally formed by deposition onto a substrate from the vapor or solution phase in a nonequilibrium process that is challenging to describe by simple theory. Inorganic semiconductors, on the other hand, generally have ordered crystal structures that simplify prediction of electronic properties. Consequently, organic semiconductor device optimization often proceeds by trial-and-error, with material properties and processing conditions varied until a desired result is achieved. Thus, given the many applications of organic semiconductors, a more predictive approach will have major commercial and societal impacts.

One general property of almost all organic semiconductor molecules is the significant anisotropy in their shape and thus in their interactions. In principle, this molecular anisotropy can provide a handle by which structural order in organic semiconductors can be controlled. In particular, translational symmetry breaking at an interface can induce preferential orientation of anisotropic molecules [3]. Ordering (and disorder) of organic semiconductor molecules at interfaces is known to have a large effect on electronic device performance in diverse applications and it is therefore important to understand the numerous mechanisms for its control. For example, aligning molecules with a permanent dipole moment at the interface between photo-active layer and electron contact in an organic solar cell can improve the power conversion efficiency by making the contact more selective to electrons over holes [4]. The alignment of organic semiconductor molecules with respect to the dielectric surface in organic field effect transistors (OFETs) strongly impacts charge-carrier mobility [5]. In organic light-emitting diodes (OLEDs), preferential alignment of host and guest emitter molecules with respect to the substrate surface can significantly boost the out-coupling efficiency of light by aligning guest transition dipole moments [6]. In organic photovoltaics (OPVs), significant variations in device efficiency have been correlated with molecular alignment at the interfaces between nanoscale domains of electron donor and acceptor materials [7]. A schematic representation of these interfaces is shown in figure 1.

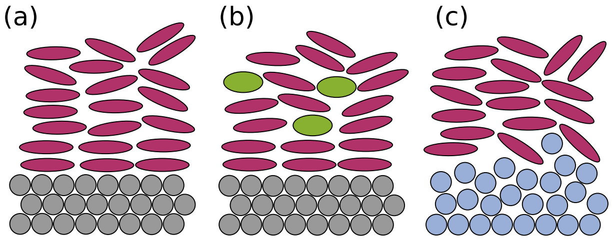

Figure 1. Schematic of general organic semiconductor interfaces addressed in this review: (a) semiconductor-dielectric interface for OFETs; (b) semiconductor host-guest mixture on a substrate for OLEDs; and (c) bulk-heterojunction electron donor-acceptor interface for OPVs.

Many examples, both experimental (e.g. [7–10]) and computational (e.g. [11–15]), of semiconducting molecules displaying preferential alignment at interfaces can be found in the literature, but few general rules for predicting interfacial orientation from chemical structure or processing conditions appear to exist. Many factors have been implicated in control of interfacial orientation, including, among others, molecular shape [14, 16–18], the presence, length, and composition of side chains [8–10, 19], backbone planarity [20], temperature [14, 15, 17], and solvent choice [14, 20, 21] and understanding the reasons behind these factors is important for the rational design of high performing organic semiconductors.

Although these interfaces are clearly important for understanding electronic processes in organic semiconductor-based devices, they are generally buried, making them experimentally difficult to characterize [22, 23]. While bulk morphology is relatively simple to characterize, morphology at the interface has been shown to often be different to that in the bulk, with changes in bulk morphology not necessarily correlated with that at the interface, and vice versa [24–26]. Although microstructural information can be gleaned from experimental techniques such as NEXAFS [27], X-ray diffraction rocking [24], GIXD [25], and soft X-ray scattering techniques such as R-SoXS and P-SoXS [28], molecular simulation can provide greater detail of the structures and processes occurring at these interfaces, with the advantage that it can often be directly coupled to an analysis of electronic structure and exciton and charge-carrier dynamics.

The use of molecular simulation to study organic-semiconductor interfaces has been recently reviewed [29], so it is not our goal to analyze in great depth the methods commonly used to study these systems, nor the general morphology at the interfaces. Instead we aim to provide an overview of the general role of molecular anisotropy at these interfaces and how it can be controlled to improve device performance through an understanding of the general physical principles that affect the interfacial microstructure. Additionally, we touch on the links between physical structure at the interfaces and electronic structure and charge transport characteristics to better understand the factors that improve or reduce device performance.

We also do not specifically focus on organic semiconductor single crystals, which have been extensively and comprehensively reviewed previously [30–37]. Studies of single crystals have provided much important insight into the control of the bulk morphology of single-component small-molecule organic-semiconductor systems and the interfacial morphology of semiconductor–substrate interfaces with matching lattices, in which orientation with respect to the substrate is controlled by matching lattice vectors of a particular semiconductor crystal plane with those of the substrate surface, resulting in aligned epitaxial growth [35]. However, such findings are not generally applicable to understanding the principles that govern interfacial microstructure and orientational ordering across different organic–semiconductor materials and device types, which are often significantly disordered and/or consist of multiple components. Even for a single crystal, the interface with a substrate is generally expected to be disordered and may even have a different structure from the bulk due to mismatched lattices and semiconductor–substrate interactions. Thus, such interfaces are expected and in some cases have been shown to be governed the same principles and processes discussed below for general organic-semiconductor systems with disorder.

The outline of this review is as follows. We initially describe the theoretical background relevant to the ordering of anisotropic molecules at interfaces in section 2 before examining the role of these interfaces and the effects of molecular alignment at these interfaces in OFETs, OLEDs, and bulk heterojunction (BHJ) OPVs in section 3. In section 4 we survey the available literature on interfacial orientational ordering of organic semiconductors with the aim of identifying general physical principles for predicting interfacial orientation. Finally, in section 5, we discuss computer simulation methods for improving understanding of the structure and supramolecular assembly of organic-semiconductor interfaces, along with the challenges associated with accurately capturing experimentally relevant length and time scales in these simulations.

The chemical structures of molecules and functional groups relevant to this work are shown in figure 2.

2. Theoretical Background

The interesting optoelectronic properties of organic semiconductors arise from significant delocalization of π electrons due to extended conjugation (alternation of single and double or triple bonds) in the molecular structure, as illustrated in figure 2. Accordingly, organic semiconductor molecules generally consist of highly anisotropic rigid subunits such as fused aromatic rings. This molecular shape anisotropy has consequences for the interfacial supramolecular assembly of organic semiconductors and optoelectronic processes, as detailed in this and the following sections.

The presence of an interface between a system of anisotropic particles with another phase (e.g. a gas, solid, liquid) breaks the translational symmetry of the system and can induce orientational ordering at the interface, even when the bulk phase is isotropic. For a collection of biaxially anisotropic particles, in which each particle has three inequivalent principal axes, the possible preferred orientations with respect to the interface can be classified into three extremes – end-on, face-on, or edge-on (figure 3) – with the actual orientation for a specific system possibly being intermediate between these extremes. For conjugated molecules such

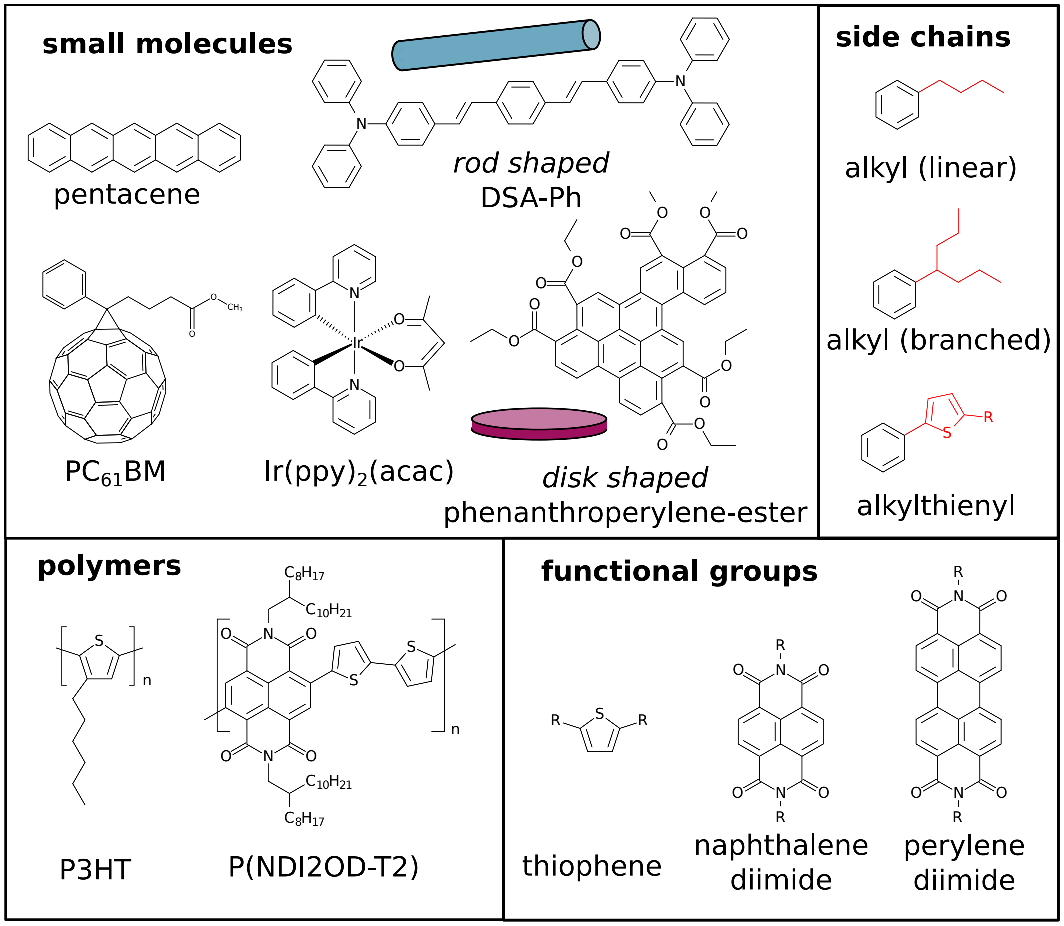

Figure 2. Chemical structures of a number of molecules and functional groups relevant to this work.

as organic semiconductors, variations in the preferred orientation will change the orientation of the π-stacking direction with respect to the interface, which has implications for exciton and charge dynamics.

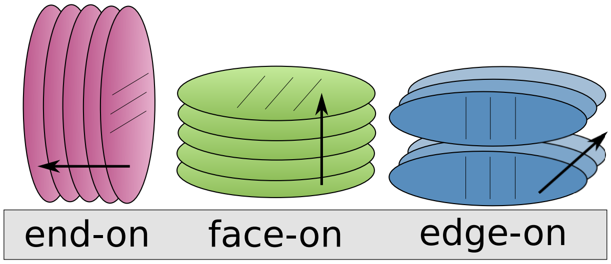

Figure 3. Classification of orientations of a collection of biaxially anisotropic particles with respect to a surface. Arrows indicate the direction of the shortest molecular axis, which is generally the π-stacking direction in organic semiconductors. The surface is shown in grey.

Orientational ordering of anisotropic particles at interfaces has long been studied, particularly in the domain of liquid crystals [3], in which experimental, theoretical, and computational studies on this topic have been extensively reviewed [38–41]. Most of this work has focused on the equilibrium behavior of single-component fluids of uniaxial mesogens, in which each molecule has one inequivalent and two equivalent principal axes. Thus, the full complexity of organic-semiconductor systems, which often comprise multi-component blends of biaxial molecules whose microstructure is formed under non-equilibrium conditions, cannot be fully understood based on these studies. Nevertheless, this extensive body of work provides a basic conceptual framework for understanding interfacial alignment of organic semiconductors.

In the field of liquid crystals, orientational ordering with respect to an interface is called surface anchoring [38], and is classified as homeotropic, planar, or tilted, depending on whether the (non-equivalent) axis of the (uniaxial) molecule is perpendicular, parallel, or oblique to the plane of the interface. Early Landau–de Gennes-type phenomenological theories [42], in which the free energy is expanded in powers of a nematic order parameter, have provided useful insight into surface anchoring, but do not lend themselves to simple interpretation in terms of the microscopic properties of the intermolecular interactions. With more recent work using molecular field theories (e.g. generalised van der Waals theories and classical density functional theories) [39] and molecular simulations [40], a clearer picture is emerging of the molecular parameters that govern interfacial orientational ordering of liquid crystals.

One general finding of these studies is that the direction of interfacial alignment of liquid crystals is non-universal [40, 43], and depends on the details of the intermolecular interactions, such as the competition between anisotropic repulsive and attractive interactions [44]. Using a generalised van der Waals theory, it has even been shown that different terms in a spherical harmonic expansion of the anisotropic attractive interactions of a model mesogen can have opposite effects on interfacial alignment [43], revealing the subtle interplay of factors that control orientational ordering. Nevertheless, some general trends can be gleaned from theoretical and computational studies of model liquid crystal interfaces.

Most theoretical and computational studies have focused on the liquid–vapor interface or nematic–isotropic interface between coexisting nematic and isotropic liquid phases of a single-component fluid. For purely repulsive intermolecular interactions, orientational ordering is governed by excluded-volume entropic effects, which result in perpendicular alignment of prolate molecules at the vapor interface [43, 44]. On the other hand, for molecules with both (short-range) repulsive interactions and (longer range) attractive interactions, various alignments are obtained depending on the anisotropy of the molecular shape and interaction strength. Most molecular simulations of liquid crystals with attractive interactions have used the Gay–Berne (GB) potential [40, 45], which is a general anisotropic potential energy function that depends on the relative position and orientation of pairs of ellipsoidal molecules. For a uniaxial molecule, the molecular shape anisotropy in the GB potential is characterized by the parameter κ, which is the ratio of the molecule length to breadth, while the interaction strength anisotropy is characterized by the parameter κ', which is the ratio of the attractive well depth for side-to-side versus end-to-end interactions. For both prolate [46–48] and oblate spheroids [48] for a range of temperatures and κ and κ' values, alignment at the vapor interface has been shown to be controlled by the κ/κ' ratio, with

$\kappa/\kappa' > 1$ yielding planar (parallel) alignment and $\kappa/\kappa' < 1$ giving perpendicular alignment. This behavior was rationalized based on the relative energies of different cleavage planes of close-packed ordered arrays of molecules. This essentially amounts to the exposed interface being the one with the lowest interfacial tension, and suggests that interfacial ordering is energetically rather than entropically controlled by the parameters chosen in these systems.

Compared with the vapor interface, orientational ordering of a liquid crystal at a solid interface is complicated by the influence of the interaction with the solid. Thus, theoretical and computational studies of this situation have been more limited and a general theoretical understanding is lacking [39]. For purely repulsive hard-core interactions between prolate molecules and with a solid surface, entropic excluded-volume effects favor planar alignment with the surface [49], opposite to the perpendicular alignment found for similar molecules at the vapor interface [44]. Similarly, semiflexible polymers, which in a sense can be considered highly anisotropic prolate molecules, confined by a repulsive solid surface tend to align parallel to it [50]. For molecules with both repulsive and attractive interactions with each other and with the solid substrate, the interfacial ordering depends on the details of the substrate–molecule interaction strength and anisotropy [51]. For example, planar anchoring is observed for strong coupling between model GB ellipsoidal particles and a solid substrate at which the substrate–molecule interactions favor this alignment. On the other hand, for a fluid confined between solid and vapor interfaces that is weakly coupled to a solid, the alignment at the solid surface is controlled by that at the vapor interface at temperatures below the nematic–isotropic transition [51].

For interactions of anisotropic particles at the interface with another fluid, the strength of the interactions between the particles is, again, an important factor for controlling interfacial alignment [52], and so general predictive rules for orientational ordering have to our knowledge not been developed. For purely repulsive interactions between a mixture of hard spheres and vanishingly thin needles, classical density functional theory has shown that the needles have a slight preference for planar anchoring at the sphere–needle interface in the demixed state [53]. On the other hand, for molecules with both repulsive and attractive interactions, molecular dynamics (MD) simulations of a system of model GB rods and Lennard-Jones (LJ) spheres have shown that increasing the strength of the interactions between the size of the rod and the spheres gives a preference for planar anchoring, while stronger interactions between the end of the rod and the spheres gives perpendicular alignment [52]. These effects are summarized in figure 4.

3. Role of interfaces and supramolecular assembly

It has long been known that molecular anisotropy at interfaces is important for enhancing charge transport and device performance, with Sirringhaus et al. [54] reporting significantly higher field-effect transistor (FET) mobility with edge-on orientations of poly(3-hexylthiophene-2,5-diyl) (P3HT) than face-on orientations of the same molecule almost 20 years ago [54]. Since then, many studies of have found similar correlations between orientation and device performance for OLED [6, 55–57], OPV [7–9], and OFET [5, 58, 59]

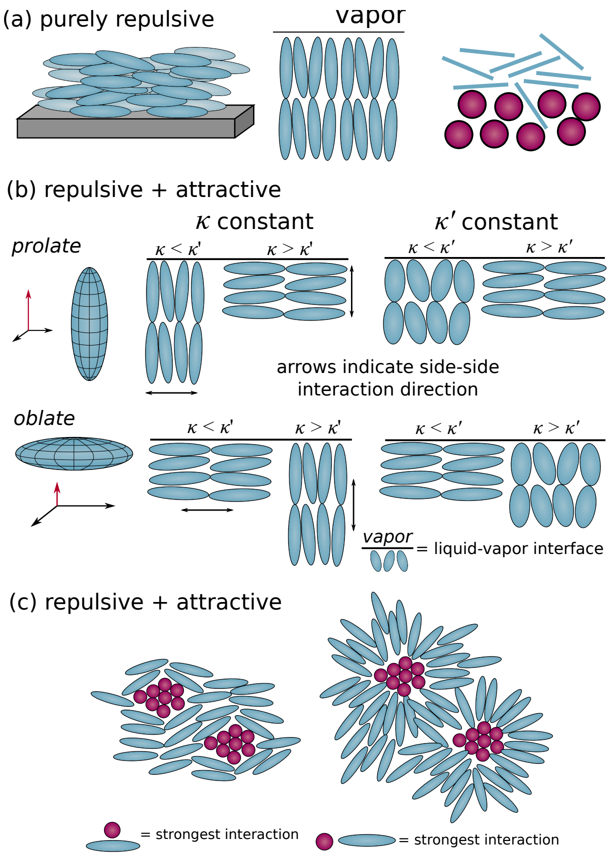

Figure 4. (a) Orientation of (left) hard rods at the interface with a solid substrate, or (center) a vapor, and (right) needles at a fluid interface. An ellipsoid with purely repulsive interactions has been shown to have a preference for parallel alignment at the solid and fluid interface, and perpendicular at the vapor. (b) Orientation of an ellipsoid, having both attractive and repulsive interactions, with its vapor, and (c) with a spherical fluid. For an ellipsoid at the vapor interface (b), increasing the side–side interaction strength (decreasing κ', left) or increasing aspect ratio (increasing κ, right) gives a parallel orientation for both prolate (top) and oblate (bottom) ellipsoids. The red arrow indicates the axis that defines orientation. The direction perpendicular to this defines the side–side direction. At the interface with a fluid (c), orientation depends on the strength of the interactions between either the end or side of the ellipsoid with the spheres.

devices. In general, in-plane alignment of the transition dipole moment of emitter molecules with respect to the substrate gives better optical properties in OLEDs [55], a face-on alignment at donor–acceptor interfaces appears to be generaly preferred for good performance in BHJ organic solar cells (OSCs) [7–9], and edge-on alignment is found in most high-performance OFETs [54, 60], although face-on structures may still give good mobility in some cases [61, 62]. It is therefore important that alignment at these interfaces can be controlled.

3.1. Semiconductor–substrate interfaces in organic transistors

In organic transistors, charge transport occurs in an organic semiconductor material that has been deposited onto the surface of a dielectric, with transport restricted to an accumulation layer within a few nm of the semiconductor–dielectric interface [63–66]. The microstructure at this interface therefore has a significant effect on the charge-carrier mobility, which is the key performance metric of OFETs and also plays an important role in OLEDs and OPVs. Indeed, a linear correlation between molecular tilt angle at the interface and OFET saturation mobility has recently been shown [58]. Additionally, a number of studies have shown that, although semicrystalline semiconductors show similar charge mobilities on different dielectric surfaces, the mobility of amorphous semiconductors depends strongly on the properties of the dielectric [62, 67–70]. Thus, understanding the structures at the interface, which can differ significantly from that in the bulk [25, 27], is important for improving device performance. Thus, the many studies on bulk morphology are not necessarily relevant for correlating electronic processes and morphology in these devices.

The orientational order (edge-on or face-on) and, for polymers, the direction of the backbone with respect to the source and drain electrodes play a significant role in organic transistor performance. An edge-on alignment to the dielectric surface, where the π-stacking direction is parallel to the substrate, is expected to enhance charge mobility. This is due to the much higher mobility of charge carriers in the π-stacking direction, related to the substantial overlap of the π-orbitals, than through the insulating aliphatic chains (figure 5), which would occur in a face-on orientation [71]. For polymers, a backbone direction parallel to the charge-transport direction (i.e. between source and drain electrodes) will give the fastest charge transport, as charge carriers can move along the backbone (figure 5) [71]; however, this will be a function of chain length as shorter polymer chains will require more interchain hops along this direction [71]. On the other hand, small molecules give the greatest performance when the π-stacking direction is the same direction as charge transport, as this facilitates hopping between adjacent small molecules in the desired direction [72]. Indeed, when methods that induce order in certain directions are used for the generation of films, highly anisotropic charge transport has been observed [73, 74].

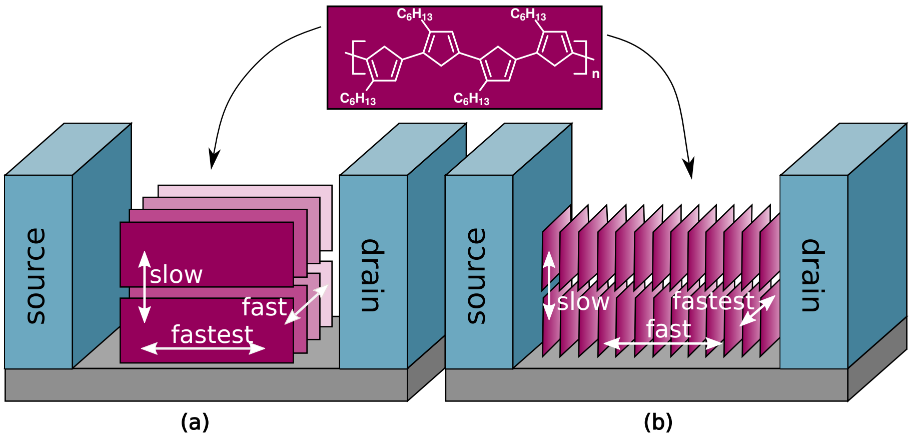

Figure 5. Architecture of a bottom-gate bottom-contact OFET at the dielectric interface. Polymers are shown in an edge-on conformation with backbone either (a) parallel or (b) perpendicular to the required charge transport direction. Charge transport is fastest along the polymer backbone, slower, but still fast, in the π-stacking direction, and slowest along the lamellar stacking direction.

The effect of liquid-crystalline order in organic semiconductors on charge transport has been comprehensively reviewed [72], from which some general conclusions can be drawn about the influence of molecular anisotropy. Disc-shaped molecules give one-dimensional columnar structures featuring good π-orbital overlap and high charge transport, but also a large susceptibility to defects [72]. Rod-like mesogens on the other hand, give smectic phases that do not pack as closely as the columnar phases formed by discs but are more resilient to defects due to the possibility of two-dimensional charge transport. Finally, board-like polymers, such as polythiophenes, combine both the close π-stacking of the discs with the two-dimensional charge transport of rods, giving enhanced charge carrier mobility [72].

A number of factors have been shown to influence edge-on versus face-on orientation with respect to the dielectric interface, ranging from the molecular weight (for polymers) [27, 75, 76], to the side chain [5, 16] and backbone [16, 20] structure, the substrate composition [11, 16, 60, 74, 77, 78], deposition technique [71, 73, 79, 80], and the solubility of the material [16, 20, 21, 27, 58, 74, 81]. These methods will be discussed in greater detail in following section in the general context of controlling anisotropy in organic semiconductors. However, as the direction of the backbone of polymer semiconductors with respect to source and drain electrodes is uniquely applicable to organic transistors, this factor will be be examined here.

The solubility of organic polymers has been shown to be an important consideration when considering device morphology as the choice of solvent can either drive or prevent self-aggregation leading to significant changes in directionality, influencing the charge transport. For example, for bar-coated films of the commonly used semiconducting polymer poly[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene) (P(NDI2OD-T2)), it was found that when a solvent was used in which significant pre-aggregation in the solution occurred, charge transport was highly anisotropic, being significantly greater parallel to the deposition direction than perpendicular to it [74]. The same effect was not observed for the same polymer in a solvent in which the extent of pre-aggregation was lower, with similar mobilities in both directions, indicating a more isotropic film. The mobility in the deposition direction was almost an order of magnitude higher than that for a film prepared by spin-coating, which would be expected to produce more isotropic films. By contrast, in the perpendicular direction the mobility was significantly lower, emphasizing the importance of this anisotropy for high-performing devices [74].

For molecules with a permanent dipole moment, preferential alignment of these dipole moments has implications for energetic disorder and thus for charge-carrier mobility [82, 83]. Energetic disorder can also be affected by interactions with the dielectric, which can be controlled by interfacial orientation. Richards et al. [84] showed using a simple analytical model that the electronic structure at the semiconductor–dielectric interface can differ significantly from that in the bulk and is significantly influenced by the dielectric constant of the dielectric material [84]: a higher dielectric constant caused a broadening of the density of states and greater energetic disorder due to the interaction between the randomly oriented dipoles in the gate dielectric and the charges in the semiconductor, leading to a reduction in mobility. However, the effect was shown to decay rapidly with distance (within a few Å from the interface), so could be limited through the introduction of something separating the semiconductor backbone and dielectric, such as a self-assembled monolayer (SAM) of an insulating material. The inclusion of a SAM was shown to give a more ordered energetic landscape and improved performance [85]. Even a thin layer of alkyl chains, such as the side-chains of an edge-on orienting polymer, has been shown to be sufficient to reduce the broadening of the density of states and effectively remove the dependence of charge mobility on substrate dielectric constant [67], highlighting again the importance of interface orientation on transistor performance.

3.2. Host–guest/substrate interfaces in organic light-emitting diodes

The active layer of an OLED is composed predominantly of a host charge-transporting material, commonly a conjugated small molecule but sometimes a polymer, doped with an emitter material. These materials are vacuum or solution deposited onto a solid substrate to make the device. The orientation of both the emitter and the host with respect to the substrate are therefore relevant, although they are expected to be influenced by similar factors.

The orientation of the emitter molecule in OLEDs has a significant effect on device performance, with in-plane (horizontal) alignment of the molecule's transition dipole moment with respect to the substrate, corresponding to light emission in the perpendicular (vertical) direction, increasing light out-coupling efficiency and external electroluminescence quantum efficiency and thus boosting performance [6, 55–57]. Controlling emitter orientation has thus been the subject of extensive study in recent years. A number of factors have been shown to influence the alignment of emitter molecules with respect to their substrate, including the choice of host [18, 86], the shape of the emitter molecule [14, 18], strength of interactions with the substrate [14, 82, 83], emitter chemical structure [87], the presence of permanent dipole moments [88], processing technique [87, 89], and temperature [14, 15, 17, 56, 90–93].

OLED devices are often produced by vapor deposition, through which good control of in-plane alignment can be achieved. The active layers of these materials often lack long-range crystalline order, and can be considered glasses. The anisotropy of vapor-deposited organic glasses has been extensively studied and found to be primarily controlled by the ratio of the substrate temperature (T_{sub}) to the glass transition temperature (T_{g}). For a series of rod- [17] and disc-like [93] small molecules of various aspect ratios, at $T_{\mathrm{sub}} \ll T_{\mathrm{g}}$ a significant preference for face-on alignment with respect to the substrate was found. At temperatures just below T_{g}, the rod-like molecules transitioned towards end-on structures, before becoming isotropic at and above T_{g}, although disc-shaped mesogens were found to form robust columnar phases in an end-on orientation even above T_{g} [93]. Similarly, rod-like mesogen itraconazole was also found to maintain end-on structure at and above T_{g} [94]. Greater orientational anisotropy around T_{g} was also found for longer molecules [14, 17, 55]. Additionally, all-atom MD simulations of ethylbenzene, a model glassy system which can be considered to have similar structural properties to common organic semiconductors showed the same dependence on T_{sub} [90]. Furthermore, coarse-grained (CG) MD simulations of rod-like or disc-like molecules showed the same trends as found experimentally despite the models only being parameterized to reproduce the molecular shape and not the specific interactions of the experimentally studied molecules [15, 17, 91]. This dependence on temperature also agrees with MD studies of vapor-deposited glasses of $\mathrm{Alq_3}$, a common host material in OLEDs [12], further atomistic MD studies on a series of rod-shaped molecules [14], and experimental studies of a similar, but shorter, rod-shaped molecule in a randomly oriented host [56]. It should be noted that the aforementioned studies predominantly examined single-component systems, while the active layer in OLEDs contains an emitter molecule doped into a host matrix, generally at low concentrations. However similar trends have been observed for two-component systems. Jiang et al. [92] showed, through experimental studies of the blue light emitter DSA-Ph, a rod-like small molecule, in $\mathrm{Alq_3}$, a similar dependence on the T_{sub}:T_{g} ratio, which was effectively independent of concentration. The T_{sub} dependence described is outlined in figure 6.

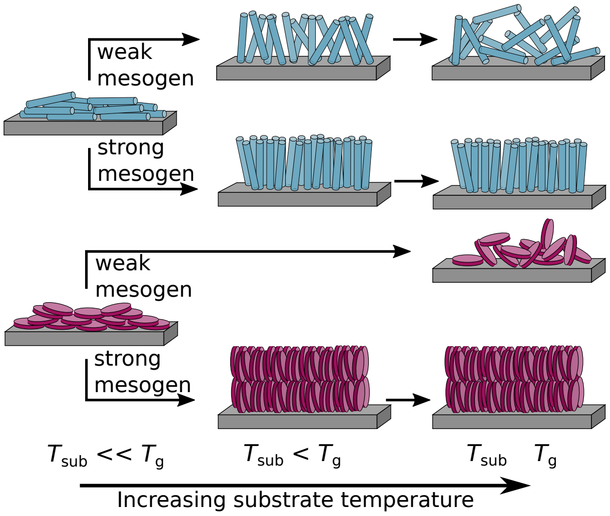

Figure 6. Effect of substrate temperature of the orientation of (top) rod- and (bottom) disc-like molecules with both solid and vapor interfaces. While both rod- and disc-shaped molecules are initially deposited in a face-on orientation at the solid substrate, at sufficiently high temperatures reorientation of rod-shaped molecules towards a end-on structure has been observed, before becoming isotropic at $T_{\mathrm{sub}} \approx T_{\mathrm{g}}$. Disc-shaped molecules did not show such a marked preference for end-on at intermediate temperatures and formed isotropic glasses at higher temperature. Strong mesogens of both shapes were shown to form robust end-on structures at intermediate temperatures that are maintained up to and up to above T_{g}.

To explain these trends, deposition has been proposed to proceed by a 'surface equilibration mechanism'. The free surface of the deposited glass has been shown to have significantly higher mobility than the bulk so that as deposition occurs, for sufficiently high substrate temperatures, molecules near the surface are able to reorient towards the equilibrium orientation for this interface [95]. Interestingly, for the range of molecules studied, this preferred orientation was end-on, which is consistent with the orientation expected for mesogens with purely repulsive intermolecular interactions at the vapor interface (section 2), although the attractive interactions present in real systems may mean that this behaviour is not universal. At low substrate temperatures, the deposition of additional layers kinetically traps the layers below in the face-on orientation that molecules most likely adopt when they first collide with the surface. This effect, as well as other factors that effect orientation in anisotropic organic glasses, has been recently reviewed [95, 96] and the reader is referred to these for further details.

Although mechanisms for achieving good control over parallel alignment are known for vapor-deposition processing methods, films fabricated through solution processing techniques have been shown to give generally isotropic films [87, 89]. As solution processability is one of the reasons organic semiconductors are so attractive, controlling alignment through these methods is of general interest. Senes et al. [18] recently investigated some methods for controlling the orientation of the transition dipole moment of a rod-like molecule in solution-processed OLEDs, finding that better parallel alignment of the transition dipole moment, which was aligned with the long axis of the molecule, could be achieved through the use of a semiflexible polymeric host molecule that showed preferential alignment in the plane of the substrate, as expected from the discussion in section 2. Thermal annealing of the system was shown to further increase anisotropy to levels comparable with vacuum-deposited layers. Additionally, through comparison of a number of different emitter molecules with different backbone shapes, they found that molecules with elongated, more rod-like, backbones more readily formed parallel aligned structures, an effect which has also been observed for vapor-deposited films [14, 17, 55].

3.3. Bulk-heterojunction donor–acceptor interfaces in organic photovoltaics

The photoactive layer of OPV devices generally consists of a blend of an electron donor and an electron acceptor material called a BHJ that is phase separated on the nanoscale [28]. Charge separation and recombination at the donor–acceptor interface is a major factor limiting device efficiency [97]. The microstructure, including molecular orientation, at electron donor–acceptor interfaces in BHJ OPVs plays a potentially important, but as yet unclear, role in determining good device performance. Charge generation at donor–acceptor interfaces is known to be more efficient than predicted by classical electrostatic models at a structureless interface [98], suggesting that the inhomogeneity of the interface may play a role in enhancing charge separation. Indeed, changes in orientation have been implicated in increasing the efficiency of charge generation [99], improving efficiency of separation and charge transport away from the interface [100], and reducing exciton recombination during charge separation [7, 9].

A number of possible mechanisms for enhanced charge separation and reduced recombination have been proposed (which potentially all play a role) that depend on the interfacial microstructure. For example, the electron–hole binding free energy at the interface has been shown theoretically to be reduced by delocalization of charges [98] or by increased energetic disorder [101], which would be expected to be enhanced and diminished, respectively, by increased structural order at the interface. Structural variations at the interfaces could also induce electronic-energy gradients that promote charge separation [102]. Computational studies have also shown that the electric field due to aligned molecular quadrupoles at the interface can drive charge separation [100], with the direction of the field and thus the spatial variation of the interfacial electronic energies sensitive to the molecular orientation at the interface [103, 104]. Furthermore, interfacial alignment will affect the electronic coupling between donor and acceptor. It has been suggested that a face-on orientation at the interface is generally preferred, as it increases orbital overlap between donor and acceptor [7, 9]. Additionally, the energy of interfacial charge transfer states (CTSs) is very sensitive to the arrangement of donor and acceptor at the interface [105]; for a pentacene:C_{60} interface, a face-on orientation has been shown computationally to give a higher energy CTS, attributed largely to a change in the electron affinity of the C_{60} acceptor due to the induced electrical field, which is expected to reduce non-radiative recombination and voltage loss in an OPV device [106].

With the myriad potential roles of molecular orientation at OPV heterojunction interfaces, controlling orientation at these interfaces is an important step towards better predictability and reproducibility of device properties. Furthermore, the ability to measure or predict the interfacial molecular orientation is crucial to clarifying the relative importance of the various charge-separation mechanisms discussed above. Measurements of orientational order at donor–acceptor interfaces have only recently become possible with the development of polarized soft X-ray scattering (P-SoXS) techniques [28], and so data relating interface orientation to molecular structure or processing conditions remains limited. As described in section 2, controlling intermolecular interactions between materials at the interface is important for directing orientation. Increasing the planarity of the molecule is one means to do this, as it would increase the extent of the interaction between donor and acceptor. This has been achieved by adding fluorine atoms along the conjugated polymer backbone, which has been shown to give a preference for a face-on orientation and better device performance [7]. In this case, intramolecular interaction between appropriately positioned fluorine and backbone sulfur atoms restrict backbone rotation, increasing planarity of the conjugated backbone [107]. Alternatively, increasing the extent of conjugation, such as by the substitution of alkyl side chains for conjugated alkylthienyl ones, would likewise be expected to enhance interactions between molecules, and has indeed been shown to increase the extent of face-on orientation and enhance performance for a mixture of polymer-donor and non-fullerene acceptor [8, 9].

4. Towards general principles for controlling interfacial orientation

As noted in the previous section, the orientation of semiconductors with respect to their interfaces is an important property for improving performance in a variety of organic-electronic device types, from BHJ organic solar cells to OLEDs and organic transistors. In this section, we examine the factors that have been shown to influence the interfacial orientation of organic semiconductors and attempt to unify these observations into some general rules for controlling molecular orientation. These factors will be broadly classified into material properties, and thermodynamic and processing conditions. While Osaka and Takimiya [10] have recently reviewed structural and processing methods for controlling backbone orientation in semiconducting polymers, we aim to extend this more broadly to non-polymeric organic semiconductors and to other factors that have been shown to influence anisotropy in both in-plane and out-of-plane directions at interfaces. While not an exhaustive review of the literature of control of interface anisotropy, we have endeavored to identify the key properties that to influence interface orientation based on research to date.

4.1. Material properties

The properties of the molecules themselves (semiconductors, substrates, and solvents) play an important role in controlling the orientation of semiconductors at interfaces. Through modification of the molecular shape, both energetic and entropic driving forces can be modulated to give preference to different orientations, while intermolecular interactions can also directly influence the alignment properties of semiconductors.

4.1.1. Shape anisotropy

Rod-shaped molecules: aspect ratio As explained in section 2, hard prolate particles, with purely repulsive interactions, preferentially align perpendicular to a vapor interface [43, 44], and parallel to a solid interface [49] due to excluded-volume entropic effects (figure 4). This type of behaviour has been observed experimentally in a number of real systems for a range of molecules of different shapes and lengths. Studies of vapor deposition, in which molecules were deposited from the gas phase onto a solid substrate, have shown that rods of various lengths prefer to orient perpendicularly to the vapor interface following deposition [14, 17, 93, 95]. In this case, as they were deposited, the molecules oriented parallel to the substrate, but at higher temperatures the surface molecules (at the vapor interface) reoriented towards an end-on (perpendicular) orientation, and, if mesogenic, formed strongly end-on liquid-crystalline phases [93, 94]. This mechanism is discussed in greater detail in section 3.2. The orientation preferences described are not unexpected, having been shown to be the preferred orientation for purely repulsive prolate particles. Given that the influence of attractive interactions are expected to effect orientational preference [47, 48], it is interesting to note that all of the molecules studied exhibited the same alignment behavior. Coarse-grained molecular simulations of particles parameterized just to reproduce molecular shape have shown similar trends to both experimental and all-atom simulations [15, 17], indicating that molecular shape is an important parameter for determining orientation at the vapor interface.

In addition, longer molecules have been shown, through computationally studies, to show stronger orientational anisotropy than their shorter counterparts [14, 17]. We note that these studies did not distinguish between face-on and edge-on orientations as they generally used models with uniaxial symmetry, but it seems reasonable that a similar argument can be applied to this additional orientational anisotropy and that high aspect-ratio molecules will initially orient with a face-on preference in vapor deposition.

Rods vs discs As for molecules with other shapes, vapor-deposited disc-shaped molecules of varying size have also been shown, through MD simulation, to orient predominantly face-on to the substrate at low temperatures [15, 93]. At high temperatures, again, orientation becomes isotropic, but for disks that are strong mesogens, a transition to an edge-on columnar stacking at T_{sub} close to and above T_{g} has been observed [93]. As with the rods, this is consistent with the reorientation of ordered structures when free to rotate to give the equilibrium end-on structure.

Backbone length and planarity As described above, increasing the length of the molecular backbone has been shown to give more extreme orientational preference, whether parallel or end-on. Alternatively, for polymers, the planarity of the backbone has also been shown to play a role in interfacial orientation. Chen et al. [20] found that while coplanar backbones can give either face-on or edge-on orientation depending on the solubility of the compound, slight deviations from coplanarity predominantly gives edge-on orientation.

4.1.2. Intermolecular interactions As discussed in section 2, changes to non-bonded (attractive) intermolecular interactions for fixed molecular-shape anisotropy can lead to dramatic changes to surface anchoring (e.g. from planar to perpendicular). Thus, these interactions are expected to strongly influence molecular orientation at organic semiconductor interfaces. Strong attraction between the face of an organic semiconductor and a solid or another molecule would give a face-on orientation, whereas if the interactions between the face of the conjugated molecule and the substrate were unfavorable, or the interactions of the substrate with the molecules edges stronger, an edge-on orientation would be preferred. This is consistent with reports from molecular simulation of a semiconducting polymer at different solid interfaces where low substrate–semiconductor interaction strength gives edge-on oriented polymer and high interaction strength gives face-on [11]. In addition to influencing the orientation at the interface, the strength of the interaction can also influence the distance from the interface to which the orientational order is maintained, with stronger van der Waals (vdW) interactions between substrate and semiconductor have been shown to give a thicker oriented interface [14].

In the organic-semiconductor field, intermolecular interactions at interfaces are often characterized in terms of surface energy. Correlations between substrate surface energy and interfacial alignment have recently been observed for semiconducting polymer films, with lower surface energy associated a more edge-on interfacial orientation than a higher energy surface [108]. This is consistent with favourable interactions between the polymer alkyl side chains with the similar sidechains of a low-energy SAM-treated surface, which is maximized in the edge-on orientation. Similar correlations have been observed in the organic single-crystal literature, with crystal orientation and grain morphology showing a strong dependence on substrate properties [109], and orientated growth being achieved through adjustment of surface energy and epitaxial growth due to similar lattice parameters [30, 35]. In line with the results of semicrystalline polymers, crystalline pentacene, for example, has been shown to adopt a perpendicular orientation with respect to a low surface energy substrate, as this exposes its lowest energy face to the substrate, while adopting a face-on interaction with high-energy substrates where its higher energy face interacts with the substrate [109].

As described in section 2 for molecules at a vapor interface, increasing end–end interaction strength has been shown to give greater parallel alignment. Practically, one means of achieving this is through the use of rod-like molecules that are able to form weak hydrogen bonding networks end-to-end with each other. These stronger end–end interactions have been shown to give more horizontally aligned vapor deposited films than otherwise very similar molecules without the hydrogen bonding capability [110]. A number of other means of tuning interaction strength between semiconductor and substrate exist, including factors such as changing the chemical composition of the backbone, side chain modification, and changes in molecular shape, which will be discussed in detail in the subsequent sections.

Atomic substitution: fluorination Atomic substitution, such as the substitution of hydrogen for the highly electronegative fluorine is a powerful means for tuning interaction strength. As fluorine is fairly small, the substitution can be made without adversely impacting steric constraints. The addition of intramolecular non-bonded interactions between backbone fluorine and sulfur atoms has been shown, for example, to be a useful method for inducing liquid-crystalline order in solution-processed conjugated polymers as it induces backbone planarization at high concentration, promoting the formation of aggregates displaying liquid crystal-like behaviour [107] (figure 7). At donor–acceptor interfaces in polymer–fullerene solar cells, face-on orientation of fluorinated polymer at the interface has been observed, while the non-fluorinated equivalent was slightly edge-on [7, 10].

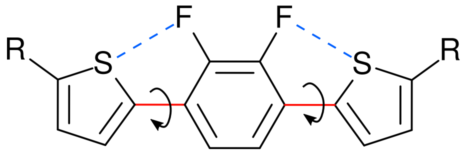

Figure 7. Restriction of backbone rotation due to F–S interactions (dashed blue). The red bonds, indicated with an arrow, are less free to rotate in the fluorinated molecule.

Side chains Side chains for organic semiconductors are predominantly engineered to alter the solubility and thus influence the aggregation properties of the molecule in solution, which can be directly tuned by changing side chain density, length, or connectivity. The effect of aggregation on orientation will be discussed later in the context of solubility, but we note that side chain arrangements that are likely to prevent aggregation, such as bulky and densely distributed alkyl chains, have been shown to give face-on morphologies for conjugated polymers at a solid surface, while those that promote ordered packing, such as linear, sparsely distributed chains are more likely to give edge-on structures [10, 16]. Additionally, Osaka et al. [19] reported that difference in side chain length for a polymer with two different side chains on each monomer can strongly impact orientation at the substrate interface. Side chains that were approximately the same length were found to give face-on structures, while if the side chains were significantly different in length an edge-on orientation was preferred [19]. Finally, polymer regioregularity, where the monomers are all coupled in the same head-to-tail fashion in the polymer chain, should enhance the formation of ordered aggregates which may also influence anisotropy [111].

While factors such as side chain length and density affect packing through changes to steric interactions, changing the side chains to modulate the strength of interactions at a semiconductor interface is also an interesting method to influence orientation. For example, stronger interactions could be introduced between molecules at the interface by replacing pure alkyl side chains with alkylthienyl chains to give 2D conjugated structures. This has been shown to give a more face-on orientation at the donor–acceptor interface in all-polymer solar cells [8, 9].

4.1.3. Polymer specific factors: molecular weight and chain stiffness Polymer molecular weight (MW) is known to have a substantial effect on device performance [27, 76, 112–116] with higher MW polymers generally (although not always) giving better performance. Although not applicable to small-molecule semiconductors, polymer MW is known to affect whether the molecule orients edge-on or face-on with respect to its substrate, which may at least in part explain its effect on device performance. Osaka and Takimiya [10] previously surveyed the literature for the effect of MW on backbone orientation and found that in general, high MW polymers form edge-on morphologies with respect to their interfaces, while low MW generally gives randomly oriented polymers. It should be noted, however, that this depends on the polymer itself, and may not be completely generalizable for all polymers. For example, more recently, Nahid et al. [58] found that for semiconducting polymer P(NDI2OD-T2), the presence of rod-like aggregates formed by low MW polymers in poor solvents [27] gave a more edge-on orientation at the polymer–air interface and better mobility than their higher MW counterparts. However, they also noted that although decreasing MW gave a more edge-on orientation in the bulk, there was little difference at the dielectric interface, which remained predominantly edge-on over all MWs. Nevertheless, this indicates that different classes of polymer may behave differently with respect to MW, and other factors may need to be considered, in particular the shape and size of aggregates formed, which will be discussed in greater detail below.

In their MD and theoretical studies of generic conjugated polymers at substrate interfaces, Zhang et al. [117] found that increasing MW increased the distance from the substrate at which polymers were still aligned. Although isotropic in the bulk, when coming in contact with the surface, the polymers aligned parallel to the surface, to a distance approximately equal to the polymer's persistence length for polymers longer than this length. For longer and stiffer chains, this ordered layer was found to be thicker, due to a larger nematic coupling parameter, with longer molecules retaining some order even slightly beyond the persistence length. They found that a higher MW was associated with a greater preference for the parallel orientation. However, as their simulations considered uniaxial molecules, they were unable to distinguish between edge-on and face-on orientations of the polymer.

4.2. Thermodynamic and processing conditions

4.2.1. Temperature Temperature is an important property for controlling interface orientation as it controls both the equilibrium microstructure and the rate at which the structure evolves towards equilibrium. Considering the example of vapor deposition, T_{sub} significantly lower than semiconductor T_g has been shown to give parallel alignment of a range of disk- and rod-shaped molecules, while an increase in temperature to just below T_g shifts the alignment of rods towards perpendicular. A further increase in temperature beyond T_g leads to isotropic phases [12, 14, 15, 17, 56, 90–93]. As discussed previously, this is attributed to a surface equilibration mechanism in which only the top couple layers of the deposited film are sufficiently mobile to allow realignment of molecules [95]. The molecules are initially deposited in the face-on orientation and then have only a finite amount of time to realign before they are buried. At low temperatures, the molecules are kinetically trapped in the as-deposited face-on orientation. As the temperature is increased, the molecules can reorient towards the equilibrium orientation, which appears to be edge-on for a range of small-molecule organic semiconductors, before their orientation is trapped by the deposition of further layers on top. Above T_g interactions between molecules are generally not strong enough to maintain order and anisotropy is lost. Although this phenomenon may also be explained by a change in the thermodynamically favoured morphology with temperature as the balance of entropy to enthalpy changes, studies of deposition rate found [95] at lower deposition rates a favored edge-on orientation was reached at lower T_{sub}, which suggests that the ability to reorganize before becoming trapped under additional layers is the driving factor for the observed temperature dependence.

Temperature in other processing methods may also be expected to influence semiconductor alignment for similar reasons. As devices are often fabricated under non-equilibrium conditions, the orientation they are initially deposited at (either from vapor or solution) can potentially become kinetically trapped. For semiconducting polymer P(NDI2OD-T2), annealing of a solution processed system above its melting point has been shown to change the orientation at the top surface and in the bulk from face-on to edge-on [118], while blade coating at similar temperatures has been shown to induce a greater degree of edge-on polymer [73]. For P3HT at the donor-acceptor interface with a fullerene, interfacial orientation has similarly been shown to shift towards edge-on with annealing [10, 119]. For these cases, it is interesting to note that in all cases of which we are aware the edge-on orientation appears to be the equilibrium structure, but as surface anchoring orientation is not expected to be universal, this may not be favored in general. Further investigation into the equilibrium structures of anisotropic particles (both polymeric and single molecule) at interfaces is necessary to better understand this.

4.2.2. Solvent As solution processing methods are common in the production of organic-electronic devices, solvent is a simple parameter to tune, and is known to have a significant effect on polymer conformation. It has been proposed that high mobility in polymer semiconductors can be achieved using poor solvents that induce a greater degree of pre-aggregation (aggregation in solution prior to deposition on the substrate), as these can give enhanced liquid-crystalline ordering [21], which is generally associated with more regular alignment. Even for non-liquid-crystalline materials, the formation of large aggregates has been observed to give rise to edge-on orientations at the substrate interface [16, 73]. The larger the aggregate, the greater the effect and the stronger the preference for edge-on structures [73]. This is consistent with recent reports of correlation between the extent of aggregation of P(NDI2OD-T2) in solution and edge-on orientation at the film–air interface [58]. However, previous reports have observed the opposite trend for the same polymer, with pre-aggregation leading to a predominantly face-on orientation, though not specifically at the interface [120]. These opposing trends can be reconciled with the knowledge that this polymer has been shown to preferentially display edge-on orientation at the film–air interface, and face-on orientation relative to the air interface in the bulk [121], suggesting that the orientation at the substrate surface may be templated by the orientation at the vapor interface or in the bulk depending on the deposition conditions.

As with temperature, although the molecules examined seem to consistently favour edge-on orientations when aggregates are formed, there is no obvious physical principle that describes this dependency, nor is it clear whether an edge-on orientation for aggregates is preferred more generally. Again, studies employing generic models may be useful for elucidating the effects of aggregate formation on interfacial orientation. As solubility can be tuned by a number of factors, such as side-chain modifications or choice of solvent and solvent additives, this provides a relatively simple way of controlling interface orientation, so a more thorough understanding of how it affects interfacial ordering would be beneficial.

4.2.3. Processing techniques: external forces Processing techniques are well known to influence the anisotropy of molecular interfaces with techniques that introduce shear or flow forces, such as blade or bar coating, giving more anisotropic films than, for example, spin coating [73, 80, 87, 89]. These non-equilibrium methods rely on the introduction of orientation-specific forces to promote different morphologies and alignment directions. Methods such as blade coating are able to give extended alignment of both fiber direction and orientation of polymeric materials, with significant alignment of chains in the shear direction observed [71, 73, 80]. Similarly, the application of an external magnetic field has been shown to give alignment of the backbone of a conjugated polymer [122] or discotic mesogen [123] parallel to the field due to anisotropy in the molecule's diamagnetic susceptibility. Likewise, alignment of P3HT fibres in the direction of an applied electric field has been observed, giving increased charge mobility [124]. Light has also been shown to be able to specifically align liquid crystals [125] although has not been studied explicitly in relation to organic semiconductors. A number of other methods for aligning and orienting polymer films by means of processing conditions and techniques have been recently reviewed [71] and the reader is referred to that work for greater detail.

Additionally, these processing techniques have been extensively used for crystalline organic semiconductors, with mechanical stretching, external magnetic- or electric-fields and solution deposition methods such as zone casting all having been shown to give good control over orientation [30]. Alternatively, concentration and temperature gradients, tilted substrates, and solution shearing have all also been shown to allow for control of crystallization direction [34]. Modulation of the shear rate, for example, has been shown to change the packing density of small molecule TIPS-pentacene, with the optimal rate giving a closer π–π stacking distance and enhanced charge carrier mobility [34].

4.3. Summary

From the preceding discussion, it should be clear that, although there are many factors which have been shown to influence interfacial anisotropy of organic semiconductors, many of them have not yet been systematically studied. Although some interesting trends are starting to develop further study is required if general principles for controlling molecular alignment at semiconductor interfaces are desired. While compelling mechanisms for some effects have been proposed, such as the surface equilibration mechanism for vapor deposited films, others, such as the effect of solution aggregation or processing temperature on orientation cannot yet be described universally through general physical principles. Likewise, although orientation of uniaxial repulsive particles at the vapor interface, and to a lesser extent solid and fluid interfaces, is fairly well understood, the role of attractive interactions, which are important for real materials, and the balance between repulsive and attractive interactions, is less clear. A better understanding of these interactions may enhance our understanding of the preferential alignment observed in relation to modifications such as aggregation, fluorination, and backbone structure.

5. Modeling organic semiconductor interfaces

As the microstructure at interfaces in organic semiconductor devices is known to be important for device performance, being able to characterize the interfacial microstructure and its relationship to electronic processes would facilitate the design of better devices. Although possible, it is often experimentally challenging to characterize these interfaces as they are generally buried within the device [22, 23]. Additionally, it is difficult, if not impossible, to extract molecular-level detail from experimental data of organic semiconductor films due to their significant disorder. With the ability to directly simulate and visualize these interfaces on an atomic scale, computer simulations are an attractive method for uncovering the intricacies of structure and assembly mechanisms of organic semiconductor interfaces. This section reviews applications of computer simulations to elucidate the microstructure and assembly of organic semiconductor interfaces. Since most of the computer-simulation techniques discussed in this section and their general use to study organic-semiconductor morphology has previously been comprehensively reviewed previously [29, 126, 127], the techniques themselves will only briefly be described here, with the focus being on applications that clarify the role of interface anisotropy.

We will also not go into detail on methods for simulating the electronic structure and electronic processes at organic semiconductor interfaces, as these methods have been extensively reviewed in the past [104, 128, 129]. Since fully quantum-mechanical simulations that account for both nuclear and electronic degrees of freedom are unfeasible for simulating microstructure formation, a general computational approach that has been widely adopted for investigating the microstructure dependence of electronic processes in organic semiconductors is to use computationally efficient classical methods that do not explicitly account for electronic degrees of freedom to simulate the physical structure and structural evolution and then to apply a quantum-mechanical or mixed quantum–classical approach [104, 128, 129] to the obtained physical structure to calculate electronic properties. This approach is expected to be reasonable, as the structural dynamics responsible for microstructure formation are generally not expected to be strongly influenced by the electronic processes in these systems. Thus, this section will focus only on the first step of this approach: the simulation of the physical structure of organic-semiconductor interfaces.

5.1. All-atom simulations

A number of different methods can be applied to simulate molecular systems and provide geometries that can be used for detailed electronic calculations. Broadly, these can be classified as MD or Monte Carlo (MC) simulations. MD is particularly useful for the study of organic semiconductor interfaces as it allows direct study of the system dynamics and can therefore capture nonequilibrium processes that can be important in organic-semiconductor interface formation. On the other hand, MC algorithms generally sample configurations from an equilibrium statistical ensemble and therefore are most adapted to simulating equilibrium states. Nevertheless, hybrid grand canonical (GC) MC–MD simulations, which involve MC particle insertion and deletion steps, can be effective for studying nonequilibrium interface formation in the presence of processes such as solvent evaporation. For further details on these methods, the reader is referred to [130] and [131].

A distinction should be made between atomistic (all-atom) and CG particle-based simulations. In atomistic simulations, every atom is treated explicitly, whereas CG models group atoms together into a single interaction site, decreasing the degrees of freedom of the system at the expense of atomic resolution with the goal of reducing computational expense. Both methods will be discussed here.

5.1.1. Background of molecular dynamics Classical MD is a molecular-simulation technique that in essence integrates Newton's classical equations of motion to study the evolution of a molecular system over time [130, 131]. Interactions between particles are defined through a force field which is used to give the total potential energy as the sum of all bonded and non-bonded interactions in a system. A number of standard force fields exist which are generally transferable between a large number of molecules. However, these force fields often need to be modified in order to accurately model the intermonomer dihedral-angle potentials in polymers, which are strongly affected by the π conjugation inherent to organic semiconductors [132, 133].

5.1.2. Study of physical structure and assembly The use of atomistic MD simulation to study the physical structure and assembly at organic semiconductor interfaces is becoming more common as computational power increases. In particular, the process of vapor deposition has been extensively studied by MD for a variety of substrates and small molecules [13–15, 57, 90, 134–138] (figure 8). While these simulations generally agree well with experimentally observed phenomena, such as the dependence of orientation on T_{sub}, they also provide further insight into the mechanisms of the process. Muccioli et al. [13], for example, simulated vapor deposition of pentacene onto a C_{60} substrate. As pentacene molecules were added, they found that they initially lay flat on the surface, before diffusing rapidly and beginning to aggregate. As the aggregates on the surface grew, they coalesced into a film covering the surface with random horizontal alignment. As more pentacenes are added to the first monolayer, the molecules rearranged to form an end-on morphology with a herringbone pattern. Additional layers then follow a similar mechanism [13].

In a similar vein, the deposition of host–emitter systems onto a substrate, relevant to OLEDs, has been studied using atomistic MD simulation [57, 135]. Emitter molecules with different degrees of molecular anistropy, Ir(ppy)_3 and $\text{Ir(ppy)}_2\text{(acac)}$, were found to have a preferred orientation with respect to a graphene substrate, resulting in anisotropy in the alignment of the transition dipole moment for phosphescent emission (obtained from quantum-chemical calculations of isolated emitters) that was consistent with experimental light-outcoupling measurements [57] (figure 8). The alignment of the highly symmetric Ir(ppy)_3 in particular was proposed to be driven by alignment of the anisotropic host material 4,4'-bis(*N*-carbazolyl)biphenyl (CBP) [57].

MD simulations have also recently been used to study the preferred orientation of a semiconducting oligmer in solution at various interfaces. At the solution vapor interface, the orientation of the oligomer was found to be edge-on, while when sandwiched between two solid substrates weak semiconductor-substrate interactions gave edge-on orientation and strong interactions face-on. When between a solid substrate and a free vapor interface, edge-on orientation was observed at the vapor interface and either edge- or face-on at the solid surface depending on the substrate [11]. From these simulations it was concluded that if interaction between the π-conjugated plane (face) of the molecules was more energetically favourable than the interactions of the same plane with the interface (either gas phase or solid), the edge-on configuration was preferred. On the other hand, face-on orientation with respect to the substrate was preferred if interactions with substrate surface were stronger than interactions between the conjugated faces of the molecules [11].

In OPVs, the size of BHJ domains is generally too large to be feasibly simulated atomisitically, being on the order of 10 nm [139]. However, simulations of model systems representative of sections of these interfaces have provided valuable insight. For example, calculations of the open-circuit voltage (V_{OC}), based on quantum-chemical calculations of electronic energies using configurations obtained from short MD simulations of planar interfaces of a number of different molecules in specific orientations at a C_{60} surface, have given excellent agreement with experimental values; this allowed the authors to rationalize the high performance of a particularly high-performing series of organic semiconductor through

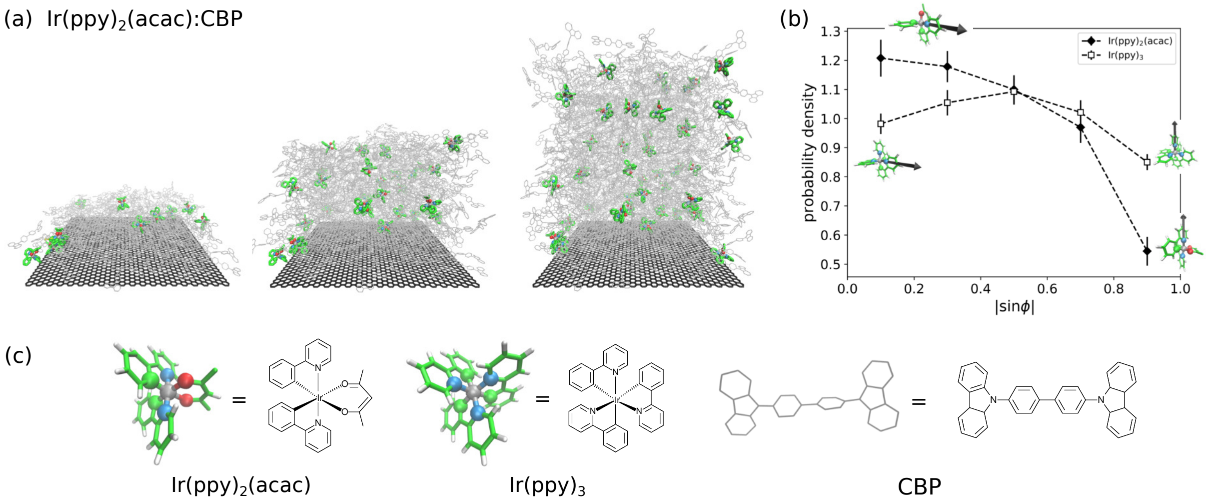

Figure 8. (a) Snapshots of a simulation of vapor deposition of a host–emitter OLED system onto a graphene substrate (black, thick line representation) [57]. The host is CBP (grey lines) and the emitter is Ir(ppy)$_2$(acac) (green). Hydrogens are omitted for clarity. (b) Transition dipole moment (TDM) orientation for Ir(ppy)$_2$(acac) (filled diamonds) and Ir(ppy)$_3$ (unfilled squares) from deposition simulations [57]. A value of $|\sin\phi|$ of 0 corresponds to horizontal alignment of the transition dipole moment and 1 to vertical, as shown in the overlaid structures. The TDMs for both molecules are assumed to lie along the Ir–N bonds. In the structures, only one TDM is shown for clarity as a black arrow. (c) Chemical structures of Ir(ppy)$_2$(acac), Ir(ppy)$_3$, and CPB. For the iridium complexes: green = carbon, blue = nitrogen, red = oxygen, grey = iridium, white = hydrogen. The molecules in (a) are colored accordingly.

the favourable energetic effects induced by its interfacial orientation [100]. Elsewhere, MD simulations have shown that at a pentacene–C$_{60}$ interface, C$_{60}$ molecules are able to burrow into the surface of face-on, but not end-on, oriented pentacenes [140], giving a more disordered region and the type of interphase structures shown elsewhere to lead to enhanced charge separation [141].

5.1.3. Challenges for all-atom simulation of interfaces Despite these successes, there are still a number of challenges associated with all-atom simulations of organic semiconductor interfaces. Potentially the largest of these challenges is accessing the relevant length and time scales for modeling processes in organic semiconductor materials, which can contain many millions (or more) of atoms and involve processes occurring on up to the second scale, or even longer for annealing processes. Although simulations of up to 100 million atoms (for 100 ns) [142], or up to the millisecond timescale for smaller systems using specialized hardware [143], are possible, typical simulations can only study a couple million atoms on the nanosecond (or microsecond at best) timescale, meaning that slower processes occurring on longer timescales are not able to be explicitly studied. This is particularly relevant when considering the scale of structural variations at interfaces, which generally involve large systems whose assembly occurs over large time periods, which can be unfeasible to simulate atomistically. All-atom simulations of polymers have also generally been limited to chain lengths of 10s of monomers, which is 1–2 orders of magnitude smaller than those studied experimentally in organic semiconductor systems, limiting the ability to realistically capture polymer microstructure using such models.

In order to deal with the problems of size and time scale, while still maintaining atomistic detail, a number of approaches may be taken, potentially at a cost to quantitative accuracy. Wang et al. [144], in their study of a polymer-fullerene system representative of a BHJ donor–acceptor interface, point out that a phase-segregated morphology cannot be fully achieved with the system sizes available to MD. They instead used a higher fullerene concentration than would be used experimentally to be able to qualitatively understand the behaviour at the interface [144]. Alternatively, Yoo et al. [137] proposed the 'frozen-bulk' method for studies of interfaces in vapor-deposition simulations. They proposed that, at large distances from the interface and at a temperature lower than T_g, the orientation of the bulk region does not significantly change. The motion of these regions was therefore frozen to allow for more efficient simulation [137]. Ratcliff et al. [136] also used positional fixing to enhance computational efficiency for the MC simulation of vapor deposition. In this work, once the molecules were deposited their positions were fixed. However, it has since been shown that there should still be quite significant movement of the molecules after deposition so this method may not accurately capture all the details of the deposition process [135]. Bagchi et al. [12] looked at the problem slightly more abstractly, and, as the surface structure of vapor-deposited glasses has been shown to be very similar to that of the equilibrium liquid [17, 95], simulated this equilibrium liquid surface, which is likely to display much faster dynamics than the glass, instead.

5.2. *Coarse-grained molecular simulations*

While atomistic simulations provide details of specific interactions at interfaces, and give an atomic understanding of the processes occurring at these interfaces, they are often limited by the size of the system and time scales of the processes of interest. A common way to address these problems is the use of CG molecular simulations, in which the number of degrees of freedom in the system is greatly reduced by approximating a collection of atoms as a single interacting site, increasing the simulation efficiency of the calculation. It is especially important that larger length scales than are feasible atomistically to be reached when one considers, for example, the molecular weight dependence of interface morphology of polymer semiconductors [24, 27, 75, 76] or the domain sizes in BHJs which are typically on the order of around 10 nm [139]. In contrast to all-atom simulations, CG simulations have been shown to be able to reach appropriate length scales with enough accuracy to model aggregation of conjugated polymer chains in solution [145] and phase separation in conjugated polymer BHJs [114, 146, 147] (see figure 9).

5.2.1. Background of coarse-grained molecular dynamics (CG MD) simulations The process of coarse-graining is summarized schematically in figure 10. Groups of atoms expected to have correlated motion are grouped into larger sites whose interactions are parametrized to (hopefully) capture the behavior of the real all-atom system. The

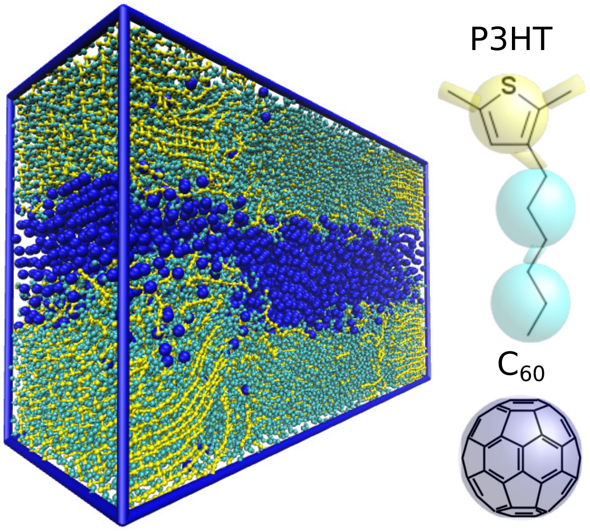

Figure 9. BHJ P3HT:C_{60} donor–acceptor interface from CG MD simulation [146].

total potential energy of the system is calculated as a sum of bonded and non-bonded interactions between CG sites. Two general approaches have been used to parameterize CG interactions: the top-down approach, in which interactions are chosen to reproduce experimental thermodynamic data [147], or the bottom-up approach, in which the interactions are tuned to reproduce the physical and thermodynamic properties of an all-atom model [148]. A number of systematic bottom-up CG methods have been developed, with the goal being to achieve thermodynamic consistency between the CG and all-atom models, e.g. by matching forces [149] or structural distribution functions[150] or minimizing the relative entropy [151] between the two models. Readers are referred to [148] for a comprehensive review of coarse-graining methods.

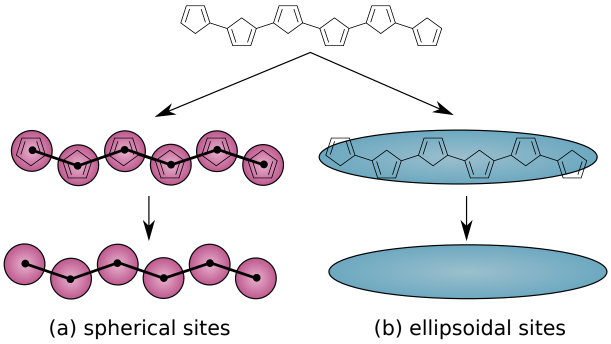

Figure 10. An example of coarse graining of small conjugated molecule sexithiophene into (a) six spherical sites, or (b) a single ellipsoidal site. The spherical model represents each thiophene unit as a sphere connected by their centers of mass (black lines to black dots), while the ellipsoidal model is a representation of how this molecule could be coarse-grained into a single anisotropic particle.

5.2.2. Spherical vs anisotropic sites and potentials To date, CG models have predominantly employed spherical sites for the calculation of non-bonded pair interactions. Although these models have been able to reproduce experimental anisotropic behaviour when the overall molecule (an accumulation of isotropic CG sites) is anisotropic (figure 9) [15, 17, 91, 117, 145], many organic semiconductors consist of large planar subunits with very rigid backbones, so representing them as a collection of spheres may not be accurate or efficient. This is especially problematic when considering properties such as π-stacking distance, which are known to be important for device performance. An alternative is to use anisotropic, either ellipsoidal [152, 153] or disc-shaped [154], particles. As these sites now have a quantifiable orientation, anisotropic non-bonded potentials are required to model the inter-site interactions as a function not only of distance, but also of orientation. Although these anisotropic interactions are slower to calculate than isotropic ones, a reduction in the number of sites (figure 10) for a given level of accuracy can compensate for this. Interpretation of simulation results of an anisotropic model with fewer degrees of freedom and parameters is also potentially simpler. A number of anisotropic non-bonded potentials exist that account for both the distance and orientation dependence of the potential energy when considering ellipsoidal sites. Most commonly used are the GB [45, 155], and RE-squared [156–158] potentials, which are effective for ellipsoidal particles. Further details can be found in the literature [156–159].

An alternative potential, more suited to the flat disc-like molecules common for organic semiconductors, has been recently reported [154]. Although not a new potential, being originally published over 40 years ago [160], the S-function expansion has only recently been applied to organic semiconductors, and with good success [154]. Again, details of this potential can be found elsewhere [154, 160] so will not be discussed here, other than to note that it may better describe the interactions between these disk-like particles than either the GB or RE-squared potentials.

5.2.3. Study of physical structure and assembly CG MD models can give valuable insights into mechanistic details of microstructure and assembly processes in organic semiconducting device that cannot be easily studied experimentally and may be computationally inaccessible by all-atom models. CG models have only been applied in the last decade or so to studying organic-semiconductor structure and so, compared with all-atom simulations, CG simulations of organic-semiconductor interfaces remain quite limited.

Simple CG simulations, using general models with interactions that were not parameterized to match any specific system, but rather just to reproduce the shape of the molecules of interest, have helped to provide a molecular understanding of the dependence of orientation at the interface on T_{sub} for vapor-deposited glasses [15, 17, 91]. Lyubimov et al. [91] showed, through the use of a rod-like model of small-molecule semiconductor N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD), represented as six spherical sites connected by springs to maintain the desired shape, similar behaviour as observed experimentally for these systems (horizontal orientation at low T_{sub} and a slight vertical preference at T_{sub} just below T_{g}), and were able to propose the surface equilibration mechanism described in section 3.2. Significantly, this and related work [15, 17] showed that even without explicit parameterization for atomistic systems, and not including the effects of dipole moments or polarizability, CG models that approximately represent molecular shape and interaction strength are able to reproduce anisotropic structural characteristics consistent with experiments.

Using a generic CG MD model, Zhang et al. [117] simulated a semiflexible polymer melt at a disordered, impenetrable interface to examine the effect of nematic coupling, influenced by chain length and stiffness, on surface-induced alignment. They showed that the polymer preferentially orients parallel to the surface, forming an aligned layer of about a persistence length thick. For longer and stiffer chains, the thickness of the aligned layer is increased due to stronger nematic coupling. From this, it is predicted that the conjugated polymer P3HT can form an alignment layer of approximately 4.5 nm thick, with stiffer polymers likely forming even thicker layers. This sort of orientational alignment is especially relevent for charge transport in OFETs, for which order near the interface is more important than that in the bulk.

Both bottom-up [146, 153, 161–166] and top-down [147] CG MD models have been used to simulate the microstructure and formation of BHJ donor–acceptor interfaces for both small molecules [153, 166] and polymers [146, 147, 161–165], a process that would be very challenging to study using an all-atom model. Even using a CG model, realistically simulating BHJ formation is difficult, and most of these studies simulated donor–acceptor interface formation in the liquid phase at elevated temperatures rather than simulating the process of solvent evaporation normally involved in BHJ formation. Even when solvent evaporation has been considered [147, 153], solvent evaporation rates have been many times those in experiments.

Nevertheless, these simulations provide useful molecular-level insight into the donor–acceptor interface, although only a couple of these studies have addressed the issue of interfacial molecular orientation. In particular, CG simulations of model P3HT:PCBM polymer:fullerene interfaces, in which the polymer chains were oriented edge-on, face-on, or end-on to the interface, or in which the polymer chains were amorphous, indicated that the interfacial energy was lower for the ordered configurations than in the amorphous one and that the energy was lowest at the face-on interface [165]. This suggested that ordering was favored at the interface compared with the bulk, which was indeed observed, and that the face-on interface was the most stable [165]. These results have implications for OPVs, as the face-on configuration is widely believed to optimize charge separation. On the other hand, Lee and Pao [153] used an ellipsoidal-site CG model of the anisotropic small-molecule semiconductor 2,5-di(2-ethylhexyl)-3,6-bis(5”-*n*-hexy-[2,2’,5’,2”]terthiophen-5-yl)-pyrrolo[3,4-c]pyrrolo-1,4-dione (SMDPPEH) blended with [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) in the solvent chlorobenzene, the latter two represented by CG spheres, to simulate the effects on the nanomorphology of solvent evaporation and shear forces mimicking the process of blade-coating. They showed that increasing the shear rate led to more stacking of the SMDPPEH, which is likely to promote hole transport, but also results in larger isolated $PC_{61}BM$ domains, hindering exciton dissociation. Thus, they concluded that an optimal shear rate exists that balances these two characteristics, and gives the greatest charge transport [153].

5.2.4. Challenges for coarse-grained simulation of organic semiconductors As with atomistic MD simulations, CG simulations are not without their challenges. In particular, the loss of molecular detail can be problematic as details about specific interactions, which may be important for understanding device properties, may be lost in the CGing procedure. It is therefore important that the desire for efficiency (fewer sites) be balanced with the need for accuracy. For good predictions, the model must be able to capture important intra- and intermolecular rearranglements which may necessitate a greater number of sites in order to prevent information loss [167, 168].

Another desirable feature of a CG model, which is not necessarily easy to achieve, is transferability to thermodynamic conditions beyond which it was parameterized. Again, a model that is able to capture the molecular rearrangements that occur at changing tempteratures is important [167]. Although this is generally likely to require a greater number of sites, transferability may also be improved with the use of anisotropic sites which may retain the relevant degrees of freedom and better describe rotations of planar molecules which cannot be captured with spherical sites. Indeed, Bowen et al. [154] noted that their anisotropic disc model for fused ring perylene diimides (PDIs) was likely to be more transferable than other CG models due to the significant amount of detail that is able to be maintained by the anisotropic sites [154]. This was due to the sections that were CGed into discs being rigid moieties that generally did not show drastic rearrangements. Accordingly, little information was lost in the CGing procedure and the model was expected to behave more like its atomistic counterpart.

A further degree of transferability that can be challenging in CG models is that of a force field for a specific molecule to other molecules in the same class, which maybe differ by just a side chain. For example, the three-site P3HT model of Huang et al. [146] shows good accuracy for the structural properties of the molecule for which it was parameterized, but on extension to other poly(3-alkylthiophene)s (P3ATs) with longer alkyl chains it has been shown that this model is no longer able to reproduce experimental properties [168]. Slight adjustments to this model, by changing the strength of the interactions between side-chain sites and those between backbone sites, were able to give qualitative agreement with experimental properties, but were still unable to achieve quantitative accuracy [168]. Root et al. [168] noted that, again, the anisotropic shape of the thiophene ring may be important for accurately predicting structural properties and a spherical site model may not be sufficient.

Additionally, despite their increase in accessible time scale relative to atomistic MD, CG models are still unable to achieve the time scales relevant to processes such as solvent-based film deposition. Although as computing power increases these time scales should begin to become more accessible, alternative methods, such as the continuum methods discussed below or hybrid approaches using CG semiconductors and a continuum or implicit solvent will likely be necessary to realistically model such processes. However, care must be taken to account for hydrodynamic interactions (particularly for polymers) [169] and the concentration dependence of the CG interactions when solvent degrees of freedom are integrated out.

5.3. Continuum simulations

Continuum or field-based models of fluid structure, such as classical density functional theories [170] or statistical field theories (including self-consistent field theory (SCFT)) [171] describe the fluid in terms of a spatially varying probability density field instead of by the coordinates of discrete particles, in contrast to the all-atom and coarse-grained particle models described in the preceding sections. In practice, such continuum models are solved numerically on a discrete lattice. They offer distinct advantages over particle-based models, in particular in being able to access much longer length and time scales, which is especially relevant for modeling long polymer chains at high densities, for which relaxation times can be prohibitively long even for simulations of CG particle-based models.

Nevertheless, applications of continuum models to studying organic-semiconductor microstructure, let alone the ordering of organic semiconudctors at interfaces, have been very limited. This is in part due to the (arguably) greater theoretical complexity of these models compared with particle-based models and the lack of freely available, general-purpose software for solving such models numerically [172], with no such software existing to our knowledge that accounts for orientational degrees of freedom. Furthermore, these continuum theories generally assume equilibrium conditions, with the solution to the model being the set of field variables (e.g. the probability density of a particular molecule type at a position and orientation) that minimizes a system free energy that is a functional of the fields. Although dynamic variants of continuum models have been developed [170, 171], they generally assume time evolution of the field variables on the equilibrium free energy surface, which is not obviously correct far from equilibrium. This may limit applicability for modeling the microstructure of the significant proportion of organic-semiconductor systems formed under non-equilibrium conditions.

Most continuum simulations of organic semiconductors (e.g [173, 174]) have used models in which the field variables depend only on position and not on orientation, and so are incapable of modeling orientational ordering. Only a handful of studies[117, 175, 176] have accounted for molecular orientation.

Zhang et al. [117] studied the orientational ordering of semiflexible polymer chains at an impenetrable surface using an SCFT model of Gaussian chains in which the chain configuration depended on both the position and orientation with respect to the surface. The model was parameterized to represent chains of the conjugated polymer P3HT. Consistent with previous findings for semiflexible polymers [50], the surface was found to induce alignment of the chains parallel to the surface, with the thickness of the aligned layer on the order of the persistence length. Nevertheless, since the model did not account for monomer orientation, it was not able to distinguish edge-on versus face-on alignment of interest in electronic applications.

Shah and Ganesan [175] used SCFT to model the self-assembled bulk-heterojunction morphologies of donor–acceptor rod–coil block copolymers between two surfaces representing solar-cell electrodes. Their model included a Flory–Huggins term for the rod–coil repuslive interaction, a Gaussian stretching energy for the coil blocks, and the anisotropic

Maier–Saupe potential for orientational ordering of the rod blocks. The solar-cell device properties were simulated using a classical drift–diffusion model of charge and exciton dynamics that accounted for the effect of orientational anisotropy through a hole mobility that was a function of the orientational order parameter in the rod block obtained from the SCFT model. Using these simulations, the effect of substrate–polymer interactions, rod–coil miscibility, and the degree of orientation order on solar-cell performance was studied. Nevertheless, the consideration of only block copolymers, which allows microphase separation to be observed at equilibrium, constrains the orientational order at the donor–acceptor interface by chain connectivity; so the model is of limited utility for understanding orientational ordering at interfaces between donors and acceptors on different molecules, which are used in most bulk-heterojunction devices.

6. Summary and outlook

As highlighted in this review, the structure at interfaces in organic semiconductor based devices is known to be important for device function with, for example, in-plane alignment with respect to the substrate of the transition dipole moment in OLEDs giving better optical properties, face-on alignment at donor–acceptor interfaces in BHJ OSCs, and edge-on alignment at the dielectric interface in OFETs generally associated with increased performance. It is therefore important to develop an understanding of the potential ways to control interface structure for the realization of efficient, commercializable, organic electronics. Although many specific examples exist of orientational ordering of organic semiconductors at interfaces and its consequences for electronic processes and device properties, a general understanding of the factors that control interfacial alignment in these systems remains lacking, even for equilibrium systems. While the alignment of uniaxial nematics at the vapor interface has been widely studied [43, 44, 47, 48], their alignment at solid and fluid interfaces is less well understood, particularly when both repulsive and attractive intermolecular interactions are present. For biaxial nematics, which are more representative of organic semiconductors, the literature is even more sparse with few, if any, studies on their general alignment at either solid, fluid, or vapor interfaces.

In this work we have attempted to collate the many observations, from both experimental and computational work, about factors that affect interfacial microstructure and reconcile these, where possible, with general physical principles to develop some general guidelines for achieving orientational control. In general, it can be concluded that

(i) vapor deposition of small molecules is controlled by substrate temperature, with higher substrate temperatures giving a slight preference to end-on orientation at the air interface, consistent with studies of purely repulsive anisotropic particles at the vapor interface (although the effect that strong attractive interactions in a real system would have on this alignment is unclear),

(ii) annealing of solution-processed polymer films appears to give preference to edge-on structure at the solid interface in many cases, although it is unclear whether this is universal and further study is required to explain this observation,

(iii) the strength of attractive interactions between the side or end of the molecule with other molecules and a solid or fluid can control orientation,

(iv) aggregation of polymers in solution prior to deposition appears to generally favor edge-on orientations while single molecules favor face-on, although the reasons for this, and whether it is is a general property beyond the systems studied, is unclear,

(v) and, for semiconductors that display liquid-crystalline properties, the use of external forces, such as shear or magnetic fields, is a potentially powerful method for controlling orientation.

We note that in many cases the studies used to determine these properties generally only focus on a specific polymer or small molecule. Further studies using simple generic models of semiconductor-like molecules, in addition to systematic experimental studies, would be of great use in better understanding the interplay between the properties described above, and developing a general framework for deliberate and precise control of interfacial orientation. For BHJ OPVs in particular, very little experimental data is available on the structure at donor–acceptor interfaces. With the advent of polarized soft X-ray scattering techniques that allow for experimental characterization of buried interfaces, systematic experimental studies would be of great value in both verifying computational models and developing greater understanding and accurate predictions of interface structure. Computationally, the use of CG models, parameterized to model the typical range of interactions in organic semiconductors, would be useful to extend the known surface-anchoring effects of equilibrium systems of uniaxial molecules to biaxial molecules (where face-, end-, and edge-on orientations can be distinguished), nonequilibrium conditions, and the examination of the interplay of attractive and repulsive interactions. Particularly in cases in which trends are beginning to emerge but for which universality has not yet been confirmed, such as in the influence of solution aggregation or temperature on interfacial orientation, these systematic studies have the potential to be of great worth. A more thorough understanding of the physical principles underlying the observed orientational preferences, coupled with knowledge of how these structural changes correlate with changes in electronic properties and device efficiency, is therefore the next logical step towards improving the performance of organic semiconductors. The ability to predict solid-state microstructure and electronic properties and processes from the molecular structure of the component materials promises to facilitate a first-principles approach to the design of high-performance organic semiconductors with application in next-generation electronic devices.

Finally, the use of computer simulations to study organic semiconductor-substrate interfaces is a very powerful method to correlate structural anisotropy with electronic processes, as well as directly visualizing molecular structure in the regions of interest. There are a number of challenges associated with both atomistic (accessing the relevant length and time scales), and CG (transferability, loss of information) simulations, but these are rapidly being addressed. The use of anisotropic CG sites is of particular interest as these should better be able represent the important structural features of the predominantly disk-like molecules prominent in the organic semiconductor literature and enable the significantly longer simulations required to capture the second-scale (or longer) processes important for self-assembly at interfaces. Further development of continuum models that can describe orientation order or hybrid CG–continuum models could be particularly fruitful for realistically modelling the nonequilibrium deposition processes involved in the formation of organic-semiconductor interfaces.

Acknowledgments

This work was supported by the Australian Research Council under the *Discovery Projects* funding scheme (DP190102100). BJB acknowledges The University of Adelaide for the Joyner and Constance Fraser scholarships and the Playford Memorial Trust for a PhD scholarship. HTLN thanks The University of Adelaide for a Master of Philosophy (No Honours) International Scholarship.

References

[1] Ana Claudia Arias, J. Devin MacKenzie, Iain McCulloch, Jonathan Rivnay, and Alberto Salleo. Materials and Applications for Large Area Electronics: Solution-Based Approaches. *Chem. Rev.*, 110(1):3–24, January 2010. doi: 10.1021/cr900150b.

[2] Murad J. Y. Tayebjee, Dane R. McCamey, and Timothy W. Schmidt. Beyond Shockley–Queisser: Molecular Approaches to High-Efficiency Photovoltaics. *J. Phys. Chem. Lett.*, 6(12):2367–2378, 2015. doi: 10.1021/acs.jpclett.5b00716.

[3] P.G. de Gennes and J. Prost. *The Physics of Liquid Crystals*. Oxford University Press, Oxford, New York, 1995.

[4] Uli Würfel, Martin Seßler, Moritz Unmüssig, Nils Hofmann, Mathias List, Eric Mankel, Thomas Mayer, Günter Reiter, Jean-Luc Bubendorff, Laurent Simon, and Markus Kohlstädt. How Molecules with Dipole Moments Enhance the Selectivity of Electrodes in Organic Solar Cells – A Combined Experimental and Theoretical Approach. *Adv. Energy Mater.*, 6(19):1600594, 2016. doi: 10.1002/aenm.201600594.

[5] Xinran Zhang, Lee J. Richter, Dean M. DeLongchamp, R. Joseph Kline, Matthew R. Hammond, Iain McCulloch, Martin Heeney, Raja S. Ashraf, Jeremy N. Smith, Thomas D. Anthopoulos, Bob Schroeder, Yves H. Geerts, Daniel A. Fischer, and Michael F. Toney. Molecular Packing of High-Mobility Diketo Pyrrolo-Pyrrole Polymer Semiconductors with Branched Alkyl Side Chains. *J. Am. Chem. Soc.*, 133 (38):15073–15084, September 2011. doi: 10.1021/ja204515s.

[6] Kwon-Hyeon Kim, Sunghun Lee, Chang-Ki Moon, Sei-Yong Kim, Young-Seo Park, Jeong-Hwan Lee, Jin Woo Lee, June Huh, Youngmin You, and Jang-Joo Kim. Phosphorescent dye-based supramolecules for high-efficiency organic light-emitting diodes. *Nat. Commun.*, 5:4769, September 2014.

[7] John R. Tumbleston, Brian A. Collins, Liqiang Yang, Andrew C. Stuart, Eliot Gann, Wei Ma, Wei You, and Harald Ade. The influence of molecular orientation on organic bulk heterojunction solar cells. *Nat. Photon.*, 8(5):385–391, May 2014.

[8] Changyeon Lee, Thota Giridhar, Joonhyeong Choi, Seonha Kim, Youngwoong Kim, Taesu Kim, Wonho Lee, Han-Hee Cho, Cheng Wang, Harald Ade, and Bumjoon J. Kim. Importance of 2D Conjugated Side Chains of Benzodithiophene-Based Polymers in Controlling Polymer Packing, Interfacial Ordering, and Composition Variations of All-Polymer Solar Cells. *Chem. Mater.*, 29(21):9407–9415, November 2017. doi: 10.1021/acs.chemmater.7b03495.

[9] Long Ye, Xuechen Jiao, Meng Zhou, Shaoqing Zhang, Huifeng Yao, Wenchao Zhao, Andong Xia, Harald Ade, and Jianhui Hou. Manipulating Aggregation and Molecular Orientation in All-Polymer Photovoltaic Cells. *Adv. Mater.*, 27(39):6046–6054, 2015. doi: 10.1002/adma.201503218.

[10] Itaru Osaka and Kazuo Takimiya. Backbone orientation in semiconducting polymers. *Polymer*, 59:A1–A15, February 2015. doi: 10.1016/j.polymer.2014.12.066.

[11] Makoto Yoneya, Satoshi Matsuoka, Jun'ya Tsutsumi, and Tatsuo Hasegawa. Self-assembly of donor–acceptor semiconducting polymers in solution thin films: A molecular dynamics simulation study. *J. Mater. Chem. C*, 5(37):9602–9610, September 2017. doi: 10.1039/C7TC01014A.

[12] Kushal Bagchi, Nicholas E. Jackson, Ankit Gujral, Chengbin Huang, Michael F. Toney, Lian Yu, Juan J. de Pablo, and M. D. Ediger. Origin of Anisotropic Molecular Packing in Vapor-Deposited Alq3 Glasses. *J. Phys. Chem. Lett.*, 10(2):164–170, January 2019. doi: 10.1021/acs.jpclett.8b03582.

[13] Luca Muccioli, Gabriele D'Avino, and Claudio Zannoni. Simulation of Vapor-Phase Deposition and Growth of a Pentacene Thin Film on C60 (001). *Adv. Mater.*, 23(39): 4532–4536, 2011. doi: 10.1002/adma.201101652.

[14] Yong Youn, Dongsun Yoo, Hochul Song, Youngho Kang, Kye Yeop Kim, Sang Ho Jeon, Youngmi Cho, Kyungchan Chae, and Seungwu Han. All-atom simulation of molecular orientation in vapor-deposited organic light-emitting diodes. *J. Mater. Chem. C*, 6(5):1015–1022, February 2018. doi: 10.1039/C7TC05278B.

[15] Diane M. Walters, Lucas Antony, Juan J. de Pablo, and M. D. Ediger. Influence of Molecular Shape on the Thermal Stability and Molecular Orientation of Vapor-Deposited Organic Semiconductors. *J. Phys. Chem. Lett.*, 8(14):3380–3386, July 2017. doi: 10.1021/acs.jpclett.7b01097.

[16] Mark S. Chen, Olivia P. Lee, Jeremy R. Niskala, Alan T. Yiu, Christopher J. Tassone, Kristin Schmidt, Pierre M. Beaujuge, Seita S. Onishi, Michael F. Toney, Alex Zettl, and Jean M. J. Fréchet. Enhanced Solid-State Order and Field-Effect Hole Mobility through Control of Nanoscale Polymer Aggregation. *J. Am. Chem. Soc.*, 135(51):19229–19236, December 2013. doi: 10.1021/ja4088665.

[17] Shakeel S. Dalal, Diane M. Walters, Ivan Lyubimov, Juan J. de Pablo, and M. D.

Ediger. Tunable molecular orientation and elevated thermal stability of vapor-deposited organic semiconductors. *PNAS*, 112(14):4227–4232, April 2015. doi: 10.1073/pnas.1421042112.

[18] Alessia Senes, Stefan C. J. Meskers, Horst Greiner, Katsuaki Suzuki, Hironori Kaji, Chihaya Adachi, Joanne S. Wilson, and Rene A. J. Janssen. Increasing the horizontal orientation of transition dipole moments in solution processed small molecular emitters. *J. Mater. Chem. C*, 5(26):6555–6562, 2017. doi: 10.1039/C7TC01568B.

[19] Itaru Osaka, Masahiko Saito, Tomoyuki Koganezawa, and Kazuo Takimiya. Thiophene–Thiazolothiazole Copolymers: Significant Impact of Side Chain Composition on Backbone Orientation and Solar Cell Performances. *Adv. Mater.*, 26(2):331–338, 2014. doi: 10.1002/adma.201303059.

[20] Mark S. Chen, Jeremy R. Niskala, David A. Unruh, Crystal K. Chu, Olivia P. Lee, and Jean M. J. Fréchet. Control of Polymer-Packing Orientation in Thin Films through Synthetic Tailoring of Backbone Coplanarity. *Chem. Mater.*, 25(20):4088–4096, October 2013. doi: 10.1021/cm402489a.

[21] Alessandro Luzio, Luigino Criante, Valerio D'Innocenzo, and Mario Caironi. Control of charge transport in a semiconducting copolymer by solvent-induced long-range order. *Sci. Rep.*, 3:3425, December 2013. doi: 10.1038/srep03425.

[22] Alberto Salleo. Charge transport in polymeric transistors. *Mater. Today*, 10(3):38–45, March 2007. doi: 10.1016/S1369-7021(07)70018-4.

[23] Alberto Salleo, R. Joseph Kline, Dean M. DeLongchamp, and Michael L. Chabinyc. Microstructural Characterization and Charge Transport in Thin Films of Conjugated Polymers. *Adv. Mater.*, 22(34):3812–3838, 2010. doi: 10.1002/adma.200903712.

[24] R. Joseph Kline, Michael D. McGehee, and Michael F. Toney. Highly oriented crystals at the buried interface in polythiophene thin-film transistors. *Nat. Mater.*, 5(3):222–228, March 2006. doi: 10.1038/nmat1590.

[25] Duc T. Duong, Michael F. Toney, and Alberto Salleo. Role of confinement and aggregation in charge transport in semicrystalline polythiophene thin films. *Phys. Rev. B*, 86(20):205205, November 2012. doi: 10.1103/PhysRevB.86.205205.

[26] Matthew R. Hammond, R. Joseph Kline, Andrew A. Herzing, Lee J. Richter, David S. Germack, Hyun-Wook Ro, Christopher L. Soles, Daniel A. Fischer, Tao Xu, Luping Yu, Michael F. Toney, and Dean M. DeLongchamp. Molecular Order in High-Efficiency Polymer/Fullerene Bulk Heterojunction Solar Cells. *ACS Nano*, 5(10): 8248–8257, October 2011. doi: 10.1021/nn202951e.

[27] Masrur M. Nahid, Rukiya Matsidik, Adam Welford, Eliot Gann, Lars Thomsen, Michael Sommer, and Christopher R. McNeill. Unconventional Molecular Weight Dependence of Charge Transport in the High Mobility n-type Semiconducting Polymer P(NDI2OD-T2). *Adv. Funct. Mater.*, 27(9):1604744, 2017. doi: 10.1002/adfm.201604744.

[28] Xuechen Jiao, Long Ye, and Harald Ade. Quantitative Morphology–Performance Correlations in Organic Solar Cells: Insights from Soft X-Ray Scattering. *Adv. Energy Mater.*, 7(18):1700084, September 2017. doi: 10.1002/aenm.201700084.

[29] Luca Muccioli, Gabriele D'Avino, Roberto Berardi, Silvia Orlandi, Antonio Pizzirusso, Matteo Ricci, Otello Maria Roscioni, and Claudio Zannoni. Supramolecular Organization of Functional Organic Materials in the Bulk and at Organic/Organic Interfaces: A Modeling and Computer Simulation Approach. In David Beljonne and Jerome Cornil, editors, *Multiscale Modelling of Organic and Hybrid Photovoltaics*, Topics in Current Chemistry, pages 39–101. Springer, Berlin, Heidelberg, 2014.

[30] Shuhong Liu, Wechung Maria Wang, Alejandro L. Briseno, Stefan C. B. Mannsfeld, and Zhenan Bao. Controlled deposition of crystalline organic semiconductors for field-effect-transistor applications. *Adv. Mater.*, 21(12):1217–1232, 2009. doi: 10.1002/adma.200802202.

[31] A. A. Virkar, S. Mannsfeld, Z. Bao, and N. Stingelin. Organic semiconductor growth and morphology considerations for organic thin-film transistors. *Adv. Mater.*, 22(34): 3857–3875, 2010. doi: 10.1002/adma.200903193.

[32] Chengliang Wang, Huanli Dong, Wenping Hu, Yunqi Liu, and Daoben Zhu. Semiconducting π-conjugated systems in field-effect transistors: A material odyssey of organic electronics. *Chem. Rev.*, 112(4):2208–2267, 2012. doi: 10.1021/cr100380z.

[33] Huanli Dong, Xiaolong Fu, Jie Liu, Zongrui Wang, and Wenping Hu. 25th anniversary article: Key points for high-mobility organic field-effect transistors. *Adv. Mater.*, 25 (43):6158–6183, May 2013. doi: 10.1002/adma.201302514.

[34] Qin-Fen Li, Shuang Liu, Hong-Zheng Chen, and Han-Ying Li. Alignment and patterning of organic single crystals for field-effect transistors. *Chin. Chem. Lett.*, 27 (8):1421–1428, 2016. doi: 10.1016/j.cclet.2016.06.027.

[35] Xiaotao Zhang, Huanli Dong, and Wenping Hu. Organic semiconductor single crystals for electronics and photonics. *Adv. Mater.*, 30(44):1801048, 2018. doi: 10.1002/adma.201801048.

[36] Chengliang Wang, Huanli Dong, Lang Jiang, and Wenping Hu. Organic semiconductor crystals. *Chem. Soc. Rev.*, 47:422–500, 2018. doi: 10.1039/C7CS00490G.

[37] Yu Wang, Lingjie Sun, Cong Wang, Fangxu Yang, Xiaochen Ren, Xiaotao Zhang, Huanli Dong, and Wenping Hu. Organic crystalline materials in flexible electronics. *Chem. Soc. Rev.*, 48(6):1492–1530, March 2019. doi: 10.1039/C8CS00406D.

[38] B Jerome. Surface effects and anchoring in liquid crystals. *Rep. Prog. Phys.*, 54(3): 391–451, March 1991. doi: 10.1088/0034-4885/54/3/002.

[39] M. M. Telo Da Gama. *Liquid Crystal Interfaces*, pages 243–292. Springer Netherlands, Dordrecht, 1995.

[40] M. A. Bates and G. R. Luckhurst. *Liquid Crystals I*, chapter Computer Simulation of Liquid Crystal Phases Formed by Gay-Berne Mesogens, pages 65–137. Springer Berlin Heidelberg, Berlin, Heidelberg, 1999.

[41] Seong Ho Ryu and Dong Ki Yoon. Liquid crystal phases in confined geometries. *Liq. Cryst.*, 43(13-15):1951–1972, December 2016. doi: 10.1080/02678292.2016.1205674.

[42] P. G. De Gennes. Short range order effects in the isotropic phase of nematics and cholesterics. *Mol. Cryst. Liq. Cryst.*, 12(3):193–214, 1971. doi: 10.1080/15421407108082773.

[43] E. Martín del Río, M. M. Telo da Gama, E. de Miguel, and L. F. Rull. Surface-induced alignment at model nematic interfaces. *Phys. Rev. E*, 52:5028–5039, Nov 1995. doi: 10.1103/PhysRevE.52.5028.

[44] Hatsuo Kimura and Huzio Nakano. Statistical theory of surface tension and molecular orientations at the free surface in nematic liquid crystals. *J. Phys. Soc. Jpn.*, 54(5): 1730–1736, 1985. doi: 10.1143/JPSJ.54.1730.

[45] J.G. Gay and B.J. Berne. Modification of the overlap potential to mimic a linear site-site potential. *J. Chem. Phys.*, 74(6):3316–3319, 1981. doi: 10.1063/1.441483.

[46] Stuart J. Mills, Christopher M. Care, Maureen P. Neal, and Douglas J. Cleaver. Computer simulation of an unconfined liquid crystal film. *Phys. Rev. E*, 58(3):3284–3294, September 1998. doi: 10.1103/PhysRevE.58.3284.

[47] E. Martín del Río and E. de Miguel. Computer simulation study of the free surfaces of a liquid crystal model. *Phys. Rev. E*, 55:2916–2924, Mar 1997. doi: 10.1103/PhysRevE.55.2916.

[48] Luis F. Rull and José Manuel Romero-Enrique. Computer simulation study of the nematic–vapour interface in the Gay–Berne model. *Mol. Phys.*, 115(9-12):1214–1224, June 2017. doi: 10.1080/00268976.2016.1274437.

[49] Koji Okano. Anisotropic excluded volume effect and alignment of nematic liquid crystal in a sandwich cell. *Jpn. J. Appl. Phys.*, 22(Part 2, No. 6):L343–L344, jun 1983. doi: 10.1143/jjap.22.l343.

[50] A. Sergei Egorov, Andrey Milchev, and Kurt Binder. Semiflexible polymers in the bulk and confined by planar walls. *Polymers*, 8(8):–, 2016.

[51] G. D. Wall and D. J. Cleaver. Computer simulations of adsorbed liquid crystal films. *Mol. Phys.*, 101(8):1105–1112, April 2003. doi: 10.1080/0026897031000068514.

[52] Dmytro Antypov and Douglas J. Cleaver. The role of attractive interactions in rod–sphere mixtures. *J. Chem. Phys.*, 120(21):10307–10316, 2004. doi: 10.1063/1.1718181.

[53] Joseph M. Brader, Ansgar Esztermann, and Matthias Schmidt. Colloidal rod-sphere mixtures: Fluid-fluid interfaces and the onsager limit. *Phys. Rev. E*, 66:031401, Sep 2002. doi: 10.1103/PhysRevE.66.031401.

[54] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. a. J. Janssen, E. W. Meijer, P. Herwig, and D. M. de Leeuw. Two-dimensional charge transport in self-organized, high-mobility conjugated polymers. *Nature*, 401(6754):685–688, October 1999. doi: 10.1038/44359.

[55] Daisuke Yokoyama. Molecular orientation in small-molecule organic light-emitting diodes. *J. Mater. Chem.*, 21(48):19187–19202, 2011. doi: 10.1039/C1JM13417E.

[56] Takeshi Komino, Hiroyuki Tanaka, and Chihaya Adachi. Selectively Controlled Orientational Order in Linear-Shaped Thermally Activated Delayed Fluorescent Dopants. *Chem. Mater.*, 26(12):3665–3671, June 2014. doi: 10.1021/cm500802p.

[57] Thomas Lee, Bertrand Caron, Martin Stroet, David M. Huang, Paul L. Burn, and Alan E. Mark. The Molecular Origin of Anisotropic Emission in an Organic Light-Emitting Diode. *Nano Lett.*, 17(10):6464–6468, October 2017. doi: 10.1021/acs.nanolett.7b03528.

[58] Masrur M. Nahid, Adam Welford, Eliot Gann, Lars Thomsen, Kamendra P. Sharma, and Christopher R. McNeill. Nature and Extent of Solution Aggregation Determines the Performance of P(NDI2OD-T2) Thin-Film Transistors. *Adv. Electron. Mater.*, 4(4): 1700559, 2018. doi: 10.1002/aelm.201700559.

[59] Cheng-Fang Liu, Yan Lin, Wen-Yong Lai, and Wei Huang. Understanding the dependence of performance on the dielectric-semiconductor interface in pentacene-based organic field-effect transistors. *Mater. Lett.*, 189:286–289, February 2017. doi: 10.1016/j.matlet.2016.12.011.

[60] R. Joseph Kline, Dean M. DeLongchamp, Daniel A. Fischer, Eric K. Lin, Martin Heeney, Iain McCulloch, and Michael F. Toney. Significant dependence of morphology and charge carrier mobility on substrate surface chemistry in high performance polythiophene semiconductor films. *Appl. Phys. Lett.*, 90(6):062117, February 2007. doi: 10.1063/1.2472533.

[61] Jonathan Rivnay, Michael F. Toney, Yan Zheng, Isaac V. Kauvar, Zhihua Chen, Veit Wagner, Antonio Facchetti, and Alberto Salleo. Unconventional Face-On Texture and Exceptional In-Plane Order of a High Mobility n-Type Polymer. *Adv. Mater.*, 22(39): 4359–4363, October 2010. doi: 10.1002/adma.201001202.

[62] Jinhua Li, Jun Du, Jianbin Xu, Helen L. W. Chan, and Feng Yan. The influence of gate dielectrics on a high-mobility n-type conjugated polymer in organic thin-film transistors. *Appl. Phys. Lett.*, 100(3):033301, January 2012. doi: 10.1063/1.3678196.

[63] Gilles Horowitz. Organic Field-Effect Transistors. *Adv. Mater.*, 10(5):365–377, 1998. doi: 10.1002/(SICI)1521-4095(199803)10:5<365::AID-ADMA365>3.0.CO;2-U.

[64] Gilles Horowitz. Organic thin film transistors: From theory to real devices. *J. Mater. Res.*, 19(07):1946–1962, July 2004. doi: 10.1557/JMR.2004.0266.

[65] Franco Dinelli, Mauro Murgia, Pablo Levy, Massimiliano Cavallini, Fabio Biscarini, and Dago M. de Leeuw. Spatially Correlated Charge Transport in Organic Thin Film Transistors. *Phys. Rev. Lett.*, 92(11):116802, March 2004. doi: 10.1103/PhysRevLett.92.116802.

[66] Manabu Kiguchi, Manabu Nakayama, Kohei Fujiwara, Keiji Ueno, Toshihiro Shimada, and Koichiro Saiki. Accumulation and Depletion Layer Thicknesses in Organic Field

Effect Transistors. *Jpn. J. Appl. Phys.*, 42(12A):L1408–L1410, November 2003. doi: 10.1143/JJAP.42.L1408.

[67] N. Zhao, Y.-Y. Noh, J.-F. Chang, M. Heeney, I. McCulloch, and H. Sirringhaus. Polaron Localization at Interfaces in High-Mobility Microcrystalline Conjugated Polymers. *Adv. Mater.*, 21(37):3759–3763, 2009. doi: 10.1002/adma.200900326.

[68] Mario Caironi, Matt Bird, Daniele Fazzi, Zhihua Chen, Riccardo Di Pietro, Christopher Newman, Antonio Facchetti, and Henning Sirringhaus. Very Low Degree of Energetic Disorder as the Origin of High Mobility in an n-channel Polymer Semiconductor. *Adv. Funct. Mater.*, 21(17):3371–3381, 2011. doi: 10.1002/adfm.201100592.

[69] Kouji Suemori, Sei Uemura, Manabu Yoshida, Satoshi Hoshino, Noriyuki Takada, Takehito Kodzasa, and Toshihide Kamata. Influence of fine roughness of insulator surface on threshold voltage stability of organic field-effect transistors. *Appl. Phys. Lett.*, 93(3):033308, July 2008. doi: 10.1063/1.2957987.

[70] Leslie H. Jimison, Alberto Salleo, Michael L. Chabinyc, David P. Bernstein, and Michael F. Toney. Correlating the microstructure of thin films of poly[5,5-bis(3-dodecyl-2-thienyl)-2,2-bithiophene] with charge transport: Effect of dielectric surface energy and thermal annealing. *Phys. Rev. B*, 78(12):125319, September 2008. doi: 10.1103/PhysRevB.78.125319.

[71] Dongyoon Khim, Alessandro Luzio, Giorgio Ernesto Bonacchini, Giuseppina Pace, Mi-Jung Lee, Yong-Young Noh, and Mario Caironi. Uniaxial Alignment of Conjugated Polymer Films for High-Performance Organic Field-Effect Transistors. *Adv. Mater.*, 30 (20):1705463, May 2018. doi: 10.1002/adma.201705463.

[72] Wojciech Pisula, Matthias Zorn, Ji Young Chang, Klaus Müllen, and Rudolf Zentel. Liquid Crystalline Ordering and Charge Transport in Semiconducting Materials. *Macromol. Rapid Commun.*, 30(14):1179–1202, 2009. doi: 10.1002/marc.200900251.

[73] Daniel Trefz, Yannic M. Gross, Carsten Dingler, Roman Tkachov, Amer Hamidi-Sakr, Anton Kiriy, Christopher R. McNeill, Martin Brinkmann, and Sabine Ludwigs. Tuning Orientational Order of Highly Aggregating P(NDI2OD-T2) by Solvent Vapor Annealing and Blade Coating. *Macromolecules*, 52(1):43–54, January 2019. doi: 10.1021/acs.macromol.8b02176.

[74] Sadir G. Bucella, Alessandro Luzio, Eliot Gann, Lars Thomsen, Christopher R. McNeill, Giuseppina Pace, Andrea Perinot, Zhihua Chen, Antonio Facchetti, and Mario Caironi. Macroscopic and high-throughput printing of aligned nanostructured polymer semiconductors for MHz large-area electronics. *Nat. Commun.*, 6:8394, 2015. doi: 10.1038/ncomms9394.

[75] Rodrigo Noriega, Jonathan Rivnay, Koen Vandewal, Felix P. V. Koch, Natalie Stingelin, Paul Smith, Michael F. Toney, and Alberto Salleo. A general relationship between disorder, aggregation and charge transport in conjugated polymers. *Nat. Mater.*, 12 (11):1038–1044, 2013. doi: 10.1038/nmat3722.

[76] R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu, and J. M. J. Fréchet. Controlling

the Field-Effect Mobility of Regioregular Polythiophene by Changing the Molecular Weight. *Adv. Mater.*, 15(18):1519–1522, 2003. doi: 10.1002/adma.200305275.

[77] Nguyen Ngan Nguyen, Sae Byeok Jo, Seong Kyu Lee, Dong Hun Sin, Boseok Kang, Hyun Ho Kim, Hansol Lee, and Kilwon Cho. Atomically Thin Epitaxial Template for Organic Crystal Growth Using Graphene with Controlled Surface Wettability. *Nano Lett.*, 15(4):2474–2484, April 2015. doi: 10.1021/nl504958e.

[78] Hongping Yan, Torben Schuettfort, Auke J. Kronemeijer, Christopher R. McNeill, and Harald W. Ade. Influence of dielectric-dependent interfacial widths on device performance in top-gate P(NDI2OD-T2) field-effect transistors. *Appl. Phys. Lett.*, 101 (9):093308, August 2012. doi: 10.1063/1.4748976.

[79] Wi Hyoung Lee, Jeong Ho Cho, and Kilwon Cho. Control of mesoscale and nanoscale ordering of organic semiconductors at the gate dielectric/semiconductor interface for organic transistors. *J. Mater. Chem.*, 20(13):2549–2561, 2010. doi: 10.1039/B924415H.

[80] Iris Wurzbach, Christian Rothe, Kirsten Bruchlos, Sabine Ludwigs, and Frank Giesselmann. Shear alignment and 2D charge transport of tilted smectic liquid crystalline phases – XRD and FET studies. *J. Mater. Chem. C*, 7(9):2615–2624, February 2019. doi: 10.1039/C8TC04536D.

[81] Marni Sapolsky, John McFaddin, and David Boucher. Aggregation Behavior of Poly(3-hexylthiophene) in Solvent Mixtures: Linear Solvation Energy Relationship (LSER) Modeling and COSMO-RS Calculations. *Macromol. Chem. Phys.*, 219(8):1700545, 2018. doi: 10.1002/macp.201700545.

[82] Pascal Friederich, Reinder Coehoorn, and Wolfgang Wenzel. Molecular Origin of the Anisotropic Dye Orientation in Emissive Layers of Organic Light Emitting Diodes. *Chem. Mater.*, 29(21):9528–9535, November 2017. doi: 10.1021/acs.chemmater.7b03742.

[83] Pascal Friederich, Vadim Rodin, Florian von Wrochem, and Wolfgang Wenzel. Built-In Potentials Induced by Molecular Order in Amorphous Organic Thin Films. *ACS Appl. Mater. Interfaces*, 10(2):1881–1887, January 2018. doi: 10.1021/acsami.7b11762.

[84] Tim Richards, Matthew Bird, and Henning Sirringhaus. A quantitative analytical model for static dipolar disorder broadening of the density of states at organic heterointerfaces. *J. Chem. Phys.*, 128(23):234905, June 2008. doi: 10.1063/1.2937729.

[85] Henning Sirringhaus, Matt Bird, and Ni Zhao. Charge Transport Physics of Conjugated Polymer Field-Effect Transistors. *Adv. Mater.*, 22(34):3893–3898, 2010. doi: 10.1002/adma.200902857.

[86] Chang-Ki Moon, Kwon-Hyeon Kim, Jin Woo Lee, and Jang-Joo Kim. Influence of Host Molecules on Emitting Dipole Orientation of Phosphorescent Iridium Complexes. *Chem. Mater.*, 27(8):2767–2769, April 2015. doi: 10.1021/acs.chemmater.5b00469.

[87] Matthew J. Jurow, Christian Mayr, Tobias D. Schmidt, Thomas Lampe, Peter I. Djurovich, Wolfgang Brütting, and Mark E. Thompson. Understanding and predicting

the orientation of heteroleptic phosphors in organic light-emitting materials. *Nat. Mater.*, 15(1):85–91, January 2016. doi: 10.1038/nmat4428.

[88] Yutaka Noguchi, Yukimasa Miyazaki, Yuya Tanaka, Naoki Sato, Yasuo Nakayama, Tobias D. Schmidt, Wolfgang Brütting, and Hisao Ishii. Charge accumulation at organic semiconductor interfaces due to a permanent dipole moment and its orientational order in bilayer devices. *J. Appl. Phys.*, 111(11):114508, June 2012. doi: 10.1063/1.4724349.

[89] Thomas Lampe, Tobias D. Schmidt, Matthew J. Jurow, Peter I. Djurovich, Mark E. Thompson, and Wolfgang Brütting. Dependence of Phosphorescent Emitter Orientation on Deposition Technique in Doped Organic Films. *Chem. Mater.*, 28(3): 712–715, February 2016. doi: 10.1021/acs.chemmater.5b04607.

[90] Lucas W. Antony, Nicholas E. Jackson, Ivan Lyubimov, Venkatram Vishwanath, Mark D. Ediger, and Juan J. de Pablo. Influence of Vapor Deposition on Structural and Charge Transport Properties of Ethylbenzene Films. *ACS Cent. Sci.*, 3(5):415–424, May 2017. doi: 10.1021/acscentsci.7b00041.

[91] Ivan Lyubimov, Lucas Antony, Diane M. Walters, David Rodney, M. D. Ediger, and Juan J. de Pablo. Orientational anisotropy in simulated vapor-deposited molecular glasses. *J. Chem. Phys.*, 143(9):094502, September 2015. doi: 10.1063/1.4928523.

[92] J. Jiang, D. M. Walters, D. Zhou, and M. D. Ediger. Substrate temperature controls molecular orientation in two-component vapor-deposited glasses. *Soft Matter*, 12(13): 3265–3270, March 2016. doi: 10.1039/C6SM00262E.

[93] Ankit Gujral, Jaritza Gómez, Shigang Ruan, Michael F. Toney, Harald Bock, Lian Yu, and M.D. Ediger. Vapor-Deposited Glasses with Long-Range Columnar Liquid Crystalline Order. *Chem. Mater.*, 29(21):9110–9119, November 2017. doi: 10.1021/acs.chemmater.7b02852.

[94] Jaritza Gómez, Jing Jiang, Ankit Gujral, Chengbin Huang, Lian Yu, and M. D. Ediger. Vapor deposition of a smectic liquid crystal: Highly anisotropic, homogeneous glasses with tunable molecular orientation. *Soft Matter*, 12(11):2942–2947, March 2016. doi: 10.1039/C5SM02944A.

[95] M. D. Ediger, Juan de Pablo, and Lian Yu. Anisotropic Vapor-Deposited Glasses: Hybrid Organic Solids. *Acc. Chem. Res.*, 52(2):407–414, February 2019. doi: 10.1021/acs.accounts.8b00513.

[96] Ankit Gujral, Lian Yu, and M. D. Ediger. Anisotropic organic glasses. *Curr. Opin. Solid State Mater. Sci.*, 22(2):49–57, April 2018. doi: 10.1016/j.cossms.2017.11.001.

[97] S. Matthew Menke, Niva A. Ran, Guillermo C. Bazan, and Richard H. Friend. Understanding energy loss in organic solar cells: Toward a new efficiency regime. *Joule*, 2(1):25–35, 2018. doi: 10.1016/j.joule.2017.09.020.

[98] Carsten Deibel, Thomas Strobel, and Vladimir Dyakonov. Origin of the Efficient Polaron-Pair Dissociation in Polymer-Fullerene Blends. *Phys. Rev. Lett.*, 103(3): 036402, July 2009. doi: 10.1103/PhysRevLett.103.036402.

[99] Niva A. Ran, Steffen Roland, John A. Love, Victoria Savikhin, Christopher J. Takacs, Yao-Tsung Fu, Hong Li, Veaceslav Coropceanu, Xiaofeng Liu, Jean-Luc Brédas, Guillermo C. Bazan, Michael F. Toney, Dieter Neher, and Thuc-Quyen Nguyen. Impact of interfacial molecular orientation on radiative recombination and charge generation efficiency. *Nat. Commun.*, 8(1):79, July 2017. doi: 10.1038/s41467-017-00107-4.

[100] Carl Poelking, Max Tietze, Chris Elschner, Selina Olthof, Dirk Hertel, Björn Baumeier, Frank Würthner, Klaus Meerholz, Karl Leo, and Denis Andrienko. Impact of mesoscale order on open-circuit voltage in organic solar cells. *Nat. Mater.*, 14(4): 434–439, April 2015. doi: 10.1038/nmat4167.

[101] Samantha N. Hood and Ivan Kassal. Entropy and Disorder Enable Charge Separation in Organic Solar Cells. *J. Phys. Chem. Lett.*, 7(22):4495–4500, November 2016. doi: 10.1021/acs.jpclett.6b02178.

[102] Fiona C. Jamieson, Ester Buchaca Domingo, Thomas McCarthy-Ward, Martin Heeney, Natalie Stingelin, and James R. Durrant. Fullerene crystallisation as a key driver of charge separation in polymer/fullerene bulk heterojunction solar cells. *Chem. Sci.*, 3 (2):485–492, 2012. doi: 10.1039/C1SC00674F.

[103] Stijn Verlaak, David Beljonne, David Cheyns, Cedric Rolin, Mathieu Linares, Frédéric Castet, Jérôme Cornil, and Paul Heremans. Electronic Structure and Geminate Pair Energetics at Organic–Organic Interfaces: The Case of Pentacene/C60 Heterojunctions. *Adv. Funct. Mater.*, 19(23):3809–3814, 2009. doi: 10.1002/adfm.200901233.

[104] Gabriele D'Avino, Luca Muccioli, Frédéric Castet, Carl Poelking, Denis Andrienko, Zoltán G. Soos, Jérôme Cornil, and David Beljonne. Electrostatic phenomena in organic semiconductors: Fundamentals and implications for photovoltaics. *J. Phys.: Condens. Matter*, 28(43):433002, September 2016. doi: 10.1088/0953-8984/28/43/433002.

[105] Björn Baumeier, Denis Andrienko, and Michael Rohlfing. Frenkel and Charge-Transfer Excitations in Donor–acceptor Complexes from Many-Body Green's Functions Theory. *J. Chem. Theory Comput.*, 8(8):2790–2795, August 2012. doi: 10.1021/ct300311x.

[106] Xian-Kai Chen, Mahesh Kumar Ravva, Hong Li, Sean M. Ryno, and Jean-Luc Brédas. Effect of Molecular Packing and Charge Delocalization on the Nonradiative Recombination of Charge-Transfer States in Organic Solar Cells. *Adv. Energy Mater.*, 6(24):1601325, 2016. doi: 10.1002/aenm.201601325.

[107] Bong-Gi Kim, Eun Jeong Jeong, Jong Won Chung, Sungbaek Seo, Bonwon Koo, and Jinsang Kim. A molecular design principle of lyotropic liquid-crystalline conjugated polymers with directed alignment capability for plastic electronics. *Nat. Mater.*, 12(7): 659–664, July 2013. doi: 10.1038/nmat3595.

[108] Fengjiao Zhang, Erfan Mohammadi, Xuyi Luo, Joseph Strzalka, Jianguo Mei, and Ying Diao. Critical Role of Surface Energy in Guiding Crystallization of Solution-Coated

Conjugated Polymer Thin Films. *Langmuir*, 34(3):1109–1122, January 2018. doi: 10.1021/acs.langmuir.7b02807.

[109] Yeong Don Park, Jung Ah Lim, Hwa Sung Lee, and Kilwon Cho. Interface engineering in organic transistors. *Mater. Today*, 10(3):46–54, March 2007. doi: 10.1016/S1369-7021(07)70019-6.

[110] Yuichiro Watanabe, Daisuke Yokoyama, Tomoyuki Koganezawa, Hiroshi Katagiri, Takashi Ito, Satoru Ohisa, Takayuki Chiba, Hisahiro Sasabe, and Junji Kido. Control of Molecular Orientation in Organic Semiconductor Films using Weak Hydrogen Bonds. *Adv. Mater.*, March 2019. doi: 10.1002/adma.201808300. in press.

[111] Youngkyoo Kim, Steffan Cook, Sachetan M. Tuladhar, Stelios A. Choulis, Jenny Nelson, James R. Durrant, Donal D. C. Bradley, Mark Giles, Iain McCulloch, Chang-Sik Ha, and Moonhor Ree. A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene:fullerene solar cells. *Nat. Mater.*, 5 (3):197–203, March 2006. doi: 10.1038/nmat1574.

[112] Hyunbum Kang, Mohammad Afsar Uddin, Changyeon Lee, Ki-Hyun Kim, Thanh Luan Nguyen, Wonho Lee, Yuxiang Li, Cheng Wang, Han Young Woo, and Bumjoon J. Kim. Determining the Role of Polymer Molecular Weight for High-Performance All-Polymer Solar Cells: Its Effect on Polymer Aggregation and Phase Separation. *J. Am. Chem. Soc.*, 137(6):2359–2365, February 2015. doi: 10.1021/ja5123182.

[113] Itaru Osaka, Masahiko Saito, Hiroki Mori, Tomoyuki Koganezawa, and Kazuo Takimiya. Drastic Change of Molecular Orientation in a Thiazolothiazole Copolymer by Molecular-Weight Control and Blending with PC61BM Leads to High Efficiencies in Solar Cells. *Adv. Mater.*, 24(3):425–430, 2012. doi: 10.1002/adma.201103065.

[114] Nanjia Zhou, Alexander S. Dudnik, Ting I. N. G. Li, Eric F. Manley, Thomas J. Aldrich, Peijun Guo, Hsueh-Chung Liao, Zhihua Chen, Lin X. Chen, Robert P. H. Chang, Antonio Facchetti, Monica Olvera de la Cruz, and Tobin J. Marks. All-Polymer Solar Cell Performance Optimized via Systematic Molecular Weight Tuning of Both Donor and Acceptor Polymers. *J. Am. Chem. Soc.*, 138(4):1240–1251, 2016. doi: 10.1021/jacs.5b10735.

[115] Baobing Fan, Lei Ying, Zhenfeng Wang, Baitian He, Xiao-Fang Jiang, Fei Huang, and Yong Cao. Optimisation of processing solvent and molecular weight for the production of green-solvent-processed all-polymer solar cells with a power conversion efficiency over 9%. *Energy Environ. Sci.*, 10(5):1243–1251, 2017. doi: 10.1039/C7EE00619E.

[116] Jonathan A. Bartelt, Jessica D. Douglas, William R. Mateker, Abdulrahman El Labban, Christopher J. Tassone, Michael F. Toney, Jean M. J. Fréchet, Pierre M. Beaujuge, and Michael D. McGehee. Controlling Solution-Phase Polymer Aggregation with Molecular Weight and Solvent Additives to Optimize Polymer-Fullerene Bulk Heterojunction Solar Cells. *Adv. Energy Mater.*, 4(9):1301733, June 2014. doi: 10.1002/aenm.201301733.

[117] Wenlin Zhang, Enrique D. Gomez, and Scott T. Milner. Surface-Induced Chain Alignment of Semiflexible Polymers. *Macromolecules*, 49(3):963–971, February 2016. doi: 10.1021/acs.macromol.5b02173.

[118] Jonathan Rivnay, Robert Steyrleuthner, Leslie H. Jimison, Alberto Casadei, Zhihua Chen, Michael F. Toney, Antonio Facchetti, Dieter Neher, and Alberto Salleo. Drastic Control of Texture in a High Performance n-Type Polymeric Semiconductor and Implications for Charge Transport. *Macromolecules*, 44(13):5246–5255, July 2011. doi: 10.1021/ma200864s.

[119] Dhritiman Bhattacharyya, Angelo Montenegro, Purnim Dhar, Muhammet Mammetkuliyev, Robert M. Pankow, Moon Chul Jung, Mark E. Thompson, Barry C. Thompson, and Alexander V. Benderskii. Molecular Orientation of Poly-3-hexylthiophene at the Buried Interface with Fullerene. *J. Phys. Chem. Lett.*, pages 1757–1762, March 2019. doi: 10.1021/acs.jpclett.9b00498.

[120] Robert Steyrleuthner, Riccardo Di Pietro, Brian A. Collins, Frank Polzer, Scott Himmelberger, Marcel Schubert, Zhihua Chen, Shiming Zhang, Alberto Salleo, Harald Ade, Antonio Facchetti, and Dieter Neher. The Role of Regioregularity, Crystallinity, and Chain Orientation on Electron Transport in a High-Mobility n-Type Copolymer. *J. Am. Chem. Soc.*, 136(11):4245–4256, 2014. doi: 10.1021/ja4118736.

[121] Torben Schuettfort, Lars Thomsen, and Christopher R. McNeill. Observation of a Distinct Surface Molecular Orientation in Films of a High Mobility Conjugated Polymer. *J. Am. Chem. Soc.*, 135(3):1092–1101, January 2013. doi: 10.1021/ja310240q.

[122] Guoxing Pan, Fei Chen, Lin Hu, Kejun Zhang, Jianming Dai, and Fapei Zhang. Effective Controlling of Film Texture and Carrier Transport of a High-Performance Polymeric Semiconductor by Magnetic Alignment. *Adv. Funct. Mater.*, 25(32):5126–5133, 2015. doi: 10.1002/adfm.201500643.

[123] Igor O. Shklyarevskiy, Pascal Jonkheijm, Natalie Stutzmann, Dorothee Wasserberg, Harry J. Wondergem, Peter C. M. Christianen, Albertus P. H. J. Schenning, Dago M. de Leeuw, Željko Tomović, Jishan Wu, Klaus Müllen, and Jan C. Maan. High Anisotropy of the Field-Effect Transistor Mobility in Magnetically Aligned Discotic Liquid-Crystalline Semiconductors. *J. Am. Chem. Soc.*, 127(46):16233–16237, November 2005. doi: 10.1021/ja054694t.

[124] M. Mas-Torrent, D. den Boer, M. Durkut, P. Hadley, and A. P. H. J. Schenning. Field effect transistors based on poly(3-hexylthiophene) at different length scales. *Nanotechnology*, 15(4):S265–S269, March 2004. doi: 10.1088/0957-4484/15/4/028.

[125] F Simoni and O Francescangeli. Effects of light on molecular orientation of liquid crystals. *J. Phys.: Condens. Matter*, 11(41):R439–R487, oct 1999. doi: 10.1088/0953-8984/11/41/201.

[126] Varuni Dantanarayana, David M. Huang, Jennifer A. Staton, Adam J. Moulé, and Roland Faller. Multi-scale modeling of bulk heterojunctions for organic photovoltaic

applications. In Vasilis Fthenakis, editor, *Third Generation Photovoltaics*, chapter 2. IntechOpen, Rijeka, 2012. doi: 10.5772/26068.

[127] Thomas E. Gartner and Arthi Jayaraman. Modeling and simulations of polymers: A roadmap. *Macromolecules*, 52(3):755–786, 2019. doi: 10.1021/acs.macromol.8b01836.

[128] David Beljonne, Jérôme Cornil, Luca Muccioli, Claudio Zannoni, Jean-Luc Brédas, and Frédéric Castet. Electronic processes at organic−organic interfaces: Insight from modeling and implications for opto-electronic devices†. *Chem. Mater.*, 23(3):591–609, November 2011. doi: 10.1021/cm1023426.

[129] Sheridan Few, Jarvist M. Frost, and Jenny Nelson. Models of charge pair generation in organic solar cells. *Phys. Chem. Chem. Phys.*, 17(4):2311–2325, December 2014. doi: 10.1039/C4CP03663H.

[130] Daan Frenkel and Berend Smit. *Understanding Molecular Simulation*. Academic Press, Inc., Orlando, FL, USA, 2nd edition, 2001. ISBN 0122673514.

[131] M. P. Allen and D. J. Tildesley. *Computer Simulation of Liquids*. Clarendon, Oxford, 1987.

[132] Kateri H. DuBay, Michelle Lynn Hall, Thomas F. Hughes, Chuanjie Wu, David R. Reichman, and Richard A. Friesner. Accurate Force Field Development for Modeling Conjugated Polymers. *J. Chem. Theory Comput.*, 8(11):4556–4569, 2012. doi: 10.1021/ct300175w.

[133] Nicholas E. Jackson, Kevin L. Kohlstedt, Brett M. Savoie, Monica Olvera de la Cruz, George C. Schatz, Lin X. Chen, and Mark A. Ratner. Conformational Order in Aggregates of Conjugated Polymers. *J. Am. Chem. Soc.*, 137(19):6254–6262, 2015. doi: 10.1021/jacs.5b00493.

[134] Taiping Hu, Guangchao Han, Zeyi Tu, Ruihong Duan, and Yuanping Yi. Origin of High Efficiencies for Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes: Atomistic Insight into Molecular Orientation and Torsional Disorder. *J. Phys. Chem. C*, 122(48):27191–27197, December 2018. doi: 10.1021/acs.jpcc.8b08169.

[135] Claire Tonnelé, Martin Stroet, Bertrand Caron, Andrew J. Clulow, Ravi C. R. Nagiri, Alpeshkumar K. Malde, Paul L. Burn, Ian R. Gentle, Alan E. Mark, and Benjamin J. Powell. Elucidating the Spatial Arrangement of Emitter Molecules in Organic Light-Emitting Diode Films. *Angew. Chem. Int. Ed.*, 56(29):8402–8406, July 2017. doi: 10.1002/anie.201610727.

[136] Laura E. Ratcliff, Luca Grisanti, Luigi Genovese, Thierry Deutsch, Tobias Neumann, Denis Danilov, Wolfgang Wenzel, David Beljonne, and Jérôme Cornil. Toward Fast and Accurate Evaluation of Charge On-Site Energies and Transfer Integrals in Supramolecular Architectures Using Linear Constrained Density Functional Theory (CDFT)-Based Methods. *J. Chem. Theory Comput.*, 11(5):2077–2086, May 2015. doi: 10.1021/acs.jctc.5b00057.

[137] Dongsun Yoo, Hochul Song, Yong Youn, Sang Ho Jeon, Youngmi Cho, and Seungwu Han. A molecular dynamics study on the interface morphology of vapor-deposited amorphous organic thin films. *Phys. Chem. Chem. Phys.*, 21:1484–1490, 2019. doi: 10.1039/C8CP05294H.

[138] Guangchao Han, Xingxing Shen, and Yuanping Yi. Deposition Growth and Morphologies of C60 on DTDCTB Surfaces: An Atomistic Insight into the Integrated Impact of Surface Stability, Landscape, and Molecular Orientation. *Adv. Mater. Interfaces*, 2(17):1500329, November 2015. doi: 10.1002/admi.201500329.

[139] Benjamin P. Lyons, Nigel Clarke, and Chris Groves. The relative importance of domain size, domain purity and domain interfaces to the performance of bulk-heterojunction organic photovoltaics. *Energy Environ. Sci.*, 5(6):7657–7663, May 2012. doi: 10.1039/C2EE21327C.

[140] Yao-Tsung Fu, Chad Risko, and Jean-Luc Brédas. Intermixing at the Pentacene-Fullerene Bilayer Interface: A Molecular Dynamics Study. *Adv. Mater.*, 25(6):878–882, 2013. doi: 10.1002/adma.201203412.

[141] Carl Poelking and Denis Andrienko. Design Rules for Organic Donor–Acceptor Heterojunctions: Pathway for Charge Splitting and Detrapping. *J. Am. Chem. Soc.*, 137(19):6320–6326, May 2015. doi: 10.1021/jacs.5b02130.

[142] Melih Sener, Johan Strumpfer, Abhishek Singharoy, C Neil Hunter, and Klaus Schulten. Overall energy conversion efficiency of a photosynthetic vesicle. *eLife*, 5: e09541, August 2016. doi: 10.7554/eLife.09541.

[143] David E. Shaw, Paul Maragakis, Kresten Lindorff-Larsen, Stefano Piana, Ron O. Dror, Michael P. Eastwood, Joseph A. Bank, John M. Jumper, John K. Salmon, Yibing Shan, and Willy Wriggers. Atomic-Level Characterization of the Structural Dynamics of Proteins. *Science*, 330(6002):341–346, October 2010. doi: 10.1126/science.1187409.

[144] Tonghui Wang, Mahesh Kumar Ravva, and Jean-Luc Brédas. Impact of the Nature of the Side-Chains on the Polymer-Fullerene Packing in the Mixed Regions of Bulk Heterojunction Solar Cells. *Adv. Funct. Mater.*, 26(32):5913–5921, 2016. doi: 10.1002/adfm.201601134.

[145] Kyra N. Schwarz, Tak W. Kee, and David M. Huang. Coarse-grained simulations of the solution-phase self-assembly of poly(3-hexylthiophene) nanostructures. *Nanoscale*, 5 (5):2017–2027, 2013. doi: 10.1039/C3NR33324H.

[146] David M. Huang, Roland Faller, Khanh Do, and Adam J. Moulé. Coarse-Grained Computer Simulations of Polymer/Fullerene Bulk Heterojunctions for Organic Photovoltaic Applications. *J. Chem. Theory Comput.*, 6(2):526–537, 2010. doi: 10.1021/ct900496t.

[147] Riccardo Alessandri, Jaakko J. Uusitalo, Alex H. de Vries, Remco W. A. Havenith, and Siewert J. Marrink. Bulk Heterojunction Morphologies with Atomistic Resolution from Coarse-Grain Solvent Evaporation Simulations. *J. Am. Chem. Soc.*, 139(10): 3697–3705, March 2017. doi: 10.1021/jacs.6b11717.

[148] W. G. Noid. Perspective: Coarse-grained models for biomolecular systems. *J. Chem. Phys.*, 139(9):090901, September 2013. doi: 10.1063/1.4818908.

[149] Sergei Izvekov and Gregory A. Voth. A Multiscale Coarse-Graining Method for Biomolecular System. *J. Phys. Chem. B*, 109(7):2469–2473, 2005. doi: 10.1021/jp044629q.

[150] Dirk Reith, Mathias Pütz, and Florian Müller-Plathe. Deriving effective mesoscale potentials from atomistic simulations. *J. Comput. Chem.*, 24(13):1624–1636, October 2003. doi: 10.1002/jcc.10307.

[151] M. Scott Shell. The relative entropy is fundamental to multiscale and inverse thermodynamic problems. *J. Chem. Phys.*, 129(14):144108, 2008. doi: 10.1063/1.2992060.

[152] Cheng K. Lee, Chi C. Hua, and Show A. Chen. An ellipsoid-chain model for conjugated polymer solutions. *J. Chem. Phys.*, 136(8):084901, February 2012. doi: 10.1063/1.3687241.

[153] Cheng-Kuang Lee and Chun-Wei Pao. Multiscale Molecular Simulation of Solution Processing of SMDPPEH: PCBM Small-Molecule Organic Solar Cells. *ACS Appl. Mater. Interfaces*, 8(32):20691–20700, 2016. doi: 10.1021/acsami.6b05027.

[154] Alec S. Bowen, Nicholas E. Jackson, Daniel R. Reid, and Juan J. de Pablo. Structural Correlations and Percolation in Twisted Perylene Diimides Using a Simple Anisotropic Coarse-Grained Model. *J. Chem. Theory Comput.*, November 2018. doi: 10.1021/acs.jctc.8b00742.

[155] R. Berardi, C. Fava, and C. Zannoni. A generalized Gay-Berne intermolecular potential for biaxial particles. *Chem. Phys. Lett.*, 236(4):462–468, April 1995. doi: 10.1016/0009-2614(95)00212-M.

[156] R. Everaers and M. R. Ejtehadi. Interaction potentials for soft and hard ellipsoids. *Phys. Rev. E*, 67(4):041710, April 2003. doi: 10.1103/PhysRevE.67.041710.

[157] M. Babadi, R. Everaers, and M. R. Ejtehadi. Coarse-grained interaction potentials for anisotropic molecules. *J. Chem. Phys.*, 124(17):174708, May 2006. doi: 10.1063/1.2179075.

[158] M. Babadi, M. R. Ejtehadi, and R. Everaers. Analytical first derivatives of the RE-squared interaction potential. *J. Comput. Phys.*, 219(2):770–779, December 2006. doi: 10.1016/j.jcp.2006.04.014.

[159] W. Michael Brown, Matt K. Petersen, Steven J. Plimpton, and Gary S. Grest. Liquid crystal nanodroplets in solution. *J. Chem. Phys.*, 130(4):044901, January 2009. doi: 10.1063/1.3058435.

[160] A. J. Stone. The description of bimolecular potentials, forces and torques: The S and V function expansions. *Mol. Phys.*, 36(1):241–256, July 1978. doi: 10.1080/00268977800101541.

[161] Cheng-Kuang Lee, Chun-Wei Pao, and Chih-Wei Chu. Multiscale molecular simulations of the nanoscale morphologies of P3HT:PCBM blends for bulk

heterojunction organic photovoltaic cells. *Energy Environ. Sci.*, 4(10):4124–4132, September 2011. doi: 10.1039/C1EE01508G.

[162] Cheng-Kuang Lee and Chun-Wei Pao. Solubility of [6,6]-phenyl-c61-butyric acid methyl ester and optimal blending ratio of bulk heterojunction polymer solar cells. *J. Phys. Chem. C*, 116(23):12455–12461, 2012/06/14 2012. doi: 10.1021/jp3028947.

[163] Chih-Cheng Lin, Po-Hsun Ho, Chi-Liang Huang, Chao-Hung Du, Chen-Chieh Yu, Hsuen-Li Chen, Yun-Chieh Yeh, Shao-Sian Li, Cheng-Kuang Lee, Chun-Wei Pao, Ching-Pin Chang, Ming-Wen Chu, and Chun-Wei Chen. Dependence of nanocrystal dimensionality on the polymer nanomorphology, anisotropic optical absorption, and carrier transport in p3Ht:tio2 Bulk heterojunctions. *J. Phys. Chem. C*, 116(47):25081–25088, 2012/11/29 2012. doi: 10.1021/jp306921e.

[164] Eric Jankowski, Hilary S. Marsh, and Arthi Jayaraman. Computationally linking molecular features of conjugated polymers and fullerene derivatives to bulk heterojunction morphology. *Macromolecules*, 46(14):5775–5785, 2013/07/24 2013. doi: 10.1021/ma400724e.

[165] T. T. To and S. Adams. Modelling of p3Ht:pcbm interface using coarse-grained forcefield derived from accurate atomistic forcefield. *Phys. Chem. Chem. Phys.*, 16 (10):4653–4663, 2014. doi: 10.1039/C3CP54308K.

[166] Guankui Long, Rui Shi, Yecheng Zhou, Ailin Li, Bin Kan, Wei-Ru Wu, U-Ser Jeng, Tao Xu, Tianying Yan, Mingtao Zhang, Xuan Yang, Xin Ke, Litao Sun, Angus Gray-Weale, Xiangjian Wan, Hongtao Zhang, Chenxi Li, Yanting Wang, and Yongsheng Chen. Molecular origin of donor- and acceptor-rich domain formation in bulk-heterojunction solar cells with an enhanced charge transport efficiency. *J. Phys. Chem. C*, 121(11):5864–5870, 2017. doi: 10.1021/acs.jpcc.6b11824.

[167] Paola Carbone, Hossein Ali Karimi Varzaneh, Xiaoyu Chen, and Florian Müller-Plathe. Transferability of coarse-grained force fields: The polymer case. *J. Chem. Phys.*, 128 (6):064904, February 2008. doi: 10.1063/1.2829409.

[168] Samuel E. Root, Suchol Savagatrup, Christopher J. Pais, Gaurav Arya, and Darren J. Lipomi. Predicting the Mechanical Properties of Organic Semiconductors Using Coarse-Grained Molecular Dynamics Simulations. *Macromolecules*, 49(7):2886–2894, April 2016. doi: 10.1021/acs.macromol.6b00204.

[169] Burkhard Dünweg and Anthony J. C. Ladd. Lattice boltzmann simulations of soft matter systems. *Adv. Polym. Sci.*, 221:89–166, 2008. doi: 10.1007/12_2008_4.

[170] Jianzhong Wu and Zhidong Li. Density-functional theory for complex fluids. *Annu. Rev. Phys. Chem.*, 58(1):85–112, 2007. doi: 10.1146/annurev.physchem.58.032806.104650.

[171] G. H. Fredrickson, V. Ganesan, and F. Drolet. Field-theoretic computer simulation methods for polymers and complex fluids. *Macromolecules*, 35(1):16–39, January 2002.

[172] Akash Arora, Jian Qin, David C. Morse, Kris T. Delaney, Glenn H. Fredrickson, Frank S. Bates, and Kevin D. Dorfman. Broadly accessible self-consistent field theory for block polymer materials discovery. *Macromolecules*, 49(13):4675–4690, 2016. doi: 10.1021/acs.macromol.6b00107.

[173] G. A. Buxton and N. Clarke. Predicting structure and property relations in polymeric photovoltaic devices. *Phys. Rev. B*, 74(8):085207, August 2006.

[174] Junwei Xue, Tingjun Hou, and Youyong Li. Optimal parameters for morphology of bulk heterojunction solar cells from simulations. *Appl. Phys. Lett.*, 100(5):053307, January 2012. doi: 10.1063/1.3681947.

[175] Manas Shah and Venkat Ganesan. Correlations between morphologies and photovoltaic properties of rod−coil block copolymers. *Macromolecules*, 43(1):543–552, December 2010. doi: 10.1021/ma9020467.

[176] Wenlin Zhang, Enrique D. Gomez, and Scott T. Milner. Predicting nematic phases of semiflexible polymers. *Macromolecules*, 48(5):1454–1462, 2015. doi: 10.1021/acs.macromol.5b00013.