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Design strategies for organic semiconductors beyond the molecular formula

Zachary B. Henson[1], Klaus Müllen[2]* and Guillermo C. Bazan[1]*

Organic semiconducting materials based on polymers and molecular systems containing an electronically delocalized structure are the basis of emerging optoelectronic technologies such as plastic solar cells and flexible transistors. For isolated molecules, guidelines exist that rely on the molecular formula to tailor the frontier (highest occupied or lowest unoccupied) molecular orbital energy levels and optical absorption profiles. Much less control can be achieved over relevant properties, however, as one makes the transition to the ensemble behaviour characteristic of the solid state. Polymeric materials are also challenging owing to the statistical description of the average number of repeat units. Here we draw attention to the limitations of molecular formulae as predictive tools for achieving properties relevant to device performances. Illustrative examples highlight the relevance of organization across multiple length scales, and how device performances — although relevant for practical applications — poorly reflect the success of molecular design.

There are widespread efforts in scientific and engineering disciplines towards developing new technologies to make use of organic semiconductors[1]. It is an area of research where organic, organometallic and polymer synthesis converge for the molecular design and preparation of the active components in devices such as light-emitting diodes (LEDs), field-effect transistors (FETs) and solar cells. The active semiconducting materials can be broken into two broad classes: π-conjugated molecular systems[2,3], with precisely defined structures, and π-conjugated polymers[4], which are described by a repeating unit and a molecular weight distribution. To achieve the maximum potential of these devices, challenges arise from considerations that reach beyond the molecular formula[5]. In this Perspective, we include selected examples that highlight these difficulties and some recent successes in structural control across multiple length scales that are proving essential for the push towards practical implementation. We do not aim at comprehensive coverage of the literature; there are several relevant reviews available[2–8]. Our purpose is to provide a succinct summary of some pressing and important challenges that those interested in entering this exciting area of research may initially find difficult to appreciate, given the vast body of previous work.

Before we consider the molecular formula and question what it tells us about the electronic and optical properties of the active component of a device, one important point has to be made: this formula stands for a wide family of possible species. For conjugated polymers, these can differ in molecular weight, in polydispersity and in the chemical groups that make up the chain ends. Increasing molecular weight has been shown to improve device performance, which ultimately relates to the supramolecular order and morphology[9] (see below). A related conclusion can be drawn for the polydispersity, because it is expected to affect the ordering of polymer chains into, for example, a lamella-type packing. Even for small molecules, which circumvent these structural considerations, one finds that geometrical factors such as molecular size and shape affect the solid-state arrangement and the resulting properties and function. Scrupulous purification is mandatory throughout, because impurities of either organic or inorganic origin may act as charge-carrier traps or exciton quenching sites[10,11].

When considering the use of (i) an electroluminescent layer in a LED, (ii) a p-type, n-type or ambipolar semiconductor in a FET, or (iii) a donor or acceptor component in a solar cell, the chemist has three useful structural handles: the olefinic or aromatic framework that describes the backbone repeat unit; the size and manner in which the repeat unit is propagated; and the solubilizing side chains (Fig. 1). Structures that stabilize the quinoidal form and/or use alternating electron-rich and electron-poor units to introduce a strong intramolecular charge-transfer band allow one to achieve desirable absorption/emission profiles and molecular orbital energy levels[4,6]. Nonetheless, the literature is replete with examples of semiconducting materials that fit what one would consider to be optimal molecular properties, yet do not yield devices with correspondingly high performances. Another challenge therefore arises: the transition from the well-understood characteristics of an isolated molecule or polymer chain (that is, 'molecular' properties) to the collective behaviour of multiple units in active-layer thin films (that is, 'material' properties) is not fully understood and lacks straightforward rules (Fig. 1, middle).

What determines a 'material' property for a given conjugated molecular or polymeric system is a well-defined macroscopic state of matter. These states can exist within fibres, films or crystals, and can even be defined in conjunction with interfaces. The packing of the molecular components in these various situations mediates their electronic coupling. How the size and orientation of the repeat unit can be used to control this organization a priori is poorly understood. Side chains are another important consideration, as their size, topology, chemical make-up and distribution within the molecular framework dictate to what extent the molecules can be solution-processed and play an important role in directing self-assembly. For instance, in a FET, the mode of packing and the degree of supramolecular order are crucial for high charge-carrier mobility (μ). Moreover, it is worth recalling that the FET charge-carrier mobility depends critically on the packing in the first few layers adjacent to the dielectric interface; this adds yet another consideration to supramolecular control[12]. Values of charge-carrier mobility have increased on average by one order of magnitude in the past decade

[1]Department of Chemistry & Biochemistry, Department of Materials, Center for Polymers and Organic Solids, University of California Santa Barbara, California 93106, USA; [2]Max Planck Institute for Polymer Research, Ackermannweg 10 D-55021 Mainz, Germany. *e-mail: muellen@mpip-mainz.mpg.de; bazan@chem.ucsb.edu

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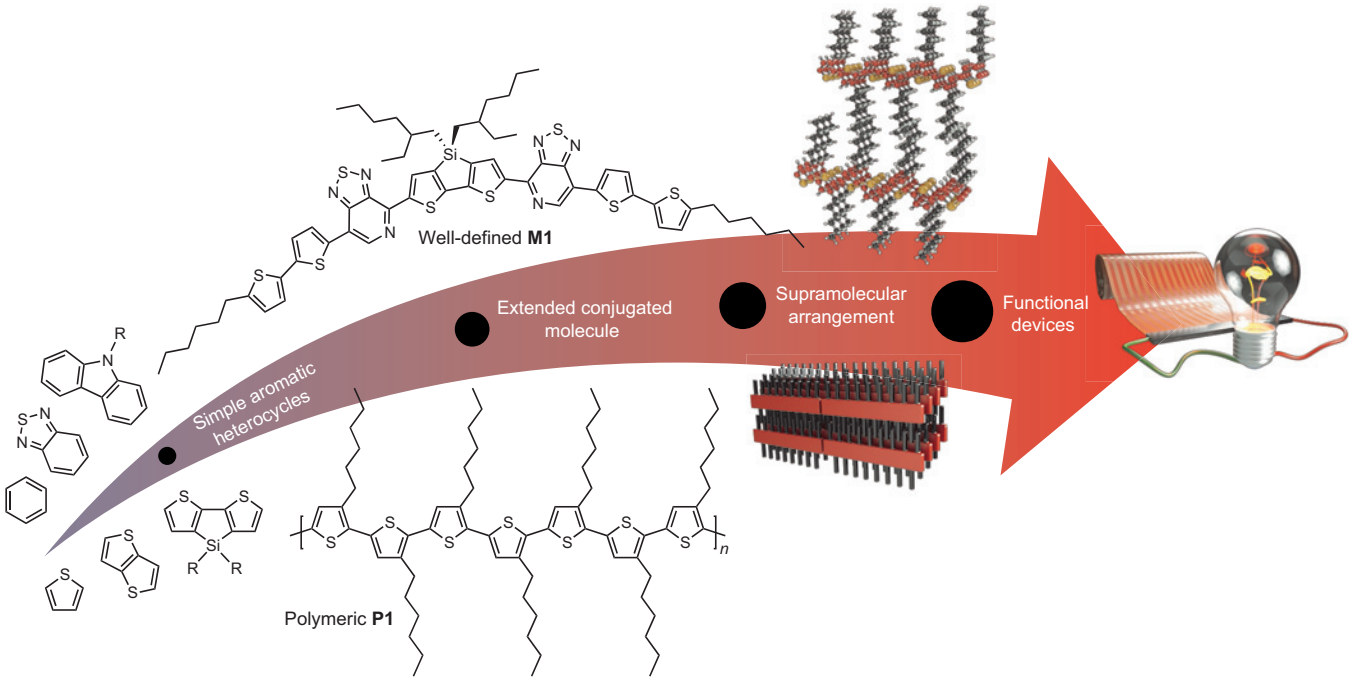

Figure 1 | Beyond the molecular level. An important challenge in organic semiconducting materials research is to understand the transition from simple conjugated building blocks to extended semiconducting molecules with predictable properties, and ultimately to the collective behaviour of multiple components in functional devices.

through improved synthesis, purification and processing. In the widely studied bulk heterojunction solar cells, the complexity of the active thin film increases, as two components are involved[4]. Their nanophase separation defines the occurrence of separate percolation pathways for holes and electrons. Apparently trivial changes in the solvent composition[13], the underlying substrate[14] and the thermal management history influence the film characteristics and can ultimately define the final optoelectronic performance. One essential challenge is thus to learn to predict and control these levels of order. Introduction of new building blocks will be unlikely to push organic optoelectronic devices to higher levels of performance in a rational manner unless design principles are found that provide control over parameters beyond the properties of the isolated chromophore[15].

Although daunting at this stage, the challenges described above lead to important new lines of scientific inquiry, and indicate that we need new paradigms for considering how the chemical structure can be used not only to achieve appropriate optoelectronic properties, but also to help as a design element when the material is incorporated into a device. The interplay of convoluted forces involved in determining intermolecular organization, particularly from solution and as a function of substrate and deposition methods cannot be managed at this time, and it has only recently

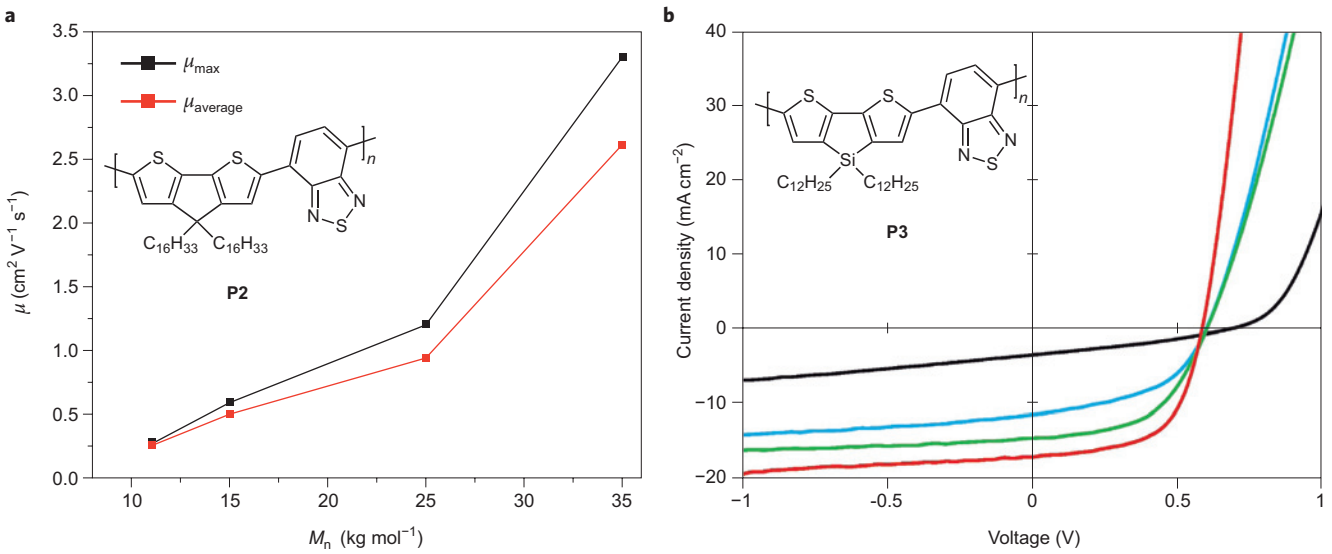

Figure 2 | Molecular weight characteristics substantially influence performance in polymer electronic devices. a, Graphical illustration of the relationship between number-average molecular weight (M_n) and average ($\mu_{average}$) and maximum (μ_{max}) saturated hole mobilities for **P2**. **b**, Current density–voltage characteristics of **P3**:**PC$_{71}$BM** solar cells as a function of the number-average molecular weight (M_n); black line: M_n = 7 kg mol^{-1}; blue line: 14 kg mol^{-1}; green line: 25 kg mol^{-1}; red line: 34 kg mol^{-1}. Figures reproduced with permission from: **a**, ref. 9. © 2011 ACS; **b**, ref. 17. © 2009 NPG.

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become possible to obtain detailed structural characterization of the active thin-film components[16].

In this Perspective we provide a brief summary of the possibilities and limitations of simple chemical descriptions for predicting device performance and fundamental properties of interest. We highlight some critical attributes beyond the molecular formula that have been shown to affect the performance of materials when incorporated into devices. We also draw attention to recent work on molecular systems that overcome many of the structural inconsistencies in polymers, but still provide the challenge of coordinating the collective behaviour. Finally, we stress how examination of device performance, although relevant from a 'bottom line' practical perspective, is not an accurate foundation for determining the success of molecular design.

Statistics of single and multi-chain structures

Because polymer samples are mixtures of structurally related macromolecules that differ in number and distribution of repeat units per chain, one finds that a given polymer structure (as simply described by a molecular drawing) can give rise to a range of materials. There is a considerable challenge in finding how best to couple the statistical nature of macromolecules with the properties of the repeat unit and somehow incorporate the choice of processing.

Influence of molecular weight characteristics. Considerable improvements in the electronic properties of conjugated polymers have been realized by optimizing organic and organometallic reaction conditions to achieve high molecular weights and high purity[17–21]. For one of the most studied conjugated polymers, poly(3-hexylthiophene) (P3HT, **P1**), the optoelectronic performance has repeatedly been shown to depend on the molecular weight, with higher values leading to better device performance[22]. The increased performances are accompanied by important changes in the thin-film morphology: systems with high molecular weight often exhibit reduced crystallinity and more isotropic films, potentially leading to larger values for charge-carrier mobility[22].

More recently, the influence of molecular weight on morphology and electronic properties of donor–acceptor conjugated copolymers has been studied, with field-effect mobilities and solar cell performance improving significantly with increasing molecular weight for **P2** and **P3** (poly[(4,4-dihexadecylcyclopenta-[2,1-b:3,4-b′]dithiophene)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] and poly[(4,4-didodecyldithieno[3,2-b:2′,3′-d]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl], respectively; Fig. 2)[9,17]. **P2** and **P3** are structurally related, possessing a dialkyl-substituted fused thiophene donor unit and benzothiadiazole acceptor unit. In **P3**, silicon is substituted for carbon as the bithiophene bridging atom. As shown in Fig. 2a, thin-film transistors using **P2** with molecular weight of 11, 16, 25 and 35 kg mol^{-1} exhibited hole mobilities of 0.28, 0.59, 1.2 and 3.3 cm^2 V^{-1} s^{-1}, respectively, displaying a nearly linear increase in transistor performance with increasing molecular weight[9]. For solar cells consisting of **P3**/**PC$_{71}$BM** bulk heterojunction active layers (where **PC$_{71}$BM** is phenyl-C$_{71}$-butyric acid methyl ester) the short-circuit current was increased from 4.2 to 17.3 mA cm^{-2} and the fill factor rose from 0.35 to 0.61 as the molecular weight increased from 7 to 34 kg mol^{-1}. These changes resulted in nearly a fivefold enhancement in the power conversion efficiency (PCE) from 1.2 to 5.9% (ref. 17).

End-group contributions and extrinsic impurities. As well as the size and distribution of polymer samples, the chain-terminating functional groups offer a further structural consideration[23]. These end groups may influence device parameters by acting as chemical traps, quenching photogenerated excitons, disrupting chain packing (sterically or by the introduction of dipoles) or accelerating degradation[24–26]. A comparison of bromine and hydrogen end-capped **P1** showed reduced optical absorption, increased rate of exciton quenching and inferior solar cell performance for the bromide-substituted derivative[24]. Similar results were found for **P3**, in that thiophene-capped samples showed greater device performance and stability when compared with unfunctionalized **P3**, containing residual tin and bromide end caps that trace their origins from the Pd-mediated Stille-coupling polymerization procedures[25]. It has also been suggested that a polymer's surface energy can be systematically modified through changes to the end group, which creates the potential to modify molecular orientation relative to different substrates and to control phase separation within polymer-blend films[23,26].

The above discussion on end-group contributions should be taken as part of the general issue of purity. There are excellent demonstrations that the presence of extrinsic contamination can have a serious negative impact on the function of organic semiconductors

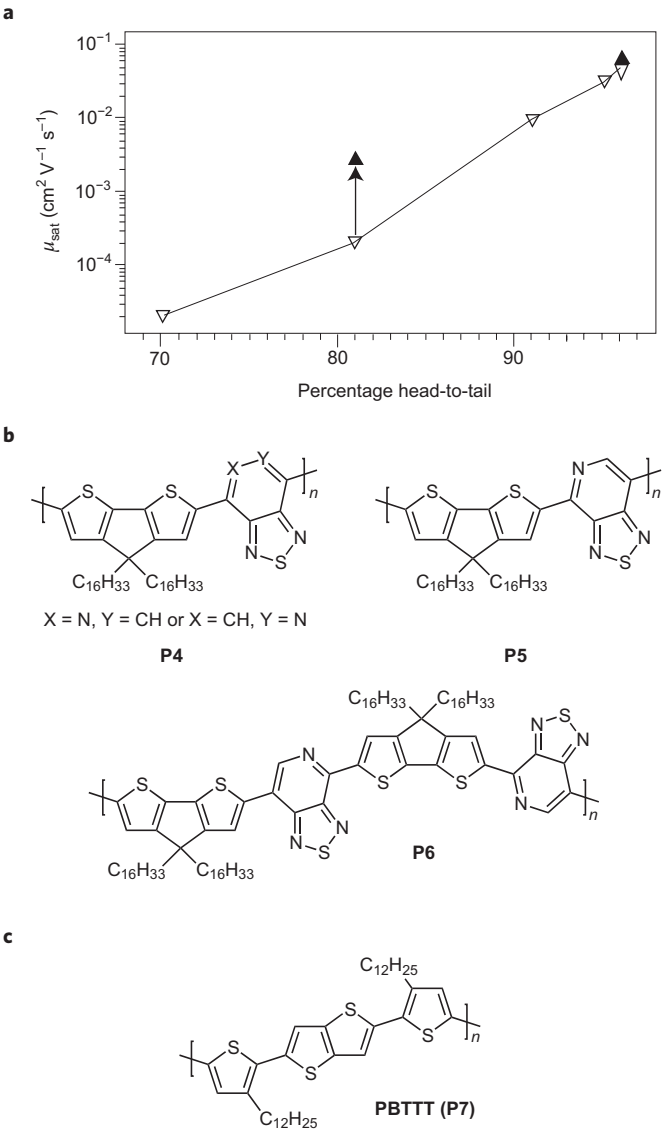

Figure 3 | Methods for controlling intra- and intermolecular order and the influence on thin-film morphology or electronic properties. a, Charge-carrier mobility of spin-coated (downward triangles) and solution-cast (upward triangles) **P1** as a function of regioregularity. **b**, Regiochemical considerations based on conjugated backbone heteroatom organization; **P4**, **P5** and **P6** are regioregular polymers, with **P4** being less ordered. **c**, Example of a polymer chain with built-in symmetry from the reactive monomer. Part **a** reproduced with permission from ref. 27. © 1999 NPG.

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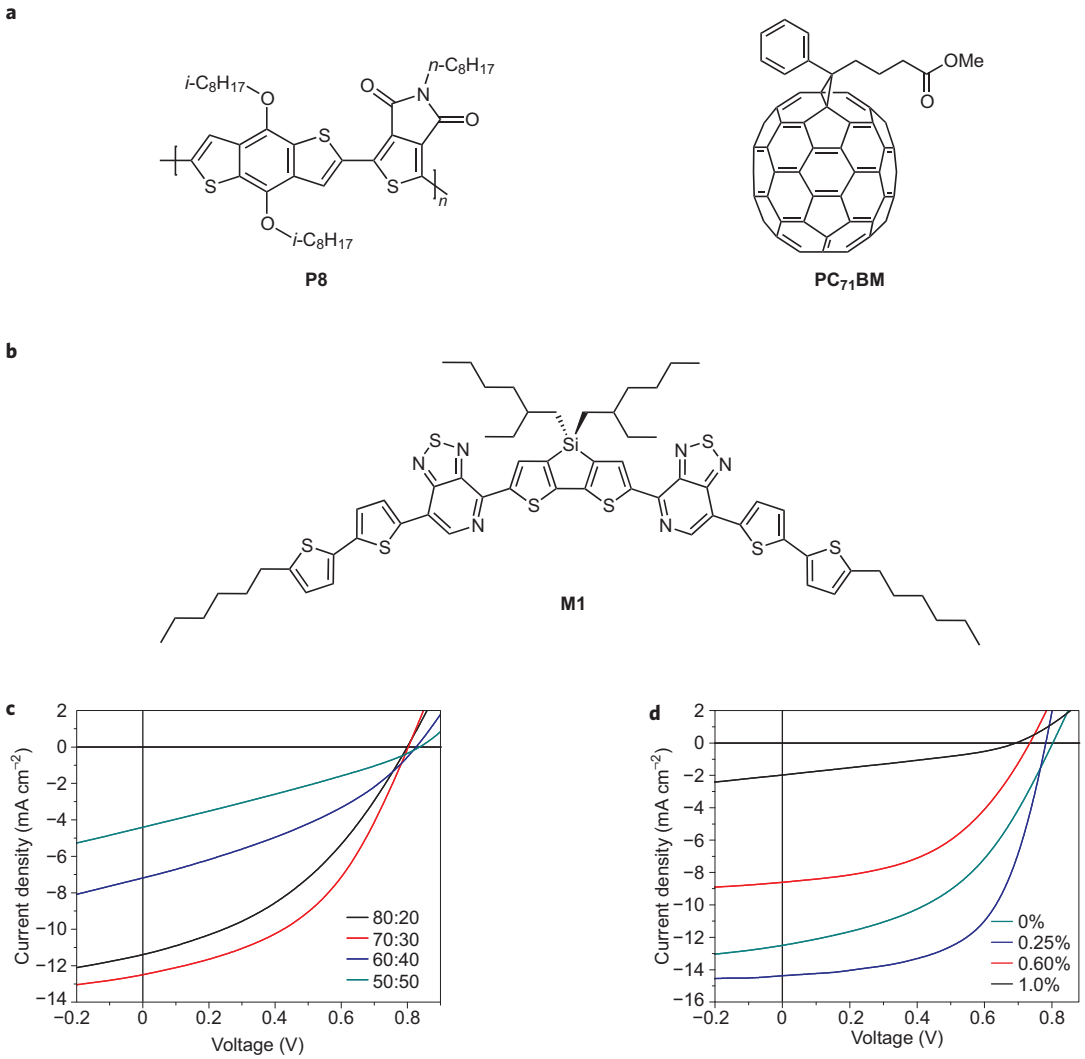

Figure 4 | Device performance of polymer and molecular samples with identical structures and similar molecular weight characteristics vary widely as a result of different processing conditions. a, Molecular structures of **P8** (PBDTTPD) and **$PC_{71}BM$**. **b**, Molecular structure of **M1** (DTS($PTTh_2$)$_2$). **c**,**d**, Summary of solar-cell results for **M1**:**$PC_{71}BM$** blends as a function of (**c**) **M1**:**$PC_{71}BM$** ratio and (**d**) volume per cent of diiodooctane additive used. Part **c** reproduced with permission from ref. 45. © 2012 NPG.

within a device[10,11]. Thus, from a synthetic perspective, preparative routes that minimize difficult-to-remove by-products are growing in importance[19,20].

Effect of intra- and intermolecular order on charge transport. Simple changes to the orientation of the repeat units along the backbone vector affect the bulk film order and electronic behaviour. In the case of the previously discussed **P1**, which possesses a non-centrosymmetric repeat unit (Fig. 1, middle), increased order and device performance have been observed following enhancement of the regioregularity, whereby monomers alternate precisely in head-to-tail fashion (Fig. 3a)[21,27]. One early study showed an increase by three orders of magnitude, from 10^{-4} to 10^{-1}, in charge-carrier mobility as the degree of regioregularity was increased (Fig. 3a)[27]. Note also in Fig. 3a how the mode of film deposition influences charge carrier mobility. For photovoltaics, a study of 91%, 93% and 95% regioregular **P1** samples exhibited power conversion efficiency values of 0.7%, 1.8% and 2.4%, respectively[28]. The improved performance was explained on the basis of improved charge transport in samples with higher regioregularity, owing to improvements in interchain packing (Fig. 1)[28]. Thus, the way in which monomeric units are arranged throughout the polymer chain should be carefully considered.

The orientation of asymmetric donor or acceptor building blocks in the backbone of narrow-bandgap conjugated polymers need also be considered, as demonstrated for the pyridylthiadiazole (PT) unit (Fig. 3c)[29]. Two regioregular polymers of poly[(4,4-dihexadecylcyclopenta-[2,1-b:3,4-b′]dithiophene)-2,6-diyl-*alt*-([1,2,5]thiadiazolo[3,4-c]pyridine)-4,7-diyl] (**P5**, **P6**) with alternative spatial orientation of the PT unit and a sample with less regiochemical precision (**P4**) have been prepared (Fig. 3b). Each regioregular sample shows a greater degree of structural order, and charge-carrier mobility two orders of magnitude larger than in the regiorandom sample. Design of symmetric monomeric units, as achieved in the case of **P7** (poly(2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene); Fig. 3c), is one route to ensure more order within the bulk and decrease the demands on the selectivity of polymerization reactions[30]. **P7** also has decreased alkyl chain density relative to **P1**, allowing for greater side-chain interdigitation and closer packing (Fig. 1). Thin-film diffraction measurements indicate that as-cast **P7** films possess ordered crystalline domains, and post-deposition annealing can be used to influence the size of the crystalline domains[31]. Molecular arrangements with respect to the substrate surface play an important role in device characteristics, and a more thorough understanding of structural features that

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guide preferential orientations will be needed to select the appropriate combination of active layer, substrate and, if necessary, modifying interlayers for desired applications.

Isoelectronic substitutions. Replacement of individual atoms in building blocks with isoelectronic atoms can yield materials with widely different properties. One class concerns conjugated molecules built upon Group 16 aromatic heterocycles, namely furan[32], thiophene[21], selenophene[33] and tellurophene[34], wherein the heteroatom choice influences molecular geometry, HOMO–LUMO gap, ionization potential, intermolecular interactions and supramolecular organization. Another example concerns polymers composed of bithiophene systems fused by group 14 atoms C, Si and Ge (for example **P2** and **P3** in Fig. 2). In these systems, Si for C substitution leads to improved solid state ordering and is a likely explanation for the enhanced transport observed[17,35,36]. One hypothesis for the enhanced ordering in Si-containing relative to C-containing systems is that the longer Si–C bond places the solubilizing alkyl side groups further from the π-conjugated backbone and allows more intimate chain–chain interactions. With this in mind a dithienogermole analogue was synthesized and demonstrated excellent organic photovoltaic performance[37].

Device performance versus success in molecular design

Beyond the design of promising conjugated polymer materials, the influence of processing conditions in determining the final bulk properties cannot be understated. In films cast from solution, issues such as nucleation, phase formation and wetting/dewetting are important. The solution composition and substrate serve as additional controls in this case and post-deposition treatments also play a large role. A case in point is **P1**, which one might think from the number of publications must have been exhaustively optimized, but which continues to be further refined[38]. Recent reports on **P8** (poly[(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b′]dithiophene)-2,6-diyl-*alt*-(5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione)-1,3-diyl]; Fig. 4a) highlight the difficulties in evaluating the potential of a given molecular structure. Three independent groups simultaneously reported the synthesis and organic photovoltaic performance of **P8**. When incorporated into a solar cell, the same polymer structure resulted in power conversion efficiencies ranging from 4.2% to 6.6%, largely owing to differences in fill factor and short-circuit current, with no obvious trends due to molecular weight discrepancies. This shows how inaccurately the device performance reflects the capability and potential of a given polymer structure[39–41].

Considering the complex matrix of device optimization strategies available, and the present emphasis on device performance, the straightforward optimization of individually promising materials has become increasingly time-consuming. Whereas synthetic chemistry allows straightforward and rapid synthesis of functional molecules, thin-film engineering continues to demand an Edisonian, trial-and-error approach[38,42]. Strategies for directed supramolecular assembly to attain active layers with optimal and stable morphological and transport characteristics without post-deposition treatments will simplify incorporation into less sensitive, more reproducible devices[43].

Supramolecular assembly in molecular semiconductors

Molecular systems are gaining popularity as a design tool to circumvent complications inherent to the molecular weight distributions of polymers[2,3,44,45]. Most of these systems consists of repeat units similar to those encountered in conjugated polymers, and the influence of each unit on the overall optical and electronic properties is an emerging area of study, particularly within the context of solar cell research[2,3,46]. Molecular semiconductors are expected not to suffer from batch-to-batch variability, and their structural features can be comprehensively characterized using conventional spectroscopic techniques. Additionally, single-crystal X-ray diffraction measurements are possible, and provide key information related to packing motifs, grain boundaries and side-chain interactions[47]. These additional characterization methods may make the transition from the single chain to bulk molecular properties more straightforward to understand and promise to reduce some of the trial and error in device optimization.

Despite this, the challenge of understanding how weak forces come together to determine bulk organization of molecular semiconductor systems remains unsolved. Indeed, the handles available to the chemist may become even more important, as the influence of individual fragments can be identified more easily, and more options for structural modification exist, as one is no longer limited by the propagation of a single repeat unit. For example, the position of the solubilizing side chains relative to the π-conjugated backbone (that is, parallel versus perpendicular) becomes increasingly important. Similarly to polymers, the side chains serve two roles: (i) enabling dissolution of the chromophore and (ii) directing self-assembly, and thus a balance between desired molecular features and synthetic complexity must be found.

Some of the best-performing molecular solar cells suggest that molecular systems may be more sensitive to deposition conditions than are polymeric materials. For example, in a recent high-performing molecular solar cell consisting of **M1** (5,5′-bis[(4-(7-hexylthiophen-2-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine]-3,3′-di-2-ethylhexylsilylene-2,2′-bithiophene) and **PC$_{71}$BM** (Fig. 4b), incorporation of only 0.25% v/v diiodooctane additive into the pre-deposition solution of an optimized blend ratio (Fig. 4c) resulted in a nearly 50% increase in power conversion efficiency, from 4.5 to 6.7% (Fig. 4d), owing to an adjustment in the sizes of donor and acceptor domains[45]. Whether this observation holds generally for newly developed systems remains to be determined.

Concluding remarks

Successes in molecular design and understanding of materials properties have made organic semiconducting materials a lively area of academic and industrial research. Practical implementation of this class of materials still requires further control over the transition between well-understood 'molecular' and desirable 'material' properties. Thin-film characterization techniques, including grazing-incidence X-ray scattering[48], solid-state nuclear magnetic resonance spectroscopy[9] (particularly for understanding relationships between the 'inert' solubilizing side groups), energy-filtered transmission electron microscopy[49] and tomographic techniques[50], are increasingly being developed to provide insight into the nanoscale and intermolecular organizations as a function of material and processing conditions. This information should aid in reaching the ultimate goal of making a rational connection between molecular structure, bulk organization, the forces that control self-assembly and device performance.

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Additional information

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Competing financial interests

The authors declare no competing financial interests.

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