



Conjugated polymers based on selenophene building blocks

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Abstract

The intrinsic flexibility, solution processability, and optoelectronic properties of semiconducting conjugated polymers make them ideal candidates for use in a wide range of next-generation electronic devices. A virtually unlimited chemical design space has led to diverse polymeric architectures made from combinations of smaller molecular building blocks with desirable functionalities. Of these, thiophene is undoubtedly the most common due to its mixture of synthetic versatility, polymer backbone planarizing effects, and good optoelectronic characteristics. However, the success of thiophene has meant that other heterocycles, such as selenophene, remain relatively underexplored. This focus review discusses the challenges and material advantages of incorporating selenophene into conjugated polymer systems within the context of our contributions to the field. The early studies of poorly performing electrochemically synthesized polyselenophenes are outlined, progressing onto the model chemically synthesized alkylated homopolymers that revealed the key consequences of selenophene addition. We then review the various donor and donor-acceptor copolymer strategies that have exploited the properties of the selenium atom to enhance the performance of solar cells, transistors, and other organic electronic devices. Finally, we give our perspective on the state of the field and the fundamental material optimization studies required to realize the full potential of selenophene-containing conjugated polymers.

Introduction

From the discovery of semiconducting phenomena in the early nineteenth century through the introduction of band theory and commercialization of the first transistor devices, semiconductors almost exclusively comprised inorganic compounds and high purity metalloids. In the last 60 years, however, the scope has grown immensely through the development of organic semiconductors, motivated by the desire to achieve ever better electrical, mechanical, and optical properties from ever more economical materials and processes. Of these, conjugated polymers have attracted the most widespread attention. Their unique advantages over inorganic counterparts, including solution processability,

low cost, and compatibility with flexible substrates, coupled with a virtually limitless structural design space have made these polymeric semiconductors the preferred materials for a variety of next-generation electronic devices [1].

Conjugated polymers generally consist of a π -conjugated sp^2 carbon-based backbone surrounded by aliphatic side chains, responsible for, to a first approximation, the optoelectronic properties and solution processability, respectively (Fig. 1). The former remains the focus of much of the research in this area, largely due to the inferiority of these materials relative to inorganic semiconductors on many optoelectronic performance metrics. This performance can be enhanced through judicious design of the conjugated backbone to tune the frontier molecular orbitals (and therefore the band gap) for the desired application and to maximize the π -orbital overlap between polymer chains to aid charge carrier mobility. In pursuit of these aims, myriad inventive and complex architectures have been reported, built from combinations of simpler molecular building blocks. One such building block is thiophene, an electron-rich heterocycle that is prevalent in the organic electronics literature [2, 3]. Thiophene aids planarization and rigidification of conjugated backbones (increasing the conjugation length), while the polarizability of the sulfur atom increases intermolecular contacts (helping to stack

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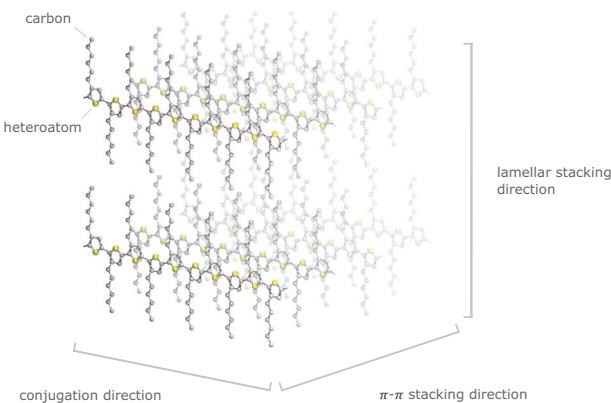


Fig. 1 Structure, packing, and molecular design principles of a model heterocycle-based alkylated conjugated homopolymer (e.g., P3HT). Hydrogen atoms were removed for clarity

polymer chains) and π -orbital overlap between chains. It is also easily substituted and polymerized via a range of techniques. Indeed, while no longer the best performing example, poly(3-hexylthiophene) (P3HT) is undoubtedly the most well-known and studied conjugated polymer (chemical structures of all polymers abbreviated in this Focus Review are provided in Supplementary Table 1 of the Supplementary Information).

Despite the efficacy of thiophene, however, a combination of practical, synthetic, and material challenges has meant that most of the other chalcogen-containing heterocycles remain relatively underexplored in conjugated polymer research. Furans are generally unstable in the presence of light and oxygen except when combined with electron-withdrawing groups or annulated with other π -conjugated systems [4], and tellurium compounds have poor photostability relative to the sulfur or selenium analogs [5]. In the case of selenophenes, however, the stability and chemistry are broadly similar to those of thiophenes, enabling direct substitution in conjugated systems. This strategy of heteroatom substitution is an effective means of tuning the organic electronic material properties without increasing the carbon content [6], which may adversely impact the cost and processability. Accordingly, in the last couple of decades, replacing thiophene with selenophene has been explored as a rational approach to enhancing the optoelectronic properties of conjugated polymers and, indeed, small molecule materials [7–12].

This focus review combines our research with the key works of others to provide an overview of the selenophene-containing conjugated polymer literature. First, the early homopolymer studies that elucidated the general effects of selenophene incorporation are discussed, followed by a comprehensive analysis of the optoelectronic and material properties of the selenophene analog of P3HT, poly(3-hexylselenophene) (P3HS). Attempts to synergistically combine the properties of selenophene with other molecular

building blocks in donor and donor-acceptor copolymer systems are reported, and the performance of all these materials in organic electronic devices is summarized. Finally, we provide our perspective on the future development of selenophene-containing conjugated polymers.

Early polyselenophene exploration

Early studies exploring the incorporation of selenophene into conjugated polymer systems were focused on the electrochemical preparation of polyselenophenes [13]. Applying an electrical potential to an organic solution containing selenophene and an electrolyte (LiClO_4) yielded films of polyselenophene (PSe) on the surface of the anode with a thickness, quality, and conductivity similar to those of similarly prepared polythiophene [14, 15]. Upon chemical oxidation (commonly known as doping) using ClO_4^- or I_2 , the conductivity increased dramatically from $\sim 10^{-10}$ to $\sim 10^{-3} \text{ S cm}^{-1}$; however, even at saturated doping concentrations, this was significantly lower than that of doped polythiophene. Studies of 3-methyl and 3-methoxy-substituted polyselenophenes revealed similar trends [16]. Electron spin resonance spectroscopic analyses of PSe suggested that charge transfer between neighboring heterocycles and delocalization of π -electrons in the chain were suppressed [14, 15]. It was proposed that, unlike the case for polythiophene, the size and preferred bonding angle of the Se atom would limit both the chain length and coplanarity of the constituent ring systems, thus reducing the conjugation length and electrical conductivity [14]. This hypothesis was later supported by ultraviolet-visible (UV-vis) absorption spectroscopic investigations of electrochemically synthesized P3HS, which revealed a larger optical band-gap compared to that of P3HT (2.4 eV and 2.5 eV, respectively, in solution) [17]. Moreover, unlike P3HT [18], the absorbance of P3HS was found to be independent of temperature, which suggested limited planarity of the backbone and conjugation between neighboring monomer units due to unfavorable interactions between the Se atom and nearby alkyl chains [17]. P3HS synthesized via oxidative polymerization with FeCl_3 catalyst showed similar behavior [19].

These initial explorations into polyselenophenes revealed largely disappointing properties; however, they utilized the – only available – hard-to-control polymerization methods that, although not reported, likely yielded polymers with low regioregularity. This point was underlined by the first report of well-defined, chemically synthesized oligoselenophenes [20]. Using a range of Ullmann and Stille couplings, all oligoselenophenes from the monomer to the pentamer were synthesized and obtained in high purity (Fig. 2).

An investigation of the optical properties showed that the absorbance related to the $\pi-\pi^*$ transition was

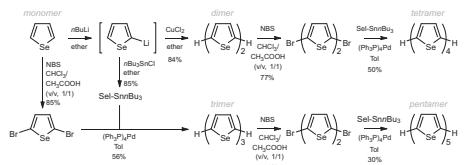


Fig. 2 Ullmann and Stille synthetic routes to oligoselenophenes (from monomer to pentamer)

bathochromically shifted with increasing chain length. The absorption maxima of the oligomers were consistently ~30 nm than their thiophene counterparts, suggesting, in contrast to previous studies, distinct stabilization of these absorption bands upon selenium incorporation. Moreover, the conductivities of I₂-doped samples were comparable to those of thiophene equivalents, which clearly demonstrated that, at least in the case of well-controlled, 2-2'-linked oligomeric samples, selenophene was not detrimental to optoelectronic properties [20]. Computational analyses provided theoretical support for these findings. A conformational study of selenophene oligomers predicted a planar *anti* form structure for PSe [21]. Separately, and in conflict with electrochemical polymerization studies, an analysis of the bonding in heterocycle homopolymers suggested that less electronegative and more polarizable π -donating heteroatoms (i.e., selenium relative to sulfur) had a stabilizing effect on the lowest unoccupied molecular orbital (LUMO) and a minimal (but destabilizing) effect on the highest occupied molecular orbital (HOMO) [22]. Accordingly, the intrinsic band gap of PSe was expected to be lower than that of polythiophene [22, 23] and the conductivity was expected to be greater, assuming similar interchain interactions.

Chemically synthesized selenophene homopolymers

Based on the preceding literature, we hypothesized that the reported performances of PSe and other selenophene homopolymers were limited by the polymer lengths, mis-couplings, and relative regiochemistry (of the side chains) arising from the relatively uncontrolled electrochemical synthetic techniques. Accordingly, we developed a Grignard metathesis route to head-to-tail coupled P3HS (Fig. 3a) [24]. The dibrominated 3-hexyl-selenophene was treated with ~1 equivalent of n-butylmagnesium chloride to yield a mix of mono-Grignard products (with preferential substitution at the 5-position). Addition of Ni(dppe)Cl₂ enabled smooth conversion to the polymer in high yield, proceeding via a regiospecific mechanism controlled by catalyst-chain π -interactions, as outlined by Yokoyama [25] and McCullough [26].

The average molecular weights (M_w s, as measured by gel-permeation chromatography against polystyrene standards) of the polymers were 70,000 to 200,000 g mol⁻¹, and nuclear magnetic resonance spectroscopic (NMR) investigations revealed a high regioregularity of 97%. Both in solution and the solid-state, the absorbance-onset wavelength for P3HS was lower than that for P3HT, indicating a correspondingly smaller band gap (1.6 eV and 1.9 eV for P3HS and P3HT, respectively, Fig. 3b) [24]. Cyclic voltammetry (CV) studies suggested that this reduction was most likely due to stabilization of the LUMO due to selenium incorporation, with minimal changes to the HOMO (Fig. 3c), as predicted by theory [22]. It was later shown that substitution of sulfur with selenium reduces interring bond lengths with a larger contribution from quinoidal resonance structures in the ground state, which makes poly-selenophene backbones rigid and hard to twist [27, 28]. Films of P3HS displayed crystalline structures with a higher photostability than P3HT, which was ascribed to the deeper LUMO and p-type behavior in organic field-effect transistors (OFETs) (Fig. 3d).

Given this combination of reduced band gap, good film morphology, and high stability, we anticipated that P3HS may be amenable to photovoltaic applications as a donor material and undertook a series of studies on P3HS/[6,6]-phenyl-C61-butric acid (PCBM) films in comparison to P3HT equivalents. As in the case of P3HT, PCBM introduction into P3HS led to a bathochromic shift in the absorbance, which was partially restored by annealing and the corresponding π - π stacking self-organization of the P3HS domains [29]. The optimal annealing temperature was higher for P3HS as a result of a higher glass transition temperature due to stronger interchain interactions. In solar cell devices, the spectral coverage of the P3HS:PCBM device was notably larger than that for the P3HT:PCBM device (due to the narrower band gap), while the peak external quantum efficiency (EQE) was lower [29], likely due to the lower hole mobility for P3HS relative to P3HT [24]. The comparable HOMO levels of the two polymers led to similar open-circuit voltage (V_{OC}) values, but P3HS displayed a larger short-circuit current density (J_{SC}) due to its broad absorbance. However, the fill factor (FF) for the P3HS:PCBM device was lower, leading to a slightly inferior power conversion efficiency (PCE) relative to that of P3HT:PCBM (2.7 and 3.0%, respectively). Our subsequent study, in which we investigated the fundamental reasons for the poorer performance of P3HS:PCBM devices, showed that while P3HS is highly crystalline and forms a eutectic composition with PCBM (Fig. 4a, b), these blends have lower crystallinity and phase purity than P3HT, partly due to the high miscibility with PCBM (Fig. 4c, d) [28, 30]. We demonstrated that this morphology increased non-geminate recombination, which is detrimental to V_{OC} , FF ,

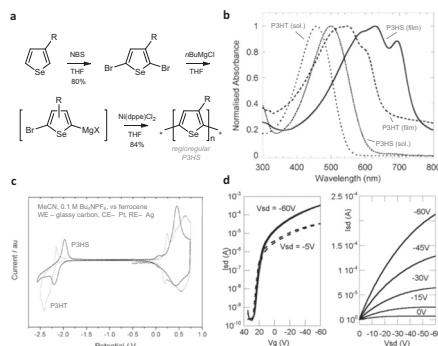


Fig. 3 Chemical synthesis and material study of regioregular P3HS. **a** Grignard metathesis route to regioregular P3HS. **b** Solution and thin film UV–vis absorption spectra of P3HT and P3HS showing distinct redshifts and increasing vibronic character (due to chain ordering) upon film formation. **c** Thin film CV of P3HT and P3HS. **d** Transfer (left) and output (right) characteristics of P3HS OFET devices; saturated carrier mobility of 0.02–0.04 cm² V⁻¹ s⁻¹. V_g = gate voltage, I_{sd} = source-drain current, V_{sd} = source-drain bias voltage. Reproduced from ref. [24] with permission from the Royal Society of Chemistry

and therefore PCE. Thus, fine control of the blend microstructure with processing conditions different from those used with P3HT was needed to maximize the PCE of P3HS-containing solar cells. One successful approach to improving the PCE of P3HS cells was to reduce the miscibility of the fullerene derivative by changing from PCBM to 1,4-diaryl-1,4-dihydro[60]fullerenes with varying alkyl lengths on the aryl substituents. Decreasing the miscibility increased the volume fraction of fullerene-rich domains, which increased the charge collection efficiency and therefore FF [31].

The discovery of the relatively low-lying LUMOs of selenophene polymers compared to thiophene analogs prompted us to explore their use as electron transport materials. While organic semiconductors are intrinsically ambipolar [32], it is challenging to fabricate n-channel transistors from materials with high-lying LUMOs (e.g., P3HT) because of the lack of stable low work-function metals and their sensitivity to trap states [33]. We synthesized poly(3,3'-di-*n*-decyltertseleophene) (PSSS-C10), the selenophene analog of poly(3,3'-didecylterthiophene) (PTT), a high hole mobility polymer shown to self-assemble into a charge transport-conducive three-dimensional lamellar π-stacking arrangement with a backbone that is “edge-on” with respect to the substrate due to side-chain interdigitation [34, 35]. In an OFET, electron injection was facilitated by the low-lying LUMO of PSSS-C10. Balanced electron and hole mobilities of 0.03 cm² V⁻¹ s⁻¹ were achieved; at the time among the best reported mobilities for a solution-processed ambipolar organic semiconductor [35]. Significantly larger threshold voltages were observed for electron versus hole transport due to a combination of

higher injection barriers and greater trapping of electrons versus holes [36]. Nevertheless, complementary-like inverters were constructed from two identical ambipolar OFETs with unparalleled (at that time) switching gain values, demonstrating the utility of heteroatom substitution in achieving new functionalities for organic electronic devices.

These studies, in addition to those on other chemically synthesized low band gap conducting polyselenophenes reported around this time [37, 38], showed that well-defined (i.e., regioregular) selenophene-containing polymers could, in fact, realize material properties that were comparable and even surpassed those of thiophene analogs. Since that time, we have continued to explore selenophene incorporation into conjugated copolymers as a means of enhancing the functional properties of organic electronic materials.

Donor copolymers

Given the identical Grignard metathesis approach used to synthesize both regioregular P3HT and P3HS, it was natural to question whether the functional properties of these homopolymers could be enhanced through copolymerization. Seferos and coworkers first addressed this in the preparation of block and statistical P3HS:P3HT copolymers using approximately 50:50 ratios of selenophene and thiophene monomers [39]. The solution-based UV–vis absorption peak for the block copolymer (P3HS-*b*-P3HT) was broad and consistent with a linear combination of the peaks of the two homopolymers, whereas the statistical copolymer (P3HS-*ran*-P3HT) had an absorption onset and maximum between the two extremes. Optical investigations comparing the absorbance of as-spun and annealed block and statistical P3HT-P3HS films showed that while the statistical copolymer displayed limited structural morphology, P3HS-*b*-P3HT showed π-stacking bands of both P3HT and P3HS, consistent with heterocycle-induced phase separation [39]. Such ordering in conjugated polymers had previously been observed only with materials functionalized with non-conjugated blocks or pendant groups. Strong selenophene-selenophene π-π interactions were found to promote phase separation and formation of nanofiber-like structures in high-M_w samples (~18,000 g mol⁻¹) while hindering aggregation in low-M_w samples (~10,000 g mol⁻¹). Intermolecular bonding is common in selenophene polymers, as are interchain Se-Se close contacts [40], which can aid charge transfer [7]. These selenophene-promoted solid-state nanostructures led to increased thermal stability and PCE for P3HS-*b*-P3HT/PCBM solar cells relative to P3HS/PCBM and compositionally equivalent P3HS/P3HT/PCBM blends (2.69%, 2.14%, and 2.05%, respectively; the P3HT/PCBM blend still had the highest PCE of 3.28%) [41]. Subsequent work by the Seferos group demonstrated how

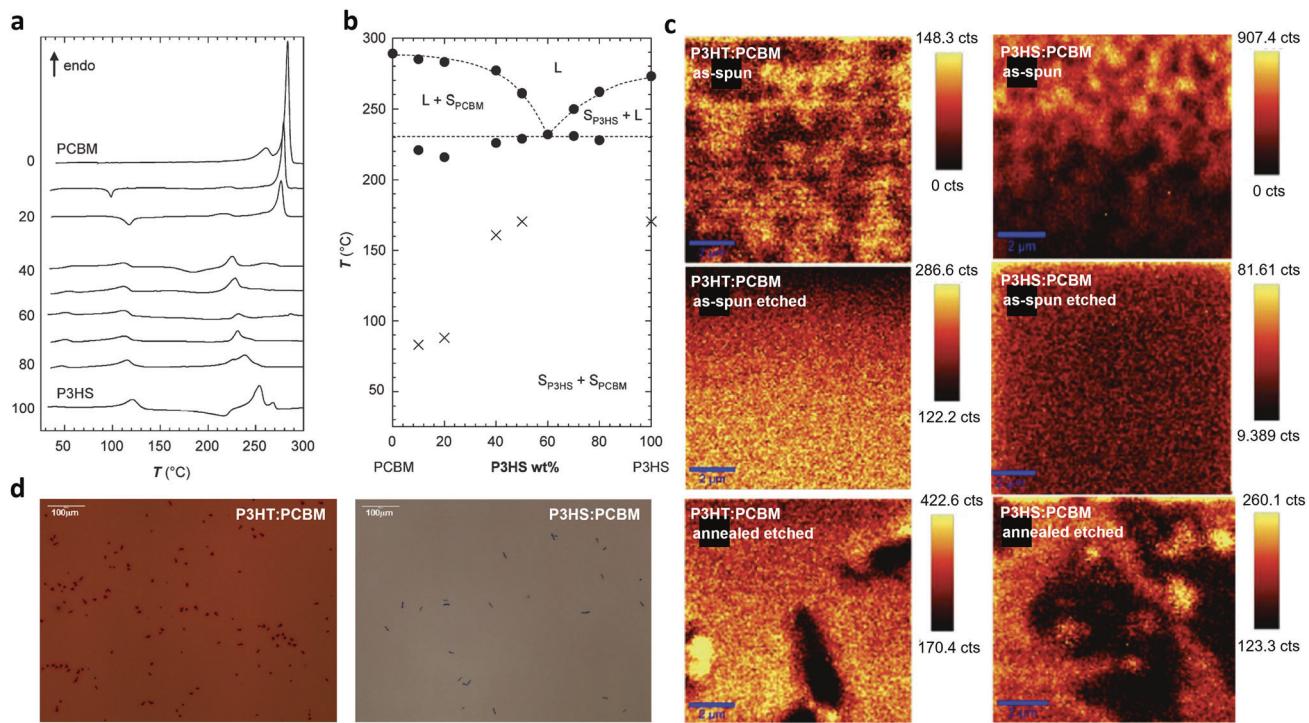


Fig. 4 Investigations of the morphologies of P3HS:PCBM films. **a, b** DSC heating thermograms (**a**) and corresponding temperature/composition diagram of the P3HS:PCBM system, featuring simple eutectic phase behavior; L = liquid phase, S = solid phase. **c** Raman images of P3HT:PCBM (50 wt% PCBM; left) and P3HS:PCBM (50 wt% PCBM; right) for as-spun (top), as-spun etched (middle), and annealed etched (bottom) films. The top 15–20 nm of the films was removed in etched samples. After annealing, coarser phase separation

was observed for both blends, but phase separation into the neat components was far less complete for P3HS:PCBM. **d** Optical images of P3HT:PCBM (50 wt% PCBM; left) and P3HS:PCBM (50 wt% PCBM; right) films after thermal annealing. More finely dispersed PCBM is observed in P3HS:PCBM relative to P3HT:PCBM blends, which is detrimental to charge separation and transport. Reprinted (adapted) with permission from ref. [30], Copyright 2010 American Chemical Society

the microstructures of the block copolymers could be engineered via modification of the sidechains or block length [42, 43].

Following this work, we demonstrated that, when using a droplet-based flow microreactor approach to vary the ratio of the monomers (Fig. 5a, b), statistical copolymers of P3HT and P3HS adhered closely to ideal Bernoullian behavior; that is, they were fully random, as the coupling probability was independent of the heteroatom throughout the polymerization [44]. Similar reactivity behavior for both Grignard and Suzuki polymerizations has been reported elsewhere [45, 46].

The average M_ws of the copolymers were 36,000 to 44,000 g mol⁻¹ with low dispersity and excellent regioregularity (as shown by NMR), which decreased slightly from 96 to 94% with increasing selenophene proportions (Fig. 5c). Accordingly, through this readily scalable synthetic approach, the band gap of P3HS-*ran*-P3HT could be precisely tuned between those of the two homopolymers through control of the monomer feed ratio (Fig. 5d).

The effect of greater ordering for selenophene-incorporated samples was also observed in our study of poly(3-alkyl selenophenylene-vinylene) (P3SeV). Using

synthetic conditions previously reported for the hexyl-substituted thiophene analog, low M_ws were observed for P3HSV, which was attributed to poor solubility of the growing chain [47]. By using longer decyl side chains, larger M_ws were achieved, and the polymer was soluble in organic solvents. Optical studies suggested a degree of structural order even in solution that was enhanced in the solid state. The narrower band gap and lower LUMO of the polymer enabled balanced ambipolar transport (~0.01 cm² V⁻¹ s⁻¹), as expected from reports on P3HS discussed earlier and many others subsequently reported in the literature [48–51]. A systematic investigation of the three dodecyl-substituted chalcogenophenylene-vinylene polymers P3SV, P3SeV, and P3TeV showed that while solid-state ordering increased inversely with solubility (solubility of S > Se > Te), P3SeV exhibited the highest hole mobility (the poor solubility of P3TeV severely affected film formation); [52] as an aside, detailed analyses of the excited state dynamics of these materials showed that heavy heteroatom substitution had a subtle effect on the photophysics of intramolecular singlet fission, suggesting possibilities for using Se- and Te-incorporated conjugated polymers in spintronic applications [53, 54].

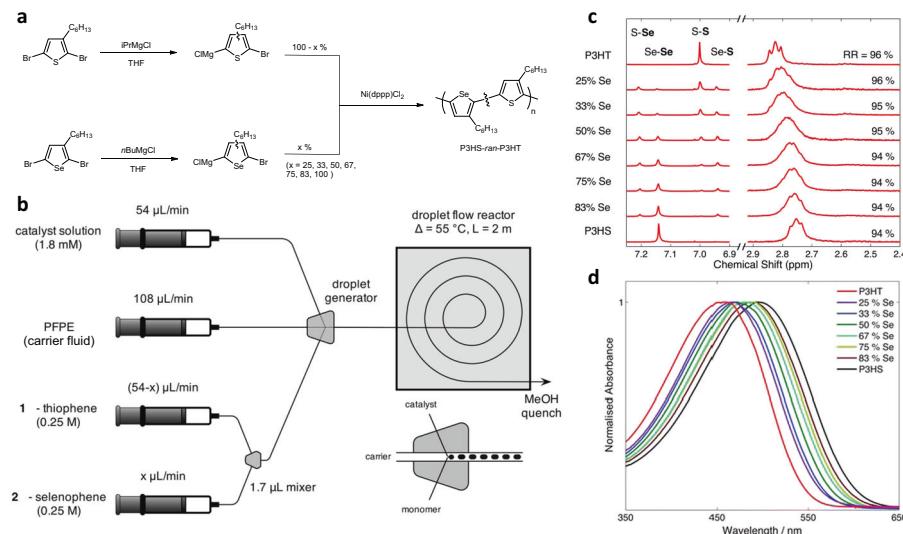


Fig. 5 **a** Grignard metathesis route to P3HS-ran-P3HT copolymers. **b** Schematic illustration of the droplet-based microreactor approach to copolymers varying in ratio from 100% P3HS to 100% P3HT. **c** ^1H NMR study showing the high regioregularity of the P3HS-ran-P3HT copolymers, which decreased slightly with increasing selenophene

ratio. **d** UV-vis absorption spectra of homo- and P3HS-ran-P3HT copolymers with distinct redshift in absorption onsets and maxima with increasing P3HS composition. Reproduced from ref. [44] with permission from the Royal Society of Chemistry

These studies showed that copolymerization of donor materials with electron-rich selenophenes was a successful approach toward tuning the optoelectronic and structural properties of conjugated polymer materials and, accordingly, enhancing organic electronic device performance. They also provided a platform from which to explore selenophene incorporation into the promising area of low band gap donor-acceptor polymers.

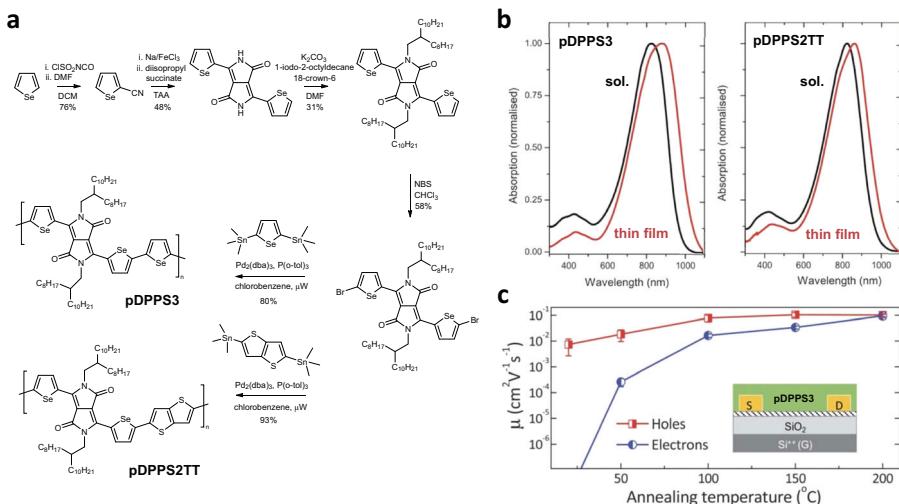
Donor-acceptor copolymers

One of the key advances in conjugated polymer design was the use of donor-acceptor copolymerization strategies to tune the band gap [55]. Combining an electron-rich donor monomer with an electron-deficient acceptor monomer leads to molecular orbital mixing in the copolymer and the formation of a new set of hybridized molecular orbitals with a smaller effective band gap than the individual units. In these structures, the polymer HOMO is mainly influenced by the donor unit, while the polymer LUMO is strongly influenced by the acceptor; therefore, stronger donating groups and strong accepting groups can be used to raise and lower the HOMO and LUMO, respectively. Accordingly, donor-acceptor polymers have readily tunable band gaps that are dependent on the monomer species. This approach has been exploited with great success in the development of high-performance conjugated polymers for photovoltaic (where the band gap is reduced to enhance spectral coverage) [56] and transistor applications (where the HOMO and LUMO are tuned for charge injection and extraction) [57].

Diketopyrrolopyrrole (DPP) is a well-studied acceptor unit for donor-acceptor polymers. It is electron-deficient and planar, capable of forming charge transporting π - π stacks, and has shown promise in low band gap ambipolar charge transport donor-acceptor copolymers [58]. However, electron transport is generally inferior to hole transport in DPP materials due to a combination of factors, including relatively high LUMO levels. We envisioned that the LUMO-lowering and band gap-narrowing effects of selenophene incorporation into donor copolymers could extend to donor-acceptor systems and boost electron transport. Accordingly, we prepared the polymers poly(3-(2,2'-biselenophen-5,5'-yl)-2,5-di(2-octyldodecyl)-6-(selenophen-2,5-yl)-1,4-diketopyrrolo[3,4-c]pyrrole (pDPPS3) and poly(3-(2,2'-biselenophen-5,5'-yl)-2,5-di(2-octyldodecyl)-6-(thieno[3,2-b]thiophen-2,5-yl)-1,4-diketopyrrolo[3,4-c]pyrrole (pDPPS2TT), as shown in Fig. 6a [59].

A clear redshift in the absorbance relative to thiophene analogs was observed and, in conjunction with photoelectron spectroscopy measurements, the LUMOs of pDPPS3 (4.0 eV) and pDPPS2TT (3.9 eV) were found to be sufficiently low for electron and hole injection from Au electrodes. Solid-state ordering was observed, with a redshift in the UV-vis absorbance and vibronic character upon film formation (Fig. 6b). Excellent (for the time) ambipolar charge transport was observed for thermally-annealed OFETs, with both hole and electron transport higher for pDPPS3 ($0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for both charge carriers, Fig. 6c) relative to the thiophene equivalent (0.04 and $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, for holes and electrons, respectively) [60] and enhanced electron transport for pDPPS2TT [59]. Changing the comonomer to

Fig. 6 **a** Synthesis of the selenophene-flanked DPP donor-acceptor polymers pDPPS3 and pDPPS2TT. **b** Solution and thin film UV-vis absorptions of pDPPS3 and pDPPS2TT, which showed redshifts upon film formation. **c** Average saturation-regime OFET mobilities of holes and electrons from five bottom-gate bottom-contact pDPPS3 OFETs after annealing at 200 °C for 30 min. Reproduced from ref. [59] with permission from the Royal Society of Chemistry



electron-deficient 2,1,3-benzothiadiazole resulted in significantly improved ambipolar performance, with the selenophene polymer exhibiting saturated charge carrier mobilities of 0.46 and 0.84 cm² V⁻¹ s⁻¹ for holes and electrons, respectively [61]. The enhancement due to selenophene incorporation enabled the demonstration of CMOS-like logic in inverters fabricated with high gains and three-stage ring oscillators that showed stable oscillation at an unprecedentedly high maximum frequency of 182 kHz when using a supply voltage of just 50 V.

We also performed a direct comparison of selenophene and thiophene donor-acceptor polymers in solar cell applications, with our initial example examining selenophene- and thiophene-flanked DPP copolymers with the extended fused aromatic dithieno[3,2-b:2',3'-d]thiophene. The selenophene polymers again exhibited absorption redshifts in comparison to the thiophene polymer, but blends with PCBM exhibited a lower efficiency (4.1%) than their thiophene analogs (5.1%), principally due to a lower open circuit voltage (V_{OC}). Our exploration of an electron-rich diseleno[3,2-b:2',3'-d]germole monomer, in which both Ge and Se heteroatoms were introduced to enhance structural order and narrow the band gap, copolymerized with the acceptor unit thienopyrrolodione (PDSGTPD) yielded a slightly better PCE in a PCBM device (5.2%), but it was still lower than when the higher V_{OC} Ge and S-containing polymer was used (PDTGTPD; 7.3%) [62]. The same general trend of a lower V_{OC} for SeDPP polymers versus their thiophene analogs was later reported by Yang and coworkers for benzodithiophene copolymers, although in their case, this was compensated by a higher photocurrent leading to an enhanced PCE [63]. A similar trend was observed for thieno[3,2-b]thiophene-flanked DPP monomers copolymerized with S, Se, and Te chalcogenophene comonomers [64].

In recent years, the charge carrier mobilities of DPP-based polymers have continued to rise; [65] however, the

poor solubility of this acceptor constitutes a distinct drawback for commercial application. The utilization of covalently linked aromatic ladder-type monomers with alkyl chains at the bridging points has been a successful alternative approach for thiophene-based polymers such as indacenodithiophene-co-benzothiadiazole (IDTBT) [66]. We anticipated that these properties could be enhanced with selenophene-based ladder monomers coupled with long side chains to compensate for the decreased solubility. Consequently, we developed the novel ladder-type monomers selenophene-based cyclopenta[2,1-b:3,4-b']diselenophene (CPDS) and indaceno[1,2-b:5,6-b']diselenophene (IDSe) and copolymerized them with the strong acceptor unit 2,1,3-benzothiadiazole (BT) to form PCPDSBT and PIDSeBT, respectively [67]. The syntheses of these ladder-type selenophene materials were challenging, as the acid-catalyzed Friedel-Crafts acylation usually employed for installing the planarizing methylene bridges is harsh and low-yielding for chalcogenophenes. To avoid these conditions, we developed an acid-free route using a Suzuki ring closing strategy to obtain the monomers in high yield (Fig. 7a) [67].

The copolymers exhibited highly coplanar backbones with significantly redshifted optical gaps relative to the thiophene analogs (the optical band gap of PCPDSBT was a remarkably low 1.18 eV, Fig. 7b, c). The OFET hole mobilities for PCPDSBT and PIDSeBT were 0.15 and 6.4 cm² V⁻¹ s⁻¹ (Fig. 7d, e), respectively, at low gate voltages. The latter is still one of the highest mobilities reported for polymers deposited from a nonchlorinated solvent (tetralin), and this was aided by significant backbone ordering [67]. Similar effects were observed in our study of an electron-rich polymer formed from diseleno[3,2-b:2',3'-d]selenophene coupled with an alkylated 2,2'-dithienyl-ethylene comonomer [68]. Very strong interchain Se-Se interactions were found to promote edge-on ordering, while the participation of Se nonbonding electrons was suggested to promote charge delocalization,

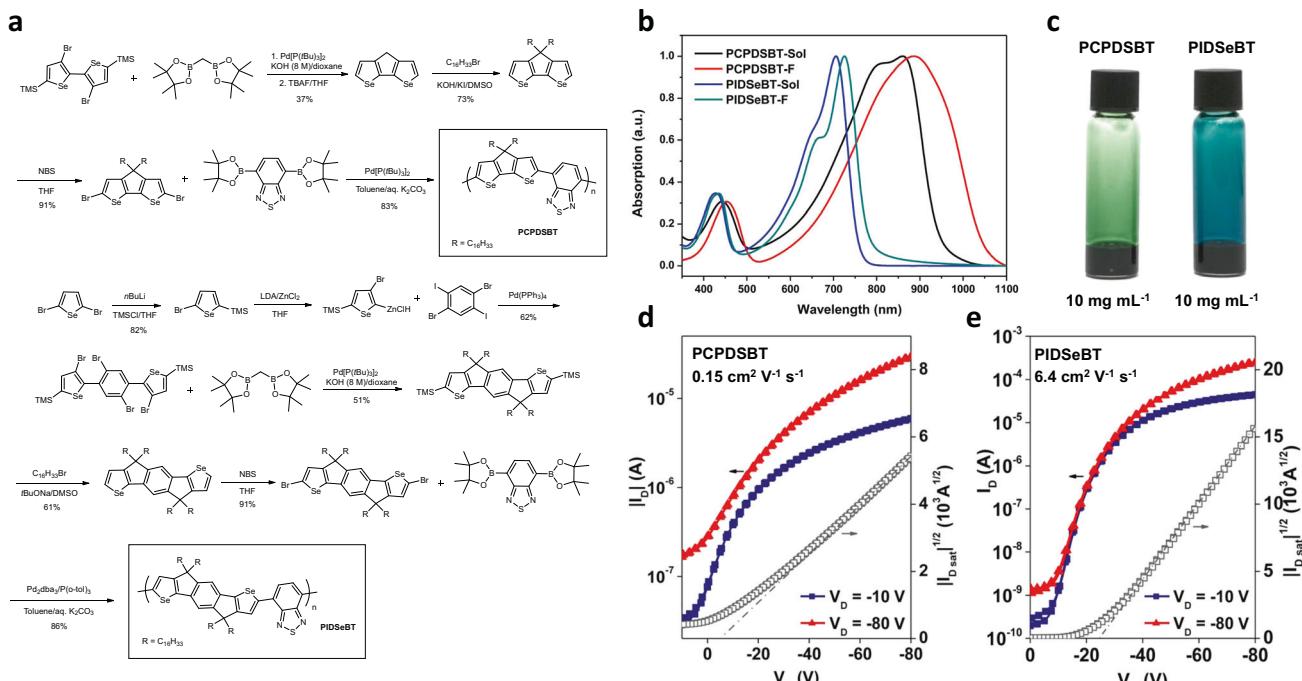


Fig. 7 **a** Synthesis of PCPDSBT and PIDSeBT polymers using a Suzuki ring closing strategy to avoid conventionally used, chalcogenophene unstable, acidic Friedel-Crafts conditions. **b** Solution and thin film UV–vis absorption of PCPDSBT and PIDSeBT showing low energy absorption onsets with vibronic character (corresponding to ordering) for both polymers that are enhanced upon film formation. **c** Photographs of the polymers in tetralin solution at room temperature.

which enabled an OFET hole mobility of $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at a gate voltage of -30 V .

Arguably, incorporation of selenophene into donor–acceptor polymers has provided the greatest demonstration of the advantages of heteroatom substitution; a combination of frontier molecular orbital tuning, enhanced solid-state packing and interchain interactions have enabled definitive advances in OFET device performance (especially with respect to ambipolarity). However, we have found limited benefits in applying this strategy to solar cell materials due to a combination of an often poor V_{OC} and the challenges in blending highly ordered selenophene polymers with other active layer materials in these devices [69].

Summary and perspective

Through the work outlined in this focus review and the continually expanding literature on this subject, we now know much about the effects of selenophene incorporation on the material properties of conjugated polymers. Relative to thiophene analogs, selenophenes have been shown to exhibit (1) lower band gaps, increased photostabilities and improved injection and transport as a result of mild HOMO destabilization but strong LUMO stabilization; (2) increased planarity

and conjugation lengths due to more rigid backbones; (3) reduced solubility but increased crystallinity of films, often enabling better charge transport in devices owing to strong intermolecular Se–Se and selenophene–selenophene π – π interactions; and (4) singlet fission due to larger heteroatom spin-orbit coupling. Given all these positives, one must question why selenophenes are not as ubiquitous in organic electronics research as their thiophene counterparts.

A common answer is that selenophene chemistry is more challenging and limited than thiophene chemistry. While this is undoubtedly the case for tellurophene, although conjugated polymers containing tellurium are by no means scant in the literature [6], in recent years, selenophene chemistry has become highly developed [70]. Indeed, of the novel materials covered in this review, few required significant changes (if any) to the synthetic pathway used for the thiophene analog. We note, however, that the paucity and expense of commercially available building blocks can necessitate additional synthetic steps. Another commonly cited issue is the toxicity of selenophene. Selenophene is indeed toxic; however, substituted selenophenes are important compounds in medicinal chemistry given their pharmaceutical and biological activities as antitumor, anti-bacterial, and anti-depressant agents (among many others) [71]. As selenium is an essential trace element in humans

[72], clearly, it is the dose and structure that makes the poison [73]. Finally, it is often reported that selenophene-incorporated conjugated polymers tend to perform less well in organic electronic devices than the thiophene equivalents. We hope that the literature presented in this focus review demonstrates that this is not always the case; however, there is certainly some truth to this assertion. M_w is a key variable for organic electronic material performance [74] that is often left out of heteroatom comparison studies, likely as a result of the difficulty in obtaining samples with comparable M_w s. This is especially important in the context of the selenophene literature given that these polymers are generally less soluble and, accordingly, synthesized samples tend to have shorter chain lengths than the thiophene equivalents. These problems with comparison aside, in our view, the primary reason underlying this issue is not intrinsic deficiencies in the properties of the polymers but that the various solid-state and device optimization approaches that have been developed over decades for thiophene polymers are simply not ideally tuned for selenophenes, as should be expected given the remarkable changes introduced by heteroatom substitution. Accordingly, we believe that more research is needed to better understand, control, and enhance the bulk properties of these materials. Only in doing so will we enable full realization of the outstanding potential of selenophene-containing conjugated polymers.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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