Polymer additive controlled morphology for high performance organic thin film transistors

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Solution-crystallizable small-molecule organic semiconductors, such as 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS pentacene), 5,11-bis(triethylgermylethynyl)anthradithiophene (diF-TEG-ADT), 2,7-dioctyl-[1]benzothieno[3,2-*b*][1]benzothiophene (C$_8$-BTBT), and *N,N'*-1*H*,1*H*-perfluorobutyl dicyanoperylene-carboxydiimide (PDIF-CN$_2$), demonstrate various practical advantages including high mobility, air stability and solution processibility. In this article, we review various polymer additive based approaches to control the crystal morphology and the resultant charge transport of some bench-mark, high performance, solution crystallizable, small-molecule organic semiconductors. The polymer additives are discussed under the categories of non-conjugated polymers and conjugated polymers. The approaches and structure-performance correlations that we discussed here may be applied far beyond the examples shown in this review and have important implications for high performance organic semiconductors in general.

1. Background and challenges

Solution-processed high-performance small-molecule organic semicoductors have attracted significant attention because they are potentially compatible with high-throughput and low-cost fabrication methods over large areas on flexible substrates.[1–11]

However, the crystalline films of these small-molecule organic semiconductors typically exhibit the issues of poor film uniformity, large grain boundary density, and thermal cracks, which lead to anisotropic charge transport and large performance variations of organic thin film transistors (OTFTs).[9,10,12,13] Therefore, the controllable crystal morphology of these small molecules in solution plays a critical role and needs to be realized in order to fabricate high-performance organic electronic devices.

Over the last decade, researchers have developed different additive-based approaches to control the crystal morphology and address these aforementioned issues of the solution-processed small-molecule semiconductors. In this article, these approaches and their resultant crystal alignment and device performance are reviewed. The first section of this review uses TIPS pentacene as an example to showcase the unique advantages of solution processed, small molecule organic semiconductors, including excellent air and operational stability, versatile solubility, and high mobility.[12] The second section of this article reviews various polymer additive-based methods to control crystal morphology. Crystal morphology of TIPS pentacene in solution

is examined in the presence of various nonconjugated and conjugated polymeric additives. In particular, the different phase segregation modes that occur between the small-molecule semiconductors and polymers are discussed for the common polymer additives. Throughout these specific examples, we demonstrate the importance of polymer additive-based controllable strategies in optimizing crystal structure, improving thin film morphology and enhancing charge transport of high performance, small molecule organic semiconductors.

1.1 Small molecule organic semiconductor

Organic semiconductors are becoming increasingly attractive because they can be solution-processable and there is potentially no requirement for high temperature and vacuum manufacturing steps.[10] Conjugated-polymer-type organic semiconductors typically have better film formation capability and lower charge transport performance than their small-molecule counterparts.[14] Therefore, this review is focused on small-molecule organic semiconductors only.

Great progress has been achieved in the morphology and charge transport studies of these small-molecule organic semiconductors, enabling their charge-carrier mobilities to increase close to or even surpass that of amorphous silicon. For example, multiple studies have reported mobility values close to or above 1 cm^2 V^{-1} s^{-1}, from OTFTs based on small-molecule organic semiconductors including 6,13-bis(triisopropylsilyl-ethynyl)pentacene (TIPS pentacene),[15–21] rubrene,[22–26] and *N,N'*-1*H*,1*H*-perfluorobutyl dicyanoperylenecarboxydiimide (PDIF-CN$_2$).[27–34] In particular, a recent study by Rocha *et al.* demonstrated a hole mobility of up to 6.7 cm^2 V^{-1} s^{-1} from TIPS pentacene crystals with a solution-shearing alignment method.[35]

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Diao *et al.* reported a mobility of up to 11 cm^2 V^{-1} s^{-1} from single-crystalline TIPS pentacene films based on a "fluid-enhanced crystal engineering" approach.[36] Peng *et al.* reported mobility of 10.4 cm^2 V^{-1} s^{-1} from C$_{10}$-DNTT crystals using a dual solution-shearing method.[37] Zhao *et al.* reported a mobility of up to 8.7 cm^2 V^{-1} s^{-1} obtained from one-dimensional 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C$_8$-BTBT) crystal arrays, which were aligned using a "asymmetric-wettability topographical template".[38] Niazi *et al.* reported a mobility of 6.7 cm^2 V^{-1} s^{-1} based on diF-TES-ADT crystals with solvent additives of different polarities.[39]

In the following section, we will use TIPS pentacene as a benchmark semiconductor to illustrate the various advantages of small-molecule organic semiconductor in general. TIPS pentacene, a soluble derivative based on pentacene, has been developed as a p-type organic semiconductor,[17,40–43] and demonstrates solution processability, high hole mobility and excellent air stability.[44–49] TIPS pentacene molecules adopt the alignment with their acene units edge-on to the substrate, with two bulky side groups touching down the substrate (Fig. 1).[50] The substitution of two bulky side groups to the aromatic ring disrupts the edge-to-face interaction of the aromatic ring, avoids the herringbone packing motif in neat pentacene, and protects the middle acene from oxidation and degradation.[51] This largely increases the solubility of TIPS pentacene, allowing it to be soluble in common solvents.[52] Also, the carbon–carbon triple bond keeps the bulky side group

substitution away from the aromatic ring. This allows face-to-face (π–π stacking) interaction between adjacent TIPS pentacene molecules and results into improved π-orbital coupling, facilitating charge transport between acene units.[53] The molecule structures of TIPS pentacene, along with of other high performance, solution crystallizable, small molecule organic semiconductors under examination in this work, including PDIF-CN$_2$ (n-type semiconductor) and C$_8$-BTBT (p-type semiconductor), are shown in Fig. 1.

Similar to many other solution-processable organic semiconductors, TIPS pentacene shows good solubility in a host of organic solvents, which include chlorobenzene,[54–56] anisole,[57,58] chloroform,[50,59–61] and toluene.[62–65] In addition, a number of mixture solvents have been investigated for the deposition of TIPS pentacene as active layers in OTFTs.[66]

1.2 Air and operational stability

Solution processed, small molecule organic semiconductors exhibit a range of air and operational stability depending upon their chemical structure and device configuration. Here we continue to use TIPS pentacene as an example in our discussion to demonstrate the effect of various factors, such as side-group substitution (as compared to pentacene), illumination, channel dimension, and active layer thickness, on the charge transport of the semiconductor.

As mentioned earlier, TIPS pentacene demonstrated enhanced air stability when compared to the plain pentacene. The operational and environmental stability of the TIPS pentacene based OTFTs was investigated by Park *et al.*[56] For the environmental stability test, the effects from both ambient environment and illumination were investigated, and the results were presented in Fig. 2. It was found that the devices, when exposed in air and dark conditions, exhibit slightly reduced mobility and increased threshold voltage and sub-threshold slopes. In contrast, when exposed in air and illuminated conditions, the devices demonstrated increased drain current and sub-threshold voltage but a larger shift of threshold voltage. Results from the repeated cycling test demonstrate that devices with shorter channel length exhibit greater shift in threshold voltage and a reduction in both mobility and current with repeated cycling. For OTFTs with short channel length, the devices undergo significant degradation for the bias-stress test. These observations are attributed to the device
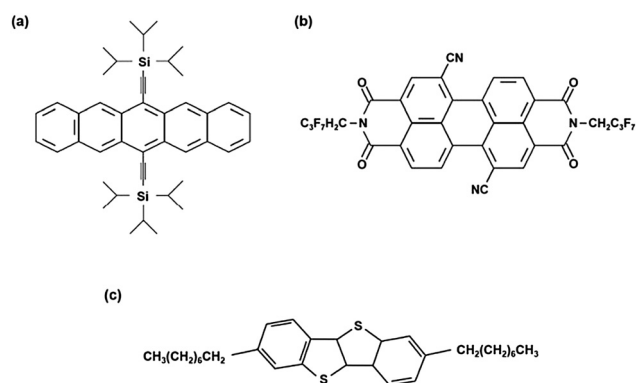

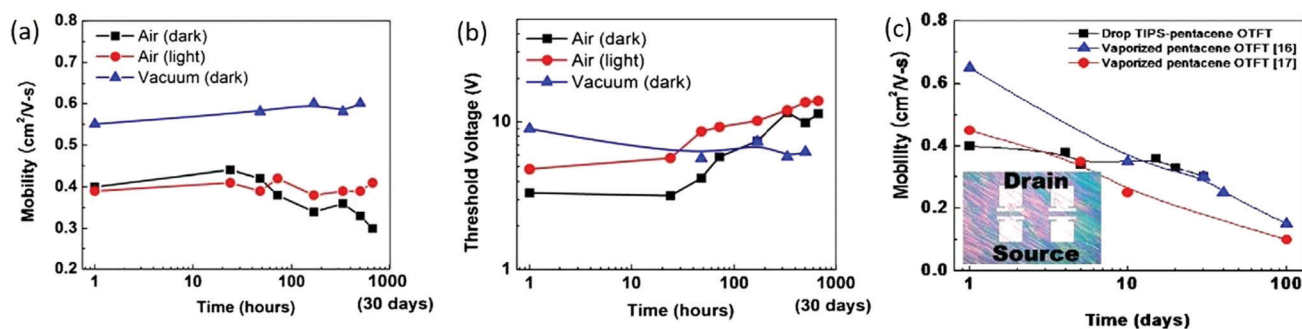Fig. 1 Molecular structures of (a) TIPS pentacene, (b) PDIF-CN$_2$, and (c) C$_8$-BTBT.

Fig. 2 Environmental stability test of TIPS pentacene based OTFTs: the change of (a) hole mobility and (b) threshold voltage with time. (c) Comparison of environmental stability test results with reference data. Reproduced from ref. 56 with permission from Elsevier.

operation at large currents, large local power dissipation, and build-in charges in the channel region. Ambient oxygen causes the pentacene molecules to oxidize, while water and polar molecules may create traps at the grain boundaries, reducing the hole mobility and degrading device performances of OTFTs. The molecules of vapor-deposited pentacene film pack in a herringbone stacking, exhibiting molecular backbone spacing about 4 Å in thin film phase.[56] In contrast, the molecular backbone spacing for TIPS pentacene molecules, which adopt two-dimensional π–π stacking, decreases to 3.5 Å. This change significantly reduces the diffusion of water and oxygen into the channel region. Also, the functional groups at both 6 and 13 positions effectively prevent the diffusion of oxygen and absorption of water, leading to improved air stability.

The incorporation of polymer additives into small-molecule organic semiconductor has been reported to enhance the air stability of the organic thin film transistors, mainly through the vertical phase segregation between the semiconductor and polymer additives. As a result, the following processes may occur: (1) the polymer additives may form a polymeric encapsulation layer, which prevents the semiconductor layer from being exposed to the ambient environment and thereby improves the device stability; and (2) the hydrophobic nature of the polymer additive repels the air and moistures of the ambient environment away from the charge transport channel. For example, Kim *et al.* reported that the addition of PαMS polymer led to the formation of an encapsulation layer and enhanced the device operational stability of diF-TESADT based OTFTs.[67] Arias *et al.* reported that an insulation polymer PMMA was blended with poly[5,5-bis(3-dodecyl-2-thienyl)-2,2-bithiophene] (PQT-12) semiconductor.[68] The blending of the PMMA polymer facilitated a vertical phase segregation between the polymer additive and semiconductor, which caused the formation of a polymeric encapsulation layer, minimized the exposure of the semiconducting channel to the environment and consequently enhanced the device air stability. Similarly, such stability enhancement due to the formation of encapsulation layer was also demonstrated on PαMS/ TIPS pentacene blends,[69] and P3HT/polyethylene (PE) blends.[70] Ohe *et al.* reported that addition of PαMS polymer into TIPS pentacene semiconducting thin film induced a vertical phase segregation with a TIPS pentacene/PαMS rich/TIPS pentacene trilayer structure.[71] This was found to help suppress the structural-phase transition of TIPS pentacene when exposed to an elevated temperature. As a result, the TIPS pentacene based OTFTs with PαMS polymer demonstrated enhanced heat stability when the devices were heated up to 180 °C. Qiu *et al.* reported that when PS was blended with a p-type semiconductor P3HT, it resulted in a vertical phase segregation structure with P3HT nanowires embedded in the PS polymer, and led to enhanced air stability of the OTFTs.[72–74] Similar improvement of device air stability was also observed by Lim *et al.* who reported P3HT/PS blend based OTFTs fabricated by using an inkjet technique.[75] In a more recent study, the effect of various polymer additives, including hydrophobic polymers, such as PαMS and PMMA, and hydrophilic polymer, such as PVA, was studied to improve the air stability of n-type small-molecule organic semiconductor PDIF-CN$_2$.[34] While the mobilities of pristine PDIF-CN$_2$ based OTFTs had decreased by ~77.2% over

30 days, the pre-deposition of the PαMS and PMMA polymers only resulted in a decrease of ~43.6% and ~67.6% in mobilities over the same period of time. In contrast, the hydrophilic polymer PVA led to one order of magnitude reduction in mobilities. The results clearly indicated a correlation between the hydrophobic nature of polymer additives with enhanced air stability of small-molecule semiconductor based OTFTs.

2. Polymer additive controlled crystal morphology

Polymer additives have been demonstrated to effectively control the crystal morphology and charge transport of organic semiconductors. Polymers such as poly(alpha-methylstyrene) (PαMS),[69,71,76–83] poly(methyl methacrylate) (PMMA),[84–86] polystyrene (PS),[57,77,80,87–89] poly(4-vinylpyridine) (P4VP),[76] and poly(tri-arylamine) (PTAA),[76,82,90–96] and the polyacrylate polymer series,[97] were used to enhance film formation, and at the same time, to manipulate the vertical and lateral phase separation between the small-molecule semiconductor and the polymer additives. New film structures can be resulted from polymer mediated small molecule organic semiconductor crystal morphology from blend solution, leading to opportunities for charge transport enhancement.

2.1 Effect of polymer additive on semiconductor crystal morphology

Small-molecule semiconductor/polymer blends have been widely studied as intriguing active layer systems to enhance the device performance of OTFTs. By blending the small-molecule organic semiconductors with polymer additives, it may have the following effects on the crystal morphology and charge transport of the semiconductors.

First, the polymer/semiconductor blends can take advantage of both the uniformity property of the polymer and the excellent charge transport property of the small-molecule semiconductor. Various polymer additives such as PαMS[67,98,99] and PS[35,87] have been reported to blend with small-molecule organic semiconductors, which resulted in an enhancement of both thin film morphology uniformity and device performance of the small-molecule semiconductor based OTFTs.

Second, the phase segregation between the small-molecule semiconductors and various non-conjugated, amorphous polymer additives is another advantage of this blend system that has been shown to improve the charge transport of the small-molecule semiconductors. Two types of phase segregation, including lateral phase segregation and vertical phase segregation, can occur from the addition of various non-conjugated, amorphous polymers, which is dictated by the thermodynamics kinetic interaction between the polymer and semiconductor.[14,97] Multiple benefits can result from such a vertical phase segregation: it can provide an effective confinement of the anisotropic crystal orientation of the small-molecule semiconductor;[97] the vertical phase segregation can facilitate the semiconductor to move towards the charge

transport channel, favoring charge transport and device performance of the OTFTs.[71,100]

Third, the addition of conjugated polymer additives can also induce intermolecular interactions between the polymer and certain small-molecule organic semiconductors, which provides a unique path to modulate the polymorphism and crystal morphology of the semiconductors.[14] Depending on the different intermolecular interactions between the polymer and semiconductor, distinct polymorphism and thin film morphology of the small-molecule organic semiconductor can be obtained, which can further lead to different modes of charge transport and device performance of the small-molecule based organic thin film transistors.

Fourth, the addition of polymer additives can enhance the air stability of the small-molecule semiconductor based OTFTs. This was mainly due to (1) the formation of a polymeric encapsulation layer, which can protect the semiconductor layer from being exposed to the ambient environment;[67–70] (2) or due to the hydrophobicity of the polymer additives, which can repel the ambient air and moistures away from the channel.[34]

The following section will review the common polymers that have been reported to blend with small-molecule semiconductors as additives, which have demonstrated to effectively control the crystal morphology and charge transport of small-molecule semiconductors. These polymers will be discussed in the categories of non-conjugated polymer additives such as poly(α-methylstyrene) (PαMS), poly-(methyl methacrylate) (PMMA), and polystyrene (PS), and of conjugated polymer additives such as poly(triaryl amine) (PTAA) and P3HT.

2.2 Non-conjugated polymer additives

Kang et al. reported that blending TIPS pentacene with poly(α-methylstyrene) (PαMS) would result in a trilayer structure, and PαMS with two relative number average molecular mass were studied. Neutron reflectometry was employed to measure the depth profile and understand the composition of the blend film with nanometer-scale resolution (Fig. 3).[69] The TIPS

pentacene/PαMS blend film with lower PαMS relative number average molecular mass ($M_{r,n}$ = 1300 g mol^{-1}) exhibits a trilayer structure with a TIPS pentacene-rich layer of ~177 Å thick on the top, a PαMS-rich layer of ~326 Å thick in the middle, and again a TIPS pentacene-rich layer of ~70 Å thick in the bottom. On the other hand, when the TIPS pentacene/PαMS blend film contains higher PαMS relative number average molecular mass ($M_{r,n}$ = 575 000 g mol^{-1}), the thickness of the top and bottom layers changes to ~134 Å and ~117 Å, respectively, indicating a strong phase segregation between the semiconductor and polymer at both interfaces. A thicker layer of TIPS pentacene in the bottom is beneficial for charge transport, contributing to the highest average hole mobility of 0.3 cm^2 V^{-1} s^{-1}, as compared to 0.05 cm^2 V^{-1} s^{-1} from the pure TIPS pentacene OTFTs.

Similarly, Ohe et al. reported that the spin coating of a blend solution of TIPS pentacene and PαMS causes a vertical phase separation between the semiconductor and polymer.[71] In order to investigate the composition of the vertically segregated structure, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was employed to examine the semiconductor/polymer blend film. The secondary ions of Si$^-$ and SiH$^-$, which only originate from TIPS pentacene, are utilized as a marker of TIPS pentacene. The three-dimensional Si$^-$ ion distribution map indicates that the semiconductor/polymer blend film consists of a trilayer structure with a TIPS pentacene-rich layer on the top and also in the bottom, plus a TIPS pentacene-poor layer in the middle. Furthermore, in order to locate the PαMS polymer component, the blend film was mechanically shaven, which allows the examination of the cross-section of the blend film without breaking the molecular structures. The distribution of $C_8H_9^+$ ions, which only originate from PαMS, indicates that most PαMS lies in the middle layer while only negligible amount of PαMS is in the top and bottom layer of the trilayer structure. The TIPS pentacene/PαMS based OTFTs demonstrate a mobility of 0.12 cm^2 V^{-1} s^{-1}, threshold voltage of ~0 V, current on/off of above 10^5. Besides, the ratio of the average of
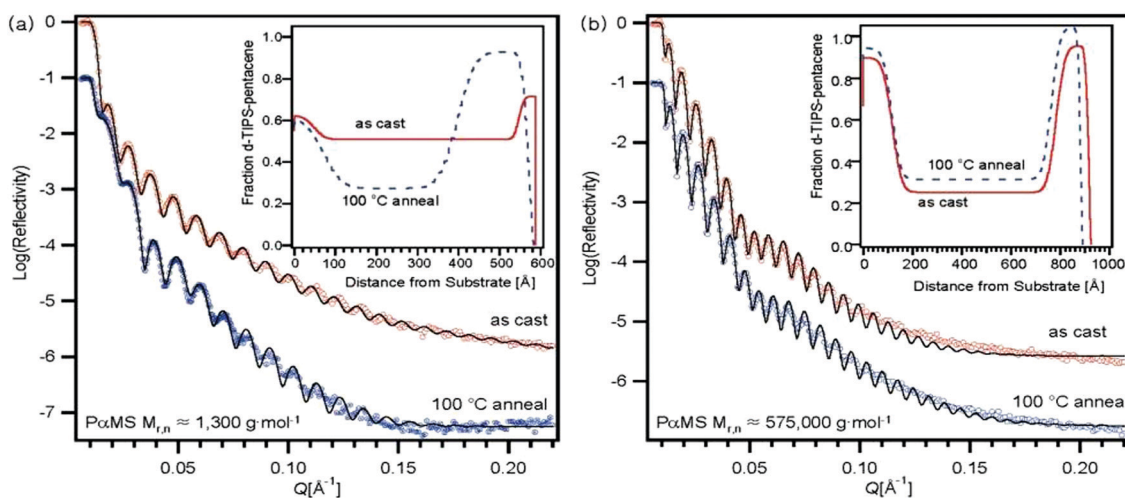

Fig. 3 Neutron reflectivity profiles of d–TIPS pentacene/PαMS blend films with different PαMS relative number average molecular mass $M_{r,n}$ of (a) 1300 g mol^{-1} and (b) 575 000 g mol^{-1}. The black solid lines represent the reflectivity curves fitted from the modeled density profiles. The insets show the fitted concentration profiles. Reproduced from ref. 69 with permission from American Chemical Society.

on-current standard deviation σ_{on} to the average of on-current $\langle I_{on} \rangle$ was used to represent the performance uniformity of the OTFTs. The TIPS pentacene/PαMS based OTFTs demonstrate remarkable reduction in $\sigma_{on}/\langle I_{on} \rangle$ as compared to those based on pure TIPS pentacene, implying that the addition of PαMS enhances the film uniformity and performance consistency of OTFTs.

Asare-Yeboah *et al.* combined the addition of PαMS polymer with a temperature gradient technique to align TIPS pentacene crystals.[98] The temperature gradient technique allows the substrate to be heated in a way that the temperature of one end is higher than that of the other, which causes a difference in the solubility of the TIPS pentacene semiconductor. As the solvent evaporates, the solution reaches saturation first on the lower temperature end and facilitates the deposition of nucleation seeds. As a result, TIPS pentacene crystals are well aligned from the lower temperature end of the substrate towards the higher temperature end. In the meanwhile, the PαMS polymer additive was further blended with TIPS pentacene in order to enhance the film morphology and to address an issue of the thermal cracks, which were caused by the thermal stress. As can be seen from Fig. 4, the addition of the PαMS polymer has reduced the crystal width and effectively eliminated the generation of the thermal cracks, which can be attributed to its polymer matrix property. This combined method of PαMS polymer additive with a temperature gradient technique was demonstrated for organic thin film transistor fabrication based on both silicon and ITO/PET flexible substrate, leading to a mobility of about 0.1 cm^2 V^{-1} s^{-1} and 0.5 cm^2 V^{-1} s^{-1}, respectively.

He *et al.* demonstrated a method to improve the TIPS pentacene film uniformity and crystal orientation in TIPS pentacene films simply by blending the semiconductor with polyacrylate polymer additives.[97] Three polyacrylate polymers, including poly(ethyl acrylate) (PEA), poly(butylacrylate) (PBA), and poly(2-ethylhexyl acrylate) (P2EHA), possess similar molecular structures but have hydrophobic side group with different carbon chain length, ranging from two, to four and to eight carbons, respectively. Mixing TIPS pentacene with these polymers leads to different phase separation modes, which can be attributed to the polymer hydrophobicity and the intermolecular interactions between TIPS pentacene and the polymer. It was discovered that a polymer additive with a shorter hydrophobic side chain, such as PEA, tends to facilitate lateral phase separation, which provides only limited confinement of crystal misorientation. A polymer additive with a longer hydrophobic side chain, such as P2EAH, contributes to vertical phase separation, effectively aligns TIPS pentacene crystals and enhances film coverage, which was responsible for the improved charge transport and reduced performance variations. An average mobility of 0.14 cm^2 V^{-1} s^{-1}, 0.16 cm^2 V^{-1} s^{-1}, and 0.35 cm^2 V^{-1} s^{-1} was achieved with the loading of PEA, PBA and P2EHA polymer additive, respectively.

Energy filtered transmission electron microscopy (EF-TEM) was carried out in order to reveal the effect of polyacrylate polymer additives on charge transport and device performance of the TIPS pentacene OTFTs. As shown in Fig. 5, the regions rich of TIPS pentacene are darker in elastic (0 eV) image due to the TIPS pentacene crystallinity and higher electron density, but at the same time brighter in the 20 eV image due to its low-eV plasmon contribution. The different features in the elastic image are also represented by the 20 eV image and thickness map. The featureless appearances of the TIPS pentacene/P2EHA blend film in both elastic image and thickness map, as well as the broad edges in 20 eV image, indicate vertical phase separation and rich interpenetration between the TIPS pentacene and P2EHA components. TIPS pentacene/PEA blend film shares identical features for all 0 eV image, 20 eV image and thickness map, indicating a dominating lateral phase separation. Detailed features in the 20 eV image of TIPS pentacene/PBA film, as highlighted by the white circles, are absent in the elastic image and thickness map, implying mainly lateral (and some small amount of vertical) phase separations between TIPS pentacene and PBA.
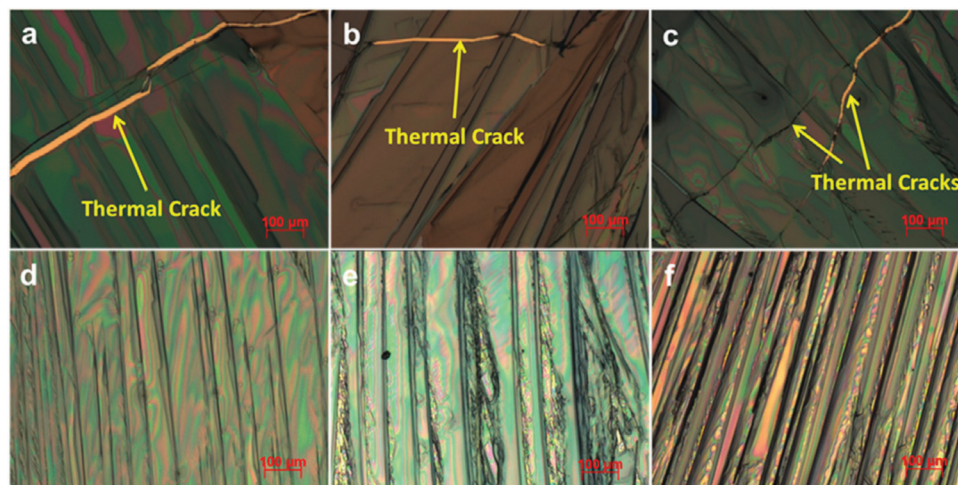

Fig. 4 Polarized optical images of well-aligned TIPS pentacene crystals using the temperature gradient technique (a–c) without and (d–f) with the addition of the PαMS polymer additive, which show the PαMS polymer has effectively eliminated thermal cracks and also enhanced film morphology. Reproduced from ref. 98 with permission from Elsevier.
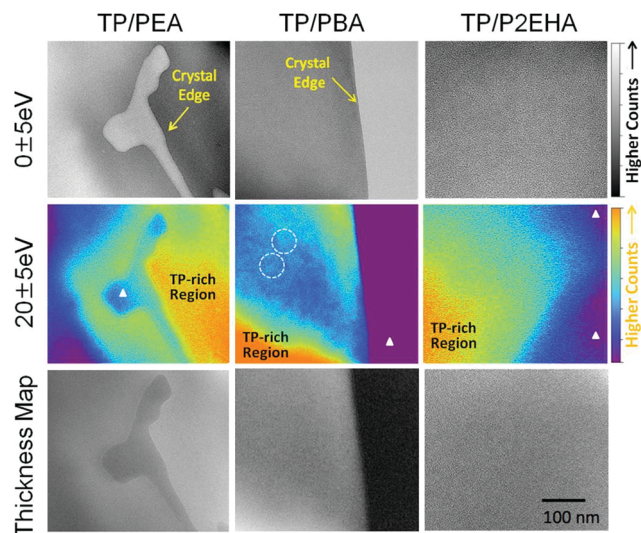
Fig. 5 Energy filtered TEM results of TIPS pentacene films with different polymer additives. Scale bar is 100 nm for all images, as shown bottom right. Regions rich of TIPS pentacene are darker in the 0 ± 5 eV (elastic) image, but brighter in the 20 eV image. White triangles represent regions deficient of TIPS pentacene. Reproduced from ref. 97 with permission from American Institute of Physics.

Park *et al.* combined an isotactic (i-) poly-(methyl methacrylate) (i-PMMA) blend method with a vertical flow approach *via* pipette writing to obtain well-aligned TIPS pentacene crystals.[86] i-PMMA was blended with TIPS pentacene due to its properties such as good leakage protection and hysteresis minimization. The TIPS pentacene/i-PMMA blend solution was applied across a HMDS treated substrate, as shown in Fig. 6(a) and (b). Since the surface energy of i-PMMA is similar to that of the HMDS treated substrate, i-PMMA moves close to the substrate surface *via* self-assembly, forming a bilayer structure with i-PMMA in the bottom and TIPS pentacene on the top. As shown in the optical images of Fig. 6(c) and (d), well-aligned highly-crystalline
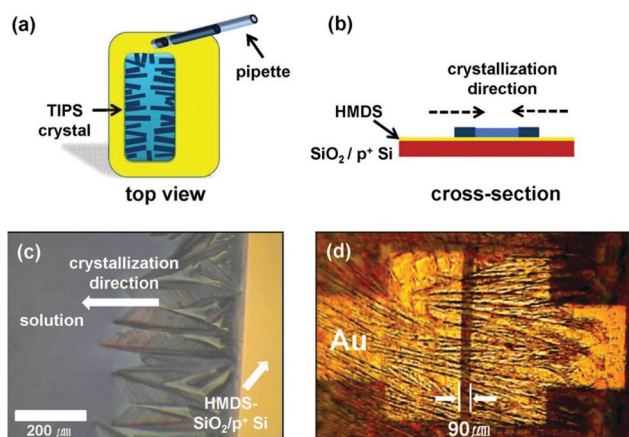
TIPS pentacene crystals were obtained by using this method, resulting in a mobility of 0.34 cm^2 V^{-1} s^{-1}.

Yuan *et al.* demonstrated highly-crystalline 2,7-dioctyl[1]ben-zo-thieno[3,2-*b*][1]benzothiophene (C$_8$-BTBT) films by spin coating the C$_8$-BTBT/polystyrene (PS) blends with an off-center coating method, and obtained a field-effect hole mobility of up to 43 cm^2 V^{-1} s^{-1}.[101] The mechanism of the off-center coating method is illustrated in Fig. 7(a). This method resulted in a vertical phase segregation with a C$_8$-BTBT layer on the top and PS polymer layer in the bottom, as indicated by the cross-sectional TEM image of Fig. 7(b). The C$_8$-BTBT layer is a dark thin film because of its high crystallinity and electron density. The obtained ultra-high hole mobility was attributed to the alignment of C$_8$-BTBT highly crystal-line films, the slight reduction of in-plane intermolecular spacing, and the passivation effect from the bottom PS layer. In addition, the C$_8$-BTBT based OTFTs are highly transparent for above 90% of the visible spectrum, implying great potential for transparent flexible electronics.

Niazi *et al.* demonstrated the addition of both poly(α-methyl-styrene) and polystyrene amorphous polymer additives, along with the application of a solution shearing method, in order to obtain orientated crystals of diF-TES-ADT.[39] The electrical performance of the diF-TES-ADT based OTFTs was found to be dependent on various important parameters including the polymer additive molecular weight, the speed of solution shearing, the vertical stratification between semiconductor and polymer layer, as well as the formation of long-range, defect-free, coherent domains. By optimizing these important parameters, the authors reported a charge-carrier mobility of up to 6.7 cm^2 V^{-1} s^{-1} from diF-TES-ADT OTFTs.

He *et al.* studied the effect of various insulation polymers on the crystal morphology of *N,N′*-1*H*,1*H*-perfluorobutyl dicyano-perylenecarboxydiimide (PDIF-CN$_2$), which is a high-performance

Fig. 6 (a) Top view and (b) cross-section view of the schematic of using the "vertical flow" method to form the TIPS pentacene/i-PMMA blend film. (c and d) Optical image of the TIPS pentacene/i-PMMA blend film obtained with the "vertical flow" method. Reproduced from ref. 86 with permission from Elsevier.
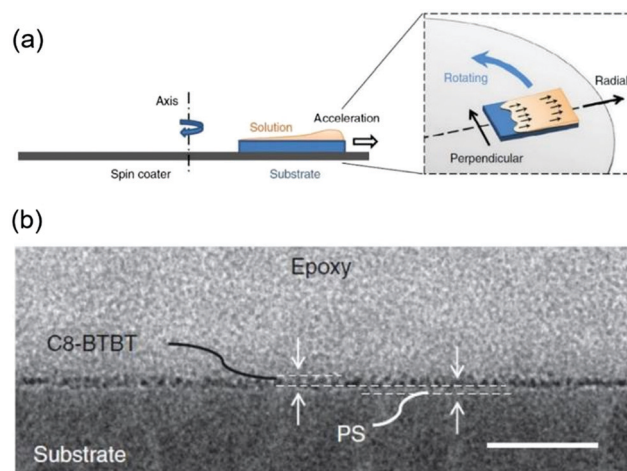

Fig. 7 (a) A schematic illustrating the mechanism of the off-center spin coating method used to deposit C$_8$-BTBT/PS blends. (b) Cross-sectional TEM image of C$_8$-BTBT/PS blend film without energy filtering, showing vertical phase segregations between C$_8$-BTBT and PS. The C$_8$-BTBT layer is observed as a dark thin layer because of the high crystallinity and electron density of C$_8$-BTBT. The scale bar is 100 nm. Reproduced from ref. 101 with permission from Nature Publishing Group.
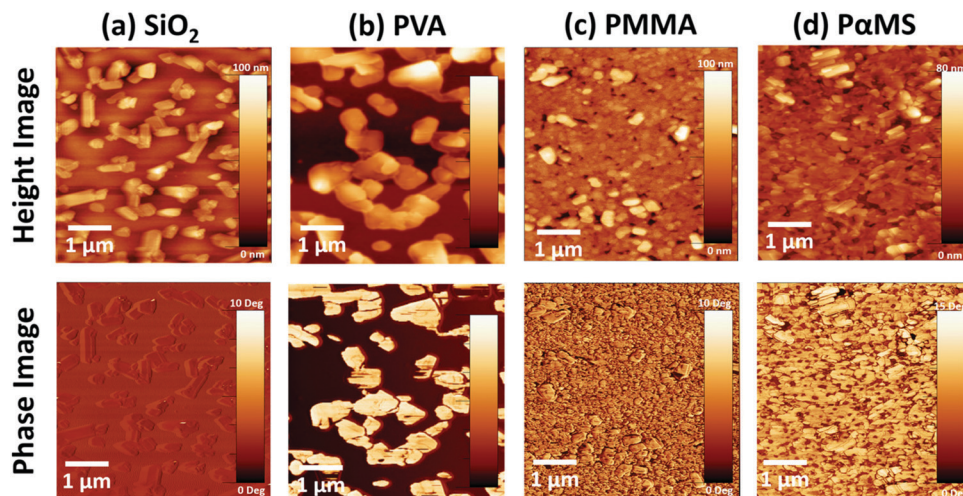
Fig. 8 AFM images of the spin-coated PDIF-CN$_2$ films on pre-coated (a) SiO$_2$, (b) PVA, (c) PMMA, and (d) PαMS polymer. Reproduced from ref. 34 with permission from American Institute of Physics.

n-type semiconductor.[34] Three different types of insulation polymers, *i.e.* poly(alpha-methylstyrene) (PαMS), poly(methyl methacrylate) (PMMA), and poly(vinyl alcohol) (PVA), were pre-coated on the substrate as an insulation layer, followed by depositing the semiconductor PDIF-CN$_2$ as an active layer for the OTFTs. As shown in the Atomic Force Microscope results of Fig. 8, the pre-deposition of the insulation polymers leads to different morphology of the spin-coated PDIF-CN$_2$ film. The incorporation of both PMMA and PαMS polymers enhanced crystalline connection and domain size. As a result, while the PDIF-CN$_2$ OTFTs without the insulation polymers exhibited an average electron mobility of 0.03 ± 0.02 cm^2 V^{-1} s^{-1}, these based on the pre-deposition of PMMA and PαMS polymers showed a mobility to 0.23 ± 0.14 cm^2 V^{-1} s^{-1} and 0.09 ± 0.03 cm^2 V^{-1} s^{-1},

respectively. Specifically, a mobility of up to 0.55 cm^2 V^{-1} s^{-1} was obtained based on the PDIF-CN$_2$ OTFTs with PαMS polymer as an insulation layer.

The various amorphous, non-conjugated polymer additives, their process and result discussed in this section are summarized in Table 1.

2.3 Conjugated polymer additives

Similar to amorphous, non-conjugated polymers, conjugated polymer additives can enhance the film uniformity, induce lateral/vertical phase segregation between the semiconductor and polymer additive, and improve the charge transport and mobilities of the small-molecule organic semiconductors. Apart from these benefits, conjugated polymer additives can

Table 1 Summary of the various amorphous, non-conjugated polymers additives discussed in this section

Material	Author	Process	Result
TIPS pentacene	Kang *et al.* and Ohe *et al.*	Blend with poly(α-methylstyrene) (PαMS) polymer additive	Vertical phase segregation occurred with a TP/PαMS/TP structure, mobility of up to 0.3 cm^2 V^{-1} s^{-1} obtained from TIPS pentacene/PαMS OTFTs
TIPS pentacene	Asare-Yeboah *et al.*	Blend with PαMS polymer additive, along with a temperature gradient method	The addition of PαMS polymer eliminates thermal cracks and reduces crystal width, leading to a mobility of 0.1 and 0.5 cm^2 V^{-1} s^{-1} from OTFTs based on silicon and ITO/PET flexible substrate, respectively
TIPS pentacene	He *et al.*	Blend with polymer additives, including poly(ethyl acrylate) (PEA), poly(butylacrylate) (PBA), and poly(2-ethylhexyl acrylate) (P2EHA)	Lateral and vertical phase separation occurred between TIPS pentacene and polymer; average mobility of 0.14 cm^2 V^{-1} s^{-1}, 0.16 cm^2 V^{-1} s^{-1}, and 0.35 cm^2 V^{-1} s^{-1} obtained with PEA, PBA and P2EHA additive, respectively
TIPS pentacene	Park *et al.*	Blend with isotactic poly(methyl methacrylate) (i-PMMA) polymer additive, combined with a vertical flow approach *via* pipette writing	Vertical flow approach along with i-PMMA additive aligned TIPS pentacene crystals, leading to mobility of 0.34 cm^2 V^{-1} s^{-1}
C$_8$-BTBT	Yuan *et al.*	Blend with PS polymer additive, along with an off-center spin coating method	Vertical phase segregation occurred between C$_8$-BTBT and PS additive, leading to a mobility of up to 43 cm^2 V^{-1} s^{-1}
diF-TES-ADT	Niazi *et al.*	Blend with PαMS, polystyrene (PS), combined with a solution-shearing method	diF-TES-ADT crystals aligned by the solution shearing method, leading to mobility of with the addition of different polarities
PDIF-CN$_2$	He *et al.*	Employ various insulation polymers, including poly(vinyl alcohol) (PVA), PMMA and PαMS to tune the crystalline film morphology of the semiconductor	Enhanced crystal connection and domain size achieved with PMMA and PαMS polymer addition, leading to an electron mobility of up to 0.55 cm^2 V^{-1} s^{-1}

also provide a unique path to tune the crystal morphology, the polymorphism and charge transport of the semiconductor *via* the intermolecular interactions between the conjugated polymer and semiconductor.[14] The following section will be discussed through the specific examples of PTAA and P3HT conjugated polymer additives.

Smith *et al.* reported the fabrication of top-gate, bottom-contact OTFTs based on TIPS pentacene and poly(triaryl amine) (PTAA) blends.[91] Fluoropolymer CYTOP is used as the dielectric layer, while either PET or Melinex film is served as the substrate. The high surface energy of the substrate results into a bilayer structure with strong phase segregation between TIPS pentacene and PTAA. This further leads to an increased concentration of TIPS pentacene in the top layer, which favors charge transport and enhances device performance of the top-gate OTFTs. As a result, a mobility of up to 1.13 ± 0.05 cm^2 V^{-1} s^{-1}, threshold voltage between -5 and -10 V, and current on/off between 10^4 and 10^5 were obtained. Although by using a top gate device configuration, the effect from the substrate on the charge transport interface can be largely suppressed, the substrate is still demonstrated to affect the conduction channel interface. Since the PET film has higher surface energy than the Melinex film, the vertical phase segregation between TIPS pentacene and PTAA is more strongly facilitated on the PET substrate, resulting in a greater concentration of TIPS pentacene moving towards the CYTOP dielectric layer and consequently a higher hole mobility.

Similarly, Kwon *et al.* reported that three different polymer binders, including PαMS, PTAA and poly(4-vinylbiphenyl) (PVBP), were blended with TIPS pentacene for OTFT fabrication.[76] These three polymers serve as adhesion layers and also as nonpolar capping layers, which can effectively improve the poor compatibility of TIPS pentacene with the gate dielectric layer. Moreover, PTAA can serve as a good hole conductor between the semiconductor and the contact electrodes, lowering the energy barrier for hole injection from the electrodes to the semiconductor. The best device performance is from the TIPS pentacene/PTAA based OTFTs, showing a mobility of up to 0.027 cm^2 V^{-1} s^{-1}, threshold voltage of -0.2 V, and current on/off of 8.42×10^4.

Mei *et al.* blended semiconductor diF-TEG ADT with a polymer additive poly(triarylamine) (PTAA) and studied the device performance consistency of diF-TEG ADT based OTFTs.[102] Although diF-TEG ADT had a trialkylsilyl substituent replaced with a trialkylgermyl group and showed distinctively different molecular packing, the diF-TEG ADT based OTFTs exhibited an average mobility of 2.3 ± 1.1 cm^2 V^{-1} s^{-1}, indicating significant variations in mobility and device performance. In order to improve device performance consistency, poly(triarylamine) was blended with diF-TEG ADT, which initiated a phase segregation between the two components upon spin coating. Top-gate, bottom-contact OTFTs based on the poly(triarylamine)/diF-TEG ADT blends exhibited greatly reduced variation of average mobility of 1.28 ± 0.05 cm^2 V^{-1} s^{-1}.

Chen *et al.* demonstrated the mediation of TIPS pentacene polymorphism by blending TIPS pentacene with two conjugated polymer additives: poly(3-hexylthiophene) (P3HT, $M_n \sim 20\,000$ g mol^{-1}) and regiorandom pentacene-bithiophene
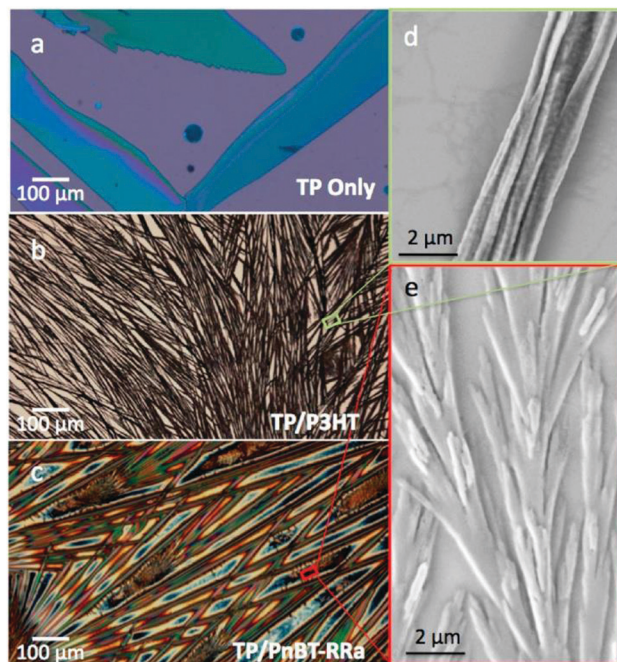

Fig. 9 Optical micrographs of (a) pristine TIPS pentacene films, and TIPS pentacene blended with (b) P3HT and (c) PnBT-RRa. The corresponding SEM images of the selected areas in (b) and (c) are presented in (d) and (e), respectively. Reproduced from ref. 14 with permission from American Chemical Society.

polymer (PnBT-RRa, $M_n = 20\,000$–$30\,000$ g mol^{-1}).[14] The optical images of TIPS pentacene film, and TIPS pentacene/P3HT, and TIPS pentacene/PnBT-RRa blend films (at 1:1 weight/weight) are shown in Fig. 9(a)–(c), respectively. The pure TIPS pentacene film shows large needle-shaped crystals with poor coverage and random orientation. The addition of P3HT changes the TIPS pentacene film morphology to a bundle of grass-like, curved microwires with enhanced long-range order, whereas the mixing of PnBT-RRa results in the formation of "interwoven" straight needles with a significant enhancement of both areal coverage and crystal orientation. The SEM images of selected areas in Fig. 9(b) and (c) are shown in Fig. 9(d) and (e), respectively. While the pure TIPS pentacene based OTFTs show an average mobility of 0.02 cm^2 V^{-1} s^{-1}, the mixing of PnBT-RRa and P3HT enhances the average mobility to 0.12 cm^2 V^{-1} s^{-1} and 0.17 cm^2 V^{-1} s^{-1}, respectively.

Bi *et al.* reported for the first time the addition of P3HT to tune the crystal morphology of a small-molecule organic semiconductor 2,5-Di-(2-ethylhexyl)-3,6-bis-(5″-*n*-hexyl-[2,2′,5′,2″]terthiophen-5-yl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (SMDPPEH).[103] When deposited *via* the method of drop casting, pristine SMDPPEH crystallized into randomly oriented needles. As a contrast, when P3HT was added to modify its crystal morphology, the addition of SMDPPEH at different weight ratios, including 1:1, 5:5 and 10:1 has in general led to the formation of crystal needles with enhanced alignment and long-range order, as shown in Fig. 10. Apart from enhancing the crystal orientation and film uniformity, XRD results also indicated that the addition of P3HT polymer additive increased the crystallinity of the SMDPPEH film. As a result, the SMDPPEH
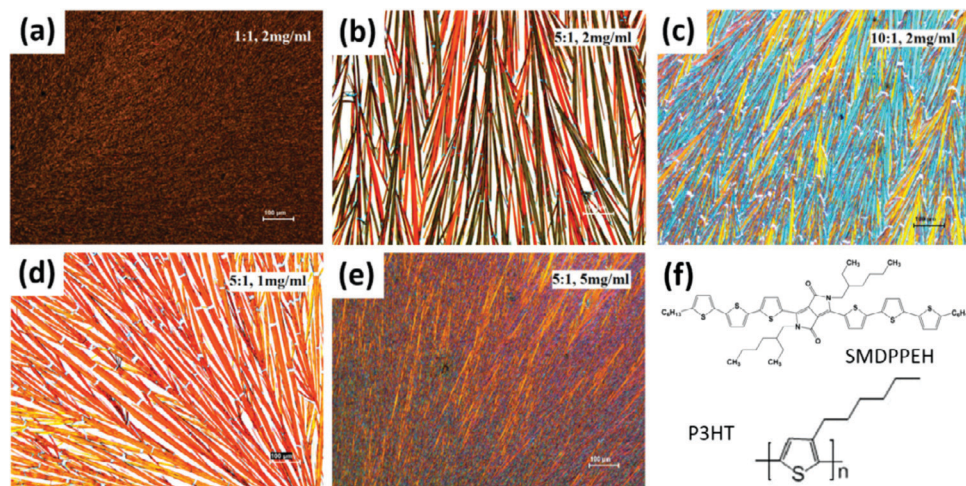
Fig. 10 (a–e) Optical images of SMDPPEH crystals with different weight ratios of P3HT conjugated polymer additive and different solute concentrations. The addition of P3HT additive has in general enhanced the crystal orientation and long-range order of SMDPPEH crystals. (f) Molecular structures of P3HT and SMDPPEH. Reproduced from ref. 103 with permission from Elsevier.

Table 2 Summary of the various conjugated polymers additives discussed in this section

TIPS pentacene	Smith *et al.*	Blend with poly(triaryl)amine (PTAA) polymer additive	Vertical phase segregation occurred between TP and PTAA, average mobility of 1.13 ± 0.05 cm^2 V^{-1} s^{-1} obtained from TIPS pentacene/PTAA OTFTs
TIPS pentacene	Kwon *et al.*	Blend with PαMS, PTAA and poly(4-vinylbiphenyl) (PVBP) polymer additives	Polymer additive served as adhesion layers and improved compatibility between TP and gate dielectric, mobility of 0.027 cm^2 V^{-1} s^{-1} obtained from TP/PTAA OTFTs
diF-TEG ADT	Mei *et al.*	Blend with PTAA polymer additive	Phase separation occurred between diF-TEG and polymer blends, leading to a mobility of 5.4 cm^2 V^{-1} s^{-1}
TIPS pentacene	Chen *et al.*	Blend with poly(3-hexylthiophene) (P3HT) and regiorandom pentacene-bithiophene (PnBT-RRa) polymer additives	Different polymorphism patterns discovered based on different polymer additive, with mobility of up to 0.12 cm^2 V^{-1} s^{-1} and 0.17 cm^2 V^{-1} s^{-1} obtained with PnBT-RRa and P3HT additive, respectively
SMDPPEH	Bi *et al.*	Blend with poly(3-hexylthiophene) (P3HT) polymer additive	Crystal alignment and long-range order achieved for the SMDPPEH semi-conductor with the P3HT polymer additive and a double-solvent system, leading to two orders of magnitude enhancement of mobility.
PDI	Bu *et al.*	Blend with poly(3-hexylthiophene) (P3HT) conjugated polymer additive	Coupled crystal formation between P3HT and PDI led to a "shish-kebabs" donor/acceptor pattern and tunable nanostructures. Further, P3HT when combined with a sonocrystallization method resulted in colloidally stable PDI nanowires with well-controlled structures.

based OTFTs with P3HT additive demonstrated a mobility that is two orders of magnitude higher than that of devices based on pristine SMDPPEH.

Bu *et al.* reported the use of poly(3-hexyl thiophene) (P3HT) conjugated polymer to tune the crystal morphology of a perylene tetracarboxy diimide (PDI) semiconductor.[104] The crystal formation of P3HT and PDI was coupled by solvent evaporation and thereby had a mutual modification of each other, leading to the formation of a "shish-kebabs" donor/acceptor pattern and tunable nanostructures. In particular, the addition of P3HT led to a kinetic stabilization of supersaturated solution of PDI and facilitated PDI to form into extended shish nanowires. These PDI nanowires further formed as heterogeneous nucleation sites from which fibrillar P3HT kebabs grew. The same authors also reported the combination of P3HT conjugated polymer with a sonocrystallization method to obtain colloidally stable PDI nanowires with well-controlled structures.[105] While the application of ultrasound helped increase the rate of crystal nucleation, the addition of the P3HT polymer as "a soluble

crystal modifier" led to a dramatic reduction of the PDI crystal formation rate *via* its preferential adsorption on the lateral crystal faces, resulting in PDI nanocrystals with sub-20 nm width. Various important factors, such as the ratio between P3HT and PDI concentrations, the molecular weight of P3HT and sonication temperature, were found to impact the size and shape of PDI crystals.

The various conjugated polymer additives, their process and result discussed in this section are summarized in Table 2.

3. Summary and outlook

In summary, this review paper examined controllable solution-based crystal morphology of various small-molecule organic semiconductors. We review additive based approaches of controllable crystal morphology and the resultant charge transport of some bench-mark, high performance, solution crystallizable, small molecule organic semiconductors. In particular, different

nanoparticle, small-molecule, and polymer additives are discussed through the specific examples of TIPS pentacene, diF-TES-ADT, PDIF-CN$_2$ and C$_8$-BTBT. The approaches that we discussed in this review may be utilized far beyond these specific examples and have important applications for future-generation high performance organic semiconductors.

The future organic electronic products will be based on high-performance organic thin film transistors that are light weight and suitable with human wearability in daily life. Therefore, the future challenges are mainly exploring and studying new semiconducting materials that are compatible with flexible substrates, nontoxic and ecofriendly, and demonstrate exceptional charge carrier mobilities. Also, since most current organic semiconducting materials show fast degradation when exposed in air, efforts are still needed to improve the environmental and air stability of these semiconductors.

Previous studies of semiconductor/polymer blends were dominantly focused on amorphous polymer additives, such as PαMS, PMMA and PS, as discussed in this work. However, there has been very few reports regarding to the effect of conjugated polymers on controlling the crystal morphology and charge transport of the small-molecule organic semiconductors. Conjugated polymers as additives can provide a unique pathway to tune the crystal morphology and enhance charge transport *via* their intermolecular interactions with the semiconductors, which is not accessible by solely adding amorphous polymer additives nor applying external alignment techniques. By engineering the conjugated polymer structures, the intermolecular interactions between the polymer and semiconductor can be correspondingly tuned, which may lead to distinctly different polymorphism and optimize film morphology and charge transport of the semiconductor. Therefore, future studies on conjugated polymers will yield more exciting discoveries.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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