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ARTICLE

Semiconducting:insulating polymer blends for optoelectronic applications — a review of recent advances

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In recent years, immense efforts in the organic electronics field have led to unprecedented progress and to devices of ever increasing performance. Despite these advances, new opportunities are sought in order to widen the applications of organic-based technologies and expand their functionalities and features. For this purpose, use of multicomponent systems seems an interesting approach in view of, *e.g.*, increasing the mechanical flexibility and stability of organic electronic products as well as introducing other features such as self-encapsulation. One specific strategy is based on blending polymeric *insulators* with organic semiconductors; which has led to a desired improvement of the mechanical properties of organic devices, producing in certain scenarios robust and stable architectures. Here we discuss the working principle of semiconductor:insulator blends, examining the different approaches that have recently been reported in literature. We illustrate how organic field-effect transistors (OFET)s and organic solar cells (OPV)s can be fabricated with such systems without detrimental effects on the resulting device characteristics even at high contents of the insulator. Furthermore, we review the various properties that can be enhanced and/or manipulated by blending including air stability, mechanical toughness, H- vs. J-aggregation, *etc.*

Organic-based electronic technologies, which promise low fabrication cost, flexibility, light weight, and simple and straight-forward manufacturing over large areas, have attracted increasing attention over the last few decades. Thanks to substantial efforts by academia and industry alike, new materials and devices have been advanced, driving technology like organic light-emitting diodes (OLED)s to the market. Moreover, great improvements have been achieved in other applications such as organic field-effect transistors and organic photovoltaics. New fields are also being explored—with great promise—including sensor applications and bioelectronics applications.

In this review, recent progress in blending organic semiconductors with insulators will be summarised. We begin the review by describing the mechanical properties of such blends and continue discussing the influence of the second component on the optical properties of the semiconductor, such as the blend absorption behaviour and exciton delocalization. We will then address the importance of solidification sequence and the role of degree of crystallinity of the insulator to obtain beneficial structures, *e.g.* to sustain bulk charge transport, as well as describe the stabilizing effect that addition of an insulator can have with respect to exposure to air. The general goal of this article is to underline the fact that blending approach allows for a wealth of opportunities for inducing desirable features in organic semiconductor-based structures

and emphasise the simplicity of blending strategies and the various opportunities they offer in the flexible electronics area.

The potential advantages and benefits of using organic compounds in the electronics area can be numerous. They often result from the many desired features commodity ‘plastics’ provide which has led to the widespread use of the latter class of materials in our everyday life. However, while organic semiconductors promise a similar versatility and breadth as the commodity polymers, their application scenario can become more challenging compared to bulk materials. An example of these differences between classical polymer products and plastic electronics technologies is given by the comparison of poly(3-hexylthiophene) (P3HT)—one of the most studied organic semiconductors—and high density polyethylene (HDPE), possibly the most widely-used commodity plastic world-wide. HDPE is a tough, ductile material, with a high elongation at break. This is evident from the stress-elongation curve displayed in Fig. 1. P3HT, on the other hand, exhibits often poor mechanical properties, with a limited elongation at break. This is due to the low molecular weight of many conjugated polymers used in organic electronic applications including most P3HTs, leading to an ‘oligomer-like’, brittle behaviour rather than a plastic performance that is typical for macromolecular matter of a molecular weight above the entanglement limit. Blending or copolymerization with an insulator of sufficiently high molecular weight can overcome this issue.¹

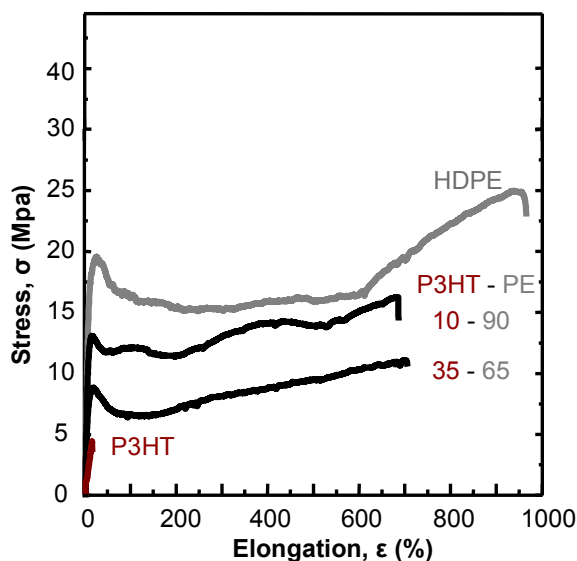


Figure 1: Stress-elongation curve for neat P3HT of a weight-average molecular weight, M_w , of 22 kg/mol (red), HDPE (grey; $M_w \approx 120$ kg/mol) and two diblock-co-polymers comprising blocks of similar molecular weights as the neat materials. The relatively weight content of the individual blocks is given in the graph. The elongation at break of HDPE is considerably higher compared to P3HT, which features a brittle behaviour. This illustrates that blends or copolymers can display performance similar to the neat insulator (adapted from Ref. 1).

Similarly, the viscosity of many organic semiconductor solutions is limited to a regime of 1-5 mPa·s because the materials used generally are of low molecular weight. This renders them incompatible with a range of deposition techniques used in the bulk commodity world as Table 1 illustrates.^{2,3} Low viscosities can represent, therefore, in certain cases an undesirable, technologically limiting factor. This can be avoided by use of materials of higher molecular weights, as the example of P3HT displayed in Fig. 2 shows.⁴ A more versatile approach is to blend an insulator of sufficiently high molecular weight with the semiconductor, analogous to the strategy described above to improve the mechanical toughness of such systems. Addition of insulating polymers thereby allows reaching a wider range of viscosities, depending on the molecular weight of the insulator, its concentration in the solution and relative composition of the materials constituting the final blend. The commodity polymer acts thereby as an “additive” with the objective to introduce the typical benefits of plastic products (plasticity and mechanical stability; tunable viscosity) without sacrificing the optoelectronic properties of the semiconductor.

Table 1: Viscosities range for commonly used solution-based coating techniques^{2,3}

Technique	Viscosity (mPa·s)
Spin coating	< 10
Doctor blade	< 10
Ink jet printing	< 10
Spray coating	10 – 1000
Gravure printing	10-1000
Flexo printing	10-1000
Slot die	10 - 100000
Knife-over-edge	100 - 100000
Screen printing	100 - 100000

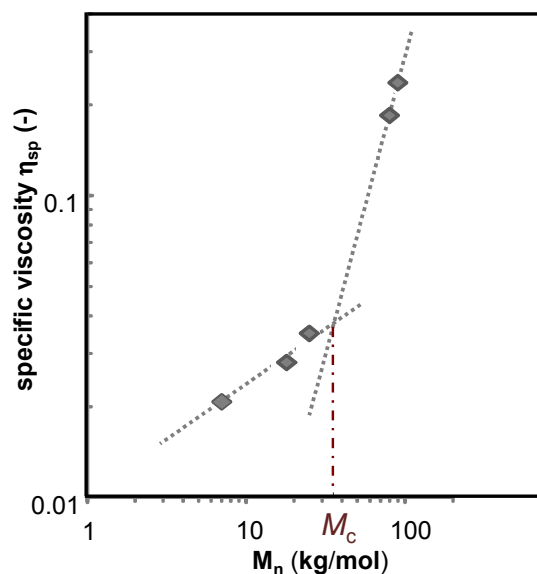


Figure 2: Specific viscosity (η_{sp}) of P3HT solutions in chlorobenzene (0.1 wt% at 21°C) as a function of number-average molecular weight (M_n) of the polymer, measured using an Ubbelohde viscometer (adapted from Ref. 4).

While addition of an insulator can have many obvious benefits, as outlined above, it is of course important to not negatively affect the optoelectronic properties of the semiconductor upon blending. Indeed, intuitively, one may expect the introduction of an insulator to detrimentally influence the desired features of the active component and, hence, the resulting device performance of semiconducting: insulating blend structures. A number of groups have, however, convincingly shown that devices and structures of characteristics comparable to those fabricated from neat materials can be produced by blending.⁵⁻¹⁴ Intriguing examples are in this context OFETs fabricated with blends comprising up to 95 wt% of an insulator, which were displaying essentially identical—if not improved—device performance than the neat semiconductor,¹¹ and ternary donor:acceptor:insulator organic solar cells where an insulator content of ~ 50 wt% allowed fabrication of solar cells of an increased thickness without sacrificing device performance,¹³ as will be discussed in details later in this article.

Blending an insulator with an organic semiconductor can also lead to other, interesting, and often desirable, features: for instance, it can strongly influence the system's optical response.^{15,16} Hellmann and co-workers have, e.g., shown that the absorption spectra of a broad range of semiconducting polymers are strongly affected by the presence of polar media, such as polyethylene oxide (PEO).¹⁵ Indeed, the absorption of P3HT:PEO blends was found to be red shifted compared to the neat P3HT (from ~ 602 to ~ 633 nm; i.e. from ~ 2.06 to ~ 1.96 eV). More strikingly, the binary films also featured a highly pronounced 0-0 transition compared to the single-component system, as the optical absorption spectra presented in Fig. 3 demonstrate. This increase in the 0-0/0-1 intensity ratio (in absorption) upon addition of the PEO could be further manipulated with the selection of the molecular weight of the P3HT as well as suitable post-deposition treatments, giving a means to control the sensitive competition between inter- and intrachain exciton coupling (leading to the different 0-0/0-1 intensity ratios) in such systems.

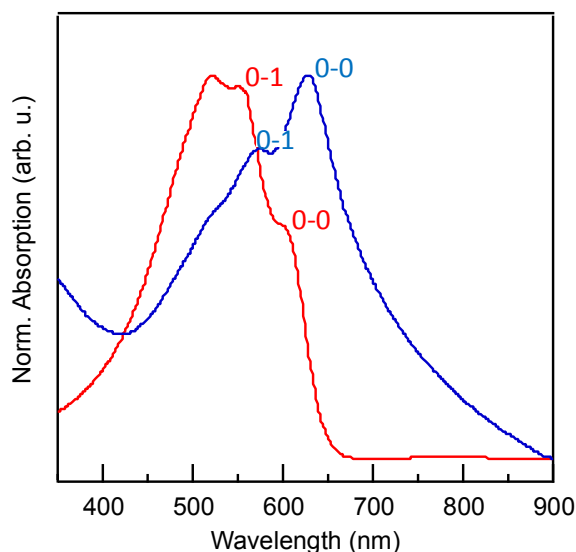


Figure 3: Normalized absorption spectra of P3HT (red) and P3HT:PEO (blue). The blend spectrum is red shifted and features a more intense 0-0 absorption (adapted from Ref. 15).

Another interesting aspect of blending organic semiconductors with an insulator is that this can lead to a certain self-encapsulation of the resulting structures and devices, leading to an increased air stability compared to neat semiconductors.^{5,11,12,14} Indeed, it is well known that organic semiconductors can suffer from photo-oxidation in the presence of oxygen and light and, as a consequence, most commercial applications of organic electronic products require encapsulation.¹⁷ An improved environmental resistance is therefore technologically highly interesting: beside a general beneficial effect during long-term usage, it also can facilitate the device fabrication due to the increased stability between different step of production before encapsulation..

Prominent examples for such self-encapsulating blends include work by Arias and co-workers, who studied a binary blend between poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene] (PQT-12) and poly(methyl methacrylate) (PMMA).¹⁴ For transistors fabricated with neat PQT-12, storage in air for 20h led to a noticeable degradation of the characteristic, evidenced by a reduced I_{ON}/I_{OFF} ratio and a substantial shift of the threshold voltage (V_{th}) to positive values. In strong contrast, PQT-12:PMMA blend devices exhibited no degradation after being in air for 48h. Exposure to air for 20 days led, however, to a threshold voltage shift of 7V (see Fig. 3), which is markedly smaller compared to the threshold voltage shift observed in neat systems only after one day. These observations are supported by work by Qiu *et al.* who reported similar results for P3HT:PS blend devices: they found that devices produced from neat P3HT featured a radical reduction of performance after one week of exposure to air, while P3HT:PS transistors displayed an essentially unchanged I_{ON}/I_{OFF} ratio and a lower V_{th} shift compared to neat P3HT.

The apparent stabilization effect when introducing an insulator in the active layer of organic optoelectronic devices is not restricted to the performance of field-effect transistors where charge transport occurs parallel to the substrate at the interface to the gate insulator and, as a consequence, some enrichment of the semiconductor at this surface may be beneficial for device performance (see below). Kumar *et al.* have,

e.g., monitored the *bulk* charge transport of P3HT and P3HT:HDPE blends via time-of-flight (TOF) photoconductivity measurements and found that charge-carrier mobilities of the blends remained basically unaltered after 4 months storage in air while P3HT samples deteriorated within hours. This is exemplified by Fig. 3 (bottom panel) where the TOF photoconductivity data for P3HT and P3HT:HDPE blend films exposed to air for two weeks are shown (adapted from Ref. 12).

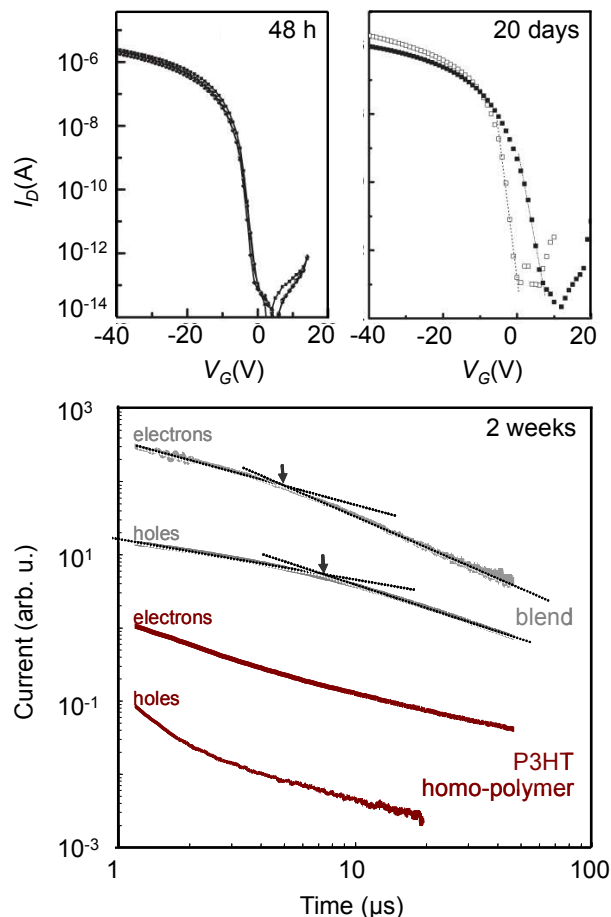


Figure 4 Top panel: Transistor transfer characteristics of bottom-gate bottom-contact devices fabricated with a PQT-12:PMMA blend. Left: Devices exposed to air for 48h feature essentially identical characteristics compare to as-cast transistors. Right: Devices exposed to air for 20 days display some degradation features; these are still significantly lower than what is observed for neat PQT-12 devices after only one day of exposure (adapted from Ref. 14). Bottom panel: Time-of-flight (TOF) photoconductivity transients for P3HT and P3HT:HDPE blend films exposed to air for two weeks (adapted from Ref. 12).

In order to exploit the beneficial effect of blending an organic semiconductor with an insulating polymer, various aspects need to be considered during materials' selection and thin film deposition, including molecular weight of the materials (alluded to above for P3HT:PEO systems), the degree of crystallinity of the insulating polymer, crystallization sequence and crystallization kinetics, *etc.* In case a *semicrystalline* insulator is used in blends with a semiconductor (rather than an amorphous polymer), the crystallization sequence of the blend components needs to be controlled; this determines not only the phase morphology of the resulting architectures but also the final degree of crystallinity of the semiconducting polymer.

The importance of control solidification/crystallisation sequence can be illustrated by the work by Goffri and co-workers who have analysed different combinations of insulators and the semiconductor P3HT, controlling the crystallisation sequence by selection of deposition temperature; *i.e.* casting at room temperature or 125 °C.¹¹ They showed that in case the insulating component, *e.g.*, HDPE or isotactic polystyrene (*i*-PS), is allowed to crystallise prior to the semiconductor (blue path in Fig. 5, top panel), a poor OFET performance is obtained. In strong contrast, when P3HT was allowed to crystallise before HDPE or *i*-PS (red path in Fig. 5, top panel), then excellent OFETs could be obtained with blends of an insulator content of up to 95 wt%. [We refer the reader to *Ref.* 11 for a detailed description of the two solidification pathways.] This stark difference in device performance was attributed to the fact that when the solidification of the semiconductor occurred in an environment of crystallised HDPE (or *i*-PS), the semiconducting polymer was not able to molecularly order in an efficient way and percolate. *Vice versa*, the ultra-low percolation limit of samples, where the semiconductor was permitted to crystallise first, was ascribed to a ‘double-percolation’-like mechanism, where the final solid-state structure of the blends is the result of multiple phase separation, first in the liquid state, followed by segregation of the—already solidified—semiconducting component caused by crystallization of the insulating matrix material. This picture is supported by grazing-angle X-ray diffraction data (Fig. 5; bottom panel), where it is evident that the P3HT component exhibited a high degree of crystallinity when it was allowed to solidify first, as can be deduced from the well-defined and characteristic reflections, both in-plane and out-of-plane.

The degree of molecular order of the insulating matrix seemed to also affect the percolation of the semiconductor in the above described systems: addition of amorphous insulators, such as atactic polystyrene (*a*-PS), to P3HT caused a rather drastic decrease of the OFET performances even at low contents of insulator, independent of the solidification sequence selected. This was explained by the between semiconductor and insulator miscibility in the liquid phase, which is higher when an amorphous insulator is used preventing a double-percolating effect to occur. It was therefore speculated that a semicrystalline insulating polymer is preferable to assist in inducing a segregation of the semiconductor by the crystallization of the insulating matrix.

In agreement with this picture are observations by Xu *et al.* who showed that casting a P3HT:*a*-PS solution from chloroform solutions seemed to prevent formation of a crystalline, network-like structure of P3HT.¹⁸ Heating such thin-film structures at temperatures above the melting point T_m of the polymers could however induce recrystallisation of P3HT – provided a low molecular weight *a*-PS (1 kg/mol or less) was used. When an *a*-PS of higher molecular weight was employed formation of high quality P3HT aggregates was prevented. This was assigned to the higher entanglement density (and hence, melt viscosity), hindering the molecular mobility of P3HT chains during heating above T_m . The lower miscibility of the two components is likely to contribute to the observed effect.

It is important to note here that blending of an organic semiconductor with an *amorphous* insulators not necessarily leads to a degradation of device performance. Qiu *et al.* have, for instance, reported P3HT:*a*-PS blends for use in OFETs where addition of the *a*-PS did not result in a loss of performance, also when high insulator contents (up to 90-95

wt%) were used.⁵ Solvent selection seems to be highly important in this case. During casting the blend from a ‘bad solvent’ for P3HT (here: dichloromethane), solvent evaporation leads to rapid aggregation and crystallisation of the P3HT because its solubility limit is reached rapidly. Since the insulator has a higher solubility than P3HT, it only solidifies after the semiconductor. As a result of such solvent-assisted solidification-sequence control, a microstructure of interconnected P3HT ‘whiskers’ (or: nanowires) that are embedded in an *a*-PS matrix is obtained, as Fig. 6 (bottom panel) visualises. Conversely, when a ‘good solvent’ was used for the deposition of such P3HT:*a*-PS blends (using in this case chloroform), an entirely different microstructure is realised, comprised of ‘droplets’ of P3HT in an *a*-PS matrix. This leads to a low OFET performance.

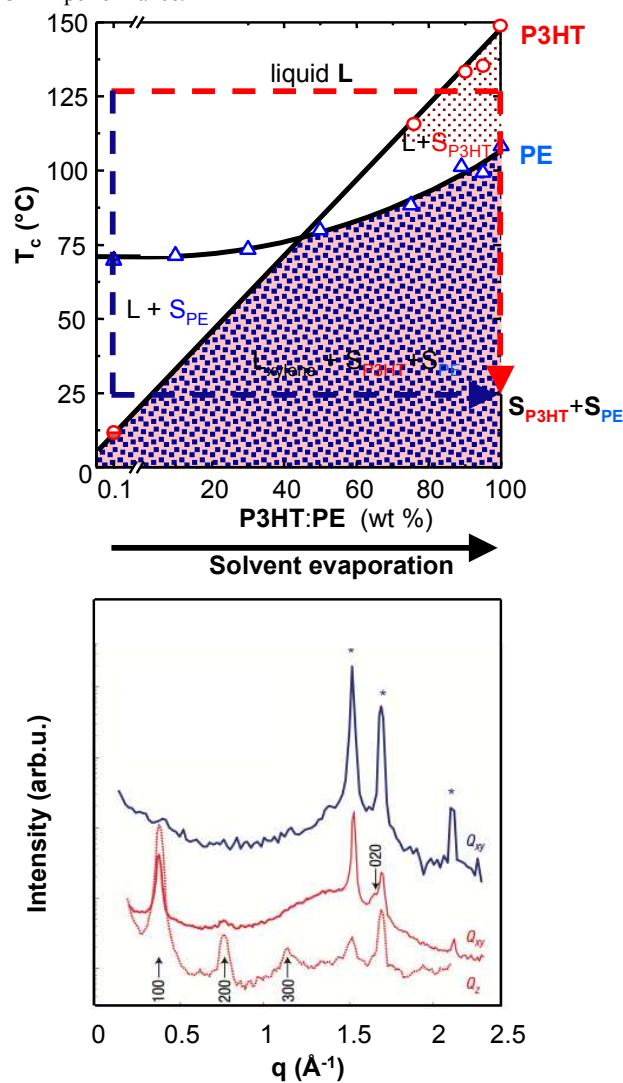


Figure 5: Top panel: Possible solidification pathways of P3HT:HDPE blends, controlled by the deposition temperature. When plotting the crystallisation temperature as a function of solvent content, it is evident that P3HT crystallises prior to the HDPE when elevated deposition temperatures are selected (red), while at low deposition temperatures the HDPE crystallises first (blue). For more details we refer the reader to *Ref.* 11. Bottom panel: GIXD diffractograms that illustrate that blends processed under conditions for which P3HT crystallises prior to the insulating polymer feature well-defined P3HT diffractions both out-of-plane (red, dotted line) and in-plane (red, solid line). These characteristic diffractions are not present in films in which the insulator crystallised prior to the

P3HT (in-plane diffraction for P3HT-HDPE: blue, solid line). The asterisks indicate the main HDPE diffractions (adapted from *Ref.* 11).

It is obvious from the above examples that a range of means exist to manipulate the solidification sequence of blends. This is important for their use in a range of optoelectronic devices, including transistors. Qiu *et al.* exploited the different solubility of the insulator and semiconductor in a given solvent, while Goffri *et al.* made use of the crystallisation of the insulating matrix to create percolating structures. The common feature in both scenarios is that the semiconducting polymer is allowed to solidify prior to the insulating matrix. As a consequence, comparable device performance is obtained to the neat system – and indeed, in specific cases improved device characteristics are recorded. For instance, I_{OFF} is often found to be drastically reduced, leading to higher ON/OFF ratios, and the field-effect mobilities increases in certain blend films.^{6,19}

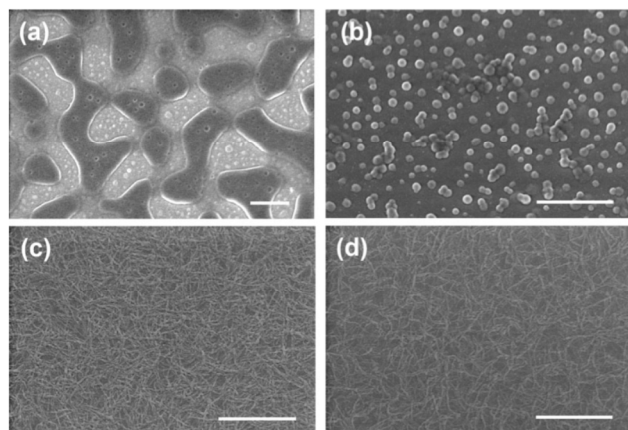


Figure 6: Scanning-electron micrographs of P3HT:α-PS blends. Top panel: Films cast from chloroform of different composition: a) 60 wt% P3HT and b) 10 wt% P3HT. Bottom panel: Films cast from dichloromethane: c) 10 wt% P3HT and d) 5 wt% P3HT (adapted from *Ref.* 5).

So far we have discussed semiconducting:insulating blends used in field-effect transistors where functioning devices were obtained when no significant vertical phase segregation needed to occur and percolating networks were sought to be realised (although some enrichment of the semiconductor at the interface with the gate dielectric cannot be excluded). Another compelling option that blending of an organic semiconductor with an insulator offers is to induce an asymmetric segregation of the two components. This can lead to bi- or multilayer structures of the various components.⁷ It also can be used for surface self-assembly that induces patterns of stratified layers of semiconductor and insulator.⁸ Qiu *et al.* employed, for instance, P3HT in combination with PMMA. The difference in surface tension between the two polymers led to a bilayer structure with the insulating polymers segregating to the bottom interphase. This stratification improved the blend OFET performance.⁷ Salleo *et al.* further exploited this behaviour and cast a PQT-12:PMMA solution onto a pre-patterned OTS substrate. This resulted in a bilayer with PQT-12 at the bottom interface exclusively where OTS was present. On the rest of the substrate, the blend structure consisted of a PMMA matrix with PQT-12 droplets embedded in it.⁸

When used in FETs, we like to point finally to another intriguing benefit semiconductor:insulator blends can offer. Lu *et al.* reported that two-component systems comprising up to 95 wt% α-PS or PMMA displayed

a poor transistor operation when as-prepared and measured in a glovebox. However upon exposure to air, all the device parameters improved and exceeded those of the neat semiconductor.⁹ The authors attributed this behaviour to a moderate oxygen-induced doping of the semiconductor as a result of a vertical phase segregation. It is important to note, though, that further exposure to air did not change the OFET characteristics. The origin for this beneficial effect seems to be still unclear. What is also remarkable for this case in point is that excellent device performance were also obtained when films were cast from a good solvent where a less favourable crystallisation of the semiconductor is expected to occur in the presence of a high content of insulator (95 wt%), as discussed above.

From these examples, it is apparent that semiconductor:insulator blends can provide an interesting landscape for microstructural control and manipulation of various features when used in transistor devices. Thereby it is important to note that the blending strategy seems widely applicable: it is not limited to polymer:polymer blends only, but can also be used for multicomponent systems comprising an insulating polymer and a *small-molecular* semiconductor,^{20–26} or copolymers comprising semiconducting and insulating moieties. For the latter structures, very similar observations have been made as for blends.^{1,27–31} For instance, copolymers including block copolymers comprising polyethylene,¹ polystyrene,²⁹ poly(methyl acrylate),³⁰ or poly(fluorinated alkyl methacrylate)-segments³¹ have been studied. In many cases, excellent bulk conductivities and field-effect mobilities were reported for such semiconducting-insulating systems. This has been attributed to a favourable microphase separation leading to optimal percolating pathways. In addition, for selected materials, increased stability was found, similar to semiconducting:insulating blends.

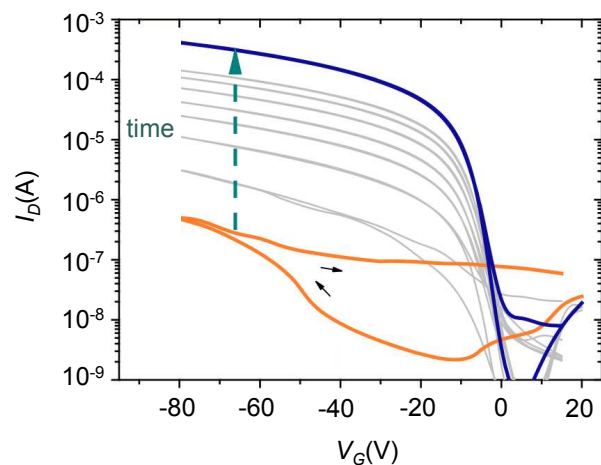


Figure 7: Transistor transfer characteristics of a top-contact bottom-gate device fabricated with a P3HT:PS blend (5 wt% HDPE). Evolution of the characteristics in the linear regime ($V_{\text{DS}} = -5\text{V}$) over time under exposure in a N_2 atmosphere (O_2 concentration ≈ 1 p.p.m; and H_2O concentration ≈ 1 p.p.m). Blue data set refers to a 1447 min exposure (adapted from *Ref.* 9).

As mentioned above, multicomponent systems comprising insulating polymers have also been investigated for use in photovoltaic applications. Here charge-transport through bulk of the solar cell is relevant — as measured *e.g.* in TOF photoconductivity experiments described above and requiring an interpenetrating network of *n*-type (electron) and *p*-type (holes) pathways. OPV performance can thus often

be more challenging to be manipulated when compared to active layers used in OFETs because of the delicate interplay of optoelectronic processes (charge generation, charge transport, charge extraction, *etc.*) that needs to be optimised in OPV structures. These processes and phenomena strongly depend on the microstructure of the active layer,^{32,33} which will be affected by the addition of an insulator and consists of a blend of a donor and an acceptor material—generally, a fullerene derivative such as [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM). A conjugated polymer or a small-molecular organic compound is employed in many cases as donor material. Use of blends comprising beside the donor and acceptor also an insulator can therefore open interesting options. Ferenczi *et al.* showed, for instance, based on the well-studied P3HT:PCBM system, in combination with HDPE and *i*-PS that solar cells of an insulator content of up to 50 wt% can be produced without resulting in a noticeable reduction in device performance.¹³ Moreover thick devices (~300nm) could be produced when using a ternary blend. This assisted to overcome the reduction in optical density compared to devices comprising no insulator because of the introduction of the insulating, non-absorbing material. More importantly, an increase in the thickness of the active layers is useful for obtaining a more reliable manufacture of organic solar cells, and it also bodes well with activities targeted to produce mechanically stable and robust devices. Further research is, however, needed. In contrast to OFETs, the amount of insulating component that can be added to donor:acceptor blends has so far been limited to ~50 wt%; at higher insulator content, device performance rapidly degrades. This has been attributed to the percolation-behaviour of PCBM: at high fractions of the insulator, no continuous pathway for electrons can be created due to the small-molecular nature of this acceptor, limiting charge extraction. This threshold composition, at which device performance is lost, seems to depend on the insulator matrix used. While up to 50 wt% of semicrystalline insulators can be added, device performance degrade already at small content of the amorphous *a*-PS, very similar to observations made on semiconductor:insulator OFET blends. New possibilities can therefore be developed also in the OPV field when introducing insulator moieties and components to donor:acceptor systems, and various approaches have already been considered and tested in the OPV area, including application of block copolymers comprising semiconducting and insulating segments used in combination with fullerene derivatives;³⁴ addition of copolymers to donor:acceptor blends to manipulate the crystallisation of P3HT and PCBM, to control the donor:acceptor phase morphology;³⁵ or the introduction of a short, insulating (*a*-PS)-side chain to isoindigo-based polymers to tune solubility and processability.³⁶

Conclusions

We have shown here on various examples that semiconducting:insulating blends and related systems such as copolymers comprising semiconducting and insulating segments provide a versatile and rich platform for materials exploration and realisation of a range of device architectures. Classical properties of plastics of bulk ‘pastics’, such as toughness and mechanical robustness can be introduced to organic semiconducting systems, which generally feature a rather brittle behaviour. Thereby the electronic properties of the semiconducting

component can be maintained: excellent OFET characteristics have been reported even when a very low weight fraction of semiconductor is used. Either semicrystalline or amorphous insulators can be employed as long as the semiconductor is allowed to solidify before the insulator. Similar rationales apply for use of blends and multicomponent systems for OPV fabrication: devices can be produced at insulator content of up to 50 wt%, allowing for the thickness of the active layers to be increased. Clearly, the possibilities are vast and more opportunities for such semiconductor:insulator blends will arise, for instance in areas such as bioelectronics, organic-based thermoelectrics and beyond.

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Notes and references

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