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Doped organic field-effect transistors

Abstract

Organic semiconductors and electronic devices based on these materials continue attracting great interest due to their excellent and unique optoelectronic properties as well as the advantageous possibilities of realizing flexible, light-weight, low-cost, and transparent optoelectronic devices fabricated on ultra-thin and solution-processible active layers. However, their poor electronic performance and unstable operation under ambient conditions limit their application in consumer electronics. This paper presents a brief introduction to doping of organic semiconductors and organic field-effect transistors. The description of the issues regarding charge carrier transport and other optoelectronic properties of organic semiconductors is also provided. The doping agents and methods commonly applied for organic semiconductors along with their fundamental mechanisms are introduced.

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Introduction

Organic semiconductors (OSCs) due to their unique mechanical and optoelectronic properties combined with structural and chemical benefits that come naturally, continue being the center of attention. More and more scientific investigations revolve around the development of organic semiconducting materials as they paved a path for developing a range of organic devices such as organic photovoltaics (OPVs), organic field-effect transistors (OFETs), and organic light–emitting diodes (OLEDs), etc. Their main advantages over the inorganic semiconductors include unique physical and mechanical properties which in turn open great opportunities for realization of flexible, light–weight, transparent, ultra-thin, printable and even paper-based devices. Organic materials are also very easily processed. They offer fabrication methods ranging from conventional thermal evaporation to solution–processing that enables simple fabrication steps such as spin–coating, drop–casting, inkjet–printing and so on, at temperatures as low as room temperature. Also organic materials are plenty and hundreds of them are synthesized every year. They offer a great range of options for synthesizers. In particular, constant performance progress is possible by optimization of the molecular structures using organic chemistry to achieve the desired requirements and functionality. Numerous OSCs have been developed to extend the opportunities to explore new applications.

But the main advantage of the organic materials and devices is that they themselves and the processes they go through are not as expensive and complicated as those of their inorganic counterparts. However, OSCs suffer from very serious issues related to their limited electronic properties and unstable operation in ambient environments. Although organic semiconductors offer a great range of application fields, these two issues make them fall behind the inorganic semiconductors. In order to address the above mentioned problems, material scientists and engineers have developed several ways for the last few decades since the organic electronics appeared. Some of these ways have proved themselves to be really straightforward methods for the improvement of the electrical properties and stability of organic semiconducting materials. These methods include doping in the first place, and then dielectric engineering, contact engineering, process engineering and so on. Doping has already been demonstrated and applied as the best improvement method for inorganic electronics including silicon technology, for more than 40 years now. Doping of OSCs by introducing small amount of impurities into functional films has also become a simple and effective way to resolve the limitations of organic semiconductors without sacrificing their unique advantages. Recent progress in the field of organic electronics confirms that molecular doping of OSCs successfully contributes to commercialization of the devices such as OLEDs by promoting efficient charge injection. The charge carrier concentration, charge polarity, mobility, stability and other related intrinsic electrical properties can be significantly improved and enhanced by several orders of magnitude via doping. As an example we can show a very famous organic electron transporting material, C_{60}, intrinsic conductivity of which was enhanced from $3.80x10^{-8}$ up to the value of $7.90x10^{-3}$ by doping. However, the doping techniques in organic electronics are completely different from those of inorganic electronics. While doping of inorganic materials involves replacement of matrix atoms by the impurity atoms, doping of organic materials is nothing more than simple charge transfer process.

There are two main conventional processing methods for doping organic semiconductors: co-evaporation and solution processing. In co-evaporation, organic matrix molecules and the doping agent are thermally co-evaporated. This method is particularly suitable for insoluble or less soluble organic matrices that consist mostly of small-molecule materials (oligomers). However, it requires expensive deposition machines and is not well suited for polymer semiconductors. Solution processed doping, on the other hand, is a simple and expedient fabrication method (from an economic point of view). The host and dopant molecules can be coated onto any kind of substrate from a blended solution or separate solutions to form a single or separate films, respectively. The latter is applied when the host and dopant molecules are not compatible to be blended together in one solvent.[1] Some dopants, mostly inorganic salts or oxides, will not dissolve in any organic solvent, which makes it impossible to use them as dopants for semiconducting polymers. Other dopants form aggregates in the solution when mixed with the host molecule which limits the doping effects and can even cause degradation of the device performance. Therefore, a great challenge for material scientists is to find suitable dopants for solution based doping. A wide range of organic and inorganic materials, such as salts, conjugated small molecules and polymers, alkali metal compounds, and metal oxides, have been studied as potential dopants for OSCs.[2,3] And once again, it is much more challenging to find reliable n-type doping agents than p-type doping agents. Nevertheless, inorganic dopants involving alkali metals such as alkali metal salts, and organic dopants, such as cobaltocene, have been successfully employed as n-channel dopants. As with inorganic electronics, OSC doping also provides the host material with extra electrons (n-type doping) or holes (p-type doping). Since the doping process involves the whole molecule rather than individual atoms, achievement of the desired doping type for organic electronics depends strongly on the energy levels, i.e., the HOMO and LUMO levels of the matrix and dopant molecules.[1,4]

To achieve p-type doping, the HOMO level of the organic matrix molecule should be higher than the LUMO level of the doping agent. In this case, the dopant molecule is referred to as an acceptor while the host molecule is the donor. In n-type doping, the donor must be the dopant molecule. Therefore, its HOMO level should be higher than the LUMO level of the matrix molecule, which is the acceptor in this case. Depending on the type of doping and energy levels of materials used, it is even possible to apply the same dopant both as a donor or an acceptor for different host materials when their energy levels are compatible. There are several common methods for doping organic polymers. They are for example, chemical doping, which is the first doping mechanism ever used, electrochemical doping, interfacial doping, photo–induced doping, etc. In chemical doping, organic matrix molecule and the doping agent can be either blended in a solution or thermally co-evaporated. Although electrochemical doping is not common for OFETs, there have been some reports on the OFETs based on electrolyte–gate dielectrics where possibly this kind of doping process takes place. Interfacial doping involves injection of relative charge carriers (holes or electrons) which depends on the polarity of the gate voltage, from metal contacts into the organic semiconductor. Among all the above-mentioned, the last doping mechanism, photo–induced doping, may be considered the most complicated and time–demanding method for doping, as it involves several complicated steps such as thermal co–evaporation, extra light excitement in order to excite the electron to jump to a level much higher than its binding energy, then yet, another step like hydride or another ion transfer to the dopant molecule, is needed to prevent this electron to fall back again to its former energetic state as it is lower than its current state.

Below some reported doping results from different scientific groups will be reviewed briefly. Chuan et al. have demonstrated significantly improved mobility, on/off current ratio, crystallinity, injection and reliability in n-type polymer P(NDI2OD-T2) based OFETs via molecular doping.[2] They applied P(NDI2OD-T2), also known as N2200, which is a conjugated electron transporting polymer with a very low lying LUMO level (around -4.0 eV) which makes it very suitable for n-type doping. By using two different classes of organic and inorganic dopants, namely, cobaltocene ($CoCp_2$) and cesium fluoride (CsF), respectively, they were able to enhance the FET mobility twice and decrease the threshold voltage almost four times. Both dopants resulted in an increase in carrier concentration which in turn, smoothed the path for free charge carriers as the result of filled traps by introduced extra carriers. The Fermi level was effectively shifted towards the LUMO level of the host material. Remarkably, both dopants exhibited the same tendency in mobility change. Mobility continuously increased by increasing the dopant concentration as the significant number of trap states became filled due to the extra charge carriers introduced via doping. Nevertheless, after some critical point which was 0.5 wt% dopant concentration in said research, additional concentration did not improve the mobility but decreased it even below the intrinsic value. This phenomenon was attributed to the molecular structure disturbance because of the introduction of too many impurity carriers which in such a case play also the role of additional trap sites.

Another impressive work was done by Dongyyoon Khim and his colleagues in 2014.[3] He demonstrated an effective way for controlling polarity of charge transport in OFETs by selective molecular doping. Via blending a small amount of two different molecular dopants, F4-TCNQ for p- channel doping and CsF for n–channel doping, he could selectively tune the operational polarity of intrinsically ambipolar methanofullerene [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) from ambipolar transport to unipolar, either electron– or hole–transport in OFETs. This method is very effective for complementary integrated circuits based on organic semiconductors. By this doping process the same organic material can be doped both ways to comprise a p–n junction just as in silicon electronics. Yuan Zhang et al.,[5] by using an n–channel dopant decamethylcobaltocene (DMC), achieved a trap–free space charge limited electron transport in a conjugated polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) which is intrinsically, a p–type semiconductor as the electrons are strongly trapped in its backbone. The deep traps in the polymer's structure were effectively deactivated (filled) by the dopant–induced carriers.[5] Nollau et al.,[6] reported a controlled n-type doping of OSCs by co-sublimation of two semiconducting materials: a strong electron acceptor and electron transport material, 1,4,5,8-Naphthalene-tetracarboxylic-dianhydride (NTCDA), as the host structure; and the charge transfer salt, bis(ethylenedithio)-tetrathiaflvalene (BEDT-TTF), which is a semiconducting material itself, as the dopant.[6] Yabinq Qi et al.,[7] obtained air–stable n–type doping with $[RhCp_2]_2$ and $[Cp^*Ru(TEB)]_2$ for polymeric organic semiconductors such as P(NDI2OD-T2) and small molecule organic semiconductors such as TIPS-pentacene, current density, conductivity and stability of which increased several orders of magnitude via doping.[7]

Results of Calvin K. Chan et al. confirmed once again that, strong reducing agents such as $CoCp_2$ are effective n-type dopants.[8] Their doping process was a little different from conventional solution or co–evaporation doping methods. CoCp2 was incorporated as a vaporized dopant in a single layer grown by thermally evaporating cobaltocene and the host material. This type of doping can be referred to as a gas–phase or vapor doping. Another group of scientists, Selina Olthof et al.,[9] managed to achieve a controlled passivation of acceptor tail states that act as charge traps, in fullerene C_{60} by ultralow molecular n-doping. By successfully filling the traps with very small amount of dopant material, they were able to obtain increased conductivity, mobility, and decreased activation energy. Fermi level position and work function of the material were also effectively controlled by this doping.[9] Another class of organic materials that have been used as molecular n–channel dopants by some research groups[10–14] are cationic dyes which are basically organic salts. The doping process involving these organic dyes has been photo-induced doping so far which has already been discussed in the introduction part of doping fundamentals. Both the host and the doping molecules were thermally co–evaporated to form a uniform film. During the co–evaporation process, the dopant organic dyes undergo oxidation and form their leuco bases which act as the basic doping agents. The host materials used for the study have included non–polymeric organic semiconductors such as NTCDA, $F_{16}ZnPc$, TCNQ, F4-TCNQ, and C_{60} which are very strong electron acceptors. The cationic dyes reported as n-type doping agents via photo-induced doping, include Pyronin B (PyB), Crystal Violet (CV), Acridine Orange (AO), Malachite Green (MG), and their leuco–bases. N-doping effects of these cationic species was only due to the process they went through to be reduced to their electron donating leuco states which contain partially filled LUMO level. The electrons were added to the host molecules from this partially filled LUMO which was termed as the singly occupied molecular orbital (SOMO) in this case.

N-type doping

As it was already mentioned, in organic electronics, the energy levels, namely the HOMO and LUMO levels of both the matrix

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and the dopant molecules play the essential part in doping process. In n-type doping, the dopant molecule plays the role of the donor and its HOMO level or partially or completely occupied LUMO level should be higher than the LUMO level of the matrix molecule which, in this case, is the acceptor. Figure 1 illustrates n-type doping process in organic semiconducting materials. N-type doping can also be achieved using Lewis bases, the chemical species with a filled orbital that contains an unbound electron pair capable to form bonding with other species via electron transfer. Thus they are good electron donors and can be employed for an effective n-type doping of organic semiconductors. This is especially effective for the materials with high lying LUMO levels that for n-type doping, would require a dopant with a HOMO level lying even higher than its LUMO which is impossible to find. A large number of inorganic and organic reducing salts acting as Lewis bases were applied as effective n-type dopants. They include but are not limited to lithium fluoride (LiF), sodium fluoride (NaF), $CoCp_2$, etc.[8,15,16]

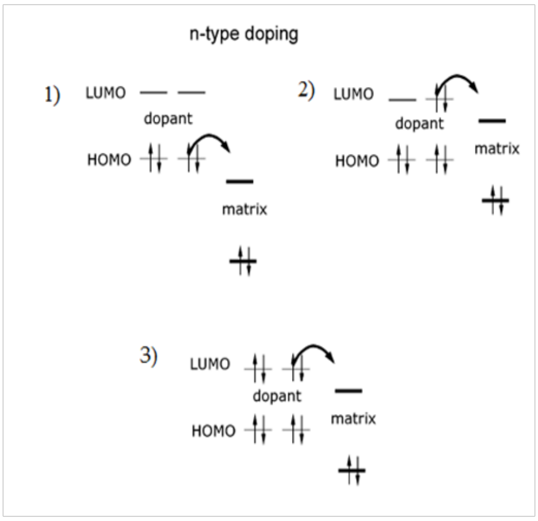

Figure 1 Schematic illustration of molecular n–type doping mechanisms.

P-type doping

In case of p-type doping, the HOMO level of the organic matrix molecule should lie higher than the LUMO level of the doping agent. In this case, the dopant molecule is referred to as an acceptor while the host molecule is the donor. Figure 2 illustrates p-type doping process in organic semiconducting materials. P-type doping can also be achieved by employing Lewis acids, the chemical species with an empty orbital capable of accepting electrons. They are electron acceptors and the effect of electron-withdrawing tendency of Lewis acids leads to effective p-type doping of organic semiconductors. For this purpose, a number of materials including iron chloride ($FeCl_3$) and cationic dyes, have been successfully applied for p-channel doping of OFETs and FETs based on carbon nanotubes.[17–20] It is especially effective for host materials with very low lying HOMO levels which would otherwise logically require a dopant that has a very low lying LUMO level for standard charge-transfer doping, that is almost impossible to achieve.

Evaluation and confirmation methods for doping efficiency

When it comes to checking doping efficiency and confirmation of doping, the Fermi level is the key parameter to investigate as doping efficiently can tune its position by shifting it towards the desired energy level (HOMO or LUMO). For organic semiconductors, the Fermi level can be understood as available energy states (chemical potential) that can be occupied by electrons. The position of the Fermi level is what defines the materials polarity. If it is near the CB (LUMO, respectively), then the material exhibits good electron transporting properties (n-type), if it is located near the VB (HOMO, respectively), the material is a good hole–transport semiconductor (p-type). For ambipolar semiconductors, this level is considered to be somewhere in the middle of the band gap between the CB and VB. Figure 3 illustrates the position of the Fermi level in different types of organic semiconductors. Determination of the Fermi level position is a common way to study and estimate doping efficiency. Among other methods enabling measurement of electrical conductivity in materials and examining doping levels, ultraviolet photoelectron spectroscopy (UPS) has been effectively used by scientists to study doping. It is a higly surface sensitive technique used to analyze the positions of the VB maximum (HOMO) and Fermi level. In p-type doping, Fermi level shifts towards the lowest half (towards HOMO) of the bandgap while in n-type doping, Fermi level moves away from HOMO closer to the upper part (towards LUMO). According to the changes in the Fermi level positon after doping, doping can be effectively estimated. Another widely used technique for characterization of doped films, is X-ray photoelectron spectroscopy (XPS). It is employed to determine doping levels by characterizing the nature and concentration of doping species in doped films and electronic properties of both pristine and doped materials. XPS spectra can effectively reveal the chemical surface modifications as well as bonding and distribution of dopant species in doped organic materials. Investigation of the crystal structure after doping is also a good method to study doping on microstructural scale. X-ray diffraction (XRD) is used to analyze doping effects on XRD peak intensities and positions (d-spacing) in doped samples compared to pristine ones. Another attractive method for characterization of doped films is ultraviolet-visible absorption spectroscopy (UV-vis absorption spectroscopy). The changes in the bandgap after doping can be effectively measured by this technique according to the changes in the spectra of the doped materials.

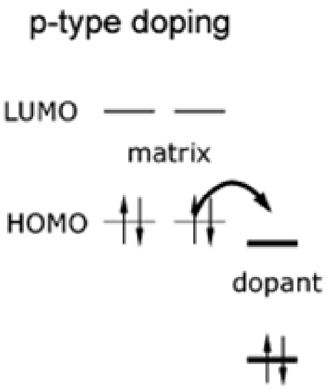

Figure 2 Schematic illustration of molecular p–type doping mechanism.

Conclusion

This paper has discussed the molecular doping of OFETs by the means of co–solvent blending and co–evaporation. For doping of organic materials both organic and inorganic materials can be

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employed. The doping mechanism used for organic electronics is totally different from that of inorganic electronics. The structural and electrical properties as well as stability of organic semiconducting materials including both small and macro molecules, can be remarkably improved by doping techniques. The resultant materials with enhanced properties can be applied to a wide range of electronic devices such as OLEDs, OFETs, CMOS–like integrated circuits, etc. However, there are still some points that should be cleared and understood in doping of organic semiconductors. In addition, even though doping improves and enhances the device performance, organic electronics still falls behind the inorganic electronics. Therefore, new, powerful and reliable dopants for organic materials have to be developed.

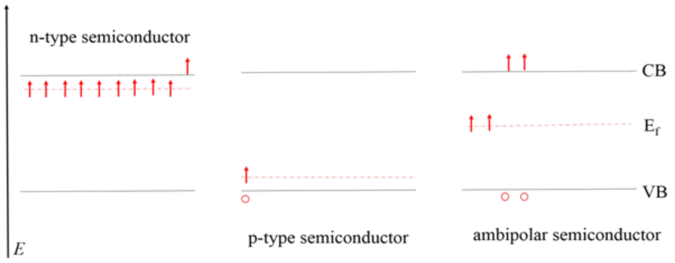

Figure 3 The Fermi level positions in n-, p-type and ambipolar semiconductors.

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Conflicts of interest

Authors declare that there is no conflicts of interest.

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