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DOPING METHODS FOR ORGANIC SEMICONDUCTORS

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ABSTRACT For many years, the idea of electronic doping in organic materials was ambiguous. Early on in the search for high electrical conductivity organic substances, it attracted a lot of interest, which helped to set the groundwork for the groundbreaking research on pure organic semiconductors (OSCs) and their ultimate wide range of uses. Despite this, development and widespread use of dopants have gone hand in hand with current advancements in organic electronics. An overview of significant developments in organic semiconductors doping and its applications is discussed here. This article begins by reviewing pertinent literature and talking about established mechanisms and processes involved in doping organic semiconductors. At last concluding the article, how doping can improve the performance of different types of organic electronics

Keywords: *Semiconductors; Ion; Charge; Doping; Organic*

INTRODUCTION

Organic semiconductors are very important and interesting from a technological standpoint, having functions and properties in a broad range of optoelectronics, including organic light-emitting diodes, organic photo-voltaics and organic field-effect transistors, in addition new developing technologies, including bio-electronics. The arrangement of the solid-state subunits in Organic Semiconductor substances, either molecular or polymeric, determines the properties applicable for device performance. Organic electronics, such as light emitting diodes, field-effect transistors, solar cells, photo-detectors, logic circuits, memory devices, chemical sensors, and many more, can be appealing in comparison with their inorganic substitutes for various reasons. OSCs are excellent than inorganic in the field of large-area and low-cost, because of their wide range of optoelectronics, make customized materials feasible. For instance, there are organic dyes that have remarkably intense visual absorption co-efficient, which make it possible to create incredibly thin photovoltaic cells and photo-detectors. Organic fluorescent dyes with significant, absorption to emission red-shifts and low refraction indices can help prevent reabsorption losses, one of the main issues with inorganic LEDs. Furthermore, because of their saturated electron systems, organic semiconductors disordered systems provide a less concentration of intrinsic defects, whereas high trap density is produced by the dangling bonds found in inorganic amorphous semiconductors. Ultimately, processing OSCs is simple. For instance, they can be deposited at room temperature on flexible substrates. Organic semiconducting materials are the most significant component in device configuration due to their ease of structural alteration, which optimizes the ensuing optoelectronic properties to match the needs for individual devices. During the last few decades, synthetic modification has been able to greatly increase device performance. Specifically, organic field-effect transistors have shown charge carrier mobility of over 10 cm^2 V−1 and the maximum power conversion efficiency of 17.3% was attained in bulk heterojunction (BHJ) solar cells (Yi, Wang, & Liu, 2015). For several decades, researchers have been investigating molecular dopants for organic semiconductors; nevertheless, they did not advanced as quickly as intrinsic organic semiconductors (Yi et al., 2015). Small oxidants molecules such as Br_2, I_2 and AsF_5, vapors were used to dope organic semiconductors. This significantly increased polyacetylene conductivity from $\sigma \sim 10^{-6}\ \Omega^{-1}cm^{-1}$ to $\sigma > 10\ \Omega^{-1}cm^{-1}$ (Shirakawa, Louis, MacDiarmid, Chiang, & Heeger, 1977).Intrinsic semiconductors are pure semiconductors. But in the majority of cases, the semiconductor is doped to change the material's Fermi energy or to enhance its electron or hole conductivity. Doping in inorganic semiconductors refers to the addition substitution of an atom that is interstitial within the crystalline matrix. Either by giving electrons to donor states near the conduction band edge (n-type doping), which produces free electrons, or by offering empty acceptor states near the valence band edge (p-type doping), which produces free holes. Although the term "bands" is used in OSCs, it is incorrect since organic molecules have significantly stronger bonds in their electronic states than crystalline inorganic semiconductors. Conversely, chemicals that donate electrons to electron acceptor molecules with more electrons or to the lowest unoccupied molecular orbital (LUMO) of the OSC remove electrons from the highest occupied molecular orbital (HOMO). In organic semiconductors, dopants come in a wide range of ionic and molecular species, such as bases and acids. These species molecular nature enables more precise control over diffusion, for example, through covalent anchoring or modifying the size or shape of the molecules. For example, a strong Bronsted acid, polystyrene sulphonic acid (PSS) is often used to doped the polymer polyethylenedioxythiophene (PEDOT) (Elschner, Kirchmeyer, Lovenich, Merker, & Reuter, 2010). A low ionization energy (IE) molecule functions as an electron donor in n-type doping and a high electron affinity (EA) molecule as an electron acceptor in p-type doping in neutral molecular dopants. Since there is only an electrical interaction between the dopant and organic semiconductors and no secondary chemical reactions involved, doping organic semiconductors with neutral molecular dopants is similar to atomic doping in inorganic semiconductors. (Jacobs & Moulé, 2017).

Basic Principles of Doping

The process of formation charge transfer product, such as the Charge Transfer Complex Formation (CPX) and Ion Pair Formation (IPA), always marks start of molecular doping process.

Ion Pair Formation (IPA) The crucial idea in IPA is that the acceptor's electron affinity (EA) in p-type doping must be at least as high as the ionization energy (IE) of the OSC. Because of this, one electron can move from the highest occupied molecular orbital (HOMO) of the OSC to the lowest unoccupied molecular orbital (LUMO) of the acceptor (see Figure 1), forming an anion of acceptor and cation of an OSC, or the ion pair (Gao & Kahn, 2003). When the dopant electron affinity (EA) is smaller than the host ionization potential (IP), there is an integer charge transfer between the dopant and host, leading to p-type doping via ion pair formation(IPA) (Yan & Ma, 2022).The microscopic electrostatic analysis indicates that the interactions between the molecular environment and the doping-induced charges can redefine the energy levels. Through the elimination of the unfavorable energy offset, the net Coulomb attraction (V_{eh}) stabilizes the IPA state. Furthermore, upon charging, the energy level position can be further modified by the structural reorganization (λ). In light of this, the IPA formation criterion has been revised to IP_{host}-EA_{dopant}+V_{he}-$\lambda > 0$. (Li et.al 2019) Considering that organic semiconductors have low dielectric constants (between 3 and 4), which lead to significant binding energies of electron-hole pair of several hundred meV (Bässler & Köhler, 2012). Understanding how IPA give rise to mobile charge carriers requires an understanding of the IPA levels' relative to the energies level of surrounding neutral OSC's. This can be accomplished for the majority of OSCs by using the picture of charged molecules. The EA of a cation is greater than that of a neutral molecule even after considering the fact that OSCs react to charging by altering bond length and at the same time stabilizing the frontier molecular orbital levels by the relaxation energy λ. Hubbard U term is used to describe the energy difference between the electron affinity and ionization energy of the cation (EA+, IE+) as a result of on-site Coulombs Interaction. In doing so, the cations unoccupied and occupied HOMO-derived sublevels are divided (Winkler et al., 2015).

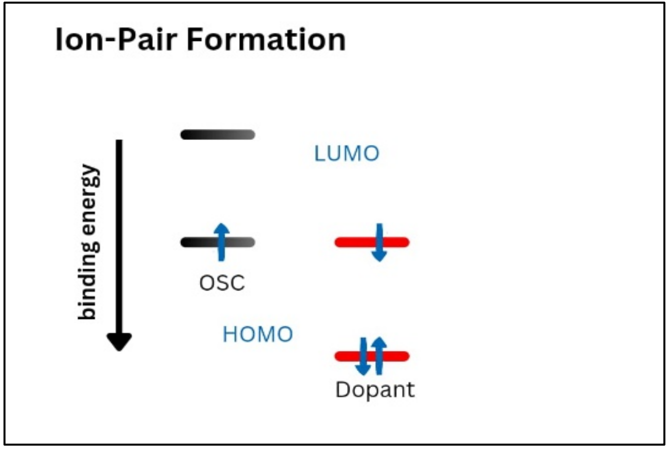

Figure 1: IPA (Ion Pair Formation)

Charge Transfer Complex Formation (CPX) When there is an off-set of unfavorable energy, doping occurs through CPX product creation through frontier orbital hybridization. Because both of the host ion pair electrons are in the new hybrid orbital, CPX is electrically neutral (Yan & Ma, 2022).Ground state charge transfer complex production is responsible for the creation of mobile carrier density in molecularly doped OSCs. An OSC molecule and a dopant hybridize to create a new set of occupied bonding and vacant anti-bonding border molecular orbitals (Figure 2). The quantity of charge transfer, δ, which can now take on non-integer values, is determined by the relative amplitude of the HOMO and LUMO of the CPX on the parent molecules. The CPX is charge-neutral overall. The energy of the CPX's frontier levels, $E_{CPX,\,H}$ and $E_{CPX,\,L}$, in a Hückel-type model is given by

$$\mathbf{E_{CPX,\,H/L}} = \frac{\boldsymbol{Hosc+Ldop}}{\mathbf{2}} \pm \sqrt{(\boldsymbol{Hosc - Ldop})^{\mathbf{2}} + \mathbf{4}\boldsymbol{\beta}^{\mathbf{2}}}$$

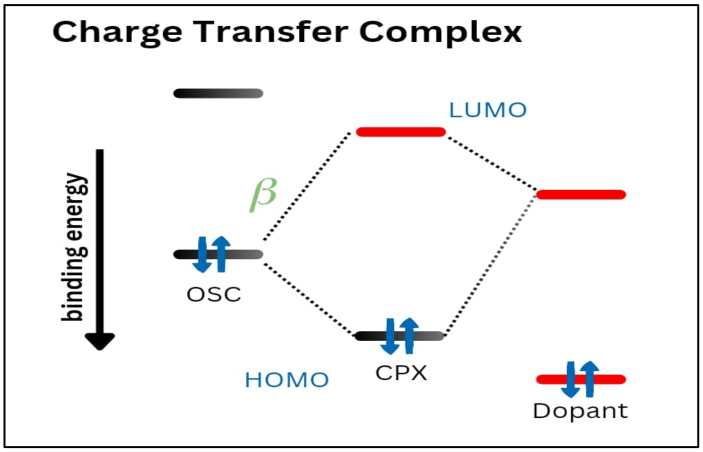

Figure 2: CPX (Formation of Charge Transfer Complex)

Conclusion

Both inorganic and organic elements can be used to dope organic compounds. Compared to inorganic electronics, organic electronics use a completely different doping method. Doping procedures can significantly improve the structural, electrical, and stability properties of organic semiconducting materials. The breakthrough of organic electronics has been greatly aided by organic doping. In particular, organic doping helps to increase the efficiency of optoelectronic devices and the reproducibility of device processing. Moreover, in organic transistors and organic cells doping is used less frequently, despite its effectiveness in optoelectronic devices, which presents numerous potentials for future research.

Abbreviations

OSC: Organic Semi-Conductor
IE: Ionization Energy
EA: Electron Affinity
LUMO: Lowest Unoccupied Molecular Orbital
HOMO: Highest Occupied Molecular Orbital
IPA: Ion Pair FormationCPX: Charge Transfer Complex

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