

Materials and Processes for Air-Stable n-Channel Organic Transistors

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1. Introduction

Organic thin-film transistors (OTFTs) have attracted a great deal of attention during the past decade as they are promising components for low-cost, large-area, and flexible electronics. To make full use of organic circuitry, it is essential to combine p-channel transistors with n-channel transistors for the fabrication of organic complementary circuits which offer lower power dissipation and greater operating speed. Less than five years ago n-channel semiconductors were far less developed compared to p-channel materials [1, 2]. In recent years, however, there has been a remarkable progress in the molecular design, device performance and stability for n-channel OTFTs [3-11]. Herein we report recent progress in materials design and processes for high-performance air-stable n-channel OTFTs, mainly focusing on the development of most-commonly used n-channel semiconductors, i.e., perylene diimide (PDI) and naphthalene diimide (NDI) derivatives.

2. Results & Discussions

Materials Design and Process Optimization for High-Performance n-Channel OTFTs

Since the initial demonstration of n-channel OTFTs using metal-phthalocyanines as the semiconductor in 1990 [12], a large number of n-channel organic semiconductors have been synthesized, mainly based on five kinds of small molecular frameworks such as metal-phthalocyanines, fullerenes, oligothiophenes, NDIs and PDIs, as well as polymers composed of these small molecular monomer units. Among them, NDIs and PDIs have received particular interest due to their high electron affinity, large π -orbital overlap in the solid state, and tunability of the optoelectronic property.

The current strategies to stabilize field-induced electron charge carriers in n-channel OTFTs can be divided into three approaches: i) molecular design to lower the LUMO level and/or to form a kinetic barrier in the semiconductor thin film, ii) electrode contact modification, and iii) interface engineering between the dielectric and semiconductor. The first strategy is to make π -conjugated cores of organic semiconductors electron-deficient (electron-accepting) and to reduce trapping of electron charge carriers by substitution with strong electron-withdrawing and/or hydrophobic substituents such as F [2], CN [10], Cl [13], alkanoyl [14], perfluorobenzene [15], and fluoroalkyl groups [1]. It enables air-stable n-channel operation by significantly lo-

wering the LUMO of the resulting molecule to resist ambient oxidation and/or by forming a kinetic barrier against the diffusion of ambient oxidants into the channel. The second approach, in terms of charge injection, is to minimize the injection energy barrier from the electrode to the LUMO by employing electrodes with low workfunctions [16]. The third, developed more recently, is to eliminate deep electron trapping sites by passivating the dielectric/semiconductor interface [4].

Considering these backgrounds, we have synthesized a series of core-halogenated NDI and PDI derivatives with varying fluorinated imide substituents. We have carried out a detailed evaluation aimed at a better comprehension of the influence of bay and imide substituents of perylene dyes on the crystal packing and their use as n-type organic semiconductors in electronic devices. The single crystal structural analysis, thin film morphological analysis, and optoelectronic characteristics were thoroughly investigated to reveal structure-property correlations.

The molecular packing of core-chlorinated NDIs showed various advantageous characteristics for charge transport including the marginal core distortion ($\leq 7^\circ$), close π -plane distance (3.3–3.4 Å), large π -orbital overlap (slipping angle $\sim 62^\circ$) and high packing density. These features of core-chlorinated NDIs lead to excellent electron mobilities up to $1.43 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in air. For several PDIs with a flat aromatic core owing to the presence of only up to two fluorine substituents at the PDI bay positions, we could obtain n-channel transistors with field effect mobilities between 0.5 and $1.44 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and on-to-off current ratios ($I_{\text{on}}/I_{\text{off}} > 10^6$) [8]. In contrast, PDIs with a distorted aromatic core evoked by four halogen substituents at the PDI bay positions showed lower mobilities and $I_{\text{on}}/I_{\text{off}}$. This is attributed to packing constraints arising from the distorted core that encumber the formation of extended highly crystalline grains. However, increasing the number of chlorine substituents at the perylene core from four to eight (“molecular engineering”) afforded a substantial lowering of the LUMO level while the combination of hydrogen-bonding and contortion of the π -core allows two-dimensional π - π -stacked percolation paths for electron transport (“crystal engineering”, Fig. 1) [7]. As a consequence of this molecular design, core-octachlorinated PDI-based TFTs operated in air with excellent electron mobility of almost $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and high $I_{\text{on}}/I_{\text{off}} > 10^6$.

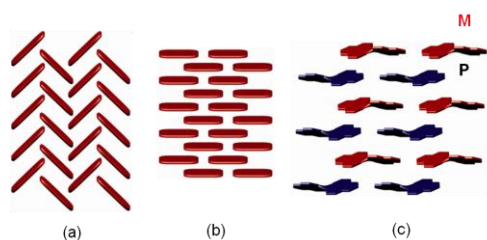


Fig. 1 Crystal engineering concepts to change the common 1-D π -stacking herringbone motif (a) with planar (b) or contorted (c) brickstone arrangements that enables 2-D percolation paths for charge transport.

Single-Crystalline Nano/Microwires for *n*-Channel OTFTs

Although single-crystalline organic semiconductor nano/microwires (NWs/MWs) have great potential as active materials in solution-formed high-performance transistors, the technology to integrate these elements into functional networks with controlled alignment and density has lagged far behind their inorganic counterparts. We have recently developed a novel solution-processing approach to achieve high-performance air-stable *n*-channel organic transistors (the field-effect mobility (μ) up to $0.24 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for MW networks) comprising high mobility, solution-synthesized single-crystalline organic semiconducting MWs (μ as high as $1.4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for individual MWs) and a new filtration-and-transfer (FAT) alignment method [17]. The FAT method enables facile control over both alignment and density of MWs. This approach presents a new route toward solution-processed, high-performance organic transistors and could be used for directed assembly of various functional organic and inorganic NWs/MWs.

N-Type Doping for Air-Stable *n*-Channel OTFTs

The ambient traps result in a significant decrease of the density of mobile electrons in *n*-channel OTFTs and thus, poor air-stability. We hypothesized that controlled *n*-type doping might compensate for the trapped charges. Previous attempts at intentional doping have increased film conductivities as a result of increased charge carrier density. However, the design of *n*-type (vs. *p*-type) dopants is considerably challenging owing to the requirement of high-lying dopant highest occupied molecular orbital (HOMO) levels, making *n*-type dopants unstable against ambient oxidants.

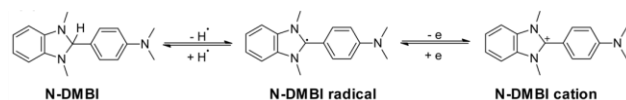


Fig. 2 The *n*-type doping mechanism of N-DMBI.

We developed a new solution-processable *n*-type dopant 4-(1,3-dimethyl-2,3-dihydro-1*H*-benzimidazole-2-yl)-phenyl)-dimethyl-amine (N-DMBI) (Fig. 2) [18]. N-DMBI neutral radicals were found to be the key species enabling *n*-type doping. Furthermore, we utilized this dopant to enable, and improve the air-stability of *n*-channel OTFTs, via

compensation for the ambiently trapped electron charge carriers. Our successful demonstration of *n*-type doping opens up new opportunities for the development of air-stable *n*-channel semiconductors.

3. Conclusions

We believe that our systematic studies on a series of core-halogenated NDI and PDI derivatives provide guidelines for the molecular design and process strategies towards air-stable *n*-channel organic transistors, which involve crystal engineering concepts for charge transport, and aligned single-crystalline wire transistors, and intentional *n*-type doped transistors.

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