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Digest paper

Molecular design of n-type organic semiconductors for high-performance thin film transistors

Bowen Shan [a], Qian Miao [a,b,*]

[a] Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China
[b] Institute of Molecular Functional Materials, Area of Excellence Scheme, University Grants Committee, Hong Kong, China

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ABSTRACT

This digest aims to provide organic chemists with an overview of recent progress on n-type organic semiconductors for application in organic thin film transistors (OTFTs) with an emphasis on molecular design. Herein, we survey n-type organic semiconductors with field effect mobility of 1 cm^2/Vs or higher in OTFTs after a brief introduction to the structure and operation of OTFTs and discussion of two key factors (frontier molecular orbitals and molecular packing) of organic semiconductors. On the basis of this survey, we finally reach conclusions on the current status of n-type organic semiconductors for OTFTs and provide an outlook for molecular design.

Contents

Introduction

This review aims to provide organic chemists with an overview of recent progress on n-type organic semiconductors for application in organic thin film transistors (OTFTs) with an emphasis on the concepts and challenges of molecular design. Organic semiconductors, unlike conventional inorganic semiconductors, are mechanically flexible, compatible with inexpensive solution-based fabrication over large areas and capable of various functionalities through molecular design and organic synthesis. With these advantages, light-weight, flexible and low-cost organic electronic devices that utilize organic semiconductors as key components are of great fundamental interests in materials science and are also recognized as a growing market for industry. Organic semiconductors, including both small molecules and polymers, are commonly classified as p-type and n-type materials, in which the major charge carrier is hole and electron, respectively. Organic semiconductors that can transport both holes and electrons are ambipolar.

* Corresponding author at: Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China.
E-mail address: miaoqian@cuhk.edu.hk (Q. Miao).

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P-type organic semiconductors are electron donors with a high-lying highest occupied molecular orbital (HOMO), while n-type organic semiconductors are electron acceptors with a low-lying lowest unoccupied molecular orbital (LUMO). Chemically speaking, electrical conduction in p- and n-type semiconductors is associated with oxidation of a neutral molecule to a cation and reduction of a neutral molecule to an anion, respectively.

Organic thin film transistors (OTFTs) are one of the most important elemental devices for organic semiconductors. Organic integrated circuits that are composed of OTFTs as elemental units are used, for example, to operate radio-frequency identification (RFID) tags and sensors and to drive individual pixels in light-weight and flexible displays.[1] OTFTs are classified into p- and n-channel transistors, which are based on p- and n-type organic semiconductors, respectively. The most important parameter to characterize the performance of OTFTs is field effect mobility (μ_{FET}), which quantifies the average charge carrier (hole or electron) drift velocity per unit electric field. Higher field effect mobility allows OTFTs to be used for wider applications. OTFTs with field effect mobility exceeding 1 cm^2/Vs, the mobility of amorphous silicon, are considered as high-performance devices, which can be used for applications requiring fast switching and sharp turn-on. Both n- and p-channel OTFTs with comparable performance are indispensable components of low-power complementary circuits for organic electronics.[2,3] One challenge in the research of organic semiconductors is that n-type organic semiconductors are currently underdeveloped in comparison to the p-type counterparts, partially due to the inherent instability of organic anions, particularly, in the presence of air and water. Without extra electron-withdrawing substituting groups, most of the commonly used π-building blocks for organic semiconductors, such as benzene and thiophene, are electron-rich and thus suitable for p-type organic semiconductors but not for n-type semiconductors. In this review, we survey n-type organic semiconductors with field effect mobility of 1 cm^2/Vs or higher in OTFTs after a brief introduction to the structure and operation of OTFTs and discussion of two key factors of organic semiconductors. On the basis of this survey with an emphasis on structure-property relationship, we finally reach conclusions on the current status of n-type organic semiconductors for OTFTs and provide an outlook for molecular design.

Structure and operation of OTFTs

To fabricate OTFTs, organic semiconductors can be processed by vacuum deposition or more desirably by solution-based methods, which are compatible with roll-to-roll and ink-jet printing techniques at low cost. An OTFT typically consists of a thin film of organic semiconductors, three electrodes (gate, drain and source) and a dielectric layer between the semiconductor and the gate electrode. OTFTs are classified as bottom- or top-gate devices when the gate is placed below or above the semiconductor, respectively; or they are classified as bottom- or top-contact devices depending on whether the drain and source electrodes are placed below or above the semiconductor, respectively. Fig. 1 shows an OTFT with a bottom-gate and top-contact configuration, which is widely used in high-performance devices. OTFTs essentially act as an on/off switch, where the electrical current between the drain and source electrodes (I_{DS}) depends on not only the voltage between the drain and source electrodes (V_{DS}) but also the voltage between the gate and source electrodes (V_{GS}). When no voltage is applied on the gate (V_{GS} = 0), the OTFT is in its "off" state with ideally no source-drain current or practically a very low source-drain current known as the *off* current. When a sufficiently high voltage (higher than the so-called "threshold voltage") is applied on the gate, mobile charges are accumulated at the interface between the semiconductor and dielectric layer, analogous to charging a capacitor. As a result, the OTFT is switched to its "on" state with a high source-drain current known as the *on* current. P-channel OTFTs achieve their "on" state with a negative gate voltage, while n-channel OTFTs achieve their "on" state with a positive gate voltage. The drain-source current ratio between the "on" and "off" states is defined as the *on/off* ratio, which is another important parameter for OTFTs.

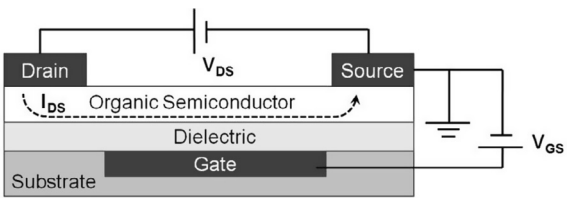

Fig. 1. Schematic structure of an OTFT (top-contact and bottom-gate) showing applied voltage (V_{DS} and V_{GS}) and source-drain current (I_{DS}).

OTFTs are interface devices with their performance highly dependent on the semiconductor-dielectric interface and the semiconductor-electrode interface. At the interface between the organic semiconductors and the dielectrics, the first few molecular layers of organic semiconductors are the locus of charge transport and responsible for current modulation. Most of OTFTs are bottom-gate devices, which have organic semiconductors directly deposited on the dielectric surface. Therefore the dielectric surface has large impacts on the performance of OTFTs in two aspects. First, during fabrication of semiconductor films, the properties of the dielectric surface, such as surface energy and surface roughness, largely determine the structures of organic semiconductor films in terms of molecular ordering,[4] orientation and film morphology. Second, the properties of the dielectric surface, such as surface dipole and trap states, greatly affect the accumulation and transport of charge carriers in organic semiconductors at the interface.[5] Therefore, control of interface structures and properties are as important as development of new semiconductor materials to the improvement of the OTFTs' performance. In virtue of their strong ability of manipulating the surface properties, self-assembled monolayers (SAMs) of organosilanes and phosphonic acids[6,7] have been developed as a powerful tool to modify the dielectric oxide surface in OTFTs.

Two key factors of organic semiconductors

Organic semiconductors generally owe their electrical conductivity to delocalized π-orbitals, which are energetically accessible for charge injection and allow charge transporting between neighboring molecules by orbital overlap. As a result, two key factors of organic semiconductors that determine their performance in OTFTs are frontier molecular orbitals (in terms of both energy level and electronic distribution) and molecular packing in the solid state. The HOMO and LUMO energy levels of organic semiconductors in the vacuum scale are commonly obtained by measuring the oxidation and reduction potentials, respectively, with cyclic voltammetry (CV) in organic solution. However, as pointed out by Bazan and co-authors in their critical review,[8] large inconsistencies have appeared on how the electrochemical potentials are correlated to orbital energies in the vacuum scale since different electrochemical scales were applied in literature. The most widely used standard redox couple for measurement of electrochemical potentials in non-aqueous solvents, as recommended by the IUPAC, is ferrocenium/ferrocene (Fc^+/Fc). When the oxidation and reduction potentials (E_{ox} and E_{red}, respectively) of a compound are measured against the electrochemical potential of Fc^+/Fc, its HOMO and LUMO energy levels (E_{HOMO} and E_{LUMO}, respectively) can be calculated using the following equations: