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Applicable p-Type Organic Semiconducting Materials

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Abstract

The functions of π-conjugated compounds are originated from rational molecular designs. To develop practical organic semiconducting materials, a series of sulfur-bridged N-shaped π-conjugated cores are newly designed and studied regarding their syntheses, fundamental properties, aggregated structures, theoretical calculations and carrier transporting capability in single-crystalline thin-film transistors.

1. Introduction

Organic field-effect transistors (OFETs)[1] have gained intense attention as organic semiconductor (OSC)-based technology due to their advantages such as being lightweight, mechanically flexible and low-cost compared to the currently used inorganic semiconductor-based counterparts. The development of practical OSCs for OFETs paves the way to next-generation organic-based electronics. Toward this goal, OSCs should meet the following requirements; 1) high carrier mobility (>10 cm^2/Vs), 2) high chemical stability, 3) appropriate solubility in organic solvents for solution processes, and 4) thermal durability for device usage environment.

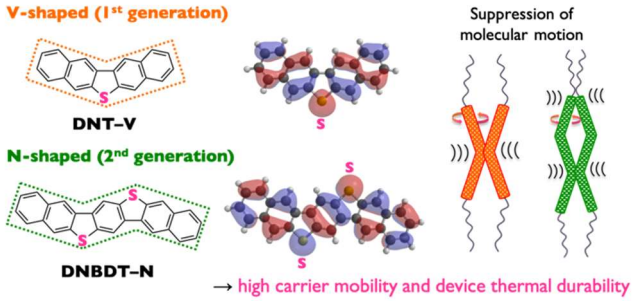
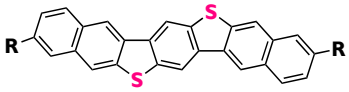


Fig. 1 Molecular design of bent-shaped organic semiconductors.

Our group has demonstrated a unique and innovative molecular design strategy. By means of both chemical and device engineering approaches, we have been focusing on molecular shapes and developed conceptually-new "bent"-shaped π-cores (Fig. 1). Suflur-bridged V-shaped π-cores are the first generation bent-shaped π-cores[2]. Effective intermolecular orbital overlaps between the central prominent sulfur atoms in the highest occupied molecular orbital (HOMO) as well as suppressed molecular vibrations along the long axis by the V-shaped feature may realize high carrier mobility. Furthermore, suppressing intermolecular vibrations should contribute to the thermal stability of the aggregated form, leading to high thermal durability of the device. To improve intermolecular orbital overlaps between molecules and suppress intermolecular vibrations, the N-shaped π-core, which is the second generation bent-shaped π-core, has been developed[3-6]. In this paper, the sulfur-bridged N-shaped π-cores are described regarding their synthesis, fundamental properties, aggregated structures, theoretical calculations, and device evaluation of solution processed single-crystalline-film-based transistors.

2. Results and discussion

The syntheses of N-shaped derivatives, DNBDT–N and alkyl-substituted DNBDT–NW (C_n–DNBDT–NW) (Fig. 2), can be realized in excellent yields via the same key reactions as V-shaped cases. First, the solubility of N-shaped derivatives, C_n–DNBDT–NW, were tested in toluene at 60 °C. C_{10}–DNBDT–NW shows at least one order of magnitude higher solubility (ca. 0.03 wt% in toluene at 60 ºC) than the decyl-substituted DNTT. To evaluate the chemical stability in the molecular and aggregated forms, UV-vis spectra were continuously collected over two weeks in evaporated thin films. Although all derivatives were stocked under ambient air, their spectra did not alter during the measuring period, suggesting that they can be handled in ambient air without special care.



DNBDT–N (R = H)
C_n–DNBDT–NW
(R = C_nH_{2n+1}, n = 8,9,10)

Fig. 2 Chemical structures of DNBDT–N derivatives.

Simultaneous measurements of thermogravimetry (TG) and differential thermal analysis (DTA) were performed to investigate their thermal stabilities. TG-DTA measurements under nitrogen gas flow revealed that the series of N-shaped derivatives vaporized without decomposition, indicating their thermal stability. Furthermore, phase transition temperatures

from the initial crystal phase are around 250 °C for alkyl-substituted C*n*–DNBDT–NW. These values are much higher than those of reported alkyl-substituted C_n–Pen[7], C_n–BTBT[8] and C_n–DNTT[9]. These findings suggest that N-shaped π-cores interact more effectively to suppress molecular motions. Their highly stabilized crystal phase is important for OSC applications. Furthermore, PYS reveals that the ionization potential of C_{10}–DNBDT–NW is 5.24 eV. The value is slightly larger than the work function of the Au electrode (~5.0 eV), indicating that the materials work as p-type organic semiconductors.

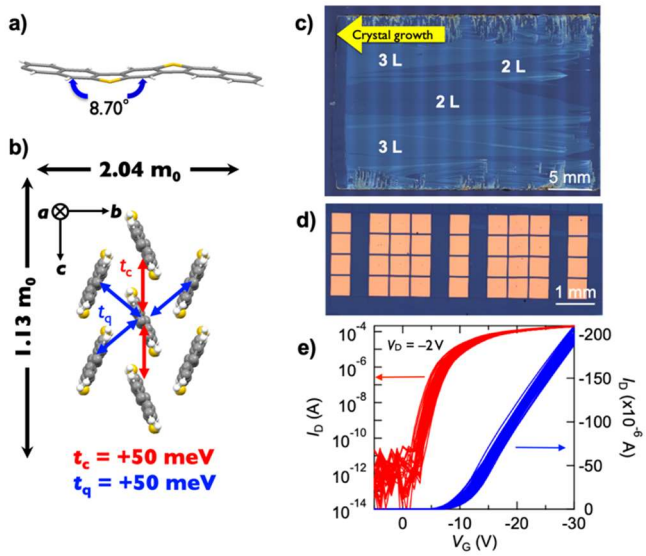


Fig. 3 a) Molecular, b) packing structure, and transfer integrals of C_n–DNBDT–NW. c) Microscopic image of C_9–DNBDT–NW thin film grown by continuous edge-casting method (2L = two layers, 3L = three layers). d) A few layer-based transistor array and e) its transfer characteristics (μ_{ave} ~10.6 ± 0.3 cm^2/Vs, V_D = –2 V, linear).

Fig. 3a-b illustrates the molecular and packing structures of C_n–DNBDT–NW (n = 8, 9, 10) in a single crystal. C_n–DNBDT–NW, exhibits a distorted molecular structure at the two thiophene rings, a lamellar structure in the direction of the long molecular axis, and a two-dimensional herringbone-type packing structure in the layer. The transfer integrals are large and over +50 meV in all directions, which are calculated at PBEPBE/6-31G(d) level. Furthermore, the band structures and effective masses were also calculated at the same level. The aggregated structure of C_n–DNBDT–NW has effective masses of 1.13m_0 and 2.04m_0 in the column direction and the transverse direction, respectively.

Finally, OFETs based on their single crystalline films were evaluated. For the soluble C_n–DNBDT–NW materials, their crystalline films were constructed by either an edge casting or a continuous edge casting technique[10-11]. The transistor structures were fabricated as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4–TCNQ, 2 nm) and gold (40 nm) were deposited through a metal mask onto the crystalline films. The mobility in the saturation region, μ_{sat}, was calculated using the formula based on a gradual channel approximation, $I_D = (1/2) \cdot \mu_{sat} \cdot C \cdot (W/L) \cdot (V_G - V_{th})^2$, where C is the capacitance of the gate insulator, and L and W are the length and width of the channel, respectively. As characteristics of several OFETs based on obtained crystalline films (Fig. 3c), Fig. 3d-e shows the transfer characteristics based on the C_9–DNBDT–NW solution-processed crystalline film. C_9–DNBDT–NW shows quite high mobility (16 cm^2/Vs at the highest and 10.6 cm^2/Vs as an average).

For OFETs based on high mobility C_n–DNBDT–NW crystalline films, thermal stress tests were performed. These transistor performances were measured at room temperature after heating at each temperature for five minutes. Transistors based on C_n–DNBDT–NW did not show any remarkable mobility degradation below 200 °C. Furthermore, storage tests and bias stress tests were also performed. The mobility of the OFET does not remarkably degrade. Thus, organic semiconductor performance of C_n–DNBDT–NW is stable against stress in the operating environment.

3. Conclusions

A series of N-shaped π-cores are easily furnished with excellent yields. The π-core has sufficient solubility for solution processes, high thermal stability, and high mobility necessary to semiconductors applicable for next-generation organic-based electronics. In particular, the N-shaped OSCs are developed based on advances in organic materials sciences and have the potential for practical use. Thus, the N-shaped π-core based on bent-shaped molecular design concept is innovative for high-performance OSCs and should pioneer a new field of development of OSCs as a foundation for next-generation electronics.

Acknowledgements

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