Design strategy for air-stable organic semiconductors applicable to high-performance field-effect transistors

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Abstract

Electronic structure of air-stable, high-performance organic field-effect transistor (OFET) material, 2,7-diphenyl[1]benzothieno[3,2-b]benzothiophene (DPh-BTBT), was discussed based on the molecular orbital calculations. It was suggested that the stability is originated from relatively low-lying HOMO level, despite the fact that the molecule contains highly \(\pi\)-extended aromatic core ([1]benzothieno[3,2-b]benzothiophene, BTBT) with four fused aromatic rings like naphthacene. This is rationalized by the consideration that the BTBT core is not isoelectronic with naphthacene but with chrysene, a cata-condensed phene with four benzene rings. It is well known that the acene-type compound is unstable among its structural isomers with the same number of benzene rings. Therefore, polycyclic aromatic compounds possessing the phene-substructure will be good candidates for stable organic semiconductors. Considering synthetic easiness, we suggest that the BTBT-substructure is the molecular structure of choice for developing air-stable organic semiconductors.

Keywords: Organic field-effect transistor; Organic semiconductors; Highest occupied molecular orbital; Stability; Molecular orbital calculations

1. Introduction

Organic field-effect transistors (OFETs) have attracted current attention owing to their potential applications as cheap alternative for the amorphous-silicon-based thin-film transistors (TFTs) \cite{1}. Although the primary issue facing OFETs for practical use is the enhancement of field-effect mobility (\(\mu_{\text{FET}}\)), recent intensive research efforts have significantly improved the \(\mu_{\text{FET}}\). For thin-film-based OFETs, pentacene is the best compound giving highest mobility (\(\mu_{\text{FET}} > 1.0 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}\)): the performance of pentacene-based OFETs almost meets the criteria for substituting the amorphous-silicon-based TFTs \cite{2}. However, the stability and durability of pentacene-OFETs under ambient conditions are problematic, thus stable organic semiconductors have been eagerly desired.

From the structural and theoretical points of view, oligoacenes including pentacene and naphthacene are advantageous as OFET materials because of (i) their expanded \(\pi\)-framework enabling strong intermolecular overlap which enhances the carrier transport in the solid state and (ii) a strong tendency to take herringbone packing which is suitable to construct two-dimensional electronic structure on the substrate when fabricated in thin-film-based devices \cite{3}. Fig. 1 shows frontier orbitals of oligoacenes obtained by DFT-MO calculation with B3LYP/6-31G(d) level \cite{4}. In the series of oligoacenes, it is obvious that when the number of benzene rings increases, the HOMO level becomes higher and the HOMO–LUMO gap becomes narrower. The instability of pentacene-based OFETs can be partially understood by high-lying HOMO level and narrow HOMO–LUMO gap. Such high-lying HOMO level makes the molecule susceptible to air-oxidation in ambient...
conditions, and narrow HOMO–LUMO gap will cause readily photo-induced excitation that may lead subsequent chemical reactions. In order to circumvent the instability of pentacene-based OFETs, new organic semiconductors employing lower acene homologues, such as anthracene [5] or naphthacene [6], in larger π-conjugated backbone have been recently developed (Fig. 2), and their OFETs are reported to show both high performance (\( \sim 1.0 \text{cm}^2\text{V}^{-1}\text{s}^{-1} \)) and reasonable stability. Experimentally determined HOMO levels of these compounds are relatively low, which corroborates the stability of their OFET devices under ambient conditions [5,6].

2. Results and discussions

We have been developing new organic semiconductors employing chalcogenophene-fused aromatic substructures. Our idea behind this strategy is that heavy chalcogen atoms such as sulfur and selenium having larger atomic orbitals and higher polarizability can contribute to intermolecular interaction enabling effective intermolecular overlap in the solid state that is highly desirable for effective carrier transport. Thus developed organic semiconductors showing high-performance OFET characteristics are 2,6-diphenylbenzo[1,2-\( b \):4,5-\( b ' \)]dichalcogenophenes (DPh-BDXs, \( \mu_{\text{FET}} \sim 0.2 \text{cm}^2\text{V}^{-1}\text{s}^{-1} \)) [7], 2,6-diarylnaphtho[1,8-\( bc \):5,4-\( b'c' \)]dithiophenes (DAr-NDTs, \( \mu_{\text{FET}} \sim 0.1 \text{cm}^2\text{V}^{-1}\text{s}^{-1} \)) [8], and 2,7-diphenyl[1]benzochalcogenopheno[3,2-\( b \):4,5-\( b' \)]bencchochalcogenophene (DPh-BXBX, \( \mu_{\text{FET}} \sim 2.0 \text{cm}^2\text{V}^{-1}\text{s}^{-1} \)) [9,10] (Fig. 3). Among these novel organic semiconductors, the most remarkable one is 2,7-diphenyl[1]benzothieno[3,2-\( b \)]benzothiophene (DPh-BTBT) showing \( \mu_{\text{FET}} \sim 2.0 \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) under ambient conditions. Furthermore, its superior device characteristics were preserved for long period of time (\( \sim 250 \) days) without significant changes [10]. Since this material can be considered as one of the best p-channel OFET materials so far reported, it is interesting to investigate its electronic structure and correlate its structural features and properties, which may provide a new concept for air-stable organic semiconductors.

Fig. 4 shows the frontier orbitals of DPh-BTBT based on optimized molecular structure with DFT B3LYP/6-31G(d) level [4]. Its HOMO energy level (\(-5.41 \text{eV}\)) is fairly lower than that of pentacene and is comparable with that of anthracene (see Fig. 1). Such stabilization of HOMO of DPh-BTBT can explain qualitatively the stability of its FET devices under ambient conditions. However, its central benzothieno[3,2-\( b \)]benzothiophene (BTBT) core contains four consecutive aromatic rings in fused-manner like naphthacene does; how can such highly extended π-electron system stabilize its HOMO? This can be rationalized by consideration of the electronic structure of BTBT that is isoelectronic with chrysene, not with naphthacene: in general, sulfur atoms supply two π-electrons in five-membered aromatic ring system to complete the aromatic sextet, and thus isoelectronic hydrocarbon of BTBT corresponds to chrysene (Fig. 5).

Electronic absorption spectroscopy (UV–vis spectra) is a convenient method to evaluate the electronic structure of aromatic hydrocarbons. Fig. 6 shows UV–vis spectra of the...
parent BTBT, chrysene, and naphthacene. Although the shape of the absorption bands of BTBT is somewhat different from those of chrysene, the absorption edges of these two compounds are almost the same (∼350 nm), indicating that the energy gaps between HOMO and LUMO in these compounds are similar. On the other hand, the absorption spectrum of naphthacene is characteristic in terms of remarkably red-shifted absorption bands up to ca. 490 nm. These results clearly support that the electronic structure of BTBT is quite similar to that of chrysene, but not to naphthacene.

In the polycyclic phene series such as chrysene and phenanthrene, increase of the number of benzene rings does not drastically destabilize HOMO and stabilize LUMO (Fig. 7). This is in sharp contrast to the tendency observed in the acene series (Fig. 1), where HOMO is rapidly destabilized with increasing the number of benzene rings. Therefore, it can be suggested that employing the phene-substructure in π-extended aromatic system will be one of the effective strategies to keep HOMO level low and thus to develop air-stable organic semiconductors.

3. Summary and outlook

We have demonstrated that consideration of electronic structures supported by MO calculations can give a good prospect for the stability of organic semiconductors for p-channel OFET application. Although higher polyacenes have been historically important materials in the field of OFETs, the polycyclic phenes can be alternative candidates as stable organic semiconductors. However, the chrysene-like substructure is not easily accessible by the conventional organic synthetic methods. For these reasons, the BTBTS-substructure is rather practical choice for developing new π-extended organic semiconductors with reasonable stability. One of such compounds is dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophenes (DNTT; Fig. 8), the calculated HOMO level of which is 5.19 eV below the vacuum level.
level [4]. In order to confirm our working hypothesis and to develop new stable, high-performance OFET materials, experimental efforts to synthesize DNTT are now underway.

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