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BODIPY derivatives as n-type organic semiconductors: Isomer effect on carrier mobility

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ABSTRACT

In the present work, two dipyrro-boradiazaindacenes (BODIPY) derivatives functioning as novel high-performance organic semiconductors are investigated by theoretical method. These two isomeric complexes are demonstrated to have large electron-transfer mobility, which means they are favor to be n-type organic semiconductors. The highest electron-transfer mobility appears at the same packing style in two crystals. The intermolecular distances of the packing style are nearly same, 4.994 Å in crystal 1 and 5.283 Å in crystal 2. However, their electron-transfer mobility changes significantly. The mobility of crystal 2 with better planar molecular structure is 0.291 $cm^2 V^{-1} s^{-1}$, which is 13 times larger than that of crystal 1 as 0.022 $cm^2 V^{-1} s^{-1}$. The significant difference of carrier mobility is ascribed to the little structural difference of these two isomers. It has been demonstrated that both crystal 1 and 2 show remarkable anisotropic behavior. This study will undoubtedly provide a new understanding of isomerization on designing novel organic semiconductors.

1. Introduction

In the past decades, molecular organic semiconductors is the object of much interest because of their applications in new generations of (opto)electronic devices [1–8]. The development of single-crystal organic field effect transistors (SCOFETs) makes it possible to explore intrinsic properties of these materials [9–11]. p-Type organic semiconductors such as pentacene, rubrene and derivatives of them have been investigated widely [12–27]. The recently improved theoretical understandings of organic semiconductors have even addressed the design rule of organics with high hole mobilities [28–31]. However, n-type semiconductors are not fully developed, and their field effect transistors (FETs) performance is not satisfactory yet. Fluorinated perylene diimide as a novel organic n-type material was reported by Heremans and coworkers in 2005 [32]. They also did research on the influence of the contact metal on the performance of n-type carbonyl-functionalized quaterthiophene organic thin-film transistors [33]. Kahn and coworkers used direct and inverse photoemission spectroscopy and some other experimental methods to study the n-type doping of an electron transport materials in 2006 [34,35]. Recently, they have reported a new acetylenic n-type organic semiconductor: fluoro-substituted phenyleneethynylenes with high performance [36]. Among intrinsic properties of organic semiconductors, the electrical anisotropy of organic materials has attracted much attention [9,37–47]. The anisotropic effects in rubrene crystals were first observed by Sundar et al. in 2004 [9]. Deng and Han have investigated the quantitative structure–activity relationships of transport properties in a series of organic semiconductors such as acene, acene derivatives and rubrene by first-principles-based simulation based on Marcus-Hush theory [48–51]. They provide systematically anisotropic mobility of each

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material above, which agree with experiments very well [48–51].

As we all know, dipyrro-boradiazaindacenes (BODIPY) is fluorescence sensor with good function. The properties of BODIPY and its derivatives have been studied widely [52–58]. Herein, we investigate the properties of two derivatives of BODIPY function as organic semiconductor. These two compounds are isomers with only little difference of the structure as shown in Fig. 1. Our simulations demonstrate that this kind of BODIPY derivative has better mobility function as n-type organic semiconductor comparing with p-type. On the other hand, complex 2 has larger electron mobility than complex 1, though there's only little different of their monomers and crystal structures. This obvious difference indicates that isomerization has significant influence on the mobility. The favorable performance as n-type organic semiconductor of both complex 1 and 2 is assigned to the high electron affinity of F atoms in the molecule. The better planar structure of complex 2 is demonstrated to be responsible for large electron mobility of crystal 2.

2. Theory and computational methods

Our simulation model is based on first-principle quantum mechanics (QM) calculations combined with Marcus-Hush theory [59,60]. For the calculations of the intermolecular effective electronic coupling, we calculate the spatial overlap (S_{ij}), charge transfer integrals (J_{ij}), and site energies (e_i, e_j):

$$e_{(}ij) = \langle \psi_{i(j)} \mid H \mid \psi_{(i)j} \rangle \tag{1}$$

$$S_{(ij)} = \langle \psi_i \mid \psi_j \rangle \tag{2}$$

$$J_{ij} = \langle \psi_i \mid H \mid \psi_j \rangle \tag{3}$$

where H is the system Kohn–Sham Hamiltonian of the dimer system, and $\Psi_{i(j)}$ means the monomer HOMOs (for hole transport) or LUMOs (for electron transport) with Löwdin's symmetric transformation, which can be used as the orthogonal basis set for calculation [61]. Then the intermolecular electronic coupling V_{ij} can be written as

$$V_{ij} = (J_{ij} - 0.5(e_i + e_j)S_{ij})/(1 - S_{ij}^2) \tag{4}$$

The calculations of all electronic couplings in different molecular packing dimers are performed with the PW91/TZ2P of density functional theory (DFT) implemented in the Amsterdam density functional (ADF) program [62]. The reorganization energy λ associated with charge transport process in organic solid materials is evaluated by the adiabatic potential energy surface method:

$$\lambda = (E_+^* - E_+) + (E^* - E) \tag{5}$$

or

$$\lambda = (E_-^* - E_-) + (E^* - E) \tag{6}$$

where E and E_+ (E_-) represent the energies of the neutral and cation (anion) species in their lowest energy geometries, respectively; E* are the energies of the neutral and cation (anion) species with the geometries of the cation (in Eq. (5)) and anion (in Eq. (6)). E_+^* (E_-^*) are the energies of cation (anion) species with the geometries of neutral species, respectively. Then the adiabatic ionization potential (IP) and affinities (EA) can be calculated as

$$IP = E_+ - E \tag{7}$$

$$EA = E_- - E \tag{8}$$

Full geometry optimizations of the monomer molecules and the reorganization energy calculations are carried out using the B3LYP functional in conjunction with the 6-31G(d,p) basis set [63]. These calculations are performed with the Gaussian09 package [64]. The reorganization energy consists of intra- and intermolecular contributions. Here we focus on the intramolecular contributions. However, the neglect of intermolecular contribution of reorganization energy will result in the overestimation of the hopping rate Eq. (10) and sequentially the absolute value of mobility Eq. (9) and (11). Previous research [65] suggested a method to evaluate the intermolecular geometric relaxation energy based on the electronic polarization P_+ that results from the interaction of the excess charge with both permanent and induced multipoles in surrounding molecules, and the P_+ can be obtained from the ultraviolet photoelectron spectroscopic (UPS) data of gas and solid phases [66,67]. Herein, we pay our attention to indicate which kind of organic semiconductor complex 1 and 2 could be function as, the n-type or p-type and which one has better functions. The total same method is chose for calculation of each compound. Therefore, the systematic error will be eliminated by comparison and the absolute value is not so important. At room temperature, it is generally accepted that the transport in organic materials occures via charge carrier hopping between adjacent molecules. Assuming no correlation between charge hopping events and charge motion is a homogeneous random walk, the maximum values of drift mobility for charge carrier (hole/electron) transport in semiconductor can be written as [28,49].

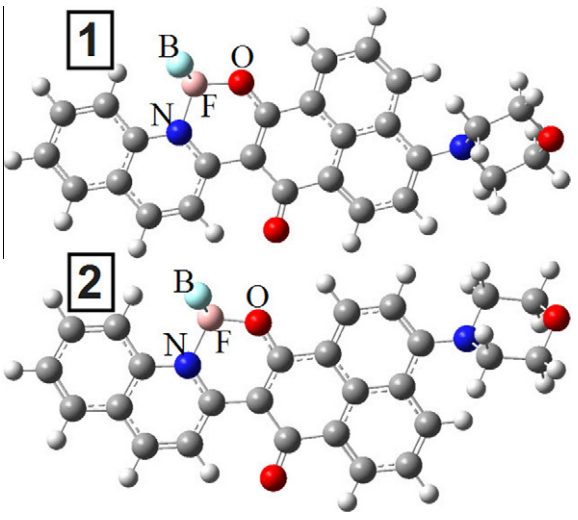

Fig. 1. Optimized structures of monomer 1 and 2 in crystal 1 and 2, respectively.