



Impact of the halogenated substituent on electronic and charge transport properties of organic semiconductors: A theoretical study



Shuo Chai ^{a,b,*}, Jin-Dou Huang ^{b,c}

^a School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, China

^b State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^c School of Physics and Materials Engineering, Dalian Nationalities University, Dalian 116600, China

ARTICLE INFO

Article history:

Received 29 April 2015

Received in revised form 6 July 2015

Accepted 6 July 2015

Available online 18 July 2015

Keywords:

Mobility

Halogenated substituent

Organic semiconductors

Intermolecular interaction

Molecular packing

ABSTRACT

The electronic and charge transport properties of the derivatives based on tetracene with aryl and halogenated aryl substituents have been investigated theoretically. This kind of functionalization is demonstrated to have a significant effect to stabilize the molecular orbital, densify the molecular packing, enhance the electronic coupling, and further lead to a high mobility, though it would also cause some increases in the reorganization energy. The packing modes of FPPT and PPT crystals are analyzed in details and effective coupling projected areas are put forward to understand the intermolecular interactions. Interestingly, FPPT is found to have a well-ordered packing as well as the improved hole mobility of $4.67 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In addition, the contributions of different frequencies of vibration to the total reorganization energies are also discussed with the normal mode analysis. This study clarifies the halogenated substituent effect on transport properties and provides the guide for molecular design of novel functional materials.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Organic semiconductors (OS) have been taken as one of the most promising materials in modern chemistry and organic electronics [1–9]. The outstanding features of low cost, flexible structures as well as convenient preparation technologies have drawn the great interests of scientists and engineers [7,9–14]. The high-performance OS materials with considerable charge mobilities can be employed in a great deal of electronic devices, such as organic field effect transistors (OFET), organic photovoltaic solar cells and organic light emitting diodes (OLED) [15–19]. The widely investigated semiconductors, including acenes, bisimide perylenes and fullerene derivatives, have been proved to have favorable charge transport performances in applications in the past decades [5,20–24]. Generally, these materials have the π -conjugated structures and the charge carriers transport between the adjacent molecules forced by the intermolecular π - π conjugated interactions. However, many OS materials cannot be used in practical applications due to low mobilities. In search of the proper OS materials with high performance in electronic devices becomes the crucial

target in organic electronics. The proper molecular modifications were demonstrated to be an effective method to enhance the intermolecular interactions and improve the charge mobilities of semiconductors [25–29]. Some n-type transport materials have been successfully exploited based on efficient p-type ones with electron-withdrawing substituents. It was widely reported that the modified materials of perylene diimide derivatives, halogenated acenes have satisfying electron mobilities [25–28].

Generally, the experimental factors influencing the charge mobility are very complicated, including the external factors (temperature, pressure, electric fields, etc.) and the internal ones (disorder, purity, density of charge carrier, molecular packing, etc.). For the OS material in a fixed condition, the charge mobilities are strongly dependent on two parameters: reorganization energy and intermolecular electronic coupling. The low reorganization energy combined with strong electronic coupling would contribute to a high mobility. The short intermolecular distances and large coupling areas of conjugated molecules in single crystal are desirable to enhance the intermolecular electronic couplings. Therefore, the molecular modification is developed in order to improve the intermolecular interactions and hence charge transport mobilities.

It is widely known that the π - π conjugated interaction plays a key role in the photochemical properties of organic semiconductors in crystals. Other weak interactions, such as hydrogen bond,

* Corresponding author at: School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, China.

E-mail address: chaishuo@dlut.edu.cn (S. Chai).

electrostatic force and solvation, are also demonstrated to influence the material properties [30–32]. Zhao et al. explored the hydrogen bonding interactions between the neighbored molecules of organic semiconductors in solid state and confirmed the improvement effect on mobilities [31,33]. The substituents with fluoro groups were demonstrated as the effective tool to design n-type transport materials [34,35]. A series of C–F···F–C and C–H···F–C interactions of organic long-chain molecules were investigated by Atoms-in-Molecules (AIM) experiments as well as quantum chemistry calculations [30]. Okamoto et al. synthesized tetracene derivatives with aryl and fluoroaryl substituents and performed the photoconductivity and OTFT measurements [36]. They found this kind of substituent is responsible for close packing of the organic crystal and high mobility. Zhang et al. theoretically investigated the fluorine substituent effect on the hole transport mobilities of tetracene derivatives [37].

In the present work the functionalization of tetracene with aryl and halogenated aryl moieties have been investigated theoretically to identify the substituent effect on the electronic and charge transport properties by using density functional theory (DFT) combined with Marcus–Hush theory methods. The substituents of tetracene (TETR) are categorized into three types and the investigated materials are: the derivative with two aryl groups: 5, 11-phenol tetracene (PPT); the ones with aryl and halogenated aryl: 5-perfluorophenol-11-phenol tetracene (FPPT), ClPPT and BrPPT; and the ones with two halogenated aryls: 5,11-perfluorophenol tetracene (2FPPT), 2ClPPT and 2BrPPT. The dihedral angles of substituted plane with central conjugated plane are numbered as DA₁ and DA₂. The chemical structures of the investigated compounds as well as the related dihedral angles are shown in Fig. 1. The compounds in bold font represent the ones of which single crystals are available from Cambridge Crystallographic Data Centre (CCDC). Both the adiabatic potential energy surface method and normal mode analysis are employed to investigate the charge transport reorganization energy. The effects of different substituted halogen atoms on the reorganization energy are discussed. In addition to π – π conjugated interaction, C–H···F–C interaction has been explored in calculations. The concept of effective coupling projected area is put forward to understand the intermolecular interactions of conjugated neighboring molecules and the hole and electron mobilities of available crystals are obtained theoretically.

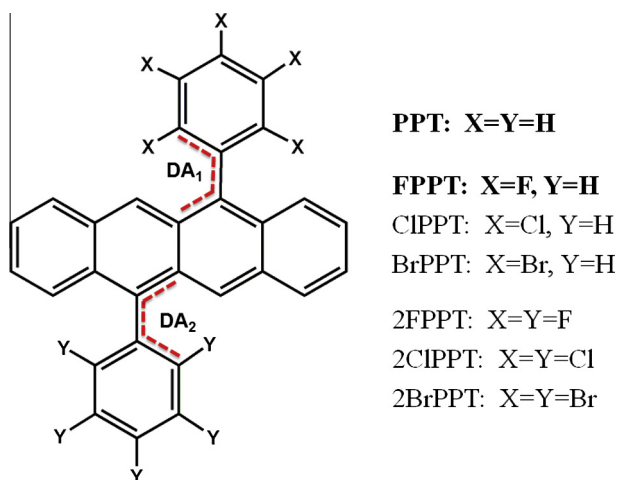


Fig. 1. Chemical structures of the investigated compounds with different substituent atoms, the dihedral angles between the substituted ring and conjugated acene plane are signed as DA₁ and DA₂.

2. Theoretical methods

Our theoretical tools are based on first-principle quantum chemistry calculations as well as Marcus–Hush theory [38–41]. The geometric, electronic and transport properties of organic monomers are investigated with density functional theory by Gaussian 09 program package [42]. The theoretical level of B3LYP functional with 6-311g (d, p) basis set is employed in our calculations. The reorganization energy denotes the internal energy relaxation of charge transport. For the single crystals the contribution from environment to reorganization energy can be neglected [43]. The hole and electron transport reorganization energies could be evaluated with the help of the idea of adiabatic potential energy surface and written as [44]:

$$\lambda_{hole} = \lambda_0^+ + \lambda_+ = (E_0^* - E_0) + (E_+^* - E_+) \quad (1)$$

$$\lambda_{electron} = \lambda_0^- + \lambda_- = (E_0^* - E_0) + (E_-^* - E_-) \quad (2)$$

where E_0 and E_+/E_- denote the energies of the neutral and cation/anion molecules with optimized geometries, E_0^* and E_+^*/E_-^* are the energies of neutral and cation/anion monomers with cation/anion and neutral geometries, respectively.

There is also another method to calculate the reorganization energy which is based on the normal mode analysis of both the neutral and charged molecular states. The total relaxation energy (polaron reorganization energy) could be given by the sum of the contributions from each vibrational mode:

$$\lambda = \sum_i \lambda_i = \sum_i \frac{1}{2} \omega_i^2 \Delta Q_i^2 \quad (3)$$

Here, ΔQ_i denotes the displacement along the normal coordinate Q_i between the optimized geometries of the donor and acceptor electronic states, and ω_i is the corresponding frequency. When making the orthogonal transformation between the normal coordinate and atomic coordinate, the square root of reduced mass is introduced to the normal coordinate term. The calculation of reorganization energy with normal mode analysis is performed by the DUSHIN program [45].

Another important parameter correlating with mobility is intermolecular electronic coupling. It is deduced with entire dimer Hamiltonian model and expressed with the charge transfer integral J , the overlap matrix S and the site energy E of monomer, as described in Ref. [46]:

$$t = \frac{J_{12} - S_{12}(E_1 + E_2)/2}{1 - S_{12}^2} \quad (4)$$

The molecular orbitals of monomer with orthogonalization are applied as basis sets of the Hamiltonian of molecular dimer. For the hole and electron transport, J_{12} , S_{12} , E_1 and E_2 can be expressed as:

$$J_{12} = \langle \varphi_1^{H/L} | h | \varphi_2^{H/L} \rangle \quad (5)$$

$$S_{12} = \langle \varphi_1^{H/L} | \varphi_2^{H/L} \rangle \quad (6)$$

$$E_{1(2)} = \langle \varphi_{1(2)}^{H/L} | h | \varphi_{1(2)}^{H/L} \rangle \quad (7)$$

Here h is the Kohn–Sham Hamiltonian of the dimer system, φ_1^H , φ_2^H are the highest occupied molecular orbitals (HOMOs) and φ_1^L , φ_2^L are the lowest unoccupied molecular orbitals (LUMOs) of two monomers, respectively.

The crystal structures of PPT and FPPT are obtained from the online Cambridge Crystallographic Data Centre (CCDC 804405 and 804406). The calculations for electronic couplings are

Download English Version:

<https://daneshyari.com/en/article/5393159>

Download Persian Version:

<https://daneshyari.com/article/5393159>

[Daneshyari.com](https://daneshyari.com)