



Theoretical investigation of fluorination effect on the charge carrier transport properties of fused anthra-tetrathiophene and its derivatives



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ABSTRACT

The crystal structures of known anthra-tetrathiophene (ATT) and its three fluorinated derivatives (ATT1, ATT2 and ATT3) were predicted by the Monte Carlo-simulated annealing method with the embedded electrostatic potential (ESP) charges. The most stable crystal structures were further optimized by the density functional theory with the dispersion energy (DFT-D) method. In addition, the effect of the electron-withdrawing fluorine atoms on the molecular geometry, molecular stacking, electronic and transport properties of title compounds were investigated by the density functional theory and the incoherent charge-hopping model. The calculated results show that the introduction of fluorine atoms does not affect the molecular planarity but decreases the HOMO-LUMO gap, which is beneficial to electron injection and provides more charge carrier stabilization. The improved electron mobility from ATT to ATT3 is attributed to the favorable molecular packing with strong π - π interaction and the short stacking distance. ATT2 and ATT3 exhibit remarkable angular dependence of mobilities and anisotropic behaviors. The band structures reveal that all the paths with larger transfer integrals are along the directions of large dispersions in the valence band (VB) and conduction band (CB). ATT3 has the largest electron mobility ($0.48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) among the four compounds, indicating that fluorination is an effective approach to improve electron transport.

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1. Introduction

Recently organic semiconductors have played an important role in the field of electronic and optoelectronic materials owing to their low manufacturing costs, large-area coverage, mechanical flexibility and lightweight [1–3]. Generally, oligothiophenes and arene derivatives have shown high hole mobility and good air-stability due to their large π -conjugation and outstanding chemical and physical properties [4]. However, the development of ambient-stable *n*-type semiconductors has largely lagged behind that of *p*-type ones due to a lack of considerable electron mobility [5]. On account of this, past few years several research groups have been working on the design and synthesis of high-performance *n*-type π -conjugated organic semiconductors. Recently, Liu et al. devised a simple synthesis of two sulfur-rich anthra-[1,2-*b*:4,3-*b'*:5,6-*b''*:8,7-*b'''*]tetrathiophene-based heteroarenes (ATT) with favorable π - π

interactions [6]. In which, fused heteroarene unit, anthra-[1,2-*b*:4,3-*b'*:5,6-*b''*:8,7-*b'''*] tetrathiophene serves as the basic skeleton of π -extended planar systems and facilitates molecular self-association through π - π stacking. ATT has shown a good stability at ambient temperature due to its favorable overlap packing and large π -conjugation. Additionally, the sulfur-sulfur interactions, originating from the high polarizability of sulfur atom in thiophene rings, could strongly affect the solid-state packing of the compounds and determine the transport network [7,8]. Over the past decades, experimental and theoretical investigations have shown that functionalizing *p*-type semiconductor with electron-withdrawing groups was a promising way to convert them into *n*-type ones [7,9]. Attaching electron-withdrawing substituents such as Cl, Br, and F to the π -conjugated ring can lower the molecular orbital energy level and provide stronger electron affinities, which will facilitate the injection of electrons [10,11]. Based on this, we design three ATT derivatives (ATT1, ATT2 and ATT3) with the strong electron-withdrawing fluorine substituents based on the precursor molecule ATT to shed light on molecular design for

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n-type organic semiconductor through simple chemical structural modification.

Motivated by the interesting fact that the slight modification of organic molecules could induce different optical and electrochemical performances, we investigated the transport properties of the fluorinated ATT derivatives based on the density functional theory (DFT) coupled with the incoherent charge-hopping model to explore the effect of the number and location of fluorine atoms on the charge transfer property of ATT. In this work, three fluorinated ATT molecules ATT1, ATT2 and ATT3 are optimized by the GGA/PBE functional. Then, the optimized molecules ATT1, ATT2 and ATT3 with electrostatic potential-fitted charge are simulated using the Monte Carlo-simulated annealing method based on the molecular mechanics (MM) to search for reasonable crystal structures. Afterwards, the predicted ATT1, ATT2 and ATT3 crystal structures with the lower energy were selected for further optimized calculations by the DFT-D method at the PBE level. A quantum chemistry and molecular mechanic combined approach is applied to investigate the geometries, molecular orbitals, electron affinities, ionization potentials and reorganization energies of the ATT derivatives. The intermolecular transfer integrals and charge transport mobilities at room temperature have been deduced with the predicted single crystal structures. This work is to elucidate the carrier transport behavior, and to formulate structure-property relationships and proceeding further with rational design of high-performance *n*-type organic semiconductors.

2. Theoretical and computational methodology

2.1. Theoretical methodology

There are mainly two types of charge transport mechanisms in organic electronic materials at present: the incoherent hopping and the coherent band mechanism [12]. The charge transport is governed by hopping mechanism when the system is disordered at room temperature. According to hopping mechanism, each hopping step has been considered as a nonadiabatic electron-transfer reaction involving a self-exchange charge from a charged molecule to an adjacent neutral one. The rate of charge transfer between neighboring molecules, k , can be expressed by the standard Marcus equation in terms of the reorganization energy λ , the transfer integral V , and the temperature T as [13]:

$$k = \frac{2\pi V^2}{h} \left(\frac{\pi}{\lambda k_B T} \right)^{\frac{1}{2}} \exp \left(-\frac{\lambda}{4k_B T} \right) \quad (1)$$

where h and k_B are the Planck and Boltzmann constants, respectively.

The reorganization energy λ consists of intramolecular reorganization energy and intermolecular reorganization energy. However, intermolecular reorganization energy is much smaller than intramolecular one in organic solid [14,15]. Herein, the intramolecular reorganization energy, which reflects the deformation of the molecular geometry in charge transfer process, is only considered in this study. Thus, the reorganization energy could be expressed by the adiabatic potential (AP) energy surface approach [16]:

$$\lambda_{\pm} = E_0(Q_{\pm}) - E_0(Q_0) + E_{\pm}(Q_0) - E_{\pm}(Q_{\pm}) \quad (2)$$

where E is energy and Q is geometry. The subscripts 0, + and – denote neutral, cationic, and anionic states, respectively. For example, $E_+(Q_0)$ is the energy of cation with geometry of the optimized neutral molecule. Then, the ionic state properties such as vertical ionization potential (IP_V), adiabatic ionization potential (IP_a), ver-

tical electron affinities (EA_V), and adiabatic electron affinities (EA_a) were calculated by the following formulas [17]:

$$\frac{IP_V}{IP_a} = \frac{E_+(Q_0)}{E_+(Q_+) - E_0(Q_0)} \quad \frac{EA_V}{EA_a} = \frac{E_0(Q_0) - E_-(Q_0)}{E_-(Q_-)} \quad (3)$$

The evolution of transfer integral V is based on the molecular orbitals of the conjugated molecules. The coupling matrix element could be expressed by the site-energy corrected method [18]:

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

here, the transfer integral V could be written with charge transfer integral J , overlap matrix S and site energy of monomer E , respectively.

In the calculation of transfer integral in single crystal, the monomer orbitals with proper orthogonalization are used as basis sets for the Hamiltonian of the dimer system. For hole transport the highest occupied molecular orbitals (HOMOs) of monomers are used as the basis function while for electron transport the lowest unoccupied molecular orbitals (LUMOs) are used correspondingly, and then S , J and E could be expressed as [19]:

$$J_{12} = \langle \varphi_1^{H/L} | h | \varphi_2^{H/L} \rangle S_{12} = \langle \varphi_1^{H/L} | \varphi_2^{H/L} \rangle E_1 = \langle \varphi_1^{H/L} | h | \varphi_1^{H/L} \rangle E_2 \\ = \langle \varphi_2^{H/L} | h | \varphi_2^{H/L} \rangle \quad (5)$$

where h is the Kohn–Sham Hamiltonian of a dimer and $\phi_1^{H/L}$, $\phi_2^{H/L}$ are the localized molecular orbitals of adjacent monomers.

Assuming that there is no correlation between charge hopping events and charge motion is a homogeneous random walk, the diffusion coefficient D could be evaluated from the hopping rate as:

$$D = \frac{1}{2n} \sum_i r_i^2 k_i P_i \quad (6)$$

where n is the spatial dimensionally (usually n is equal to 3), r_i is the centroid distance of the hopping channel i , and P_i is the hopping probability for the specific path i , which is calculated as:

$$P_i = k_i \left(\sum_i k_i \right)^{-1} \quad (7)$$

Here, the drift mobility for charge carrier transport in organic semiconductor, μ , can be evaluated from Einstein relation [20]:

$$\mu = \frac{e}{k_B T} D \quad (8)$$

In the organic single crystals, the orientation function describing the mobility in a specific conducting direction on a specific surface can be written as the following equation, which is known as the angular resolution anisotropic mobility [21]:

$$\mu_{\Phi} = \frac{e}{2k_B T} \sum_i r_i^2 k_i P_i \cos^2 \gamma_i \cos^2(\theta_i - \Phi) \quad (9)$$

here γ_i is the angle of hopping path relative to the plane of molecular stacking layer, Φ is the orientation angle of the transistor channel relative to the specific crystallographic axis and θ_i is the angle of the projected hopping path relative to the specific axis.

2.2. Computational details

For molecules ATT, ATT1, ATT2 and ATT3, the optimized geometry has been obtained by DFT calculations at the GGA/PBE level, and Gaussian electrostatic potential (ESP) charges of all atoms were obtained. The crystal structure prediction, based on the embedded ESP charges, was performed by employing the Dreiding force field

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