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Different electronic and charge-transport properties of four organic semiconductors Tetraazaperopyrenes derivatives

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HIGHLIGHTS

- We theoretically calculated the charge-transport and electrochemical data of the TAPP derivatives.
- Our calculation is based on the Marcus–Hush electron-transfer theory with DFT calculations.
- The core substitution of TAPPs has a drastic influence on the charge-transport mobilities.
- Our work makes a profound study on the effect of the different substitution of the TAPPs in the different positions.

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ABSTRACT

Tetraazaperopyrenes (TAPPs) derivatives are high-performance n-type organic semiconductor material families with the remarkable long-term stabilities. The charge carrier mobilities in TAPPs derivatives crystals were calculated by the density functional theory (DFT) method combined with the Marcus–Hush electron-transfer theory. The existence of considerable C–H…F–C bonding defines the conformation of the molecular structure and contributes to its stability. We illustrated how it is possible to control the electronic and charge-transport parameters of TAPPs derivatives as a function of the positions, a type of the substituents. It is found that the core substitution of TAPPs has a drastic influence on the charge-transport mobilities. The maximum electron mobility value of the core-brominated 2,9-bis (perfluoroalkyl)-substituted TAPPs is 0.521 $cm^2\,V^{-1}\,s^{-1}$, which appear in the orientation angle 95° and 275°. The results demonstrate that the TAPPs with bromine substituents in *ortho* positions exhibit the best charge-transfer efficiency among the four different TAPP derivatives.

Introduction

In the past twenty years, a great deal of progress has been made in organic semiconductors and their device applications. Organic semiconductors have been successfully employed as a new class of electronic materials for applications in electronic devices such as organic thin-film transistors (TFTs), organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs) [1–7]. The most critical organic semiconductor for electronic devices is p-type semiconductors or n-type semiconductors. The performance of p-type semiconductors has been found to comply with the requirements of many applications with high hole mobilities in extensive investigations. However, there has been considerably less development of n-type semiconductors because of challenges such as the low mobility, instability in the air and large barrier to electron injection [8–12]. The n-type semiconductors materials are therefore becoming more and more important in field effect transistor applications for developing circuitry.

The TAPPs derivatives have outstanding merits as an investigated familie of air-stable n-type organic semiconductors for organic thin-film transistors [13,14]. Till Riehm and his coworkers have synthesized these semiconductors by treating 4,9-diamino-3-10-perylenequinone diimine (DPDI) with some experimental studies in previous reports [15,16]. Recently, DPDI has been synthesized by oxidative coupling with two 1,8-diaminonaphthalene molecules [17]. Susanne C. Martens and coworkers have reported the crystal structures, synthesis, electronic structures and organic complementary circuits of 2,9-bisperfluoroalkyl-1,3,8,10-tetraazaperopyrenes (TAPPs) and their derivatives by direct experimental methods as shown in Fig. 1. Moreover, 1,3,8,10-tetraazaperopyrenes (TAPPs) have been promised candidates for the development of n-type semiconductors because of their obvious electrochemical behavior [18].

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Sonja Geib studied the semiconducting properties of the core-brominated TAPPs as n-channel semiconductors for organic complementary circuits [19]. The maximum electron mobilities of two TAPPs derivatives were measured steadily at 0.05 $cm^2 V^{-1} s^{-1}$ and 0.14 $cm^2 V^{-1} s^{-1}$ during air exposure relatively [18]. These results show that the introduction of electron-withdrawing substituents makes these TAPPs derivative materials promising candidates for the development of n-type semiconductors.

Theoretical investigations on organic semiconductors are incessantly enriched and updated in the course of development [20,21]. For example, Han and coworkers developed a quantum mechanics (QM) calculation method to simulate the angular resolution anisotropic mobility with Marcus–Hush theory [22–25]. Han, Zhang and Deng et al. have theoretically investigated some types of organic semiconductors, such as the DADF, DADK and rubrene in order to understand the relationship between molecular packing and charge transport [26,27]. Recently, our group has systematically investigated the electrical anisotropy properties of two ladder-type semiconductors [28]. Although the research of the charge transport properties has attracted a lot of attention, a systemic investigation of electron transfer mobilities is still lacking in many ways.

In this work, the charge mobilities of four Tetraazaperopyrene (TAPP) derivatives were theoretically studied and the angular-resolution anisotropic mobilities were simulated. The four molecular models of TAPPs derivatives were analyzed and discussed. We consider the possibility of tuning the electronic properties of the materials via the considerable C–H…F–C bonding interaction between the two moleculars model systems. Through the first-principles quantum mechanics (QM) calculations and Marcus–Hush theory, the study reports the data about molecular orbitals (lowest unoccupied molecular orbital (LUMO), electron affinities (EAs) and ionization potential (IP) as well as the energy gaps), the absorption spectra properties and the angular-resolution anisotropic mobility curves of the four different compounds 1–4.

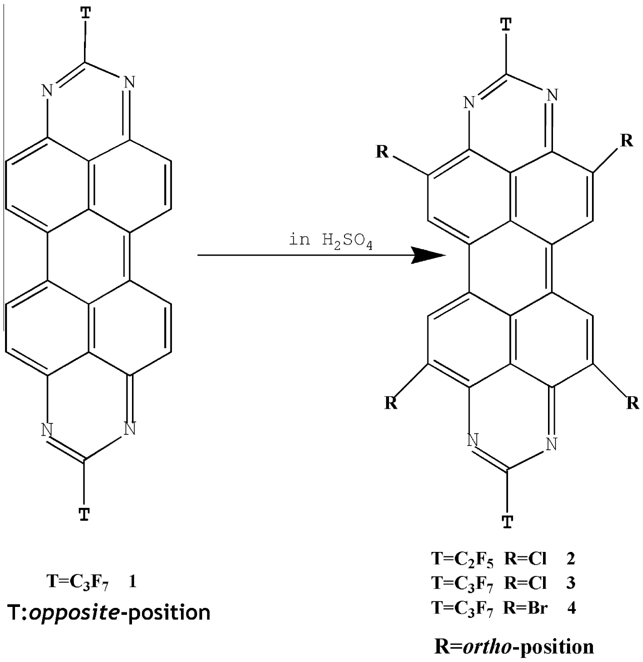

Fig. 1. Synthesis of the core-chlorinated and core-brominated TAPP derivatives 2-4 and two different substituted positions of TAPPs: *opposite*-position and *ortho*-position.

Theoretical methods

This work is based on Marsh–Hush electron transfer theory and first-principle QM calculation. The study of geometric structures was conducted with density functional theory (DFT) and the absorption spectra can be simulated by using time-dependent density functional theory (TDDFT). The geometric structures (in the neutral and charged states) were optimized by using the DFT method with B3PW91 functional. The reorganization energies, ionization potential and electron affinities were calculated from the relevant points on the potential energy surfaces. The calculations were carried out by the Gaussian 09 program package with 6-31g (d, p) throughout the whole process [29]. The transfer integrals were calculated by using fragment orbital approach for the neighbor molecular pairs. The calculations of electronic coupling were implemented by the PW91 gradient corrections and TZ2P basis set in the Amsterdam density functional (ADF) program [30]. Finally, we computed the mobilities of the TAPPs derivatives with the deduced analytic function.

Anisotropic mobility

Using the standard Marcus–Hush theory, we obtain the following expression for the hole (or electron) charge-transfer rate [31]

$$W = \frac{V^2}{\hbar}\left(\frac{\pi}{\lambda k_B T}\right)^{1/2} exp\left(-\frac{\lambda}{4k_B T}\right) \tag{1}$$

where λ is the reorganization energy, k_B is the Boltzmann constant, T is the temperature(T is 350 K in our article) and V is the coupling matrix element between neighboring molecules.

The drift mobility of hopping for charge carrier transport (μ) can be evaluated from the Einstein relation in organic semiconductors,

$$\mu = \frac{e}{k_B T} D = \frac{e}{2nk_B T}\sum_i r_i^2 W_i P_i \tag{2}$$

The anisotropic mobility is an intrinsic character in organic semiconductors, and the magnitude depends on the organic crystal specific surface. The anisotropic mobility (μ_ϕ) can be analyzed by forecasting the different hopping pathways. The following equation provides an analytic function to calculate the anisotropic mobilities by relating the intermolecular electron coupling V to the measuring channel angle ϕ for any organic semiconductor [24,25].

$$\mu_\phi = \frac{e}{2k_B T}\sum_i W_i r_i^2 P_i \cos^2\gamma_i \cos^2(\theta_i - \phi) \tag{3}$$

In these parameters, r_i is the hopping distance, γ_i is the angle of the hopping jumps between adjacent molecules relative to the plane of interest (the values of γ_i are 0°), ϕ is the orientation angle of the transistor channel relative to the reference axis, and θ_i is the angle of the projected electronic coupling pathways of different dimer types relative to the same reference axis (generally the crystallographic axis). Therefore, we can draw the $\theta_i - \phi$ reflects the angle between pathways and the conducting channels.

Reorganization energy calculation

The reorganization energy λ can be divided into two types: the inner and outer contributions (λ_1 and λ_2).

$$\lambda = \lambda_1 + \lambda_2 \tag{4}$$

The former is caused by the change in equilibrium geometry of the donor and acceptor sites consecutive to the gain or loss of electronic charge upon electron-transfer, and the latter is the energy change of the electronic and nuclear polarization (relaxation) due to the surrounding solvent molecules upon electron transfer.