



# Theoretical study on the electron transport properties of chlorinated pentacene derivatives



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## ABSTRACT

The effects of chlorination on the geometries, electronic structures and transport properties for some chlorinated pentacene derivatives ( $n\text{Cl-PENT-}n$ ) have been theoretically investigated by using density functional theory calculations and Marcus-Hush theory. Compared with PF-PENT, introducing chlorine atoms into pentacene, remarkably decreases the frontier molecular orbital energies while scarcely increases the internal reorganization energy, therefore improves their air-stability and ability of electron injection. Based on the experimental crystal parameters, the predicted hole and electron mobility ( $\mu_h = 0.46 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $\mu_e = 0.61 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) values for 6,13-dichloropentacene (DCP) crystal indicate that DCP crystal may be a promising candidate as ambipolar OFET materials. After the present work the results indicate that 4Cl-PENT-1 should be good n-channel material ( $\mu_e = 2.74 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). In addition, the angular dependent simulation for electron mobility shows that the electron transport is remarkably anisotropic in the studied molecular crystals and the maximum  $\mu_e$  appears along the crystal axis direction since molecules along this direction exhibit the close face-to-face stacking arrangement with short interplanar distances ( $\sim 3.7\text{--}5.3 \text{ \AA}$ ), which induces large electronic couplings.

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## 1. Introduction

Organic field-effect transistors (OFETs) have received much attention in recent decades due to their advantages such as high flexibility, lightweight, and easy fabrication for potential application in numerous electronic devices [1–4]. Although, significant progress has been made in the study of OFET devices, the development of n-type materials has lagged far behind p-type ones due to their instability at the air condition and lower charge carrier mobility [5,6]. Therefore, developing ambient stability and high-performance novel n-type materials is currently hot topic and also a crucial challenge [7–9].

The principal design strategy for developing n-type organic semiconductors is to realize a low-lying energy level of the lowest unoccupied molecular orbital (LUMO), and provide large electron affinities (EAs). Chao et al. [10] have theoretically verified that chlorination can considerably activate the n-channel conduction in terms of the large EAs and ionization potentials (IPs). Also Bao et al. [11] have considered that chlorinated molecules behave as well or better than their fluorinated compounds in terms of electron mobility and ambient stability. Recently, chlorinated chrysene

[12] and coronene derivatives [13] have been investigated which are all shown larger EAs to facilitate the electron injection from the metallic electrode. As compared to polycyclic aromatic hydrocarbons (PAHs) and heteroacenes, chlorinated linear acenes are rarely studied systematically. And the previous works mainly based on investigating the reorganization energy ( $\lambda$ ), IP, EA and the frontier molecular orbital to evaluate the effect of chlorination. In this study, we have systematically analyzed the influence of chlorine substitution on the geometries, electronic properties and charge transport parameters for a set of designed pentacene derivatives from the number of chlorine atoms and the position of chlorine introduced. Moreover, crystal structures have been predicted to estimate the corresponding charge transfer rates, the electron mobilities and anisotropy of the designed molecules.

## 2. Methods

### 2.1. Theoretical models

In organic crystals and films, due to the weak interaction of adjacent molecules and the strong electronic–vibrational coupling, the coherent band model is not suitable in describing the charge transfer properties at high temperature [14,15]. In such cases, the

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dynamic disorder may strongly localize the charge carrier, and the incoherent hopping model is often employed [16,17]. In this model, the charge-transfer rate constant ( $k$ ) between adjacent molecules can be calculated using the Marcus theory [14,18]

$$k = \frac{2\pi^2}{h} \frac{1}{\sqrt{\pi(\lambda_{\text{int}} + \lambda_{\text{out}})k_{\text{B}}T}} V^2 \exp\left(-\frac{(\lambda_{\text{int}} + \lambda_{\text{out}})}{4k_{\text{B}}T}\right) \quad (1)$$

where  $h$ ,  $k_{\text{B}}$  and  $T$  denote the Planck, Boltzmann constants and temperature, respectively.  $\lambda_{\text{int}}$  is the internal (intramolecular) reorganization energy,  $\lambda_{\text{out}}$  is the external (intermolecular) reorganization energy,  $V$  is the effective charge transfer integral. As illustrated in Eq. (1), the  $k$  is mainly determined by two key parameters at a given temperature: the  $\lambda$  ( $\lambda_{\text{out}}$  and  $\lambda_{\text{int}}$ ) and the  $V$ . The  $\lambda_{\text{out}}$  induced the polarization of the medium is very small in compared with the  $\lambda_{\text{int}}$  [19–21], which is usually neglected in theoretical studies [21,22]. The  $\lambda_{\text{int}}$  is caused by the change of the internal nuclear coordinates from the reactant to the product, which can be evaluated from the adiabatic potential energy surfaces [23,24]

$$\lambda_{\text{int}} = [E^0(\text{M}^c) - E^0(\text{M}^0)] + [E^c(\text{M}^0) - E^c(\text{M}^c)] \quad (2)$$

where  $E^0(\text{M}^0)$  is the energy of the neutral state with the optimized geometry of neutral molecule,  $E^c(\text{M}^c)$  is the energy of the charged states with the optimized charged geometry,  $E^c(\text{M}^0)$  is the energy of the charged states with the optimized geometry of the neutral molecule, and  $E^0(\text{M}^c)$  is the energy of the neutral state with the optimized charged geometry. The  $V$  is another important parameter determining the charge transfer rate according to Eq. (1). In this work, the  $V$  is calculated on the direct coupling approach. In terms of this scheme, the  $V$  between molecules  $i$  and  $j$  can be estimated by the spatial overlap integral ( $S_{ij}$ ), charge transfer integral ( $T_{ij}$ ), and site energy ( $e_{i(j)}$ ) [25,26]

$$V_{ij} = \frac{T_{ij} - 0.5(e_i + e_j)S_{ij}}{1 - S_{ij}^2} \quad (3)$$

where the  $S_{ij}$ ,  $T_{ij}$ , and  $e_{i(j)}$  terms can be obtained by the following equations [27]:

$$S_{ij} = \langle \psi_i | \psi_j \rangle = \sum_{\mu\nu} c_{i,\mu} c_{j,\nu} S_{\mu\nu} \quad (4)$$

$$T_{ij} = \langle \psi_i | F^{\text{KS}} | \psi_j \rangle = \sum_{\mu\nu} c_{i,\mu} c_{j,\nu} F_{\mu\nu}^{\text{KS}} \quad (5)$$

$$e_{i(j)} = \langle \psi_{i(j)} | F^{\text{KS}} | \psi_{i(j)} \rangle = \sum_{\mu\nu} c_{i(j),\mu} c_{i(j),\nu} F_{\mu\nu}^{\text{KS}} \quad (6)$$

Among them,  $\psi_{i(j)}$  is the Highest Occupied Molecular Orbital (HOMO, for hole transfer) or Lowest Unoccupied Molecular Orbital (LUMO, for electron transfer) of the isolated molecule  $i(j)$ ,  $c_{i,\mu}$  and  $c_{j,\nu}$  are the isolated molecular-orbital coefficients for atomic basis functions  $\mu$  on molecule  $i$  and  $\nu$  on molecule  $j$ ,  $S_{\mu\nu}$  is the atomic-orbital overlap matrix, and  $F^{\text{KS}}$  is the Kohn–Sham Hamiltonian of the dimer system, which can be calculated by the following equation [28]:

$$F^{\text{KS}} = SC\varepsilon C^{-1} \quad (7)$$

where  $S$  is the intermolecular overlap matrix,  $C$  is the molecular orbital coefficient matrix from the isolated monomer, and  $\varepsilon$  is the orbital energy from one-step diagonalization without iteration.

At a fixed temperature ( $T$ ), the drift mobility is expressed as the Einstein relation [28,29]

$$\mu = \frac{eD}{k_{\text{B}}T} \quad (8)$$

where  $e$  is the electronic charge,  $D$  is the diffusion coefficient, which is related to the charge-transfer rate  $k$ , and it can be approximately evaluated as [30]

$$D = \lim_{t \rightarrow \infty} \frac{1}{2n} \frac{\langle x(t)^2 \rangle}{t} \approx \frac{1}{2n} \sum_i d_i^2 k_i P_i \quad (9)$$

where  $n = 3$  is the dimensionality,  $i$  represents a specific hopping pathway with  $d_i$  being the hopping centroid distance. Here, we assume that the charge hopping occurs only between nearest-neighbor molecules.  $P_i$  is the relative probability for charge carrier to a particular  $i$ th neighbor

$$P_i = k_i / \left( \sum_i k_i \right) \quad (10)$$

The anisotropic mobility is an important intrinsic property of the charge transport in organic semiconductors, which intensively depends on the specific surface of the organic crystal [31]. Yin et al. [32] have proposed to compute the anisotropic mobility ( $\mu_{\Phi}$ ) by solving the steady-state master equation approach [33]. The kinetics of charge transport through a solid material with many possible resident sites can be expressed by the following master equation [34]:

$$\frac{dp_i}{dt} = - \sum_{j \neq i} [k_{ij} p_i (1 - p_j) - k_{ji} p_j (1 - p_i)] \quad (11)$$

where  $k_{ij}$  is the charge transfer (CT) rate from site  $i$  to site  $j$  in the crystal,  $p_i$  is the charge occupied density on site  $i$ , and  $1 - p_i$  is the Coulomb penalty factor, which prevents two or more charges simultaneously to occupy the same site. When the charge transport reaches the so-called steady state,  $dp_i/dt = 0$ , the  $p_i$  can be obtained by an efficient iterative procedure given a full set of CT constant  $k_{ij}$  [35]. When an electronic field  $E$  is applied to the material, the charge carrier will drift accordingly, and the mobility can be determined via the velocity  $v$  as the linear response of the motion to the perturbation [36]:

$$\mu_{\Phi} = \frac{v}{|\mathbf{E}|} = \frac{\sum_{ij} k_{ij} p_i (1 - p_j) R_{ij} \hat{\mathbf{E}}}{p_{\text{tot}} |\mathbf{E}|} \quad (12)$$

where  $\hat{\mathbf{E}}$  is the unit vector of applied electric field,  $p_{\text{tot}}$  is the total carrier population,  $R_{ij}$  is the hopping distance between site  $i$  and site  $j$  projected onto the direction of the applied electronic field vector. The  $R_{ij}$  can be obtained according to the following equation:

$$R_{ij} = \frac{\mathbf{R}_{ij} \cdot \mathbf{E}}{|\mathbf{E}|} \quad (13)$$

where  $\mathbf{R}_{ij}$  is the distance vector from site  $i$  and site  $j$ .

All simulations are performed using the periodic boundary condition to model an infinite molecular crystal. In addition, to reduce the influence of the electric field on the  $\mu$  as possible, the  $\hat{\mathbf{E}}$  is set as a very small value of  $1.0 \times 10^{-3} \text{ V \AA}^{-1}$ .

## 2.2. Computational details

It is well known that the B3LYP hybrid functional can present rational description for the geometric relaxation of  $\pi$ -conjugated organic molecules in charge transfer process [37–41]. As a result, for the studied molecules, the geometry optimizations and the electronic structures are calculated with B3LYP hybrid functional [28,42] and the 6-31+G(d,p) basis set. It is shown that there are no imaginary frequencies in all derivatives. The  $V$  values for the charge transfer in all nearest-neighbor molecular pairs are calculated with the PW91PW91/6-31G(d) method, which has been shown to provide the reasonable result at the DFT level [43–45]. All the quantum chemistry calculations are carried out with the Gaussian 09 software package [46]. The crystal structure prediction has been performed for  $n\text{Cl-PENT-}n$  by using the polymorph predictor (PP) module in the Accelrys package Materials Studio

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