Chemical Physics 478 (2016) 130–138

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Dimer and cluster approach for the evaluation of electronic couplings governing charge transport: Application to two pentacene polymorphs

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ARTICLE INFO

Article history:
Available online 9 April 2016

Keywords:
Organic semiconductors
Charge transport anisotropy
Quantum-chemistry
Embedding effects
Electronic couplings

ABSTRACT

Hole transport properties are modeled for two polymorphs of pentacene: the single crystal polymorph and the thin film polymorph relevant for organic thin-film transistor applications. Electronic couplings are evaluated in the standard dimer approach but also considering a cluster approach in which the central molecule is surrounded by a large number of molecules quantum-chemically described. The effective electronic couplings suitable for the parametrization of a tight-binding model are derived either from the orthogonalization scheme limited to HOMO orbitals and from the orthogonalization of the full basis of molecular orbitals. The angular dependent mobilities estimated for the two polymorphs using the predicted pattern of couplings display different anisotropy characteristics as suggested from experimental investigations.

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1. Introduction

The electronic structure of organic semiconducting materials has received considerable attention from the viewpoint of both fundamental research and device fabrication and performance. Pentacene, in particular, has become an important reference in organic-semiconductor materials, with potential applications in thin-film transistors and single crystals, due to its high mobility.

The intrinsic charge transport properties of organic crystals depend strongly on the molecular packing and arrangement in the crystal. In this regard, pentacene, showing one of the highest charge carrier mobilities among organic semiconductors, is known to crystallize in at least four polymorphs, which can be distinguished by their layer periodicity *d* [1,2].

Various structure determinations on single crystals grown in different ways have revealed different triclinic structures for pentacene [3]. Polymorphism in pentacene, on the other hand, has been observed also in thin-film growth experiments. In all of these phases, pentacene molecules align their long axis approximately perpendicular to the film surface but different interlayer spacings (*d*-spacing) perpendicular to the thin-film surface have been observed, with values of 14.1, 14.5, 15.0, and 15.4 Å, sometimes used to label the different polymorphs. The shortest *d*-spacing of 14.1 Å, is consistent with the recent room-temperature single-crystal structure of pentacene, and the 14.5 Å *d*-spacing is consistent with the initial structure reported by Campbell [4] and with the high-temperature polymorph stable above 463 K [3].

Thin films fabricated on insulating layers often show a unique structure called the "thin film" phase that is characterized by an interlayer spacing of $d = 15.4$ Å. The substrate-induced 15.4 Å polymorph is the most relevant for organic thin-film transistor (OTFT) applications [5] because this polymorph is usually present in the working layers of pentacene OFETs [6]. The complete lattice parameters for the thin film phase of pentacene have been determined recently for various substrates [5,6].

Recently the angle resolved photoemission spectroscopy measurements of thin film phase pentacene, (identical to that of the thin film phase grown on SiO_2) have been reported [7] and used to fit a tight-binding model from which effective masses have been derived. The effective masses indicated a less marked charge transport anisotropy compared to that reported for the single crystal phase of pentacene, from field effect mobility measurements [8].

Charge mobility calculations have been reported for pentacene, encompassing band theory and hopping approaches and computed electronic couplings have been discussed by several groups [9–15]. The band structure for different polymorphs of pentacene and their hole mobilities were determined in recent computational investigations [10,11]. Charge mobility and mobility anisotropy has been predicted also in the framework of the hopping approach, but only for the single crystal structure of pentacene [12–15] and generally

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http://dx.doi.org/10.1016/j.chemphys.2016.04.004
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using the classical Marcus equation to estimate charge transfer rate constants.

Here we have reconsidered the single crystal polymorph [1] but we have also included the thin film polymorph whose structure and molecular orientation on SiO_2 has become available [5] (see Fig. 1). We determined electronic couplings for the two different polymorphs and used them to model charge transport. Recently, we investigated the combined effect of intra- and inter- molecular properties on the charge transport and localization of several organic semiconductors [16–20]. We successfully reproduced the trends in *n*-type charge transport of some fluorinated and chlorinated perylene diimide derivatives and fluoro-alkylated naphthalene diimide [18–20]. More recently we adopted the same computational approach to investigate the *p*-type charge transport properties and anisotropy of a thienoacene and its derivatives [21,22]. In our previous work the electronic couplings were estimated with the common dimer approach [23]. Nonetheless, in the case of one thienoacene [21], we employed a cluster approach to estimate the solid phase embedding effects on the small HOMO/HOMO-1 energy difference which influences charge transport. Here we explore the use, for the first time, of the cluster approach (beside the dimer approach) also for estimating electronic couplings between the central molecule and surrounding molecules in the cluster.

2. Computational methods

Equilibrium structures of neutral and charged species were obtained from quantum chemical calculations performed at B3LYP/6-31G* level of theory. The nature of the stationary points obtained by structure optimization was assessed by vibrational frequencies calculations at the optimized structure. Vibrational frequencies were also employed to estimate the vibrational contributions to the intramolecular reorganization energy through the calculations of Huang–Rhys parameters [24,25] (see below). All quantum-chemical calculations were performed using the Gaussian09 suite of programs [26].

The charge transport properties were investigated within the non-adiabatic hopping mechanism, according to which the charge transfer occurs between a pair of molecules (dimer). The molecular materials considered here are in crystalline form, therefore the dimers were identified by evaluating the distances between the centers of mass of the molecules surrounding a central reference molecule in the crystal. The reliability of the model depends on the relative magnitude of the electronic couplings (or charge transfer integrals) V_{ij} and the reorganization energy λ, with V_{ij} required to be much smaller than λ [27,28] and we anticipate that pentacene is critical in this sense. As a result, absolute values of computed mobilities are not the objective of this work and will have to be taken with caution. The most suitable formulation of the charge transfer kinetic constant k_{eT}, for a dimer, is the Marcus–Levich–Jortner (MLJ) equation [29,30] which represents a quantum correction of the Marcus equation since it includes the quantum nature of the vibrational modes most active in molecular reorganization:

$$k_{eT} = \frac{2\pi}{\hbar} V_{ij}^2 \frac{1}{\sqrt{4\pi\lambda_o k_B T}} \sum_{v=0}^{\infty} \left[\exp(-S_{eff}) \frac{S_{eff}^{v}}{v!} \times \exp\left(-\frac{(\Delta G^o + \lambda_o + v\hbar\omega_{eff})^2}{4\lambda_o k_B T} \right) \right] \tag{1}$$

In the above expression the reorganization energy is composed of an intramolecular term λ_i and an "outer" contribution λ_o due to the interaction with the surrounding molecules in the crystal. λ_i was computed at B3LYP/6-31G* level of theory, either with the

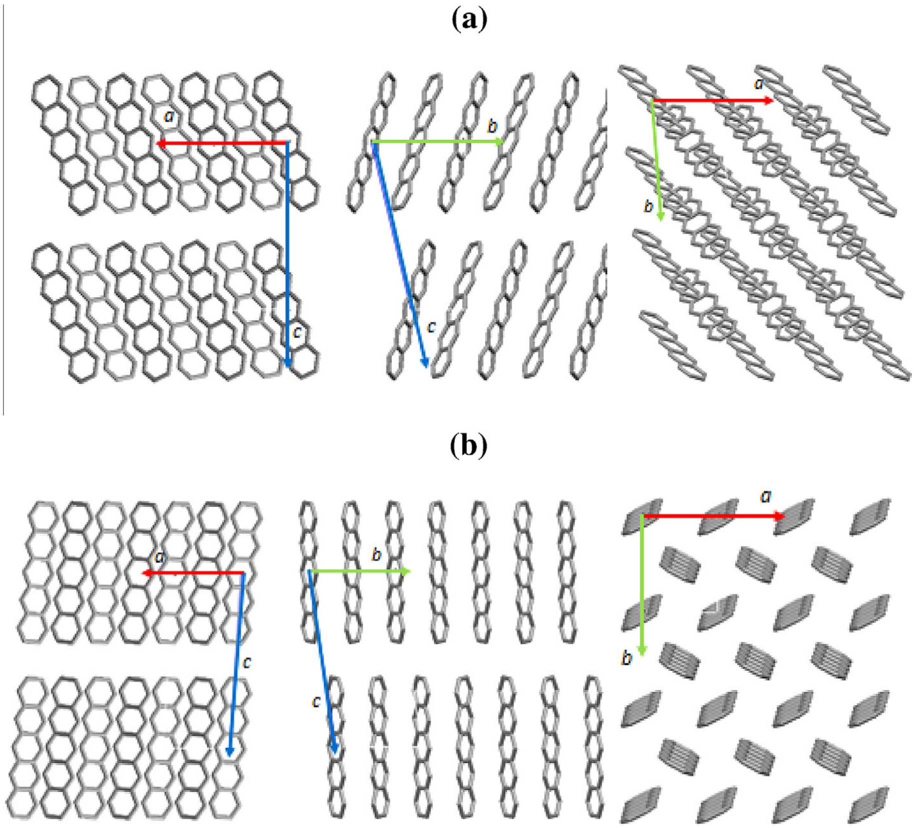

Fig. 1. Portion of the two polymorphs of pentacene investigated in this work: (a) single crystal polymorph, (b) thin film polymorph. Views along the *b* axis (left), *a* axis (center) and *c* axis (right). Hydrogens are not shown.

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