Large bandwidths in synthetic one-dimensional stacks of biological molecules

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We present ab initio calculations of the electronic and transport properties of one-dimensional π-conjugated stacks of guanine- and melanin-based molecules. The electron and hole bandwidths are found to be very large for these organic materials (up to 2 eV), and the effective masses of the charge carriers are rather small. Since these material parameters basically determine the intermolecular charge-transport properties, we predict highly ordered self-assembled one-dimensional stacks of such biological molecules to be promising candidates for applications in organic electronics.

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I. INTRODUCTION

Organic semiconductors with π conjugation represent a highly attractive class of materials for low-cost and easy- to-process (opto)electronic devices such as organic field-effect transistors (OFETs),1,2 organic light-emitting devices (OLEDs),3 and organic solar cells.4 In order to improve the performance of all these devices, the understanding and optimization of the charge transport through the organic material is highly important as it governs, e.g., the switching frequency of OFETs. During the last few years, tremendous progress has been achieved by several groups towards a better fundamental description of the charge-carrier transport in organic semiconductors.5–11 In particular, predictions about electron and hole mobilities as a function of temperature, direction, and disorder in various organic molecular crystals have been made recently.7–11

An important conclusion from these previous investigations was that the charge-transport properties can be improved especially by (i) the proper choice of a molecule with a large π-electron system, (ii) the maximization of the wave-function overlap between adjacent molecules, and (iii) the reduction of structural disorder throughout the entire arrangement of all molecules as, e.g., in a perfect molecular crystal. This concept is commonly referred to as the structure-property relationship5 and serves as an important starting point for theoretical predictions and experimental guidelines. For a long time, the above criteria could experimentally only be fulfilled simultaneously for highly purified vapor-grown three-dimensional (3D) bulk crystals of, e.g., oligoacenes or rubrene (see, e.g., Refs. 2,12–14). More recently, experimental work has also focused on two-dimensional (2D) organic structures. For example, as an important proof of concept, it has been demonstrated that highly ordered organic monolayers on conducting substrates can be achieved through the proper use of anchoring groups in combination with the self-assembling properties of organic molecules.15 Following this spirit, we propose in the present paper to consider also self-assembled one-dimensional (1D) structures built up from biological molecules such as guanine and melanin.

II. THEORETICAL AND COMPUTATIONAL METHODS

Our ab initio calculations are based on density functional theory (DFT) as implemented in the VIENNA AB INITIO SIMULATION PACKAGE (VASP)25 using a plane-wave basis set and projector augmented wave pseudopotentials for the description of the electronic states.
of the electron-ion interaction. Thereby an energy cutoff of 750 eV for the plane-wave expansion has been used. The various 1D stacks are modeled within the supercell approach using very large supercell dimensions of 20 Å (guanine) and 30 Å (melanin) in order to prevent artificial interactions between neighboring stacks. The Kohn-Sham equations are solved by treating exchange and correlation effects on the level of the local-density approximation (LDA). We stress that the typical band-gap problem in LDA is less relevant for the purpose of the present work as we will mainly focus on determining bandwidths and effective masses. These quantities can still be extracted with high accuracy because the band dispersions remain quite reliable using LDA.26

For the subsequent calculation of the quantum transport along the stacks, we follow the idea of Landauer and Böttiker27 and reduce the conduction problem to the calculation of the transmission function \( T(E) \). Using the Green’s function technique, this quantity is expressed as \( T(E) = \frac{\text{Tr}(\Gamma_L C^{-1}_R \Gamma_R G^{-1}_C)}{\pi} \), where \( G^{-1}_C \) are the retarded and advanced Green’s functions of the conductor and \( \Gamma_L/R \) are the coupling between the conductor and the left (L) and right (R) leads, respectively. This rather complicated and abstract formula can be significantly simplified for an infinite 1D (or quasi-1D) conducting wire, such as the stacks considered in the present work, where the conductor and the leads consist of the same material. Then, the problem is reduced to the solution of a periodic 1D (or quasi-1D) chain where an evaluation in \( k \) space is directly possible and advantageous. As outlined in more detail in our previous work,28 the above quantities can then be simplified into \( G^{\text{ret/adv}}_C(E) = [E - E_C(k) \mp i\gamma]^{-1} \) and \( \Gamma_L/R(E) = -\gamma \), where only the band structure \( E_C(k) \) and a broadening parameter \( \gamma \) enter. In the limit of ballistic transport \( (\gamma \to 0) \), the transmission becomes simply

\[
T(E) = \sum_k \gamma^2 \gamma^2 \rightarrow 0 \sum_k \delta_{E,E_C(k)} = N(E).
\]

Consequently, the transmission function at a particular energy can be immediately identified with the number of states \( N(E) \) at this energy and is therefore directly accessible from the \textit{ab initio} band structure. Therefore, in order to convert the band structures numerically into the transmission functions of the various stacks, we make use of Eq. (1) by performing the \( k \)-point summations on grids of dimension 321 \( \times 1 \times 1 \) and by making the (numerically necessary) broadening very small, i.e., \( \gamma \leq 20 \) meV.

III. RESULTS AND DISCUSSION

Using the above methodology, we present in Fig. 2(a) the results for stacks of cofacially aligned guanine molecules. While this particular molecular arrangement may not occur naturally, it may be stabilized using anchoring groups or scaffolds (e.g., using an experimental technique similar to the one recently presented in Ref. 15) and has been considered as a reference model system before.18 Here, we do not fix the stacking height but perform a structural relaxation of the stack and obtain the equilibrium intermolecular distance as 3.67 Å. From the band structure, we recognize the semiconducting behavior of the guanine stack (LDA gap: 2.65 eV). The bands relevant for the charge transport of electrons and holes are the lowest conduction band and the highest valence band, which exhibit bandwidths of 0.55 and 0.74 eV, respectively. These bandwidth values are of the same order as those in 3D bulk guanine crystals16 and very close to the ones reported in Ref. 18 even though there the lattice constant was fixed at a much smaller value of 3.37 Å. These bands, which are comparably wide for an organic semiconductor, are also easily recognizable in the corresponding transmission function [see Fig. 2(a)] as pronounced plateaus over a wide spectral region. Since the bandwidth is mainly determined by the intermolecular transfer integrals, this implies a strong \( \pi-\pi \) wave-function overlap and hence potentially good charge transport along the stacking direction. This conclusion is further confirmed by the calculated values of the effective masses of electrons \( m^* = 1.11 m_0 \) and holes \( m^*_h = 1.44 m_0 \), which are on the order of the free electron mass and thereby rather small for an organic material, indicating potentially large carrier mobilities for transport along the stack.

It is interesting to contrast these results with similar structures based on eumelanin building blocks. In Figs. 2(b)–2(d), we proceed with studies of three slightly different molecules that are components of eumelanin, namely, quinone methide (MQ), indolequinone (IQ) and 5,6-dihydroxy-indolequinone (HQ). Again, we consider cofacially aligned 1D stacks built up from these planar molecules. The stacking heights calculated after the structural relaxation of the stacks are 3.08 Å (MQ), 3.82 Å (IQ), and 3.70 Å (HQ). While the latter two are comparable to the guanine value, the stacking height for MQ is...
FIG. 2. (Color online) Stack geometries, transmission functions, band structures, and bandwidths for 1D stacks built from the molecules of Fig. 1. The Fermi energy $E_F$ is used as energy zero. The widths of the relevant bands in the one-dimensional Brillouin zone (BZ) are given in units of eV.

surprisingly small and might indicate some overbinding caused by the use of LDA. However, recently similar melanin-like structures with a comparably small lattice constant of 3.20 Å could be successfully synthesized.29 From the band structure, we see that the MQ molecule has a dominating influence in the region around the Fermi level. Similar to the MQ stacks, we observe also here a metallic behavior, large transmission coefficients, and huge bandwidths between 1.72 and 1.80 eV. As in the case of the pure MQ stacks, these huge bandwidths arise from the small stacking height and accompanied strong $\pi-\pi$ coupling. They can be interpreted as precursors for high mobilities, but due to the improved overall structural stability of the HQ-MQ-HQ-MQ rings, these stacks might be somewhat more realistic with respect to practical applications for organic electronics.

IV. SUMMARY

In conclusion, we have presented ab initio studies of various one-dimensional stacks of biological molecules. Especially, we have calculated the electronic and transport properties of guanine and several melanin-like stacks based on DFT using the supercell method and $k$-space number-of-states approach. We have found that all stacks exhibit very large bandwidths for electrons and holes (up to 2 eV) and, accordingly, small effective masses for the charge carriers. This makes these highly ordered synthetic structures and, in particular, the HQ-MQ-HQ-MQ rings of Figs. 1(e) and 2(e) very promising candidates for high-mobility organic materials.

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