

Large bandwidths in synthetic one-dimensional stacks of biological moleculesBjörn Oetzel,¹ Frank Ortmann,^{2,3} Lars Matthes,¹ Falk Tandetzky,^{1,4} Friedhelm Bechstedt,¹ and Karsten Hannewald^{1,*}¹*Institut für Festkörperteorie und –optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany and European Theoretical Spectroscopy Facility (ETSF)*²*INAC, SPRAM, Commissariat à l’Energie Atomique et aux Energies Alternatives (CEA) Grenoble, 17 Rue des Martyrs, 38054 Grenoble Cedex 9, France*³*CIN2 (ICN-CSIC) and Universitat Autònoma de Barcelona, Catalan Institute of Nanotechnology, Campus de la UAB, E-08193 Bellaterra (Barcelona), Spain*⁴*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany*

(Received 2 February 2012; revised manuscript received 15 October 2012; published 5 November 2012)

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.

DOI: [10.1103/PhysRevB.86.195407](https://doi.org/10.1103/PhysRevB.86.195407)

PACS number(s): 73.63.–b, 71.20.Rv, 72.80.Le

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.

As one of the four DNA base molecules, guanine has already been investigated for its prominent role played in the charge transport through DNA and in the quantum transport of short artificial DNA-like structures.^{16–19} Additionally, well-ordered monohydrate guanine crystals were suggested recently as high-mobility materials for organic electronics.¹⁰ They exhibit surprisingly large electron and hole bandwidths which, in turn, translate into small effective carrier masses that favor the charge transport through the crystal. Moreover, the dominant transport channels were identified as being mainly along the π -stacking direction. Therefore, it is natural to directly consider the corresponding 1D structure itself, i.e., stacks of cofacially aligned guanine molecules, as another potential candidate for efficient charge transport.

Similar to guanine, the physical and (photo)chemical properties of the human pigment melanin have been investigated by various groups^{20–24} but so far mainly with respect to their biological consequences. In particular, the relationship between the various molecular components of eumelanin and its optical absorption properties has received a lot of attention.^{22–24} However, recent suggestions for possible natural realizations of 1D eumelanin stacks²⁴ appear also worthwhile to investigate with respect to their potential for organic electronics applications.

Therefore, in the present paper, we investigate the electronic and transport properties of 1D guanine and melanin-like stacks (based on the molecules shown in Fig. 1) by means of *ab initio* calculations. Hereby, the focus will be on those material properties that mainly govern the charge transport through these artificial stacks. Especially, the electron and hole bandwidths, the effective carrier masses, and the resulting transport coefficients will be calculated and discussed with respect to their potential for organic electronics.

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

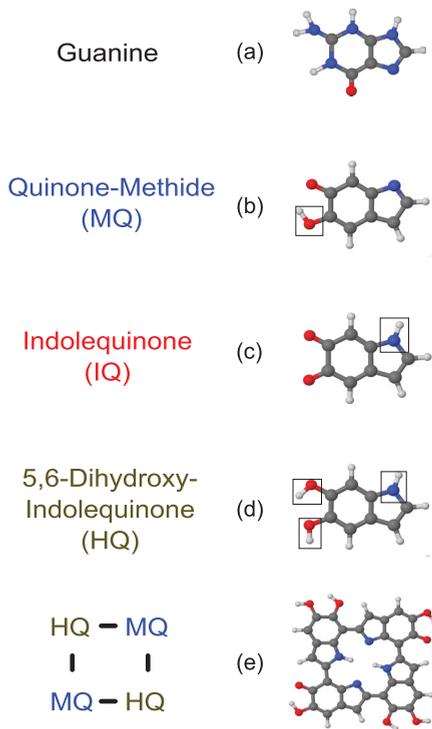


FIG. 1. (Color online) Chemical structures of the studied guanine- and melanin-based molecules. The slight differences between MQ, IQ, and HQ are highlighted. Dark gray: carbon; light gray: hydrogen; blue: nitrogen; red: oxygen.

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 Büttiker²⁷ 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 $T(E) = \text{Tr}(\Gamma_L G_C^{\text{ret}} \Gamma_R G_C^{\text{adv}})$, where $G_C^{\text{ret/adv}}(E)$ are the retarded and advanced Green's functions of the conductor and $\Gamma_{L/R}(E)$ are the coupling between the conductor C 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 \mathbf{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 $G_C^{\text{ret/adv}}(E) = [E - E_C(\mathbf{k}) \mp i\gamma]^{-1}$ and $\Gamma_{L/R}(E) = -\gamma$, where only the band structure $E_C(\mathbf{k})$ and a broadening parameter γ enter. In the limit of ballistic transport ($\gamma \rightarrow 0$), the transmission becomes simply

$$T(E) = \sum_{\mathbf{k}} \frac{\gamma^2}{[E - E_C(\mathbf{k})]^2 + \gamma^2} \xrightarrow{\gamma \rightarrow 0} \sum_{\mathbf{k}} \delta_{E, E_C(\mathbf{k})} = N(E). \quad (1)$$

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 *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 \mathbf{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 crystals¹⁰ 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 π - π 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 ($m_e^* = 1.11 m_0$) 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

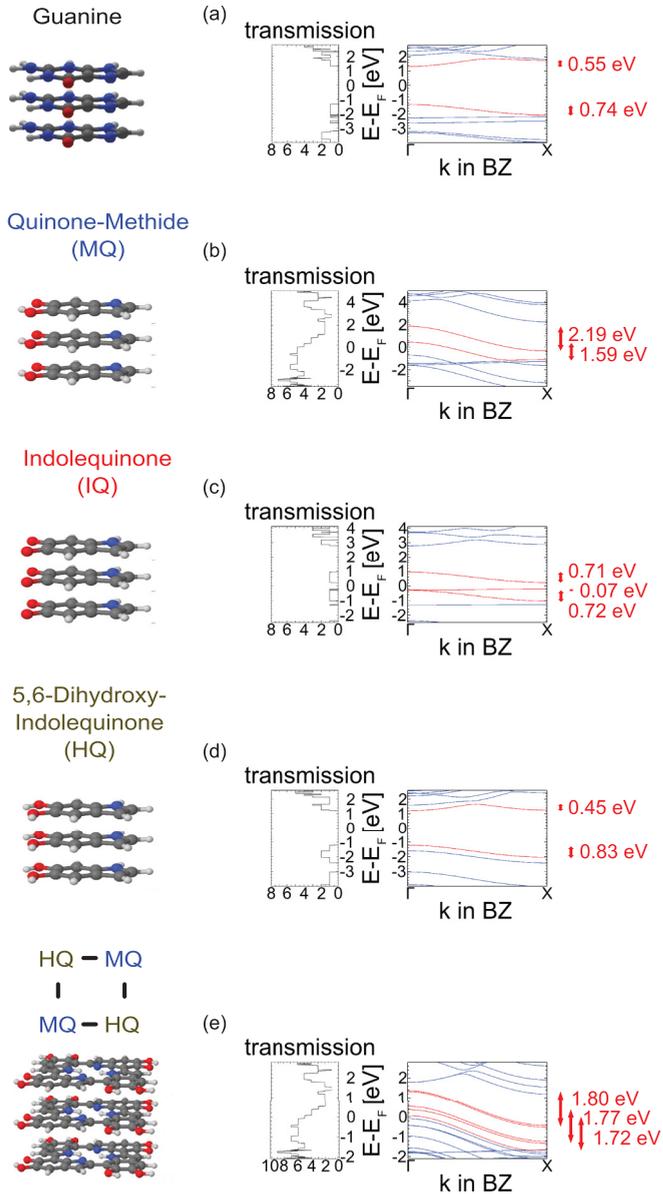


FIG. 2. (Color online) Stack geometries, transmission functions, band structures, and bandwidths for 1D stacks built from the molecules of Fig. 1. The Fermi energy E_F is used as energy zero. The widths of the relevant bands in the one-dimensional Brillouin zone (BZ) are given in units of eV.

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 corresponding band structure calculations, we obtain semiconducting structures with LDA gaps of 0.44 eV for IQ stacks and 2.42 eV for HQ stacks but a metallic behavior for the MQ stacks. In principle, this interesting finding deserves further investigation on a higher level of theory, in particular, its robustness with respect to the choice of the exchange-correlation functional and quasiparticle corrections. However, as stated above, the transport properties of electrons and holes are mainly determined by the bandwidths rather than the band gap. Technically, the gap could be simply corrected for by the

adoption of the scissors-operator approach²⁶ without affecting the actual bandwidths. In this sense, we can extract here useful transport parameters even for MQ stacks. Indeed, we find huge bandwidths for all three types of stacks of up to 0.72 eV for IQ, up to 0.83 eV for HQ, and even up to 2.19 eV for MQ. Already, the values for IQ and HQ are slightly larger than that for guanine, thus indicating even stronger π - π coupling. Again, these broad bands can also be seen nicely as plateaus in the corresponding transmission functions in Fig. 2. The resulting effective masses of $m_e^* = 1.39 m_0$ and $m_h^* = 15.03 m_0$ for IQ as well as $m_e^* = 1.09 m_0$ and $m_h^* = 1.25 m_0$ for HQ are also mostly rather small, indicating efficient charge transport through these stacks. The bandwidths for the MQ stack are even much larger, which is a direct consequence of the smaller lattice constant and hence the larger intermolecular transfer integrals.³⁰ In fact, the bands are so much broader for MQ that, even if one would correct for the possible LDA overbinding of a few percent, the bandwidths would still be significantly larger than for the other stacks. Therefore, we conclude that these types of stacks are very good candidates for high-mobility transport.

Finally, in Fig. 2(e), we combine HQ and MQ molecules into a ring structure, which has recently been proposed as a central structural element of the human pigment eumelanin.²⁴ For the 1D stacks of these rings, we obtain a stacking height of 3.24 Å, in excellent agreement with experimental data on similar melanin-like structures.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 π - π 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 \mathbf{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.

ACKNOWLEDGMENTS

We thank Clara Santato for bringing melanin-based structures to our attention. This work was supported by the European Community within the framework of the European Theoretical Spectroscopy Facility ETSF (GA No. 211956). B.O. would also like to acknowledge the financial support from the Carl-Zeiss-Stiftung and the Graduiertenkolleg GK 1523. F.O. would like to thank the European Commission for support through a Marie Curie fellowship.

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