Electronic properties of one-dimensional pentacene crystals

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Abstract

The electronic properties of an infinite row of freestanding, aligned side-by-side, pentacene molecules are derived as a function of the intermolecular overlap integral and the chemical potential shift. We use a semiclassical approximation and a first principles tight binding method to obtain conductance and mobility of this one-dimensional crystal as a function of temperature and gate voltage. For two values of the intermolecular overlap, energy bands show a metallic behavior. For all the other values, a bandgap is present and evolves with the intermolecular overlap following a typical modulation. The magnitude of the scattering parameters estimated by the observed conductivity is coherent with the existing literature values. These findings could be relevant for the implementation of organic-based sensors.

List of symbols

\( a \) carbon bond length in the pentacene molecule
\( R \) distance between molecules (no-tilt case)
\( D \) length of the repeating unit cell, \( D = 2a + R \)
\( W \) width of the unit cell of the 1D molecular crystal (=10\( a \))
\( L \) length of the crystal sample \( L = nD (n \text{ integer}, n \to \infty) \)
\( \gamma \) transfer integral between pentacene molecule carbon atoms
\( \Gamma \) transfer integral between molecules
\( k' \) wavenumber, \((\text{m}^{-1})\)
\( k = k'D/\pi \) dimensionless wavenumber
\( E_\alpha(k) \) \( \alpha \)-th subband energy in eV
\( N_\alpha(E) \) density of states in eV\(^{-1}\) cm\(^{-2}\)
\( N_\alpha^u(E) \) density of states in the unit cell eV\(^{-1}\)
\( f \) equilibrium Fermi distribution
\( n_\alpha \) carrier concentration in the \( \alpha \)-th subband (carriers cm\(^{-2}\))
\( g_\alpha \) contribution of the \( \alpha \)-th subband to the 1D, length \( L \), crystal sample conductance (\( \mu \text{S} \))
\( I_\alpha \) contribution of the \( \alpha \)-th subband to the current \( I \)
\( \sum_\alpha n_\alpha \) total carrier concentration (carriers cm\(^{-2}\))
\( g = \sum_\alpha g_\alpha \) conductance \([\text{m}^2/\text{V}]\) of the length \( L \) crystal sample (\( \mu \text{S} \)) (output conductance)
\( E_F \) Fermi level

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carrier velocity in the $\alpha$-th subband

relaxation time

mean free path in the $\alpha$-th subband (m)

an adjustable energy parameter for the numerical determination of the Dirac $\delta$’s

carrier mobility [tq/m] in the $\alpha$-th subband (cm$^2$/Vs)

carrier mobility averaged over all the subbands

$G_0 = \frac{2e^2}{h} = 7.74 \times 10^{-5}$S conductance quantum

electric field (Volt/m)

number of points in the k space used in calculations

1. Introduction

The working principles of devices and sensors based on organic semiconductors are often borrowed from conventional semiconductor electronics. However the molecular nature of devices based on organics enables unusual conduction mechanisms which only an interdisciplinary approach can bring to light. As a matter of fact, seventy years of silicon based electronics progresses do not grant the same physics applies in this rapidly developing field. In fact, despite the undeniable progress achieved, much remains to be understood in order for organic semiconductors compete on an even footing with standard semiconductor electronics.

The mechanism of charge transport in organic semiconductors is still not fully understood\cite{1,2}, the main debate still revolving between free charge and polaronic transport mechanism. Even assuming a free charge mechanism, experiments can hardly distinguish between a classical energy band transport and a charge transport based on hopping\cite{3}. This complexity is not exactly a drawback and opens to the real challenging perspective of the field: the possibility that materials meeting particular demands can be chemically synthesized when needed.

Indeed, organic semiconductors and organic semiconductor crystals are emerging as an important platform related to new electronic and optoelectronic functions. Most interestingly, in this regard, decisive advances in material processing techniques have enabled fabrication of few-monolayered 2D nanostructures in which this exploration is facilitated\cite{4}.

In the organic semiconductor applications, carrier mobility is probably the most important figure of merit to evaluate the performance of an organic semiconductor. Pentacene (C$_{22}$H$_{14}$S$_2$), and pentacene-like molecules like DNTT (C$_{22}$H$_{14}$S$_2$)\cite{5}, are in many respect very attractive materials from this point of view\cite{6,7}. Pentacene mobility reaches 1cm$^2$/Vs in poly-crystalline films and 35 cm$^2$/Vs in single crystals\cite{8}. Furthermore there are many indications supporting in these materials a charge transport mechanism close to a conventional energy band transport (see\cite{9} and references therein).

In this paper we model the charge transport in a gated pentacene artificial aggregate with a view to gain insight into thin film organic semiconductor transistor behaviour based on pentacene. Our emphasis is on fundamental physics and conceptual issues. In particular, we discuss the conductivity change of a linear chain of side-by-side coupled pentacene molecules as a function of the intermolecular coupling strength.

As is well known, under carefully controlled conditions of deposition, pentacene forms a regular two-dimensional herringbone (Van der Waals) solid\cite{10}, even though most of the times, deposited pentacene films present only partial order and/or defects typical of weakly interacting molecules.

In the regular pentacene solid, a and b crystalline axis directions are preferred charge-transfer pathways made by linear chains or rows of freestanding molecules\cite{3}. Even far from the solid phase, i.e. in conditions of lower packing density, linear molecular chains can still exist due to residual partial order or interaction with the substrate\cite{11,12} and play a fundamental role in charge transfer.

It has also been found\cite{13} that, on particular substrates like TiO$_2$, pentacene grows in form of lying-down molecules coupled side-by-side into long mono-layer stripes. Optimal charge transport along the monolayer stripes of lying-down molecules has been suggested and the question arises whether the band structure of these pentacene aggregates may efficiently support the electric transport in field effect devices.

The aforementioned evidences suggest that the characterization of the transport properties of linear arrays of pentacene molecules may provide some clues in understanding the intricate physics of the organic semiconductors. Thus, in this work, we provide a detailed analysis about the transport properties of a one-dimensional crystal resulting from a side-by-side coupling of pentacene molecules (see figure 1(a)). We assume variable degree of molecular packing, ranging from a close packing molecular crystal to a loose packing one,
characterized by a descending value of the intermolecular overlap integral $\Gamma$. Lower overlap integrals correspond either to larger intermolecular distances or to a nonzero tilt of the molecular planes (see figures 1(b), (c)).

Within this idealized framework, we proceed in evaluating key transport properties showing internal consistency of results and agreement with existing experiments. Firstly, by using a nearest neighbour tight binding method \[14\], the energy band structure of the 1D crystal as a function of the intermolecular overlap integral is calculated. Then, assuming that defects and molecular vibrations frequently scatter charge carriers, we use a quasi-classical relaxation time formula to calculate the conductance of the 1D crystal. Next, the carrier density is evaluated as a function of the temperature, the Fermi level $E_F$ and the overlap integral value $\Gamma$ and the mobility is evaluated. Gate action by an external electrostatic gate is simulated by evaluating the dependence of the conductance and mobility on the position of the Fermi level. Strictly related to the study presented here, is the important work by Cornil et al \[15\] who first studied the relation between transport properties and electronic structure in 3D pentacene crystals. Compared to the Cornil’s work, we deal with a simple linear arrangement of molecules and neglect the Coulomb interaction influence (Hartree–Fock terms). Despite these limitations, the molecular arrangement considered in this work may be relevant in defining the transport properties of pentacene-based devices, the latter observation being the main motivation of this work.

2. Electronic properties

Unlike inorganic materials, such as silicon semiconductors, organic materials are formed with very weak Van der Waals interactions between molecules. For typical organic semiconductors, the intermolecular bonding energies are small, in the range of 10–100 meV \[16\]. However, due to different circumstances and conditions, mainly related to the molecules/substrate or molecules/environment interaction, these energies can be much greater. In what follows we will ideally extend this energy range up to the electron-volts.
2.1. The model
Figure 1 shows schematically the system we have in mind incorporating all the described features. In figure 1(a), pentacene molecules are aligned side by side to form an (infinitely extended) array or a 1D crystal similar to an armchair graphene nanoribbon with \( N = 11 \) [17], \( N \) being the number of atoms in transverse direction. Figures 1(b) and (c), illustrate how \( \Gamma \) is influenced by the reciprocal distance and tilt, respectively. Panel d) schematically shows relevant pathways, made by linear chains, in the typical herringbone pentacene solid.

Each pentacene molecule is characterized by five benzene rings with carbon atoms spaced out by \( a \) along the ring and intramolecular (between carbon atoms) overlap integral \( \gamma \). As said, the interaction between molecules is evaluated as overlap integrals between carbon atoms belonging to adjacent molecules spaced out by \( R \), and attributed a value \( \Gamma \) (intermolecular overlap integral). The 1D pentacene crystal is characterized by a rectangular periodic unit cell of length \( D = 2a + R \) and width \( W \). The case \( \Gamma = \gamma \) corresponds to the armchair graphene nanoribbon structure for which \( D = 3a \).

As usual in the present approximation, only \( \pi \) orbital (normal to the plane of the molecule) electrons are free to propagate along the crystal. The electrons comprising the configuration \( 2s^2 2p_x^2 2p_y^2 \) of the carbon atom, having orbitals lying in the plane of the molecule, remain strongly localized and are simply involved in \( \sigma \)-bonding resulting from the \( sp^2 \)-hybridization [18]. For simplicity, we consider free standing molecules on a substrate, as effectively observed for pentacene on SiO\(_2\) [19], and neglect the presence of hydrogens. This arrangement minimizes the influence of the substrate on the molecule, even though the latter can still remain relevant. To this regard, note that several kind of interactions with the substrate could be introduced. This however would be invariably made at the expense of the minimal complexity principle we want adopt in this paper.

2.2. Tight binding Hamiltonian and band structure
The dispersion relations \( E_n(k') \) for the pentacene crystal (we deserve the symbol \( k \) to indicate the dimensionless wavenumber), that is, its band structure, are obtained by considering the Hamiltonian of the crystal. Starting point is the unit cell Hamiltonian \( \hat{H} = \sum_{ij} t_{ij} |i\rangle \langle j| \) i.e. the Hamiltonian of the isolated pentacene molecule, and the tight binding equations for the molecular crystal:

\[
\hat{H} \Psi_n + \hat{\Gamma}^j \Psi_{n+1} + \hat{\Gamma}^i \Psi_{n-1} = E \Psi_n,
\]

in which \( \hat{\Gamma}^j \) represents the hermitian conjugated of the translation operator \( \hat{\Gamma} \), this latter being parameterized by \( \Gamma \). It is clear that the matrix \( t_{ij} \) reflects, in a unique manner, the topology and the connection structure of the atomic sites comprising the molecule. The element \( t_{ij} \) with \( i \neq j \), is the intramolecular overlap integral \( \gamma \) (hopping parameter), while the Dirac notation \( |i| \) stands for a localized orbital on site \( i \).

The Bloch form of the wavefunction allows \( \Psi_n \) to be written in terms of eigenfunctions of the translation operator on the chain, \( \Psi_n \sim e^{ikn} \). Substitution of \( \Psi_n \) into the above equation yields a secular equation through which the subbands \( E_n(k') \) of the solid can be determined. The number of subbands obtained is the same of the number of levels of the isolated single molecule (appendix A). Within our assumptions, the minimal pentacene model implies the presence of 22 subbands. Throughout this paper, \( t_{ij} \) is set to \( \gamma = 3 \) eV (see for instance [20, 21]) when \( i \) and \( j \) are nearest neighbors, while it is fixed to zero otherwise. When \( i = j \), \( t_{ij} \) is the on-site orbital energy \( \epsilon \). This latter is also the level from which all the energies are calculated. We set it at zero (\( \epsilon = 0 \)) without loosing generality. Furthermore, in what follows, all the energies, starting with \( E_n(k') \) and \( \Gamma \), will be expressed in units of \( \gamma \) (set at 3 eV).

The 22 subbands \( E_n(k') \) are obtained as a function of the intermolecular overlap integral \( \Gamma \). In this way we hypothesize a basic pentacene linear aggregate with molecules more or less interacting according to the value of \( \Gamma \). To illustrate this, in figure 2(a), all the subbands are shown as a function of the intermolecular overlap integral \( \Gamma \). As said, these quantities have been normalized to \( \gamma \) in the figure. In particular, \( \Gamma \) diminishes starting from the value \( \Gamma = 1 \), characterizing the armchair graphene nanoribbon (figure 2(a)), which is a semimetal (zero energy gap), till to the small value (\( \Gamma = 0.1 \)) characterizing the band structure of a loose-packed crystal (figure 2(g)).

The two main features observed in the sequence of figure 2(a) are a flattening of the subbands and the formation of an energy bandgap. Two flat non-dispersive subbands, given by \( E_{n+} = +\gamma \) and \( E_{n-} = -\gamma \), are also observed (see the horizontal dashed lines in figures 2(a), (b) and also in figures 3(a), (b), (c)).

To better illustrate the evolution of the bandgap as \( \Gamma \) varies from 1 to 0, the first ten subbands around the Fermi level are shown in figure 2(b). The deformation of the bands is not uniform: some of the bands move towards the Fermi level while others move away the Fermi level. The energy bandgap grows in amplitude till it reaches a maximum value when \( \Gamma \approx 0.5803 \). This \( \Gamma \) value characterizes the cross-over of the HOMO-LUMO levels and the secondary HOMO-LUMO levels: they cross each other at this value after which the energy bandgap reduces back again. Noteworthy, due to this mechanism, the energy gap disappears again at \( \Gamma \approx 0.2679 \) (second metallic point).

The energy bandgap value of 1.314 eV obtained for a vanishing \( \Gamma \) value refers to the HOMO-LUMO gap of the isolated molecule (see appendix A). This latter does not differ too much from the absolute maximum gap.
obtained for $\Gamma = 0.5803 (~1.74$ eV, in real units), i.e. $\sim 1.4$ eV. The evolution of the band gap with $\Gamma$ is shown in figure 3(d), where the metallic points are indicated with $\alpha$ and $\beta$. The reported zig-zag modulation of the band gap is typical: it mirrors results obtained by using more sophisticated models than the present one in the context of strained graphene nanoribbons [22–24], the latter condition sharing similarities with the present case.

Nakayama et al [25] have experimentally investigated the $E(k)$ dispersion relation of a 3D pentacene single-crystal in the valence-band. In that work the value of the transfer integral $\Gamma$ results from the measurements, and a value of 43 meV (from the first band) at room temperature was found. The corresponding measured bandwidth was about two times larger ($\sim 2\Gamma$). This 2 to 1 ratio between bandwidth and transfer integral value can be observed roughly in our model at low $\Gamma$’s (from few tens of meV up to hundreds of meV). For instance, from panel g in figure 2, which corresponds to $\Gamma = 0.1$ (300 meV in real units), one can appreciate a bandwidth for the LUMO of 510 meV, a 1.7:1 ratio.

2.3. Density of states

For the $\alpha$-th subband the partial density of states (states per unit cell per eV in the $\alpha$-th subband) can be defined as

$$N_{\alpha}^u(E) = \frac{1}{2} \int \delta(E_{\alpha}(k) - E)dk.$$  (2)

Then the total density of states (DOS) of the 1D pentacene crystal is given by

$$\text{DOS}(E) = \sum_{\alpha} N_{\alpha}^u(E).$$  (3)

Here $k = k'D/\pi$ is the dimensionless wavenumber, $k'$ is the wavenumber [m$^{-1}$] and the first Brillouin zone is defined by the interval $-1 \leq k \leq 1$. The actual method of computation of these quantities is described in appendix B. For the sake of illustration figures 3(a), (b), (c) shows the density of states (number of states per unit cell per normalized energy units) of three noteworthy configurations of the crystal: the two metallic stages ($\Gamma = 1, \Gamma = 0.2179$) and the maximum gap semiconductor stage ($\Gamma = 0.5803$). The figure also shows the corresponding energy band curves a, b, c, from which the densities of states derive. Dividing $N_{\alpha}^u$ by the surface of
the unit cell $WD$ gives the density of states per eV per cm$^2$, $N_\alpha(E) = N^0_\alpha / WD$. The surface of the repeating unit cell can be estimated by observing that it is of the order of magnitude of the unit cell of a graphene nanoribbon, that is, since $W \approx 10a$ and $a \approx 0.15$ nm, $WD = 3aW \approx 6.7 \times 10^{-15}$ cm$^2$.

3. Relaxation time approximation for the transport properties

In a macroscopic size sample (micrometric or longer pentacene chain), one in which the present theory applies, the charge carriers are frequently scattered by dynamical disorder induced by molecular vibrations and by static disorder, such as defects and charged impurities in the lattice. Since the organic semiconductor is formed in few molecular layers on a dielectric insulator surface, the presence of local dipoles in the substrate should be individuated as a specific further source of static disorder affecting the transport properties [16].

In what follows implicit assumptions are that distance between scatterers is much greater than wavelength and that the phase relaxes at every scattering event. In this regime the Boltzmann theory of transport, or semiclassical theory, is an adequate theoretical framework [26]. In particular, the conductance of the channel can be easily derived in this theory, which is a directly accessible quantity in typical experiments made on field effect transistors.
3.1. Conductance

Therefore, having calculated the band structure and the corresponding density of states, we are in position for calculating the conductance of a pentacene 1D crystal sample of assigned length $L$ depicted in figure 1(a). Assuming no band exchanging scattering processes, for each sub-band $E_\alpha(k)$, the $\alpha$-th contribution to the conductance $g$ (Siemens) of the sample, in the relaxation time approximation [26], is given by (see appendix C):

$$ g_\alpha = -q^2 W_\alpha \int \tau v^{*}_\alpha(E) N_{\alpha}(E) \frac{d\varepsilon}{dE} dE. \tag{4} $$

Here $v_\alpha = \frac{\partial E_\alpha}{\partial k}$ is the group velocity of the wavepacket for the $\alpha$-th subband, $N_{\alpha}$ is the density of states calculated previously (in eV$^{-1}$ cm$^{-2}$) and $\tau$ the relaxation time ($10^{-14}$–$10^{-16}$ s at room temperature). The relaxation time is an energy-dependent quantity which contains information on the relaxation processes relative to electrons and holes. In real systems, these processes are not perfectly symmetric and different values of the relaxation time can be used for electrons and holes. When this complication is included in the model, an element of asymmetry is introduced. In order to minimize the model parameters, we neglect these effects and consider a single energy-independent relaxation time. Introducing dimensionless quantities, i.e. $\bar{v}_\alpha = (\hbar \pi / \gamma D) v_\alpha$ and $\bar{N}_\alpha = \gamma WD N_{\alpha} = \gamma N_{\alpha}^{\gamma}$ the above equation can be written in the following form

$$ g_\alpha = - \frac{\tau \gamma D q^2}{2L^2 \pi^2 \hbar^2} \int \tau v^{*}_\alpha(E) \bar{N}_{\alpha}(E) \frac{d\varepsilon}{dE} dE \tag{5} $$

where the dimensionless integral is a temperature-dependent quantity which is affected by the Fermi energy $E_F$ and the intermolecular hopping parameter $\Gamma$. In the above equations $f$ is the equilibrium Fermi distribution,

$$ f = \frac{1}{1 + \exp \left( \frac{E_F - E_k}{kT} \right)}. \tag{6} $$

The total conductance of the pentacene 1D crystal of length $L$ is given by the sum of all the non-zero subband contributions

$$ g = \sum_\alpha g_\alpha. \tag{7} $$

To this end we explicitly note that the non-dispersive subbands $E_\alpha = \pm 1$ are irrelevant for the sum in equation (7). In fact these bands do not contribute neither to the conductance nor to the free carrier density or the mobility.

Most of the information on the electronic transport properties of organic semiconductors comes from measurements done on field effect transistors [27, 28]. In a FET the electric field generated by the gate excites the semiconducting active layer, or channel, to control the device current. In practice the energy bands (the HOMO LUMO levels of the semiconductor) are shifted downward or upward with respect to the Fermi level, while local charge transfers between metallic electrodes and semiconductor deform the energy bands [29].

In the present model we neglect band deformation effects induced at (metal electrode)-(semiconductor channel) interface and focus our attention on the field effect which induces band shifting of the pentacene channel. This shifting is achieved in our model by allowing the Fermi level to sweep the energy gap, the conduction and the valence bands, whereas these latter are kept fixed. The sweep range chosen is that in which a meaningful gate action occurs.

Figure 4, panels A-F, shows the room temperature conductance curves. This figure is obtained by setting $\tau = 10^{-15}$ s, which is here used as a free parameter to be deduced from the best agreement with experiments [8]. The values of $\Gamma$ chosen are those corresponding to the points A, B, C, D, E, $F$ in figure 3(d), which mark six representative values of the energy gap of the semiconducting 1D crystal. The conductance scale is referred to a one dimensional micrometric sample of two thousand unit cells, i.e. $L = 2000D$.

As shown further on when calculating the crystal mobility, points like $D$ and $E$ in figure 3(d) ($\Gamma = 0.5$, $\beta = 0.4$), located on the curve branch between the maximum bandgap point $C$ and the second metallic point $\beta$, give results in agreement with observed experimental values in pentacene crystals. Values of $\Gamma \lesssim 0.2$ refer to a very weakly coupled crystal (see figure 4(F)) for which the conductance pattern shows the fingerprint of the energy levels of the isolated molecule and the presence of secondary bandgaps in the energy band structure.

Let us finally note that, in principle, each $\Gamma$ value corresponds to a specific intermolecular distance $R$ of the 1D crystal. This latter can be roughly estimated on the basis of simple calculations (see appendix 1). For instance, when an intermolecular distance of $R = 3a \sim 0.45$ nm (corresponding to a unit cell length of $D = 2a + R = 5a \sim 0.75$ nm) is considered, the overlap parameter $\Gamma \sim 0.4$ is found.
3.2. Carrier concentration and mobility

The carrier concentrations in the $\alpha$-th band are given by

\[ n_\alpha = \int f(E) N_\alpha(E) dE \]

\[ p_\alpha = \int (1 - f(E)) N_\alpha(E) dE \]

where we have distinguished between hole concentration $p_\alpha$ and electron concentration $n_\alpha$ as usually done for a common undoped semiconductor. When $E_F = 0$, the Fermi level lies in the middle of the HOMO—LUMO gap and we have perfect carrier sign symmetry, i.e. $n_\alpha = p_\alpha$. A gate operation consists in fact in shifting the $E_F$ level. Figure 5 shows the total carrier density of the pentacene crystal as a function of the temperature (figure 5(a)). Figures 5(b) and (c) show the carrier concentration as a function of the Fermi level. Two values of $\Gamma$ are considered: $\Gamma = 0.5$ and $\Gamma = 0.4$ (respectively, 0.15 eV and 0.12 eV, in real units) corresponding to the points D and E in figure 3(d) already highlighted in the discussion about the conductance. The Arrhenius plots in figure 5(a) show a typical exponential dependence of the carriers concentration on temperature.

To calculate the contribution of the $\alpha$-th subband to the mobility of our pentacene crystal, the formula (see appendix E)

\[ \mu_\alpha = \frac{L}{W q n_\alpha} \]

Figure 4. Conductance (calculated by means of equation (5)) of a 2000 unit cell long pentacene crystal vs chemical potential for descending value of the overlap integral $\Gamma$. The energy bandgap values corresponding to the curves in panels A, B, C, D, E, F are $E_g = 0.3, 0.96, 1.39, 1.05, 0.6, 0.3$ eV, respectively. A relaxation time $\tau$ of $10^{-15}$ s was used. A rough quantitative relationship between $\Gamma$ and $R$, as presented in appendix D, indicates that 2000 unit cells correspond to a sample long $L \sim 1$ $\mu$m in the case reported in panel A ($\Gamma = 0.9$) and to a sample long $L \sim 1.8$ $\mu$m in the case reported in panel F ($\Gamma = 0.2$). The dashed line in panel A is for the reference gapless case curve with $\Gamma = 1$. 

Figure 5 shows the total carrier density of the pentacene crystal as a function of the temperature (figure 5(a)). Figures 5(b) and (c) show the carrier concentration as a function of the Fermi level. Two values of $\Gamma$ are considered: $\Gamma = 0.5$ and $\Gamma = 0.4$ (respectively, 0.15 eV and 0.12 eV, in real units) corresponding to the points D and E in figure 3(d) already highlighted in the discussion about the conductance. The Arrhenius plots in figure 5(a) show a typical exponential dependence of the carriers concentration on temperature.

To calculate the contribution of the $\alpha$-th subband to the mobility of our pentacene crystal, the formula (see appendix E)
neglecting hydrogens, we have calculated the energy band structure of the solid system allowing for a variable

We have studied the electronic properties of a 1D pentacene crystal. In the tight binding approximation, and

4. Summary

Here is used, where \( n_\alpha \) is the \( \alpha \)-th subband electron or hole concentration in cm\(^{-2}\). The above formula may be also written as:

\[
\mu_\alpha = \frac{\tau q D^2}{2 \pi^2 \hbar^2} \int_0^\infty \left( \frac{d}{dE} \right)^2 \rho(E) \frac{\rho(E)}{\partial E} \frac{dE}{n_\alpha}
\]

where \( n_\alpha = n_\alpha \cdot WD \) is the number of carriers per unit cell in the \( \alpha \) band.

Finally, the mobility (cm\(^2\)/Vs), meant as an observable quantity to compare with experiments, is calculated as the weighted average over the carrier concentration of the single dispersive subbands:[30]

\[
\mu = \frac{\sum \alpha n_\alpha \mu_\alpha}{\sum \alpha n_\alpha}
\]

Here \( \sum \alpha n_\alpha \) the total carrier concentration given by the sum of the \( \alpha \)-th subband contributions \( n_\alpha \).

Figures 6(a), (b), (c) shows the mobility of the pentacene crystal as a function of the Fermi level for the case \( \Gamma = 0.5 \) and \( \Gamma = 0.4 \) (respectively, 0.15 eV and 0.12 eV, in real units) as calculated by using equation (12). The obtained mobility values span the range between 10 cm\(^2\)/Vs and 50 cm\(^2\)/Vs which is compatible with the accepted experimental values from the literature [8]. Interestingly enough, in close vicinity of the Fermi level (figures 6(b) and (c)) of the pristine system \( (E_F = 0) \) channel conductance can be effectively controlled by using a back gate, the latter observation being relevant to set the device working point for applications. Note, finally, that the rapid modulation of the mobility with the Fermi level present in figure 6(a), is a consequence of having chosen a sharp density of states by fixing a small value of the quantity \( \Delta E \) (see appendix B). The latter choice is appropriate to describe an ideal crystal whose density of states is poorly affected by the presence of defects. Larger \( \Delta E \) values can be used to model experimental conditions in which the system is strongly hybridized with substrate states or defect states. Under the latter condition, a broadened density of states is obtained. More broadened densities of states (larger values of \( \Delta E \)) makes the mobility a milder function of the Fermi level. When strong disorder is considered (very high values of \( \Delta E \)), the density of states broadening tends to cancel any trace of the band gap. Under this extreme condition, the device channel cannot be effectively controlled by acting with a back gate and thus a negligible conductance modulation is achieved. The absence or a relevant reduction of the conductance modulation is a detrimental condition for the operation of a field effect device and thus the limitation of the disorder effects is an important technological issue.

4. Summary

We have studied the electronic properties of a 1D pentacene crystal. In the tight binding approximation, and neglecting hydrogens, we have calculated the energy band structure of the solid system allowing for a variable
coupling $\Gamma$ between molecules. In this way we can range from the coupling of a tight packing structure, close to that of a graphene nanoribbon ($\Gamma \sim 3$ eV), to the loose packing one of a weak interacting pentacene crystal ($\Gamma \rightarrow 0$ eV). We have illustrated how an energy bandgap opens up and evolve in amplitude, reaching a maximum of $\sim 1.4$ eV in correspondence of $\Gamma = 1.74$ eV. This maximum value is characterized by a crossover in the energy bands between HOMO LUMO and secondary HOMO LUMO levels. The subsequent evolution with $\Gamma$ consists in a lowering of the bandgap amplitude, up to zero (second metallic point) and a regrowth, up to the energy difference between HOMO and LUMO of an isolated pentacene molecule ($1.3$ eV). Next, we have calculated the conductance of an assigned micrometric length portion of our crystal and simulated a gate operation in a voltage range of a few ten of volts. No specific disordered has been introduced in the regular crystal structure, while we have considered a generic scattering mechanism represented by a phenomenological relaxation time $\tau$. We have obtained typical conductance values of $0.01$–$0.2 \mu$S with a relaxation time of $1$ fs. After having derived the relationship between conductance and mobility in this 1D model, we have obtained mobility values as a function of the gate voltage for two significant cases of semiconductive crystals with moderately low overlap integrals: $\Gamma = 0.15$ eV and $\Gamma = 0.12$ eV (corresponding to a bandgap of $E_g = 1.05$ eV and $E_g = 0.6$ eV, respectively), obtaining mobility values in very good agreement with the observed values of literature.

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Appendix A. Pentacene levels

The tight binding calculation for the isolated pentacene molecule $C_{22}H_{14}$, neglecting the hydrogen, gives 22 energy levels indicated in table A1. These energies are measured from the carbon on site orbital energy $\epsilon$, set to $\epsilon = 0$. 

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Figure 6. 1D pentacene crystal mobility as a function of the Fermi level calculated in the present model. Panel (a): comparison between curves obtained with $\Gamma = 0.5$ and $\Gamma = 0.4$. Panel (b) and (c): restricted range of gate operation for the same curves in panel (a). The temperature is 300 K.
Appendix B. Density of states

In the actual numerical calculation of the DOS in the $\alpha$-th subband, we use the approximate form for the delta function:

$$
\delta(E_\alpha(k) - E) \approx \frac{1}{2\sqrt{\pi} \Delta E} \exp \left[ \frac{(E_\alpha(k) - E)^2}{4\Delta E^2} \right]
$$

and

$$
dk \sim \Delta k = \frac{2}{M-1} \sim \frac{2}{M}; \quad (M \to \infty)
$$

such that

$$
N_{\alpha}^L = \frac{1}{2} \int \delta(E_\alpha(k) - E) dk \approx \frac{1}{M-1} \sum_{k} \frac{1}{2\sqrt{\pi} \Delta E} \exp \left[ \frac{(E_\alpha(k) - E)^2}{4\Delta E^2} \right]
$$

Here $k = k\prime D/\pi$ is the dimensionless wavenumber, $k\prime$ is the wavenumber, $M$ the number of points considered in k-space. The energy $\Delta E$ is an adjustable parameter useful to turn in a recognizable broad continuum the sharp, discrete spikes of the delta function. Throughout this paper, it has been set to 0.015 eV.

Table A1. Energy levels in the isolated pentacene molecule.

| level | energy $^*$ | degeneracy |
|-------|-------------|-------------|
| 1     | 2.495       | single      |
| 2     | 2.302       | "           |
| 3     | 2           | "           |
| 4     | 1.618       | "           |
| 5     | 1.495       | "           |
| 6     | 1.302       | "           |
| 7     | 1.219       | "           |
| 8     | 1           | double      |
| 9     | 0.618       | single      |
| 10    | 0.219       | "           |
| 11    | −0.219      | "           |
| 12    | −0.618      | "           |
| 13    | −1          | double      |
| 14    | −1.219      | single      |
| 15    | −1.302      | "           |
| 16    | −1.495      | "           |
| 17    | −1.618      | "           |
| 18    | −2          | "           |
| 19    | −2.302      | "           |
| 20    | −2.495      | "           |

$^*$ normalized to $\gamma = 3$ eV, carbon site energy $\epsilon = 0$.

Appendix C. Formula for the conductance of a 1D pentacene crystal of length $L$, (equation (4))

Let us assume a one-dimensional pentacene crystal of total length $L$ made of aligned pentacene molecules of a distance $R$ far apart each other. The width $W$ of the crystal coincides with the height of the pentacene molecule, i.e. $W \sim 1.5$ nm. A voltage difference $\phi L$ is applied between the two extremes of the crystal, where $\phi$ is the resulting electric field$^4$. The current $I$ in the crystal is the sum of the current contributions of the single energy bands $I = \sum I_\alpha$. Each contribution is given by the Ohm’s law $I_\alpha = g_{\alpha} \phi L$ and serves to define the conductance $g_{\alpha}$ of the 1D crystal in the $\alpha$-th subband:

$^4$ A note on the boundary conditions. The considered system is infinitely extended along the propagation direction and spatially periodic, with a repeating unit cell of assigned length $D$. Under these conditions, the tight binding equations for the molecular crystal, equations (1), were diagonalized by using periodic boundary conditions. The transport properties obtained can be thought as referred to a single unit cell. The result, in terms of a crystal sample conductance, can be applied to a finite part of the system of length $L = nD$, made by an integer number $n$ of basic unit cells. In this way the finite length $L$ of the sample enters the conductance, equation (5), only as a geometrical factor.
\[ I_\alpha = g_\alpha \varepsilon L = -\frac{q}{2\pi} \int dk \nu_\alpha (k)f(k) \approx -\frac{q}{2\pi} \int dk \nu_\alpha (k) \left(f_0(k) + \frac{q\tau}{h} \frac{\partial f_0}{\partial k}\right), \]  
\[ \text{(C1)} \]

where \( q = -|e| \) is the electron charge. In writing the second line of equation (C1) we have used the linearized solution of the Boltzmann equation written for a uniform electric field \( \varepsilon \). The symbol \( \tau \) represents the time constant at which the system returns to equilibrium (relaxation time). \( f_0(k) \) is the distribution function at equilibrium. The first integral in the sum is zero (symmetric interval of integration around zero of an even function). Then as
\[ \frac{\partial f_0}{\partial k'} = \frac{\partial f_0}{\partial E_\alpha} \frac{\partial E_\alpha}{\partial k'} = \frac{\partial f_0}{\partial E_\alpha} \nu_\alpha, \]  
\[ \text{(C2)} \]

the current in the \( \alpha \)-th band, equation (C1), can be simplified to:
\[ I_\alpha = g_\alpha \varepsilon L \approx -\frac{q^2\varepsilon}{2\pi} \int dk' \nu_\alpha^2 \frac{\partial f_0}{\partial E_\alpha}. \]  
\[ \text{(C3)} \]

The last integral can be written as an integral over the energy introducing once more the density of states \((eV^{-1}\text{cm}^{-2})N_\alpha(E) = \frac{1}{\pi W} \frac{d\nu}{dE}\). Then
\[ I_\alpha = g_\alpha \varepsilon L \approx -\frac{q^2\varepsilon W}{2} \int dE \nu_\alpha^2 N_\alpha(E) \frac{\partial f_0}{\partial E} \]  
\[ \text{(C4)} \]

from which equation (4) is obtained.

Appendix D. Overlap integral and intermolecular distance

An estimate of the intermolecular distance corresponding to the value of the overlap integral \( \Gamma \) can be obtained, in the absence of molecular tilting, through the formula [31] for the overlap integrals between 1s-orbitals on centres separated by \( R \):
\[ \frac{\Gamma(R)}{\gamma} = \frac{3}{7}(e^{-R/a})(1 + \frac{R}{a} + \frac{R^2}{3a^2}); \quad R \geq a \]  
\[ \text{(D1)} \]

which assumes \( a \) as the minimum distance and \( \Gamma(a) = \gamma \). Table D1 reports estimates of the overlap integral as a function of the intermolecular distance.

Appendix E. Formula for the mobility, (equation 10)

The relationship between conductance and mobility equation (10) derives from the following argument. The current in the \( \alpha \)-th band in the 1D pentacene crystal can be written as
\[ I_\alpha = Wq\nu_\alpha \langle v_\alpha \rangle \]  
\[ \text{(E1)} \]

where \( \langle v_\alpha \rangle \) is the average drift velocity in the band \( \alpha \), or by introducing the mobility \( \mu_\alpha \),
\[ I_\alpha = Wq\mu_\alpha \varepsilon L. \]  
\[ \text{(E2)} \]

Furthermore this same current can be expressed through the Ohm’s law as
\[ I_\alpha = g_\alpha \varepsilon L. \]  
\[ \text{(E3)} \]

Thus, equating the two expressions, one get the desired result:
\[ \mu_\alpha = \frac{L}{Wqg_\alpha}. \]  
\[ \text{(E4)} \]

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