ARTICLE TYPE

Explaining Different Experimental Hole Mobilities: Influence of Polymorphism on Dynamic Disorder in Pentacene[†]

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The effect of polymorphism (i.e. the ability of accessing different packing structures) on the fluctuations of transfer integrals is quantified for a prototypical molecule, pentacene. Computed mobilities for different polymorphs match the broad range of measured mobilities in organic field-effect transistors (OFET), suggesting that the large spread of experimental values reported in the literature, even when resorting to the same experimental setup, can be related to polymorphism in the samples. This finding is especially significant in new materials, where polymorphism is not known, as it could lead to a spread of results across groups and processing conditions, ultimately slowing down the research towards better semiconductors. Additionally, our analysis shows for the first time that the non-local electron-phonon coupling changes with temperature, a key finding that must be taken into account when computing the temperature dependence of the mobility; it also highlights the possibility of identifying previously unexplored ranges of temperatures, where materials display higher performances. The method here presented can be used to rapidly screen many materials and design new ones thanks to its low computational cost and its accuracy.

Introduction

Organic semiconductors have recently attracted a widespread interest because of their advantages, such as good mechanical properties, light weight, fine tunability of electronic properties, and in particular low production costs, resorting to a variety of solution-processing techniques or vacuum deposition methods[1,2]. Unfortunately, the design of new materials has relied up to now on a trial-and-error synthetic approach, although a more rational, theory-guided protocol would be highly beneficial. Indeed, the ability to rationalize, predict and improve material properties given only its atomistic structure would significantly speed up the pace of the discovery of new semiconductors[1,3,4]. Progresses in this area have been slowed down in particular for two reasons: (i) the most appropriate theoretical approach to model charge transport in organic semiconductors is still actively debated[5–7] and (ii) there is a quite large spread of experimental mobility val-

ues reported in the literature by different groups[8,9], a puzzling evidence that makes it difficult to access to the intrinsic charge transport properties of the material. The first point has been intensively studied[5,6], leading to the conclusion that the dynamic disorder, i.e. the large fluctuations of the transfer integrals because of thermal motions is the factor ultimately limiting charge mobility in organic materials[5,9,10].

The second point, i.e. the broad range of experimental mobility values reported in the literature, is however still a challenge. It is widely known that mobilities obtained with different experimental techniques (e.g. transistors, Space Charge Limited Current, etc.) or different systems are different[2,8,11]. Nevertheless, when one considers the most common experimental setup (transistors with SiO_2 gate) the range of measured mobility values is still very large. For example, μ of 0.5[12], 1.5[13], 2[14], 3[15], 6[16] $cm^2V^{-1}s^{-1}$, have been reported for pentacene transistors.

One key aspect explaining this discrepancy could be the presence of different polymorphs (i.e. different crystalline packing states) in the samples used by different groups. Indeed, in contrast to inorganic semiconductors, where covalent bonds are prominent, organic compounds are mainly bonded by non-specific interactions, like Van der Waals and quadrupoles. For that reason, several solid-state packings are accessible even at room temperature, and it has been pointed out that about one third of

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organic materials display polymorphism at ambient conditions[17]. This phenomenon is of paramount importance, since even the slightest change in molecular packing can have a huge impact on electronic properties, as demonstrated by previous works[18–26].

However, to the best of our knowledge, a study investigating the relationship between polymorphism and dynamic disorder is still missing. In this respect, we here compute the non-local electron-phonon coupling and the hole mobility for several polymorphs of a prototypical molecule, pentacene. Pentacene has been chosen as a test case because (i) the thin-film phase is different from bulk in transistors[27], (ii) a broad range of experimental mobilities have been reported, and (iii) structural data about its four known polymorphs are available[28], also at different temperatures, allowing us to analyze the effect of the temperature on the non-local electron-phonon coupling.

Methods

In the transient localization theory (TLT) framework, the charge mobility μ of an organic semiconductor can be evaluated resorting to the following equation:

$$\mu = \frac{e}{k_{\mathrm{B}}T} \frac{L^2(\tau)}{2n\tau}, \qquad (1)$$

where n is the dimensionality of the system, $k_{\mathrm{B}}T$ is the thermal energy and $L(\tau)$ is the transient localization length, i.e. the typical distance reached by a moving charge in the semiconductor on the timescale τ of the molecular fluctuations ($\tau \approx 1$ ps; this value will be used throughout this work)[9].

It has been shown[29,30] that $L(\tau)$ can be evaluated from the eigenvalues and eigenvectors of the Hamiltonian displaying static disorder given by the oscillations σ of the transfer integral V (see eq. 10 in the ESI). In other words, in order to evaluate $L(\tau)$ it is important to take into account the disorder in the materials due to thermal motions, which causes fluctuations in the transfer integral between two interacting molecules due to displacements Q_M along the phonon mode M.

To assess this effects, it is possible to compute the non-local electron-phonon coupling g_M, a measure of how the transfer integral V is modulated by the displacements Q_M along the phonon mode M:

$$V = V^{(0)} + \sum_M g_M \mathbf{Q}_M, \qquad (2)$$

where $V^{(0)}$ is the transfer integral evaluated around the equilibrium position. As explained in the ESI, it is convenient to express the non-local electron-phonon coupling as a function of ∇V, i.e. the numerical derivative of the transfer integral with respect to the Cartesian displacement of an atom k[31–33]:

$$\nabla V = \left\{ \frac{\partial V}{\partial x_k} \right\}. \qquad (3)$$

In this way, the non-local electron phonon coupling can be expressed as $g_M = \nabla V \cdot \mathbf{Q}_M$, an approach with the benefit of significantly speeding up the computations[31,32]. More importantly, from ∇V it is possible to compute the variance of the transfer integral $\sigma^2 = \left\langle (V - \langle V \rangle)^2 \right\rangle$,

$$\sigma^2 = \sum_M \frac{|\nabla V \cdot \mathbf{Q}_M|^2}{2} \coth\left(\frac{\hbar \omega_M}{2 k_{\mathrm{B}} T} \right), \qquad (4)$$

the key figure to evaluate the hole mobility μ. It is worth noting that the evaluation of σ from ∇V introduces an explicit dependence on the temperature (eq. 4) since the former is a global measure of thermal fluctuations, which are of course larger at higher temperatures.

In practice, our method can be summarized in the following steps:

1. Define the supercell of the system, that is, the positions of all molecular sites in presence of periodic boundary conditions. Obviously, the supercell must be larger than the $L(\tau)$ reached by the moving charge. This can be obtained by checking convergence for different system sizes.

2. Evaluate the oscillations of the transfer integral σ using eq.s 3 and 4 for all the interacting couples in the crystal.

3. Build a disordered Hamiltonian of the size of the supercell displaying off-diagonal disorder given by the oscillations σ

4. Diagonalize the Hamiltonian to calculate $L(\tau)$

5. Repeat steps 2-4 several times with different realizations of disorder (to take into account the random nature of the disorder in real systems) and compute average $L(\tau)$. The statistical error on $L(\tau)$ can be made arbitrarily small by increasing the number of realizations.

6. Evaluate the mobility through eq. 1

It is worth noting that this methodology, used for the first time throughout this paper and detailed in the ESI, relies on the combination of schemes introduced in previous works by some of us[9,32] which guarantee a significant decrease in the computational cost (only one day per material using an ordinary laptop with eight processors) while leading to results in excellent agreement with experimental data[9,34] or with other much slower approaches[32]. Therefore, even though we use it to study several polymorphs of the same molecule, this methodology is also suitable to rapidly and efficiently analyze databases of known organic crystals[35] to identify new semiconductors.

Results

In the following, we adopt the classification of the four known pentacene polymorphs at room temperature reported in ref. 28, taking the experimental cell parameters determined in ref.s 28 and 36 (see ESI). All the polymorphs adopt a herringbone structure with two non-equivalent molecules in the unit cell with group symmetry $P\bar{1}$, see Fig. 1 where a comparison among some of them is shown. Each of the four packings can be obtained in thin film form, depending on the substrate and on growth conditions, while polymorph II is the structure usually adopted in single crystals[28,36–38]. Like other molecular semiconductors, pentacene
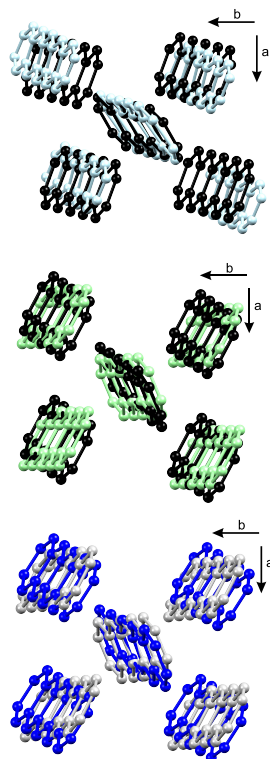
Fig. 1 Superposition of polymorphs' structures. Top: light blue = polymorph II, black = polymorph IV; middle: green = polymorph III, black = polymorph IV; bottom: white = polymorph I at 293 K, blue = polymorph I at 498 K. The structure at 90 K, almost coincident with the one at 293 K, is not shown for clarity.

possesses a high-mobility plane (ab plane), while the transfer integrals V between molecules out of this plane are one-two orders of magnitude smaller, therefore we have not considered them (see fig. 2).
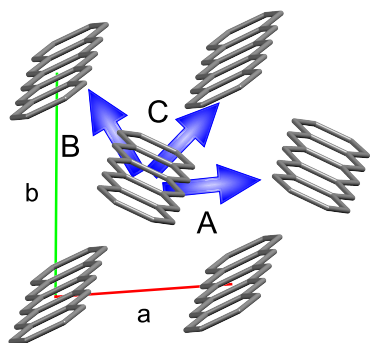
Fig. 2 Pictorial representation of the symmetry-independent charge transfer paths in the ab plane of pentacene.

According to this layout, in Table 1 we have reported the transfer integral (V), the norm of the transfer integral gradient ($|\nabla V|$), and the fluctuation of the transfer integral (σ) for each pair in the ab plane of the four pentacene polymorphs. We remark that the signs of the transfer integrals are consistent across Table 1 (that is, the phase of the molecular orbital basis is the same for all the polymorphs)[32]. This is of paramount importance, since the sign of the intermolecular coupling affects the simulation of electronic

properties such as charge mobility or band structure. We also notice that our data about the non-local electron-phonon coupling for polymorph I are in good agreement with existing ones obtained at different level of approximations (within 10% with values reported in ref.s 39 and 40). Moreover, in a previous work[32] we have evaluated the non-local electron-phonon coupling for several organic semiconductors, finding a good agreement with other groups, thus ensuring the broad applicability of our approach. Finally, we point out that, as discussed in the Methods section, the methodology here used can converge to the any desired level of accuracy[30] and the values reported in Table 1 are converged to the number of significant digits given.

Table 1 Transfer integral (V), norm of the transfer integral gradient ($|\nabla V|$), and fluctuation of the transfer integral (σ) evaluated at $T = 293$ K for each pair in the ab plane for different polymorphs. Polymorph I has been studied at three different temperatures.

Polymorph	Path	V (meV)	∇V (meV)	σ (meV)	σ/V	μ (cm^{2}V^{-1}s^{-1})
I, $T = 293$ K	A	+52.7	207	13.1	0.248	4.51
	B	+126	273	25.9	0.206	
	C	−80.5	376	27.0	0.335	
II	A	+40.2	273	19.4	0.483	2.26
	B	−75.5	265	18.9	0.251	
	C	+44.6	394	31.2	0.700	
III	A	+90.1	389	34.3	0.381	3.75
	B	+132	281	27.3	0.207	
	C	−54.3	376	36.4	0.670	
IV	A	+102	465	29.4	0.288	6.88
	B	+159	292	27.1	0.170	
	C	−41.9	667	39.6	0.945	
I, $T = 90$ K	A	+60.1	220			
	B	+137	299			
	C	−88.3	408			
I, $T = 498$ K	A	+26	201			
	B	+84	239			
	C	−43	318			

To the best of our knowledge, this is the first time that the thermal disorder σ has been evaluated for different polymorphs and that allows us to investigate the effects of the solid-state packing on this quantity. Indeed, it is apparent that polymorphs are an excellent way to study the fundamentals of charge transport since they display in some cases, e.g. polymorphs III and IV, essentially the same transfer integrals V but different fluctuations σ. Moreover, the relative changes in these two quantities appear to be completely uncorrelated; for example, path B always displays a lower σ/V than path C for all the structures, but this ratio varies widely, in particular for the latter (from 0.33 to 0.95). These results suggest that the study of polymorphs allows to analyze the effect of non-local electron-phonon coupling in isolation.

A careful inspection of table 1 shows that, rather than depending on the transfer integrals alone, the electronic properties of the material are determined by the subtle interplay between the disorder and the electronic coupling[9,10]. As a first example, we notice that polymorph IV has a higher mobility than polymorph II, a result that may well be explained by the first having higher transfer integrals than the latter. However, this explanation fails when we compare polymorph III and IV, the latter displaying μ two times higher than the first despite a quite similar transfer in-

tegral. This result points out that focusing only on this quantity, without taking into account its fluctuations could lead to misleading interpretations. Indeed, the difference in the mobility is fully justified if one considers the higher degree of disorder displayed by polymorph III, in terms of the relative fluctuation σ/V. Moreover, focusing on this quantity allows also to explain the difference between polymorph II and IV, see table 1, thus indicating that σ/V is the value ultimately determining the charge mobility. Even though the change in σ/V in different structures is quite difficult to predict a priori, in our previous work[32] we discussed in details a procedure to improve material performances during its design, by carefully studying the variation in the gradient of V, for which a map can be constructed. Indeed, using our methodology, it is possible to quickly and effectively explore the ∇V during materials design even though there is no simple rule correlating its value with molecular packing.

Another point of view offered by the data in table 1 shows the importance of having at least two paths with a low value of σ/V, while the third path can even display a high degree of disorder. For example, even if its path C has a very high σ/V, polymorph IV displays the highest mobility among the structures under study. Conversely, polymorph II exhibits low μ because it has two paths with a rather high σ/V ratio. It is worth noting that the presence of two paths with low σ/V has other positive impacts on the charge carrier mobility, ensuring the possibility of circumventing a defect in the material, or of transferring the charge through percolation paths[41] in bulk heterojunction solar cells. These results indicate a strategy for the improvement of material performances: rather than focusing only on increasing the absolute magnitude of the transfer integrals, efforts should be devoted in optimizing the relative values of σ/V so that they are as low as possible along at least two different directions. In other words, if the total σ is concentrated along only one charge transfer path rather than evenly distributed along all possible directions, the material will be less susceptible to the effects of the thermal disorder and also to extrinsic defects.

The two most interesting polymorphs for practical applications are II and IV, because the former is usually found in single crystals[36], while the latter is considered the most relevant for organic thin-film transistors, since it grows on a-SiO$_2$ substrates[42]. When comparing our predictions for these two packings with experimental findings, we find an excellent agreement, thus indicating the reliability of the method used. Indeed, our μ value for polymorph II is in very good agreement with the vast majority of experimental single-crystal OFET measurements: μ ranging in the interval 0.6-2.3 cm^{2}V^{-1}s^{-1} have been reported[13–15,43,44]. At the same time, our predictions for polymorph IV are in line with experimental measurements performed on thin-film devices ($\mu \approx 6$ cm^{2}V^{-1}s^{-1})[16].
In other words, computed mobilities match the range of the experimentally measured ones, suggesting that the large spread of values reported in the literature can be accounted for by the presence of different polymorphs across groups and processing conditions. It is worth noting that polymorphism can have an even greater impact on experimental measurements since (i) interconversion towards different polymorphs is strongly influenced by

the type and density of defects and impurities in the sample[38] and (ii) it is possible to have the coexistence of two or more polymorphs in the sample, as reported e.g. for pentacene[27,37,38]. These experimental evidences, alongside with a variable amount of defects, allow to explain the several slightly different experimental values obtained by different groups[12,13,15,16].

Finally, since it is widely recognized that even a change in temperature or pressure can induce a phase transition towards a different polymorph[37,38], we have analyzed three structures reported in the Cambridge Structural Database (CSD)[35], corresponding to polymorph I heated at 90 K, 293 K or 498 K, respectively (see bottom of fig. 1), whose experimental structures were determined in ref.s 45 and 38.

To describe the disorder effects at different temperatures we focus on the difference among ∇V values since, as discussed above, σ is proportional to this quantity but introduces an explicit temperature dependence. Inspection of table 1 shows that the low-temperature packing has electronic properties similar to the room temperature one, as expected since no significant changes in the relative position of the molecules has occurred after cooling[45]. On the other hand, the high-temperature structure shows significantly lower transfer integrals and ∇V than the room temperature one. This indicates that polymorphism is temperature dependent and since it significantly affects the non-local electron-phonon coupling, the latter becomes itself temperature dependent. While it is widely known that the electron-phonon coupling changes with temperature for two reasons, i.e. thermal expansion and polymorphism, previous studies have missed the latter effect, focusing only on the variation of the transfer integral with temperature, while the change in the non-local electron-phonon coupling has always been considered negligible[39,46].

In a first attempt to correlate experimental deformation with the electron-phonon coupling, we have computed the mobility at different temperatures in the range between 293 and 498 K for two limiting cases: (i) constant electron-phonon coupling (as assumed up to now in the literature) and (ii) electron-phonon coupling that varies linearly with temperature. In both cases the variations of transfer integrals and lattice parameters with temperature[5] are taken into account. Our results (fig. 3) show that, while in the first case the mobility monotonically diminishes as temperature increases, the behavior is completely different when taking into account electron-phonon coupling variations. Indeed, in this second case the mobility initially increases, reaching a peak around 375 K, then decreases. A similar trend has been experimentally observed in ref. 47, even though in that work the μ are quite lower than our data. These low values in ref. 47 are probably due to a significant amount of defects and/or impurities in the sample. Indeed, higher mobilities have been reported in carefully purified samples[43,44]

Despite its simplicity, this study indicates (i) the importance of taking into account the variations of the electron-phonon coupling in order to accurately reproduce the temperature dependence of the mobility and (ii) the possibility of identifying ranges of temperature where the material displays higher performances also above room temperature. This finding should not be overlooked, inasmuch as electronic components usually operates
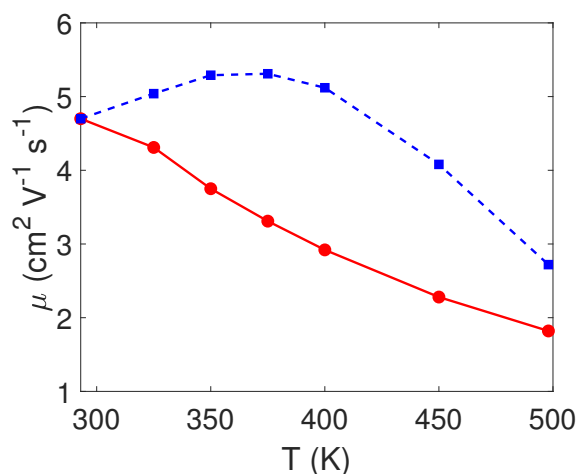
Fig. 3 Mobility vs. temperature with a constant ∇V (red dots) or a linearly varying ∇V (blue squares)

above room temperature; thus, reliably assessing their mobilities in the operational temperature range of organic electronics is of paramount importance to design new materials reaching top performances.

Conclusions

We have here discussed a methodology based on the combination of approaches which have been proven to lead to reliable results at a low computational cost. In light of these benefits, this approach could enable a more systematic selection of materials for organic electronics through the rapid screening of big databases of molecules. Moreover, thanks to the improvements in the field of crystal structure prediction [4,48], it could in principle be used to predict mobilities of new semiconductors from scratch.

Using this method, we have analyzed the influence of polymorphism on the electronic properties of pentacene. Polymorphs are an excellent way to study the fundamentals of charge transport since our data shows that some pairs of polymorphs display essentially the same transfer integrals but different non-local electron-phonon couplings, e.g. they are perfect to analyze the effect of non-local electron-phonon coupling in isolation.

We have found that the large spread of experimental OFET mobilities reported in the literature matches the range of mobility computed for different polymorphs, suggesting that the dissimilarity of results by different research groups can be related to the presence of different polymorphs. That finding is particularly significant for new materials, where polymorphism is not known, as this could be one of the causes of a spread of results across groups and processing conditions. Such an ambiguity could hinder the access to materials' intrinsic electronic performances, significantly affecting the research towards better semiconductors.

Finally, we have shown that the strength of non-local electron-phonon coupling changes with temperature, a completely unexpected finding, as in previous works it has been assumed to be constant. Our study indicates the importance of taking into account the variations of this quantity when discussing the temperature dependence of the mobility in organic materials and high-

lights the possibility of identifying previously unexplored ranges of temperatures where materials display higher performances.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgments

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TOC Graphic

μ≈7   μ≈2