

## Supporting Information for: Explaining Different Experimental Hole Mobility: Influence of Polymorphism on Dynamic Disorder in Pentacene

Alessandro Landi<sup>1,\*</sup>, Alessandro Troisi<sup>2</sup>, Andrea Peluso<sup>1</sup>

<sup>1</sup>*Dipartimento di Chimica e Biologia, Università di Salerno, I-84084 Fisciano, Salerno, Italy*

<sup>2</sup>*Department of Chemistry, University of Liverpool, Liverpool L69 3BX, U.K.*

\*e-mail: [alelandi1@unisa.it](mailto:alelandi1@unisa.it)

**The Model Hamiltonian** We use the well-known Peierls Hamiltonian [1, 2] for the description of the charge transport in organic semiconductors:

$$\begin{aligned} \mathcal{H} = & \sum_i E_i |i\rangle\langle i| + \sum_{i,j \neq i} V_{ij} |i\rangle\langle j| + \sum_M \hbar\omega_M \left( -\frac{1}{2} \frac{\partial^2}{\partial \mathbf{Q}_M^2} + \frac{1}{2} \mathbf{Q}_M^2 \right) + \\ & + \sum_i \sum_M g_{i,M} \mathbf{Q}_M |i\rangle\langle i| + \sum_{i,j \neq i} \sum_M g_{ij,M} \mathbf{Q}_M |i\rangle\langle j|, \end{aligned} \quad (1)$$

where the first two terms are the electronic part, the third the phonon part and the latter their interaction. Only one electronic state  $|i\rangle$  per molecular site is considered, e.g. the molecular HOMO for hole transport;  $E_i$  is the electronic energy of the site,  $V_{ij}$  is the transfer integral between nearest neighbour pairs and  $\mathbf{Q}_M$  is the dimensionless coordinate of the normal mode with frequency  $\omega_M$ .  $g_{i,M}$  and  $g_{ij,M}$  are respectively the local and the non-local electron-phonon couplings; the former describes the modulation of the site energies, while the latter concerns the modulation of the transfer integrals due to the normal modes  $M$ .

The  $V_{ij}$  can be evaluated as [3]:

$$V_{ij} = \langle \phi_i^0 | \mathcal{F} | \phi_j^0 \rangle, \quad (2)$$

where  $\phi_i^0$  and  $\phi_j^0$  are the localized HOMOs of states  $i$  and  $j$ , respectively, and  $\mathcal{F}$  is the Fock operator of the system. The suffix 0 indicates that the orbitals are unperturbed.

Following our previous work [4], we have represented the mode  $M$  as a vector of Cartesian displacements  $\mathbf{Q}_M = \{x_k^M\}$ , so that  $g_{ij,M}$  can be expressed as:

$$g_{ij,M} = \nabla V_{ij} \cdot \mathbf{Q}_M. \quad (3)$$

Here,  $\nabla V_{ij}$  is the Cartesian gradient of the transfer integral, i.e. the derivative of the transfer integral with respect to the Cartesian displacement of an atom  $k$ :

$$\nabla V_{ij} = \left\{ \frac{\partial V_{ij}}{\partial x_k} \right\}. \quad (4)$$

This approach is particularly suited for the development of a fast protocol because the first term of the product  $(\nabla V_{ij})$  only includes  $6N_A$  differentiations (where  $N_A$  is the number of atoms in one molecule) and the second term does not depend on the transfer integral, so it needs to be evaluated only once.

The non-local electron-phonon coupling is related to the variance of the transfer integral  $\sigma_{ij}^2 = \langle (V_{ij} - \langle V_{ij} \rangle)^2 \rangle$  via the relation [5]:

$$\sigma_{ij}^2 = \langle (V_{ij} - \langle V_{ij} \rangle)^2 \rangle = \sum_M \frac{|g_{ij,M}|^2}{2} \coth \left( \frac{\hbar\omega_M}{2k_B T} \right), \quad (5)$$

where  $k_B T$  is the thermal energy.

It is important to point out that in our discussion we have only discussed about the non-local electron-phonon coupling. Indeed, the local electron-phonon coupling is normally due to high-frequency modes (faster than the carrier) that have the effect of renormalizing both the transfer integral and its fluctuation by the same amount. In this regime of transport, the renormalization of both  $V$  and  $\sigma$  has minimal effect on the mobility, as shown in ref. 6; therefore, we have not discussed it in our work. Moreover, since we are comparing polymorphs, i.e. materials made by identical molecules, the renormalization correction is similar for all the polymorphs, that is, it does not affect the results discussed in this work.

**Theoretical models for charge transport** It has been shown that the modulation of the transfer integral as a consequence of coupling to the phonon modes is of the same order of magnitude as the transfer integral itself [1], comparable with the characteristic timescale of carrier dynamics [7, 8]. More importantly,  $\sigma$  is now considered the factor ultimately limiting charge transport [1, 9], being one of the most important quantities involved in several theories for the evaluation of the charge mobility in organic semiconductors [6, 10, 11].

These models usually start from the Green-Kubo linear response theory [12, 13], which relates the particle's mean-squared displacements to the current-current autocorrelation function  $C_{+,x}(t) = \langle \hat{J}_x(t), \hat{J}_x(0) \rangle$ , where  $\hat{J}_x$  is the current operator along a generic  $x$  direction. It is important to notice that, even if we are presenting the one-dimensional (1-D) case, generalization to 2-D or 3-D is straightforward (vide infra). Performing the time derivative and writing the current operator in terms of the position operator [14], it has been shown that  $C_{+,x}(t)$  is also related to the

diffusion coefficient  $D_x(t)$ , defined as

$$D_x(t) = \frac{1}{2} \frac{d\Delta X^2(t)}{dt}, \quad (6)$$

by the following equation:

$$D_x(t) = \frac{1}{2} \int_0^t C_{+,x}(t') dt'. \quad (7)$$

Different theories deal with this relation in different ways [10, 15–18], e.g. by factorizing the correlation function into Green's function terms and matrix element of the current operator [10], both averaged over the phononic part [15] or replacing  $C_+$  with a mean-square momentum matrix element between different states [18].

The transient localization theory (TLT)[16, 17], which has the interesting feature of explaining the band-like temperature dependence also for mobilities that are too small to be described by band transport, resorts to the relaxation time approximation (RTA) assumption. In the RTA, the dynamical properties of the actual system can be expressed in terms of those of a reference system from which it decays over time:  $C_{+,x}(t) = C_{+,x}^{ref}(t)e^{-t/\tau}$ . Usually [17] the reference system includes only static disorder, i.e. the molecular positions are frozen, and the decay time  $\tau$  is the timescale over which disorder fluctuates because of the intermolecular oscillations ( $\tau \approx 1$  ps)[6].

Substituting this decay form in eq. 7, we get

$$D_x(t) = \frac{1}{2} \int_0^t C_{+,x}^{ref}(t') e^{-t'/\tau} dt', \quad (8)$$

which has the form of a Laplace transform  $\mathcal{L}$ . Using the properties of Laplace transform, we get

$$\frac{1}{\tau} L_x^2(\tau) = \mathcal{L} \frac{d^2 \Delta X^2(t)}{dt^2}, \quad (9)$$

where  $L_x^2(\tau) = \int_0^\infty \frac{d\Delta X^2(t)}{dt} e^{-t/\tau} dt$  has been called transient localization length, since it corresponds to the typical distance covered by a charge before disorder fluctuates[17].

Resorting now to the Lehmann's representation of the velocity autocorrelation function [13],

$L_x^2(\tau)$  can be expressed as

$$L_x^2(\tau) = \frac{1}{Z} \sum_{n,m} e^{-E_n/(k_B T)} |\langle n | [\mathcal{H}, \mathcal{X}] | m \rangle|^2 \frac{2}{(\frac{1}{\tau})^2 + (E_m - E_n)^2}, \quad (10)$$

where  $|m\rangle$  and  $|n\rangle$  are two generic eigenvectors, with corresponding eigenvalues  $E_m$  and  $E_n$ , of the Hamiltonian  $\mathcal{H}$  reported in eq. 1. When dealing with realistic systems, it has been shown [9, 16, 17] that the local electron-phonon coupling  $g_i$  can be neglected, while the effect of the oscillations  $\sigma$  (eq. 5) in the transfer integral values can be accounted for as off-diagonal disorder in the Hamiltonian. Finally  $Z = \sum_n e^{-E_n/(k_B T)}$  is the partition function and  $\mathcal{X}$  is the the position operator.

$L_x^2(\tau)$  is related to the diffusion coefficient by[16]:

$$D_x(t) = \frac{L_x^2(\tau)}{2\tau} \quad (11)$$

Substituting this latter relation in the well-known Einstein-Smoluchowsky equation [19, 20] the charge mobility  $\mu$  can be evaluated as:

$$\mu_x = \frac{e}{k_B T} \frac{L_x^2(\tau)}{2n\tau}, \quad (12)$$

where  $n$  is the dimensionality of the system.

As mentioned above, we have focused on equations describing 1-dimensional charge transport; however, in most OSCs, charge migration mainly occurs in the so-called high-mobility plane,

while the mobility perpendicular to this plane is 1-2 orders of magnitude smaller [6, 21, 22]. Nevertheless, generalization of TLT to 2-dimensional charge transport is trivial [6], since the total localization length is the sum of the contributions along the two directions, say  $x$  and  $y$ :

$$L^2(\tau) = L_x^2(\tau) + L_y^2(\tau). \quad (13)$$

### Computational methods

The crystal structure for the polymorphs studied has been derived from the Cambridge Structural Database (CSD)[23], except for polymorph III and IV, whose crystallographic data have been reported in ref. 24. In the following we provide a list of the CSD codes, if any, together with structure information and the reference to original work.

- Polimorph I, T= 293 K. CSD code= 170186; ( $a = 6.266 \text{ \AA}$ ,  $b = 7.775 \text{ \AA}$ ,  $c = 14.530 \text{ \AA}$ ,  $\alpha = 76.475$ ,  $\beta = 87.682$ ,  $\gamma = 84.684$ ); ref. 25
- Polimorph II, T= 293 K. CSD code= 1230799; ( $a = 6.060 \text{ \AA}$ ,  $b = 7.900 \text{ \AA}$ ,  $c = 16.010 \text{ \AA}$ ,  $\alpha = 101.90$ ,  $\beta = 85.80$ ,  $\gamma = 112.60$ ); ref. 26
- Polimorph III, T= 293 K. ( $a = 5.89 \text{ \AA}$ ,  $b = 7.70 \text{ \AA}$ ,  $c = 15.7 \text{ \AA}$ ,  $\alpha = 77.6$ ,  $\beta = 80.3$ ,  $\gamma = 88.4$ ); ref. 24
- Polimorph IV, T= 293 K. ( $a = 5.77 \text{ \AA}$ ,  $b = 7.49 \text{ \AA}$ ,  $c = 17.2 \text{ \AA}$ ,  $\alpha = 73.5$ ,  $\beta = 75.3$ ,  $\gamma = 91.2$ ); ref. 24
- Polimorph I, T= 90 K. CSD code= 170187; ( $a = 6.239 \text{ \AA}$ ,  $b = 7.636 \text{ \AA}$ ,  $c = 14.330 \text{ \AA}$ ,  $\alpha = 76.978$ ,  $\beta = 88.136$ ,  $\gamma = 84.415$ ); ref. 25

- Polimorph I, T= 498 K. CSD code= 619982; ( $a = 6.123 \text{ \AA}$ ,  $b = 8.078 \text{ \AA}$ ,  $c = 15.134 \text{ \AA}$ ,  $\alpha = 80.802$ ,  $\beta = 76.712$ ,  $\gamma = 86.042$ ); ref. 27

Electronic structure, normal modes, and vibrational frequencies have been calculated by employing the self-consistent charge density-functional tight-binding (DFTB) method as implemented in the DFTB+ software package.[28, 29] The DFTB is a semi-empirical tight-binding method where the elements of Hamiltonian and overlap matrices are evaluated starting from precomputed values, reducing the computational time of about 3-4 orders of magnitude with respect to DFT.[29, 30]

In the case of the electronic structure calculations, the elements of the resulting general tight-binding Hamiltonian matrix are chosen to be self-consistent atomic DFT eigenvalues evaluated with the B3LYP/6-31g\* functional [29], while the off-diagonal elements are calculated in a two-center approximation as is the case of the employed 3-ob-1 Slater-Koster set parameter [31]. The atomic positions of the unit cell have been optimized keeping the experimental lattice values fixed, using the conjugate gradient method with a force-threshold criterion of  $10^{-8}$  Hartree per Bohr radius. We have used periodic boundary conditions (PBC) employing a  $4 \times 4 \times 4$  Monkhorst-Pack  $k$ -point sampling scheme.[32], resorting to the DFTB-D3 formalism [33] to take into account the weakly van der Waals interaction in the crystalline phase.

Since DFTB is known to severely underestimate transfer integrals because of the minimal basis set used [34–37], they have been evaluated at the B3LYP/3-21g\* level of theory as implemented in Gaussian 09 [38]. Since the molecule under study is usually well described at any DFT level [4, 39], we have used one of the most popular functional choice[39, 40] in conjunction with a basis set that ensures reliable results at a reasonable computational cost [4].  $\nabla V$  has been evaluated by using the finite difference 2-point approximation, using displacement of  $\pm 0.01 \text{ \AA}$ .

Lattice phonons have been evaluated as reported in our previous work [4], assuming a strict separation between intramolecular and intermolecular degrees of freedom. The first are assumed to be equal to the vibrations of the isolated molecule, while, to describe the intermolecular modes, we have considered the rigid motion of each molecule surrounded by the neighboring molecules frozen in their equilibrium position [41–43]. This corresponds to the definition of six rigid displacement modes  $q_1 \dots q_6$  (three translations and three rotations in reduced mass coordinates) and to the evaluation of a  $6 \times 6$  Hessian matrix  $P_{ij} = \partial^2 E / \partial q_i \partial q_j$ , where  $E$  is the total energy of a cluster containing a molecule surrounded by all its neighbors in van der Waals contact. The eigenvalues of  $P_{ij}$  are the square of the frequencies of intermolecular modes and the corresponding eigenvectors provide a representation of these modes as a linear combination of the original roto-translational modes  $q_1 \dots q_6$ .

## References

1. A. Troisi and G. Orlandi, *Phys. Rev. Lett.*, 2006, **96**, 086601.
2. W. P. Su, J. R. Schrieffer and A. J. Heeger, *Phys. Rev. Lett.*, 1979, **42**, 1698–1701.
3. A. Troisi and G. Orlandi, *Chem. Phys. Lett.*, 2001, **344**, 509 – 518.
4. A. Landi and A. Troisi, *J. Phys. Chem. C*, 2018, **122**, 18336–18345.
5. V. Coropceanu, R. S. Sánchez-Carrera, P. Paramonov, G. M. Day and J.-L. Brédas, *J. Phys. Chem. C*, 2009, **113**, 4679–4686.
6. S. Fratini, S. Ciuchi, D. Mayou, G. T. De Laissardière and A. Troisi, *Nat. Mater.*, 2017, **16**, 998–1002.
7. D. A. da Silva Filho, E. G. Kim and J. L. Brédas, *Adv. Mater.*, 2005, **17**, 1072–1076.
8. J. L. Brédas, J. P. Calbert, D. A. da Silva Filho and J. Cornil, *Proc. Natl. Acad. Sci.*, 2002, **99**, 5804–5809.
9. S. Fratini, D. Mayou and S. Ciuchi, *Adv. Funct. Mater.*, 2016, **26**, 2292–2315.
10. O. Gunnarson and J. E. Han, *Nature*, 2000, **405**, 1027–1030.
11. J. Dong, W. Si and C.-Q. Wu, *J. Chem. Phys.*, 2016, **144**, 144905.
12. R. Kubo, *J. Phys. Soc. Jpn.*, 1957, **12**, 570–586.
13. G. D. Mahan, *Many-Particle Physics*, Springer US, 1995.
14. D. Mayou, *Phys. Rev. Lett.*, 2000, **85**, 1290–1293.

15. F. Ortmann, F. Bechstedt and K. Hannewald, *Phys. Rev. B*, 2009, **79**, 235206.
16. S. Ciuchi, S. Fratini and D. Mayou, *Phys. Rev. B*, 2011, **83**, 081202.
17. S. Ciuchi and S. Fratini, *Phys. Rev. B*, 2012, **86**, 245201.
18. Y. Wang, D. MacKernan, D. Cubero, D. F. Coker and N. Quirke, *J. Chem. Phys.*, 2014, **140**, 154902.
19. Z. Shuai, L. Wang and C. Song, *Theory of Charge Transport in Carbon Electronic Materials*, Springer Press, 2012.
20. A. Landi, R. Borrelli, A. Capobianco, A. Velardo and A. Peluso, *J. Phys. Chem. C*, 2018, **122**, 25849–25857.
21. W. Deng, L. Sun, J. Huang, S. Chai, S. Wen and K. Han, *Nature Protocols*, 2015, **10**, 632–642.
22. B. Blülle, A. Troisi, R. Häusermann and B. Batlogg, *Phys. Rev. B*, 2016, **93**, 035205.
23. C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Cryst. B*, 2016, **72**, 171–179.
24. C. C. Mattheus, G. A. de Wijs, R. A. de Groot and T. T. M. Palstra, *J. Am. Chem. Soc.*, 2003, **125**, 6323–6330.
25. C. C. Mattheus, A. B. Dros, J. Baas, A. Meetsma, J. L. d. Boer and T. T. M. Palstra, *Acta Cryst. Sect. C*, 2001, **57**, 939–941.
26. R. B. Campbell, J. M. Robertson and J. Trotter, *Acta Cryst.*, 1962, **15**, 289–290.
27. T. Siegrist, C. Besnard, S. Haas, M. Schiltz, P. Pattison, D. Chernyshov, B. Batlogg and C. Kloc, *Adv. Mater.*, 2007, **19**, 2079–2082.
28. B. Aradi, B. Hourahine and T. Frauenheim, *J. Phys. Chem. A*, 2007, **111**, 5678–5684.

29. M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai and G. Seifert, *Phys. Rev. B*, 1998, **58**, 7260–7268.
30. G. Seifert and J. O. Joswig, *WIREs: Comput. Mol. Sci.*, 2012, **2**, 456–465.
31. M. Gaus, A. Goetz and M. Elstner, *J. Chem. Theory Comput.*, 2013, **9**, 338–354.
32. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188–5192.
33. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
34. A. Kubas, F. Gajdos, A. Heck, H. Oberhofer, M. Elstner and J. Blumberger, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14342–14354.
35. A. Kubas, F. Hoffmann, A. Heck, H. Oberhofer, M. Elstner and J. Blumberger, *J. Chem. Phys.*, 2014, **140**, 104105.
36. T. Kubar, P. B. Woiczikowski, G. Cuniberti and M. Elstner, *J. Phys. Chem. B*, 2008, **112**, 7937–7947.
37. A. F. Oliveira, G. Seifert, T. Heine and H. A. Duarte, *J. Braz. Chem. Soc.*, 2009, **20**, 1193 – 1205.
38. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma,

- V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision D.01*, Gaussian Inc. Wallingford CT 2009.
39. T. P. Nguyen, J. H. Shim and J. Y. Lee, *J. Phys. Chem. C*, 2015, **119**, 11301–11310.
40. I. Yavuz, B. N. Martin, J. Park and K. N. Houk, *J. Am. Chem. Soc.*, 2015, **137**, 2856–2866.
41. Y. Li, V. Coropceanu and J.-L. Brédas, *J. Chem. Phys.*, 2013, **138**, 204713.
42. K. Hannewald, V. M. Stojanović, J. M. T. Schellekens, P. A. Bobbert, G. Kresse and J. Hafner, *Phys. Rev. B*, 2004, **69**, 075211.
43. A. Girlando, L. Grisanti, M. Masino, I. Bilotti, A. Brillante, R. G. Della Valle and E. Venuti, *Phys. Rev. B*, 2010, **82**, 035208.