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Electrical transport and noise in polyacene semiconductors

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Abstract Measurements of electrical transport and excess current noise in semiconducting films of polyacenes revealed a superquadratic increase of the current and a sharp peak of the relative noise at voltage values corresponding to the trap-filling transition region. Recently, we formulated an explanation of these findings in terms of trapping and detrapping processes of the injected carriers by deep defect states. This interpretation was based on a phenomenological model that takes as input the measured I–V characteristic curve. Here we introduce a new percolative approach to transport and noise in these materials. In particular we develop two percolation models, differing in the voltage dependence of the trapping and detrapping rates: precisely, one model neglects and the other accounts for the Poole-Frenkel effect. We then discuss the results of both models in connections with experimental findings.

Keywords Organic semiconductors · Electrical noise · Polyacenes

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1 Introduction

Nowadays, electronic devices based on organic semiconductors, like polymeric or molecular semiconductors, are much more than a promising field. Actually, field-effect transistors, light-emitting diodes, solar cells, switches, memories, etc. made of organic semiconductors have started to replace traditional electronic devices in many applications, being competitive in terms of cost, flexibility, weight and several other features. Thus many studies have been devoted to the investigation of electrical transport properties in organic semiconductors [1–23]. In particular, it has been realized that the performances of these devices are crucially controlled by the injection of charge carriers at the molecule-metal interfaces and by their trapping-detrapping (TD) processes at defect states [1–3, 7–16, 24]. While the effect of thermal and electrical stresses on TD processes has been widely investigated [2, 3, 7–16], only a relatively small number of studies was devoted to the electrical noise in organic semiconductors [17–23].

Transport measurements in thin films of polyacenes (tetracene and pentacene) [17, 18] have evidenced a strong superquadratic increase of the current voltage (I–V) characteristic and a concomitant peak of the low-frequency relative spectral density of current noise at intermediate voltages, corresponding to the crossover between Ohmic and space charge limited currents (SCLC) regimes [17, 18, 25, 26]. A first qualitative explanation of these experiments has been given [17, 18] in terms of continuous percolation between two asymptotic regimes (Ohmic and SCLC), considered as different conducting phases. The noise increase was explained as due to the clustering of insulating regions among which current paths are constrained [17, 18].

Recently, we have proposed a complementary interpretation of these experimental findings, in terms of noise due to trapping and detrapping (TD) processes of injected carriers by deep traps in the trap filling transition (TFT) regime [27]. This second interpretation was based on a phenomenological model which makes use of the measured I–V characteristic to estimate the fraction of filled traps as a function of the applied voltage. Then, the value of this fraction is used to express the spectral density of current noise in the TFT regime. The good quantitative agreement between the behavior obtained from the phenomenological model and the experiments supports the interpretation of abscribing the sharp peak of noise in the TFT region to the fluctuating occupancy of the traps due to TD processes [27].

Here we introduce a new percolative approach to transport and noise in organic semiconductors which does not make any *a priori* assumption on the I–V characteristic curve. In particular we have developed two percolation models, differing in the voltage dependence of the trapping and detrapping rates: precisely one model neglects and the other accounts for the Poole-Frenkel effect [37–39]. In the next section we present and discuss the results of both models in connections with the experimental findings [17, 18].

2 Method

Our approach adopts the well known resistor network (RN) method [28–33]. Precisely we describe the semiconducting film as a binary mixture of two kinds of resistors linked in a two-dimensional resistor network. In particular here we consider a square-lattice with square geometry (size $N \times N$) [28–33]. Each elementary resistor $r_{i,j}$ describes a small region of the film with homogeneous electrical properties, i.e. a small region characterized by a leading mechanism of electrical transport. This leading mechanism of transport defines the "state" of the resistor.

Then, we assume that an elementary resistor can be found in two states: an Ohmic state (state 1) with resistance r_1 and a SCLC state (state 2) with resistance r_2. We indicate with N_1 and N_2 the number of resistors in the states 1 and 2 respectively, with $N_{tot} = N_1 + N_2 = 2N^2$ the total number of resistors in the network. The fraction of resistors in the state 2, $p = N_2/N_{tot}$, is the key quantity which characterizes the global network state: for $p > p_c$ the SCLC phase associated with the r_2 resistors percolates through the network, where p_c is the percolation threshold [28].

An external constant voltage V is applied to the RN through perfectly conducting bars placed at the left and right hand sides. As a consequence of this external bias, a voltage drop $v_{i,j}$ is also applied to each elementary resistor through which it flows a current $i_{i,j}$, while I is the total current flowing through the network. The network is taken to be in contact with a thermal bath at temperature T. Furthermore, to mimic the effect of trapping and detrapping process, we assume the existence of random transitions between the two resistor states, occurring with probabilities $W_{1\to 2}(v_{i,j})$ and $W_{2\to 1}(v_{i,j})$, both dependent on the local voltage drop $v_{i,j}$. In other terms, each resistor behaves as a generator of a random telegraph signal [34] with voltage dependent transition rates.

2.1 Model A

As a first approximation, by neglecting the Poole-Frenkel effect [37–39], we take:

$$W_{1\to 2} = \exp\bigl[-(E_2 - q v_{i,j})/k_B T\bigr] \tag{1}$$

and:

$$W_{2\to 1} = \exp[-E_1/k_B T] \tag{2}$$

where E_1, E_2 are two activation energies, q is an effective charge and k_B is the Boltzmann constant. Then, by adopting a mean field-like approach, similar to that described in Ref. [35], for $W_{2\to 1} \ll 1$ the average value $\langle p\rangle$ of p can be written as:

$$\langle p\rangle \approx \frac{1}{1+\frac{\langle W_{2\to 1}\rangle}{\langle W_{1\to 2}\rangle}} \equiv \frac{1}{1+\exp(a-bv)} \tag{3}$$

where: $a \equiv (E_2 - E_1)/K_B T$, $b \equiv q/K_B T$ and $v \equiv \langle v\rangle$ is the average voltage applied to an elementary resistor. Moreover, it is possible to give an approximate analytical expression for the relative resistance noise of the network:

$$\Phi(v) \equiv \frac{\langle(\delta r)^2\rangle}{\langle r\rangle^2} \approx \frac{1-\langle p\rangle}{\langle p\rangle}\,\frac{(r_1-r_2)^2}{[\frac{1-\langle p\rangle}{\langle p\rangle}r_1 + r_2]^2} \tag{4}$$

Thus:

$$\Phi(v) \approx \frac{(f_r-1)^2\exp(a-bv)}{[f_r\exp(a-bv)+1]^2} \tag{5}$$

where $f_r = r_1/r_2$. Equation (5) shows that the relative noise of the network depends only on the three parameters: f_r, a, b and on the size N (which enters in the average value v). The evolution of the network is calculated by numerical simulations performed according to an iterative procedure similar to that described in [29, 30, 32, 33] and by using constant-voltage boundary conditions. The results of this model are reported in Sect. 3 and they are obtained by adopting the following values of the parameters (chosen as reasonable values): $N = 75$, $f_r = 290$, $a = 2.5$ and $b = 210\ \mathrm{V}^{-1}$.

2.2 Model B

In highly resistive materials like polyacenes the Poole-Frenkel effect [37–39], i.e. the modification of the shape of the impurity potential by the external field, can give rise to a significant change of the generation and recombination rates of charge carriers trapped and detrapped by impurity states. This change has been modeled by Kuhn et al. [37, 38] by considering field-dependent generation and recombination rates. Therefore, according to Ref. [37, 38] we take:

$$W_{1\to 2}^{PF} \equiv \gamma(v_{i,j}) = \begin{cases} \gamma_{\text{eq}}(\frac{v_{i,j}}{v_t})\sinh(\frac{v_{i,j}}{v_t}) & \text{if } v_{i,j} < v_t \\ \gamma_{\text{eq}}(\frac{v_{i,j}}{4v_t})[\exp(2\sqrt{\frac{v_{i,j}}{v_t}}-1)(2\sqrt{\frac{v_{i,j}}{v_t}}-1) \\ \quad -2\exp(-\frac{v_{i,j}}{v_t})+e] & \text{if } v_{i,j} > v_t \end{cases} \tag{6}$$

and:

$$W_{2\to 1}^{PF} \equiv \rho(v_{i,j}) = \begin{cases} \rho_{\text{eq}}\frac{1}{1+c(\frac{v_{i,j}}{v_t})} & \text{if } v_{i,j} < v_t \\ \rho_{\text{eq}}\frac{1}{1+c(2\sqrt{\frac{v_{i,j}}{v_t}}-1)} & \text{if } v_{i,j} > v_t \end{cases} \tag{7}$$

where: $\gamma_{\text{eq}} = \exp(-E_2/k_BT)$ and $\rho_{\text{eq}} = \exp(-E_1/k_BT)$ are the equilibrium probabilities of the transitions $1 \to 2$ and $2 \to 1$ between the two states of the elementary resistors in absence of the external voltage, v_t is a voltage threshold value, while $c = 0.98$ [37, 38]. Given the form of Eqs. (6) and (7), we notice that in this case it is not possible to write simple expressions like those of Eqs. (3) and (4) and we must rely only on numerical simulations. Preliminary results concerning this model are reported in the next section. They are obtained by adopting the following values of the parameters: $N = 75$, $T = 300$ K, $f_r = 10$, $v_t = 0.0015$ V, $E_1 = 0.17$ eV, while two values of E_2 are considered: 0.043 and 0.086 eV. These values are selected as a reasonable choice just to have an insight of the peak shape resulting from the inclusion of the Poole-Frenkel effect. However, at this preliminary stage, we have not yet performed a systematic optimization of the parameter values.

3 Results

We start by considering the results provided by model A introduced in Sect. 2.1. Figure 1 shows the time evolution of the network resistance R (the time is expressed as a number of iteration steps). Several $R(t)$ signals are reported corresponding to increasing voltage values, ranging from the Ohmic regime (upper curve) up to the beginning of the SCLC regime (lower curve). We can see that a rather abrupt transition occurs for voltage values in the range $0.7 \div 1.0$ V.

Figure 2 displays the calculated I–V characteristic curve. Each I value is obtained by averaging over $R(t)$ (only the stationary portion of the signal, after the decay of the initial transient state, is considered). For comparison, the I–V curve measured in a tetracene sample at 300 K [17, 18] is also reported. After the Ohmic regimes, both the curves are characterized by a strong superlinearity in the transition region. The slopes of the SCLC regimes are 1.9 ± 0.1 for the experimental data (lowest dashed curve) and 2.4 ± 0.1 for the simulated one (highest continuous curve).

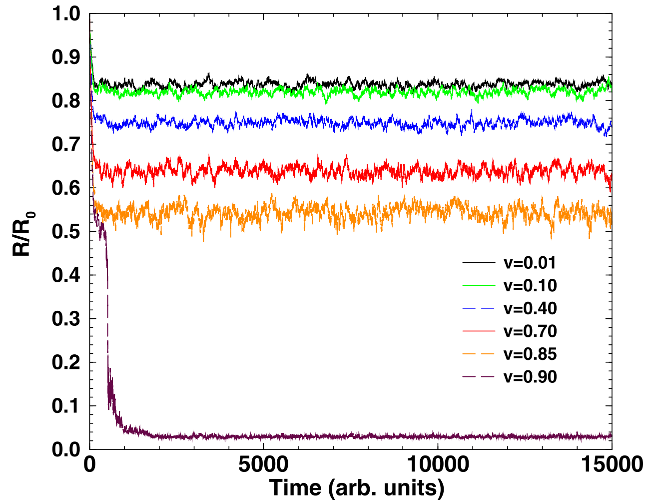

Fig. 1 Typical evolutions of the resistance (normalized to the perfect film value R_0) calculated for several values of the applied voltage, ranging from 0.01 V (*upper curve*) to 0.9 V (*lower curve*). The values of the model parameters are given in the text

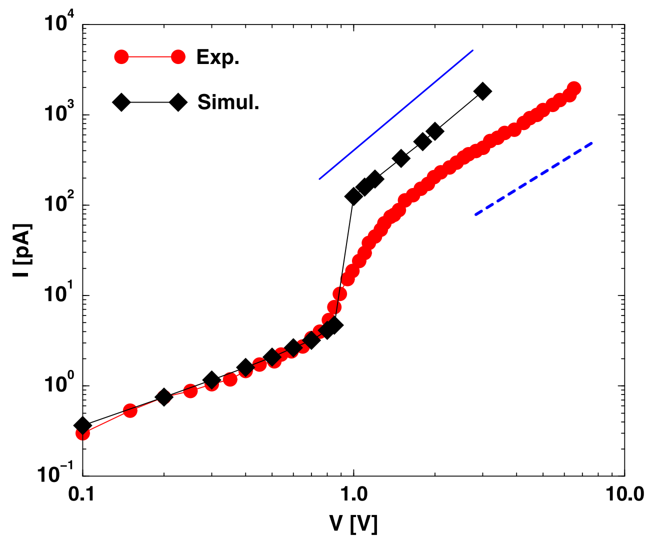

Fig. 2 *Circles*: experimental I–V characteristic measured in a tetracene sample (Refs. [17, 18]). *Diamonds*: I–V curve obtained from numerical simulations. The *dashed* and *continuous curves* correspond to the slopes 1.9 ± 0.1 and 2.4 ± 0.1, respectively

Figure 3 reports the calculated values of the relative resistance noise of the network as a function of the applied voltage. For comparison we plot also the experimental curve of the relative spectral density of current noise at 20 Hz measured for the same tetracene sample of Fig. 2 [17, 18]. The simulated values are normalized by a factor $S_{\text{norm}} = 5.26 \times 10^{-5}$ that is chosen to agree with the measured value of $S_{\max}$. Overall, Figs. 2 and 3 show a satisfactory agreement between experiments and the model predictions.

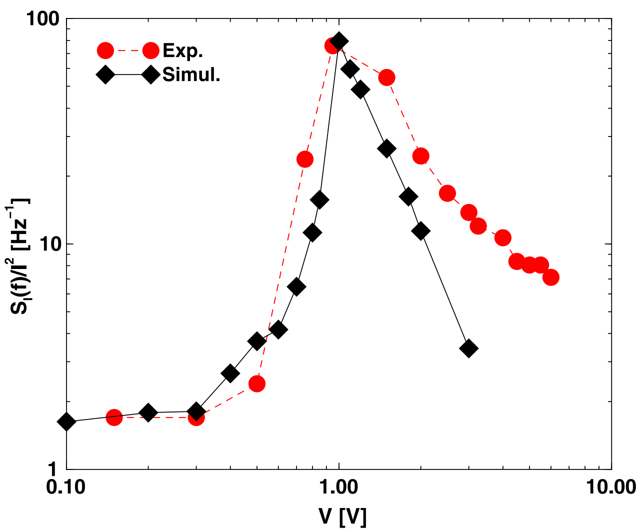

Fig. 3 *Circles*: experimental values of $S(f)$ (Refs. [17, 18]). *Diamonds*: relative current noise S_{sim} obtained from numerical simulations

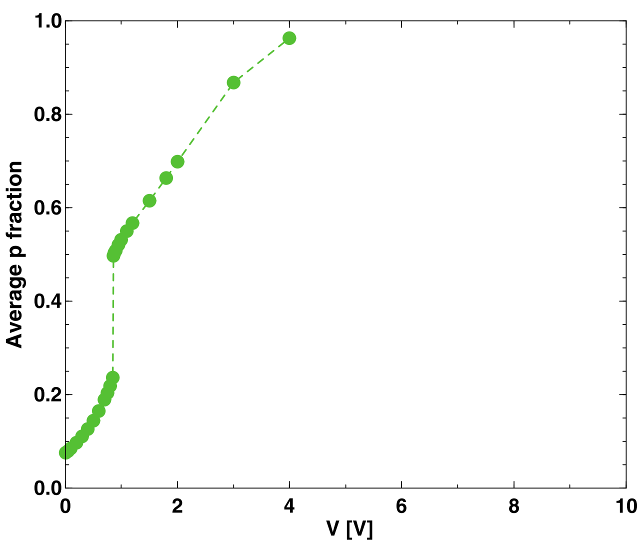

Fig. 4 Average fraction $\langle p\rangle$ of r_2 resistors calculated as a function of the applied voltage. The *dashed line* is a guide to the eyes

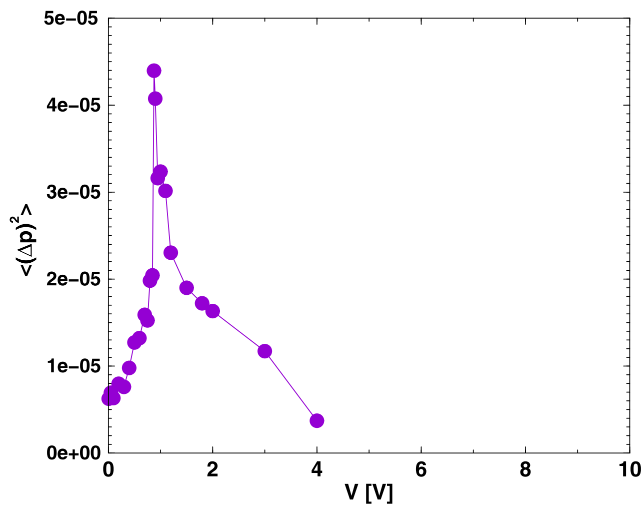

Fig. 5 Variance of the r_2 resistor fraction calculated as a function of the applied voltage. The *dashed line* is a guide to the eyes

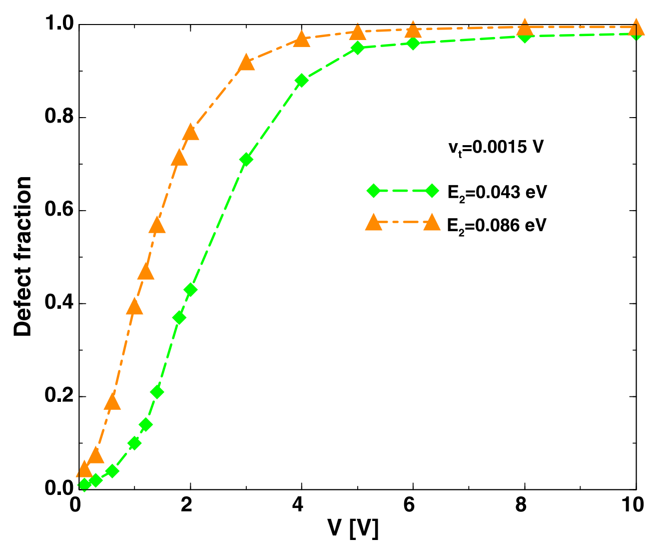

Fig. 6 Average fraction $\langle p\rangle$ of r_2 resistors as a function of the applied voltage and calculated by accounting for the Poole-Frenkel correction of the generation and recombination rates (see text). The *two curves* correspond to two different values of the activation energies E_2 of the recombination process

Figure 4 displays the average fraction $\langle p\rangle$ of resistors in the state 2 as a function of the voltage applied to the network. The abrupt change of $\langle p\rangle$ for $V \approx 0.9$ V points out the first order character of the transition [36].

This abrupt variation of the average fraction $\langle p\rangle$ has its counterpart in the sharp peak of the variance of p itself, which is shown in Fig. 5 for the same voltage value. Thus, Fig. 5 emphasizes the key role played by the fluctuations of the p fraction due to TD processes, as described by Eqs. (1) and (2), in the peak of the relative noise shown in Fig. 3 and observed in the experiments.

In the following we present some preliminary results obtained from model B of Sect. 2.2, i.e. by accounting for the Poole-Frenkel effect on the generation and recombination rates. Figure 6 shows the average fraction $\langle p\rangle$ of resistors in the state 2 as a function of the applied voltage. We can see that the abrupt change of $\langle p\rangle$ in the trap-filling region provided by model A now disappears and the transition becomes much smoother as shown by the continuous behavior of $\langle p\rangle$.

The calculated I–V characteristic is reported in Fig. 7, where the two curves correspond to different values of the energy E_2. We remark that in this case the I–V curve becomes linear above the trap-filling transition, at least for the region of parameter values that we have explored (see the

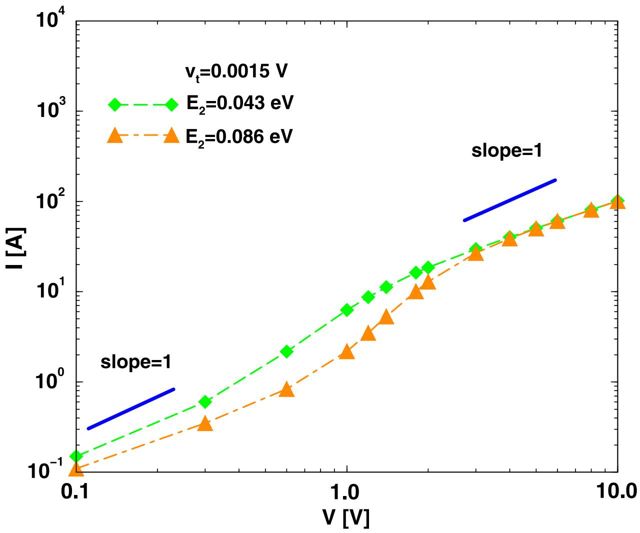

Fig. 7 I–V characteristics obtained from simulations by accounting for the Poole-Frenkel correction of the generation and recombination rates (see text). The *two curves* correspond to two different E_2 values

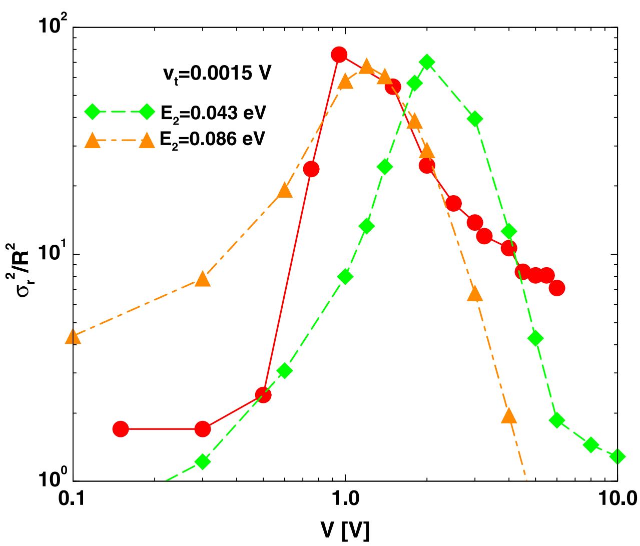

Fig. 8 Relative variance of the total resistance fluctuations S calculated as a function of the applied voltage by accounting for the Poole-Frenkel correction (*dashed* and *dot-dashed curves* correspond to two different E_2 values. The *solid curve with circles* shows the experimental curve (the same of Fig. 3)

discussion below). A feature that overall worsens the agreement with experiments, even if it should be noticed that the model does not attempt at all to describe the SCLC transport regime. Finally, Fig. 8 displays the calculated values of the relative resistance noise as a function of the applied voltage, again for two different values of E_2. The experimental curve of the relative spectral density of current noise for a tetracene sample (the same curve shown in Fig. 2) is also reported for a direct comparison. Here, the simulated values of S are normalized by a factor $S_{\text{norm}} = 1.7 \times 10^5$ to agree with the measured value of $S_{\max}$. Consistently with the smoother character of the trap-filling transition provided by model B, now the shape of the noise peak is more rounded and, at least for what concerns this feature, it better reproduces the experimental one. However, the rather complicated analytical expressions of the probabilities $W_{1\to 2}^{PF}$ and $W_{2\to 1}^{PF}$ make more tricky the optimization of the parameters of model B. This optimization was not performed at this preliminary stage. Therefore, comparing Figs. 3 and 8, it seems that the inclusion of the Poole-Frenkel correction worsens the agreement with the experiments in contrast to what one would expect. Further investigations could clarify this point.

4 Conclusion

The paper reports a theoretical investigation on the I–V characteristic and the sharp peak of the relative spectral density of current noise which have been observed in polyacene semiconductors as a function of the applied voltage [17, 18]. Recently [27], we have formulated an interpretation of these experiments on the basis of a phenomenological model, in terms of TD processes of the injected carriers. This model made use of the measured I–V curve to estimate the fraction of filled traps as a function of the applied voltage and it provides a good agreement with the experiments [27]. Here we have adopted a percolative approach which does not make any *a priori* assumption on the I–V characteristic. In particular we have introduced two percolation models, differing in the voltage dependence of the trapping and detrapping rates. Model A neglects and model B accounts for the Poole-Frenkel effect [37–39] on generation and recombination rates. We notice that the inclusion of the Poole-Frenkel effect at this stage does not improve significantly the agreement between theory and experiments. Overall, the numerical simulation results presented here support the conclusions of the phenomenological model.

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References

1. Pope, M., Swemberg, C.E.: Electronic Processes in Organic Crystals and Polymers. Oxford University Press, Oxford (1998)
2. Lang, D.V., Chi, X., Siegrist, T., Sergent, A.M., Ramirez, A.P.: Bias-dependent generation and quenching of defects in pentacene. Phys. Rev. Lett. **93**, 076601 (2004)
3. Miyadera, T., Wang, S.D., Minari, T., Tsukagoshi, K., Aoyagi, Y.: Charge trapping induced current instability in pentacene thin film transistors: trapping barrier and effect of surface treatment. Appl. Phys. Lett. **93**, 033304 (2008)
4. Cacelli, I., Ferretti, A., Girlanda, M., Macucci, M.: I/V characteristics of molecular switch. Chem. Phys. **333**, 26 (2007)

5. Girlanda, M., Macucci, M.: Theoretical analysis and numerical simulation of intramolecular barriers in polyphenyl-based molecular devices. J. Phys. Chem. A **107**, 706 (2003)
6. Fiori, G., Lebèque, S., Betti, A., Michetti, P., Klintenberg, M., Eriksson, O., Iannaccone, G.: Simulation of hydrogenated graphene field-effect transistors through a multiscale approach. Phys. Rev. B **82**, 153404 (2010)
7. Koch, N., Elschner, A., Johnson, R.L., Rabe, J.P.: Energy level alignment at interfaces with pentacene: metal versus conducting polymers. Appl. Surf. Sci. **244**, 593 (2005)
8. Yang, Y.S., Kim, S.H., Lee, J.I., Chu, H.Y., Do, L.M., Lee, H., Oh, J., Zyung, T.: Deep-level defect characteristics in pentacene organic thin films. Appl. Phys. Lett. **80**, 1595 (2002)
9. Knipp, D., Street, R.A., Volkel, A.R.: Morphology and electronic transport of polycrystalline pentacene thin-film transistors. Appl. Phys. Lett. **82**, 3907 (2003)
10. Dinelli, F., Murgia, M., Levy, P., Cavallini, M., Biscarini, F.: Spatially correlated charge transport in organic thin film transistors. Phys. Rev. Lett. **92**, 116802 (2004)
11. Schwalb, C.H., Sachs, S., Marks, M., Schõll, A., Reinert, F., Umbach, E., Hõfer, U.: Electron lifetime in Shockley-type metal-organic interface state. Phys. Rev. Lett. **101**, 146801 (2008)
12. De Boer, R.W.I., Jochemsen, M., Klapwijk, T.M., Morpurgo, A.F., Niemax, J., Tripathi, A.K., Pflaum, J.: Space charge limited transport and time of flight measurements in tetracen single crystals: a comparative study. J. Appl. Phys. **95**, 1196 (2004)
13. Kang, J.H.D.: Shallow trap states in pentacene thin films from molecular sliding. Appl. Phys. Lett. **86**, 152115 (2005)
14. Chandra, W., Ang, L.K., Pey, K.L.: Two-dimensional analytical Mott-Gurney law for a trap-filled solid. Appl. Phys. Lett. **90**, 153505 (2007)
15. Giulianini, M., Waclawik, E.R., Bell, J.B., Motta, N.: Current-voltage characteristics of poly(3-hexylthiophene) diodes at room temperature. Appl. Phys. Lett. **94**, 083302 (2009)
16. Torres, I., Taylor, D.M., Itoh, E.: Interfaces states and depletion-induced threshold voltage instability in organic metal-insulator-semiconductor structures. Appl. Phys. Lett. **85**, 314 (2004)
17. Carbone, A., Kotowska, B.K., Kotowski, D.: Space-charge-limited current fluctuations in organic semiconductors. Phys. Rev. Lett. **95**, 236601 (2005)
18. Carbone, A., Kotowska, B.K., Kotowski, D.: $f^{-\gamma}$ current fluctuations in organic semiconductors: evidence for percolation. Eur. Phys. J. B **50**, 77 (2006)
19. Jurchescu, O.D., Hamadani, B.H., Xiong, H.D., Park, S.K., Subramanian, S., Zimmerman, N.M., Anthony, J.E., Jackson, T.N., Gundlach, D.J.: Correlation between microstructure, electronic properties and flicker noise in organic thin film transistors. Appl. Phys. Lett. **92**, 132103 (2008)
20. Martin, S., Dodabalapur, A., Bao, Z., Crone, B., Katz, H.E., Li, W., Passner, A., Rogers, J.A.: Flicker noise properties of organic thin-films transistors. J. Appl. Phys. **87**, 3381 (2000)
21. Necliudov, V., Rumyantsev, S.L., Shur, M.S., Gundlach, D.J., Jackson, T.N.: 1/f noise in pentacene organic thin film transistors. J. Appl. Phys. **88**, 5395 (2000)
22. Sampietro, M., Ferrari, G., Natali, D.: Tracking of conduction phenomena and degradation in organic light emitting diodes by current noise measurements. Appl. Phys. Lett. **78**, 3262 (2001)
23. Vandamme, L.K.J., Feyaerts, R., Tref/'an, G., Detcheverry, C.: 1/f noise in pentacene and poly-thienylene vinylene thin film transistors. Appl. Phys. Lett. **91**, 719 (2002)
24. Van Vliet, C.M.: Electronic noise due to multiple trap levels in homogeneous solids and in space charge layers. J. Appl. Phys. **93**, 6068 (2003)
25. Kleinpenning, T.M.G.: Physica B **94**, 141 (1978)
26. Hooge, F.N., Kleinpenning, T.G.M., Vandamme, L.K.J.: Experimental studies on 1/f noise. Rep. Prog. Phys. **44**, 479 (1981)
27. Carbone, A., Pennetta, C., Reggiani, L.: Trapping-detrapping fluctuations in organic space-charge layers. Appl. Phys. Lett. **95**, 233303 (2009)
28. Stauffer, D., Aharony, A.: Introduction to Percolation Theory. Taylor and Francis, London (1992)
29. Pennetta, C.: Resistance noise near to electrical breakdown: steady state of random networks as a function of the bias. Fluct. Noise Lett. **2**, R29 (2002)
30. Pennetta, C., Reggiani, L., Trefán, G., Alfinito, E.: Resistance and resistance fluctuations in random resistor networks under biased percolation. Phys. Rev. E **65**, 066119 (2002)
31. Pennetta, C., Gingl, Z., Kiss, L.B., Reggiani, L.: Biased percolation and electrical breakdown. Semicond. Sci. Technol. **12**, 1057 (1997)
32. Pennetta, C., Alfinito, E., Reggiani, L., Fantini, F., De Munari, I., Scorzoni, A.: A biased resistor network model for electromigration phenomena in metallic lines. Phys. Rev. B **70**, 174305 (2004)
33. Pennetta, C., Reggiani, L., Trefan, G., Fantini, F., Scorzoni, A., De Munari, I.: A percolative approach to electromigration of metallic lines. J. Phys. D, Appl. Phys. **34**, 1421 (2001)
34. Kogan, Sh.: Electronic Noise and Fluctuations in Solids. Cambridge Univ. Press, Cambridge (1996)
35. Pennetta, C., Alfinito, E., Reggiani, L.: Tuning the correlation decay in the resistance fluctautions of multi-species networks. J. Stat. Mech. **2009**, P02053 (2009)
36. Pennetta, C., Alfinito, E., Reggiani, L., Ruffo, S.: Non-Gaussianity of resistance fluctuations near electrical breakdown. Physica A **340**, 380 (2004)
37. Varani, L., Reggiani, L.: Microscopic theory of electronic noise in semiconductor unipolar structures. Riv. Nuovo Cimento **7**, 1–110 (1994)
38. Kuhn, Reggiani, L., Varani, L., Mitin, V.: Monte Carlo method for the simulation of electronic noise in semiconductors. Phys. Rev. B **42**, 5702 (1990)
39. Ieda, M., Sawa, G., Kato, S.: A consideration of Poole-Frenkel effect on electric conduction in insulators. J. Appl. Phys. **42**, 3737 (1971)