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Influence of fillers concentration on electrical properties of polystyrene matrix doped by gold nanoparticles and 8HQ

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Abstract. The analysis of the electrical properties of polystyrene films containing gold nanoparticles capped with 1-dodecanethiol and 8-hydroxyquinoline molecules is reported. The conductivity of the nanocomposite as a function of the doping level has been investigated both in planar and stacked configurations. While the former configuration evidenced low field tunneling between nanoparticles in the polymer matrix, stacked devices allowed us to investigate the main phenomena ruling the transport properties when switching effects are present close to critical electric fields. In particular, through the analysis of current-voltage characteristics we studied the charge transport at different fillers concentrations and sketched a physical picture of conductivity in such nanocomposite systems.

PACS. 34.70.+e Charge transfer – 77.80.Fm Switching phenomena – 91.60.Tn Transport properties – 82.35.Np Nanoparticles in polymers

1 Introduction

Nanocomposites formed by a conducting phase dispersed in a polymeric matrix have attracted a considerable attention from different research areas interested in organic electronics. This is mainly motivated by the strong potential of these materials to be the active layer in almost all kinds of organic electronic devices, such as LEDs [1], photovoltaic cells [2], transistors [3] and memory devices [4].

Depending on the conducting filler amount and the related distribution inside the polymer matrix, the physical properties of the composite can be largely tuned. In particular, at very low filler fractions, the mean distance between the conducting fillers is quite large, and the electrical conductivity is mainly determined by the host matrix. When the filler concentration gets some critical value, fillers form linkages resulting in conductive paths in the whole material: the corresponding filler content is named percolation threshold. Near this critical value, small changes of the fillers amount can induce conductivity modification up to several orders of magnitude. On the other hand, at higher filler concentrations, the larger number of conducting paths forms a complete three-dimensional network. In this way, the resulting conductivity is noticeably increased and much less sensitive to

any change in the filler fraction. Among the different possible materials, many investigation efforts have been devoted to a polymer composite consisting of a polystyrene matrix (PS) filled with gold nanoparticles capped with 1-dodecanethiol (Au-DT-NPs) and small molecules of 8-hydroxyquinoline (8HQ) in different weight percentages.

Owing to the presence of two conductivity states which differ by several orders of magnitude, Yang et al. [5] demonstrated the possibility to use such a nanocomposite as the basic material for programmable non-volatile memory devices (NVM). By the analysis of the electrical transport properties of various realized devices, the electronic transition between the two conducting states was attributed to the electric-field-induced charge transfer between Au-DT-NPs and the 8HQ molecules.

In order to investigate the physical nature of such conductivity states, in this paper we report on a complete electrical characterization of the polystyrene composite at different Au-DT NPs and 8HQ weight percentage. The electrical conductivity as a function of the filler content has been measured in planar configuration, while the electrical behavior of stacked devices fabricated at different filler concentrations allowed us to investigate the role of the applied electric field close to critical switching values.

In particular, Section 2 describes the fabrication procedure of both in-plane and stacked devices. Experimental results in terms of current-voltage characteristics (IVCs)

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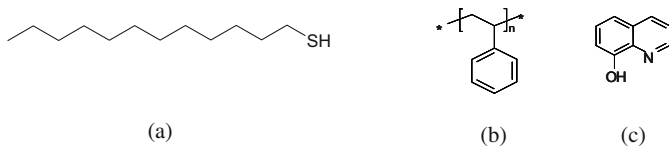(a)   (b)   (c)

Fig. 1. Chemical structure of: (a) 1-dodecanethiol (DT); (b) polystyrene (PS); (c) 8-hydroxyquinoline (8HQ).

at different fillers concentrations for both configurations are reported in Section 3. In Section 4 data from stacked devices are analyzed according to electron transport models, leading to a physical picture of the charge transport in such composite systems, as a function of gold nanoparticles and 8HQ content.

2 Device fabrication

The polymeric composite of interest in this work consists of polystyrene (PS) film containing gold nanoparticles capped with 1-dodecanethiol (Au-DT NP) and small molecules conjugated of 8-hydroxyquinoline (8HQ). The chemical structures of these materials are shown in Figure 1.

The metal nanoparticles were prepared by the two-phase arrested growth method [6]. We dissolved 0.4 g $HAuCl_4 \cdot 3H_2O$ in 25 ml water and mixed it with 80 ml toluene solution of 1.4 g tetraoctylammonium bromide. The organic phase was isolated and 0.24 ml dodecanethiol was added.

The formation of the gold nanoparticles was completed by adding 25 ml aqueous solution of 0.38 g NaBH4 drop-wise into the organic solution under vigorous stirring. The nanoparticles were purified by washing with 80 ml ethanol and 150 ml acetone. Nanoparticles were characterized by Transmission Electron Microscopy (TEM). The Au-DT NPs show a narrow size distribution centered at about 4 nm (Fig. 2).

The material conductivity was assessed by planar structures with Ag electrodes (100 μm spaced, 80 nm thick, 5 mm long) sputtered on a glass substrate. The active layer was formed by spin coating a solution of PS, Au-DT NPs and 8HQ in chloroform. The films were then annealed at 80 °C for 30 min. In order to evaluate the conductive properties of PS-AuNPs-8HQ blend, the active layers were realized with different filler contents. The PS content was fixed to 0.8 wt%, while the nanoparticles and 8HQ wt%, in the same measure, varied from 0.013 to 0.405 wt%.

The electrical properties were also tested by the basic stacked architecture sketched in Figure 3, where the polymer film was sandwiched between two metal electrodes. In this case, the glass substrate was cleaned by sonication in acetone for 10 min and then in isopropyl alcohol for 10 min. Afterward, the bottom Al electrode was sputtered onto the substrate at a vacuum pressure of 10^{-6} mbar. Next, the active layer was formed by spin-coating the solution at different concentrations. Typical
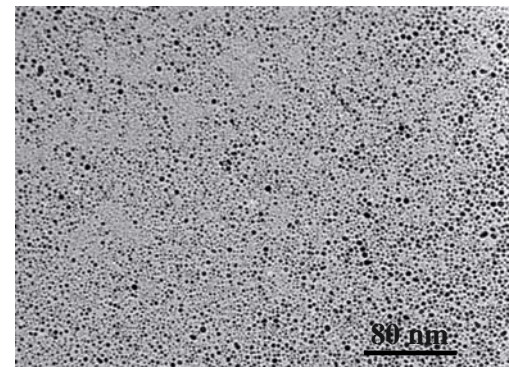
(a)
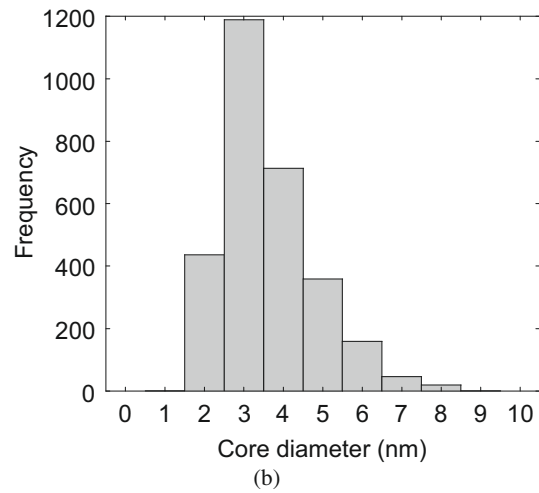
(b)

Fig. 2. (a) TEM image and (b) size histogram of Au-DT NPs.

polymer film thickness was about 100 nm with a roughness nearly 0.4 nm. Finally, the device was completed by thermal evaporation of the top Al electrode in perpendicular orientation respect to the bottom contact. In this way, devices with effective area of 0.04 or 1 mm^2 were realized.

The IVCs of both in-plane and stacked devices were tested with an Agilent 4155C parameter analyzer. Samples were contacted by 1 μm metallic tips of a Karl Suss PM5 probe station. Device testing in controlled atmosphere highlighted no significant differences from air exposure, and then most of the measurements have been done in air.

3 Experimental results

The electrical conductivity of polymeric matrix with different amounts of the conducting filler was tested by measuring the IVCs of planar samples. For all the prepared samples, the IVCs characteristics show a linear behavior through the whole explored voltage range (up to 100 V, corresponding to an electric field of few MV/m). Hence, the conductivity has been evaluated by basic Ohm's law. In Figure 4 the IVCs of samples at different concentrations are reported, while Table 1 summarizes the averaged conductivity data at different Au-DT/8HQ concentrations.
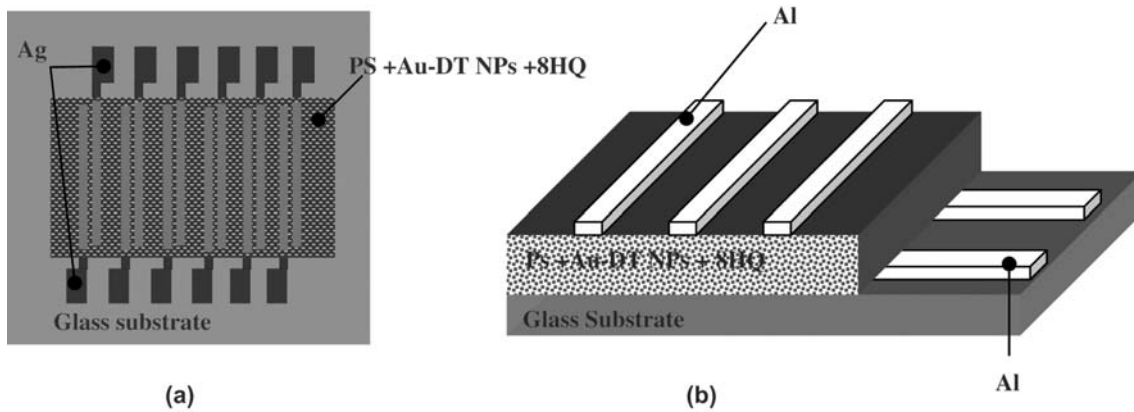
Fig. 3. Structures of the planar (a) and stacked (b) devices: Al/ PS +Au-DT NPs +8HQ/Al.
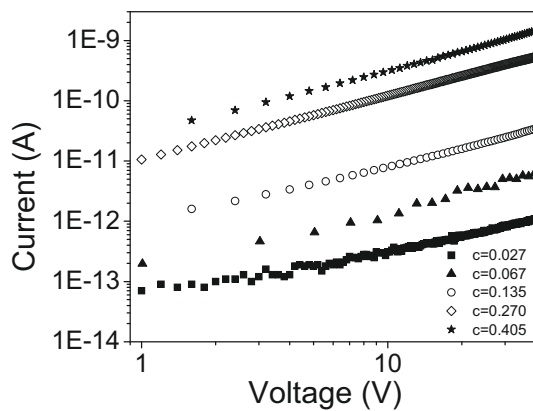

Fig. 4. IVCs for positive voltages at different concentrations of Au-DT NPs and 8HQ, the curve at lower concentration of $c = 0.013$ was omitted because the overlap with the $c = 0.027$ curve.

Fig. 5. IVC of a 1 mm^2 Al/PS-Au-DT NPs-8HQ/Al device with 0.027% Au-DT NPs/8HQ filler concentration in 0.8 wt% of PS.

Table 1. Averaged conductivity values for different Au-DT NPs and 8HQ amount.

(Au DT/8HQ)%	Conductivity (S/cm)
0.013	(1.0 ± 0.5) E-10
0.027	(2.4 ± 1.8) E-10
0.063	(2.9 ± 1.8) E-10
0.135	(6.7 ± 5.0) E-9
0.200	(1.4 ± 0.5) E-8
0.270	(2.0 ± 1.4) E-8
0.405	(7.6 ± 4.9) E-8

When the Au-DT-NPs and 8HQ wt% in the PS matrix is below 0.063%, experimental data are comparable with our set-up resolution. Differently, for concentrations between 0.063% and 0.135% the conductivity displays a sudden increase and further add of filler contents provides a three orders of magnitude increase in the conductivity values.

This behavior indicates that, for weight fraction of Au-DT and 8HQ below 0.063 wt%, nanoparticles and molecules are insulated and the overall electrical properties are dominated by host polymer matrix. As the filler content increases, the average distance between the par-
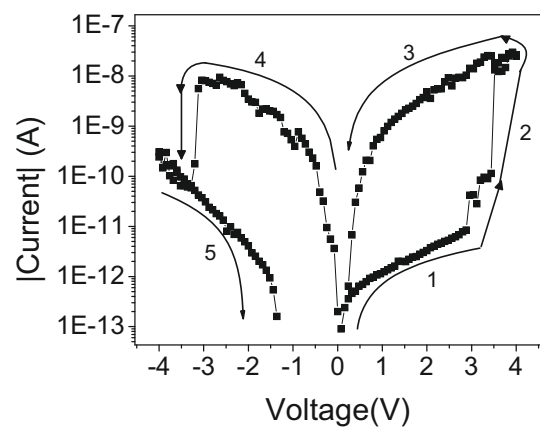
ticles decreases, until it becomes so small that tunneling or hopping processes can occur. In previous work [7] conductivity data for Au-DT and 8HQ weight fraction higher than 0.135 wt% have been analyzed according to the percolation theory [8]. Data analysis suggested that conduction in the polymeric matrix is due to a three dimensional network of conductive paths between spherical and conducting fillers separated from the insulating phase. As a result the nanoparticles as well as the 8HQ molecules are well separated between them and do not form aggregates. All the results converge to a 3D network of Au NPs surrounded by the DT shell and 8HQ molecules, with a regular lattice structure. This scenario indicates that, in the low voltage limit, the main role in the nanocomposite conduction is played by tunneling events between nanoparticles.

To deeply investigate the electrical properties of the nanocomposite, stacked devices were realized at the same Au-DT-NPs and 8HQ concentrations. Since the high values of the applied electric fields, up to $\sim$100 MV/m, a non linear behavior in the IVCs was observed and, as expected [9] a hysteresis for some of the investigated concentrations was detected. In Figure 5, a typical IVC for a device with 0.027 wt% Au-DT NPs is shown. Devices
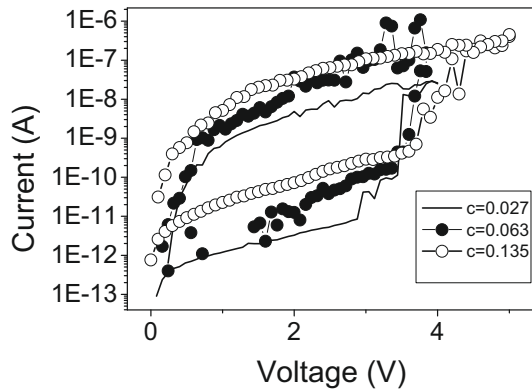
Fig. 6. IVC of a 1 mm² Al/PS-Au-DT NPs-8HQ/Al device at different concentration of Au-DT NPs and 8HQ.

exhibit two different conducting states resulting in hysteretic IVCs, depending both on the applied electric field and on the scan direction. The device switches from a low to a high conducting state when the voltage increases from 0 to 4 V, and then it resets to the low conducting state after the application of a negative bias of about –4 V. This behavior has been detected for all the devices containing 0.027% of Au-DT NPs and 8HQ, with stable and reproducible performances for several cycles of measurements.

Hysteretic behavior in IVCs was observed for all the investigated concentrations with the exception of 0.405 wt% of Au-DT/8HQ devices, exhibiting only one conducting state. Moreover, for Au-DT NPs and 8HQ concentrations lower than 0.027%, the two states are not completely separated and some detected hysteresis seems to be due to polarization effects in the insulating compound. For concentration higher than 0.027%, the devices IVCs show two different states of conductivity, but device behavior depends quite critically on the Au-DT NPs/8HQ wt%. In Figure 6 the IVCs of some of the investigated samples are reported. The increase in the Au-DT NPs and 8HQ concentration produces higher currents both in the low and in the high conducting state nevertheless this one seems weakly affected, accordingly to the results on similar devices [10]. In addition the value of fillers concentration critically affect reset voltages, since for concentrations above 0.1% the devices reset from the high to the low conducting state when the applied voltage is zero, showing that these concentrations are not suitable for non volatile memory applications.

Moreover the conductivity of the material in the stacked low conducting state is lower than the planar one, suggesting that the Aluminum bottom electrode limits the current injection probably due to the presence oxide barriers and defects at the interface polymer/electrode.

4 Discussion

The investigated devices, i.e. Al/PS-Au-DT Nps-8HQ/Al, represent a quite complex system, including several interfaces and structures. Due to such a complexity, any modelling appears challenging and theoretical approaches

are often not completely appropriate to investigated problems. Nevertheless, electronic properties can be lead back to an elementary structure, i.e. metal/polymer/metal (MPM), extensively investigated in the past [11,12]. This is the case of charge transfer between gold nanoparticles separated by thiols, 8HQ molecules, PS or simply between metal electrodes separated by an insulating polymer, as discussed in the following. In steady state conditions, the current in an MPM device is governed by the less effective process between carrier injection from the electrodes into the polymer, and charge transport through the polymeric film [13]. The injection of charges depends both on the potential energy barrier at the metal/polymer interface, and on the transport properties of the polymer. In particular, if the thermal energy is close to the height of the energy barrier, a field assisted thermionic emission can take place. There are several formulations of the current injection at the metal/semiconductor interface [14] depending on the characteristics of the interface and on the mechanisms taken into account. Considering the image-force lowering, the Richardson-Schottky model (RS) is well described by the following equation [15]:

$$J = AT^2 \exp\left(-\frac{\Phi_B}{k_B T}\right) \exp\left[\left(\frac{q^3 V}{4\pi \varepsilon_0 \varepsilon_r d}\right)^{1/2} \bigg/ k_B T\right] \tag{1}$$

where $A = 4\pi q m^* k_B^2/h^3$ is the Richardson-Schottky constant, k_B the Boltzmann's constant, h the Planck's constant, Φ_B is the energy difference between the conduction band edge in the semiconductor and the Fermi level in the metal, m^* the effective electron mass, d the film thickness, ε_0 the vacuum permittivity, ε_r the optical dielectric constant, and q the electron charge.

On the other hand, if the applied field is lower than the barrier height, the charge injection can occur by tunneling and the IVC is well described by the Fowler-Nordheim theory (FN) [16] which leads to:

$$J = \frac{q^3}{8\pi h \varphi} E^2 \exp\left(-\frac{8\pi\sqrt{2m^*}\varphi^{3/2}}{3hqE}\right) \tag{2}$$

where φ is the barrier height, E the applied electric field.

Previous experiments [17] performed on Al/Au-DT NPs+8HQ+PS/Al demonstrate the existence of a critical electric field for the activation of the charge transfer by tunneling between Au nanoparticles and 8HQ HOMO level. As a consequence, the HOMO of the 8HQ is partially filled, and the composite now exhibits a high conductivity state after charge transfer due to tunneling between 8HQ molecules.

Within this framework, we analyzed the IVCs of stacked devices with different Au-DT NPs/8HQ filler concentrations. Fitting procedures used the Levenberg-Marquardt algorithm for chi-square minimization [18]. At 0.027% Au-DT NPs/8HQ concentration, in the low conducting state IVCs are well fitted by the RS model, with an energy barrier higher than $\Phi_B = 0.96$ eV, under the assumption that $m^* = m_e$ and starting from an ε_r value close to 3 comparable to the optical dielectric constant of
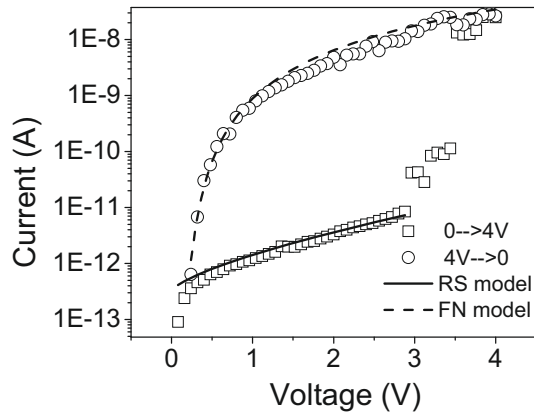
Fig. 7. Current-voltage characteristic of a 1 mm² Al/PS-Au-DT Nps-8HQ/Al device with 0.027% A DT/8HQ filler concentration in 0.8 wt% of PS. Different symbols have been adopted for the low (square and high (circles) conducting state. The solid and dotted lines are the data fits of RS and FN modelin respectively.

the polystyrene. The poor conduction ($J < 1$ nA/cm²) is related to the small number of carriers able to overcome the interface energy barrier up to the critical field $\sim 3 \times 10^5$ V/cm, a value very close to the value 7×10^5 V/cm as reported in reference [17].

At bias fields larger than the above threshold, the device undergoes a switch to a high conducting state. According to references [5,17], the IVCs are now well fitted by FN-type tunneling (see Fig. 7) in the presence of a triangular barrier characterized by an average energy height $\varphi = (0.4 \pm 0.1)$ eV. This value was obtained by fixing the value of the barrier thickness over which the electric field is active to 1nm according to reference [5], and with $m^* = m_e$. This latter approximation is due to the fact that, to our knowledge, the value of the effective electron mass in such composite systems is unknown, and hence according to other similar approaches reported in literature we fixed it to the value of the free electron mass.

Despite the two fitting functions give similar looking curves, each of them cannot be applied to describe both the states without leading to unphysical values of estimated energy barriers.

At higher concentrations (i.e. 0.8% PS, 0.135% Au-DT NPs, 0.135% 8HQ), the situation is quite similar to the 0.027% Au-DT NPs/8HQ case, experimental and fitting data are showed in Figure 8.

Further increases of the Au-DT/8HQ concentration produce higher current densities but similar IVCs in term of switching properties. This is true up to a filler content of 0.405 wt%, when the hysteresis in the IVCs disappears. In this case, the best fit of experimental data was obtained using the RS equation with $\Phi_B = 0.9$ eV, $d = 1$ nm.

The increase of the number of Au-DT NPs and 8HQ molecules inside the composite does not produce a serious change of the estimated energy barrier: this is an indication that charge transport takes place mainly between NPs forming chains between two electrodes. Moreover the activation of the charge transport between 8HQ molecules
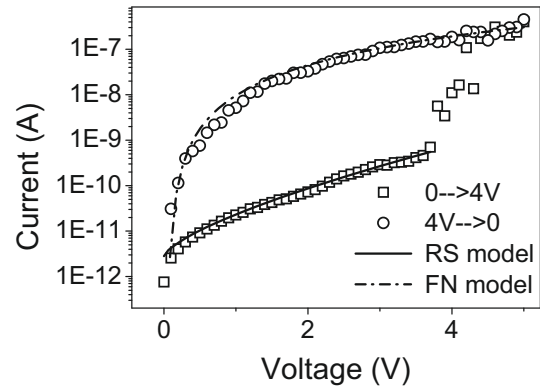

Fig. 8. IVCs of a 1 mm² Al/PS-Au-DT Nps-8HQ/Al device with 0.135% Au-DT/8HQ filler concentration in 0.8 wt% of PS. Different symbols have been adopted for the low (squares) and high (circles) conducting state. The solid and dotted lines are the data fits of RS and FN modeling, respectively.
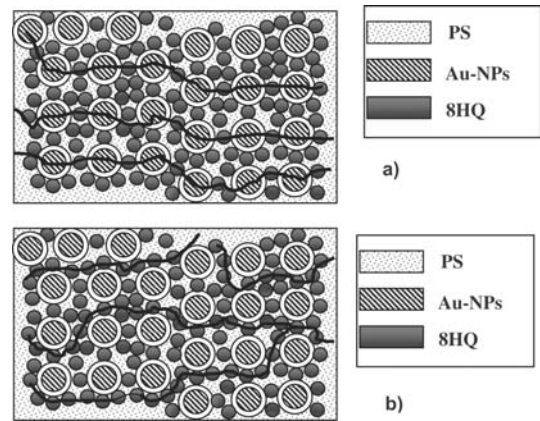

Fig. 9. Schematic picture of the (a) low conducting state of the composite showing tunneling between NPs and 8HQ, and (b) high conducting state, where 8HQ molecules produce paths between electrodes.

is less effective as suggested by the absence of any switching in the IVCs.

The physical picture that emerges from the above analysis can be sketched as follows. At concentrations lower than the percolation threshold, the current is due to electrons which pass from the metal electrodes trough the insulating composite. Near to the percolation threshold, devices exhibit two clear conducting states as evidenced by transport measurements. In the low conducting state the current is limited by the presence of an interface energy barrier ($\Phi_B = 0.9$ eV) that we relate to the interface between Au nanoparticles and 8HQ molecules (see Fig. 9a). At critical value of the applied voltages, charge transfer between Au-DT NPs and 8HQ molecules was activated and the excess charge into the 8HQ molecules produces changes into the density of states of the molecule toward an enhanced conductivity. The high density of 8HQ molecules produces now a large number of conducting paths inside the composite, and charge transport is likely to take place through direct tunneling between 8HQ molecules (see Fig. 9b). According to reference [17] thanks

to the thiols insulating shell the charges cannot recombine after electric field removal and it needs to apply a suitable reverse polarization to allow the electrons come back from the nanoparticles to $8HQ^+$ molecules. In this condition the low-conducting state is restored as shown in the IVC of Figure 5 for negative voltages.

At very large filler concentrations, there is again a single conducting state in the composite as evidenced by the IVCs, and the charge transport is likely to take place through NPs without investing 8HQ molecules.

5 Conclusions

We presented a systematic study of the conducting properties of a PS matrix doped by Au-DT NPs and 8HQ. The conductivity vs. filler concentration has been obtained by a planar electrodes configuration, showing that the charge transport between Au NPs separated by the insulating DT and 8HQ molecules is governed by low field tunneling. Experimental results from stacked devices confirmed the presence of two conducting states of the composite, as requested for non volatile memory organic devices. Despite the absence of any general theory able to exhaustively describe the electrical behavior of such complex hybrid devices, the analysis of their IVCs has been performed according to transport models usually adopted in semiconducting devices. In particular, we demonstrated the existence of a percolation threshold at a critical filler concentration of about 0.05 wt%, below which the composite behaves as an insulating material. Close to the percolation threshold, in agreement with other experiments reported in literature, IVCs show clear hysteresis, related to the existence of two conducting states. Data analysis suggests that in the low conducting state the charge transport involves a thermionic emission mechanism between Au nanoparticles and 8HQ molecules. When a bias critical field is reached, the 8HQ molecules undergo an electronic transition, and the charge transport between electrodes takes place along 8HQ paths. At concentrations much larger than the percolation threshold, a single conducting state is now observed, which corresponds in our picture to a direct transport between Au nanoparticles.

Experimental results confirm the high potential of such nanocomposites toward the realization of advanced non volatile memory organic devices, and contribute to the understanding of the role of filler concentration on both the occurrence and the control of the electrical bi-stability phenomena.

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