

Increased conductivity of a hole transport layer due to oxidation by a molecular nanomagnet

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Thin film transistors based on polyarylamine poly(*N,N'*-diphenyl-*N,N'*bis(4-hexylphenyl)-[1,1'-biphenyl]-4,4'-diamine (pTPD)) were fabricated using spin coating in order to measure the mobility of pTPD upon oxidation. Partially oxidized pTPD with a molecular magnetic cluster showed an increase in mobility of over two orders of magnitude. A transition in the mobility of pTPD upon doping could also be observed by the presence of a maximum obtained for a given oxidant ratio and subsequent decrease for a higher ratio. Such result agrees well with a previously reported model based on the combined effect of dipolar broadening of the density of states and transport manifold filling. © 2008 American Institute of Physics. [DOI: 10.1063/1.2917304]

In recent years, there have been increasing interests and research activities in the field of organic light-emitting devices (OLEDs). The promise of the use of this technology in flat panel displays through the fabrication of low-cost and flexible electronic devices has been the main driving force. Although enormous progress has been achieved in improving the luminance efficiency, color fidelity, and device lifetime, there is a continuous effort for a better stability of the device toward commercialization. Interface engineering between the electrodes and the emitting layer is important for the improvement of the device lifetime as well as luminous efficiency in OLEDs and has led to the fabrication of multilayer devices, with charge transport and charge injection layer (HIL) deposited by vacuum sublimation technique.^{1,2} In terms of solution processable OLEDs, such as polymer based light emitting devices (PLEDs), the use of a PEDOT-PSS layer as the HIL is well known to improve the hole injection from the indium tin oxide (ITO) as well as planarizing the ITO surface and has been well studied.^{3,4} Although it has shown improved device performance such as lower operational voltage and higher luminance efficiency, other problems render it not suitable for device stability. For example, it is found that the ITO/PEDOT-PSS interface is not stable due to the etching of ITO by the strong acidic nature of PSS.⁵ Therefore, at this stage of PLED development, the search for other better solution processable HIL material is needed and it is much required to modify the HIL to further improve the device lifetime as well as its efficiency. Following such an approach, recent results by Bolink *et al.*⁶ have shown that a solution processable HIL material can be used for PLEDs and showed improved performance as when using PEDOT-PSS. Such HIL material is based on a polyarylamine poly(*N,N'*-diphenyl-*N,N'*bis(4-hexylphenyl)-[1,1'-biphenyl]-4,4'-diamine (pTPD)) which was

doped with a molecular magnet and showed tunable conductivity depending on the level of doping. The diamine derivative pTPD resembles very closely to the well known and intensively used organic molecule *N,N'*-diphenyl-*N,N'*bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), while being processable by the spin coating technique and showing a lower conjugation length. In pTPD, the arylamine units are chemically linked to each other, however, due to the angle between the adjacent phenyl rings, the conjugation is limited and does only extend slightly along the chain direction. However, such a slight extended conjugation can result in slightly increased hole mobilities than in the case of TPD. Mobilities of the order of 10^{-5} cm²/V s and 2.4×10^{-5} cm²/V s can be obtained usually for spin coated TPD and pTPD-based films, respectively, showing slightly better mobility for pTPD material as expected. More recently, doping TPD or partially oxidizing it have shown possible enhancement of its charge mobility^{7,8} and resulted in OLED devices exhibiting very low driving voltages.^{9,10}

In this study we chose to investigate the pTPD diamine derivative and determine its mobility in the normal and oxidized state using thin film transistors (TFT). We will show here that it is possible to improve quite significantly the charge mobility of pTPD, using a simple methodology. An enhancement of two orders of magnitude in the holes mobility of pTPD films have been achieved by oxidation of the pTPD solution with a molecular magnetic cluster [Mn₁₂O₁₂(H₂O)₄(C₆F₅COO)₁₆].

pTPD was commercially available from American Dye Sources (98% purity) with no further purification steps. A solution of 20 mg/ml of pTPD was made in chlorobenzene. 100 nm thin films were obtained by spin coating the filtered solutions at 1500 rpm. The molecular magnetic cluster [Mn₁₂O₁₂(H₂O)₄(C₆F₅COO)₁₆], abbreviated as Mn₁₂, was prepared using the ligand substitution method.¹¹ The preparation of the Mn₁₂:pTPD solution in chlorobenzene was done by adding small amounts of Mn₁₂ diluted dichlo-

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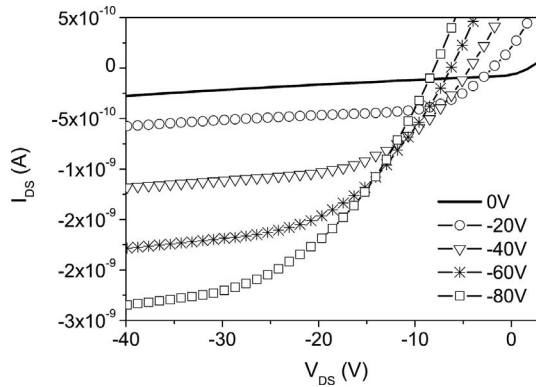


FIG. 1. Output characteristics of an OTFT device based on spin coated pTPD.

romethane solution to the pTPD solution. The pTPD films with varying amounts of Mn_{12} were spin coated from chlorobenzene solution onto SiO_2 coated Si substrates. Highly doped *p*-type silicon wafers with 200 nm thick thermal SiO_2 were used as the substrate of the bottom contact TFT device structure with gold drain and source electrodes. The electrical characterization of the TFTs was performed at room temperature in air using a 4156 Agilent semiconductor parameter analyzer in a slow scan mode.

Several doped pTPD-based OTFTs were fabricated and characterized in order to study their performance in function of the dopant level. All devices exhibited the operating characteristics of a *p*-channel field-effect transistor. In Fig. 1, the output characteristics of the pTPD OTFTs fabricated are shown. Figure 2(a) shows the I_{DS} plotted on a log scale as a function of V_{GS} for a V_{DS} of -50 V (transfer characteristic). The field-effect mobility (μ) and the threshold voltage V_T can be obtained from the saturation characteristics given by the equation $I_D \cong (\mu WC_0/2L) \cdot (V_{GS} - V_T)^2$, where W and L are the channel width and length of the TFT and C_0 is the capacitance of the insulator per area unit of 1.725×10^{-8} F/cm². Figure 2(b) shows the curve of $|I_{DS}|^{1/2}$ versus V_{GS} in the saturation regime used for the calculation. Mobilities (μ) were estimated to be around 2.4×10^{-5} cm²/V s for pTPD, with positive values of 1 V for the threshold voltage. The measured μ and V_T values obtained for pTPD are consistent with results reported for OTFTs measured in ambient conditions and deposited on a SiO_2 dielectric layer (reported field-effect mobilities between 10^{-5} and 10^{-4} cm²/V s).¹²⁻¹⁴

The possibility of improving the mobility of such materials has been demonstrated and reported using various approaches.^{7,8,12-15} For example, it is possible to modify the polymer chain by anchoring end-capping groups,¹² to use them as dopant for inert polymers such as polystyrene or polycarbonate,^{7,13,14} or to oxidize the arylamines with strong oxidant molecules such as ClO_4^- and $AgSbF_6$.^{8,15} Recently, Bolink *et al.*^{6,16} have shown that pTPD properties can be modified by oxidizing it with a molecular magnetic cluster $[Mn_{12}O_{12}(H_2O)_4(C_6F_5COO)_{16}]$. They have shown improved conductivity as a function of the concentration of Mn_{12} used in the pTPD solution as well as improved OLED device performance using Mn_{12} /pTPD as the hole-injection material. They demonstrated that the performance of a blue PLED

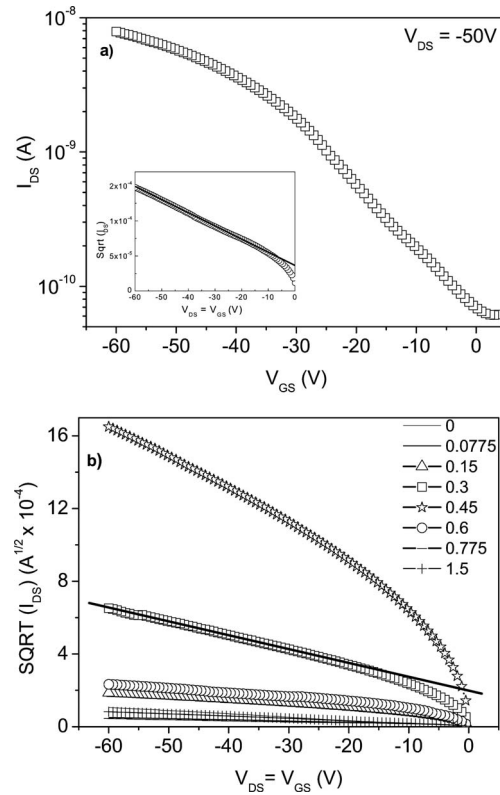


FIG. 2. (a) Transfer characteristics of a (\square), for a V_D of -50 V. The inset shows the saturation regime curve (\circ), from which the mobility and threshold voltage can be deduced. (b) Saturation regime curve as a function of the ratio of Mn_{12} to pTPD in the solution. A linear fit to the curves, used for calculating the mobility, is shown for the Mn_{12} ratio of 0.3.

can be optimized by fine-tuning the composition of this hybrid hole-injection material, reaching efficacies of 3.5 cd/A at 5000 cd/m². The conductivity of the hole-injection material is tunable and ranges from 10^{-8} S/cm for the unoxidized pTPD to 0.01 S/cm at relatively low levels of oxidation.¹⁶ Following these previous results, pTPD was oxidized by Mn_{12} , using a wide range of concentrations and TFTs were fabricated based on such solutions in order to obtain values for the mobility of the oxidized pTPD. The mobilities of oxidized arylamine materials are not a trivial thing to determine as no precise models exist to deduce them from direct current current-voltage characteristics. In fact, the partial oxidation of arylamines, although resulting in an increase in conductivity, is still not completely understood. In their paper, Shen *et al.*¹⁵ describe the competing influence of at least three processes on the increase in conductivity. These are the increase of the width of the distribution of the density of states (DOS) due to an increased polarity by the partial oxidation, the Coulombic interaction between the delocalized charge on the arylamine and its counterion and the partial filling of the transport manifold. The first two processes in fact should decrease the mobility, whereas the latter is believed to be responsible for an increase in the materials mobility. Therefore, we attempted to determine the hole mobilities of partially oxidized pTPD via the preparation of TFTs. Interestingly we were able to deduce the hole mobilities as a function of oxidation ratio. Their dependence on the proportion of Mn_{12} present in the solution is shown in Fig. 3. As

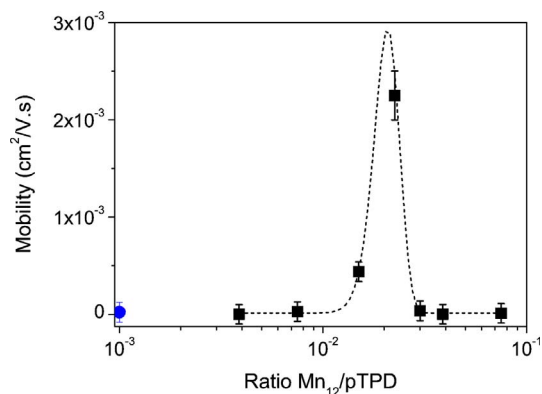


FIG. 3. (Color online) Field-effect mobility of pTPD:Mn₁₂ as a function of the ratio of Mn₁₂ to pTPD in the solution. The mobility of pTPD alone was measured to be $\mu = 2.5 \times 10^{-5}$ cm²/V s and is represented as a round dot on the graph. A Gaussian fit is added just for an indication of the dependence behavior.

mentioned previously, in this work, the mobility of pTPD alone was found to be 2.4×10^{-5} cm²/V s. As can be seen, when a small amount of Mn₁₂ is introduced in the pTPD solution (ratio of Mn₁₂/pTPD less than 0.01), an initial decrease in mobility can be observed. As the proportion of Mn₁₂ is increased, so is the mobility. A maximum mobility of 2.4×10^{-3} cm²/V s is obtained for a ratio of Mn₁₂/pTPD of 0.0225, which consists of an improvement of about two orders of magnitude compared to pTPD alone. Then as the proportion of Mn₁₂ is further increased, the mobility decreases again down to 2.4×10^{-5} cm²/V s for ratios of Mn₁₂/pTPD above 0.03. Up to this high ratio of dopant, a TFT behavior could be observed and therefore meaningful values for the mobility could be obtained. The nonlinear behavior of the mobility of the oxidized pTPD as a function of the dopant ratio exactly follows the prediction made from the model put forward by Shen *et al.*,¹⁵ which is due to a combined effect of dipolar broadening of the DOS and manifold filling. The initial decrease in mobility can be explained by the increase in the broadening of the transport manifold due to the enhanced disorder coming from the dopant. At higher oxidation ratios, the manifold filling becomes more important and the mobility increases until the polarity gets so high for a higher oxidation ratio that Coulombic effects appear and reduce the mobility again. Such nonlinear behavior is quite common in organic blends, where an optimized system (in terms of luminescence efficiency, conductivity, mobility, etc.) is obtained for a certain concentration of dopant and decreases for further increase in concentration. This can also be clearly seen in the transition observed in the device operation when using such material for the HIL.¹⁶ It goes from a hole-limited device (ratio of Mn₁₂/pTPD lower than 0.01) to a charge balance device (ratio 0.01) and eventually to a device which is electron limited (ratio above 0.01).¹⁶

Finally, it is important to report that significant improvement in the pTPD mobility has previously been reported using other dopants, such as polyhedral oligomeric silsesquioxanes¹¹ (POSS), where an increase in mobility of one order of magnitude was also obtained (around 10^{-2} cm²/V s). In that case, the mobility improvement was

only observed when the POSS was added to the main chain of the polymer via chemical synthesis. The pTPD:Mn₁₂ blend offers a simpler technique to obtain improved mobilities compared to the latter one. The pTPD polymer really presents attractive properties for device applications such as a spin coating technology, nice uniform films, and mobility (and conductivity) that can be improved to reach up to 10^{-3} – 10^{-2} cm²/V s by using either organic or inorganic dopants.

In conclusion, we have shown that the mobility of pTPD can be improved by two orders of magnitude by oxidizing the solution with a molecular magnetic cluster Mn₁₂. Such enhanced mobility is not linear with the proportion of Mn₁₂ present in the solution and a maximum was obtained for a ratio of Mn₁₂/pTPD of 0.0225. It can be explained by a combined effect of dipolar broadening of the DOS due to the increased disorder coming from the dopant and the transport manifold filling. This model was already put forward to explain the variation of the conductivity of the oxidized polymer in function of the oxidant ratio. Such results are important in order to understand the phenomena at stake in the transport mechanism for doped or oxidized polymers. Furthermore, a polymer such as pTPD really presents attractive properties for device applications such as spin coating technology, nice uniform films, a lower conjugation length than TPD, and mobility (and conductivity) that can be improved to reach up to 10^{-3} – 10^{-2} cm²/V s by using either organic or inorganic dopants.

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