

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Determination of charge carrier mobility of hole transporting polytriarylamine-based diodes

Eva M. Barea^a, Germà Garcia-Belmonte^{a,*}, Michael Sommer^b, Sven Hüttner^b,
Henk J. Bolink^c, Mukundan Thelakkat^{b,*}

^a Photovoltaic and Optoelectronic Devices Group, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain

^b Applied Functional Polymers, Universität Bayreuth, 95440 Bayreuth, Germany

^c Molecular Science Institute-Universitat de València, Polígon La Coma s/n, 46980 Paterna, València, Spain

ARTICLE INFO

Article history:

Received 29 December 2008

Received in revised form 5 August 2009

Accepted 1 October 2009

Available online 13 October 2009

Keywords:

Poly(triarylamines)

Hole-transporting materials

Mobility

Organic electronics

ABSTRACT

Hole transport properties of three different side chain poly(triarylamines) have been determined by means of the analysis of steady-state current–voltage characteristics using co-planar diode structures. The interpretation is based on space-charge limited models with field-dependent mobility. Mobilities between $\sim 10^{-8}$ and $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are obtained. The highest mobility is achieved for poly(tetraphenylbenzidine) devices and the lowest for poly(triphenylamine) devices. Electron-rich methoxy substituents increase the mobility of poly(triphenylamine)s. A comparison of the mobility values with those obtained using organic field-effect transistors is also given.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Triarylamines (TAAs) comprise an important class of hole conducting materials (HTM) that are widely used in organic photovoltaics [1] or light emitting diodes [2]. Polymeric TAAs (PTAAs) exhibit enhanced processing properties compared to their low molecular weight analogs, and crystallization is impeded which is a prerequisite for the long term stability of such devices [3]. Classification can be made by distinguishing simple poly(triphenylamine)s PTPAs and poly(tetraphenylbenzidine)s PTPDs, in which the active group is composed of two TPA units. Also, main chain polymeric structures can be compared to side-chain architectures. Polymeric side chain triphenylamines exhibit enhanced solubility and living polymerization methods can be employed in order to synthesize defined molecular weights and narrow molecular weight distributions [2,4,5]. Recently, amorphous side chain polytriarylamines polymers have been used as hole conducting building blocks for the synthesis of donor-acceptor block copolymers and large differences in the device performance were found as a function of the hole conductor and the molecular weight [4,6].

The charge carrier mobility of organic electronic materials can be determined by a variety of methods, including time-of-flight [7], analysis of space-charge limited currents (SCLC) in steady-state conditions [8], interpretation of transients in dark injection SCLC, [7]

measurement of transient electroluminescence [9], and analysis of organic field-effect transistor (OFET) performance [10,11]. Alternatively, mobility-related parameters can be extracted from ac capacitance measurements [12]. The adopted technique to measure mobility has to be selected in relation to the final device structure. In order to gain information of the hole mobility in a photovoltaic device, techniques capable of measuring transport vertical to the film plane should be used. This excludes the analysis of OFET mobility and makes the interpretation of steady-state current–voltage (J – V) characteristics a simple, straightforward method.

The aim of this work is the measurement of the hole mobility of different polymeric triarylamines in diode device architectures. It is generally known that TPA based hole conductors exhibit lower charge mobilities than the analogous TPD materials, but no report exists in which such materials with comparable polymer architectures are compared. We thus seek to explore the influence of the substitution pattern on the final transport parameters.

2. Materials and device preparation

The structures analyzed in this work are drawn in Fig. 1. Three polymers are used, namely poly(vinyltriphenylamine) PvTPA, poly[bis(4-methoxyphenyl)-4'-vinylphenylamine] PvDMTPA, and poly[N,N'-bis(4-methoxyphenyl)-N-phenyl-N'-4-vinylphenyl-(1,1'-biphenyl)-4,4'-diamine] PvDMTPD. The polymers were prepared by nitroxide mediated radical polymerization allowing the preparation of well-defined and narrow-distributed materials. The molecular weights of PvTPA, PvDMTPA and PvDMTPD are 39.0 kg/mol, 23.0 kg/mol and 22.4 kg/mol,

* Corresponding authors.

E-mail addresses: garcia@uji.es (G. Garcia-Belmonte), mukundan.thelakkat@uni-bayreuth.de (M. Thelakkat).

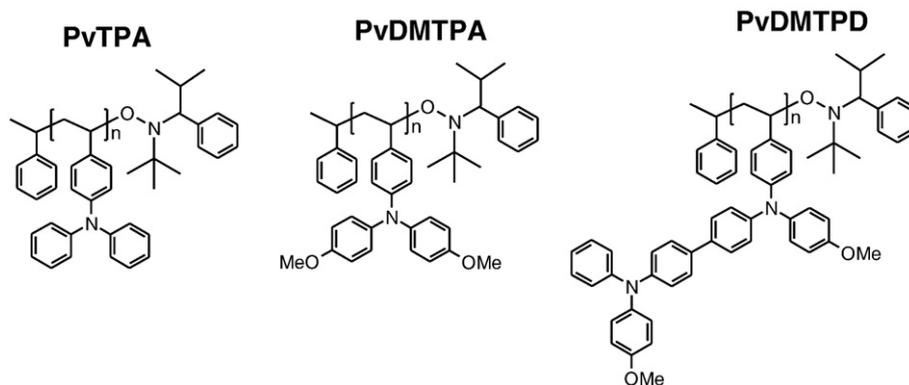


Fig. 1. Chemical structures of analyzed donor polymers.

and the polydispersity indices are 1.23, 1.51, and 1.24, respectively. The higher-occupied molecular-orbital (HOMO) levels of PvTPA is 5.2 eV and PvDMTPA and PvDMTPD both show the same value of 5.0 eV, as measured by cyclic voltammetry in solution. All polymers exhibit a glass transition temperature T_g of 150 °C, 129 °C and 163 °C, respectively. Devices of co-planar structure indium-doped tin oxide ITO/HTM/Au (diode configuration) were prepared under standard conditions in ambient atmosphere (clean room). Pre-patterned ITO glass plates were extensively cleaned, using chemical and UV–ozone methods, just before the deposition of the organic layers. Solutions of the polymers were prepared in chloroform (32 mg of polymer in 1.5–2 ml of chloroform) and the spin speed was 1000 rpm. The thickness of the organic films, deposited by spin coating from a chloroform solution, was determined using an Ambios XP1 profilometer, resulting in film thicknesses between 90 nm and 280 nm. No annealing treatments were applied. Au was thermally evaporated to a layer thickness of 70 nm using temperature controlled sources and an evaporation chamber integrated in an inert atmosphere glove box (0.1 ppm O₂ and H₂O). J – V characteristics were registered using a Keithley 2400 electrometer.

3. Transport model and results

The measured J – V characteristics in polymer and small-molecule electronic devices in reverse and forward bias direction up to approximately the built-in potential V_{bi} often exhibits ohmic response. This behavior is believed to be caused by additional leakage currents flowing in parallel with useful currents responsible for the device operation, $J_{tot} = J_{oper} + J_{leakage}$. For voltages more positive than V_{bi} an increase in current indicates the potential-driven enhancement in charge carrier injection. For the studied hole-transporting materials, the device current is determined by the transport of holes since the potential barrier at the anode is sufficiently low to form ohmic contacts. Under this assumption the hole transport is space-charge limited (SCLC) because the material is considered to be undoped. J – V characteristics can be analyzed by means of the approximation of Murgatroyd [13],

$$J_{oper} = \frac{9 \epsilon \mu_0}{8 L^3} V^2 \exp(0.89 \gamma \sqrt{V/L}) \quad (1)$$

Here V corresponds to the operating voltage (subtracting the built-in voltage, $V = V_{bias} - V_{bi}$), L represents the layer thickness, ϵ stands for the permittivity of the organic layer ($\epsilon \approx 3\epsilon_0$ for most polymers), μ_0 is the zero-field hole mobility, and γ the field coefficient. These last two parameters are related to the field dependence of the mobility [14,15]

$$\mu(E) = \mu_0 \exp(\gamma \sqrt{E}), \quad (2)$$

which is in agreement with the Poole–Frenkel effect [16] and hopping transport models in an energetically and spatially disordered system [17,18]. For the calculation of the Murgatroyd's approximation the electrical field in Eq. (2) can be stated as $E = V/L$ and considered to be constant along the active layer thickness.

Fig. 2 shows an example of the J – V characteristics of the analyzed hole-transporting materials. A leakage current is observed in the low and reverse bias region, which can be approximated by an ohmic contribution in addition to the operating current of Eq. (1). At more positive potentials the onset current is situated around 0.5–1.8 V, depending on the material of the layer. The variation is usually attributed to changes of V_{bi} caused by differences between the ITO and Au effective work functions, which might be largely altered by the presence of interface dipoles [19]. In case of PvTPA we found V_{bi} values around 1.8 V. This parameter results lower ($V_{bi} \sim 0.5$ – 0.9 V) for PvDMTPA, and practically disappears ($V_{bi} \approx 0$ V) when PvDMTPD is used. Since the ITO work function (~ 4.7 – 5.0 eV) fairly aligns with the polycrystal Au work function (~ 5.1 eV) [20], one can infer that contacts between PvDMTPD molecules and ITO or Au do not form significant interface dipoles able to shift energetic levels. Therefore the electronic levels of the contact materials align with the HOMO levels of the organic layers (5.2–5.0 eV). The influence of interface dipoles would be more pronounced in case of PvTPA-based devices, which results in $V_{bi} > 1$ V. However, it is also evident in Fig. 2 that leakage current is higher for PvTPA than that observed for PvDMTPD-based devices. High leakage

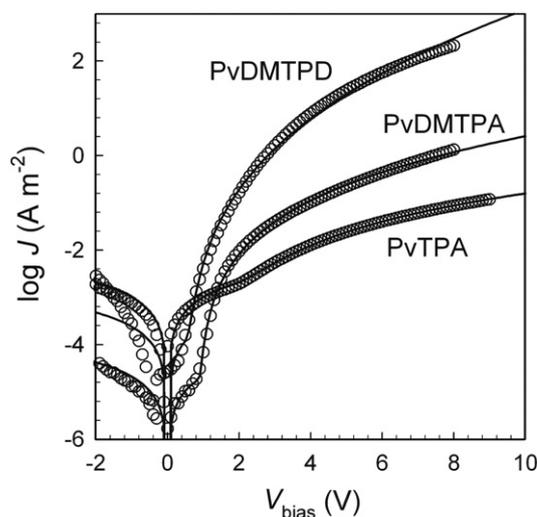


Fig. 2. Measured J – V characteristics (dots) and fitting curve (line) of the polymers of Fig. 1. Analysis is based on Eq. (1) and an additional ohmic leakage current which dominates at low voltages. Correlation coefficient resulted in all cases $R > 0.996$, and relative errors of parameters obtained from fitting were always below 4%.

currents might hide the actual operating current onset being the obtained $V_{bi} > 1$ V just an apparent value rather than a real one.

As one can observe in Fig. 2, there are large differences in the current exhibited by PvTPA and that of other two polymers. Fitting by using Eq. (1) matches experimental data as observed in Fig. 1, which informs on the agreement between SCLC approach [Eq. (1)] and the experimental J - V characteristics. For fitting purposes an ohmic leakage current has been assumed flowing in parallel to J_{oper} . The results are summarized in Table 1. Simpler structures such as PvTPA exhibit low zero-field mobility values of the order of $5 \times 10^{-10} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas PvDMTPA and PvDMTPD show enhanced values in the range of 10^{-9} – $10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. As encountered for other hole conducting polymers [21] the field coefficient γ [Eq. (2)] lies within the order of $10^{-4} \text{ m}^{1/2} \text{ V}^{-1/2}$.

4. Discussion

The charge carrier mobility μ_0 of PvTPA, PvDMTPA and PvDMTPD increases from $5.3 \times 10^{-10} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $7.7 \times 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and finally to $1.0 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, for devices of similar thickness (around 220 nm). Interestingly, the mobility of PvDMTPA is more than three times higher than that of PvTPA, which is ascribed to the electron-enriching effect of the methoxygroups in PvDMTPA. Since the molecular weights of PvTPA and PvDMTPA do not differ excessively (39 kg/mol and 23 kg/mol, respectively), molecular weight seems not to affect the hole mobility of these materials considerably, and the differences should be related to above mentioned electron-enriching effect. Unlike in conjugated polymers [22], the molecular weight of a side chain polymer is unlikely to affect the charge transport properties. The highest mobilities are achieved in devices made of PvDMTPD, and thus the common trend of a higher hole mobility in TPD based materials compared to the TPA analog is also seen here [23,24].

It is also interesting to compare our results listed in Table 1 with those resulting from alternative methods. A common technique to evaluate mobility in organic materials makes use of an organic field-effect transistor (OFET) configuration. Instead of a transport across the active layer (diode configuration), OFET measurements are performed in a planar structure. As usually recognized, mobility extracted from OFET (μ_{FE} field-effect mobility) always results superior than that obtained from diode structures [25]. It has been recently demonstrated that such discrepancy is related to the improvement in mobility caused by the high increment of carrier concentration achieved in OFETs at high gate voltages [25]. Mobility is believed to be highly dependent on the charge carrier density as derived from hopping percolation models in disordered systems [26]. In our case such difference between mobility calculated using diode and OFET architectures is also found (Fig. 3). The μ_{FE} extracted in our analysis results some orders of magnitude larger than μ_0 . However, it is worth noticing that the general trends are indeed reproduced. In both types of configurations (OFET and diode) PvDMTPD exhibits the highest mobility values. The mobility calculated for an electrical field of 10 MV m^{-1} by means of Eq. (2) are also plotted in Fig. 3 for comparison. Such electrical field value corresponds to that encountered in usual operation of solar cells (around 1 V in 100 nm-thick layers). This entails that one can expect mobilities values around $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when PvDMTPD is employed as hole transporting material in operating photovoltaic devices.

Table 1

Mobility parameters resulting from fits for J - V characteristics in Fig. 2.

HTM	μ_0 (cm^2/Vs)	γ ($\text{m}^{1/2}/\text{V}^{1/2}$)	Thickness (nm)	μ_{FE} (cm^2/Vs)
PvTPA	5.3×10^{-10}	6.4×10^{-4}	277	3.1×10^{-6}
PvDMTPA	7.7×10^{-9}	4.0×10^{-4}	204	2.5×10^{-5}
PvDMTPD	1.0×10^{-8}	14×10^{-4}	220	8.5×10^{-5}

The OFETs were prepared by spincoating the materials the same way as described in Ref. [27]. The mobility was extracted in the saturation regime.

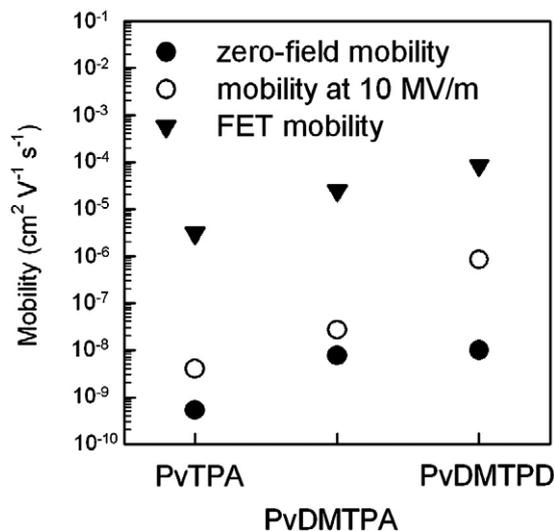


Fig. 3. Comparison of the mobility values resulting from fits, calculated for usual operating conditions using Eq. (2) for 10 MV m^{-1} , and those reported for OFET configurations.

5. Conclusions

The analysis of space-charge limited currents (SCLC) in steady-state conditions of several polytriarylamine-based diodes has allowed us to extract mobility-related parameters of hole transport. We have given a comparison between TPA and TPD based amorphous side chain polymers and encountered that devices made from poly(tetraphenylbenzidine) exhibit a mobility of $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in usual operating conditions (~ 1 V in 100 nm-thick layers), which is around two orders of magnitude higher compared to that of the TPA polymer ($\sim 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). When methoxygroups are attached at the para position of the TPA polymer, the mobility results 5 times greater. The OFET mobilities of the same materials result in values that are two orders of magnitude higher, however the same trend is reproduced.

Acknowledgments

We thank the financial support from Ministerio de Educacion y Ciencia under project HOPE CSD2007-00007 (Consolider-Ingenio 2010), from ESF EUROCORES SONS Programme (MAT2006-28187-E), from Universitat Jaume I (P1.1B2008-32), and from the Deutsche Forschungsgemeinschaft (SFB 481). G.G.B. acknowledges an ESF Short Visit Grant (ORGANISOLAR 1716).

References

- [1] C.S. Karthikeyan, M. Thelakkat, Inorg. Chim. Acta 361 (2008) 635.
- [2] E. Bellmann, S.E. Shaheen, R.H. Grubbs, S.R. Marder, B. Kippelen, N. Peyghambarian, Chem. Mater. 11 (1999) 399.
- [3] M. Thelakkat, Macromol. Mater. Eng. 287 (2002) 442.
- [4] M. Sommer, S.M. Lindner, M. Thelakkat, Adv. Funct. Mater. 17 (2007) 1493.
- [5] S.M. Lindner, M. Thelakkat, Macromolecules 37 (2004) 8832.
- [6] M. Sommer, M. Thelakkat, Eur. Phys. J., Appl. Phys. 36 (2006) 245.
- [7] M.A. Lampert, P. Mark, Current Injection in Solids, Academic Press, New York, 1970.
- [8] Z. An, J. Yu, S.C. Jones, S. Barlow, S. Yoo, B. Domercq, B. Prins, L.D.A. Siebbeles, B. Kippelen, S.R. Marder, Adv. Mater. 17 (2005) 2580.
- [9] S. Karg, V. Dyakonov, M. Meir, W. Riess, G. Paasch, Synth. Met. 67 (1994) 165.
- [10] S.M. Sze, Physics of Semiconductor Devices, John Wiley and Sons, New York, 1981.
- [11] Y. Shirota, H. Kageyama, Chem. Rev. 107 (2007) 953.
- [12] J.M. Montero, J. Bisquert, G. Garcia-Belmonte, H.J. Bolink, E.M. Barea, Phys. Status Solidi (a) 204 (2007) 2402.
- [13] P.N. Murgatroyd, J. Phys. C. Solid State Phys. 3 (1970) 151.
- [14] D.M. Pai, J. Phys. Chem. 52 (1970) 2285.
- [15] P.S. Davids, I.H. Campbell, D.L. Smith, J. Appl. Phys. 82 (1997) 6319.
- [16] W.D. Gill, J. Appl. Phys. 43 (1972) 5033.
- [17] H. Bässler, Phys. Stat. Sol. (b) 175 (1993) 15.
- [18] S.V. Novikov, D.H. Dunlap, V.M. Kenkre, P.E. Parris, A.V. Vannikov, Phys. Rev. Lett. 81/20 (1998) 4472.

- [19] W.R. Salaneck, K. Seki, A. Kahn, J.-J. Pireaux (Eds.), *Conjugated Polymer and Molecular Interfaces, Science and Technology for Photonic and Optoelectronic Applications*, Marcel Dekker, New York, 2002.
- [20] J. Hölzl, F.K. Schulte, *Work Function of Metals in Solid State Physics*, Springer-Verlag, Berlin, 1979.
- [21] L. Bozano, A. Carter, J.C. Scott, G.G. Malliaras, P.J. Brock, *Appl. Phys. Lett.* 74 (1999) 1132.
- [22] R.J. Kline, M.D. McGehee, J. Kadnikova, J. Liu, J.M.J. Fréchet, *Adv. Mater.* 15 (2003) 1519.
- [23] M. Stolka, D.M. Pai, D.S. Renfer, J.F. Yanus, *J. Polym. Sci., Polym. Chem.* 21 (1983) 969.
- [24] M. Abkowitz, D.M. Pai, *Philos. Mag.*, B 53 (1986) 193.
- [25] C. Tanase, E.J. Meijer, P.W.M. Blom, D.M. de Leeuw, *Phys. Rev. Lett.* 91/21 (2003) 216601.
- [26] M.C.J.M. Vissenberg, *M. Matters, Phys. Rev.*, B 57 (1998) 12964.
- [27] S. Hüttner, M. Sommer, M. Thelakkat, *Appl. Phys. Lett.* 92 (2008) 093302.