Electron and hole transport in an anthracene-based conjugated polymer

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The bulk transport properties of an anthracene-containing poly(*p*-phenylene-ethynylene)-alt-poly (*p*-phenylene-vinylene) (AnE-PV*stat*) were investigated by small-signal time-of-flight. AnE-PV*stat* exhibited a very good ambipolar behaviour, consistent with the high delocalization of both frontier molecular orbitals. The transport of negative carriers was found to be even faster than that of positive carriers, with an electron drift mobility of about six times higher than that evaluated for holes, suggesting that conjugated polymers with carbon-carbon triple bonds could represent a promising platform toward high performance ambipolar materials for plastic electronics. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4742738]

Charge transport properties constitute a major determining factor for the operation of any electronic device, and mainly for organic electronics. Indeed, the much worse mobility of charge carriers (μ) in organic materials, compared to that in conventional semiconductors, represents a critical parameter for organic devices. Among organic semiconducting materials, solution-processable π-conjugated polymers are attracting considerable attention for large-area, cost-effective, and high throughput production of flexible electronics.[1] Contrary to the general belief of the past, the intrinsic ability of π-conjugated polymers to transport both positive and negative charge carriers has been pretty well ascertained in the last years.[2,3] Though organic field effect transistors (OFETs) using polymers as active materials and showing high and balanced hole and electron mobilities have been recently demonstrated,[4,5] the availability of conjugated polymers able to efficiently transport negative carriers is still a challenge.

The observation of ambipolar transport in OFET structures relies on the efficient injection of both holes and electrons from the metal contacts (usually both in gold) into the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) level of the investigated polymer, respectively. For this reason, a careful tuning of the position of the polymer energy levels is usually required for achieving an effective ambipolar behaviour in OFETs.[6,7] Moreover, it is well established that charge carrier mobility in organic materials is highly dependent on charge carrier density,[8] being orders of magnitude higher in OFETs compared to that flowing in diode-like devices such as organic light emitting diodes and solar cells. As a consequence, field-effect mobility is often found to be much higher than that measured in diode structures by using the so-called bulk techniques.[9] Among bulk techniques, time-of-flight (TOF)[10]

is considered the "direct" method for the investigation of bulk transport properties in disordered materials, with the great advantage over the OFET technique of being an injection-free method, thus not limited by the position of the energy levels of the materials.

In this Letter, we report the very good ambipolar behaviour of films made of an anthracene-containing poly(*p*-phenylene-ethynylene)-alt-poly(*p*-phenylene-vinylene) (PPE-PPV). The ambipolar charge transport properties of the polymer, here denoted as AnE-PV*stat*[11] (Figure 1(a)), were investigated by small-signal TOF technique. The advantage of the triple bond in the polymer structure, due to its cylindrical symmetry, is the preservation of the conjugation between aromatic groups in case of rotation of the aromatic plane, though it is maximum in the planar conformation.[12,13] It has been shown that PPE-PPVs are characterized by an enhancement of both backbone stiffness and electron affinity, as compared to parent PPV, due to the incorporation of the electron-withdrawing ethynylene units into the polymer backbone.[14] Indeed, the triple bond acts as a bridge for the
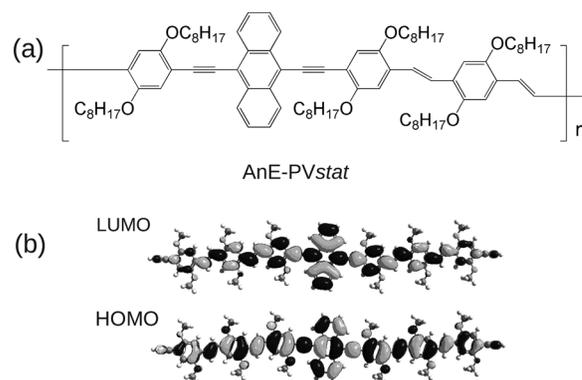

FIG. 1. (a) Molecular structure of AnE-PV*stat* (octyl and 2-ethylhexyl side-chains are randomly distributed). (b) HOMO/LUMO electron density plots calculated by B3LYP/6-31G* for the energy-minimized model structure of the methoxy-substituted trimer.

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electrons of two aromatic systems also by means of π-π^* hyperconjugation.

AnE-PV*stat* is capable of both easy oxidation and reduction, as demonstrated by the reversible oxidation and reduction peaks observed in its cyclic voltammogram,[11] this being a pre-requisite for ambipolar transport. A further evidence for ambipolar transport ability is given by the electron-state-distribution of the HOMO/LUMO levels of AnE-PV*stat*, computed by B3LYP/6-31G* (Ref. [15]) density functional theory, which shows a very good delocalization of both energy levels (Figure 1(b)). Indeed, the TOF experiments performed on sandwich-type devices indium-tin-oxide (ITO)/AnE-PV*stat*/Al yielded a room-temperature electron mobility of 1.2×10^{-3} cm^2 V^{-1} s^{-1} at the electric field (E) of 1.1×10^5 V cm^{-1}. This value is among the highest reported for the bulk electron mobility of a conjugated polymer, though lower than the record of 6.0×10^{-2} cm^2 V^{-1} s^{-1}, recently achieved for highly ordered films of poly(N,N-bis 2-octyldodecyl-naphthalene-1,4,5,8-bis dicarboximide-2,6-diyl-*alt*-5,5-2,2-bithiophene).[16] However, differently from other good electron-transporting polymers, which in best cases exhibit very close bulk hole and electron mobilities, the transport of negative carriers in as-cast films of AnE-PV*stat* is six times faster than the transport of holes.

The devices for TOF experiments were realized onto patterned glass/ITO substrates. AnE-PV*stat* films (3.6 μm thick) were deposited by drop-casting from 1,2-dichlorobenzene solution (30 gl^{-1}). The device structure was completed with a vacuum evaporated semitransparent aluminium layer (18 nm), acting as the illuminated electrode. A nitrogen laser ($\lambda = 337$ nm) with a pulse duration of 6–7 ns was used in single-pulse mode to photogenerate charge carriers. The absorption coefficient of AnE-PVstat at the excitation wavelength was 2.39×10^4 cm^{-1}, so most of light was absorbed within the first 420 nm of the polymer film. A variable DC potential was applied to the samples and, in order to ensure a uniform electric field inside the device, the total photogenerated charge was kept less than 0.1 CV, where C is the sample capacitance and V the applied potential. The photocurrent was monitored across a variable load resistance by using a Tektronix TDS620A digital oscilloscope. The TOF experiments were performed at room temperature, under dynamic vacuum (8×10^{-6} mbar).

A typical photocurrent transient for holes is shown in Figure 2(a), for the applied field of 4.2×10^4 V cm^{-1}. Transport of holes is not affected by high dispersion in cast-films of AnE-PV*stat* and the transit time of carriers, τ, can be detected also in a linear scale, mainly at higher fields. The low dispersion of TOF signals is consistent with the multi-crystalline character of this copolymer.[17] By reversing the polarity of the illuminated semitransparent Al electrode, the signal reported in Figure 2(b) was observed for electrons, clearly showing that current due to negative carriers decreases more rapidly and indicating that the time required for electrons to travel through the same sample is much shorter than that for holes. The comparison of the two signals of Figure 2 confirms the usual finding that transport of electrons is more dispersed than that of positive carriers in conjugated polymers,[18] commonly attributed to trapping effects. Indeed, with the LUMO level at -3.04 eV,[11] electron transport states of AnE-PV*stat* are expected to lie close to the
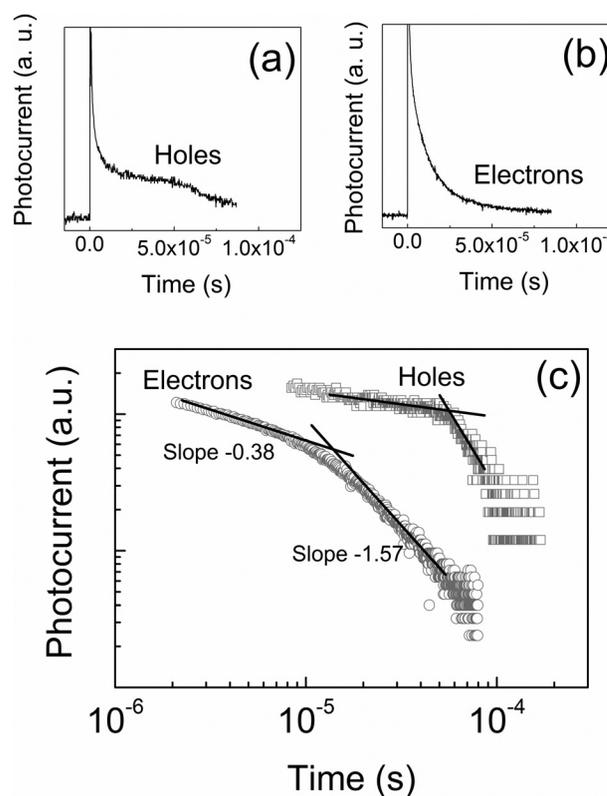

FIG. 2. Linear plots of photocurrent signals for an ITO/AnE-PV*stat*/Al device with the illuminated semitransparent Al electrode: (a) positively biased and (b) negatively biased. In both cases, the applied field was 4.2×10^4 V cm^{-1}. (c) The same signals shown in a double logarithmic scale, in which the slopes before and after the transit time are also indicated for electrons signal. Thickness of the polymer layer: 3.6 μm.

typical impurities acting as trapping states for negative carriers.[19] Though the dispersion of photocurrent signals, two different slopes were clearly observed also for electrons in the double-logarithmic representation, as shown in Figure 2(c), with slopes far below -1 for times shorter than τ and much higher than -1 for longer times and whose sum was very close to -2, as predicted by the Scher-Montroll theory.[20] Both for electron and hole TOF signals, charge carrier transit times were determined from the intersection point between the two straight lines with different slopes, which τ represents the arrival time of fastest carriers.

The values of charge carrier mobility were calculated through the well-known expression $\mu = d/\tau E$, where d is the thickness of the polymer layer, and are displayed as a function of the square root of E in Figure 3. The bulk electron mobility in as-cast AnE-PV*stat* films is roughly six times higher than hole mobility in the investigated range of field. For example, at the same field of 1.1×10^5 V cm^{-1}, an electron mobility of 1.2×10^{-3} cm^2 V^{-1} s^{-1} was calculated, against 2.0×10^{-4} cm^2 V^{-1} s^{-1} for holes. Both for electron and hole mobility, a good linear trend of μ with E$^{1/2}$ was obtained (Figure 3), indicating a Poole-Frenkel behaviour $\mu = \mu_0 \exp(\gamma \sqrt{E})$, where μ_0 denotes the mobility at zero field and γ is the Pool-Frenkel factor, describing how strong is the field dependence. Such a behaviour has been frequently observed in organic materials and could be attributed to the effects of energetic and positional disorder on the hopping conduction in disordered molecular solids.[21] The parameters
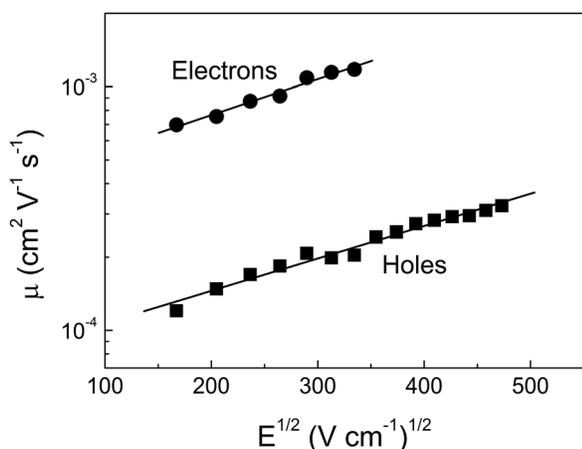
FIG. 3. Room-temperature TOF mobility as a function of the square root of field for an as-cast AnE-PV*stat* film 3.6 μm thick. The lines indicate the linear fits to the experimental data.

for the Poole-Frenkel fit to mobility data of Figure 3 are $\mu_0 = 3.9 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and $\gamma = 3.4 \times 10^{-3}\,\mathrm{(V\,cm^{-1})^{-1/2}}$ for electrons and $\mu_0 = 7.9 \times 10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and $\gamma = 3.1 \times 10^{-3}\,\mathrm{(V\,cm^{-1})^{-1/2}}$ for holes. The values of γ are rather usual for conjugated polymers and indicate a moderate field-dependence of charge carrier mobility in AnE-PV*stat*. That of electron mobility is however a bit stronger than that for holes, consistent with increased/different trapping processes.[22]

In conclusion, AnE-PV*stat*, showing reversible electrochemical oxidation and reduction peaks as well as a very good delocalization of HOMO and LUMO levels, exhibits a very good ambipolar charge transport behaviour. However, differently from other good ambipolar conjugated polymers already reported in the literature, the bulk transport of negative carriers is much faster than that of positive carriers, with a drift mobility of fastest electrons of about six times higher than that evaluated for fastest holes in the investigated field range. These results suggest that conjugated polymers with carbon-carbon triple bonds, rarely considered and investigated, could represent a promising platform toward high performance ambipolar materials for printable and plastic electronics.

[1]*Printed Organic and Molecular Electronics*, edited by D. R. Gamota, P. Brazis, K. Kalyanasundaram, and J. Zhang (Kluwer Academic, Norwell, 2004).

[2]L.-L. Chua, J. Zaumseil, J.-F. Chang, E. C. W. Ou, P. K. H. Ho, H. Sirringhaus, and R. H. Friend, Nature (London) **434**, 194 (2005).

[3]H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dötz, M. Kastelr, and A. Facchetti, Nature (London) **457**, 679 (2009).

[4]S. Cho, J. Lee, M. Tong, J. H. Seo, and C. Yang, Adv. Funct. Mater. **21**, 1910 (2011).

[5]Z. Chen, M. J. Lee, R. S. Ashraf, Y. Gu, S. Albert-Seifried, M. M. Nielsen, B. Schroeder, T. D. Anthopoulos, M. Heeney, I. McCulloch, and H. Sirringhaus, Adv. Mater. **24**, 647 (2012).

[6]J. Zaumseil and H. Sirringhaus, Chem. Rev. **107**, 1297 (2007).

[7]H. Usta, A. Facchetti, and T. J. Marks, Acc. Chem. Res. **44**, 501 (2011).

[8]C. Tanase, E. J. Meijer, P. W. M. Blom, and D. M. de Leeuw, Phys. Rev. Lett. **91**, 216601 (2003).

[9]S. Tiwari and N. C. Greenham, Opt. Quantum Electron. **41**, 69 (2009).

[10]P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Xerography* (Marcel Dekker, New York, 1998), Ch. 4.

[11]D. A. M. Egbe, G. Adam, A. Pivrikas, A. M. Ramil, E. Birckner, V. Cimrova, H. Hoppe, and N. S. Sariciftci, J. Mater. Chem. **20**, 9726 (2010).

[12]S. Saebø, J. Almlöf, J. E. Boggs, and J. G. Stark, J. Mol. Struct.: TEOCHEM **200**, 361 (1989).

[13]M. Levitus, K. Schmieder, H. Ricks, K. D. Shimizu, U. H. F. Bunz, and M. A. Garcia-Garibay, J. Am. Chem. Soc. **123**, 4259 (2001).

[14]D. A. M. Egbe, B. Carbonnier, E. Birckner, and U.-W. Grummt, Prog. Polym. Sci. **34**, 1023 (2009).

[15]A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[16]J. C. Blakesley, M. Schubert, R. Steyrleuthner, Z. Chen, A. Facchetti, and D. Neher, Appl. Phys. Lett. **99**, 183310 (2011).

[17]S. Rathgeber, D. Bastos de Toledo, E. Birckner, H. Hoppe, and D. A. M. Egbe, Macromolecules **43**, 306 (2010).

[18]A. J. Campbell, D. D. C. Bradley, and H. Antoniadis, Appl. Phys. Lett. **79**, 2133 (2001).

[19]A. J. Campbell, D. D. C. Bradley, and D. G. Lidzey, J. Appl. Phys. **82**, 6326 (1997).

[20]H. Scher and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975).

[21]H. Bässler, Phys. Status Solidi B **175**, 15 (1993).

[22]P. E. Parris, D. H. Dunlap, and V. M. Kenkre, Phys. Status Solidi B **218**, 47 (2000).