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Published in:
Journal of Applied Physics

DOI:
[10.1063/1.2938057](https://doi.org/10.1063/1.2938057)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Parshin, M. A., Ollevier, J., Van der Auweraer, M., de Kok, M. M., Nicolai, H. T., Hof, A. J., & Blom, P. W. M. (2008). Hole transport in blue and white emitting polymers. *Journal of Applied Physics*, 103(11), 113711-1 - 113711-7. [113711]. <https://doi.org/10.1063/1.2938057>

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Hole transport in blue and white emitting polymers

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(Received 16 November 2007; accepted 4 April 2008; published online 11 June 2008)

Hole transport in a blue emitting polyspirobifluorene polymer and in a white emitting polymer consisting of a polyspirobifluorene backbone and two dyes (green and red) was studied. The hole mobility was measured using the time-of-flight method as a function of the electric field and temperature in the range 10^5 – 10^6 V/cm and 285–335 K, respectively. The observed temperature and electric field dependence of the hole mobility was analyzed in the framework of the Bässler disorder model. Also, steady-state current-voltage characteristics were measured over a wide range of electric fields and temperatures and the hole mobility was determined. Our measurements have shown that the hole mobility in the white emitting polymer is the same as in the blue emitting polymer. The performed disorder model analysis gives the same values for the effective energetic disorder (115 meV) and for the positional disorder (1.85) for both polymers. Therefore, we have concluded that the added green and red dyes do not act as hole traps as they have no influence on the hole mobility. It can therefore be concluded that their highest occupied molecular orbital (HOMO) levels are aligned with the HOMO level of the polyspirobifluorene backbone.

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I. INTRODUCTION

Organic light-emitting diodes (OLEDs) are of great interest because they can be used in new low-cost high-efficiency displays (including flexible displays) and for solid-state lighting.^{1,2} There are two classes of materials used in OLEDs: small molecules and polymers. Semiconducting polymers have an advantage in comparison with small molecular weight organic materials due to a simpler manufacturing process. Diodes of such type can be easily fabricated by solution processing the light-emitting polymer onto the indium tin oxide (ITO)-coated glass at room temperature.

Polyfluorenes are known as an important class of semiconducting light-emitting polymers.³ They are efficient blue emitters. Moreover, they can be used as a host material to achieve white emission by blending with other polymers⁴ or by doping with phosphorescent dyes⁵ due to effective energy transfer to green and red emitters. Therefore, they are promising materials for the development of the new efficient white OLEDs that can be used for lighting.

One of the important parameters in OLEDs is the charge carrier mobility in light-emitting organic layers, because it determines the limiting current, the charge carrier balance, and as a consequence, the efficiency of OLEDs. The hole transport in the polyspirobifluorene homopolymer and copolymer was studied by Laquai *et al.*⁶ Their measurements have shown nondispersive charge transport in both polymers. However, the incorporation of 10% of a triarylamine-biphenyl comonomer in polyspirobifluorene homopolymer leads to a substantial increase of the energetic and positional

disorder, and as a result, to a decrease of the hole mobility. The zero-field hole mobility at room temperature of the spirohomopolymer was found to be about 2×10^{-6} cm²/V s, whereas the copolymer has showed a considerably lower hole mobility of 6×10^{-8} cm²/V s.

In this work we present the hole transport study in two polyspirobifluorene copolymers: the first one is analogous to the polyspirobifluorene copolymer studied in Ref. 6, and the second one is a polyspirobifluorene copolymer containing a small amount of red and green dyes and emitting white light. The aim is to investigate how charge carrier transport will change with the incorporation of the dyes.

II. EXPERIMENTAL

The polymers studied in this work were provided by Merck KGaA and developed in the framework of the European project OLLA. The blue emitting polymer is analogous to polyspirobifluorene-triarylamine copolymer described in Ref. 6 with a slightly modified structure of the polyspirobifluorene backbone. The white emitting copolymer is made of the blue backbone, chemically doped with two dyes: green and red, with a molar content of 0.1 and 0.02%, respectively.^{7,8} The green and red emitting chromophores were copolymerized into the polymer chain. The structures of the comonomers and the compositions of the blue and white emitting polymers are presented on Fig. 1. Films for time-of-flight (TOF) measurements were spincoated at 900 and 1050 rpm onto cleaned indium tin oxide (ITO) substrates from toluene solutions, using concentrations of 5 and 4 wt % for the blue and for the white emitting polymer, respectively. The film thickness was 1.25 μ m. Then semitransparent alu-

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FIG. 1. Chemical structure of the blue and white emitting polyspirobifluorene copolymers studied in this work. The compositions are $m=50\%$, $n=40\%$, and $o=10\%$ for the blue emitting polymer, and $m=50\%$, $n=39.88\%$, $o=10\%$, $p=0.1\%$, and $q=0.02\%$ for the white one.

minum electrodes (20 nm) were thermally evaporated through a shadow mask at a pressure of 10^{-6} mbar.

For the TOF measurements a nitrogen laser with a wavelength of 337 nm and a pulse duration of 4 ns was used. Excitation occurred through the positive Al top electrode and the current transient was measured from the bottom ITO electrode with a LeCroy 9400A digital oscilloscope triggered by the laser pulse. The resistance-capacitance time of the measurement circuit was chosen more than 50 times shorter than the transit time. The excitation intensity was regulated by two polarizers. The total charge of the photocarriers was always less than 10% of the capacitor charge to avoid space-charge effects. The sample was mounted in a vacuum chamber with a quartz window. The temperature in the vacuum chamber is regulated by using a flow-water thermostat connected to the back of the chamber. The temperature of the sample was measured by a thermocouple with an accuracy of 0.5 K.

Absorption spectra in thin films of the blue and white emitting polymers were measured with a Lambda 950 UV-vis spectrometer in the range from 190 to 780 nm. Polymer films of 80 nm were spin-coated on quartz substrates from a 10 mg/ml toluene solution. The absorption spectra are presented in Fig. 2. One can see that they are almost identical and that the absorption is determined by the blue backbone. The absorption coefficients at the excitation wavelength of 337 nm are $1.0 \times 10^5 \text{ cm}^{-1}$ in the blue emitting polymer and $9.6 \times 10^4 \text{ cm}^{-1}$ in the white emitting polymer. It means that the width of an optically generated charge sheet for the TOF measurements is about 100 nm, which is much less than the film thickness.

For the study of the hole mobility from space-charge-limited current-voltage measurements, a LED structure with a thin film of the blue or white emitting polymer was used. To obtain the ohmic injecting contact for holes, patterned

ITO substrates were precoated with a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). Subsequently the polymer was spin-coated from a toluene solution in a nitrogen atmosphere. The thickness of the polymer film was 150 and 130 nm for the blue and for the white emitting polymer, respectively. To fabricate hole-only devices, a high work function material such as palladium was used as a cathode. Palladium top contacts were deposited by thermal evaporation through a shadow mask at a pressure of 10^{-6} mbar.

Steady-state current-voltage characteristics were measured with a computer-controlled Keithley source-measure-unit 237. The samples were mounted in the homemade nitrogen cryostat. The results of the measurements were independent of the scanning rate, indicating that deep trapping is not significant.

FIG. 2. Absorption spectra in thin films (80 nm) of the blue (solid line) and white (dash line) emitting polymers.

FIG. 3. Transient photocurrent signals at room temperature: (a) for the blue emitting polymer; (b) for the white emitting polymer. The electric field was 7.2×10^5 V/cm. Insets show double-logarithmic plots of the photocurrents (the transit time is determined from the intersection point of the two asymptotes).

III. RESULTS AND DISCUSSION

Transient photocurrent signals for holes in blue and white emitting polymers at room temperature and for an electric field 7.2×10^5 V/cm are shown in Fig. 3. Both transient photocurrents have a well-defined plateau on a double-logarithmic plot and show a well-defined deflection point on a linear plot indicating the nondispersive hole transport. To increase the signal to noise ratio, five transients were averaged. The transit time was determined from the intersection point of the two asymptotes in the double-logarithmic plot of the transient photocurrent (as shown in the insets in Fig. 3). One can see that the shapes of the transient photocurrents for blue and white emitting polymers are very similar. Also, the transit times are almost the same for both polymers. The hole mobility was calculated using

$$\mu = \frac{d}{t_{tr}E}, \quad (1)$$

where d is the film thickness, t_{tr} is the transit time, and E is the applied electric field.

To obtain detailed information concerning the hole transport in blue and white emitting polymers, the hole mobilities were measured as a function of electric field and temperature in the range 10^5 – 10^6 V/cm and 285–335 K, respectively. Figure 4 presents the field dependencies of the hole mobility

FIG. 4. The field dependence of the hole mobility at different temperatures (semilogarithmic plot): (a) in the blue emitting polymer; (b) in the white emitting polymer. Solid lines show linear fits to the Poole-Frenkel law for different temperatures.

in the blue and white emitting polymers at different temperatures. The field dependence of the mobility could be fitted to Poole-Frenkel-type behavior,

$$\ln \mu = \ln \mu_0 + \beta \sqrt{E}, \quad (2)$$

where μ_0 increases and β decreases upon increasing the temperature. The solid lines in Fig. 4 show linear fits to the Poole-Frenkel-type plots. The correlation factor (R) for these fits varies from 0.991 to 0.998 for the blue emitting polymer and from 0.986 to 0.997 for the white emitting polymer. It is remarkable that the hole mobility and its field dependence were almost identical in the blue and white emitting polymers at different temperatures.

A small sigmoidal deviation from Poole-Frenkel-type behavior at temperatures above room temperature is observed. This deviation is connected with a cusp in transient photocurrents developing at temperatures above room temperature. The cusp was more pronounced at lower electric fields and smoothed out at higher fields. Due to the cusp a small overestimation of the mobility at lower electric fields could be possible, as the position of the intersection point of the asymptotes in a double-logarithmic plot of transient photocurrents with the cusp is shifted to shorter times. A similar cusp was also observed in the blue emitting polyspirobifluorene-triarylamine copolymer, analogous to

our blue one⁶ and in polyspirobifluorene-anthracene copolymer.⁹ In the last polymer a similar sigmoidal deviation from Poole-Frenkel-type behavior at temperatures 323 and 343 K was observed. The origin of the cusp was discussed in the literature.^{9–11} It was shown that the cusp is an intrinsic feature of the charge carrier transport within a disordered distribution of transport sites.

The observed field and temperature dependence of the mobility were analyzed in the framework of the Gaussian disorder model developed by Bässler *et al.*,^{12,13}

$$\mu = \mu_{00} \exp \left[- \left(\frac{2\sigma}{3kT} \right)^2 \right] \exp \left[C \sqrt{E} \left(\left(\frac{\sigma}{kT} \right)^2 - \Sigma^2 \right) \right], \quad (3)$$

where μ_{00} is the mobility extrapolated to zero field and infinite temperature, σ is the energetic disorder parameter (describes the spread of energy levels associated with transport), Σ is the positional disorder parameter describing the fluctuation of intersite distances and coupling between sites, and C is an empirical constant depending on the hopping distance. The main idea of this model is that charge transport occurs via hopping through a manifold of localized states with superimposed energetic and positional disorder. It assumes that the distribution of site energies and distances is Gaussian and the jump rates are described by the Miller-Abrahams expression.¹⁴ The Gaussian disorder model was developed for pure amorphous organic materials, but can be applied formally for doped materials.¹⁵ In the last case the doping leads to the appearance of extrinsic traps if the highest occupied molecular orbital (HOMO) levels of dopant molecules are not aligned with the HOMO level of the host polymer. Monte Carlo simulations have shown¹⁵ that the existence of extrinsic traps can be phenomenologically accounted for by the introduction of an effective width of the Gaussian density of states (DOS) in the disorder model. This effective width σ_{eff} replaces the original width σ of Gaussian DOS for trap-free system. Its square increases linearly with the average trap depth and logarithmically with trap concentration.

As one can see from Eq. (3), the key parameters of the disorder model σ and Σ can be derived from the field and temperature dependencies of the mobility. From the fits presented in Fig. 4, we have obtained values for the zero-field hole mobility (μ_0) and the slope β of the field dependence of the hole mobility [see Eq. (2)] for different temperatures. Then, the logarithm of the zero-field mobility ($\ln \mu_0$) was plotted as a function of $(1/T)^2$. Figure 5 presents these plots for blue and white emitting polymers. According to Eq. (3), the energetic disorder parameter σ and the mobility prefactor μ_{00} can be determined from the linear fit to this plot. This analysis gives the same values for the energetic disorder parameter $\sigma=115$ meV and the mobility prefactor $\mu_{00}=1.1 \times 10^{-3}$ cm²/V s for both polymers. Also, we have fitted the logarithm of the zero-field mobility to an Arrhenius plot $(1/T)$ and found that the linear fits are marginally worse than the fits presented in Fig. 5. The correlation factors (R) for Arrhenius and Gaussian fits were, respectively, 0.986 and 0.989 for the blue emitting polymer, 0.989 and 0.992 for the white emitting polymer. To determine positional disorder Σ and parameter C , the slope β of the Poole-Frenkel field dependence was plotted versus $(\sigma/kT)^2$. Table I summarizes all

FIG. 5. The disorder model analysis of the hole mobility in blue and white emitting polymers: the logarithm of the zero field mobility ($\ln \mu_0$, μ_0 in cm²/V s) vs $(1/T)^2$. Solid and dashed lines show linear fits for the experimental data for the blue and for the white emitting polymer, respectively.

the parameters obtained from the disorder model analysis. For a comparison, we pointed out in the last row the results obtained in Ref. 6 for the polyspirobifluorene-triarylamine copolymer analogous to our blue emitting polymer.

One can see that the disorder model parameters are almost the same for both polymers studied. Moreover, the energetic disorder and the positional disorder parameters are very close to the values obtained by Laquai *et al.*⁶ for the polyspirobifluorene-triarylamine copolymer, analogous to our blue emitting one. However, the mobility prefactor μ_{00} is 7 times higher for our polymers. Also, the constant C , being proportional to the square root of the hopping distance, is 40% smaller. There are two main reasons for the observed difference: the first one is a slightly modified structure of the blue emitting polymer (see Fig. 1), and the second one is the influence of preparation conditions on the film morphology. The observed increase in the mobility prefactor μ_{00} can be related to an increase of the effective overlap of wave functions of neighboring molecules taking into account the structure difference of the blue emitting polymer. Also, the reduced empirical constant C indicates the shorter hopping distance. According to Eq. (3), the shorter hopping distance leads to a smoother field dependence of the hole mobility. Indeed, room-temperature mobilities in our polymers at high electric fields ($E=5 \times 10^5$ V/cm) were 1.4×10^{-6} cm²/V s, which is two times lower than the value measured in Ref. 6 in the blue emitting polyspirobifluorene-triarylamine copolymer: 2.7×10^{-6} cm²/V s. However, the zero-field mobility

TABLE I. Disorder model parameters for blue and white emitting polymers and for the polyspirobifluorene-triarylamine copolymer from Ref. 6, analogous to our blue emitting polymer.

Polymer	μ_{00} (cm ² /V s)	σ (eV)	C (cm/V) ^{1/2}	Σ
Blue	1.1×10^{-3}	0.115	2.15×10^{-4}	1.88
White	1.1×10^{-3}	0.115	2.01×10^{-4}	1.83
Spiroco-TAD (Ref. 6)	1.5×10^{-4}	0.107	3.60×10^{-4}	1.8

at room temperature in our polymers was higher than that in the previous study: 1.3×10^{-7} and 6.2×10^{-8} cm²/V s, respectively.

The same value of the energetic disorder parameter obtained for the blue and white emitting polymers demonstrates that the green and red chromophores copolymerized into the blue emitting backbone do not create additional traps for holes. It means that the HOMO levels of the red and green comonomers are aligned with or below that of the blue emitting backbone. Also, the positional disorder and the hopping distance do not change. The equal values of the empirical constant C for the blue and white emitting polymers demonstrate that the hopping distance for holes is the same in both polymers. The concentration of the green and red chromophores is about 0.1%. It is not sufficient to allow hopping via dyes. Therefore, we conclude that the hole transport in the white emitting polymer occurs via the same way as in the blue emitting polymer: along blue backbone chains and hopping between adjacent chains when there is sufficient overlap of wave functions.

As shown in a comparative study of hole transport in polyspirobifluorene homopolymer and copolymer,⁶ the incorporation of a triarylamine-biphenyl comonomer in polyspirobifluorene homopolymer increases the energetic disorder from 0.086 to 0.107 eV and the positional disorder from 0 to 1.8. As a result, the hole mobility at room temperature decreases more than one order of magnitude. However, it leads to an increase in efficiency of polymer LEDs from 1.6 to 3.8 cd/A due to the enhanced charge carrier balance.⁶ Also, the triarylamine-biphenyl moiety is necessary for increased stability.

Another important question is the influence of the dyes on electron transport. From the presented analysis of the hole transport we come to the conclusion that the HOMO levels of the red and green chromophores are aligned with or below that of the blue emitting backbone. Hence, taking into account that they have a smaller band gap than that of the blue backbone, their lowest unoccupied molecular orbital (LUMO) levels will be much below the blue backbone's LUMO level. Therefore, they are expected to act as electron traps. TOF measurements for electrons showed very dispersive transient photocurrents in both polymers,¹⁶ which is characteristic of the trap-controlled transport. Furthermore, high electric fields were needed to extract photogenerated electrons that indicate the presence of deep traps already for the blue emitting polymer. The amount of extracted charge at low electric fields (2×10^5 V/cm) was about 10% of the photogenerated charge in both polymers. However, at high electric fields (1×10^6 V/cm) this amount was 50% in the blue emitting polymer and still only 10% in the white emitting polymer. This could be related to the larger concentration of deep electron traps in the white emitting polymer, which are associated with the red and green emitting chromophores. Electrons trapped on these traps cannot be released on an experimental time scale even at high electric fields. The room-temperature mobility of the untrapped (mobile) electrons at high electric fields (7×10^5 – 1×10^6 V/cm) in the blue emitting polymer was 2 times higher than the hole mobility. In the white emitting polymer

FIG. 6. Current-voltage characteristics for hole-only devices at different temperatures (semilogarithmic plot): (a) for the blue emitting polymer; (b) for the white emitting polymer. Solid lines show fits according to Eq. (4) for different temperatures.

the room-temperature mobility of mobile electrons at high electric fields was about 40% higher than the hole mobility. This indicates that in the white emitting polymer the red and green emitting chromophores increase the deep trapping without influence on the mobility of the mobile electrons.

Steady-state current-voltage (I - V) characteristics at different temperatures for hole-only devices with the blue and the white emitting polymer are shown in Fig. 6. To analyze the I - V curves in the framework of a space-charge-limited current (SCLC) density, a built-in voltage of 1 V should be subtracted from the applied voltage. The value of 1 V was higher than the value expected from the difference between anode and cathode work functions. Let us discuss this important issue. The built-in voltage (V_{bi}), being governed by the difference in work functions of the anode and cathode, can be directly determined from the I - V measurements: for ap-

TABLE II. Hole mobility parameters at room temperature for blue and white emitting polymers obtained from the TOF measurements and the steady-state current-voltage (I - V) measurements.

Polymer	$\mu_0(\text{TOF})$ ($\text{cm}^2/\text{V s}$)	$\mu_0(I-V)$ ($\text{cm}^2/\text{V s}$)	$\beta(\text{TOF})$ ($\text{cm}/\text{V})^{1/2}$	$\beta(I-V)$ ($\text{cm}/\text{V})^{1/2}$
Blue	1.3×10^{-7}	2×10^{-7}	3.45×10^{-3}	3×10^{-3}
White	1.3×10^{-7}	8×10^{-8}	3.45×10^{-3}	3×10^{-3}

plied voltages lower than V_{bi} the electric field in the device is in the opposite direction of the current, and the current is dominated by diffusion. Such a diffusion-dominated current is characterized by an exponential increase with voltage. For voltages larger than V_{bi} the current is space-charge limited and dominated by drift. The crossover from a diffusion-limited current to a space-charge-limited current is therefore a good measure for the V_{bi} . In a I - V measurement the built-in voltage is represented by the voltage at which the current starts to deviate from the exponential shape.¹⁷ Using this method resulted in a measured built-in voltage of approximately 1.0 V, with a typical error of ± 0.05 V. A variation of 0.1 V in the built-in voltage does not affect the parameters for the mobility that we obtain from fitting the I - V curves. From the difference in work functions between PEDOT:PSS (≈ 5.1 eV) and palladium (≈ 4.6 eV), one would expect a built-in voltage of only approximately 0.5 V. The fact that the measured built-in voltage is higher could have a number of causes, such as charge trapping at the Pd/polymer interface.

At low voltages, the current shows a quadratic dependence with voltage characteristic of SCLC. At higher voltages it is observed that the current increase is steeper, indicating the mobility enhancement. It can be attributed to a field dependence of the mobility¹⁸ or to a carrier density dependence of the mobility.¹⁹ To compare the hole mobility in our polymers, we assume in the analysis of I - V curves a field-dependent mobility. In this case, SCLC can be approximated by the equation²⁰

$$J = \frac{9}{8} \epsilon_0 \epsilon \frac{V^2}{d^3} \mu_0 \exp \left[\beta \sqrt{\frac{V}{d}} \right], \quad (4)$$

where ϵ is the dielectric constant of the polymer ($\epsilon \approx 3$), μ_0 is the zero-field hole mobility, β is the field activation factor, d is the film thickness, and V is the applied voltage. We have fitted the measured current densities for our polymers using Eq. (4) (solid lines in Fig. 6).

Table II presents the comparison between the hole mobility and its field dependence obtained from the TOF measurements and the I - V measurements for $T=295$ K. The values of the zero-field mobility μ_0 and the slope β of the Poole-Frenkel plot [Eq. (2)] determined from I - V measurements at room temperature are in accordance with the TOF values for both studied polymers. The observed accordance between TOF and I - V hole mobilities indicates the nondispersive hole transport which is independent of the sample thickness at room temperature. The sample thicknesses were 1250 and 130–150 nm for TOF and I - V measurements, respectively.

FIG. 7. Comparison of the zero-field hole mobilities ($\ln \mu_0$, μ_0 in $\text{cm}^2/\text{V s}$) obtained from the TOF (circles) and I - V (diamonds) measurements for the blue emitting polymer. Solid and dotted lines show linear fits for the dispersive and nondispersive transport regimes. The arrow indicates the transition from nondispersive to dispersive transport.

Figure 7 presents zero-field hole mobilities ($\ln \mu_0$) versus $(1/T^2)$ obtained from the TOF and I - V measurements for the blue emitting polymer. A transition from the nondispersive to the dispersive hole transport associated with the change of slope in this dependence is observed at about 250 K. Studies of the transition from nondispersive to dispersive transport combining both Monte Carlo simulation and experiment^{21,22} give a simple relation to calculate the critical temperature (T_c) when this transition occurs,

$$\left(\frac{\sigma}{kT_c} \right)^2 = 44.8 + 6.7 \log d, \quad (5)$$

where σ is the energetic disorder and d is the film thickness in centimeters.

Using Eq. (5), we calculate the critical temperature for the blue emitting polymer: $T_c = 309$ K for the film thickness of 1.25 μm , although for samples with the thickness of 130–150 nm this critical temperature should be higher. According to this value the transition from the nondispersive to dispersive hole transport should be observed already at 309 K. However, we did not observe the dispersive character of the transient photocurrent in the temperature range 285–335 K. Also, Fig. 5 does not show any change in the $1/T^2$ dependence of the zero-field mobility ($\ln \mu_0$) at temperatures below 309 K. Moreover, the hole mobilities derived from I - V characteristics in the thin sample (150 nm) are very close to the values obtained from TOF measurements, indicating the nondispersive transport at room temperature. The experimental transition temperature (251 K) shown in Fig. 7 is much lower than the calculated value of T_c . The main reason for this discrepancy is that the positional disorder is not taken into account in Eq. (5). As it was mentioned,²¹ the positional disorder leads to an additional carrier relaxation mechanism, which should be taken into account to derive the nondispersive to dispersive charge transport transition. An agreement between theory and experiment was observed only for materials with a very weak positional disorder. Also, in Ref. 6 a

good agreement was observed for a polyspirobifluorene homopolymer with the positional disorder equal to zero. However, for the polyspirobifluorene-triarylamine copolymer analogous to our blue emitting polymer, the same discrepancy was observed.

IV. CONCLUSIONS

Hole transport in white and blue light-emitting polymers was studied using TOF and *I-V* measurements. White emission is achieved by the chemical doping of the blue emitting polyspirobifluorene-triarylamine copolymer with two dyes: green and red, with a molar content of 0.1%. Our measurements have shown the nondispersive character of hole transport at temperatures above 250 K. The hole mobility was the same for the white and blue emitting polymers: electric field dependencies at different temperatures are almost identical. Disorder model analysis gives the same values of the energetic and positional disorder for the studied polymers: $\sigma = 115$ meV, and $\Sigma = 1.83 - 1.88$. These data demonstrate that the added green and red emitters in the white emitting polymer are not involved in hole trapping. We conclude that the HOMO levels of the red and green emitting comonomers are aligned with or below that of the blue emitting backbone. Taking into account that the red and green emitting comonomers are characterized by a smaller band gap, they act as deep electron traps. This was confirmed by the recent TOF measurements.

ACKNOWLEDGMENTS

The authors are grateful to Merck KGaA for the polymer synthesis. This work has been done in the framework of the IP OLLA (EU) (Organic LEDs for Light Applications) and

the project GOA 2006/2 of the research council of K.U. Leuven.

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