Electro-optical properties of poly(1-(difluorophenyl)-2-(4-alkylcyclohexyl phenyl)acetylene) organic light-emitting diodes

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Abstract

For organic light-emitting diodes (OLEDs) applications, we have investigated novel polymers, using substituted polyacetylenes (PA), poly(1-(fluorophenyl)-2-(alkylcyclohexylphenyl)acetylene) (PDPA-nF) ($n=1$ or $n=2$) which exhibit air stability, better solubility in common organic solvent and higher luminescence than polyacetylene. In this study, we have used poly[(1-(3,4-difluorophenyl)-2-(4-pentylcyclohexylphenyl) acetylene)] (PDPA-2F) as an emitter in OLEDs and their performance was determined by measuring the current–voltage–luminance characteristic. The devices have a maximum brightness of 827 candela (cd)/m^2 at 12 V and a maximum current efficiency of 0.78 cd/A at 9 V with a maximum luminescence at 536 nm. Influence of the metal electrode on the charge injection was studied using several cathode configurations (Ca, Al and Au) for the devices. Furthermore, the charge injection and transport processes were correlated to the presence of traps inside the polymer, determined by deep level transient spectroscopy (DLTS).
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1. Introduction

Conjugated polymers have been studied since the early 60s. The discovery of high electrical conductivity in doped polyacetylene (PA) in 1977 [1] has lead to the investigation of new field of conjugated polymers. Although PA shows a very high conductivity by doping, it has rarely been used as a polymer based electronic devices, because of the insolubility, infusibility and instability in air of non-substituted polyacetylene. In addition, this polymer exhibits almost no photoluminescence (PL) in the visible region.

Recently, several investigations [2–5] have succeeded in the synthesis of a series of substituted polyacetylene derivatives, which are stable in air and soluble in organic solvents. In addition, these polymers show luminescence properties in the visible wavelength region. The most commonly substituents used in these derivatives are the alkyl and phenyl groups allowing light emission in a wide range of colors, from red to blue. These derivatives polymers are used as an active material

in polymer light-emitting diodes (PLED) [6]. Among these derivatives, the poly-diphenylacetylene (PDPA) systems made into single-layer devices which exhibit a stable green light emission, but with a weak intensity [3].

In this work, we have investigated the electro-optical properties of a polyacetylene derivative: poly[(1-(3,4-difluorophenyl)-2-(4-pentylcyclohexylphenyl)acetylene)] (PDPA-2F). The characteristics of organic light-emitting diodes using this polymer were measured and analysed. Furthermore, as traps in the polymer material play a key role in charge transport process, it is important to evaluate trap parameters in the studied devices in order to control their electrical and optical performance [7]. For this purpose, the charge-based deep-level transient spectroscopy (Q-DLTS) has been applied to investigate the trap states in PDPA-2F.

2. Experimental

Poly[(1-(3,4-difluorophenyl)-2-(4-pentylcyclohexylphenyl) acetylene)] (PDPA-2F) was synthesized following the method described elsewhere [8]. The polymer structure is shown in the inset of Fig. 1. The polymer powder is soluble at room

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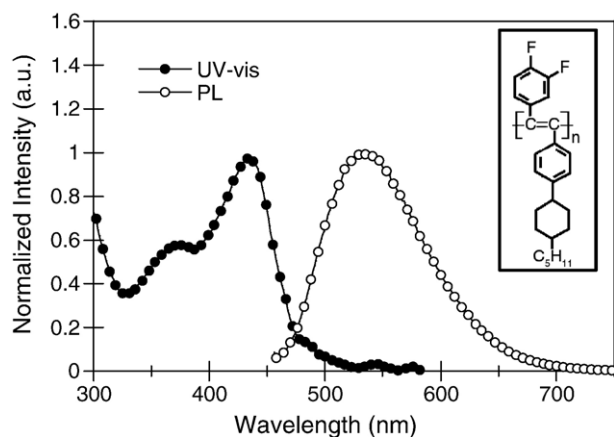 *E-mail address:* nguyen@cnrs-imn.fr (T.-P. Nguyen).

Fig. 1. UV–VIS and PL spectra of PDPA-2F at $T=300$ K. Inset is the chemical structure of PDPA-2F.

Fig. 2. Band energy diagram of a ITO/PEDOT:PSS/PDPA-2F/Ca/Al device.

temperature, in common organic solvents such as chloroform, toluene, and xylene.

For the device fabrication, an ITO-coated glass substrate was used as anode, which was pre-cleaned and treated with UV ozone before use. A polyethylene dioxythiophene:polystyrene sulfonate (PEDOT:PSS) layer of thickness 40–50 nm was spin-coated on the ITO substrate, which was then annealed at 150 °C under a vacuum for 1 h. PDPA-2F powder was dissolved in toluene (6 mg/1 mL) and polymer films of 70–80 nm thick were deposited by spin-coating over the PEDOT:PSS layer. Final structures ITO/PEDOT:PSS/PDPA-2F/Ca/Al were obtained by deposition under high vacuum conditions of a calcium layer (~35 nm) over the polymer film, followed by an aluminum one (~100 nm) serving as a protective layer of the cathode.

The UV–Visible absorption and the photoluminescence spectra were measured from an HP 8453 spectrometer and a Hitachi F4500 luminescence spectrometer, respectively. Current–voltage characteristics of the diodes were measured using a Keithley 2400 source meter, and brightness and efficiency of the devices by a Photo Research PR650 spectrometer. Trap parameters in devices were investigated by mean of charge-based deep-level transient spectroscopy (Q-DLTS). An auto-mated system ASMEC-02, supplied by InOmTech Inc. was utilized to perform Q-DLTS measurements with the sample placed under vacuum in the 210–315 K temperature range.

3. Results and discussion

Fig. 1 shows the UV–Visible and PL spectra of PDPA-2F thin films. The absorption spectrum has two maximum peaks at 365 and 435 nm, similar to the results previously obtained for poly[1-(p-n-butylphenyl)-2-phenylacetylene (PDPA-nBu) [9]. The PL spectrum of PDPA-2F exhibits high PL intensity at 536 nm with a green–yellow light.

To determine the energy levels of electronic states, electro-chemical study of the polymer was carried out using Bu_4NBF_4 in acetonitrile. The ionization potential (IP) and bandgap energy (E_g) were calculated from the oxidation onset potential and absorption onset wavelength in the UV–VIS spectra. Fig. 2 shows the band energy diagram of a ITO/PEDOT:PSS/PDPA-2F/Ca/Al structure
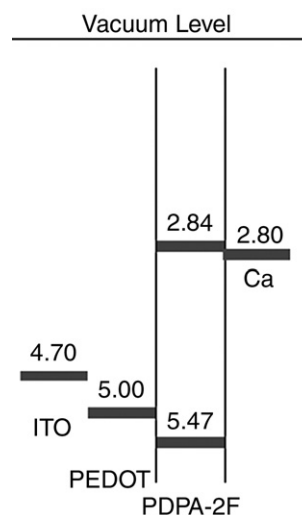
with the energetic position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the polymer. It can be seen that the LUMO level of PDPA-2F (2.84 eV) is close to the cathode (Ca) Fermi level indicating a favorable electron injection into the polymer.

The brightness and efficiency of a two-layer device ITO/PEDOT:PSS/PDPA-2F/Ca/Al are shown in Fig. 3. The device has a maximum brightness of 827 candela (cd)/m^2 at 12 V and a maximum current efficiency of 0.78 cd/A at 9 V with a current density of ~35 mA/cm^2. Compared to previously reported PDPA derivative based devices, the performance of the used diode is better. The coordinates of the electroluminescence spectrum (not shown) determined in the C.I.E. (Commission Internationale de l'Eclairage) diagram are (0.35, 0.54).

For comparison, diodes having a similar structure but with different cathode metals (Au, Al) were also studied. A strong dependence of the current–voltage characteristics (not shown) on the nature of the cathode electrode was observed: the turn-on voltage of diodes increased from Ca (of work function $\psi_{Ca}=2.84$ eV), to Al ($\psi_{Al}=4.3$ eV) and Au ($\psi_{Au}=5.2$ eV). The behavior of the devices is comparable to that observed in poly (2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene) (MEH-
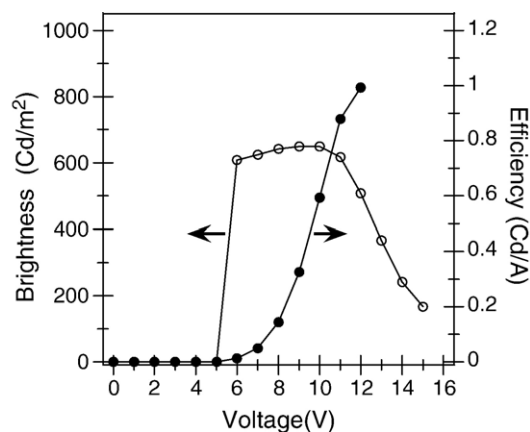

Fig. 3. Brightness and efficiency of a ITO/PEDOT:PSS/PDPA-2F/Ca/Al device.

PPV) based diodes [10], for which an charge carrier tunneling mechanism has been proposed to explain the electrical characteristics. When plotting the $I–V$ characteristics of a ITO/PEDOT:PSS/PDPA-2F/Ca/Al structure, using the logarithmic scale (Fig. 4), we observe that the current presents three distinct regions with different variation behaviors. An ohmic conduction can be considered at low forward applied voltages (region A: $V < 2$ V), and a trap-free charge space limited conduction (SCLC) at high voltages (region C: $V > 5$ V). In-between, the current variation in the intermediate region B can be considered to correspond to trap filling process.

In order to investigate the carrier trapping in devices, we used the charge based deep level transient spectroscopy (Q-DLTS). This technique is similar to the conventional DLTS but the released charge variation is measured instead of the capacitance one. We briefly recall hereafter the description of the technique. It consists of applying a charging voltage ΔV during a short period t_C (charging time) in order to fill the trap centers. Then, the bias is set to zero, and the trapped carriers are thermally released. The related transient charges are recorded at two successive times t_1 and t_2, which defines the rate window by:

$$\tau = (t_2 - t_1)/\ln(t_2/t_1) \qquad (1)$$

The Q-DLTS spectrum is the plot of the discharge $\Delta Q = Q(t_1) - Q(t_2)$ as a function of the rate window τ. Assuming that the transient charge is an exponential function of time and providing a ratio t_1/t_2 constant, it can be demonstrated that the charge variation ΔQ goes through a maximum when the rate window τ matches the relaxation time τ_m of the trap at the measurement temperature T. The thermally released charges from a discrete trap level without re-trapping can be written as [11,12]:

$$Q(t) = Q_0[1 - \exp e_{n(p)}t] \qquad (2)$$

where Q_0 is the initial trapped charges during the filling process and $e_{n(p)}$ is the electron (hole) emission rate given by:

$$e_{n(p)} = \sigma \Gamma_{n(p)} T^2 \exp(-E_A/kT) \qquad (3)$$

σ is the capture cross section, E_A is the activation energy, and $\Gamma_{n(p)}$ is a constant depending on the effect of mass of the carriers.
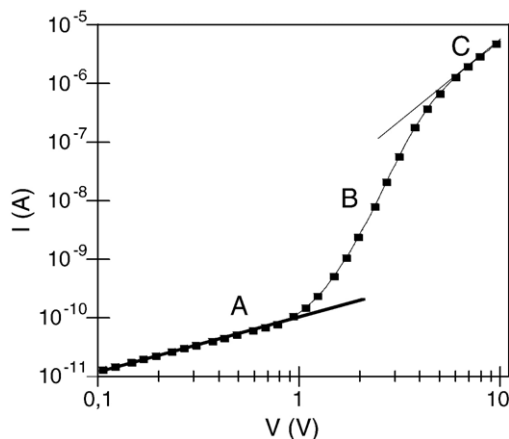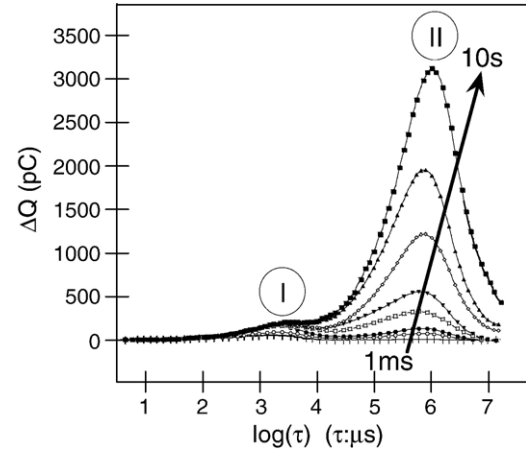

Fig. 5. Q-DLTS spectra measured at 300 K on a ITO/PEDOT:PSS/PDPA-2F/Ca/Al device using an offset $V_0 = 0$ V and a charging voltage $\Delta V = +8$ V for increasing charging times t_C from 1 ms to 10 s.

It can be shown that the spectrum $\Delta Q(\tau)$ goes through a maximum when the window rate t^{-1} matches the trap emission one. Therefore, recording the Q-DLTS spectra as a function of the temperature and from Eq. (3), both σ and E_A can be determined. Furthermore, the trap density N_t can also be evaluated from the measurements of the maximum value ΔQ_M of the Q-DLTS signal [11,12].

By measuring a Q-DLTS spectrum at different temperatures, a set of relaxation time τ_m is obtained. The activation energy E_A and capture cross-section σ are determined from the slope and the intercept of an Arrhenius plot of $\ln(\tau_m^{-1} T^2)$ vs. $1000/T$. The trap density can be obtained from the maximum value of the Q-DLTS spectrum.

The Q-DLTS spectra of a ITO/PEDOT:PSS/PDPA-2F/Ca/Al structure using a pulse of $\Delta V = +8$ V show two distinct peaks, labeled peaks I and II, suggesting that at least two types of traps are present in ITO/PEDOT:PSS/PDPA-2F/Ca/Al structure (Fig. 5). Peak I occurs at $\tau = 2.5$ ms and becomes saturated for
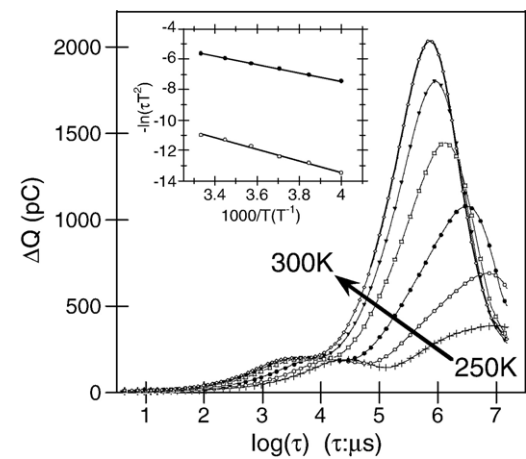

Fig. 4. $I–V$ characteristic at $T = 300$ K of a ITO/PEDOT:PSS/PDPA-2F/Ca/Al device using double logarithmic scale.

Fig. 6. Q-DLTS spectra measured on a ITO/PEDOT:PSS/PDPA-2F/Ca/Al device using an offset $V_0 = 0$ V, a charging time $t_C = 1$ s and a charging voltage $\Delta V = +8$ V for different temperatures in the range 300-250 K. (Inset) Arrhenius plots for type I (●) and type II traps (○).

the charging time values upper 50 ms suggesting that the type I traps are entirely filled. The type II traps have an approximated relaxation time of 800 ms at 300 K and could not be filled even when using the maximum available rate window $\tau_c = 10$ s of the experimental set-up.

The trap parameters were determined by recording the Q-DLTS spectra as function of temperature. Fig. 6 shows the evolution of the spectra in the 250–300 K range for $\Delta V = +8$ V, for peaks I and II, respectively. From the position of the peaks at different temperatures, the Arrhenius curves are plotted in the inset.

For the type I traps, we obtained the following trap parameters: average activation energy $E_{T1} \sim 0.24$ eV, capture cross-section $\sigma_1 \sim 10^{-20}$ cm^2 and trap density $N_{T1} \sim 2 \times 10^{15}$ cm^{-3}. The type II traps are located at $E_{T2} \sim 0.33$ eV from the band edge with a capture cross-section $\sigma_2 \sim 10^{-20}$ cm^2 and a low limit value of density $N_{T2} \sim 1 \times 10^{16}$ cm^{-3}. The trap parameters found in PDPA-2F are comparable to those obtained in poly(phenylene vinylene) (PPV) or its derivatives [13].

It is interesting to consider the energetic level of the type II traps in relation with the electroluminescence spectrum. In fact, using the band diagram of Fig. 2 and considering the trap level, we evaluate the energy difference between the band edge from HOMO (for hole traps) or LUMO (electron traps) to be $\Delta E = 2.63$ eV. This value corresponds fairly to the energy of the PL and EL peak spectra (~ 536 nm), suggesting that the trapping sites would act as emissive recombination centers. Such emissive traps have been already observed in polyfluorene emitting materials, in which defects were supposed to have structural origin, and were introduced to the polymer backbone by photooxidation process [14]. It should be stressed that oxidation process is frequently observed in polymers, leading to the formation of carbonyl or keto groups, which can act as defect sites. We also note that these traps are not entirely filled when using a long charging time (10 s) and their intensity is increasing with the charging voltage (up to $+8$ V in this experiment). The turn-on voltage of the diodes was $V_{to} \sim +5$ V. As the traps continue to be filled when the applied voltage exceeds V_{to}, it can be assumed that these traps are electron-like traps, which would be explained by the oxygen contamination of the polymer film. As for the type I traps, their nature is not known from the present study, and further investigations are necessary to clearly identify the trap types in the studied polymer.

4. Conclusion

The performance of PDPA-2F emitting materials has been examined by optical and electrical characterizations of ITO/PEDOT:PSS/PDPA-2F/Ca/Al devices. Good efficiency combined with high luminance makes this polymer a promising candidate material for light-emitting devices.

Using the charge based deep level transient spectroscopy, we have determined the trap states in the polymers, which occupy two distinct energy levels, at $E_{T1} = 0.24$ eV and $E_{T2} = 0.33$ eV from the edge of HOMO or LUMO energy, respectively. The traps in E_{T2} level are tentatively assigned to electron-like traps, which result from oxidation process and act as emissive recombination centers in the polymer film. The nature of the traps in E_{T1} level could not be clearly identified by the present study.

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