Absorption cross-sections of hole polarons in glassy and β-phase polyfluorene

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ABSTRACT

Absorption induced by electrochemically injected holes is studied in poly-9,9-dioctylfluorene (PFO) films. Injected charges form positive polarons which are delocalised over four fluorene units in the glassy phase and about seven fluorene units in its β-phase. Polaron absorption cross-sections at the 640 nm peak are similar to the published values of chemically reduced oligofluorenes in solution. The absorption cross-section of polaron in the β-phase at 470 nm is about eight times smaller than the stimulated emission cross-section derived from published data. This indicates that β-phase-rich PFO is an attractive candidate for a light-emitting layer in double-heterostructure organic laser diodes.

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1. Introduction

The optical properties of charged excitations are important for understanding organic semiconductor photophysics. The injection of electric charge into organic materials polarizes the surroundings and changes the bond lengths around it, such an excitation is defined as a charged polaron. Absorption of light and fluorescence quenching by polarons are important issues in the operation of organic optoelectronic devices. It is particularly relevant to the development of electrically pumped lasers. With recent advances in materials properties and optical design the lasing threshold of organic structures under optical pumping is now low enough to enable pumping by inorganic laser diodes [1–3] and LEDs [4] which is promising for fabrication of very sensitive low-cost devices for biosensing and chemosensing [5,6]. However, light absorption by injected charges has been reported to be the major obstacle to electrically pumped lasing [7]. Injected charges can also quench luminescence as they accept energy from excitons by resonant dipole–dipole interactions and this is an important loss mechanism in organic LEDs as well as in lasers. Absorption cross-sections of polarons are not known to the desired accuracy because of the difficulty of quantifying the charge density injected into the film. Previous studies used controlled electrical injection of charges in unipolar devices through contacting electrodes and field-dependent charge mobility measurements to estimate the charge densities which were compared with the values obtained by capacitance–voltage analysis and the two results differed by a factor of three [8,9].

In this letter we adapted electrochemical techniques [10,11] for a controlled oxidation of poly(9,9-dioctylfluorene-2,7-diyl) (PFO) films with different amounts of β-phase which allows us to quantify absorption of hole polarons in glassy and β-phases. Absorption cross-sections obtained from these measurements show very good agreement with the published values of chemically reduced oligofluorenes. We also find that the absorption cross-section of hole polarons in β-phase PFO at 470 nm is about eight times smaller than the stimulated emission cross-section of singlet excitons. Fluorene-based polymers have previously been used to make optically pumped low threshold polymer lasers [1,3,4,12] including structures with charge-injecting electrodes [13,14] and high gain optical amplifiers [15]. Some polyfluorenes show relatively high charge carrier mobility up to 0.06 $cm^2V^{-1}s^{-1}$, as well as high optical gain and may be suitable for electrical pumping [16]. Our results suggest that β-phase-rich PFO could be used as a light-emitting layer in double-heterostructure organic laser diodes.

2. Materials and methods

PFO was purchased from American Dye Source (product ADS129BE). All the solvents (Chloroform, THF, Acetonitrile) were anhydrous grade grade from Aldrich. Tetrabutylammonium tetrafluoroborate (TFB-TBA, electrochemical grade) was from Aldrich. Indium-tin oxide (ITO) covered glass substrates (Delta, 60 S cm^{-1}) were used as working electrodes for the electrochemical characterization of the conjugated polymer. Prior to its use, the ITO glass was cleaned by sonication in an acetone bath. Polymer films were spin-coated from solutions in THF and chloroform (1 mg mL^{-1})

over transparent ITO electrodes. The film thickness was determined using spectral ellipsometry and found l = 30 nm for the films prepared from THF and l = 90 nm for the film prepared from chloroform.

The electrochemical measurements were performed with a Dropsens µStat400 potentiostat–galvanostat. The injected charge was quantified by integrating the oxidation current in PFO film drop-casted on ITO electrode using 5 g of the polymer and assuming a density of polymer film of 1 g cm^{-3}. Absorption spectra were measured with a spectrophotometer Varian Cary 300 and fluorescence spectra with a Jobin–Yvon Fluoromax 2.

The Electrochemically-Induced Absorption (ECIA) spectra presented are the difference between absorption spectra measured at a controlled potential and the reference spectrum at 0.2 V vs ferrocene. Platinum wire was used as a counter-electrode. Silver wire was used as pseudo-reference electrode. The reference electrode was calibrated against ferrocene (Fc).

3. Results and discussion

The charge concentration in the polymer film was measured by integrating the oxidation current in the forward scan of the stabilized voltammogram which is shown in Figure 1. The current shows a rise from 0.6 V, which corresponds to the onset of hole injection into the PFO film. The voltammetric scan was reversed at 1.05 V and the corresponding counter processes were observed. A negative current appears which is related to the de-doping process that finishes at a potential <0.5 V.

Absorption spectra of pristine films used in this study are shown in Figure 2, the peak at 437 nm corresponds to a 0→0 vibronic transition in β phase PFO whereas absorption from both phases overlap at <420 nm. The fraction of repeat units which adopt β phase in spin-coated films from THF and chloroform solutions was determined to be ~33% and ~8% respectively by subtracting the glassy film absorbance shown by dashed lines from the measured absorbance after normalization at 354 nm as described previously [17,18].

Figure 3 shows electrochemically induced absorption (ECIA) spectra in a β-phase-rich PFO film which were obtained by taking a difference of the absorption spectrum with injected charge and the absorption spectrum of a neutral film. At low-doping levels (top panel) two negative absorption bleaching bands appear at 407 and 438 nm that correspond to bleaching of the neutral β phase PFO absorption, which indicates that positive injected charges reside predominantly in the β phase. Concurrently an absorption band appears with a peak at 643 nm and is assigned to charge carrier absorption in the β phase. This band is similar to photoinduced absorption spectra observed in β-phase-rich PFO

Figure 2. Absorption spectra (solid lines) of PFO films deposited from THF with 33% of the β phase (a) and from chloroform with 8% of the β phase (b). Dashed line shows the absorbance of the glassy phase in each film which was subtracted from the total absorbance to estimate the fraction of the repeat units which adopt β phase. This estimation is based on observation that the absorption transition dipole moment of chromophores in glassy and β phase is similar for the same number of repeat units [25].

films [19–22]. The peak at 643 nm and a shoulder at around 590 nm can be attributed to the 0→0 and 0→1 vibronic transitions of charge absorption respectively, and from their amplitude ratio the Huang–Rhys factor for the hole polaron absorption is S = 0.6.

At intermediate doping levels (middle panel in Figure 3) the bleaching of the 438 nm peak saturates at >0.05 charge per fluorene unit indicating that all β phase chromophores are filled with charge and the glassy phase absorption at <420 nm starts to bleach. The growth of a positive band at ~580 nm is also observed and is attributed to charge absorption in the glassy phase.

At high-doping levels (bottom panel in Figure 3) the bleaching of the neutral polymer absorption at <420 nm increases further and indicates that extra charge is injected into the glassy phase. The positive absorption band at 580 nm progressively shifts to shorter wavelengths at >0.22 charges per fluorene unit. This observation is similar to that by Takeda et al. who studied the evolution of the absorption spectra of polyfluorene in solution upon chemical reduction with sodium [23]. They proposed that Coulombic repulsion between adjacent negative polarons in highly doped samples produce a blue shift of absorption due to compression of polarons and estimated the delocalisation length of an electron polaron to be between four and five fluorene repeat units. Zaikowski et al. have shown that polaron delocalisation in long oligofluorenes is also between four and five fluorene repeat units [24]. Our observation of the blue shift of absorption at >0.22 charge per fluorene unit (1 charge injected per 4.5 fluorene unit) suggests that delocalisation of a positive polaron in the
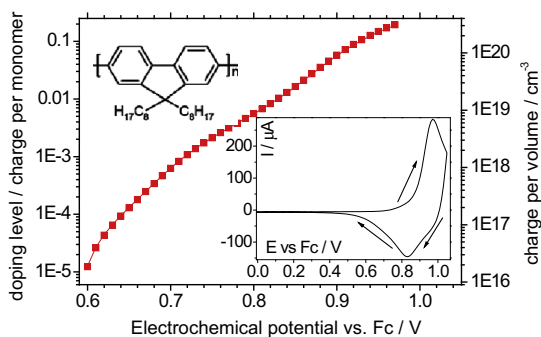

Figure 1. Number of positive charges per fluorene unit *vs* the potential of an ITO/PFO electrode in acetonitrile +0.1 M TFB-TBA. The inset shows the chemical structure of PFO and the cyclic voltammogram.
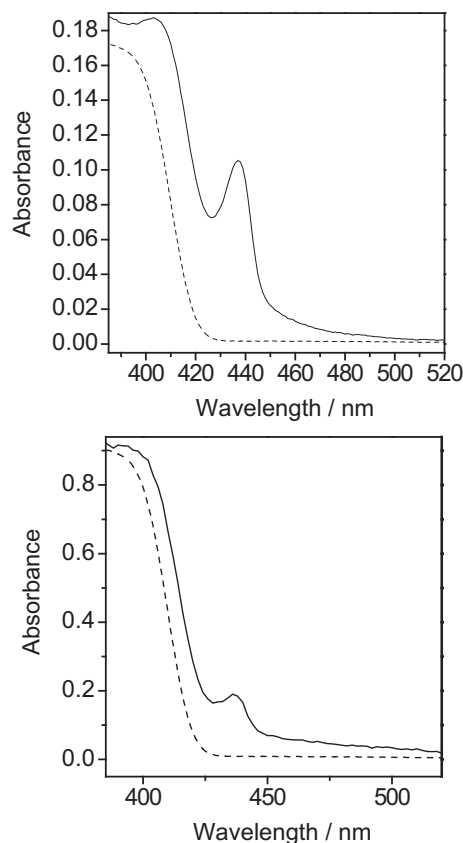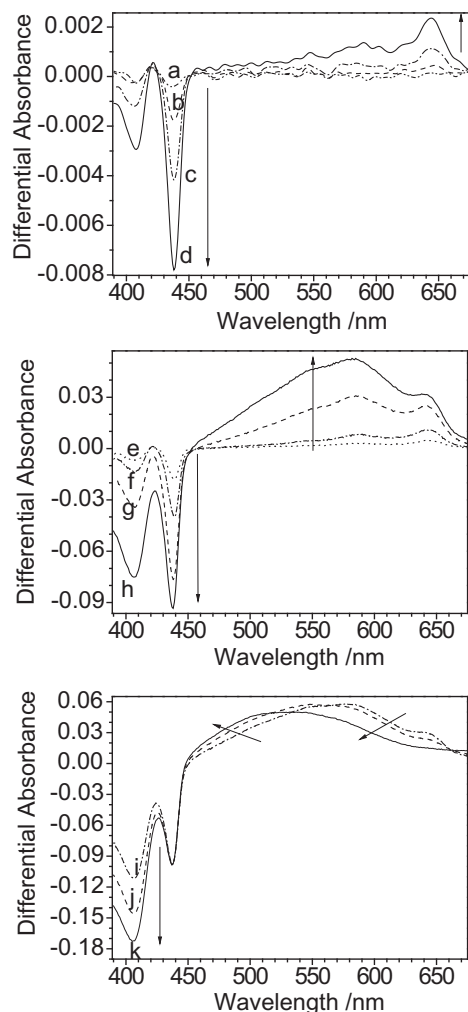
Figure 4. Differential absorption spectrum of electrochemically doped PFO film (33% β phase) at 2.1×10^{-3} charges per monomer (solid line, left axis, note that the negative differential absorption values are inverted for clarity) and the fluorescence spectrum of the same undoped film (dashed line).

tween 0→0 peaks of absorption and fluorescence is zero which indicates that geometrical relaxation between the aromatic ground state structure and the quinoidal structure of the neutral excited state does not change the energy of the β phase chromophore in PFO.

Figure 5 shows a similar experiment performed in a PFO film with a low amount of the β phase (8%). The saturation of the β phase bleach at 438 nm is observed when charge concentration exceeds 0.01 per fluorene unit but the characteristic polaron absorption in the glassy phase is already observed at a half of this concentration. This and is consistent with stronger bleach of the 400 nm band than in the sample with 33% of the β phase and indicates that some charge is injected into the glassy phase at concentrations lower than those needed to fully fill the β phase and can be explained by incomplete charge transfer from the glassy to the highly diluted β phase.

Figure 3. ECIA spectra of the PFO film with 33% of the β phase at different doping levels (expressed in the number of charges per fluorene repeat unit). Top panel: (a) 1.2×10^{-5}, (b) 1.3×10^{-4}, (c) 6.3×10^{-4} (d) 2.1×10^{-3}; middle panel: (e) 5.6×10^{-3}, (f) 0.016, (g) 0.057, (h) 0.15; bottom panel: (i) 0.22, (j) 0.28, (k) 0.41.

glassy phase of PFO films is similar to the previously observed negative polaron in solution.

It has been shown that the transition dipole moment for absorption of chromophores in glassy and β phase is similar for the same number of repeat units [25], which means that the integrated absorption spectrum of each phase can be taken as a measure of the number of repeat units in that particular phase. Saturation of the β phase bleach in the film with 33% of the β phase is observed at 0.05 charge injected per repeat unit which corresponds to 0.15 charge per repeat unit of the β phase because all injected charges reside in this phase. This indicates that one elementary charge injected into the film bleaches the absorption of about seven repeat units which can be used as an estimate of polaron delocalisation. It is nearly twice longer than in the glassy phase. Larger delocalisation of the polaron in the β phase is consistent with a planar chain conformation which allows undisrupted π-conjugation of the backbone.

The electrochemically induced bleaching spectrum shown in Figure 4 gives a good representation of the neutral β phase absorption with the 0→0 vibronic peak at 438 nm and the 0→1 vibronic peak at 407 nm. The Huang–Rhys factor of β phase absorption $S \approx 0.3$ is obtained from the ratio of vibronic peaks and is about the same as that of the fluorescence spectrum. The Stokes-shift be-
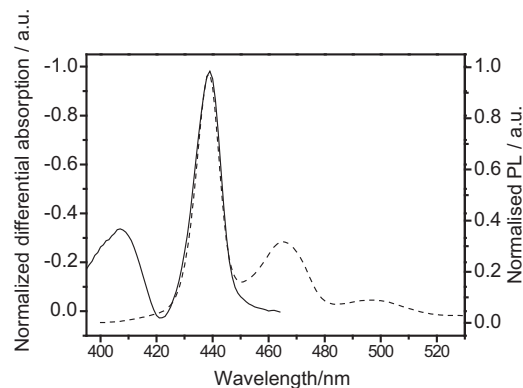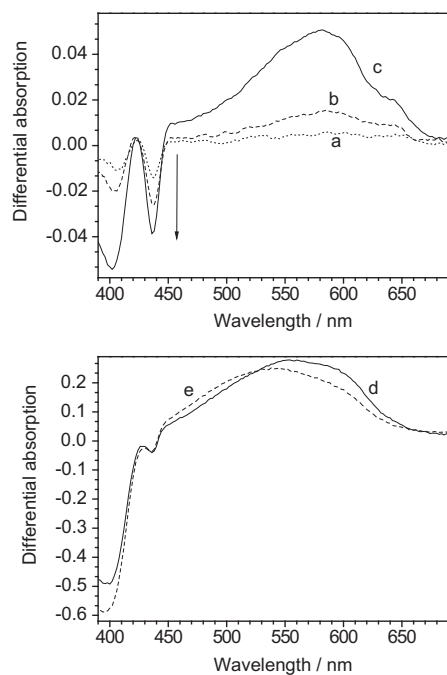

Figure 5. ECIA spectra of the PFO film with 8% of the β phase at different doping levels (expressed in the number of charges per fluorene repeat unit). Top panel: (a) 0.005; (b) 0.009; (c) 0.02. Bottom panel: (d) 0.03, (e) 0.1.

We can determine the absorption cross section σ of the injected charge at a particular wavelength using the expression derived from the Beer–Lambert law

$$\sigma = \frac{2.302 \, \Delta A}{Nl} \qquad (1)$$

where ΔA is the electrochemically induced absorbance, N is the concentration of injected charges and l is the film thickness. Figure 6 shows the evolution of the $\Delta A/l$ ratio as a function of N in PFO films with 33% and 8% of the β phase. This ratio at 640 nm corresponds to charge absorption in the β phase and it shows a linear dependence on N up to $\sim 15 \times 10^{18}$ charges per cm³ (0.01 charge per fluorene unit) in both films. From the linear part we obtain $\sigma = 4 \times 10^{-16}$ cm² for the β phase at 640 nm. This value is consistent with the published molar extinction coefficient of polaron absorption $\varepsilon = 6 \times 10^4$ dm³ mol⁻¹ cm⁻¹ at its peak in oligofluorenes with three to ten repeat units [20]. Converting it using $\sigma[\text{cm}^2] = 2302\varepsilon/N_A$, where N_A is the Avogadro constant, gives $\sigma = 2.3 \times 10^{-16}$ cm² for the charge in oligofluorenes. The oscillator strength of an optical transition is proportional to the spectrally-integrated molar extinction coefficient. For this reason the β phase of the polymer is expected to show a higher value on the peak of absorption than an oligomer because the polaron absorption spectrum in the oligomer is broader [20], thus, we consider that agreement with published values is very good. This validates use of electrochemical charge injection to control charge concentration in polymer films and also shows that polarons have similar optical properties in film and solution. Saturation of $\Delta A/l$ ratio at 640 nm for $N > 20 \times 10^{18}$ cm⁻³ in the film with 8% of the β phase indicates that all β phase is filled with charge and is consistent with a sharp increase of charge absorption in the glassy phase at its 580 nm peak. From the latter we estimate $\sigma = 8 \times 10^{-16}$ cm² for the hole polaron in the glassy phase at 580 nm. An apparent decrease of absorption cross-section at 580 nm at the charge concentration of 120×10^{18} cm⁻³ (0.08 charge per repeat unit) in the sample with 8% of the β phase is a result of the blue-shift of polaron absorption spectra which is clearly

seen in the bottom panel in Figure 5. We attribute it to Coulombic repulsion between adjacent hole polarons positioned on the same conjugated segment which forces polarons to compress. It is striking that in the sample with 33% of the β phase such a blue-shift is observed at a twice higher charge concentration as compared to the sample with 8% of the β phase (see bottom panel in Figure 3). This indicates that more polarons can be injected into β-phase-rich films before electrostatic interaction starts altering energetics of electronic states and can be explained assuming that β-phase can accommodate more polarons than the glassy phase for the same number of repeat units. This assumption is justified by much longer conjugation length of the β phase chains.

In order to evaluate the feasibility of electrically pumped lasing we have to estimate losses associated with carrier and triplet absorption at a lasing wavelength and compare them with the optical gain observed in a laser structure under optical excitation. Amplified spontaneous emission and lasing in PFO films with >5% of β phase is generally observed at 470 nm and corresponds to a $0\rightarrow1$ vibronic peak of the PL spectrum of the β phase [26–28]. The $\Delta A/l$ ratio at 470 nm (Figure 7) in both films is similar up to $N\sim20\times10^{18}$ cm⁻³ and increases sharply at higher N in the film with 8% of the β phase. The onset of this sharp increase corresponds to saturation of the β phase with charge and indicates that charge absorption at 470 nm in the glassy phase is higher than in the β phase.

We estimate an effective charge absorption cross-section in the β phase at 470 nm (which is a superposition of charge absorption and an overlapping bleaching of the neutral polymer absorption) $\sigma = 2 \times 10^{-17}$ cm² using a linear fit to the $\Delta A/l$ ratio in Figure 7 for $N < 25\times10^{18}$ cm⁻³. Bleaching of the β phase shows a slight saturation in this charge concentration range (Figure 8) which indicates that some of the charge is also injected into the glassy phase and gives stronger absorption at 470 nm than the polaron in the β phase, therefore, our estimate of σ should be considered as an upper limit. As a side result we estimate $\sigma = 1.2\times10^{-15}$ cm² for the neutral β phase at 439 nm from Figure 8 for $N < 25\times10^{18}$ cm⁻³. This is very similar to the value estimated for the maximum stimulated emission/absorption cross section of 1.5×10^{-15} cm² in the β phase at 440 nm using the experimental fluorescence lineshape and the radiative lifetime [13]. Good agreement of the absorption cross-section on the peak with the published results of the electron polaron [24] indicates that holes and electrons have similar absorption strength and in the following discussion we refer to both as σ_{carrier}. The stimulated emission cross-section σ_{SE} has been shown to be similar for both phases [26,27] which is consistent with the transition dipole moments being very similar for both phases [25]. Comparing our value of $\sigma_{\text{carrier}} = 2 \times 10^{-17}$ cm² at
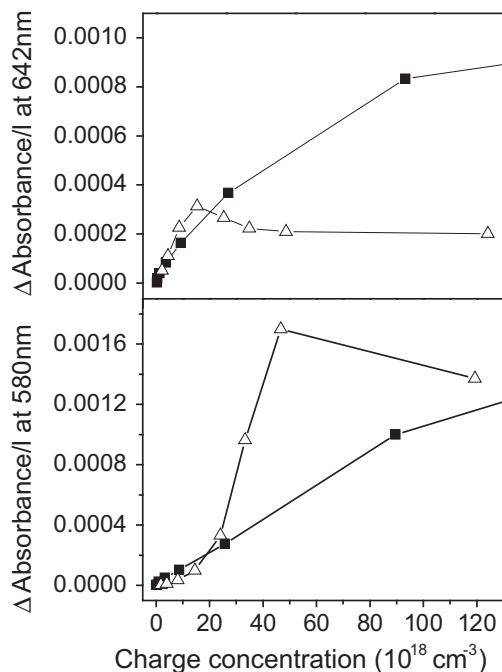

Figure 6. Electrochemically induced absorption normalized to the film thickness ($\Delta A/l$, where l in nm) at 640 nm (top panel) and at 580 nm (bottom panel) vs the injected charge in PFO films with 33% of β phase (solid squares) and 8% of β phase (open triangles).
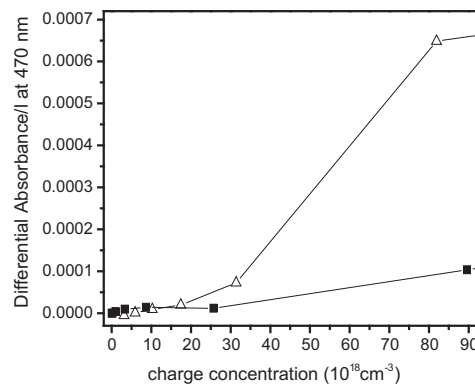

Figure 7. Electrochemically induced absorption at 470 nm normalized to the film thickness ($\Delta A/l$, where l in nm) as a function of the injected charge in PFO films with 33% of β phase (solid squares) and 8% of the β phase (open triangles).
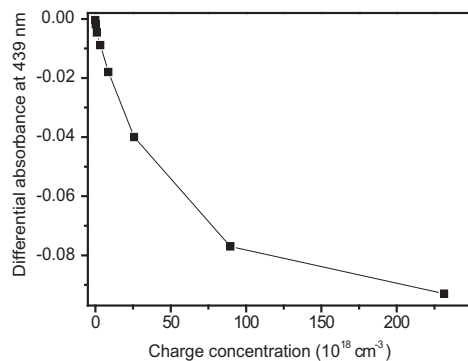
Figure 8. Electrochemically induced bleaching of the neutral β phase absorbance at 439 nm as a function of the injected charge in PFO film with 33% of the β phase.

470 nm with the published $\sigma_{SE} = 1.7 \times 10^{-16}$ cm^2[29] we get $\sigma_{SE} = 8\sigma_{carrier}$ for the charge injected in the β phase at $N < 25 \times 10^{18}$ cm^{-3}. Numerical simulations reported by C. Gärtner et al. [7] showed that in order to reach lasing threshold in a double-heterostructure laser diode with an emissive layer sandwiched between the electron and hole transporting layers for $\sigma_{SE} = 8\sigma_{carrier}$ in the emissive layer the mobility of both electrons and holes should be at least 1×10^{-3} cm^2 V^{-1} s^{-1} assuming that absorption by triplet states at the lasing wavelength is negligible or triplets are efficiently scavenged. The required mobility is four times higher than a photocurrent time-of-flight (TOF) hole mobility of 2.7×10^{-4} cm^2 V^{-1} s^{-1} measured in PFO films with $\sim$1 µs transit time [16]. Higher mobility of 0.01 cm^2 V^{-1} s^{-1} has been reported for electrons in PFO-based field-effect transistors [30]. We must also note that recent time-resolved measurements showed that the sum of the hole and electron mobility on a picosecond time scale is as high as 0.1 cm^2 V^{-1} s^{-1} in a fluorene copolymer and exceeds the microsecond TOF mobility by four orders of magnitude [31]. Other polyfluorene derivatives similar to PFO show microsecond TOF hole mobility up to 0.06 cm^2 V^{-1} s^{-1} (200 times higher than in PFO) and slightly higher optical gain than PFO [16], so, the required charge mobilities may be achievable. PFO films can be made with a large amount of the β phase (up to 40% demonstrated) [17] which should be able to support high macroscopic carrier mobility. We conclude that β-phase-rich PFO could be used as a light-emitting layer in double-heterostructure organic laser diodes in combination with suitable loss-less charge transporting layers.

4. Conclusions

We have showed that spectroelectrochemistry enables quantitative measurements of the charge carrier absorption cross-sections and spectra in polymer films. Results are reported for glassy and β-phase poly-9,9-dioctylfluorene (PFO). We found that the effective absorption cross-section of charge injected into β-phase-rich PFO is at least eight times smaller than the stimulated emission cross-section derived from previously published data. Our results show that β-phase-rich PFO could possibly be used as a light-emitting layer in double-heterostructure organic laser diodes.

References

[1] T. Riedl et al., Appl. Phys. Lett. 88 (2006).
[2] A.E. Vasdekis, G. Tsiminis, J.C. Ribierre, L. O'Faolain, T.F. Krauss, G.A. Turnbull, I.D.W. Samuel, Opt. Express 14 (2006) 9211.
[3] C. Karnutsch, M. Stroisch, M. Punke, U. Lemmer, J. Wang, T. Weimann, IEEE Photonics Technol. Lett. 19 (2007) 741.
[4] Y. Yang, G.A. Turnbull, I.D.W. Samuel, Appl. Phys. Lett. 92 (2008).
[5] A. Rose, Z.G. Zhu, C.F. Madigan, T.M. Swager, V. Bulovic, Nature 434 (2005) 876.
[6] Y. Wang, N.B. McKeown, K.J. Msayib, G.A. Turnbull, I.D.W. Samuel, Sensors 11 (2011) 2478.
[7] C. Gärtner, C. Karnutsch, C. Pflumm, U. Lemmer, IEEE J. Quantum Electron. 43 (2007) 1006.
[8] M. Lehnhardt, S. Hamwi, M. Hoping, J. Reinker, T. Riedl, W. Kowalsky, Appl. Phys. Lett. 96 (2010).
[9] T. Rabe, P. Gorrn, M. Lehnhardt, M. Tilgner, T. Riedl, W. Kowalsky, Phys. Rev. Lett. 102 (2009).
[10] F. Montilla, R. Mallavia, J. Phys. Chem. B 110 (2006) 25791.
[11] F. Montilla et al., Electrochim. Acta 58 (2011) 215.
[12] G. Ryu, P.N. Stavrinou, D.D.C. Bradley, Adv. Funct. Mater. 19 (2009) 3237.
[13] C. Rothe, F. Galbrecht, U. Scherf, A. Monkman, Adv. Mater. 18 (2006) 2137.
[14] B.H. Wallikewitz, M. de la Rosa, J.H.W.M. Kremer, D. Hertel, K. Meerholz, Adv. Mater. 22 (2010) 531.
[15] D. Amarasinghe, A. Ruseckas, A.E. Vasdekis, G.A. Turnbull, I.D.W. Samuel, Adv. Mater. 21 (2009) 107.
[16] B.K. Yap, R.D. Xia, M. Campoy-Quiles, P.N. Stavrinou, D.D.C. Bradley, Nat. Mater. 7 (2008) 376.
[17] J. Peet, E. Brocker, Y.H. Xu, G.C. Bazan, Adv. Mater. 20 (2008) 1882.
[18] A.K. Bansal, A. Ruseckas, P.E. Shaw, I.D.W. Samuel, J. Phys. Chem. C 114 (2010) 17864.
[19] A.J. Cadby et al., Phys. Rev. B 62 (2000) 15604.
[20] A. Wohlgenannt, Z.V. Vardeny, Synth. Met. 125 (2001) 55.
[21] M. Ariu, D.G. Lidzey, M. Sims, A.J. Cadby, P.A. Lane, D.D.C. Bradley, J. Phys. Condens. Matter 14 (2002) 9975.
[22] A. Hayer, A.L.T. Khan, R.H. Friend, A. Kohler, Phys. Rev. B 71 (2005).
[23] N. Takeda, S. Asaoka, J.R. Miller, J. Am. Chem. Soc. 128 (2006) 16073.
[24] L. Zaikowski et al., J. Am. Chem. Soc. 134 (2012) 10852.
[25] S. Schumacher et al., J. Chem. Phys. 131 (2009).
[26] G. Ryu, R. Xia, D.D.C. Bradley, J. Phys. Condens. Matter 19 (2007).
[27] M. Anni, Appl. Phys. Lett. 93 (2008).
[28] D.W. Bright, F. Galbrecht, U. Scherf, A.P. Monkman, Macromolecules 43 (2010) 7860.
[29] H. Marciniak et al., Phys. Rev. B 85 (2012) 214204.
[30] L.L. Chua et al., Nature 434 (2005) 194.
[31] A. Devizis, A. Serbenta, K. Meerholz, D. Hertel, V. Gulbinas, Phys. Rev. Lett. 103 (2009).