

Understanding Fundamental Processes in Poly(9,9-Dioctylfluorene) Light-Emitting Diodes via Ultrafast Electric-Field-Assisted Pump-Probe Spectroscopy

T. Virgili,* G. Cerullo, L. Lüer, and G. Lanzani

Dipartimento di Fisica-INFN, IFN-CNR, Politecnico di Milano, Piazza L. Da Vinci 32, I-20133 Milan, Italy

C. Gadermaier

Christian Doppler Laboratory, Petersgasse 16/I, Advanced Functional Materials A-8010 Graz, Austria

D. D. C. Bradley[†]

Experimental Solid State Group & Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College, Prince Consort Road, London SW7 2BW

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Femtosecond electric-field-assisted pump-probe measurements are a new approach to the study of fundamental processes within organic optoelectronic devices. Here we report a detailed study of organic light-emitting diodes based on poly(9,9-dioctylfluorene), using both temporal and spectral information to investigate polaron generation, due to field-induced singlet dissociation, and their subsequent recombination. The fundamental event in electroluminescence is time resolved: we find that initially free polarons coalesce into intermediate pairs of both singlets and triplets multiplicity which subsequently decay into the neutral state. Our results indicate that the efficiency of singlet formation, $\beta \approx 0.7$, is much higher than expected from simple state degeneracy arguments ($\beta \approx 0.25$).

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In recent years polymer semiconductors have attracted considerable interest as the active constituents in a wide range of optoelectronic devices. Many of the ideas concerning the physics of these materials have been transferred from earlier studies of small organic molecules, often in solution. It is now emerging, however, that this correspondence is not always exact. There are several reports [1–3] which demonstrate that the 25% limit imposed by the spin statistics does not appear to apply in polymer LEDs, and several investigations of such phenomena have been undertaken [3–6]. These data suggest that π -conjugated polymers may have an important advantage over their small molecule equivalents when it comes to LED applications [4].

To date much of the information about the fundamental dynamics of the processes involved in polymer devices has been collected from experiments on thin film samples and/or using (quasi) steady state measurements, often at low temperature. However, local electric fields, interfaces with inorganic (including metallic) electrodes, optical interference effects, and geometric constraints on the material structure can all affect the fundamental physics that governs the performance of the material within the device. In addition, the time scales appropriate for events in a device may be significantly different from those that apply for nondevice samples. As a consequence, it is advantageous to directly study device structures with time-resolved spectroscopy. In this Letter, we report the use of electric field-assisted femtosecond pump-probe measurements performed on organic light-emitting devices based on poly(9,9-dioctylfluorene) (PFO) (the chemical structure of PFO is shown in the inset of

Fig. 1). We show that this new technique can selectively probe the dynamics of elementary processes in device structures with 150 fs time resolution. PFO is the prototypical member of an increasingly important family of fluorene based polymers. It has been widely studied and shows a number of interesting features [7–9]. PFO has also been previously studied by standard ultrafast pump-probe experiments so that the basic spectral features and their assignments are known [10,11].

Pump pulses at 390 nm were focused to a 100 μm diameter spot, giving an excitation energy density of 0.39 mJ/cm² and corresponding pump fluence of 7×10^{14} cm⁻² photons per pulse. Electric field-assisted pump-probe experiments were carried out in the visible and near-infrared spectral regions. To protect the sample from photo-oxidation during the experiment it was kept in vacuum ($\approx 10^{-4}$ mbar). The sample comprised a PFO LED, consisting of a glass substrate coated with an indium-tin-oxide (ITO) anode, a 100 nm thickness PFO film (spin coated from a 20 mg/ml toluene solution), and a thermally evaporated aluminum cathode. In the experiment the pump and the probe beams both pass through the glass, ITO, and polymer layers and are then reflected from the aluminum. The reflected beam is then focused onto a photodiode. Conventional ultrafast pump-probe experiments [12], were performed on thin film samples of PFO or unbiased LEDs (the results are indistinguishable). Measurements [13] of the corresponding quantity $(\Delta T/T)_F$ in the presence of an electric field were performed on reverse biased LEDs. In order to detect small field-induced changes in ΔT , we applied a modulated electric field (1.7 MV/cm, 470 Hz) to the device and

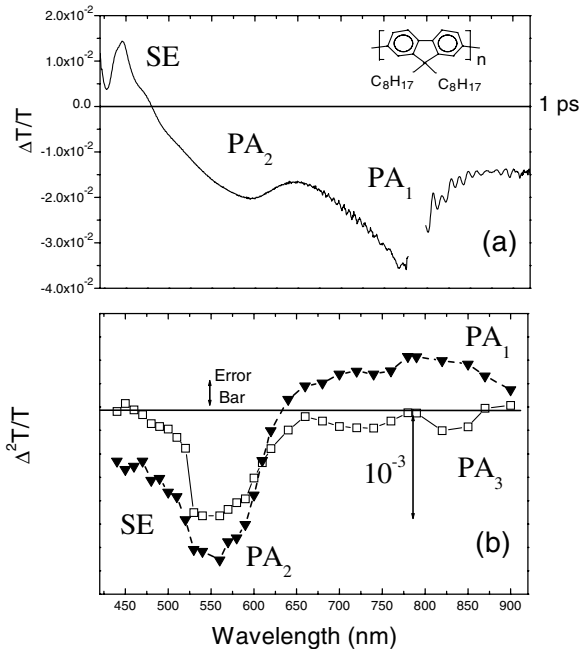


FIG. 1. (a) The chirp-free transient absorption spectrum ($\Delta T/T$) of a layer of PFO at 1 ps pump-probe delay. The chemical structure of PFO is shown in the inset. The nature of the spectral features (labeled PA_1 , PA_2 , SE) is discussed in the text. (b) The field-induced change ($\Delta^2 T/T$) in the differential transmission spectrum for a PFO film at two different pump-probe delays at 2 ps (filled triangles + dashed line) and 200 ps (open squares + solid line).

used standard phase-sensitive detection schemes. Field-induced changes in the $\Delta T/T$ spectra, namely $\Delta^2 T/T = (\Delta T/T)_F - \Delta T/T$, were then deduced. For photobleaching (PB) or stimulated emission (SE), a positive $\Delta^2 T/T$ signal corresponds to a field-induced increase in the corresponding population density, while a negative $\Delta^2 T/T$ signal corresponds to a field-induced quenching. The opposite situation holds for photoinduced absorption (PA).

Figure 1(a) displays the chirp-free pump-probe spectrum at a probe decay of 1 ps for a PFO film spin coated on a glass substrate. This spectrum reproduces earlier results and simply serves as a reference for the following discussion of field-induced changes. The spectrum consists of three distinct features, namely, a SE band at 440 nm (~ 2.85 eV), and two PA bands labeled PA_1 and PA_2 at 780 nm (~ 1.59 eV) and 580 nm (~ 2.14 eV), respectively. The PA_1 band is assigned to S_1-S_n transitions of singlet excitons [10,11] and PA_2 to D_0-D_1 transitions of polarons created by very fast exciton dissociation, probably mediated by S_n states reached via two step excitation [14]. Figure 1(b) shows the corresponding $\Delta^2 T/T$ for the PFO LED at two different probe delays, namely, 2 ps (filled triangles + dashed line) and 200 ps (open squares + solid line). The resulting spectral variations help, by comparison with Fig. 1(a), to identify the origin of the field-induced changes in the visible and near-infrared regions at fixed pump-probe delay.

At 2 ps probe delay, the $\Delta^2 T/T$ signal is negative at wavelengths corresponding to the SE and PA_2 features of Fig. 1(a) and positive in the region of the PA_1 band. These results are readily interpreted: The electric field within the LED dissociates singlet states and consequently reduces SE and S_1-S_n absorption (PA_1). There is a corresponding increase in the signal at 580 nm (PA_2) which indicates that polarons result from singlet dissociation. At 200 ps probe delay the $\Delta^2 T/T$ signal at the PA_2 band position decreases in strength. The $\Delta^2 T/T$ signal at SE wavelengths is no longer apparent, indicating that changes in the singlet population are recovered. There is, however, an interesting change of sign for the $\Delta^2 T/T$ signal in the spectral region beyond 650 nm. This indicates the presence, at long probe delays, of a new absorption band (labeled PA_3), apparently not correlated to SE and singlets.

These features are further evident from the data in Fig. 2 which show the temporal evolution of the (normalized) $\Delta^2 T/T$ signal at two wavelengths: 680 nm (solid line) and 820 nm (open squares and line). The inset shows the corresponding evolution of the (normalized) $\Delta T/T$ signal (no-field applied) at the same wavelengths. While in the latter case both signals have the same dynamics, consistent with their common origin in the singlet exciton population, the two $\Delta^2 T/T$ signals show quite different behavior. The signal at 820 nm changes sign after about 50 ps at which point that at 680 nm has already decayed to zero. The transitions responsible for the negative $\Delta^2 T/T$ signal cannot therefore be attributed to the singlet exciton population. We note, however, that a triplet PA band has been observed in the same wavelength range by Cadby *et al.* [15] using (quasi) steady state photoinduced absorption spectroscopy. This result allows us to postulate that the new PA_3 absorption band arises from the formation of a triplet population, in about 50 ps, by nongeminate recombination of the initially field-induced polarons. (Geminate recombination of singlet polaron pairs cannot lead to triplet states in our time scale. The spin flip rate for doublet states happens in time scales of the order of 1 μ s [16]. Intersystem crossing in PFO is negligible, we do not see any triplet-triplet absorption in our $\Delta T/T$ spectra.) With this interpretation we can model the $\Delta^2 T/T$ data to determine the efficiency, β , for polaron recombination into singlets and thence also that for triplet generation ($1-\beta$).

The formation of triplet states in the presence of an external field can be rationalized by the generation of free charges from singlets dissociation due to the applied electric field. We think that those charges, in a very short time, undergo a *pairing* process. Such intermediate pairs will eventually decay, without further interaction, into lowest neutral states (singlets and triplets). During the pairing of the free charges a fraction β will form singlet polaron pairs and the remaining will form triplet polaron pairs. With our numerical fitting to the experimental data we can thus find out the value of the branching ratio β .

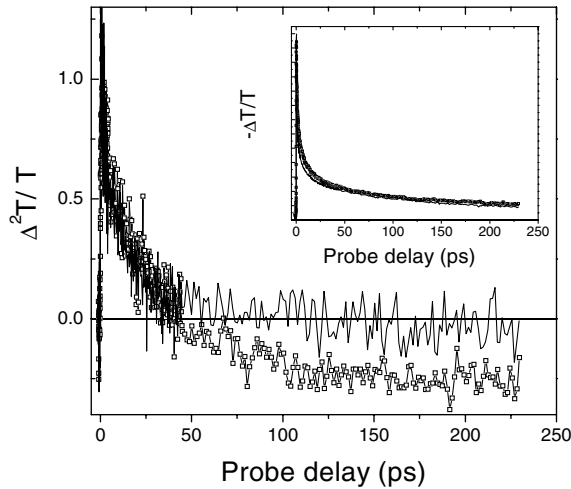


FIG. 2. $\Delta^2 T/T$ dynamics at 680 nm (solid line) and at 820 nm (open squares + solid line). The $\Delta T/T$ dynamics are shown at the same wavelengths in the inset (same symbols apply).

Figure 3 shows the temporal evolution (normalized) of (a) the polaron population (probed at 580 nm) in a LED structure ($\Delta^2 T/T$, solid squares) with an applied field, and the signal at 820 nm showing the contributions of singlet and triplet populations ($\Delta^2 T/T$, open square), (b) the directly photogenerated singlet population (probed at 680 nm, $\Delta T/T$, filled squares) and the reduction in the singlet population resulting from dissociation but ameliorated by subsequent recombination of field generated polarons ($\Delta^2 T/T$, open squares). Fits to the data (see below) are shown by the lines.

Figure 4 shows the decay traces of the polaron population at 580 nm in LED structure ($\Delta^2 T/T$) with an applied field at three different excitation densities: 1.67 mJ/cm² (filled squares), 0.44 mJ/cm² (open squares), and 0.18 mJ/cm² (solid line). Even though the population of polarons grows with excitation density, showing that saturation is *not* taking place, the decay kinetics does not change. This is due to the fact that bimolecular recombination happens in the excitation time scale (200 fs), while what we observe is the monomolecular pairs recombination, possibly due to intrapair electron tunneling.

A kinetic analysis of the $\Delta T/T$ and $\Delta^2 T/T$ decay traces was carried out in order to extract quantitative information, in particular, on the polaron recombination rate and the corresponding singlet-triplet branching ratio. Since the dependence of the $\Delta T/T$ decay kinetics on pump pulse intensity is weak, we exclude any significant contribution from bimolecular decay channels to the $\Delta T/T$ decay kinetics of singlet. We assume first-order decay of singlet states with a rate coefficient $k_l(t)$ [17]. We assume that under the influence of an electric field, predominantly free charge carriers D_F during the pump pulse are formed, which subsequently undergo nongeminate pairing according to second order kinetics with rate

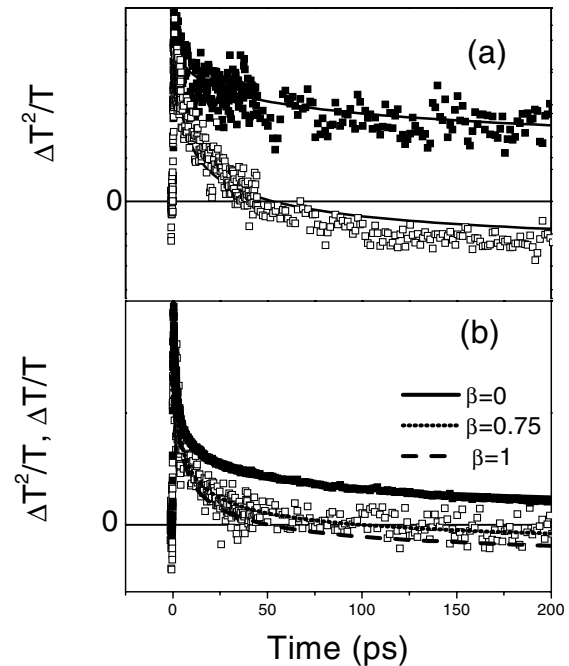


FIG. 3. The temporal evolution of (a) the polaron population (probed at 580 nm) in a LED structure ($\Delta^2 T/T$, solid squares) and the trace decay at 820 nm ($\Delta^2 T/T$, open squares); (b) the directly photogenerated singlet population (probed at 680 nm) without ($\Delta T/T$, filled squares) and with ($\Delta^2 T/T$, open squares) an applied field. Fits to the data are shown by solid lines and are discussed more extensively in the text.

constant k_d to form singlets and triplets polaron pairs in a ratio $\beta/1-\beta$. This population of polaron pairs decays with first-order kinetics, at rate $k_g(t)$ [17] to singlets and to triplets states.

This decay does not depend on the pump intensity as seen in Fig. 4. In order to reproduce our data we have to introduce an intermediate step between the free charges and their recombination in singlet and triplet states: the formation of polaron pairs. At the initial concentration of free carriers (about 10^{18} cm⁻³) the Coulomb capture radius (≈ 20 nm) is about twice the average distance. Free carriers can thus interact given their high mobility (see estimation below). The efficiency of field-induced polarons creation from singlets separation is found to be 3%. The singlet efficiency β can be varied in order to fit $\Delta^2 T/T$, once the other parameters are determined by fitting the no-field ($\Delta T/T$) data and the $\Delta^2 T/T$ polaron data. The best fit is found for $\beta = 0.7 \pm 0.1$. The extracted β value is unquestionably larger than the 0.25 value expected for a spin-independent recombination process. Qualitatively, this is consistent with the results of Wohlgenannt *et al.* [3], namely $\beta = 0.57$.

Finally, we note that the $\Delta^2 T/T$ kinetics also allow an estimate of the microscopic mobility for free charge carriers. The bimolecular recombination rate for polarons in molecular solids is expected [18] to be related to the charge carrier mobility μ :

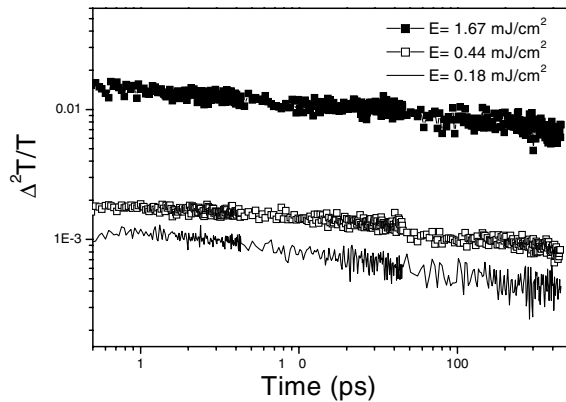


FIG. 4. The temporal evolution of the polaron population in a LED structure with the presence of an applied electric field at three different excitation densities: 1.67 mJ/cm² (filled squares), 0.44 mJ/cm² (open squares), and 0.18 mJ/cm² (solid line).

$$k_d = \frac{e\mu}{\varepsilon\varepsilon_0}$$

If we assume $\varepsilon \approx 4$ [19] and use the lower limit value of k_d (0.25×10^{-17} cm³/s) found from our fit to Fig. 3(a), we can extract a lower limit of $\mu \approx 5$ cm²/V s. This high value can be due to transport within a single chain, but also to interchain hopping of hot, nonthermalized carriers. The range of mobility values obtained here is more than 4 orders of magnitude higher than obtained by time-of-flight mobility measurements nonstandard films of PFO [9] ($\mu \approx 4 \times 10^{-4}$ cm²/V s). However, we note that even partial liquid crystalline order increases μ to $\approx 8 \times 10^{-3}$ cm²/V s [20] and that the infinite temperature, zero field mobility extracted from a Gaussian disorder model [21] analysis of the temperature dependence of the mobility is $\mu_0 \approx 0.4$ cm²/V s [22]. In addition, a value $\mu = 0.74$ cm²/V s, similar to the upper limit found here, was reported by Grozema *et al.* [23] from time-resolved μ -wave conductivity experiments (another microscopic electrodeless technique) on a homopolymer polyfluorene with branched octyl side chains.

In summary, we report novel femtosecond electric field-assisted pump-probe measurements on blue light-emitting poly(9,9-dioctylfluorene) diodes. Details on the fundamental event in electroluminescence are singled out, showing that free charges form an intermediate state before falling into S_1 of T_1 . Modeling within a simple kinetic scheme allows extraction of important parameters that can be compared with estimates based on completely different techniques. The proposed polaron recombination efficiency to form singlets, namely $\beta \approx 70\%$, is in agreement with a variety of less direct measurements reported in the literature [3–5].

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*Email address: tersilla.virgili@polimi.it

Corresponding author.

†Email address: D.Bradley@ic.ac.uk

Corresponding author

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