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Spectroscopy of Conjugated Polymers: Phosphorescence and Delayed Fluorescence

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SUMMARY: We report on the observation of delayed fluorescence (DF) and phosphorescence (P) from films and dilute frozen solutions of various conjugated polymers of the PPP-type. The materials differ with respect to the rotational freedom along the polymer backbone. Upon pulsed optical excitation into the $S_1 \leftarrow S_0$ transition of the materials, delayed emission occurs on a time scale of µs to ms in solid films at 80 K. The phosphorescence in dilute frozen solution decays monoexponentially with a radiative lifetime on the order of one second. The data analysis reveals that the DF is caused by recombination of geminate electron hole pairs rather than triplet-triplet annihilation. This conclusion is supported by investigations of the response of the DF to an applied electric field.

Introduction

In molecular crystals the elementary excitations are Frenkel excitons of singlet and triplet character [1]. At sufficiently large concentrations bimolecular annihilation of triplets can give rise to delayed fluorescence from the first excited singlet state. The singlet-triplet gap is on the order of 1 eV and a signature of the exchange interactions as indicated by the red-shift of the phosphorescence spectrum with respect to the fluorescence. In single component molecular crystals formation of charge transfer states costs several 0.1 eV in excess of the singlet energy and complete dissociation into a pair of free charges costs another half of an eV. This is because the dielectric constant is 3 to 4 implying that coulombic effects are important. A direct valance to conduction band transition is not observed.

Not long ago the general belief was that conjugated polymers behave very different, resembling an one-dimensional semiconductor [2]. The assumption was that optical

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absorption creates a pair of unbound charge carriers dressed by a large chain relaxation, i. e. a polaron pair. This implies negligible coulomb and exchange interaction. If so, there should be no singlet-triplet gap. Meanwhile there is abundant evidence against this notion. How else could it be that recombination of injected electrons and holes in a light emitting diode leads to electroluminescence or, rather electrofluorescence [3]. It turns out that conjugated polymers behave very similar to their oligomeric counterpart structures [4].

The conventional notion has been that conjugated polymers do not phosphoresce although there must be triplet excitations. Spin statistics predict that in electroluminescence three quarter of all recombination events produce triplets rather than singlets [5]. Considering the important role the triplet state plays as nonradiative decay channel which limits the quantum efficiency of fluorescent light emitting diodes (LEDs), it is necessary to gain information about the energetic position of T_1 and its population and depopulation mechanisms. To know how the position of T_1 changes with chemical structure is also useful if one aims at harvesting of triplet excitons for the improvement of LEDs, as it has been demonstrated recently [6, 7]. Obviously, if one could harvest triplets one might enhance the efficiency of LEDs significantly. Meanwhile indirect evidence for triplet excitations in conjugated polymers has been inferred from triplet-triplet absorption experiments [8-10] and optical detected magnetic resonance (ODMR) [11].

The conjugated polymers under investigation are the methyl-substituted ladder-type poly(para-phenylene) (MeLPPP) and poly(2,7-(9,9-bis(2-ethylhexyl)fluorene)) (PF2/6). The methylene bridges in MeLPPP force the PPP backbone into a rigid, almost planar configuration. The rigidity leads to narrow line width of the optical transitions and well resolved vibronic structure compared with conventional conjugated polymers. Although there is a large number of studies on the photophysics of the MeLPPP [12], little is known about the delayed emission in MeLPPP in particular and conjugated polymers in general. Led by the notion that reducing the disorder of a non-crystalline conjugated polymer would enhance TT annihilation we investigated the delayed emission properties of MeLPPP. It turned out that delayed luminescence is indeed observable and its spectrum is a superposition of delayed fluorescence and phosphorescence. The response of DF to the application of an electric field is used to disentangle the routes by which the DF is generated. The results will be compared to delayed emission from PF2/6, where the torsional freedom along the polymer backbone is increased with respect to MeLPPP which corresponds to a larger energetic disorder.

Experimental

The synthesis of the methyl- substituted ladder- type poly(para-phenylene) (MeLPPP) and poly(2,7-(9,9-bis(2-ethylhexyl)fluorene)) (PF2/6) have been described elsewhere [13, 14]. Data and structure of O-MeLPPP, PIF and DDO-PPP can be found in [15].

In order to fabricate 100 nm thin films of high optical quality, the materials were spun cast from toluene solution on fused silica substrates.

In the present spectroscopic studies either an excimer pumped dye laser or an optical parametric oscillator pumped by the third harmonic of a Nd-YAG laser were used as excitation source. The duration of the light pulses are 5 ns and 10 ns, respectively. Both lasers were driven at a repetition rate of 10 Hz.

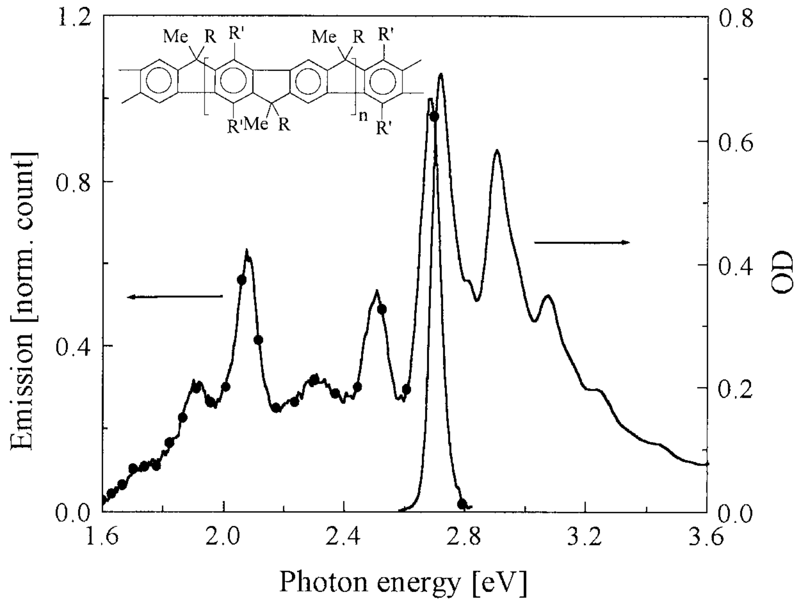

Fig. 1: Phosphorescence/delayed fluorescence of a MeLPPP film (solid line with circles) at 80 K recorded with a time delay of 5 μs after excitation at 2.73 eV. Absorption spectrum (solid line) of the same film at 80 K. The inset shows the molecular structure of MeLPPP.

The luminescence from a illuminated spot size of 3 mm in diameter was passed through a monochromator with a spectral resolution of 2 nm onto an optical multichannel analyzer. The detection window of 10 ms width of the intensified diode array detector was operated synchronously but delayed with respect to the laser pulse. A variable gate of 10 ns to 10 ms after optical excitation allowed the detection of weak delayed luminescence after the intense prompt fluorescence. Delayed luminescence experiments with an applied electric field were done on ITO/MeLPPP/Al sandwich structures. Films of 150 nm thickness were spun from chloroform solution (1 % by weight) onto indium tin oxide (ITO) glass. After storage in vacuum (10^{-6} mbar) for 12 hours to remove residual solvent the diode structure was completed by thermal evaporation of Aluminum on top of the film. The size of the contact was 3 mm in diameter. A pulse generator provided voltage pulses of variable length from 100 ns to 10 ms and variable amplitudes of up to 30 V, which corresponds to an electric field of 2×10^6 V/cm, applied to the device. To eliminate electroluminescence from the film and to reduce the quenching of optical excitations by charge carriers the diode was used under reversed bias, i. e. Al positive and ITO negative. Dilute solutions were prepared by dissolving the compounds (conc. 0.002 to 0.02 mg/mL) in 2-methyl-tetrahydrofuran (MTHF), which was dried over sodium for several days to remove water and then distilled under argon atmosphere. The solutions were transfer to a sealed cuvette immediately. All measurements were done in a cryostat under dynamic vacuum of 10^{-5} mbar.

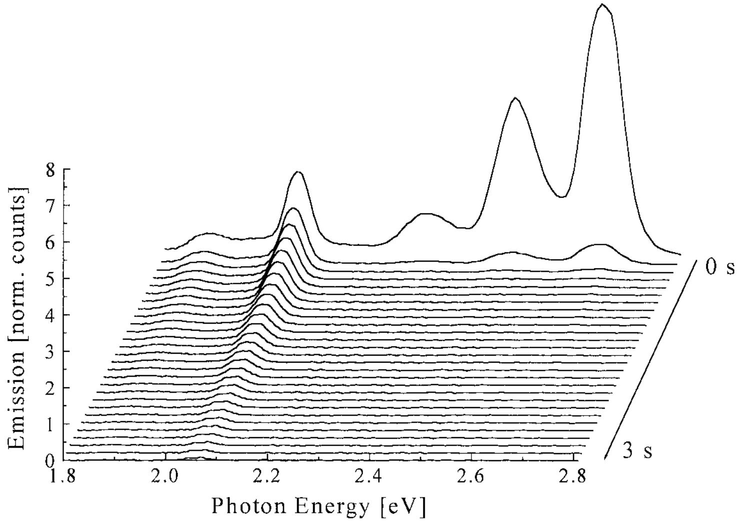

Fig. 2: Phosphorescence and delayed fluorescence of MeLPPP in MTHF at 80 K. The first spectrum is recorded 100 ms after excitation at 2.73 eV. The delay is increased in increments of 100 ms.

Results and Discussion

In the inset of fig. 1 the molecular structure of MeLPPP is depicted. The methylene-bridges between the phenyl rings lock the polymer backbone into a very rigid configuration. As a consequence MeLPPP exhibits a low degree of disorder compared with other conjugated polymers as demonstrated by the absorption spectrum of a MeLPPP film (fig. 1). The inhomogeneously broadened $S_1 \leftarrow S_0$ (0-0) transition at 2.72 eV shows a well-resolved vibronic progression, barely seen in most other conventional conjugated polymers. The main vibronic splitting being 180 meV due to the C=C stretch of the phenyl ring [16]. By introducing a time gate between the exciting laser pulse and the detection window of the spectrometer delayed emission (fig. 1) can be detected. The delayed emission component at 2.69 eV has been assigned to DF from the S_1 state its spectrum being coincident with the prompt fluorescence and was discussed in detail previously [17, 18]. The low energy part of the delayed emission shows a pronounced peak at 2.08 eV and a second peak at 1.90 eV. Because this emission is red-shifted with respect to the fluorescence and is absent at room temperature it is assigned to phosphorescence from T_1 [17, 19]. Furthermore, the vibronic splitting of the triplet emission is the same as that of DF. The value of T_1 is in good agreement with the estimated triplet energy obtained by energy transfer experiments (T_1 ~2.15 eV [20]).
The $S_1 \leftarrow S_0$ (0-0) transition of a dilute solution of PF2/6 is centered at around 3.00 eV (fig. 3) the vibronic splitting is dominated by the C=C stretch. The absorption in dilute solution exhibits a bathochromic shift as compared to the film absorption (fig. 3), which is related to an increased conjugation length in solution, whereas in the PF2/6 film the interchain interactions lead to shorter conjugation length along the polymer chain. From the absorption of the PF2/6 film (fig. 3) it becomes evident that the PF2/6 is much more disordered than the MeLPPP in the solid state. The absorption spectrum with a maximum at 3.15 eV shows only weak vibronic structure and a large inhomogeneous broadening. This is, obviously, a consequence of the energetic disorder in the material and is related to the molecular structure (inset fig. 3). Note that PF2/6 has only two bridged phenylene rings in the monomer unit, whereas MeLPPP is fully planarized. Nevertheless after optical excitation delayed emission can be seen in the dilute solution (fig. 3) and in the film (fig. 3). It shows a well resolved vibronic structure and two different contributions can be distinguished. Both delayed emissions have a dominant vibrational mode of 180 meV. The first peak at 2.93 eV is coincident with the spectral position of the $S_0 \leftarrow S_1$ (0-0) transition in the prompt fluorescence spectrum and it is assigned to DF. In dilute solution the low energy emission is shifted by

0.75 eV with respect to the first peak of the DF. This emission shows all signatures of phosphorescence from the T_1 state of PF2/6. Although the delayed emission in the PF2/6 film (fig. 3) is also due to DF and phosphorescence, a remarkable difference concerns the position of the triplet state in the film (2.1 eV) and dilute solution (2.18 eV), leading to a S_1-T_1 gap of $\Delta E_{ST} \approx 0.84$ eV for the film. Apparently the transition from isolated chains to a bulk film affects the phosphorescence spectrum more than the DF.

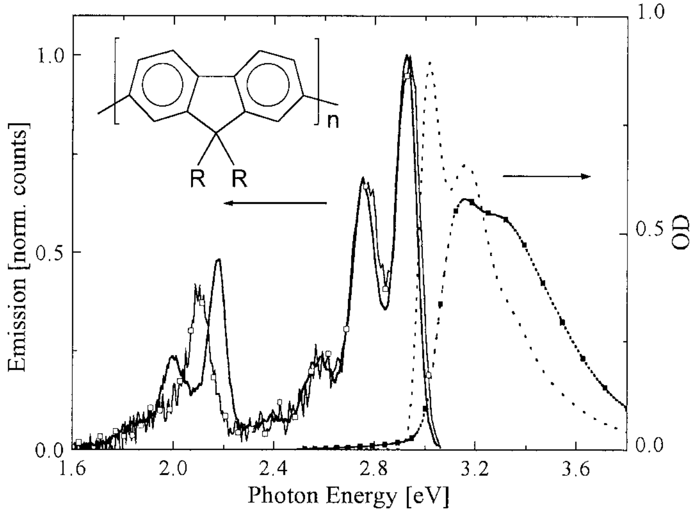

Fig. 3: The absorption spectra of PF2/6 in MTHF (dotted line) and a PF2/6 film (dotted line with solid squares) at 80 K. Delayed emission of the PF2/6 in MTHF (solid line) and a PF2/6 film (solid line with open squares) at 80 K detected after 5 ms delay following excitation. The inset depicts the molecular structure of PF2/6.

It is noteworthy to mention that the red-shift of the phosphorescence in the film spectra increases with increasing inhomogeneous broadening of the optical transitions and, concomitantly, with disorder. In MeLPPP where the inhomogeneous broadening is smallest no shift in the phosphorescence of the film with respect to solution is observed. Since the increase in inhomogeneous broadening corresponds to a broadening of the density of states (DOS) the obvious explanation of this phenomenon invokes spectral migration of the long lived triplet excitons to tail states of the DOS on a microsecond to millisecond time scale [21, 22]. Even though spectral diffusion would also take place in frozen solution, the hopping motion is restricted to hops along the isolated chain, where the lowest energy sites might not be accessed.

In fig. 4 the energies of the S_1 and T_1 states of the materials are plotted versus the inverse number of phenyl rings. The data of PIF, DDO-PPP were taken from [15]. For the DDO-PPP the singlet energy was calculated taking into account the structural relaxation occurring upon electronic excitation. The fits were obtained by taking only the MeLPPP oligomer data into consideration. Apparently the S_1 and T_1 energies of the oligomers can be expressed as $E(n) = E_\infty + E/n$, where n is the number of phenyl rings. Under the premise that the torsional freedom in PIF, PF2/6 and DDO-PPP leads to distortion of the conjugation as compared to MeLPPP they can be viewed as "oligomers".

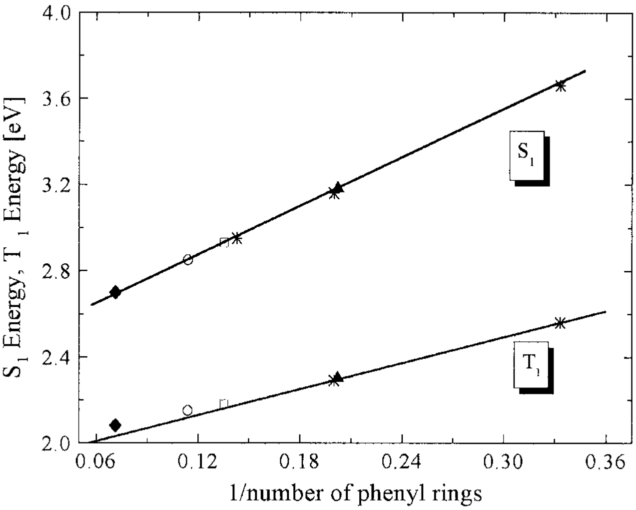

Fig. 4: The energies of S_1 and T_1 plotted versus the inverse number of phenyl rings. The fit of S_1 vs. 1/n was obtained by using the data of O-MeLPPP MeLPPP-dimer [23] and MeLPPP-trimer [23], whereas only O-MeLPPP and MeLPPP-dimer [19] triplet energies were used to fit T_1 vs. 1/n. For the polymer S_1 transitions the n values were adjusted to fit the straight line. See text for details.

By taking the measured S_1 energies of the polymers and adjusting n to fit the above relation one arrives at n~5 (DDO-PPP), n~7.5 (PF2/6), n~9 (PIF) and n~14 (MeLPPP) phenyl rings. That this approximation does not hold for T_1 is evident from fig. 4. Except for DDO-PPP the measured T_1 values of the polymers deviate from the expected value obtained by extrapolation of the oligomer data (fig. 4). The smoother slope for the triplet energies indicates that T_1 is less extended as has also been shown by semiempirical calculations [24]. The singlet triplet gap for PF2/6, PIF and MeLPPP are more or less the same, consistent with data reported for polyynes [25].

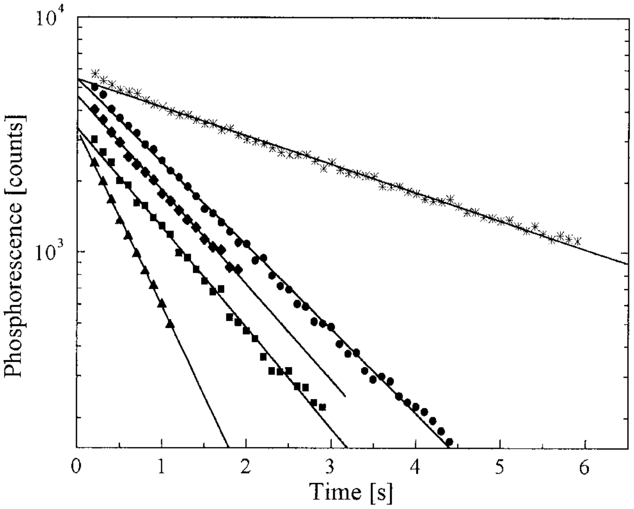

Fig. 5: The decay of the phosphorescence of O-MeLPPP [15] (crosses), PIF [15] (circles), MeLPPP (diamonds), PF2/6 (squares) and DDO-PPP [15] (triangles) in MTHF at 80 K. The first data point was taken 200 ms after laser excitation.

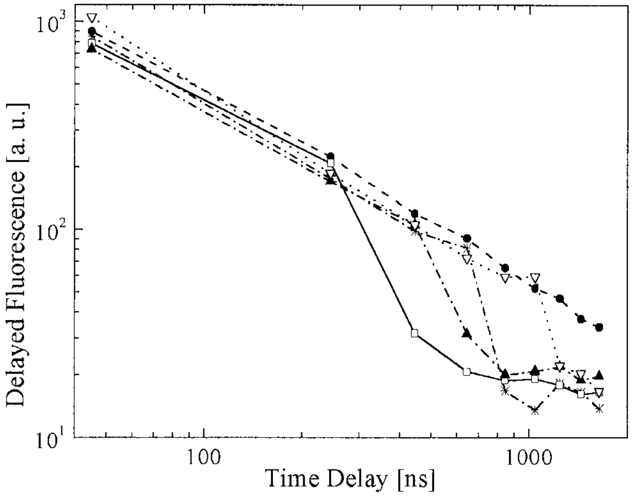

Fig. 6: The decay of the delayed fluorescence intensity with and without applied electric field of MeLPPP at 80 K. The excitation energy was 2.73 eV. The top curve (circles) corresponds to the field-free case, whereas in the other curves a voltage pulse to the ITO/MeLPPP/Al device (E=2x10^6 V/cm reversed bias) was applied 400 ns (squares), 600 ns (up triangles), 800 ns (stars) and 1200 ns (down triangles) after optical excitation.

The radiative phosphorescence decay times τ_P of the materials in frozen MTHF are on the order of one second (fig. 5). Only the lifetime in DDO-PPP is significantly shorter although the S_1-T_1 gap is larger. The reason might be that spin orbit coupling introduced by the oxygen atom in the repeat unit is enhanced, resulting in a shorter decay time. At variance with the measurements in films [18] the phosphorescence in dilute solution decays monoexponentially over the entire time range, as expected when the decay of the triplet reflects the intrinsic decay time. The long intrinsic lifetime of the phosphorescence favors nonradiative quenching at defects or impurities in the polymer film, therefore the radiative decay is orders of magnitude shorter and the emission intensity is much weaker in the film.

The decay of the delayed fluorescence intensity with and without applied electric field at short times from 40 ns to 1.6 μs is shown in fig. 5. Without an electric field the DF decays according to a power law $I^{DF} \propto t^{-n}$ with n close to unity as observed for longer delay times (fig. 4). There is a remarkable response of the DF intensity to an electric field applied several hundred ns after optical excitation. The DF intensity is quenched instantaneous after turn on of the electric field. This is compelling evidence against TT fusion as the predominant route for DF. It is apparent that triplets would not respond to an electric field while charge carriers do. Therefore we conclude that under pulsed excitation DF is due to GP recombination, produced via singlet-singlet annihilation [18].

In conclusion, we have shown that phosphorescence and DF are common phenomena in conjugated polyphenylenes, its radiative lifetime in frozen dilute solution being on the order of one second. The T_1 of these materials is approximately 0.7 eV below the first excited singlet state, which demonstrates the importance of electron-electron interactions in conjugated polymers. Concerning all these properties conjugated polymers behave like smaller π-conjugated molecules.

Acknowledgements

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