Photophysics of Poly[*p*-(2,5-didodecylphenylene)ethynylene] in Thin Films

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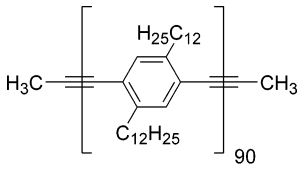
ABSTRACT: The optical properties of thin films of poly[*p*-(2,5-didodecylphenylene)ethynylene] (DPPE) have been investigated. In chloroform solution the DPPE exhibit structured blue emission with a lifetime of 0.4 ns. In contrast to the solution, pristine DPPE films show a broad featureless green fluorescence with a nonexponential decay with time constants of 1.15 ns (8%) and 5.9 ns (92%). Upon annealing, the emission spectrum returns to a structured blue emission similar to the solution, and the fluorescence decay is nonexponential with a component at 0.45 ns (38%) and 90 ps (62%). Both spin-cast and annealed films possess similar absorption spectra, suggesting that the lifetime difference is due to an excimer-like state in the pristine film and efficient fluorescence from isolated chains within the annealed films. The decrease of the fluorescence lifetime from 0.4 ns (DPPE in solution) to 90 ps (annealed DPPE films) is further attributed to the lack of conformational disorder found within the ordered solid state.

Introduction

We describe the effect of annealing upon the UV−vis and fluorescence spectra of thin films of poly[*p*-(2,5-didodecylphenylene)ethynylene] (DPPE). Excimer fluorescence ($\tau_{/2} = 4.5$ ns) is observed in pristine films of DPPE; thermally annealed films yield a blue-shifted emission with $\tau_{/2} = 90$ ps.



DPPE

Aggregation is a term often used in macromolecular science describing two related yet different processes. The general term "aggregation" refers to the agglomeration of polymer chains in a poor solvent. In this broad meaning it is applicable to *any* polymer including polystyrene or polyethylene. The only prerequisite for this process is the existence of a solvent which induces the agglomeration of polymer chains.[1] The second meaning of the term aggregate is an electronic one and means the interaction of two or more chromophores in the ground state.[2] Such ground-state aggregates or electronic aggregates are known in dye chemistry are well studied for perylenes and include the H- and J-type aggregates of cyanine-type dyes.[3] In these aggregates bathochromic or hypsochromic shifts are observed in absorption when comparing unaggregated with aggregated forms. Electronic aggregates *can* form but are not compulsory in conjugated polymers even if large shifts in absorption and emission are observed upon agglomeration of polymer backbones. Chain conformation is a mechanism that can explain spectral shifts in agglomerated conjugated polymers.[4] However, conformational effects and electronic aggregation are not mutually exclusive but could be both at work in a specific conjugated polymer. Dialkyl-PPEs specifically show large spectral responses upon change of solvent composition or when comparing electronic spectra in chloroform, a good solvent, to those obtained from thin films.[5] In the case of the PPEs there is a controversy if their agglomeration is concomitant with ground-state aggregate formation.[6,7] We herein illuminate this problem for the specific case of the DPPE pars pro toto for the whole class of all dialkyl-PPEs. We will show that DPPE forms excimer-like states in thin films, but we cannot detect electronic ground-state aggregates in solution or in thin films.

Results

Figure 1 gives an overview of the spectral responses in absorption and emission that can be elicited from DPPE samples in dilute and concentrated solution and in spin-cast and annealed films. The DPPE we utilized shows a melting point of 180 °C. Dialkyl-PPEs are stable at these temperatures in air.[6b] In Figure 1a absorption and emission of DPPE in chloroform are shown (0.5 mg/L). The spectral data are identical to those reported in the literature.[6] The emission decay of DPPE in chloroform is single exponential with a lifetime of 400 ps, in excellent agreement with literature values.[8] Upon increasing the concentration (0.5 g/L) a second peak shows up in absorption at 439 nm and in emission at 480 nm (Figure 1b). When spin-cast films of DPPE are investigated (Figure 1c), the spectral properties are significantly different. In absorption a sharp maximum at 450 nm appears with a second feature at 410 nm. The emission is broad and centered at 540 nm. The time-resolved fluorescence shows the decay is now nonexponential (see Supporting Information). The decay is well

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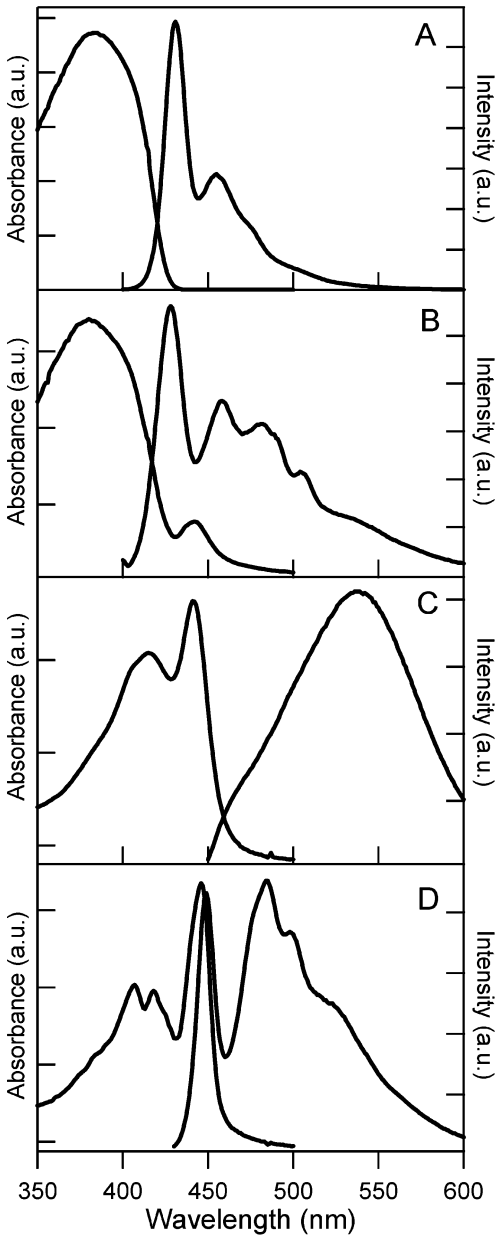

Figure 1. Normalized absorption and emission spectra from DPPE in (A) dilute chloroform solution, (B) concentrated chloroform solution, (C) a pristine spin-cast thin film, and (D) a thermally annealed thin film.

fit by a double-exponential $t_1 = 1.14$ ns (8%) and $t_2 = 5.9$ ns (92%). The longer time dominates the decay and is more than 10-fold slower when compared to the lifetime of the DPPE in solution. Upon annealing the film of DPPE to 160 °C or by heating to 200 °C ($mp_{DPPE} = 180$ °C) into an isotropic liquid phase and cooling (9−10 min, 20 °C/min) to room temperature, the absorption spectrum sharpens somewhat, but the peak maxima are virtually unchanged. The effect of annealing is visible for the high-energy band; the low-energy band at 449 nm is unchanged. However, the emission spectra of the annealed and the pristine, spin-cast samples are dramatically different. Upon annealing, the fluorescence is blue-shifted to 450 nm and is mirror symmetric to the absorption spectrum with a vanishing Stokes shift. The time-resolved fluorescence decay is dramatically increased compared with the pristine film. The annealed film's decay is again nonexponential and well fit by a

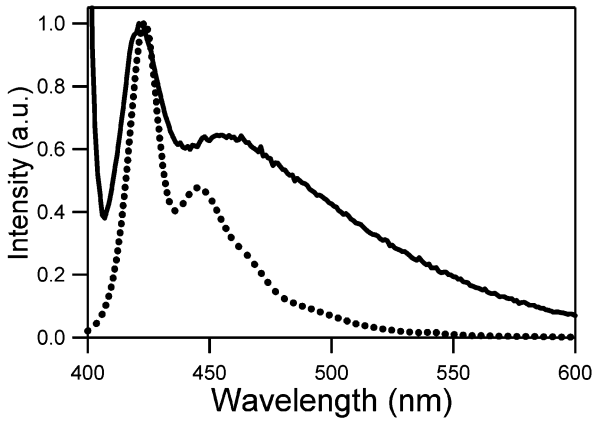

Figure 2. Normalized fluorescence emission profiles of DPPE in a well-solvated solution (plain) and a molten film at 180 °C (bold).

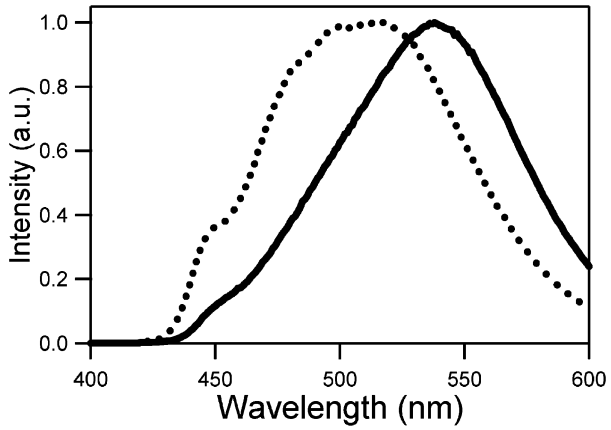

Figure 3. Normalized fluorescence emission profiles of pristine DPPE film (bold) and a molten film flash frozen in 0 °C ice bath (plain).

double exponential, $t_1 = 90$ ps (62%) and $t_2 = 0.45$ ns (38%). Compared with the pristine films, the annealed films have a quantum yield for emission that is nearly identical. Excitation spectra of the pristine and annealed films are similar at all emission wavelengths and nearly identical to the absorption spectra (Supporting Information).

We have investigated the emission of DPPE in the melt (Figure 2). It resembles that of DPPE in dilute solution, although a red-shifted tail is visible. Upon melting, DPPE is highly viscous, and it was possible (Figure 3) to prepare a flash frozen film by submerging the quartz slide with the molten film into ice water. Under these conditions, an emission spectrum similar to that obtained by spin-casting of DPPE is observed (Figure 3). Both the pristine and the annealed films were analyzed by polarization NSOM (Figure 4). The pristine film shows no birefringence and only very little molecular order, but the annealed sample is highly birefringent and possesses large microscale domains with significant polarization anisotropy. This observation was corroborated by an independent powder diffraction X-ray study. Pristine samples or samples that were molten and flash-frozen did not show any diffraction pattern; they are fully amorphous. However, annealed samples of DPPE showed the distinct lamellar diffraction pattern reported earlier by Bunz et al.[9]

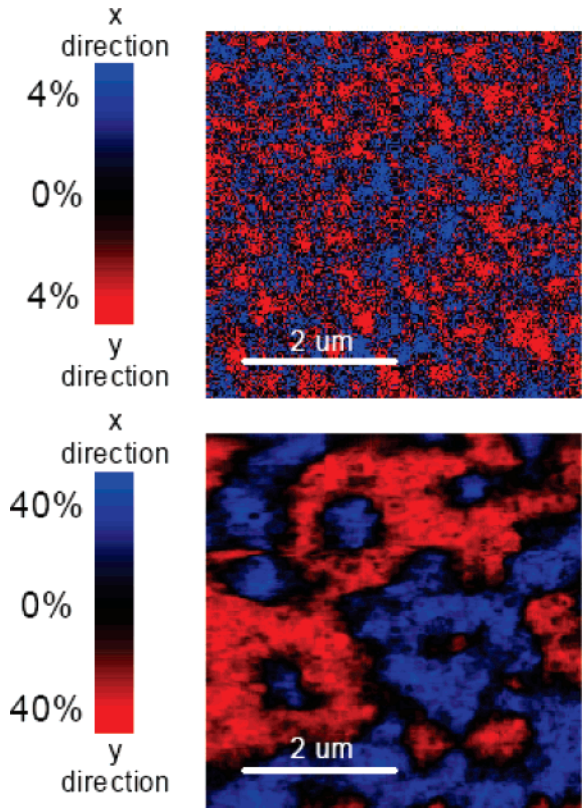

Figure 4. Fluorescence anisotropy images obtained using polarization NSOM. A pristine film with little molecular order is presented in the top image, and a significantly more ordered, thermally annealed, film possessing large microscale domains is shown in the lower image.

Discussion

When comparing spectral properties of a dilute solution of DPPE with that of an amorphous spin-cast film, one finds that absorption and emission are both red-shifted. The absorption of the thin film sample is much more structured (Figure 1). The emission is broad and featureless with an emissive lifetime of 4.49 ns. The increased lifetime and the lack of structure in the emission suggest an excimer-like state to be populated in the amorphous solid.[2] Noteworthy is that the lack of order does not interfere with excimer formation; i.e., contact of the π-systems and amorphous morphology of the film do not seem to be mutually exclusive.

Figure 5 shows a model of the proposed packing of the polymer chains of DPPE in the spin-cast films. In this model, the planarized PPE chains are similar to a heap of flat boards that are stacked on top of each other. Multiple contacts between the π-conjugated backbones exist, and therefore, excimeric states are easily accessible. The lack of order in this phase is corroborated by NSOM and powder diffraction measurements.

If such a sample is heated above its melting point and slowly cooled to room temperature, the changes in the absorption spectrum are only marginal, and λ_{max} is unchanged. The only visible effect in the UV−vis spectrum of the annealed sample is that the high-energy part of the absorption is more structured. Powder diffraction, electron diffraction, and NSOM microscopy all show the annealed samples to be highly ordered.[9] The emission spectrum of the annealed sample is different from that of the amorphous films. It is highly structured and has a vanishing Stokes shift, and the emission lifetime is shortened, excluding excimer-type states. When looking at the spectra of the annealed sample (Figure 1d) without any other information, one could construe a similarity to the formation of Scheibe-type aggregates.[3] These show sharp absorption and emission bands with a vanishing Stokes shift, and one could conclude that electronic aggregates have formed. However, when looking at the excimer-type dominated emission spectrum of the pristine film, this conclusion breaks down. The pristine and annealed samples have very similar absorption spectra, suggesting that the ground-state interactions in both species are identical. In the amorphous films we see excimer-like emission and conclude that in the pristine films there is no significant ground-state chromophore−chromophore interaction. Upon annealing, the excimer-type emission vanishes, and we obtain a highly ordered sample, but with an unchanged absorption spectrum. If upon annealing the absorption is unchanged, and the pristine films do not show ground-state aggregates (but excimer types), then the annealed samples can neither form ground-state electronic aggregates. Additionally, the loss of excimer emission suggests a reduction of interchain interactions rather than an increase as the polymer chains become ordered. Temperature-dependent studies show these changes are continuous as the system evolves from one dominated by excimer emission

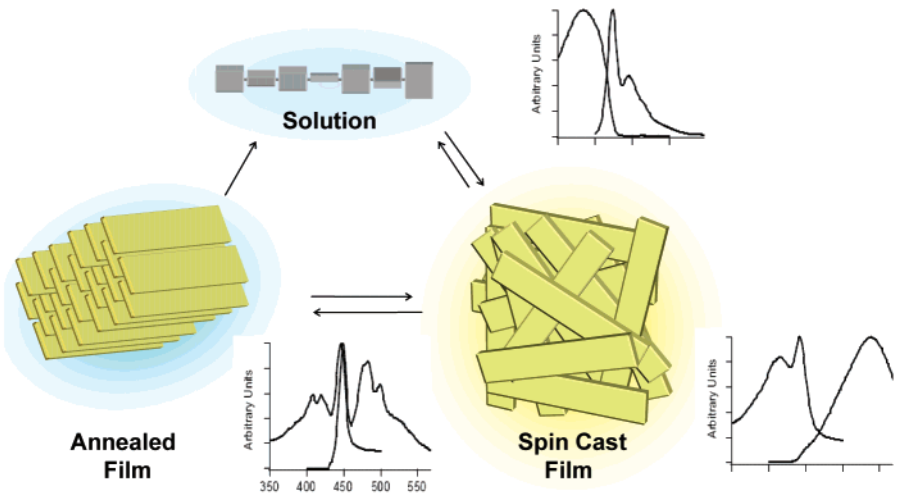

Figure 5. Optical behavior of didodecyl-PPE in solution and in the solid state.

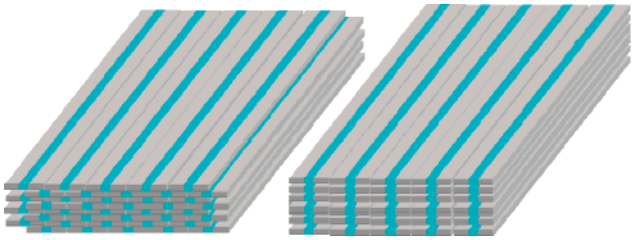

Figure 6. Two possible packing motifs of lamellarly ordered DPPE. Left: maximum distance leads to a brick-wall-type packing motif in PPEs. Right: packing model in which the conjugated backbones are stacked on top of each other and interchromophore interactions are maximized. Gray represents the dodecyl side chains, while turquoise represents the emissive backbone. According to X-ray powder diffraction, the planarized conjugated backbones are 1.3−1.4 nm apart in the brick-wall structure (left), while in the parallel structure the planarized backbones are 0.4 nm apart (right).[9a]

to one that is dominated by single chain emission with increasing polymer order.

In the annealed samples it seems, despite high order, there are no significant chromophore interactions. With the powder diffraction data, it is possible to construct two lamellar packing models that cannot be discerned well (Figure 6). In one model the backbones of the PPEs are stacked on top of each other, while in the second model the backbones are positioned such that the chromophores go on maximum distance with respect to each other; according to powder X-ray diffraction ≈1.3−1.4 nm in the diagonal and 0.7−0.8 nm in the vertical direction. Which one is correct? Benzene rings do not like to be stacked parallel on top of each other; direct contact of the π-systems of two benzene rings is unfavorable, and, unless a pair of donor and acceptor substituted arenes is used, a perpendicular packing of benzene is energetically preferred. We would therefore assume that a lamellar packing of the brick-wall type, in which the conjugated backbones avoid direct contact to each other is preferred. In this model the chromophores of DPPE are insulated from each other by the dodecyl side chains. This packing model would explain the absence of electronic ground-state aggregates in dialkyl-PPEs.[9a]

The above interpretation of DPPE's spectral properties leaves several questions open that have to be accommodated without contradiction: What causes the red shift in absorption when going from dilute solution to thin films? Planarization of the backbones with increased conjugation length will lead to red shifts in absorption and emission.[6b] Polythiophenes and polydiacetylenes[4] show a similar behavior in which planarization is significant for the observed red shift in absorption when going from solution into the solid state. In a melt of DPPE an absorption spectrum results that is almost superimposable to that observed for a dilute solution of DPPE in chloroform. Band-gap calculations suggest that the HOMO−LUMO gap of PPE oligomers is dramatically dependent upon the twist angle of neighboring benzene rings, with the planar forms showing the smaller band gaps.[6b] More structural information is available from a single-crystal X-ray structure of a pentameric model compound:[11] All of the phenyl rings are coplanar with respect to each other, leading to a brick-wall-type packing that is very similar to that proposed for DPPE.

How can the short emissive lifetimes of the annealed samples be explained? Compared to solution, the emissive lifetime decreases from 400 to 70 ps. What is the reason for the change? In solution the rotationally disordered PPE chains have to planarize before they emit, while in the solid state the PPE chains are already planarized and no significant geometric reorganization between ground and excited state is necessary.[8] That alone will lead to a reduced emissive lifetime. While one might expect an increase in the quantum yield with a faster radiative rate, the quantum yield in the annealed films is comparable to that of the pristine films. The high order in these lamellar phases allows the exciton to access energy traps and nonradiative defect sites much easier due to a degenerated fluorescence resonance energy transfer (FRET)-type interaction that is very efficient in three dimensions, suggesting an only weakly bound Frenkel exciton. Swager has shown that FRET from a conjugated polymer to a dye is effective in the solid state over several nanometers distance. This FRET mechanism is probably general for all PPEs.[12]

Conclusions

In contrast with many other conjugated polymer systems, the photophysics of DPPE shows larger interchain interactions in amorphous pristine films than in highly ordered annealed samples. The emission from the amorphous pristine films is dominated by interchain excimer-like species, while in the lamellarly ordered annealed films it is best explained by single chain absorption and emission. The lack of ground state interaction in the highly ordered annealed films is explained by a brick-wall-type lamellar packing motif in which the planarized benzene rings of the conjugated main chain are positioned apart as far as possible without compromising the requirement for optimum space filling. In effect, the chromophores are insulated by the surrounding dodecyl groups. Electronic ground state aggregates, however, can be excluded in thin solid films of DPPE and probably in all other dialkyl-PPEs. In donor−acceptor-substituted PPEs this situation may be different.[7]

Experimental Section

All work in the current study was conducted on the fluorescent conjugated polymer system, DPPE. The material was synthesized as previously described.[13] The average polymer length is 90 repeat units as determined by gel-permeation chromatography. Dilute solution phase samples (0.005 wt % DPPE in chloroform) were prepared to examine the spectral properties of isolated single macromolecules. Pristine polymer films were prepared via spin-casting (2000 rpm) from organic solution (0.5 wt % DPPE in chloroform). The polymer samples were deposited onto base-cleaned glass microscope coverslip substrates. All samples were spin-cast from solutions that had been briefly heated before spin deposition to produce transparent clear casting solutions. The resulting yellow films were subsequently placed under high vacuum (10^{-6} Torr for 1 h) to remove residual solvent from the condensed phase systems. A second group of spin-cast films were prepared and heated to 200 °C, 20 °C above DPPE's melting temperature.[13] The heated samples were allowed to cool back to room temperature at a rate of 20 °C/min to yield thermally annealed DPPE films. Both pristine and annealed films possessed thicknesses of ∼70 nm as determined with AFM step height measurements.

Absorption data were acquired using a diode array spectrophotometer (Hewlett-Packard model 8453). Temperature-controlled spectra were taken after equipping the instrument with a home-built heat exchange manifold. Temperatures between 25 and 200 °C could be set and regulated within 10 °C using the system. All fluorescence measurements, except temperature dependent data, were acquired with a right-angle

fluorometer (Photon Technologies International Quanta Master model C). Samples were excited at 400 nm, and fluorescence beyond 420 nm was collected. The excitation beam was filtered using a 400 nm band-pass filter to minimize the effects of any imperfections in the excitation monochromator. The fluorescence signal was also filtered using a series of long pass filters to prevent both scattered and transmitted excitation light from reaching the instrument detector. Film samples were analyzed in a reflection-type geometry. Attempts were made to limit reflection of the excitation source and maximize the overall fluorescence signal. Film fluorescence depended greatly upon the orientation of the sample in the fluorometer chamber, and attempts were made to minimize angular variation between analyses of different films. Temperature-dependent fluorescence data of thin-film samples were obtained employing a dual monochromator fluorometer (Spex FluoroLog) adapted with a home-built temperature regulating film sample cell. The cell could effectively regulate within 10 °C the sample temperature between 25 and 200 °C.

Microscopic measurements were made using a compound optical microscope (Olympus model BX60) equipped with crossed polarizers and fluorescence filter cubes. High-resolution near-field scanning optical microscopy (NSOM) (Thermomicroscopes Aurora) was employed to make quantitative measurements of film order in both pristine and thermally annealed samples with spatial resolution approaching 85 nm. A configuration employing two detectors oriented to collect sample fluorescence emission at orthogonal polarizations was used to obtain fluorescence anisotropy data. The instrument has been detailed elsewhere.[15]

Time-correlated single photon counting (TCSPC) data were collected from pristine and annealed polymer films as well as dilute solution phase samples of DPPE using a TCSPC module with 30 ps time resolution. The instrument employs both a tunable optical parametric oscillator (Coherent, Inc., Mira OPO) and a multichannel plate photodiode (Hamamatsu MCP) to achieve maximum time resolution. Samples were excited at 400 nm, and time-resolved fluorescence measurements were made above 420 nm in pristine samples, above 450 or 500 nm in annealed films, and above 410 nm in solutions. The decays were fit to single- and double-exponential decays convolved with the instrument response function. Percentages reported for the double-exponential decays are based on the product of the amplitude and the time constant for each exponential.

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Supporting Information Available: Figures of the excitation and absorption spectra of annealed and pristine films of DPPEs and fluorescence lifetime decay curves for DPPE in solution, pristine films, and annealed films. This material is available free of charge via the Internet at http://pubs.acs.org.

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