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Abstract

Single molecule confocal fluorescence microscopy was used to perform photoluminescence spectroscopy on single, isolated molecules of derivatives of the conjugated polymer poly(*p*-phenylenevinylene). We show that the fluorescence from single chains of these electroluminescent polymers depends strongly on chain conformation. Extended chains show emission from multiple segments, while tightly-folded chains emit only from few distinct sites. The tight coil in folded chains enables the polymer to funnel excitons to highly aggregated low energy regions via three-dimensional Foerster-type energy transfer. This strong intrachain coupling causes these polymers to mimic the photophysical behavior of single chromophores and leads to localized emission and fluorescence intermittency.

Polymer molecules that have specifically designed steric hindrance for backbone contacts show higher resistance to solvent-induced interaction between its segments. Only the introduction of non-solvents to such systems forces the polymer to stack its backbone and form aggregates. The luminescence of these buckled polymer chains shows distinctly red-shifted emission presumably due to excimer-formation. These results have significant implications for photophysics and photochemistry of conjugated polymers and their application in thin film electronic devices. Published by Elsevier Science B.V.

Keywords: Single molecules; Photoluminescence spectroscopy; Conjugated polymers; Aggregates

1. Introduction

Conjugated polymers are a new class of semiconductor-like material that are able to transport charge and that luminescence quite efficiently in the solid state [1]. Their organic constitution makes them soluble in common organic solvents and allows for easy processing and inexpensive mass production of thin film devices. The photophysical and electronic properties of these films, however, depend strongly on processing conditions such as solvent polarity, concentration or spin speed and are currently under extensive investigation [2,3]. Briefly, film properties are dominated by the amount of interchain interaction introduced by different processing conditions [3,4]. The study presented here, was undertaken to understand how aggregation of polymer chains influences their photophysical properties on a molecular scale.

In an oversimplified picture, a conjugated polymer can be described as a flexible chain of quasi-independent chromophores or segments that are created by twists and kinks or chemical defects of a fully conjugated backbone. The chemical properties of these polymers depend almost solely on the sidechains that are attached to this backbone. The size and relative flexibility of polymer molecules allow them to form aggregates to lower their energy. Conjugated polymer film studies show that aggregation leads to the formation of weakly emissive interchain species in thin films that significantly reduce the quantum yield of thin film devices [4]. The formation yield of interchain species remains a subject of study [5] but there is emerging a consensus that the strong processing dependence of luminescence yields results from film morphology [2,3]. Indeed, the conformation of chains in films has been shown to be correlated to the molecular conformation in solution [2].

Aggregation of polymer chains begins at the molecular level. Already two molecules can entangle their π-conjugated backbones close enough to form interchain species such as excimers or exciplexes. If the molecules exceed a certain size, even a single molecule can fold back onto itself and self-aggregate. This implies that a thorough investigation of molecular aggregation should ideally be focused on the study of isolated single molecules or aggregates. Fortunately, the past decade has seen a number of improvements in low-level light detection that have made the detection of single fluorescent molecules possible [6]. During the last few years, a number of different concepts, which all share the common feature of efficient background suppression in addition to high luminescence collection efficiency have led to the almost

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routine detection and spectroscopy of single fluorescent molecules [6–8]. Recently, conjugated polymers have become the object of single molecule studies and some surprising observations have been made [9]. The photoluminescence of a single chain of the conjugated copolymer PPV–PPyV showed fluorescence intermittency, i.e. millisecond jumps between fluorescent and dark states. In addition, discrete photoluminescence emission levels were reported [9]. These quantum phenomena indicated strong coupling between the over thousand chromophores that constitute the polymer chain and were attributed to efficient energy migration along the chain to photochemically generated quencher sites. On the other hand, however, it has been shown that one-dimensional energy diffusion along the chain is very slow [10,11]. It seems thus rather unlikely, that a single defect site could quench the entire chain. A different model that allows for three-dimensional energy transfer between closely packed segments appears to be more appropriate to describe the observed behavior [5].

A recent study of polymer chains isolated in channels of mesoporous silica glass has shown, that energy flow in conjugated polymers can be directed by nano-engineering and migration along the conjugated polymer backbone occurs more slowly than energy transfer between polymer chains [11]. These results support our recent observation, that the photophysical behavior of single polymer chains depends strongly on their conformation [12]. It is well known that polymer chains form close coils in unfavorable solvents to minimize their exposure to the solvent. It would thus be expected, that the close packing of chromophores in a tightly coiled polymer chain should have strong impact on its photophysical properties. On the other hand, however, dilute solutions of conjugated polymers in different solvents, where polymer molecules are isolated and have little interaction, show very similar spectra with just a slight spectral shift due to changes in their average conjugation lengths [2]. This only subtle difference is most likely due to an averaging effect over many molecules. Thus, ensemble-averaged studies cannot account for quantum effects like fluorescence blinking.

In this report, we will show that the influence of chain conformation on single molecule spectra and emission properties is quite significant. Single, folded polymer chains show all evidence for very efficient intersegmental energy transfer of the primary photoexcitations to the sites of lowest energy, i.e. the longest segments. Extended polymer chains, on the other hand, emit from multiple sites and reveal therefore very different temporal emission properties and spectroscopy. In the second part of this report, we will show, that the addition of dendritic sidegroups to the conjugated polymer backbone significantly decreases the number of intersegmental interactions, although the steric hindrance caused by these sidegroups is only two-dimensional. Solvent polarity has little influence on their spectroscopy.

2. Materials and methods

2.1. Experimental setup

On the excitation side of our setup, the 488 nm or 514.5 nm line of a water-cooled argon-ion laser (Coherent, Innova 90c) serves as light source. The laser light is coupled into a single-mode optical fiber and guided to an optical table mounted above an upright optical microscope (Nikon). After passing a narrow bandpass filter that rejects any Raman scattering or fluorescence from the fiber, the circularly polarized beam is directed toward a pellicle beamsplitter that reflects 10% of the beam to the microscope tube. The transmitted 90% are being dumped at a beam stop. The use of the broadband reflecting beamsplitter allows rapid switching of the excitation light source without the need to change a dichroic mirror — at the expense of loosing most of the excitation power. The excitation beam is finally focused to a diffraction-limited spot by an oil immersion objective lens with high numerical aperture (Zeiss, Plan-Apochromat $100\times$, 1.4 NA).

On the detection side, the locally excited fluorescence is collected by the same microscope objective. The collimated beam passes the pellicle beamsplitter and is then separated in two parts by a 50/50 broadband beamsplitter cube. One arm passes a holographic notch filter (Kaiser, HSPF-488-1) and is then focused through the entrance slit of an imaging monochromator (SPEX, Triax 320) that disperses the light onto a liquid nitrogen cooled back-thinned charge coupled device camera (Princeton Instruments, LN/CCD-1340/100). The other arm passes a longpass optical filter (Omega Optical, ALPE498 or ALPE520) mounted in a remote controlled filter wheel (Oriel). An antireflection-coated lens with a focus length of $f = 300$ mm focuses the fluorescence onto a photon-counting avalanche photodiode (APD) (Perkin-Elmer, SPCM-AQR-141), whose active area with a diameter of 170 μm serves as confocal aperture. If needed, other optical elements such as a dichroic mirror or polarizing beamsplitter can be mounted behind the lens, and redirect the two components to two APDs. For imaging and positioning purposes, the sample is held on a three-axis scan stage (Physik Instrumente, P-517.3CL) with 100 μm lateral scan range and closed-loop feedback. This stage allows to obtain photoluminescence images of samples by scanning them through the focus of the excitation beam. Once an image at low power (70 W/cm^2) has been acquired, individual spots can be addressed by the scan stage for local spectroscopy. The excitation power is then increased to 200 W/cm^2 and spectra with 5 s integration time and a spectral resolution of 1.5 nm are taken until the molecules undergo final photobleaching. Scan motion and data acquisition are provided by a scanning probe microscope controller equipped with a dual-channel pulse counting board (Digital Instruments, Nanoscope IIIa).
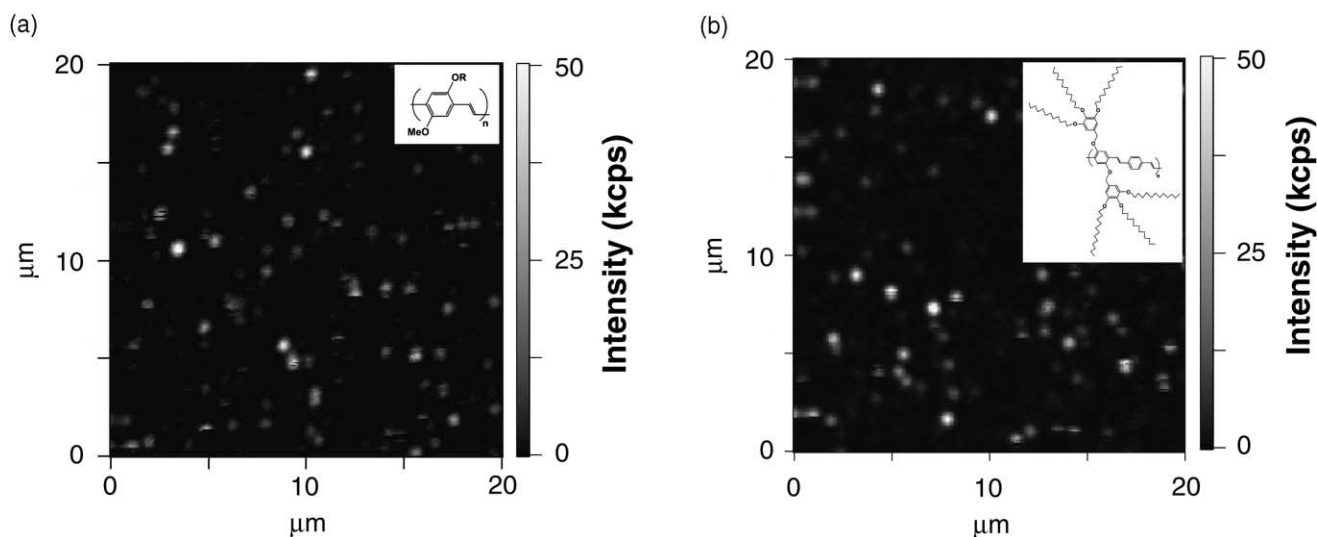
Fig. 1. Photoluminescence images of single conjugated polymers on glass. (a) MEH-PPV spun-cast from dilute toluene solution. Inset shows the structure of MEH-PPV; (b) dPPV (see text) spun-cast from dilute toluene solution. Inset shows the structure of dPPV. Photoluminescence of the molecules was excited with 200 W/cm^2 at 488 nm with circular polarization. The intensity variation between the molecules may be due to polydispersity of the molecular weights.

2.2. Sample preparation

All polymers used in this study are derivatives of poly(p-phenylene–vinylene) (PPV) and were synthesized at the University of Rochester (MEH-PPV, poly[2-methoxy, 5-(2′-ethyl-hexyloxy)-p-phenylene–vinylene]) and Bell Labs, Lucent Technologies (phenylene–vinylene backbone with dendritic sidegroups; we will use the term dPPV as a short form for this polymer). Chemical formulas of MEH-PPV and dPPV are shown in Fig. 1a and b, respectively. Molecular weights of the polymers are approximately 1,000,000 for MEH-PPV and 1552 for dPPV. Dilute solutions of the conjugated polymers in toluene (J.T. Baker, Baker analyzed) and chloroform (Aldrich, 99.8%, spectrophotometric grade) were prepared by dissolving a few milligram of the polymer in each solvent for at least 24 h and subsequent extensive ultrasound treatment at 40–50°C. These solutions were then further diluted to achieve final concentrations of 10^{-9} or 10^{-10} M. Microscope cover slips (Fisher Scientific, Fisherbrand Circle 25 mm, #1) were cleaned by sonicating them for 30 min in a 2% solution of an alkaline cleaning agent (Fisher Scientific, Hellmanex) and subsequent extensive rinsing with deionised water. The clean cover glasses were dried with a nitrogen purge. An amount of 20 µl of the dilute polymer solution was then spun-cast onto the cover slips rotating at 7500 rpm. The high spin speed ensures fast evaporation of the solvent and preserves the solution-conformation of the polymer on the glass substrate. This preparation resulted in surface coverages of roughly 10–20 polymer molecules per 10 µm × 10 µm. Finally, a 70 nm cap layer of polyvinylbutyral (PVB) (Aldrich, poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate)) was spun-cast on top of the sample to prevent fast photodegra-

dation of the conjugated polymer. The PVB solutions were prepared from the same solvents as the conjugated polymer solutions, respectively, and were spun at the same spin speeds.

3. Results and discussion

Fig. 1a shows a representative photoluminescence image of a MEH-PPV sample. In Fig. 1b, a similar image obtained from a dPPV sample is displayed. The diffraction-limited spots observed in these single molecule images are attributed to single polymer molecules since the number of spots varies linearly with concentration. Moreover, the number of spots on the surface equals roughly the density of molecules that is expected for the given concentrations of the solutions.

3.1. Conformation-dependent photoluminescence of single MEH-PPV molecules

MEH-PPV in the non-polar solvent toluene tends to form a tight coil to minimize solvent interactions, while in the more polar solvent chloroform the polymer chains are expected to have an extended conformation [2]. We have examined over 100 molecules spun from each solvent. The photophysical behavior we observed for all these molecules was similar with respect to the solvent.

Fig. 2a shows a representative intensity transient and Fig. 2b the independently acquired temporal evolution of photoluminescence spectra of a single MEH-PPV molecule spun-cast from toluene (MEH-PPV/Tol). Fig. 2c and d display intensity transient and spectra for a molecule spun-cast from chloroform (MEH-PPV/Clf). The intensity transient of the MEH-PPV/Tol molecule reveals intermittent
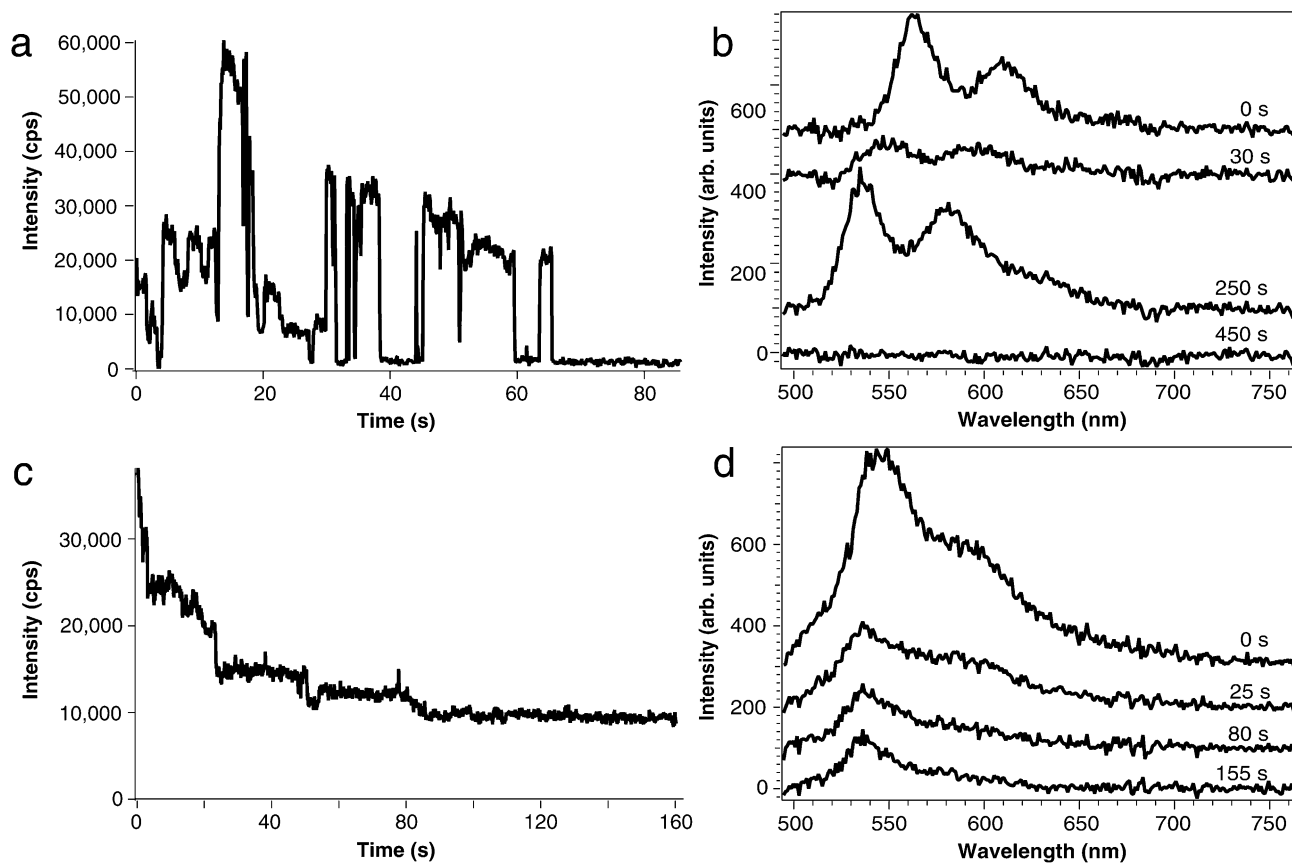
Fig. 2. (a–c) Representative intensity transients of a MEH-PPV molecule spun from toluene and chloroform solution, respectively; (b–d) time-evolution of spectra of a MEH-PPV molecule spun from toluene and chloroform, respectively, obtained under continuous excitation. Integration time for each spectrum was 5 s with a spectral resolution of 1.5 nm. Spectra are offset in vertical direction for clarity and labeled with the start time at which they were taken.

fluorescence similar to what has recently been observed by VandenBout et al. [9]. The photoluminescence intensity switches rapidly between on- and off-states while different discrete intensity levels are assumed.

VandenBout et al. have explained this behavior by the creation of photogenerated defects that quench excitations *along* the entire chain [9]. Fig. 2c, however, shows a very different behavior. The intensity transient for this MEH-PPV/Clf molecule reveals an initial exponential decrease in its photoluminescence intensity without discrete jumps to the background level. This behavior is representative for all MEH-PPV/Clf molecules we measured. The time constants for the exponential intensity decrease vary from 0.1 to 2 s. After a few seconds, jumps in the intensity occur, but never to the background level. The further reduction of the intensity to the background level occurs gradually and on much longer timescales than that for MEH-PPV/Tol molecules.

To understand the physical origin of this very different behavior, we have analyzed photoluminescence spectra obtained simultaneously with the intensity transients. MEH-PPV/Tol molecules (cf. Fig. 2b) show well-resolved vibronic structure. The position of the first vibrational peak (0–0) lies typically at about 570 nm. Surprisingly,

the spectra shift at continued excitation by up to 50 nm to lower wavelengths, while the separation between the first and second vibrational peak remains constant with an energy spacing of 0.16 eV corresponding to the backbone stretching mode. Fig. 2b gives an example of this behavior where the initially red emission shifts to shorter wavelengths until the final photobleaching step occurs. In addition, some of the MEH-PPV/Tol spectra have an initial blue component that disappears fully after few seconds (data not shown, cf. [12]). A total of 75% of the approximately 120 MEH-PPV/Tol molecules that we examined show fully red-shifted spectra as in Fig. 2b. Only 25% of the spectra have an additional blue component.

Fig. 2d shows the representative temporal evolution of the spectrum of a single MEH-PPV/Clf molecule. The emission is relatively broad and without much vibronic structure. Its peak emission lies at about 550 nm. The intensity (area under the spectra) decreases exponentially with the spectral mean fluctuating around its average value. Also, 16% of all MEH-PPV/Clf spectra that we have measured show some initial vibronic structure superimposed to a broad background. This structure, however, is lost after a few seconds of continuous exposure.
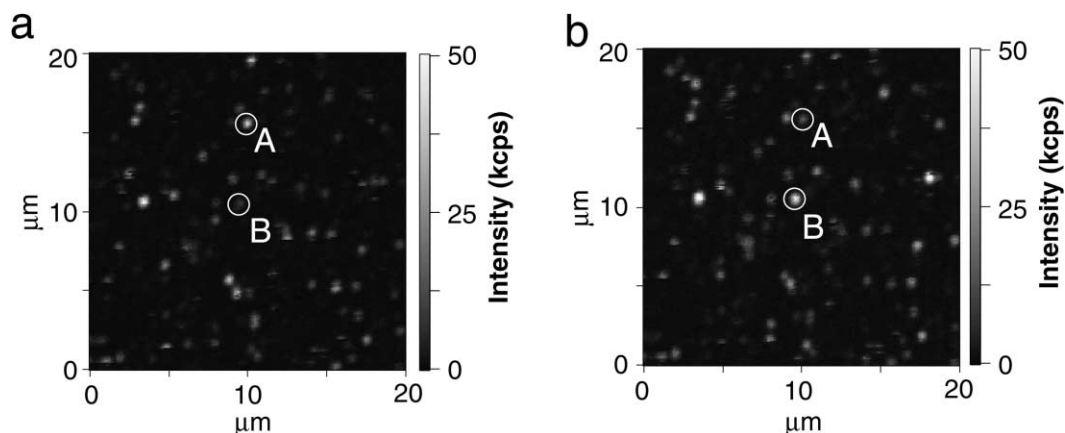
Fig. 3. Simultaneously acquired photoluminescence images at orthogonal polarization for MEH-PPV molecules spun-cast from toluene solution. The molecule labeled A emitted most of its fluorescence into the first channel and the molecule labeled B emitted most of its fluorescence to the opposite channel. MEH-PPV molecules prepared from toluene-solution show high anisotropy of their emission dipole moments.

In addition to spectroscopy, polarization studies also provide a means to better understand molecular conformations and their influence on photophysical properties of conjugated polymers. In a recent report, single molecules of MEH-PPV were shown to reveal a high degree of anisotropy of their absorption and emission dipole moments [13]. We investigated this behavior further by separating the photoluminescence into two channels with orthogonal polarization. The ratio between these two channels provides information on the orientation of the emission dipole moment relative to the excitation polarization (circular in our case). Fig. 3a and b show photoluminescence images of a MEH-PPV/Tol sample acquired simultaneously at two orthogonal emission polarizations. As can be seen from these images, the emission dipole moments of MEH-PPV/Tol molecules show large anisotropy. Molecules that have a high intensity at one detector are barely visible in the other channel with perpendicular polarization as is indicated for two spots labeled A and B in Fig. 3. Recently, we have shown that anisotropy values $(I_1 - I_2)/(I_1 + I_2)$ from such images, where I_1 is the intensity in channel 1 and I_2 the intensity in channel 2 are evenly spread between -1 and 1 [12]. This indicates that MEH-PPV/Tol molecules have a well-defined emission dipole moment. For MEH-PPV/Clf molecules the anisotropy values show a Gaussian distribution around zero, what indicates random emission (equal intensity at the two polarization sensitive detectors), and thus no well-defined emission dipole moment.

We have explained the differences in time-dependent emission, spectroscopy and polarization of MEH-PPV by a model of conformation-dependent intramolecular energy transfer [12]. A prerequisite for this model is the fact that MEH-PPV remembers its solution configuration prior to deposition on the substrate. This has been demonstrated by Nguyen et al. in studies of films prepared from different solvents [2]. Polymer molecules in dilute toluene solution tend to form a tightly-folded chain while those in chloro-

form take on a more extended conformation. This behavior has been verified for MEH-PPV by light-scattering experiments [2]. A tightly-coiled molecule allows for interactions between its closely packed segments thus facilitating efficient three-dimensional exciton diffusion [5]. In addition, interactions between stacked segments appear to be responsible for the reduction in luminescence yields and red-shifted spectra characteristic of longer conjugation in packed regions [3,4,14,15].

In the case of MEH-PPV/Tol, where the chains form a tight coil and intersegment interactions are promoted, the excitation energy is efficiently transferred to the longest segments. In the majority of cases (75%) the longest segments are the only emissive species. Only 25% of all molecules show partial energy transfer as indicated by a weak emission from shorter segments. These, presumably, represent parts of the chain that are dangling out of the coiled region and cannot transfer their energy to the longer segments. Since in the aggregated region energy transfer from the shorter conjugated segments to longer segments is very efficient and occurs within few picoseconds [11,16], only the longest segments have a substantial occupancy of excited states. Thus, only these will be subject to excited state photoreactions that create photochemical defects. Once all the longer segments are photo-bleached, energy transfer to these segments is prohibited and the shorter segments become emissive as indicated by the spectral blue-shift in Fig. 2b. The high polarization anisotropy for MEH-PPV/Tol furthermore indicates a fixed emission dipole moment. For a polymer molecule with such high molecular weight, the creation of a fixed dipole moment can only be achieved by a well-organized folding of the polymer chain. Remarkably, polarization memory is retained even after the longest segments are photodegraded. This indicates that the emission from segments with shorter conjugation length still derives from chain segments that are oriented within the folded polymer. Our model suggests, that MEH-PPV/Tol forms a

self-aggregated polymer molecule with well-stacked segments. The high efficiency of intramolecular inter-segment energy transfer for self-aggregated molecules explains its intermittent fluorescence [9]. If the low energy regions harbor a reversibly photogenerated quenching site such as charge separation on adjacent conjugated segments (polaron pair formation), the entire molecule's fluorescence can be temporarily quenched until charge recombination occurs [5]. Similar processes are held responsible for the intermittent fluorescence of semiconductor nanocrystals [17]. Efficient intramolecular energy transfer also explains the efficient photoluminescence quenching of polymer chains by extremely low amounts of cationic electron acceptors [18] and their permanent loss of photoluminescence.

The spectroscopy of the initial emission in the toluene-cast MEH-PPV (Fig. 2b) is also informative. Often, a higher intensity of the 0–0 peak with respect to the 0–1 peak is observed than what is seen for the blue-shifted spectra that result after prolonged exposure or those in the chloroform case. This indicates that the steric hindrance from packing makes the optical transition more vertical since the excited and ground states are driven towards having similar geometries. In addition, the suppression of torsional motion results in an increase in effective conjugation length and hence redder emission spectra.

Molecules spun-cast from chloroform, however, assume an extended conformation. In this case, energy migration along the chain becomes a more important pathway for energy transfer. Dipoles from segments along a chain are poorly situated for efficient Foerster transfer and quasi one-dimensional diffusion along the chain direction is slow [10,11]. Therefore, the photoluminescence spectrum of a MEH-PPV molecule with extended conformation as shown in Fig. 2d exhibits a broad emission from multiple emitting segments. The shape of the emission spectrum, therefore, results from a distribution of chromophores with a variety of conjugation lengths. Since energy transfer is inefficient,

the emission of multiple segments with different conjugation lengths leads to nearly homogeneous photobleaching of all segments. Thus, the intensity transient in Fig. 2c shows an exponential decrease. Furthermore, a polarization anisotropy value of zero indicates random emission from all segments. This is the expected result for a random, extended coil. It should be pointed out, however, that we obtained diffraction-limited spots with a diameter of about 400 nm even though the completely extended chain would be over 1 μm long, what implies that these too must to some extent be coiled. This is in accordance with the light-scattering data, where the physical size of molecules in a polar solvent was only about twice that in a non-polar solvent [2]. The loose coil obviously does not allow for efficient three-dimensional energy transfer and energy migration along the chain plays an important role [11].

The deposition of polymer molecules on glass substrates, however, comes at some cost as is demonstrated in Fig. 4. Here, we compare the emission of dilute solutions of MEH-PPV in chloroform and toluene to averaged spectra of 30 molecules spun-cast from the same solvents. The dilute solution spectra show a similar behavior as what has been observed by Nguyen et al. [2] for chlorobenzene and tetrahydrofuran. The solution spectrum of MEH-PPV in toluene (main peak at 557 nm) is slightly blue-shifted with respect to the spectrum in chloroform (main peak at 561 nm). This behavior has been explained with the shorter average conjugation length in the less favorable solvent [2], i.e. toluene in our case. The averaged single molecule spectra, however, show a very different behavior. In the case of MEH-PPV/Clf, the averaged spectrum is blue-shifted by almost 20 nm with respect to the solution spectrum. The MEH-PPV/Tol spectrum on the other hand is red-shifted by 12 nm relative to the solution spectrum. The overall shapes of the solution spectra are well reflected by the average single molecule spectra. In particular, the slightly more expressed second vibrational (0–1) peak in the toluene case is
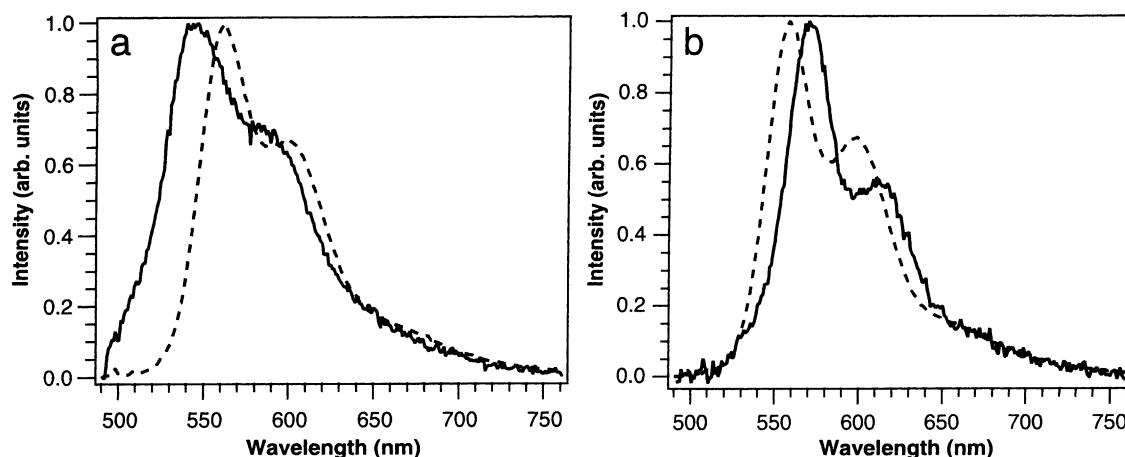

Fig. 4. Comparison of spectra of MEH-PPV in dilute solution (dashed lines) and averaged spectra of 30 single molecules adsorbed to a glass surface (solid lines), respectively. (a) MEH-PPV in chloroform vs. averaged spectrum of MEH-PPV molecules spun-cast from chloroform; (b) MEH-PPV in toluene vs. averaged spectrum of MEH-PPV molecules spun-cast from toluene.
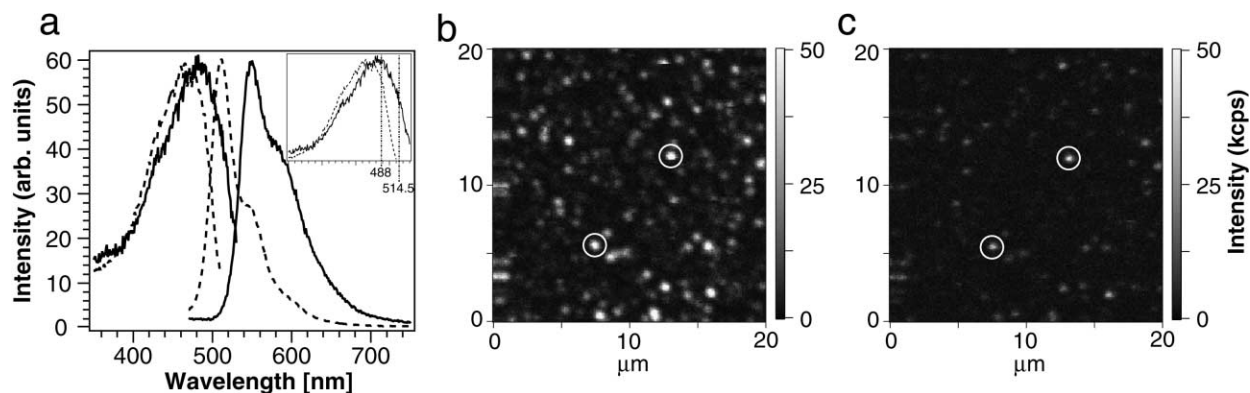
Fig. 5. Influence of excitation at different wavelengths on dPPV emission. (a) Photoluminescence excitation and photoluminescence spectra of dilute dPPV/chloroform solution (dashed line) and of a dPPV thin film (solid line). Inset shows differences in photoluminescence excitation in more detail: only the thin film can be efficiently excited at 514.5 nm. (b) Single dPPV molecules excited at 488 nm. (c) The same single dPPV molecules as in (b), but excited at 514.5 nm.

well reproduced. The differences between single molecule and solution spectra are most likely induced by the presence of the rigid substrate. Generally speaking, molecules in dilute solution have a high mobility for rotational and diffusional motion, but also for conformational reconfiguration. Thus, a MEH-PPV molecule in toluene solution is constantly attacked and buckled by solvent molecules. The solvent interaction constantly bends and twists the polymer chain and results in a short average conjugation length with little coupling between different segments. The spun-cast MEH-PPV/Tol molecules, however, are in a quasi-frozen state on the substrate and their close and steady packing leads to strong three-dimensional energy transfer to the lowest energy sites as has been explained above, thus, resulting in an initially red-shifted spectrum. On the other hand, an extended MEH-PPV molecule in chloroform solution has a long average conjugation length, thus, leading to a red-shifted spectrum with respect to the polymer solution in toluene. When such a molecule is spun onto the glass surface the averaged spectra in Fig. 4a suggest, that its average conjugation length is shorter than in solution. This might be caused by a buckling of the backbone during the spin-process.

3.2. Photoluminescence of single chains of a phenylenevinylene derivative with dendritic sidegroups

The intention of designing a conjugated polymer with dendritic sidechains, i.e. dPPV in our case, is to separate adjacent PPV backbones in thin films [19]. This physical separation should prevent unfavorable interchain interactions that severely decrease the luminescence efficiency of polymer thin films [4].

As shown in Fig. 5a, however, photoluminescence spectra from spun-cast film and dilute solution of such a polymer show similar behavior as in conventional conjugated polymers such as MEH-PPV. Photoluminescence excitation and photoluminescence spectra of thin films of dPPV are

red-shifted with respect to solution spectra. Obviously, the plain dPPV molecule can only prevent interchain interactions in two dimensions, but suffers from π-stacking in the third dimension.

The spectral shift between thin film and solution in the photoluminescence excitation spectra presents itself as a good means to distinguish between aggregated and non-aggregated molecules with a tunable argon-ion laser. As can be seen from the spectra in the inset to Fig. 5a, excitation at a wavelength of 488 nm should excite both aggregated and non-aggregated molecules. Excitation at 514.5 nm, on the other hand, should only sufficiently excite aggregated molecules. Thus, images of single molecules taken at these two excitation wavelengths should allow us to identify aggregated molecules. This is demonstrated by the photoluminescence images in Fig. 5b and c. Fig. 5b was obtained by scanning a range of $20\,\mu m \times 20\,\mu m$ with 488 nm, while Fig. 5c was obtained by scanning the exact same location with 514.5 nm excitation. In this case, the sample was spun-cast from a 10^{-9} M solution of dPPV in toluene and covered with a 70 nm PVB cap layer. As can be seen from the comparison between Fig. 5b and c, spin-casting dPPV from toluene solution creates only few aggregated molecules. A similar result was obtained for dPPV spun from chloroform. The two solvents that produced well-distinguishable results for MEH-PPV, as demonstrated above, are basically identical for dPPV. This result is further supported by the spectroscopy of dPPV molecules prepared from different solvents. Fig. 6a shows the temporal evolution of the spectrum of a single dPPV molecule prepared from chloroform solution. The spectrum reveals well-expressed vibrational structure, that decays steadily with time until the molecule is photobleached. Since the molecular weight of dPPV is relatively low, it seems reasonable to assume that its variation in conjugation lengths is rather small, thus, leading to a sharper spectrum. Fig. 6b displays spectra obtained from a molecule identified as being aggregated according to the 488/514.5 nm
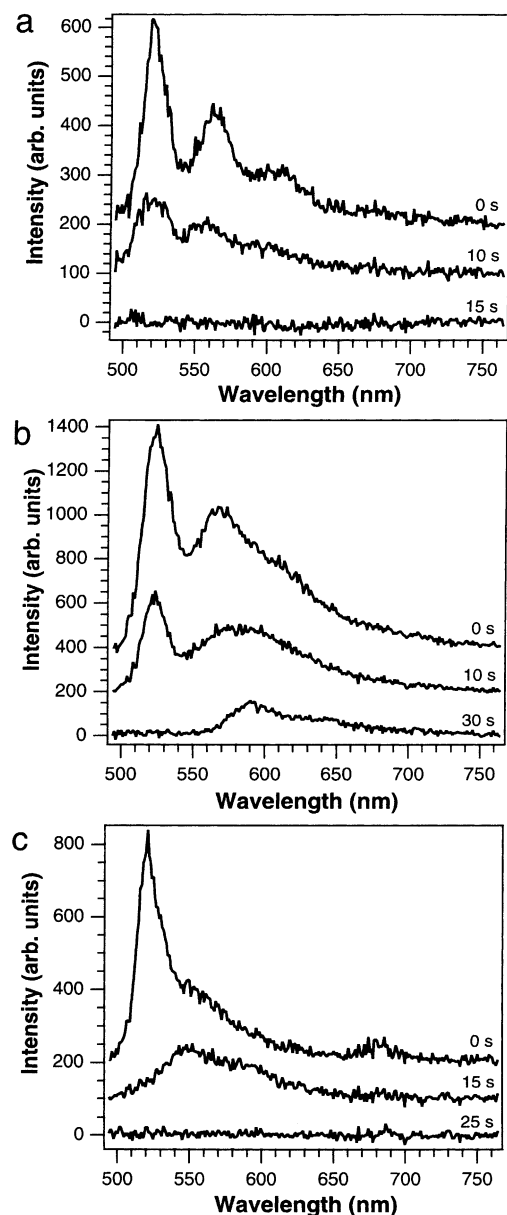
Fig. 6. Temporal evolution of spectra of single dPPV molecules. (a) Single dPPV molecule spun-cast from chloroform solution. (b) Another dPPV molecule spin-cast from chloroform, but identified as being self-aggregated by the photoluminescence excitation criterion. (c) Single dPPV molecule spun-cast from the unfavorable solvent mixture 50% toluene/50% dimethylsulfoxide.

excitation criterion. This molecule shows a strong 0–0 peak at 525 nm on top of a broad and red-shifted band that peaks between 570–590 nm.

With prolonged exposure, the peak at 525 nm decays completely and just the broad background remains. We assign this behavior to π-stacking of the conjugated backbone onto itself. Part of the dPPV molecule is folded back onto itself and creates the broad red-shifted emission due to interchain interactions. Only that part of the molecule that is not in contact with a neighboring chain produces the ini-

tial pure singlet emission. The percentage of molecules that show such a behavior is relatively small (∼10%) and does not depend on solvent polarity. This suggests that the physical separation of conjugated polymer backbones by dendritic sidegroups is quite effective. There is, however, still a good chance for π-stacking in thin films, that leads to red-shifted excitation and emission as illustrated in Fig. 5a. To force and study molecular aggregation of dPPV we have prepared a mixed solvent solution. dPPV was first dissolved in toluene and after the polymer had completely dissolved, dimethylsulfoxide (DMSO), a non-solvent for dPPV, was added to the solution. The final solution had a concentration of 10^{-9} M dPPV in 50% toluene and 50% DMSO (by volume). Fig. 6c represents the spectral evolution of a dPPV molecule prepared from this solution. This molecule shows a very similar behavior as the self-aggregated molecule in Fig. 6b. The addition of DMSO causes the majority of dPPV molecules to form self-aggregates as can be seen from 488/514.5 nm image scans (data not shown). The freely dangling non-aggregated PPV residue gives a strong blue emission at the position of the 0–0 vibrational peak of the non-aggregated molecules (cf. Fig. 6a). After this part of the polymer has been photobleached, the only photoluminescence derives from the supposedly stacked part with an excimer-like red-shifted and weak emission. These results suggest, that the two-dimensionally extended molecule created by the introduction of denritic sidegroups allows for either full interaction of its π-conjugated segments or none. These back-folded molecules obviously stabilize themselves against twists and bends and lead to full contact between adjacent segments. These form excimers and show their characteristic red-shifted luminescence, which is otherwise only observed at low temperatures [4].

4. Conclusions

In conclusion, we have shown, that chain conformation has significant impact on conjugated polymer photophysics. The preparation of MEH-PPV molecules from solvents with different polarity, where these molecules take on extended or folded conformations [2], leads to distinctive changes in their spectroscopy. The photophysical behavior of coiled or densely-folded polymers is dominated by three-dimensional intramolecular energy transfer and only the segments in lowest energy states are emissive. In addition, polarization anisotropy and the strong dipole–dipole interactions indicate, that the folding of polymer molecules occurs in a well-organized pattern. The strong coupling in folded polymers explains the recently observed intermittent emission and strong quenching by cations [18]. In this case, small parts of the polymer chain dominate its entire photophysics. This property is desirable for applications such as antenna complex design for energy transduction or biological sensing where attachment to an appropriate site can quench the luminescence of thousands of absorbing chromophores.

Extended, relaxed chains on the other hand show little interaction between neighboring segments. Foerster-type energy transfer is prohibited by their heads-on dipole orientation and energy migration can only take place by thermally induced electron-hopping [11]. Consequently, these chains emit from multiple sites. Clearly, this is more desirable in the fabrication of electroluminescent films where interchain interactions both reduce luminescence yield and facilitate rapid excitation transport to quench sites that form preferentially in low energy regions. The addition of dendritic side-groups to PPV-type polymers helps to significantly reduce intersegmental contact. Little influence of solvent polarity on the spectroscopy of these polymers has been found. The addition of non-solvents, however, leads to excimer-like emission presumably due to π-stacking of the chain onto itself.

This work has shown, that the conformation of conjugated polymers plays an important role in single chain photophysics and should not be neglected in the design of thin-film devices.

Acknowledgements

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