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Excitonic Processes in a Conjugated Polyelectrolyte Complex

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Abstract

In aqueous solution, a di-sulphonated phenylenevinylene polymer (DPS-PPV) forms a complex with non-ionic poly(vinyl alcohol) (PVA) leading to absorption spectral shifts and a dramatic (6-fold) increase in DPS-PPV fluorescence intensity. Spectroscopic investigations demonstrate that the complexation with PVA and other neutral polymers results in conformational changes in the DPS-PPV chains that lead to the removal of non-fluorescent energy traps and resulting in the observed increase in fluorescence in bulk solution. Single molecule fluorescence measurements of DPS-PPV chains dispersed on glass and in PVA films confirm that efficient exciton energy transfer occurs within each photo-excited DPS-PPV chain and that the observed increase in fluorescence intensity in the PVA film environment is also associated with fewer quenching sites. The results highlight the importance of conjugated polyelectrolyte conformation on exciton relaxation pathways.

Introduction

Polymers with a conjugated polymer backbone often exhibit semi-conducting properties that have been exploited in the development of optical light emitting diodes (OLEDs) and organic solar cells (OSCs).[1-4] A well-studied example is poly(2-methoxy-5-(-2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) which has been extensively characterized and investigated for OLED and OSC applications.[5,6] The main chain backbone conjugation in these polymers is interrupted by conformational defects so that the polymers consist of a distribution of conjugation lengths and it is these segments which make up the light absorbing chromophores within the polymer chain.[7,8] It has been shown that photoexcitation of the polymer leads to excitation energy transfer between the conjugated sequences resulting in fluorescence arising from excitons located on lower energy conjugated segments.[9] Single molecule fluorescence studies by our group and others have demonstrated that changes to the conformation of single chains of MEH-PPV and related polymers can modify the exciton energy transfer process.[10-12] Thus for extended MEH-PPV chains dispersed in poly(styrene) film, emission arises from multiple chromophores of the chain whereas for the coiled conformations adopted in poly(methyl methacrylate) films, where intra-chain energy transfer is efficient, a low energy single chromophore is the primary emitter.[11]

Water soluble variants of these polymers also show interesting behaviour that have led to their application as fluorescence sensors and interfacial coatings in opto-electronics.[13,14] We have described previously the properties of the conjugated polyelectrolyte poly(2,5-dipropoxy-sulphonato-1,4-phenylenevinylene) (DPS-PPV)(see Figure 1).[15] In this work we report that DPS-PPV forms an interpolymer complex with non-ionic poly(vinyl alcohol) (PVA) (Figure 1) in aqueous solution leading to a remarkable increase in fluorescence intensity. Spectroscopic and single molecule fluorescence studies have been applied to investigate and identify the origin of these photophysical changes.

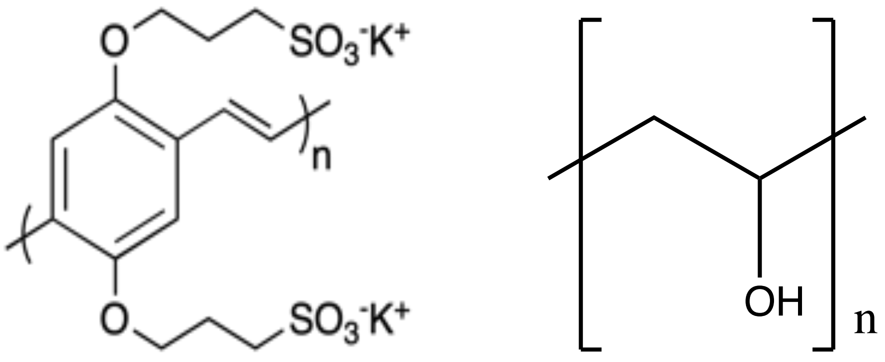

Figure 1. Chemical structures of DPS-PPV (left) and PVA (right)

Experimental

The potassium salt of DPS-PPV synthesized in our laboratories and characterized previously was used in this investigation.[15, 16] Molecular weight analyses using analytical ultracentrifugation techniques determined a weight average molecular weight of 24,800.[16] As the concentration in water increases, the apparent molecular weight also increases due to the formation of interpolymer chain aggregates[16] but at the very low concentrations (~10^{-7} M in polymer chains) used in this work inter-chain aggregation should be minimal. Aqueous solutions for study were made up by dilution of stock solutions of DPS-PPV and PVA (Sigma Aldrich) in Milli-Q water so that the concentration of DPS-PPV chains was kept constant at 4.0×10^{-7} M (2.4×10^{-5} M in monomer units).

Absorption and corrected fluorescence spectra were recorded on a Cary 50 UV-Vis spectrophotometer and Cary Eclipse fluorimeter respectively. Fluorescence quantum yields were determined relative to fluorescein in 0.1 M NaOH ($\Phi_f = 0.925$).[17] Fluorescence lifetimes were measured using the time-correlated single photon counting technique as described previously[18] using the frequency doubled output of a cavity dumped mode-locked Coherent Mira/PulseSwitch laser operating at 400 nm as the pulsed excitation source. Fluorescence decay curves were analysed using FAST software (Edinburgh Instruments). The wide-field single molecule fluorescence measurements were recorded using an instrument described elsewhere[11] based on an Olympus IX71 inverted microscope with fluorescence image detection by a Princeton Instruments PhotonMax 512 CCD camera.

Excitation was with either a 473 nm diode laser (Shanghai Laser & Optics Century Ltd, Model BL4737-150) or 532 nm diode laser (Shanghai Dream Lasers Technology Pty Ltd, Model 532-200T). DPS-PPV (~10^{-9} M concentration in water) was either spin-coated directly onto glass cover-slips or dispersed in PVA films on cover slips by spin-coating with 10 mg/ml PVA (500 rpm for 10 minutes then 2000 rpm for 100 seconds). The final DPS-PPV:PVA films were ~70nm thick as measured by a Dektak 150 profilometer. The films were studied under nitrogen.

Results and Discussion

Additions of PVA to aqueous solutions of DPS-PPV (4.0×10^{-7} M) leads to a red-shift in the absorption maximum and a small increase in absorption coefficient (Figure 2). The maximum absorption changes are reached at a molar ratio of PVA:DPS-PPV of ~10:1. There is an isosbestic point at 455 nm consistent with a transformation between two species. Under the same conditions, the fluorescence of the DPS-PPV solution excited at the isosbestic wavelength of 455 nm shows a dramatic increase in intensity with addition of PVA (Figure 3) that also reaches its maximum at the same molar ratio. The fluorescence yield of DPS-PPV increases from 0.073 to 0.46 over the addition range, a factor of 6.3. The final solution is highly fluorescent to the eye. The average fluorescence lifetime measured by time-correlated single photon counting (See Supplementary Material, S1) increased only slightly with the addition of PVA, from 0.59 to 0.62 nanoseconds.

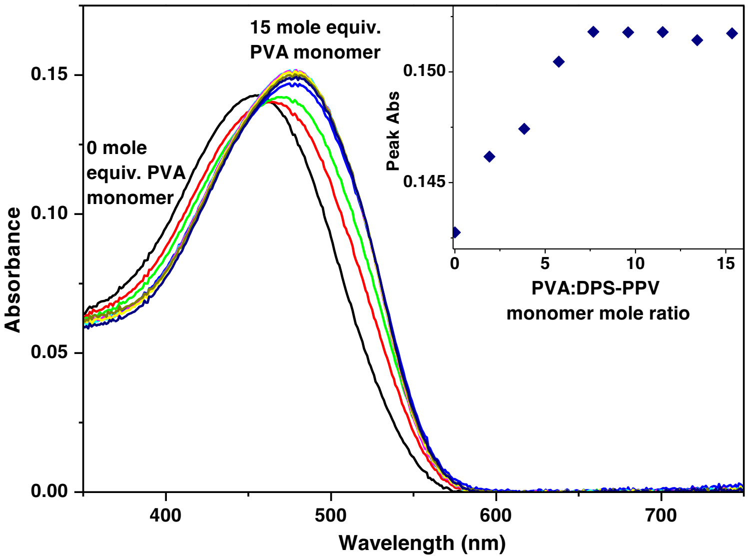

Figure 2. Absorption spectra of aqueous DPS-PPV (4.0 x 10^{-7} M) with additions of PVA. Inset: maximum absorbance vs. mole ratio PVA:DPS-PPV.

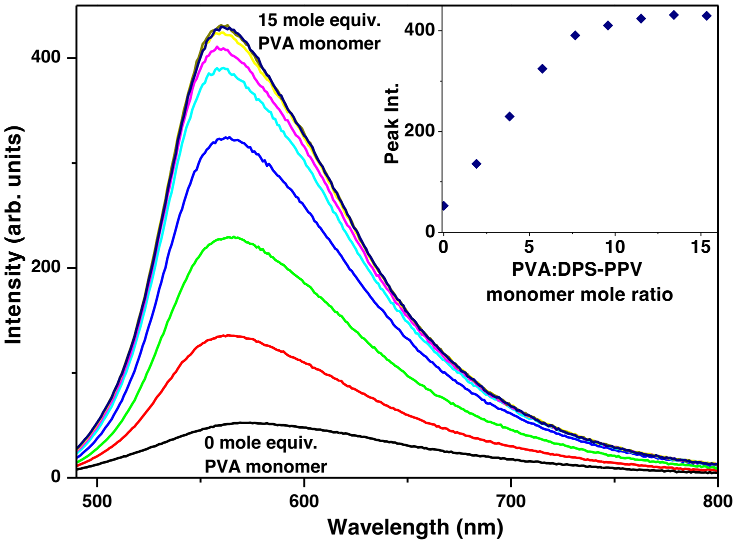

Figure 3. Fluorescence spectra of aqueous DPS-PPV (4.0 x 10^{-7} M) with additions of PVA. Excitation wavelength 455nm. Inset: fluorescence intensity vs. mole ratio PVA:DPS-PPV.

These bulk solution observations are consistent with complex formation between DPS-PPV and the non-ionic polymer PVA that leads to a major change in exciton relaxation pathways of the conjugated polymer. Complex formation has been reported previously for a mono-sulphonated analogue, MPS-PPV, with the surfactant sodium dodecyl sulphate[19] and cationic surfactants[20] leading to changes in fluorescence and solubility properties. For the non-ionic polymer PVA, charged interactions with the anionic DPS-PPV polymer are not possible. Similar spectral changes occur in solutions of DPS-PPV with poly(acrylic acid) (PAA) in its neutral (protonated) form at pH 3.5 (at pH 9, when PAA is a polyanion, interaction is much reduced, see Supplementary Material S2). Hydrogen bonding interactions with the PVA hydroxyl or PAA carboxylic acid groups could be excluded as similar complexation and fluorescence increase was also observed in the presence of the neutral, aprotic polymer poly(vinyl pyrrolidone) (PVP) (Figure 4).

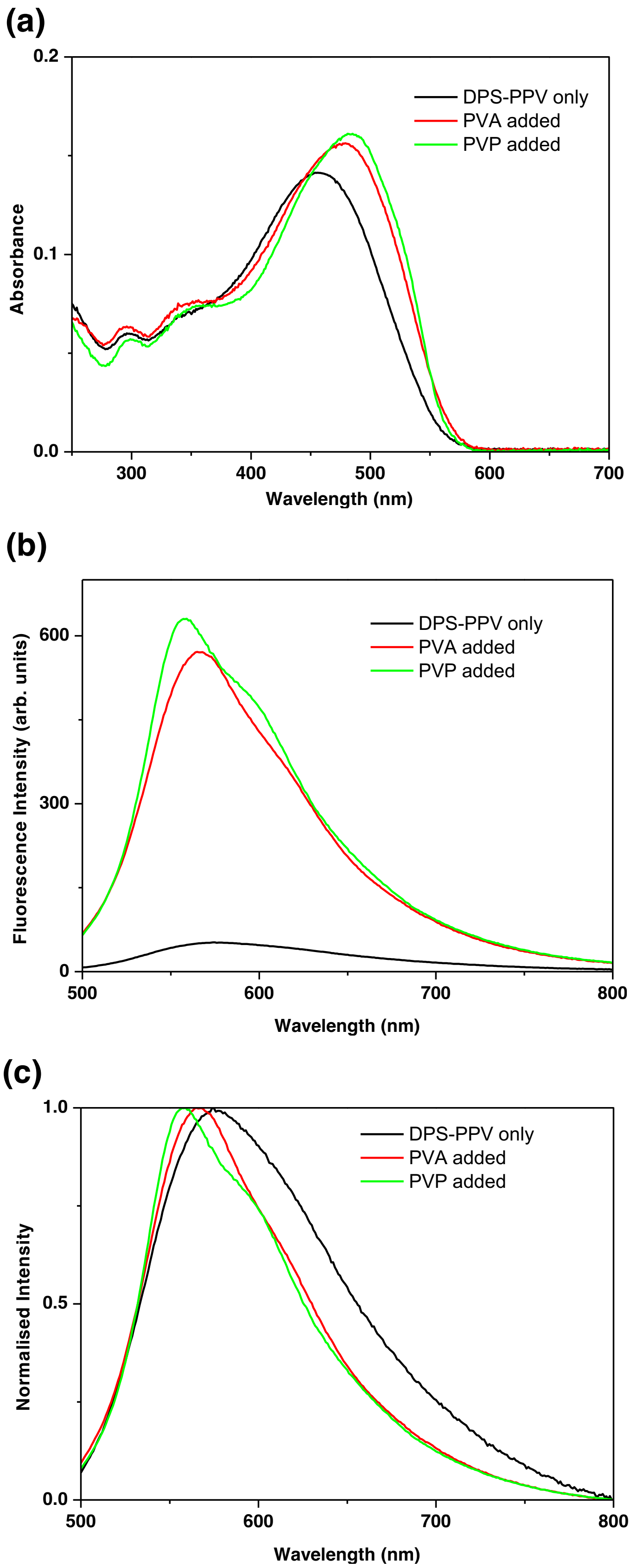

Figure 4. Absorbance (a) and absolute (b) and normalised (c) fluorescence spectra for DPS-PPV (4.0 x 10^{-7} M) in water, and in water with 1 mg/ml PVA and PVP (ex. 455 nm).

The most likely origin of the interaction with PVA is thermodynamically driven association between the polymers (hydrophobic effect) as proposed for other aqueous polymer complexes.[21] The non-polar backbone of DPS-PPV will tend to avoid the polar aqueous environment leading to coiling of each polymer chain into tight clusters with the anionic sulfonate groups surrounded by solvation shells of water. Non-ionic PVA can associate with and envelop the DPS-PPV polymer chains, reducing water interactions with the backbone and allowing the conjugated polymer clusters to expand so the chains become more extended within a PVA envelope. The high mole ratio of PVA:DPS-PPV (~10:1) required to achieve the maximum effect supports the mechanism of solvent displacement.

Changes in the spectral energies and line-shapes of DPS-PPV (Figure 4) upon complexation with PVA, protonated PAA, and PVP, lend strength to this uncoiling hypothesis. The red-shift in the absorption spectrum is consistent with extension of the DPS-PPV chains, leading to longer conjugation length sequences of DPS-PPV monomer units which are of lower energy. Delocalisation of excitation energy over larger number of monomer units redistributes spectral intensities into the 0,0 Franck-Condon transitions.22 The reduction in relaxation leads to a sharpening of absorption and emission bands, an effective blue-shift of the fluorescence maximum, and a reduced Stokes Shift, all of which are observed here for the DPS-PPV/polymer complexes. Complexation with PVP shows enhanced effects (fluorescence blue shift and intensity increase) than PVA which can be attributed to additional extension of the DPS-PPV polymer chains. Although not explored further in this work it might be expected that the magnitude of the hydrophobic effect and extent of uncoiling will depend on the relative ability of the polymer complex formed to reduce water interactions with DPS-PPV. Tensile drawing of MEH-PPV films reported elsewhere led to similar spectral changes to those observed here and also attributed to chain extension.23

The question then arises as to the origin of the striking increase in fluorescence intensity of DPS-PPV in the presence of PVA and other neutral polymers. In the tight clusters of the un-complexed polymer, close association and aggregation of the DPS-PPV chromophores will be favoured. This can lead to the formation of non-fluorescent dimers and higher aggregates that can act as low energy traps. Efficient energy transfer among the tightly packed chromophores will further favour rapid re-location of the absorbed light energy to these trap sites. Such non-fluorescent dimers and excimer traps have been proposed previously for conjugated polymer systems.[24, 25] Addition of PVA and formation of the interpolymer complex leads to uncoiling of the DPS-PPV clusters and removal of these trap sites. Consistent with this proposal is that the fluorescence lifetime of the polymer is not affected greatly by addition of PVA. In the absence of PVA, fluorescence arises from a few unquenched chromophores in sections of polymer that are unable to transfer energy to the trap sites. Addition of PVA, with the associated uncoiling of the DPS-PPV and removal of non-fluorescent traps, allows many more chromophores in the DPS-PPV to fluoresce. In the coiled state in the absence of PVA, DPS-PPV chromophores thus effectively undergo a static quenching process (at least on the time scale of our fluorescence lifetime measurements) due to the presence of energy traps formed by close association of the polymer chain segments. The much stronger enhancement of fluorescence observed in this work compared to the effects of conformational change reported for the non-polyelectrolyte MEH-PPV in various organic solvents,[10] is likely associated with the strong quenching of the coiled polymer in aqueous solution and the large chain extension that occurs with complexation.

In order to investigate further the effect of conformation of individual DPS-PPV chains on exciton relaxation pathways, single molecule fluorescence studies were undertaken in the absence and presence of PVA. The fluorescence from single polymer chains can be studied by spin coating very dilute solutions of the polymer (~10^{-9} M) on to glass cover slips and imaging the resulting emission through a fluorescence microscope equipped with a sensitive CCD detector.[11, 26] Since the single chains deposited from such dilute solutions are spatially separated by several microns, fluorescence from each molecule can be identified and monitored. We anticipated that DPS-PPV chains dispersed from aqueous solutions on to glass slides should retain the coiled, compact conformation. However, when the conjugated polymer was spin-coated from PVA solutions to form a film on the glass substrates, the more extended conformations would be favoured. We have previously reported wide-field single molecule studies of MEH-PPV dispersed in various polymer films.[11] In particular defocussed images of single molecule fluorescence can provide insight into the extent of energy transfer within a polymer chain. By degrading the image by defocussing (i.e. achieved by moving the objective towards the sample by ~1 micron from the focused position), the image patterns observed are characteristic of single chromophore or multiple chromophore emission from an individual polymer chain.[27-29] Typical focussed and defocussed fluorescence images of a single chain are shown in Figure 5. Under focussed conditions a single diffraction limited fluorescence spot is observed. However, with defocussing a bi-lobe patterned image arises for a single chromophore emitter. This pattern is associated with the angular spatial distribution of emitted light intensity from a single in-plane emission transition dipole.[29] If the polymer has multiple emitters with their transition dipoles in different orientations, a superimposition of single emitter patterns leads to a characteristic “doughnut” shape pattern (Figure 5).[29]

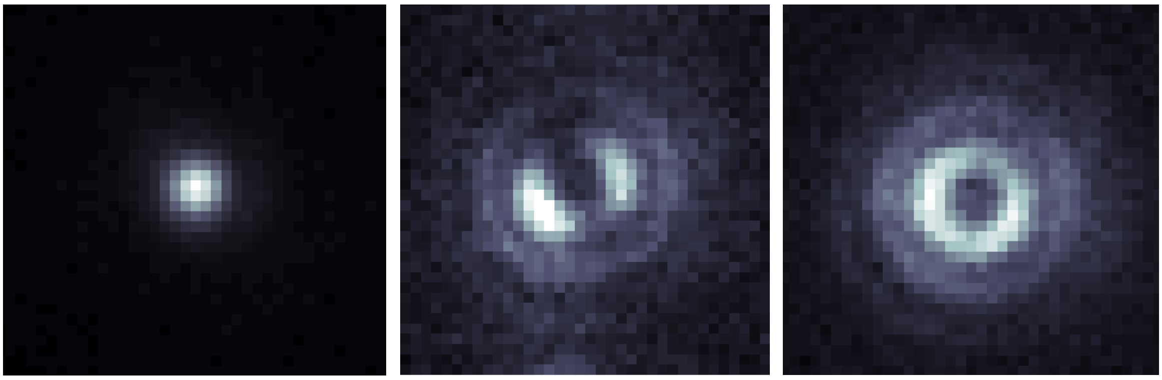

Figure 5. Diffraction limited focussed fluorescence image of a single polymer chain (left), defocussed image pattern for a single chromophore emitter (centre), and defocussed image pattern arising from multiple emitters in a single chain (right). The size of each image is 2.3 x 2.3 microns with excitation at 532 nm.

Widefield single molecule micrographs for DPS-PPV on glass and DPS-PPV:PVA films are provided in Figure 6. Unlike bulk measurements which report the ensemble average fluorescence properties, single molecule experiments reveal a distribution of fluorescence behaviour arising from the range of conformations and excited state properties unique to each molecule. The images of many molecules need to be analysed to measure this distribution. For DPS-PPV molecules dispersed on glass the emitters observed were almost exclusively single chromophore emitters (217 of 218 measured) while for DPS-PPV:PVA films the vast majority (198 of 209 measured) were also single emitters. For DPS-PPV which is composed of multiple chromophores that are repeatedly excited during the image collection, the observation of single emitters is consistent with efficient energy transfer to a single emitting chromophore site.[11] The laser power at the sample for the measurements with 532 nm excitation was 2.6 mW (power density ~ 0.5 kWcm^{-2}). Increasing the power by an order of magnitude decreased the survival time of the emitters but did not affect the preponderance of single emitters. Previous single molecule studies for the water insoluble analogue MEH-PPV (molecular weight 1 x 10^6) have reported multi-emitters in extended polymer chains attributed to inefficient energy transport.[10] The molecular weight of DPS-PPV (24,000) is much lower than used in these studies and one might expect more efficient energy transfer among the fewer chomophores that comprise the polymer chain.

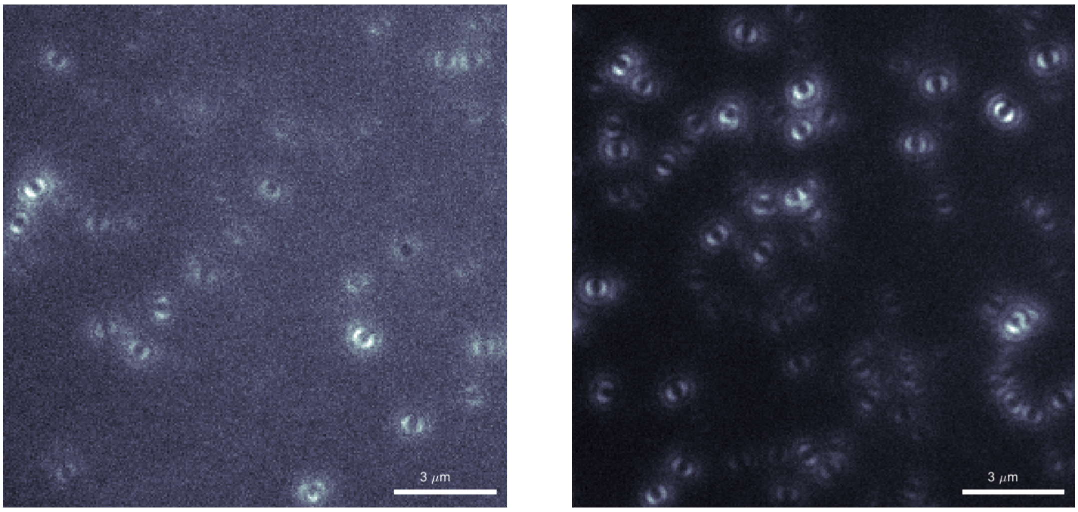

Figure 6. Defocussed widefield single molecule fluorescence images of DPS-PPV deposited on glass (left) and in DPS-PPV:PVA film (right). The size of each image is 17.4 x 17.4 microns (excitation at 532 nm, 1 second integration time). The contrast for the image on the right is 2x greater than the image on the left.

It was observed that the DPS-PPV:PVA fluorescence images appeared significantly brighter and were more stable over time than the DPS-PPV on glass single molecule images. The relative brightness was quantified by measuring the maximum fluorescence intensity of many diffraction limited fluorescence spots for both samples with the resulting histograms shown in Figure 7. The histograms show a clear bias for higher intensities for the DPS-PPV:PVA sample. The mean (median) maximum fluorescence intensity was 11,500 (10,320) for DPS-PPV on glass and 30,000 (25,600) for DPS-PPV:PVA films. These single molecule results demonstrate that (i) energy transfer is an efficient process in isolated DPS-PPV polymer chains and (ii) that there is quenched emission for the DPS-PPV chains on glass. Non-emissive (totally quenched) chains will not be observed in the single molecule fluorescence experiments and the reduced emission of those molecules that are detected on glass suggests there is a quenching process during the collection time of the image (~300ms) that is not present in the PVA environment. The results are consistent with a coiled conformation for DPS-PPV chains on glass that provides additional quenching opportunities compared to the DPS-PPV:PVA film.

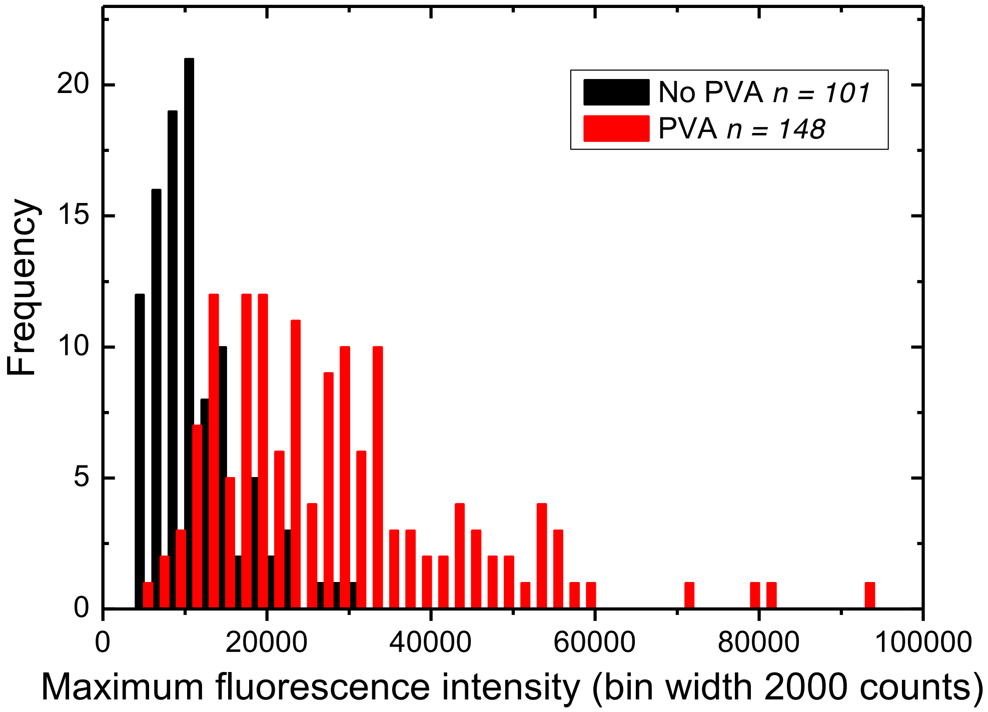

Figure 7: Histogram of the maximum fluorescence intensity of individual single molecule emitters for DPS-PPV on glass and DPS-PPV:PVA films (excitation at 473 nm).

A further interesting observation was the marked difference in single molecule emission time trajectories for the two samples (see Figure 8). Most single molecules of DPS-PPV:PVA displayed a prolonged stepwise decay in intensity over 10's of seconds. Such trajectories are typical of the gradual bleaching of chromophores in the polymer chain (i.e. once the lowest energy emitter is bleached, it is replaced by emission from another conjugated segment until all chromophores are bleached).[30] On the other hand, for the DPS-PPV on glass sample, the majority of single emitters displayed a very rapid fall-off of in intensity with exposure time (Figure 8). Preliminary single molecule measurements for DPS-PPV:PVP films were similar to the results obtained for DPS-PPV on glass alone. While a full explanation for these observations is beyond the scope of the present work, this lower photostability of the DPS-PPV emitters on glass and in PVP could reflect an increased exposure to residual atmospheric oxygen (compared to DPS-PPV embedded in PVA) or specific bleaching interactions with the glass surface or PVP film environment.

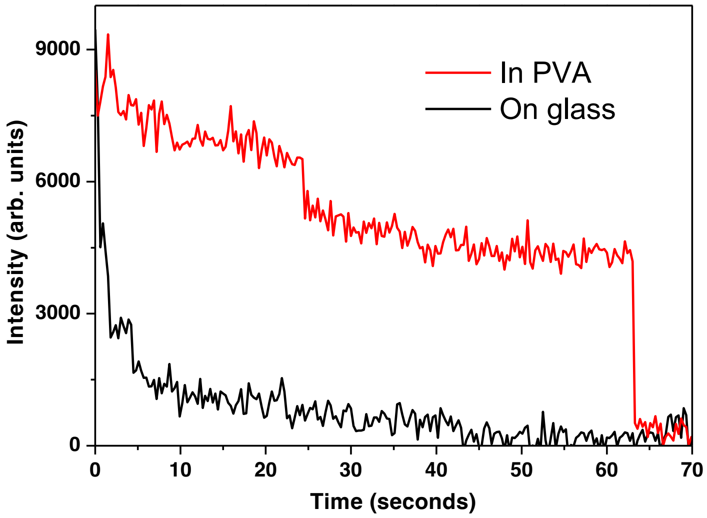

Figure 8: Examples of single molecule fluorescence intensity-time trajectories for DPS-PPV chains on glass and in PVA film (excitation at 473nm).

Conclusion

The conjugated polyelectrolyte DPS-PPV readily forms a complex with non-ionic poly (vinyl alcohol) in water. Associated with complex formation is a dramatic increase in DPS-PPV fluorescence intensity. The spectroscopic results presented here imply that the increased fluorescence intensity is associated with a collapse of compact polymer conformations and an extension of the DPS-PPV chain when PVA is present. The reduction in quenching dimer/aggregate trap sites accompanying extension of the polymer chains is proposed as the likely reason for the observed increase in fluorescence. The different polymer conformations of DPS-PPV on glass and in PVA film have also been probed by single molecule fluorescence measurements. In the PVA film environment higher fluorescence intensities and increased photostability of single molecules are observed. While bulk and single molecule measurements confirm that efficient exciton energy transfer in DPS-PPV chains occurs, coiling of DPS-PPV chains are conducive for the formation of quenching trap sites that decrease fluorescence. These results highlight the important role of polymer chain conformation on the fate of excitation energy in conjugated polyelectrolytes.

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Graphical Abstract

Addition of poly(vinyl alcohol) (PVA) to aqueous solutions of the conjugated polyelectrolyte DPS-PPV ‘turns on’ fluorescence intensity due to complexation and associated changes in DPS-PPV conformation.