

Single Molecule Nanoparticles of the Conjugated Polymer MEH–PPV, Preparation and Characterization by Near-Field Scanning Optical Microscopy

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We have developed a straightforward method for producing a stable, aqueous suspension of hydrophobic, fluorescent π -conjugated polymer nanoparticles consisting primarily of individual conjugated polymer molecules. Features of the method are the facile preparation, purity, unique optical properties, and small size (~ 5 – 10 nm) of the resulting nanoparticles. The results of TEM, scanning force microscopy, and near-field scanning optical microscopy of particles cast from the suspension indicate that the particles are single conjugated polymer molecules. The NSOM results yield estimates of the optical cross-sections of individual conjugated polymer molecules. The UV–vis absorption spectra of the nanoparticle suspensions indicate a reduction in conjugation length attributed to deformations of the polymer backbone. Fluorescence spectra of the aqueous nanoparticle suspensions indicate interactions between segments of the polymer chain and intramolecular energy transfer.

Introduction

Fluorescent conjugated polymers have been demonstrated in a wide range of electrical device applications.^{1–3} There is considerable current interest in improving control of nanoscale composition in conjugated polymer blends to improve the efficiency of polymer LEDs and photovoltaics.^{4–6} Recently, a mini-emulsion method was employed to prepare submicron sized conjugated polymer particles (~ 0.1 μm diameter), and device layers were fabricated from aqueous suspensions of the conjugated polymer particles as a strategy for obtaining improved control over composition in device films.^{7–9} Fluorescent nanoparticles are also of interest for biomolecule labeling and sensing owing to the high brightness and photostability of fluorescent nanoparticles as compared to conventional fluorescent dyes.^{10,11} Most fluorescent nanoparticles to date are based on inorganic semiconductors^{10,11} or dye-loaded beads.¹² Here, we present a novel, facile method for preparing aqueous dispersions of hydrophobic, fluorescent conjugated polymer nanoparticles consisting primarily of single conjugated polymer molecules. Possible applications for these nanoparticles include nanocomposite electrooptical devices and fluorescent labels. Conjugated polymer nanoparticles possess several advantageous properties for fluorescence labeling applications such as a short excited-state lifetime (which minimizes saturation effects), quantum yields approaching unity,¹³ and a large absorption cross-section per particle. Additionally, conjugated polymers are of particular interest for fluorescence-based sensing due to the high fluorescence quenching efficiency associated with multiple energy transfer between segments of the polymer chain.^{14–16} For example, sensitive solution-based fluorescent DNA probes based

on multiple energy transfer in ionic conjugated polymers have been demonstrated.¹⁵

There is a complex relationship between molecular conformation and the optical and electrical properties of conjugated polymers. Conjugated polymer conformation determines the interactions between segments of polymer chains. These interactions give rise to interchain species such as dimers, excimers, and exciplexes. The effects of conjugated polymer conformation and interchain interactions on the optical properties of solutions and films have been probed using a variety of optical techniques.^{13,17–24} Recently, near-field scanning optical microscopy (NSOM) and single molecule spectroscopy have emerged as powerful tools for determining how structure governs optical properties in conjugated polymers and polymer blends.^{25–38} The typical red shift in the absorption and fluorescence of the film compared to that in solution is attributed to interchain interactions and rapid energy transfer to a small number of red-shifted chromophores. The ability to probe the photophysics of molecules of conjugated polymers in aqueous suspension provides a unique point for comparison to studies of the optical properties of conjugated polymers in various organic solvents and in bulk films. For a dilute aqueous suspension of hydrophobic polymer molecules, the interaction between molecules is miniscule, but the interactions between different segments of a given polymer chain increase. The aqueous suspension thus provides a way to eliminate interchain effects and determine the optical properties associated with intrachain interactions in individual collapsed polymer chains.

Here we demonstrate for the first time a simple, general method for preparing a pure, surfactant-free, stable, aqueous dispersion of fluorescent, conjugated polymer nanoparticles, starting from commercially available device-grade conjugated

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polymers. The well-studied conjugated polymer poly[2-methoxy-5-((2-ethylhexyl)oxy)-*p*-phenylenevinylene] (MEH-PPV) was chosen for the experiments reported here. The method is based on addition of the conjugated polymer dissolved in an organic, water-miscible solvent to water, followed by rapid mixing. Preparation does not involve emulsion polymerization or surfactants and can be applied to a wide variety of conjugated polymers that are soluble in organic solvents. In addition, the nanoparticles produced are typically 5–10 nm in diameter, consistent with single polymer molecules and an order of magnitude smaller than particles produced by other methods.^{7–9} Fluorescence and absorbance spectra provide evidence of significant interactions between segments of the polymer chain, intraparticle energy transfer, and decreased mean conjugation length.

Experimental Section

Suspensions of polymer nanoparticles were produced as follows. MEH-PPV with an average molecular weight of 200 000 amu was purchased from ADS Dyes, Inc. and was used without further purification. The polymer was dissolved by stirring overnight in HPLC grade THF under inert atmosphere. The solution was then filtered through a 1.6 μm filter and further diluted to a concentration of 0.005 wt %. A 2 mL quantity of the MEH-PPV/THF solution was added quickly to 8 mL of deionized water while the mixture was sonicated. The resulting suspension was filtered with a 0.2 μm membrane filter. The THF was removed by evaporation under vacuum, followed by filtration through a 0.2 μm filter. The resulting suspensions were clear (not turbid), with an orange color. On the basis of investigations of the degree of aggregation in the aqueous suspension (determined by spectroscopy and filtration) as a function of the concentration of the MEH-PPV/THF solution, it was determined that little aggregation occurs if the concentration of the MEH-PPV/THF solution is at or below 0.005 wt %. Therefore, all experiments were performed on suspensions prepared from a 0.005% solution. The suspensions were found to be stable for weeks at a time, with no evidence of aggregation. The suspensions were also stable upon concentration by water evaporation. Complete removal of water resulted in a film that was insoluble in water, perhaps due to coalescence as observed in previous reports of films cast from aqueous suspensions of larger (0.1 μm) conjugated polymer particles.⁸

The fluorescence spectra of thin film and solution samples were recorded using a cooled CCD spectrograph (488 nm excitation). Thin film samples were placed at an angle of approximately 45° with respect to the excitation beam. Additional fluorescence spectra were recorded on a commercial fluorometer system and yielded similar results. TEM images of nanoparticles drop-cast onto metal grids were obtained. Thin films cast from THF were obtained by spin-coating the 0.1 wt % solution onto cleaned microscope cover glass. Partial layers of nanoparticles for NSOM studies were prepared by drop-casting the aqueous suspension onto cleaned microscope cover glass and drying under a nitrogen flow. Near-field fluorescence and transmission microscopy of the nanoparticles was performed on a modified Aurora 2 NSOM microscope. Excitation was provided by the 488 nm line of an argon ion laser, coupled to the optical fiber probe. Near-field transmission and fluorescence light were collected with a 50X objective mounted underneath the sample and focused onto a single-photon-counting avalanche diode. For fluorescence images, the collected light was passed through a 550 nm long-pass filter to remove the excitation light.

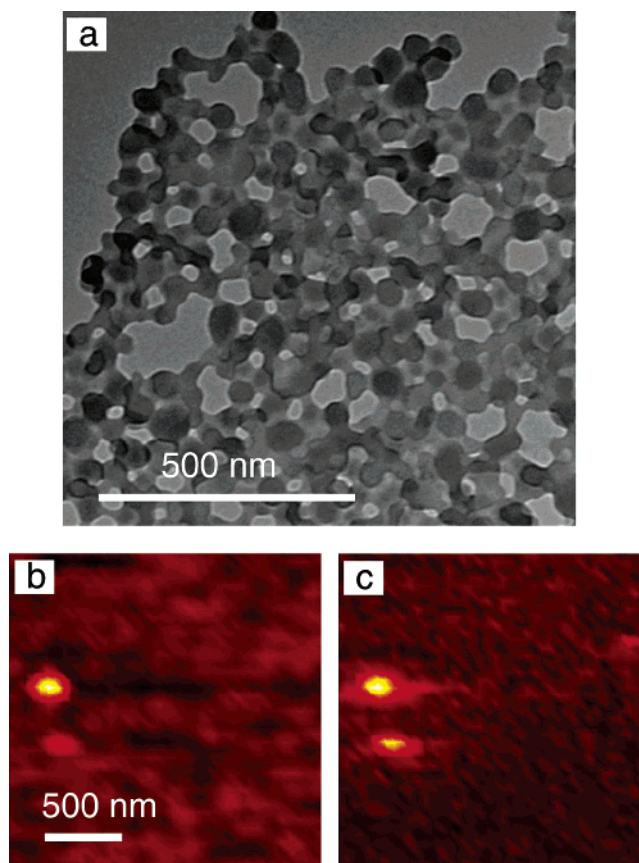


Figure 1. TEM image (a) of a dense island of nanoparticles. Correlated scanning force (b) and fluorescence NSOM (c) of a sparse nanoparticle film.

Results and Discussion

TEM was used to determine particle size and morphology (Figure 1). The drop-cast films formed large islands of roughly spherical particles with diameters ranging from a few nanometers to 30 nm. The islands were similar in overall appearance to results obtained by Landfester et al. for larger conjugated polymer particles.⁷ In the interior of the islands, the particles appear to coalesce to form an interconnected network. This is consistent with our observations that evaporated films are insoluble in water. Such high surface-area networks are considered ideal for polymer photovoltaic applications.^{39,40} Further characterization of well-separated particles on a glass substrate was performed using NSOM, an ultraresolution microscopy technique that combines the nanoscale resolution of scanning probe microscopy with the chemical specificity of optical spectroscopy.^{28,41,42} NSOM was employed to measure the size distribution of nanoparticles as well as for obtaining fluorescence and absorbance images of individual nanoparticles. The resulting images (Figures 1b,c and 2a,b) indicate the presence of primarily isolated nanoparticles. In contrast with the TEM results, few large islands were observed on the films drop-cast onto glass, likely due to differences in casting conditions and substrate. Transmission NSOM images were analyzed to obtain a direct measure of the optical cross-section of individual conjugated polymer nanoparticles as a function of particle diameter (Figure 2c). On the basis of the UV-vis absorption of the solution and the average molecular weight of 200 000, the optical cross-section of an MEH-PPV molecule is approximately 4 nm². If we assume the NSOM probe acts as a simple aperture, the fraction of photons absorbed by a particle within the near field aperture is given by the ratio of the optical

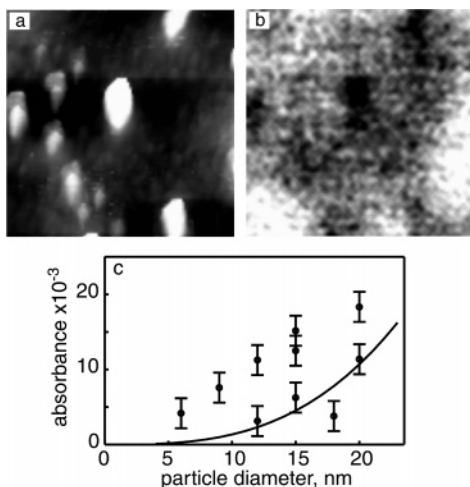


Figure 2. (a) Topography and (b) transmission NSOM images of a nanoparticle film, $2 \times 2 \mu\text{m}$ area. (c) NSOM absorbance versus particle diameter (circles), compared to the estimate based on known absorptivity of MEH-PPV in solution. The error bars represent photon counting noise.

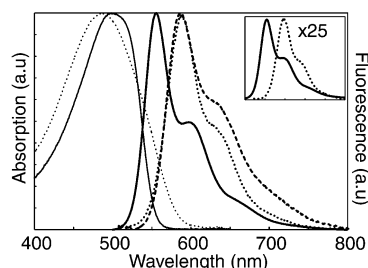


Figure 3. (left) Normalized absorption spectra and (right) fluorescence spectra comparing MEH-PPV suspended in water (solid lines) and dissolved in THF (dotted line). The dashed fluorescence curve is the thin film fluorescence. The inset is a comparison of the fluorescence intensities of MEH-PPV dissolved in THF (solid line) versus nanoparticles suspended in water (dashed line), multiplied by a factor of 25.

cross section to the illuminated area. The measured diameters (estimated from the particle heights) ranged from 5 to 30 nm with the majority between 5 and 10 nm. The measured absorbance NSOM versus particle diameter approximately follows the predictions of the simple aperture model assuming an NSOM aperture diameter of 50 nm and assuming the optical cross-section scales linearly with particle volume. To our knowledge, these results represent the first application of NSOM to estimate the optical absorption cross-sections of individual conjugated polymer molecules. The scatter in the results can be ascribed to particle aggregates, inhomogeneous photobleaching, uncertainties in the measured particle diameters (including deviations from the assumed spherical shape), and near-field effects. The small diameters (5–10 nm) are evidence that the majority of the nanoparticles consist of a single molecule of polymer with an average molecular weight of $\sim 200\,000$. The small fraction of larger particles observed may be due to aggregates or represent the tail of the molecular weight distribution of the polymer. It should be noted that though the size range of the nanoparticles is roughly consistent with single polymer molecules, it is not possible, given the available data, to determine whether a given nanoparticle is a single molecule or an aggregate of smaller molecules, due to the large polydispersity of the polymer sample.

In Figure 3, the UV-vis absorption spectrum of the aqueous suspension of MEH-PPV nanoparticles is compared to the

spectrum of MEH-PPV dissolved in THF. The absorption peak of the polymer nanoparticles is slightly blue-shifted and the spectrum is broadened as compared to that of the polymer dissolved in THF. The observed blue shift of the absorption spectrum of the nanoparticles is consistent with an overall decrease in the conjugation length.²³ Because the nanoparticles possess a compact, approximately spherical structure, the reduced conjugation length can be attributed to bending or kinking of the polymer backbone. The results of electronic structure calculations suggest that PPV-type polymers are more flexible than is generally believed, with a low barrier to spontaneous formation of tetrahedral defects.⁴³ Such defects exhibit a blue-shifted spectrum, consistent with our conclusions. In contrast, the absorption spectra of thin films (and aggregates) are typically red-shifted as compared to that of the solution due to reduced bending of the polymer backbone and increased interchain interactions.²² The nanoparticle absorption spectrum also exhibits a long red tail, indicating some red-shifted chromophores, likely due to intrachain interactions in the collapsed, folded polymer structure.

The conformation of stiff, rodlike polymers under various conditions is a subject of intense practical and fundamental interest.^{35,43–46} Theoretical results indicate that a wide variety of conformations can be obtained, depending on the rigidity of the backbone and other factors. Although the results presented here indicate a roughly spherical shape, this is likely a quenched, metastable conformation produced by the rapid mixing process. Further studies of the structure of the single conjugated polymer nanoparticles are necessary.

In Figure 3, the fluorescence spectrum of the colloidal suspension of nanoparticles is compared to that of MEH-PPV dissolved in THF and that of the thin film. The fluorescence spectra of the thin film and the nanoparticles are quite similar, with a large Stokes shift. The large Stokes shift for films is attributed to energy transfer to low-energy chromophores and weakly fluorescent aggregates.²² The fluorescence yield of the aqueous suspension was also reduced as compared to that of the solution, in agreement with reports of decreased, red-shifted fluorescence of MEH-PPV in solvent mixtures containing methanol, attributed to energy transfer to weakly fluorescent intrachain aggregates.²⁴

The absorption spectrum of the nanoparticles suggests that the fraction of intrachain aggregates is small, yet the majority of the fluorescence signal is attributed to intrachain aggregates. Therefore it is appropriate to consider whether energy transfer to intrachain aggregates is expected to be sufficiently efficient to partly account for the red-shifted fluorescence spectra. The measured exciton diffusion length of MEH-PPV is approximately 20 nm,⁴⁷ larger than the average particle size and sufficiently large that a small number of red-shifted aggregates per particle can act as energy acceptors for a large majority of chromophores. This conclusion is also supported by reports of efficient quenching of conjugated polymer fluorescence by a variety of quencher molecules^{14–16} and polarons,^{29,48} and by reports of intermittent fluorescence in individual tightly coiled conjugated polymer molecules.^{33–38}

Conclusion

We have demonstrated a facile method for the preparation of an aqueous suspension of single conjugated polymer molecule nanoparticles. The particle diameters, determined by TEM and NSOM, and optical properties, determined by NSOM, UV-vis, and fluorescence spectroscopy, are evidence that the nanoparticles consist primarily of single molecules of conjugated

polymer. The NSOM results also provide a measure of the optical cross-section of single conjugated polymer molecules. The spectroscopy of the suspended nanoparticles reveals a reduction in the mean conjugation length associated with bending or kinking of the polymer backbone as well as energy transfer to intrachain aggregate states. Intrachain energy transfer is important for possible nanoparticle applications such as sensors based on fluorescence quenching.

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