

Oriented luminescent nanostructures from single molecules of conjugated polymers

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ABSTRACT

Dipole emission pattern imaging experiments on single chains of common conjugated polymers (solubilized poly phenylene vinylenes) isolated by ink-jet printing techniques have revealed surprising uniformity in transition moment orientation *perpendicular* to the support substrate. In addition to uniform orientation, these species show a number of striking differences in photochemical stability, polarization anisotropy,[1] and spectral signatures[2] with respect to similar (well-studied) similar molecules dispersed in dilute thin-films. Combined with molecular mechanics simulation, these results point to a structural picture of a folded macromolecule as a highly ordered cylindrical nanostructure whose long-axis (approximately collinear with the conjugation axis) is oriented, by an electrostatic interaction, perpendicular to the coverglass substrate. These results suggest a number of important applications in nanoscale photonics and molecular-scale optoelectronics.

INTRODUCTION

Nanophotonics – or molecular-scale optoelectronics – is a rapidly emerging new area of research that combines nanoscale optical elements (e.g., single-molecules, or quantum dots)[3,4] and molecular scale electronics.[5] For these and other applications, one needs nanoscale components with well-defined transition energies and dipole moment orientation for spatially selective addressability, as well as robust photostability and facile charge transport properties.[6] Because of the inherent size scalability, and long history in mesoscale photonics,[7,8] semiconducting polymers[9] make attractive candidates for nanoscale optoelectronics. However, in conventional thin film formats, these species usually assume random in-plane orientation with a distribution of chain morphologies,[10] and tend to be quite fragile with respect to repeated optical excitation under ambient conditions. Despite the extensive literature on semiconducting polymers and their photophysical properties in thin films, a number of important questions remain as to strategies for controlling chain organization

and alignment in nano- and mesostructured media [11], as well as to how one would characterize at a molecular-level of detail the morphology of such structures.

Recently, work in our laboratory (ORNL) has focused on microdroplet techniques to form polymer- and polymer blend nanoparticles with a tunable size and phase structure.[12] The absence of wall/surface interactions and three-dimensional confinement combine to make polymer particles with properties very different from those observed in thin-films. The work described here was motivated by questions as to how conducting polymers might behave in an isolated nanoparticle environment (i.e. the absence of potentially interfering host material), effect of 3-D confinement and surface energy in an evaporating nanodroplet, and how such an environment might affect chain organization in single-molecules of conjugated polymers.

EXPERIMENTAL

Our experiments reported here combine atomic force microscopy, and recently developed emission pattern imaging tools to probe the morphology and orientation of MEH-PPV nanoparticles formed from micron-sized liquid droplets of dilute solution. We used ink-jet printing methods to isolate single conducting polymer chains in microdroplets of solution typically less than 5- μm initial diameter that evaporate en route to the coverglass substrate. The MEH-PPV used in our experiments was obtained commercially (H. W. Sands Corp. OPA9576) without further purification, and had an average molecular weight of 270,000 (polydispersity $M_n/M_w \approx 8$). Droplets of ultradilute MEH-PPV solution (5 μm nominal diameter, and concentration of $10^{-11} - 10^{-12}$ M) in doubly distilled tetrahydrofuran (THF) were generated from a piezoelectric on-demand droplet generator, dried en route to clean glass coverslips in a 20-cm vented drying tube. At this concentration, the average number of MEH-PPV molecules per droplet is about 0.05 suggesting negligible probability of multichain aggregates forming within a single droplet.

Single MEH-PPV molecules isolated from microdroplets were probed using emission pattern imaging techniques.[13] The measured patterns from a single chromophore derive from a combination of transition moment orientation and coupling to the high-index substrate. Near the coverslip-air dielectric boundary, most of the emitted molecular fluorescence ($\approx 80\%$) is coupled into the glass at orientation-specific angles, instead of isotropically into the air above the coverslip.[14] Because single molecules emit light with a sine-squared distribution relative to the emission dipole orientation, molecules with transition moments aligned along the optic axis emit light only at very high angles relative to the optic axis giving rise to a toroidal or “donut” emission pattern. Conversely, molecules perpendicular to the optic axis emit primarily at shallow angles directly into the microscope objective and give rise to a non-circularly symmetric “wing”-like pattern which can be seen with a small defocusing (≈ 200 nm) of the oil objective.

Figure 1 shows a high-resolution fluorescence image (each pixel corresponds to ≈ 30 nm real-space distance) from isolated single MEH-PPV molecules. The toroidal spatial intensity patterns we observe derive from the fact that emission is forbidden at angles along the optic axis for z-orientation of the transition dipole, resulting in the central intensity node for a given nanoparticle fluorescence image. This result is the exact opposite of the dipole orientation of these species in spun-cast thin films that lie randomly oriented (in ϕ) nearly parallel to the

substrate. Since the transition moment for poly (phenylene vinylenes) lie nearly collinear with the conjugation axis,[15] the observation of uniform z-orientation implies a high degree of intramolecular organization since random-coil geometries would be expected to produce a broad distribution of transition moment orientations even in the event single-dipole emission were observed.[16]

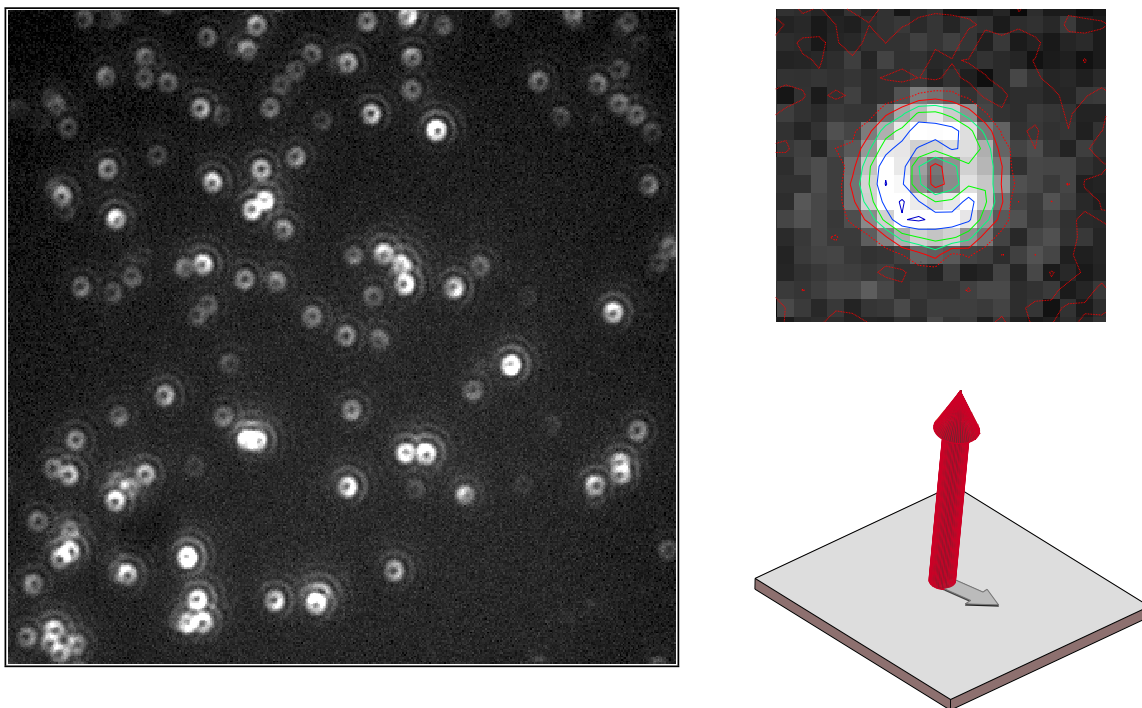


Figure 1. Fluorescence of single MEH-PPV molecules isolated from microdroplets and excited by an expanded Ar^+ laser beam with an intraobjective (1.4 N.A. 100x), total internal reflection (TIR) geometry. Fluorescence was collected through the same high NA objective used to focus the excitation light, and passed through a dichroic filter with a band-edge (50% transmission) at 530 nm. The upper right shows a close-up of a selected emission pattern from the z-oriented sample superimposed with a simulated image from classical electrodynamics (see Ref. 13) from which 3D dipole orientation (lower right) can be obtained.

DISCUSSION

While luminescence dynamics carry important information on the nature of the emissive site within the molecule, polarization modulated single-molecule fluorescence excitation measurements have provided new insights into intramolecular structure.¹⁰ The connection between excitation polarization anisotropy and intramolecular structure in these systems is based on the idea that excitonic excitation can occur in any one of many local conjugated segments within the molecule, followed by rapid intramolecular energy transfer to lower lying radiative trap states. That is, while radiative recombination in the molecule may be highly

localized (as evidenced by dipolar emission patterns, on-off blinking, etc.), the excitation may occur in many different possible sites within the molecule, where the degree of intramolecular order is manifested in contrast in luminescence efficiency between orthogonal polarizations.

To make analogous polarization anisotropy measurements on the z-oriented samples, we modulated the z-component of the evanescent excitation field at the air-coverglass interface by rotating between *S*-(transverse electric) and *P* (transverse-magnetic) input polarizations with a half-wave plate. Multiple *P-S* rotations were made during individual nanoparticle measurements where we obtained polarization anisotropy parameters, *M*, from $[I(P) - I(S)] / [I(P) + I(S)]$ where $I(P,S)$ is the spatially integrated fluorescence intensity for the two input polarizations for each complete rotation cycle. Control measurements on dye-doped polymer nanospheres (Molecular Probes) indicate negligible intensity bias Figure 2 shows representative data for polarization-modulated fluorescence of an isolated z-oriented MEH-PPV nanoparticle compared with a background reference. In this particular example, the frame-averaged polarization modulation parameters were 0.88, 0.89, and 0.84 (± 0.04) for the 3 *P-S* rotation cycles respectively.

Additional evidence for highly ordered intramolecular structures is given by the histogram of anisotropy parameters compared with approximations of simulated distributions for different single-molecule morphological families as well as experimental thin-film results.[10] Our experimental histogram on the z-oriented samples differs significantly in peak value from the simulation of rod-shaped (cylindrical) molecules (0.92 vs. 0.7). As yet, the origin of this difference is not clear, however the interpretation of highly ordered intramolecular structure is supported by hybrid molecular-mechanics simulation. Comparison of the total energy of a MEH-PPV chain in the linear versus folded (at sp^3 defect sites in the chain) cylindrical configuration indicates a significant energy lowering in the folded configuration by 10's of kcal/mol relative to a random coil. Experiments performed on cyano-substituted polyphenylene vinylenes and with different solvents have led to the the conclusion that solution phase morphology plays a dominant role in forming the highly ordered nanostructures observed here. MEH-PPV is known to adopt compact structural forms in THF and nebulization experiments with solvents that are known to support expanded chain configurations (such as methylene chloride or chlorobenzene[11]) do not result in oriented polymer nanostructures. Third, the absence of a host polymer allows the structural organization

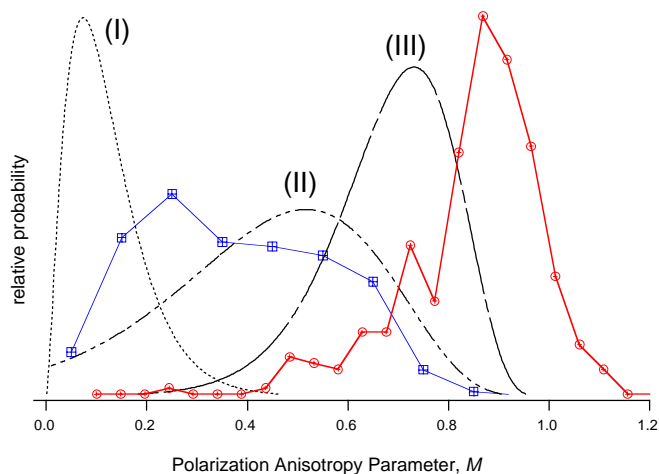


Figure 2. Histogram of measured linear dichroism parameters (red squares) determined from $M = (I_p - I_s) / (I_p + I_s)$, where I_p, I_s are the spatially integrated fluorescence intensity for excitation with z-component (p) and no z-component (s). Thin film results from Ref (10) are shown in blue, and approximations of Monte Carlo simulation of distributions for random coil (I), defect cylinder (II), and rod-shaped (III) molecular configurations (also from Ref. (10)) are shown as solid lines.

to take place without other material potentially interfering with the collapse. The observation of similar orientational behavior for other conjugated polymers and polymer-blend nanoparticles (MEH-PPV and polystyrene) indicate that the behavior is not unique to isolated MEH-PPV, but may be applicable to a broad range of polymeric systems confined to nanoscale domains.

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