

Photon Antibunching from Oriented Semiconducting Polymer Nanostructures

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Semiconducting polymers have been widely studied both in fundamental and photonics applications contexts.¹ However, difficulties in controlling the intramolecular organization often introduce a significant heterogeneity in their photophysical properties. Single-molecule fluorescence studies of conjugated polymers have yielded a great deal of new insight into the problem of correlating luminescence properties with chain configuration.^{2,3} In compact conformations, these species often show fluorescence instabilities (on-off blinking) and discrete photobleaching behavior that resemble that of single chromophoric molecules. These observations have led to a mechanistic picture of localized emissive trap sites (conjugated segments) within a single conjugated polymer chain, fed by excitonic energy transfer from other parts of the molecule.^{4,5} However, to our knowledge, definitive evidence of emission from single localized sites has not been observed.

Fluorescence intensity correlation techniques offer a powerful method for addressing the question of single- vs multiple-site emission from single polymer chains. Here, the distribution of photon detection coincidences separated by a time interval τ is measured. On a time scale of a few fluorescence lifetimes, this distribution approximates the intensity correlation function $g^2(\tau)$ and may be approximated by the expression

$$g^2(\tau) = 1 - (1/N) \exp(-(W_p + \Gamma_f)\tau) \quad (1)$$

where W_p is the pumping rate, Γ_f is the fluorescence decay rate, and N is the number of emissive sites within the nanostructure.^{6,8} For large N , $g^2(\tau = 0)$ approaches unity and the emitted radiation appears classical; for single-quantum emitters ($N = 1$), $g^2(0) \rightarrow 0$, a phenomenon known as photon antibunching.⁷ However, to resolve $g^2(0)$ with reasonable accuracy from a single fluorescent entity requires high fluorescence count rates (> 10 kHz) sustained on time scales of tens of minutes if not hours. For most conjugated polymers in thin films, the relatively poor photostability precludes such measurements from a single polymer chain. Recently, Huser and co-workers,⁸ reported nonclassical emission ($g^2(0) \approx 0.6$) from single MEH-PPV molecules in a thin film by summing contributions from ~ 1000 different molecules, suggesting an average number of emissive sites per polymer chain of ~ 3 .

In this Communication, we show for the first time definitive evidence of a single emissive site from individual oriented conjugated polymer nanostructures formed from single polymer

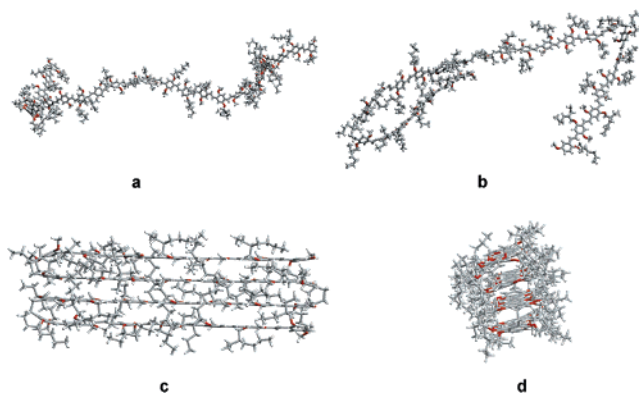


Figure 1. Snapshots of chain organization of a PPV oligomer in solution (a and b) and side and end-on views of the minimum-energy geometry (c and d) from molecular mechanics simulation.

chains isolated from microdroplets of dilute solution.⁹ The uniform z -orientation of the transition moment at the glass surface occurs as a result of an electrostatic interaction between the particle and stray charges on the substrate. The polymer system studied here is cyano-substituted polyphenylene vinylene (CN-PPV (H. W. Sands Corp.), MW 100 000 g/mol), a polymer commonly used in OLED applications. Nanoparticle samples were generated by nebulizing a 10^{-12} M CN-PPV solution in toluene from a $5 \mu\text{m}$ quartz nozzle under flow of dry N_2 . This produces toluene aerosol droplets roughly $5\text{--}10 \mu\text{m}$ in diameter that evaporate on a time scale of a few tens of milliseconds, and the dry polymer nanoparticles are collected on clean glass coverslips. All of the experiments described here were performed on neat nanoparticle samples (no support polymer film) and under ambient temperature and pressure conditions.

Figure 1 shows “snapshots” from a high-level molecular mechanics simulation of the self-organization of a single conjugated polymer chain, where folding occurs at sp^3 defect sites. These defects, observed in NMR studies,¹⁰ result from synthetic artifacts or oxidation of ethenic linkages. The high degree of molecular order suggested by this simulation is consistent with previous linear dichroism measurements^{9a} and expected to lead to facile energy transfer within the nanostructure. We find that CN-PPV is more stable photochemically than z -oriented MEH-PPV (ref 8) by about a factor of 2, an effect that presumably derives from a smaller separation between conjugated segments.¹¹

Figure 2 shows a high-resolution fluorescence image of CN-PPV polymer nanostructures deposited on a glass coverslip. The “donut”-like spatial intensity patterns are characteristic of transition moment orientation along the optic axis.¹² z -Oriented nanostructure luminescence was selected with a confocal aperture on the side-

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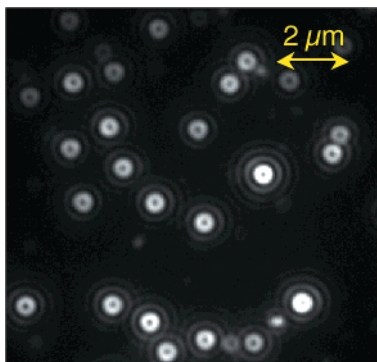


Figure 2. High-resolution fluorescence image of z-oriented CN-PPV nanostructures on a glass coverslip from nebulized toluene solution. Particle fluorescence was excited with a 514.5 nm Ar⁺ laser line in a total internal reflection illumination geometry and imaged through a 605 ± 15 nm band-pass filter.

port of our microscope, collimated through a 50/50 beam-splitter and imaged onto two photon-counting avalanche photodiodes (APD, Perkin-Elmer SPCM-AQR-14). The time intervals between APD detection events were measured with a PC-based time-to-digital converter (TDC, TimeHarp 200, PicoQuant GmbH, 34 ps resolution). Typical fluorescence count rates from single z-oriented CN-PPV nanostructures were ~50 kHz at pump intensities of 5 kW/cm² that can be sustained on time scales of ≤1 h. This allows us to measure photon-pair coincidences at rates of up to 500 cps from individual polymer nanostructures.

Figure 3 shows representative measured $g^2(\tau)$ from a single z-oriented CN-PPV nanostructure at three different (cw) laser powers. In this particular example, more than 10⁸ photons were detected from a single particle; the three data sets shown were acquired in about 20 min. The antibunching feature is clearly evident with $g^2(0)$ (at the highest pump intensity) = 0.1 (± 0.02) and an exponential parameter ($W_p + \Gamma_f$) that is essentially independent of pump intensity above ~1 kW/cm² and reproducible to within a few percent from particle to particle. Interestingly, the rise time (8.8 ns) seen in our $g^2(\tau)$ measurements corresponds to a fluorescence lifetime considerably longer than seen in solution-phase or film samples (≤2 ns). This effect derives from a combination of interfacial and dielectric confinement effects and will be described elsewhere.

In summary, we have shown for the first time, definitive evidence of single localized emissive site within a polymer nanostructure. This result suggests a rich application potential in photonics and quantum information processing, as well as providing new insight into the photophysics of this important class of materials.

Acknowledgment. This research was sponsored by the Advanced Research and Development Activity (ARDA) under contract number A849-RA-DE01 and by the Division of Chemical Sciences,

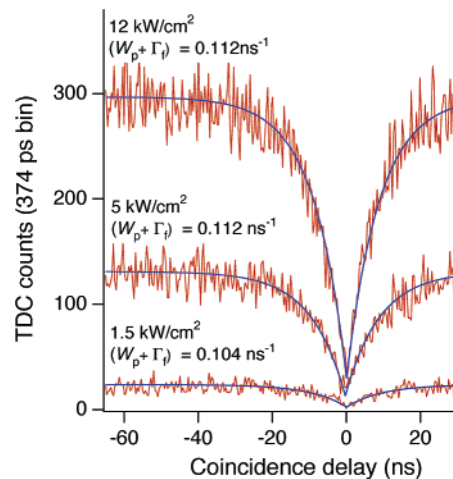


Figure 3. Intensity correlation functions, $g^2(\tau)$, as a function of coincidence delay from a single z-oriented CN-PPV nanostructure. Data are shown on a scale of binned time-to-digital counts (374 ps bin width); the normalized modulation depth is approximately the same in all three cases (≥90%) with rise times independent of pump intensity above ~1 kW/cm².

Office of Basic Energy Sciences, U.S. Department of Energy, with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. R.M. Dickson acknowledges financial support from the National Science Foundation (CHE-9984507) and the Alfred P. Sloan and Camille and Henry Dreyfus Foundations and partial support from the Blanchard and Vassar-Wooley Foundation.

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JA031921N