

Comparison of the morphology between isolated polymer chains and aggregates by using excitation polarization spectroscopy

T. Stangl, Chair Prof. Lupton, Institute of Experimental and Applied Physics, University of Regensburg, Germany (December 2015)



Application Note

Introduction:

Many applications of conjugated polymers depend critically on excitation energy transport. Although bulk measurements regarding these processes have the inherent disadvantage of averaging over interesting areas, single-molecule spectroscopy is limited to single conjugated polymer chains, which may not reveal bulk-related mechanisms. Both experimental techniques have their unique advantages and have served tremendously in obtaining a detailed understanding of organic materials. Here we used in situ solvent vapor annealing (SVA) to generate aggregates composed of several individual poly(para-phenylene-ethynylene-butadiynylene) (PPEB) chains to advance into the regime between a single chain and bulk film, that is, the mesoscopic size regime.¹ This material-class is well known to demonstrate a drastic change in photoluminescence (PL) characteristics in going from well-dissolved single chains to bulk film,² making it especially useful to follow the evolution from a single chain towards a mesoscopic object. The changes in PL are supposed to be connected with a change in morphology and we aimed to follow these morphological changes by employing excitation polarization spectroscopy.³

Experimental setup

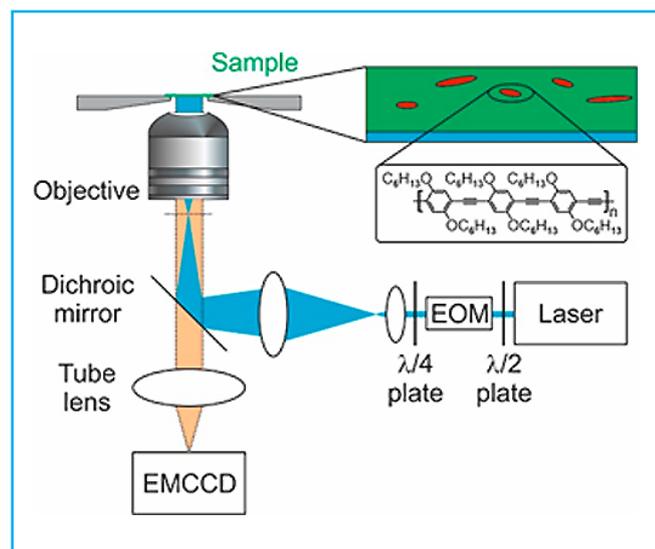


Figure 1. Schematic illustration of a typical widefield setup used for excitation polarization spectroscopy. (EMCCD electron multiplying charge coupled device, EOM electro optical modulator).

A custom-designed inverted fluorescence microscope was built for wide-field excitation and capable of detecting single molecules (Figure 1). A fiber-coupled diode laser was used in continuous wave mode. The laser light source was passed through a clean-up filter and a Glan-Thompson polarizer to provide linearly polarized excitation light. The polarization of the excitation light was rotated by an electro-optical modulator and an additional $\lambda/4$ waveplate. The laser beam was expanded and focused by a lens system onto the back-focal plane of the 1.35 NA oil immersion objective in the microscope. An excitation area of $\sim 80 \times 80 \mu\text{m}^2$ was generated in the focal plane and the fluorescence of the sample is collected by the same objective. The fluorescence signal was imaged on an EMCCD camera (Andor iXon3 DU897-DCS-BV) after an additional magnification of 1.6x and after passing a fluorescence filter. The excitation intensity was set to 100 mW/cm^2 and the overall magnification results in a resolution of 160 nm^2 per pixel leading to diffraction limited spots of approximately 2×2 pixels ($16 \times 16 \mu\text{m}^2$) for a single molecule.

Experiment

We compared the morphology of isolated chains and aggregates using excitation polarization spectroscopy, which reports on the overall anisotropy in absorption.³ The polarization of the excitation light was rotated in the x-y-plane by 180° at periods of 20 seconds and the fluorescence intensity of each individual fluorescent spot was recorded as a function of the polarization angle (Figure 2) for 200 seconds.

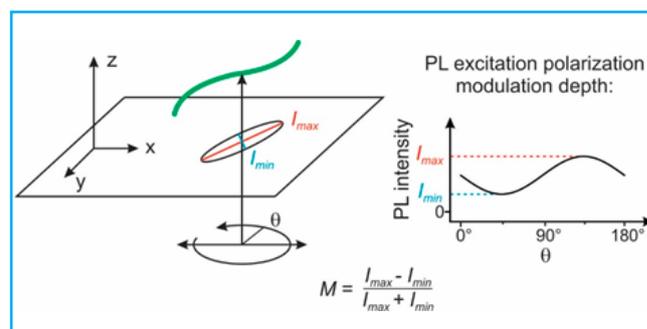


Figure 2. Schematic representation of the excitation polarization measurement procedure and definition of the modulation depth, M .

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The excitation polarization modulation depth, M , was obtained by fitting the fluorescence intensity, I , as a function of polarization angle, θ , to Malus' law,

$$I(\theta) \propto 1 + M \cos 2(\theta - \Phi)$$

where Φ is the orientation of the net dipole moment of the molecule, when the emission is maximized. For each single spot, M was acquired and yielding a histogram as shown in Figure 3a and b for single PPEB chains (green) and aggregates (red), respectively.

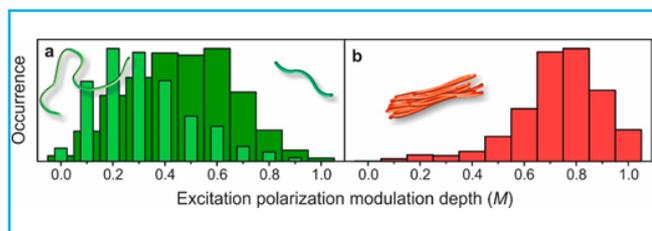


Figure 3. Excitation polarization histograms for single PPEB chains and aggregates. (a) Modulation depth, M , values for single chains with an average molecular weight of 40 kDa (dark green, 562 spots measured) and 210 kDa (light green, 1686 spots measured). (b) M values for single aggregates (1340 spots measured).

Since molecular weight affects chain morphology we compared two different weights of PPEB. The histogram shaded in dark green shows the distribution of modulation depth values for short chains ($M_n \approx 40$ kDa). The light shaded histogram reports on long chains with $M_n \approx 210$ kDa. The anisotropy decreases as chain length increases since longer chains fold more. This behavior is in contrast to that of isolated aggregates shown in Figure 3b. The resulting modulation depth histogram has a maximum at $M \approx 0.8$. We conclude that PPEB undergoes aggregation-induced ordering during SVA, leading to the first building blocks of crystalline structures which characterize the bulk film.

Performance

A general problem for acquiring meaningful modulation depth histograms is photo-bleaching of parts of the conjugated polymers or aggregates under investigation. Therefore, very low excitation intensities are employed, which can be, in principle, compensated for by long integration times of the detector. Additionally, a detector is needed, which provides the highest detection efficiency possible, to circumvent photo-degradation over time. For this reason we obtained a back-illuminated EMCCD camera (Andor iXon3 DU897-DCS-BV), with which we could find the best compromise between excitation intensity, photo-stability and detection signal.

References:

- (1) Vogelsang, J.; Adachi, T.; Brazard, J.; Bout, D. A. V.; Barbara, P. F. *Nature Mater.* 2011, 10, 942.
- (2) Bunz, U. H. F. *Macromol. Rapid Commun.* 2009, 30, 772.
- (3) Hu, D. H.; Yu, J.; Wong, K.; Bagchi, B.; Rosky, P. J.; Barbara, P. F. *Nature* 2000, 405, 1030.

Contact

Thomas Stangl
Institute of Experimental and Applied Physics
Faculty of Physics
University of Regensburg
Universitätsstraße 31
93053 Regensburg, Germany

Phone: +49 941 943-2062
E-mail: thomas.stangl@physik.uni-regensburg.de
www.physik.uni-regensburg.de/forschung/lupton/lupton/index.php