

## COMMENTS

## Comment on “X-ray and Electron Induced Oligomerization of Condensed 3-Hexylthiophene”

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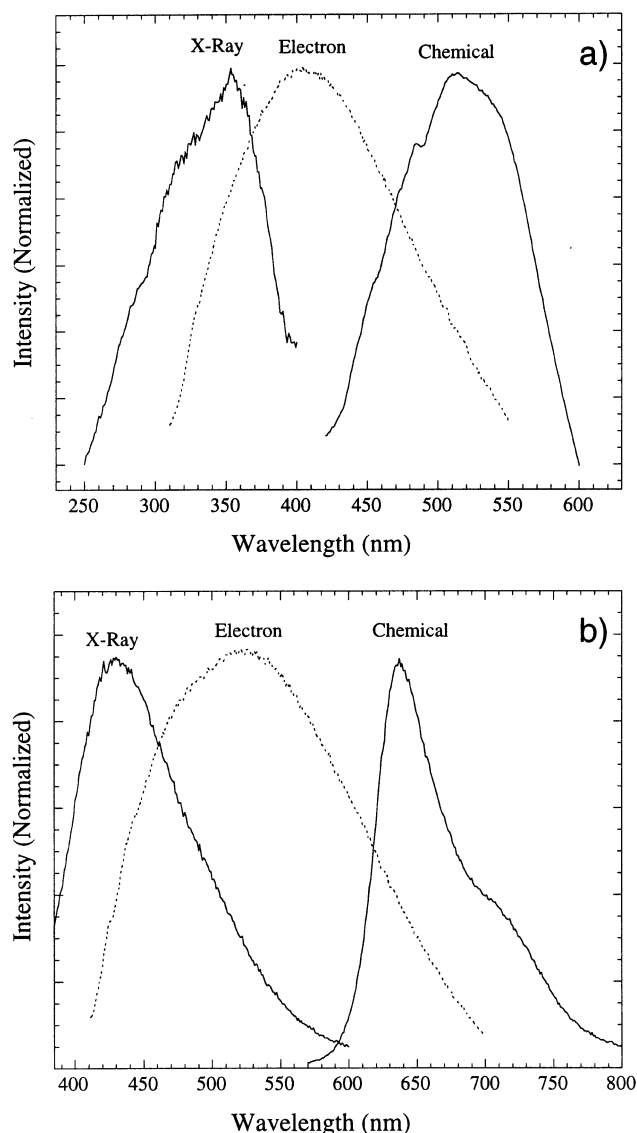
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We recently reported<sup>1</sup> that MgK $\alpha$  X-ray and electron irradiation of 3-hexylthiophene cryogenically condensed onto conducting substrates results in the formation of oligomeric films. X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and infrared reflection absorption spectroscopy demonstrated similarity to chemically synthesized poly(3-hexylthiophene) with clear retention of conjugation. Related studies have shown that this phenomenon also occurs for thiophene.<sup>2–5</sup> However in the case of ref 1, films as thick as 1 micron were formed by adsorbing very thick physisorbed layers prior to electron beam irradiation.

In this comment, we report the first photoluminescence measurements of X-ray and electron beam-formed conjugated oligomers. In some cases fluorescence from the lithographically formed structures is bright enough to be seen with the naked eye when held under an ultraviolet lamp. This result is significant in that few methods exist for lithographically forming conjugated polymers/oligomers. Existing techniques include using a plasma to deposit hydrophilic patterns on a surface, followed by selective adsorption of substituted poly(phenylene vinylene),<sup>6</sup> and the use of a scanning tunneling microscope to lithographically polymerize precursors of this polymer.<sup>7</sup> Unfortunately, in the latter case the polymers are not photoluminescent, presumably because of quenching by carbonyl groups, formed by oxidation from ambient oxygen. Poly(phenylene vinylene) has also been patterned with line widths of 200 nm by Visconti et al.<sup>8</sup> in a three-step process consisting of photoresist deposition on top of the conjugated polymer, multiple holographic exposures to produce a mask, and plasma etching to remove the photoresist.

The methods used to form the X-ray and electron beam oligomerized samples were described in ref 1. Briefly, gold-coated Si(111) substrates were cooled to 135 K in ultrahigh vacuum, 3-hexylthiophene (hereafter, 3HT) vapor was leaked into the chamber for a specified exposure, and the samples were irradiated either with X-rays or electrons. The samples were then warmed to room temperature and removed from vacuum. Excitation and emission spectra were recorded using a JY Horiba “Spex Fluorolog” instrument operating in reflection mode with a 22.5° angle between the excitation source and detector. A substrate for conductivity measurements was prepared by coating a piece of sapphire with gold, except for a 0.25 mm stripe in the middle of the sample. 3HT was condensed on the substrate, and the gap and surrounding sides were bombarded with electrons. After warming and removing the sample from vacuum, the conductivity was determined by measuring the current flowing across the gap for a particular voltage. Fluorescence



**Figure 1.** Fluorescence excitation (a) and emission (b) spectra of X-ray- and 5 keV electron oligomerized 3HT films and regioregular P3HT. For the excitation spectra, the emission wavelengths were 430, 550, and 632 nm, respectively. For the emission spectra, the excitation wavelengths were 365, 380, and 550 nm, respectively. The excitation and emission slit widths were 1 mm.

rescence images were acquired with a Nikon Eclipse microscope equipped with a mercury arc lamp and emission and excitation cubes. For comparison experiments with poly(3-hexylthiophene) (hereafter, P3HT), samples were spin-coated from regioregular P3HT (Aldrich), with an average molecular weight of ca. 87 000, dissolved in chloroform.

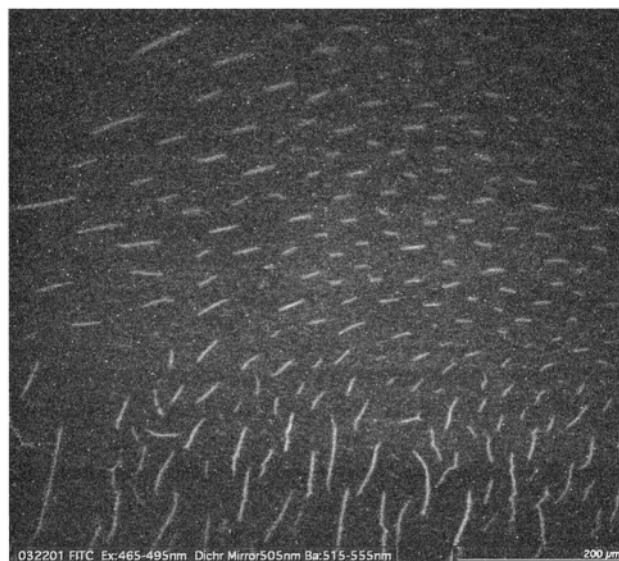
Figure 1 shows reflection excitation and emission spectra of MgK $\alpha$  X-ray- and 5 keV electron-formed 3HT films. Data for a 350 Å spin-coated film of chemically synthesized regioregular P3HT, referred to as “chemical”, are also included for comparison. In the case of X-rays, an exposure time of 75 min (source conditions of 12kV and 20 mA) was used. For the

electron-formed sample, the electron dose was  $4 \times 10^{16}$  electrons/cm<sup>2</sup>. The X-ray- and electron beam-formed films are approximately 100 Å and 10 microns thick, respectively. In the former case, the thickness was estimated from the intensity of the Au substrate XPS signal;<sup>1</sup> for the electron sample, it was determined by profilometry. The excitation maxima are 350, 405, and 510 nm for the X-ray, electron, and chemically synthesized samples, respectively. The corresponding emission maxima are 430, 525, and 640 nm. The shorter wavelengths for the beam-polymerized samples indicate shorter average conjugation lengths, consistent with oligomerization rather than polymerization. Comparison to photoluminescence data for films of unsubstituted thiophene oligomers<sup>9</sup> suggests an average conjugation length corresponding to less than four units, with the X-ray sample being less conjugated than the electron-formed one. The emission spectra are substantially broader than those corresponding to chemically synthesized oligomers, suggesting less homogeneous conjugation lengths. On the bases of emission spectra signals, the relative fluorescence intensities for the samples are approximately 10.5, 3.5, and 1.0 for regioregular P3HT, electron-oligomerized 3HT, and X-ray oligomerized 3HT, respectively.

Fluorescence microscopy of X-ray- and electron-induced films has also been performed, and we have observed a variety of morphologies depending on monomer thickness, beam irradiation time, and sample temperature during irradiation. Figure 2 shows an image of a typical sample, formed using the conditions described in the caption. Profilometry reveals an inhomogeneous overall film thickness ranging from 2300 to 3800 Å. The bright wormlike features are due to oligomerized 3HT islands surrounded by a fluorescently weaker background. Atomic force microscopy indicates that the highly fluorescent structures have an average height and width of ca. 200 nm and 2–5 microns, respectively. A wide distribution of lengths is observed, ranging from less than 10 to over 100 microns. The less fluorescent background surrounding the oligomer islands is organic in nature (i.e., not the gold substrate), as verified by the absence of gold features in an Auger electron spectrum of the film.

Vacuum-deposited short oligothiophenes, such as terthiophene and quaterthiophene, are known to have high diffusion rates relative to longer ones and to form islands and crystallites on a variety of substrates,<sup>10,11</sup> presumably coalescing via van der Waals forces. The results of Figure 2 indicate that a similar type of nucleation may be occurring in the case of the beam-oligomerized samples. This may take place after irradiation, as the substrate is warmed, or may be due to the morphology of the condensed 3HT prior to irradiation.

Electrical measurements indicate poor conductivity of the oligomerized film. For a sample made in a similar fashion as



**Figure 2.** Fluorescence microscope image of a  $670 \times 760$  micron<sup>2</sup> region of an electron-oligomerized film formed by 3.5 keV electron bombardment ( $1.8 \times 10^{16}$  electrons/cm<sup>2</sup>) of 3HT condensed at 135 K on a Au/Si(111) substrate (exposure of ca. 4000 L). The excitation and emission wavelength ranges were 465–495 and 515–555 nm, respectively.

that corresponding to Figure 2, the conductivity was on the order of  $10^{-9}$  cm<sup>-1</sup> ohm<sup>-1</sup>. A comparable measurement in our laboratory for (undoped) regioregular P3HT gave a value of  $10^{-3}$  cm<sup>-1</sup> ohm<sup>-1</sup>. The poor conductivity of the electron-formed film is consistent with the formation of electrically isolated islands.

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