



Temperature dependent analysis of three classes of fluorescence spectra from *p*-6P nanofiber films

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ARTICLE INFO

Article history:

Received 17 September 2008

Received in revised form

5 February 2009

Accepted 12 February 2009

Available online 28 February 2009

Keywords:

Muscovite mica

Organic molecules

para-Hexaphenylene (*p*-6P)

Nanofibers

Fluorescence

ABSTRACT

Discontinuous nanofiber films of *para*-hexaphenylene molecules can be routinely fabricated via vacuum deposition on muscovite mica. The fibers emit upon UV illumination blue fluorescence with excitonic spectral peaks. Their intense fluorescence makes them very attractive for the use in photonic devices, given that the spectra are reproducible for varying surface temperatures. A detailed investigation as a function of surface temperature variation from 300 to 30 K reveals three classes of spectra: (a) spectra with well resolved excitonic peaks, which shift 35 meV to the blue with decreasing temperature, (b) similar spectra with an additional intermediate broadening around 150 K, and (c) excitonic spectra similar to (b), but with a green defect emission band. Quantitative fitting of type (a) spectra results in an exciton–phonon coupling factor of 80 ± 10 meV and an average phonon temperature of $\theta = 670 \pm 70$ K. The Huang–Rhys factor decreases linearly from 1.2 at 300 K to 1.0 at 30 K. Fitting of type (b) spectra reveals that the apparent intermediate temperature broadening is due to additional fluorescence peaks, the relative importance of which increasing with decreasing temperature.

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1. Introduction

Vacuum deposition of conjugated organic molecules such as *para*-phenylenes [1–3], *para*-functionalized *para*-phenylenes [4], α -thiophenes [5] as well as phenylene-thiophene co-oligomers [6–8] on muscovite mica substrates leads to the formation of needle-like crystallites (“fibers”). The fibers are grown together with clusters and sometimes a wetting layer made of lying molecules and/or flat islands from upright molecules [9,10]. These fibers, either as ensembles or as single entities, have a promising application potential in future optoelectronic devices [11,12]. Because of the peculiar growth mechanism both the fibers and the clusters emit polarized light after UV excitation.

Similar to many other organic crystals the optical properties of such *para*-hexaphenylene (*p*-6P) aggregates are to a certain degree determined by the optical properties of the building blocks, i.e. the intramolecular optical properties [13,14], but also by interactions between electronic states of neighboring molecules and by collective properties of the crystal lattice [15,16]. Packing effects like the planarization of the molecules and interchain interactions have been described on the basis of theoretical calculations for *p*-6P [17,18]. An aggregate-size dependence of the optical

properties has been observed for organic nanocrystals [19] and even for *p*-6P nanofibers [20].

For *p*-6P the fluorescence spectra are dominated by several excitonic transitions between the electronic ground state S_0 and the first excited singlet state S_1 [21], i.e. display vibronic progression series. In the gasphase *p*-6P molecules are nonplanar with torsion angles of 30° – 40° [17]. In the solid phase, however, the *p*-6P molecules are on average flat [22–24]. Planarization depends on temperature: molecules are more planar at higher temperatures [25]. That way the HOMO–LUMO gap also decreases with increasing temperature [6,26]. With decreasing temperature a structural phase transition has been observed for *p*-6P crystallites between 143 and 110 K [27], which results in a quadrupled size of the unit cell. Hints for a structural phase transition at room temperature have been extracted from Raman spectra of thin films [23]. For *para*-quaterphenylene the effects of a similar structural phase transition on absorption and fluorescence spectra have also been described [28,29]. In addition a green emission band in the fluorescence spectra has been observed occasionally and has been attributed to the emission from molecular aggregates, stemming from structural defects [30].

A detailed understanding of the optics of phenylene thin films is of importance for optical applications which include, e.g., superradiance [31] or electroluminescence [32,33]. In this article, we improve insight into the steady-state optical properties of *p*-6P needle films grown on muscovite mica by comparing samples prepared under very similar conditions, which however result in

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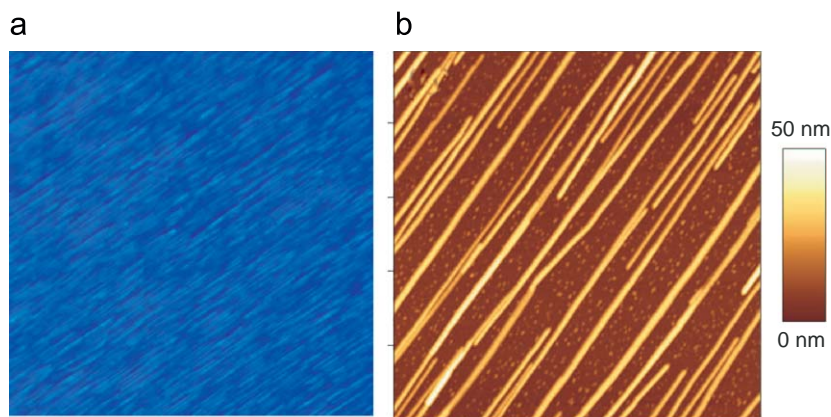


Fig. 1. $100 \times 100 \mu\text{m}^2$ fluorescence microscope image (a), excitation wavelength $\lambda_{\text{exc}} = 365 \text{ nm}$, and $10 \times 10 \mu\text{m}^2$ atomic force microscope image (b) of a typical sample of *p*-6P grown on muscovite mica. The AFM image shows also small clusters in between the mutual parallel needles. A simultaneously existing wetting layer is observed by LEED, only.

quite different fluorescence spectra. These spectra and their temperature dependence can be classified to belong to three different types, induced by slight modifications of the subtle organic adsorbate/substrate system.

2. Experimental

The growth substrate muscovite mica (Structure Probe, Inc., West Chester, PA) is cleaved in air and transferred within seconds into a high vacuum chamber with a base pressure of $p \approx 2 \times 10^8 \text{ mbar}$. *p*-6P is purchased from TCI America. Before deposition onto the substrate from a Knudsen cell the adsorbate is outgassed just below the sublimation temperature to remove water and other contaminants. It has been shown by mass spectrometry that for larger molecular weight and thus higher sublimation temperature than *p*-6P octaphenyl and dodecaphenyl are main contaminants (less than 2%) [34].

Deposition takes place at a pressure of $2 \times 10^7 \text{ mbar}$ with a deposition rate of $0.1\text{--}0.2 \text{ \AA/s}$ at a surface temperature of approximately 390 K, leading to films with well separated needles. In situ the grown samples are characterized by low-energy electron diffraction (MCP-LEED, Omicron), ex situ by fluorescence microscopy and atomic force microscopy (JPK NanoWizard). The overall thickness of the organic deposit is monitored by a water cooled quartz microbalance (Inficon XTC/2) positioned close to the substrate. Transferred back into ambient air temperature dependent measurements of *p*-6P fluorescence spectra between room temperature and 30 K are performed in a closed cycle He-cryostat (vacuum $5 \times 10^5 \text{ mbar}$) with a 0.25 m spectrograph and a cooled CCD camera, after excitation with a multiline-UV Ar⁺ laser (excitation wavelength 310–351 nm). The laser intensity is chosen in a way that bleaching [35] of the samples within the measurement time is negligible.

3. Results and discussion

In Fig. 1a fluorescence micrograph (a) together with an atomic force microscope image (b) of a typical sample of *p*-6P grown on muscovite mica is shown. Needles from *p*-6P together with clusters are clearly visible in the AFM image, the typical height of the needles being 50 nm. The blue fluorescence is polarized approximately perpendicular to the long needle axis [2,10]. LEED

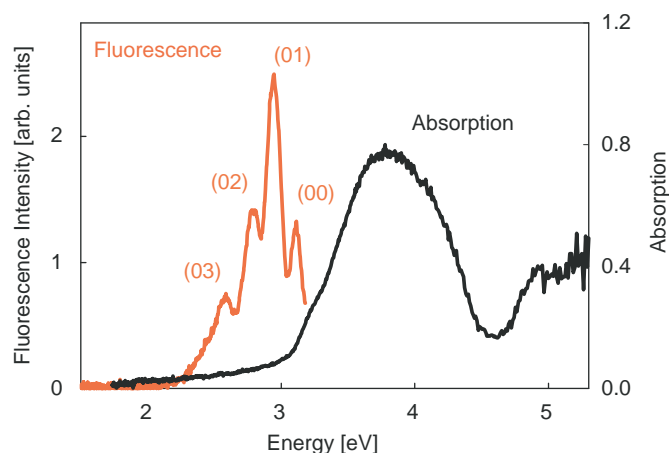


Fig. 2. Absorption and fluorescence ($E_{\text{exc}} = 3.4 \text{ eV}$) from a film of lying *p*-6P molecules on KCl at room temperature. Pairs (00)–(03) mark the different excitonic transitions.

displays a strong diffraction pattern from the wetting layer of lying *p*-6P molecules [3,36].

It has been shown experimentally [14,37–41] as well as theoretically [22,42] that the direction of the lowest energy transition dipole of *p*-6P is oriented along the long molecular axis. Therefore, by either absorption or emission spectroscopy and by variation of the angle of incidence of the irradiating light one can easily discriminate between molecules lying on the surface and upright ones. In Fig. 2 an absorption spectrum together with an emission spectrum (excitation energy $E_{\text{exc}} = 3.4 \text{ eV}$) of lying *p*-6P molecules on KCl are given, both taken at room temperature under normal incidence and with unpolarized light. KCl is favored over muscovite as the growth substrate for this experiment because of its higher optical transparency in the ultraviolet spectral range. The broad absorption band between 3 and 4.5 eV is characteristic for a sample consisting of lying molecules [39,41]. The absorption spectrum is structureless due to conformational disorder, a typical feature for oligo-phenylenes [43,44]. In emission vibronic peaks with energetic differences of $160 \pm 10 \text{ meV}$ are resolved, the energetic distance between the maximum in absorption and the first maximum in emission being approximately 0.7 eV. The sample emits at 3.09, 2.94, 2.77, and 2.62 eV, the corresponding transitions are labeled as (00), (01), (02), and (03). These are transitions between the vibrational

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