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Temperature dependent interplay between emitting species in highly ordered P3HT single crystals

Dr. Agumba O. John

University of Science & Technology, Kenya, Email: agumba.john@gmail.com

Abstract

In this study, the temperature dependent photoluminescence (PL) spectra measurement has provided us a feasible means to elucidate the nature of the emissive species and the melt transitions in P3HT single crystals. This has been achieved by performing in situ temperature dependent photoluminescence measurements followed by detailed spectral analysis. Spectrally resolved PL lineshapes through multipeak Gaussian functions simulating 0-0, 0-1, 0-n peaks have revealed multiple vibrational replicas yielding two and three emitting species (states) between 30°C–220°C and 240°C–290°C, respectively. Highly ordered crystalline domains with melt transition at ~302°C are suggested to form the structural and electronic origin of the species 1 emission while the less ordered domains with melt transition at ~240°C are suggested to form the origin of species 2 emission. At high temperatures, disordered domains whose PL lineshapes resembles that of P3HT solution emerged between 240°C and 310°C and is seen to be responsible for species 3 emission (single chromospheres emissions). This observation has further been corroborated by the temperature dependent birefringence measurements. We suggest that the temperature dependent vibronic progressions arise from different electronic origins i.e. different species (fluorophores) due to multiple crystalline polymorphs within the crystal with varied coupling of the excited states. We conclude that it is not sufficient to invoke only the intramolecular interactions to explain the nature of both the absorption and PL spectra of highly ordered P3HT single crystals which are widely dominated by both interchain and intrachain interactions.

Introduction:

The optical response of polymer aggregates has been described by considering coulombic interactions of transition dipoles which will couple in either a side-by-side orientation, (H-aggregates), or aligned along one dimension (J-aggregates). For thin-films of polythiophenes, it's been reported that both optical absorption and therefore the photoluminescence spectra are often well explained by weakly coupled H-aggregates. this is often thanks to dense π-stacking of the polymer chains with short distances between them. consistent with Kasha’s rule, vibrational relaxation to rock bottom excited state takes place on a way shorter duration than the lifetime of an exciton. The photon emission thus takes place from rock bottom energy excited state. In ideal H-aggregates consisting of rigid molecules, the optical transition from the band bottom of rock bottom excited state is optically forbidden, hence these aggregates don't show any fluorescence. The absorption and PL spectra of polythiophenes,are usually described in terms of intramolecular interactions coupled to only one phononic mode. However, for highly organized/ordered single crystals of polythiopheses like P3HT, this model is so simplistic and can't fully describe the PL spectra thanks to the presence of both the intramolecular and intermolecular couplings exposure within the absorption and emission spectra. during this study, the temperature dependent PL spectra measurement has provided us a feasible means to elucidate the character of the emissive species and therefore the melt transitions in other polythiophenes. the consequences of thermal fluctuation on different phases of a bulky substituted poly (3-(2, 5-dioctylphenyl) thiophene) (PDOPT) and Poly(3 hexylthiopne-2 5diyl) (P3HT) are systematically investigated using photoluminescence spectroscopy. This has been achieved by performing in-situ temperature dependent photoluminescence measurements followed by detailed spectral analysis of the polythiophenes. For PDOPT, the temperaturedependent optical spectroscopy on as-cast thin films and spherulitic crystals was wiped out order to elucidate the connection between emission probability and changes in morphology from ordered crystalline regions to disordered molten chains. From the study, the intensities of the emitted species varied as a function of temperature that determine degrees of order. Wellorderedspherulitic crystals emitted strongly in lower energies as against less ordered films and spherulitic crystals. From the deconvoluted PL spectra, it had been declare that, the emitting energy bands remained constant with shift of intensity. The ordered crystals emitted strongly in higher wavelengths as compared to their disordered counterparts that emitted strongly in lower wavelengths. On the opposite hand, so as to elucidate the changes within the PL spectra with temperature and to elucidate the origins of the PL peaks more qualitatively and quantitatively for P3HT films and single crystals, Gaussian fittings of the PL spectra were necessary. Before fitting the spectra, an assumption was made that the vibronic progressions were arising from different electronic origins i.e. different species (fluorophores). The vibronic progressions were then fitted using multipeak Gaussian functions simulating 0-0, 0-1, 0-n peaks with the energy spacing between them taken approximately 170meV like the energy of the C-C symmetric vinyl stretch since within a vibronic family, the spectral width should be a continuing for every 0-n transition. The electronic origin of the 0-0 peak and therefore the PL intensity were considered as adjustable parameters so as to achieve the simplest fit the experimental data. However, the energy spacing between the peaks was kept at ~170meV during the fitting process. During the fitting process, the FWHM and therefore the energy spacing between the vibronic progressions were slightly adjusted so as to achieve an honest fit the experimental data. We suggest that the temperature dependent vibronic advancements arise from different electronic origins i.e. different species (fluorophores) thanks to differentufficient crystalline polymorphs within the crystal with varied coupling of the excited states. This phenomenon has been explained using the weakly coupled H-aggregate model for polythiophenes. during this model, static disorder caused by temperature variation breaks the symmetry of the dipole and this enables emission to the vibrationless state , which is strictly forbidden in perfect H-aggregates. Hence, increasing disorder increases the intensity of the 0-0 emission peak. It should be noted that the sideband intensities also increase although at a slower rate, which suggests that increases with disorder. From our observation, we've shown that for highly organized/ordered polthiophene aggregates like spherulitic and single crystals, a model that considers only intramolecular interactions is so simplistic and can't satisfactorily describe the spectra because in such structures, there's presence of both the intramolecular and intermolecular couplings exposure within the emission spectra. thanks to such couplings, there are multiple vibrational replicas yielding different emitting species arising from different electronic origins. These emitting states arise from domains with different crystalline ordering resulting from 2D molecular coupling within the ordered domains. Thermal treatment has thus provided a feasible route to elucidate the emission origins in ordered polythiophenes and has revealed that the PL spectra can't be considered as an emission from one electronic state thanks to the various crystalline ordering (domains) in highly crystalline polythiophenes. We conclude that it's not satisfactory to invoke only the intra molecular interactions in explaining the character of PL spectra of highly ordered polythiophenes which are widely dominated by both inter chain and intra chain interactions. The aggregation of π-conjugated materials significantly impacts the photo physics and performance of optoelectronic devices. Nevertheless, little is understood about the laws governing exaggerate formation of π-conjugated materials from solution. during this angle, we compare, discuss, and summarize how aggregates form for 3 differing types of compounds, that is, homo-polymers, donor–acceptor type polymers, and low relative molecular mass compounds. to the present end, we employ temperature-dependent optical spectroscopy, which may be a simple yet powerful tool to research aggregate formation. we discover the mixture formation to proceed an equivalent altogether these compounds by a coil-to-globule-like first order phase of transition. Particularly, the chain expands before it collapses into a highly ordered dense state. From our conclusion, we conclude that it's not sufficient to invoke only the intra molecular interactions in explaining the character of PL spectra of highly ordered polythiophenes which are widely dominated by both inter chain and intra chain interactions.