

Temperature Dependent Interplay between Emitting Species in Highly Ordered Poly (thiophenes) as Revealed by Optical Spectroscopy

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The optical response of polymer aggregates has been described by considering coulombic interactions of transition dipoles that can couple in either a side-by-side orientation, (H-aggregates), or aligned along one dimension (J-aggregates). For thin-films of polythiophenes, it has been reported that both optical absorption and the photoluminescence spectra can be well explained by weakly coupled H-aggregates. This is due to dense π -stacking of the polymer chains with short distances between them. According to Kasha's rule, vibrational relaxation to the lowest excited state takes place on a much shorter time scale than the lifetime of an exciton. The photon emission thus takes place from the lowest energy excited state. In ideal H-aggregates consisting of rigid molecules, the optical transition from the band bottom of the lowest excited state is optically forbidden, hence these aggregates do not show any fluorescence. The absorption and PL spectra of polythiophenes, are usually described in terms of intramolecular interactions coupled to only a single phononic mode. However, for highly organized/ordered single crystals of polythiophenes such as P3HT, this model is so simplistic and cannot fully describe the PL spectra due to the presence of both the intramolecular and intermolecular couplings showing up in the absorption and emission spectra. In this study, the temperature dependent PL spectra measurement has provided us a feasible means to elucidate the nature of the emissive species and the melt transitions in other polythiophenes. The effects of thermal fluctuation on different phases of a bulky substituted poly (3-(2,5-dioctylphenyl) thiophene) (PDOPT) and Poly(3 hexylthiophene-2,5-diyl) (P3HT) have been 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 temperature-dependent optical spectroscopy on as-cast thin films and spherulitic crystals was done in order to elucidate the relationship 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. Wellordered spherulitic crystals emitted strongly in lower energies as opposed to less ordered films and spherulitic crystals. From the deconvoluted PL spectra, it was declared 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 other hand, in order to elucidate the changes in the PL spectra with temperature and to explain 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 corresponding to the energy of the C-C symmetric vinyl stretch since within a vibronic family, the spectral width should be a constant for each 0-n transition. The electronic origin of the

0-0 peak and the PL intensity were considered as adjustable parameters in order to attain the best fit to the experimental data. However, the energy spacing between the peaks was kept at \sim 170meV during the fitting process. During the fitting process, the FWHM and the energy spacing between the vibronic progressions were slightly adjusted in order to attain a good fit to the experimental data. We suggest that the temperature dependent vibronic advancements arise from different electronic origins i.e. different species (fluorophores) due to different sufficient 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. In this model, static disorder caused by temperature variation breaks the symmetry of the dipole and this allows emission to the vibrationless ground 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 means that increases with disorder. From our observation, we have shown that for highly organized/ordered polythiophene aggregates such as spherulitic and single crystals, a model that considers only intramolecular interactions is so simplistic and cannot satisfactorily describe the spectra because in such structures, there is presence of both the intramolecular and intermolecular couplings showing up in the emission spectra. Due 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 cannot be considered as an emission from a single electronic state due to the different crystalline ordering (domains) in highly crystalline polythiophenes. We conclude that it is not satisfactory to invoke only the intramolecular interactions in explaining the nature of PL spectra of highly ordered polythiophenes which are widely dominated by both interchain and intrachain interactions. The aggregation of π -conjugated materials significantly impacts the photophysics and performance of optoelectronic devices. Nevertheless, little is known about the laws governing exaggerate formation of π -conjugated materials from solution. In this angle, we compare, discuss, and summarize how aggregates form for three different types of compounds, that is, homopolymers, donor-acceptor type polymers, and low molecular weight compounds. To this end, we employ temperature-dependent optical spectroscopy, which is a simple yet powerful tool to investigate aggregate formation. We find the aggregate formation to proceed the same in all 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 is not sufficient to invoke only the intramolecular interactions in explaining the nature of PL spectra of highly ordered polythiophenes which are widely dominated by both interchain and intrachain interactions.