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Temperature dependent interplay between emitting species in highly ordered poly(thiophenes) as revealed by optical spectroscopy

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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 different polythiophenes. The effects of thermal fluctuation on different phases of a bulky substituted poly (3-(2, 5-dioctylphenyl) thiophene) (PDOPT) and Poly(3 hexylthiopne-2 5diyl) (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. For PDOPT, the intensities of the emitted species varied as a function of temperature that determine degrees of order. Well-ordered crystals emitted strongly in lower energies as opposed to less ordered films and spherulitic crystals. From the deconvoluted PL spectra, it was revealed that, the emitting energy bands remained constant with shift of intensity with ordered crystals emitting strongly in higher wavelengths as compared to their disordered counterparts that emit strongly in lower wavelengths. On the other hand, for P3HT, the spectrally resolved PL lineshapes through multipeak Gaussian functions simulating 0-0, 0-1, 0-n peaks have revealed multiple vibrational replicas yielding different emitting species (states). 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. From our observation, 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.

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