Interplay between Förster energy migration and defect concentration in shaping a photochemical funnel in PPV

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1. Introduction

The opto-electronic devices, for example light - emitting diodes, photovoltaic cells and optical sensors fabricated from conjugated polymers (CPs) are far less costly than inorganic semiconductor based devices. The efficiency of intrachain and interchain transport of excitation energy determines the performance of CP based opto-electronic devices. At this juncture, it is important to realize the strong correlation between the optical properties of CPs and, the degree of defects and disorder along a CP chain [1]. The single molecule experiments carried on poly[2-methoxy-5-(20-ethylhexyl)oxy-1,4-phenylenevinylene] (MEH-PPV) have explored this correlation and suggested the existence of a photochemical funnel in the photophysics of CPs [2]. The conformational and/or chemical defects along the polymer chain leads to length distribution of chromophores along the chain [3]. Efficient non-radiative energy transfer among these chromophore segments is considered to be the origin of photochemical funnel. To establish the existence of photochemical funnel, we studied excitation energy dynamics along PPV chains [4].

2. Methodology

To study the excitation energy dynamics along PPV, we modelled PPV chain as a polymer with the length distribution of chromophores given either by a Gaussian or by a Poissonian distribution. We observe that the Poisson distribution of the segment lengths explains the photophysics of PPV better than the Gaussian distribution. An extended 'particle-in-a-box' model is used to calculate the exciton energies and the transition dipole moments of the chromophores, and a master equation to describe the excitation energy transfer among different chromophores. The rate of energy transfer within first approximation is assumed to be given by the well-known Förster expression [5].

3. Results

The observed excitation population dynamics confirms the photochemical funneling of excitation energy from shorter to longer chromophores of the polymer chain. However, the difference between computed emission spectra under steady state and equilibrium conditions indicate that the excitation energy may not always migrate towards the longest chromophores in the polymer chain instead there exist local domains in the polymer chain within which the non-radiative energy transfer from shorter to longer chromophores take place. These results are found to be in agreement with the experimental reports [6, 7]. The time scale of spectral shift and energy transfer for our model polymer, with realistic values of optical parameters, is in the range of 200–300 ps.
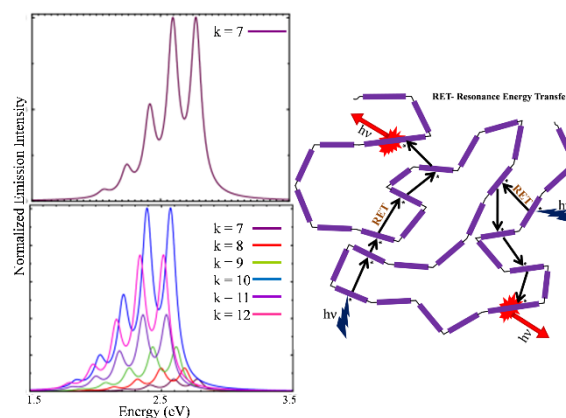

Figure 1: Excitation energy dynamics showing the existence of photochemical funnel and local domains in CPs.

4. Conclusions

Using a simple model, we have been able to capture the semi-quantitative features of energy transfer dynamics in conjugated polymers. We observe that defects have profound influence on the optical properties of CPs.

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