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Exciton diffusion dynamics in an organic semiconductor nanostructure

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1 Introduction

Polymeric semiconductors are now finding commercial applications in optoelectronic devices such as light-emitting diodes and photovoltaic diodes. Here, we investigate exciton dynamics in chiral helices of an oligo-*p*-phenylenevinylene derivative monofunctionalized with a ureido-*s*-triazine (MOPV, see Fig. 1(a) for the molecular structure). The latter functional group leads to oligomer dimerization by hydrogen bonding in dodecane solution, resulting in reversible supramolecular assembly by solvophobic and π - π interactions [1]. MOPV is a model system to study exciton transfer dynamics as it is possible to investigate the effect of intermolecular interactions by comparing optical properties in the dissolved phase (above the transition temperature) and the supramolecular assemblies.

2 Experimental

The synthesis of MOPV has been described in detail elsewhere [1]. The material was dissolved in anhydrous dodecane at a concentration of 1.6×10^{-4} M and then kept under inert atmosphere except during absorption (Abs) measurements. Measurements were carried out using a temperature-controlled Abs cuvette. The transient photoluminescence (PL) and Abs apparatus have been described in detail previously [2,3].

3 Results and Discussion

We have undertaken transient PL and Abs studies of MOPV in dodecane solution at sufficiently low concentration to explore exciton dynamics within *isolated* supramolecular assemblies. Fig. 1(b) plots the PL intensity as a function of time at various solution temperatures, at the peak of the PL spectrum. Below the transition temperature for supramolecular assembly (65°C), nonexponential decay is

observed, which we have assigned to diffusion-assisted exciton quenching at defect sites [2]. This is accompanied by a dynamic red shift of the PL spectrum and by PL depolarization, both assigned to the exciton diffusion process [2]. Fig. 1(c) displays photoinduced Abs transients at a photon energy that probes Abs of the lowest exciton, with higher excitation fluence than used in the transient PL measurements. An intensity-dependent picosecond component is assigned to exciton bimolecular annihilation dynamics [3]. Both of these sets of results indicate that exciton diffusion in MOPV stacks in solution occurs on picosecond timescales. We have developed a simple Monte-Carlo simulation (MC) in order to obtain

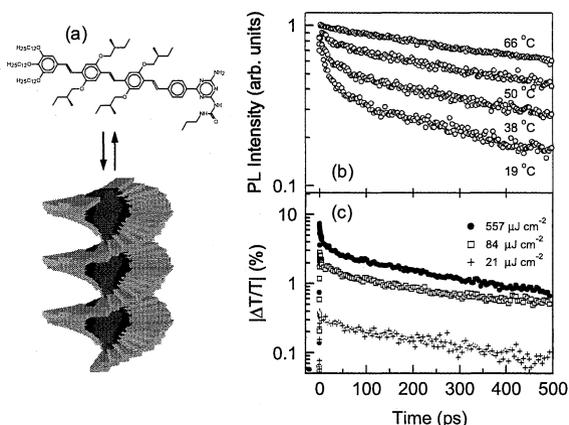


Fig. 1. (a) Chemical structure of MOPV and schematic representation of a MOPV supramolecular stack. (b) PL decay kinetics at 2.226 eV photon energy at various temperatures. (c) Abs transients with 1.46 eV probe photon energy at 14°C and at various pump fluences.

a microscopic understanding of these dynamics. The model generates randomly orientated helicoidal packs of oligomers with uncorrelated random energies (following a Gaussian law). The excitons are created at random positions and can then diffuse on the supramolecular nanostructures. At any time step, any exciton can transfer to another unoccupied site, annihilate with any other exciton or decay with a constant probability (the inverse of the lifetime). The hopping and the annihilation events are treated as resonance energy transfer events and modelled with a Forster-type probability law using a line-dipole approximation. The latter is a refinement of the point-dipole approximation and is needed as the stacks are very closely packed. In this scheme, each oligomer is divided into small segments used to calculate the electronic coupling using a point dipole approximation (see [4] for a discussion). The transfer rate includes an overlap integral of the homogeneous PL and Abs spectra which depends on the difference in site energies. Several parameters were deduced independently from previous measurements. The PL, Abs and CD spectra were fitted with two vibronic progressions and a Gaussian broadening to obtain the homogeneous spectra (the

transfer probabilities follow a detailed balance principle). The model allows us to extract the decays of the exciton population (see Fig. 2(a)), of the average exciton energy (see Fig. 2(b)) and of the PL polarisation anisotropy (see Fig. 2(c)).

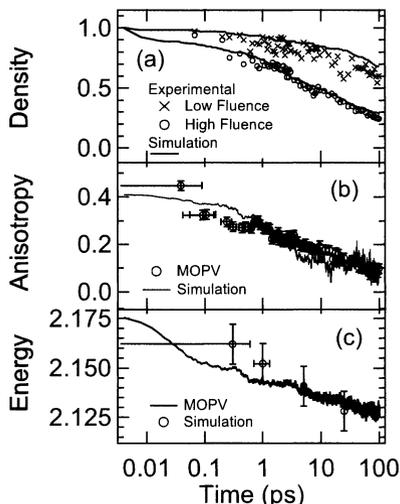


Fig. 2. (a) The symbols are the normalised exciton population decays at high and low excitation fluences. The curves are the decays from the MC simulation. (b) The circles are the polarisation anisotropy of the exciton Abs, while the curve is from the MC simulation. (c) The circles are the PL average energy measured with PL up-conversion, while the curve is from the MC simulation.

4 Conclusion

The model allows to extract microscopic informations such as the average exciton hopping annihilation rates. We believe that this model allows us to describe quantitatively the exciton dynamics on supramolecular architectures from sub-picosecond to nanosecond timescales.

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