Project: Exciton Transport in Molecular Crystals: The Role of Dynamic Disorder

Contact: Juan Arago (J.Arago-March@warwick.ac.uk)

Alessandro Troisi (A.Troisi@warwick.ac.uk)

Summary Report:

The main goal of the scientific project (EXTMOC, 329513) was *the development of an accurate theoretical model to describe the exciton diffusion in molecular crystals* and, therefore, during these two years a significant progress in the theoretical description of excitons in organic crystals has been attained. Exciton diffusion in molecular crystals or aggregates is a fundamental physical process taking place in many organic electronic devices including light emitting diodes and solar cells. For example, a long exciton diffusion length is a prerequisite for efficient organic solar cells, where excitons should diffuse to a donor-acceptor interface to initiate the process of charge separation and, consequently, the generation of photocurrent.

The distinctive characteristic of this project is the introduction of thermal molecular motions (*dynamic disorder*) in the approximation developed to study exciton diffusion and its relevance for an accurate description. To carry out our goal we have followed several steps: i) development of a proper diabatization scheme to compute excitonic couplings, ii) evaluation of the fluctuation of the excitonic couplings due to the thermal nuclear motions, and iii) theoretical models to study exciton diffusion in coherent and incoherent regimes incorporating the fluctuations of the excitonic couplings.

Below, the main results during these two years are briefly summarized:

1. **Dynamics of the Excitonic Coupling in Organic Crystals**.

We have showed that the excitonic coupling in molecular crystals undergoes a very large fluctuation at room temperature as a result of the combined thermal motions of the nuclei. This observation dramatically affects the description of exciton transport in organic crystals and any other phenomenon (like singlet fission or exciton dissociation) that originates from an exciton in a molecular crystal or thin film. This unexpected result is due to the predominance of the short-range excitonic coupling mechanisms (exchange, overlap, and charge-transfer mediated) over the Coulombic excitonic coupling for molecules in van der Waals contact. To quantify this effect we develop a procedure to evaluate accurately the short-range excitonic coupling (via a diabatization scheme) along a molecular dynamics trajectory of the representative molecular crystals of anthracene and tetracene.

2. **Excitonic couplings between molecular crystal pairs by a multistate approximation**.

We have developed a diabatization scheme to compute the excitonic couplings between an arbitrary number of states in molecular pairs. The method is based on an algebraic procedure to find the diabatic states with a desired property as close as possible to that of some reference states. In common with other diabatization schemes, this method captures the physics of the important short-range contributions (exchange, overlap, and charge-transfer mediated terms) but it becomes particularly suitable in presence of more than two states of interest. The method is formulated to be usable with any level of electronic structure calculations and to diabatize different types of states by selecting different molecular properties. These features make the diabatization scheme presented here especially appropriate in the context of organic crystals, where several excitons localized on the same molecular pair may be found close in energy. The method was validated on the tetracene crystal dimer, a well characterized case where the charge transfer (CT) states are closer in energy to the Frenkel excitons (FE). The test system was studied as a function of an external electric field (to explore the effect of changing the relative energy of the CT excited state) and as a function of different intermolecular distances (to probe the strength of the coupling between FE and CT states). Additionally, we illustrated how the approximation can be used to include the environment polarization effect.

3. A very general rate expression for charge hopping in semiconducting polymers.

We proposed an expression of the hopping rate between localized states in semiconducting disordered polymers that contain the most used rates in the literature as special cases. We stress that these rates cannot be obtained directly from electron transfer rate theories as it is not possible to define diabatic localized states if the localization is caused by disorder, as in most polymers, rather than nuclear polarization effects. After defining the separate classes of accepting and inducing nuclear modes in the system, we obtain a general expression of the hopping rate. We show that, under the appropriate limits, this expression reduces to (i) a single-phonon rate expression or (ii) the Miller-Abrahams rate or (iii) a multi-phonon expression. The description of these limits from a more general expression is useful to interpolate between them, to validate the assumptions of each limiting case, and to define the simplest rate expression that still captures the main features of the charge transport. When the rate expression is fed with a range of realistic parameters the deviation from the Miller-Abrahams rate is large or extremely large, especially for hopping toward lower energy states, due to the energy gap law.

4. Charge Dynamics in Organic Photovoltaic Materials: Interplay between Quantum Diffusion and Quantum Relaxation.

We discussed the mechanism of generation of free charges in organic photovoltaic cells (OPV) from electrostatically bound electron−hole pairs. The efficiency of this process is explained when interfacial charge- transfer (CT) states are generated by direct optical excitation. We used semiclassical quantum dynamics at a short time scale (∼100 fs) and Redfield theory at a relatively long time scale (∼10−100 ps) to cover both the process of dissociation and the relaxation to the lowest energy state. Our calculations suggest that a CT state with an intermediate electron−hole separation can evolve into a charge-separated (CS) state on ultrafast time scales (∼100 fs) as a result of quantum diffusion. On long time scales, however, the CS states ultimately relax to the low-energy CT states due to the interaction with the thermal bath, indicating that the yield of free charge carrier generation is determined by the interplay between ultrafast charge separation, due to quantum diffusion, and the much slower quantum relaxation process.

5. Regimes of Exciton Transport in Molecular Crystals in the Presence of Dynamic Disorder.

We showed that thermal motions in molecular crystals cause substantial fluctuation of the excitonic coupling between neighboring molecules (dynamic disorder). We explore the effect of such fluctuation on the exciton dynamics in two limiting cases, exemplified by the crystals of anthracene and a heteropentacene derivative. When the excitonic coupling is small in comparison with the electron phonon coupling, the exciton diffusion is incoherent and the inclusion of excitonic coupling fluctuation does not alter the exciton physics but can improve the agreement between computed and experimental diffusion coefficients. For large excitonic couplings, when the transport becomes coherent, the thermal motions determine the diffusivity of the exciton, which can be several orders of magnitude larger than in the incoherent case. The coherent regime is less frequent but potentially of great technological importance.

The five projects briefly described gave rise to five high-impact peer-review publications (Phys. Rev. Lett., J. Chem. Phys. J. Phys. Chem. C and Adv. Funct. Mater.). It is important to note that, although the fluctuation of the excitonic couplings owing to the thermal motions is a very intuitive effect for the exciton diffusion in molecular materials, it has not been incorporated in the most popular theories to study exciton transport. Our results clearly show that this is an important effect and should be taken into account for a proper exciton diffusion description. In addition, the timescale of the excitonic coupling fluctuation and its magnitude hamper the use of the traditional theories that may account for the excitonic coupling fluctuation. We proposed suitable approximations in the limiting transport regimes (incoherent and coherent) able to study the exciton diffusion taken into account all the needed effects.