Exciton formation via transition dipole coupling

Conjugated polymers possess unique energetic characteristics due to the extended -conjugation (alternating single and double bonds) along the polymer backbone. Upon absorption of a photon, an electron is excited from the  to \* electronic band, generating a neutral excitation that is delocalized (through strongly coupled transition dipoles) along a segment of the polymer, known as a Frenkel (or molecular) exciton. This conjugated segment is referred to as a chromophore, which is typically comprised of 2-8 monomer units in CPs and CPNs.

Transition dipole coupling strength determines whether or not excitons form in CPs, as well as chromophore size in CPs. Transition dipole coupling also facilitates several types of energy transport depending on the magnitude of the coupling strength, temperature, and the amount of disorder in the polymer. The interactions between transition dipoles of two or more degenerate monomer units can be described using perturbation theory. The coupling strength is quantified via the perturbation to the energy of the electronic states of the interacting monomers. As a brief review, it can be shown that given a perturbed Hamiltonian that solves the Schrödinger equation , where is the unperturbed Hamiltonian, corresponds to the amount of perturbation applied, varying between 0 and 1 (taken to be 1 for simplicity), and is the perturbation, the first-order energy corrections to the *D* degenerate monomer states are the roots of the corresponding secular determinant for *n, m* = 1,2,…D where (if the degeneracy is removed completely in first-order), and it is assumed that the correct zero-order wavefunctions that diagonalize the secular determinant are used.{Levine, 2000 #182} Thus, the perturbation acting on a set of degenerate electronic states results in either partial or complete splitting of the previously degenerate energy levels of the individual monomers sharing the excitation (Davydov splitting), which leads to energy shifting of the UV-Vis and fluorescence spectra of CPs in the aggregate (e.g. nanoparticle or thin film) state. In the simplest case of two identical interacting monomers, the first-order energy corrections and are , respectively, where is the dipole-dipole interaction potential. For intermolecular separations R, .

Excitons are able to migrate along or between polymer chains via several processes, including incoherent processes such as Förster resonance energy transfer (FRET) and Dexter electron transfer (described in detail in section 1.4), or by coherent energy transfer; all of these processes encompass what is often referred to as “exciton diffusion.”[ref] To understand the nature of coherent transfer, we can calculate the time-dependent probability of an electron tunneling from one monomer to another. For the aforementioned two-molecule system, the probability amplitude of an electron tunneling from molecule a to molecule b , where , and is the reduced Planck constant . The resulting probability is given by . Thus, the probability of finding the excited state electron on one of the participating monomers oscillates back and forth between the coupled monomer units with a tunneling (energy transfer) rate constant of . This tunneling process occurs on the femtosecond time scale, and is the basis of exciton diffusion.[Kasha] Given a set of monomer units (or chromophores) with strongly coupled transition dipoles, an excitation on one of the monomers will yield an oscillating excitation across the set of interacting monomers (or the set of chromophores). The relative contributions of FRET, Dexter transfer, and coherent transfer can be understood by inspecting , where is the Boltzmann constant times temperature. For , exciton formation dominates, and coherent transfer is the primary means of energy transport. If , neighboring monomers (and chromophores) do not interact strongly, thus limiting chromophore size and/or coherent transfer between like chromophores. [find a ref, maybe Kasha] It is important to note that Dexter transfer and FRET between like chromophores (homo-FRET) still contributes to exciton transport for all coupling strengths. For low coupling strengths, homo-FRET and/or Dexter transfer dominate, depending on the degree of molecular orbital overlap and alignment of transition dipoles. However, for high coupling strengths, the contributions of FRET and Dexter transfer are smaller by comparison. [Kasha, other refs]

Temperature and disorder in CPs and CPNs also affect the rate of exciton transport. At high temperatures (e.g. room temperature) excitons are thermally activated, leading to exciton-phonon coupling, which blue shifts emission, and increases the exciton diffusion length LD (i.e., the average distance travelled by an exciton during its excited state lifetime, discussed in detail in chapter 3). Reducing temperature (<150 K) eliminates exciton-phonon coupling, leading to a reduction in exciton diffusion and a red-shift of emission, due to the absence of additional thermal energy.[Nguyen, Bassler] Disorder can be understood as the presence of conformational defects or chemical defects along CP chains. Conformational defects (i.e., bends or kinks in the polymer chain) arise most commonly in aggregated CP samples such as nanoparticles or thin films; whereas chemical defects in CPs are often the result of oxidation of the polymer (e.g. fluorenone/keto defects in polyfluorenes).[refs] The presence of various defects result in conjugation breaks along CP chains, which in turn yields inhomogeneous broadening of optical spectra due to the distribution of exciton energies associated with a random distribution of conjugation lengths within the polymer. Disorder also broadens the distribution of fluorescence lifetimes within CPs and CPNs, leading to fluorescence intensity decays characterized by complex exponential functions.