The excimer dimer: mechanisms involving local and nonlocal intermolecular vibrational coupling to charge transfer states

Abstract:

Excimers, a species often associated with low-energy "trap states" and low quantum yields in material design of organic photovoltaics, are rather enigmatic outside of the original solution-phase studies performed on a series of small aromatic organic chromophores. While some excimers display a traditionally broad, structureless and red-shifted photoluminescence (PL) peak, sometimes the PL spectra exhibit a competition between vibronically structured and unstructured components. This is commonly attributed to an equilibrium between monomeric and aggregated species, even though there are cases where the presence of monomers can be excluded. In our recent work, we apply a Holstein-Peierls Hamiltonian to quantum mechanically account for not only a local vibronic coupling to a fast intramolecular vibrational mode but also local and nonlocal coupling of the charge transfer (CT) states to a slow intermolecular vibrational mode. This model simulates both the absorption and excimer emission spectra from the same set of parameters. Furthermore, it offers mechanistic insight into the origins of excimer spectral signatures without the need for an equilibrium between different species, where one observes an evolution from a structured to unstructured PL spectrum by either 1) increasing the nonlocal Frenkel exciton-CT coupling, or 2) by stabilization of the diabatic CT energy relative to that of the Frenkel exciton. Using this model's physical insight, we justify different experimental spectral features of to two different bis-perylene diimide dyes.