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Exciton coupling and energy transfer in perylene-based systems

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Abstract

Understanding the nature of photoinduced processes in organic molecules is essential for the design and synthesis of compounds with desired photochemical properties. This dissertation aims for gaining knowledge and mechanistic understanding of energy transfer in perylene-based systems. The investigations were performed using isomeric Donor-bridge-Acceptor systems, where perylene is used as an acceptor. Identifying the correlations between the molecular structure of the dyads and their photophysical properties allowed to gain an in-depth understanding of the mechanistic differences present in those. Both Förster and Dexter types of energy transfer were shown to be highly sensitive towards relative molecular orientations This work shows the first experimental proof of triplet-to-singlet energy transfer that was verified within the theoretical framework of Förster formalism.

This thesis also demonstrates a new solubilising strategy for rylene-based chromophores using bay-alkylation of perylene. This allowed to obtain soluble quaterrylene and subsequently form superradiant near-infrared J-aggregates. The delocalized nature of excited states in J-aggregates allowed to overcome the energy gap law and gain high fluorescence in the near-infrared region of the electromagnetic spectrum. That opens a previously unexplored pathway towards highly emissive near-infrared chromophores, where emission efficiency was restricted by the framework of the energy gap law.

The research results presented in this thesis contribute to the understanding of the fundamental photophysics behind such processes as multiplicity conversion, directional energy funnelling, switching between the energy transfer pathways and aggregation-induced enhanced emission. Such advanced molecular functions are of practical importance in smart materials of the future.

Keywords: perylene, triplet-to-singlet energy transfer, Förster resonance energy transfer, J-aggregates, exciton coupling