MODULATING CHARGE TRANSFER INTERACTIONS IN STRONGLY COUPLED PORPHYRIN ENSEMBLES

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In photosynthesis, cascades of short-range energy transfer and electron transfer events occur between well-arranged organic pigments (*i.e.*, light harvesting antenna ensemble and photosynthetic reaction center (PRC)) and other cofactors. Thereby the antenna portion captures light and transduces the resulting excitation energy, *via* singlet-singlet energy transfer, to the PRC. In the PRC charges are then separated with remarkable efficiency to yield a spatially and electronically well-isolated radical pair. Owing to the importance and complexity of natural photosynthesis, the study thereof necessitates suitable simpler models. The ultimate goal is to design and assemble artificial systems, which can efficiently process solar energy, replicating the natural analog.

Mimicking the primary events in natural photosynthesis mandates the use of suitable donor-acceptor couples, separated by adequate linkages. The fundamental advantage for the fabrication of tailored architectures is the control over composition, alignment, orientation and separation between individual constituents at a molecular level.

Fullerenes and porphyrins are molecular architectures ideally suited for devising integrated, multicomponent model systems to transmit and process solar energy.

The rich and extensive absorptions (*i.e.*, π-π^* transitions) seen in porphyrinoid systems - the pigments of life - holds particular promise for increased absorptive cross sections and, thus, an efficient use of the solar spectrum. Their high electronic excitation energy, typically exceeding 2.0 eV, powers a strongly exergonic electron transfer, which subsequently intercedes the conversion between light and chemical / electrical energy.

Implementation of C_{60}, on the other hand, as a 3-dimensional electron acceptor bears great promises on account of their small reorganization energy in electron transfer reactions and has exerted a noteworthy impact on the improvement of light-induced charge-separation.

This contribution describes how the specific composition of porphyrin chromophores linked to C_{60} - yielding artificial light harvesting antenna and reaction center mimics - have been elegantly utilized to tune the electronic couplings between donor and acceptor sites and the total reorganization energy. In particular, the effects that these parameters have on the rate, yield and lifetime of energetic charge-separated states are considered.