Clustered Geometries Exploiting Quantum Coherence Effects for Efficient Energy Transfer in Light Harvesting

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Excitation energy transfer (EET) is a fundamentally quantum mechanical phenomenon crucial in photosynthesis, solar-energy conversion, and organic electronics, however, conventional descriptions of energy transfer in nanoscale molecular systems are often based on a classical picture. In this work we aim to develop novel quantum theoretical methods for EET in molecular systems in order to investigate quantum coherence effects and quantum control of energy flow. To this end, we generalized the modified Redfield theory to derive a coherent modified Redfield theory (CMRT) that treats coherent quantum evolution in EET dynamics. We then applied this method to investigate optimal geometry for EET in a linear chain of chlorophylls mimicking an artificial energy-transporting wire in artificial light harvesting. For this specific topology, the optimized geometrical parameters for EET from one end to the other were investigated to reveal that the efficiency is maximized if the donor and acceptor pairs are dimerized with closer intra-pair spacing. This result is non-trivial because a classical approach such as the Förster resonance energy transfer theory would predict that an equally spaced linear geometry should give rise to the optimal efficiency. We reveal that energy tuning due to coherent delocalization of photo-excitations is mainly responsible for the efficiency optimization. This coherence-assisted energy tuning mechanism also explains the energetics and chlorophyll arrangements in the widely studied Fenna-Matthews-Olson complex. We argue that a clustered network with rapid energy relaxation among donors and resonant energy transfer from donor to acceptor states provides a basic formula for constructing efficient light-harvesting systems, and the general principles revealed here can be generalized to larger systems and benefit future innovation of efficient molecular light-harvesting materials.