NONEQUILIBRIUM EXCITATION ENERGY TRANSFER IN ORGANIZED MOLECULAR SYSTEMS

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Sequential and cooperative excitation energy transfer has been studied with Langmuir-Blodgett multilayer films which were prepared by successive deposition of monomolecular layers contained in each layer different dye molecules. Six functional dye molecules are stacked along the transfer channel, as denoted by N1, N2 ···· in the order of decreasing the S_1 energy level of dye (see Figures). The distance between adjacent layer is 25 Å, and the Förster critical transfer distance falls in between 50 and 70 Å. Taking an interchromophore distance of 25 Å as an optimal D-A pair, the excitation transfer should occur in 1~10 ps. From analyses of the ps time-resolved fluorescence spectra, the time course in every emission component of N1, N2 ···· revealed that the fluorescence rises sharply in 15~20 ps and then slowly at later time 100~200 ps, while in the decay part the fast and slow decays appear. For the fast kinetic components, the decay time of donor corresponds to the rise time of acceptor and also to the fluorescence anisotropy decay constants. Striking features are that the fluorescence decay and anisotropy decay of N1 become faster in going from two (N1-N2) to four (N1-N2-N3-N4) layer systems, and the transfer efficiency of N1→ N2 increases as one goes from the two to the four layer systems.

These observation can be accounted for by assuming participation of a reversible transfer process. The reversible transfer may occur through a dipole-dipole interaction of the Förster mechanism (the medium coupling case) which is considerably larger in the interaction energy than the weak coupling case. The ultrafast transfer should compete with the vibrational relaxation (~10 ps) within the vibrational manifolds in S_1 initially populated, and involves a transfer from vibrationally unrelaxed levels. In relation to biological molecular systems, such non-equilibrium excitation transfer should involve in the excitation transport in the photosynthetic light-harvesting antenna systems.