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Molecular Cooperation in Photo-Induced Electron Transfer in Monolayer Assemblies

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Molecular Cooperation in Photo-Induced Electron Transfer in Monolayer Assemblies

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Quenching of fluorescence due to electron transfer is observed in monolayer assemblies when electron donor D and electron acceptor A are either at the same interface or separated by one spacer monolayer. When the donor and acceptor monolayers are separated by two or more fatty acid interlayers no fluorescence quenching is detected.

Contrary to the situation in solution where electron transfer occurs on collision of donor D and acceptor A[1] the donor and acceptor molecules are immobile in monolayer assemblies. Donor and acceptor are incorporated in different mixed monolayers and fixed in the rigid matrix constituted by long chain fatty acid molecules. During the assembling of the monolayers a fraction of the donor molecules may form mixed dimers with acceptor molecules.[2] In this situation of contact the electron transfer can occur as in solution. In systems without mixed dimers the quenching of fluorescence indicates electron transfer from the donor to a separated acceptor molecule. The electron has to tunnel through the potential barrier between the donor and the acceptor molecule. Consequently, the efficiency of electron transfer must depend strongly on the energetic position of donor and acceptor levels with respect to the barrier, the lifetime of the excited species, and on the spatial separation.

Two types of photo-induced electron transfer have been studied:

1) The donor is excited and the electron is transferred from the S_1 state of the donor into the lowest unoccupied orbital of the acceptor. The donor fluorescence is quenched.

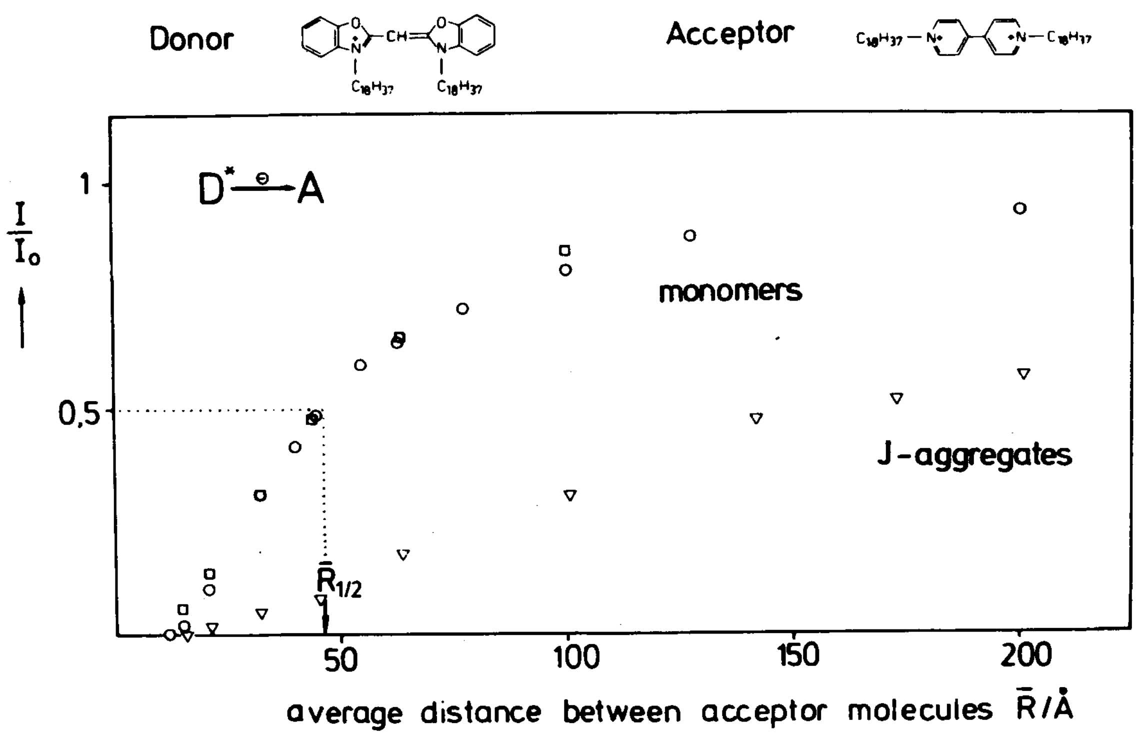

FIGURE 1 Relative flourescence intensities I/I_0 of the excited donor D* plotted against the average distance $\bar{R}$ between acceptor A molecules. Circles: Monomers of D, acceptor in the adjacent monolayer, D and A at the same interface. Squares: Monomers of D, acceptor mixed into the donor monolayer. Triangles: Donor organized in J-aggregates, A in the adjacent monolayer, D and A at the same interface. Efficiency of electron transfer strongly enhanced by organization of D in extended cooperative systems.

2) The acceptor is excited and the electron is transferred from the S_0 state of the donor into the highest occupied orbital of the acceptor. The acceptor fluorescence is quenched. In both processes the initial situation is recovered by back transfer of an electron from the reduced acceptor to the highest occupied orbital of the donor.

In the case (1) the efficiency of the electron transfer was studied by varying the concentration of A in the acceptor layer. The fluorescence quenching depends on the average distance $\bar{R}$ between acceptor molecules as calculated from the molar mixing ratio and the molecular areas of acceptor and fatty acid in the mixed monolayer. Values of $\bar{R}_{1/2}$ (average distance in the acceptor layer at which the fluorescence intensity is half of the intensity without electron transfer) have been determined.

In Figure 1 the relative fluorescence intensities I/I_0 (I in presence of A, I_0 in absence of A) are plotted against $\bar{R}$ for differently organized donor monolayers. The results represented by circles and squares have been obtained with monolayers of D constituted by monomeric dye. In one experimental set (squares) the acceptor molecules are incorporated in the same monolayer as D, whereas in the other set (circles) the molecules of A are in the adjacent monolayer with D and A at the same interface. The triangles represent values of I/I_0 obtained with monolayers of D organized in J-aggregates, D and A at the same interface.

From Figure 1 it is obvious that the efficiency of the electron transfer from the excited donor to the acceptor is strongly enhanced by organizing the dye molecules in extended cooperative systems (J-aggregates).

The values of $\bar{R}_{1/2}$ observed with the acceptor shown in Figure 1 and with monolayers of various monomeric donors depend on the energetic position of the electron donating level as calculated from electrochemical and spectroscopic data.[3]

In mixed monolayers of a long chain substituted pyrene and arachidic acid the chromophores are located at the hydrophobic interface constituted by the methyl end groups of the hydrocarbon chains. The acceptor can then be separated from the donor by a spacer monolayer of well defined thickness. The quenching of the pyrene excimer luminescence in such systems was found to depend on the thickness of the insulating spacer layer as would be expected for a tunneling mechanism of the electron transfer.

In systems of cyanine dyes selected to avoid energy transfer the fluorescence quenching of the excited electron acceptor according to case (2) has been studied. In these systems, the relative fluorescence intensity I/I_0 of the acceptor depends on the average distance between electron donor molecules in the adjacent monolayer.

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