Photoinduced Electron-Transfer Processes in Monolayer Assemblies. Supersensitization in a Three-Component System[1]

Thomas L. Penner*[2] and Dietmar Möbius

Contribution from the Max-Planck-Institut für biophysikalische Chemie, Abteilung Molekularer Systemaufbau, D3400 Göttingen-Nikolausberg, Am Fassberg, West Germany.
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Abstract: Electron-transfer reactions involving oxidation and reduction of a photoexcited cyanine dye have been investigated in monolayer assemblies. In photooxidation, the formation of the electron-adduct product of a surfactant viologen acceptor has been detected and measured quantitatively. The yield of this species can be enhanced or supersensitized by the incorporation of an electron donor as a third component into the monolayer assembly containing dye and viologen. For such supersensitization to occur the dye molecules must be organized into aggregates. The results can be understood in terms of energy and charge migration within the dye aggregate and sequential electron-transfer reactions between dye and acceptor or donor.

I. Introduction

Photoinduced electron transfer involving organic molecules has received much attention in recent years (reaction 1).[3] One common feature of such reactions, under a great variety of conditions, is the high efficiency of the dark reaction of recombination 2, which is facilitated by the energetics and the initial proximity of the reactants. As an example consider the photoreduction of an electron acceptor (A) by a photoexcited sensitizer (C*):

$$C^* + A \rightarrow C^+ + A^- \quad (1)$$

$$C^+ + A^- \rightarrow C + A \quad (2)$$

Maximization of the yield of electron transfer is often desirable, and techniques to minimize recombination have been much studied. These techniques have generally involved physically separating the products of photoreaction,[4] neutralizing or removing one of them by means of added substances,[5] or combinations of these.[6] Additives used to neutralize or remove C^+ from the system are generally good reducing agents or electron donors (D). Thus

$$D + C^+ \rightarrow D^+ + C \quad (3)$$

The overall reaction in such a three-component system is

$$D + C^* + A \rightarrow D^+ + C + A^- \quad (4)$$

Such an enhancement of electron transfer from C* to A by an electron donor which cannot directly reduce A is known as supersensitization.[7]

Reaction 4 has lost all mechanistic information present in reactions 1–3. In fact, the same overall result can occur by the following sequence:

$$D + C^* \rightarrow D^+ + C^- \quad (5)$$

$$D^+ + C^- \rightarrow D + C \quad (6)$$

$$C^- + A \rightarrow C + A^- \quad (7)$$

Both of these mechanisms of supersensitization have been extensively discussed in the literature.[8] Sequence 5–7 involves prereduction of the excited sensitizer so that it is necessary for D to be an electron-transfer quencher of C* for this mechanism to be possible. For the alternative process involving the sensitizer regeneration reaction 3 to occur, the donor must be able to reduce the photooxidized sensitizer C^+. If this condition is met, supersensitization via reactions 1–3 is possible independent of whether the donor can photoreduce C*, since the reduction potentials of C^+ and C* are generally different. Thus, if a donor cannot photoreduce C*, mechanism 5–7 is excluded. However, the ability of D to photoreduce C* does not exclude the regeneration mechanism of reactions 1–3. In this case both mechanisms are, in principle, possible.

Multicomponent electron-transfer reactions exhibiting supersensitization have been studied in a wide variety of systems involving homogeneous solutions,[5,9] heterogeneous fluids such as micelles,[10] and semiconductors both at the solid–liquid interface[11] and, less frequently, in solids.[12] Although of particular interest for applications, the solid systems are physically complex and difficult to characterize precisely. Because of this, fluid systems have provided the most substantial mechanistic data. The applicability of these mechanisms to the solid state is often limited; solid-state systems exhibit charge-migration and -transfer processes without molecular diffusion, a dominant process in solution.

We have investigated photoinduced electron-transfer reactions such as those discussed above, but in monolayer assemblies. The detailed information that can be obtained with such assemblies where reaction systems are well-defined at molecular dimensions has been well documented.[13] Processes of energy and charge migration in such systems resemble those in the solid state, because molecular diffusion is minimal. Monolayer assemblies can be fabricated in simple geometries in which parameters such as molecular spacing can be varied systematically and thus provide model systems for the study of the individual steps of energy- or electron-transfer processes of more complex solid-state systems.

Electron transfer from excited molecules in monolayer assemblies has usually been studied through the quenching of

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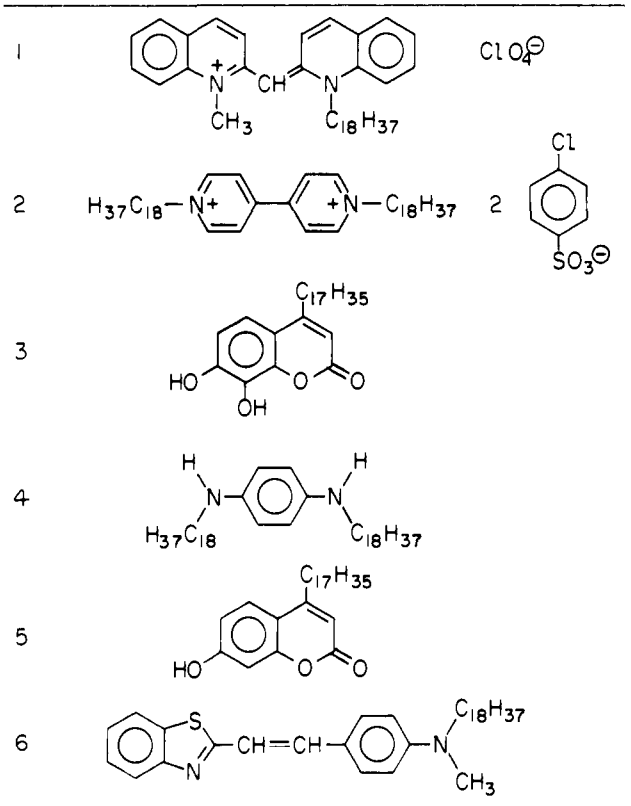
Table I. Structures of Compounds



fluorescence from the photoexcited component C*.[14,15] Reduced electron acceptor A⁻ has also been detected in some systems, both optically[16] and by ESR,[17] but no systematic quantitative investigation has been reported. Limited evidence for reaction 5 in monolayers also exists.[18] But the process described by reaction 4, i.e., the synergistic interaction of three components to enhance or supersensitize the yield of product from photoinduced electron transfer with all components fixed in a monolayer assembly, has not been observed previously. Our objective has been to find conditions under which such supersensitization occurs in monolayer assemblies and to study its dependence on system parameters in order to provide insight into the mechanisms applicable to more complex circumstances such as in spectral sensitization of solid-state systems.

II. Experimental Section

Arachidic acid and methyl stearate were purchased from E. Merck, Darmstadt. The acid was recrystallized from ethanol, and the ester was used as received. The remaining compounds are listed in Table I. Compounds **1–3** and **5** were synthesized by J. Sondermann, and compound **4** was synthesized by U. Lehman, both of the Max-Planck-Institut für biophysikalische Chemie, Abteilung Molekularer Systemaufbau. Compound **6** was synthesized by D. W. Heseltine and co-workers of the Kodak Research Laboratories. Techniques for preparing monolayers, cleaning glassware, and purifying water have been described.[19] Some modifications were made in manipulation procedures, because the preparation of good monolayers of aggregated cyanine dyes requires special conditions. The dye layers were formed on water in the absence of heavy-metal ions. Although ions such as Cd^{2+} stabilize fatty acid monolayer structure, they interfere with aggregate formation of cationic chromophores. Water with sodium phosphate buffer to give the desired pH was used. Total buffer concentration was 4×10^{-3} M. The cyanine dye (**1**) was mixed in a 1:1 molar ratio with methyl stearate, spread in chloroform solution, compressed to 35 dyn cm^{-1}, and allowed to equilibrate for 10–15 min. The aggregate layers thus formed were too viscous to transfer by the conventional immersion–withdrawal technique. They were coated by manually lowering a glass slide, made hydrophobic with a monolayer of arachidic acid, horizontally into contact with the spread layer and then immersing it into the aqueous subphase. The slide was then clamped vertically under water, the water surface was cleaned, and the next layer was coated conventionally by withdrawal. The adjacent layers then always have the relative orientation shown schematically in Figure 1. Monolayers of this cyanine dye can be made without forming J aggregates by using the *N,N'*-dioctadecyl analogue of **1** and diluting the layer with arachidic acid, restricting dye concentration to less than 10 mol %. The positions of the absorption bands of monomer and dimer (also J aggregate at higher concentration) for this analogue are identical with those of **1**. The choice of molecules with either one or two octadecyl chains was based on the greater tendency of the former to aggregate. All monolayers other than those containing aggregated dye were transferred at a surface pressure of 30 dyn cm^{-1}.

The equipment for measuring absorption and fluorescence spectra has been described.[15] Viologen radical production was measured in a spectrophotometer chamber that was continuously flushed with high-purity nitrogen. Illumination was through a window with a 200-W high-pressure mercury lamp and an interference filter to isolate the 545-nm light. All monolayer fabrications and experiments were done at room temperature, ca. 20 °C. Measurements were made on freshly prepared samples, less than 1 h old.

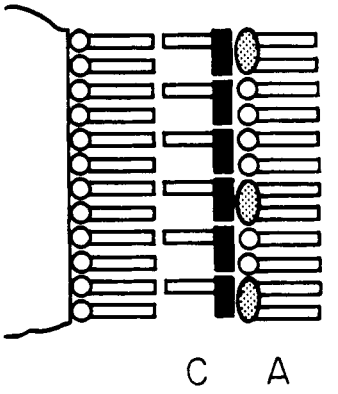


Figure 1. Arrangement of layers in monolayer assembly of cyanine dye **1** (C) and viologen electron acceptor **2** (A) on a glass plate with a spacer layer of arachidic acid.

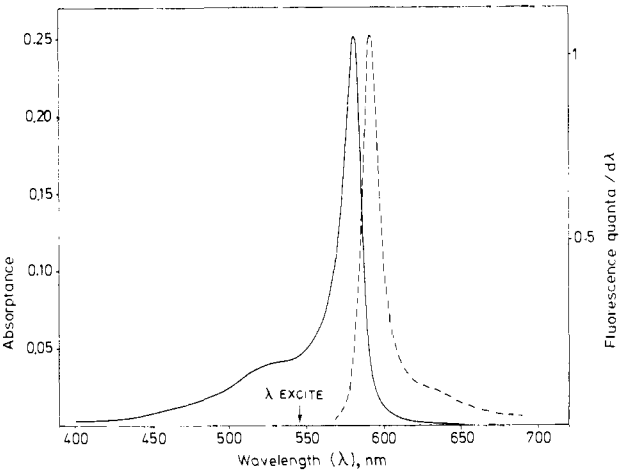


Figure 2. Absorption and normalized fluorescence spectra of a single monolayer of cyanine dye **1** in J-aggregated form.

III. Results and Discussion

1. Two-Component Sensitizer–Acceptor System. Cyanine dye **1** was used as the photosensitizer. Of great importance to the properties of the system is that the dye can be incorporated into

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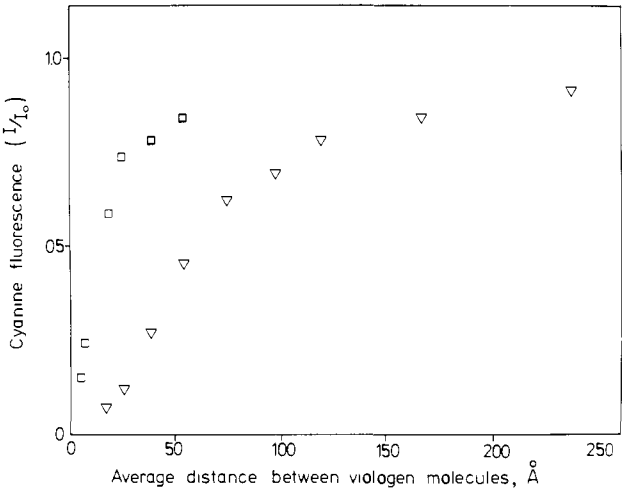

Figure 3. Dependence of cyanine J-aggregate (▽) or monomer (□) fluorescence on the average distance between viologen molecules in the adjacent layer when the dye layer is organized respectively into J aggregates or monomer plus dimer.

the monolayer as J aggregates.[20] When a cyanine dye forms J aggregates, the molecules are close-packed in an extended, regular brickwork array so that they exhibit cooperative excitonic absorption leading to an intense narrow band, bathochromically shifted from the monomeric absorption.[21] The excited-state lifetime is short (for **1** it is $<10^{-10}$ s[22]) and exhibits fluorescence with a small Stokes shift. Figure 2 shows the fractional absorption and emission spectra of a single monolayer of **1** mixed in equimolar amounts with methyl arachidate. The assembly was fabricated in the configuration of Figure 1, but without electron acceptor. The molecular area of **1** in compressed monolayers on the water surface or transferred onto glass as described is 45 ± 2 Å^2, indicating that the molecules are aligned with their molecular planes perpendicular to and their long axes parallel to the surface of the support. It is known that the formation of J aggregates drastically alters the excitation or electron-transfer properties of a cyanine dye in monolayer assemblies.[23]

Before we studied the three-component system, we examined electron transfer in the two-component cyanine dye–electron acceptor assembly. As previously,[15] the *N,N'*-dioctadecyl derivative (**2**) of the viologen molecule was used as an electron acceptor. This compound, with no absorption overlap with the dye fluorescence, is an analogue of paraquat, a strong electron acceptor.[24] The amount of viologen was restricted to ≤10 mol %, diluted with arachidic acid. The surface concentration of J-aggregated cyanine dye was then always at least 5 times that of the viologen.

Fluorescence Quenching. Figure 3 shows the quenching of the cyanine fluorescence as a function of the average distance between viologen molecules in the layer adjacent to the dye, calculated by using the molecular areas of the constituent molecules as measured from pressure–area isotherms and assuming a random two-dimensional distribution.[13b] The chromophores were in head-to-head contact at the interface as depicted in Figure 1. The data show that, when the dye was aggregated, it required much less viologen to quench the fluorescence than when in the monomeric–dimeric form. In fact, aggregate fluorescence was 50% quenched when acceptor molecules were 60 Å apart. When

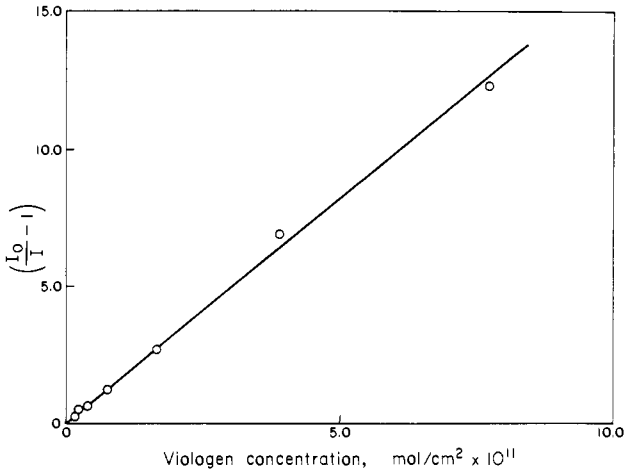

Figure 4. Dependence of cyanine J-aggregate fluorescence on the concentration of viologen in the adjacent layer.

monomer fluorescence was monitored, the dioctadecyl analogue of **1** was used to avoid forming the aggregate, as discussed in the Experimental Section. Both monomer and dimer were present, with absorption maxima at 530 and 490 nm, respectively. In this case 50% quenching occurred at an average acceptor spacing of about 15 Å. High concentrations are needed so that an acceptor molecule is near to one of the excited dye monomers or dimers, which are isolated by arachidic acid molecules. The comparison demonstrates the extensive excitation migration within the J aggregate and its consequent sensitivity to electron-transfer processes. In Figure 4 the data of Figure 3 for J-aggregate luminescence have been replotted to test the quenching equation derived below. This equation is based on the premise that the exciton is mobile over the aggregate and that its probability of encountering an electron-acceptor molecule is directly proportional to the surface concentration of acceptor. Considering then the following set of reactions, where k_f and k_{nr} are the fluorescence and nonradiative deactivation rate constants of C*

$$C^* \xrightarrow{k_f} C + \text{fluorescence} \quad (8)$$

$$C^* \xrightarrow{k_{nr}} C \quad (9)$$

$$C^* + A \xrightarrow{k_A} C^+ + A^- \quad (10)$$

one can derive the dependence of cyanine dye fluorescence on electron-acceptor concentration

$$I_0/I - 1 = k_A[A]/(k_f + k_{nr}) = \tau k_A[A] \quad (11)$$

where τ is the lifetime of C* in the absence of A. This equation predicts that a plot of $I_0/I - 1$ vs. acceptor concentration will be a straight line through the origin. The good fit of the data shows that the fluorescence quenching by the viologen is straightforward, linearly dependent on the number of quencher molecules.

The slope in Figure 4 is $(1.6 \pm 0.2) \times 10^{11}$ cm^2 mol^{-1}. (The error limits are based on the reproducibility of the fluorescence measurements.) With 10^{-10} s as an upper limit to the excited-state lifetime, from this slope can be calculated a lower limit to the electron-transfer rate constant k_A of 3×10^{-3} cm^2 molecule^{-1} s^{-1}. This is $\sim 10^3$ faster than a recent estimate of diffusion control in monolayers.[25] Thus, although the quenching equation has the form of Stern–Volmer kinetics,[26] exciton migration within the dye layer rather than molecular diffusion is involved.

Formation of Viologen Radical. The fluorescence quenching monitors reaction 1, the primary electron transfer. But to measure the extent to which electron transfer escapes the back-reaction, one must measure the yield of A$^-$ directly. On exposure in a

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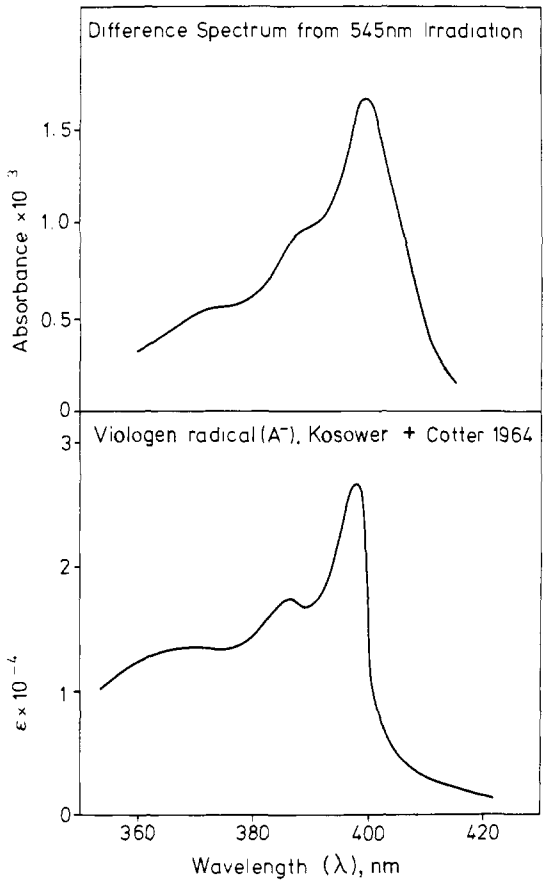

Figure 5. Photosensitized absorption induced by illumination of dye–viologen monolayer assembly at 545 nm compared with a literature spectrum of the one-electron adduct of methylviologen (ref 23).

nitrogen atmosphere of the dye aggregate–viologen system described above to light of 545 nm, which was absorbed only by the dye, we could detect the growth of the viologen radical produced by electron transfer. The radical was stable for many minutes, and its absorption spectrum could be measured around 400 nm where there is a window in the dye absorption. This spectrum corresponded to the radical formed by addition of an electron to the viologen[27] (Figure 5). The formation of this product, which we call persistent radical, was followed as a function of illumination time and reached a maximum yield that could not be increased by further exposure (Figure 6). The amount of this radical formed at steady state was directly proportional to the concentration of viologen molecules in the layer, at least up to the 10 mol % maximum used. Thus, the same fraction of viologen was converted to persistent radical at all concentrations if no other conditions were changed. In the case in Figure 6, this was calculated to be 40% of the viologen present, based on the known extinction coefficient of the viologen radical.[28] The shape of the spectrum remained unchanged with concentration. (No radical dimer (λ_{max} = 370 nm)[27] was detected.)

Since cyanine fluorescence was about 90% quenched by the viologen under the conditions of Figure 6, reaction 1 must occur on a time scale $<10^{-10}$ s. Yet the production of persistent radical occurred over minutes with an initial quantum yield of about 0.01, based on the light absorbed by the cyanine dye. Such a result can be rationalized if the fluorescence is quenched in a fast electron-transfer process that is followed by a slow reaction leading to the persistent radical in competition with efficient recombination. It can be envisioned that a physical reorientation of the initially produced radical is required to make it immune to recombination. Alternatively, the slow reaction competing with recombination may be the diffusion of the positive charge (hole)

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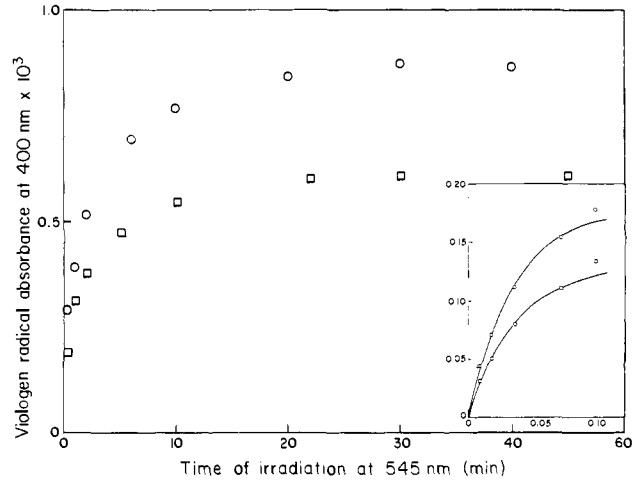

Figure 6. Time-dependent growth and steady-stage yield of radical absorption for the dye aggregate–viologen (□) and donor–dye aggregate–viologen (○) assemblies. Donor and acceptor levels are each 5 mol % mixed with arachidic acid; subphase pH 11.

away from the original electron-transfer site.

It is not possible to clarify these mechanistic details without direct detection of the intermediate species involved. However, a closer examination of the formation rate of persistent radical does provide some information on the overall process. The growth kinetics of this radical absorption show that it is more complex than the three-reaction scheme just described. Such a simple mechanism would result in an expression of the form

$$[A^-] \propto (1 - e^{-kt}) \tag{12}$$

to describe the time dependence of radical buildup. In fact, the process does follow such an expression, as shown by the curves in the expanded time scale inset in Figure 6, but only at low conversion (<20% of the final yield). To fit the entire time scale requires a sum of such growth curves:

$$[A^-] = \sum_{i=1}^{n} a_i(1 - e^{-k_i t}) \tag{13}$$

Generally three sets of parameters, i.e., $n = 3$, are sufficient to characterize the entire curve. The rate constants are different enough so that at short times the curve fits the simple form. Such a series of growth curves implies that there are several populations of viologen molecules with different rates of stabilization (or possibly recombination). This is plausible for a nonhomogeneous system such as the present one where viologen molecules may be located at different sites relative to the dye aggregates, e.g., near aggregate boundaries vs. the interior, or with different relative orientations.

The radical produced was not entirely stable, decaying over hours in a nitrogen atmosphere with the light turned off. Because it was photostable, presumably it is this slow dark decay that ultimately limits the extent of viologen conversion to less than 100%. The unconverted portion represents those populations where the stabilization rate is too slow, or recombination too fast, for radical production to exceed the dark decay. Also, a certain portion of the viologen could be simply unreactive, as seen in other photochemical reactions in monolayer assemblies.[29] But as shown later, a variety of factors can influence the maximum conversion at a given concentration of acceptor. The steady-state condition thus appears to be a dynamic equilibrium, albeit slowly established because of low rates of radical formation and decay. Little is known about this dark decay. It presumably regenerates viologen, since, as long as illumination continues, no loss of radical absorption is observed over several hours. (This represents 10^4 turnovers of C*. The quantum yield for photodegradation of the cyanine sensitizer is $<10^{-5}$.)

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The initial rate of growth of persistent radical increased linearly as light intensity was increased from 0.05 to 1.5 photons s^{-1} absorbed per dye molecule. Although such a linear response does not unequivocally prove that the process is a single-photon reaction, the low light levels used would require that any intermediates must have a lifetime on the order of seconds for the intensity dependence to appear linear. We detected no buildup of the persistent radical after illumination was interrupted (0.5-s resolution).

Without the availability of a direct measurement of the recombination reaction 2, it does not appear to be worthwhile to attempt a more detailed analysis of these kinetics. The results are consistent with the three-reaction scheme proposed, with the added complication that there is a distribution of rate constants for the overall process and a slow dark decay of radical, apparently regenerating viologen.

2. Two-Component Sensitizer–Donor System. As discussed in the Introduction, it is not necessary for the donor to be able to photoreduce the sensitizer to have supersensitization. For example, reaction 3 could be involved. However, the study of cyanine photoreduction reaction 5 in comparison with the photooxidation reaction 1 is of interest in its own right. Furthermore, if a donor can photoreduce the dye excited state, it probably will also reduce the cation (reaction 3). Thus, a molecule that can photoreduce C* should be a good supersensitizer, although the photoreduction may not be involved in the mechanism. Several reducing agents were found that quench the dye-aggregate fluorescence when incorporated in a monolayer diluted with arachidic acid in contact with dye chromophores. Compound **3**, the 4-heptadecyl derivative of daphnetin (7,8-dihydroxycoumarin) was studied in detail. For convenience, we use the name daphnetin for **3**. It was approximately $^1/_4$ as effective a quencher as the viologen electron acceptor, based on the concentration required to quench half of the dye-aggregate fluorescence when the monolayers were prepared under identical conditions at pH 11 (see below).

Influence of Subphase pH. An interesting feature of the action of this donor is that its ability to quench dye fluorescence was dependent on the pH of the aqueous subphase from which the layers were coated. (As with all other experiments, the actual fluorescence measurements were done on dry, transferred assemblies, not in contact with the subphase.) Since daphnetin is a substituted catechol, it is reasonable that it shows an acid–base equilibrium and that these two species have different electron-donor properties. The deprotonated form should be a better reducing agent. If one assumes a scheme such as that outlined below, an equation can be derived relating fluorescence quenching to pH. In addition to reactions 8 and 9, the following reactions can be written, where BH is a quencher in its acid form and B^- is the conjugate base:

$$BH \overset{K_a}{\rightleftharpoons} B^- + H^+ \tag{14}$$

$$C^* + BH \xrightarrow{k_{BH}} C^- + BH^+ \tag{15}$$

$$C^* + B^- \xrightarrow{k_{B^-}} C^- + B\cdot \tag{16}$$

The expression for fluorescence quantum yield can be derived and from this the equation for the quenching of fluorescence intensity, as already done for the electron acceptor.

From mass balance and the definition of K_a, the ionization constant, the pH dependence of fluorescence quenching is obtained:

$$\frac{I_0}{I} - 1 = \frac{a + b[H^+]/K_a}{1 + [H^+]/K_a} \tag{17}$$

where $a = \tau k_B C_0$ and $b = \tau k_{BH} C_0$. C_0 is the total concentration of quencher in acid and base form and τ is the fluorescent lifetime with $C_0 = 0$. The terms a and b represent the limiting cases when all fluorescence quenching is due to basic or acidic forms of the donor, respectively. They were derived experimentally from results at high and low pH ($a = 3.2$ and $b = 0.3$).

The curve in Figure 7 is based on the above general equation with only K_a as an adjustable parameter. The value $pK_a = 10.5$

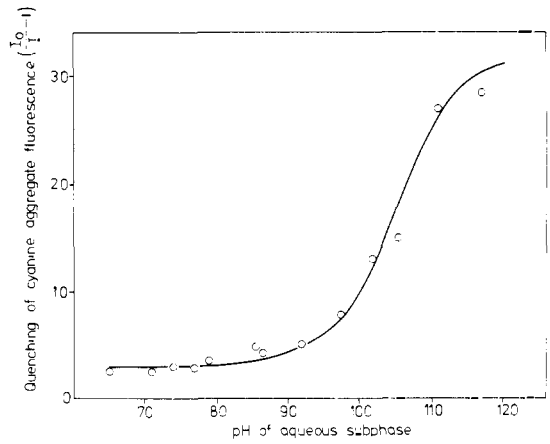

Figure 7. Dependence of the donor quenching of cyanine-aggregate fluorescence on the pH of the aqueous subphase from which monolayers were transferred. Curve is based on eq 17. Donor level was 10 mol % mixed with arachidic acid.

defines an "effective" equilibrium constant in the monolayer system, which can be different from that in the aqueous subphase.[30] The good fit of the fluorescence quenching data to this "titration curve" supports the above interpretation. Further, it shows that the deprotonation equilibrium of the donor molecules established at the subphase interface is not drastically changed upon deposition onto the J-aggregated dye layer. The ratio $a/b = k_B/k_{BH} = 10$ means that the rate constant for fluorescence quenching is 10 times greater for the basic form than for the neutral molecule. This supports the idea that the fluorescence quencher acts by donating an electron to excited dye.

Irradiation of cyanine dye–daphnetin donor systems with 545-nm light under nitrogen did not produce any detectable absorption at 400 nm.

3. Three-Component Donor–Cyanine Aggregate–Acceptor Assembly. Supersensitization. Having characterized the component systems involved in reactions 1 and 5, we combined them into a system in which both donor and acceptor are incorporated into the assembly. Because of the techniques of monolayer fabrication, it was not possible to place donor and acceptor layers on opposite sides of the dye layer without the imposition of fatty acid layers, which strongly inhibit electron transfer.[18] They were usually mixed together into the same layer in contact with the dye layer although, as described below, in some experiments the donor was in the dye layer.

The yield of viologen radical absorption at 400 nm was measured for such a three-component system in which the monolayers were spread on a subphase at pH 11. As shown in Figure 6, the presence of the donor substantially increased the persistent radical yield when this assembly was irradiated under identical conditions as the two-component dye–acceptor system containing the same amount of viologen. The spectrum remained unchanged. Examination of the kinetics of radical formation revealed that the initial rate and the eventual steady-state yield were increased in the same proportion by addition of donor. The donor had supersensitized the stable radical yield by a factor of 1.4. This relative enhancement was independent of viologen concentration, if enough donor had been added. Donor concentrations >20% that of acceptor were needed for a substantial influence. Levels of donor >50% of the acceptor concentration showed no further increase. The data in Figure 6 were obtained with 5 mol % each of donor and acceptor.

Mechanism of Supersensitization. As discussed, the initial growth rate of persistent radical can be described by a single rate constant, but the entire curve requires several. Thus, the increase in initial rate on the addition of donor to the system reflects the increase in the first rate constant, which represents about 20% of the total conversion, whereas the increase in steady-state yield

(30) (a) Fernandez, M. S.; Fromherz, P. *J. Phys. Chem.* **1977**, *81*, 1755. (b) Fromherz, P.; Arden, W. *J. Am. Chem. Soc.* **1980**, *102*, 6211.

reflects the cumulative change in all the rates. The fact that these two values, initial rate and steady-state yield, are increased in the same proportion by the addition of donor (both by a factor of 1.4 under the conditions of Figure 6) implies that all the rates are increased in about the same proportion as the initial one. Discussion of the influence of the donor on steady-state yield in terms of kinetics is thus justified. The donor does not influence the extent of fluorescence quenching by the acceptor (see below). Therefore, it does not act on the initial electron-transfer reaction 1. It must influence the balance between recombination and the slow radical stabilization. Because this donor is itself a quencher of dye fluorescence, the mechanism could involve either reaction 3 or 5 or both.

Whatever the sequence of these events, reaction 4 results in a net electron transfer from donor to acceptor through the mediation of excited dye. Lateral diffusion of the molecules is not possible, but preassociation of donor and acceptor could occur, as has been detected in solution between viologen and dihydroxybenzenes.[31] Low levels of such charge-transfer complexes would be difficult to detect in monolayers. However, the following observations argue against the involvement of ground-state complexes:

1. The quenching of cyanine-aggregate fluorescence by donor and acceptor was additive.[32] From the quenching data of the individual components their additive effect can be calculated. These calculated values agreed with those measured for a wide variety of donor and acceptor mixtures to within the 10% reproducibility of the measurement.

2. By restricting its concentration to a maximum of 1 mol %, the donor could be incorporated into the cyanine layer without disrupting the aggregate. The supersensitizing effect was the same as when the donor was incorporated at the same surface concentration into the adjacent layer containing a constant concentration of 2 mol % acceptor. Enhancement values were 1.56 and 1.52, respectively. With donor added to the dye layer at ≤1 mol % and acceptor in the adjacent layer at 2 mol %, it is unlikely that molecules of the two are close enough to form a ground-state complex.

When electron-acceptor and -donor levels were diluted even further, it was possible to demonstrate that, on addition of donor to the acceptor or dye layer, this enhancement in radical yield, or supersensitization, remained constant down to concentrations where the average donor–acceptor spacing was greater than 40 Å. (Since the actual radical yield decreases on lowering viologen concentration (see section III.1), we were unable to measure radical yields sufficiently accurately at concentrations representing greater separations.) The net overall supersensitization reaction 4 is electron transfer from donor to acceptor through mediation of excited dye. In view of the average donor–acceptor spacing at which this enhancement is still observed, we conclude that charge is transferred over rather large molecular distances from donor to acceptor. We propose that this occurs via electron migration through the dye aggregate. Although the net electron-transfer reaction 4 does not involve ionized dye, the actual steps in either mechanism, represented by reactions 1 and 3 or 5 and 7, include charge generation in the dye layer. It is not unreasonable that this could migrate through the aggregate. Distances of about 40 Å imply the involvement of at least four to five dye molecules in the transfer of electrons from donor to acceptor.

This hypothesis is supported by experiments with the dioctadecyl analogue of cyanine dye **1** incorporated into the layer with no J aggregation (i.e., only monomer plus dimer). With sufficient

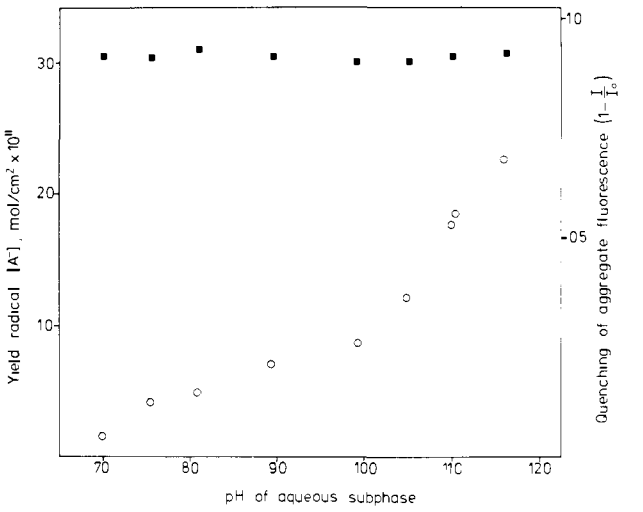

Figure 8. Dependence of steady-state radical yield (○) and the fraction of cyanine-aggregate fluorescence quenched (■) on the pH of the subphase from which the monolayers of the cyanine dye–viologen assembly were transferred. Viologen level was 10 mol % mixed with arachidic acid.

viologen to quench 50% of the fluorescence, the persistent radical was generated upon illumination of the dye. However, it was not possible to increase its yield by the addition of any of the electron donors that are effective supersensitizers when the dye is aggregated. It appears that the dye must be J aggregated for supersensitization. This supports the model involving electron migration through the dye aggregate. When diluted with arachidic acid to prevent aggregation, the dye monomer or dimer molecules are isolated and electron migration within the dye layer is inefficient. The enhancement of lateral photoconductivity in a monolayer upon dye aggregation has been reported for merocyanines.[33]

Influence of pH on Supersensitization. The multilayers used in the preceding supersensitization experiments were fabricated with a subphase of pH 11 because the daphnetin electron donor is most active at high pH. These are not the conventional conditions for fabricating monolayer assemblies. Multilayers of dye and electron acceptor had initially been prepared on pure water (pH 5.6), and the acceptor was equally effective as a fluorescence quencher as at high pH. However, the steady-state yield of stable radical was small, less than 10% that at pH 11. A systematic investigation led to the results shown in Figure 8. Fluorescence quenching by acceptor is pH independent. In fact, the dye-aggregate fluorescence spectrum and intensity in the absence of any acceptor as well as its absorption properties are essentially independent of the pH of the subphase on which the layers are spread. In contrast, the yield of persistent radical is strongly increased at high pH although no donor has been added. In effect the yield of radical has been "pH supersensitized" by a mechanism that does not involve dye fluorescence quenching. Examination of the kinetics of radical formation shows that the initial rate of formation changes in the same proportion as the steady-state yield as a function of pH, analogous to the addition of donor. Thus, here too the variation in steady-state yield reflects a kinetic effect. Effects such as an acid–base equilibrium in the viologen radical can be excluded, because its extinction coefficient is independent of pH over the range used.[28] The most likely explanation is a supersensitization by an unidentified donor via reaction 3, which does not involve fluorescence quenching. Recent information demonstrates that water is incorporated in the outer layers during the fabrication of a multilayer fatty acid assembly,[34] so that ions might be transported in an aqueous phase into our coatings. It is unlikely that phosphate ions from the buffer are involved since similar results are obtained with carbonate buffer. One possibility is that hydroxide ions act as electron donors. Although we have

(31) White, B. G. *Trans. Faraday Soc.* **1969**, *65*, 200.

(32) When two species quench fluorescence independently and additively, their combined effect is given by

$$I_0/I_{A,D} - 1 = (I_0/I_A - 1) + (I_0/I_D - 1)$$

where $I_{A,D}$ is the fluorescence measured in the presence of both donor and acceptor, and I_A and I_D are the values at the same concentrations for acceptor and donor, each alone.

(33) Sugi, M.; Fukui, T.; Iizima, S.; Iriyama, K. *Mol. Cryst. Liq. Cryst.* **1980**, *62*, 165.

(34) Windreich, S.; Silberberg, A. *J. Colloid Interface Sci.* **1980**, *77*, 427.

Table II. Comparison of Donors as Supersensitizers of Viologen Radical Formation and as Quenchers of Dye-Aggregate Fluorescence

donor	supersensitization	I_D/I_0
5	1.3	0.96
3	1.9	0.90
6	2.4	0.77
4	3.5	0.24

no direct evidence, precedent exists in the literature for this suggestion. The photoinduced electron transfer from dyes to methylviologen in aqueous solution[35] and the enhancement of chlorophyll-sensitized photocurrent in an aqueous-monolayer-semiconductor electrode system[36] at high pH have been attributed to such a mechanism. Alternatively, the interfacial energy states that are proposed to exist between adjacent monolayers[37] may be either more numerous or occupied by electrons to a greater extent when the layers are fabricated at high pH. These could then act as a source of supersensitizing electrons. The nature of the states is not known. Whatever the source of the electrons, the system appears to be highly self-supersensitized at high pH without any added reducing agent. If this is true, an added donor would have small additional effect. Then by lowering the pH and therefore the radical yield in the absence of supersensitizer, one might expect to obtain conditions where an added donor has a greater influence than at pH 11.

For the daphnetin the situation is complicated because it is a poorer donor at lower pH. Thus we investigated another donor, *N,N'*-dioctadecyl-*p*-phenylenediamine (**4**). The pK_a of this compound appears to be well below 8 in the monolayer system, since it is as effective a fluorescence quencher at pH 8 as at pH 11. At the high pH it is about as good a quencher as daphnetin at the same concentration.

We compared persistent radical yield with and without donor incorporated into the acceptor layer in contact with dye aggregate (donor and acceptor concentrations were 5 mol %). At pH 8 the *p*-phenylenediamine derivative enhanced the yield by a factor of 3.5 and the daphnetin by a factor of 1.9. The corresponding values at pH 11 were 1.5 and 1.4 (from Figure 6), respectively. (The large enhancements in radical yield at pH 8 are accompanied by equal increases in initial formation rate.) Clearly, added donors have a greater supersensitizing effect when the pH enhancement of radical yield is small. It is significant that the daphnetin is still a reasonably good supersensitizer at pH 8 even though it is then a poor fluorescence quencher (I_D/I_0 = 0.9).

Supersensitization by Various Donors. In view of the above result, we investigated the supersensitizing ability of two additional compounds in order to form a series of donors that quench the dye-aggregate fluorescence to various degrees. Table II compares these compounds which, in addition to **3** and **4** already discussed, include **5**, the monohydroxy analogue of **3**, and **6**, a known supersensitizer of photographic spectral sensitization.[38] There is no overlap between the absorption spectra of these compounds and the fluorescence band of the cyanine dye aggregate.

The comparisons in Table II were made with each donor at the same concentration as that of viologen (5 mol %) and located in the same layer. The subphase was at pH 8. Supersensitization values represent the ratio of persistent radical yield in the presence of donor to that measured in its absence. The value I_D/I_0 is the ratio of dye-aggregate fluorescence in the presence of 5 mol % donor to that in its absence, with no viologen present in either case.

Qualitatively, the supersensitization by the donors parallels their fluorescence quenching ability. However, both donors **3** and **5** give appreciable supersensitization although they are poor quenchers of dye fluorescence under these conditions. They presumably supersensitize by reaction 3. We do not know if this is also the mechanism for the other electron donors which do quench dye fluorescence. The parallel increases in fluorescence quenching and supersensitization reflect increasing reducing ability of the donors. However, as discussed in the Introduction, this does not necessarily mean that photoreduction of excited dye is involved in supersensitization. The two processes may even be competitive.

IV. Summary

Photooxidation and photoreduction of an excited cyanine dye were demonstrated in a monolayer assembly through fluorescence quenching when an electron acceptor or an electron donor, respectively, was incorporated into the adjacent layer in head-to-head contact. When the dye is J aggregated, it undergoes electron-transfer fluorescence quenching at much lower acceptor concentrations than when in monomeric and dimeric form. This is attributed to extensive migration of excitation in the aggregate.

Electron-transfer quenching by viologen leads to the buildup of its radical in quantitatively measurable amounts. The slow formation of this persistent radical can be explained by a scheme involving a rapid photoredox reaction, an efficient back-reaction (recombination), and a reaction of low probability leading to optically detectable radical. When both donor and acceptor are incorporated into the assembly, the yield of radical from acceptor is enhanced. That is, the electron transfer from excited dye to acceptor is supersensitized by the electron donor. Depending on the particular donor and conditions, an enhancement as large as a factor of 3.5 is obtained. No supersensitization occurs when the dye is not J aggregated. Together with the high dilutions of donor and acceptor at which supersensitization is still observable, this leads us to conclude that charge migration through the aggregate for distances as large as 40 Å is involved in the supersensitization.

In addition to enhancement by added donors, the yield of acceptor radical can be markedly increased by raising the pH of the subphase from which the dye aggregate–electron acceptor assembly is fabricated.

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Registry No. **1**, 78693-33-1; **2**, 83705-07-1; **3**, 83705-08-2; **4**, 55621-26-6; **5**, 26038-83-5; **6**, 83705-09-3.

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(38) Muenter, A. A.; Cooper, W. *Photogr. Sci. Eng.* **1976**, *20*, 121.