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Controlled Transfer of Excitation Energy Through Thin Layers†

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In biological systems the molecules are in a distinct order and entirely new properties are caused by this organization at the molecular level. The synthesis of molecular aggregates of a planned order is an important new task for chemists. The chemist has methods for the synthesis of very complicated molecules but he has no methods for synthesizing aggregates of molecules of a given order or organization, of such systems which we may call organizates. He needs a kind of pincette for picking out single molecules and arranging them in a planned manner. The task of synthesizing organizates may be seen in two aspects: One may try to imitate simple biological structures or one may try to build any planned arrangement of molecules that has useful properties depending on the details of the arrangement of the molecules.

The goal of the experiments described here is to synthesize very simple organizates of molecules A, B, C, D ... by arranging them in the strict order ABCD .... This may be done by bringing a monolayer of molecules A on a support (Fig. 1a) superimposing a monolayer of molecules B (Fig. 1b) and then a monolayer of molecules C (Fig. 1c) and so on. In this way molecular arrays of any planned order in the sequence of molecules might be constructed.

Blodgett and Langmuir[1] were able to build multilayers of fatty

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† This paper is based on a lecture presented by H. Kuhn at the Third Annual Symposium on the Organic Solid State, The Franklin Institute, Philadelphia, Pennsylvania on September 20, 1965.

acid salts such as barium stearate on a glass plate by bringing first a monolayer of the fatty acid salt on the surface of water. By dipping the glass plate in the water and taking it out again a first monolayer of the fatty acid salt is fixed on the plate, and by dipping it in again and taking it out again a second and a third monolayer is attached; by repeating this procedure again and again an almost arbitrary number of monolayers may be laid upon each other.

According to Singer and Ries[2] such monolayers have holes as found by the electron microscope, and according to Sobotka[3] the fatty acid molecules may diffuse through many monolayers (as shown by radioactive tracer studies). Each part of the layer is in a continuous thermal movement and the diffusion arises by opening and closing of pores. Langmuir[4] has concluded from his work that in many cases the layers rearrange after the plate is taken out of the water.

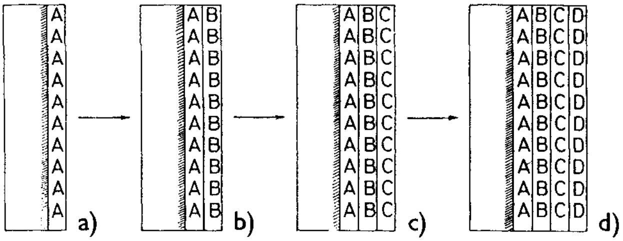
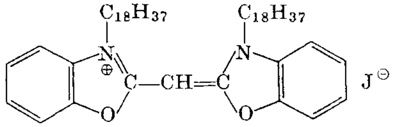


Figure 1.

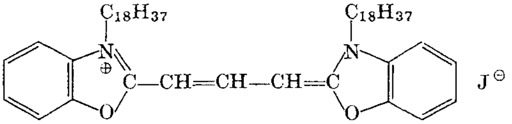
It does not seem very hopeful therefore that organizates can be obtained in this way. However, from the experiments to be described here we will come to the conclusion that systems of monolayers suitable for this purpose may be obtained by appropriately changing the Langmuir Blodgett technique.

A. Preparation of Systems of Monolayers of Ionic Dyes with Long Chain Hydrocarbon Substituents

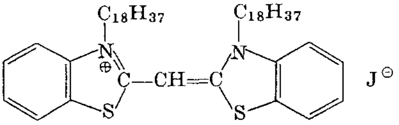
We have synthesized ionic dyes with long chain paraffin substituents such as



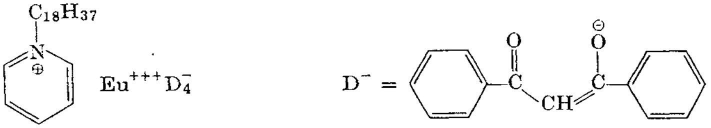
I



II



III



IV

As well as a fatty acid such a dye containing a hydrophilic and a hydrophobic part may be spread on water. A solution of the dye or dye plus fatty acid in an organic solvent is dropped on a surface of water; the solvent evaporates; a tension of 30 dyn/cm is applied and a monolayer of the dye (or a mixed dye and fatty acid monolayer) is thus obtained (Fig. 2). In the case of a fluorescent dye this monolayer may be seen as a glow of the surface of the water when it is irradiated with an ultraviolet lamp (Fig. 3a, p. 215). When a glass plate is dipped in the water, no layer is attached because glass is hydrophilic; when it is taken out again the hydrophilic chromophoric part of the dye sticks to the glass surface and the monolayer is attached as seen by the fluorescence of the section of the glass covered by the dye (Fig. 3a, b, p. 215). By dipping in the lower part of the glass plate a second layer of the dye is attached to the surface of the plate which is now hydrophobic, and by taking it out again a

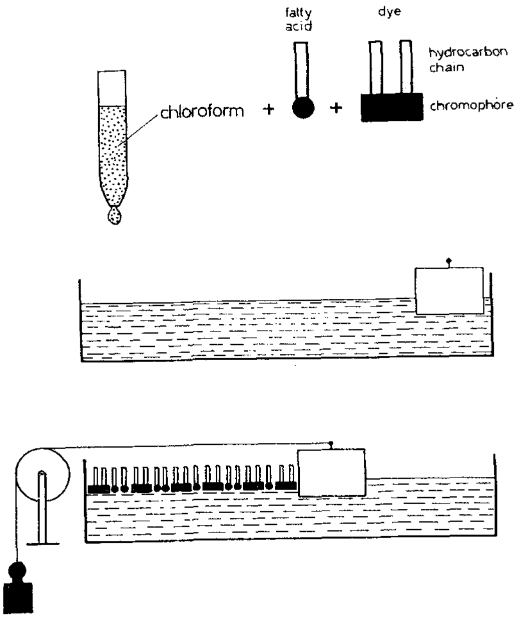


Figure 2. Preparation of mixed dye and fatty acid salt monolayers by spreading solution on water surface.

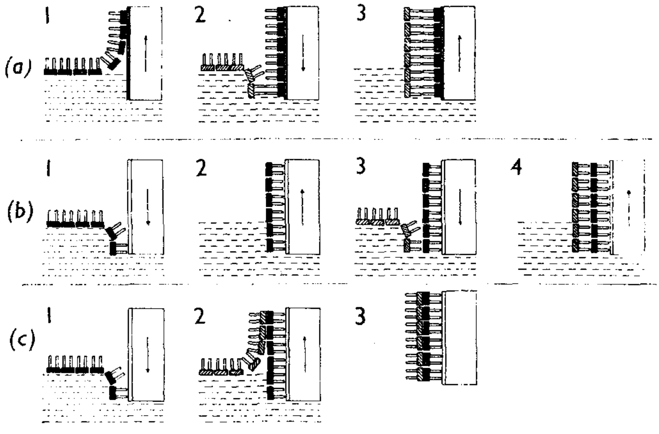


Figure 4. Preparation of three different arrangements of a layer of dye A (chromophore: solid rectangle) and a layer of dye B (chromophore: shaded rectangle). Layers of chromophores A and B in a distance of 60 Å (a), 30 Å(b) and in direct contact (c). Schematic representation. Actually we have used mixed dye and fatty acid salt monolayers prepared according to Figure 2.

third layer is attached. This is seen in the light of the ultraviolet lamp by the strong fluorescence of the lower part of the plate. (Fig. 3c, p. 215).

We may imagine many combinations of monolayers of such dyes representing most simple organizates. Figure 4 shows a few combinations that may actually be realized.

The water may be covered by a monolayer of such dye molecules A, the molecules sticking their ionic chromophor heads into the water and the paraffin legs towards the surface. By dipping in a glass plate with a hydrophilic surface and by taking it out again a monolayer of the dye is attached to the plate as mentioned before (Fig. 4a, step 1). This plate may now be dipped into water covered by a monolayer of dye B; the monolayer will be attached to the surface of the plate, the paraffin legs of dye B being attached to the paraffin legs of dye A (Fig. 4a, step 2). The monolayer on the water may be removed and the plate may be taken out of the water (Fig. 4a, step 3). In this case the chromophoric parts of dyes A and B are separated by the paraffin legs of both dyes.

However, when dipping a plate with a hydrophobic surface in water covered by a monolayer of dye A, the layer will be attached to the plate (Fig. 4b, step 1). The monolayer may then be removed from the surface of the water and the plate may be taken out of the water (Fig. 4b, step 2). This plate may then be dipped in water with a surface covered by a monolayer of dye B. Surprisingly enough, this plate is then covered by the monolayer, its surface thus behaves as being hydrophobic (Fig. 4b, step 3). The monolayer on the water surface may then be removed and the plate may be taken out (Fig. 4b, step 4). In this case the chromophoric parts of dyes A and B are separated by the paraffin legs of dye B only.

Another possibility of arranging dyes A and B is obtained by first proceeding as in Fig. 4b, step 1, getting a plate covered by dye A (Fig. 4c, step 1). We may then cover the water surface with a monolayer of dye B and take out the plate which then will be covered by a monolayer of dye B, the chromophores of dyes A and B now being in direct contact (Fig. 4c, step 2 and 3). In this manner as many monolayers as we like of a great number of different compounds may be laid upon each other in the ways considered.

However, according to the present view taken from our knowledge of fatty acid monolayers, it appears that the picture discussed above is very unrealistic. From the work of Langmuir[4] (who had concluded that fatty acid salt monolayers with carboxyl groups at the surface between monolayers and air will be rearranged in a way that the paraffin ends turn to the surface) one might expect a rearrangement in the case of Fig. 4a and b. For instance in the case of Fig. 4b there will be a rearrangement to the case of Fig. 4c. From the work of Sobotka[3] it might appear that the molecules will be mixed by diffusion processes. Thus the properties of the systems should be the same in all three cases shown in Fig. 4.

The main concern of this paper is to demonstrate that the view given in Fig. 4 is a realistic one; the properties of such systems are drastically and predictably dependent on how the monolayers have been assembled.

B. Proof of Predicted Order in the Arrangement of the Molecules in Systems of Monolayers

(*a*) ENERGY TRANSFER FROM SENSITIZER DYE MOLECULE S TO ACCEPTOR A AS A MEASURE OF THE DISTANCE OF THE CHROMOPHORIC PARTS OF S AND A

(1) *Fluorescence Quenching of S and Sensitized Fluorescence of A*

For demonstrating the view given above, we must have methods to control whether or not the chromophores of the molecules A and B are at the distance assumed in each case, and thus we will be looking for properties depending strongly on the distance of chromophores A and B. Such a property is the fluorescence quenching by the transfer of excitation energy from sensitizer molecule S to acceptor molecule A: S may be absorbing in the ultraviolet and fluorescing in the blue, and A may be absorbing in the blue and fluorescing in the yellow (Fig. 5), and we shall irradiate the system with ultraviolet light. In the case of a sufficiently large distance of S and A the blue fluorescence of S appears, since A does not absorb the light, and in the case of a sufficiently small distance the excitation energy of S is transferred to A and we will find the yellow fluorescence of A.[5] We have made the three arrangements of Fig. 4a to c using the blue fluorescent dye I as the sensitizer and the yellow fluorescent dye II as the acceptor. In the case of Fig. 4a, where the chromophores of the sensitizer and the acceptor are in a distance *d* of about 60 Å the system is expected to show predominantly the blue fluorescence of S, and in the case of Fig. 4b where *d* is about 30 Å a moderate energy transfer should occur and a green fluorescence resulting from the blue fluorescence of S and the yellow fluorescence of A is expected, and in the case of Fig. 4c a complete energy transfer from S to A and thus the yellow fluorescence of A is expected.

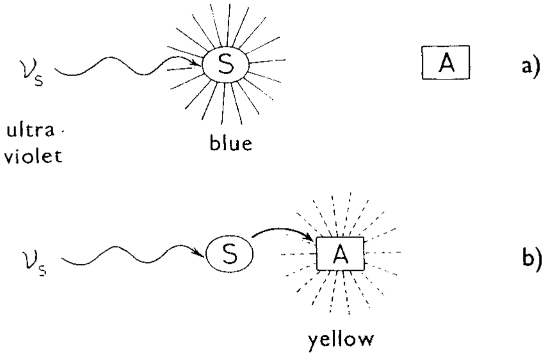


Figure 5. Dye molecules S and A. S absorbs ultraviolet light of frequency ν_S and emits a blue fluorescence. A absorbs blue light and emits a yellow fluorescence. Molecules S and A are assumed to be irradiated simultaneously with light of frequency ν_S. If S and A are not in too close proximity, only the blue fluorescence of S is seen (a). If S and A are brought into close proximity (b) energy transfer from S to A occurs and the yellow fluorescence of A is seen. Sensitizer S and acceptor A form a molecular function unit: The system of cooperating dye molecules S and A has a property not present in either of its substituents (i.e. to show yellow fluorescence when illuminated with ultraviolet light).

Figure 6 (p. 215) shows a colour photograph of the three plates when irradiated with ultraviolet light, and the corresponding fluorescence spectra. The expected behaviour is found in all three cases. Diffusion, holes and rearrangement of the molecules would lead to a levelling out effect.

Such an arrangement of a sensitizer molecule S and an acceptor molecule A as well as a similar arrangement obtained before[6, 7, 8] in a less controlled manner, is an extremely simple case of an organizate: Similar to a pair of scissors this unit of S and A being in proximity to each other has entirely new properties not found in either of its substituents depending on the way the molecules are assembled; this unit is a simple molecular function unit.

A distance of, say, 60 Å between sensitizer and acceptor may be kept in many different ways, as demonstrated in Fig. 7, using the legs of the dyes and cadmium arachidate as distance keeper, and, as expected, in all cases the same fluorescence colour is found.† When using a fatty acid monolayer of increasing length of paraffin chain as a distance keeper a distinct change of fluorescence in the expected direction is observed, that is an increased fluorescence of the sensitizer and a decreased fluorescence of the acceptor.

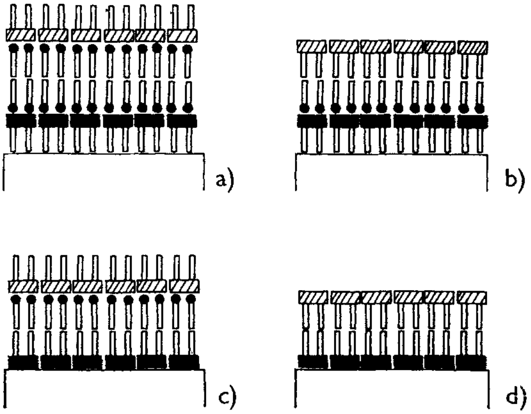


Figure 7. Cross-cut through different arrangements to keep a distance of 60 Å between the layers of the chromophores of dyes S and A. Symbols according to Figs. 2 and 4. Schematic representation. Actually we have used mixed dye and fatty acid salt monolayers instead of dye layers.

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† By measuring the intensity of the fluorescence of S we may distinguish even between some of these cases. In the case of Figs. 7b and c (distance between the planes of the chromophores of S and A, $d = 54$ Å) this intensity is measurably stronger than in the case of Fig. 7d ($d = 51$ Å), and measurably weaker than in the case of Fig. 7a ($d = 57$ Å).

Instead of a dye, an evaporated film of a metal or a semiconductor may be used as an acceptor. On a glass plate covered by a very thin gold film of a transmittance of, say, 95%, we put two, four and six monolayers of Cadmium arachidate on a section to the left, in the middle and to the right, and then we covered the plate by a monolayer of dye I (Fig. 8). On irradiation with ultraviolet light we found a strong, moderate and weak quenching of the fluorescence of S in the section where the distance of S and gold is 2, 4 and 6 times 27 Å respectively.

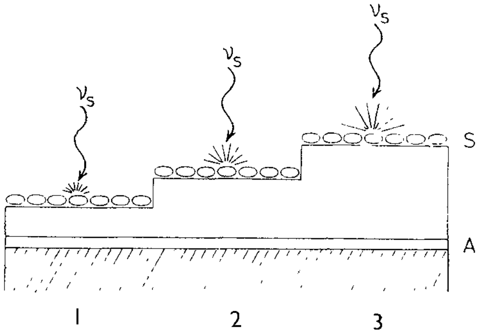

Figure 8. Cross-cut through a glass slide with an evaporated gold film covered by arachidate monolayers and a monolayer of sensitizer dye S (dye I and cadmium arachidate in molar ratio 1:10). The arachidate monolayers keep the plane of the chromophores of S in a distance of 54 Å + 27 Å (section 1), 108 Å + 27 Å (section 2) and 162 Å + 27 Å (section 3) from the gold film. In section 1 a strong energy transfer from dye S to gold occurs and the fluorescence of S is strongly quenched. In section 2 this energy transfer and thus the quenching of fluorescence of S is moderate, in section 3 weak.

For a quantitative examination plates are used covered by layers of S and A; one half of the plate is used as a standard and the layers are kept at a great distance by arachidate layers; in the other half they are kept at the distance d considered. The fluorescence is excited by a narrow beam moving from left to right. The signal of a multiplier measuring the fluorescence is recorded. An example is given in Fig. 10 showing the fluorescence to be reasonably homogeneous over the plate. The ratio J_d/J_∞ of the fluorescence intensities for the distance d considered (J_d) and for a relatively large distance (J_∞) is thus obtained. The results are shown in Figs. 11a and 12a for the systems dye I/dye III and dye I/gold (extinction 0.027). Figures 11b and 12b give the measured value of

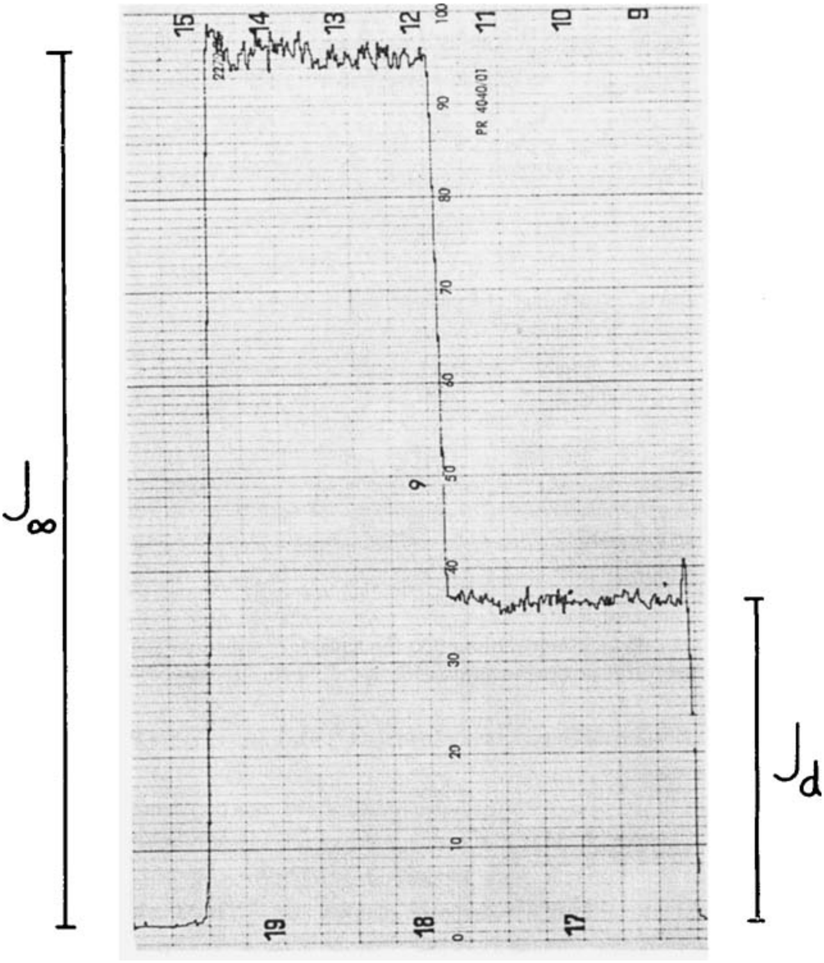

Figure 10. Fluorescence intensity of a glass slide covered by monolayers of sensitizer S and acceptor A in a distance d considered (J_d, right half of the slide) and in a large distance (J_∞, left half of the slide). A narrow beam of exciting light is moving from left to right. Record of signal of multiplier measuring fluorescence.

d_0 (that is the distance of layers S and A for which J_d/J_∞ equals $\frac{1}{2}$) as a function of the extinction E_{AS} of the acceptor layer. d_0 is clearly increased by increasing the molar ratio of the acceptor dye

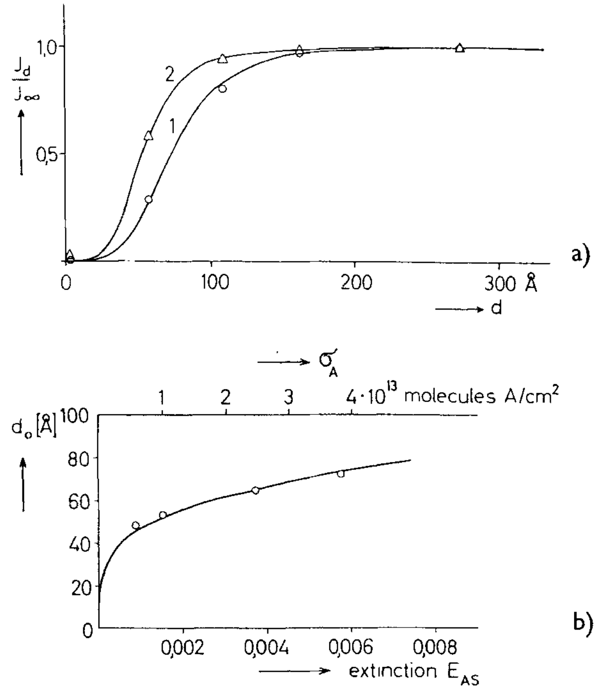

Figure 11. System of monolayer of S (dye I and cadmium arachidate in molar ratio $r_S = \frac{1}{20}$) and monolayer of A (dye III and cadmium arachidate in molar ratio r_A) in distance d. (a) J_d/J_∞ (relative fluorescence intensity of S) against d. Curve 1 (circles), $r_A = \frac{1}{10}$; curve 2 (triangles), $r_A = \frac{1}{50}$. (b) d_0 (value of d corresponding to $J_d/J_\infty = \frac{1}{2}$) against σ_A (scale above) or E_{AS} (extinction of monolayer of A; scale below). The curves follow Eqs. (1) (2).

in the mixed dye and arachidate monolayer (Fig. 11b), or the thickness of the gold layer (Fig. 12b).

We may compare this result with theory and begin with a very simple theoretical picture. Let us consider the sensitizer molecule as an oscillating dipole of the frequency of the maximum of the fluorescence band, corresponding to a wavelength λ_S^* in the medium surrounding the dipole. Now let us put an absorber n the proximity field of the radiating dipole. The alternating field of the dipole acts in each volume element of the absorber. The energy dissipation in the absorber and thus the ratio J_d/J_∞ may be calculated. In the case of an absorbing layer of a thickness small compared to the distance of the dipole from the layer the result

$$\frac{J_d}{J_\infty} = \left[1+\left(\frac{d_0}{d}\right)^4\right]^{-1} \tag{1}$$

is obtained where

$$d_0 = \alpha\lambda_S q_S^{1/4} E_{AS}^{1/4} \tag{2}$$

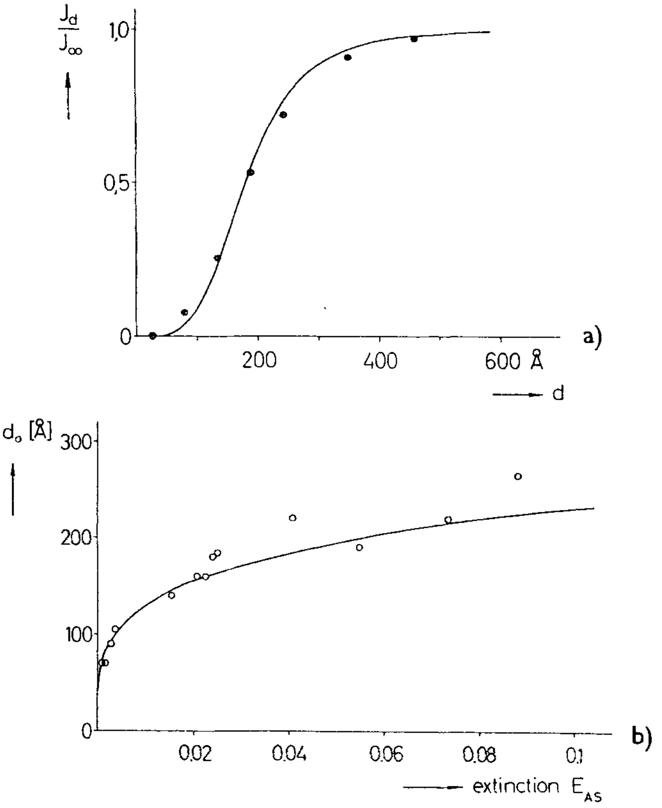

Figure 12. System of monolayer of S (dye I and cadmium arachidate in molar ratio r_S) and evaporated gold film (extinction E_{AS} at 430 nm) in distance d. (a) J_d/J_∞ against d for $r_S = \frac{1}{1000}$ and $E_{AS} = 0.024$ (an extinction $E_{AS} = 0.024$ corresponds to a thickness $\Delta = 10$ Å of the gold film). (b) d_0 against E_{AS} for $r_S = \frac{1}{10}$. The curves follow Eqs. (1) (2).

q_S is the quantum yield of the fluorescence of S, A being absent, and E_{AS} is the extinction of layer A at wavelength λ_S^*; α is a numerical factor; $\alpha = 0.12$ in the case of S and A being polarized in the lamellar plane, and $\alpha = 0.14$ in the case of S being polarized in the lamellar plane and A being unpolarized.

The current theory of energy transfer by Förster[5] (radiationless resonance energy transfer, very weak coupling case) gives an equation which agrees with Eqs. (1) and (2) in the case of a narrow fluorescence band. The theories of Perrin[9] and Förster[5] and the more recent theories[10] of long range energy transfer are based on the idea of resonance between S and A. According to the above treatment it is possible to approach the long range energy transfer also in a simple classical way which does not depend on resonance of S and A. The absorber may be considered for instance as a classical metal consisting of free electrons restricted by frictional forces, i.e., by a system that has no resonance frequency.

In the more general case not limited to a narrow fluorescence band, according to Förster, E_{AS} must be exchanged for

$$\int_0^\infty f_S(\nu)\, E_A(\nu) \left(\frac{\nu_S}{\nu}\right)^4 d\nu$$

where ν_S is the frequency of the maximum of the fluorescence band of S and f_S is the distribution function of the quantum spectrum of the fluorescence of S normalized according to $\int_0^\infty f_S\, d\nu = 1$. $E_A(\nu)$ is the extinction of A at frequency ν. However, by introducing this refinement the value calculated for d_0 is influenced by only a few per cent in all practical cases.

The curves in Figs. 11 and 12 are obtained from (1) and (2) assuming a quantum yield $q_S = 0.3$ and 1 respectively. A good agreement of theory and experiment is thus found, again pointing to the correctness of the basic assumption of a rigid structure of these layers.†

† This good agreement might be partially fortuitous, since the assumptions $q_S = 0.3$ and 1 respectively might not be justified. However, since $d_0 \sim q_S^{1/4}$, the result is not very dependent upon the value of q_S.

Equation (1) is valid only in the case of d being large compared to the average distance of two nearest neighbour acceptor molecules, a_A. In the case of a_A being large compared to d, the probability of an energy transfer from S to A is indepedent on d. Even in the case $d = 0$ no energy transfer occurs as long as $a_A \gg r_0$, where r_0 is the distance of a molecule of S and a molecule of A characterized by a 50% probability of the energy transfer from S to A. In the case $a_A/3 = r_0$ and $d = 0$ the energy transfer should occur with about a 50% probability, i.e. $J_0/J_\infty \simeq \frac{1}{2}$ for $a_A/3 = r_0$. $a_A/3$ is a good approximation for the average distance of an S molecule and its nearest neighbour A molecule in the case $d = 0$. The length a_A depends on σ_A, the number of molecules A per unit area $[(a_A/2)^2 \pi\sigma_A \simeq 1]$, and $r_0 = 50$ Å in the example of dyes I and III considered here.‡ Thus a value of $J_0/J_\infty \simeq \frac{1}{2}$ is expected for

$$\sigma_A = \frac{1}{(3r_0/2)^2\pi} = \frac{1}{\pi(75 \times 10^{-8}\ \text{cm})^2} = 6 \times 10^{11}\ \text{cm}^{-2}.$$

It is actually found in the case of $\sigma_A = 5 \times 10^{11}$ cm^{-2} that J_d/J_∞ by decreasing d decreases much less than according to (1) and by going to $d = 0$ the value $J_0/J_\infty = 0.55$ is obtained.

It is useful to consider additional methods to prove the absence of the disturbing effects considered in the beginning which might result in each sensitizer molecule seeing the layer of the acceptor somewhat differently. A method to show that all sensitizer molecules are the same distance from the layer of the acceptor is obtained by measuring the decay function of the fluorescence.

(2) *Decay Time of Fluorescence of S*

By decreasing the distance of S and A, the fluorescence intensity of S is decreased, since a larger portion of the excited molecules is deactivated by the energy transfer process: The life time of the excited molecules is shortened and thus the decay time of the fluorescence is shortened. This may be demonstrated particularly

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‡ In the case where the transition moments of S and A are statistically distributed in the lamellar plane, $r_0^6 = (20/3\pi)d_0^4/\sigma_A$, and according to Fig. 11 $d_0 = 70$ Å for $\sigma_A = 4 \times 10^{13}$ cm^{-2}. Thus we find for monolayers of dyes I and III the value $r_0 = 50$ Å.

easily if S is the europium complex IV since this complex has a decay time of its red fluorescence of about 10^{-3} sec, which is easily measurable.

Such systems are obtained by evaporating a gold film on a glass plate, covering it by a given number of cadmium arachidate monolayers and by a monolayer of europium complex IV. The intensity J of the fluorescence may be measured as a function of the time t after the flash illumination. Figure 13 shows J and log J as a function of t for a distance $d = 185$ Å of the gold film A from the europium complex layer S.

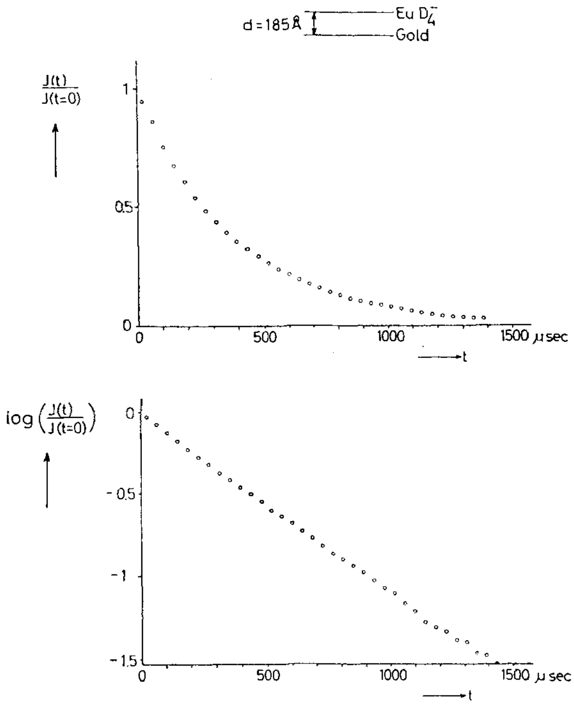


Figure 13. System of monolayer S (Eu-complex IV) and evaporated gold film (thickness $\Delta = 5$ Å) in distance $d = 185$ Å. J (intensity of fluorescence) against t (time after flash illumination).

In the logarithmic plot, the experimental points are seen to be on a straight line. An analogous result is found for all other distances d considered. Thus the decay process is described by an exponential function or by a single decay time: To each molecule of the sensitizer S we must attribute the same decay time and thus each S molecule sees the acceptor layer in the same way. Any of the monolayer defects considered before would result in a curve with positive curvature in the logarithmic plot of Fig. 13. From the slope of the straight line in Fig. 13 the decay time τ_d may be obtained for

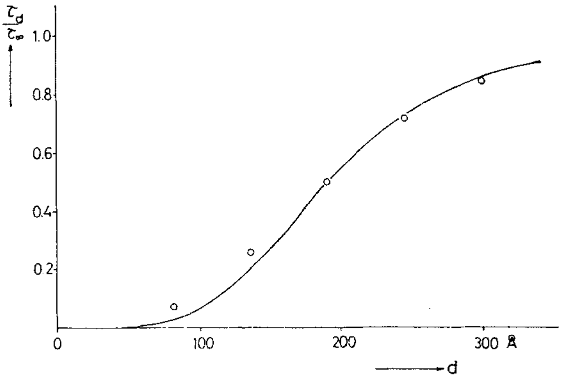


Figure 14. Decay time shortening of S by A. System of monolayer S (Eu-complex IV) and evaporated gold film (thickness $\Delta = 5$ Å) in distance d. τ_d/τ_∞ (τ_d = decay time, τ_∞ = decay time for $d = \infty$) against d. Experimental points and theoretical curve.

the distance between sensitizer and acceptor layer, d, considered. In Fig. 14 the ratio τ_d/τ_∞ is plotted against d, where τ_∞ is the value of τ_d for large distances d (points). Theoretically, $\tau_d/\tau_\infty = J_d/J_\infty$ and J_d/J_∞ is given by (1) and (2). Assuming again $q_S = 1$ the value $d_0 = 186$ Å and the curve in Fig. 14 is obtained. A good agreement between theory and experiment is thus observed.

(b) INTERFERENCE EXPERIMENTS FOR DETERMINING THE POSITION OF A DYE MOLECULE IN THE LAYER SYSTEM AND FOR MEASURING THE THICKNESS OF A MONOLAYER DIELECTRIC

When light falls on a mirror we obtain standing light waves by the interference of the direct and reflected beam, and when a

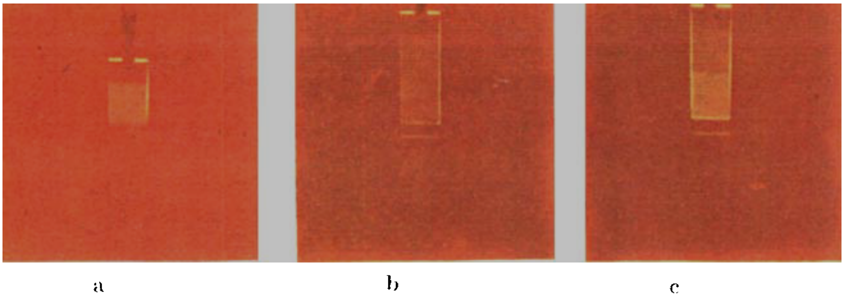


Figure 3. Preparation of built up multilayers of dyes on glass slide. The red fluorescence of the monolayers of IV in the ultraviolet light is seen in Figs. 3a to c for three succeeding steps of the preparation.

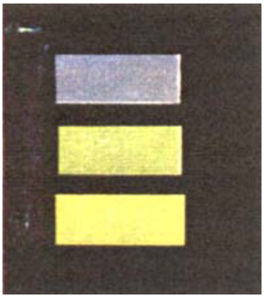


Figure 6

Figure 6. Glass slide covered with a monolayer of sensitizer dye S (dye I and cadmium arachidate in molar ratio 1:10) and a monolayer of acceptor dye A (dye II and cadmium arachidate in molar ratio 1:10). The layers of Fig. 6a, b, c are obtained according to Fig. 4a, b, c, respectively. Color photograph of fluorescence observed in the ultraviolet lamp. The ultraviolet light is absorbed by S. (a) Layers of chromophores of S and A in a distance of 60 Å. Blue fluorescence of S. (b) Layers of chromophores of S and A in a distance of 30 Å. Blue fluorescence of S and yellow fluorescence of A (=green fluorescence). Moderate transfer of excitation energy from S to A. (c) Layers of chromophores of S and A in direct contact. Yellow fluorescence of A. Complete transfer of excitation energy from S to A.

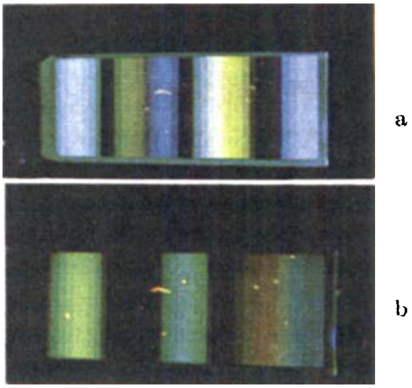


Figure 17. Color photograph of the arrangement indicated in Fig. 16. (a) $\lambda_e = 366$ nm; (b) $\lambda_e = 435$ nm. The fluorescence of the dye is absent at the positions where the dye is in a node.

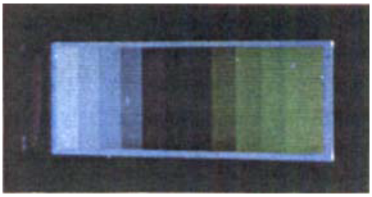


Figure 18. Color photograph of arrangement according to Fig. 16, with a step interval of two monolayers of cadmium arachidate and steps in the proximity of the first node in front of the mirror. The step at the node appears black. A clear fluorescence is seen already at the nearest neighbour steps.

fluorescent dye is brought to an antinode it will absorb and thus emit fluorescent light; when it is brought to a node, it will not absorb and thus not be fluorescent (Fig. 15). Such experiments have been made by Nernst and Drude,[11] and they can now be carried out very easily and with greatly improved resolution by using monolayers. On a glass plate covered by an evaporated silver mirror a stair-like succession of cadmium arachidate layers is constructed according to Fig. 16, each step consisting of four monolayers and covered by a mixed monolayer of dyes I and III.

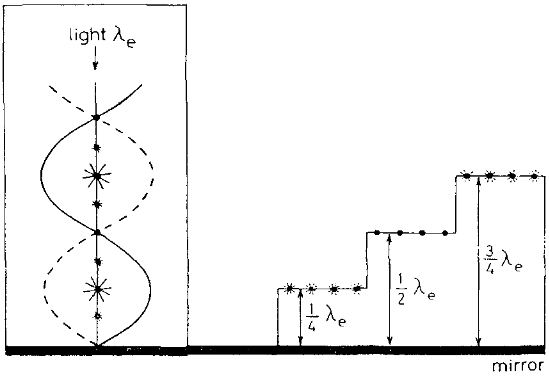


Figure 15. In front of a mirror irradiated with light, standing light waves are formed which are able to excite fluorescence of dye molecules situated at the antinodes, while fluorescence can not be excited when the molecules are at the nodes.

In a beam of light of wavelength $\lambda_e = 366$ nm falling perpendicular to the mirror the dye on the three stair steps indicated in Fig. 16a is expected to be almost at a node. These stair steps should appear almost black and this is actually the case (Fig. 17a, p. 216). If λ_e is equal to 435 nm, the two stair steps indicated in Fig. 16b should appear black and this is found to be the case (Fig. 17b, p. 216). In a similar arrangement, where, however, each step corresponds to only two cadmium arachidate layers, one step appears completely dark, while the neighbouring steps show a measurable intensity of the fluorescence (Fig. 18, p. 216). This pattern would be much less pronounced if appreciable irregularities in the geometry of the layers or diffusion of the dye through the layers were present.

We find from Figs. 17 and 18 that the fluorescence colour is not by any means uniform over the plate and that the fluorescence intensity is not equally large in each antinode. Both effects are caused by an interference phenomenon of the fluorescence light (wide angle interference of a substance placed at a small distance in front of a mirror studied by Selenyi and Kossel[12]). By considering carefully this phenomenon the colour and intensity distribution thus obtained may be explained. This may be seen in the case of Fig. 17a for the stairs where the incident light (wavelength λ_e) has its first and second antinode in front of the mirror (first intensity

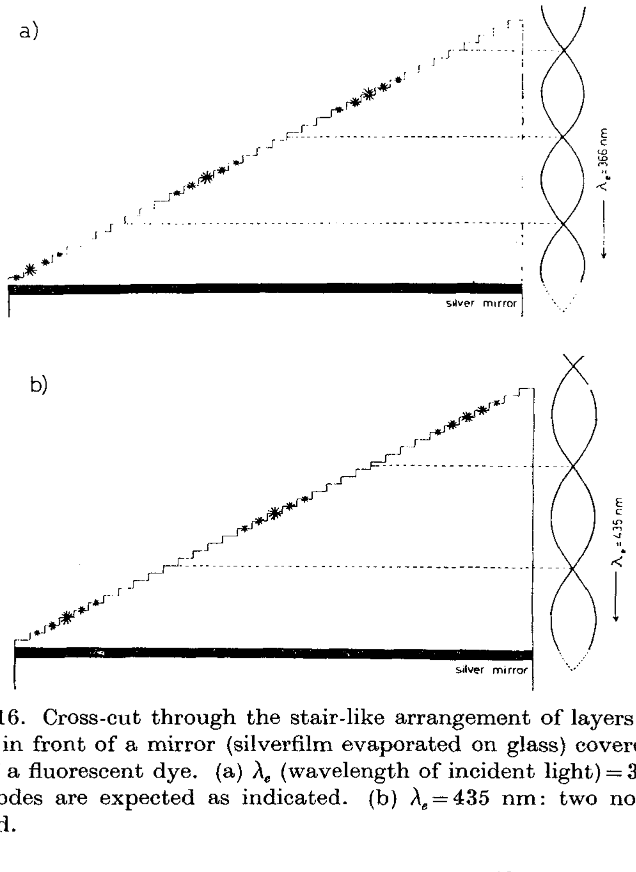


Figure 16. Cross-cut through the stair-like arrangement of layers of arachidate in front of a mirror (silverfilm evaporated on glass) covered by a layer of a fluorescent dye. (a) λ_e (wavelength of incident light) = 366 nm: three nodes are expected as indicated. (b) $\lambda_e = 435$ nm: two nodes are expected.

maximum to the left of Fig. 17a, and second maximum). The direct and reflected fluorescence light (wavelength $\lambda_f \simeq \frac{3}{2}\lambda_e$) interferes in both cases (Fig. 19) and an amplification is obtained in the first case and an attenuation in the second case (the intensity in the first maximum to the left of Fig. 17a is much higher than in the second maximum).

The phase relation of the direct and reflected beam and thus the resulting intensity of the fluorescence depends on the direction of observation. A monolayer of europium complex IV (which has the advantage of having a very narrow fluorescent band) is kept at a distance *d* in front of a gold mirror by cadmium arachidate monolayers. The sample is placed in a cylindrical cuvette and is immersed in a solution of the same refractive index as cadmium arachidate (Fig. 20). The fluorescence is excited by ultraviolet light and its directional pattern is measured by turning a multiplier as shown in Fig. 20. Figure 21 gives for several values of *d* the

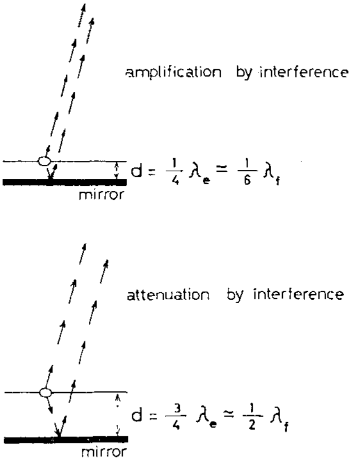


Figure 19. The fluorescent light emitted by a dye in front of a mirror may travel to the point of observation via the direct path or via the indirect path containing a reflection from the mirror surface. The beams interfere and an amplification or attenuation is obtained depending on the distance *d* of dye and mirror and on the angle of observation.

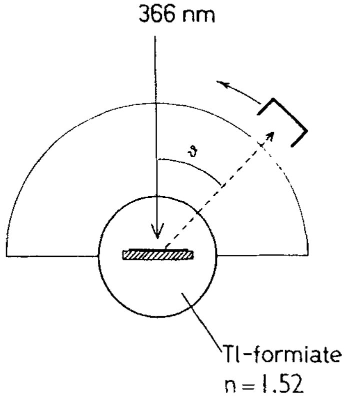


Figure 20. Arrangement for measuring the directional pattern of the fluorescence of a dye monolayer in front of a mirror.

intensity of the fluorescent light as a function of the angle ϑ between the direction perpendicular to the lamellar plane and the direction of observation. The intensity of the component with electric vector oscillating perpendicular to the plane of angle ϑ and in this plane

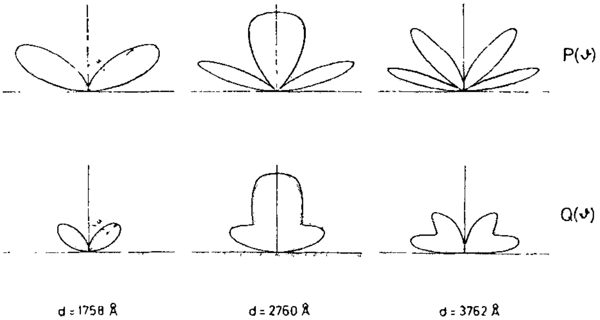
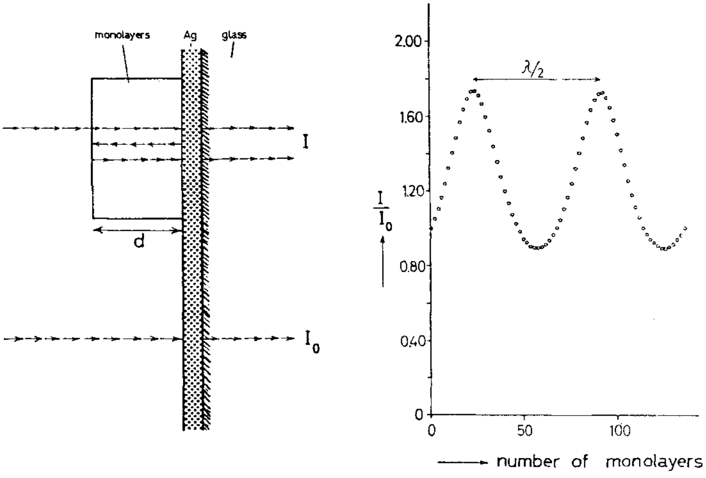


Figure 21. Directional pattern of fluorescence of Eu-complex IV ($\lambda_f = 612$ nm) in front of a silver mirror for $d = 1758$ Å; $d = 2760$ Å; $d = 3762$ Å. Full line, experimental; dotted line, theoretical. Component with electric vector of light oscillating perpendicular (above) and parallel (below) to the plane of angle ϑ. This pattern is analogous to that of a dipole radio antenna at a certain elevation above the conducting ground surface. Diffusion of the dye molecules or irregularities in the layer system would distort these interference effects.

is given above and below respectively (full line). Excellent agreement with the theoretical expectation (dotted line) is obtained.

These experiments represent good evidence for the electric dipole nature of the radiation emitted by europium, since in each case different directional patterns are to be expected for electric quadrupole or magnetic dipole radiation. The directional distribution of the fluorescence light depends on the distance *d* in a very sensitive manner and thus the experimental verification of an expected pattern is a good test to prove the absence of an effect that changes this distance.



a) b)

Figure 22. Transmittance of a thin silver film covered by a cadmium arachidate multilayer of thickness *d*. Wavelength 546.1 nm. I/I_0 against $d.I$ is strongly dependent on *d* and the arrangement is a sensitive method for measuring *d*.

The experiments considered above do not rule out the possibility that a thin impurity layer of constant thickness may be present and thus enhance the distance between sensitizer and acceptor.

We found the interference experiment pictured in Fig. 22a very valuable for controlling the absence of an impurity layer and of irregularities in the arachidate layer. A thin silver film (transmittance 0.24 in the case of Fig. 22) is covered by an arachidate multilayer of thickness *d*. The direct and reflected light interferes and the intensity of the outcoming beam depends in a sensitive way upon the thickness *d* of the arachidate layer. This is shown in Fig. 22b, where the measured intensity is plotted against *d* for light of wavelength 546.1 nm. For $d = 54$ Å and $d = 108$ Å respectively the intensity ratio $J(108\ \text{Å})/J(54\ \text{Å})$ is found to be 1.0515 ± 0.0002. This exemplifies the great sensitivity of this test.

(c) THICKNESS OF MONOLAYER DIELECTRIC FROM MEASUREMENT OF CAPACITANCE

Another way to control the absence of an impurity layer and of irregularities in the fatty acid salt layer is obtained by measuring the capacitance of the capacitors obtained by covering an evaporated Al-film with fatty acid salt monolayers and by again depositing an Al-film on top of these layers. The capacitance of such condensers may easily be measured, and it is amazing that this is the case even for a single monolayer sandwiched between the metal films. The capacitance C should be given by the equation

$$\frac{1}{C} = \frac{4\pi d}{DF} = \frac{4\pi}{DF}.n\delta \qquad (3)$$

where F is the area, D the dielectric constant, d the thickness of the dielectric, δ the thickness of a monolayer and n the number of monolayers. In Fig. 23 $1/C$ (for capacitors with $F = 2\ \text{cm}^2$) is plotted against the number of monolayers of cadmium stearate (C_{18}) and cadmium arachidate (C_{20}). According to (3) $1/C$ is proportional to d and thus it should increase linearly with increasing number of monolayers, n, and for a given number of monolayers it should increase linearly with increasing length of fatty acid chain, δ. Figure 23 shows that this is the case. By introducing the value $D = 2.40$ (square of the value of the refractive index of barium stearate[13]) in (3) the straight lines in Fig. 23 are obtained. In both cases (C_{18} and C_{20}) the experimental points are almost on the corresponding line. A layer of a dielectric impurity would increase d and thus $1/C$.

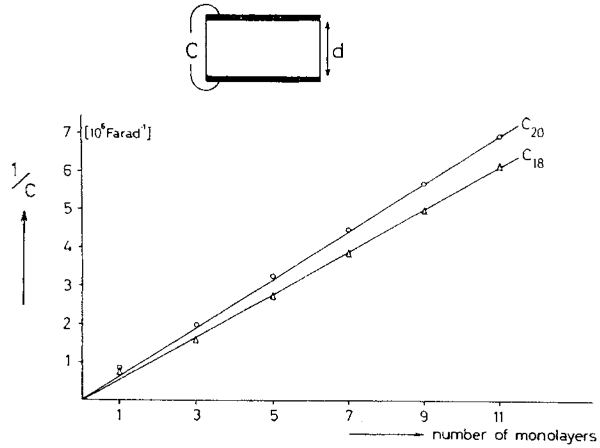


Figure 23. Cross-cut through a capacitor formed by two evaporated metal films separated by n layers of cadmium stearate (C_{18}) or cadmium arachidate (C_{20}). The inverse of the experimental capacity C is plotted against n (triangles and circles). The straight lines result from the theoretical equation

$$\frac{1}{C} = \frac{4\pi d}{DF} = \frac{4\pi}{DF} n\delta$$

($D = 2.40$ dielectric constant, $F = 2\ \mathrm{cm}^2$ area of the metal electrodes, δ thickness of a monolayer of cadmium stearate ($\delta = 24.6$ Å) or arachidate ($\delta = 26.6$ Å)).

(d) SPECTROSCOPIC CONTROL OF THE CONDITIONS OF THE DYE MOLECULES IN THE MONOLAYERS

After having controlled the technique used to obtain simple organizates we may want to have more information on the state of the dye molecules in the monolayer.

Valuable information is obtained from the spectra of the monolayer in the visible. The spectrum of the extinction E of a mixed monolayer of a dye such as I or II and cadmium arachidate is

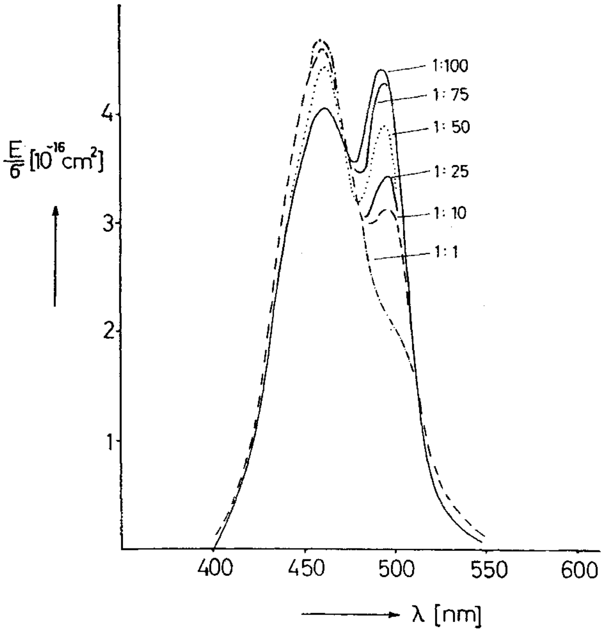


Figure 24. Mixed monolayer of dye II and cadmium arachidate on glass substrate. E/σ (E = extinction, σ number of dye molecules per cm^2) against λ (wavelength) for r (molar ratio of dye and arachidate) = 1; $\frac{1}{10}$; $\frac{1}{25}$; $\frac{1}{50}$, $\frac{1}{75}$; $\frac{1}{100}$.

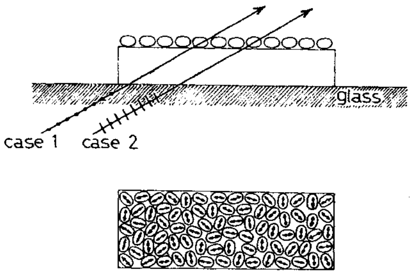


Figure 25. Upper part: cross-cut through a monolayer of dye molecules which is traversed at an oblique angle by a beam of polarized light. When the electric vector oscillates parallel to the plane of the monolayer (case 1) the beam is found to be attenuated more strongly than when it oscillates in the incident plane (case 2). Lower part: Orientation of the dye molecules I, II, III in the monolayer as inferred from the above type of experiment. The molecules lie flat on the surface of the substrate with random orientation of their long axis.

dependent on the mixing ratio and thus on the number σ of dye molecules per cm^2. In Fig 24 E/σ is plotted against wave length λ for the molar ratio of dye and arachidate of 1:1; 1:10; 1:25; 1:50; 1:75; 1:100. The curves have an isosbestic point showing that aggregates of a certain degree of association n must be present

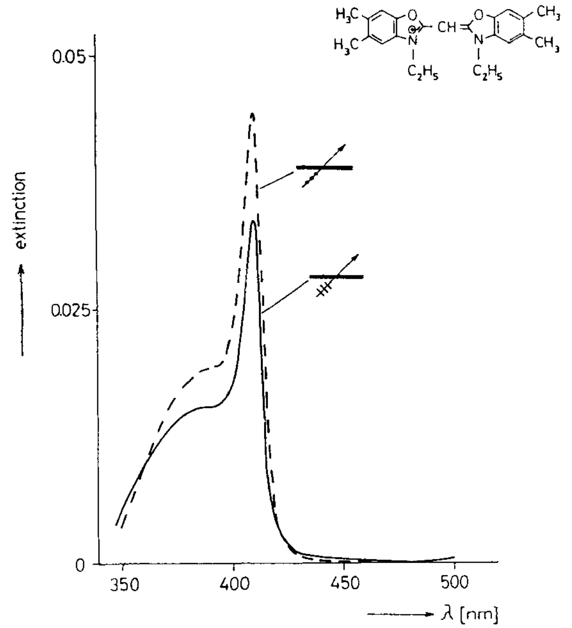


Figure 26. Absorption spectrum of monolayer of N,N'-diethyl-5,6,5′,6′-tetramethyloxacyaninetosylate for case 1 and case 2 of Fig. 25. Narrow and high band assigned to dye polymers with head to tail association of monomers.

besides monomers. By plotting $\log(E-E_n)$ against $\log(E_1-E)$ for the maximum at longer waves (E_1 and E_n being the extinction of pure monomers and pure associates) a straight line of slope 1/2 is obtained, and thus $n=2$. It may be concluded that monomers and dimers are in a (frozen) equilibrium in the monolayer. This example shows that the usual methods of solution spectroscopy may be extended to the study of monolayers.

In the arrangements of Fig. 25 the orientation of the molecules in the monolayer can be investigated. It is found with dye I, II or III that the absorption in the main band is stronger in case 1 than in case 2 (Fig. 25) and it can be concluded that the transition moment must be in the plane of the layers as indicated in Fig. 25. On the other hand it is known that the main absorption band is parallel to the long axes of the molecules and we can justify that these long axes must be parallel to the surface of the layer.

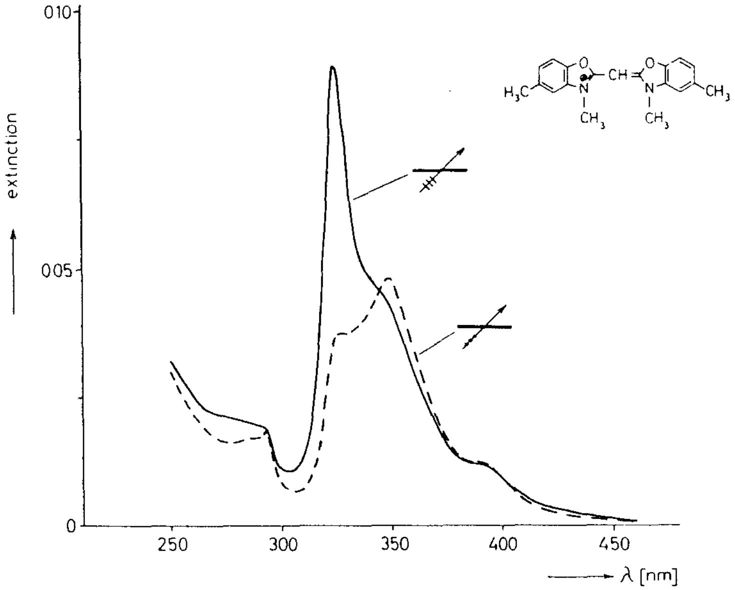


Figure 27. Absorption spectrum of monolayer of *N*,*N*′,5,5′-tetramethyloxacyaninetosylate for case 1 and case 2 of Fig. 25. Narrow and high band assigned to dye polymers with head to head association of monomers.

In some of the dyes with paraffin substituents and in many other dyes the appearance of a high and narrow peak on the long wavelength side of the main band of the dimer has been observed. This corresponds to the band that Scheibe and Jelley[14] found in solution spectra and that were attributed to dye polymers with head to tail association of the monomers.[15]

From the polarization of the polymer band (see for example Fig. 26) it may be concluded that the transition moment of this band (and thus the long axis of the polymer) is roughly parallel to the lamellar plane.

In the case of Fig. 27 a sharp band on the short wavelength side of the dimer band is observed. It is not seen in the case 1 of Fig. 25 and appears strongly in case 2; the transition moment is thus perpendicular to the lamellar plane. Such a band is expected for a dye polymer with head to head association of the monomers[15] and should be polarized perpendicular to the long axis of the polymer in the direction of the transition moments of the main band of the monomer subunit. Thus it may be presumed that the long axis of the polymer is in the lamellar plane, and that the long axis of the monomer subunits is perpendicular to this plane. Similar but less narrow bands have been observed in solution of other dyes[16]. The dye polymer considered here might exist only under the stabilizing influence of the surface.

C. Assembling Composite Energy Transfer Arrangemens

The technique now being controlled by these different methods we may try to build up somewhat more complicated organizates by assembling composite energy transfer arrangements. Let us look at a system of sensitizer S and acceptor A and add another acceptor A′ (Fig. 28). A′ may steal the excitation energy from S (case 1) or from A (case 2). Case 1 (A and A′ competing) is given when the absorption band of A′ overlaps with the fluorescence band of S, case 2 (A′ parasite of A) when A is fluorescent and when the absorption band of A′ overlaps with the fluorescence band of A. When A is removed, the fluorescence of A′ in case 1 is enhanced because a nasty competitor is absent, and it is quenched in case 2 because the host is absent.

Case 1 is exemplified by S = dye I, A = gold and A′ = dye II. A plate according to Fig. 29 is made and a color photograph is taken with illumination from an ultraviolet lamp: In section 1 the blue fluorescence of S appears. This fluorescence is partly quenched in section 2 (energy transfer S→A); it is almost

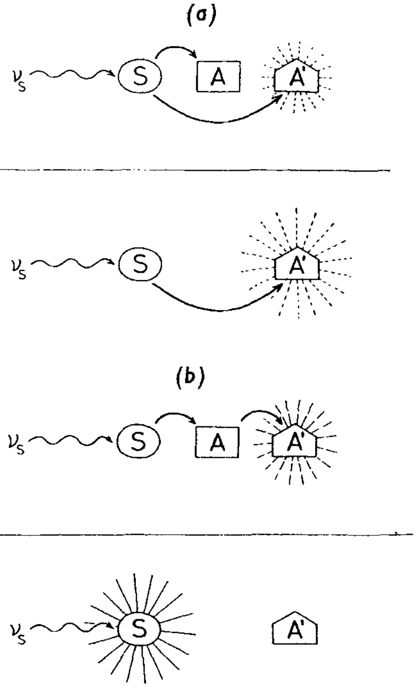


Figure 28. Sensitizer S, acceptors A and A′. (a) A and A′ competitors. Fluorescence of A′ enhanced by removing A. (b) A′ parasite of A, Fluorescence of A′ quenched by removing A.

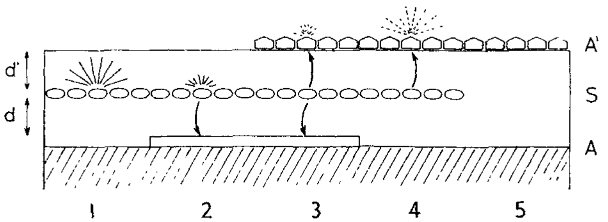


Figure 29. Cross-cut through arrangement to demonstrate competition of A and A′. S = dye I, A = gold, A′ = dye II. Section 1: fluorescence of S; section 2: fluorescence of S partially quenched by energy transfer S→A; section 3: weak fluorescence of A′ resulting from energy transfer S→A′ competing with transfer S→A; section 4: strong fluorescence of A′ obtained by energy transfer S→A′; section 5: no fluorescence since sensitizer S is absent.

quenched in section 3 where a weak yellow fluorescence of A′ appears (energy transfer S→A and S→A′); the fluorescence of A′ is much stronger in section 4 where quencher A is missing; section 5 appears black because A′ does not absorb the incident light and thus is not fluorescent. The intensity $J_{d,d'}$ of the fluorescence of S in systems of S, A and A′, relative to the intensity J_{∞} in a system of S without acceptor, is given in Table 1 for different values of distance d between the monolayers S and A, and distance d' between S and A′. These values are compared in Table 1 with the values obtained from the equation

$$\left(\frac{J_{\infty}}{J_{d,d'}}-1\right)=\left(\frac{J_{\infty}}{J_{d}}-1\right)+\left(\frac{J_{\infty}}{J_{d'}}-1\right) \tag{4}$$

where J_d is the fluorescence intensity in a system of monolayers S and A in a distance d, and $J_{d'}$ the corresponding intensity in a system of S and A′ in a distance d'.

TABLE 1

d Å	d' Å	$J_{dd'}/J_{\infty}$ Exp.	$J_{dd'}/J_{\infty}$ Theor.
27	54	0.02	0.02
135	54	0.18	0.21
135	108	0.42	0.43
189	162	0.67	0.70

Case 2 has been exemplified in Ref. 7.

We hope to be able to construct, in this way, much more complicated organizates than the very simple systems considered here, with much more interesting properties determined by the step by step assembling of molecules.

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