

INFORMATION, ELECTRON AND ENERGY TRANSFER IN SURFACE LAYERS

Hans Kuhn

Max-Planck-Institut für biophysikalische Chemie
Karl-Friedrich-Bonhoeffer-Institut, Molekularer Systemaufbau
D 3400 Göttingen-Nikolausberg, Germany

Abstract - The formation of interlayer-dimers of dye molecules and the cleavage between monomolecular layers are studied and considered as the basis of a device for copying information at the molecular level and for separating the copy from the original. Information at the submicron level is copied by contacting a dye monolayer with a template. On illumination the dye is bleached except in the proximity of the template where it is stabilized by energy transfer. Simple models demonstrating signal transduction and transfer based on the planned cooperation of a few molecules are constructed by superimposing appropriate monolayers. Arrangements are obtained that represent systems of correlated switches acting as new entities where entirely independent reactions are coupled at the molecular level.

INTRODUCTION

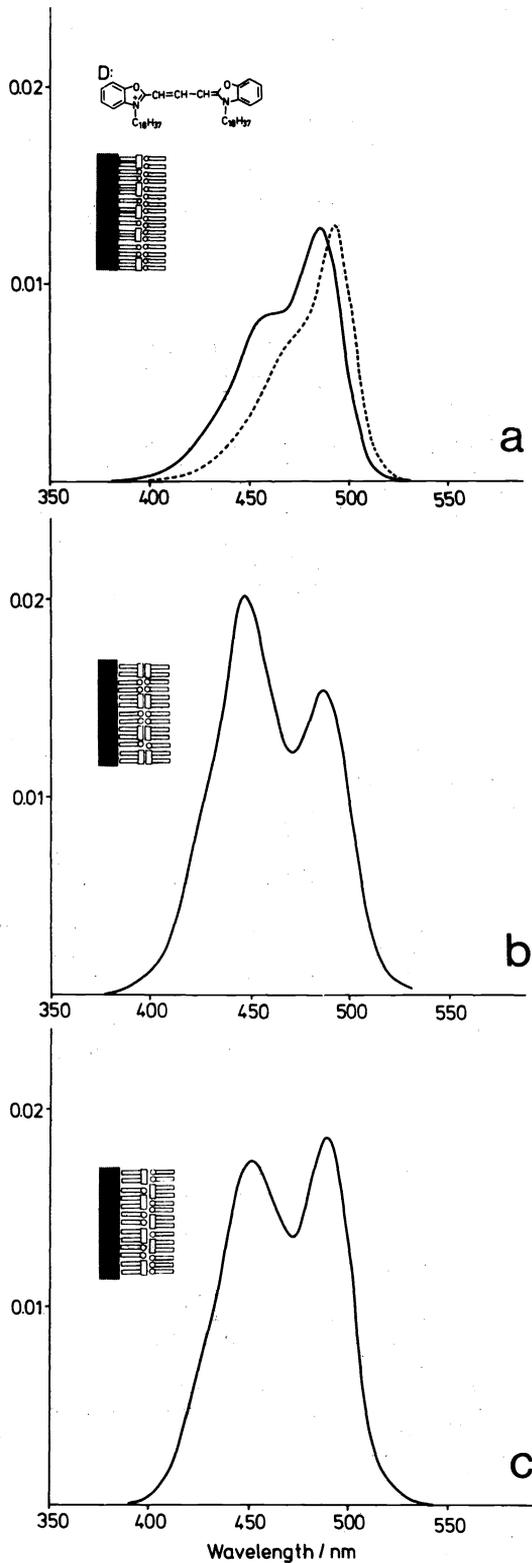
In biological systems signals are transduced and transferred by molecular mechanisms, and information is stored and translated in devices of molecular size. It is of interest to construct artificial systems in which similar processes are taking place and therefore methods are needed to arrange molecules in defined geometry. Such organized arrangements of molecules (organizates) can be obtained by inserting the various functional component molecules in monolayers of appropriate matrix molecules, and by superimposing the monolayers in planned succession on a glass slide (Refs. 1, 2, 3).

It is important for constructing functional devices to use rigid component monolayers that consist of well ordered molecular arrays and to investigate the arrangements in various ways for obtaining information concerning the presence of the intended molecular architecture, normally by measuring the surface pressure area isotherm and using spectroscopic and microscopic techniques for testing the quality of the layers on the water surface and after deposition on the glass slide.

Another possibility to obtain organizates should be to construct functionalized micelles or vesicles (Ref. 4). The difficulty in this case is the permanently changing size and molecular architecture. The lack of information concerning the assembly architecture makes an interpretation of effects on functionalized systems of this type uncertain. Based on a recent micelle model by Fromherz (Ref. 5) many effects observed in functionalized micelles should be reinterpreted. The construction of functionalized micelles and vesicles of well-defined geometry should be a great challenge. It would be necessary for that purpose to use component molecules of different kinds that are tightly interlocking with each other and that are constructed appropriately to form planned intermolecular links for stabilizing the intended arrangements. In the following we restrict ourselves to a discussion of the monolayer assembly techniques. The results obtained by these techniques should be of interest also in investigating future possibilities for constructing functionalized micelles and vesicles of more defined architecture.

STORING AND COPYING INFORMATION AT THE MOLECULAR LEVEL

In biosystems information is stored in a linear array, it is copied by matrix dependent strand synthesis, and original and copy are removed from each other for further information processing. A similar process in a two dimensional array can be imagined. Let us assume that the information is stored on a sur-



face at molecular dimensions, and that an appropriate monolayer is deposited on that surface. The molecules in the monolayer may diffuse in such a way that they form a pattern complementary to the original. The monolayer may then be rigidized by some means and separated from the original. For investigating possibilities to reach that aim it seems advantageous to use dye molecules with the chromophores in the layer plane as carriers of information, and the formation of sandwich dimers of dye molecules as the principle on which a copying procedure can be based. Each bit of information can be represented by the direction of the chromophore axis (Ref. 6). Sandwich dimers can be easily obtained and investigated in monolayer organizations (Refs. 1, 7). A solution of dye D in Fig. 1, methylester of stearic acid (SME) and Behenic acid (C₂₂) (in the molar ratio D:SME:C₂₂ = 1:20:5) in chloroform is spread on a water surface. The solvent evaporates and a monolayer is formed in which the dye molecules are homogeneously distributed and tightly packed in the SME/C₂₂ matrix. This is known from the absorption spectrum which shows the band of the monomer (Fig. 1a), and from the surface pressure area of similar systems (Fig. 2). The area covered by the dye corresponds to the cross

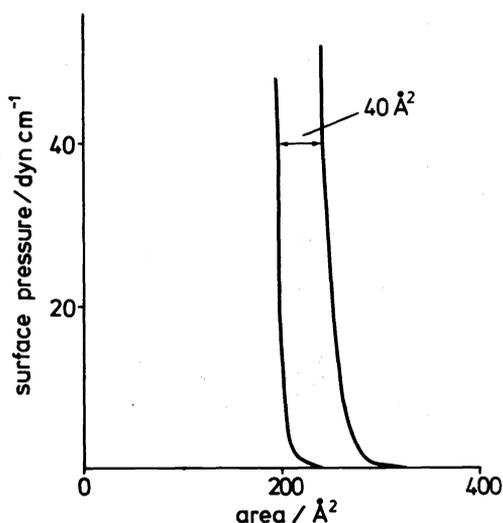


Fig. 2 Surface pressure versus area per 10 matrix molecules. Subphase bidistilled water.
 curve 1: matrix (SME:C₂₂ = 4:1).
 curve 2: matrix + dye (one dye molecule per 10 matrix molecules). The additional area (40 Å²) corresponds to the cross section of the two hydrocarbon substituents of the dye.

section of the hydrocarbon substituents indicating that these substituents are tightly packed in the hydrocarbon matrix and the chromophore has no influence on the area covered by the layer. The monolayer is deposited on a glass slide with hydrophobic surface by dipping in the slide. By taking out the slide a second layer is deposited on top of the first one. The monomer band almost disappears and a band corresponding to interlayer dimers is observed (Fig. 1b). The quantum mechanical calculation (Ref. 7) predicts a shift of -36 nm for a sandwich dimer with parallel axes of the chromophores, in good agreement with the observation (-40 nm). The effect is seen even at high dilution of the dye in the matrix (mixing ratio of dye and matrix molecules 1:1000). This demonstrates that the dye molecules are able to diffuse over distances of the order of 100 Å to find a partner.

If the interlayer dimer formation is used for copying information conditions must be carefully designed in such a way that the molecules in the first layer are in a rigid matrix in order to keep the information, whereas again the molecules in the second layer must be sufficiently mobile to diffuse within the layer and form sandwich pairs with the molecules of the first layer.

For that purpose the matrix of the first layer is made more rigid by introducing Cd^{2+} in the subphase when forming the layer. By the formation of the Cd^{2+} salt of the fatty acid the layer is strongly rigidized. This has almost no influence on the spectra of the arrangements of Figs. 1a and b, showing that the dimers are still formed. However, if the second layer is rigidized, the dimer band is smaller indicating the increasing difficulty in the interlayer dimer formation (Fig. 1c).

A more direct method to check the possibility of the intended information transfer would be to introduce a preferential orientation of the chromophore axes of the dye in the first layer. The chromophore axes of the dye in the second layer should then orient themselves in the same direction when depositing this layer. This effect would indicate the possibility of copying the information represented by the orientation of each molecule in the rigid matrix of the first layer. The orientation of the dye molecules can be checked very easily by measuring the absorption with polarized light and determining the anisotropy.

The dye molecules in the first layer can be oriented by coating a freshly cleaved gypsum crystal very slowly (speed 2 mm/minute) at 18° C with the layer (Fig. 3a) (Ref. 2). The chromophore axes orient preferentially in the direction of the a axis of the gypsum crystal, and they retain their orientation when the monolayer is separated from the gypsum crystal, transferred to the water surface (Fig. 3b, c), deposited on a glass slide with hydrophobic surface (Fig. 3d, e) and coated with a monolayer of fatty acid (Fig. 3f, g) for avoiding a reorganization which would occur if a monolayer assembly with a hydrophilic surface would be removed from the water. A reasonably strong anisotropy of the absorption is observed in the case of dye A in Fig. 4a. If instead of a fatty acid monolayer a monolayer of dye B in Fig. 4 is transferred to the slide an anisotropy of the absorption is observed also in the band of this dye (Fig. 4a).

The composition of monolayer and subphase are important. If the conditions are appropriate the monolayer separates from the gypsum crystal within a second, and the layer must then immediately come in contact with the glass plate. Otherwise the anisotropy is smaller. When the dye monolayer is separated from the gypsum the water must be covered with a monolayer at a surface pressure of 30 dyn/cm. Otherwise the dye layer would fall apart on the water surface when being removed from the gypsum crystal.

It is of interest to separate the copy from the original. This is necessary for further information processing or for making further copies by using the original or the copy as template. A cleavage between layers deposited on a glass slide is easily possible at a hydrophobic interface (Ref. 8), but in particular cases a separation can also be achieved at a hydrophilic interface (Ref. 6). A new technique is indicated in Fig. 5.

A glass slide with hydrophobic surface is covered subsequently by a monolayer of dye A and dye B, each in a matrix. This sample is sandwiched with a quartz slide with hydrophobic surface that has been obtained by depositing a fatty acid monolayer on the slide (Fig. 5a), and the etch of this pair of slides is dipped in a 0.1 n HCl-0.1 n NaCl solution. A zone dividing the wetted and the dry section appears (Fig. 5b) which moves to the top in a few seconds. The pair of slides is now immersed in water and the slides can be separated (Fig. 5c). The second layer with dye B is quantitatively transferred to the second slide and the first layer stays on the first slide. Both layers are undamaged. This is seen by inspecting the fluorescence which is entirely homogeneous. The first slide has no fluorescence in the UV and fluoresces red in blue light (dye A with no traces of B). The second layer fluoresces blue in the UV (dye B with no traces of A). The separation process can easily be traced by inspecting the movement of the zone between the dry region where the layers are in contact (red fluorescence in UV due to energy transfer from B to A) and the wetted region where they are separated (blue fluorescence of B in UV). These phenomena are also observed if the sample is prepared according to Fig. 3a-g.

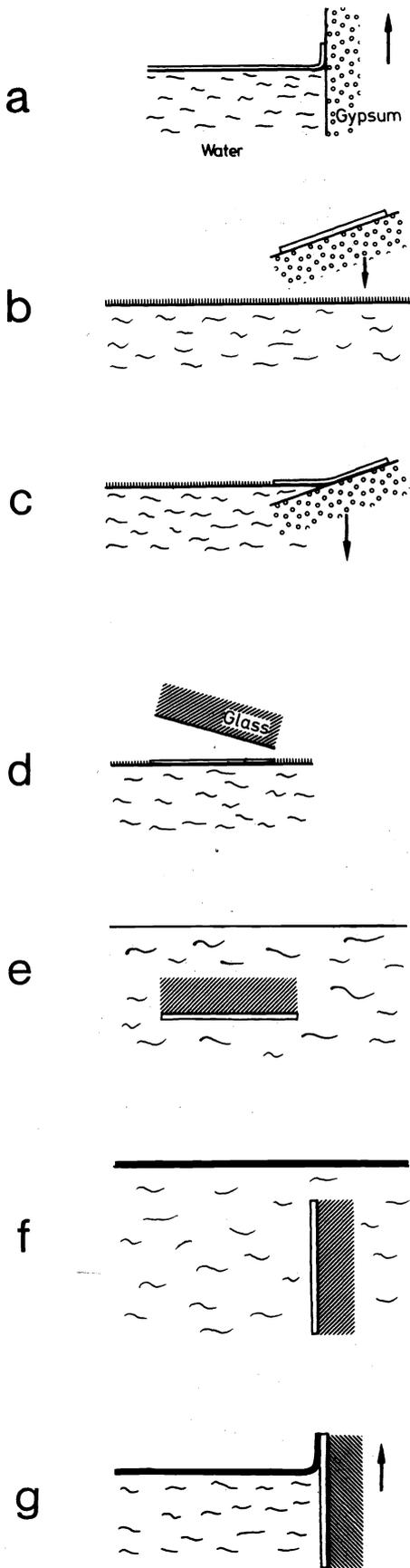


Fig. 3 Preferential orientation of chromophore axes at crystal surface

a) monolayer deposition on gypsum

b)-c) separating monolayer from gypsum, transfer to water surface

d)-e) monolayer deposition on glass or quartz slide. A quartz slide is needed for realizing a subsequent cleavage according to Fig. 6

f)-g) deposition of second monolayer

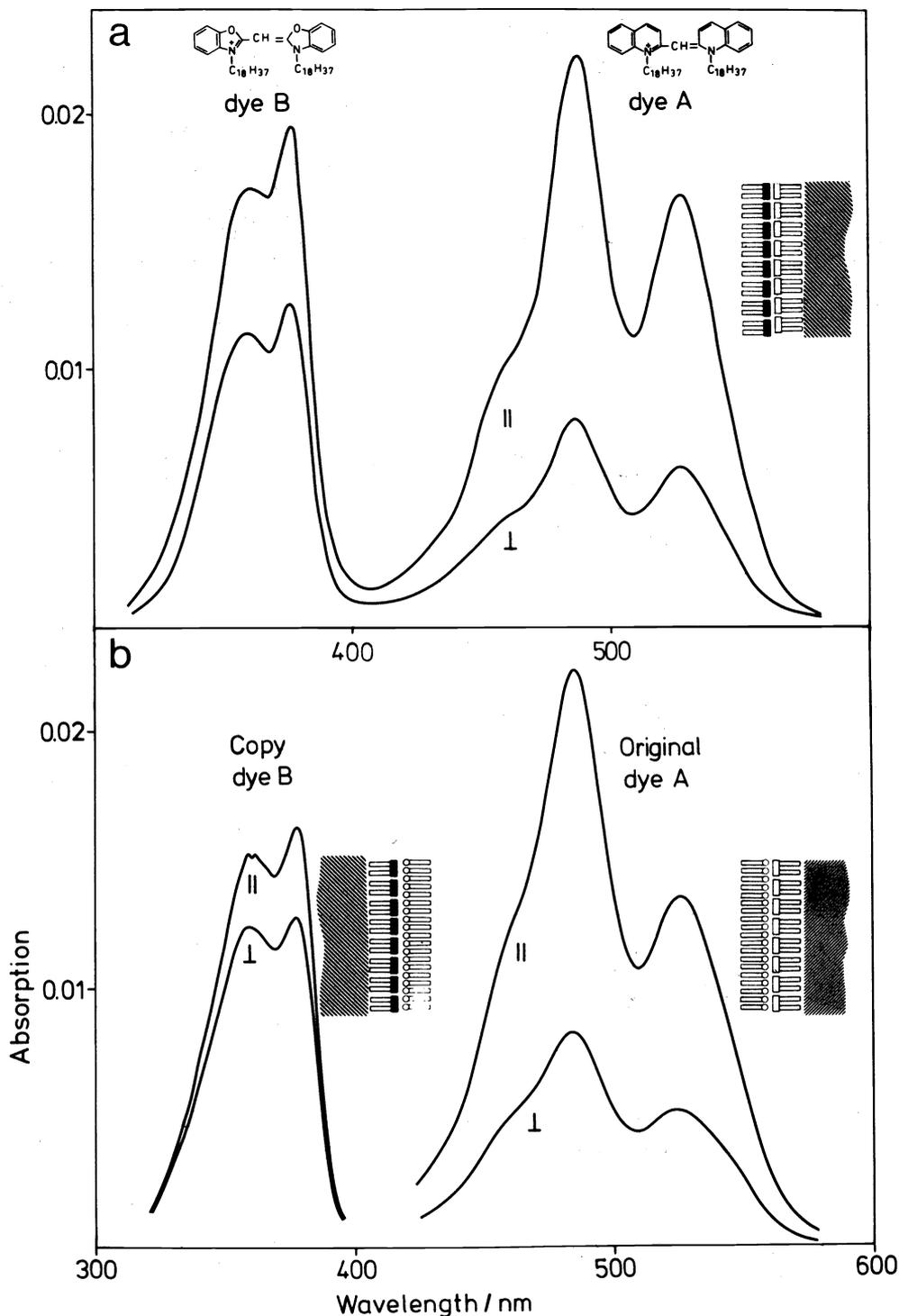


Fig. 4 Transfer of orientation in samples obtained according to Fig. 3. Layer of dye A (B) and matrix molecules (methyl ester of arachidic acid (AME), arachidic acid (C₂₀), behenic acid (C₂₂) in molar ratio A: AME:C₂₀ = 1:9:1 (B:C₂₂ = 1:10). Absorption for light with electric vector in layer plane in the direction that coincided originally with the *a* axis of the gypsum crystal (II), and with electric vector in layer plane perpendicular to that direction (I). Schematic representation of assemblies omitting matrix molecules.

a) dye A monolayer in contact with dye B monolayer

b) dye A monolayer and dye B monolayer separated according to Fig. 6.

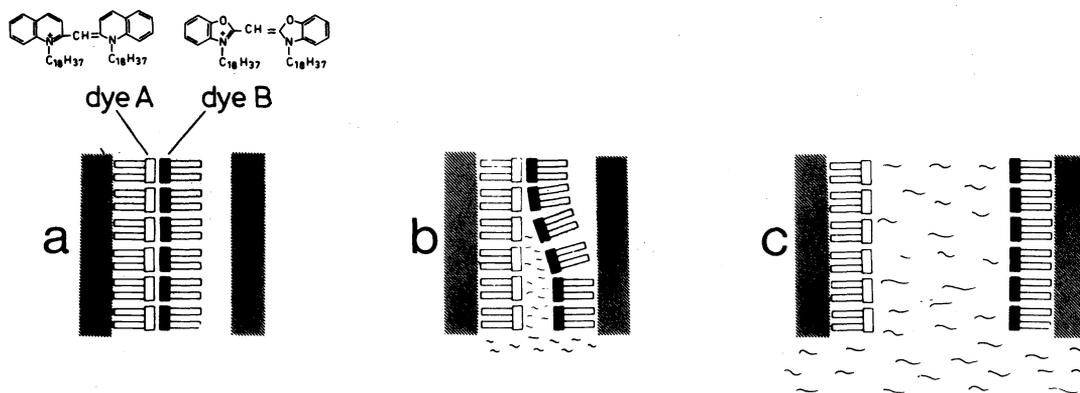


Fig. 5 Cleavage between monolayers of dyes A and B. The second layer is transferred to a quartz slide with hydrophobic surface. Schematic representation of monolayers omitting matrix molecules.

The orientation of the dye in the first layer is retained after removal of the second layer. However, no dichroism of the absorption is observed on the slide with the second layer. It must be concluded that this layer is fully reorganized in the process of transfer from the first to the second slide (Fig. 5b).

The procedure used to separate the monolayer from gypsum should be a more adequate way to avoid reorganization during the cleavage. Indeed, a separation is possible under similar conditions, but with an acidic aqueous sub-phase (0.1 n HCl-0.1 n NaCl) at 10⁰ C (Fig. 6).

The anisotropy of absorption of both slides, the slide with the original monolayer and the slide with the copy (Fig. 4b), are only slightly smaller than before separation (compare Fig. 4a with Fig. 4b). The processes can be performed only under very restricted conditions allowing an orientation at the matrix on one hand, and a subsequent removal of the layer on the other hand. The layers in Fig. 4 are too rigid to allow interlayer dimer formation as observed in the case of the dye of Fig. 1. This can be concluded from the fact that the spectrum in Fig. 4a is roughly the superposition of the spectra in Fig. 4b, while the formation of heterodimers between the two dyes would result in small shifts and changes in intensity of the bands. This was demonstrated in an earlier paper (Ref. 7), where sandwich heterodimers of several cyanine dyes were obtained by using a more mobile matrix. Unfortunately, a cleavage could not yet be observed in cases, where the typical spectral shifts for sandwich interlayer heterodimers and the special layer properties required for copying purposes were present simultaneously. But even in the case of Fig. 4 the strong dichroism in the absorption band of dye B demonstrates information transfer at the molecular level; the orientation of a dye molecule in the second layer is determined by its particular molecular neighborhood in the first layer.

These results show that the information transfer from one monolayer to another is feasible. Although the storage and processing of meaningful information at the molecular level is a remote aim, the main features should be mentioned. In computers information is deposited in a storage system and retrieved from it. It is difficult to see possibilities to do this with storage elements of molecular size. However, this is not what happens basically in the genetic information processing in biosystems. In this case the information is not introduced into a given storage system. It is present and is copied, and it is translated. The translation product is a functional unit, the individual. The individual is subject to selection. The information carried by the selected forms is again copied. The process is repeated again and again. Occasional errors in the copying procedure give rise to changes and by selection the forms continuously adapt to the environment. Messages of increasing sophistication develop and in this way information is produced.

The principle of this biological information processing device is very simple and information stored in monolayers could be processed in similar ways. Mo-

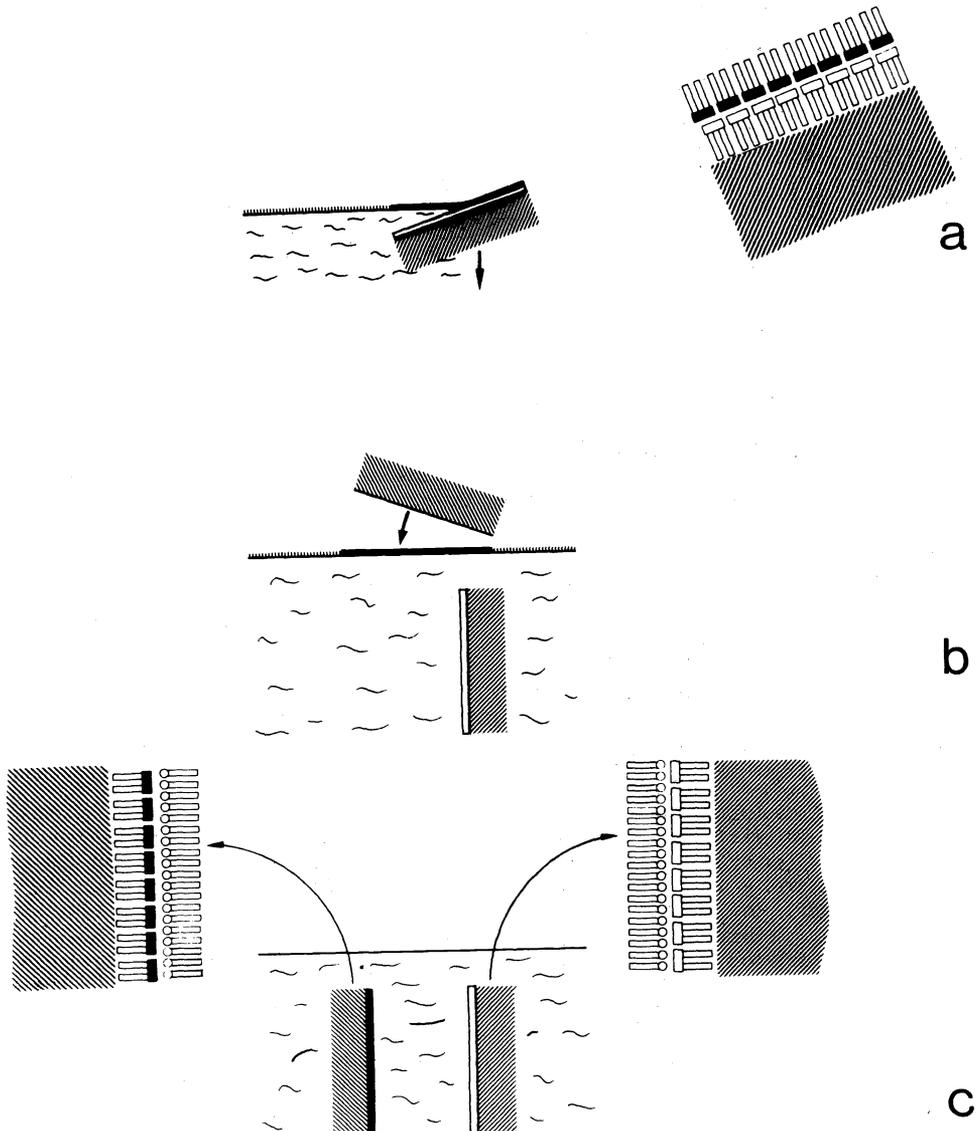


Fig. 6 Cleavage between monolayers of dyes A and B at 10° C (a); depositing layer B on slide with hydrophobic surface (b); coating both samples with fatty acid (c).

lecules can be imagined that bind to some arrangement of possible carriers of information (such as the dye chromophores in our examples). If a certain message would be present on a surface, represented by a particular arrangement of information carriers, and if the appropriate molecules would be in a surrounding solution, a complex arrangement could build up by the appropriate attachment of these molecules to the surface. This arrangement could have particular functionalities, e. g. a specific catalytic activity. The most efficient specimen could be selected and copied. This procedure could be repeated again and again. We would have an evolving system that would become increasingly efficient with respect to its particular functionality.

STORING AND COPYING INFORMATION AT THE SUBMICRON LEVEL

Monolayer assemblies are also of interest for storing information in a more conventional sense in small areas and copying this information. A bit can be stored in an area of 100 nm diameter. It can be deposited on a surface by an electron beam and read by an electron beam. The monolayer assembly techniques allow to copy an information at the 0.1 μm level (Ref. 9). For simplicity, the template is not made by an electron beam, but by evaporating platinum on a glass slide through a nucleopore filter, removing the filter, coating the sample with a polystyrene film and removing the glass by hydrofluoric acid treatment. A template with platinum specks of 8 μm diameter and 1-2 nm thickness is thus obtained. This template is brought in contact with a monolayer of the dye deposited on a glass slide covered with a polystyrene film (Fig. 7). The system is illuminated and the dye is bleached except in the

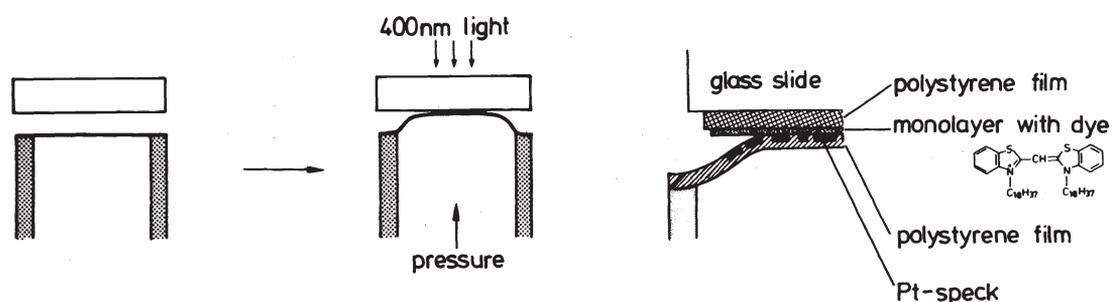


Fig. 7 Contacting template with monolayers and copying message by illumination. The monolayer is deposited on a glass slide coated by a polymer film (Ref. 9).

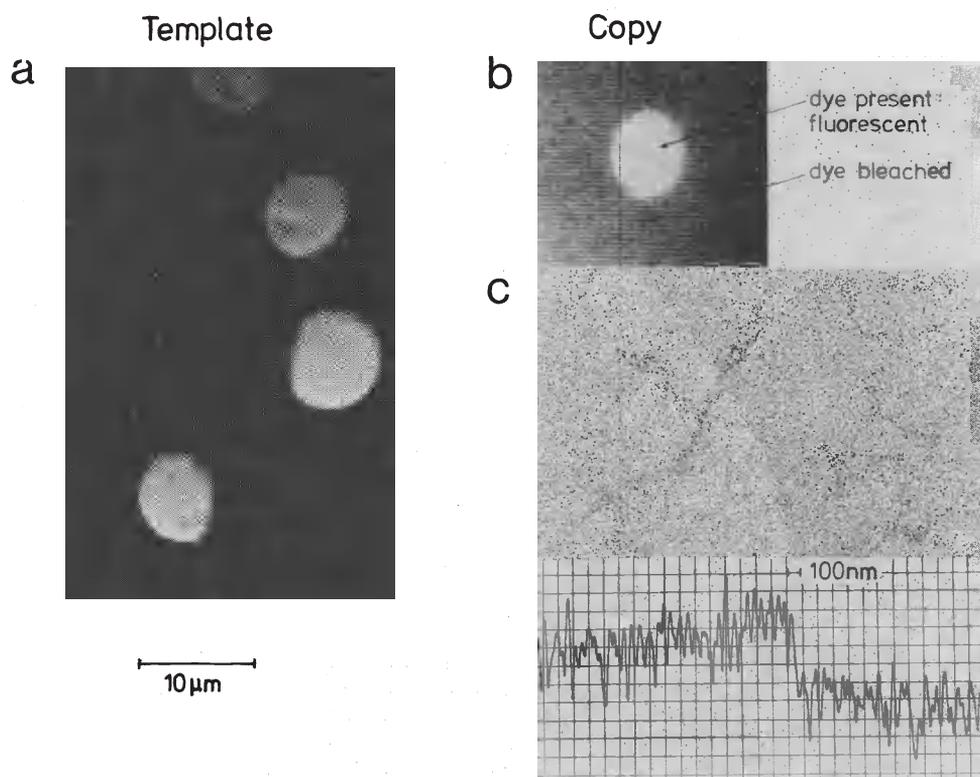


Fig. 8 Microscopic picture of template (a) and copy (b and c). The copy shown in the fluorescence microscope (b) is decorated with silver and observed in the electron microscope (c). The resolution (see densitometer plot) is below 100 nm (Ref. 9).

ultimate proximity of a platinum speck, where the dye molecules are specifically deactivated by transfer of energy to the platinum. The glass slide with the monolayer is separated from the mask. The unbleached dye is seen by its fluorescence (Fig. 8b) at the sections which were in contact with the Pt specks of the template (Fig. 8a). Silver is deposited by evaporation (it adheres preferentially to the sections of the monolayer where the dye has been bleached). The polystyrene film with the decorated monolayer is separated from the glass slide and inspected in the electron microscope. The resolution is better than 100 nm (Fig. 8c). The same mask can be used more than 20 times. This experiment demonstrates that the resolution of a device for processing light induced signals is well below the wavelength of light, since the transfer of energy from the excited dye to an acceptor covers a range of about 10 nm.

TRANSDUCTION OF SIGNALS AND TRANSFER OF ENERGY AND ELECTRONS IN MONOLAYER ASSEMBLIES

Signal processing devices of molecular size are the principle elements of the biological machinery, and simple models demonstrating signal transduction and transfer based on the planned cooperation of a few molecules are of interest. Simple examples are indicated in Fig. 9. A monolayer of dye D, deposited on a glass plate, is covered by two monolayers of fatty acid and a monolayer of dye E (Fig. 9a). The fatty acid interlayer keeps the chromophores of D and E at a planned distance, such as 50 Å. The sample is illuminated with UV radiation. Dye D is excited, a quantum of energy is transferred from the excited molecule D to E and E emits a quantum of fluorescent light. The strong yellow fluorescence of E appears while in the absence of E the sample shows the blue fluorescence of D. E acts as energy acceptor of D. Another example is the combination of a monolayer of dye D with a monolayer of electron acceptor A (Fig. 9b). Dye D is excited. It would normally fluoresce, but the fluorescence is quenched, since the excited electron is transferred to acceptor A.

This effect can be used to construct a more complex signal processing element consisting of a layer of chromophores D_1 at a distance of 50 Å from the pair of layers D and A in Fig. 9b, now called D_2 and A (Fig. 9c) (Ref. 10). Dye D_1 is continuously excited with 545 nm light and its red fluorescence is observed. When dye D_2 is excited with 366 nm light an electron is transferred to trap A and a colored radical is formed. This radical disappears by returning the accepted electron to dye D_2 when the light is turned off. By selection of the kind of trap the radical is energetically adjusted to act as acceptor of the excitation energy of dye D_1 : It therefore quenches the fluorescence of D_1 . As a result the fluorescence emission of dye D_1 can be modulated by exciting D_2 with the 366 nm light. The arrangement represents a system of correlated switches acting as a new entity with properties which are not present in the molecular constituents. Entirely independent reactions - a reversible photoreaction and energy transfer - are coupled in such a way that the first reaction triggers the second at a molecular level.

A similar molecular device is obtained in the arrangement of a photochromic substance (colored form E, non-colored form N) combined with a dye acting as the energy donor D of E (Fig. 9d) (Ref. 11). Dye D is excited with blue light (405 nm) and fluoresces green if E is absent. This fluorescence is quenched by E. The photochromic substance acts as flip-flop element turned on with 366 nm radiation and turned off with 545 nm light. The fluorescence of D is quenched as long as the flip-flop element is turned on.

Another example is the combination of an energy donor D and an energy acceptor E in contact with a semiconductor. The energy donor is excited by light, the excitation energy is transferred to the acceptor, and the excited acceptor injects the electron into the semiconductor. The semiconductor can be silver bromide (Fig. 9e). In this case the injected electrons produce a latent image which can be developed in the photographic process. Or the semiconductor can be indium-tin oxide and the injected electrons produce a photocurrent which can be measured (Fig. 9f) (Ref. 12). In this case the sample is inserted in an electrolyte with the counter electrode. By an electron donating substance present in the electrolyte the oxidized dye is reduced and in this way the illuminated system is continuously recovered. A dye D that can be protonated to DH^+ has been used as the energy donor of E. In the protonated form it cannot act anymore as the energy donor of E and it can therefore be used as flip-flop element. By changing pH, the photocurrent can be controlled by a sequence of cooperating steps that can be stimulated

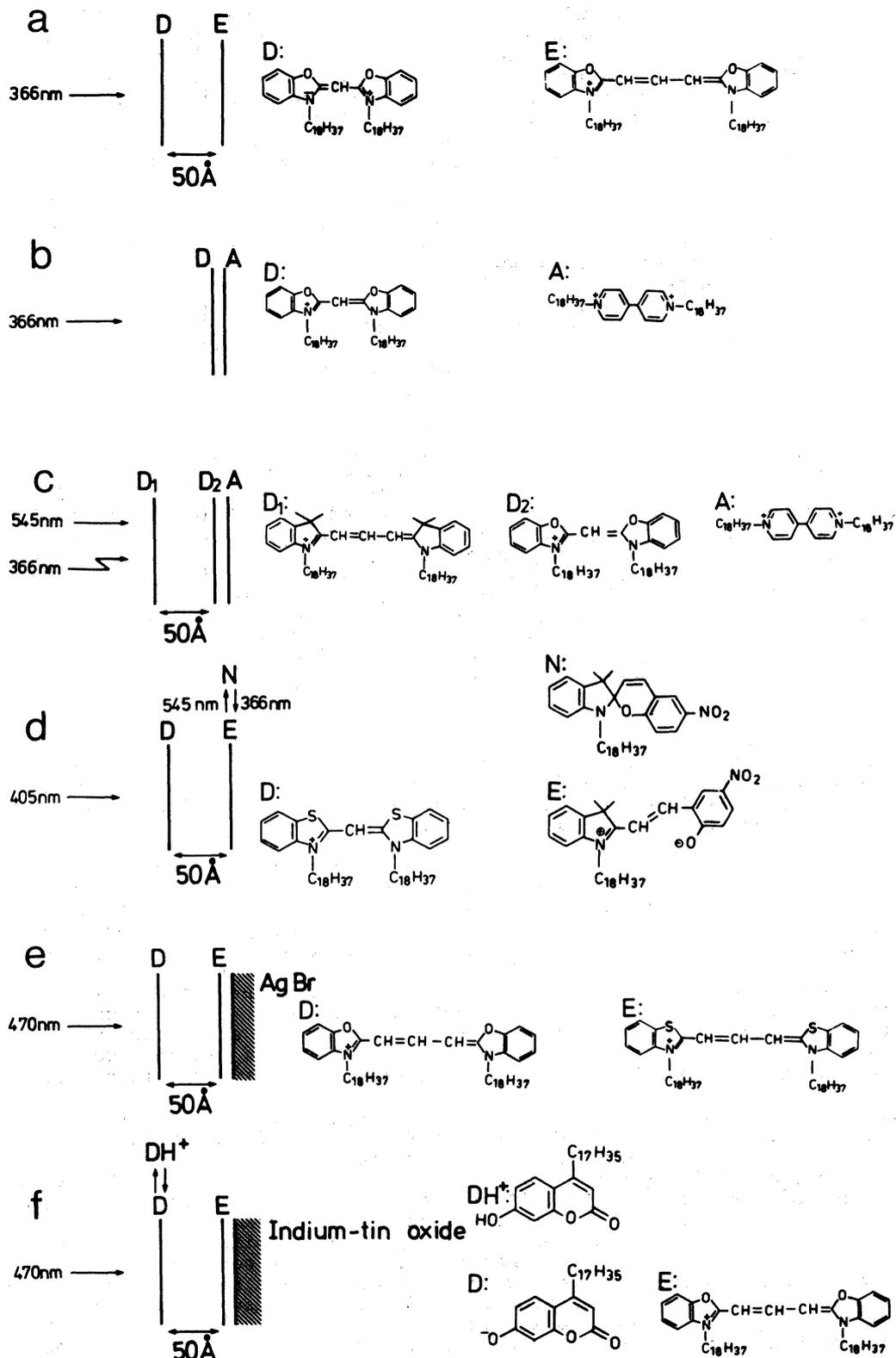


Fig. 9 Examples demonstrating signal transduction and transfer. Schematic representation of monolayer arrangements. Cooperating molecules D (energy or electron donor), E (energy acceptor), A (electron acceptor), DH⁺ and N inactivated species (Refs. 10-13).

independently. The spatial and energetical matching of each component and the tuning of each step to each other are essential. The machinery can be made even more complex by adding an enzyme that produces protons in the reaction with the substrate (Ref. 13). The enzyme can be bound to a monolayer with the proton-sensitive dye and the added substrate can trigger the fluorescence of the dye by stimulating the local proton concentration.

We have discussed cases where the energy acceptor E is at the semiconductor surface and the energy donor D at 50 Å distance. Alternatively, the energy donor can be at the semiconductor surface and the energy acceptor at 50 Å. Dye D at the surface is excited and can deactivate by electron or energy transfer to the semiconductor (AgBr), or by energy transfer to energy acceptor dye E. Dye E and the semiconductor are competitors in this case. We compare the six situations in Fig. 10 (Ref. 14).

Dye D is excited. In case a) it is deactivated by fluorescence or thermal deactivation (rate constant $k_{f,th}$). In case b) it is in addition deactivated by energy transfer to E; the fluorescence is quenched to 10 % of its value in a), and therefore rate constant $k_{DE} = 10 k_{f,th}$. In cases c) - f) the excited dye D can be deactivated via AgBr and then a latent image is produced which is developed. Taking case c) as a standard the sensitization of the photographic process is reduced in case d) to one half, in case e) to 1/100 and in case f) to 1/1000. The result in case d) (reduction of sensitization to 1/2 of that in case c) means that the deactivation of an excited molecule of dye D occurs via dye E (rate constant k_{DE}) and via AgBr (rate constant k_{DAgBr}) with equal probabilities, and therefore $k_{DAgBr} = k_{DE}$. It follows that $k_{DAgBr} = 10 k_{f,th}$, and that consequently, the dye in case c) is mainly deactivated via AgBr. In case e) the dye is separated from the AgBr surface by 50 Å and the sensitization of AgBr is 1/100 of that in case c). Therefore in case e) k_{DAgBr} must be 1/100 of $k_{f,th}$ and consequently k_{DAgBr} (case e) = 1/1000 k_{DAgBr} (case c). If energy acceptor E is added (proceeding from e) to f)) the lifetime of D* should be reduced to 1/10 since $k_{DE} = 10 k_{f,th}$. Therefore, the sensitizing action in f) (as compared to e)) should be reduced to 1/10, as is actually observed.

In case f) energy acceptor E has a much stronger effect on the sensitizing action of dye D than in case d). This is because in case d) the deactivation via dye E (k_{DE}) and the deactivation via AgBr (k_{DAgBr}) are the main competitive paths, while in case f) these paths are the deactivation via E (k_{DE}) and the deactivation by radiative emission and thermal collision ($k_{f,th}$).

This material was presented to give a demonstration of the high quality of these layers. Let us first consider that some dye molecules in cases e) and f) might have reached the AgBr surface by diffusion or reorganization effects and that these molecules are responsible for the sensitization. Then the observed sensitization in case e) (1 % of that in case c)) would mean that 1 % of the dye molecules have reached the surface. However, if these molecules should be responsible for the sensitization of AgBr dye E would be ineffective as competitor, the sensitization would be the same in cases e) and f). The observed competing effect of E in case f) shows that even such small effects as the sensitization by a dye at 50 Å distance can be measured without interference with effects based on layer imperfections.

Another quality test is obtained from the arrangements in Fig. 11; arrangement a) is similar to that in Fig. 10c, but now dye D is mixed in the monolayer with electron acceptor A. Dye D has no sensitizing action in this arrangement, and this is not surprising, since A is a strong competitor to AgBr. In the arrangement in Fig. 11b the acceptor is at direct contact and dye D at 50 Å distance. The layer of electron acceptor A has no effect on the sensitizing action of the dye (nearly the same sensitization is found in Fig. 10e and Fig. 11b). This demonstrates again the sensitization by the dye at 50 Å distance. Dye molecules that might have reached the surface cannot sensitize since the acceptor is present. If the sensitization in the case of Fig. 10e would be due to traces of dye that have reached the surface of the AgBr by diffusion or undesired rearrangements we would observe no sensitization in the case of Fig. 11b.

Of particular interest is the energy and electron transfer in monolayer assemblies with aggregates of tightly packed dye chromophores characterized by a narrow absorption band and an almost coinciding fluorescence band. The fluorescence is quenched by traces of molecules acting as exciton trap. The most effective trap that has been investigated quenched the fluorescence

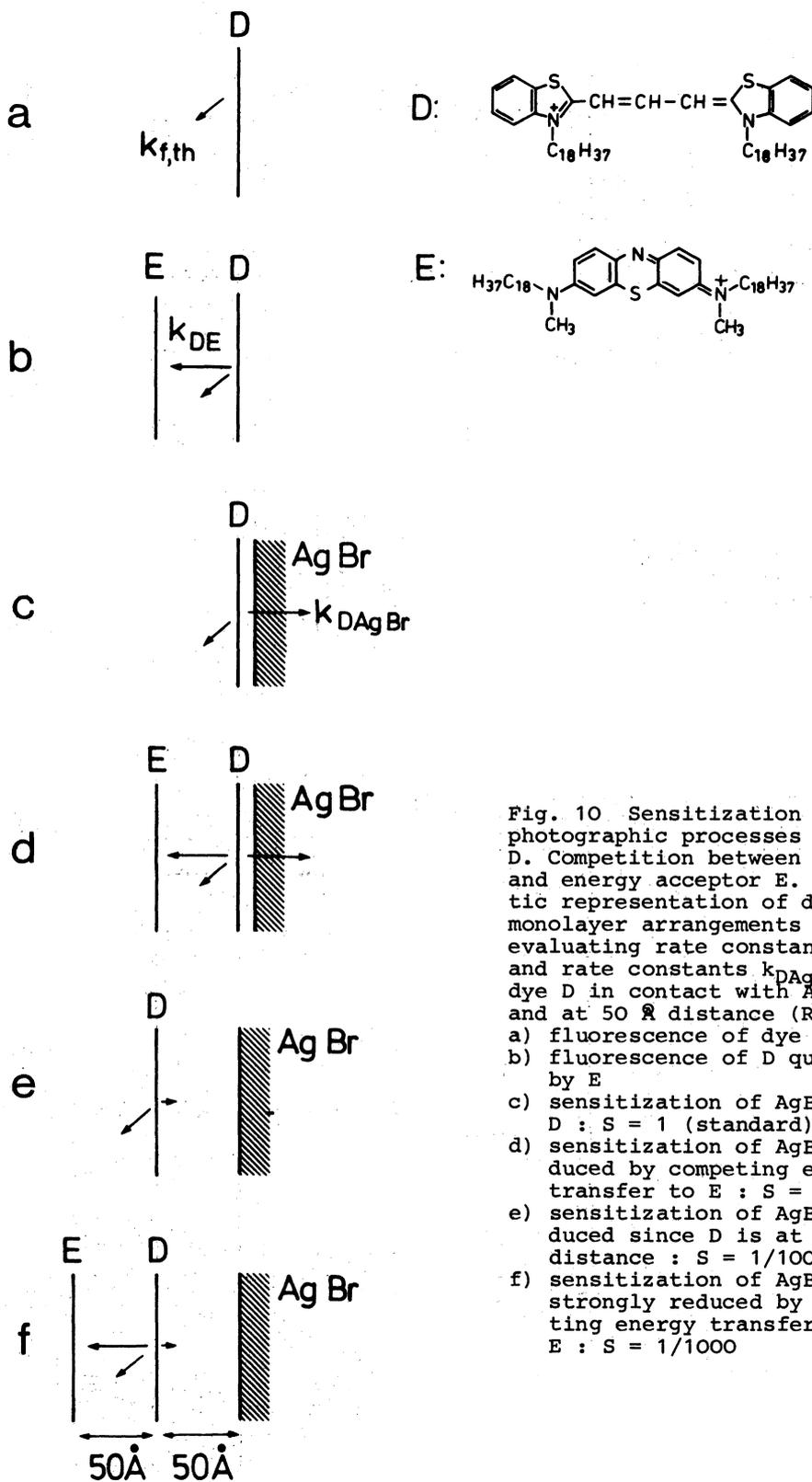


Fig. 10 Sensitization of photographic processes by dye D. Competition between AgBr and energy acceptor E. Schematic representation of different monolayer arrangements for evaluating rate constant k_{DE} and rate constants k_{DAgBr} for dye D in contact with AgBr and at 50 Å distance (Ref. 14).

a) fluorescence of dye D
 b) fluorescence of D quenched by E
 c) sensitization of AgBr by D : S = 1 (standard)
 d) sensitization of AgBr reduced by competing energy transfer to E : S = 1/2
 e) sensitization of AgBr reduced since D is at 50 Å distance : S = 1/100
 f) sensitization of AgBr strongly reduced by competing energy transfer to E : S = 1/1000

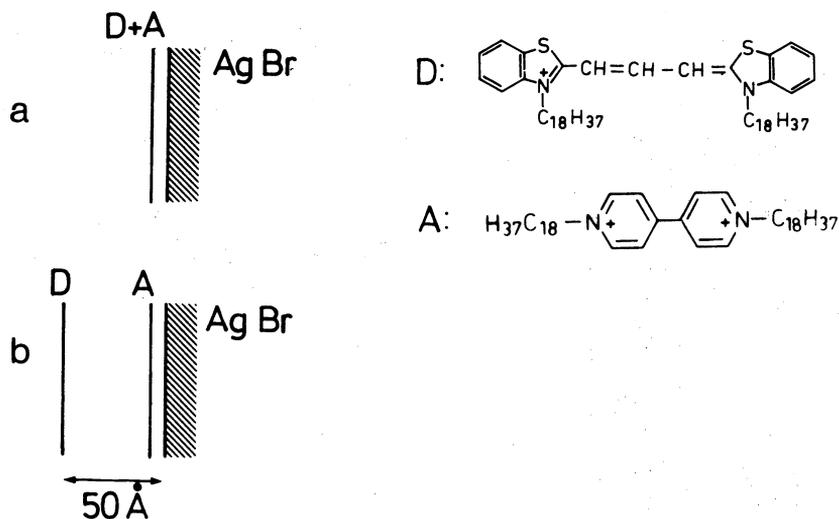


Fig. 11 Arrangements similar to Figs. 10c and e, and with additional electron acceptor A (Ref. 14).

- a) dye D sensitization of AgBr fully suppressed by A : S = 0
 b) dye D sensitization of AgBr not influenced by A (if a correction for the desensitizing action of A has been performed) : S = 1/100 (such as in Fig. 10e).

of the aggregate to one half at a concentration of one trap per 10 000 dye molecules (Ref. 10). This is a demonstration for the high cooperativity of the system. The trap can be excited by the exciton approaching it (Ref. 15) (trap E) or it can be reduced (trap A) or oxidized (trap B) (Fig. 12).

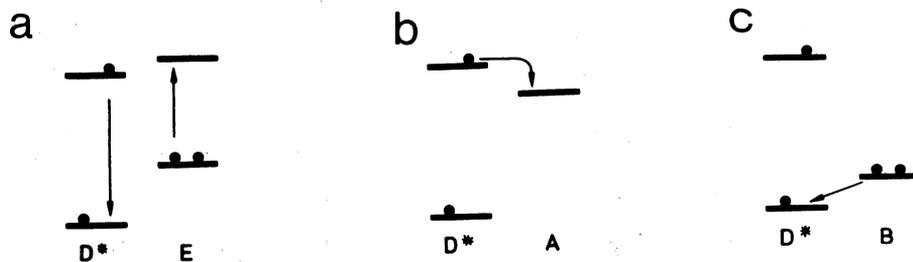


Fig. 12 Exciton encountering trap represented by energy acceptor E (a); electron acceptor A (b); electron donor B (c).

We discuss some experiments with an aggregate of dye D (Fig. 13) combined with an electron accepting species A and an electron donating species B (Ref. 16). Dye D was mixed in 1:1 molar ratio with methyl stearate and compressed to 35 dyne/cm for 10-15 minutes to obtain the well organized arrangement. The aggregate layer thus formed is too viscous to coat by the conventional technique and the method of Fig. 3c-d was applied. The desired contact layer (C₂₀-AME matrix) is coated in a conventional manner by withdrawal as in Fig. 3f. The absorption and fluorescence spectra are given in Fig. 14. The fluorescence intensity is quenched by traces of A or B in the contact layer. By measuring the fluorescence quenching by the donor and acceptor in the mixture and alone at the same concentration it can be

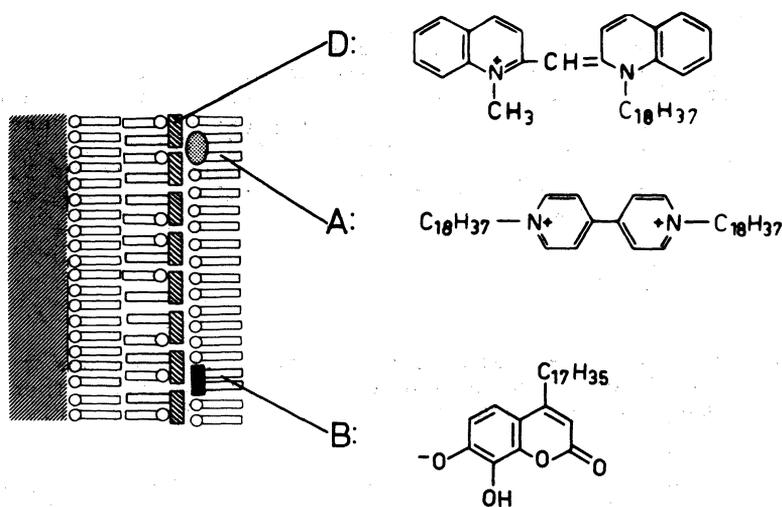


Fig. 13 Monolayer of dye aggregate (D) and contact layer of matrix molecules with traces of electron acceptor (A) and electron donor (B).

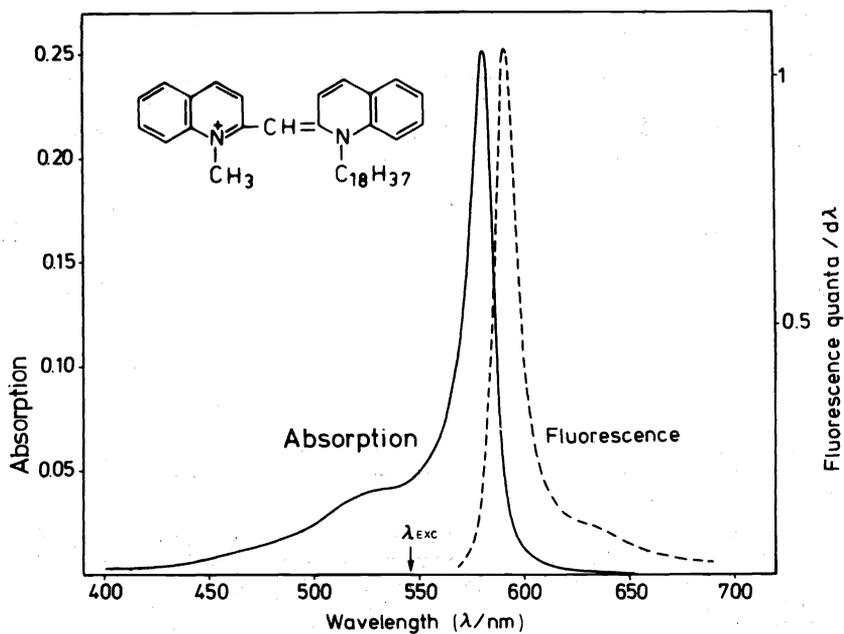


Fig. 14 Monolayer of dye aggregate. Absorption and fluorescence spectra (Ref. 16).

shown that the two quenchers act independently, since the relation holds

$$\left(\frac{I_0}{I_{AB}} - 1\right) = \left(\frac{I_0}{I_A} - 1\right) + \left(\frac{I_0}{I_B} - 1\right)$$

where I_0 is the fluorescence intensity in the absence of quenchers, while I_A , I_B and I_{AB} are the intensities in the presence of A, B and A plus B respectively. The relation follows from the fact that the relative fluorescence intensity I_A/I_0 is given by the ratio $k_{f,th}/(k_{f,th}+k_{DA})$ and therefore $(I_0/I_A - 1) = k_{DA}/k_{f,th}$. The same holds for I_B and similarly $(I_0/I_{AB} - 1) = (k_{DA}+k_{DB})/k_{f,th}$. Furthermore, the dependence of I_A on the dilution of A (measured by the number N_A of molecules D per molecule A) can be expressed by the equation

$$\frac{I_0}{I_A} - 1 = \frac{\text{const}}{N_A}$$

which is obtained if it is assumed that the mobile exciton has a certain chance to be trapped when encountering an acceptor molecule. Therefore, k_{DA} must be proportional to the concentration $1/N_A$, and consequently $I_0/I_A - 1$ must be proportional to $1/N_A$.

When A has trapped an exciton by capturing the excited electron, it will usually return this electron to the dye molecule (Fig. 15a). This is indicated

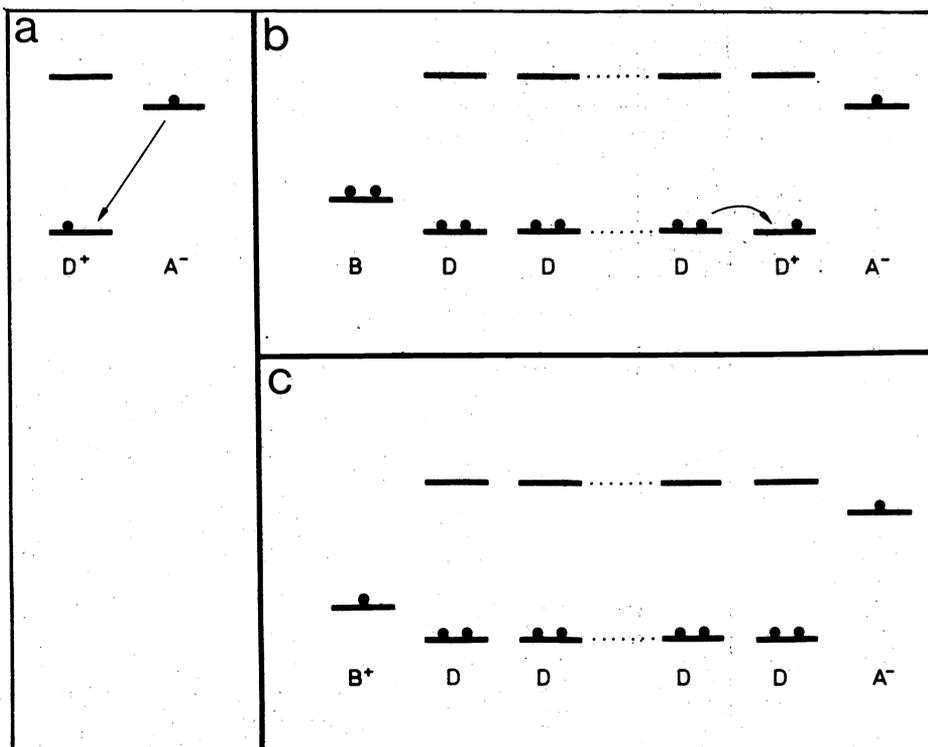


Fig. 15 Electron of reduced acceptor (A^-) returns to adjacent oxidized dye D^+ (a), or electron of adjacent molecule D migrates to D^+ (b), and finally the positive hole is captured at electron donor B (c).

by the fact, that the concentration of the radical A^- does not build up in a fast process as expected from the amount of quenching, but in a slow process within minutes (Fig. 16). It was concluded from the quenching of the fluorescence that the donor acts as competitor in the process of trapping the exciton. The rate of formation of A^- is therefore diminished by adding the donor

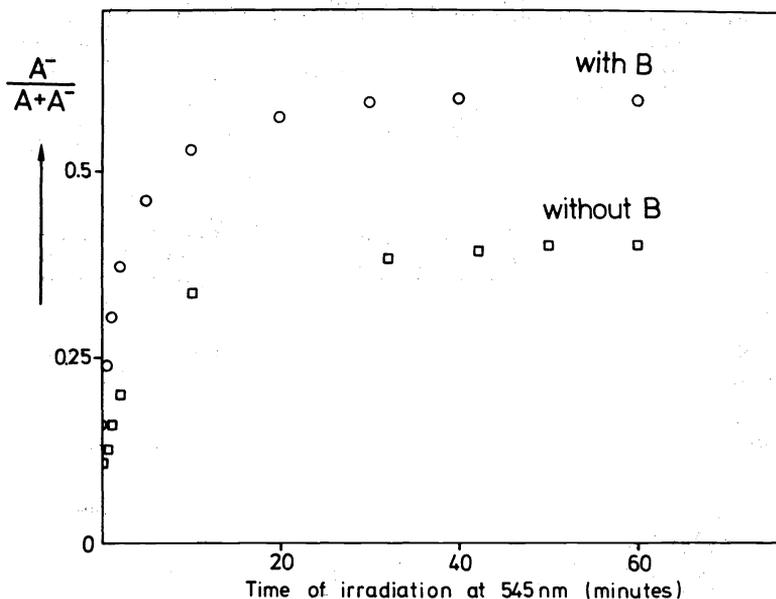


Fig. 16 Monolayer dye aggregate with traces of acceptor. Ratio of acceptor present as radical (A^-) versus time of illustration. Squares: donor absent, circles: donor present in the same concentration as acceptor (Ref. 16).

and one might expect a decreased build up process of A^- . The contrary is true (Fig. 16). This fact can be explained by hole migration from the oxidized dye molecule D^+ adjacent to A^- (Fig. 15b) across the aggregate to trap B (Fig. 15c). Then, no empty state is available in the dye molecule adjacent to A^- . The donor B therefore helps stabilizing A^- and this is much more effective than the competition of exciton trapping.

The process is effectively a photoinduced electron transfer from the donor to the acceptor. Reactions of this type are useful for studying photo energy conversion processes where intermediate storage devices preceding chemical dark reactions are particularly interesting (Ref. 17).

Molecular devices are based on elaborate strategies for achieving the intended cooperations in molecular dimensions. Each manipulation must be carefully planned and controlled since subtle changes in the conditions have strong effects on the molecular organization. The cleavage experiments discussed in the first section are particularly sensitive on details of the procedure, e. g. it is important to use quartz not glass slides that have been cleaned immediately before use and the bidistilled water in the trough must be replaced each day, etc.

The aim was the construction of molecular systems and therefore many surprising phenomena of interest to surface chemists observed during the development of the techniques have not been further investigated. For instance the deposition of a monolayer with the hydrophilic groups on the hydrophobic surface of the preceding monolayer is not possible if this preceding monolayer consists of a fatty acid. However, the deposition can be achieved if 1/10 of the fatty acid is replaced by the methylester of the fatty acid (Fig. 17) (Ref. 2). The monolayer deposited in this way is appropriate for

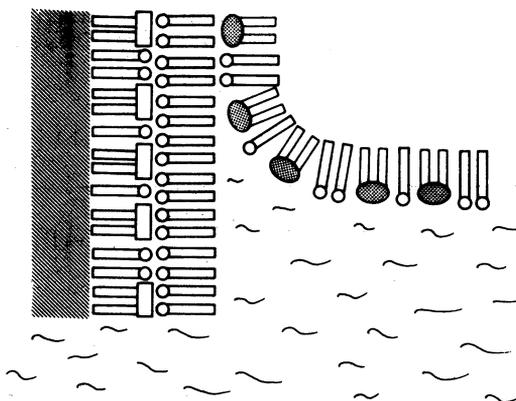


Fig. 17 Deposition of monolayer with hydrophilic groups on hydrophobic surface. The deposition is only possible for very particular sublayer composition. Electron donor D and acceptor A according to Fig. 9b, fatty acid spacer layer, sublayer D:AME:C₂₀ = 1:10:90, top layer A:AME:C₂₀ = 2:1:9 [Ref. 2].

subtle experiments, such as electron tunneling. The technique has been developed for tunneling measurements which are extremely sensitive to imperfections in the structure of the assembly and therefore tunneling measurements are valuable tests of the molecular architecture of the organization. Assemblies for electron tunneling processes are of particular interest also in the development of possibilities of photo energy conversion. In this case the charge separation is the crucial event and to avoid the back reaction by quantum mechanical tunneling is of principle importance.

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