

SYNTHETIC MOLECULAR ORGANIZATES*

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Summary

Organized systems of molecules (organizates) can be obtained by assembling monolayers of planned composition and architecture. Appropriately constructed monolayer assemblies can be used to study light-induced vectorial charge separation. Such systems are of interest in designing devices for solar energy conversion.

Possibilities of such devices are discussed and experiments are presented to demonstrate light-induced charge separation. Charge separation is limited by the quantum mechanical tunnelling effect which cannot be avoided at molecular dimensions. Experiments to study that effect are described.

Monolayer assemblies to discriminate between different mechanisms of spectral sensitization of photoeffects by dyes are discussed and cases are considered where an increased spectral sensitization is achieved by cooperation of different dye molecules.

1. General aspects

The phrase "synthetic molecular organizate" was introduced to indicate a new aim [1, 2]. An organized aggregate or organizate is not just an aggregate — a monolayer, a micelle, a vesicle etc. — but a monolayer, a micelle or a vesicle consisting of molecules of different sorts interlocking specifically to form a functional unit. A functional unit is a system of molecules acting as an entity in a purposeful manner. A synthetic molecular organizate then is a molecular aggregate of specifically designed architecture.

In biological systems we find extremely sophisticated organized aggregates of molecules and it seems fascinating as a new task to make simple artificial organized systems of molecules by synthesizing different sorts of appropriate component molecules. These component molecules may then interlock to form functional units.

Synthetic organizates are promising for solar energy conversion: light can excite a molecule and a subsequent separation of charges may occur. In a system for energy conversion these charges should be kept separated for a

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certain time. This seems important for efficient energy storage since the desired dark reactions should be possible without much loss of free energy and this means they should be sufficiently slow. To approach these requirements does not seem easy and it should be of interest to design an artificial organized structure similar to the structure necessary for the primary process in plant photosynthesis.

We can think of several possible ways of obtaining organizates. Appropriate surface active molecules can be adsorbed on a hydrophilic solid surface by dipping the solid in an organic solvent containing the molecules. It should be possible in this way to make complicated organized assemblies with planned functions by using many different sorts of specifically interlocking component molecules. Soap molecules form micelles, and it should be possible to get micellar organizates of practical interest [3]. However, the task of designing useful functional systems, which are simply formed by self-assembly of different sorts of interlocking molecules in solution, appears to be a tiresome puzzle. Its solution will require much effort by preparative chemists.

A simplified procedure is to design appropriate monolayer assemblies. Different sorts of molecules which are insoluble in water but which have a hydrophilic group are spread on a water surface and are pushed together, thus forming a monolayer of well-defined architecture (Fig. 1). The monolayers of different composition can be deposited on top of each other. By planning the sequence, designed monolayer assemblies can be obtained [1, 2].

The trick in this approach is to give the molecules some help to organize. They need to be less specific than for self-assembling in solution. Monolayer assemblies are suitable for studying possibilities of self-assembly, and on this basis increasingly sophisticated functional systems can be made in a more and more self-assembling manner. This approach should lead gradually to the development of self-assembling functional systems which are promising for future applications. Solar energy converting devices covering large areas can

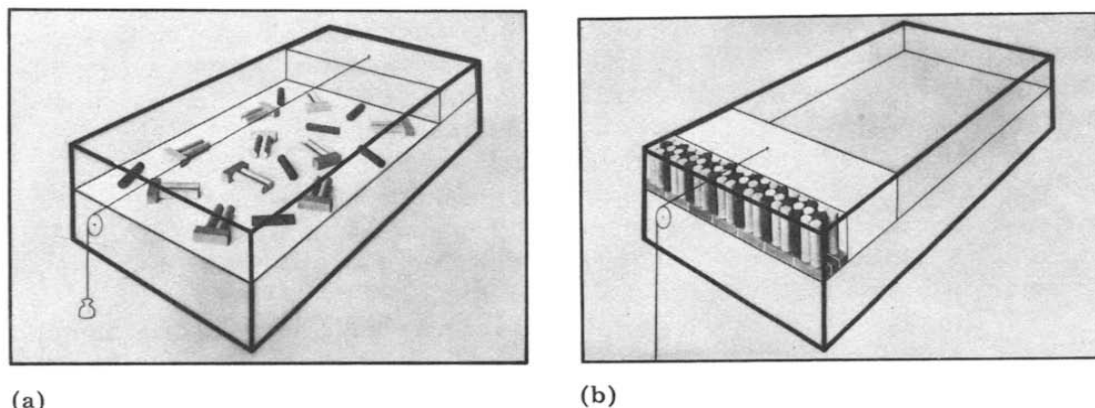


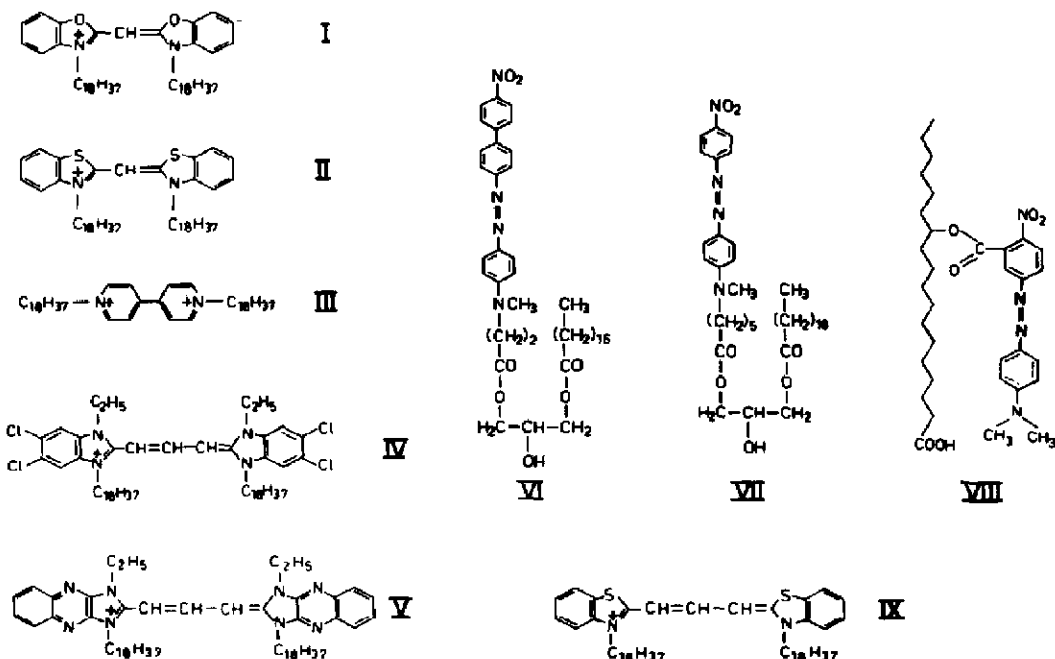
Fig. 1. Dye I and octadecane (a) spread on a water surface and (b) compressed by applying a pressure of 30 dyn cm^{-1} .

be imagined as consisting of powder particles covered by an appropriately designed organized layer obtained by adsorption from solution.

In the case of simple fatty acids methods of obtaining monolayers and of depositing them on plates have been known for several decades. Pockels [4] made monolayers of fatty acids on a water surface and Langmuir [4] showed how to deposit such layers on a plate. These old techniques can be used and modified for the more recent aim of producing synthetic molecular organizes [5, 6].

2. Monolayer assemblies for exciton channelling

A system harvesting light energy and channelling the energy should be of interest as a component in any proposed device for solar energy conversion. In a monolayer of dye I (host) with traces of dye II (guest) the host is harvesting light energy and the guest, which absorbs at longer wavelength, is trapping the energy. The energy migration in the layer of the host depends strongly on the interaction of the molecules. For fast exciton motion the chromophores of the host must be in a compact arrangement, and this is reached by spreading the dye and the long chain hydrocarbon octadecane in a 1:1 mixture (Fig. 1). The dye chromophores are hydrophilic and the hydrocarbon substituents hydrophobic. The octadecane chains fill the empty spaces between the hydrocarbon substituents of the dye molecules and in this way a compact arrangement in the chromophore part and simultaneously a com-



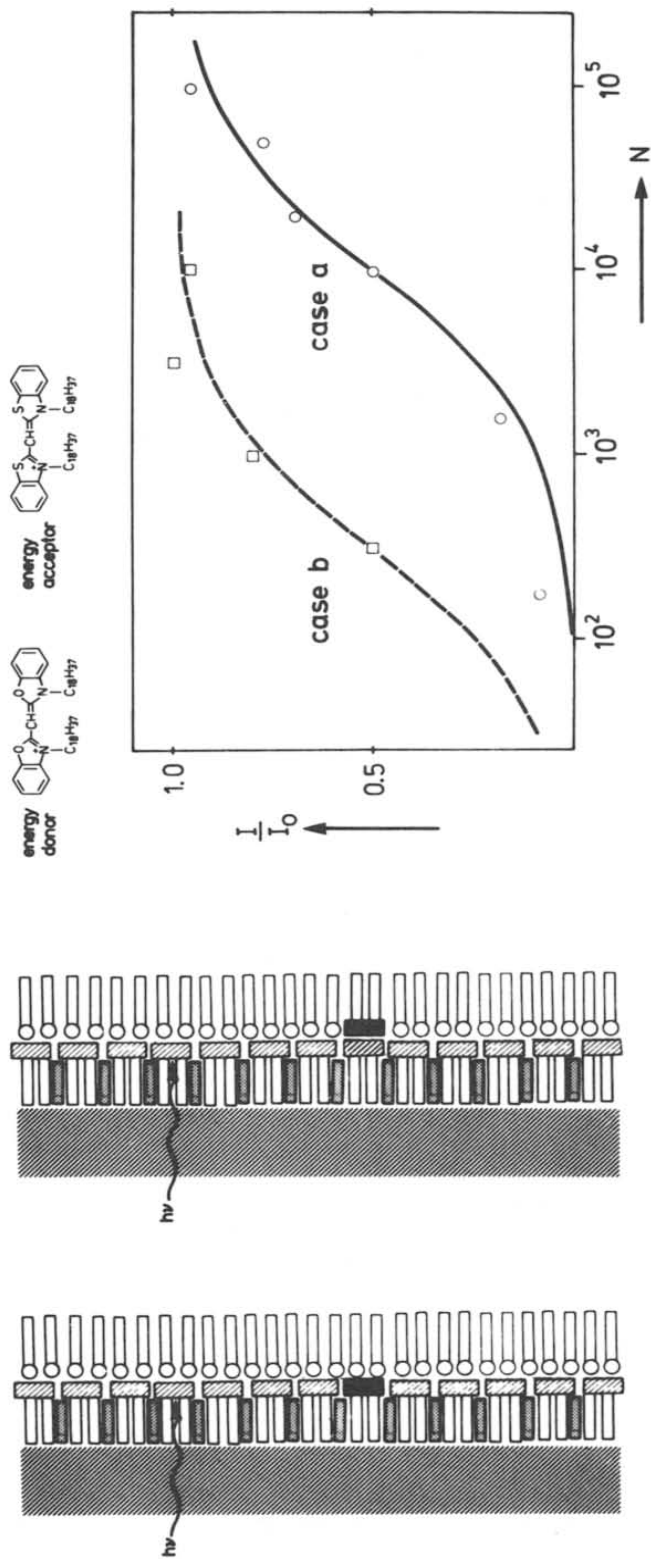
compact arrangement in the hydrocarbon part are reached [5]. It can be demonstrated by a quantum mechanical calculation that the exciton hopping time in this very compact arrangement of chromophores is $\Delta t = 10^{-13}$ s. In terms of the uncertainty principle, this corresponds to a natural bandwidth of 5 nm, and in fact the narrow absorption and almost coincident fluorescence band of the host in this arrangement have a bandwidth of 8 - 9 nm. Since the fluorescence time of the single molecule is 10^4 times longer than Δt , we can expect an unusually long exciton diffusion path. If an exciton trap is exactly interlocking in this structure the coupling should be sufficiently strong to get a trapping of the energy absorbed by the host even if there is one molecule of the guest among 10^4 molecules of the host. This condition should be fulfilled in the present case where dye II differs from I only by two sulphur instead of two oxygen atoms. The molecule can substitute a molecule of the host in the lattice. The same effect is predicted when coherent exciton motion is assumed instead of hopping. This predicted effect can easily be demonstrated [7].

The monolayer is deposited on a glass plate and illuminated with UV light, which can excite the host only. A plate where the guest is missing shows the violet fluorescence of the host. A plate where one molecule of the guest is among 5000 molecules of the host shows strong blue fluorescence demonstrating the energy channelling to the guest (Fig. 2(a)). The fluorescence quantum yield of the host and the guest are nearly unity and therefore we expect that for each missing fluorescence quantum of the host a fluorescence quantum of the guest should appear, *i.e.* the quantum yield should be the same for both plates. This is the case. A considerable quenching of the fluorescence of I and a sensitized fluorescence of II is seen even if only one among 50 000 molecules of I is exchanged by a molecule of II (Fig. 2). This shows that the system must be free of larger imperfections. It should be noted that this artificial device for channelling energy is far more efficient than the device used in plant photosynthesis where there is one energy trap among 300 chlorophyll molecules harvesting energy.

Perfect positioning of the guest in the lattice of the host is essential for energy channelling. If we deposit on a layer of aggregated dye I a layer of fatty acid containing traces of dye II (Fig. 2(b)) then the fluorescence of II is much less quenched. To reach the same amount of quenching a 30 times higher surface density of II is needed (Fig. 2). The striking difference between the two cases can be made plausible very easily on the basis of the extended dipole model [8] and follows from a quantum mechanical computation. If I and I_0 are the intensity of the fluorescence of the host in the presence and in the absence of the guest respectively we can write

$$I = I_0 \frac{k_d}{k_d + k_{en}}$$

where k_d is the rate of deactivation by fluorescence and thermal collisions and k_{en} is the rate of energy transfer. Since k_{en} is proportional to the surface



(a)

(b)

Fig. 2. Harvesting of light energy by I and trapping by II. The trap is 30 times more efficient in case (a) than in case (b). The graph gives a plot of I/I_0 (relative fluorescence intensity of I) against N (number of molecules of I) for cases (a) (circles) and (b) (squares).

density of the guest (inversely proportional to N where N is the number of molecules of host per molecule of guest) then

$$\frac{I}{I_0} = \frac{1}{1 + \text{const.}/N}$$

Using the values $\text{const.} = 10^4$ and $\text{const.} = 300$ for cases (a) and (b) respectively we obtain the full and broken curves in Fig. 2. This example shows the importance of a well-defined architecture of the monolayer assembly. Each arrangement must be studied very carefully before it can be used as a functional component.

3. Vectorial separation of charges in monolayer assemblies

In a proposed device for converting solar energy the exciton should be channelled to a dye molecule D and this particular dye molecule may transfer the excited electron to an acceptor A (Fig. 3). In judging possibilities of using organizes for solar energy conversion it seems important to ask: can the charge separation be maintained between D^+ and A^- for a sufficiently long time? To store an appreciable part of the absorbed solar energy in a monolayer assembly, it should be possible to maintain a potential drop across a monolayer of more than 1 V. This can easily be achieved [9 - 11].

In any proposed device for energy conversion it is important to minimize the losses in the reduction and oxidation reactions that follow charge separation. Therefore these reactions should be as slow as possible for approaching reversibility. From this point of view the charges should be kept separated as much as possible. However, the system should have recovered by the time the next light quantum is absorbed and channelled. Otherwise, the system would not be ready to convert the energy of that quantum. Therefore,

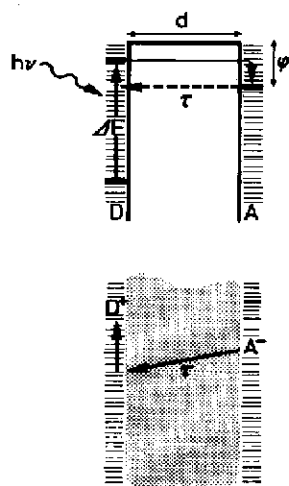


Fig. 3. Dye D is excited. An electron moves from D to acceptor A. The back reaction (electron tunnelling from A^- to some site at the interlayer of D^+ and to D^+ in a subsequent fast process) should be avoided.

the oxidation and reduction processes must have taken place by that time. There is no sense in having a device that could keep the charges separated for a longer time.

In bright sunlight a dye molecule captures a light quantum about once per second. Therefore, if we consider a device which has one trap per 100 dye molecules (similar to the situation in plant photosynthesis), the time for recovery is 1/100 s. This should be a compromise between the opposite tendencies of keeping the number of complex devices (reaction centers) small and the time available for the dark reactions long. It seems reasonable that a system where this compromise is found evolved in nature. Consequently, a useful device for energy storage should be constructed in such a way that the charge separation is maintained for about 1/100 s. The question then arises: can such a device be realized?

4. Tunnelling in monolayer assemblies

Organized monolayer assemblies are well suited to avoiding diffusion which would lead to a back transfer of separated charges. However, the tunnelling of electrons from the reduced acceptor A^- to the oxidized donor D^+ has still to be considered. This fundamental process cannot be avoided when dimensions get small.

The tunnelling across a monolayer can easily be demonstrated. Monolayer capacitors with fatty acids of different chain lengths d can be made by coating an aluminium layer evaporated on a glass plate with a fatty acid monolayer and evaporating a second aluminium layer on top. The current at a given voltage can be measured as a function of d . This current decreases exponentially with d [9]. This has recently been investigated for fatty acids with chains of 14 - 23 carbon atoms (C_{14} to C_{23}) [10, 11]. According to this exponential dependence the resistance of a monolayer is enormously dependent on the layer thickness. If we proceed from C_{14} to C_{23} the thickness increases by 30%. The resistance does not increase by 30%, as expected for an ohmic resistance, but by a factor of a million.

This exponential dependence of the current on the thickness of the barrier is typical for the quantum mechanical tunnelling effect. Owing to its wave nature an electron in the metal has a certain chance of penetrating the barrier (Fig. 4). The probability of finding the electron on the other side of the barrier decreases exponentially with the thickness d .

The slope of the straight line in the plot of the logarithm of the conductivity σ against d measures the effective height of the potential barrier above the Fermi level in the metal and a value of about 2 eV is obtained.

For tunnelling in monolayer assemblies sites must be available which match energetically. It can be concluded from several very different types of experiment [12 - 16] that there is a considerable density of interlayer tunnelling sites, while each monolayer acts as a tunnelling barrier. Multilayer capacitors can be investigated [14]; these are obtained by a similar method

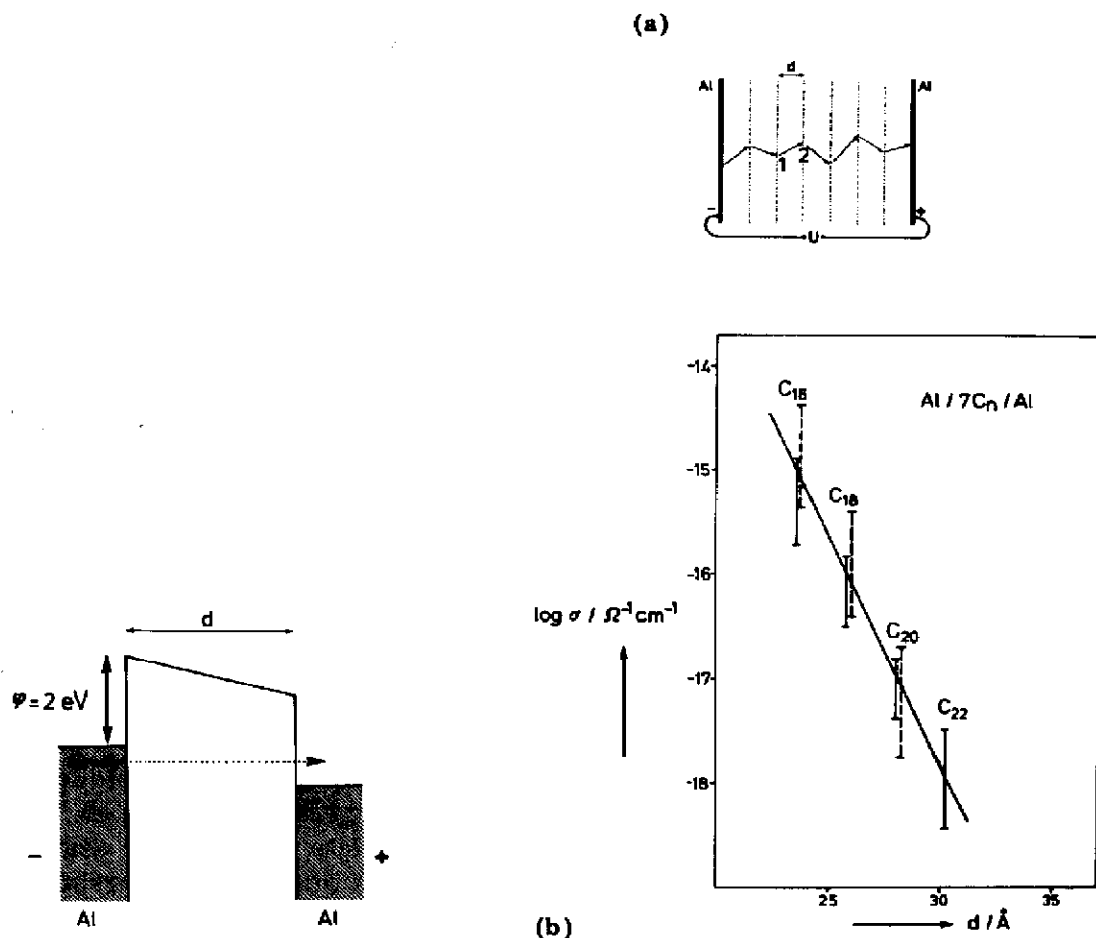


Fig. 4. The fatty acid salt monolayer (tunnelling barrier) between metal layers.

Fig. 5. Conduction in multilayers of fatty acid salts (chain length d) between aluminium electrodes. (a) Sample with seven monolayers: the electron tunnels through monolayers and is temporarily held at sites in the interlayers. (b) $\log \sigma$ against d for samples according to Fig. 5(a): broken bars, according to Sugi *et al.* [14]; full bars, according to Polymeropoulos (unpublished).

to monolayer capacitors, by depositing several fatty acid layers on top of each other (Fig. 5(a)). In Fig. 5(b) $\log \sigma$ is plotted against the thickness d per component monolayer for samples with seven monolayers sandwiched between aluminium electrodes. The conductance depends on d in the same manner as in single layer capacitors. It can be concluded that the electron jumps from one interlayer to the next (Fig. 5(a)) and the density of sites per interlayer obtained from the measured current is $N = 10^{15} \text{ eV}^{-1} \text{ cm}^{-2}$.

Let us consider an electron in some interlayer site 1 (Fig. 5(a)). The relaxation time τ to transfer this electron to some empty site 2 at the opposite side of the monolayer can be estimated. The tunnelling is only possible when the sites match energetically. In general this will not be the case and we shall have to wait for an appropriate thermal hit. The most probable tun-

nelling site of the electron will be determined by a compromise between optimal energetic fit and smallest possible tunnelling distance. In the case of poor energetic fit the density of interfacial states is high (this means that the tunnelling distance is small), but the probability of thermal activation to energetic coincidence between donor and acceptor state required for tunnelling is also small. In the case of good energetic fit the distance between donor and nearest acceptor fulfilling this requirement is large. As a result of this compromise the relation

$$\tau = Ae^{2\alpha d} \quad (1)$$

with

$$A = \tau_0 (2\alpha d)^{-3/2} \exp \{ (2\alpha/\pi NdkT)^{1/2} \} \quad N = 10^{15} \text{ eV}^{-1} \text{ cm}^{-2} \quad (2)$$

is obtained [15]; k is Boltzmann's constant, T the absolute temperature and $\tau_0 \approx 10^{-13}$ s. The slight temperature dependence to be expected from the relation ($\log \sigma$ plotted against $1/\sqrt{T}$ should be on a straight line) is actually observed in monolayer assemblies of different architecture [16, 17].

At room temperature A has typical values of the order of 10^{-13} s. If the potential barrier is described by a square well in a constant potential and the electron is described as moving in the x direction perpendicular to the barrier with momentum p_x , then

$$\alpha = (2m\phi)^{1/2} / \hbar \quad (3)$$

where m is the mass of the electron, $\hbar = h/2\pi$ and h is Planck's constant, and ϕ is the barrier height minus $p_x^2/2m$. In the case of localized states the situation is more complex but eqn. (3) is still a useful approximation. In this case ϕ can be identified with the energy to bring the electron from the state to the top of the barrier.

5. Maintenance of charge separation

We have considered a dye molecule D that has been excited; the electron has moved through a monolayer and is captured by some acceptor A (Fig. 3). The electron may now tunnel through the energy barrier given by the monolayer to some site in the interlayer where oxidized dye D^+ is positioned. From there it can easily return to D^+ . Using eqns. (1), (2) and (3) we may calculate the average tunnelling relaxation time and it is found that τ has the desired value of 1/100 s (see Section 3) for $\phi = 1$ eV at distance $d = 25$ Å, for $\phi = 0.6$ eV at distance $d = 32$ Å and for $\phi = 0.25$ eV at distance $d = 50$ Å.

If ΔE is the excitation energy of the vibronically relaxed excited molecule, the ratio $\phi/\Delta E$ of this energy is lost in the situation in Fig. 3. Therefore, the tendency in obtaining a useful device will be to choose ϕ as small as possible. However, if ϕ is smaller than some critical value, the electron will frequently jump over the barrier after a thermal collision. If we use as a rough estimate the condition $\nu_{\text{therm}} e^{-\phi/kT} = 100 \text{ s}^{-1}$ (where $\nu_{\text{therm}} \approx 10^{12} \text{ s}^{-1}$) the

critical value $\phi = 0.6$ eV is obtained. Therefore, we should be trying to construct devices with barriers near that limit, *i.e.* barriers with about $d = 30$ Å and $\phi = 0.7$ eV. Furthermore, the barrier should be carefully adjusted to the level of the electron in the vibronically relaxed excited dye D. The latter level should not be too high (otherwise we would waste energy) and it should not be too low (otherwise the electron would usually not jump over the barrier to the acceptor during the lifetime of the excited state of the dye and the vectorial charge transfer then would have a small quantum yield).

To approach the goal of constructing such a device it seems important to study possibilities of tunnelling by electrons from excited dyes through monolayers.

6. Electron transfer from excited dye D to acceptor A across a monolayer

We consider a monolayer of dye II mixed with a surplus of fatty acid. The dye is in monomeric form and is strongly fluorescing. The layer can be deposited on a glass slide and covered by a monolayer of the electron acceptor III. We consider three cases (Fig. 6): in case (1) the dye and electron acceptor are in direct contact; in case (2) they are separated by a fatty acid spacer layer sandwiched between dye and acceptor; in case (3) dye chromophore and acceptor are separated by the hydrocarbon substituents of both layers.

To obtain a sample corresponding to case (1) the dye layer is produced on a water surface by spreading dye II and fatty acid and applying a surface pressure of 30 dyn cm^{-1} (Fig. 7). The fatty acid (not shown symbolically) is important in obtaining a compact mixed layer with tightly packed straight hydrocarbon chains of dye and fatty acid. By dipping in a glass plate with a hydrophobic surface the monolayer is transferred to the plate. The chromophores are at the surface. Now the layer is removed from the water surface and a layer of the acceptor (again mixed with fatty acid) is produced at that surface. Then the sample is taken out and is covered with the layer.

To realize case (2) the plate is covered by the dye and then by a fatty acid layer of desired length in the usual manner. Now the layer is dipped in water without a surface layer, the water is then covered by an acceptor layer and the plate is taken out. This is a somewhat tricky step since rearrangements must be avoided. The plate is taken out by slowly lifting the sample in a horizontal position. The hydrophilic side of the film must be moderately hydrophilic and well adjusted in its composition to make the intended contact.

In case (3) a glass plate with hydrophilic surface is taken out when the water surface is covered by a monolayer of the dye and then the plate is dipped in water covered by a monolayer of the electron acceptor. Dye chromophore and acceptor are separated by the hydrocarbon portion of both molecules. The system is then covered with a fatty acid layer for stabilizing the structure.

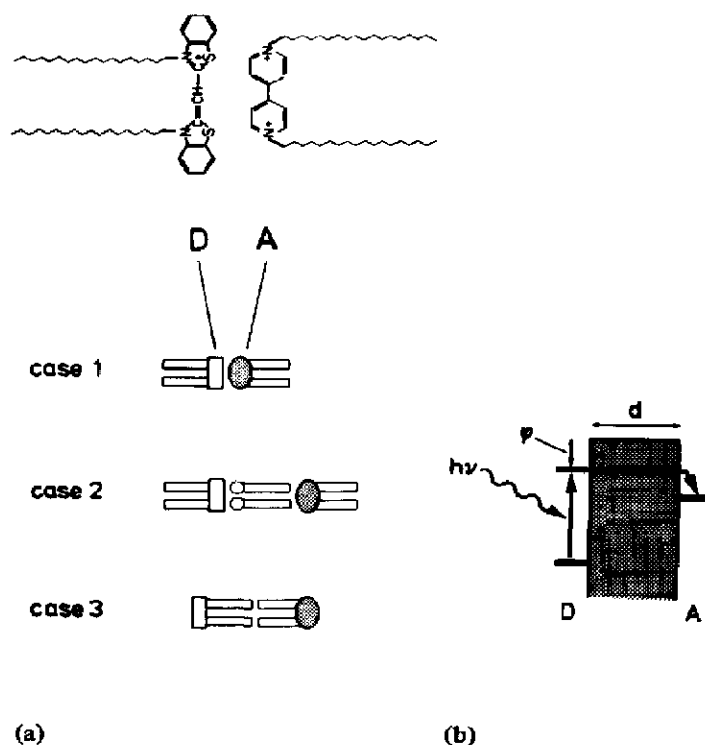


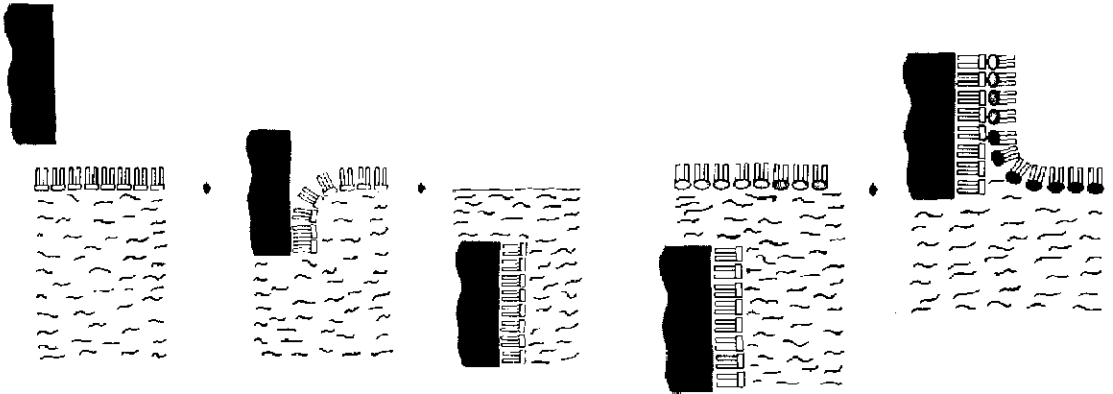
Fig. 6. Assembly of monolayers of dye D and electron acceptor A. (a) Arrangements: case 1, D and A at contact; case 2, D and A separated by one fatty acid salt monolayer; case 3, D and A separated by the hydrocarbon chain of both layers. (b) Potential barrier between D and A. The electron in D is excited, tunnels to some interlayer site near A and is trapped by A.

The plates are excited with violet light absorbed by the dye and their fluorescence is compared with the fluorescence of a plate where the acceptor is absent. This fluorescence is totally quenched in case (1), half quenched in case (2) if the C_{16} fatty acid is used as spacer layer and totally unquenched in case (3) [7].

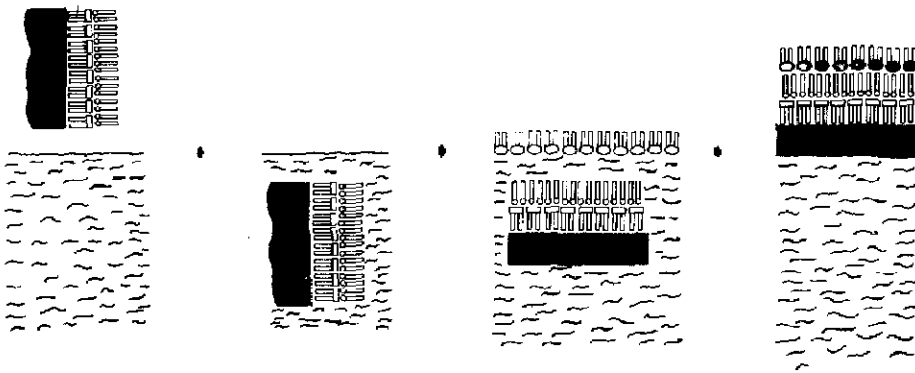
The radical cation of the acceptor is produced when the fluorescence is quenched [18]. This follows from the spectral change of the absorption when illuminating the sample, showing that the absorption spectrum of the reduced species agrees in all details with the absorption spectrum of the violet radical in solution as measured by Kosower and Gotter [19].

It is of particular interest to compare the fluorescence intensity I of samples with fatty acid spacer layers of different length. The ratio $(I_0 - I)/I$, where I_0 is the fluorescence intensity without acceptor, measures the rate of the electron transfer. This ratio is given by the ratio of the rate of electron transfer and rate of deactivation of the excited dye in the absence of the electron acceptor. If the electron transfer is purely tunnelling, the rate of electron transfer should be practically independent of temperature and decrease exponentially with increasing thickness d of spacer layer. Therefore, the logarithm of $(I_0 - I)/I$ plotted against d should form a straight line.

Case 1



Case 2



Case 3

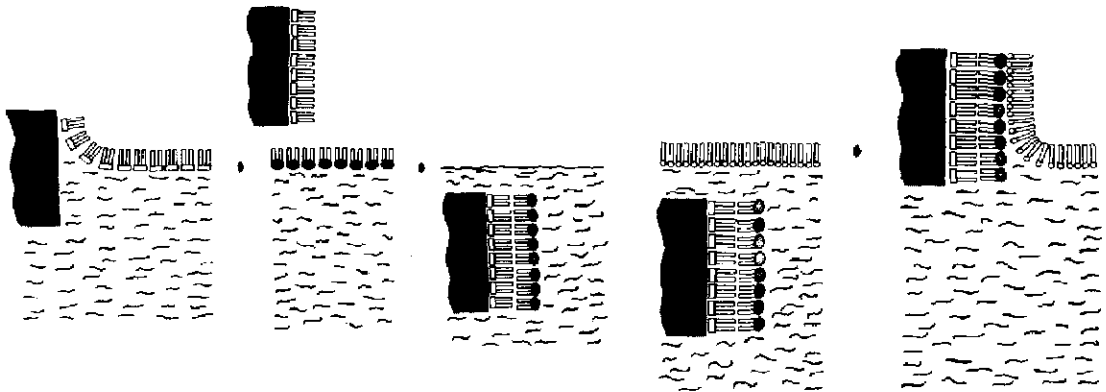


Fig. 7. Production of layer arrangements according to Fig. 6.

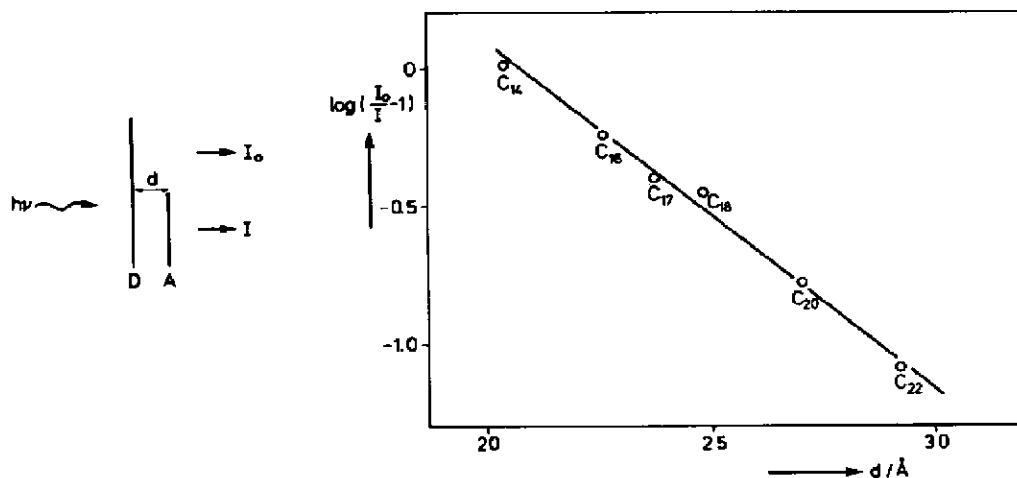


Fig. 8. Quenching of fluorescence of dye II (D) by electron acceptor III (A) in the arrangement of Fig. 2, case 2. $\log \{(I_0/I) - 1\}$ is plotted against the spacer layer thickness d for fatty acids with 14 - 22 C atoms.

Figure 8 shows that this is in fact the case for spacer layers with 14 - 22 C atoms [18]. The slope can be interpreted according to eqn. (2) with $\phi = 0.15$ eV for the barrier height indicated in Fig. 6.

In the case of pyrene as the dye and again bipyridinium cation as the electron acceptor, the linear relation of $\log \{(I_0 - I)/I\}$ against d could also be demonstrated [7]. In this case the standard technique of producing monolayer assemblies could be applied since the pyrene was bound to the methyl group at the end of a fatty acid chain while the bipyridinium cation III is at the hydrophilic head of the molecule. It is therefore easy in this case to separate chromophore and electron acceptor by a single monolayer of hydrocarbon chains.

7. Shifting an electron from source E to oxidized or excited dye D

In Section 5 we have considered the potential barrier on the right-hand side of D (Fig. 3), but there must be a higher barrier on the left to drive the electron to the right (Fig. 9). However, owing to this barrier the oxidized dye molecule is buried in the assembly and will not be available for a subsequent oxidation reaction. We need an electron source E to supply this electron. If this high barrier is sufficiently narrow, the electron should be able to tunnel through the barrier in a time short compared with the time of 1/100 s necessary for the dark reactions in a useful device (see Section 3) [21]. The dark reactions (oxidation reaction at E^+ and a reduction reaction at A^-) will need appropriate catalysers.

The shift of an electron from a source E to an excited dye D can be demonstrated easily in monolayer assemblies. Monolayers of E (dye IV) and D (dye V) are sandwiched according to Fig. 10, cases 1 and 2. Dye D is

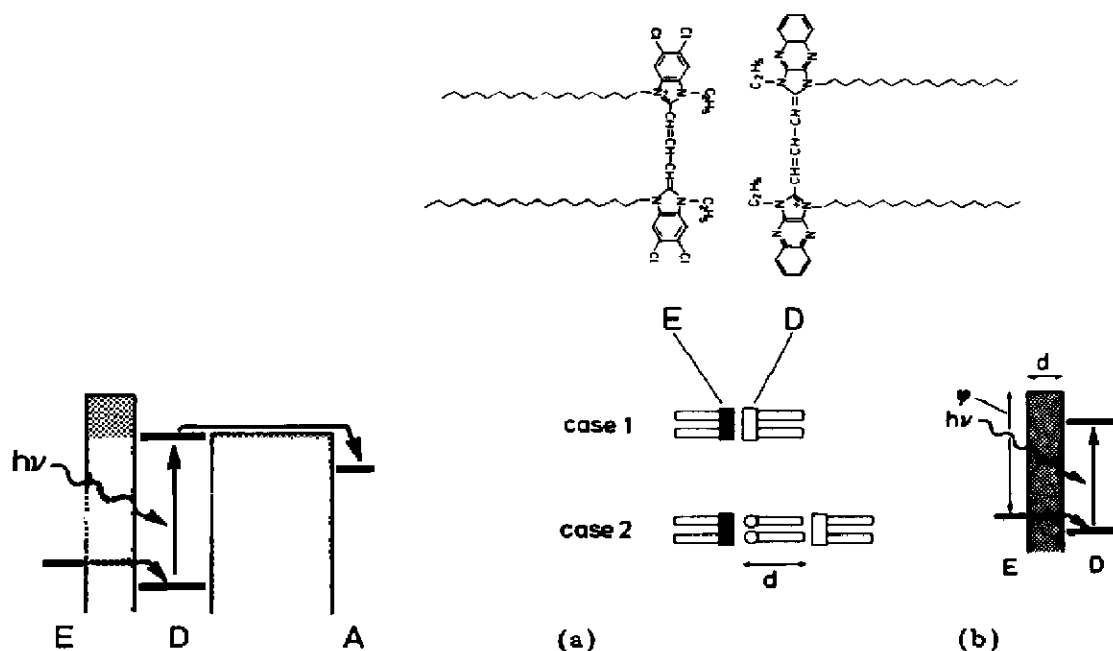


Fig. 9. Device for vectorial charge separation. D is excited by light. The low barrier conducts the electron which is then captured by A. The barrier is sufficiently broad to prevent the electron from back tunnelling. The high barrier is sufficiently narrow to allow an electron from source E to tunnel to oxidized dye D^+ . The conductance can occur by hopping between distinct intermediate states. Such states have been traced in bacterial photosynthesis [20].

Fig. 10. An assembly of monolayers of dye D and electron source E. (a) Arrangements: case 1, D and E at contact; case 2, D and E separated by one fatty acid salt monolayer. Quenching of fluorescence of D is observed only in case 1. (b) Potential barrier between E and D. An electron in D is excited. An electron is released from E and is trapped by excited dye D only if the barrier is sufficiently narrow.

excited in both cases. The fluorescence is compared with the fluorescence in the absence of electron source E. It is strongly quenched in case (1) and fully unquenched in case (2), where E and D are separated by a C_{16} fatty acid spacer layer.

This is to be expected: the potential ϕ is higher than in the case of the tunnelling to the acceptor (compare Figs. 6(b) and 10(b)); therefore α (in eqn. (3)) is larger and the tunnelling probability smaller. To reach a value of τ which is about equal to the lifetime of the excited state of the dye the barrier thickness should be about 6 Å (see eqns. (1) - (3)). This may be realized by a bulky saturated substituent as spacer instead of a fatty acid interlayer.

8. Lowering the energy barrier by a π -electron system

For realizing the lower barrier in Fig. 9 that should conduct the excited electron from photocatalyser D to electron acceptor A we may consider

using an unsaturated system. This should present a lower barrier than a hydrocarbon. We shall discuss some experiments demonstrating possibilities of constructing such molecular conducting elements. The first successful approach used a polythienyl interlayer [22]. Attempts then have been made to force a π -electron system into the hydrocarbon portion of a monolayer. In the case of dye VI the surface pressure, when diminishing the area, increases suddenly at about 35 \AA^2 [23]. This corresponds to the cross section of hydrocarbon plus chromophore. At larger areas the surface pressure is very small showing that the molecules are strongly attracting each other. They form macroscopic islands on the water surface which are seen spectroscopically. These islands are pushed together when the area is diminished and finally assemble to form the compact monolayer. The chromophores in the islands and in the compact monolayer are perpendicular to the water surface. This can be checked by measuring the absorption of light at inclined incidence, polarized first in the plane of incidence and then perpendicular to this plane. Going from dye VI to dye VII the chromophore is shortened and therefore the conformation in which the chromophore stays in the hydrocarbon part of the monolayer should be destabilized. In fact, the steep rise of the surface pressure when lowering the area is found at an area corresponding to the cross section of the hydrocarbon portion alone. This shows that the chromophores are squeezed out of the hydrocarbon portion when diminishing the surface area to form the compact monolayer. At large areas a two-dimensional gas is present and no island formation is observed. At an area of 100 \AA^2 per molecule a monolayer of the molecules in the flat-on position is reached. At a surface pressure of 8 dyn cm^{-1} a phase transition takes place. The molecules change from the flat-on position to the position where the chromophore chains are perpendicular to the water surface. Again, this transition can easily be traced by polarized absorption spectroscopy. These dyes can be used in different ways as molecular wires conducting electrons.

Another dye (VIII) devised for that purpose [23] is obtained by binding a chromophore to a fatty acid chain. Its molecular model interlocks with the model of cyanine dye IX and in fact it can be shown by the surface pressure area curve of a mixed monolayer of fatty acid with the two dyes that the cyanine dye prevents the azo dye from being squeezed out of the monolayer at high surface pressures, demonstrating the interaction of the two dyes [17].

A single monolayer containing this pair of dyes can be sandwiched between fatty acid monolayers and metal electrodes. A voltage is applied and the sample is then illuminated with light absorbed by the cyanine dye. The conduction of the excited electron of cyanine dye IX through the π -electron system of dye VIII can be studied. This arrangement was chosen to check this functional element given by the two dyes for a possible later use as a component in more complex systems.

For a comparison we consider first the system in which the conducting element is missing. A single monolayer containing the cyanine dye is sandwiched between fatty acid layers and electrodes. Figure 11(a) gives the

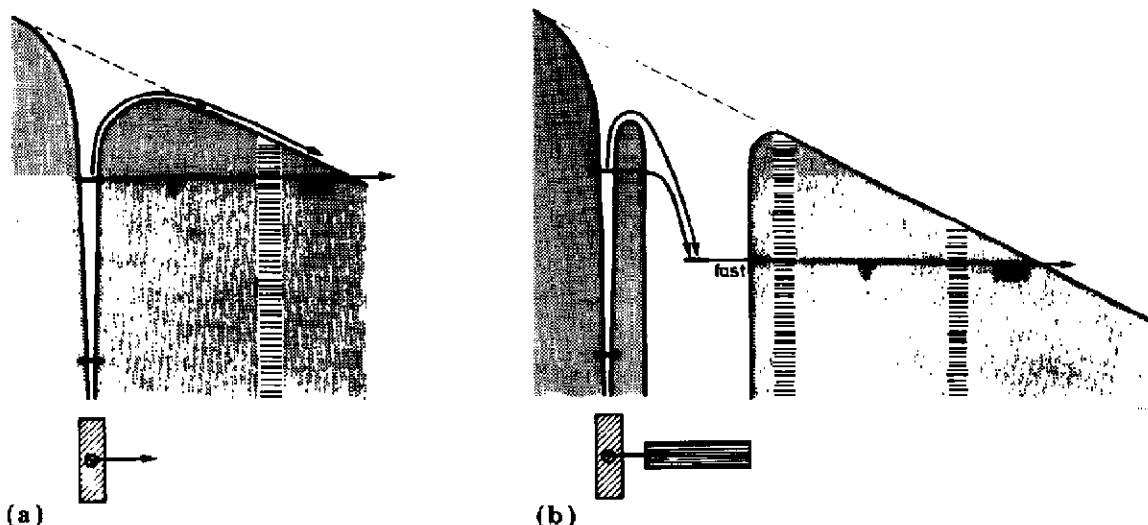


Fig. 11. A monolayer containing a light-sensitive unit is sandwiched between fatty acid salt monolayers and aluminium electrodes: potential profile when the electrode on the right is positively biased. (a) Cyanine dye IX: dye IX is excited and an electron can jump over the potential barrier or tunnel to an interlayer state and subsequently move to the electrode in a fast process. (b) Functional unit of interlocking molecules VIII and IX: dye IX is excited and the electron can proceed to VIII, tunnel to an interlayer state and subsequently move to the electrode in a fast process. The photocurrent is 10 times larger in (b) than in (a) since the excited electron of IX has to cross or surmount a much lower potential barrier and is then trapped in VIII. The tunnelling rate of the trapped electron through the high barrier on the right is sufficiently large to increase the photocurrent by this factor of 10.

potential curve when the electrode on the right is positively biased. The electron from the cyanine dye is imagined to move in the direction of the positively biased electrode. It is in the Coulomb field of the rest charge in the molecule and in the constant field of the applied voltage. If we excite the dye the electron may fall back to the ground state or it may tunnel to some site in the next interlayer, and then jump to the electrode in a fast process, or it may hop over the barrier by thermal excitation.

This model can be checked experimentally in many ways [17]. At low temperature the contribution from thermal excitation can be neglected; at high temperature this is the predominant part. The temperature dependence in the high temperature mode gives a value for the activation energy which agrees with the value obtained from the energetic position of the excited dye level and the barrier height of the hydrocarbon portion, and quite independently this same value is obtained from the measured tunnelling current at low temperature.

The voltage dependence of the current can be measured and in both temperature modes the logarithm of the current density is found to be a linear function of the square root of the applied voltage. It can be concluded from the model that this should be the case. The potential barrier height is given by the sum of the Coulomb attraction of the electron to the dye mole-

cule and the applied field. This height decreases in proportion to the square root of the applied field.

When introducing the conducting element a totally different behaviour is expected and observed. The potential is given in Fig. 11(b). The electron imagined to move from the cyanine to the right must surmount only a small barrier, then move along the chain of the conducting azo dye and finally enter the hydrocarbon portion of the next monolayer. If the dye is excited the electron may fall back into the ground state, tunnel through the narrow barrier to the conducting molecule or jump over this barrier. In a secondary process it can then tunnel through the next monolayer to some interlayer site and proceed to the electrode in a fast process.

The photocurrent is an order of magnitude larger than that without the conducting molecule. Again, a low temperature mode and a high temperature mode can be distinguished and a reasonable and self-consistent value is obtained for the height of the narrow barrier (0.25 eV). The voltage dependence of the photocurrent which is determined by the efficiency of the tunnelling through the barrier on the right should be quite different in this case compared with the case without the conducting molecule. The logarithm of the current density plotted against the applied voltage should be on a straight line, and this is actually observed. This dependence is due to the fact that the effective height of the barrier on the right is lowered in proportion to the applied voltage. This is different from the case of Fig. 11(a) where the electron is moved perpendicular to the chromophore chain of the cyanine dye while in the case of Fig. 11(b) it is moved along the chain of the azo dye. A convincing way to test the model is by varying the thickness of the critical monolayer that represents the potential barrier on the right in Fig. 11(b). The fatty acids with 14, 16 and 20 carbon atoms in the chain were introduced, and Fig. 12 gives the plot of the logarithm of current density against applied voltage. The lines are predicted, the points experimental. The variation of any other fatty acid layer is of no detectable influence.

The results demonstrate that such molecular wires can be handled experimentally and theoretically very well. This should stimulate thoughts about getting more adequate systems. It is hoped that the different components of these designed monolayer assemblies can be adjusted to each other in such a way that an efficient electron pump results. The next step then will

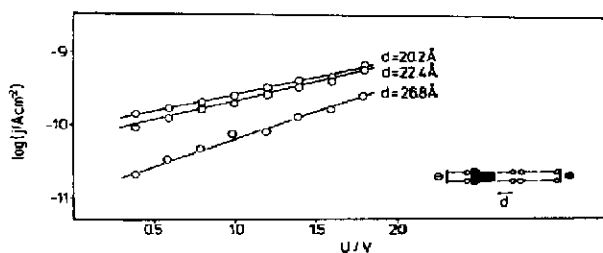


Fig. 12. Logarithm of photocurrent density against distance d for the arrangement of Fig. 11(b): lines, theory; circles, experiment.

be to introduce catalysers for the reduction and oxidation processes.

It might be advisable to use the deposition technique to obtain the desired functional systems and then to proceed to try and get the same functional systems by more self-assembling techniques. The self-assembly by adsorption at solid surfaces using intermolecular as well as chemical binding of components to the substructures appears to be particularly promising for future developments. It seems not to be hopeless that useful devices for solar energy conversion can be obtained in this way.

9. Energy transfer and electron transfer in the sensitization of photo processes

Monolayer assembly techniques are also useful in developing more conventional methods of solar energy conversion. Studies on electron tunnelling and energy transfer are important in understanding the dye sensitization of photographic and photogalvanic processes. A dye monolayer at the surface of a semiconductor such as silver bromide is illuminated with visible light (Fig. 13(a)). A dye molecule is excited and an electron is injected into the conduction band of the semiconductor. A latent image is produced which can be photographically developed. According to Section 6 the tunnelling from an excited cyanine dye should be negligible if the dye molecule is separated from the semiconductor by two spacer layers of fatty acid. However, the energy transfer to some acceptor site at the surface of the semiconductor should still be possible. In the past Möbius has demonstrated dye sensitization in this case in many different experimental arrangements [24]. In a recent experiment in cooperation with Steiger [25] a mixed layer of dye IX in a surplus of electron acceptor III was first deposited on a silver bromide layer, then the sample was illuminated with light of 570 nm wavelength absorbed by the dye and photographically developed (Fig. 14, upper section). The dye did not sensitize at all. This was not surprising, since the electron released by the excited dye should be immediately captured by the

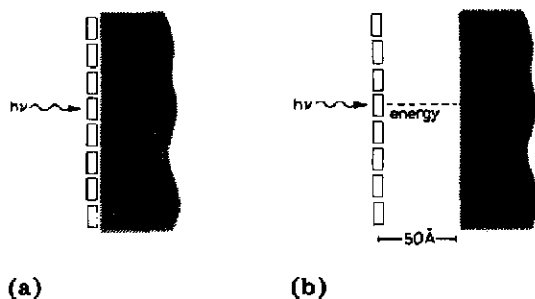


Fig. 13. Sensitization of the photographic process. Discrimination between electron injection and energy transfer mechanisms. Electron injection from excited dye to semiconductor occurs in case (a) and not in case (b); energy transfer to surface states in AgBr occurs in case (a) and case (b).

acceptor surrounding the dye. Now the silver bromide was covered with a monolayer of electron acceptor III, and then by two monolayers of the dye diluted with fatty acid to such an extent that the surface concentration was the same as in the first case (Fig. 14, lower section). After exciting with 570 nm light and developing we should expect a photographic picture only if energy transfer to assumed surface states in AgBr is possible. Such a picture was actually observed. The dye, which is ineffective at the surface of the semiconductor owing to the electron acceptor, sensitizes the photographic process when it is fixed at a small distance (50 Å).

The result demonstrates that the sensitization by the dye at a distance cannot be explained as an artefact caused by traces of dye molecules reaching the semiconductor surface by diffusion through the layer or by defects in the spacer layer. Dye molecules that might come near the surface of silver bromide because of imperfections in the layer assembly would be inefficient. They would not sensitize the photographic process, as in the part of the sample where the dye was purposely mixed with the acceptor layer (upper section in Fig. 14).

It is important for the process to fix the dye at about 50 Å from the AgBr surface. At a larger distance the energy transfer would no longer be effective; at a smaller distance the electron transfer to the acceptor would compete with sensitization. This demonstrates the necessity of a planned molecular architecture to reach certain distinct functionalities.

The silver bromide layer can be coated with a monolayer of dye with fatty acid or the dye can be positioned at 50 Å distance. In this case, which

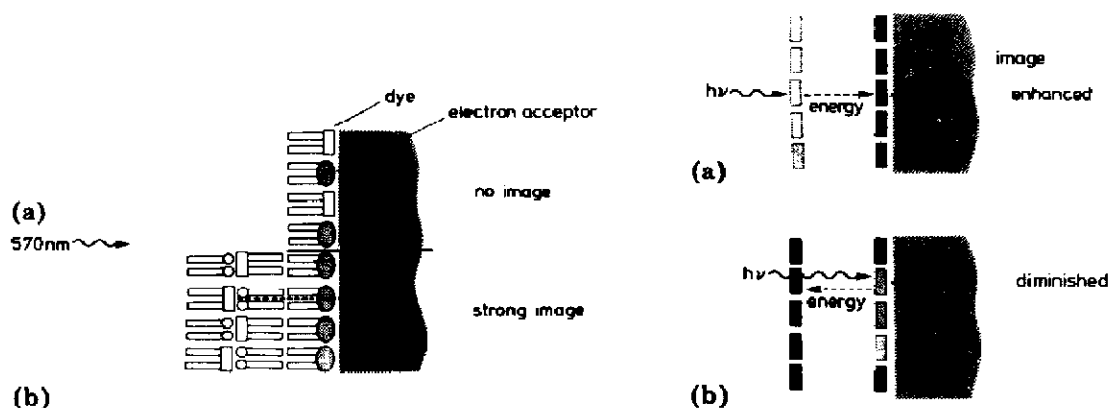


Fig. 14. Monolayer assembly on AgBr: the sample is illuminated and photographically developed. (a) Mixed monolayer of dye IX and electron acceptor III on AgBr: no image. The electron from the excited dye is captured by the acceptor. (b) Monolayer of electron acceptor III on AgBr, superimposed by a double layer containing dye IX: strong image. This is evidence for the sensitization of the photographic process by energy transfer.

Fig. 15. Sensitization of photographic or photogalvanic process by dye at the surface of a semiconductor. A second dye at 50 Å may enhance sensitization (Fig. 15(a), second dye energy donor) or reduce sensitization (Fig. 15(b), second dye energy acceptor). The dyes are chosen such that the fluorescence band of the energy donor (hatched rectangles) overlaps with the absorption band of the energy acceptor (full rectangles).

is quite different from the case considered above, the sensitizing action at contact is 120 times larger than that at 50 Å. This demonstrates that the main contribution to the sensitization is electron injection. In the case of Fig. 14, this contribution was totally suppressed by the electron acceptor and the smaller contribution by energy transfer could then easily be studied.

The contribution by energy transfer depends strongly on the nature of the photographic material. In the present case great efforts were made in the Ciba-Geigy Laboratories to obtain impurity free silver bromide samples. In earlier experiments [24] with other materials we found energy transfer to be the essential mechanism in dye sensitization.

10. Assisted sensitization of the photographic and photogalvanic processes

An important limitation in the sensitivity of a photographic or photogalvanic material is given by the fact that only a single monolayer of dye sensitizes the photographic process and an important question is: how can we increase the sensitivity to values above the limit given by the absorption of the dye monolayer? The first experiment to overstep this limit was carried out a few years ago by Möbius (see ref. 26). The sensitizing dye at the surface of the silver bromide was combined with the corresponding energy donor separated by a spacer layer (Fig. 15(a)). When illuminated with light in the absorption region of the energy donor the energy acceptor at the silver bromide surface is excited by energy transfer and an enhanced sensitization of the photographic process is reached. The opposite effect is obtained when combining the dye at the surface with an energy acceptor separated by a spacer layer (Fig. 15(b)). In this case the second dye acts as a competing deactivation channel and the sensitization of the photographic process is diminished. This effect was also realized by Möbius [24].

Both experiments have been carried out recently in our group in an alternative form [27]. Indium oxide doped with tin was used instead of silver bromide as semiconductor and the number of electrons injected into the conduction band was measured by measuring the photocurrent in a photogalvanic arrangement instead of producing a photographic picture. The oxacyanine I was used as energy donor and the thiacyanine II as energy acceptor. If the energy acceptor is at the surface of the semiconductor and the energy donor at 50 Å, then light can be absorbed by the donor and transmitted to the acceptor and a photocurrent is obtained. If the two dyes are exchanged and the energy donor, now at the semiconductor, is excited, it is partially deactivated by energy transfer to the acceptor and therefore in this case the second dye reduces the sensitizing action of the dye at the semiconductor surface.

If only one of the two dyes is present and is directly at the semiconductor surface, it sensitizes the photocurrent strongly (quantum yield 0.7). Practically no spectral sensitization is reached when the dye is fixed at a distance of 50 Å from the semiconductor surface. Therefore the situation is similar to that found in Section 9 for silver bromide.

The fluorescence of the energy donor can be measured. It reflects a diminished energy transfer to the acceptor. An energy acceptor molecule in the situation of Fig. 15(a) that has injected its electron into the semiconductor does not act as energy acceptor any more and the fluorescence of the energy donor is increased. Therefore the fluorescence of the energy donor measures the concentration of the oxidized energy acceptor. The concentration of the oxidized energy acceptor increases as the electrons are pumped away by applying a positive bias to the semiconductor electrode, and the concentration of the oxidized dye decreases if the dye is restored by adding allyl thiourea as electron source.

11. Summarizing remarks

The purpose of this discussion was to show that monolayer assemblies are quite well defined in their architecture and that this architecture can be manipulated in many ways. Organizates obtained by self-assembly would be of great interest and it seems essential for future developments that pure substances will be considered more as intermediates and that the planned synthesis of organizates will be seen more as the aim of synthetic efforts.

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