ELECTRON TRANSFER IN MONOLAYER ASSEMBLIES

Hans Kuhn

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

Abstract - Monolayer assemblies are rigid structures of speci-
fically designed architecture. Processes can be studied depen-
ding on the relative position of several molecules which in-
teract with each other to form a cooperative system. Appro-
priately constructed monolayer assemblies are useful to in-
vestigate light induced vectorial charge separation. A number
of different arrangements to study electron motions are
given, such as the transfer of an electron from an excited
dye molecule to an acceptor across the hydrocarbon portion of
a monolayer, from an electron source to an excited dye mole-
cule, or from an excited dye aggregate to an acceptor. Attempts
which have been made to model potential profiles with unsa-
turated chains are discussed. They are of interest for an
efficient charge transfer from an excited dye to an electron
acceptor.

1) INTRODUCTION

In monolayers molecules are oriented, and reacting groups can arrange speci-
fically (Ref. 1). Very high local concentration can be achieved. Chemical and
photochemical reactions in such systems are of great interest and important
and promising results have been obtained by taking advantage of these parti-
cular properties of monolayers (Refs. 2, 3).

Another possibility in using monolayers is the planned synthesis of organized
aggregates of molecules (molecular organizates) (Ref. 4). An organizate is a
cooperative system of molecules acting as a functional unit.

In solution the aggregation of molecules to designed assemblies is difficult
to achieve (very particular molecules are required, which interlock and bind
by intermolecular forces). The task of designing organizates is simplified
by using molecules that orient at an interface.

Assemblies of designed architecture can be obtained by spreading different
sorts of appropriate molecules on a water surface and pushing them together.The
monolayer formation can be manipulated by the way this is done. Monolayers
at the water surface can be transferred to a solid surface. Layers of diffe-
rent molecular architecture can be deposited on top of each other in a planned
sequence. Monolayers or packages of monolayers can be separated from a solid
subphase and transferred in various ways to another solid (Fig. 1). The ac-
curacy of these manipulations at the molecular level can be checked easily by
absorption and fluorescence spectroscopic techniques and in the past these
techniques have been used to introduce and develop various methods of sepa-
rating and joining assemblies (Refs. 4, 5).

Monolayer assemblies are of interest for studying photoinduced charge sepa-
ration. By the well defined and rigid structure of a designed assembly a
vectorial electron transport and fixation of the separated charges should be
possible, since no appreciable diffusion leading to the back reaction should
occur. In such a case the tunneling of electrons as the fundamental quantum
mechanical effect at molecular dimensions should be a limitation and there-
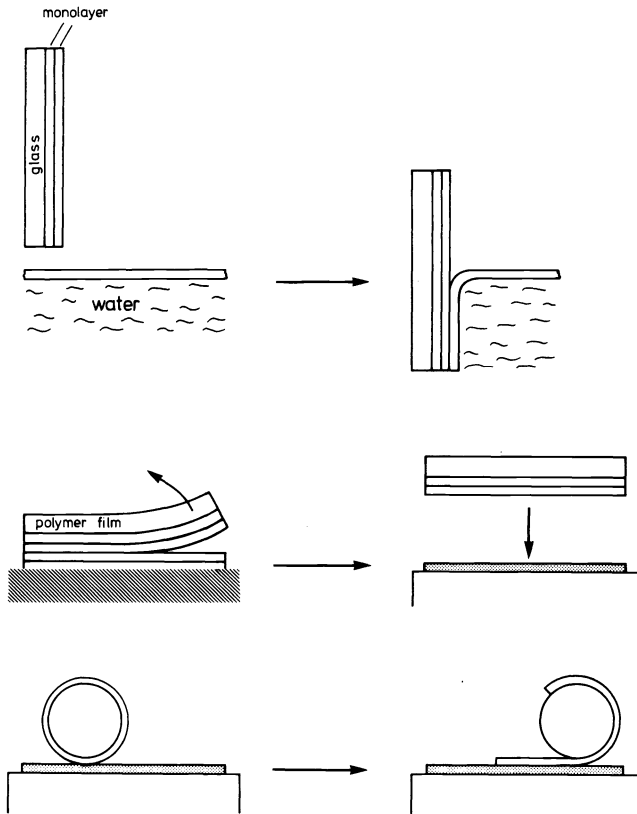fore we shall study this effect first in simple and then in more complex
assemblies.

Fig. 1 Some possibilies to make and manipulate monolayer
assemblies.

The simple layers to be discussed first are obtained by picking up a fatty
acid monolayer from the water surface and by adsorption from solution. The
study of adsorbed monolayers is of interest for future developments. On the
one hand, proposed organizates obtained by adsorption at a solid surface from
solution will require more specificity in the different sorts of interlocking
molecules than organizates obtained by spreading at the water surface and di-
minishing the area adequately. On the other hand the adsorption process would
be a much easier formation procedure, and this simplicity would be important
for possible applications.

It is known since many years that monolayers of fatty acids can be obtained
by adsorption from solution (Ref. 6). For judging the possibility to use this
method for producing organized assemblies it is important to check the quali-
ty of adsorbed layers (Refs. 7, 8). Measuring the tunneling current is an ex-
tremely sensitive test for imperfections.

        2) TUNNELING OF ELECTRONS IN MONOLAYERS AND MULTILAYERS

Tunneling across monolayers

The tunneling of an electron across a dielectric is caused by the fact that
an electron which hits a potential barrier and has not enough energy to jump
over the barrier has a certain chance to penetrate this barrier (Fig. 2a).
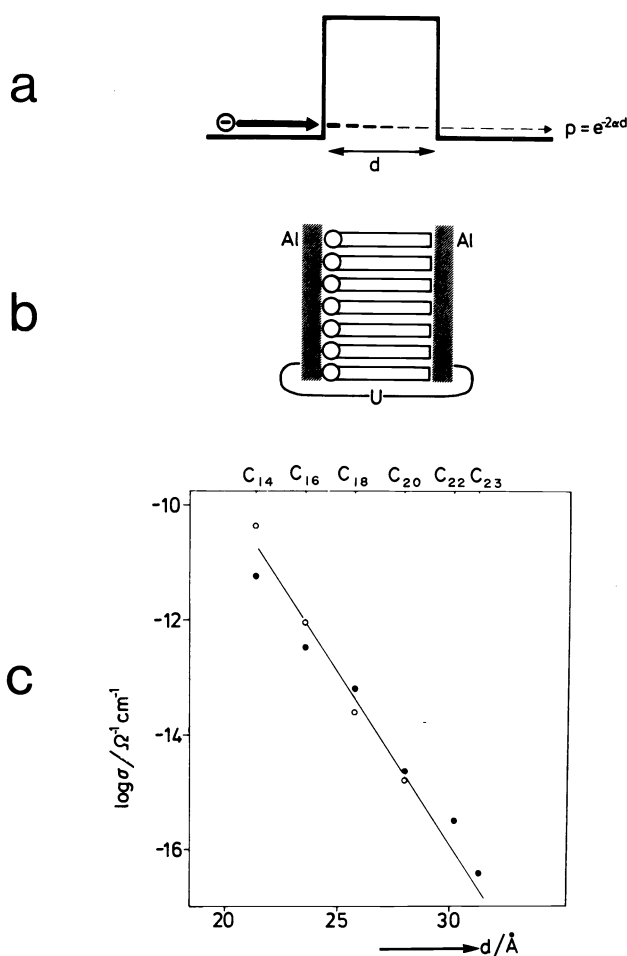
Fig. 2.   a) Electron tunneling across potential barrier
          b) Monolayer between layers of aluminum: tunneling
       barrier for metallic conduction electrons
          c) log σ against d. C_n fatty acid with n carbon atoms.
       circles: monolayer deposited from water surface
       points: monolayer adsorbed

This effect does not require pores in the material and it cannot be explained
in classical terms. The electron must be considered in a certain sense as a
wave which extends into the forbidden region, and this means that there is a
certain chance to find the electron as a particle in that region. The proba-
bility p to penetrate a rectangular barrier decreases exponentially with the
thickness d of the barrier. It is proportional to $e^{-2\alpha d}$,

$$\alpha = \sqrt{2m\gamma}/\hbar \tag{1}$$

$\hbar = h/2\pi$ and h is Planck's constant, m is the mass of the electron, γ the
height of the potential minus $p_x^2/2m$ where p_x is the momentum of the electron
in the x direction perpendicular to the barrier.

For studying the tunneling effect an aluminum layer on a glass plate is co-
vered by a fatty acid layer and a second aluminum layer is evaporated on top
(Fig. 2b). A voltage is applied and the current is measured. It can be demon-
strated that the current is purely due to tunneling. The thickness of the po-
tential barrier can be changed by changing the chain length d of the fatty
acid. According to the tunneling theory the current at a given voltage should
decrease exponentially with increasing chain length. In Fig. 2c the logarithm

of the conductivity σ is plotted against d for fatty acids with 14 to 23 carbon atoms (Refs. 8, 9, 10). In this range the resistance increases by a factor of a million, while the thickness of the dielectric increases by 30 %. This exponential dependence indicates tunneling. The circles correspond to monolayers transferred from water surface, the points to layers obtained by adsorption from a solution in n hexadecane. The slope of the straight line gives the effective height φ of the potential barrier above the Fermi level in aluminum. The value φ = 2.0 eV is obtained and this means that the electron in the dielectric is effectively 2.2 eV below vacuum.

Perfluorinated fatty acids with 7 to 10 carbon atoms can be adsorbed instead of fatty acids and similar capacitors can be made (Ref. 8). In the plot of log σ against d the points are on a straight line with larger slope than in the case of fatty acids, corresponding to a larger value of φ.

The current is almost independent on temperature in a wide range. This must be expected from simple tunneling theory, since in general the contribution by thermally excited electrons is negligible. However, at an applied voltage equals φ/e the thermally excited electrons have a shorter tunneling path than all others and contribute relatively more to the current than at lower and higher applied voltages (Fig. 3, inset). In this particular case the current then should increase with increasing temperature.
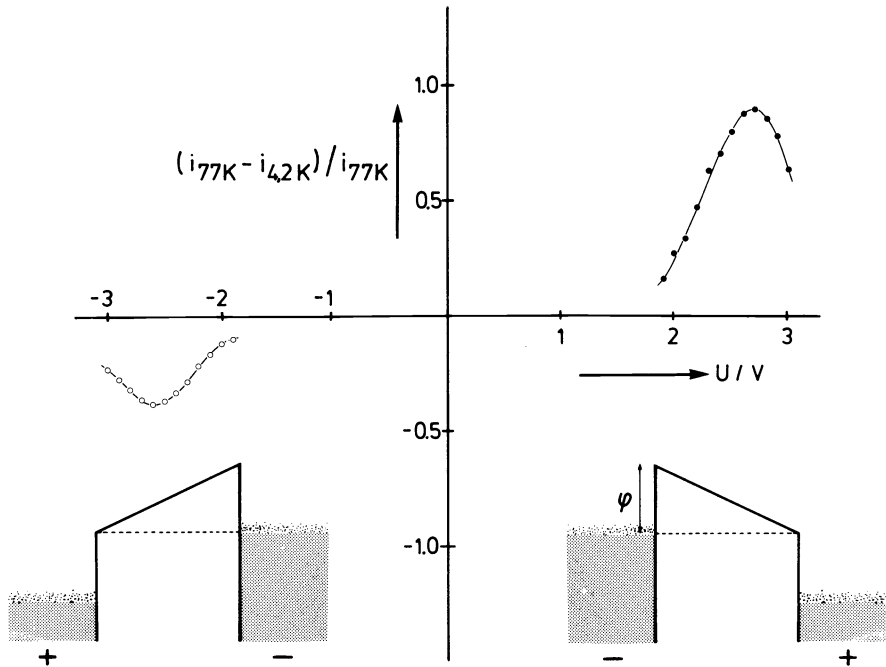

Fig. 3. $(i_{77K}-i_{4.2K})/i_{77K}$ against applied voltage U. The thermally excited electrons in the metal contribute to the currents significantly at U $\simeq$ φ/e (see insets).

This effect is observed (Ref. 8) when plotting the ratio (difference between current at 77 K and current at 4.2 K)/(current at 77 K) against the applied voltage. The ratio has a pronounced maximum at U $\simeq$ φ/e and the corresponding minimum is seen at reversed applied voltage. The approximate agreement between the barrier heights obtaind in this way and from the slope in Fig. 2c is evidence for tunneling. The φ value from Fig. 3 is somewhat higher than the value from Fig. 2c. This can be explained if image forces are considered (Ref. 8).

The capacitors used in this experiment were made with an adsorbed monolayer. In this case bias voltages up to 4 V can be applied without any signs of break-through, while discharges in the case of layers transferred from the

water surface occur at about 1.5 V. This indicates that adsorbed layers are free of larger defects like holes and crackes. The results demonstrate that compact and ordered monolayers can be made by adsorption, and adsorption therefore appears as promising for monolayer assembly construction.

Another test for electron tunneling is the typical deviation of the current at small applied voltages at low temperatures when an electrode metal becomes superconducting. At higher temperatures, when the metal is not superconducting the current is proportional to the voltage at small applied voltages. In the superconducting region a band gap appears in the metal. Less states then are available for tunneling and a distinct voltage must be applied to bring filled states of one electrode to energetic match with empty states of the other electrode. This expected deviation is indeed observed (Ref. 11) (Fig.4).
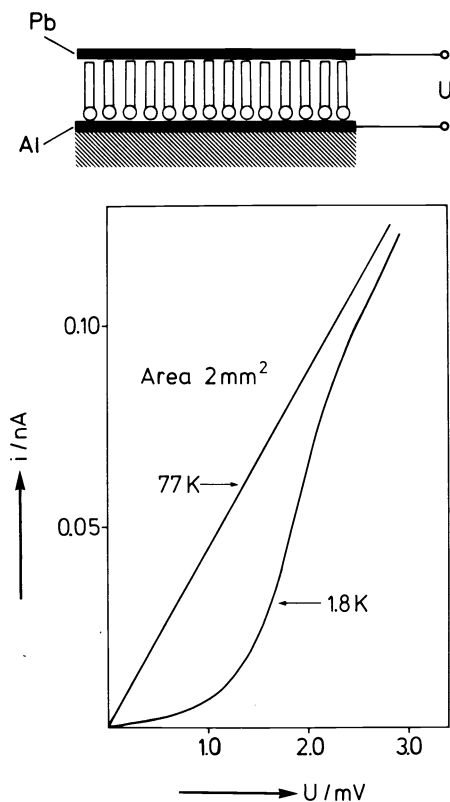

Fig. 4. Monolayer capacitor with Al as bottom electrode and Pb as top electrode. Current i against applied voltage U, for 77 K and 1.8 K. Lead is superconducting below 7.19 K. At O K at an applied voltage below 1.3 mV the electrons cannot tunnel since no states are available in the superconductor. This leads to a corresponding deviation in the superconducting region (Ref. 12). The observed deviation from proportionality at 1.8 K is strong evidence for tunneling.

Tunneling in Multilayers

An evaporated aluminum layer is covered by fatty acid layers and by mixed monolayers of a dye and fatty acid and the system is covered by an evaporated aluminum layer (Fig. 5a). The dye is excited by stationary illumination in order to produce charge carriers. An alternating voltage is applied. The frequency is varied. At a certain frequency an increment in conductance is observed. The result can be interpreted by assuming that the electrons are hopping between sites at interlayers by tunneling through single layers (Fig. 5b). An increment in current then should be observed when the time per cycle is similar to the most probable tunneling relaxation time τ. In this case the
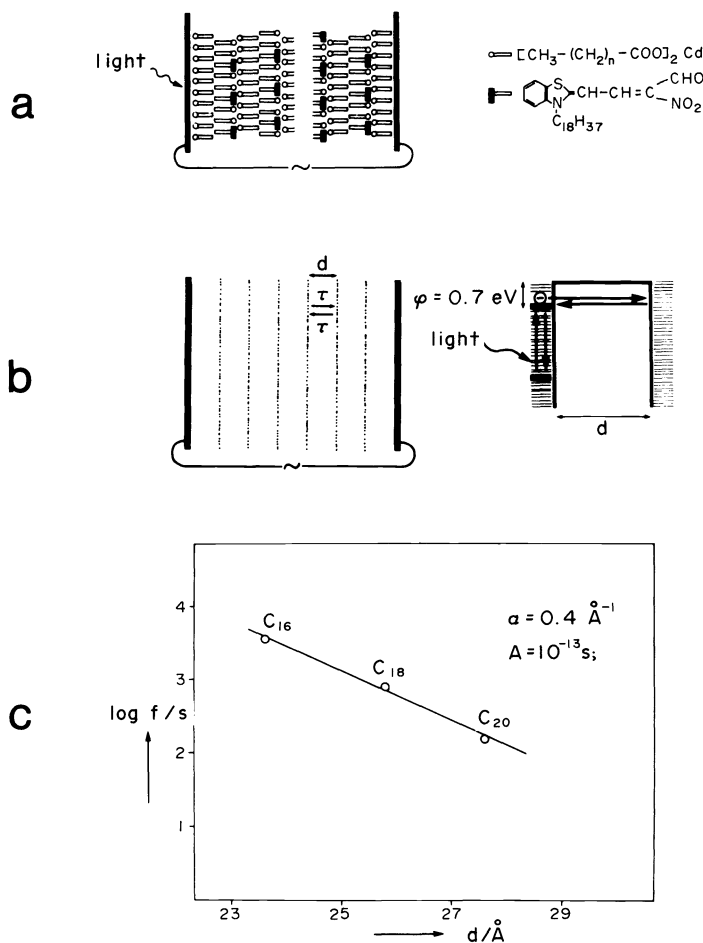
Fig. 5. a) a. c. voltage applied at capacitor with 15 dye +
fatty acid monolayers sandwiched between aluminium layers.
Stationary illumination.
b) electron tunneling between interlayer sites at the level of
the excited dye.
c) log f against d (f frequency of current increment, d thick-
ness per monolayer. C_n fatty acid with n carbon atoms. The li-
near dependence is evidence for tunneling between interlayer
sites.

charge moved by tunneling is largest. The tunneling relaxation time should be
about

$$\tau = A\, e^{2\alpha d} \tag{2}$$

where A is estimated to be about 10^{-12} to 10^{-13} s. The characteristic fre-
quency f depends strongly on the length of the fatty acid chain (3000 Hz and
200 Hz for the fatty acid with 16 and 20 C-atoms respectively) and the expec-
ted linear dependence of the logarithm of the frequency against chain length
d is indeed observed (Fig. 5c) (Ref. 13). From slope and y intercept the
values $\alpha = 0.4\ \text{\AA}^{-1}$ (corresponding to $\varphi = 0.7$ eV according to equation (1)),
$A = 10^{-13}$ s are obtained which are reasonable.

In the present case, different to the case of Fig. 2, the electron tunnels
between localized states and then φ can be considered as the energy to bring
the electron from its localized state to the top of the potential barrier.
This can be immediately seen for a H-atom like site. In this case the wave

function at distance r: $\psi \sim e^{-r/a_o}$ and therefore $\alpha = 1/a_o$. The Bohr radius $a_o = \hbar^2/me^2$ can be expressed in terms of the ionization energy $I = e^2/2a_o$. We find $Ia_o = \hbar^2/2ma_o$ and then $\alpha = \frac{1}{a_o} = \sqrt{2mI}/\hbar$. At large distances ($r \gg a_o$) we can identify I with φ .

The difference between the above value $\varphi = 0.7$ eV and the value $\varphi = 2$ eV obtained in the case of Fig. 2c is due to the fact that in the present case the electrons are continuously lifted to higher levels by the illuminating light and continuously falling back (Fig. 5b). The electrons at the level of the excited dye determine the tunneling current. They have to tunnel through a lower barrier than the electrons in the case considered first, which where at levels near the Fermi level of aluminum.

These experiments indicate, that the conduction in multilayers should be due to tunneling between sites at interlayers. This can be checked by measuring the dc-current in a capacitor obtained by covering an evaporated aluminum layer with a given number of fatty acid monolayers and an aluminum top layer. The conductivity decreases exponentially with the length of the fatty acid, exactly as in the case of the single monolayer (Fig. 2), and the barrier height obtained from the slope in the plot of log σ against d (thickness per monolayer) is again $\varphi = 2$ eV (Ref. 14). Therefore, the electron simply hopps from interlayer to interlayer using sites near the Fermi level.

3) TRANSFER OF ELECTRONS FROM EXCITED DYE TO ACCEPTOR FIXED AT DIFFERENT DISTANCES

We consider a fluorescent dye molecule (electron donor D) separated from an electron acceptor A (Fig. 6a) by a fatty acid spacer layer (thickness d). The dye is excited. It will usually emit a fluorescence quantum or thermally deactivate, and there is a certain probability that the excited electron will tunnel to the acceptor.
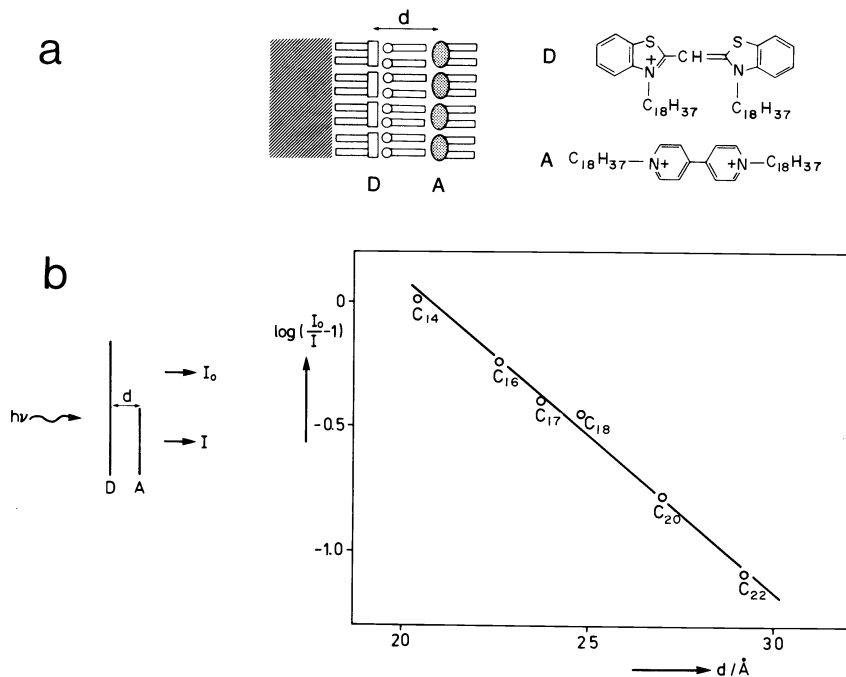

Fig. 6. Monolayer assembly of electron donor D and electron acceptor A at distance d. Quenching of fluorescence of D by A a) Assembly architecture. D and A are diluted with fatty acid (not shown symbolically).
b) log ($\frac{I_o}{I}$ -1) against d. The linear relation is evidence for the tunneling mechanism of electron transfer

The barrier height can be estimated, and the value $\psi = 0.2$ eV seems not un-
reasonable. For a rough estimate we may assume that A is decreased by a fac-
tor of 10 by the presence of the electron acceptor which produces additional
interlayer sites. Then $\tau = 0.1$ ns for d = 20 Å. This is shorter than the
lifetime of the excited state which is about 1 ns. Therefore, we may expect
that the fluorescence should be quenched by the tunneling to the acceptor.
The ratio $(I_o-I)/I$ where I is the fluorescence intensity and I_o the fluor-
escence intensity of a corresponding sample without acceptor, measures the
ratio:rate of electron transfer devided by rate of deactivation in the absence
of the electron acceptor. If electron transfer is purely tunneling the rate
should be practically independent on temperature and decrease exponentially
with increasing thickness d of the spacer layer. This is indeed observed
(Ref. 15). In Fig. 6b log $[(I_o-I)/I]$ is plotted against d for spacer layers
with 14 to 22 carbon atoms. The points are on a straight line. Slope and y
intercept can be interpreted with the values $\alpha = 0.2$ Å^{-1} ($\psi = 0.15$ eV)
$A = 10^{-14}$ s (eq. (2)).

It can be checked that the radical is actually produced when the fluorescence
is quenched. 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 violen ra-
dical in solution (Ref. 16).

Electron transfer reactions are very useful to check the architecture of a
monolayer assembly. For instance, one likes to bring a monolayer package in
contact with another package and it is important to know if molecular contact
can be achieved. In Fig. 7 the simple case of single monolayers is considered.
One monolayer (containing the acceptor) is deposited at a glass plate. The
other monolayer (containing the fluorescent dye) is at a polymer film and the
layers are brought in contact. The fluorescence of the dye is completely
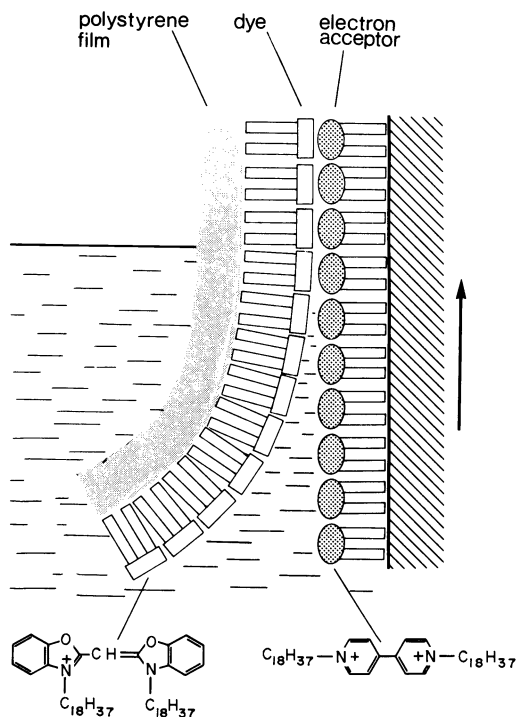quenched when contacting the layers, demonstrating molecular contact (Ref. 17).

Fig. 7. Monolayer at polymer film (with D) is contacted with
monolayer at glass plate (with A). The quenching of the fluor-
escence of D by A indicates molecular contact. D and A are di-
luted with fatty acid (not shown symbolically).

4) TRANSFER OF ELECTRONS FROM ELECTRON SOURCE TO EXCITED DYE

A monolayer of fluorescent dye D (Fig. 8) can be contacted with a monolayer
of electron source E. D is excited and an electron of source E is transferred
to D. The fluorescence of D is quenched (Ref. 15). This is only the case when
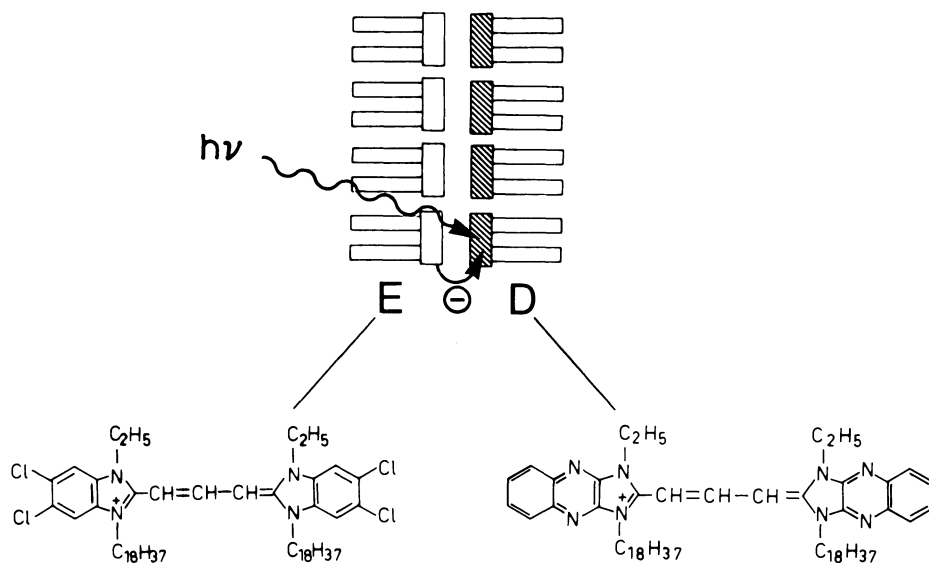

Fig. 8.   Assembly of electron source E and Dye D.

dye chromophore and electron source are at direct contact. Even when separa-
ting E and D by only one fatty acid monolayer no quenching is observed, in
contrast to what is found in dye D/electron acceptor A assemblies. This is to
be expected. The tunneling electron in the ED-system is at the ground state
level, in the DA-system at the level of the excited state. Therefore, the po-
tential V is much higher in the ED-system, α much larger, the tunneling pro-
bability much smaller.

5) ELECTRON TRANSFER IN AGGREGATING DYE MONOLAYERS

The cyanine dye in Fig. 9 can be arranged in the monolayer in very different
ways and it is observed that the rate of electron transfer to the acceptor
is strongly influenced by the arrangement of the dye molecules. The dye can
be applied in a surplus of fatty acid. In this case the chromophores are
separated from each other. By spreading a 1:1 mixture of the dye and octade-
cane a compact dye monolayer is obtained in which the hydrocarbon octadecane
fitts in the space between the hydrocarbon substituents of the dye. The chro-
mophores then are forced to arrange in a compact brick stone wall like pat-
tern (Fig. 9a).

By this close packing there should be a strong coupling between the chromo-
phores and this is reflected by the narrow absorption band and the narrow
fluorescence band almost coinciding with the absorption band (Ref. 4). The
exciton hopping time as estimated by a treatment based on the electron gas
model is $\Delta t = 10^{-13}$ s. According to the uncertainty principle this corresponds
to a natural band width of 5 nm and indeed the measured band width is 8-9 nm.

The dye monolayer (Fig. 9a) is contacted with a monolayer of fatty acid with traces of electron acceptor (Fig. 9b) and the quenching of the fluorescence is measured. It can be estimated to what dilutions the electron acceptor should be able to quench the fluorescence of the dye. For that purpose we first consider the case discussed in section 3, where the fluorescent dye was diluted with fatty acid and fixed at a certain distance d from the electron acceptor layer (Fig. 9c). The dye in Fig. 9, similar to the dye in Fig. 6, is quenched in its fluorescence by about 50 % at $d = 23$ Å. In this case $d = 23$ Å the tunneling rate then equals the decay rate of the excited state. In the case of Fig. 9b the distance between the dye chromophore and the acceptor is about $d = 6$ Å as seen from molecular models. Now if we proceed from Fig. 9c to Fig. 9b the tunneling rate should increase by a factor of $e^{2\alpha \cdot 23\,\text{Å}}/e^{2\alpha \cdot 6\,\text{Å}}$ if in Fig. 9b the exciton would stay during its lifetime at the appropriate dye molecule next to the acceptor. If we use the value

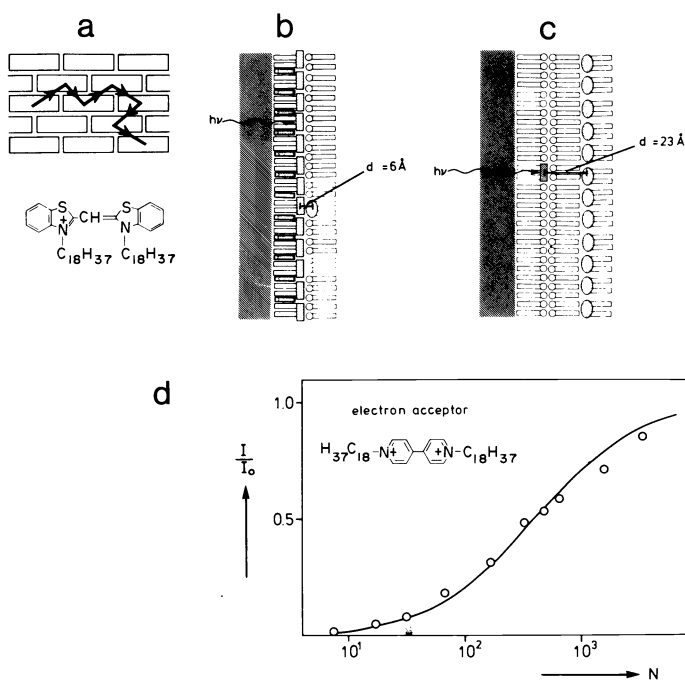

Fig. 9.   a) Dye in compact brickstone work like arrangement.
             Exciton hopping time 10^{-13} s.
          b) Dye monolayer (Fig. 9a) in contact with monolayer
             of fatty acid containing acceptor in high dilution.
          c) Monolayer of fatty acid containing dye in high
             dilution in contact with acceptor layer.
          d) Fluorescence intensity of dye in arrangement b)
             (I) relative to fluorescence intensity in arrange-
             ment without acceptor (I_o) plotted against dilu-
             tion of acceptor (N) (number of dye molecules per
             acceptor molecule).

$\alpha = 0.2$ Å^{-1} as in the case of Fig. 6 we obtain for that factor 10^3.

Now we shall consider a special case: the acceptor in the arrangement of Fig. 9b is diluted to such an extent that one molecule is among $N = 10^3$ molecules of the dye. Then the exciton should be at a dye molecule next to an acceptor molecule for 1/1000 of its lifetime. Since the tunneling rate during that time is increased by a factor of 10^3 the net probability to tunnel to the acceptor during the lifetime of the exciton should be about the same in both cases (Figs. 9b and 9c).

Therefore, it should be expected that the fluorescence of the aggregate is quenched by 50 % at a dilution $N \simeq 10^3$. Indeed I/I_o is 50 % at $N = 400$ (Fig. 9d). The consideration can be easily generalized. We can write

$$I = I_o \frac{k_d}{k_d + k_{et}}$$

where k_d is the rate of deactivation by fluorescence and thermal deactivation, and k_{et} is the electron transfer rate. k_{et} is inversly proportional to N and therefore

$$\frac{I}{I_o} = \frac{1}{1 + const/N} \tag{3}$$

The curve in Fig. 9d follows (3) with const = 400.

6) DESIGNED POTENTIAL PROFILES

It is of interest to reach a high quantum yield in charge separation and to keep the charges separated in a high energy state. Therefore, the barrier in Fig. 6a between dye and electron acceptor should be lowered and should be adjusted to the excited dye level.

It is of interest to have a π-electron chain forced to stay in the hydrocarbon portion perpendicular to the layer plane. The azo dye in Fig. 10a has this property as concluded from absorption measurements with polarized light at inclined incidence (Ref. 18). Its molecular model interlocks with the model of a cyanine dye as shown in Fig. 10a and indeed the surface pressure area curve of a mixed monolayer of fatty acid and the two dyes show 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 (Ref. 19). A single monolayer containing this functional unit can be sand-
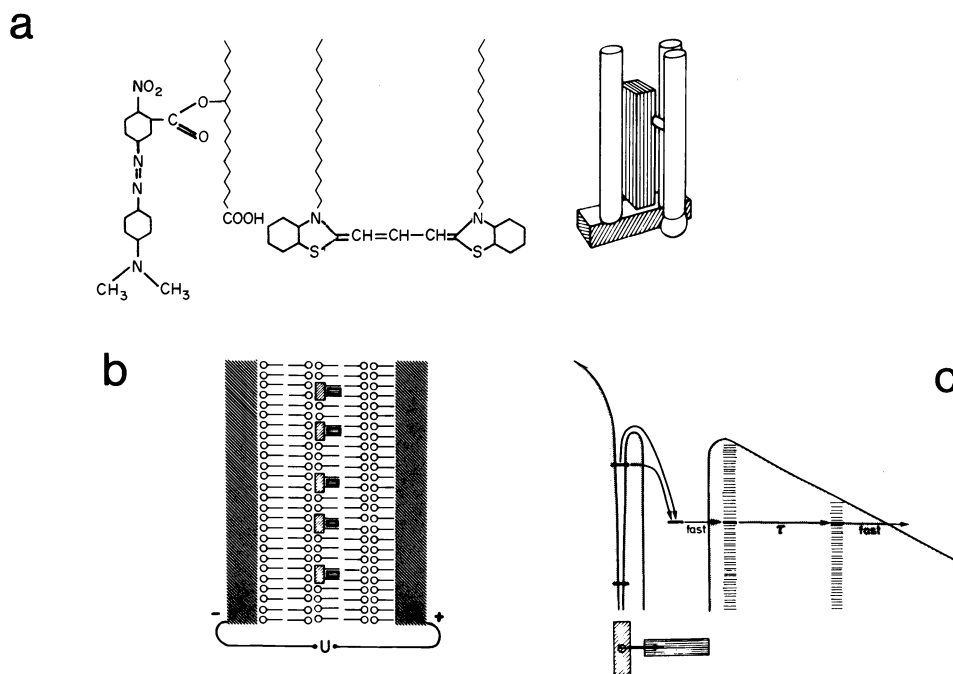

Fig. 10. Functional unit for photo electron production and conduction.
a) Interlocking cyanine dye and π-electron system. Mixed monolayer of the dyes and fatty acid.
b) Arrangement for measuring photocurrent
c) Potential profile in arrangement of Fig. 10b. Cyanine dye is excited, electron moves to conducting π-electron system, tunnels to an interlayer state and subsequently moves to the electrode.

wiched between fatty acid monolayers and electrodes (Fig. 10b). The cyanine is excited and the photocurrent is measured. The system can be investigated by variing temperature, applied voltage, and intensity and wavelength of the incident light. A detailed analysis shows (Ref. 19) that the π-electron system acts as molecular wire in the intended manner (Fig. 10c).

The results should stimulate thoughts in getting more adequate systems for vectorial charge separation. The examples should demonstrate that monolayer assembly techniques are of interest in fields where. systems are useful which have a planned molecular architecture, designed for each particular purpose. *)

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