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Molecular Cooperation in Monolayer Organizates

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In biological systems the molecules organize themselves to functional entities, e.g., the photosynthetic unit. The processes occurring in these systems are controlled by the appropriate arrangement of the components in space and energy. The function is correctly performed only when all components of the complex system operate properly. The microscopic functional unit is a machinery with cooperating components of molecular dimensions. So that artificial systems of similar complexity and with similar functions can be obtained, appropriate molecules must be organized to the adequate structure which enables the molecules to cooperate as intended.

Various methods have been developed to approach this goal, and the resulting molecular organizates differ widely in structure and dynamics. These artificial systems which contain functional components besides the inert matrix molecules are the monolayer,[1,2,3] the micelle,[4,5] the lipid bilayer,[6] monolayer membranes,[7] the vesicle,[8] the microemulsion,[5] and the monolayer organizate,[1-3] which is a layered assembly of different complex monolayers. Spectroscopic measurements[4a,9] and the study of reactions of excited molecules incorporated in theses different forms of organized environment provide information on the mobility of the excited species.[10] The monolayer organizates can be constructed to prevent rotational and translational diffusion of the components. The immobilization of the molecules and the resulting fixed structure are essential requirements for the use of these systems in the investigation of complex processes.

This Account intends to demonstrate the potential of the monolayer technique in organizing molecules into complex functional units, especially those that are characterized by the cooperation of the different molecular species.

Compared with homogeneous solution, the organization of molecules is facilitated at interfaces since the interface introduces a directionality in the molecular interactions and causes orientation of the molecules. The average separation of molecules at interfaces is generally far smaller than in bulk solution. The high local concentration increases the probability of formation of the desired molecular units. On solid surfaces dense monolayers can be formed by adsorption or by a surface chemical reaction.[11] This method has gained much interest for attaching sensitizing dye molecules to semiconductor electrodes (chemically modified electrodes[12]). In most cases, however, no well-defined monolayers have been obtained in this way.

Monolayers of water-insoluble substances like long-chain fatty acids can easily be formed at the air–water interface.[13] The transfer of monolayers from the water surface to solid substrates[14] provides the possibility of assembling monolayer organizates in a stepwise procedure. The potential of the monolayer technique in organizing different molecules to functional molecular units was realized by H. Kuhn and co-workers[3,15-18] who introduced long-chain substituted cyanine dyes into the

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(1) G. L. Gaines, Jr., "Insoluble Monolayers at Liquid-Gas Interface", Interscience, New York, 1966.
(2) W. A. Barlow, Ed., *Thin Solid Films* **1980**, *68*, No. 1, Special issue on Langmuir–Blodgett films.
(3) H. Kuhn, D. Möbius, and H. Bücher in "Physical Methods of Chemistry", Weissberger and B. Rossiter, Eds., Vol. I, Part 3B, Wiley, New York, 1972, p 577.
(4) (a) N. J. Turro, M. Grätzel, and A. M. Braun, *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675. (b) P. Fromherz, *Chem. Phys. Lett.* **1981**, *77*, 460.
(5) K. L. Mittal, Ed., "Micellization, Solubilization, and Microemulsion", Vol. 1 and 2, Plenum Press, New York, 1977.
(6) (a) H. Tien, "Bilayer Lipid Membranes; Theory and Practice", Marcel Dekker, New York, 1974; nb) D. Mauzerall, *Life Sci. Res. Rep.* **1979**, *12*, 241; (c) T. Kunitake and Y. Okahata, *J. Am. Chem. Soc.* **1980**, *102*, 549.
(7) Y. Okahata and T. Kunitake, *J. Am. Chem. Soc.* **1979**, *101*, 5231.
(8) J. Fendler, *Acc. Chem. Res.* **1980**, *13*, 7.
(9) (a) H. Wennerström and G. Lindblom, *Q. Rev. Biophys.* **1977**, *10*, 67; (b) L.B.-A.Johansson, A. Davidsson, G. Lindblom, and B. Nordén, *J. Phys. Chem.* **1978**, *82*, 2604; (c) M. Shinitzky and Y. Barenholz, *Biochim. Biophys. Acta* **1978**, *515*, 367; (d) R. H. Austin, S. S. Chan, and T. M. Jovin, *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 5650; (e) R. Greinert, H. Staerk, A. Stier, and A. Weller, *J. Biochem. Biophys. Meth.* **1979**, *1*, 77; (f) L.B.-A. Johansson and G. Lindblom, *Q. Rev. Biophys.* **1980**, *13*, 63.
(10) D. G. Whitten, *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 440.
(11) E. E. Polymeropoulos and J. Sagiv, *J. Chem. Phys.*, **1978**, *69*, 1836.
(12) R. W. Murray, *Acc. Chem. Res.* **1980**, *13*, 135.
(13) A history of monolayer research is given by S. D. Forrester and C. H. Giles, *Chem. Ind. (London)* **1979**, 469, and references therein.
(14) K. B. Blodgett and I. Langmuir, *Phys. Rev.* **1937**, *51*, 964.
(15) H. Bücher, K. H. Drexhage, M. Fleck, H. Kuhn, D. Möbius, F. P. Schäfer, J. Sondermann, W. Sperling, P. Tillmann, and J. Wiegand, *Mol. Cryst.* **1967**, *2*, 199.
(16) H. Kuhn and D. Möbius, *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 620.
(17) H. Bücher, O.v. Elsner, D. Möbius, P. Tillmann, and J. Wiegand, *Z. Phys. Chem. (Frankfurt/Main)* **1969**, *65*, 152.
(18) D. Möbius, *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 848.

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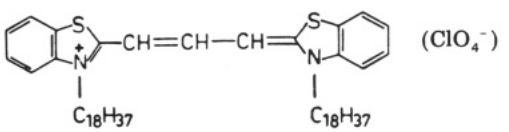
matrix of fatty acid monolayers. In this way strongly interacting molecules could be arranged either as probes or as active components in well-defined geometries by using the properties of long-chain fatty acid monolayers which are favorable for assembling complex systems.

Spreading techniques had to be improved for the formation of multicomponent monolayers. Usually, the surface-active material is brought to the surface as a solution in a volatile solvent. The molecules of most cyanine dyes are homogeneously distributed in the fatty acid monolayer matrix. A phase separation, however, was detected with mixtures of arachidic acid and a merocyanine dye.[17] In some cases the monolayers formed on the water surface become too rigid immediately after spreading to attain the equilibrium, and therefore are inhomogeneous. These difficulties have been overcome by transient modification of the environment, e.g., by cospreading of some slowly evaporating compound.[18] The classical methods of monolayer formation and transfer have been improved, e.g., by incorporation of active proteins in complex monolayer organizates.[19] With the new technique of monolayer manipulation,[20] monolayer systems can be cleaved with molecular precision at particular interfaces, and, after transfer to a new substrate, molecular contact has been achieved. The method was applied to a reinvestigation of the spectral sensitization of vacuum-deposited silver bromide layers with layer systems prefabricated on glass.[21] In this way it was possible to exclude the influence of possible defects in the monolayer systems which were assembled directly on the silver bromide as in the original investigation.[22]

Systems of increasing number of interacting components have been assembled, e.g., linking energy-transfer processes with photochemical reactions like photoisomerization[23] and photoinduced electron transfer[18] or combining proton-, photon-, and electron-transfer processes.[24]

Organization of a Complex Monolayer at the Air–Water Interface

Cyanine dyes with octadecyl substituents instead of the usual methyl or ethyl groups on the nitrogen atoms (e.g., *N,N'*-dioctadecylthiacarbocyanine, dye I) are incorporated in the monolayer matrix of arachidic acid molecules when a mixed solution is spread on the water surface. In the compressed film, the long-chain substituents of the dye molecules are aligned with the hydrocarbon chains of the fatty acid molecules, and the cationic chromophores are located at the hydrophilic



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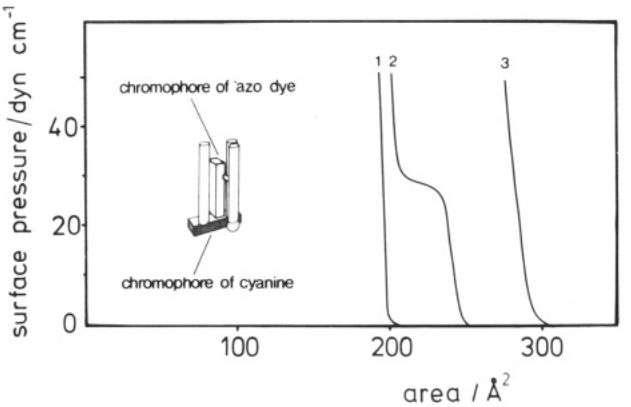
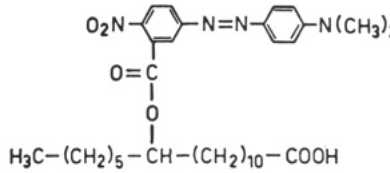


Figure 1. Interlocking of the cyanine dye I and the azo dye II (schematic representation) and surface pressure plotted vs. the area of 10 arachidic acid molecules for different monolayers. Isotherm 1, arachidic acid; isotherm 2, mixed monolayer of arachidic acid and azo dye II, molar ratio acid:azo = 10:1; isotherm 3, mixed monolayer of arachidic acid, azo dye II, and cyanine dye I, molar ratios acid:azo:cyanine = 10:1:1. The azo dye II is squeezed out of the arachidate matrix according to (2) at 25 dyn/cm, but is retained when the cyanine dye I is present.

interface together with the carboxyl groups. The optical transition moment of the dye is oriented parallel to the water surface.[3]

For many purposes it is desirable to have π-electron systems oriented parallel to the hydrocarbon chains, i.e., perpendicular to the water surface. This was achieved by linking the nonionic chromophore of an azo dye chemically to a molecule of stearic acid, dye II.[25]



II

Molecular models of the cyanine dye I and the azo dye II can be interlocked to a complex unit, as shown schematically in Figure 1, inset. The formation of such a 1:1 complex in a mixed monolayer influences the mechanical properties of the monolayer and therefore must be detectable in the surface pressure–area isotherm.

In Figure 1 the isotherms of different monolayers are shown. The surface pressure is plotted vs. the area of 10 arachidic acid molecules. The isotherm 1 refers to a monolayer of arachidic acid, which shows a steep increase of the surface pressure at 200 Å^2 on decreasing the monolayer area. This is reasonable, since the cross section of an arachidic acid molecule with perpendicular hydrocarbon chain is about 20 Å^2. The mixed monolayer of arachidic acid and the azo dye II, molar ratio acid: azo = 10:1, has the isotherm 2 with the steep increase at 240 Å^2. The shift is due to the presence of the additional azo dye molecule with a cross sectional area of about 40 Å^2 in an upright orientation. The monolayer becomes unstable at a surface pressure of about 25 dyn/cm as shown by the decrease in monolayer area. Apparently, the azo dye molecules are squeezed out of the arachidic acid matrix at this surface pressure. Isotherm 3 in Figure 1 is obtained with a

(19) (a) P. Fromherz, *Biochim. Biophys. Acta* **1971**, *225*, 382; (b) P. Fromherz and D. Marcheva, *FEBS Lett.* **1975**, *49*, 3; (c) P. Fromherz and J. Peters, *Biochim. Biophys. Acta* **1975**, *394*, 111; (d) P. Fromherz, *Rev. Sci. Instrum.* **1975**, *46*, 1380.

(20) O. Inacker, H. Kuhn, D. Möbius, and G. Debuch, *Z. Phys. Chem. (Frankfurt/Main)* **1976**, *101*, 337.

(21) D. Möbius, *Photogr. Sci. Eng.* **1974**, *18*, 413.

(22) L. v. Szentpály, D. Möbius, and H. Kuhn, *J. Chem. Phys.* **1970**, *52*, 4618.

(23) E. E. Polymeropoulos and D. Möbius, *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1215.

(24) P. Fromherz and W. Arden, *J. Am. Chem. Soc.* **1980**, *102*, 6211.

(25) J. Heesemann, *J. Am. Chem. Soc.* **1980**, *102*, 2167, 2176.

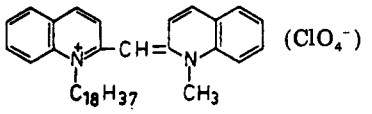
mixture of arachidic acid, the azo dye II, and the cyanine dye I in the molar ratios acid:azo:cyanine = 10:1:1. The steep increase of the surface pressure on decreasing the monolayer area is displaced to about 280 Å^2, another 40 Å^2 more with respect to isotherm 2. This additional area is occupied by the two octadecyl substituents of the cyanine dye which are tightly incorporated in the arachidic acid matrix. Since no instability is observed at 25 dyn/cm, the azo dye is no longer squeezed out of the three-component monolayer when the cyanine dye is present in at least the same molar fraction as the azo dye.[26] When the fraction of the cyanine dye is smaller than that of the azo dye, the monolayer instability is again observed. These facts clearly indicate the formation of a 1:1 molecular arrangement of the two different dyes in the fatty acid matrix.

As expected, the transition moment of the cyanine dye is oriented parallel to the water surface whereas the transition moment of the azo dye is oriented perpendicular to the surface,[26] as deduced from a measurement of the absorption of linearly polarized light under oblique incidence.[3,25] This example of molecular cooperation in a complex monolayer at the air–water interface, which results in a tight incorporation of the azo dye II in a fatty acid matrix at surface pressures exceeding 25 dyn/cm, shows that simple geometrical considerations can lead to useful concepts of molecular organization.

Extended Cooperative Systems

In most monolayer organizates the matrix consists primarily of fatty acid molecules or mixtures of different inert matrix molecules in order to provide the appropriate mechanical properties and optimal monolayer transfer. The dye molecules are only a small fraction of the monolayer. Consequently, the mobility of the dye molecules in the spread monolayer is strongly influenced by the composition of the matrix. In condensed monolayers the viscosity can be determined mainly by the interactions of the hydrophylic groups rather than by the adhesion of the hydrocarbon chains, as indicated by the results of surface viscosity measurements on monolayers of stearic acid and of stearyl alcohol on water.[27]

In cases where intimate contact of the dye chromophores is intended in order to form associates (dimers or higher aggregates), the ionic or dipolar chromophores must not be separated by the hydrophilic groups of other surfactants. Densely packed monolayers of surface-active cyanine dyes, according to the absorption spectra, are composed of monomers and dimers.[18] When a compound like hexadecane or methyl stearate is added which transiently increases the mobility of the chromophores at the interface ("molecular lubricant"), large two-dimensional arrays of ordered chromophores are formed. The additive separates the chromophores at the water surface and is slowly shifted under the applied surface pressure into the free space in the hydrophobic portion of the condensed monolayer.[28] The monolayer of dye III, organized in this way and transferred to a glass plate, reveals the strong and narrow absorption band and the resonance emission typical for large aggregates (J-aggregates[29]; see Figure 2a). This

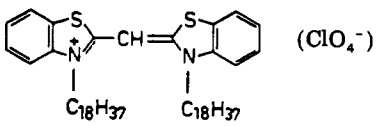


III

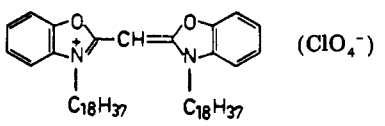
appears to be a consequence of the strong interaction between the ordered chromophores.

The condensed monolayers at the water surface (or transferred to glass plates) are like two-dimensional solids. There are, however, possibilities to vary and control the molecular mobility. The optical absorption of a J-aggregate monolayer is isotropic in the layer plane. Immediately after deposition of the monolayer on a gypsum crystal the absorption becomes anisotropic, as shown in Figure 2b. The dye chromophores align slowly along the *a* axis of the freshly cleaved gypsum surface.[30] The reorganization of the aggregate monolayer is practically completed after 24 h (Figure 2c). This totally ordered monolayer can be transferred by the techniques of monolayer manipulation via a water surface to a glass plate. The original J aggregate is re-formed without loss of preferential chromophore orientation (see Figure 2d). This experimental series demonstrates how molecular interactions can be controlled in order to achieve optimal organization for molecular cooperation.

The extension of the two-dimensionally ordered arrays can be evaluated from a study of the energy transfer from the excited J-aggregate to an appropriate energy acceptor, which can be incorporated in the aggregate without interference with the long-range order. With the *N,N'*-dioctadecylthiacyanine (IV) as acceptor,



IV



V

the fluorescence of the aggregate of the *N,N'*-dioctadecyloxacyanine (V) is quenched to half of the unquenched intensity by one acceptor molecule per 10 000 donor molecules in the aggregate.[18] The energy acceptors in these arrays are very dilute and act as energy traps, concentrating the energy absorbed anywhere in the aggregate. In this respect the organizate surpasses the energy-harvesting array in the photosynthetic unit of green plants which consists of 300–400 pigment molecules.[31]

The efficiency of the energy transfer from the excited J aggregate to the acceptor incorporated in the monolayer adjacent to the chromophores of the aggregate depends on the temperature. The experimental data were rationalized by a model of a coherent exciton extending at room temperature over a domain of about 10 donor molecules in the extended aggregate.[32] The

(26) E. E. Polymeropoulos, D. Möbius, and H. Kuhn, *J. Chem. Phys.* **1978**, *68*, 3918.
(27) B. M. Abraham and K. Miyano, in press.
(28) H. Bücher and H. Kuhn, *Chem. Phys. Lett.* **1970**, *6*, 183.
(29) (a) G. Scheibe, *Angew. Chem.* **1936**, *49*, 563; (b) E. Jelley, *Nature (London)* **1936**, *138*, 1009.
(30) G. R. Bird, G. Debuch, and D. Möbius, *J. Phys. Chem.* **1977**, *81*, 2557.
(31) J. Barber, Ed. *Top. Photosynth.* **1979**, *3*.

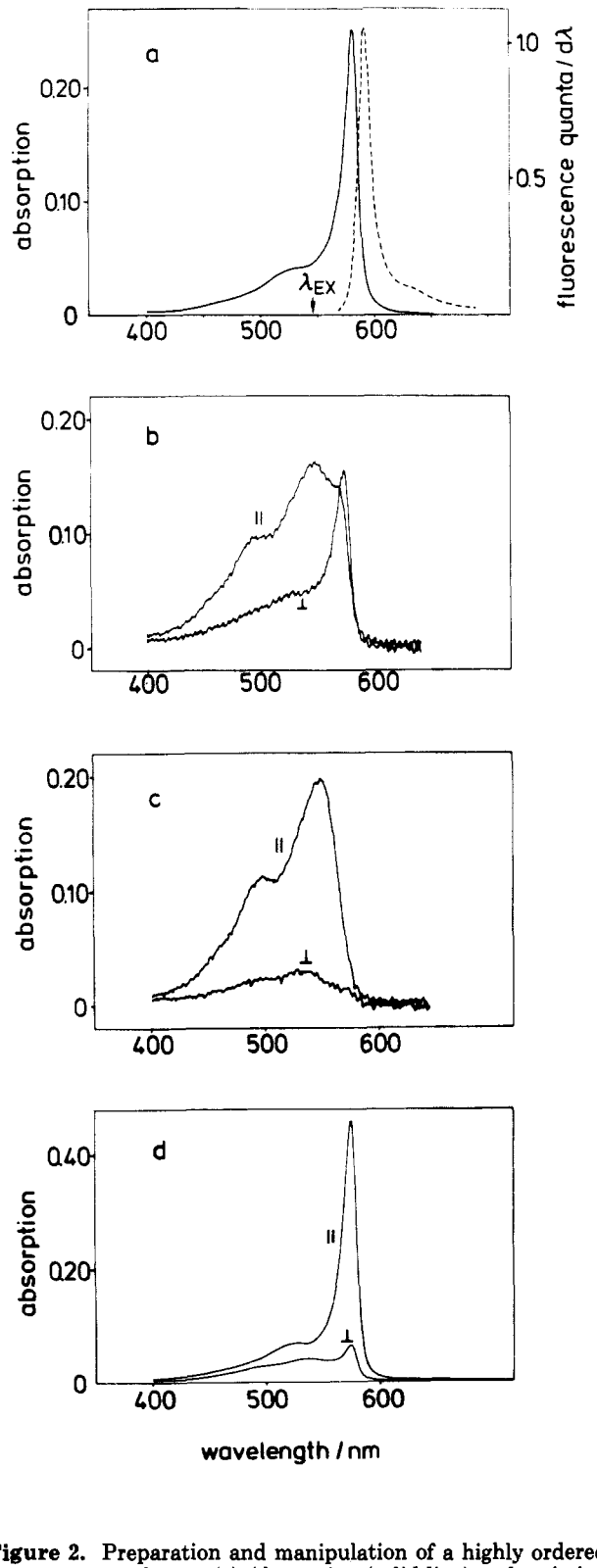


Figure 2. Preparation and manipulation of a highly ordered aggregate monolayer. (a) Absorption (solid line) and emission (dashed line) spectra of a mixed monolayer of cyanine dye III and hexadecane, molar ratio 1:1, organized in J aggregates. The absorption is isotropic in the layer plane (monolayer on glass coated with arachidate monolayers). (b) Absorption spectra parallel (‖) and perpendicular (⊥) to the *a* axis of a freshly cleaved gypsum crystal coated with a monolayer as in (a) under normal incidence of the light; dye molecules partly reorganized along the *a* axis. (c) Monolayer of (b) after 24 h in the dark; the reorganization of the dye monolayer is completed. (d) Monolayer of (c) after separation from the gypsum crystal and transfer to a glass plate via a water surface. The anisotropy is unchanged and remains constant.

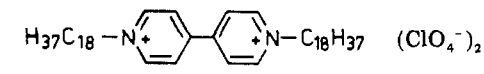
domain size increases with decreasing temperature, and as a consequence of the molecular cooperation the rate of fluorescence emission increases. This effect has not yet been directly observed.

Photoinduced Electron Transfer

In the preceding section examples of molecular cooperation within the monolayer were described. The cooperation of molecules incorporated in different monolayers that are parts of monolayer organizates will be considered here. A particularly interesting process to apply the analytical potential provided by monolayer organizates is the photoinitiated electron transfer which is the basis of the energy conversion via photosynthesis.

A molecule in the electronically excited state, either singlet or triplet, can act as electron donor since it has one electron in the excited-state orbital and also as electron acceptor since it has a vacancy in the ground-state orbital. In solution the electron transfer takes place when the donor molecule and the acceptor molecule have come close to each other by diffusion.[33] The molecular diffusion is inhibited in monolayer organizates with appropriate matrix. Therefore, the dependence of the efficiency of photoinduced electron transfer on the donor–acceptor separation can be easily investigated by variation of the distance between the interfaces at which the donor and the acceptor chromophores are located.

The use of octadecyl-substituted cyanine dyes like I and IV as electron donor and of the *N,N'*-dioctadecyl-4,4'-bipyridinium cation (VI) as electron acceptor,



VI

both located at hydrophilic interfaces, implies a practical difficulty: In monolayer organizates assembled by the usual Langmuir–Blodgett transfer method the hydrophilic interfaces are at contact or separated by an an even number of long hydrocarbon chains (Y deposition). In the case of contact of the hydrophilic interfaces with the donor and acceptor chromophores, complete quenching of the donor emission is observed if the concentration of the acceptor chromophores is sufficiently high. No fluorescence quenching, i.e., no electron transfer, is observed with the same acceptor concentration in the case of donor–acceptor separation by two arachidate monolayers, corresponding to a distance of 54 Å.[18] The hydrophilic interfaces with the donor chromophores and the acceptor cations VI (viologen) must be separated by only one fatty acid interlayer.

This can be achieved by deposition of the acceptor monolayer with its hydrophilic groups on top of the hydrophobic surface of the fatty acid interlayer, resulting in the structure shown schematically in Figure 3, top. The transfer of a single monolayer on dipping and withdrawal of the slide from the monolayer-covered water surface has been observed with fatty acid monolayers.[34] The resulting structure, however, does not yield the contact of hydrophilic and hydrophobic interfaces, since rearrangement by overturning of the

(32) D. Möbius and H. Kuhn, *Isr. J. Chem.* **1979**, *18*, 375.
(33) D. Rehm and A. Weller, *Isr. J. Chem.* **1970**, *8*, 259.
(34) K. B. Blodgett, *J. Am. Chem. Soc.* **1935**, *57*, 1007; see also ref 1, p 336.

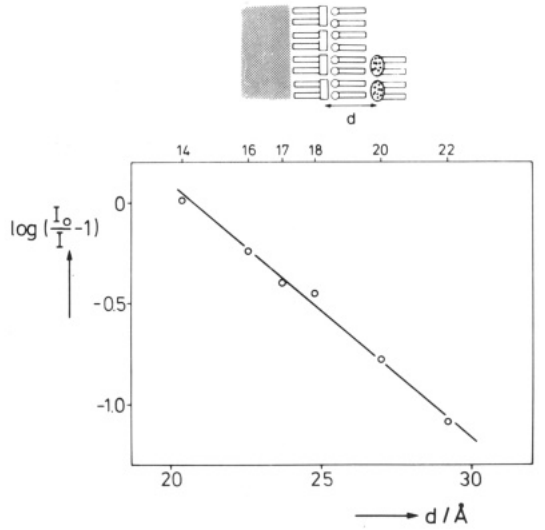


Figure 3. Photoinduced electron transfer in monolayer organizates. Layer system (schematic) with donor layer (dye IV) and fatty acid interlayer on the whole plate and acceptor layer (viologen VI) on the lower part. For clarity, the matrix molecules of the donor and acceptor layers (methyl arachidate and arachidic acid, molar ratio 1:9) are not represented. the fluorescence of the donor (intensity I_0) is reduced by the acceptor layer (I). The logarithm of $(I_0/I)-1$ is plotted vs. the distance d between donor and acceptor planes. The linear dependence indicates electron tunneling.

molecules to the usual structure occurs,[35] as deduced from X-ray diffraction measurements.[36] The procedure used for the deposition of the electron-acceptor layer in our case is classified as Z deposition.[1] The glass plate with the donor layer covered by the long-chain fatty acid monolayer is immersed in the trough through the clean water surface. Then, the acceptor monolayer is spread, compressed, and transferred to glass plate on withdrawal of the plate.

The deposition is complete if the acceptor monolayer has the appropriate composition and if the hydrophilic interface next to the hydrophobic surface has the appropriate composition. The replacement of one-tenth of the fatty acid molecules in the matrix of the donor layer by the methyl ester of the same fatty acid provides the optimal substrate for the attachment of the acceptor layer to the hydrophobic surface.[37] This is another example of the strong effects caused by subtle changes in monolayer organizates.

From the steady-state fluorescence intensities of the cyanine dye monolayer in the absence (I_0) and in the presence of the acceptor layer (I), the rate constant k_{el} of the electron transfer is obtained from

$$k_{el}\tau = (I_0/I) - 1$$

where τ is the fluorescence lifetime of the donor in the absence of the electron acceptor. The electron transfer can occur via thermal activation of the electron in the excited state to the top of the energy barrier created by the fatty acid monolayer or by electron tunneling across this barrier. In the case of electron tunneling, the rate constant k_{el} should decrease exponentially with increasing distance d between the donor chromophores and the interface with the electron acceptor.[38]

The distance dependence has been investigated with monolayers of the *N,N'*-dioctadecylthiacyanine (IV) as donor and the viologen VI as acceptor.[39,40] The values of $(I_0/I) - 1$ were calculated from the measured steady-state fluorescence intensities and are plotted logarithmically in Figure 3 vs. the thickness d of the fatty acid interlayer. The fatty acids used are indicated by the number of their carbon atoms. From Figure 3 it is obvious that the rate constant k_{el} decreases exponentially with increasing distance. Additional evidence for a tunneling mechanism of electron transfer in these monolayer organizates was obtained from an investigation of the influence of an energy acceptor reducing the electron-transfer efficiency[40] and from donor fluorescence decay measurements. With monolayers of the cyanine dye V as donor, a decrease of the fluorescence lifetime in agreement with the result of the steady-state quenching measurements has been observed for d = 25 Å.[41]

The distance of electron tunneling during the lifetime of the excited state of the cyanine dye, which is of the order of 1 ns, appears relatively large compared to results of electron-transfer experiments in disordered solids[42] or discussed in connection with photosynthesis.[43] However, the monolayer organizates differ fundamentally from many other systems investigated: The layered structure provides states at each interface[44] which primarily accept the electron and subsequently transfer it to the final acceptor, namely, viologen in the case considered here. If no subsequent reactions occur, the electron returns into the ground-state orbital of the oxidized donor, restoring the original situation. Occasionally the electron is provided by other donors in the monolayer organizate, and then the reduced acceptor, the violen radical, slowly accumulates. This species has been detected in monolayer organizates in air,[45] in inert atmosphere like argon, helium, or nitrogen,[40] and under vacuum by measuring the absorption spectrum or the ESR signal of the radical.[46]

The various observed phenomena, the donor fluorescence quenching and lifetime shortening, the appearence of the reduced acceptor radical, the influence of the interlayer thickness, and structure are determined by the cooperation of the different molecular species which in turn is controlled by the energetic and spatial organization.

Photovoltage Generation by Vectorial Photoinduced Electron Transfer

For the monolayer organizates depicted in Figure 3 the electron transfer can take place only in one spatial direction. This is quite different from the usual situation in solution or in other disordered systems. If the

(35) (a) I. Langmuir, *Science (Washington, D.C.)* **1938**, *87*, 493; (b) E. P. Honig, *J. Colloid Interface Sci.* **1973**, *43*, 66; J. F. Stephens, *ibid.* **1972**, *38*, 557.
(36) (a) G. L. Clark, R. R. Sterrett, and P. Leppla, *J. Am. Chem. Soc.* **1935**, *57*, 330; (b) C. Holley and S. Bernstein, *Phys. Rev.* **1936**, *49*, 403; (c) R. C. Ehlert, *J. Colloid Sci.* **1965**, *20*, 387.
(37) D. Möbius and W. Zeiss, unpublished.
(38) H. Kuhn, *Life Sci. Res. Rep.* **1979**, *12*, 151.
(39) H. Kuhn, *Pure Appl. Chem.* **1979**, *51*, 341.
(40) D. Möbius; a detailed publication is being prepared.
(41) D. Möbius and H. Staerk, unpublished.
(42) J. V. Beitz and J. R. Miller, *J. Chem. Phys.* **1979**, *71*, 4579.
(43) J. J. Hopfield, *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640.
(44) (a) M. Sugi, K. Nembach, D. Möbius, and H. Kuhn, *Solid State Commun.* **1974**, *15*, 1867; (b) M. Sugi, K. Nembach and D. Möbius, *Thin Solid Films* **1975**, *27*, 205.
(45) D. Möbius and G. S. Ballard, unpublished.
(46) J. Cunningham, E. E. Polymeropoulos, D. Möbius, and F. Baer in "Magnetic Resonance in Colloid and Interface Science," J. P. Faissard and H. A. *Resing*, Eds., Reidel Publishing Co., Dordrecht, Holland, 1980, p 603.

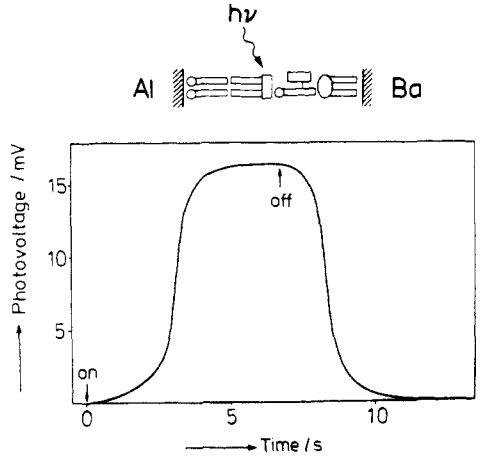
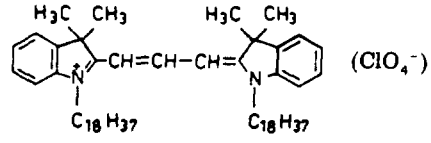


Figure 4. Photovoltage generation by vectorial photoinduced electron transfer. Structure (schematic) of the monolayer organizate with a monolayer of cadmium arachidate on aluminum (donor) covered by the monolayer of cyanine dye VII (photocatalyst), the monolayer of azo dye II (conducting π-electron system), the monolayer of the viologen VI (primary electron acceptor), and the barium electrode (acceptor). The matrix molecules of the dye and acceptor layers are not represented. Rise and decay of the photovoltage on illumination of the system with green light absorbed by the cyanine dye.

back transfer of the electron can be inhibited, the vectorial electron transfer results in the generation of an electrical field across the insulating monolayer. This can be achieved by appropriately shaping the potential profile of the monolayer organizate with donor, photocatalyst, and acceptor layers.[38] Starting with the system of Figure 3, an electron source (the donor) should be added on the left of the dye layer, separated by a thin insulating barrier higher than the barrier between the dye, which is now the photocatalyst, and the acceptor layer. The electrons from the donor should be capable of tunneling to the photocatalyst interface and filling the ground-state orbital of the photocatalyst after excitation. The electron in the excited-state orbital is transferred to the acceptor, thereby loosing some energy in order to inhibit the back reaction.

An effort to construct a monolayer organizate along these lines has been untertaken recently.[47] The photocatalyst was *N,N'*-dioctadecylindocarbocyanine (VII),



VII

and the viologen VI was used as intermediate acceptor. The system was arranged between a semitransparent aluminum electrode as donor and a barium electrode as ultimate electron acceptor. The fatty acid monolayer between the cyanine and the viologen was modified by incorporation of the azo dye II as a conducting element. This provides a low-lying unoccupied orbital for the transfer of the electron from the excited photocatalyst to the interface with the viologen as primary acceptor.

(47) E. E. Polymeropoulos, D. Möbius, and H. Kuhn, *Thin Solid Films* 1980, *68*, 173.

The function of the azo dye π-electron system oriented parallel to the fatty acid hydrocarbon chains as a "molecular wire" has been demonstrated in an investigation of the photoconduction in monolayer organizates between aluminium electrodes.[26] The complete system is shown schematically in Figure 4 (top). The dye and viologen monolayers are in fact mixed monolayers, but for simplicity the matrix molecules (methyl arachidate and arachidic acid, molar ratio ester: acid r = 1:1 for cyanine VII, r = 0:1 for azo dye, r = 1:9 for viologen) are not represented.

On illumination of the organizate under vacuum with light absorbed by the cyanine dye, a photovoltage is generated which decays when the light is turned off, as shown in Figure 4. The photovoltage action spectrum corresponds to the absorption spectrum of the cyanine dye, and the steady-state photovoltage is proportional to the light intensity in the range covered by the experiments.[47] The kinetics has not yet been analyzed in detail. However, the initial phases of photovoltage rise and decay are probably influence by the slow filling and emptying, respectively, of electron traps in the monolayer organizate.

Qualitatively, the monolayer organizate shows the anticipated behavior. The electron transfer has the expected directionality as a consequence of the cooperation of the different components appropriately selected to fulfill the energetic requirements and properly arranged in space.

Concluding Remarks

The controlled incorporation of various active and passive molecular components into inert monolayer matrices has made available modules which can readily be assembled to a planned functional unit. A few examples have been selected from the experimentally investigated monolayer organizates to demonstrate the strategy and methods for achieving cooperation in molecular dimensions. The dominant features of monolayer organizates are the simplicity in structure and the possibility of systematic variation of the parameters controlling the phenomenon under investigation. These are the reasons for the high potential of these artificial systems in the analysis of complex processes and in assembling molecular machines with photons, electrons, protons, or molecules as mobile parts. The structural requirements for the components of a planned molecular functional unit can be efficiently evaluated.

The ultimate goal should be the construction of the molecular machinery by spontaneous organization of the molecules in homogeneous solution or at interfaces by a series of surface chemical reactions. It is a challenge to modern chemistry to conceive and synthesize the adequate molecules which combine more and more functions. The monolayer technique which uses external stimulus like the surface pressure exerted on a monolayer at the air–water interface to interlock appropriately shaped molecules provides methods to facilitate and accelerate the evolution of such artificial functional units that might be used in solar energy conversion, in information storage and processing systems, or in medical applications.