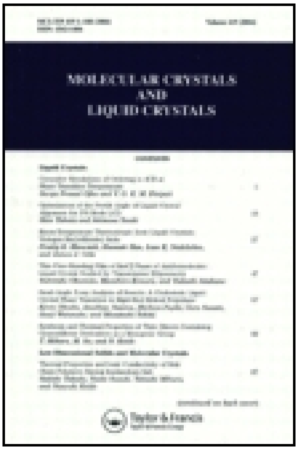

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Hans Kuhn [a]
[a] Max-Planck-Institut für biophysikalische Chemie Molekularer Systemaufbau, Am Faßberg D 3400 Göttingen-Nikolausberg, Germany

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DEVELOPMENT OF ORGANIZED MONOMOLECULAR LAYER ASSEMBLIES

HANS KUHN
Max-Planck-Institut für biophysikalische Chemie
Molekularer Systemaufbau, Am Faßberg
D 3400 Göttingen-Nikolausberg, Germany

Abstract Methods are described to assemble molecules of different kinds into organized systems where individual molecules cooperate forming functional units. The aim of constructing organized assemblies is to study new types of phenomena that depend on the molecular organization, to develop arrangements of potential technological interest (high density information storage and processing, energy conversion), and to construct adequate models for simulating processes in complex biological structures. In order to approach this goal films of the thickness of one molecule are superimposed upon each other in various ways. The resulting assemblies of molecules can be applied to the study of complex photochemical reactions, e. g. the investigation of the mechanism of the spectral sensitization of the photographic process. Energy and electron transfer processes can be systematically analyzed since the geometry of the interacting molecules can be varied in a controlled manner. Systems can be constructed where independent reactions are coupled in complex ways.

First attempts to construct organized molecular assemblies were based on the idea of using monolayers for carrying individual molecules of different kinds and arranging them according to a given plan[1]. A monolayer of molecules of a first kind in some matrix can be produced on the surface of water, the layer is deposited on a solid support, a monolayer with molecules of a second kind is deposited on top of this layer, etc. In this manner simple functional systems are constructed where individual molecules act as solid parts, electrons, photons, protons as mobile parts of a simple machinery [2]. Such monolayers can be manipulated in many ways. By appropriately choosing the layer composition the layer system can be cleaved at a planned location. The arrangement in Fig. 1, given as an example, is composed

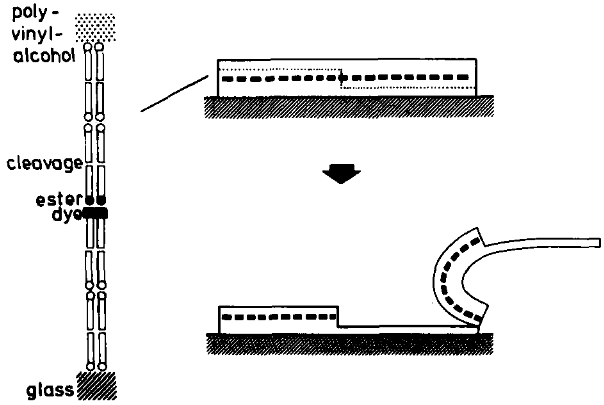

FIGURE 1. Cleavage of monolayer assembly in a precisely defined manner. The assembly was obtained by depositing monolayers of appropriate composition on a glass slide and by producing a polymer film on top.

of layers with fatty acid as matrix compound with the exception of one layer which is composed of fatty acid ester. In the section on the left this ester layer is positioned above the layer containing a fluorescent dye (indicated by a broken line), in the section on the right below the dye layer. The assembly cleaves precisely between the ester layer and the next layer, and this is easily seen by inspecting the fluorescence [3].

Electron Transfer in Monolayer Assemblies

The development of organized systems that mimic photosynthesis is of interest in studying possibilities of solar energy conversion and for that purpose it is important to investigate in some detail the photoinduced electron transfer in monolayer assemblies. An arrangement shown in Fig. 2 can be built up on a glass slide [4]: A layer of a cyanine dye D, a spacer layer and a layer of an acceptor A (viologen). If the acceptor is separated from the donor by only 2 nm using a fatty acid interlayer with 14 carbon atoms in the hydrocarbon chain, the fluorescence is strongly quenched. The interlayer thickness d can be varied by using fatty acids of various chain lengths, and for each system the amount of quenching is measured.

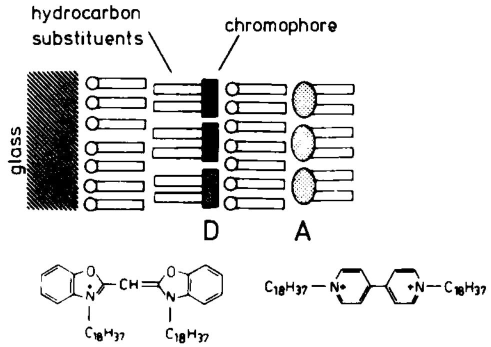

FIGURE 2. Photoinduced electron transfer from cyanine dye (D) to viologen (A) by tunneling through fatty acid spacer layer. D and A are incorporated in a mixed methyl-arachidate and Cd-arachidate matrix omitted in the symbolic representation of the assembly architecture.

One difficulty arises in realizing such systems. The hydrophilic groups in the acceptor layer do not easily bind to the hydrophobic surface of the fatty acid spacer layer. The deposition of the acceptor layer is easily possible if the surface of the spacer layer is made partially hydrophilic by incorporating a monoester of a dicarboxylic acid, such as $HOOC(CH_2)_{16}COOCH_3$. When spreading this monoester and fatty acid at the water surface the ester groups first turn to the water surface; when increasing the surface pressure the ester groups are forced to move to the monolayer/air interface (Fig. 3)[5]. This layer is deposited on a glass slide on top of a layer of the donor and it is covered by a layer of the acceptor.

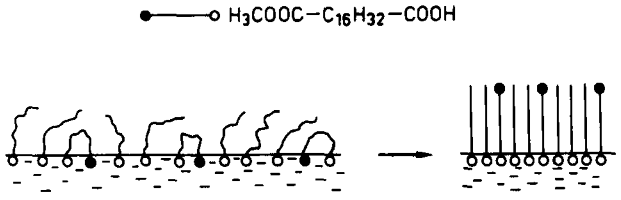

FIGURE 3. Production of mixed layer of fatty acid and octadecane dicarboxylic acid monoester. Layer used as spacer in the arrangement of Fig. 2.

Tests to check the architecture of the monolayer assembly are important. The possibility must be excluded that acceptor molecules give rise to fluorescence quenching that are located at smaller distance to the donor than intended (due to pinholes, diffusion or rearrangements). A test is given by measuring the quenching of the fluorescence as a function of the surface density of the donor. The fluorescence intensity I relative to the intensity I_o of a sample without acceptor should be independent of the density of the donor and this is actually the case [6] (Fig. 4, circles).

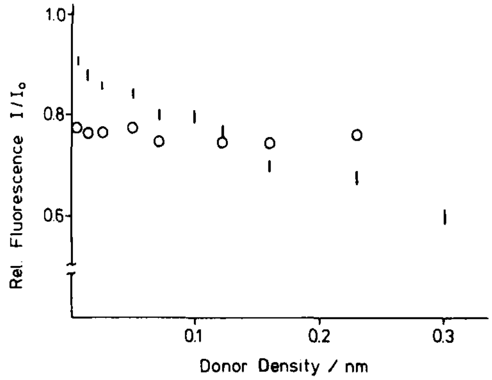

FIGURE 4. Quenching of fluorescence of electron donor by acceptor. Relative fluorescence intensity I/I_o plotted against surface density of donor (σ_D) at constant surface density of acceptor (σ_A).
circles: arrangement according to Fig. 2 (d = 2.3 nm; $\sigma_A = 0.43\ \text{nm}^{-2}$)
bars: arrangement according to Fig. 2, but without spacer layer ($\sigma_A = 0.01\ \text{nm}^{-2}$).

On the other hand, in systems where donor and acceptor are located at the same layer the quenching of the donor fluorescence at constant acceptor density is strongly increased by increasing the surface density of the donor (bars). At high surface density of the donor excitonscan hop between donor molecules and then reach the acceptor more easily than at low density.

The amount of quenching is strongly dependent on the thickness of the spacer layer. For 2.0 nm the fluorescence is quenched by 70 %,for 2.2 nm by 50 %,for 2.7 nm by 10 %. From the amount of fluorescence quenching the rate of electron transfer k_{DA} relative to the decay rate without acceptor, k, can be given ($k_{DA}/k = I_o/I - 1$). The rate k_{DA} thus obtained is found to decrease exponentially with increasing interlayer thickness [4]. An independent way to demonstrate the exponential

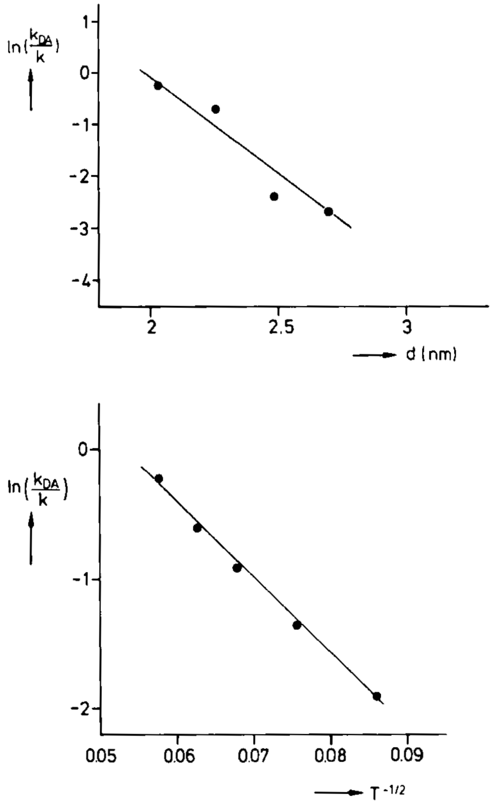

FIGURE 5. Rate constant for electron transfer (k_{DA}) in arrangement of Fig. 2 obtained from lifetime of fluorescence

a) $\ln(k_{DA}/k)$ versus d at T = 300 K b) $\ln(k_{DA}/k)$ versus $T^{-1/2}$ at d = 2.2 nm. Surface density of acceptor $\sigma_A = 0.43\ nm^{-2}$.

dependence of the rate constant k_{DA} on the distance d is given by measuring the fluorescence lifetime of the donor, which should be shortened due to the electron transfer, because the electron transfer competes with the fluorescence emission. The fluorescence lifetime shortening is a measure of the rate constant of electron transfer ($k_{DA}/k = \tau_o/\tau - 1$ (τ and τ_o are the fluorescence lifetimes with and without A respectively)), and again this rate is found to decrease exponentially with distance d of donor and acceptor (Fig. 3 (Fig. 5a)[7]. The electron transfer rate decreases with decreasing temperature. A linear relation is observed between the logarithm of the rate constant (obtained from lifetime measurements) and $1/\sqrt{T}$ (Fig. 5b). The observed exponential decrease of the electron transfer rate with increasing distance d and increasing values of $T^{-1/2}$ indicate quantum mechanical tunneling of electrons through the energy barrier representing the fatty acid ester interlayer. However, in evaluating the data given in Fig. 5 some unexpected results appear which should be of a more general interest in discussing electron transfer reactions. It is found[8] that eq. (1) is relevant in the present case which differs in an important point from standard expressions describing electron tunneling[9].

$$k_{DA} = \frac{1}{t_c} \varepsilon S \text{ (for } k_B T > \varepsilon > h/8t_c) \qquad (1)$$

k_{DA} is the electron transfer rate from D to A at distance r in the case $\varepsilon > h/8t_c$, t_c is the time between thermal collisions (10^{-12} s). ε is the perturbation energy of donor and acceptor. In the present case donor and acceptor are π electron systems with their molecular planes in the layer plane

(Fig. 6). If the wave functions at long distance from the centers are described by hydrogen like $2p_x$ atomic orbitals

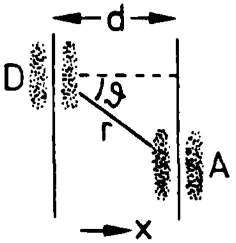

FIGURE 6. Tunneling of a π electron from D to A. Wave function at long distance described by superposition of $2p_x$ atomic wave functions.

and if only the highest power of αr is considered we obtain

$$\varepsilon = \kappa \varphi (\alpha r)^3 e^{-\alpha r} \cos^2 \vartheta \cdot \qquad (2)$$

where $\alpha = \sqrt{2m\varphi}/\hbar$. φ is the barrier height, m the mass of the electron, $\hbar = h/2\pi$ and h Planck's constant and $\kappa = \frac{2}{5}$. If both wave functions are expressed as a superposition of such orbitals, each related to an antinode of the molecular orbital and if these orbitals are described in the approximation of the free electron model we obtain in the present case, after averaging over all different orientations of D and A within the monolayer plane, the approximate relation $\kappa = 0.6 \sin \vartheta$ (I am indebted to Dr. Orrit for the calculation).

ε and not ε^2 (as in standard procedures) enters eq.(1). The factor S in eq. (1) is given by

$$S = \sum_{vw} \langle \psi_{Do} \psi'_{Dv} \rangle^2 \langle \psi_{Ao} \psi'_{Aw} \rangle^2 \frac{1}{k_B T} e^{-\frac{\Delta_{vw}}{k_B T}} \qquad (3)$$

$\langle \psi_{Do} \psi'_{Dv} \rangle^2$ is the probability that the donor, after removal of the electron, is in vibronic state v, $\langle \psi_{Ao} \psi'_{Aw} \rangle^2$ the probability that the acceptor, after having captured the electron, is in vibronic state w. Δ_{vw} is the activation energy needed to reach energetic match. k_B is Boltzmann's constant, T the absolute temperature.

For a layer assembly where several acceptor molecules are in the range of a donor we obtain from (1)-(3)

$$k_{DA} = A\, e^{-\alpha d - \beta (Td)^{-1/2}} \tag{4}$$

$$A = \frac{1}{t_c} \cdot \frac{1}{k_B T} \cdot \bar{\kappa}\, \varphi\, (\alpha d)^3 \langle \psi_{Do}\, \psi'_{Dv} \rangle^2 \langle \psi_{Ao}\, \psi'_{Aw} \rangle^2 \tag{5}$$

$$\beta = \left(\frac{\ln 2\, \Delta E \alpha}{\pi \sigma_A\, k_B} \right)^{1/2} \tag{6}$$

where d is the distance of donor and acceptor layers. ΔE is the energy difference between vibronic levels, σ_A the surface density of the acceptor. The reaction is assumed to be exergonic. $\bar{\kappa} \cong 0.3$.

Equation (4) agrees with the experimental finding (Fig. 5) and the values

$A = 1.5 \cdot 10^{15}\ s^{-1}$, $\alpha = 4.7\ nm^{-1}$, $\beta = 88\ K^{1/2}\ nm^{1/2}$

are obtained from the data given in Fig. 5 and the experimental value $k=1.5\ 10^9 s^{-1}$.* We shall compare the values thus obtained with the theoretical expectation. In the case of a H-atomic 2p orbital $\alpha = 1/(2a_o)$ where $a_o = 53$ pm is Bohr's radius. In the present case (medium of dielectric constant 2.5 between donor and acceptor **) $\alpha \cong 1/(2.5 \cdot 2a_o) = 3.8\ nm^{-1}$, in good agreement with the experimental value $\alpha = 4.7\ nm^{-1}$.

* The data given in ref. 8, Fig. 7a, were obtained by using N,N'-dioctadecyl-thiacyanine, and not N,N'-dioctadecyl-oxacyanine as stated there. By this inconsistency the parameter values given in ref. 8 are somewhat different from those given here. The numerical factor 3/20 in eq. (5) in ref. 8 should be exchanged for κ given in the present paper. The numerical values given for ε and t_{DA} in ref. 8 (after eq. 5) relate to the values $\varphi = 0.84$ eV and $\alpha = 4.7\ nm^{-1}$ given here and not, as stated there, to $\varphi = 0.36$ eV, $\alpha = 3.1\ nm^{-1}$.

** It was shown in many cases [10] that the correlation of π electrons can be treated very successfully by considering the σ electrons as dielectric of dielectric constant 2.5.

A similar value $\alpha = 4\ \mathrm{nm}^{-1}$ is obtained from (1) by estimating φ from the height of the barrier by a fatty acid layer (2.3 eV below vacuum * [11]) and the level of the excited state of dye D (2.9 eV below vacuum [12]).

With the values $\alpha = 4.7\ \mathrm{nm}^{-1}$, $\sigma_A = 0.43\ \mathrm{nm}^{-2}$ (Fig. 5) $\Delta E = 0.17$ eV ($\Delta E = h\nu_o$ where ν_o is the frequency of the C-C valence vibration) $k_B = 8.62 \cdot 10^{-5}\ \mathrm{eV\ K}^{-1}$ we obtain from (6) $\beta = 69\ \mathrm{K}^{1/2}\mathrm{nm}^{1/2}$ in good agreement with experimental finding ($\beta = 88\ \mathrm{K}^{1/2}\mathrm{nm}^{1/2}$). Finally, by introducing the values given above and the value $\Sigma <\psi_{Do}\,\psi'_{Dv}>^2<\psi_{Ao}\,\psi'_{Av}>^2 = 0.1$ obtained from a free electron model approximation into (5) we obtain A-values between $10^{14}\ \mathrm{s}^{-1}$ and $10^{15}\ \mathrm{s}^{-1}$ in the temperature and distance range considered, in good agreement with the experimental value ($A = 1.5 \cdot 10^{15}\ \mathrm{s}^{-1}$). On the other hand, the standard procedure leads to an A value which is larger than the experimental value by 7 orders of magnitude [8].

Some Applications of Monolayer Assembly Techniques

While the probability of tunneling from an excited dye molecule to an acceptor at 5 nm is negligibly small, energy transfer is easily possible if an appropriate acceptor is present. This allows to discriminate between the two processes. This was demonstrated in the case of the photographic process which is sensitized by dyes at the silver bromide surface. Using the monolayer assembly technique, the dye molecules can be fixed at defined distances from the silver bromide surface [13]. It is important in evaluating such experiments to make sure that the sensitization of the

* It should be mentioned that this value reflects the dielectric nature of the hydrocarbon portion and not the energetic position of acceptor states in hydrocarbon.

photographic process measured in such arrangements is due to dye molecules present in the intended architecture and not due to molecules that have reached the silver bromide surface by imperfections of the assembly or by undesired rearrangement processes.

This possibility can be excluded in different ways. One way is to add an energy acceptor to the organized assembly at a distance of 5 nm from the sensitizing dye. It acts as competitor of well defined strength depending on its surface density. If the sensitization would be due to imperfections or layer reorganization,the energy acceptor would be ineffective as a competitor.

The contributions of energy transfer and electron injection to the spectral sensitization of AgBr vary strongly with the energetic position of the excited dye level and with the amount of neutral silver atoms at the silver bromide surface acting as acceptors for the excitation energy of the dye. With increasing surface density of these acceptors energy transfer becomes increasingly favourable as compared to electron injection, going from pure electron injection in one case to pure energy transfer in another case. This has been demonstrated recently by Steiger [14]. Some results are summarized in Fig. 7. They confirm our early experiments with monolayer assemblies on AgBr [15], which were strongly criticized [16]. (The criticism could be rejected in all points [17]). Thus an old controversial problem in photographic science has been finally resolved.

The possibility offered by the monolayer technique to arrange molecules in planned geometry has been used in many ways to determine molecular parameters and to study important physical phenomena. Dye molecules in a monolayer can be sandwiched between electrodes and fatty acid interlayers. The electrodes are evaporated films of aluminum (Fig. 8). The absorption band of the dye can be measured.

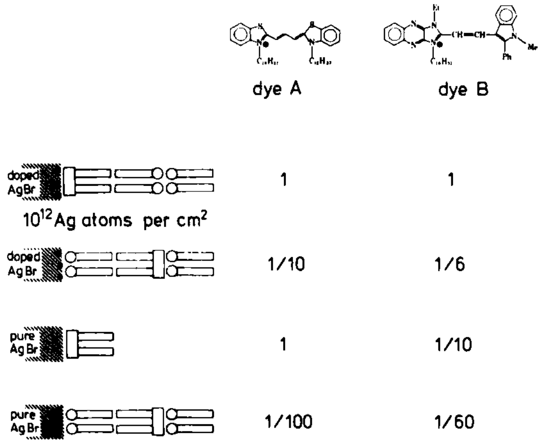

FIGURE 7. Spectral sensitization of photographic process. Effect of doping AgBr by neutral Ag atoms (according to Steiger [14]).

Dye A (excited dye level within conduction band of AgBr). At contact: No effect by doping; dye acts by electron injection. At 5 nm: Strongly enhanced spectral sensitization by doping; dye acts by energy transfer to neutral Ag atoms.

Dye B (excited dye level below conduction band of AgBr). At contact and at 5 nm: Strong enhancement of spectral sensitization by doping; dye acts by energy transfer in both cases.

It is shifted by an applied voltage. The shift depends on the extent by which the dipole moment and the polarizability in the excited state of the dye molecule differ from the dipole moment and the polarizability in the ground state. The change in dipole moment produces a shift proportional

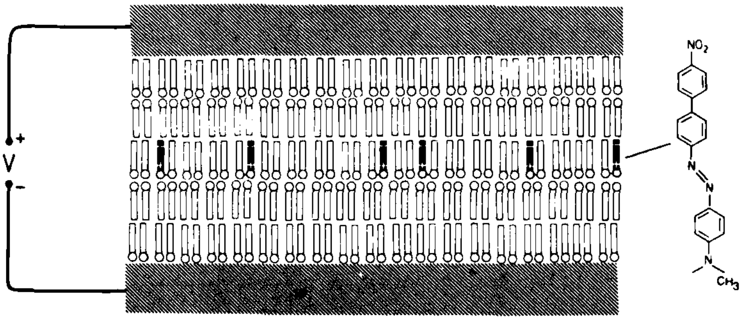

FIGURE 8. Monolayer assembly to measure shift of absorption band by electric field

to the applied field, the change in polarizability a shift proportional to the square of the field [18]. The monolayer assembly technique thus offers a method of measuring in a direct manner the dipole moment and the polarizability of the excited state of a molecule. Important is the fact that a molecule can be placed in strict orientation in an electric field by this technique.

In other similar arrangements quantum mechanical tunneling of electrons through a monolayer sandwiched between aluminum electrodes or between an aluminum and a superconducting lead electrode could be established [19]. Quantum mechanical hopping was studied in various superstructures under the influence of a constant or an alternating external electric field [20]. These measurements provide important information for the design of model potential profiles with the monolayer technique which is of great interest in many applications.

The interaction of a molecule with another molecule placed nearby can be used in many ways to study important physical phenomena. The interaction between two dye molecules changes the intensity and position of the absorption bands of both molecules in a typical manner [21]. The observed changes agree well with the result of quantum mechanical calculation. The energy of an excited molecule can be transferred to a specific singlet or triplet acceptor fixed at a certain distance [22] and even a molecule with no detectable luminescence can be stimulated to transfer its excitation energy to an appropriate acceptor [23]. In this case the architecture of the assembly must be designed in such a way that the energy transfer from the donor to the acceptor competes successfully with the transition from a higher vibronic level of the excited singlet state to lower levels which occurs in about 10^{-12} sec. The monolayer technique then allows to manipulate some processes in the pico second range. Monolayer arrangements have been investigated where the path of deexcitation of a molecule can be dramatically changed by proximity effects.

Another interesting aspect of monolayer assemblies is the manipulation of excitation processes by organizing the more distant environment of a molecule. This can be demonstrated in the case of a layer containing luminescent molecules covered by a number of fatty acid layers. The average lifetime of the excited state of each molecule can be measured for samples with different numbers of fatty acid layers. It is found to be markedly dependent on the distance of the luminescent species from the surface [24]. The emitted light wave is reflected at the surface and the echo-wave interacts with the source. The phase relation between echo-wave and source is relevant for the average lifetime of the excited state. The echo is retarded by a time of the order of 10^{-15} sec. This is then a very simple technique to investigate process in the femto second range.

This example demonstrates the possibility of modelling the electromagnetic field in the proximity of a luminescent molecule. Many different arrangements to demonstrate such phase relations have been investigated. Surface plasmon oscillation can be excited in an arrangement of a metal layer and a monolayer assembly with dye molecules at a given distance[25]. The sensitized excitation of surface plasmons by energy transfer from the dye to the metal is strongest at a certain distance of the dye molecule from the metal surface and is zero if the dye is placed near the surface[26]. This illustrates how the design of monolayer assemblies leads to new approaches in thin film optic research. The ability to manipulate excitation processes provides new ways to channel energy; in this case the surface plasmon can be excited via dye molecules that harvest the energy of the incident light.

These examples demonstrate the importance of methods allowing exact positioning of molecules. The synthesis of molecules that interlock forming designed assemblies to be used as tools of molecular size should be a challenging new field of great interest in future technologies in many different areas. The monolayer assembly techniques thus have certainly a great number of possibilities but the difficulties in building practical molecular electronic devices should not be underestimated.

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