256. Electron Transfer in Monolayer Assemblies with Incorporated Ruthenium (II) Complexes

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Herrn Dr. *Guido Schetty* zum 65. Geburtstag freundlich zugeeignet

(3.X.77)

Summary

An arrangement for light induced vectorial charge separation is discussed in which the electron of the excited dye is transferred to an acceptor and the dye is recovered by electron tunneling through a high and narrow potential barrier. The possible relevance of the model in connection with photosynthesis is considered. Monolayers of Ru(II)-bipyridine complexes with long chain hydrocarbon substituents were investigated which may be useful as component in such arrangements.

The surface pressure area isotherms of the monolayers were measured for various ionic compositions of the subphase, and the results demonstrate a strong effect of these ions on the structure of the layers. The layers were deposited on different substrates. The luminescence and its change by contacting the sample with water and by subsequent drying were found to be strongly dependent on the architecture of the layer assembly. Attempts of a photochemical cleavage of water with these assemblies failed.

The pH-dependence of the absorption and the luminescence of a Ru(II) bipyridine-dicarboxylic acid complex in solution is interpreted by assuming that the electron in the excited state is localized in one pyridine part of the substituted ligand, the conjugation with the second half of the bipyridine carboxylic acid being negligible. Monolayer assemblies for measuring the energy transfer from the ruthenium complex to an adequate energy acceptor and from an adequate energy donor to the ruthenium complex were investigated. The results demonstrate that the deactivation of the excited ruthenium complex occurs mainly by passing the luminescent state.

Assemblies were investigated for measuring the electron transfer from the excited ruthenium complex to an appropriate electron acceptor positioned in the carboxylate portion at the same interface as the electron donor. With bipyridinium ions as acceptor the ruthenium complex luminescence is quenched at average distances between acceptor molecules of about 10 Å, while this distance is 30, 60 und 75 Å for different cyanine dyes used instead of the ruthenium complex. A correlation between this distance and the ionization energy in the excited state of the donor is observed.

Introduction. – In attempting a photolytic cleavage of water, arrangements of specific molecular organization are of interest which allow the photo-electron to shift along a distinct path. An electron source and an electron sink are obtained where the aimed reduction and oxidation processes, respectively, should take place, if adequate catalysts are present. This directionality of the motion of electrons can be achieved by providing an adequate potential profile of the insulating barrier. A thin and high barrier should separate the excited dye and the electron donor, and prevent the photo-electron to move towards the donor. A lower and broader barrier should allow the excited electron to reach the acceptor and prevent its return to the oxidized dye. The thin barrier between dye molecule and donor, on the other hand, should permit an electron to tunnel from the donor to the oxidized dye molecule thus regenerating the original unexcited state *(Fig. 1)*.

This arrangement was discussed as a possible model for the primary step in photosynthesis and as a guideline in aiming at energy converting systems [1] [2] and it will be further considered here in connection with some experiments on the electron transfer in monolayer assemblies.

After excitation of dye **b** and subsequent transfer of the electron to **c** the system should recover by the transfer of an electron from **a** to **b** in a time τ_1 which is small compared to the time t_o until the next excitation of dye molecule **b** takes place. Therefore, $t_o \gg \tau_1$ where τ_1 is the tunneling relaxation time.

The subsequent reactions of the oxidized and reduced species should have taken place when the next quantum appears (time t_o). On the other hand these reactions should be as slow as possible, since reversibility of these reactions should be approached for keeping the loss of free energy as low as possible. Therefore they should take part within the time t_o.

Following a preceding paper [3] we assume interface traps at **b** (density $N_t = 10^{15}$ cm^{-2} eV^{-1}). If the tunneling from **a** to such a trap is the time determining step, the tunneling relaxation time is given by

$$\tau_1^{-1} = \tau_o^{-1}(2a_1 l_1)^{3/2} \exp\{-2a_1 l_1 - (4a_1/\pi N_t l_1 kT)^{1/2}\} \quad (1)$$

where kT is the thermal energy and $\tau_o = 10^{-12}$–10^{-13} s; a_1 is the damping constan of the electron wave function given by

$$a_1 = (2mV_1)^{1/2}/\hbar \quad (1a)$$

m is the mass of the electron, $\hbar = h/2\pi$ and h is *Planck*'s constant[1]), V_1 is the height of the tunneling barrier.

This equation which derives from the *Miller-Abrahams* equation [4] was found to be useful in the interpretation of a number of effects in monolayer assemblies [5].

If we assume that the top of the narrow barrier is at the level of the hydrocarbon portion of a fatty acid monolayer (at $\kappa \simeq 2.3$ eV below the energy of the electron in the vacuum [6],[7]) and that the electron donor site is $\simeq 4.5$ eV below vacuum, we obtain $V_1 = 2.2$ eV and therefore, in the case of a barrier thickness of $l_1 = 14$ Å, $\tau_1 \simeq 10^{-3}$s. In this case the condition $t_o \gg \tau_1$ is fulfilled for usual excitation rates.

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[1]) In [1] the simple equation $\tau_1^{-1} = \tau_0^{-1} \exp\{-2a_1 l_1\}$ was used. The results derived in the following are only slightly changed by using this equation instead of eq. (1).

The time τ_2 for tunneling from electron acceptor **c** to a trap at layer plane **b** is given by eq. (1) with index 2 instead of 1. Using the same values for N_t, V_1 and l_1 we find that the condition $\tau_2 \geq \tau_1$ is fulfilled for $l_2 = 25$ Å if $V_2 \geq 1$ eV and for $l_2 = 35$ Å if $V_2 \geq 0.6$ eV. Smaller values of V_2 than about 0.6 eV would not anymore prevent a back reaction by thermal excitation in the time interval considered. This example shows that the level of the electron acceptor must be low enough (V_2 large enough) to prevent back tunneling or a back reaction by thermal activation.

In the case of the photosynthesis the donor of photosystem I is at about 4.4 eV below vacuum. This follows from the redox potential at pH = 7 of cytochrome f ($E_o' = 0.38$ V; $E_o' = E_o + 0.42$ V) since the standard potential E_o in the case of an aqueous solution and the *Fermi* energy ε are related by $\varepsilon = -E_o e - 4.5$ eV (-4.5 ± 0.15 eV is the energy difference between an electron in the gas phase and the *Fermi* level of a standard hydrogen electrode [8]). The condition $t_o \gg \tau_1$ is fulfilled since $t_o \simeq 10^{-2}$ s in bright sunlight (each chlorophyll molecule is excited about once per second, and about 300 chlorophyll molecules transfer their excitation energy to the site where the electron is pumped), and in fact the system has recovered in about 1/50 s after each flash [9]. It seems reasonable to assume that the potential profile is represented by a protein molecule and then l_2 should not be much larger than about 25 Å. The barrier V_1 might be represented by some hydrocarbon portion. As shown above this distance corresponds to a value $V_2 = 1$ eV. With a threshold excitation energy of $\Delta\varepsilon = 1.77$ eV [9] [10] the available free energy is $\Delta\varepsilon - V_2 = 0.8$ eV. This might explain why in plant photosynthesis the electron pump reaches a potential difference which corresponds to only about half the available excitation energy of 1.77 eV.[2])

As mentioned above this model is based on assuming the existence of interlayer states at **b** of the same density as in artificial monolayer assemblies, where we had to assume such states for explaining the observed electron tunneling over distances as large as 28 Å. On the other hand, *Hopfield & Potasek* [12] disregard the existence of such states and therefore find typical tunneling distances of 8–10 Å.

The principle of the proposed mechanism is unchanged if intermediate states are assumed in the transition from **b** to **c** (dashed arrows in *Fig. 1*). Indications for such intermediate state have been found in photosynthesis. In the case of bacterial photosynthesis [13] it was concluded recently from the magnetic field dependence of the primary photochemical reaction [14] that the electron transfer following the excitation of P (probably a bacteriochlorophyll dimer) to acceptor X (probably an iron ubiquinon complex) *via* a primary acceptor I (probably bacteriopheophytin, 0.12 eV below P*) occurs in a nanosecond. This high rate constant supports the principle mechanism proposed above and in [1].

Monolayer assemblies are particularly promising in attempting to construct an artificial electron pump by modelling an appropriate potential profile. The

[2]) It seems not unreasonable to consider reduced cytochrome f as donor at **a** *(Fig. 1)* which can pass an electron to P 700$^+$ at **b** *via* plastocyanine at **b** or directly. Some evidence is given by observations on flash signals with half times 10 µs and 0.2–0.3 ms when cytochrome f and plastocyanine were partially reduced (reduction potential 340 mV and 385 mV respectively): The 10 µs signal was attributed to plastocyanine, the 0.2–0.3 ms signal to cytochrome f [9]. Both signals were confirmed by following the decay of the light induced ESR. signal of P 700$^+$ [11].

assembly technique [15] allows to construct planned organized arrangements of appropriate molecules. The monolayer assembly can be planned for charge separation across the layers as well as for charge separation within the layer plane. In both cases we intend to represent the high barrier by the hydrocarbon portion of a fatty acid monolayer. In the first case the low barrier is aimed to be modelled by chain like π-electron systems that can be fixed in a monolayer assembly with their long axes perpendicular to the layer plane [16]. In the second case the low barrier is constituted by the carboxylate portion of the fatty acid monolayer.

In preliminary studies for this second possibility a monolayer of a dye containing a hydrophilic chromophore and hydrocarbon chains is deposited on a glass plate with hydrophobic surface which is then coated by a monolayer of fatty acid containing an electron acceptor *(Fig. 2)*. By varying the mixing ratio of acceptor and fatty acid the efficiency of the acceptor can be studied, and this efficiency is found to depend clearly on the relative energetic position of electron-donor and -acceptor levels [17].

In the following we discuss arrangements according to *Figure 2*, containing the ruthenium bipyridine complex **1** investigated by *Sprintschnik et al.* [18] [19] as photo-electron source. The strong luminescence of the complex in the monolayer assembly is partially quenched in the presence of the electron acceptor (1,1′-dioctadecyl)-(4,4′-bipyridinium) perchlorate.

The energy transfer from ruthenium complex **1** to an appropriate acceptor and from an appropriate donor to **1** used as acceptor are investigated for obtaining information on the path of deactivation by comparing the quantum yields q′ (ratio between the number of emitted and absorbed quanta) and q (ratio between the number of emitted quanta and the number of molecules that reached the luminescent excited state).

Experimental data by *Wrighton et al.* [20] on Ru(II)-(2,2′-bipyridine)$_2$-(2,2′-bipyridine-4,4′-dicarboxylic acid)$^{2+}$ in aqueous solutions are discussed and results

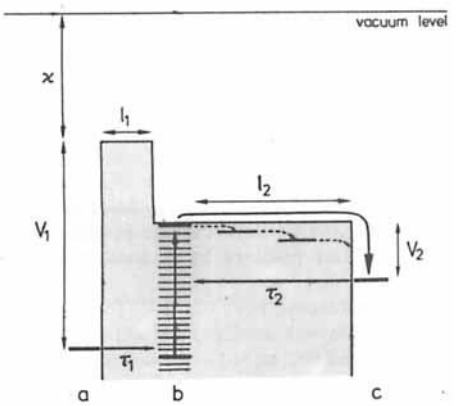
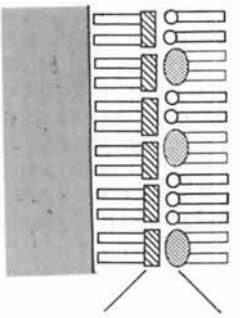


Fig. 1. *Potential profile of a possible arrangement for light driven charge separation.* Light induced electron transfer from **b** to **c** and recovery by transferring electron from **a** to **b** tunneling through high, but thin barrier.



Dye or complex **1** Electron-acceptor **8**

Fig. 2. *Monolayer assembly for investigating charge separation within layer plane*

on the electron localization in the luminescent excited state are obtained which are of interest in discussing possible reactions in the excited state.

The oxidation potential of the excited $Ru(II)(bipy)_3^{2+}$ (-0.56 V [21]) is slightly more negative than the potential necessary for the evolution of gaseous hydrogen in neutral water (-0.41 V). Investigations of photochemical oxidation and reduction processes in solutions of Ru(II)-(bipyridine)$_3^{2+}$ [22] indicate, that ruthenium complexes may be used for energy storage [23]. Recently *Whitten et al.* [24] found in Ru(II) complexes, where the charged Ru(bipyridine)$_3^{2+}$ core is surrounded by aliphatic substituents, that the complex is photoreduced by appropriate electron donors to $Ru(bipy)_3^{+1}$ and that the back reaction is almost entirely avoided. A high energy and reactive product could be isolated [24]. Assemblies of appropriately designed architecture with incorporated ruthenium complexes may be suitable in experiments for attempting a photolytic cleavage of water. *Sprintschnik et al.* observed a strong quenching of the luminescence of monolayers of the ruthenium complex **1** deposited on a glass slide when dipping the sample in water and they reported an evolution of H_2 and O_2 to take place when illuminating the submersed sample with a mercury lamp or with sun light.

In carrying out similar experiments we were not able to confirm a photolytic cleavage of water, as shown below. The effect found by *Sprintschnik et al.* might be dependent on unexplored details determining the structure of the assembly such as the influence of certain impurities. Some effects of impurities on the structure of assemblies are discussed below.

Experimental Part

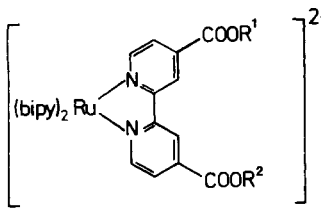
Materials. – Three preparations of surfactant derivatives of tris(2,2′-bipyridine) ruthenium complexes have been used. Two different preparations of the Ruthenium(2,2′-bipyridine)$_2$-(4,4′-dioctadecyl-carboxyl-2,2′-bipyridine)$^{2+}$ perchlorate:

Preparation **1a** obtained from *D. G. Whitten* in 1974; preparation **1b** by Dr. *Steiner, Ciba-Geigy AG*, Basel, which was cleaned by chromatography; ($C_{68}H_{96}Cl_2N_6O_{12}Ru$; Calc: C 59.99; H 7.11; Cl 5.21; N 6.17; Ru 7.42; Found: C 60.1; H 7.1; N 6.2; Cl 5.3; Ru 7.2; H_2O: 0.5%).

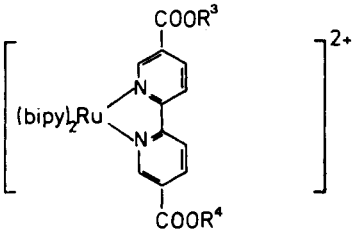
Preparation **2** of the analogue 5,5′-dioctadecylester ($C_{68}H_{96}Cl_2N_6O_{12}Ru$; Calc. C 59.99; H 7.11; N 6.17; Cl 5.21. Found C 60.1; H 7.1; N 6.6; Cl 5.7; H_2O: 0.4%) and of the 4-octadecyl-4′-ethylester **3** were also supplied by Dr. *E. Steiner.* The liquid chromatography spectrum of preparation **1b** kindly supplied to us by Dr. *G. L. Gaines*, General Electric, Schenectady, indicates complex **1** with only traces of other compounds. The arachidic acid ($C_{19}H_{39}COOH$) from *E. Merck*, Darmstadt, *p.a.*, was used after recrystallization from ethanol (m.p. 74.5–75.3°) for coating glass plates prior to transfer of ruthenium complex monolayers or for preparation of mixed monolayers. The electron acceptor (1,1′-dioctadecyl)-(4,4′-bipyridinium) perchlorate **8**, the energy acceptor 1,1′-dioctadecyl-4,4′-carbocyanine perchlorate **6** and the energy donor 1,1′-dioctadecyloxacyanine perchlorate **7** were prepared by *J. Sondermann* in this laboratory [25].

The solvents (chloroform, tetrahydrofurane), *Baker Analyzed Reagent*, were run through a column of Al_2O_3 (Aluminia, *Woelm* B-Super I) before use. The chloroform was stabilized by addition of 2% *(v/v)* ethanol. The salts ($CdCl_2$, $NaHCO_3$, NaCl, KSCN, NaF, KI) and HCl added to the bidistilled water (monolayer subphase) were *p.a.* from *Merck*, Darmstadt. The water was cleaned as described in [15].

Surface Pressure – Area – Isotherms. – The isotherms of spread monolayers of the ruthenium complex were determined at 22° with the circular *Langmuir* balance described in [15]. A volume of 0.04 ml of spreading solution (concentration of the ruthenium complex 1×10^{-3} M in $CHCl_3$) was delivered to the water surface by means of a glass syringe *(Agla)* within about 10 s on an area of 1000 cm^2. Immediately after spreading the area was decreased at a rate of 14 Å^2 molecule^{-1} min^{-1}.



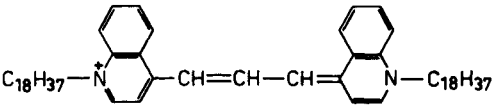
1 $R^1 = R^2 = C_{18}H_{37}$
3 $R^1 = C_{18}H_{37}$ $R^2 = C_2H_5$
4 $R^1 = R^2 = H$



2 $R^3 = R^4 = C_{18}H_{37}$

5 $R^3 = R^4 = H$

6



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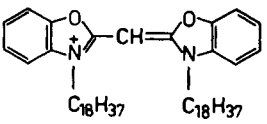

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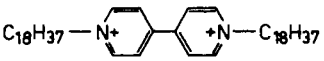


9 $Ru(bipy)_3(ClO_4)_2$

Preparation of the support. – The different solid substrates for monolayers or multilayer systems in spectroscopic measurements, corrosion and photolysis experiments were plates of glass, glass treated with $Si(CH_3)_2Cl_2$, glass coated with cadmium arachidate layers, quartz plates, and polystyrene films treated with sulfuric acid. The dimensions of the supports were 38 mm × 12 mm × 1 mm in spectroscopic measurements and in determining the loss of monolayer material during illumination under water. In the photolysis experiments coated supports of the dimensions 76 mm × 24 mm × 1 mm or thin (0.1 mm) glass plates (38 mm × 38 mm) were placed in the reaction vessel.

Cleaning procedures of the solid substrates. – a) *Ultrasonic cleaning with alcaline surfactant.* The glass plates were put in a stainless steel plate holder where contact between glass and holder occurred at the plate edges only. The holder with 40 plates was immersed in a tank with 1 l of aqueous solution of *Trokil* 764 (*Benckiser*, 10 g/l). The plates were sonicated for 7 min at 80° (40 kHz). The cleaning solution was removed from the tank and the plates were sonicated with distilled water. This procedure was repeated 5 times. Finally, the plates were individually rinsed with bidistilled water which was pressed through a *Millipore* filter and dried in heated air flow.

b) *Cleaning with chromic sulfuric acid.* The glass plates were placed in a plate holder made from glass and put in chromic sulfuric acid (*p.a.* $K_2Cr_2O_7$ saturated in *p.a.* H_2SO_4) at 90° for 2 h. Then, the plates were transferred with the holder into a beaker with bidistilled water, standing in the ultrasonic tank in bidistilled water and sonicated for 2 min. The water in the beaker was replaced 4 times by fresh bidistilled water. This was followed by ultrasonic treatment in *p.a.* concentrated H_2SO_4 and another 5 ultrasonic washes in bidistilled water. Then, the plates were treated in the ultrasonic tank with NaOH (5% in water) and washed as before 5 times with bidistilled water in the ultrasonic tank.

c) *Acid cleaning.* The glass plates were put in a plate holder made of glass and immersed in a mixture of 97% (by volume) H_2SO_4 conc. *(p.a.)*, 2% HNO_3 conc. and 1% HCl conc. for 1 h at 80°. Then the glass plates were transferred as in procedure b into bidistilled water and washed in the ultrasonic tank. The wash was repeated 6 times with fresh bidistilled water.

d) *Treatment with nitric acid after cleaning according to procedure a.* The glass plates in the plate holder were immersed in conc. nitric acid for 24 h at room temperature. Subsequently, the plates were washed under ultrasonic action as in procedure 3 with bidistilled water (5 times).

For treatment with dimethyldichlorosilane sets of 18 cleaned glass plates were put for 10 min into 250 ml of $Si(CH_3)_2Cl_2/CHCl_3$ 1:1. The plates were then transferred into 300 ml methanol. After 2 min the plates were put in 500 ml water. The water surface was then cleaned by sucking off about 200 ml of water. The plates, on removal from the remaining water should emerge completely dry. In case of water droplets or patches on the solid surface the plates were discarded.

Sulfonation of the polystyrene films. – For spectroscopic measurements pieces with the dimensions $38 \times 12 \times 0.6$ mm^3 were used. In water photolysis experiments coated films (thickness 0.1 mm) of 200×32 mm^2 were folded to form a package of approximately 30×32 mm^2. The polystyrene (PS) pieces were put in the glass holder used for cleaning glass plates and treated with a mixture of 95% (by volume) of H_2SO_4 conc. *p.a.* and 5% Oleum, *p.a.* at temperatures between 60 and 70° for 80–100 s. The reaction mixture was vigorously stirred by means of a teflon coated magnet with a magnetic stirrer. The thin (0.1 mm) PS film was put on a glass grid and treated in the same way. Subsequently the PS pieces or films, respectively, were immersed in a 2% (by weight) solution of sodium hydrogencarbonate in bidistilled water for 10 min at 22°. Then, the PS was washed six times with bidistilled water (without ultrasonic treatment), immersed for 10 min at 22° in 500 ml 1N HCl and washed another five times with bidistilled water. The PS films or pieces were kept under water und coated the same day with monolayer systems.

Monolayer stability and transfer. – For measurement of the stability of spread monolayers on the water surface under a defined surface pressure an automatic device was used for maintaining a constant pressure and recording the area occupied by the monolayer. This device consisted of a rectangular trough (11.35×39 cm^2, 5 mm deep) made from polytetrafluorethylene and provided, with a hole for dipping glass plates. The surface pressure was measured with a *Wilhelmy* balance similar to the type described earlier [26], and *via* a feed-back loop a movable barrier (also made from *Teflon*) was activated to maintain constant surface pressure. The position of this barrier is recorded which defines the area occupied by the monolayer. This device was also used in the measurement of the monolayer transfer ratio r_R, *i.e.* the ratio of the decrease of monolayer area on withdrawal of the solid substrate and the geometrical area of the coated solid.

The plates used for spectroscopic measurements and for water photolysis experiments were coated by using simple mechanical troughs of the type described in [15]. The surface pressure is applied to the floating barrier *via* a pulley by means of the defined weight.

For lowering and raising the plates a simple motor driven lift was used at a rate of 15 mm/min. In the measurements of the transfer ratio r_R a device with motor-generator described by *Fromherz* [27] was used.

Absorption and luminescence spectra. – Absorption spectra of solutions were measured in a *Cary* 118 spectrophotometer. The absorption spectra of monolayers transferred on glass plates were measured in the photometer described in [15]. Luminescence spectra of solutions were measured in a *Fica* 55 spectrofluorometer and luminescence spectra of transferred layer-systems were measured in the spectrofluorometer described in [15], which was provided with a different excitation part and corrected for detection monochromator transmission and photomultiplier response (*EMI* 9669 QB). In these measurements the exciting light from a 100 W super pressure mercury lamp (air cooled) was focussed by a quartz lens on the slit of a *Bausch & Lomb* 250 mm grating monochromator. The luminescence of the monolayers was excited under normal incidence und measured under an angle of 45°. In experiments to determine the luminescence quenching of ruthenium complex monolayers due to contact with a monolayer containing the electron acceptor **8**, slides were coated in part without the acceptor layer (reference area). Then the luminescence intensity I of the complex along the long axis of the glass plate was measured by moving the glass plate, and the ratio I (with acceptor)/I_0 (without acceptor) was determined. The additional quenching by contact with water was then determined by using a special cuvette with

interchangeable front plate [27]. This device was also used in determining the temperature dependence of the luminescence spectra and relative intensities of monolayers on glass in contact with water.

For recovery of the luminescence after quenching by contact with water, the plates with the monolayer of preparation **1b** were dried in high vacuum (6×10^{-7} Torr) at 25° or 50° for 30 min. Then, the luminescence intensity (excitation at $\lambda=435$ nm, luminescence at λ 690 nm) was measured in room air.

Water photolysis experiments. – Three different types of reaction vessels have been used in experiments to detect water photolysis catalysed by the excited ruthenium complex in monolayers.

Arrangement 1. A water filled glass bell (⌀= 80 mm) with a small closed glass tube (⌀8 mm) on top was loaded with 29 coated glass slides of the size 76×26 mm^2 in a plate holder. This bottomless reaction vessel was put in a dish filled with water. The total volume of the vessel was 700 ml. This assembly corresponds to that used by *Sprintschnik et al.* without stopcock at the top glass tube. The assembly was illuminated through a heat filter (*Schott* KG 3, 3 mm) with a 200 W super pressure mercury lamp at integrated intensities between 55 and 140 mW/cm^2.

Arrangement 2. This is intended to reduce the volume to monolayer surface ratio and to prevent gas exchange with the atmosphere. A 50 ml glass flask was loaded with maximal 120 coated glass plates (cover glass, 0.1 mm thick, 24×32 mm) which were separated from each other at about 0.3 mm. This assembly was illuminated with a 200 W super pressure mercury lamp provided with a concave mirror, a collecting lens and a heat filter (*Schott* KG 3, 3 mm or 55 mm water). The photon flux absorbed by the ruthenium complex monolayers on the glass plates was calculated to approximately 5×10^{-9} Einstein/s.

Arrangement 3. The reaction vessel was intended for electrochemical determination of oxygen and hydrogen dissolved in the water. A glass cylinder (see *Fig. 3*) was provided with fittings for two electrodes. The ends of the cylinder were closed by quartz plates using *Viton* rings. The volume (36 ml) was loaded with up to 35 coated glass plates (32×26 mm^2) which were placed in a *Teflon* holder for keeping the plates apart. The assembly was illuminated with a 200 W super pressure mercury lamp through heat filters (*Schott* KG 3, 3 mm) and a filter glass for cutting off the yellow and red part of the spectrum (*Schott*, BG 12, 3 mm). The photon flux absorbed by the ruthenium complex was between 2 and 5×10^{-9} Einstein/s.

The oxygen concentration in the water was determined in a part of the experiment with a commercial *Clark* electrode (WTW, Type E_0 16 and for more sensitive measurements Orbisphere model 2711) which was calibrated by measuring a series of solutions with oxygen concentrations between 0 and 8 mg/l. An increase of the oxygen concentration of 15 μg/l and 0.5 μg/l, respectively, was detectable.

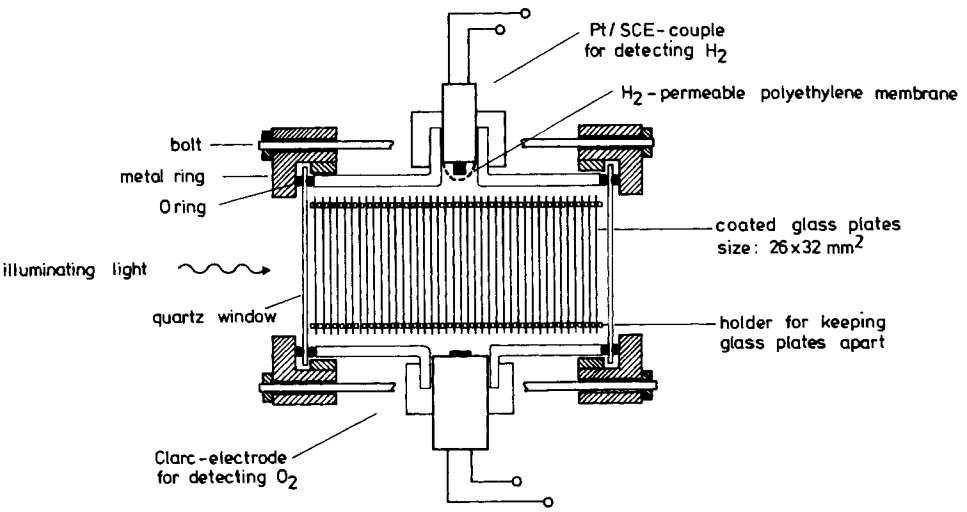


Fig. 3. *Arrangement for investigating photochemical cleavage of water*

Hydrogen does not interfere in these oxygen measurements. The concentration of hydrogen dissolved in the water was determined by measuring the potential of an activated platinum electrode with respect to a saturated calomel reference electrode (SCE). The electrode couple was separated from the photolysis solution by a hydrogen permeable polyethylene membrane and kept in a buffered solution at pH 6.9. The potential due to the hydrogen in the water depends further on pH, temperature and oxygen content [28]. This dependence was evaluated for the used platinum-SCE couple, and a partial pressure of hydrogen as low as 2 Torr H_2 (4 μg/l) could be detected. The activity of the electrode was checked after each photolysis experiment by adding small volumes of water, saturated with hydrogen, to the reaction vessel.

Some monolayer material is removed from the support on immersion in water under illumination and also when kept in the dark. The fraction of monolayer material in the aqueous phase after a period of immersion of the coated support was determined after addition of tetrahydrofurane (THF/water 1:10, *v/v*) to dissolve the material, by measuring the absorption at the wavelengths $\lambda = 436$ nm and $\lambda = 470$ nm. At these wavelengths the absorption is independent of the ratio of diester to saponified material which might be formed.

Surface pressure-area isotherms. – *Sprintschnik et al.* [18] [19] reported a cleavage of water after photoexcitation of two ruthenium bipyridine complexes organized in monolayers on glass plates which were immersed in water, and it was assumed that the reported action of the excited complex might be due to a specific organization in the monolayer.

An indication for the molecular organization in a spread monolayer on a water surface is the surface pressure (π)-area (A)-isotherm. The isotherm of the ruthenium bipyridine complex on water containing $CdCl_2$ and $NaHCO_3$ at pH 6.2, given in [18] differs considerably from that measured by *Gaines et al.* [29]. We have reproduced the isotherm given by *Sprintschnik et al.* with the original preparation **1a**, but found for preparation **1b** under the same conditions an isotherm similar to that of *Gaines et al. (Fig. 4)*. Further, monolayers of both preparations on bidistilled water, pH 5.6, under a constant surface pressure of 30 dyn/cm exhibit quite different decrease in monolayer area with time. In case of preparation **1a** the area per molecule immediately after reaching 30 dyn/cm (at compression rate of 190 Å^2/molecule min.) is $A_{1a}(o) = 51$ Å^2 and after 10 min $A_{1a}(10) = 28.6$ Å^2. In the case of preparation **1b** the decrease in monolayer area is negligible ($A_{1b}(o) = 73$ Å^2 and $A_{1b}(10) = 69.4$ Å^2). The dissolution of monolayer material from preparation **1a** under a surface pressure of 30 dyn/cm was detected by observing the fluorescence of the complex in the subphase on excitation with blue light.

The shape of the π/A-isotherm and consequently the molecular organization within the monolayer depends strongly on the composition of the subphase. *Gaines et al.* [29] have reported isotherms of the ruthenium bipyridine complex **1** on 0.1M HCl subphase which differ considerably from those on a subphase at pH 6.8 containing 2.5×10^{-4}M $CdCl_2$ and 5×10^{-5}M $NaHCO_3$. We have measured π-A-isotherms with various anions at different concentrations in the subphase. The results are shown in *Fig. 5* for HCl(a), NaCl(b), NaF(c), KSCN(d) and KI(e), $CaCl_2$(f), $CdCl_2$(g). In the case of NaOH increasing concentration led to monolayer instability presumably due to hydrolysis. In agreement with *Valenty & Gaines* [29] we found that at pH = 12 the hydrolysis occurs within 1 min.

From *Fig. 5* it is seen, that subphase anion concentrations as small as 10^{-5}M are sufficient to change the monolayer organization. In the cases of the anions Cl^- and F^- the shape of the isotherms depends strongly on the concentration of the added salt up to 10^{-2}M in the subphase whereas in the cases of SCN^- and I^- only slight changes of the isotherms are observed at concentrations higher than 10^{-5}M. Compared with the isotherms measured on bidistilled water the addition of salt to the subphase results in an expansion effect below 30 dyn/cm which decreases with decreasing hydratization in the series $F^- > Cl^- > I^- > SCN^-$. This is in agreement with *Goddard et al.* [30] who have studied counterion effects on positively charged monolayers, *e.g.* of trimethyldocosylammonium-ions. They obtained expansion effects of the counter-ion in the subphase in the series $F^- > Cl^- > Br^- > NO_3^- > I^- > SCN^-$.

In the cases given in *Figure 5* the area at a given surface pressure is independent of the compression rate in the range between 14 Å^2 molecule^{-1} min^{-1} and 70 Å^2 molecule^{-1} min^{-1}. The monolayer area at constant surface pressure decreases with time and reaches a constant value. In the case of complex preparation **1b** this relaxation process is fast compared to the compression. In the case of the complex with chloride counter-ion this relaxation process is slow and influences the measured π-A-curve.

Monolayer Transfer. – Monolayers of preparation **1b** and complex **2** were transferred at $\pi =$ 30 dyn/cm and a rate of 15 mm/min onto glass surfaces and onto glass coated with two layers of

arachidate on withdrawal of the immersed plate. The transfer ratio r_R was found on coating glass from bidistilled water, pH = 5.6, $r_R = 0.88$ (preparation **1**) and $r_R = 0.99$ (complex **2**). In the case of glass coated with two arachidate layers the layers were transferred from bidistilled water with 2.5×10^{-4} M $CdCl_2$ and 4×10^{-5} M $NaHCO_3$, pH 6.4, and the values $r_R = 0.95$ (preparation **1b**) and $r_R = 0.99$ (complex **2**) were obtained.

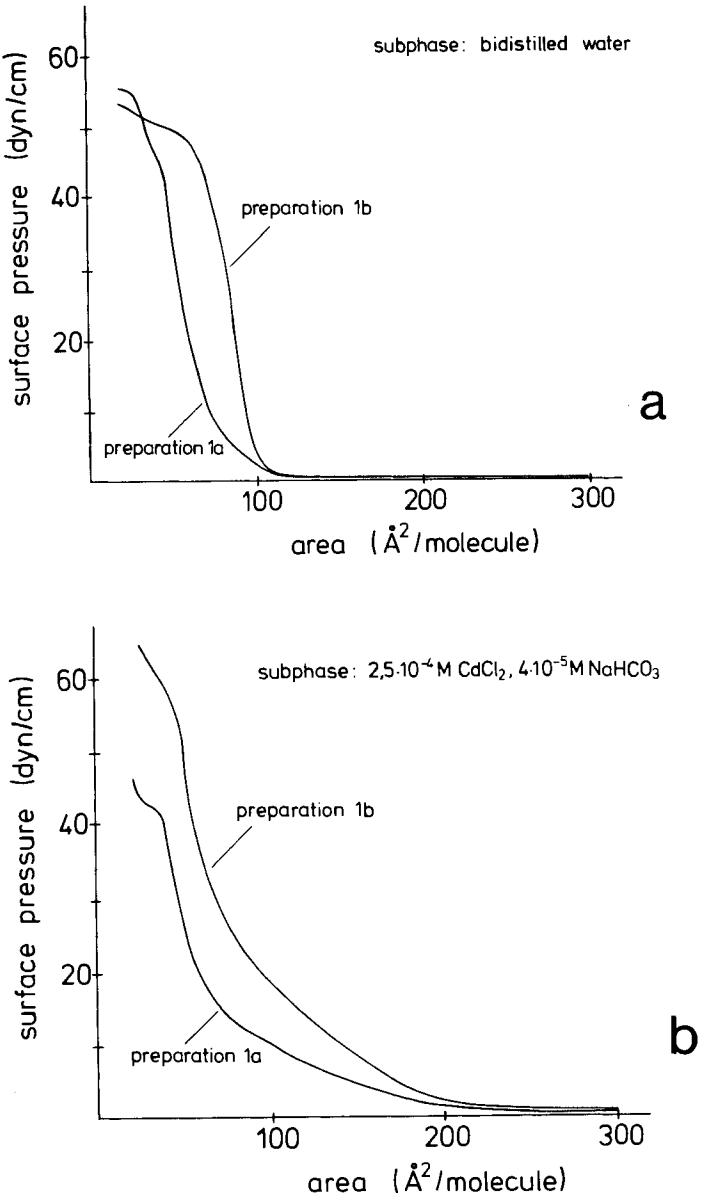
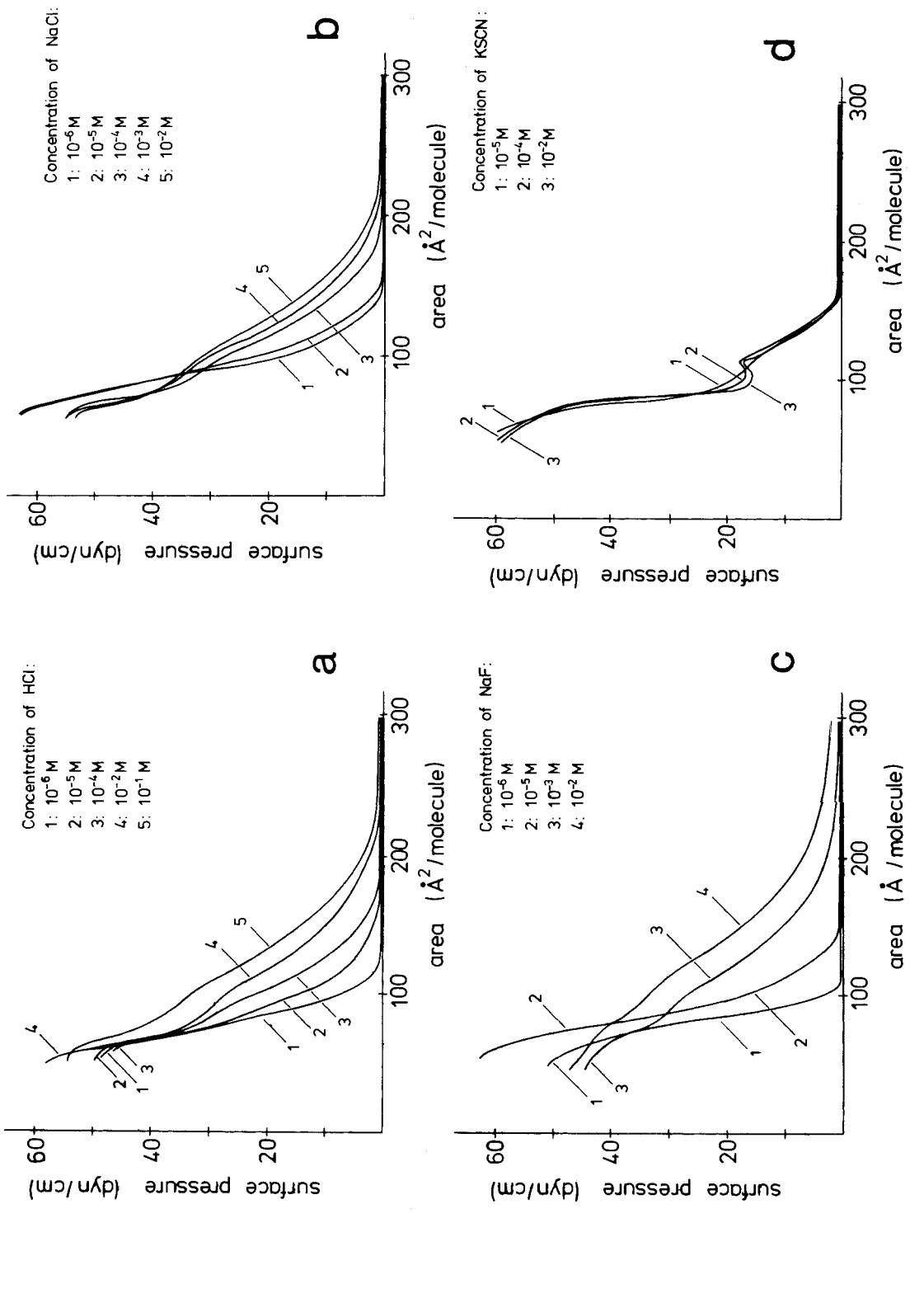
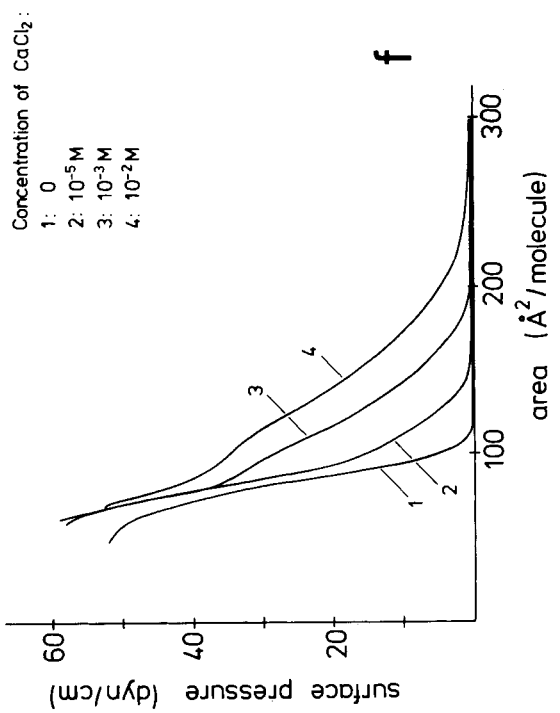
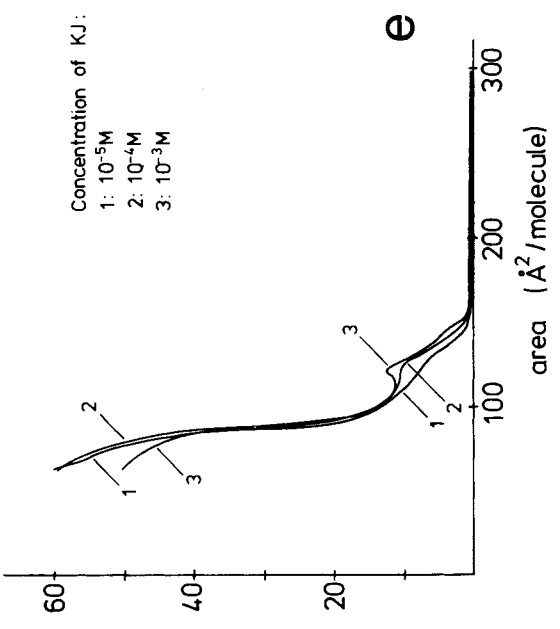


Fig. 4. Ru(II) complex **1** monolayers, preparations **1a** and **1b**. Surface pressure vs area per molecule at 24°. [a]) On bidistilled H_2O, pH: 5.6. [b]) On 2.5×10^{-3} M $CdCl_2$ and 5×10^{-5} M $NaHCO_3$ at pH 6.8.


a
Concentration of HCl:
1: 10^{-6} M
2: 10^{-5} M
3: 10^{-4} M
4: 10^{-2} M
5: 10^{-1} M
surface pressure (dyn/cm)
area (Å^2/molecule)
b
Concentration of NaCl:
1: 10^{-6} M
2: 10^{-5} M
3: 10^{-4} M
4: 10^{-3} M
5: 10^{-2} M
surface pressure (dyn/cm)
area (Å^2/molecule)
c
Concentration of NaF:
1: 10^{-6} M
2: 10^{-5} M
3: 10^{-3} M
4: 10^{-2} M
surface pressure (dyn/cm)
area (Å/molecule)
d
Concentration of KSCN:
1: 10^{-5} M
2: 10^{-4} M
3: 10^{-2} M
surface pressure (dyn/cm)
area (Å^2/molecule)





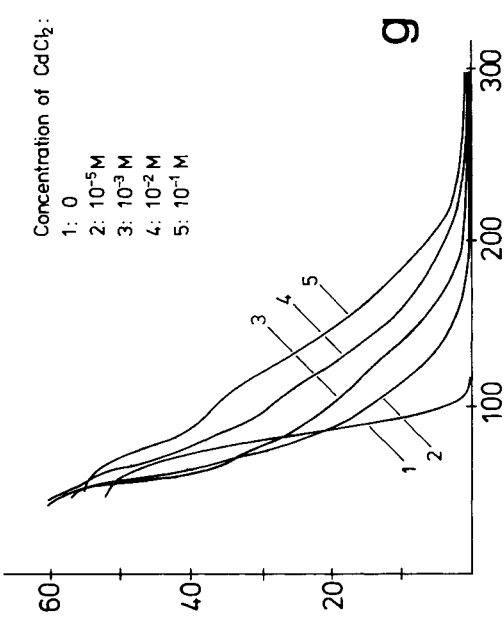


Fig. 5. Ru(II) complex **1** monolayers, preparation **1b** on subsolutions of different electrolytes at various concentrations. Surface pressure vs area per molecule at 24°, pH 5.6–5.8 (*Fig. 5a–f*), pH 6.3–6.8 (*Fig. 5g*). [a]) HCl; [b]) NaCl; [c]) NaF; [d]) KSCN; [e]) KI; [f]) $CaCl_2$; [g]) $CdCl_2$ ($NaHCO_3$ $5 \cdot 10^{-5}$ M).

Luminescence Quenching by Water and Recovery. – In *Fig. 6* absorption and luminescence spectra are plotted of monolayers on quartz of the ruthenium bipyridine complex preparations **1a**, **1b** and **2**. The spectra of complex **2** differ markedly from those of preparations **1a** and **1b**.

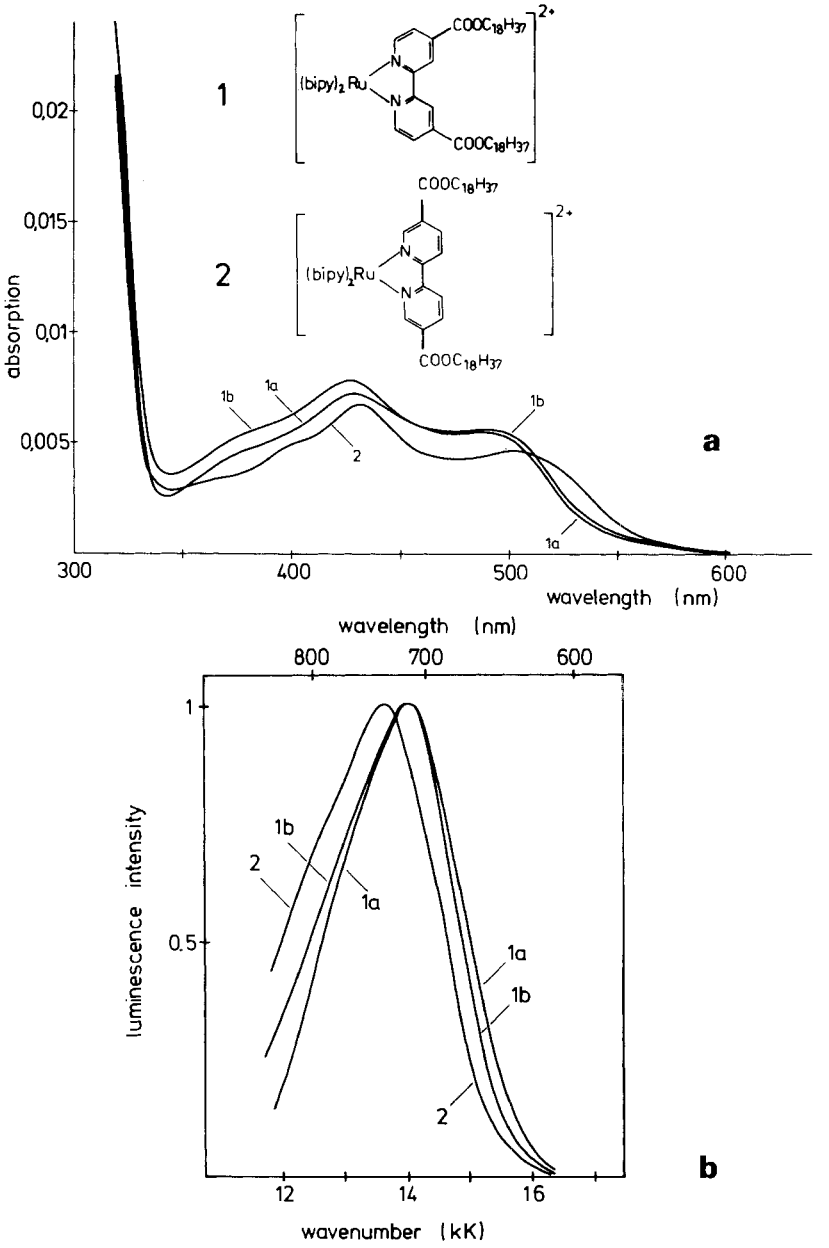


Fig. 6. *Monolayer of complex* 1, *preparations* (1a), (1b) *and complex* (2) *on quartz substrate.* [a]) absorption, [b]) luminescence (photons per wavenumber interval, arbitrary units)

Further, we observed only small differences due to different substrates, *e.g.* glass and glass coated with two arachidate layers, and sulfonated polystyrene. The luminescence intensity of monolayers of complex **2** is about 100 times smaller than that of preparations 1a and 1b.

Liquid water in contact with monolayers of the ruthenium bipyridine complex quenches the luminescence almost entirely according to *Sprintschnik et al.* [18] [19] and the luminescence is regenerated when drying the sample by heating *in vacuo* (3 Torr at 70°).

We have measured the changes in luminescence intensity ($\lambda_{excitation} = 435$ nm, $\lambda_{luminescence} = 690$ nm) for different preparations and substrates:

I_o (before contact with water), I_W (immersed in water), $I_{W,d}$ (after drying, as described in the experimental section, of the slides that were immersed) and $I_{o,d}$ (intensity of the original layers, treated in high vacuum). The results are given in *Table 1* and *2*. We find a marked difference between the I_W/I_o values of complexes **1** and **2** and the values depend considerably on the architecture of the assembly. The quenching effect of D_2O is somewhat smaller than that of H_2O. A stronger isotope effect was observed in solutions of $Ru(bipy)_3Cl_2$ [31].

Sprintschnik et al. investigated the luminescence in solution and found no quenching on substitution of Dioxan or THF by Dioxan/water and THF/water respectively. They concluded that the specific organization of the complex in monolayer assemblies is essential for the luminescence quenching by water. We measured the relative integral emission intensity of preparation **1b** and of the corresponding

Table 1. *Luminescence quenching by water.* Ratio of luminescence intensities I_W/I_o (I_o before contact with water, I_W immersed in water).

Monolayer arrangement	Preparation		
	1a	**1b**	**2**
G	0.1	0.14 (0.18[a])	0.55
Q	0.15	0.30 (0.36[a])	0.6
G	0.1	0.12	–
G	–	0.11	–
G	–	0.4	–
G	–	0.3	–
G	–	0.4	–
G	–	0.26	–
G	–	0.25	–
SPS	0.35	0.34	–
GH	–	0.41	–

Symbols: G = glass, Q = quartz, GH = silanated glass, SPS = sulfonated polystyrene.
[a]) Immersed in D_2O.

Table 2. *Monolayers of preparation* (1b) *on quartz.* Recovery of luminescence by drying in high vacuum at different temperatures after immersion in water (symbols see text).

°C	I_W/I_o	$I_{W,d}/I_o$	$I_{o,d}/I_o$
25	0.35	0.95	1.30
50	0.35	1.05	1.35

carboxylic acid complex **4**, complex **5** and complex **9** in different solvents (exciting light at 435 nm, probes adjusted to the same optical density 0.34, concentrations in the range 2.5 to 3×10^{-5} M at 20°). A solution of preparation **1b** in THF was used as standard (luminescence intensity I_0). The results are given in *Table 3.* Our data show that an appropriate mixture of preparation **1b** and the 4,4′-acid **4** would exhibit the properties observed by *Sprintschnik et al.*, and according to *Gaines et al.* the preparations used by *Sprintschnik et al.* are indeed partially hydrolysed. The weak luminescence of the 5,5′-acid **5** compared with the strong luminescence of the 4,4′-acid **4** is remarkable.

Energy Transfer Experiments. – Information on pathways of deactivation of excited molecules can readily be obtained from studies of *Förster* energy transfer from a layer of excited molecules (donor) to a layer of an appropriate energy acceptor [15] [32]).

From the distance dependence of the energy transfer the critical distance d_0 can be determined, *i.e.* the distance at which deactivation of the luminescent state by energy transfer is equal to deactivation by other processes. The distance dependence is determined by measuring the relative donor luminescence intensities.

$$\frac{I_d}{I_\infty} = \left[1 + \left(\frac{d_0}{d}\right)^4\right]^{-1} \tag{2}$$

$$d_0 = \alpha\,(\lambda_D/n) \cdot q_D^{1/4} \left(\int f(\tilde{\nu})\, A_A(\tilde{\nu})\, (\tilde{\nu}_D/\tilde{\nu})^4\, d\tilde{\nu}\right)^{1/4} \tag{3}$$

In these equations I_d and I_∞ are the luminescence intensities of the donor layer with the acceptor layer at distance d or at infinite distance, respectively, α a factor which depends on the orientation of the transition moments of donor and acceptor molecules, λ_D the wavelength of the luminescence maximum of the donor, n the refractive index of the medium, q_D the probability of photon emission of a donor molecule in the luminescent state, $f(\tilde{\nu})$ the luminescence quantum spectrum normalized according to $\int f(\tilde{\nu})\, d\tilde{\nu} = 1$, $A_A(\tilde{\nu})$ the absorption spectrum of the acceptor layer, and $\tilde{\nu}_D$, the wavenumber of the luminescence maximum of the donor. Since d_0, α, λ_D, n, $f(\tilde{\nu})$ and $\tilde{\nu}_D$ can be experimentally determined the quantity q_D can be calculated from eq. (3).

In monolayer systems with mixed layers of preparation 1b and arachidic acid (r = 1:100) as donor and mixed layers of the 1,1′-dioctadecyl-4,4′-carbocyanine (**6**) and methylarachidate and arachidic acid (r = 1:2:18) d was varied by deposition of spacer layers of arachidate between donor and acceptor layers. In *Fig. 7* the relative luminescence intensities I_d/I_∞ are plotted *vs.* d (bars). The curve represents eq. (2) with the value $d_0 = 50$ Å. In *Fig. 8* the luminescence quantum spectrum of the donor layer and the absorption spectrum of the acceptor layer are shown. Accordingly the integral in eq. (3) has the value 7.1×10^{-4}. With $\alpha = (1/4\pi)3^{1/4}$ (transition moments of donor spatially statistically distributed, of acceptor statistically distributed in layer plane [33]), $\lambda_D = 7050$ Å, n = 1.50 and $d_0 = 50$ Å the value $q_D = 0.15$ is obtained from eq. (3).

Table 3. *Relative integral emission intensities of different ruthenium bipyridine complexes in different solvents*

(**1b**)	in chloroform	3.1	(**5**)	in THF/H_2O (1:10, *v/v*)	< 0.1
(**1b**)	in THF	1	(**9**)	in H_2O	14.6
(**1b**)	in THF/H_2O (1:10, *v/v*)	0.4	(**9**)	in THF/H_2O (1:10, *v/v*)	17.8
(**4**)	in THF/H_2O (1:10, *v/v*)	9.2			

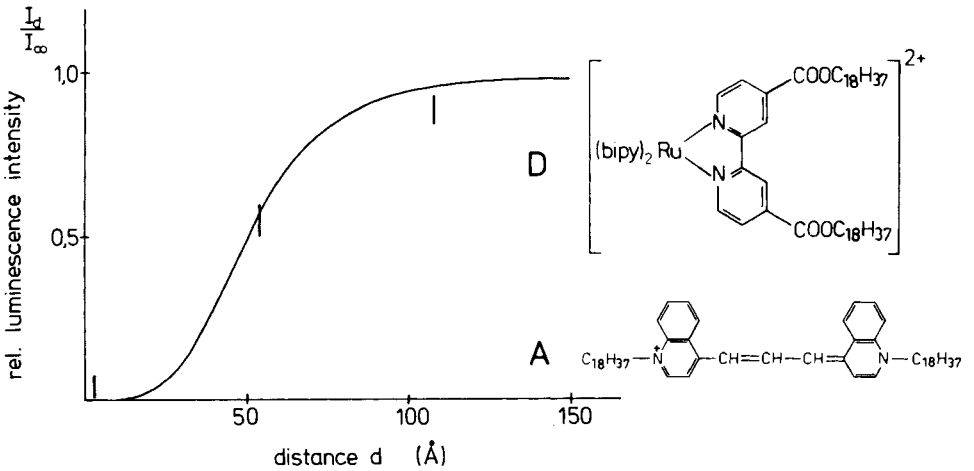


Fig. 7. *Energy transfer in layer systems.* Complex **1** as energy donor D and cyanine dye **6** as energy acceptor A. Luminescence intensity of D *vs.* distance between monolayers D and A.

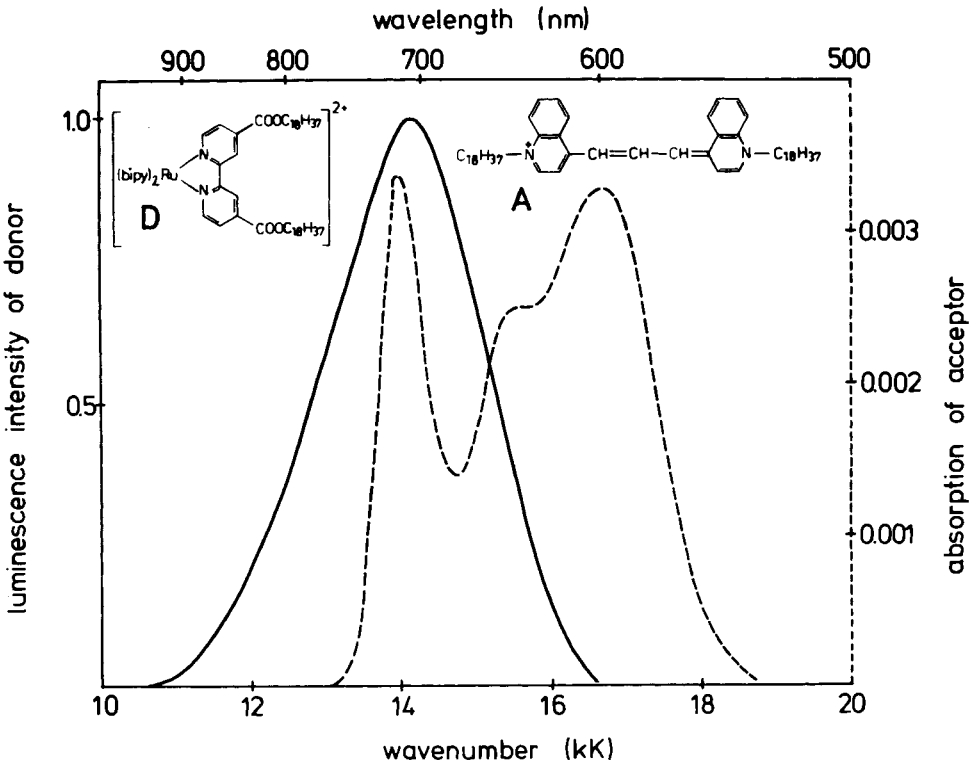


Fig. 8. *Luminescence quantum spectrum of monolayer of Ru complex* **1** (donor in system in *Fig. 7*) *and absorption spectrum of monolayer of dye* **6** (acceptor A in system in *Fig. 7*)

A comparison of the quantity q with the luminescence quantum yield, q′, defined as the ratio of emitted photons and absorbed photons per unit time may provide evidence for the occurrence of deactivation processes of the excited molecule prior to reaching the luminescent state. In monolayer systems the luminescence quantum yield can be determined indirectly by an energy transfer method [34], which does not require absolute photon flux measurements.

A donor layer (case a) and a donor acceptor assembly (case b) are illuminated under equal conditions. We first assume that the luminescence of the donor is completely quenched by the acceptor. n_D is the number of quanta per unit time emitted by D in arrangement a), n_A is the corresponding quantum number emitted by A in arrangement b). In case b) each molecule D that has reached the luminescent excited state transfers energy to A, and the fraction q'_A of excited A molecules emit a quantum of light. In case a) the fraction q_D of the molecules in the luminescent excited state emits a quantum of light. Thus, $n_A/n_D = q'_A/q_D$ and therefore

$$q'_A = q_D \frac{n_A}{n_D}$$

If the acceptor layer is at distance d the energy transfer is incomplete. Fluorescence light of the donor is still present and its intensity I_d can be compared with the intensity I_∞ in case a). The fraction transferred to A is given by $1-I_d/I_\infty$. Thus

$$\frac{n_A}{n_D} = \left(1-\frac{I_d}{I_\infty}\right) q'_A/q_D \text{ and therefore } q'_A = q_D \frac{n_A}{n_D} \cdot \left(1-\frac{I_d}{I_\infty}\right)^{-1} \quad (4)$$

The ratio of n_A/n_D is obtained from a plot of the corrected luminescence quantum spectra. According to *Figure 9* $n_A/n_D = F_A/F_D$.

This simple method is valid in the case of identical angular distributions of the emissions of D and A. This is the case for the cyanine dyes in mixed monolayers where the transition moments are in the layer plane with statistical distribution.

For measuring q′ of the ruthenium complex, this complex must be used as acceptor and combined with an appropriate donor. The transition moment can be assumed as statistically oriented in space. Therefore, the factor β has to be introduced in the right side of eq. (4) to allow for this difference. This factor is $\beta = 1.33$.

With a mixed layer of the 1,1′-dioctadecyl-oxacyanine **7**, methylarachidate and arachidic acid (r = 1:2:18) and a monolayer of preparation **1b** at distance d = 54 Å (see *Fig. 9*) we obtained $I_{54}/I_\infty = 0.25$ and $n_A/n_D = 0.15$. The value q_D was determined for donor **7** in separate measurements of energy transfer to a layer of 1,1′-dioctadecyl thiacyanine mixed with methylarachidate and arachidic acid (r = 1:2:18) and the value $q_D = 0.60$ was found. With these data from eq. (4) the quantum yield of luminescence of the ruthenium bipyridine complex monolayer, preparation **1b**, was calculated to $q'_A = 0.12$. With mixed layers of preparation **1b** and arachidic acid, mixing ratio r = 1:10 and 1:100 values of q'_A between 0.1 and 0.2 have been obtained. The values for q and q′ (0.15 and 0.1–0.2 resp.) coincide, and therefore the deactivation occurs mainly by passing the luminescent state. In the case of complex **2** the value q′ = 0.003 was obtained. The spectroscopic properties of the Ru(II)-(bipyridine)$_3^{2+}$ complex have been investigated [35] and in EPA-solution the quantum yield q′ = 0.28 [36] was found at 12°.

Electron Transfer Experiments. – The luminescence of a monolayer of excited dye molecules in contact with a monolayer of an appropriate electron acceptor is quenched due to electron transfer from the dye to the acceptor. As in the investi-

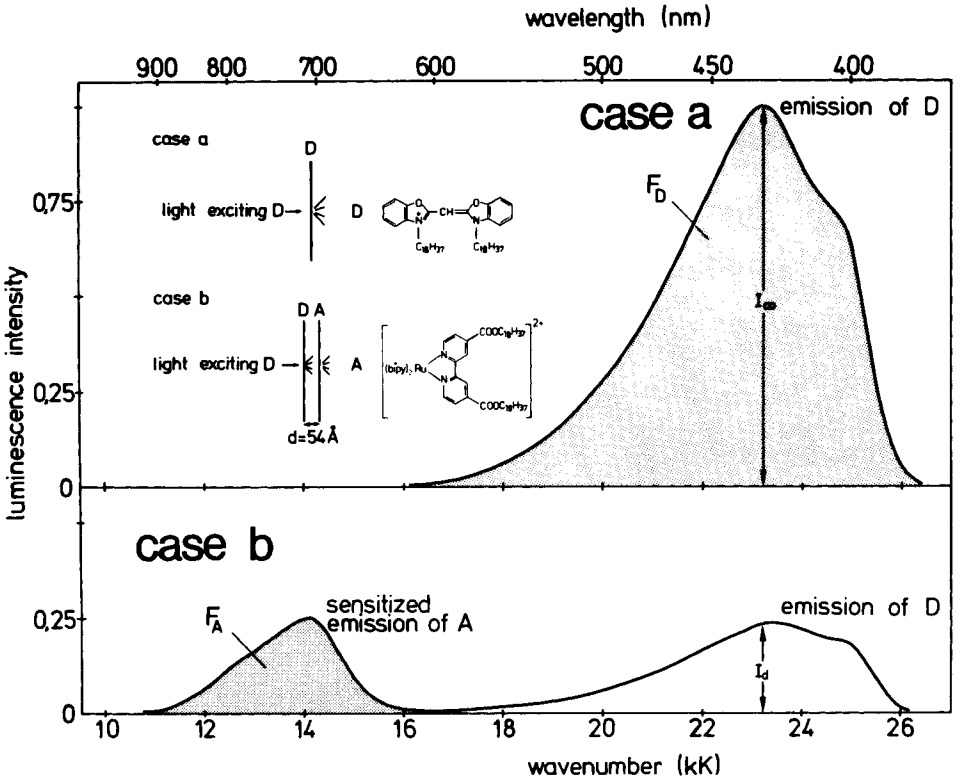


Fig. 9. *Energy transfer in layer systems.* Cyanine dye **7** as energy donor D and Ru-complex **1** as energy acceptor A. Corrected luminescence quantum spectrum. [a]) Layer of D, [b]) Layers of D and A at distance d = 54 Å.

gation of energy transfer the ratio of luminescence intensities I/I_0 can be determined (I in presence of the electron acceptor, I_0 in the absence of the electron acceptor). The luminescence quenching depends on the density of acceptor molecules in the monolayer which can be varied by varying the mixing ratio of acceptor to inert matrix molecules (methylarachidate and arachidic acid) in the mixed monolayer. From the mixing ratio the average distance $\bar{R}$ between acceptor molecules can be calculated, assuming a statistical distribution.

In *Figure 10* the ratio I/I_0 is plotted against $\bar{R}$ for the electron acceptor 1,1'-dioctadecyl-4,4'-bipyridinium (**8**) and the electron donors 1,1'-dioctadecyl-oxacyanine (**7**) (circles) and the ruthenium complex, preparation **1b** (squares). In the case of the oxacyanine the electron transfer is seen to be effective up to $\bar{R} \simeq 100$ Å, whereas in the case of the ruthenium complex this separation is less than 10 Å.

We define by $\bar{R}_{1/2}$ the value of $\bar{R}$ corresponding to 50% quenching ($I/I_0 = 1/2$). In *Fig. 11* $\bar{R}_{1/2}$ of a series of donor molecules is plotted against ε^* which is a measure of the ionization energy in the excited state of the dye molecule. We define by ε^* the sum of the excitation energy $\Delta\varepsilon$ and of the *Fermi* energy ε of the redox system of

dye and its oxidized state. The value of ε is related to the oxidation potential E_o as mentioned on p. 4. Thus:

$$\varepsilon^* = -eE_o - 4.5\ eV + \Delta\varepsilon \tag{5}$$

E_o was taken from polarographic measurements [37] and $\Delta\varepsilon$ was assumed to be given by the average of the energies corresponding to the absorption and fluorescence maximum of dye molecules in solution. The level on the right in *Figure 11* corresponds to the *Fermi* energy of the redox-system paraquat/violen radical (obtained by uptake of an electron from paraquat) ($E_o = -0.41$ V, thus $\varepsilon = -4.1$ eV). The level is below the levels of each dye, and this is in harmony with the fact that the fluorescence of the dye can be quenched in each case by paraquat. If *e.g.* the 1-octadecyl-pyridinium salt is used as electron acceptor instead of the 1,1'-octadecyl-4,4'-bipyridinium salt the level is between the levels of dyes, and a quenching effect is observed only in the cases of the dyes located energetically higher than the level of the electron acceptor [17].

By measuring the quenching of the luminescence of $Ru(bipy)_3^{2+}$ by quenchers of various reduction potentials in solution, *Whitten et al.* [21] found a threshold value which allowed them to give the value of the oxidation potential of the excited complex. It agreed approximately with the value E_o-$\Delta\varepsilon/e$ where E_o is the oxidation potential in the ground state, and *Whitten et al.* concluded, that almost the full reducing power of the excited ruthenium bipyridine complex can be used for electron transfer reactions.

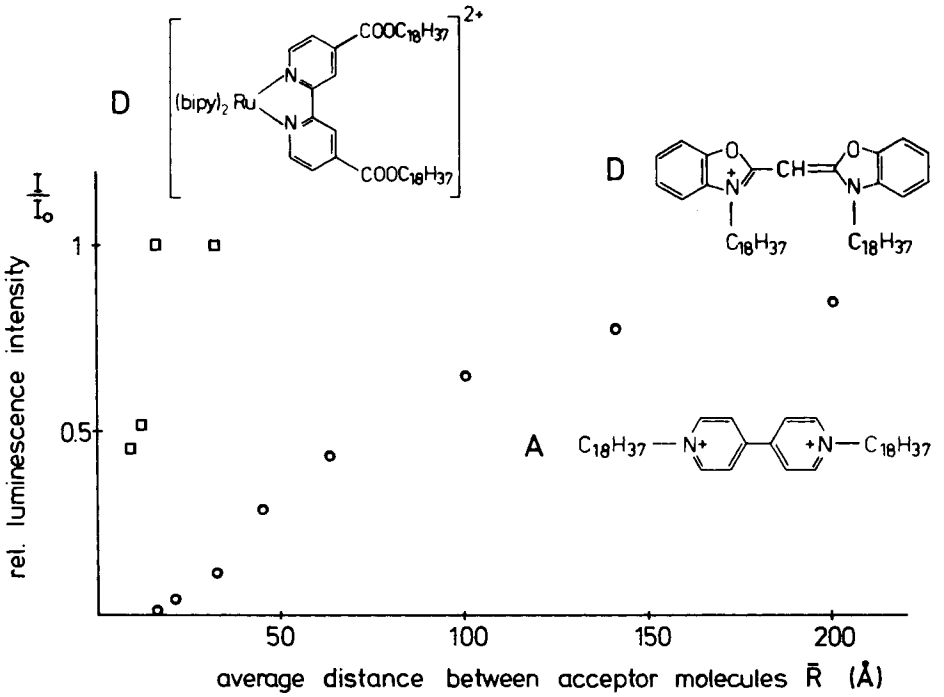


Fig. 10. *Electron transfer arrangement according to* Fig. 2. Intensity of luminescence of electron donor D *vs.* distance $\bar{R}$. $\bar{R}$ is the average distance between molecules of electron acceptor A in the mixed monolayer of A and Cd-arachidate as calculated from the mixing ratio assuming statistical distribution. Electron donor D: Ru complex **1** (squares) and dye **7** (circles), electron acceptor A: di-cation **8**.

This result is confirmed by our observations which show that all those acceptors act as quenchers which are energetically below the excited dye level.

The dashed line in *Figure 11* corresponds to the electron affinity of the hydrocarbon portion of a monolayer as obtained from tunneling measurements ($\kappa = 2.3$ eV). The levels of each dye are below that line, and this is in agreement with the observation, that the electron acceptor is inefficient when it is separated from the excited dye molecules by the hydrocarbon portion. The excited electron cannot jump over the potential of the hydrocarbon portion of the monolayer during the

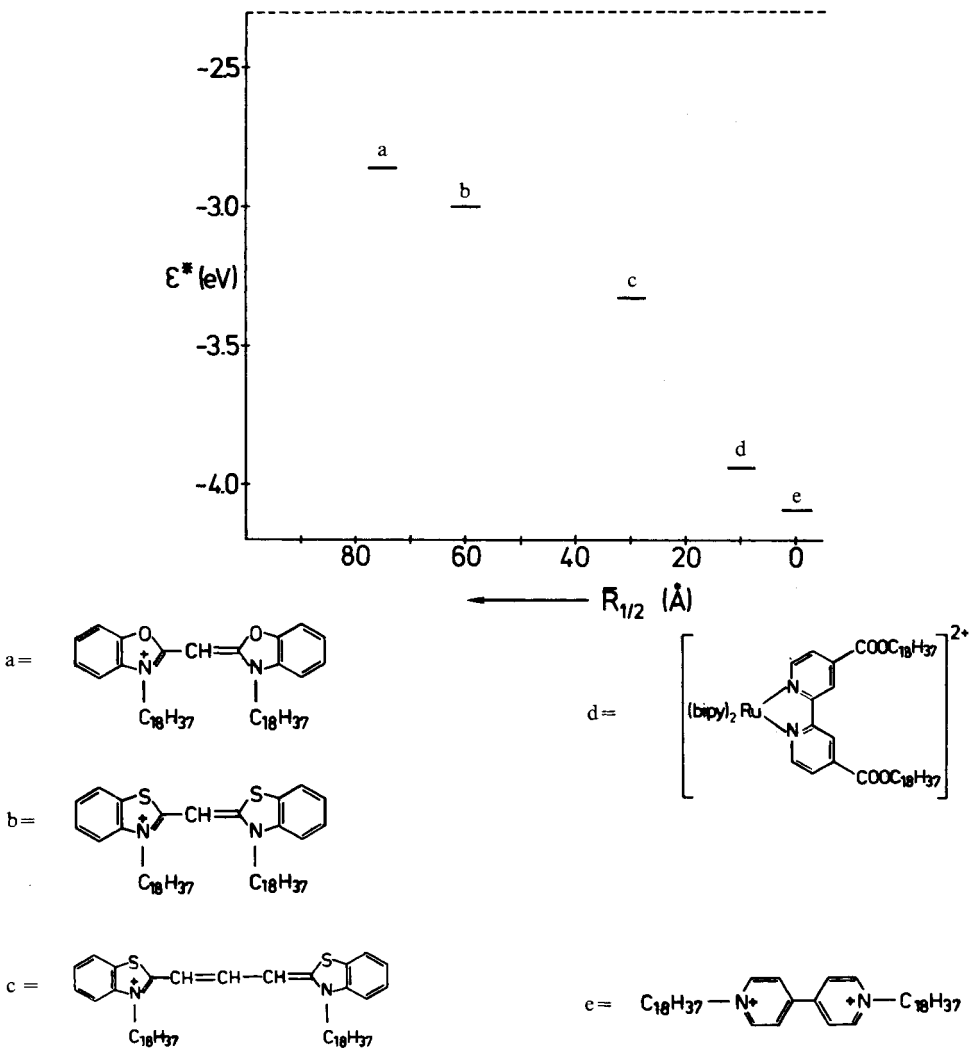


Fig. 11. ε^* vs. $\bar{R}_{1/2}$ *for different dyes as donor D and di-cation* **8** *as acceptor A.* ε^* is the excited state ionization energy (approximated from oxidation potential E_o and excitation energy $\Delta\varepsilon$, see eq. (5)). $\bar{R}_{1/2}$ is the average distance between A molecules in the case of a 50% quenching of the luminescence of D *(cf. Fig. 10).*

lifetime of the excited state [38], but can move along the ionic interlayer. Thus the electron affinity of this interlayer is larger than κ.

As *Figure 11* demonstrates, a correlation between the ionisation energy ε^* and $\bar{R}_{1/2}$ is clearly observed. It is surprising that such a simple and reasonable empirical relation can be given. Furthermore $\bar{R}_{1/2}$ should depend on the potential hight of the carboxylate portion and on the number of traps in that region.

The efficiency of electron transfer from an excited molecule to the adjacent acceptor monolayer might depend on the extent of exciton migration within the donor layer which will then be strongly reduced on separating the donor molecules by inert matrix molecules (methylarachidate and arachidic acid). The electron transfer was investigated with mixed monolayers of the ruthenium bipyridine complex. Only small differences are observed between the values obtained for pure complex monolayers and mixed monolayers (molar mixing ratio complex **1**/ arachidic acid 1:10; 1:100). Therefore, these results provide no evidence for exciton migration within the ruthenium-bipyridin-complex monolayers.

Electron Location in Excited State. – The pH dependence of the absorption and luminescence band of the Ru^{II}-(bipyridine)$_2$-(2,2′-bipyridine-4,4′-carboxylic acid)$^{2+}$ in aqueous solution has been investigated by *Wrighton et al.* [20]. They found a pK-shift between ground state and excited state species by measuring the pH-dependence of absorption and of luminescence. The authors found isosbestic points in the absorption spectra measured at various pH and concluded, that the intermediate AH^+ in the equilibrium $AH_2^{2+} \rightleftarrows AH^+ + H^+ \rightleftarrows A + 2\,H^+$ cannot be observed in the absorption spectrum. They considered the equilibrium constant $K_a = [H^+]^2[A]/[AH_2^{2+}]$ and the corresponding constant K_a^* for the excited state. The difference for the deprotonation reaction $AH_2^{2+} \rightarrow A + 2\,H^+$ in the ground state and in the excited state $(-RT\ \ln K_a^*) - (-RT\ \ln K_a) = RT \cdot 2.3\ (pK_a^* - pK_a)$ was compared with the band shift $\Delta\tilde{\nu}$ when proceeding from the protonated to the deprotonated species. *Wrighton et al.* found a considerable discrepancy between the measured pK_a change and the change calculated from this band shift

$$pK_a^* - pK_a = \frac{hc\Delta\tilde{\nu}}{2.3\,kT} \tag{6}$$

where k is *Boltzmann*'s constant, h is *Planck*'s constant and c is the velocity of light. The luminescence maximum shifts from 655 nm to 622 nm thus $\Delta\tilde{\nu} = 800\ cm^{-1}$ and from eq. (6) the difference $pK_a^* - pK_a = 1.6$ follows, whereas the measured difference is from $pK_a = 5.5$ to $pK_a^* = 8.5$. This difference is about twice the value calculated from $\Delta\tilde{\nu}$. In the absorption spectrum (*Fig. 1* in [20]) the contribution of the unsubstituted bipyridine rings interferes. Therefore, as mentioned by *Wrighton et al.*, the shift cannot be given with similar precision, but seems to be roughly the same as in the case of the luminescence.

However, in our opinion the observation must be interpreted as follows: the isosbestic points can be at first explained in two ways: 1) A is protonated directly to AH_2^{2+}, and the intermediate AH^+ does not appear in a measurable amount (for examples see [39]); 2) The absorption band can be considered as an electron

transfer from ruthenium to a pyridine nucleus, the excitation energy being independent on whether the other pyridine nucleus is protonated or not. In this case the absorption spectrum of the form AH^+ cannot be distinguished from the spectrum of an equally molar mixture of A and AH_2^{2+}.

By considering the maximum slope in the plot of the relative optical density change α against pH it can be distinguished between these two cases. According to case 1) this slope should be $(d\alpha/dpH)_{max} = 2.303/2 = 1.15$ as is easily seen from mass action law. The slope $(d\alpha/dpH)_{max} = 0.58$ is obtained from *Fig. 2* in [20] in contrast to this result. In case 2), however, the pyridine nuclei are independent species and in this case the slope $(d\alpha/dpH)_{max} = 2.303/4 = 0.58$ is expected, in agreement with experiment. (The interaction between the carboxyl groups is neglected as justified by the well known results on acidity constants of $\alpha\omega$-dicarboxylic acids).

The maximum slope in the plot of the emission intensity against pH has the same value $(d\alpha/dpH)_{max} = 0.58$. Therefore the p$K$ of the excited pyridine nucleus is independent on whether the other nucleus is protonated or not. Thus, the luminescence must be considered as an electron transition from the excited pyridine nucleus to the Ru, and the band shift by deprotonation should correspond to the difference in free energy of the deprotonation reaction $RCOOH \rightarrow RCOO^{\ominus} + H^{\oplus}$ in excited and ground state respectively (p$K^* = 4.25$ and p$K = 2.75$, see [20], *Fig. 2*). Thus, $pK^* - pK = hc\Delta\tilde{\nu}/2.3\,kT$. This difference $pK^* - pK = 1.5$ is exactly half the difference $pK_a^* - pK_a = 3$ and thus the discrepancy mentioned above has disappeared.

Thus, the electron in the excited state appears as being localized in the pyridine-carboxylic acid, the conjugation with the second half of the bipyridyl substituent being negligible.

Water Photolysis Experiments. – The different types of reaction vessels were used in order to reproduce the experiments of *Sprintschnik et al.* and to improve the methods of hydrogen and oxygen detection.

Small amounts of gas were collected during the initial 2 to 5 h with a total volume of 0.04 to 0.08 ml in the reaction vessels type 1 and 2. This gas volume decreased or remained nearly constant if deaerated water was used. In the case of water saturated with air or nitrogen this gas volume remained constant. A steady evolution of gas was not detected with any of the four preparations **1a**, **1b**, **2** and **3**. The formation of the small gas volume during the initial 2 to 5 h was also observed with samples coated with arachidate instead of ruthenium complex monolayers. Under conditions given for reaction vessel type 3 saturation of the water with hydrogen and oxygen would have been reached after 20 to 40 h in case of quantum yield 0.1 for water cleavage after photon absorption. In *Table 4* experiments are listed which have been conducted with the various schematically depicted systems in the reaction vessel 3. In no case hydrogen or oxygen production was detected.

As listed in *Table 4*, column 4, a removal of ruthenium bipyridine complex from the glass plates during illumination is observed with all systems used as detected by absorption measurement.

The monolayer arrangement, the pH in the reaction vessel and the exposure time has some influence on the removal of ruthenium complex from the layer system. The fraction of removed complex from assemblies used for photolysis experiments ranges from about 15% to 80% of the initial monolayer material. The monolayer material is lost from the solid substrate by dispersion and saponification and a part of the dispersed material is saponified subsequently. This follows from spectroscopic investigations since the diacid **4** emits a luminescence at 647 nm [29] that can be discriminated from the luminescence of the diester **1**.

In cases where the complex **1** was deposited on glass covered with even numbers of cadmiumarachidate monolayers the rate of removal increased with the number of arachidate layers.

Transferred monolayers of preparation **1b** on glass were saponified in the dark at temperature dependent rates, which increased under illumination in the range of ligand and CT absorption (intensity approximately 150 mW/cm^2) and in the infrared region (intensity 2000 mW/cm^2).

An aqueous solution of preparation **1b** (2×10^{-5}M) at pH 6.8 was saponified at 25° in the dark. Approximately 70% of the dispersed material was hydrolysed after 6 days.

Table 4. *Water cleavage experiments with monolayer systems containing different preparations of ruthenium tris(bipyridyl)complexes.* No evolved hydrogen and oxygen was detected.

Arrangement		Photolysis conditions			Remarks
		pH	time of exposure (h)	fraction of dispersed layer	
G	**1a**	5.6	70	0.2	a)e)h)
G	**1a**	6.2	68	0.25	a)f)h)l)
G	**1b**	6.2	77	0.15	a)f)i)l)
G	**1b**	6.2	84	0.6	a)f)i)l)
SPS	**1b**	5.6	124	0.25	e)h)
G	**1b**	5.6	80	0.2	b)f)g)
G	**1b**	6.0	82	0.2	b)f)i)l)
G	**1b**	6.9	92	0.3	b)f)i)l)
G	**1b**	7.5	53	0.35	b)f)i)l)
GH	**1b**	7.7	55	0.45	f)i)l)
G	**1b**	5.6	74	0.2	b)e)g)
G	**1b**	7.5	79	0.5	b)f)i)l)
G	**1b**	7.6	130	0.75	b)e)i)l)
GH	**1b**	7.4	126	0.35	f)i)l)
GH	**1b**	7.0	131	0.55	f)i)l)
G	**1b**	5.6	60	0.2	c)e)i)
G	**3**	5.7	58	0.4	c)e)i)
G	**1b**+**3**	5.6	49	0.3	c)e)i)
G	**2**	5.9	54	0.45	c)e)i)

Symbols: G = glass; GH = silanated glass; SPS = sulfonated polystyrene. Ru complex preparations **1a**, **1b**, **2**, **1b**+**3** (symbolizing **1b** and **3** in molar mixing ratio 2:3).

a)b)c)d): Cleaning of glass support according to procedure a, b, c, d, page 2613/2614, resp.; e)f): Subsolution in depositing monolayer; e): Bidistilled water (pH 5.6); f): $CdCl_2$ $2.5\cdot10^{-4}$M, $NaHCO_3$ $5\cdot10^{-5}$M, pH 6.4; g)h)i): Photolysis solution; g): Saturated with air; h): Degassed by boiling; i): Saturated with nitrogen; l): Photolysis solution: Bidistilled water, adjusted to pH by $NaHCO_3$ (*e.g.* 10^{-5}M for pH 6, $3\cdot10^{-5}$ for pH 7.5).

Conclusion. – In a large variety of monolayer systems containing the surfactant ruthenium bipyridine complex no light induced evolution of hydrogen was detected. The removal of complex from the solid substrate during illumination was in most cases moderate and cannot account for this failure. We have found no evidence for wide range exciton migration in transferred monolayers of the ruthenium bipyridine complex which might facilitate the photoinduced cleavage of water. *Whitten et al.* [19] assumed that the effects that have been observed might be dependent on unexplored details determining the structure of the layers. This structure is sensitive on small alterations of conditions as shown by the π/A-isotherms which vary strongly with changes in the subphase composition. There might exist the possibility to arrange appropriate ruthenium complexes favourably for a cooperation in the sensitized photocleavage of water.

We are indepted to Dr. *E. Steiner*, Ciba-Geigy, Basel for supplying us with ruthenium complex preparations.

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