PROCEEDINGS OF THE SYMPOSIA ON

Photoelectrochemical Processes
and
Measurement Techniques for Photoelectrochemical Solar Cells

PHOTOELECTROCHEMISTRY: FUNDAMENTAL PROCESSES AND MEASUREMENT TECHNIQUES

Edited by

William L. Wallace, Authur J. Nozik, and Satyen K. Deb
Solar Energy Research Institute
Golden, Colorado

Ronald H. Wilson
General Electric Company
Schenectady, New York

PHYSICAL ELECTROCHEMISTRY DIVISION AND ENERGY TECHNOLOGY GROUP

Proceedings Volume 82-3 1982

THE ELECTROCHEMICAL SOCIETY, INC., 10 South Main St., Pennington, NJ 08534

d-π* TRANSITIONS FOR ELECTRON INJECTION INTO THE CONDUCTION BAND OF SEMICONDUCTORS

G. Calzaferri, M. Gori, H.R. Grueniger, W. Spahni
Institute for Inorganic Chemistry, University of Bern
CH-3000 Bern 9, Switzerland

SUMMARY

The basic idea of this work is that we want to detect directly light induced charge redistribution along a well defined central atom to aromatic ligand axis and to stabilize this charge redistribution in order to build systems which provide photodiode characteristics on a molecular scale [1].

In many asymmetric transition metal complexes with only one aromatic ligand, AR, CT-transitions are known leading to charge redistribution along a well defined central atom to aromatic Ligand axis L_nM-AR. If the interaction between the two fragments L_nM and AR is not too strong, one would expect the energy needed for such transitions to be proportional to the difference of the redox potentials of the fragments. This hypothesis can be tested by keeping one of the two fragments constant and exchanging the other one, provided that solute-solvent interactions remain unchanged for different systems. This condition can be better fulfilled by exchanging the aromatic ligand AR and not the metal part of the complex. For such a transition one would expect to find

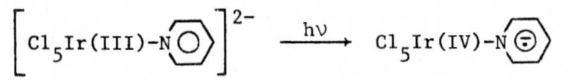
$$E_{CT} = a + b \cdot E_{AR/AR^-}$$

Since this equation can be used to fit many data, it seems that in many cases such proportionality does exist. It is this information we use in order to build systems with photodiode characteristics on a molecular scale.

Starting with trichlorosilane compounds, the ligand is in a first step attached by a C-Si-O bridge to a colorless metal oxide with semiconductor properties. The oxides have to be dried in vacuum. Once the bulk water is completely removed, enough hydroxyl groups remain on the surface to react with the trichlorosilane. We use the characteristic -C≡N stretch vibrations of benzonitrile to analyze the surface modification. In a next step the metal complex is built. Electron injection into the conduction band is detected by measuring photocurrents by applying lock-in technique.

INTRODUCTION

Klixbüll Jørgensen was the first to understand the new long wave absorption band in the pentachloro pyridine iridium(III) complex [2].



(1)

He interpreted it as charge transfer from the iridium (III) to the pyridine ligand. The point in this example is that the charge transfer appears along the well specified central atom to aromatic ligand axis.

If the interaction between the two fragments $[Cl_5Ir(III)]^{2-}$ and pyridine is not too strong, one would expect the energy needed for such transitions to be proportional to the difference of the redox potentials of the fragments.

$$E_{CT} \propto -a \cdot E^{o}_{[Ir(IV)Cl_5]^-/[Ir(III)Cl_5]^{2-}} + b \cdot E^{o}_{Py/Py^-} \qquad (2)$$

This hypothesis can be tested by keeping one of the two fragments constand and exchanging the other one provided that solute-solvent interactions remain unchanged for different systems [3]. This condition can be better fulfilled by exchanging the aromatic ligand AR and not the metal part of the complex.

$$L_nM\text{—}AR \xrightarrow{h\nu} L_n\overset{\oplus}{M}\text{—}\overset{\ominus}{AR} \qquad (3)$$

L_nM = constant
AR = variable

d-π* TRANSITIONS ALONG A WELL DEFINED MOLECULAR AXIS

For such a situation one would expect to find the following relationship [1], [3], [4]:

$$E_{CT} = a + b \cdot E_{AR/AR^-} \qquad (4)$$

This equation has been tested by several authors using pentacyano iron-(II) and pentaamineruthenium(II) systems with many similar aromatic ligands [4],[5]. The constants a and b can be interpreted within a thermodynamic analysis similar to that used for organic donor acceptor complexes [3]. The enthalpy difference between the ground state and the relaxed d-π* state is related to the maximum of the d-π* absorption band by:

$$\Delta H = h\nu_{max} - \Delta H_R \qquad (5)$$

ΔH_R may be called enthalpy of reorganization. ΔH can be calculated by means of an enthalpy cycle in solution. The dimensions used are energy per molecule. We prefer to use $h\nu_{max}$ instead of $h\nu_{00}$ since it is difficult to identify the zero-zero transition in the absorption spectra of these complexes.

$$\begin{array}{rcll} L_nM\text{—}AR & \longrightarrow & L_n\overset{+}{M}\text{—}AR + e^- & \Delta H_1 \\ AR + e^- & \longrightarrow & AR^- & -\Delta H_2 \\ L_n\overset{+}{M}\text{—}AR + AR^- & \longrightarrow & L_n\overset{+}{M}\text{—}\overset{-}{AR} + AR & \Delta H_C \\ \hline L_nM\text{—}AR & \longrightarrow & L_n\overset{+}{M}\text{—}\overset{-}{AR} & \end{array} \qquad (6)$$

$$\Delta H = \Delta H_1 - \Delta H_2 + \Delta H_C$$

By using the Gibbs-Helmholtz equation

$$H_j = \mu_j + TS_j \qquad (7)$$

the difference ΔH can be related to the differences of chemical potentials μ_j.

$$\mu_j = \mu_j^o + kT\,\ell n\, f_j \cdot c_j \;; \quad f_j = \text{activity coefficient} \qquad (8)$$

This means that H_j generally depends on the concentration of the species. This concentration dependence disappears if the activity coefficients are equal one or if their temperature dependence can be neglected.

$$\frac{\partial \mu_j}{\partial T} = \frac{\partial \mu_j^o}{\partial T} + k \cdot \ell n\, f_j \cdot c_j + kT \frac{\partial}{\partial T} \ell n\, f_j \cdot c_j$$

$$\frac{\partial \mu_j}{\partial T} = -S_j$$

If $\frac{\partial}{\partial T} \ell n\, f_j \cdot c_j$ can be neglected, S_j is given by:

$$S_j = S_j^o - k \cdot \ell n\, f_j \cdot c_j \qquad (9)$$

Inserting (9) and (8) into (7) leads to the concentration independent equation

$$H_j = \mu_j^o + TS_j^o \qquad (10)$$

Thus, under the mentioned conditions ΔH can be related to concentration independent variables.

$$\begin{aligned} \Delta H &= \Delta\mu_1^o + T\Delta S_1^o - (\Delta\mu_2^o + T\Delta S_2^o) + \Delta H_C \\ \delta S_{12} &= \Delta S_1^o - \Delta S_2^o \\ h\nu_{max} &= \Delta\mu_1^o - \Delta\mu_2^o + T\delta S_{12} + \Delta H_C \end{aligned} \qquad (11)$$

Since

$$\begin{aligned} \Delta\mu_1^o &= eE_{L_n\overset{+}{M}/L_nM} \\ \Delta\mu_2^o &= -eE_{AR/AR^-} \\ e &= 1 \end{aligned}$$

equation (11) takes the form

$$h\nu_{max} = \{E_{L_n\overset{+}{M}/L_nM} + T\delta S_{12} + \Delta H_C\} + E_{AR/AR^-} \qquad (12)$$

Therefore a and b in equation (4) are

$$a = E_{L_n\overset{+}{M}/L_nM} + T\delta S_{12} + \Delta H_C$$

$$b = 1$$

The coefficient a is not a constant if various aromatic ligands AR are combined with the fragment L_nM because ΔH_C and δS_{12} depend on the character of AR. Since equation (4) can be used to fit many data it seems that a proportionality to E_{AR/AR^-} does exist.

The pyrazine pentacyano iron(II) exhibits an interesting absorption spectrum as three completely different transitions can be distinguished [6]. The situation is similar to that observed in $[(NH_3)_5RuAR]^{2+}$ complexes described by Taube and co-workers [5]. In water the iron to pyrazine d-π* transition occurs at 22.1 kK. Since the electrons in the $(CN)_5Fe$ fragment and the electron in the π*-level of the pyrazine occupy different orbitals which are nearly localized on the two components, the singlet-triplet splitting of the CT state is therefore expected to be small. A similar behaviour is observed in organic donor-acceptor complexes [7]. At 38 kK the first π-π* transition of the pyrazine can be identified. At higher energies similar transitions as in the hexacyano iron(II) complexes are observed.

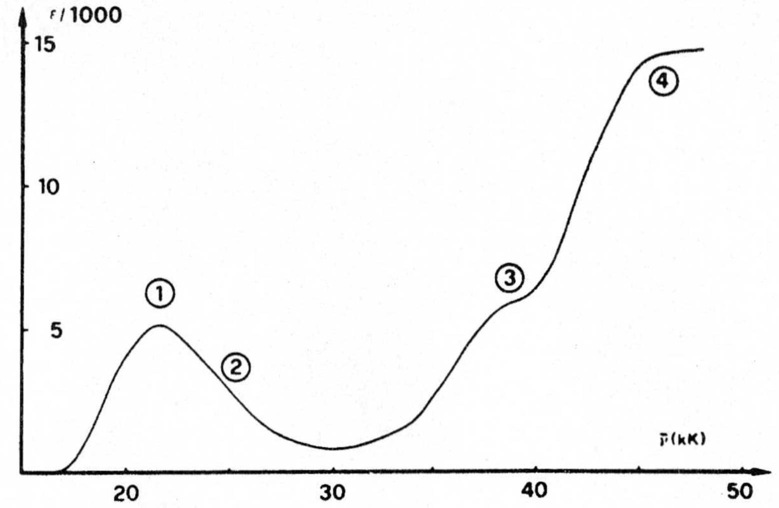


Fig. 1: Absorption spectrum of $[Fe(CN)_5Pyrazine]^{3-}$ in water at 25°C. The longest wavelength band (1) at 22 100 cm^{-1} can be identified as iron pyrazine CT transition. The band (3) (38 000 cm^{-1}) is the first pyrazine π-π^* transition. (2) probably corresponds to a d-$\sigma^*(z^2)$ absorption and (4) also occurs in the $[Fe(CN)_6]^{4-}$ [6].

We have carried out molecular orbital calculations on the extended Hückel level [8] with charge iteration [9] in order to improve the understanding of what happens in the d-π^* CT transition. One of the results is shown in Fig. 2, where the distribution of the six electrons in the highest occupied orbitals of the ground state and the CT-state is visualized. In the ground state five of these six electrons are concentrated on the iron. In the CT-state the electron distribution on the cyanide ligand does not change significantly within a first order approximation. But as we have imagined, one of the electrons from the iron is quantitatively transferred to the pyrazine, thus creating a pyrazine radical anion and iron with the formal oxidation number III.

Up to now we have not achieved a charge separation. Only CT states have been created. We do not want to speak about charge separation before a real barrier between the hole and the electron has been introduced. Let us first see what happens when we introduce the same pentacyano iron (II) fragment on both sides of the pyrazine:

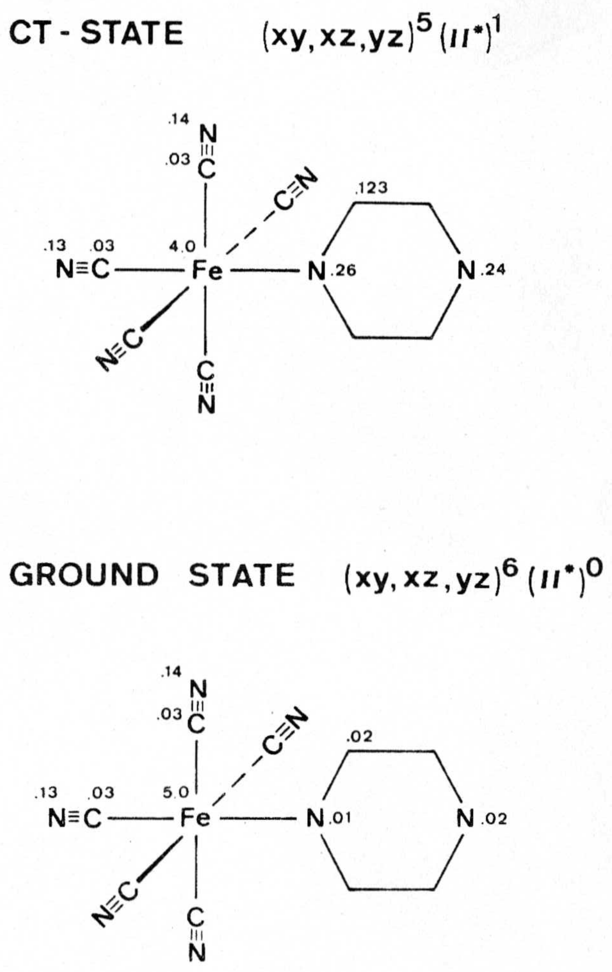


Fig. 2: Distribution of the six electrons in the highest occupied orbitals of the ground state as well as in the d-π^* CT state [6].

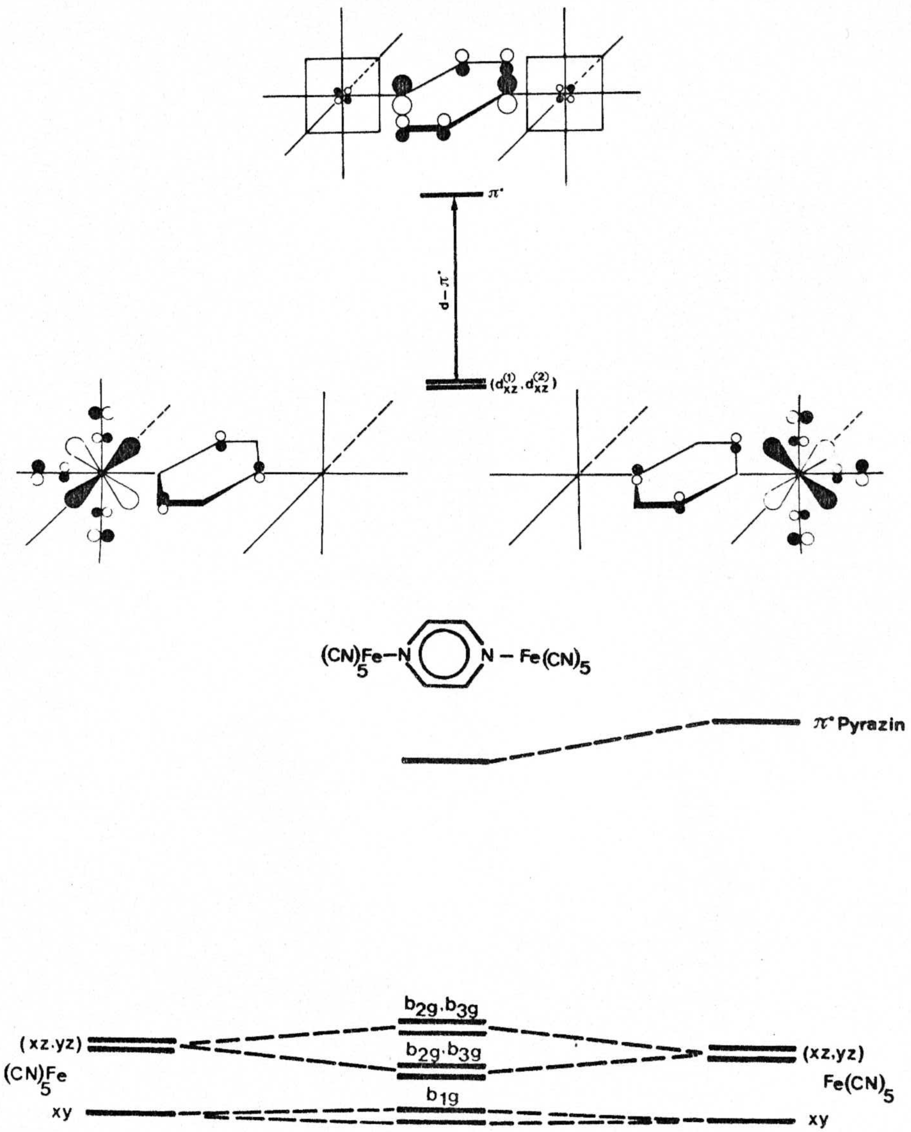


Fig. 3: Creation of a localized hole on one of the two iron sites by the d-π* transition in the binuclear di-pentacyanoferrat-μ-pyrazine complex [1, part I].

The question is: Is it possible to create an electron hole pair in a way that the hole is either located on the left or on the right iron, but not delocalized on both? One would imagine such a localized hole to oscillate at a certain frequency between the left and the right iron. If the oscillation frequency is not too high we can think in localized terms [10]. From the results obtained by applying molecular orbital theory [1], we deduce that in the CT transition observed in this binuclear complex a localized hole is created. This is shown in Figure 3.

The lifetime of such a hole in condensed phase is not known. But it is probably very small. This idea of a localized hole is supported by a recent work of Gleiter who showed that the photoelectron spectra of the biferrocenylene and the biferrocene complexes can only be interpreted if the creation of a localized hole on one of the two iron sites is assumed [11]. The ionized state of these complexes corresponds to a mixed valence state [12]. It would be very interesting to know the absorption spectra of the biferrocenylene and the biferrocene cations in gaseous phase. Several authors have tried to describe localized hole states in small molecules [13].

If we wish now to produce a charge separation out of this CT state the only thing we in principle need to do is making the complex asymmetrix as shown in Fig. 4. Depending on the nature of the bridge, mixed valence transitions are observed in the d-π* state or in the state of charge separation. For our purpose the system has to be built in a way which makes such transitions improbable since they are loss mechanisms.

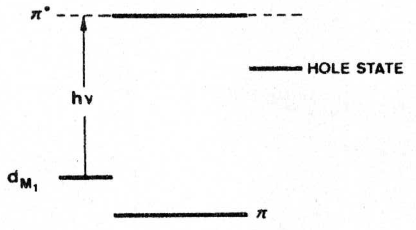
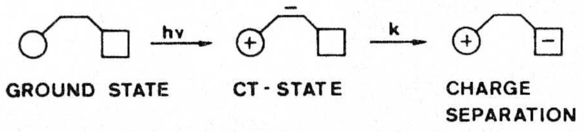


Fig. 4: Simplified one electron energy level diagram for an asymmetric binuclear complex bridged by an aromatic ligand.

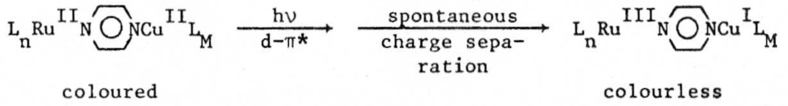


By absorption of a photon a directed CT state is created. Since the energy gap between the HOLE STATE and the π* level is much smaller than the energy gap between the d_{M1} hole and the π* level, it is highly probable that the electron will jump in a step of intramolecular deactivation from the π* level into the HOLE STATE [14]. Now a true charge separation has been created. The velocity of thermal recombination

$$\{d_{M_1}(+)\text{-bridge-HOLE STATE}(-)\} \longrightarrow \{d_{M_2}\text{-bridge-HOLE STATE}\}$$

can be estimated by considering data of innersphere redox reactions [15].

An approximation to such a photoinduced $\{d_{M1};\text{HOLE STATE}\} \rightarrow \{d_{M1}(+);\text{HOLE STATE}(-)\}$ charge separation has been published by V.A. Durante and P.C. Ford [16].



The $\{Ru^{III},Cu^{I}\}$ complex is not stable. But this example shows that the reaction scheme in Fig. 4 makes sense.

Le us now return to the description of the "directed" d-π* state. Considering the analysis of the kinetics of fluorescence quenching by electron transfer published by Rehm and Weller [17], these d-π* can be compared to the radical ion pair $^{2}F^{(+)} \ldots {}^{2}Q^{(-)}$. The main difference to such a radical ion pair is that we have an intramolecular electron hole pair which can react by an intramolecular process to a state of charge separation. Therefore, it seems probable that the theory of intramolecular relaxation can be applied [14],[18].

The main properties of the complexes shown in Fig. 5 can be rationalized by simple molecular orbital calculations [4],[6]. In the hexacyano iron(II) the d-d transition appears first and at higher energies there are CT transitions; Fig. 5. If one of the cyano ligands is replaced by an amino or an aquo group one observes a new transition which may be called $d\text{-}\sigma^*(z^2)$. In case a pyridine is introduced, the d-d and the $d\text{-}\sigma^*(z^2)$ transitions are still there but they are covered by an intense "directed" d-π* absorption. For X = benzonitrile the d-π* transition is shifted to much lower energy so that even a second d-2π* band is observed. The data reported by other authors for the benzonitrile complex are not correct. Since even at day light the colour of the complex fades, they have probably measured the absorption spectrum of the photoproduct [19]. In contrast to other [20] $[(CN)_5Fe\text{-}AR]^{3-}$ complexes, the photoreaction of the benzonitrile complex is completely reversible [4].

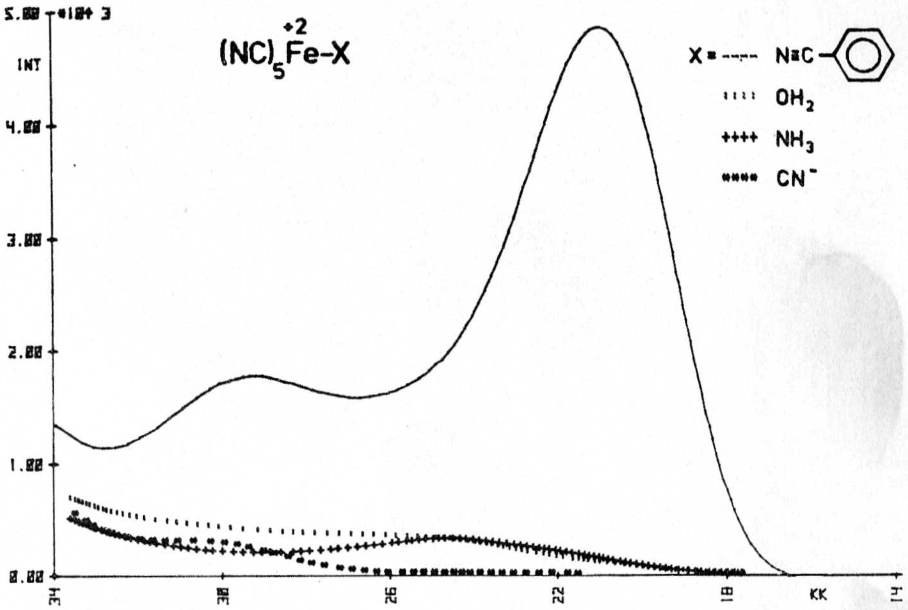


Fig. 5: Comparison of the absorption spectra of pentacyano-X-ferrate(II) complexes in water. Molar extinction [ℓ/(M·cm)] versus energy in units of 1000 cm^{-1}. 10^{-4} molar aqueous solutions.

The results of this section can be summarized as follows: In many asymmetric transition metal complexes $L_nM\text{-}AR$ with only one aromatic ligand, AR, CT transitions are known, which lead to charge redistribution along a well defined central atom to aromatic ligand axis. Under appropriate conditions, one would expect proportionality between the energy needed for the CT transition and the redox potentials of the aromatic ligand.

$$L_nM\text{—}AR \xrightarrow{h\nu} L_n\overset{+}{M}\text{—}AR^-$$

for L_nM = const and AR variables. $E_{CT}(i) = a + b\,E_{AR_i}$, many d^6 examples are known [2],[4]-[6],[21], e.g.

M = Cr^0, Mo^0, W^0, Fe^{II}, Ru^{II}, Os^{II}, Rh^{III}, Ir^{III}
AR = Pyridine, Pyrazine, Benzonitrile, 2,2'-Bipyridyl, Terpyridyl, etc.
L = CO, CN^-, NH_3, Cl^-, etc.

From theoretical and experimental results we conclude that it should be possible to find systems which show photodiode behaviour on a molecular scale.

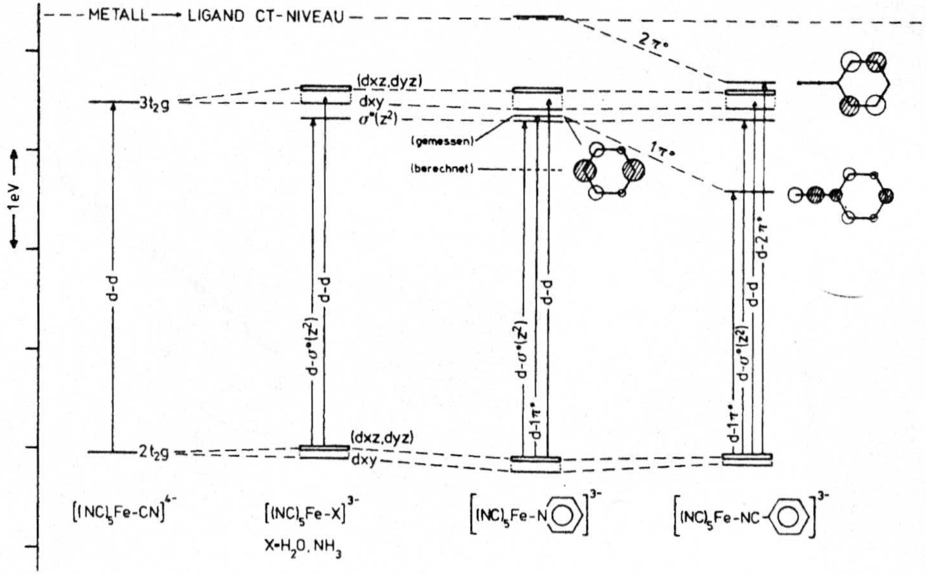


Fig. 6: One electron scheme which allows systematic interpretation of the spectra shown in Fig. 5 [4].

SURFACE MODIFICATION

It is this information we use to build systems with photoiode characteristics on a molecular scale. An interesting possibility for vectorial charge separation has been discussed by H. Kuhn and co-workers [22]. A different type of systems can be built with the help of "directed" d-π* transitions, since already during the absorption of the photon an electron hole pair is generated. Our approach is also different from the well known sensitization by dye absorption on the surface of colourless semiconductors [23].

Starting with trichlorosilane compounds we attach a ligand by stable covalent bonds on the surface of a semiconductor [24]. We take as much care as possible to achieve a well defined monomolecular surface modification. Benzonitrile ligands as shown in Fig. 7 are especially attractive for this purpose, since the CN stretch frequency can be used as label in order to analyze the surface modification by measuring attenuated infrared spectra (ATR-IR) with polarized light [25].

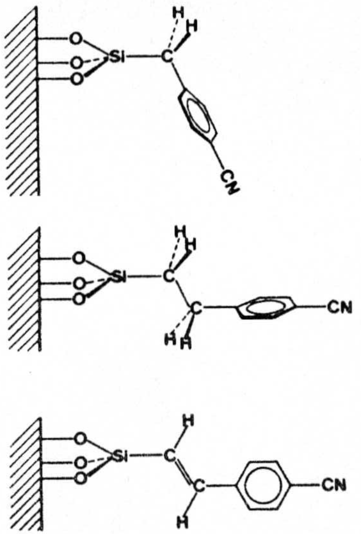


Fig. 7: Ligand system we use to analyze the monomolecular surface modification.

In Fig. 8 the parallel ∥ and vertical ⊥ ATR-IR component of the CN stretch spectra are the result of 25 reflections which have been averaged 250 times. By careful interpretation of such spectra one can get good information about the angle between the nitrile group and the surface.

Once we have the ligand on the surface, we build the complex, and finally we have all the pieces together to start photochemistry. In Figure 9 the principle of the complete system is shown.

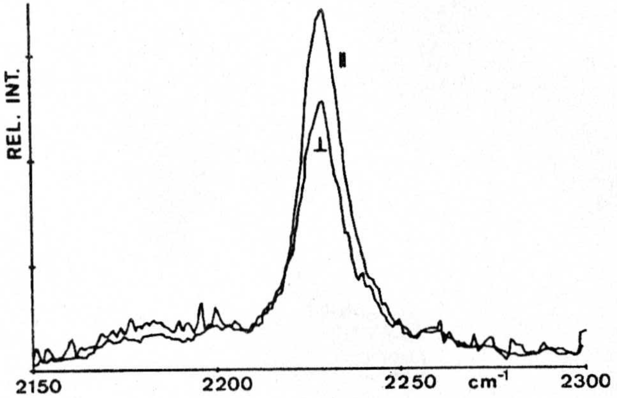


Fig. 8: Parallel ∥ and vertical ⊥ component of an ATR-IR spectrum.

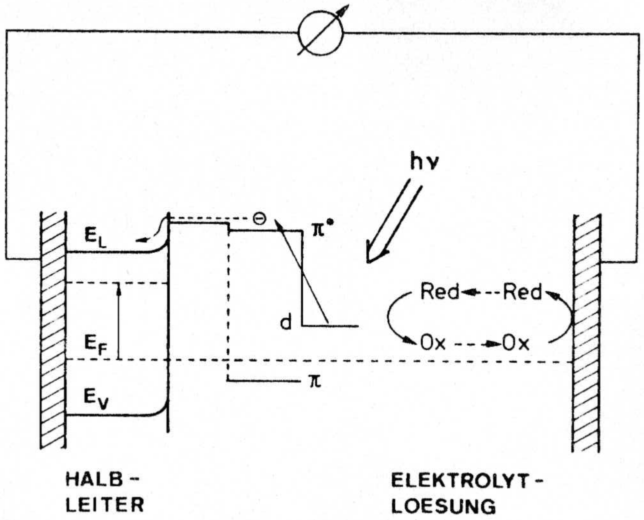


Fig. 9: Principle of the systems we prepare to detect the electron injection. The important point of this arrangement is the low energy barrier for the π*→conduction band electron transfer and the very high barrier for the recombination process from conduction band to d-hole.

By shining visible light onto the surface modified electrode, an electron from a d-level is quantitatively transferred to a π*-level. From this level it will jump with a certain probability into the conduction band E_L, leaving a d-hole behind. Notice the very high barrier for the recombination process from the conduction band to the d-hole.

The probability of the electron in the π*-level to jump into the conduction band and not to recombine with the d-hole depends very much on the way we choose the barrier between the semiconductor and the π*-level. We can develop a feeling on what has to be done, by looking at the calculated probability distribution of an electron in the π*-level of the ligands in Fig. 10.

In the first compound the probability for the electron to be on the silicon atom is high. Since the density of states in the tin dioxide is much higher than in the hole created on the iron, and since the energy gap π*-level to conduction band is smaller than the energy gap π*-level to d-hole, the electron in the d-π* state will be caught with high probability by the conduction band of the semiconductor.

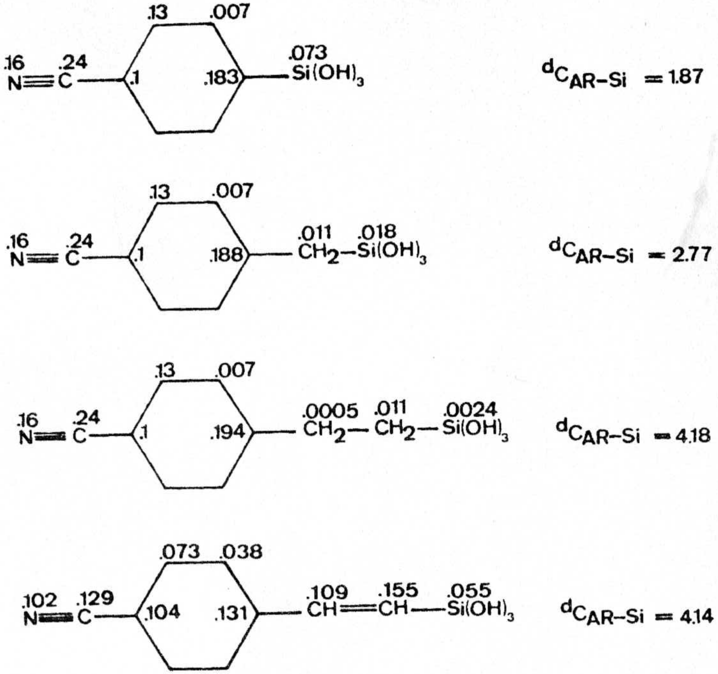


Fig. 10: Probability distribution of an electron in the π*-level.

With one CH_2 group between the aromatic ligand and the silicon atom, the electron density on the silicon atom is four times smaller, but it has still a reasonable value. If we put two CH_2 groups between the aromatic part and the silicon atom, the electron density drops to a small value. But of course if instead of an alkane group we use a conjugated bridge, the probability for the electron to be at the silicon atom is very high.

The conclusion of this result is that systems with longer alkane chains than $-(CH_2)_2-$ will not be efficient for our purpose.

There is another important point: The d-π* CT state should be the lowest excited state of the complex on the surface, since otherwise rapid relaxation to the lower lying states will occur.

Since for a monomolecular surface modification the absorption probability can be estimated to be in the order of $5 \cdot 10^{-7}$·(molar extinction coefficient) we cannot expect to observe large photocurrents. Therefore, we have built an experiments as shown in Figure 11.

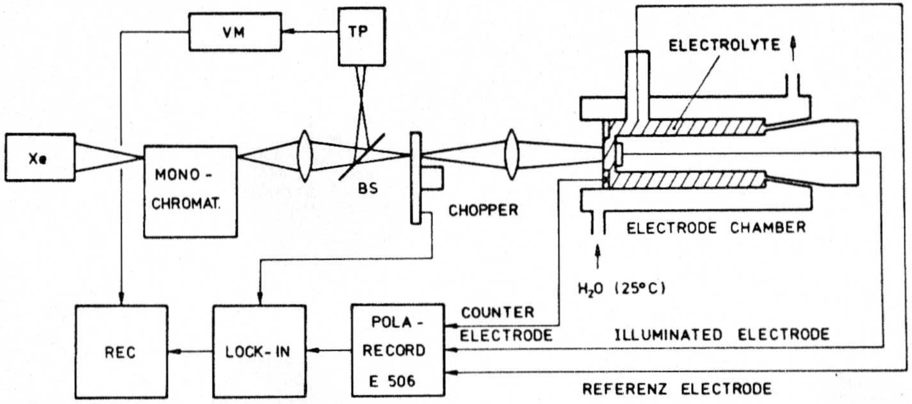


Fig. 11: Experimental set-up to measure photocurrents.

The surface modified electrode is put into a de-oxygenated electrolyte solution. To make the resistance small, the platinum counter electrode is attached to the quartz window. The distance between the window and the surface modified electrode can be varied between zero and several mm. Potential control versus an SCE reference electrode and current measurements are made with the polarograph "Polarecord E506 METROHM". In order to compensate for dark currents we apply lock-in technique using the lock-in amplifier PAR 186 A. The photocurrent is compared to the photon flux measured by means of a thermopile. The construction of the electrode is similar to that we have used for other purposes [26].

In Figure 11 preliminary results obtained on sintered tin dioxide electrodes are reported. The interpretation of measurements on sintered electrodes is not as simple as on single crystals. Since our measurements have been repeated several times on different electrodes and we have always observed similar behaviour, we are confident that these first results are significant. The tin dioxide used in these experiments has been obtained by a sintering process. It is doped with 1^{o}/oo Sb_2O_3. In order to prepare electrodes the material is pressed into tablets before sintering at 1200°C during 12 h on a Si_3N_4 substrate. The obtained tin dioxide is completely white and has a large surface. Its density is 4.5 g/cm^3. The density of single crystals is 6.95 g/cm^3. Prior to the surface modification the electrodes are carefully polished, etched for 24 h in pure concentrated hydrochlorid acid and washed for the same time

with bidistilled water. Before starting the measurements, the electrodes are polarized for 12 h at a potential of 0, Volts towards SCE. The deoxygenated electrolyte contains $3 \cdot 10^{-3}$ moles $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$ in water. The same potential is maintained when measuring the photocurrents. Results obtained with unmodified (2) and modified (1) electrodes are shown. The curves are corrected for equal photon flux and for light absorption by the electrolyte. Identical current to wavelength curves are observed many times if no oxygen is present. Comparison between modified and unmodified electrodes makes it very probable that the expected electron injection takes place. The signals at the modified electrodes are smaller than expected. This might be due to the fact that in this special case the complexation constant for the complex on the surface is too small.

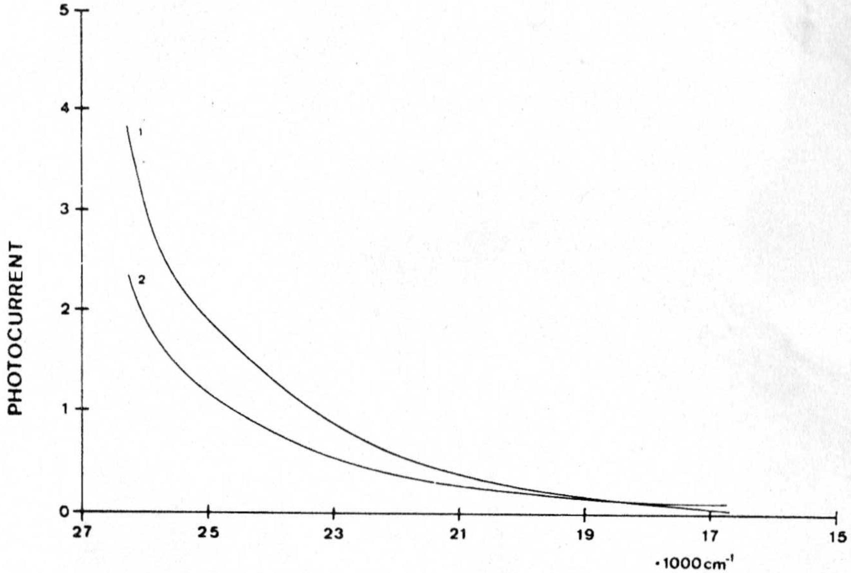
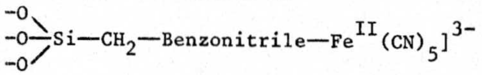


Fig. 12: Photocurrents (arbitrary units) of surface modified (1) and unmodified (2) tin dioxide of



$$\left.\begin{matrix}-O\\-O\\-O\end{matrix}\right\rangle Si-CH_2-Benzonitrile-Fe^{II}(CN)_5]^{3-}$$

ACKNOWLEDGEMENT

This paper is part of the project No. 4.340.79.04 of the Swiss National Science Foundation.

We should like to thank Professor Ernst Schumacher for support of this work.

REFERENCES

[1] G. Calzaferri, Chimia 32, 241 (1978), and 35, 209 (1981).

Many of these results have been reported by the author on the "One Day Symposium" on "Alternative Approaches to the Photodissociation of Water", Photochemistry Group, Royal Institution, London, May 29, 1980.

[2] C.K. Jørgensen, Acta chem.Scand. 11(1957)166.

[3] R.S. Mulliken & W.B. Perron, Molecular Complexes, John Wiley (1969)

[4] G. Calzaferri & H.R. Grüniger, Helv.chim.acta 62(1979)1112.

[5] P.C. Ford, F.P. Rudd, R. Gauner & H. Taube, J.Am.Chem.Soc. 90 (1968)1187.
H.E. Toma & J.M. Malin, Inorg.Chem. 12(1973)1039.
H.E. Toma, E. Giesbrecht, J.M. Malin & E. Fluck, Inorg.Chim.Acta 14(1975)11.

[6] G. Calzaferri & F. Felix, Helv.chim.acta 60(1977)730.

[7] H. Beens & A. Weller, in J.B. Birks: "Organic Molecular Photophysics", Vol. 2, p. 159 ff, 1975.

[8] R. Hoffmann, J.Chem.Phys. 39(1963)1397, and many later contributions of this author.
M. Wolfsberg & L. Helmholtz, J.Chem.Phys. 20(1952)837.

[9] C.J. Ballhausen & H.B. Gray, Molecular Orbital Theory, W.A. Benjamin Inc., New York, 1965.

[10] The Feynman Lectures on Physics, Vol. III, California Institute of Technology, 1965.

[11] M.C. Böhm & R. Gleiter, Inorg.Chem. 19(1980)1081.

[12] M.B. Robin & P. Day, in Adv.Inorg.Chem. and Radiochem. 10(1967)247.

[13] P.S. Bagus & H.F. Schäfer III, J.Chem.Phys. 56(1972)224.
R.L. Lozes, O. Goscinski, U.I. Wahlgren, Chem.Phys.Letters 63 (1979)77.

[14] R. Engleman & J. Jortner, Mol.Physics 18(1975)145.

[15] D. Gaswick & A. Haim, J.Am.Chem.Soc. 96(1974)8745.
D.A. Piering & J.M. Malin, ibid 98(1976)6045.
H.E. Toma, J.Inorg.Nucl.Chem. 37(1975)785.
H. Kreutzien & H. Taube, J.Am.Chem.Soc. 98(1976)6379.
H. Fischer, G.M. Tom & H. Taube, ibid. 98(1976)5512.

[16] V.A. Durante & P.C. Ford, J.Am.Chem.Soc. 97(1975)6898.

[17] D. Rehm & A. Weller, Ber.Bunsenges.Phys.Chem. 72(1970)834.
D. Rehm & A. Weller, Isreael J.Chem. 8(1970)259.

[18] F.K. Fong, Radiationless Processes in Molecules and Condensed Phase, Springer-Verlag, 1976.

[19] A.P. Szecsy, S.S. Miller & A. Haim, Inorg.chim.acta 28(1978)189.

[20] J.E. Figard & J.D. Petersen, Inorg.Chem. 17(1978)1059.

[21] H.D. Murdoch & R. Henzi, J.Organomet.Chem. 5(1966)166.
J.A. Connor et al., J.C.S. Dalton 1246 (1972).
G. Boxhorn, A.D. Oskam, E.P. Gibson & R. Narayanaswamy, Inorg.Chem. 20(1981)783.
R.W. Banlk, D.J. Stufkens & A.D. Oskam, Inorg.chim.acta 34(1979)267.
M.S. Wrighton, H.B. Abrahamson & D.L. Morse, J.Am.Chem.Soc. 98 (1976)4106.
R.J. Watts, Inorg.Chem. 20(1981)2302.

[22] E.E. Polymerapoulos, D. Möbius & H. Kuhn, J.Chem.Phys. 68(1978) 3918.

[23] H. Gerischer & F. Willig, Topics in Current Chemistry, Springer-Verlag, 61(1976)31.

[24] H.R. Grüniger & G. Calzaferri, Helv.chim.acta 62(1979)2547.

[25] N.J. Harric, Internal Reflection Spectroscopy, John Wiley & Sons Inc., New York, 1967.
W.N. Hansen, Internal Reflection Spectroscopy in Electrochemistry, Adv. in Electrochemistry, Vol. 9, Wiley-Interscience, 1973.

[26] J. Baumann, H.R. Grüniger & G. Calzaferri, Zeitschr. für physikalische Chemie NF 118(1979)11.