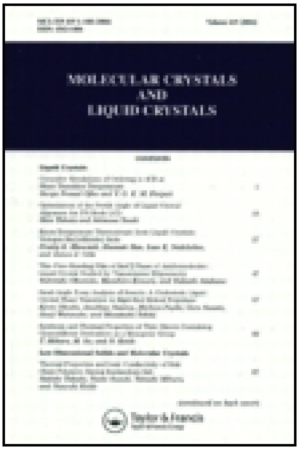

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# PHOTO-INDUCED ELECTRON TRANSFER IN AND ELECTRON INJECTION FROM TRICHROMOPHORIC MOLECULES FORMING LANGMUIR BLODGETT FILMS

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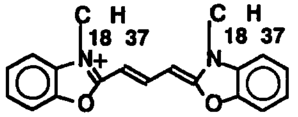
Abstract The analysis of the fluorescence decay of a cyanine dye linked covalently to two pyrene moieties suggests an excited state equilibrium between the locally excited state of the dye and a charge transfer state. Excitation of a mixed monolayer of this trichromophore and palmitic acid deposited on $SnO_2$ results in a photo-sensitized anodic current. The dependence of this photocurrent on time and hydroquinone (regenerator) concentration suggests that the alien recombination of the oxidized dye with electrons in the conduction band or in suraface states as well as the irreversible degradation of the oxidized dye are slowed down compared to systems where the charge injection is mediated by di-octadecyloxacarbocyanine.

## INTRODUCTION

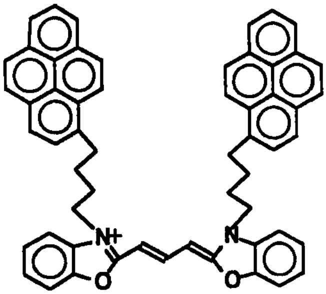
The overall quantum yield of photo-induced electron transfer in Langmuir Blodgett films is often limited by competition between the primary electron transfer and other decay processes of the excited state[1,2]. As it was demonstrated that the HOMO of alkyl chains is involved in the photo-induced electron transfer between monolayers, it was attempted to link the electron donor and acceptor by alkyl chains to increase the efficiency of the electron transfer process[3]. Therefore a trichromophoric molecule[4] (OXAPY) containing an oxacarbocyanine moiety and an two pyrene moieties has been synthesized. It was possible to incorporate this molecule in Langmuir Blodgett films[4] of palmitic acid (PAA) and myristic acid (MYA). Furthermore it can be expected that, when the trichromophoric molecule is used to inject electrons[5-10] into an n-type semiconductor the electron donor moiety will enhance the regeneration of the excited dye.

## EXPERIMENTAL

The synthesis of OXAPY will be described elsewhere[11]. Mixed monolayers of OXAPY and PAA were prepared using the procedure described earlier[4]. The monolayers were deposited on $SnO_2$ electrodes that were cleaned according to the procedure described elsewhere[9-10,12]. The dark and photocurrents were determined using a potentiostat. As the dark current was several orders of magnitude larger than the photocurrent a chopper and lock-in amplifier were used for the determination of the photocurrent[9-10]. Contrary to prior experiments the concentration of $NaClO_4$ amounted to 0.1 $moll^{-1}$ and the concentration of the buffer (phosphate or acetate) amounted to 0.01 $moll^{-1}$. All solvents were of spectroscopic or fluorescence grade and were used as received. Corrected fluorescence and excitation spectra were obtained with a SPEX Fluorolog 212. The fluorescence decays were obtained by the single photon timing technique[13-14]. Upon excitation at 514 nm the repetition rate of te modelocked argon laser was reduced using a low voltage Pockels cell (Conoptics) driven by an pulse amplifier constructed according to the design of Van Hoek[15].



OXA18



OXAPY

## RESULTS AND DISCUSSION

### Photophysics of OXAPY in solution

The absorption spectrum of OXAPY in ethanol corresponds to the sum of the absorption spectra of the individual chromophores[4]. Upon excitation of the carbocyanine moiety the observed fluorescence spectrum is a mirror image of the most bathochromic absorption band. The fluorescence quantum yield amounts to 0.23±0.03 and 0.25±0.03 in ethanol and chloroform respectively. This is of the same order of magnitude than fluorescence quantum yield of OXA18 which amounts to 0.07±0.01 and 0.20±0.02 in ethanol and chloroform respectively. Contrary to what is observed for OXA18 where the fluorescence decay can be fitted to a one exponential decay in all solvents where it was determined, the fluorescence of OXAPY decays according to a sum of two exponentials. Excitation at 295 nm (where light absorption is mainly by the pyrene moieties and at 514 nm (where light absorption is exclusively by the dye) yields similar decay times ($\gamma_1^{-1}$, $\gamma_2^{-1}$ ) and a similar ratio of preexponentials ($\alpha_1/\alpha_2$). Therefore the bi-exponential decay cannot be related to energy transfer from the pyrene moieties to the cyanine moiety. However the bi-exponential decay could also be caused by reversible electron transfer, with a rate constant $k_{21}$ from the HOMO of the pyrene moiety to the HOMO of the excited dye moiety. When the rate constant for back electron transfer yielding the singlet excited state of the dye and the ground state are given by $k_{12}$ and $k_{02}$ respectively, the sums $k_{01} + k_{21}$ and $k_{02} + k_{12}$ and the product $k_{21}k_{12}$ can be obtained from the fluorescence decay. To obtain the individual rate constants is also necessary to know $k_{01}$, the rate constant for decay of the singlet state in the absence of electron transfer.

TABLE I Analysis of the fluorescence decay of OXAPY as a sum of two exponentials $\alpha_1 \exp(-\gamma_1 t) + \alpha_2 \exp(-\gamma_2 t)$.

| | $\gamma_1$ ($10^9$s) | $\gamma_2$ ($10^8$s) | $\alpha_1/\alpha_2$ | $\chi^2$ |
|---|---|---|---|---|
| EtOH ($\lambda_{exc}$=295nm) | 1.984 | 5.000 | 0.580 | 1.161 |
| EtOH ($\lambda_{exc}$=514nm) | 1.718 | 4.520 | 0.910 | 1.184 |
| $CHCl_3$ ($\lambda_{exc}$=514nm) | 1.394 | 6.024 | 7.10 | 1.147 |

Two approaches are possible. In a first hypothesis one could assume that $k_{02}$ can be neglected compared to $k_{12}$. Table II shows that this leads to physically acceptable values of $k_{12}$ and $k_{21}$. From the fluorescence quantum yield (0.20) and fluorescence decay time (560 ps) of OXA18 in $CHCl_3$ a value of $3.55 \times 10^8 s^{-1}$ can be calculated for the radiative contribution, $k_{1f}$, to $k_{01}$. In this case the nonradiative contribution to $k_{01}$, $k_{1nr}$, amounts to $1.43 \times 10^9$ $s^{-1}$ for OXA18 in $CHCl_3$. In an analogous way the fluorescence quantum yield (0.073) and the fluorescence decay time (280 ps) of OXA18 in ethanol allow to obtain for OXA18 in ethanol a value of $2.61 \times 10^8$ $s^{-1}$ and $3.31 \times 10^9$ $s^{-1}$ for $k_{1f}$ and $k_{1nr}$ respectively. Assuming that the values of $k_{1f}$ are within the experimental error the same for OXAPY and OXA18 and that $k_{12}$ is much smaller than $k_{02}$ a value of $9.23 \times 10^8$ $s^{-1}$ and $4.35 \times 10^8$ $s^{-1}$ is obtained for $k_{1nr}$ for OXAPY in $CHCl_3$ and ethanol respectively. These values amount to 85 and 14 % of the values obtained for OXA18. This decrease could probably be due to a larger hydrodynamic drag[16] of the pyrenebutyl moiety compared to the (coiled) octadecylchain. This hypothesis leads to the maximum value that is acceptable for $k_{1nr}$ and $k_{12}$ and to the minimum value that is acceptable for $k_{21}$. The second hypothesis assumes that $k_{1nr}$ can be neglected compared to $k_{1f}$. This hypothesis leads to the maximum value that is acceptable for $k_{21}$ and $k_{02}$ and to the minimum value that is acceptable for $k_{12}$. A priori both hypotheses lead to physically acceptable values of the different rate constants. This means that the free energy change for the excited state electron transfer can vary between -0.073 eV and 0.043 eV or -0.011 eV and 0.028 eV for $CHCl_3$ and ethanol respectively. Using a value of 2.45 eV[4], 1.15±0.05 V[17] and -1.04±0.05 V[18] for the singlet energy of OXAPY, the reduction potential of the oxidized methylpyrene and the reduction potential of the cyanine moiety respectively, the free energy change for the excited state electron transfer should amount to -0.26±0.10 eV. The difference of about 0.2 eV between the values of ΔG° calculated on basis of the redox potential and the most negative values obtained from the analysis of the fluorescence decays are probably due to a different solvation of all species in $CHCl_3$ or ethanol compared to acetonitrile where the reduction potentials were determined.

TABLE II Rate constants of the processes occurring in the singlet excited state of OXAPY in solution at 298 K.

|  | EtOH[a] | $CHCl_3$[b] | EtOH[b] | $CHCl_3$[b] |
|---|---|---|---|---|
| $k_{01}$ ($10^9 s^{-1}$) | 0.261 | 0.355 | 0.696 | 1.194 |
| $k_{02}$ ($10^8 s^{-1}$) | 6.113 | 6.280 | / | / |
| $k_{21}$ ($10^8 s^{-1}$) | 7.940 | 9.413 | 3.586 | 0.968 |
| $k_{12}$ ($10^8 s^{-1}$) | 5.035 | 0.720 | 11.15 | 7.001 |
| K | 1.537 | 13.07 | 0.321 | 0.138 |

a) assuming that the radiationless contribution to $k_{01}$ can be neglected, b) assuming that $k_{02}$ can be neglected.

## Sensitized Photocurrents

In agreement to earlier observations[9,10], made for $SnO_2$ electrodes covered by mixed Langmuir Blodgett films of OXA18 and arachidic acid an anodic photocurrent could be observed upon illuminating $SnO_2$ electrodes covered by a mixed monolayer of OXAPY and palmitic acid (mixing ratio 1/5) in contact with a solution of $2.5 \times 10^{-3}$ $moll^{-1}$ hydroquinone. As observed for $SnO_2$ electrodes sensitized by OXA18 the onset of the photocurrent occurred at an electrode potential of 70±25 mV versus the SCE (saturated calomel electrode) when the pH of the solution amounts to 2.9 (phosphate buffer). When the electrode potential became more anodic the photocurrent increased until a saturation occurred at 500±50 mV versus the SCE. At electrode potentials exceeding 700 mV a decrease of the photocurrent was observed.

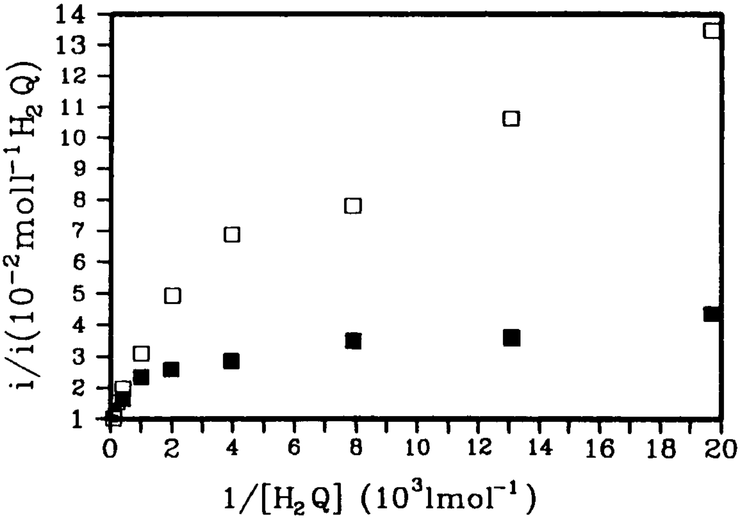


FIGURE 1 Influence of the inverse hydroquinone concentration on the photocurrent at an electrode potential of 300 mV vs. the SCE, for a $SnO_2$ electrode covered by a mixed monolayer of OXAPY and PAA with a mixing ratio 1/5 (■) and a mixed monolayer of OXA18 and ARA with a mixing ratio 1/5 (□). The photocurrent is normalized at a hydroquinone concentration of $1.0x10^{-2}$ $moll^{-1}$. Excitation occurred at 495 nm. The electrolyte pH amounted to 4.5 ($10^{-2}$ $moll^{-1}$ phosphate buffer) and the incident light intensity was equal to $3.1\pm0.3x10^{-3}$ W and $3.0\pm0.3x10^{-3}$ W for the electrodes covered by OXAPY and OXA18 respectively.

Decreasing the hydroquinone concentration decreased the maximum value of the photocurrent but neither the features of the current voltage plot nor the onset potential of the photocurrent were changed. In the absence of hydroquinone a photocurrent could still be obtained it was however much smaller for the anodic scan than for the cathodic scan. Furthermore at successive scans the photocurrent continued to drop. This suggests that consumption of the dye by some irreversible side reaction occurs. Increasing the pH of the solution shifts the onset potential of the photocurrent to -100 mV at pH 4.5 (phosphate buffer), -160 mV at pH 4.7 (acetate buffer) and - 300 mV at pH 6.6 (phosphate buffer). The electrode potential where the saturation and decrease of the photocurrent occurs does however not depend on the pH of the electrolyte solution. As observed for the sensitized photocurrent injected by mixed monolayers of OXA18 and ARA the quantum yield of the photocurrent decreases upon increasing the electrolyte pH when the electrolyte pH is higher than four.

While for monolayers of OXA18 the inverse photocurrent depends in a linear way upon the hydroquinone concentration between $1.0x10^{-3}$

$moll^{-1}$ and $1.6x10^{-3}$ $moll^{-1}$ it is in this concentration range nearly independent upon the hydroquinone concentration when a mixed mono

**Scheme 1**

| | |
|---|---|
| $D \xrightarrow{h\nu} D^*$ | light absorption |
| $D^* \xrightarrow{k_f} D + h\nu$ | fluorescence |
| $D^* \xrightarrow{\Sigma k_{nr}} D$ | radiationless decay |
| $D^* \xrightarrow{k_{red}} P$ | formation of a geminate electron-defectelectron pair |
| $P \xrightarrow{k^g_{rec}} D$ | geminate recombination |
| $P \xrightarrow{k_{ss}} D$ | recombination from a surface state |
| $P \xrightarrow{k_{-1}} e^-_{cb} + D^+$ | dissociation of the geminate electron-defectelectron pair |
| $D^+ + REG \xrightarrow{k_{reg}} D$ | regeneration of the oxidized dye |
| $e^-_{cb} + D^+ \xrightarrow{k^i_{rec}} D$ | "alien" recombination with electrons in the conduction band |
| $D^+ \xrightarrow{k_{ss}} D$ | recombination from a surface state |
| $e^-_{cb} \xrightarrow{k_{es}} j$ | escape of the electron to the bulk of the conduction band |

layer of OXAPY and PAL, is used. At lower hydroquinone concentrations a plot of the inverse photocurrent versus the inverse hydroquinone concentration shows first a sub-linear variation and at hydroquinone concentrations below $1.2x10^{-4}$ $moll^{-1}$ a levelling is observed (figure 2). For photocurrents injected by mixed monolayers of OXA18 and ARA the decrease of the photocurrent is more important and even at a concentration of $5.0x10^{-5}$ $moll^{-1}$ no saturation is observed. This behaviour does not depend on the electrolyte pH. To explain the dependence of the sensitized photocurrent on the electrode potential and the hydroquinone concentration the model presented in scheme 1 was proposed for electron injection by mixed monolayers of OXA18 and ARA. To allow for the saturation of the photocurrent at low hydroquinone concentrations one should also take into account an irreversible reaction of the oxidized dye, as was already proposed by Nasielski et al[6].

| | |
|---|---|
| $D^+ \xrightarrow{k_p} X_{ads}$ | product formation |

The process described by $k_p$ leads to an irreversible destruction of the dye and will therefore induce a decrease of the photocurrent as a function of time. This phenomenon is observed for photocurrents injected by both OXA18 and OXAPY and becomes more important a low hydroquinone concentrations. Furthermore it is more important for monolayers of OXA18 compared to OXAPY. Therefore the levelling of the inverse photocurrent at higher hydroquinone concentration cannot be explained by a larger value of $k_p$. On the other hand the larger value of the photocurrent observed for OXAPY at very low hydroquinone concentrations would suggest that the ratio $k_p/k_p+k_{ss}+k^i_{rec}$ is larger for OXAPY. This dilemma can only be solved if one considers that the sample is illuminated by chopped light. During the light part of the cycle both OXA18 and OXAPY become oxidized. However OXAPY has the possibility to distribute the defect electron between the HOMO of the cyanine moiety and that of the two pyrene moieties. While a defect-electron in the cyanine moiety will lead to an irreversible destruction of the chromophore during the light part of the cycle the oxidized pyrene is relatively stable and does not react before it is reduced by hydroquinone during the dark part of the cycle. Furthermore if the missing electron in the OXAPY molecule would be distributed between the cyanine moiety and the pyrene moiety which is farther removed from the $SnO_2$ electrode one can expect that $k_{ss}+k^i_{rec}$ will become smaller for OXAPY compared to OXA18. This will lead to a higher value of the ratio $(k_p+k_{reg}[H_2Q])/(k_{ss}+k^i_{rec}+k_p+k_{reg}[H_2Q])$ which is proportional to the photocurrent. According to this hypothesis $k_{ss}+k^i_{rec}$ must become negligible compared to $k_{reg}[H_2Q]$ at much lower hydroquinone concentrations than when the electrons are injected by a mixed monolayer of OXA18 and ARA. This explains why the photocurrent depends no longer upon the hydroquinone concentration between $1.6\text{x}10^{-3}$ $\text{moll}^{-1}$ and $8.0\text{x}10^{-3}$ $\text{moll}^{-1}$. On the other hand the lower value of $k_{ss}+k^i_{rec}$ explains why at low hydroquinone concentrations the ratio $k_p/(k_p+k_{ss}+k^i_{rec})$ is much larger for OXAPY than for OXA18 leading to a larger photocurrent. Although the oxidation potential of 1-methylpyrene (1.15 V) and that of diethyloxacarbocyanine (1.02 V)[19] in acetonitrile predict that this equilibrium should be shifted to the situation where the cyanine moiety is oxidized one should take into account that the electric field over the Helmholtz layer and the different solvation of both moieties in the monolayer can change the solvation free energy of the different species involved in this electron transfer process.

In spite of the less efficient recombination at low hydroquinone concentration the photocurrents obtained for OXAPY at higher hydroquinone concentrations are no larger than those obtained using OXA18. This is probably due to the fact the initial recombination processes are much faster than the distribution of the defectelectron over the different chromophores in the OXAPY molecule. This corresponds to recent time experiments on the photo-sensitized injection of electrons in $SnS_2$ which suggest that the initial recombination processes occur within a few tens of picoseconds[20].

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## REFERENCES

1. M.Van der Auweraer, B.Verschuere, G.Biesmans, F.C.De Schryver, Langmuir 3, 992 (1987).
2. F.Willig, R.Eichberger, K.Bitterling, W.S.Durfee, W.Storck, M.Van der Auweraer, Ber.Bunsenges.Phys.Chem., 91, 869 (1987).
3. M.Fujihira, K.Nishiyama, K.Aoki, Thin Solid Films, 160, 317 (1988).
4. D.Meerschaut, M.Van der Auweraer, W.Kools, F.C.De Schryver, A.Scheelen, A.Persoons, Thin Solid Films, 210/211, 492, (1992).
5. H.Gerischer, M.T.Spitler, F Willig, in Proceedings of the Third International Symposium on Electrode Processes, edited by S.Bruckenstein, (The Electrochemical Society; Princeton N.Y. 1979), p.115.
6. J.Nasielski, A.Kirsch-De Mesmaeker, P.Leempoel, Electrochimica Acta, 23, 605 (1978).
7. R.Memming, Far.Disc.Chem.Soc., 85, 261 (1974).
8. W.Arden, P.Fromherz, J.Electrochem.Soc., 127, 370 (1980).
9. G.Biesmans, M.Van der Auweraer, C.Cathry, D.Meerschaut, F.C.De Schryver, W.Storck, F.Willig, J.Phys.Chem., 95, 3771 (1991).
10. G.Biesmans, M.Van der Auweraer, C.Cathry, F.C.De Schryver, Y.Yonezawa and T.Sato, Chem.Phys., 60, 97, (1992).
11. M.Van der Auweraer, D.Meerschaut, F.C.De Schryver, in preparation.
12. G.Biesmans, M.Van der Auweraer and F.C.De Schryver, Langmuir, 6, 277 (1990).
13. M.M.H.Khalil, N.Boens, M.Van der Auweraer, M.Ameloot, R.Andriessen, J.Hofkens, F.C.De Schryver, J.Phys.Chem., 95, 9375 (1991).
14. N.Boens, L.Janssens, F.C.De Schryver, Biophys.Chem.33, 77 (1989).
15. A.van Hoek, A.J.W.G, Visser, Rev.Sci.Instrum., 52, 1199 (1981).
16. M.Van der Auweraer, M.Vandenzegel, N.Boens, F.C.De Schryver, F.Willig, J.Phys.Chem., 90, (1986), 1169.
17. N.Beens, A.Weller in Organic Molecular Photophysics Volume II, edited by J.B.Birks (John Wiley and Sons NY, 1975) p 159.
18. P.B.Gilman, Photograph.Sci.Eng., 18, (1974) 475.
19. R.Loutfy, J.Sharp, J.Photogr.Sci.Eng., 20, 165 (1976)
20. J.M.Lazafame, R.J.D.Miller, A.A.Muenter, B.A.Parkinson, J.Phys.Chem., 96, 2820 (1992).