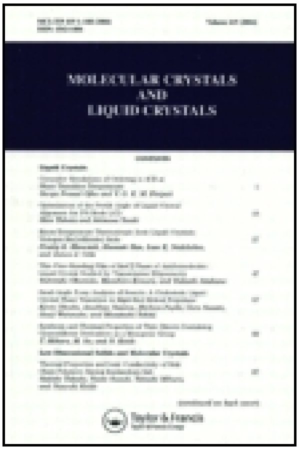

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photoinitiated Electron Wire Properties of a Face to Face Porphyrin Tetramer. Insertion in Ultrathin Membranes

J. L. Garaud [a], E. Bienvenue [a], J. M. Janot [a], G. Miquel [a], P. Seta [a], P. Maillard [b] & M. Momenteau [b]

[a] LPCSP, URA 330 CNRS, Montpellier, France

[b] Institut Curie, Centre Universitaire, Orsay, France

Version of record first published: 05 Dec 2006.

To cite this article: J. L. Garaud , E. Bienvenue , J. M. Janot , G. Miquel , P. Seta , P. Maillard & M. Momenteau (1993): Photoinitiated Electron Wire Properties of a Face to Face Porphyrin Tetramer. Insertion in Ultrathin Membranes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 235:1, 59-66

To link to this article: http://dx.doi.org/10.1080/10587259308055180

Mol. Cryst. Liq. Cryst. 1993, Vol. 235, pp. 59–66
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

PHOTOINITIATED ELECTRON WIRE PROPERTIES OF A FACE TO FACE PORPHYRIN TETRAMER. INSERTION IN ULTRATHIN MEMBRANES.

J.L. GARAUD, E. BIENVENUE, J.M. JANOT, G. MIQUEL, P. SETA
LPCSP, URA 330 CNRS, Montpellier, France.
P. MAILLARD, M. MOMENTEAU
Institut Curie, Centre Universitaire, Orsay, France.

Abstract Information processing on a molecular scale will hopefully be achieved by assemblies composed of molecules acting either as electronic components or as electron wires. A face to face porphyrin tetramer is designed here as a candidate for an electron wire. We present evidence from direct electric measurement for the electric conduction of such molecules embedded in an ultrathin membrane which spatially organize them. According to energetic considerations issued from electrochemical and spectroscopic data, an intramolecular charge shift following photoexcitation and photooxidation is more probable than transient formation of a biradical ion pair.

INTRODUCTION

The electric conduction at the molecular scale is a problem being debated since two decades in a multi-field research community. The impact of the research has shown itself in biology as well as in physical chemistry. In the domain of biology the will of knowing the mechanisms of the primary steps in photosynthesis has been recently stimulated by an advance in the knowledge of the structure of the reaction centers.[1] In the domain of physical chemistry theoretical models have rapidly emerged,that quantitatively describe the intramolecular electron transfer in systems with restricted diffusion.[2,3] Advances in supramolecular chemistry - the chemistry of molecular assemblies - rapidly contributed to a real burst in the production of organic and organometallic compounds that possess electron transfer or energy transfer properties.[4] The latter molecules constitute models of electric components in the futuristic scope of molecular computing devices.[5] In that prospect, outside the building of molecules capable of achieving the functions of components such as diodes, switches and gates, the building of a conducting molecular wire is required in order to connect those various elements. This aspect has been explored in particular in the domain of conducting polymers, but few has been done yet at the molecular scale. However, some molecular models similar to polyenes have been constructed; generally, they are based on polyenic structures placed between electroactive groups.[6,7] Other approaches concern self assembled or covalently linked systems implying stacked porphyrin or phtalocyanin derivatives in which the driving force for the intramolecular electron transfer comes from the dissymmetry of the complexed metals.[8,9] Much less attention has been paid to molecular wire properties of molecules made up of identical chromophores linked by spacers.[10] A technological advance based on the use of molecular components requires some problems to be resolved firstly, in particular the problems of the positioning of the molecular components inside a circuit architecture, and of the communication at the molecular scale (adressing and reading out the information). That is why a knowledge of the interactions between molecules is important. Monolayers and thin films are possible insertion media for molecular components. They also can be assembled in bilayer membranes[10] or L.B films[11], or deposited on electrodes.[12] Each of these systems presents an interest, either orientating the molecules, or behaving as an electric insulator between the active zones, or simply establishing an electric connection with molecules that are under study.

We present in this article data concerning a face to face porphyrin tetramer, analogous to a short polymer, and its ability to act as a conducting wire, i.e to exchange electrons with other electroactive species being in contact with its terminations. This long molecule has been immobilized in an ultrathin membrane which plays both the role of a support and of an insulator, resembling the amorphous silicon in doped semi-conductors.

EXPERIMENTAL

Synthesis

The stacked tetraporphyrin (compound 1) was prepared according to the strategy used by Collman[13] for the synthesis of face-to-face porphyrins, but here a monohandle diporphyrin compound was condensed on itself in the presence of phosgene.

Cyclic voltammetry

The oxidation and reduction potentials of compound 1 have been measured in dichloroethane with 0.1M tetra-n-butylammonium tetrafluoroborate, using a glassy carbon as working electrode and an Ag electrode as reference.

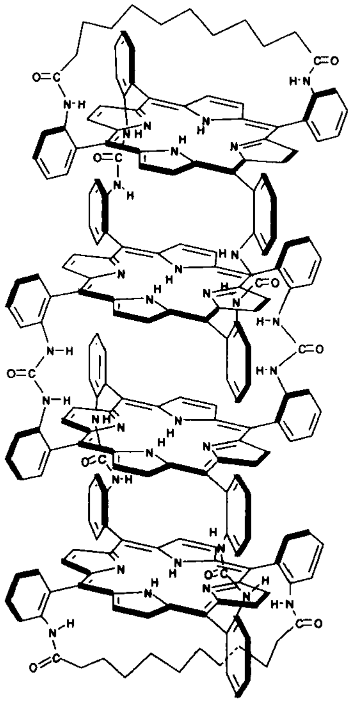

FIGURE 1 Compound 1

Electrochemical cell

The electrochemical cell is composed of two chambers separated by a Teflon film. The phosphatidylethanolamine bilayer membrane sensitized with 1.25% (mole/mole) compound 1 is formed on a 1mm diameter hole drilled in the 0.1mm thick Teflon septum. The chambers are filled with an electrolytic medium of controlled composition (10^{-1}M NaCl, 10^{-2}M potassium monophosphate buffer, pH 4.8, 10^{-2}M potassium ferricyanide, 10^{-2}M ascorbic acid). One Ag/AgCl electrode is dipped in each chamber. The membrane is photoexcited by light pulses from the beam of a CW argon laser, cut by an electromechanical shutter. The photoinduced current and potential changes are recorded in the electrical circuit between the electrodes which are used also for biasing the membrane voltage.

Spectroscopy

The absorption spectra were recorded with an UV visible spectrophotometer, Kontron Instruments model 940. The excitation and fluorescence emission spectra were obtained with a luminescence spectrophotometer Perkin-Elmer LS50.

PHOTOELECTRICAL RESULTS

The evidence for the photoconductivity of compound 1 comes from the charge flux induced by the light absorption of this chromophore. The variation of the photocurrent I at the steady state is plotted in Figure 2 versus the external bias voltage U (membrane potential) impinged by the electrodes. The I/U curve is close to linearity in the studied potential range, but, as already noticed for photoinduced vectorial charge transfer processes through ultrathin membranes, a stopping voltage U^S is observed; the photocurrent value stays at zero when the applied voltage is lowered under the stopping voltage value. The latter value is higher than the corresponding photopotential recorded on the same membrane in open circuit conditions (-29mV as compared to U^S= - 80 mV in the case of Figure 2). This fact has been attributed to the existence of an ionic leakage current accompanying the photoinduced electron flux.

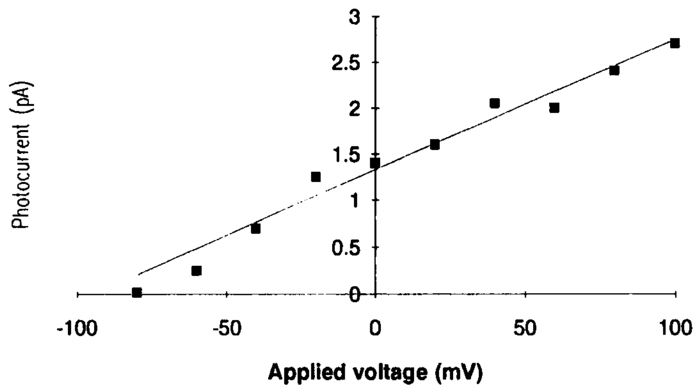

FIGURE 2 Photocurrent versus external applied voltage

It is important to stress that the part of the steady state photocurrent related to an electron transfer is relevant to a transmembrane flux achieved by the electron transport ability of compound 1 spanning the membrane.

SPECTROSCOPIC RESULTS

In order to propose a photochemical mechanism for the experimentally observed photoconductivity of the tetraporphyrin molecules embedded in the ultrathin membrane, it is important to get some insights into the nature of the excited state which is the precursor of the charge transfer process at the molecular level. If the photoexcited state was a delocalized multiplex state having a charge transfer character prior to dissociating into a radical ion pair, this excited state would show some classical features of charge separation [14]. It would show a large Stokes shift; i. e. the differences between its absorption and emission spectrum would change with the polarity of the solvent. Moreover, the energy level of the zero-zero transition of the lowest singlet excited state of the tetramer would differ from that of a single chromophore. The absorption and fluorescence emission spectra of compound **1** in toluene, chloroform and methanol are shown in Figures 3 and 4a. No significant solvent shift is observed, neither for the absorption nor for the fluorescence emission.

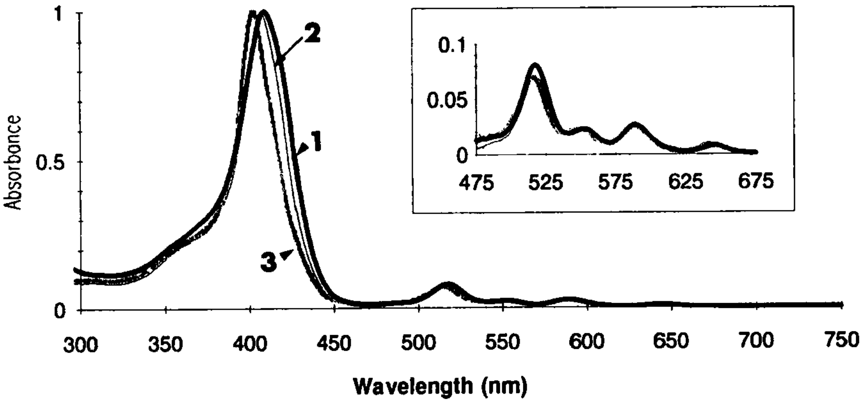

FIGURE 3 Absorption spectra of compound **1** in toluene (1), chloroform (2) and methanol (3)

Moreover the exact overlapping of the absorption and emission spectra (see Figure 4b) indicate that the conversion of the energy stored in the singlet ^2S excited state (the Soret band of the porphyrin) toward the lower ^1S state is almost complete; neither fluorescence from the ^2S state, nor other processes involving a polar state take place from this energy level, in contrast to what is observed for gable porphyrins.[15] The energy value of 1.92 eV for the zero-zero transition of the ^1S state, obtained from the overlapping between the excitation and fluorescence emission spectra is identical to that of a single porphyrin; consequently, the excited state (at least the lowest ^1S) is not a multiplex.

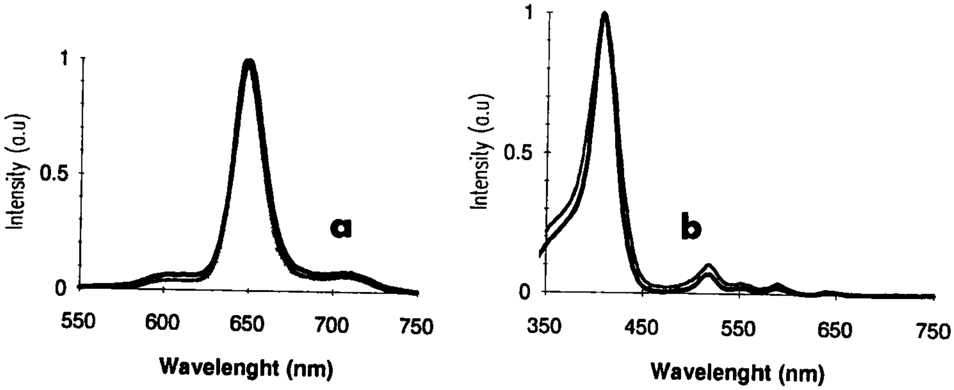

FIGURE 4 (a) Fluorescence emission spectra of compound 1 in the same solvents as in Figure 3. (b) Absorption and fluorescence excitation spectra of compound 1 in chloroform.

ELECTROCHEMICAL RESULTS

Another piece of evidence against the occurrence of a charge transfer state, is related to the lack of exergonicity of such a process for the tetraporphyrin. An intramolecular charge separation corresponds to a deactivation path of the excited state in parallel to other processes such as internal conversion, intersystem crossing etc.... The charge separation only occurs if there is a driving force for such a process, i. e. if the energy level of the excited state is higher than that of the corresponding ion pair (biradical such as P^+-P^-). The energy of this radical pair can be roughly estimated (see the voltammogram in Figure 5) as 1.8 eV from the difference in the lowest redox potentials of compound 1, i. e. $E^\circ(P^-/P)$ - $E^\circ(P/P^+)$. The resulting small negative value calculated for the Gibbs free energy of the charge separation along the tetramer molecule is in favour of a charge separated state, but the lack of solvent effect makes this possibility relatively improbable.

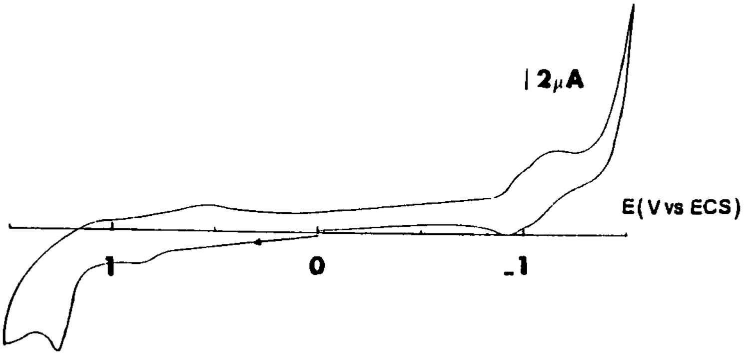

FIGURE 5 Cyclic voltammogram of compound 1 (see experimental).

MECHANISM

Relying on the spectroscopic and electrochemical results, we confirm the mechanism already proposed for the corresponding triporphyrin. Following the photoexcitation, the tetraporphyrin molecules lying near the oxidant interface are photooxidized, forming a monocation radical P^+PPP. The back displacement of the electron competes with the intramolecular migration of the charge from one porphyrin to the other until the porphyrin monocation is back reduced at the reducing interface. Thus, the molecule is back to its fondamental state, until a new photoexcitation occurs. This mechanism, equivalent to the propagation of a hole in the short pile of porphyrin macrocycles, is quite similar to the mechanism recently proposed for the electron transfer in columnar stacks of porphyrin molecules. Taking into account the value of the electron mobility given by Schouten et al.[8], the order of magnitude of the charge flux is calculated as approximately 10-20 pA in our situation assuming 1% efficiency of photoexcitation. This estimated value is slightly higher than the 2-5 pA order of magnitude of the measured photocurrent values. This can easily be explained by the longer porphyrin plane to plane distance in our case. The estimated distances are 4.9Å and 7.3Å for the columnar molecule[8] and for compound 1, respectively.[16]

CONCLUSION

The stacked tetraporphyrin, like the corresponding triporphyrin, is an example of an electron wire of the same order of length as other molecular models of molecular electronic components such as dyads or triads. The intramolecular electron transfer mechanism is the result of the formation of a cation radical on one termination of the molecule, followed by a charge shift of the cation radical from one porphyrin ring to the neighbouring one. In that way, this mechanism, although being photochemically induced, is similar to the one proposed by Lehn's group[7] concerning the electron transfer mediated by caroviologens. In the latter case, the electron transfer along the polyene spacer is the result of the chemical redox modification of one terminal viologen group of the molecule embedded in a vesicle bilayer membrane.

REFERENCES

1. J. Deisenhofer, O. Epp, K. Miki, R. Huber and H. Michel, J. Mol. Biol, 180, 385 (1984).
2. R. A. Marcus and N. Sutin, Biochim.Biophys.Acta, 818, 265 (1985).
3. J. Jortner and M. Bixon, J. Chem. Phys, 88, 167 (1988).
4. M. P. O' Neil, M.P. Niemczyk, W.A. Svec, D. Gosztola, G.L. Gaines III, and M.R. Wasielewski, Science, 257, 63 (1992).
5. Haddon and A.A. Lamola, Proc. Natl. Acad. Sci. U S A, 82, 1874, (1985).
6. V. Balzani and L. de Cola, Supramolecular Chemistry (Kluwer Academic Publishers, Dordrecht, vol. 371, 1992).
7. T. S. Arrhenius, M. Blanchard-Desce, M. Dvolaïtzky and J. M . Lehn, Proc. Natl. Acad. Sci, 83,5355 (1986).
8. P.G. Schouten, J.M. Warman, M.P. de Haas, M.A. Fox and H.G. Pan, Nature, 353, 736 (1991).
9. Fujita, J. Fajer, C.K. Chang, C.B. Wang, M. A. Bergkamp and T. L. Netzel, J. Phys. Chem, 86, 3754 (1982).
10. A. Lamrabte, M. Momenteau, P. Maillard and P. Seta, J. Mol. Electron, 6, 145 (1990).
11. M. Fujihira and H. Yamada, Thin Solid Films, 160, 125 (1988).
12. P. Collin A. Deronzier and M. Essakalli, J. Phys. Chem, 95, 5906 (1991).
13. P. Collman, C. M. Elliot, T. R. Halbert and B. S. Tovrog, Proc. Natl. Acad. Sci. U S A , 74, 18 (1977).
14. Y. Masaki, Y. Uehara, S. Yanagida and C. Pac, Chem. Lett. 315 (1992).
15. Y. Kaizu, H. Maekawa and H. Kobayashi, J. Phys. Chem, 90, 4234 (1986).
16. A. El Kasmi, Thèse de Doctorat, Université Paris VII (1991).