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Photo-Induced Energy and Electron Transfer in Porphyrin Triad and Related Dyads

TMR Large-Scale Facilities Access Programme

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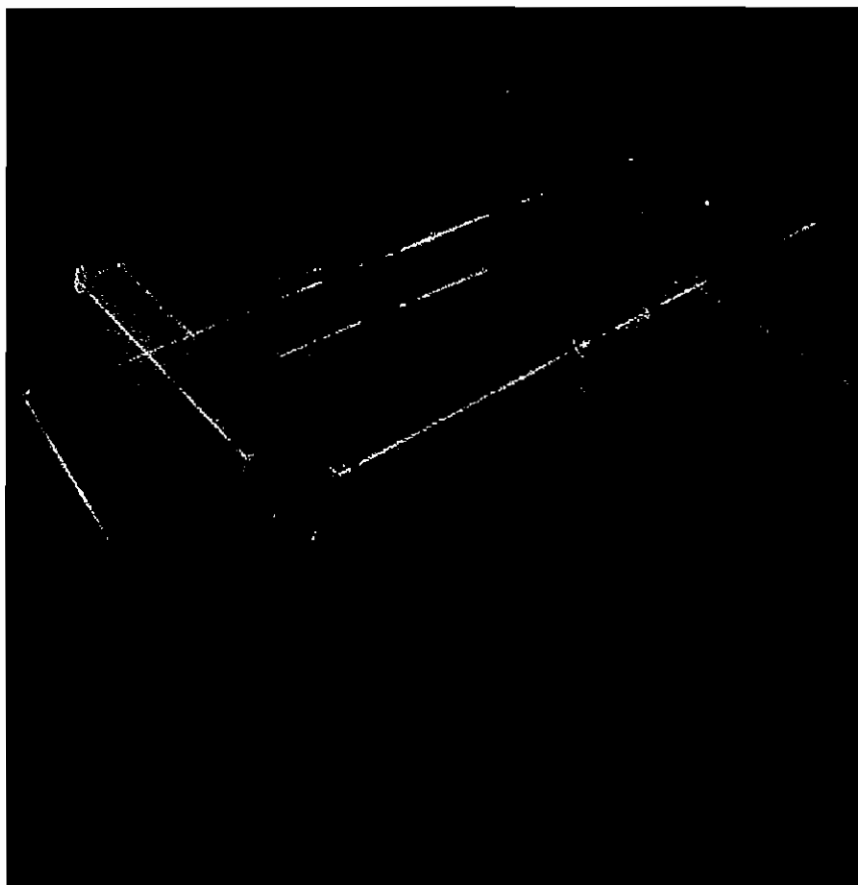
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SUMMARY

This report describes the experiment entitled 'Photo-Induced Energy and Electron Transferin Porphyrin Triad and Related Dyads; carried out at the Central Laser Facility (CLF) from the 2nd Nov to the 15th Nov 1997. The experiment, funded by the Framework IV Large-Scale Facilities Access Scheme, was proposed by Dr P Seta, Laboratoire des Materiaux et Procédés Membranaires, Montpellier and carried out by visiting researchers from the Laboratory. They were supported by researchers from the Central Laser Facility, Rutherford Appleton Laboratory.

Results Summary

- An extensive set of femtosecond transient absorption data has been successfully obtained to elucidate the electron transfer mechanism in porphyrin triads and dyads.

- These systems are important in the design of light conversion and solar energy storage devices and their investigations improve our understanding of primary steps in photosynthesis at the molecular level.

- The results will be used in conjunction with complimentary transient resonance Raman studies which are to be undertaken in near future.

Photo-Induced Energy and Electron Transfer
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INTRODUCTION

Substantial efforts have been directed over the past decades towards mimicking the vectorial photo-induced electron transfer and charge separation in photosynthetic reaction centres in view of i) -the desire to understand at the molecular level the mechanism of the primary steps in photosynthesis, ii)- the design and the development of practical systems for light conversion and solar energy storage. One approach for modelling such processes consists in the building of linked donor-acceptor molecules called polyads [1]. Most of the related studies involve porphyrins and metalloporphyrins because these molecules represent chemically stable models of the chlorophylls of the natural photosynthetic reaction centres where the absorbed light is converted into electrochemical energy by vectorial electron transfers. The stabilisation of the charge separation is generally achieved by the spatial separation of the ion-radicals produced by vectorial electron transfer, which prevents recombination of the electrical charges and by energetic considerations on the potential energy surfaces of the initial and final states described in the Marcus electron transfer theory [2].

Towards the stabilisation of the charge separation several porphyrins linked to quinone [3] or to viologen [4] moieties have been synthesised, the energy level of the charge separated final state (bi-radical) being much lower than the LUMO level, i.e the energy stored in the lower localised singlet excited state of these artificial reaction centres. In the present work we have studied a triad molecule composed of two porphyrins (a zinc and a free base porphyrin) acting as electron donor groups in the photo-excited state of the compound, and located on both sides of a two electrons acceptor group (bipyridinium), which plays the role of an electron trap. We designed this compound to understand how the electron transfer paths (from the porphyrin A or B to the respective adjacent pyridinium acceptor of the bipyridinium V^{2+} linker, see figure1) compete for the charge separation and how these steps are influenced by the possible excitation energy transfer between the two porphyrins of different LUMO levels.

In a previous work [5] we have shown by fluorescence photon counting experiments that in the triad B-V^{2+}-A as well as in the corresponding dyads B-V^+ and A-V^+ (see figure 1), the fluorescence emission is strongly quenched as compared to those of the corresponding A and B porphyrin monomers. If we take into account electrochemical data obtained with these compounds (oxidation and reduction potentials), two different charge separated states shown in figure 2 are energetically allowed. Thus the shortened fluorescence lifetimes have been tentatively explained as due to the favored electron transfers which produce the radical cations of the porphyrins and reduced forms of the bipyridinium acceptor, that would be evidenced in transient absorption spectroscopy experiments.

During the experiments at RAL we recorded, after excitation of the studied molecules in organic solution with a powerful femtosecond light pulse, the variation of absorption at different wavelengths of the different intermediate states that are formed during the deactivation process. The aim of these experiments is the evaluation of the kinetic parameters of the electron transfer and charge recombination steps from the rises and decays of the transient absorptions.
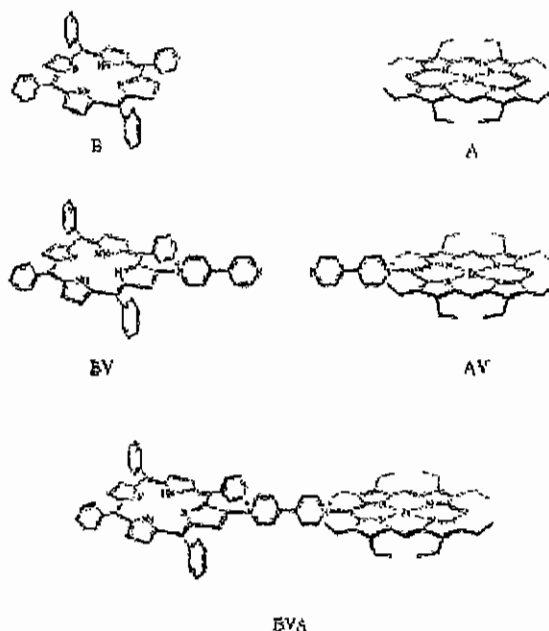

Figure 1. Triad B-V-A, related dyads B-V
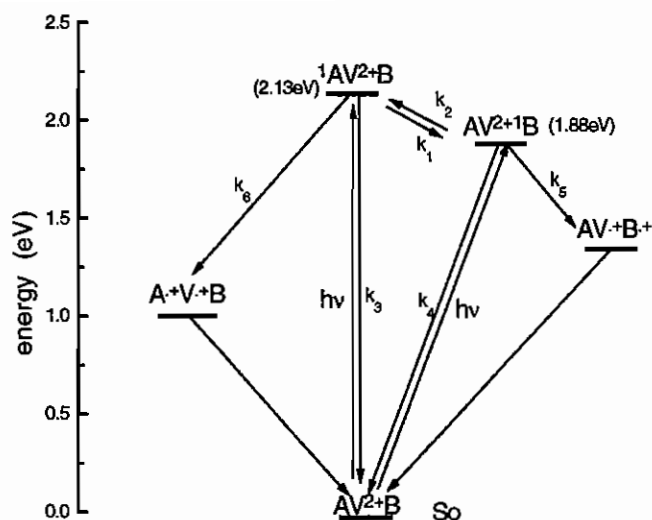and A-V and porphyrin monomers B and A.

Figure 2. Photoinduced electron transfers scheme

The transient absorption variations recorded for the dyads and the triad are represented in figure 3. The temporal profiles are different according to the values of the probe wavelength. This has to be related to the fact that these variations of absorbance do correspond to a sum of the absorbances of the different intermediate states that are weighted according to their differences in cross sections. These signals are at first characterized by a fast rise in the picosecond time scale, followed by a decay more complex than a single exponential. The decays, at least for the zinc porphyrin dyad and for the triad, are faster than the fluorescence decay times, previously measured [5]. This means that the shape of the transient absorption signals are not only due to the variations of absorption resulting of the population followed by the deactivation of a unique singlet excited state, but do result from a more complex deactivation scheme. If this was not the case, it should be impossible to explain the shorter decrease of the absorbance in the zinc dyad case as compared to the free base, taking into account the values of the fluorescence lifetimes which vary in the opposite way.

Thus, after analysis of many different schemes, the mechanism we suggest to explain our data in order to conciliate them with the fluorescence experiments has to incorporate two distinct emitting photo-excited states as drawn in figure 4. The assumption of these two ^1S states could be supported by the existence in porphyrins of two well known orthogonal transition moments of the singlet excited state.
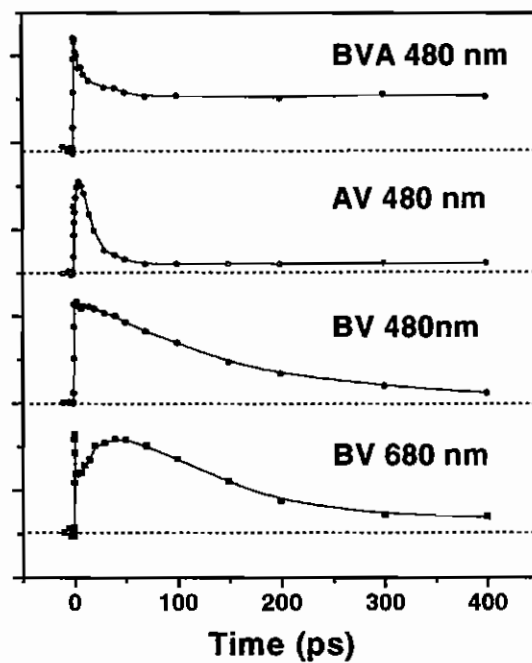
Figure 3. Transient absorption signals recorded after the excitation with a pulse at 415 nm, for the AV, BV dyads and triad AVB. The probe wavelengths are given in the figure.
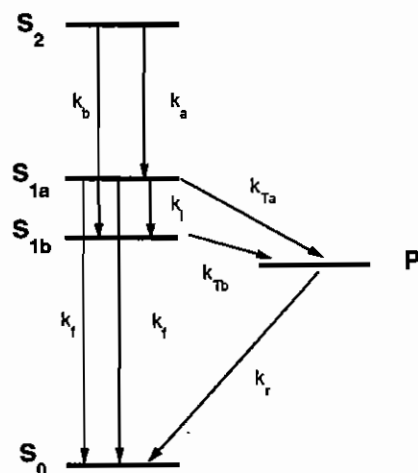

Figure 4. Photoinduced electron transfer scheme used for the fit of the transient absorption signals shown in figure 3.

This effect could be reinforced by the asymmetry imposed by the bipyridinium group. The main feature of this model is essentially that the upper excited state is rapidly quenched by electron transfer (step with rate constant k_{ta}) giving rise to a quenched luminescence lifetime of about 5-30 ps. This very short lifetime was previously interpreted as scattering light in the luminescence experiments because of the limited time resolution of the single photon counting device (≈ 20 ps). This upper excited state is in competition with a charge separation process which populates a lower singlet state with a rate constant k_i, from which electron transfer also occurs at a rate lower than that of the upper state (rate constant k_{tb}). The emission of these lower and less populated intermediate states can account for the quenched luminescence observed with these compounds. Thus the major contribution of the upper excited state is the fast charge separation which produces light absorbing radicals, and the population at a minor concentration of a lower excited singlet state which is responsible of the observed luminescence. This model also accounts for the change in the shape of the transient signals with the wavelength of the probe. The variation of absorbance is in fact the difference between the ground state absorption and the sum of the absorbancies of the different intermediate states following the excitation pulse. We know from previous photo-electrochemical experiments that the porphyrin cation radical and the formal acceptor bipyridinium anion mainly absorb at wavelengths longer than 600 nm, which is as a matter of fact the spectral domain where the transient absorption signals present a hump. On the contrary the singlet excited states of the porphyrins have strong absorptions in the 400-500 nm region. According to the model shown in figure 4, the calculated time course of the charge separated state and of the singlet state show that the signals at the lower wavelengths are dominated by the singlet excited states absorptions whereas at longer wavelengths by the radicals. The data collected with the triad resemble those recorded with the zinc porphyrin dyad. However after a fast decay the transient absorption reaches a pseudo steady state of much higher amplitude. As no evidence of triplet state formation was observed in previous experiments, the explanation we propose is the formation of a longer lived charge separation species stabilised by the attraction effect of the remaining positive charge worn by the bipyridinium. The observed faster decay as compared to that of the BV dyad, as well as the occurrence of a stabilisation of the charge separation, accounts for a favoured deactivation of the excitation by the electron path k_6 instead of k_5 (see figure 2).

CONCLUSIONS

The transient absorption experiments confirm the possible photoinduced intramolecular charge separation in this family of molecular reaction centres models. The main path for electron transfer in the triad appears to be issued from the localized zinc excited state. However the spectral attribution of the formed porphyrin radicals is not enough accurate to conclude univocally. Thus these conclusions have to be confirmed by the use of a separate powerful technique of radical identification such as transient Raman spectroscopy.

REFERENCES

1.   D Gust and TA Moore, Science, <u>35</u> 244, (1989)

2.   R.A Marcus, J. Chem. Phys. <u>24</u> 966, (1956) ; R A Marcus and N Sutin Biochim.Biophys.Acta, <u>811</u> 265, (1985)

3.   J Liu and J R Bolton, J. Phys. Chem, <u>96</u> 1718, (1992) ;
        A D Joran *et al*, Nature, <u>327</u> 508, (1987)

4.   V.Y.Shafirovitch *et al*, Chem. Phys. Lett., <u>15</u> 24, (1991)

5.   M. El Baraka *et al*, Photochem. Photobiol A, <u>113</u> 163, (1998)