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Excited State Electron Transfer in Systems with a Well-Defined Geometry

Progress Report

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Abstract

To determine what are the important criteria governing efficient light induced electron transfer, we have been studying cyclophanes formed by joining two chlorophyll macrocycles together with two covalent linkages. The properties of the cofacial dimer can be altered by adding one or two magnesium atoms. When a cyclophane containing only one metal atom is excited electron transfer takes place in under ten picoseconds. Evidence for the formation of a state having a great deal of charge transfer interaction or perhaps even a radical pair is found in the time resolved difference spectrum which shows a contribution due to a cation of the magnesium containing macrocycle and an anion of the metal free portion of the molecule. The lifetime of the charge transfer state is 2.4 nsec. This would indicate that we have stabilized the charge separation for a relatively long time. The metal free dimer has an excited state product which does not appear to be a triplet state. The lifetime of this product is very long. The identity of the product has not as yet been obtained. It too could be a charge transfer state. If this is true, we have succeeded in stabilizing the charge separation for an extremely long time. Finally we observed that the photophysical properties of the chlorophyll macrocycle are modified by reduction of the vinyl group on ring I.

I. Introduction

For the past seven months we have been studying the properties of cyclophanes formed by joining two chlorophyll macrocycles together. The structure of these cyclophanes is shown in Figure 1.¹ We have been working with three different cyclophanes: a) a cyclophane which contains two magnesium atoms and is therefore a dimer of chlorophyll; b) one does not contain any metal atoms at all and is a dimer of pheophytin; c) a third cyclophane which has only one magnesium atom, therefore containing both a chlorophyll macrocycle and a pheophytin macrocycle. The aim of our work has been to try to understand the conditions that lead to efficient charge separation in the singlet excited state and the conditions that will stabilize this charge transfer state for a period long enough to extract it to do useful chemical work. We have used a variety of techniques to understand the dynamics of these molecules. Steady state absorption and steady state fluorescence have been used to determine the amount of interaction between the two macrocycles in the ground and the excited state. Time resolved picosecond absorption spectroscopy was used to determine the extent of charge separation in the singlet excited state and also to detect the nature and the yield of the products formed due to wasteful processes. As can be seen from a review of our work, we have spent a great deal of time characterizing the three cyclophanes. The data is most complete on the monometal compound. This is because we have been able to show that it undergoes a charge separation in the excited state.

We have obtained the singlet lifetimes, fluorescent lifetimes, relative fluorescence yields, and triplet yields for the two monomers and three dimers. These data, for butyronitrile containing 5% pyridine, are summarized in Table I.

Table 1^a

System	Singlet Lifetime as determined by absorbance measurements	Singlet Lifetime as determined by fluorescence mea- surement	Relative fluorescence yield	Triplet yield
M-PChl	11 ns	11 ns	1.0 ^b	0.4
M-PPh	10 ns	10 ns	.37	0.65
Mono-metal cyclophane	2.4 ns	~ 2 ns	.12	0.15
Dimetal cyclophane	2.8 ns	3.2 ns	.42	0.1
No-metal cyclophane	0.3 ns	5.5 ns	.27	0.1-0.3

a) All data are in butyronitrile with 5% pyridine.

b) This was arbitrarily taken to equal 1.0.

II. Doubly Metallated Cyclophane

The absorption spectrum of the doubly metallated dimer is similar to that of the monomer (Figure 2,3).¹ The monomers that are used in this study are not monomers of chlorophyll a or pheophytin a, but monomeric forms of methyl mesopyrochlorophyllide a (M-PCh a) and methyl mesopheophorbide a (M-PPh a) (Figure 1). These molecules differ from chlorophyll a in that the carbomethoxy group is absent and the vinyl group is reduced. These compounds were chosen as models because they are analogous to the individual macrocycles that form the three cyclophanes we studied. The emission spectrum of the dimer is slightly red shifted with respect to the monomer fluorescence (Figs. 4,5). The absorption and fluorescence data are in agreement with previously published results. The small red shift could be due to increased interaction between the two chromophores in the singlet excited state or the mixing of a small amount of a charge transfer state with the excited singlet state. The fluorescence quantum yield of the dimer was about a factor of two less than that of the monomer.

Measurements of the singlet lifetime of the monomer indicate that it is about 11 nsec while the dimer is about 3 nsec. This factor of more than three difference in lifetime is enough to account for the difference in quantum yield between the dimer and the monomer. The very long singlet lifetime of monomeric M-PCh a is quite surprising. It is more than a factor of two larger than that of monomeric methyl pyrochlorophyllide a. The triplet quantum yield of methyl mesopyrochlorophyllide a was estimated from the stable residual bleaching at 15-30 nsec after excitation. It was found to be 0.4, which is somewhat less than the 0.6-0.7 that has been reported for monomeric chlorophyll a and pyrochlorophyll a.^{2,3}

The decrease in the triplet quantum yield coupled with the increase in singlet lifetime arises from a decrease in the rate for intersystem crossing. Thus the reduction of the vinyl group effects the photophysical properties of the macrocycle. Additional work is needed to substantiate these findings. If these are found to be correct, then it would be the first observation of a significant change in the excited state dynamics of the monomeric chlorophyll a macrocycle due to chemical modification.

The excited state difference spectrum of the monomeric M-PCh a (Figure 8a) is nearly identical to those reported earlier for chlorophyll a.⁴ There was a small difference in the spectra in the 580-600 nm region. Presumably this difference is due to the absence of the vinyl group in the meso pyrochlorophyll a molecule. The dimetal cyclophane has an excited state difference spectrum which is similar to that of the monomer. There is no compelling evidence of a charge transfer interaction or an electron transfer reaction taking place during the singlet lifetime of the dimer.

III. Metal Free Cyclophane

The absorption spectrum of the monomer (M-PPh a) and the dimer are similar. The dimer shows a small (2 nm) red shift and slight broadening of the red absorbance band. The fluorescence spectrum of the dimer has a small red shift with respect to the monomer (Figure 4,5). In addition, the dimer fluorescence has a large red tail which is indicative of an excited state interaction. The fluorescence quantum yield of the dimer is about a factor of 4 less than that of the monomer. The triplet yield for the monomer is about 0.6, while its singlet lifetime is about 4 nsec.

Time resolved absorption spectra of the initially prepared excited state of the metal free dimer show that it decays in 270 psec

in butyronitrile and in about 750 psec in toluene. The product that is produced has a lifetime in excess of 15 nsec and a yield of about 0.3. Identification of this product and its lifetime is presently underway. The primary candidate for this product would be a triplet state of the dimer. However this identification does not agree with the very short lifetime of the singlet, the significant yield for the product, the observation of only a small decrease in the fluorescence intensity, and the long fluorescence lifetime. The decrease of nearly a factor of 20 in the singlet lifetime with less than a factor of two decrease in the fluorescence yield would mean that the radiative decay rate of the dimer must be a factor of 10 times larger in the dimer than in the monomer.

All of the data are compatible with the product being a radical pair or charge transfer state. The only problem with this identification of the product is that arguments based on the redox properties of the monomers would indicate that the chlorophyll dimer should demonstrate an even greater tendency to form a charge transfer state and at present it does not seem to do so. Experiments designed to identify the product and understand this puzzle are presently underway and are described in the accompanying proposal.

IV. Monometallated Cyclophane

The absorption spectrum of the monometallated dimer, Figure 3, is similar to a solution containing 50% of each of its monomers. The dimer shows a small (2 nm) red shift and slight broadening in the red absorbance band. In butyronitrile, to which 5% pyridine has been added to prevent aggregation, the emission spectrum of the 50/50 monomer solution appears (as expected) to be a mixture of M-PCh a and M-PPh a fluorescence (Figure 5). The emission from the dimer dissolved in butyronitrile does not

resemble that of the mixture, but is much more like the fluorescence arising from the metal free macrocycle (Fig. 5). The emission intensity of the monometallated cyclophane is reduced over that of the monomer mixture by about a factor of 5. In acetone the monometallated dimer has an emission spectrum which is much more like that of M-PCh a than M-PPh a (Figure 6). Comparing the emission yield of the monometallated dimer to that of the Mg containing monomer shows that fluorescence is quenched by more than a factor of 8 in the dimer dissolved in acetone. The absorption spectrum in acetone is slightly blue shifted with respect to that in butyronitrile. The absorbance spectra of the metal and no metal containing monomers are also blue shifted in acetone. Thus the ground state absorption of the dimer still appears as a linear superposition of the monomer spectra.

The simplest interpretation of the emission data would be that the excitation energy is localized on one of the two macrocycles, with the site of localization depending on the solvent. The excited state difference spectrum of the dimer dissolved in butyronitrile (with 5% pyridine) taken after a 30 ps excitation pulse is shown in Figure 7. As can be seen from the Figure there is a negative optical density change due to both the metal containing and the metal free macrocycle. The most interesting feature of this spectrum is the dual peaks that are observed. It is almost as if the dimer absorption was split into a separate contribution from the metal bearing chromophore and one arising from the metal free chromophore. We were unable to observe this separation in the ground state absorption spectrum even when the cyclophane was cooled to 77 K. The excited state spectrum in Figure 7 could be explained by the trivial effect of exciting the Mg containing chromophore in half of the molecules and exciting the metal free macrocycle in the

remaining dimers. It would be difficult to explain the emission arising only from the metal free chromophore if half of the singlet states consist of excited chlorophyll chromophores. Also, since the absorption of the mesopyropheophytin is about a factor of 4 larger at the wavelength of the exciting laser (532 nm), we would expect to see a much larger contribution in the light minus dark difference spectrum due to monomeric M-PPh than monomeric M-PCh. This is not observed. Excitation of samples containing a 50/50 mixture of the two monomers is presently underway and should eliminate the trivial effect as an explanation of the data.

The data in Figure 7 were taken with the YAG laser system. This system utilizes a spectrograph to obtain a spectrum covering about 250 nm during a single laser pulse. This apparatus is not able to study highly fluorescent samples near the emission maximum. This problem has been overcome by adding ethyliodide to the sample. The ethyliodide should not greatly effect the singlet excited state spectra taken immediately after the picosecond flash since it is a dynamic and not a static quencher. The ethyliodide does of course decrease the singlet lifetime and increase the triplet yield. The excited state difference spectra of methyl mesopyrochlorophyllide a and methyl pyropheophorbide a in the presence of ethyliodide is shown in Figure 8 a & b. In Figure 9 we have added together the difference spectra of the two monomeric chromophores. By comparing Figure 7 and Figure 9 it becomes evident that the excited state difference spectrum of the monometal cyclophane does not arise from the excitation of two isolated chromophores.

An excited state difference spectrum of the cyclophane taken with our low resolution glass laser picosecond spectrometer is presented in Figure 10. This system cannot resolve the two peaks seen in Figure 7.

However, when the low resolution spectrum is compared to a spectrum constructed from the sum of the low resolution excited state difference spectrum of the singlet of the methyl mesopheophytin a and the singlet of methyl mesochlorophyll a (Figure 11) the two appear different.

The major difference between the cyclophane spectrum (Figure 10) and the spectrum formed from M-PChl* and M-PPh* (Figure 11) is found between 700 and 750 nm. In this region the cyclophane difference spectrum has a broad positive optical density change that is not seen in Figure 11. The broad band appears to be due to charge separation in the cyclophane following absorption of a picosecond pulse.

A cation-anion spectrum was synthesized using the data of Fajer and coworkers.⁵ The cation and anion spectra were uncorrected for the small difference in the absorption spectrum of the mesopyrochlorophyll (and mesopheophytin) compared to the chlorophyll (and pheophytin) that were used in Fajer's study. The agreement between the "synthetic" anion-cation spectrum (Figure 12) and the cyclophane spectrum (Figure 10) is excellent. The agreement between the two spectra would suggest that excitation of the cyclophane leads to a rapid formation of a state having a large amount of charge transfer character or perhaps even a radical pair.

The appearance of the absorbance in the 700-750 nm region occurs in under 6 psec indicating that at room temperature this process is very fast. The lifetime of the state that is seen is about 2.4 nsec demonstrating that the charge separation is stabilized for a relatively long time. At present there have been only two other reports of such a long charge stabilization from reactions that proceed from porphyrin excited singlet states.^{6,7} The triplet yield for the monometal cyclophane was measured to be only about 0.14. This is considerably

lower than has been observed in any of the monomers. It is in keeping with a radical pair being produced since the hyperfine interactions are not expected to produce a radical pair with a large triplet component during the few nanoseconds that the state is stabilized.⁸

In the absence of nucleophiles such as pyridine or ethanol, the singlet lifetime of the dimer appeared to be shortened by an order of magnitude. This was due to aggregation. This is not surprising except that the concentrations used (10^{-4} M) should not have been large enough to lead to extensive aggregate formation. The aggregates that were formed had a singlet lifetime much shorter than that previously seen in monomeric chlorophyll aggregates at similar concentrations. In fact the monomers we studied did not show such a decrease in singlet lifetime for concentrations similar to those used for the dimers. This finding is important for it means that aggregation leads to a new decay channel. This decay channel quenches the excitation energy and must be prevented in systems that utilized the cyclophanes as antennae or reducing or oxidizing agents.

Preliminary data indicate that the positive absorbance at 740 nm, which is seen in butyronitrile, is absent in toluene. The dielectric strength of butyronitrile is 36 while that of toluene is about 2.4. One would expect that the charge stabilization in toluene would be considerably less than that in butyronitrile. First order calculations including only the redox potentials indicate that there is enough free energy in the singlet state to lead to a charge separation. However, when the coulombic terms are included, the transfer is allowed in butyronitrile but not in toluene. Since the radical pair or charge transfer state would be stabilized more in the higher dielectric solvent, the lifetime and the triplet yields should

differ in toluene and butyronitrile because the energy gap with the ground state, the triplet state and the singlet excited state are all different. Experiments to test these ideas are underway.

V. Time and Effect of the Principal Investigator

The principle investigator devoted 33% of his time to the project. He is expected to devote 33% of his time to the project for the remainder of the contract.

VI. Publications Prepared Under This Contract

- 1) Studies of Chlorophyll in Vitro, by K. J. Kaufmann and M. R. Wasielewski, Adv. Chem. Phys., in press.
- 2) Intramolecular Charge Separation and Storage, by R. E. Overfield, M. R. Wasielewski, and K. J. Kaufmann, in preparation.

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Chlorophyll a

Methyl Mesopyrochlorophyll a ($R = CH_3$)

Cyclophane Structures

- a) $M_1 = 2H$ $M_2 = 2H$ c) $M_1 = Mg$ $M_2 = Mg$
 b) $M_1 = Mg$ $M_2 = 2H$

Figure 2: Absorption Spectra of the Three Cyclophanes.

Figure 3: Absorption Spectrum of the Monomers and Monometal Cyclophane.

Figure 4: Fluorescence of the Three Cyclophanes. Band at 605 nm is scattered exciting light.

Figure 5: Emission of the monometal cyclophane, methyl mesopyrochlorophyllide a, methyl mesopheophorbide a, and a 50/50 mixture of the monomers. Band at 605 nm is scattered exciting light.

Figure 6: Fluoresence of the monomers and the monometal cyclophane in acetone. Band at 605 nm is scattered exciting light.

MONO-METAL CYCLOPHANE IN BUTYRONITRILE

Figure 7: Excited state difference spectrum of mono-metal cyclophane taken after 30 psec excitation pulse.

M-PCHL IN BUTYRONITRILE & 20% IODOETHANE

18-DEC-79

Figure 8a: Excited state difference spectrum of methyl mesopyrochlorophyll a
in butyronitrile:ethyliodide (8:2).

M-PPH IN BUTYRONITRILE & 20% IODOETHANE

Figure 8b: Excited state difference spectrum of methyl mesopyropheophorbide a in butyronitrile:ethyl iodide (8:2).

COMBINATION M-PCH. & M-PPH. EXCITED STATES

Figure 9: Computer summation of Figure 8a and 8b.

Figure 10: Low resolution excited difference spectrum of monometal cyclophane in butyronitrile.

M-PCH AND M-PPH IN BUTYRONITRILE (GLASS).

Figure 11: Computer summation of the low resolution spectra of the singlet states of methyl mesochlorophyllide a and methyl mesopyropheophorbide a.

Figure 12: Sum of chlorophyll a cation and pheophytin a anion difference spectra from data of reference 5.