THE UNIVERSITY OF CALGARY

Studies on

Photoinduced Electron Transfer

by

Yueming Zhong

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Studies on Photoinduced Electron Transfer" submitted by Yueming Zhong in partial fulfillment of the requirements for the degree of Master of Science.

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Feb. 24, 1994

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Abstract

A linear triad molecule D-P-A, a porphyrin (P) covalently-attached with a viologen electron acceptor (A) and an N,N-dimethylaniline donor (D), and its model compounds D-P and P-A were synthesized. Electron transfer was studied utilizing UV-vis and fluorescence spectroscopy. Compound D and A both quenched the fluorescence of P via intramolecular electron transfer. The relative fluorescence quenching efficiency by A and D was explained by the Marcus theory. This represents the first study of a triad molecule using both P-A and P-D as reference compounds. Interesting relation was found between the rate constant of fluorescence quenching in D-P-A and those in P-D and P-A. For the first time, the S_2 state of P was shown to be quenched by D and A probably via an ultra-fast electron transfer mechanism.

The concept of using photoinduced electron transfer for the design of a cyclic photomagnetic molecule was also proposed.

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1. INTRODUCTION

1.1 An Overview

Photoinduced electron transfer is the transfer of electrons induced by the absorption of light by one of the reactants in a system. The importance and complexity of electron transfer in nature have led many researchers to look for ways to study the fundamental chemistry of these processes in simplified model systems. A significant part of this effort has been devoted to the study of photoinduced charge separation reactions as a means of capturing and storing solar energy. A long-term goal of this research is to develop an understanding of photoinduced electron transfer reactions that is sufficiently advanced to enable one to design laboratory systems for the conversion of solar energy into chemical potential energy. A vital part of this research is the design and synthesis of complex molecular systems which are comprised of electron donors and acceptors that mimic the charge separation function of photosynthetic proteins.

In this study, the photoinduced electron transfer reaction was utilized for the design of a photomagnetic cyclic molecule which consisted of a light absorber, an electron acceptor and an electron donor. The photomagnetic molecule was designed and the synthesis was attempted, but was unsuccessful. A linear molecule, which had a light absorber, an electron acceptor and an donor covalently linked through ester bonds was synthesized for the study of photoinduced intramolecular electron transfer. The linear molecule can be a good prototype compound for the cyclic molecule and possibly can be modified and cyclized.

1.2 A Brief Introduction to Photoinduced Electron Transfer

The general electron transfer (ET) reaction could be written as:

$$D + A \rightleftharpoons D^{+\cdot} + A^{-\cdot} \qquad (1)$$

where D is the electron donor and A is the electron acceptor. In the electron transfer reaction, D transfers an electron to A and is oxidized, while A is reduced.

If light is involved, the photoinduced electron transfer (PET) reaction could be expressed as:

$$D \xrightarrow{h\nu} D^{*} \qquad (2)$$

$$D^{*} + A \longrightarrow D^{+\cdot} + A^{-\cdot} \qquad (3)$$

or

$$A \xrightarrow{h\nu} A^{*} \qquad (4)$$

$$D + A^{*} \longrightarrow D^{+\cdot} + A^{-\cdot} \qquad (5)$$

where either D^{*} or A^{*} represents an electronically excited state. D, when excited to D^{*}, has an electron occupying a higher-lying lowest unoccupied molecular orbital (LUMO) and this electron can be transferred to the vacuum continuum with less energy than any electron in a ground-state molecular orbital. D^{*} is therefore a better reducing agent than D. Similarly, A^{*} is a stronger oxidizing agent than A because the vacancy that is created by photoexcitation in the ground-state (highest occupied molecular orbital (HOMO) increases the electron affinity of the excited state relative to that of the ground state. The light is simply used to overcome a kinetic barrier and plays the role of a catalyst. This is illustrated in Fig. 1-1[1]. The electron transfer step can proceed either by reductive quenching of the excited state of A by the donor D or by oxidative quenching of the excited state of D by the acceptor A. Most of the PET systems studied are of the latter type.

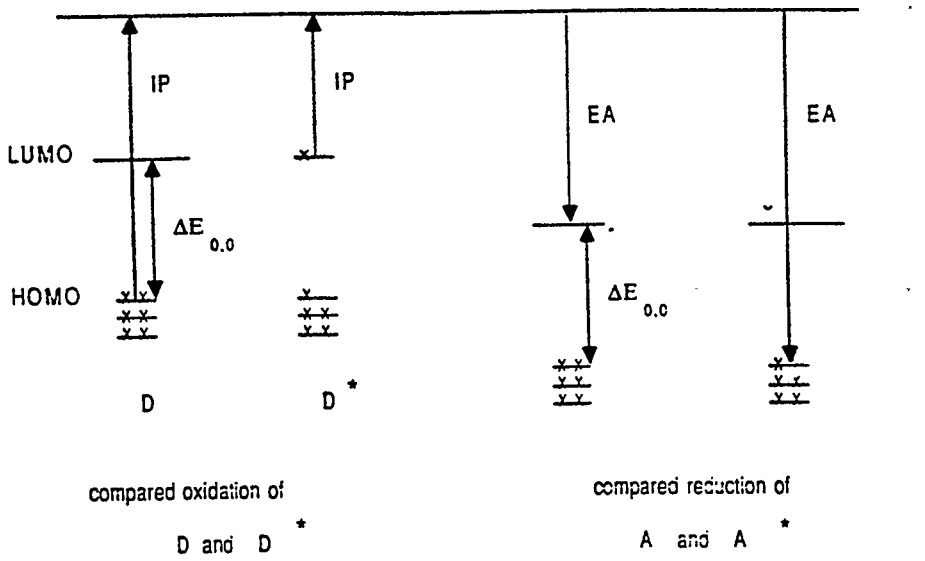


Fig.1-1 Illustration of enhancement of redox properties of excited states.

1.3 A Brief Review of Electron Transfer Reactions

Photoinduced electron transfer systems have been intensively studied in recent years, owing to their potential ability to convert or store solar energy. These systems generally consist of a light absorber (such as a porphyrin or metal bipyridine complex) and an electron acceptor and/or donor. Upon irradiation, the light absorber would absorb light and be excited to the higher energy level of electronically excited states. The resulting electron transfer between the excited light absorber and electron acceptor/donor will result in a transient charge separation radical-ion pair which will temporarily store most of the photon energy absorbed.

Many charge-separation schemes which have been studied involve intermolecular electron transfer. For example, in the study of cleavage of water into hydrogen and oxygen, ruthenium bipyridine complex, $Ru(bpy)_3^{2+}$ is often used as a light absorber and viologen as an electron acceptor.[2-5] It is well known that $Ru(bpy)_3^{2+}$ and its

alkyl-substituted derivatives can absorb ultraviolet or visible light and get excited to the metal-to-ligand charge-transfer (MLCT) state. The long-lived luminescence is due to the emission from the MLCT. The excited species, $Ru(bpy)_3^{2+*}$, is best described as $Ru^{III}(bpy)_2(bpy^{-\cdot})^{2+}$, in which a d-electron from the metal has been moved to a π^*-orbital localized on one of the bipyridines. In its excited state, $Ru(bpy)_3^{2+}$ is both a stronger reducing agent and a stronger oxidizing agent than in its ground state. As such, it is subject to either oxidative or reductive quenching, and in the presence of an electron acceptor or donor, its MLCT emission may be quenched. When an electron acceptor is present, the unpaired electron of $(bpy^{-\cdot})$ is transferred to the acceptor, reducing it. After that, an electron may also be transferred from the electron donor (usually a sacrificer) to the unoccupied metal d-orbital, thereby oxidizing the donor and reducing the $Ru(bpy)_3^{3+}$ to its initial +2 charge state. The MLCT state may also be quenched by accepting an electron from the donor and result in oxidizing the donor and reducing $Ru(bpy)_3^{2+}$ to +1 state. Among these systems, other metal polypyridine complexes often used are $Os(bpy)_3$, or $Re(bpy)_3$.[6] The electron acceptors usually used are various viologens and quinones, the electron donors usually used are N,N-dimethylaniline and N,N-diethylaniline while the sacrificers are ethylenediamine tetraacetic acid disodium salt or EDTA, both of which decompose after donating an electron.

If we use ruthenium complexes as light absorbers, and viologens (V^{2+}) and EDTA as electron acceptors and sacrificer, the process could be described as:

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \qquad (6)$$

$$Ru(bpy)_3^{2+*} + V^{2+} \longrightarrow Ru(bpy)_3^{3+} + V^{+\cdot} \qquad (7)$$

$$Ru(bpy)_3^{3+} + EDTA \longrightarrow Ru(bpy)_3^{2+} + EDTA_{ox} \qquad (8)$$

A back electron transfer reaction could easily occur, in the absence of the sacrificer,

decreasing the quantum yield for the forward electron transfer. This back electron transfer reaction could be described as:

$$Ru(bpy)_3^{3+} + V^{+\cdot} \longrightarrow Ru(bpy)_3^{2+} + V^{2+} \qquad (9)$$

A major goal in solar energy conversion systems involving photochemical electron transfer reactions is the inhibition of the back electron transfer reaction regenerating the ground state reactants. The inhibition of the back electron transfer may then allow other useful competitive chemical reactions to occur, yielding photochemical fuels. Attempts to retard back electron transfer reactions have been made by using suitable microenvironments such as micelles[7,8], vesicles[9,10], microemulsions[11], charged colloids[12] or polyelectrolytes[13-15] in the system. Polymers with pendant light absorbers and electron acceptors have also been synthesized.[16,17] In these combined systems, the relative quantum yield for forward electron transfer was remarkably increased. The effect was attributed to the enhancement of charge separation of the photon produced primary ion pair due to electron injection from the photoreactive site into the electron relay system and the succeeding electron migration.

Efficient electron transfer quenching of photoexcited species may be achieved by the use of a light absorber with a covalently linked electron acceptor or donor. More recently, intramolecular electron transfer systems have received considerable attention. While the majority are made up of a chromophore linked to either an electron acceptor or a donor, there are a few examples of molecular assemblies in which a chromophore is linked to both an electron acceptor and a donor. These systems have been shown to generate relatively long-lived photoinduced charge-separation states which improve the efficiency of electron transfer quenching of photoexcited species, and in the latter case, hinder the back electron transfer.

Simple covalently linked aromatic donor and acceptor systems[18-23] have been employed to study the dependence of electron transfer rates on the free energy change of a reaction, the donor-acceptor distance and orientation, and the solvent. In general, molecules that possess more well defined structural relationships between the donor and acceptor yield more subtle insights into electron transfer reactions.

It is known that natural photosynthesis involves macrocyclic electron donors, such as chlorophylls. Since porphyrins are easy to synthesize and the structure is similar to chlorophylls, a great deal of work has been done with porphyrins to develop supramolecular systems that mimic the stepwise nature of photosynthetic charge separation, where an initial photoinduced charge separation is followed by a sequence of dark electron transfer steps that proceed at rates sufficiently fast to compete with the series of back electron transfer process. The goal is to achieve a long-lived charge separation with a relatively high quantum yield. While this strategy is relatively simple, the fulfillment of these requirements is often difficult.

Many different quinone linked porphyrins and porphyrin metal complexes have been synthesized and studied as model compounds to mimic the process of primary charge separation in natural photosynthesis, where the porphyrin is the light absorber and quinone is the electron acceptor.[24-31] The efficiency of the intramolecular quenching process is clearly higher than that of the intermolecular process and both charge separation and charge recombination are very rapid.

Methyl viologen linked porphyrins and zinc porphyrins have also been made and studied.[32-38] It has been found that the charge recombination process is much slower than the charge separation process. Conversely, in porphyrin-quinone systems the

charge recombination is as fast or even faster than the charge separation. There are also a few studies on covalently linked non-methylated viologen zinc porphyrins where the non-methylated viologens were effective quenchers for the zinc porphyrin singlet excited states.[34]

Covalently linked viologen to ruthenium bipyridine complexes as models of a man-made photoreaction center have also been prepared and studied.[16] The intramolecular electron transfer quenching of ruthenium complexes by closely located viologen units was compared to the intermolecular quenching. It was found that the emission from the ruthenium complex in the photoreaction center was almost completely quenched by the linked viologen units. The synthesis of covalently linked tris(2,2'-bipyridine)-ruthenium(II)/diquaternary-2,2'-bipyridinium salt (diquat) complexes have also been reported.[39] The electron transfer rates have been measured for a series of these linked ruthenium/diquat complexes. The rate of electron transfer from the metal-to-ligand charge transfer (MLCT) states has been analyzed in terms of a simple kinetics model, in which the MLCT excitation hopping is fast, electron transfer to the diquat is rate limiting, and the latter occurs only from MLCT states localized on the bipyridine ligands which are linked to the diquat acceptors. Although in the acceptor attached chromophore systems the efficiency of forward electron transfer reaction is increased, the back electron transfer reaction is uncontrollable.

An electron relay system as supplied by aligned viologen units in micelles, and polymer chains, and polysoap with pendant viologen units, and CTAC micelles incorporating amphipathic viologen, were all used as electron relay systems in combination with the above described man-made photoreaction center. The study found that the charge separation efficiency is increased remarkably due to the electron injection from the

photoreaction center.[16] These electron relay systems were efficient enough to suppress the rapid back electron transfer process in the photoreaction center, which consists of a ruthenium complex and covalently linked viologen units.

In order to control the recombination of the photoproduced oxidant/reductant pair by back electron transfer, a means must be found for directing the oxidative and reductive equivalents in a spatially selective way toward different catalysts. At the molecular level, this requires a directional charge-transfer character to be built into the system.

The photochemically induced separation of oxidative and reductive equivalents has been accomplished in synthetic molecules that contain a light absorber (P) (a light absorber can absorb light and be easily excited to its electronically excited state), electron donors (D) and acceptors (A) held in appropriate spatial arrays. It was reported that a linked dimethylaniline-porphyrin-quinone system containing a fixed rigid bridge and a flexible methylene chain was synthesized.[40] These porphyrin-based systems containing both an electron acceptor and electron donor led to a relatively long lived photoinduced charge separation onto the peripheral donor and acceptor redox sites, where the redox potential is stored. Other triad molecules, such as carotenoid-porphyrin-quinone were also prepared and studied.[41,42] More recently, a carotenoid-porphyrin-bisquinone tetrad and a five-unit system of a carotenoid covalently linked to a bisporphyrin and to a bisquinone were also synthesized and studied to mimic the photosynthesis in bacteria.[43-45]

A MLCT-based chromophore (ruthenium bipyridine complex) system was also reported where the donor and acceptor were chemically attached to the chromophore.[46,47] This system was based on a ruthenium(II)trisbipyridine ($Ru(bpy)_3^{2+}$) moiety, covalently linked to a N,N'-diquaternary-2,2'-bipyridinium salt (diquat) electron acceptor and two

phenothiazine (PTZ) donors. This system was studied with different techniques and it was found that the excitation of the $Ru(bpy)_3^{2+}$ to its MLCT state leads to a long-lived charge separated state which is shown to form by oxidative quenching of the $Ru(bpy)_3^{2+}$ moiety by diquat followed by phenothiazine-to-ruthenium electron transfer. The results were compared to those obtained in the analogous $Ru(bpy)_3^{2+}$-acceptor complexes. In such molecular arrays, optical excitation, quenching, and subsequent electron transfer provide the basis for converting the incident photon energy into transiently stored, spatially separated oxidative (D^+) and reductive (A^-) redox equivalents. The light-induced redox splitting is directional at the molecular level because of the existence of an intramolecular free-energy gradient which arises from the difference in redox potentials between the excited couples and the quenched couples.

$$D\text{-}P\text{-}A \xrightarrow{h\upsilon} D\text{-}{}^*P\text{-}A \longrightarrow D^+\text{-}P\text{-}A^-$$

For the above systems, a long-lived charge-separated state was observed, the path was studied, and it was found that the initial electron transfer step was from the chromophore to the electron acceptor. Donor to chromophore electron transfer occurs only following oxidative quenching. In the case of an intramolecular assembly containing an electron acceptor and an electron donor, sequential charge transfer reactions occur resulting in a charge-separated state in which the donor is oxidized, the acceptor is reduced , and the chromophore returns to its initial ground state.

Significant progress in the development of supramolecular systems for photoinduced charge separation and storage continues to be made. As this work progresses, more and more workers come to realize that structural control is a necessary criterion for developing systems that will yield answers to questions concerning the mechanism of electron transfer. The ability to incorporate the broadly based set of ideas required in

making these molecules will be an impressive demonstration of the growing "high technology" capabilities, even if they have no economic value. The long-term goal to mimic the ability of green plants and other photosynthetic organisms in their use of sunlight to make high-energy chemicals, will someday be reached.

1.4 Objectives

The original objective of this research was to design and synthesize a photomagnetic cyclic molecule which consists of a light absorber, an electron acceptor and an electron donor. Although photoinduced electron transfer systems have been studied by many people, no report was found of the design of photomagnetic molecules.

A photomagnetic molecule could be described as a molecule that absorbs light, which induces a circulating electric current and ultimately generates a magnetic field. If the process involves the photoinduced electron transfer, the process could be as follows:

Light ⟶ Closed Circuit Electron Transfer ⟶ Magnetic Field

Photomagnetic effects in semiconductors induced by local illumination were reported by Sablikov and Sandomirskii.[48] It was shown that closed electric currents and magnetic fields can be generated in an inhomogeneous semiconductor upon local exposure to light in the region of intrinsic absorption or in a homogeneous semiconductor in the presence of an external magnetic field.

The main idea in our design is to utilize the photoinduced electron transfer reaction in a cyclic molecule with a light absorber (P), an electron acceptor (A) and an electron donor (D). In such a molecule, upon absorption of the light, the light absorber will be excited

to a higher energy excited state. The electron acceptor then accepts an electron from the excited light absorber. Next, the electron donor transfers an electron to the oxidized light absorber to return it to the original ground state. Finally an electron transfers from the reduced electron acceptor to the oxidized electron donor. In such a way, a cyclic electron transfer reaction may occur. In other words, a closed circuit current is generated in the cyclic molecule, and thus a magnetic field may be generated. The process may be described as is shown in Fig. 1-2 and Fig 1-3.

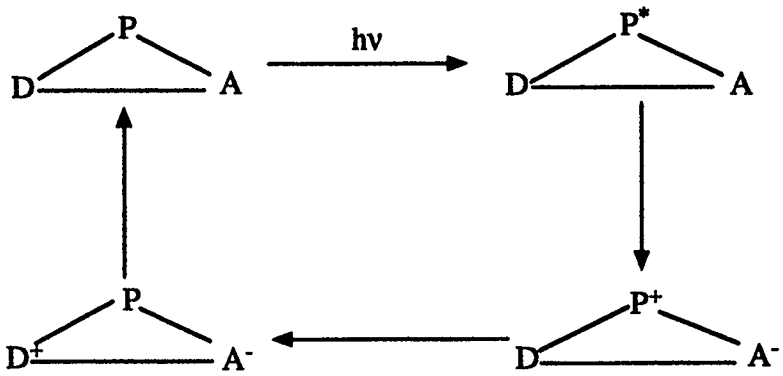


Fig. 1-2

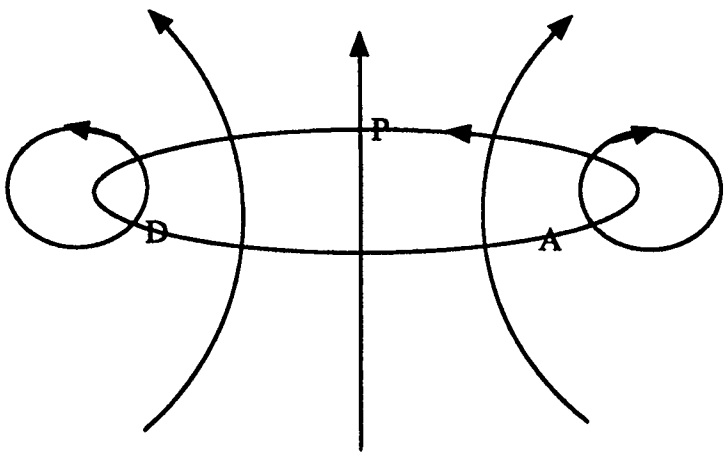


Fig. 1-3

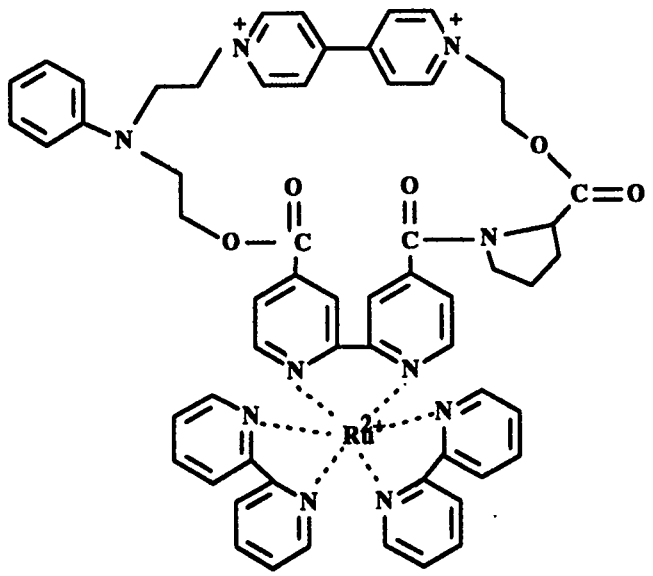
In this case, the optical energy could be transferred into magnetic field energy. This may provide a signal conversion material which converts optical signals to magnetic signals similar to the photoelectric materials.

The magnitude of the magnetic field of a single loop, B, is inversely proportional to the radius of the circular loop, a.

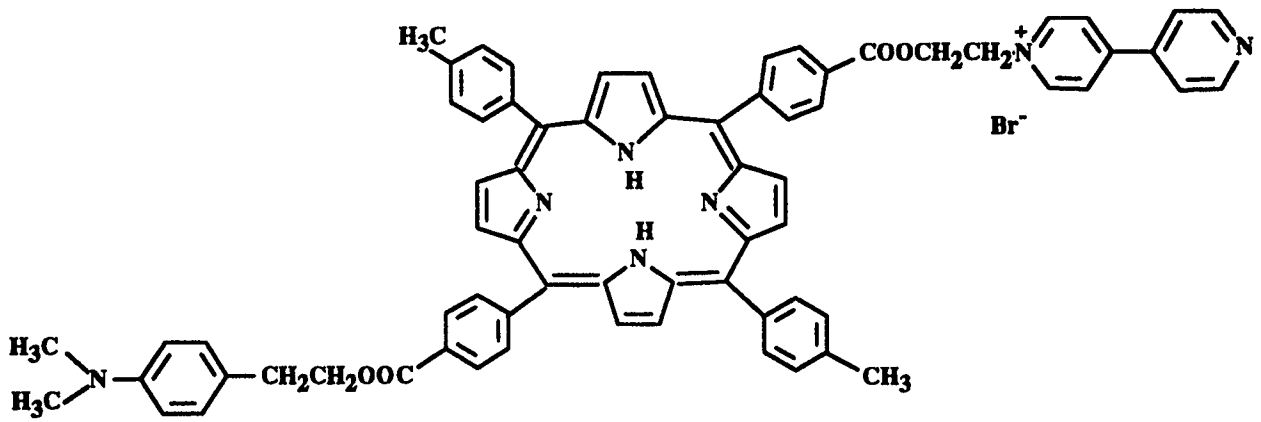
$$B = \mu_o \frac{I}{a}$$

where I is the current and $\mu_o = 4\pi \times 10^{-7}$ Tm/A. Since the radius of a cyclic molecule is so small (in the magnitude of 10^{-10} m), the magnetic field generated by electron transfer may be very large. If this kind of cyclic molecule could be aligned, it may result in a high magnetic field material.

Since the ruthenium bipyridine complex is a good chromophore (it absorbs visible light and has a very high extinction coefficient), we chose the $Ru(bpy)_3^{2+}$ as the light absorber, while the proline is used as a spacer between the light absorber and the electron acceptor. We decided to use viologen as the electron acceptor and N,N-diethylaniline as the electron donor. These components were designed to be linked via ester bonds as:



The attempted synthesis of the above cyclic molecule was not successful. As the time allowed for the research was limited, the objective was switched to the synthesis of a linear molecule, which consists of a light absorber, an electron acceptor and an electron donor, instead of a cyclic one. Such a molecule would be a good reference compound for the cyclic molecule and the study of photoinduced electron transfer in it provide a clue as to how electrons flow when it is converted to a cyclic molecule. At this stage, the porphyrin was used as the light absorber since the ruthenium complex is very hard to purify due to the +2 charge on it. Viologen was used as the electron acceptor, but N,N-dimethylaniline was used as the electron donor instead of N,N-diethylaniline in order to get a better ester linkage. The target linear molecule should have the structure as follows:



The porphyrin, porphyrin-viologen and porphyrin-dimethylaniline fragments of this structure were synthesized to compare the electron transfer behavior to the donor-porphyrin-acceptor.

Although some references have been found on the synthesis and study of a linear molecular array consisting of a light absorber, an electron acceptor, and an electron

donor, no report of the above structure has been found. Upon completion of the synthesis of this target molecule and the study of the electron transfer reaction, the structure of the linear molecule could be modified and cyclized, in order to achieve the original objective.

2. MOLECULAR DESIGN

2.1 Theories on Photoinduced Electron Transfer

2.1.1 Thermodynamics

The feasibility of a photoinduced electron transfer between a donor and an acceptor molecule is dictated by the overall change in the free energy, ΔG, which accompanies the reaction.[1-3] If ΔG of the reaction is smaller than zero, the reaction will be exergonic and spotaneous. However, the back electron transfer reaction

$$D^{+\cdot} + A^{-\cdot} \longrightarrow D + A \qquad (1)$$

is also exergonic and hence spontaneous. This is illustrated in Fig. 2-1.

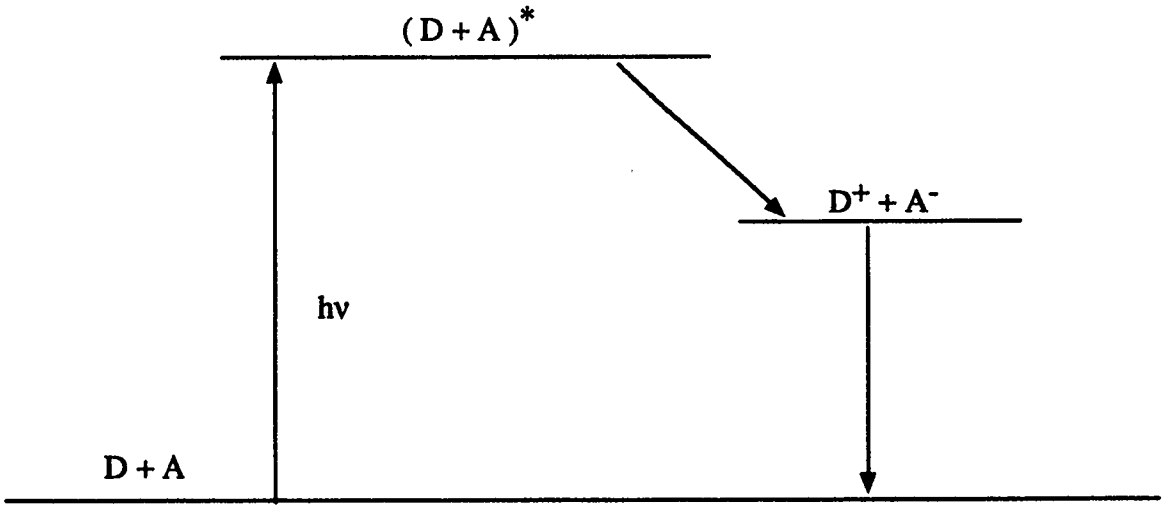


Fig. 2-1

The well known "Weller equation"[4] (2) is used to calculate the free energy change of a photoinduced electron transfer reaction when the energy difference, E^*, between the excited state and ground state of a reactant and the redox potentials of both reactants are known:

$$\Delta G\,(eV) = [\,(E^0_{D+/D} - E^o_{A/A-}) - e^2/(\epsilon d)\,] - E^* \qquad (2)$$

where $E^0_{D+/D}$ and $E^0_{A/A-}$ are the reduction potential of D and A.

This relation takes into account the free enthalpy $e^2/\epsilon d$ gained by bridging the two formed radical ions to an encounter distance d in a solvent of dielectric constant ϵ. This equation may not be valid if there are significant structural changes accompanying the electron transfer since it supposes that the geometry of the excited state does not differ from the ground state and the entropy changes are negligible.

If the solvent separated ion pair dissociates into free ions or if the solvent has a large dielectric constant, the coulombic energy term can be neglected. In acetonitrile, it is less than 0.06 eV at a separation distance exceeding 7 Å. The equation then simplifies to:

$$\Delta G\,(eV) = (E^0_{D+/D} - E^o_{A/A-}) - E^* \qquad (3)$$

It is often easier to use equation (3) to calculate the net free energy change corresponding to a photoinduced electron transfer, regardless of the pathways involved.

2.1.2 Kinetics

It is well known that not all thermodynamically favored reactions occur. A second important requirement is the kinetic criterion.

2.1.2.1 The Weller Equation

For photoinduced electron transfer, Rehm and Weller performed a series of fluorescence quenching experiments with several excited donor-acceptor couples varying in ΔG between -60 and 6 kcal/mol.[4] Fitting the experimental data yielded the following relation between the rate constant of electron transfer k_{ET} and ΔG for the reactions.

$$k_{ET} = \frac{20 \times 10^9}{1 + 0.25\,[\exp(\Delta G^{\neq}/RT) + \exp(\Delta G / RT)} \qquad (4)$$

where $\Delta G^{\neq}$ is the activation energy of the actural electron transfer. The relation is shown in Fig. 2-2.

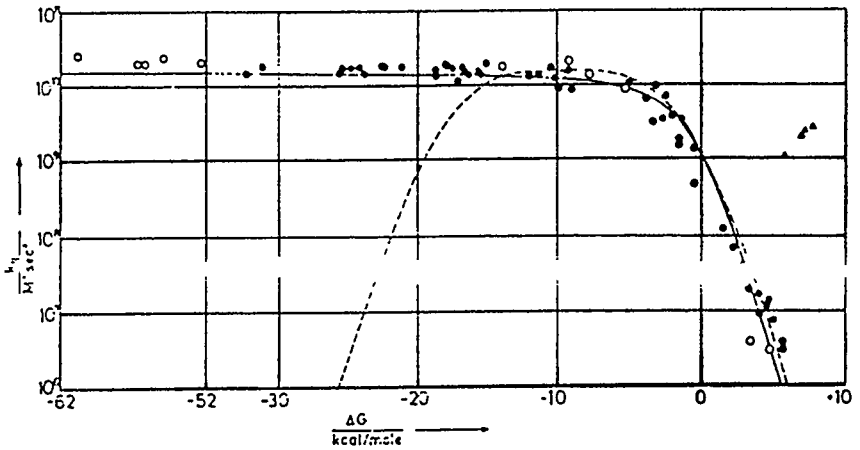


Fig.2-2 Fluorescence quenching rate constant k_q as a function of the free energy of the outer sphere electron-transfer process.[4]

The authors assumed that agreement between calculated and experimental photoinduced electron-transfer rate constants within a factor of two could be taken as evidence in favor of an outersphere, photoinduced, adiabatic, electron transfer through an encounter complex.

$$D^* + A \longrightarrow (D^{+\cdot} \ldots A^{-\cdot})$$

$$D^* + A \longrightarrow \underset{\text{encounter complex}}{D^* \ldots A} \longrightarrow \underset{\text{solvated ion pair}}{D^{+\cdot} + A^{-\cdot}} \xrightarrow{\text{decay}}$$

For the reaction, $D^* \ldots A \longrightarrow D^{+\cdot} + A^{-\cdot}$, if ΔG is between -60 and +5 kcal/mol, then $\Delta G^{\neq}$ can be expressed as:

$$\Delta G^{\neq} = \Delta G/2 + [\,(\Delta G/2)^2 + (\Delta G_0^{\neq})^2\,]^{1/2} \qquad (5)$$

Where $\Delta G_0^{\neq}$ is the activation enthalpy of the actural electron transfer when $\Delta G = 0$. In this correlation, for $\Delta G < -10$ kcal/mol, k_{ET} reaches the diffusion-controlled limit of about 2×10^{10} $M^{-1}s^{-1}$; at $\Delta G = 0$, k_{ET} is about 10^9 $M^{-1}s^{-1}$ and decreases sharply for positive ΔG values. The limiting slope when $\Delta G \geq 5$ kcal/mole is -1/2.303 RT.

A plot of k_{ET} versus the driving force of the reaction to check correspondence with the Rehm-Weller prediction has become a classical method to demonstrate that a reaction is actually a photoredox one. The rate constant k_{ET} is often called the quenching constant since it is the rate constant of the quenching of the photoexcited state. Usually it is obtained experimentally.

2.1.2.2 Marcus approach

Marcus[5-9] and Sutin[10-11] have developed a theoretical model to show the relation between the rate-constant k_{ET} for a ground state outer sphere electron transfer and the free energy change ΔG of the reaction. Fig. 2-3 illustrates this correlation.

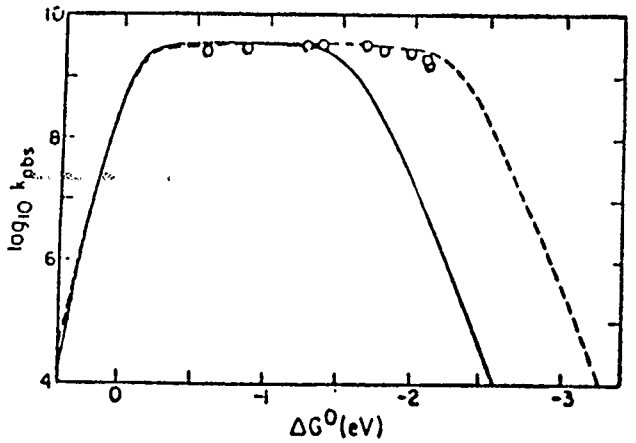


Fig. 2-3 Calculated (curves) and experimental rates (circles) of electron transfer quenching by ruthenium (II) bipyridyl vs. ΔG^{o}.[12]

Using absolute reaction rate theory as a point of departure, Marcus gives the rate constant, k_{ET}, of electron transfer in terms of a free energy of activation ΔG^* for the reaction.

$$k_{ET} = \kappa(r) Z \exp(-\Delta G^*/RT) \qquad (6)$$

where $\kappa(r)$ is the probability for the electron transfer to occur normalized to the number of times the molecule acquires the correct nuclear configuration to pass through the intersection of the potential energy surfaces of the reactants and products, r is the center-to-center distance between electron donor and acceptor, and Z is either the collision frequency in a bimolecular reaction or the vibrational frequency in a monomolecular (intramolecular) reaction. At large values of r, the value of κ is assumed to depend exponentially on r. When the molecular vibrations of the donor and acceptor required for the molecules to reach the transition state are assumed to be harmonic oscillators, the free energy of activation takes on the well-known quadratic dependence on the ΔG^o of the reaction:

$$\Delta G^* = (\lambda + \Delta G^o)^2 / 4\lambda \qquad (7)$$

where λ is the total energy of nuclear reorganization required for the system to reach the intersection. This is usually divided into contributions from oscillators within the molecules, λ_i, and solvent oscillators, λ_s, $\lambda=\lambda_i+\lambda_s$. The value of λ_i may be calculated from the force constants for all the molecular vibrations in both reactant and product, while λ_s can be determined by application of the dielectric continuum model of a solvent. In the simplest case, this model assumes that the donor and acceptor are spherical with radii a_1 and a_2, lying a center-to-center distance r apart. If ϵ_{op} and ϵ_s are the optical and static dielectric constants of the medium, respectively, then

$$\lambda_s = (\Delta e)^2 (1/2a_1 + 1/2a_2 - 1/r)(1/\epsilon_{op} - \epsilon_s) \qquad (8)$$

It is easy to see from the equation that the influence of the solvent on the rate of the electron transfer will depend strongly on the distance between the donor and acceptor in the intermediate distance regime.

According to Marcus, k_{ET} would increase up to a maximum and then decrease with increasing $-\Delta G$ values (inverted region). There has been much work to determine if it was possible to have such an inversion of rate. Recent studies have established that in solution, rates of photoinduced electron transfer do decrease for covalently-bonded donor-acceptor molecules as predicted by the Marcus model for highly exergonic reactions.

Experimental demonstration of these retardations is difficult for reactions between donor-acceptor pairs not covalently linked.[13-18] For intermolecular donor-acceptor interactions in the highly exergonic regime, side reactions may take place. These include (i) the production of vibrationally excited products[19] and (ii) the onset of exciplex formation as the dominating mechanism of fluorescence quenching.[20-21]

The rate constant of intramolecular photoinduced electron transfer for porphyrin-quinone donor-acceptor diad molecules were found to show the appearance of the inverted region for the highly exergonic charge separation and radical ion pair recombination reactions.[22-23] The same observation was done in a series of chlorophyll-quinone molecules[24] and phenothiazine-$Ru(bpy)_3^{2+}$-diquat molecules[25].

2.1.2.3 Levich's Approach[26]

Levich's semi-classical approach led to the expression for rate constants for the non-adiabatic regime. The expression is:

$$k_{ET} = \frac{J^2}{h} \left[\frac{1}{4\pi kT\lambda}\right]^2 \exp\left\{-\left[\frac{e^2}{\epsilon_s R} + \frac{1}{4\lambda}(\Delta G^o + \lambda)^2\right] / (kT)\right\} \qquad (9)$$

where k is the Boltzmann constant and h is the Plank constant.

The k_{et} can be separated into two parts: one part being characterized by the activation energy $\frac{e^2}{\epsilon_s R} + \frac{1}{4\lambda}(\Delta F^o + \lambda)^2$, the other part being the electron transmission coefficient characterized by the term J^2. The value of J is defined as:

$$J = (H_{12} - S_{12}H_{12})(1 - S_{12}^2) \qquad (10)$$

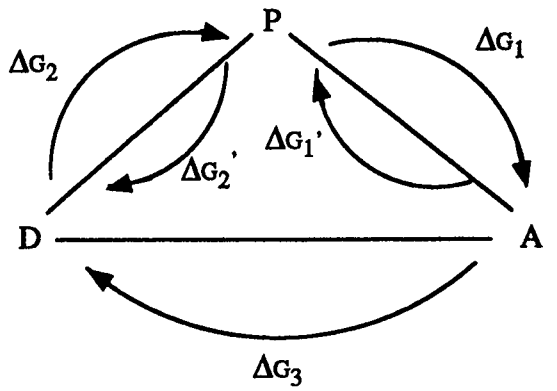
In the above equation, the initial and final states of the system (corresponding to ψ_{DA} and ψ_{D+A-}) are denoted by subscripts 1 and 2; $H_{12} = \langle\psi_1|H'|\psi_2\rangle$; $H_{11} = \langle\psi_1|H'|\psi_1\rangle$, where H' is the electronic Hamiltonian of the system, and $S_{12} = \langle\psi_1|\psi_2\rangle$.

The magnitude of J decreases with increasing separation between D and A. If the direct space overlap of the orbitals of D and A is the main contribution to the magnitude of J, then J decreases exponentially with respect to the distance of r.

2.2 Calculations

2.2.1 The Cyclic Molecule

We want to design a cyclic molecule which consists of a light absorber, an electron acceptor and an electron donor which may be expressed as:



where P is the light absorber,

D is the electron donor, and

A is the electron acceptor.

ΔG_1 is the free energy change of the electron transfer from P^* to A,

ΔG_2 is the free energy change of the electron transfer from D to P^+,

ΔG_3 is the free energy change of the electron transfer from A^- to D^+,

ΔG_1' is the free energy change of the reverse electron transfer from A^- to P^+, and

ΔG_2' is the free energy change of the electron transfer from D to P^*.

If we expect this cyclic molecule to exhibit a photoinduced electron transfer and possess photomagnetic property, a closed circuit electron transfer must occur. First, the light absorber absorbs the light and get excited to its electronic excited state. It then transfers one electron to the electron acceptor, while the electron donor transfers an electron to the oxidized light absorber. Finally the electron acceptor transfers an electron to the donor to finish the electron transfer circle. The process could be illustrated as in Fig. 2-4.

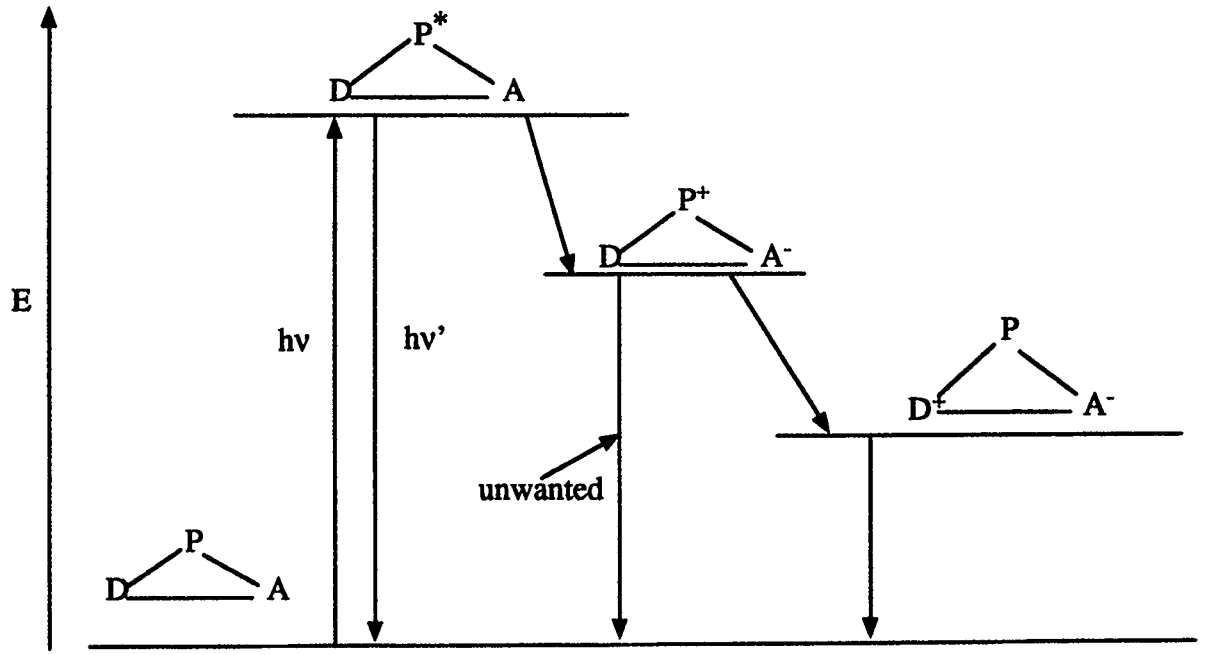


Fig. 2-4

From Fig. 2-4, the competition reaction for the electron transfer from P^* to A is the emission of fluorescence and internal conversion and intersystem crossing. The back electron transfer from A^- to P^+ is an unwanted step.

The electron transfer reaction involved should be:

$$P \xrightarrow{h\upsilon} P^*$$

$$P^* + A \longrightarrow P^+ + A^- \qquad \Delta G_1$$

$$D + P^+ \longrightarrow D^+ + P \qquad \Delta G_2$$

$$D^+ + A^- \longrightarrow D + A \qquad \Delta G_3$$

To make this desired direction of electron transfer reaction occur, the criteria of thermodynamic spontaneity must be satisfied, that is the free energy change ΔG of all these reactions should be negative. With this criterion, we can select the components of

the target molecule which satisfy the following conditions.

(1) To ensure that electrons mainly transfer from P^* to A instead of from D to P^*, we must have $\Delta G_1 < \Delta G_2'$, which means, using equation (3)

$$E_{P+/P} - E_{A/A-} - E^* < E_{D+/D} - E_{P/P-} - E^*$$

$$\therefore E_{P+/P} - E_{A/A-} < E_{D+/D} - E_{P/P-}$$

this could be satisfied by careful selection of P and A.

(2) To ensure that $D + P^+ \longrightarrow D^+ + P$ prevails over $A^- + P^+ \longrightarrow A + P$

$$E_{A/A-} - E_{P+/P} > E_{D+/D} - E_{P+/P}$$

or

$$E_{A/A\_} > E_{D+/D}$$

(3) To ensure the occurrence of

$$D^+ + A^- \longrightarrow D + A$$

$$E_{A/A-} - E_{D+/D} < 0, \quad \text{or} \quad E_{A/A-} < E_{D+/D}$$

Here condition (2) contradicts condition (3). The above conditions are all thermodynamic considerations. According to Levich's theory, the rate of electron transfer is distance dependent. If we can select the proper components and adjust the distances between P and A or D and P to make the rate of electron transfer from A^- to P^+ slower than that from D to P^+, then condition (3) can be relaxed.

The widely used tris(bipyridine) ruthenium complex was selected as the light absorber, viologen and N,N-diethylaniline as the electron acceptor and the electron donor. The

reductive potentials of these components are as follows:

$E_{P+/P} = 1.29$ V, $E_{P/P-} = -1.35$ V, $E^* = 2.12$ V[27]

$E_{A/A-} = -0.45$ V[28]

$E_{D+/D} = 0.76$ V[29]

$\Delta G_1 = 23.06\,[(E_{P+/P} - E_{A/A-}) - E^*] = 23.06\,(1.29 + 0.45 - 2.12) = -8.76$ kcal/mol

$\Delta G_2 = 23.06\,(E_{D+/D} - E_{P+/P}) = 23.06\,(0.76 - 1.29) = -12.22$ kcal/mol

$\Delta G_3 = 23.06\,(E_{A/A-} - E_{D+/D}) = 23.06\,(-0.45 - 0.76) = -27.90$ kcal/mol

We should also consider that the back electron transfer of

$$P^+ + A^- \longrightarrow P + A \qquad \Delta G_1'$$

and the electron transfer from the excited light absorber to the electron donor,

$$P^* + D \longrightarrow P^- + D^+ \qquad \Delta G_2'$$

will compete with the electron transfer reaction from the light absorber to the electron acceptor. The free energy change of these two competing reaction is:

$\Delta G_1' = 23.06\,(E_{A/A-} - E_{P+/P}) = 23.06\,(-0.45 - 1.29) = -40.12$ kcal/mol

$\Delta G_2' = 23.06\,[(E_{D+/D} - E_{P/P-}) - E^*] = 23.06\,(0.76 + 1.35 - 2.12) = -0.23$ kcal/mol

From the calculation, we have ΔG_1, ΔG_2 and $\Delta G_3 < 0$, but $\Delta G_1'$ also < 0 and $\Delta G_1' < \Delta G_1$. We know that ΔG_2, ΔG_3 and $\Delta G_1'$ are less than -10 kcal/mol and according to Weller's approach, these reaction rates are diffusion controlled at the limit at above 2×10^{10} $M^{-1}s^{-1}$. It is important to control the back electron transfer from A^- to P^+. Since the rate of electron transfer is distance dependent, we would like to use a rigid linkage of proline to connect the $Ru(bpy)_3^{2+}$ and the viologen to make the distance between P and A long. This will retard the back electron transfer reaction.

2.2.2 The Linear Molecule

A linear molecule, which consisted of a light absorber, an electron acceptor and an electron donor, was also designed and the free energy change of the electron transfer reactions calculated. There are two paths to reach the final charge-separation state as illustrated in Fig. 2-5. In the first path P^* is quenched by the acceptor and undergoes an oxidative quenching. In the second path, the excited light absorber is quenched by the donor and undergoes a reductive quenching. This kind of linear molecule can be studied to find the mechanism of electron transfer and to see which way it really occurs. The information obtained is useful for the design and understanding of the electron transfer mechanism in the future study of photomagnetic molecules .

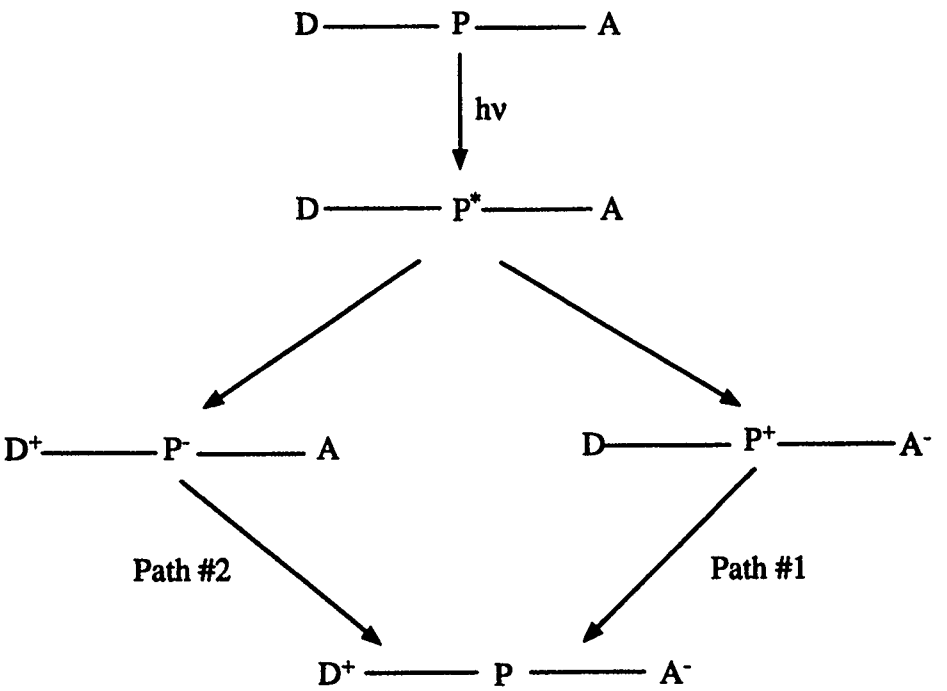


Fig. 2-5

The choices which we made for the components for this triad molecules were:

P = porphyrin,

A = viologen, and

D = N,N-dimethylaniline

Here porphyrin was chosen instead of $Ru(bpy)_3^{2+}$ because it is widely used and the purification is easier than the charged ruthenium complex. Non-methylated viologen is used as electron acceptor, since its structure is very close to the dialkylated viologen. N,N-Dimethylaniline is similar to diethylaniline. The reduction potential (in acetonitrile) of each component is as follows:

$E_{P+/P} = 1.06$ V, $E_{P/P-} = -1.06$ V, $E^* = 2.05$ V[30-31]

$E_{D+/D} = 0.81$ V[29]

$E_{A/A-} = -0.96$ V[32]

In the first path, the free energy change of the electron transfer from P^* to A, is:

$$\Delta G_1 = 23.06\,[(E_{P+/P} - E_{A/A+}) - E^*] = 23.06\,(1.06 + 0.96 - 2.05) = -0.69 \text{ kcal/mol}$$

The free energy change of electron transfer from D to P^+, is:

$$\Delta G_2 = 23.06\,(E_{D+/D} - E_{P+/P}) = 23.06\,(0.81 - 1.06) = -5.77 \text{ kcal/mol}$$

The free energy change of back electron trasnfer from A^- to P^+, is:

$$\Delta G_1' = 23.06\,(E_{A/A-} - E_{P+/P}) = 23.06\,(-0.96 - 1.06) = -46.58 \text{ kcal/mol}$$

In the second path, the electron transfer from P^* to D , is:

$$\Delta G_3 = 23.06\,[(E_{D+/D} - E_{P/P-}) - E^*] = 23.06\,(0.81 + 1.06 - 2.05) = -4.15 \text{ kcal/mol}$$

The free energy change of electron transfer from P^- to A, is:

$$\Delta G_4 = 23.06 \, (E_{P/P^-} - E_{A/A^-}) = 23.06 \, (-1.06 + 0.96) = -2.31 \text{ kcal/mol}$$

The free energy change of the back electron transfer from P^- to D^+, is:

$$\Delta G_3' = 23.06 \, (E_{P/P^-} - E_{D^+/D}) = 23.06 \, (- 1.06 - 0.81) = -43.12 \text{ kcal/mol}$$

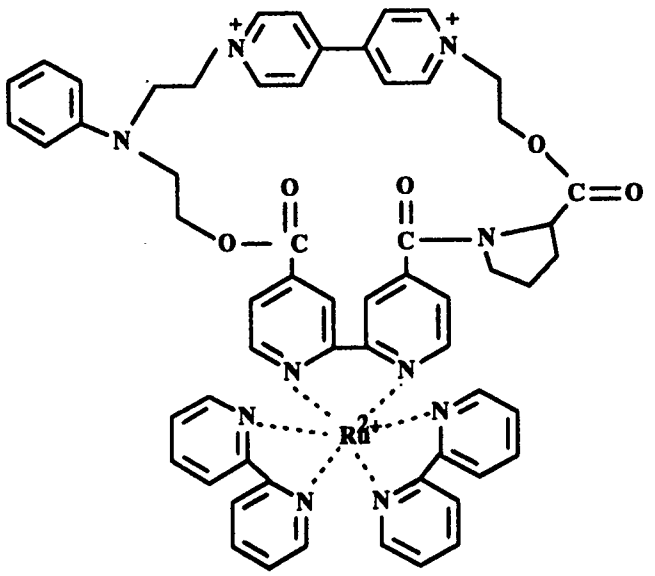
From the above calculation (based on acetonitrile as solvent), all ΔG's in the possible electron transfer reactions are negative and the reactions are thermodynamically spontaneous. Since $\Delta G_3 < \Delta G_1$, the second path should be favoured. We should determine the electron transfer path through experiments.

3. SYNTHESIS

3.1 Results and Discussion

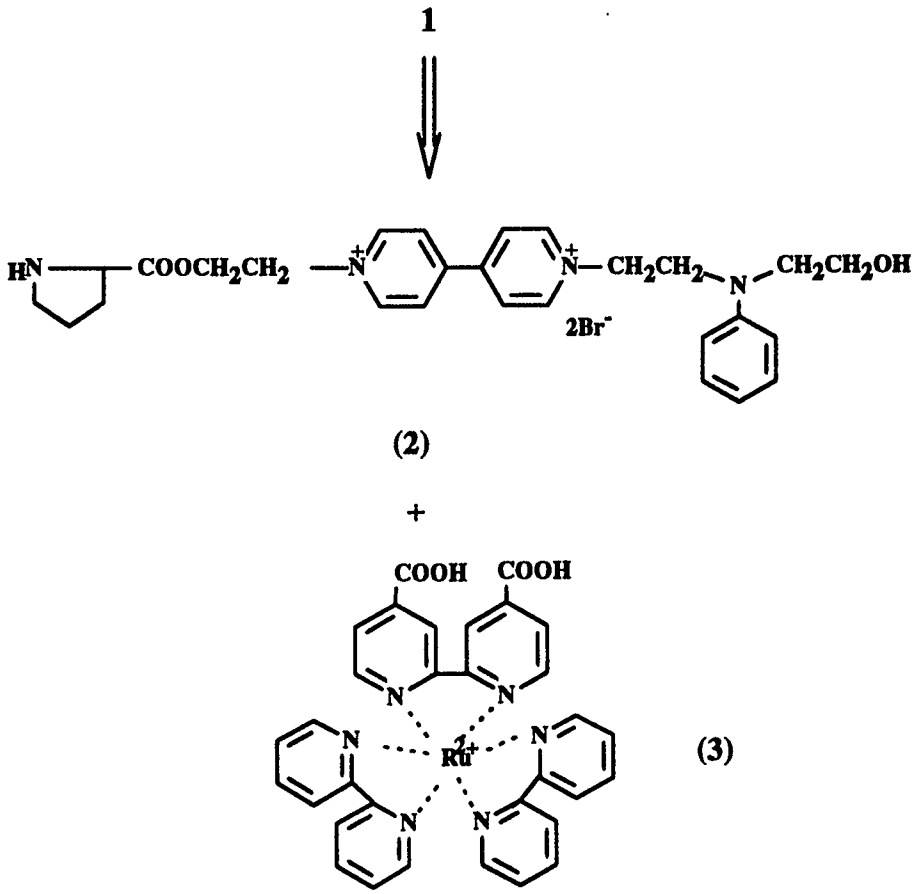
3.1.1 Attempt at Synthesis of the Cyclic Molecule

As discussed in chapter 2, a photomagnetic molecule should contain at least three parts, a light absorber, an electron acceptor and an electron donor. Supramolecule (1) meets the requirement, in which the ruthenium tripyridyl complex served as the light absorber, the viologen as the electron acceptor and the N,N-diethylaniline as the electron donor. In this molecule, the proline moiety is a spacer which adjusts the distance between the light absorber and the electron acceptor. The compound could, in principle, be made by the coupling reaction of viologen (2) and dicarboxylic acid (3), using high dilution techniques, as shown in Scheme 1.



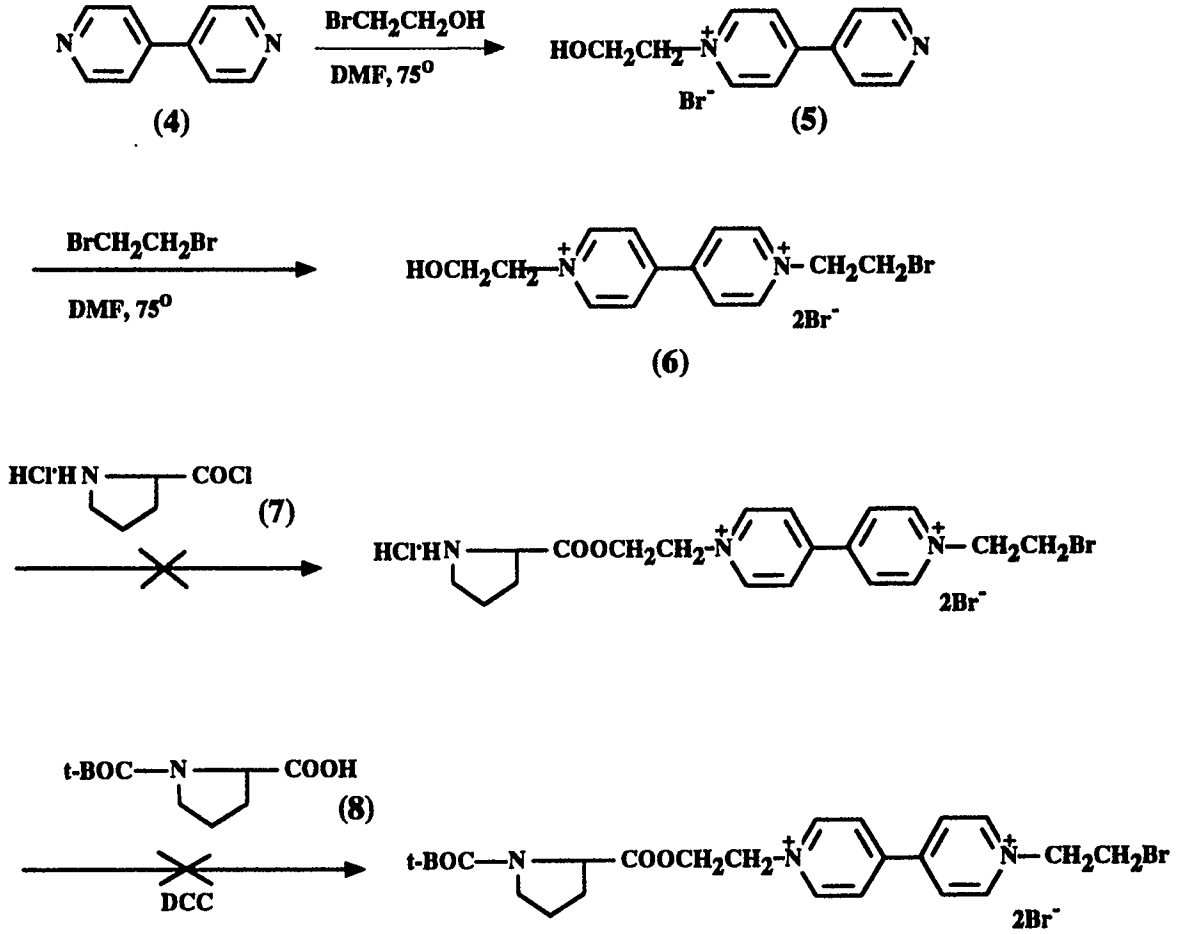
(1)

Scheme 1



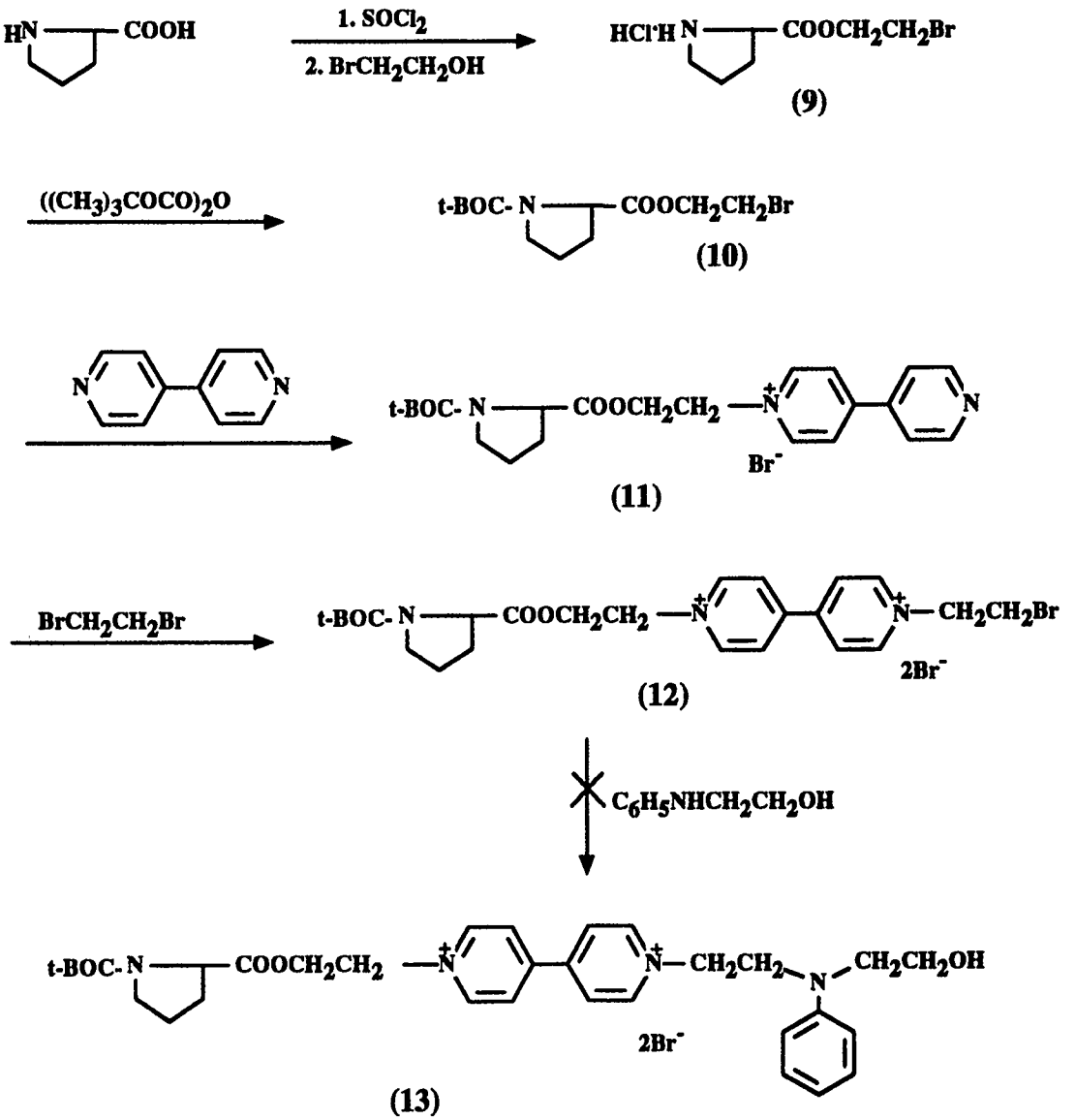
One possible approach to the synthesis of precursor **2** is shown in Scheme 2. The reaction of 4,4'-dipyridyl (**4**) and 2-bromoethanol yielded **5**, which was then treated with 1,2-dibromoethane to give the dication derivative (**6**).[1] However, attempts at the esterification of L-proline and **6** were unsuccessful. The reaction of acid chloride (**7**) with **6** did not give the desired ester, nor did the coupling reaction of acid (**8**) with **6** in the presence of dicyclohexylcarbodiimide (DCC).

Scheme 2.

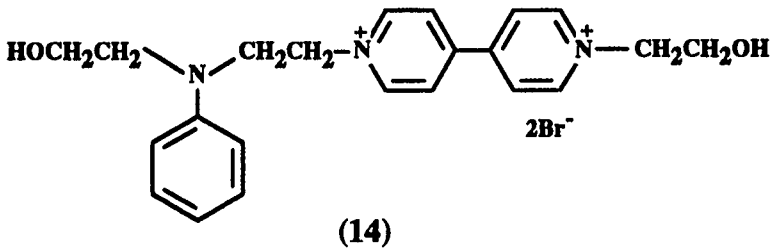


Scheme 3 shows another synthetic approach to **2**. L-Proline was first converted into the acid chloride, which was treated with 2-bromoethanol to afford compound (**9**). The free amino group in **9** was protected by reaction with di-*tert*-butyl dicarbonate to give compound (**10**).[2] Reacting 4,4'-dipyridyl (**4**) with one equivalent of 1,2-dibromoethane yielded 1-(2-bromoethyl)-4-(4'-pyridyl)pyridinium bromide, which did not react with **10** to give compound (**12**). In alternative, treatment of **10** with **4** followed by 1,2-dibromoethane then gave the dication derivative **12**. Unfortunately, attempted amination of **12** with N-(2-hydroxyethyl)aniline was unsuccessful, because a ground state electron donor-acceptor complex was formed instead of the desired product.

Scheme 3.



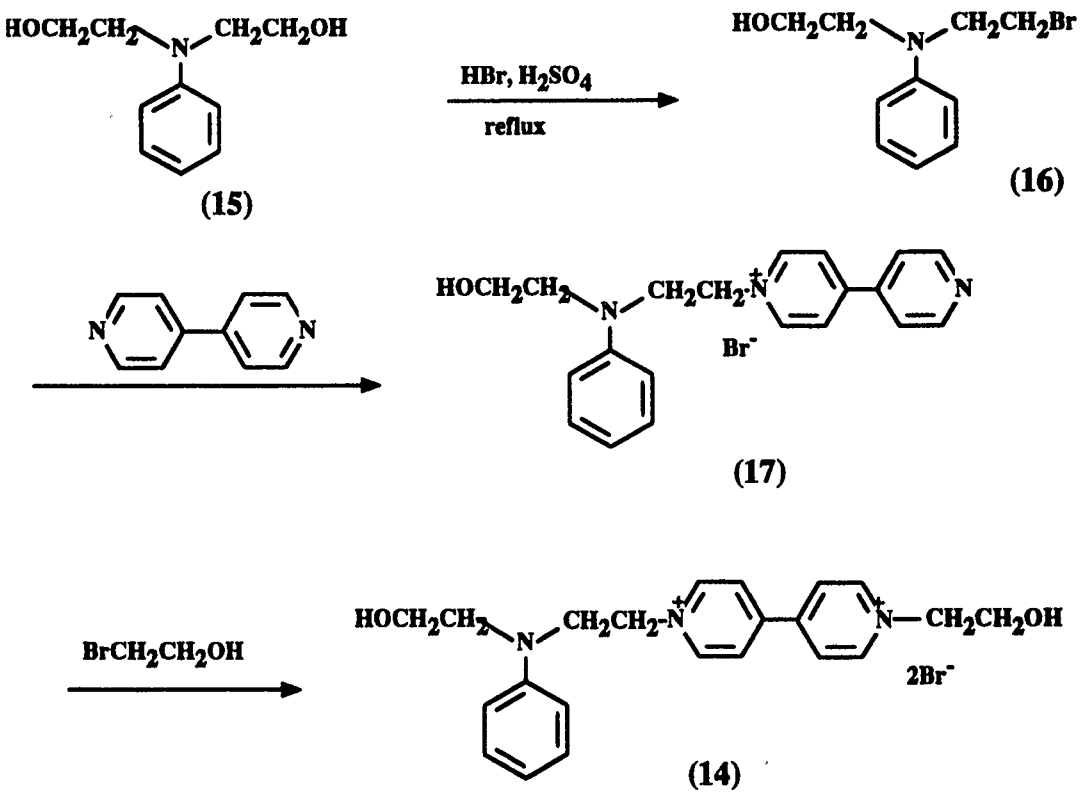
At this stage, it became evident that precursor **2** would be difficult to obtain. Although the proline moiety in **2** is theoretically important as mentioned in last chapter, my attention had to turn to the preparation of **14** as an alternative precursor for its synthetic feasibility.



(14)

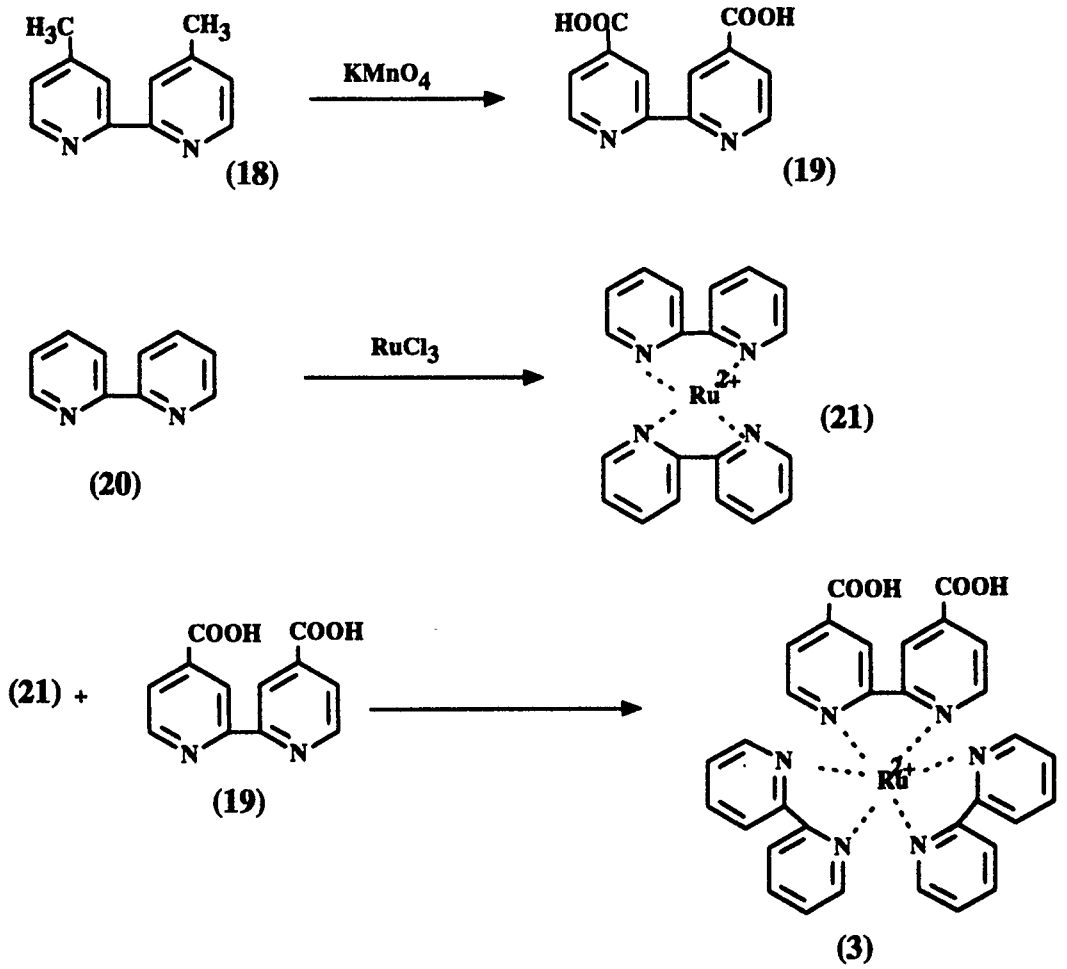
An approach to obtain **14** is shown in Scheme 4. Monobromination of N,N-bis-(2-hydroxyethyl)aniline was achieved by treatment with 48% hydrobromic acid in the presence of a catalytic amount of concentrated sulfuric acid.[3] The resulting N-(2-bromoethyl)-N-(2-hydroxyethyl) aniline (**16**) was then reacted with **4** to give **17** followed by 2-bromoethanol to afford **14.**

Scheme 4.



The other precursor **3** was synthesized according to a literature procedure[4] as shown in Scheme 5. 4,4'-Dicarboxy-2,2'-dipyridine (**19**) was obtained by oxidation of 4,4'-dimethyl-2,2'-dipyridine with potassium permanganate. Reaction of ruthenium trichloride with 2,2-dipyridine (**20**) formed *cis*-dichlorobis(bipyridine) ruthenium (**21**), which reacted with **19** to afford **3**.

Scheme 5.



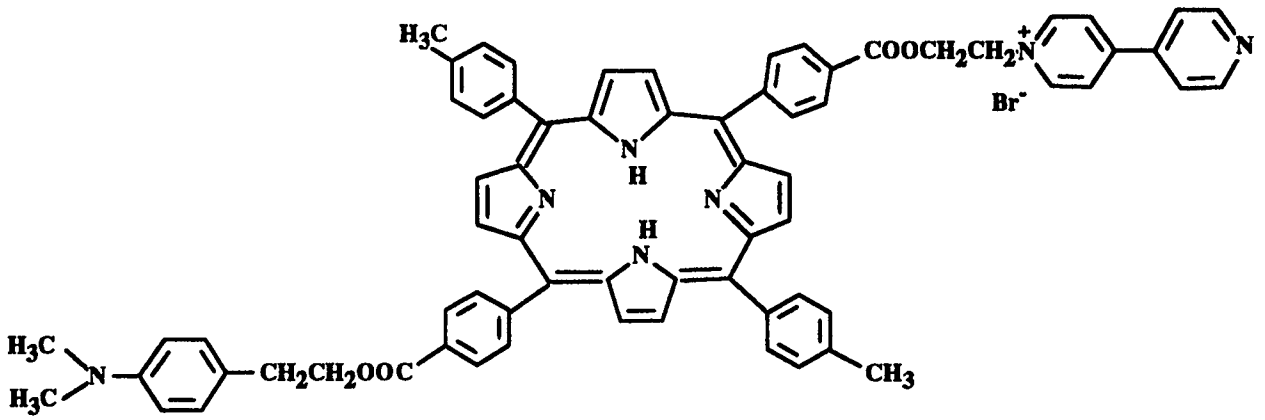
The cyclic coupling of **14** and **3** was attempted by two different procedures. *Yamaguchi's* method[5,6] was applied first. The diacid **3** was mixed with 2,4,6-trichlorobenzoyl chloride in N,N-dimethylformamide to form a mixed anhydride. To the resulting mixture was added diol **14** at high dilution. However, this reaction provided a messy mixture, which was difficult to separate due to its low solubility in normal organic solvents. After crude purification by several reprecipitations from ethyl ether and thick layer chromatography with 1-butanol:water:acetic acid (8:3:2) as eluent, all components obtained gave broad peaks in ^{1}H NMR spectra which were difficult to assign. ESR analysis indicated that the Ru(II) species was oxidized to Ru(III).

A second procedure, known for the synthesis of macrocyclic lactones,[7] was then attempted. Diacid **3** was first converted into its acid chloride. The coupling reaction of the latter with diol **14** at high dilution in N,N-dimethylformamide then yielded a mixture. Further separation of the product mixture was also difficult.

At this stage, the desired cyclic molecule had not been obtained. It was however believed that the coupling cyclization in both procedures could produce small amount of the cyclic molecule. Unfortunately, appropriate purification methods and analytical techniques were not available.

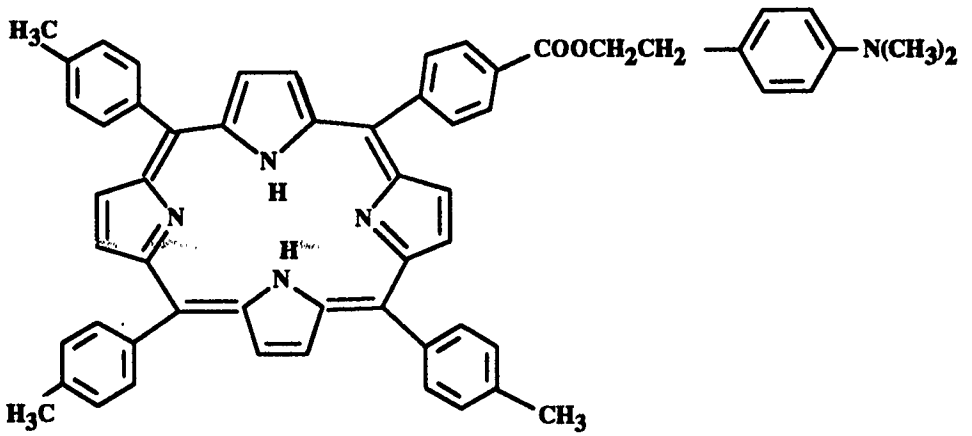
3.1.2 Synthesis of D-P-A, P-A and P-D Molecules

Due to the reason stated in chapter 2, the objective was switched to the synthesis of a linear molecule containing a porphyrin light absorber, an electron acceptor and an electron donor. The porphyrin covalently linked to the N,N-dimethylaniline electron donor and viologen electron acceptor, has the following structure:

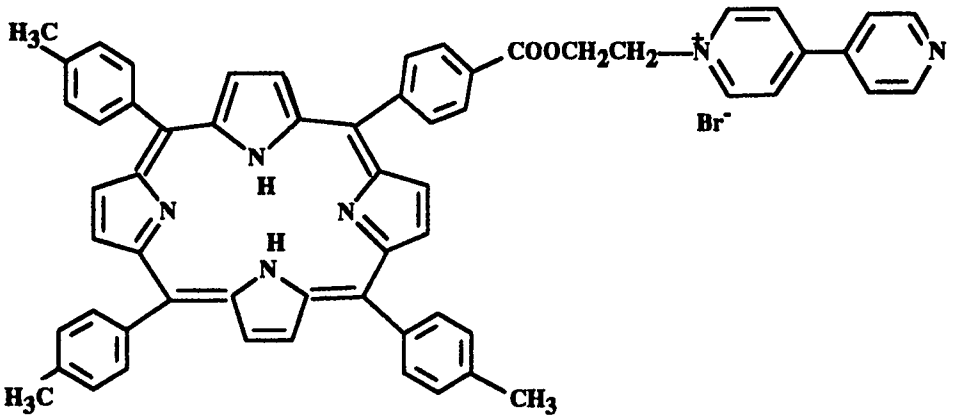


(22) D-P-A

Two reference compounds without either the electron donor or the electron acceptor, compound (23) and compound (24) , were also needed to compare the electron transfer behavior within the triad compound. They have the following structure:



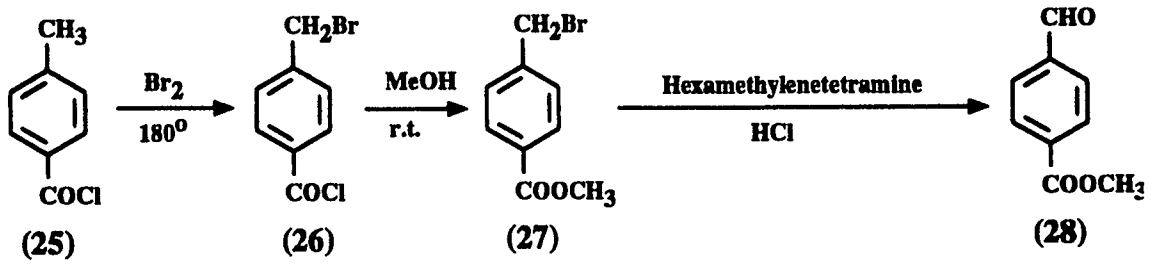
(23) P-D



(24) P-A

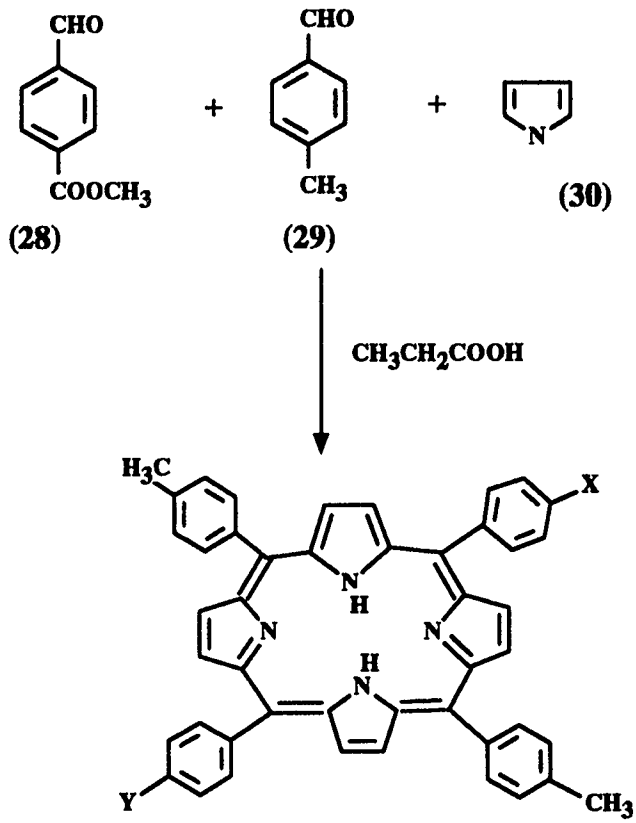
For the synthesis of these porphyrin derivatives, 4-carbomethoxybenzaldehyde (**28**) was prepared according to a literature method.[8] As shown in Scheme 6, bromination of acid chloride (**25**) followed by treatment with methanol gave bromide (**27**), which was converted into aldehyde **28** by a Sommelet reaction.

Scheme 6.



Two key porphyrin intermediates, **31a** and **31b** were prepared by using a literature method.[9] As shown in Scheme 7, heating a mixture of aldehydes, **28** and **29**, and pyrrole in propionic acid resulted in the formation of a mixture of porphyrins, which was subject to column chromatography to afford **31a** and **31b**.

Scheme 7.



(31 a): X= $COOCH_3$
Y= CH_3
(31 b): X=Y= $COOCH_3$

Porphyrin **31a** was subject to hydrolysis , which was followed by treatment with thionyl chloride to form acid chloride (**32**). The reaction of **32** with N,N-dimethyl-4-aminophenethyl-alcohol (**34**) hereby gave the reference molecule **23** as shown in Scheme 8. After the reaction, the reaction mixture was subject to gel column chromatography, but there were still some impurity peaks shown in the ^1H NMR spectrum. Further purifications were attempted. No improvements were found after recrystallization and normal phase HPLC. Purification by reverse phase HPLC (with trtrahydrofuran:water 65:35 as eluent) was then employed and the purified product gave

a much cleaner ^{1}H NMR spectrum. The purified product was, however, contaminated by 2,6-di-*tert*-butyl-4-methylphenol (BHT), a stabilizer for the eluent component tetrahydrofuran used in HPLC separation. BHT was then removed by thick layer chromatography using chloroform as eluent. The ^{1}H NMR spectrum of **23** (Fig. 3-1) clearly suggests that we obtained the desired compound. In comparison with the known compound **31 a**, the porphyrin ring structure of **23** didn't change. New peaks showed up at δ 2.97 (s, 6H, N-C<u>H</u>$_3$), 3.15 (t, 2H, J=7.1 Hz, C<u>H</u>$_2$-N), 4.68 (t, 2H, J=7.1 Hz, COOC<u>H</u>$_2$), 6.81 (d, 2H, J=8.5 Hz, aromatic C<u>H</u>) and 7.30 (d, 2H, J=8.5 Hz, aromatic C<u>H</u>), which were assigned to the protons of the new moiety incorporated with the esterification.

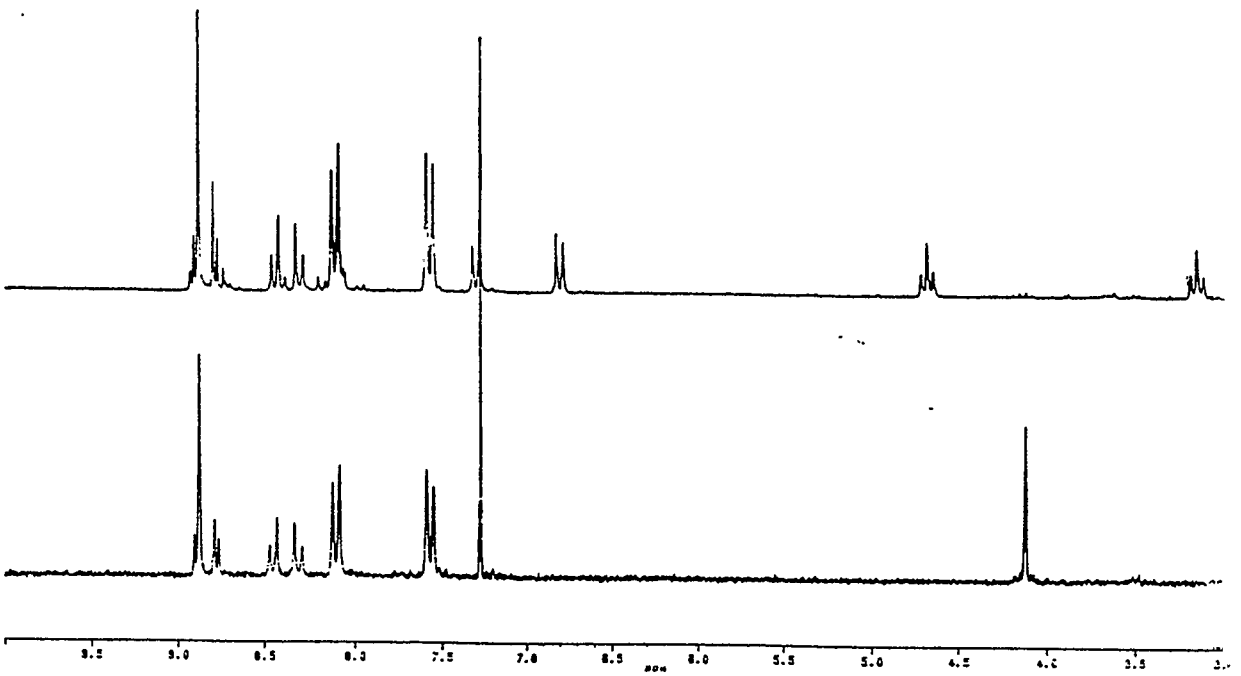
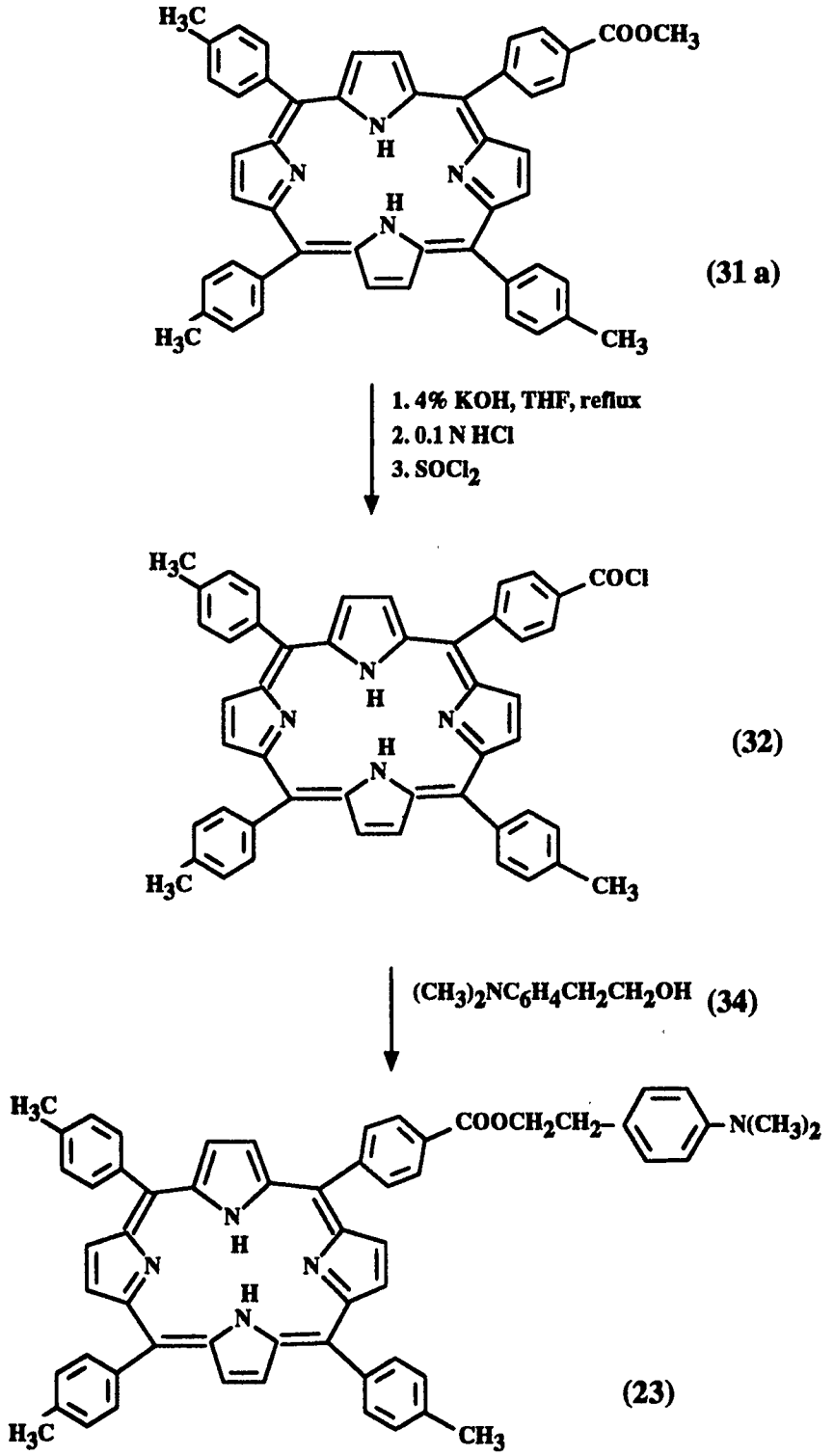


Fig. 3-1 ^{1}H NMR spectra of **23 and 31 a.**

(a) 23

(b) 31 a

Scheme 8.


H3C
COOCH3
N
H
N
N
H
N
H3C
CH3
(31 a)
1. 4% KOH, THF, reflux
2. 0.1 N HCl
3. SOCl2
H3C
COCl
N
H
N
N
H
N
H3C
CH3
(32)
(CH3)2NC6H4CH2CH2OH (34)
H3C
COOCH2CH2-
-N(CH3)2
N
H
N
N
H
N
H3C
CH3
(23)

A model reaction was carried out before the synthesis of **24**. In the model reaction, benzoyl chloride reacted with 2-bromoethanol and then with **4** to give 1-(2-benzoyloxyethyl)-4-(4'-pyridyl)pyridinium bromide. Similarly, acid chloride **32** should react with 2-bromoethanol to give **35**, which could then react with **4** to yield **24** as shown in Scheme 9.

After the esterification reaction, crude product **35** was purified by gel column chromatography, followed by recrystallization. The ^{1}H NMR spectrum of **35** is shown in Fig. 3-2. Compared with the ^{1}H NMR spectrum of **31 a**, the chemical shifts of the two new methylene groups were observed at δ 3.82 (t, 2H, J=6.1 Hz, $C\underline{H}_2Br$) and δ 4.84 (t, 2H, J=6.1 Hz, $COOC\underline{H}_2$). Crude product **24** was washed with large amount of ethyl ether to remove the excess **4**, followed by thick layer chromatography using ethyl acetate as eluent. Further purification by reverse phase HPLC was attempted, unfortunately, the sample decomposed in the column. The ^{1}H NMR spectrum of **24** is shown in Fig. 3-3. Comparing the ^{1}H NMR spectrum of **35** with that of **24** (used DMSO-d_6), new peaks showed up at δ 5.20 (br, 2H, $C\underline{H}_2$-N, compared with the $C\underline{H}_2Br$ at δ 3.82 in **35**), 8.08 (d, 2H, 7.9 Hz, overlap with 6 tolyl protons), 8.76-8.86 (m, 4H, overlap with 8 pyrrole protons) and 9.50 (d, 2H, J=6.6 Hz) ($C\underline{H}$ of the dipyridyl ring).

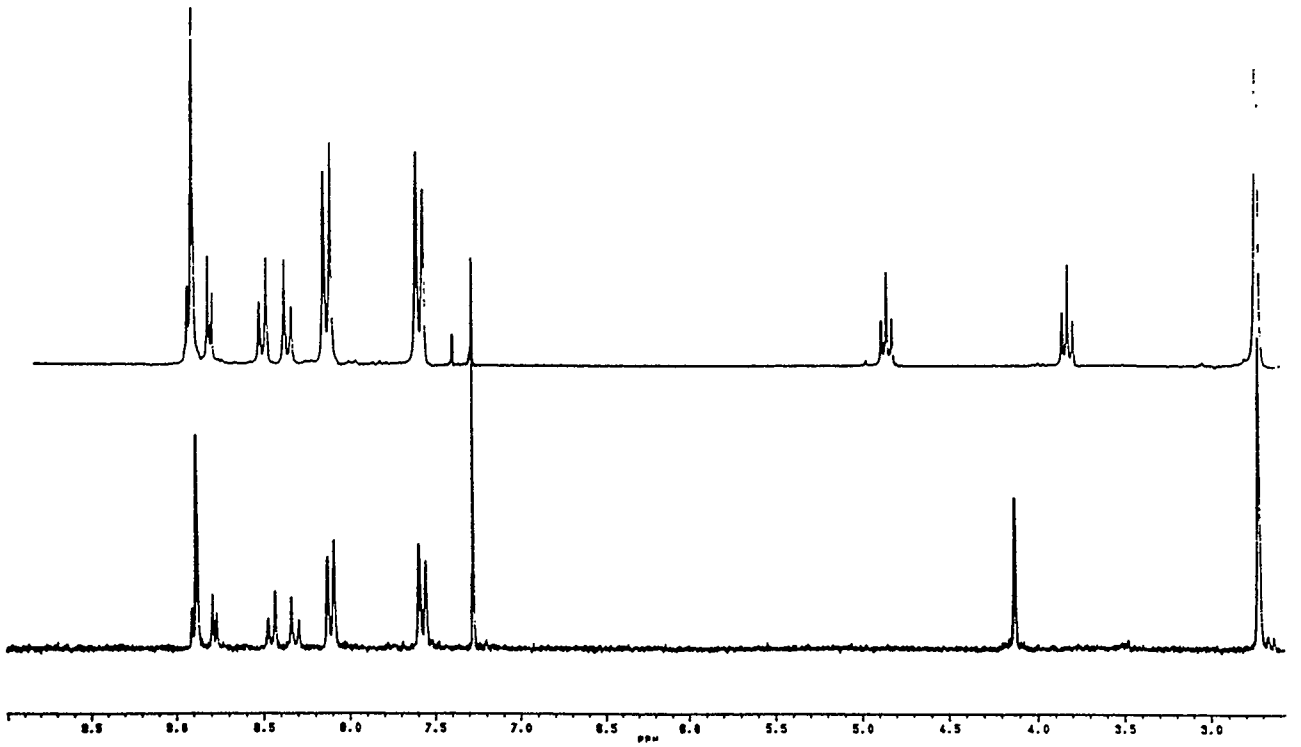


Fig. 3-2 ^{1}H NMR spectra of **35** and **31 a**

(a) **35**

(b) **31 a**

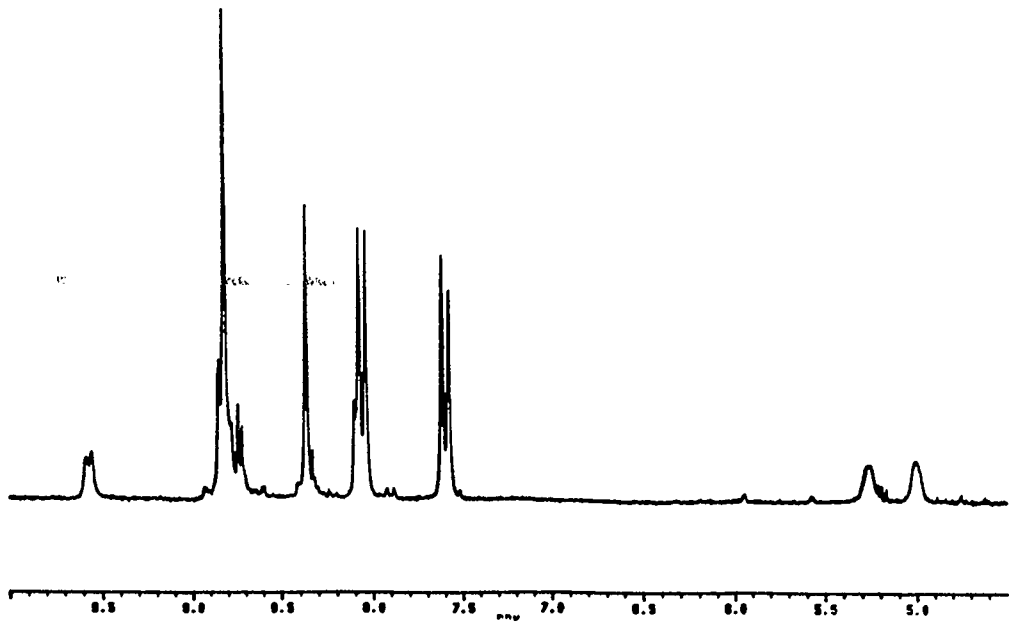
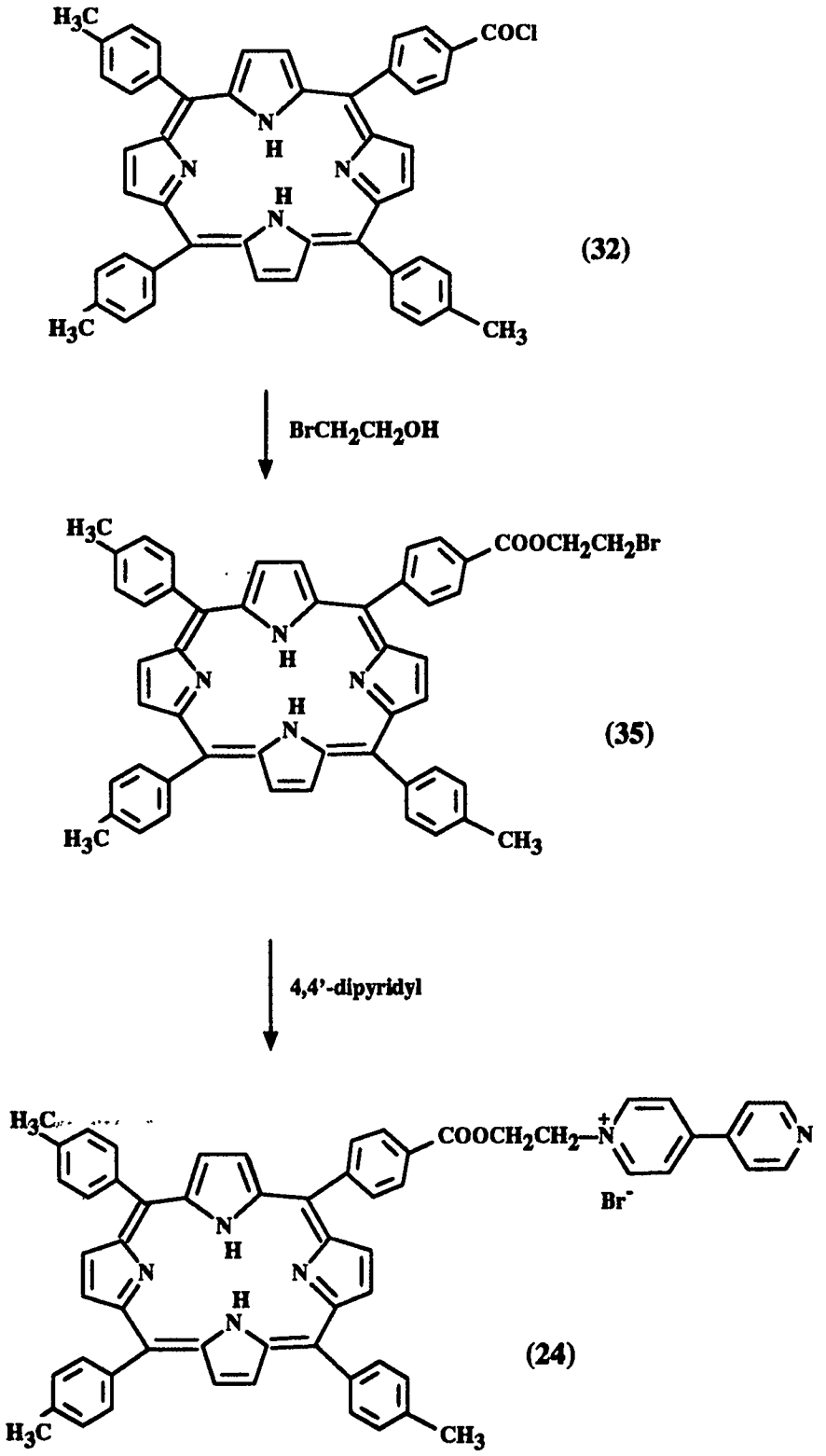


Fig. 3-3 ^{1}H NMR spectrum of **24**

Scheme 9.


H3C
COCl
N
H
N
N
H
N
H3C
CH3
(32)
BrCH2CH2OH
H3C
COOCH2CH2Br
N
H
N
N
H
N
H3C
CH3
(35)
4,4'-dipyridyl
H3C
COOCH2CH2—N+
N
Br-
N
H
N
N
H
N
H3C
CH3
(24)

Compound **22** was synthesized as shown in Scheme 10. Dimethy ester **31 b** was first converted into the corresponding acid chloride (**36**) by hydrolysis, followed by reaction with thionyl chloride. The successive treatment of **36** with **34** and 2-bromoethanol then gave **37**. After the esterification reaction, the reaction mixture was first subject to gel column chromatography to obtain the crude product of **37**. But in the ^{1}H NMR spectrum, two impurity triplet peaks showed up at δ 3.9 and 4.7 ppm and they were not removed after recrystallization and by normal phase HPLC. It was only through the use of reverse phase HPLC that the impurity peaks were removed. But the product was contaminated with BHT (introduced by tetrahydrofuran used for HPLC). The ^{1}H NMR spectrum of **37** is shown in Fig. 3-4.

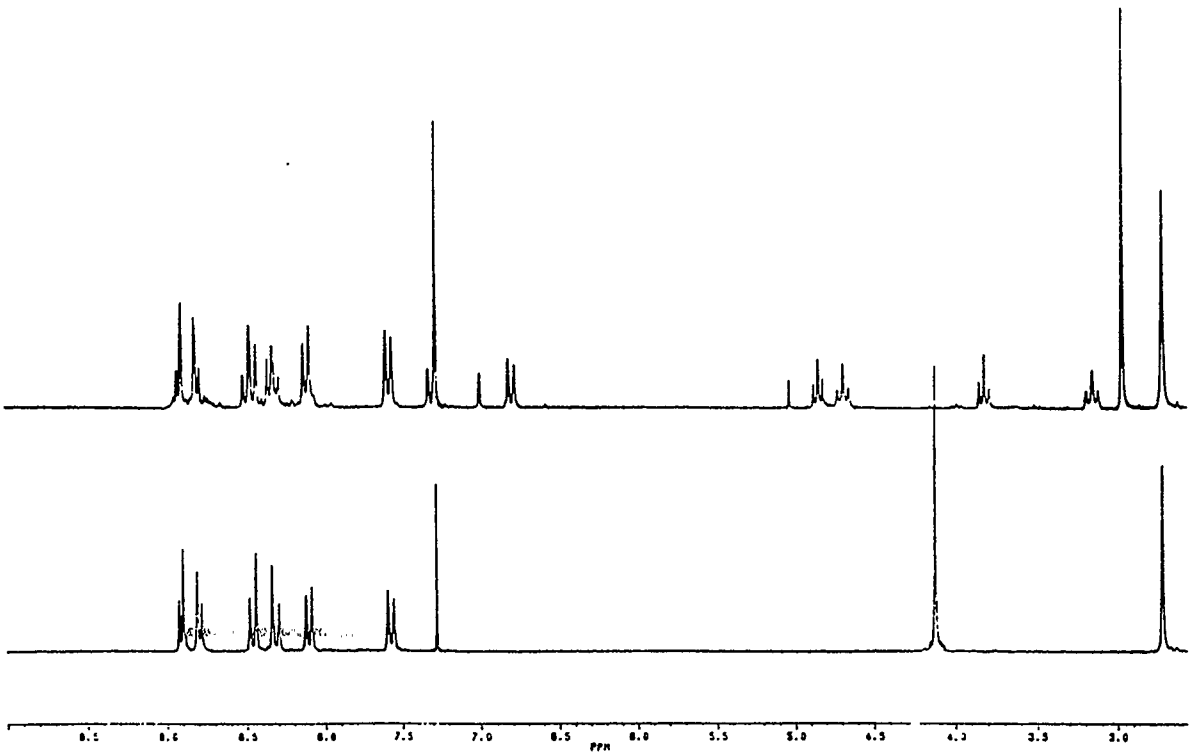


Fig. 3-4 ^{1}H NMR spectra of **37** and **31 b**

(a) **37**

(b) **31 b**

In comparison with the known compound **31 b**, new peaks showed up at δ 2.97 (s, 6H, $C\underline{H}_3$-N), 3.15 (t, 2H, J=7.1 Hz, $C\underline{H}_2$-N), 3.82 (t, 2H, J=6.0 Hz, $C\underline{H}_2Br$), 4.68 (t, 2H, J=7.1 Hz, $COOC\underline{H}_2$-CH_2N), 4.84 (t, 2H, J=6.0 Hz, $COOC\underline{H}_2CH_2Br$), 6.80 (d, 2H, J=8.7 Hz) and 7.30 (d, 2H, J=8.7 Hz) (aromatic C<u>H</u>). (Two small singlet at δ 7.0 ppm and 5.0 ppm were BHT peaks.)

Finally, compound **22** was obtained from the reaction of **37** with **4**. The crude product of **22** was first washed with a large amount of ether to remove the excess of **4**, and then followed by repeated thick layer chromatography first with chloroform as eluent to remove the unreacted **37** and then with ethyl acetate as eluent to remove trace amount of **4**. The ^1H NMR spectrum of **22** is shown in Fig. 3-5.

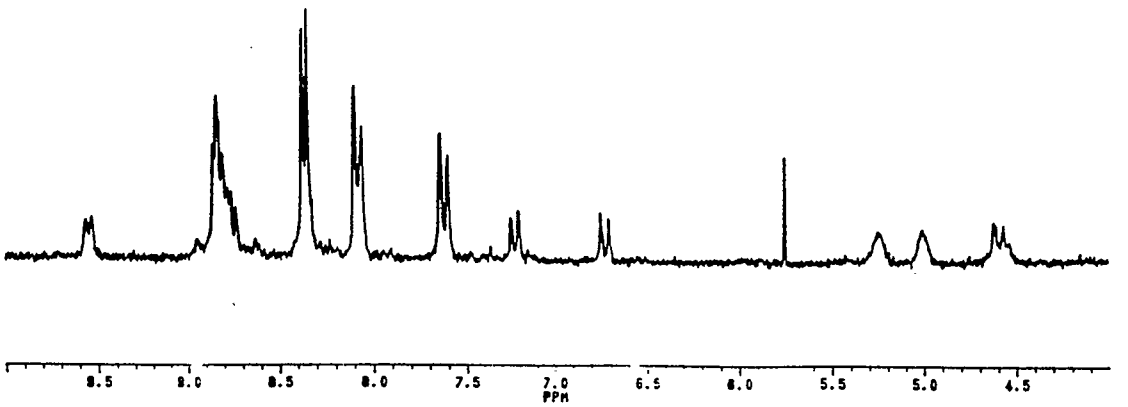
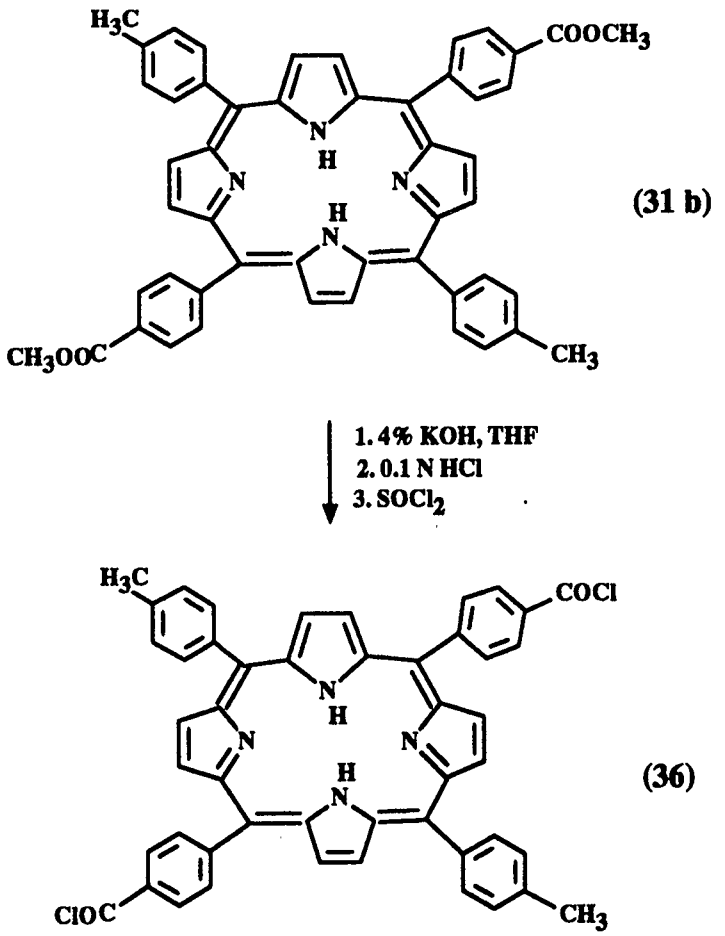


Fig. 3-5 ^1H NMR spectrum of **22**

In comparing the ^1H NMR spectrum of **22** with that of **37**, new peaks showed up at δ 5.20 (br, 2H, $C\underline{H}_2$-N, compared with the $C\underline{H}_2Br$ at 3.82 in **37**), 8.09 (d, 2H, J=8.4 Hz, overlap with 6 tolyl protons), 8.70-8.85 (m, 4H, overlap with 8 pyrrole protons) and 9.50 (d, 2H, J=6.6 Hz) (C<u>H</u> of the dipyridyl ring).

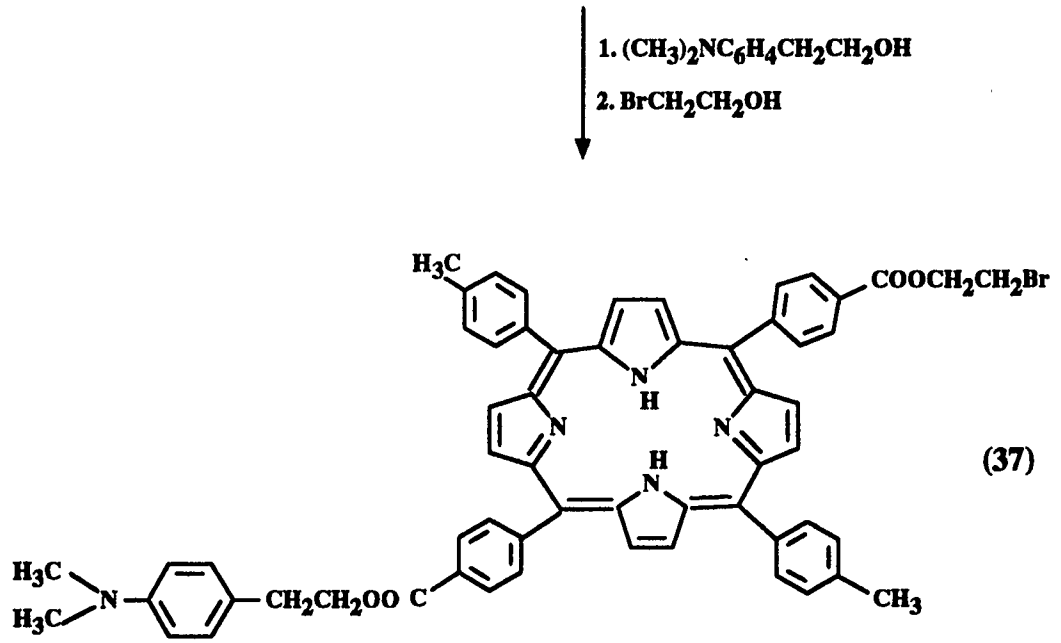
As discussed above, five new porphyrin derivatives (**22**, **23**, **24**, **35** and **37**) have been successfully synthesized and their structures were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy and by FAB mass spectroscopy. However, the elemental analyses gave lower C, H and N values than expected (also happened to **14** and **21**), which might be due to incomplete combustion (in some cases, higher H values which might be due to water). This problem has been encountered by others involved in porphyrin synthesis. We do not know the reason for this. Anton and Loach[19] reported that a satisfactory elemental analysis result of free-base porphyrins could be obtained by converting them to their Cu(II) complexes, but we did not have enough sample to try that.

Scheme 10.

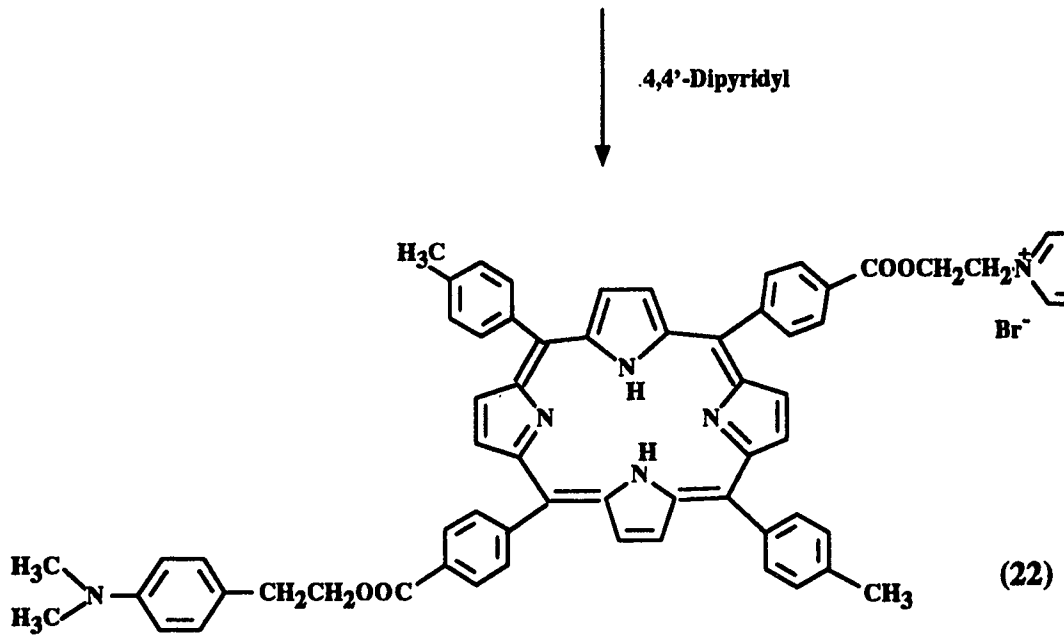


(31 b)

(36)


1. $(CH_3)_2NC_6H_4CH_2CH_2OH$
2. $BrCH_2CH_2OH$
H_3C
$COOCH_2CH_2Br$
N
H
H_3C
H_3C
$CH_2CH_2OO\ C$
CH_3

(37)


4,4'-Dipyridyl
H_3C
$COOCH_2CH_2$
Br^-
N
H
H_3C
H_3C
CH_2CH_2OOC
CH_3

(22)

3.2 Experimental

Instrumentation and Techniques

IR spectra were recorded on a Mattson 4030 spectrometer and NMR spectra were obtained on a Bruker ACE-200 or a Bruker ACE-400 instrument. Fast Atom Bombardment (FAB) mass spectra were obtained on a KRATOS MS80RFA instrument, using 2-nitrobenzyl alcohol as the matrix. Melting points were measured on a Gallenkamp melting point apparatus. HPLC was carried out on a Varian 5000 HPLC instrument. Thick layer chromatography was performed on silica gel GF, 1000 μm, supplied by Analtech. Silica gel used in column chromatography was supplied by Merck, 70-230 mesh or finer than 230 mesh. Thin layer chromatography was performed on silica gel UV 254 (250 μm) supplied by Whatman.

Materials

Unless otherwise specified, all chemicals were used without further purification. Benzene and dichloromethane were dried by distilling over calcium hydride and stored over molecular sieves. N,N-Dimethylformamide was distilled under reduced pressure over phosphorus pentoxide before use.

1-(2-Hydroxyethyl)-4-(4'-pyridyl) pyridinium bromide (5)[1]

A literature method[1] was used for the preparation of compound **5**. A mixture of 2-bromoethanol (3.17 g, 25.4 mmol) and 4,4'-dipyridine (7.81 g, 50 mmol) in 50 ml of N,N-dimethylformamide was heated at 85 °C for 15 hours. After cooling, the precipitated dication salt was filtered. The filtrate was diluted with ethyl ether and the

solid precipitate was collected (5.05 g, 60% yield). The pure product was obtained by recrystallization from ethanol/ethyl ether, m.p. 194-196 °C (lit.[1] 195-197 °C).

^{1}H NMR (DMSO-d_6): δ 3.89 (t, 2H, J=4.9 Hz), 4.70 (t, 2H, J=4.9 Hz), 8.05 (d, 2H, J=6.2 Hz), 8.64 (d, 2H, J=6.9 Hz), 8.88 (d, 2H, J=6.2 Hz), 9.16 (d, 2H, J=6.9 Hz).

1-(2-Bromoethyl)-1'-(2-hydroxyethyl)-4,4'-bipyridinium dibromide (6)

Compound **6** was prepared using the same method as above[1]. Compound **5** (2.81 g, 10 mmol) and a large excess of 1,2-dibromoethane (18.74 g, 99.7 mmol) in 30 ml of N,N-dimethylformamide were heated at 72 °C for 15 hours. After cooling, the bipyridinium salt **6** (3.0 g, 97%) was collected. The crude product was purified by recrystallizing from methanol/2-propanol.

^{1}H NMR (D_2O): δ 3.90 (t, 2H, J=5.7 Hz), 3.98 (t, 2H, J=4.9 Hz), 4.69 (t, 2H, J=4.9 Hz), 5.02 (t, 2H, J=5.7 Hz), 8.44 (t, 4H J=6.3 Hz), 8.98 (d, 2H, J=7.0 Hz), 9.04 (d, 2H, J=7.0 Hz).

Trial esterification of L-proline with 6 via acid chloride route

A mixture of L-proline (0.58 g, 5.0 mmol) and thionyl chloride (0.83 g, 6.95 mmol) in 25 ml of dry N,N-dimethylformamide was stirred at 80 °C for 3 hours. Compound **6** (1.6 g, 3.41 mmol) was added and the mixture was stirred at the same temperature overnight. Although the acid chloride of L-proline formed according to the IR analysis, the IR spectrum of the reaction mixture showed that no esterification had occurred.

Trial esterification of L-proline with 6 via DCC route

L-Proline (0.08 g, 0.7 mmol) was mixed with concentrated hydrochloric acid (0.2 ml). After removal of the volatile materials in vacuum, the L-prolinate hydrochloride was dissolved in 5 ml of dry N,N-dimethylformamide. To this solution were added

dicyclohexylcarbodiimide (DCC) (0.1 g) and **6** (0.2 g, 0.43 mmol). The reaction mixture was stirred at room temperature for 14 hours. The IR spectrum indicated that no desired product was obtained.

N-*tert*-Butyloxycarbonyl-L-proline (8)[13]

Compound **8** was prepared according to a literature method[13]. p-Nitrophenyl chloroformate (15.53 g, 77 mmol) was added in small portions at 0 °C to a solution of t-butyl alcohol (5.68 g, 76.74 mmol) in pyridine (30 ml). The reaction mixture was stirred at room temperature for 3 hours. The precipitated solid was then removed by filtration. The filtrate was poured into water (10 ml) and extracted with ethyl ether. The ether solution was washed three times each with 1 N hydrochloric acid, saturated sodium carbonate solution and saturated sodium chloride solution, followed by drying over magnesium sulfate. After evaporating to dryness, the residue was dissolved in 53 ml of ethanol, 60 ml of water was then added to give t-butyl p-nitrophenylcarbonate (9.65 g, 54%), m.p. 78-79 °C (lit.[13] 78-79 °C).

^{1}H NMR ($CDCl_3$): δ 1.59 (s, 9H), 7.37 (d, 2H, J=9.3 Hz), 8.28 (d, 2H, J=9.3 Hz).

To a mixture of L-proline (2.3 g, 20 mmol), t-butyl p-nitrophenylcarbonate (6.0 g, 25 mmol), and sodium hydroxide (2.0 g, 50 mmol) in 30 ml of t-butyl alcohol was added in 20 ml of water. The resulting reaction mixture was refluxed for 30 minutes. All the solids dissolved during this period but two liquid layers persisted. The reaction mixture was then concentrated to remove the t-butyl alcohol. After cooling, the precipitated sodium p-nitrophenolate was filtered and washed with 14 ml of water in three portions. The filtrate was adjusted to pH 5-6 with dilute hydrochloric acid, extracted with ethyl ether to remove any remaining t-butyl-p-nitrophenylcarbonate and p-nitrophenol. The aqueous portion was then adjusted to pH 1 and extracted with ethyl ether. After

evaporation of the ether, the solid residue was recrystallized from 2-butanone and petroleum ether to give compound **8** (2.39 g, 56%), m.p. 135-136 °C (lit.[13] 136-137°C).

IR (KBr): 1740 (C=O), 1659 (t-BOC) cm^{-1}.

^1H NMR ($CDCl_3$): δ 1.50 (s, 9H), 1.95 (br, 3H), 2.63 (br, 1H), 3.47 (br, 2H), 4.37 (br, 1H).

Trial esterification of N-*tert*-butyloxycarbonyl-L-proline with 6 via DCC route

A mixture of **8** (0.05 g, 0.23 mmol), dicyclohexylcarbodiimide (0.08 g, 4.85 mmol) and **6** (0.10 g, 0.21 mmol) in 5 ml of dry N,N-dimethylformamide was stirred at room temperature for 40 hours. The IR spectrum showed that no desired reaction had occurred.

Trial esterification of N-*tert*-butyloxycarbonyl-L-proline with 6 via acid chloride route

A mixture of **8** (0.14 g, 6.51 mmol) and oxalyl chloride (0.74 g, 5.8 mmol) in 10 ml of dry dichloromethane was stirred at reflux overnight. After removal of the volatile materials under reduced pressure, the acid chloride was dissolved in 3 ml of dry N,N-dimethylformamide. Into this solution were added **6** (0.24 g, 0.51 mmol) and sodium carbonate (0.06 g, 5.66 mmol), and the reaction mixture was stirred at room temperature. The yellow solution turned to dark green. The IR analysis showed that no desired reaction had occurred.

2-Bromoethyl L-prolinate hydrochloride (9)

A literature method[2] was modified to prepare compound **9**. Thionyl chloride (0.44 g, 4.3 mmol) was added slowly to L-proline (0.47 g, 4.1 mmol) in a round bottom flask which was cooled in an ice bath. The reaction mixture was then stirred at room temperature for

10 minutes. Dry dichloromethane (3 ml) and 2-bromoethanol (3.17 g, 25.4 mmol) were added and the resulting mixture was stirred at room temperature overnight. After removal of the volatile materials under reduced pressure, a brown viscous oil was obtained (0.94 g, 79.4%). The IR spectrum showed a strong absorption at 1748 cm^{-1}, assigned to the C=O ester stretch.

2-Bromoethyl N-(*tert*-butyloxycarbonyl)-L-prolinate (10)[2]

To a solution of 2-bromoethyl L-prolinate hydrochloride (**9**) (3.836 g, 14.8 mmol) in 5 ml of dichloromethane, cooled in an ice bath, were added triethylamine (3.0 g, 29.8 mmol) and di-*tert*-butyl dicarbonate (3.931 g, 18.5 mmol). The reaction mixture was stirred at 0 °C for 1 hour, warmed to room temperature and stirred overnight. It was then made acidic with a saturated citric acid solution. The dichloromethane layer was separated, washed sequentially with water, a saturated sodium bicarbonate solution and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent yielded **10** as a brown oil (3.617 g, 75 %).

IR (KBr): 1750 (ester), 1698 (t-BOC) cm^{-1}.

^1H NMR ($CDCl_3$): δ 1.46 (s, 9H), 1.75-2.35 (m, 4H), 3.32-3.90 (m, 4H), 4.25-4.65 (m, 3H).

1-(2-Bromoethyl)-4-(4'-pyridyl) pyridinium bromide

A mixture of 1,2-dibromoethane (0.392 g, 2.09 mmol) and 4,4'-dipyridine (0.56 g, 3.59 mmol) in 5 ml of N,N-dimethylformamide was stirred at 40 °C for 24 hours. After cooling to room temperature, the dication salt was filtered. Ethyl ether was added to the filtrate and the yellow precipitate was collected and dried (0.63 g, yield 51%).

^1H NMR (D_2O): δ 3.87 (t, 2H, J=5.7 Hz), 4.94 (t, 2H, J=5.7 Hz), 7.76 (d, 2H, J=6.3 Hz), 8.28 (d, 2H, J=7.0 Hz), 8.61 (d, 2H, J=6.3 Hz), 8.87 (d, 2H, J=7.0 Hz).

Trial coupling of 10 with 1-(2-bromoethyl)-4-(4'-pyridyl) pyridinium bromide

A mixture of 1-(2-bromoethyl)-4-(4'-pyridyl) pyridinium bromide (2.47 g, 7.18 mmol) and **10** (0.2 g, 0.93 mmol) in 15 ml of N,N-dimethylformamide was stirred at 75 °C for 2 days. Ether was added and the precipitate was collected. The ^{1}H NMR spectrum showed that the two starting materials remained, and no desired reaction had occurred.

1-[2-(N-t-BOC-2-pyrrolidinecarbonyloxy)ethyl]-4-(4'-pyridyl) pyridinium bromide (11)

A mixture of **10** (0.64 g, 1.99 mmol) and 4,4'-dipyridyl (0.5 g, 3.2 mmol) in 7 ml of N,N-dimethylformamide was stirred at 50 °C for 24 hours. After cooling to room temperature, the dication salt was filtered. The filtrate was diluted with ethyl ether and the precipitate was collected, washed with ether and dried under reduced pressure to give **11** (0.59 g, 62%).

^{1}H NMR (D_2O): δ 0.96-1.23 (m, 9H), 1.73 (br, 3H), 2.10 (br, 1H), 3.23 (br, 2H), 3.85-4.20 (br, 2H), 4.55 (br, 1H), 4.92 (br, 2H), 7.98 (br, 2H), 8.36 (br, 2H), 8.72 (br, 2H), 8.93 (br, 2H).

1-(2-Bromoethyl)-1'-[2-(N-t-BOC-2-pyrrolidinecarbonyloxy)ethyl]-4,4'-bipyridiniu m dibromide (12)

A mixture of **11** (0.029 g, 0.07 mmol) and 1,2-dibromoethane (0.17 g, 0.90 mmol) in 5 ml of N,N-dimethylformamide was stirred at 45 °C for three days. After cooling, the precipitate was collected, washed with ethyl ether and dried under reduced pressure to give **12** (0.016 g, 40%).

^{1}H NMR (D_2O): δ 0.97-1.23 (m, 9H), 1.73 (br, 3H), 2.10 (br, 1H), 3.24 (br, 4H), 3.90-4.22 (br, 2H), 4.54 ((br, 1H), 4.94 (br, 4H), 8.14 (br, 2H), 8.40 (br, 2H), 8.81 (br, 2H), 8.98 (br, 2H).

N-(2-Hydroxyethyl) aniline

A modification of Rindfusz and Harnack's method[14-15] was applied. A mixture of aniline (20.4 g, 0.22 mol), 2-bromoethanol (24.7 g, 0.20 mol), and anhydrous sodium carbonate (18.0 g, 0.17 mol) was stirred at 60-70 °C overnight. The reaction mixture was filtered and washed with ether. After removal of the ether and the unreacted aniline, the desired product was obtained as a lemon-coloured oil by distillation at 113-120 °C/4 mmHg, which was in agree with the literature value, (15.3 g, 56.5%).

IR (KBr): 3396 (br, OH), 1057 (C-O) cm^{-1}

^1H NMR ($CDCl_3$): δ 2.95 (s, 1H), 3.30 (t, 2H, J=5.2 Hz), 3.83 (t, 2H, J=5.2 Hz), 6.65-6.80 (m, 3H), 7.17-7.25 (m, 2H).

Trial coupling of 6 with N-(2-hydroxyethyl) aniline

A mixture of N-(2-hydroxyethyl) aniline (4.9 mg, 0.036 mmol) and **6** (17.1 mg, 0.036 mmol) in 1 ml of methanol was srirred at room temperature for 2 hours. The reaction mixture turned dark purple. The methanol was removed with a rotary evaporator. The ^1H NMR (D_2O) spectrum of the residue indicated that only the two starting materials were recovered. The UV-vis spectrum showed that upon dilution, the absorption peak at about 237 nm split into two peaks at 207 nm and 243 nm respectively. This suggests that a ground state electron donor-acceptor complex formed between the two starting materials.

4,4'-Dicarboxy-2,2'-bipyridine (19)[4]

Compound **19** was prepared according to the literature.[4] A mixture of 4,4'-dimethyl-2,2'-dipyridyl (**18**) (4.0 g, 0.217 mol) and potassium permanganate (12.5 g, 0.079 mol) in 140 ml of water was stirred at refluxing temperature for 12 hours. Removal of the brown precipitate by filtration gave a yellowish solution, which was

extracted with ether three times to remove the unreacted 4,4'-dimethyl-2,2'-dipyridyl. The aqueous layer was treated with concentrated hydrochloric acid and the white precipitate was collected, washed well with water and dried in a vacuum oven for 24 hours to yield **19** (1.1 g, 20.7%). This compound was insoluble in any organic solvents. Anal. Calcd. for $C_{12}H_8N_2O_4$: C, 59.02; H, 3.30; N, 11.47. Found: C, 58.67; H, 3.23; N, 11.14.

***cis*-Dichlorobis (bipyridine) ruthenium (21)**[4]

Compound **21** was prepared according to the literature.[4] A mixture of ruthenium trichloride (3.9 g, 18.8 mmol) and 2,2'-bipyridine (**20**) (4.7 g, 30.1 mmol) in 150 ml of N,N-dimethylformamide was stirred at refluxing temperature for 3 hours. After most of the solvent was distilled, the residue was cooled to room temperature and acetone (125 ml) was added. The solution was kept at 0 °C overnight, and the crystals were collected and washed well with water. The crude product was suspended in 625 ml of water-ethanol (1:1) solution and stirred at reflux for 1 hour. The solution was filtered to remove insoluble solid and treated carefully with 75 g of lithium chloride. After most of the ethanol was distilled, the resulting aqueous solution was cooled in an ice bath. The dark crystals were collected, washed well with water and dried in a vacuum oven for 24 hours. UV (in ethanol): λ=366.8, 533.7 nm. This compound was used for the next reaction without further purification

Anal. Calcd. for $C_{20}H_{20}N_4O_2Cl_2Ru$: C, 46.16; H, 3.87; N, 10.77. Found: C, 44.08; H, 3.80; N, 9.92.

***Bis*(bipyridine)-4,4'-dicarboxy-2,2'-bipyridineruthenium (3)**[4]

A literature method[4] was applied for the preparation of **3**. A mixture of *cis*-dichlorobis(bipyridine)ruthenium (**21**) (523 mg, 1.0 mmol),

4,4'-dicarboxy-2,2'-bipyridine (**19**) (302 mg, 1.24 mmol), and sodium bicarbonate (302 mg, 3.6 mmol) in a solution of 15 ml of water and 10 ml of methanol was refluxed for 2 hours. At the end of the reaction, aqueous ammonium hexafluorophosphate was added and the solution was refrigerated overnight. Dark red crystals were collected.

Anal. Calcd. for $C_{32}H_{24}N_6O_4P_2F_{12}Ru$: C, 40.56; H, 2.55; N, 8.87. Found: C, 41.00 ; H, 2.44; N, 8.69.

N-(2-Hydroxyethyl)-N-(2-bromoethyl) aniline (16)[3]

A literature method[3] was modified for the preparation of **16**. A mixture of **15** (3.4 g, 18.8 mmol), 48% hydrobromic acid (3.576 g, 21.2 mmol), and concentrated sulfuric acid (0.6 ml) was heated at reflux for 8 hours. The solution was cooled to room temperature, neutralized with saturated sodium bicarbonate solution, and extracted with ether. The ether solution was washed with a saturated sodium bicarbonate solution, a saturated sodium chloride solution, and dried over magnesium sulphate. After evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel with hexanes/ethyl acetate (2:1) as eluent to give compound **16** as a pale yellow viscous oil (1.157 g, yield 25.2%).

IR (KBr): 3383 (br, OH), 1038 (C-O) cm^{-1}.

^1H NMR ($CDCl_3$): δ 3.46-3.57 (m 4H), 3.73-3.82 (m 4H), 6.76-6.82 (m 3H), 7.22-7.31 (m 2H).

1-[2-(N-Hydroxyethyl-N-phenyl)ethylamino]-4-(4'-pyridyl) pyridinium bromide (17)

A mixture of **16** (0.55 g, 2.25 mmol) and 4,4'-dipyridyl (1.1 g, 7.05 mmol) in 15 ml of N,N-dimethylformamide was stirred at 75 °C for 17 hours. The solution was cooled to room temperature and poured into a large volume of ethyl ether. A light yellow solid

was collected and redissolved in a minimal amount of N,N-dimethylformamide. The mixture was filtered to remove any undissolved solid, diluted with ethyl ether, and the precipitate was collected. This crude product was purified by flash column chromatography on silica gel with methanol/water/acetic acid (6:1:1) as eluent to yield **17** (0.52 g, 57.7%). This compound was used for the next reaction without further purification.

^{1}H NMR (D_2O): δ 3.28 (t, 2H, J=5.6 Hz); 3.51 (t, 2H, J=5.6 Hz); 3.95 (t, 2H, J=5.3 Hz); 4.72 (t, 2H, J=5.3 Hz); 6.49-6.58 (m, 3H); 6.99 (t, 2H, J=8 Hz); 7.73 (d, 2H, J=6.6 Hz); 8.06 (d, 2H, J=6.6 Hz); 8.62 (d, 2H, J=6.6 Hz); 8.70 (d, 2H, J=6.6 Hz).

1-(2-Hydroxyethyl)-1'-[2-(N-hydroxyethyl-N-phenyl)ethylamino]-4,4'-dipyridinium dibromide (14)

A mixture of **17** (0.93 g, 2.33 mmol) and 2-bromoethanol (10.6 g, 84.8 mmol) in 25 ml of N,N-dimethylformamide was stirred at 75 °C for 96 hours. After the mixture was cooled to room temperature, ethyl ether was added. The precipitated sticky material was dissolved in a minimal amount of methanol and re-precipitated in chloroform. The dark red solid was collected, washed well with chloroform, and dried in vacuum. The elemental analysis result was not satisfactory. Ratioing the observed data with the theoretical data, the ratio for C,H and N were found to be all around 0.95, suggesting that the problem might be due to incomplete combustion.

^{1}H NMR (D_2O): δ 3.32 (t, 2H, J=5.6 Hz); 3.53 (t, 2H, J=5.6 Hz); 3.95-4.01 (m, 4H); 4.70 (m, 2H); 4.80 (m, 2H); 6.51-6.61 (m, 3H); 7.01 (t, 3H, J=8.0 Hz); 8.21 (d, 2H, J=6.9 Hz); 8.29 (d, 2H, J=6.9 Hz); 8.86 (d, 2H, J=6.9 Hz); 8.95 (d, 2H, J=6.9 Hz); ^{13}C NMR (DMSO-d_6): 51.4, 52.8, 57.9, 58.5, 59.9, 63.1, 112.2, 116.62, 126.1, 129.1, 146.1, 146.3, 147.2, 148.4, 148.5.

Anal Calcd. for $C_{22}H_{27}N_3O_2Br_2$: C, 50.30; H, 5.18; N, 8.00. Found: C, 48.63; H, 4.94;

N, 7.62.

Trial coupling cyclization of 3 with 14 by *Yamaguchi's* method[5-6]

To a solution of **3** (0.28 g, 0.30 mmol) in 20 ml of N,N-dimethylformamide was added 2,4,6-trichlorobenzoyl chloride (75.4 mg, 0.31 mmol) and triethylamine (0.067 g, 0.66 mmol). The reaction mixture was stirred at room temperature under argon for 20 hours. The mixture was then filtered to remove the triethylamine hydrochloride and washed with 15 ml of N,N-dimethylformamide. The filtrate was added dropwise at 74 °C to a mixture of 4-dimethylaminopyridine (0.52 g, 4.26 mmol) and **14** (0.15 g, 0.29 mmol) in 60 ml of N,N-dimethylformamide over a period of 6 hours, and the resulting reaction mixture was stirred for additional 33 hours. After most of the solvent was removed with a rotary evaporator, the residue was diluted with a large volume of ether. The solid was collected and further purified by reprecipitating with ether 3 times and with chloroform once and separated by thick layer chromatography with 1-butanol:water:acetic acid (8:3:2) as eluent. ^{1}H NMR spectra of all components showed very broad peaks which were hard to assign. The ESR spectrum indicated that the Ru^{2+} species was oxidized to Ru^{3+}.

Trial coupling cyclization of 3 with 14 via acid chloride[7]

A mixture of **3** (0.28 g, 0.30 mmol) and 10 ml of thionyl chloride in 10 ml of benzene was stirred at refluxing temperature for 24 hours. Evaporation of the volatile materials resulted in a dark brown solid which was dried in vacuum. The acid chloride was then dissolved in 25 ml of dry N,N-dimethylformamide. Meanwhile, a solution of **14** (0.16 g, 0.30 mmol) in 28 ml of N,N-dimethylformamide was prepared. The two solutions were added dropwise at 80 °C to a solution of triethylamine (0.44 g, 4.3 mmol) in 52 ml of dry N,N-dimethylformamide under argon over a period of 4 hours. The reaction mixture was

stirred at 80 °C for additional 3 days and then cooled to room temperature. The mixture was concentrated with a rotary evaporator, and the triethylamine hydrochloride was filtered. After removal of the solvent under reduced pressure, the residue was chromatographed on a preparative TLC plate with dioxane/water (1:1) as eluent. The ^1H NMR spectrum (D_2O) showed very broad peaks which were hard to analyze.

Attempted model cyclization of 14 with 19 (with triethylamine as base)

Compound **19** (0.124 g, 0.51 mmol) was refluxed with thionyl chloride (3.65 g, 30.6 mmol) for three hours. After the volatile materials were evaporated under reduced pressure, the residue was further dried in vacuum for 2 hours. The diacid chloride was then dissolved in 40 ml of benzene-N,N-dimethylformamide (1:1) in a dropping funnel. Meanwhile, compound **14** (0.26 g, 0.50 mmol) was dissolved in 44 ml of dry N,N-dimethylformamide in another dropping funnel. The two solutions were added dropwise at 80 °C to 76 ml of dry N,N-dimethylformamide, under argon, over a period of 3.5 hours, and the reaction mixture was stirred for an additional 48 hours. The reaction was monitored by thin layer chromatography using dioxane/water (4:1) as the eluent. It was found that the two starting materials still remained. Triethylamine (0.364 g, 3.6 mmol) was added and the reaction mixture turned darker. After five minutes, the colour of the solution turned from brown to blue. The reaction mixture was stirred at 80 °C for additional 24 hours. After removal of the solvent and drying in vaccum, the ^1H NMR spectrum in DMSO-d_6 showed that the chemical shifts of the aromatic protons in the viologen molecule changed. Later studies showed that compound 14 was unstable toward triethylamine under the above reaction condition.

Trial model cyclization of 14 with 19 (with pyridine as base)

The diacid chloride was prepared as above from **19** (0.096 g, 0.39 mmol). The diacid

chloride was then dissolved in a mixed solvent of dry benzene (5 ml) and dry N,N-dimethylformamide (15 ml) in a dropping funnel. Compound **14** (0.20 g, 0.38 mmol) was dissolved in 25 ml of dry N,N-dimethylformamide in another dropping funnel. The two solutions were added dropwise at 80 °C to a solution of pyridine (0.2 ml) in 60 ml of N,N-dimethylformamide under argon over a period of 3 hours, and the reaction mixture was stirred for additional 48 hours. TLC was developed by dioxane/water (4:1) and ^{1}H NMR spectrum in D_2O indicated that the two starting materials still remained.

4-(N,N-Dimethylamino)phenethyl alcohol (34)

A mixture of 4-aminophenethyl alcohol (**33**) (2.6 g, 0.019 mol), methyl iodide (15 g, 0.11 mol), and sodium hydroxide (4.0 g, 0.1 mol) in 15 ml of ethanol and 10 ml of water was stirred at room temperature for 17 hours. After most of the ethanol was evaporated with a rotary vaporator, the residue was poured into 30 ml of water, extracted with ether. The ether solution was washed well with water and dried over magnesium sulfate. Evaporation of the solvent left an oily residue which was subjected to flash column chromatography with hexanes/ethyl acetate (1:1) as eluent. The first major band was collected (1.42 g, 45.1%).

^{1}H NMR ($CDCl_3$): δ 2.79 (t, 2H, J=6.5 Hz); 2.94 (s, 6H); 3.82 (t, 2H, J=6.5 Hz); 6.74 (d, 2H, J=8.7 Hz); 7.12 (d, 2H, J=8.7 Hz).

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.49; H, 8.91; N., 8.46.

2- Bromoethyl benzoate

A mixture of benzoic acid (2.0 g, 16.4 mmol) and thionyl chloride (9.6 g, 80.7 mmol) in 20 ml of benzene was stirred at reflux overnight. Evaporation of the solvent under

reduced pressure gave benzoyl chloride which was directly used without further purification.

The benzoyl chloride (0.24 g, 1.71 mmol) was mixed with 2-bromoethanol (0.364 g, 3.6 mmol) and triethylamine (0.44 g, 3.5 mmol) in 8 ml of dry benzene, and the reaction mixture was refluxed overnight. The triethylamine hydrochloride was removed by filtration and the filtrate was washed with dilute sodium hydrogen carbonate solution and water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent yielded a pale yellow oil (3.1 g, 82.6%).

IR (KBr): 1723 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ 3.66 (t, 2H, J=6.1 Hz), 4.64 (t, 2H, J=6.1 Hz), 7.37-7.63 (m, 3H), 8.08 (d, 2H, J=8.4 Hz).

1-(2-Benzoyloxyethyl)-4-(4'-pyridyl) pyridinium bromide

A mixture of 2-bromoethyl benzoate (0.41 g, 1.79 mmol) and 4,4'-dipyridine (0.43 g, 2.76 mmol) in 11 ml of N,N-dimethylformamide was stirred at 80 °C for 24 hours. The solution was filtered to remove the dication salt. The filtrate was poured into a large volume of ethyl ether. The yellow precipitate was collected and reprecipitated with ether.

IR (KBr): 1713 (C=O) cm^{-1}.

^1H NMR (DMSO-d_6): δ 4.75-4.85 (m, 2H), 5.03-5.15 (m, 2H), 7.52 (t, 2H, J=7.4 Hz), 7.67 (t, 1 H, J=7.4 Hz), 7.94 (d, 2H, J=7.0 Hz), 8.07 (d, 2H, J=6.2 Hz), 8.71 (d, 2H, J=6.9 Hz), 8.88 (d, 2H, J=6.2Hz), 9.37 (d, 2H, J=6.9 Hz).

Methyl α-bromotoluate (27)[27]

Compound **27** was prepared according to a literature method[27]. p-Toluyl chloride was

purified by fractional distillation before use. Bromine (80.6 g, 0.50 mol) was added dropwise at 180 °C to freshly distilled p-toluyl chloride (78.3 g, 0.51 mol) over a period of 2.5 hours, and the resulting reaction mixture was stirred for an additional 1.5 hours. The brominated mixture was allowed to cool to room temperature, and then 50 ml of methanol was added dropwise. After esterification for 30 minutes, the mixture was fractionally distilled under reduced pressure. The fraction at 110-124 °C/0.2-1 mmHg was collected. The crude product was recrystallized from methanol to give **27** as colourless crystals (40.5 g, 36.7%); m.p. 53.5-54.5 °C (lit.[27] 54-55°C).

IR (KBr): 1726 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ 3.93 (s, 3H), 4.51 (s, 2H), 7.47 (d, 2H, J=8.2 Hz); 8.02 (d, 2H, J=8.2 Hz).

4-Carbomethoxybenzaldehyde (28)

4-Carbomethoxybenzaldehyde was synthesized according to the procedure used by Sankaran and Marvel.[8] Compound **27** (71.2 g, 0.31 mol) was mixed with hexamethylenetetramine (87.4 g, 0.62 mol), 194 ml of water and 155 ml of acetic acid. The mixture was refluxed with stirring for 2 hours. Concentrated hydrochloric acid (93 ml) was then added and stirring was continued at room temperature for another 15 minutes. The cooled solution was extracted with ether, and the organic phase was washed with water, dilute sodium hydrogen carbonate solution and again with water. The extract was dried over anhydrous magnesium sulfate. Evaporation of the solvent and recrystallization of the residue from hexanes gave compound **28** (39.8 g, 78%); m.p. 60.5-61.5 °C (lit.[8] 61-62°C).

IR (KBr): 1726 (C=O), 1684 (CHO) cm^{-1}.

^1H NMR ($CDCl_3$): δ 3.98 (s, 3H), 7.97 (d, 2H, J=8.4 Hz), 8.21 (d, 2H, J=8.4 Hz), 10.11 (s, 1H).

5-(4-Carbomethoxyphenyl)-10,15,20-tritolylporphyrin (31 a)

A modification of Anton and Loach's procedure[9] was used for the synthesis of **31 a**. A mixture of Compound **28** (4.58 g, 0.028 mol) and distilled p-tolualdehyde **(29)** (10.06 g, 0.084 mol) in 450 ml of propionic acid was heated to reflux. Freshly distilled pyrrole **(30)** (7.5 g, 0.112 mol) was then added over a period of 15 minutes. Refluxing was continued for another 30 minutes, at which time 230 ml of ethylene glycol was added. The reaction mixture was placed in an ice bath for 1 hour, and then filtered. The purple crystals obtained were washed repeatedly with methanol-water mixture (1:1) and finally with 15 ml of methanol. The crystals, a mixture of mono, di, tri, and tetra-substituted arylporphyrins, were dried in vacuum for 24 hours (yield 3.25 g of mixed porphyrin). Compound **31 a** was separated from the mixed porphyrins by column chromatography. A chloroform-toluene (5:3) mixture was used as eluent. The second major band was collected. Compound **31 a** (1.17 g) was obtained from 2.655g of the mixed porphyrins. The overall yield of **31 a** was 5.9%. The ^{1}H NMR data was identical to the literature values.

^{1}H NMR ($CDCl_3$): δ -2.70 (s, 2H), 2.73 (s, 9H), 4.13 (s, 3H), 7.58 (d, 6H, J=7.8 Hz), 8.11 (d, 6H, J=7.8 Hz), 8.32 (d, 2H, J=8.4 Hz), 8.46 (d, 2H, J=8.4 Hz), 8.77-8.91 (m, 8H); ^{13}C NMR: 21.5, 52.4, 118.2, 120.4, 120.7, 127.4, 127.9, 129.5, 131.1, 134.5, 134.6, 137.4, 139.17, 139.22, 147.2, 167.4.

Hydrolysis of 31 a

Datta-Gupta and Bardos' procedure[10] was modified for the hydrolysis of **31 a**. Compound **31 a** (1.17 g, 1.64 mmol) was treated with 40 ml of 4% aqueous potassium hydroxide solution in 200 ml of freshly distilled THF. The mixture was stirred at reflux in the dark for 24 hours. After the THF was removed with a rotary evaporator, 15 ml of

water was added, and the residue was acidified with 0.1 N hydrochloric acid. The crystals were collected, washed well with water, and dried in vacuum for 24 hours to give 1.0836 g (95%) of the product.

^{1}H NMR (DMSO-d_6): δ -2.95 (s, 2H), 2.65 (s, 9H), 7.61 (d, 6H, J=8.0 Hz), 8.08 (d, 6H, J=8.0 Hz), 8.28-8.39 (m, 4H), 8.79-8.92 (m, 8H).

Anal. Calcd. for $C_{48}H_{36}N_4O_2$: C, 82.29; H, 5.14; N, 8.00. Found: C, 81.32; H, 4.71; N, 7.73.

5-(4-Benzoyl chloride)-10,15,20-tritolylporphyrin (32)

Kong and Loach's method[12] was used to prepare the acid chloride. A mixture of 5-(4-carboxyphenyl)-10,15,20-tritolylporphyrin (100 mg, 0.14 mmol) and thionyl chloride (9.93 g, 83.4 mmol) in 50 ml of benzene was refluxed for 12 hours. After removal of the solvent under reduced pressure, the acid chloride was dried in vacuum for 2 hours. The acid chloride was used without further purification.

5-⟨4-[2-(N,N-Dimethyl-4-aminophenyl)]ethoxycarbonyl phenyl⟩-10,15,20-tritolyl-porphyrin (23)

A mixture of **32** (0.1 g, 0.14 mmol), **34** (0.1 g, 0.61 mmol), and triethylamine (0.073 g, 0.72 mmol) in 50 ml of dry benzene was stirred at refluxing temperature for 24 hours. The benzene solution was washed with water three times and dried over anhydrous magnesium sulfate. The solvent was evaporated with a rotary evaporator. The residue was purified with flash chromatography, using hexanes/ethyl acetate (2:1) as eluent and the third band was collected, (0.049 g, 41%). The crude product was further purified by preparative HPLC (reverse phase octadecyl-silane bonded to LiChrosorb 10 μm; 50 cm; inner diameter 8mm; eluent tetrahydrofuran;water 65:35; UV detection at 415 nm). The relevant fraction was collected, the solvent evaporated. Then the BHT contaminant was

removed by further purification with thick layer chromatography using chloroform as eluent.

IR (KBr): 1717 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ -2.76 (s, 2H), 2.72 (s, 9H), 2.97 (s, 6H), 3.15 (t, 2H, J=7.1 Hz), 4.68 (t, 2H, J=7.1 Hz), 6.81 (d, 2H, J=8.5 Hz), 7.30 (d, 2H, J=8.5 Hz), 7.57 (d, 6H, J=7.8 Hz), 8.11 (d, 6H, J=7.8 Hz), 8.30 (d, 2H, J=8.2 Hz), 8.44 (d, 2H, J=8.2 Hz), 8.74-8.93 (m, 8H); ^{13}C NMR: 21.5, 34.4 ($\underline{C}H_2C_6H_5$), 40.8 (N-$\underline{C}H_3$), 66.3 (COO$\underline{C}H_2$), 113.0 (aromatic $\underline{C}$H), 118.3, 120.4, 120.6, 125.8 ($\underline{C}$), 127.4, 127.9, 128.1, 129.7 (aromatic $\underline{C}$H), 131.1, 134.50, 134.54, 137.4, 139.18, 139.22, 147.1, 149.6 ($\underline{C}$), 166.7 ($\underline{C}$OO). (The chemical shifts which were not assigned were very close to those of **31 a**)

FAB: $(M+H)^+$, m/z = 848

Anal. Calcd. for $C_{58}H_{49}N_5O_2$: C, 82.14; H, 5.82 ; N, 8.26. Found: C, 79.64; H, 5.81; N, 7.78.

5-[4-(2-bromoethyl) toluate]-10,15,20-tritolylporphyrin (35)

A mixture of **32** (0.1 g, 0.14 mmol), 2-bromoethanol (0.088 g, 0.7 mmol) and triethylamine (0.044 g, 0.43 mmol) in 50 ml of dry benzene was refluxed for 24 hours, and then cooled to room temperature. The resulting solution was washed with water three times and dried over magnesium sulfate. The solvent was evaporated with a rotary evaporator, the residue was chromatographed with benzene as eluent to give **35** (0.034 g, 30.1%). The product was further purified by recrystallization from chloroform--methanol. Although the NMR spectra of this compound are very clean, the elemental analysis result is not satisfactory. Since the ratio of the observed value of C, H and N to the theoretical value was found to be 0.97, suggesting that the problem was due to the incomplete combustion.

IR (KBr): 1725 (C=O) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ -2.75 (s, 2H), 2.72 (s, 9H), 3.82 (t, 2H, J=6.1 Hz), 4.84 (t, 2H, J=6.1 Hz), 7.57 (d, 6H, J=7.8 Hz), 8.11 (d, 6H, J=7.8 Hz), 8.34 (d, 2H, J=8.4 Hz), 8.49 (d, 2H, J=8.4 Hz), 8.74-8.93 (m, 8H); ^{13}C NMR: ($CDCl_3$): 21.5, 28.9 ($\underline{C}H_2Br$), 64.5 ($COO\underline{C}H_2$), 118.1, 120.4, 120.7, 127.4, 128.1, 129.0, 131.2, 134.5, 134.7, 137.4, 139.16, 139.21, 147.7, 166.3 ($\underline{C}OO$). (The chemical shifts which were not assigned were very close to those of **31 a**.)

FAB: $(M+H)^+$, m/z = 807/809.

Anal. Calcd. for $C_{50}H_{39}N_4O_2Br$: C, 74.35; H, 4.83; N, 6.94. Found: C, 72.26; H, 4.65; N, 6.75.

Viologen linked porphyrin (24)

Compound **35** (0.1 g, 0.12 mmol) was mixed with 4,4'-dipyridyl (0.2 g, 1.28 mmol), which had previously recrystallized from ethyl acetate, in 7 ml of N,N-dimethylformamide. The reaction mixture was stirred at 80 °C for 72 hours and then cooled to room temperature. After most of the N,N-dimethylformamide was removed with a rotary evaporator, a large volume of ether was added to precipitate the product. The precipitated solid was collected, washed well with ether and then acetonitrile to give **24** (0.038 g, yield 35%). Then the crude product was purified by thick layer chromatography, using benzene as eluent. The above procedure was performed in the dark. A reverse phase HPLC with tetrahydrofuran-water (65:35) as eluent was also tried. It was however found that the product decomposed in the column. Further purification was performed by thick layer chramatography using ethyl acetate as eluent to remove trace amount of 4,4'-dipyridyl.

IR (KBr): 1717 (C=O) cm^{-1}.

^{1}H NMR (DMSO-d_6): δ -2.95 (s, 2H), 2.66 (s, 9H), 5.01 (br, 2H), 5.20 (br, 2H), 7.63 (d, 6H, J=7.9 Hz), 8.08 (d, 8H, J=7.9 Hz), 8.37-8.41 (m, 4H), 8.76-8.86 (m, 12H), 9.50 (d,

2H, J=6.6 Hz); ^{13}C NMR: 20.9, 60.2 ($\underline{C}H_2N$), 64.9 ($COO\underline{C}H_2$), 118.2, 120.1, 120.4, 121.8 (dipyridyl $\underline{C}H$), 125.4 (dipyridyl $\underline{C}H$), 127.5, 127.9, 128.5, 131.4, 134.0, 134.4, 137.3, 138.2 ($\underline{C}$), 140.7, 146.0 (dipyridyl $\underline{C}H$), 146.5, 150.9 (dipyridyl $\underline{C}H$), 152.9 ($\underline{C}$), 165.9 ($\underline{C}OO$). (The chemical shifts which were not assigned were very close to those of **31 a**.)

FAB: $(M+H)^+$, m/z = 962/964, $(M-Br^-)^+$, m/z = 883.

Anal.Calcd. for $C_{60}H_{47}N_6O_2Br$: C, 74.76; H, 4.91; N, 8.71. Found: C, 73.05; H, 4.94; N, 9.33.

5,15-Bis(4-carbomethoxyphenyl)-10,20-ditolylporphyrin (31 b)

A modification of Anton and Loach's procedure was applied.[9] A mixture of **28** (11 g, 0.067 mol) and distilled p-tolualdehyde (8.05 g, 0.067 mol) in 550 ml of propionic acid was heated to reflux. Freshly distilled pyrrole (9.0 g, 0.134 mol) was then added over a period of 15 minutes. Refluxing was continued for another 30 minutes and then 270 ml of ethylene glycol was added. The reaction mixture was placed in an ice bath for 1 hour, and then filtered. The purple crystals obtained were washed repeatedly with a methanol-water (1:1) mixture and finally with 15 ml of methanol. The crystals, a mixture of mono, di, tri and tetra-substituted tetra-arylporphyrins, were dried in vacuum for 24 hours (yield 4.14 g of mixed porphyrin). Desired compound **31 b** was separated from the mixed porphyrins using column chromatography. A chloroform-hexanes-ethyl acetate (2:3:1) mixture was used as eluent. The third major band was collected. Compound **31 b** was obtained from 4.14 g of the mixed porphyrin used. The overall yield for the reaction was 3.1%. The ^1H NMR data was found to be identical to the literature values.

^1H NMR ($CDCl_3$): δ -2.69 (s, 2H), 2.74 (s, 6H), 4.15 (s, 6H), 7.58 (d, 4H, J=7.9 Hz), 8.14 (d, 4H, J=7.9 Hz), 8.35 (d, 4H, J=8.2 Hz), 8.49 (d, 4H, J=8.2 Hz), 8.83-8.97 (m, 8H).

Hydrolysis of 31 b[10]

A literature was applied for the hydrolysis of **31 b**. Compound **31 b** (0.79 g, 1.04 mmol) was mixed with 135 ml of freshly distilled THF and 50 ml of 4% aqueous potassium hydroxide solution. The mixture was stirred at reflux in the dark for 24 hours. The THF was then evaporated using a rotary evaporator. Water (10 ml) was added to the residue before it was acidified with 0.1 N hydrochloric acid. The crystals were collected, washed well with water, and dried in vacuum for 26 hours to give 0.72 g (95%) of the product.

^{1}H NMR (DMSO-d_6): δ -2.69 (s, 2H), 2.66 (s, 6H), 7.62 (d, 4H, J=7.8 Hz), 8.08 (d, 4H, J=7.8 Hz), 8.32 (d, 4H, J=8.2 Hz), 8.37 (d, 4H, J=8.2 Hz), 8.80-8.86 (m, 8H).

Anal. Calcd. for $C_{48}H_{36}N_4O_4$: C, 78.9; H, 4.66; N, 7.67. Found: C, 75.33; H, 4.90; N, 7.12.

5,15-Bis(4-benzoyl chloride)-10,20-ditolylporphyrin (36)

This acid chloride was prepared by the same method as for the preparation of **32**.

5-⟨4-[2-(N,N-Dimethyl-4-aminophenyl)]ethoxycarbonylphenyl⟩-15-
-[4-(2-bromoethyl toluate)]-10,20-ditolylporphyrin (37)

A mixture of **36** (0.12 g, 0.16 mmol), 2-bromoethanol (0.018 g, 0.14 mmol), and triethylamine (0.44 g, 0.43 mmol) in 50 ml of dry benzene was refluxed for 24 hours, followed by addition of **34** (0.084 g, 0.51 mmol). The reaction mixture was stirred at reflux for another 24 hours. After cooling to room temperature, the mixture was washed three times with water, and dried over anhydrous magnesium sulfate. After the solvent was evaporaed with a rotary evaporator, the residue was subject to flash chromatography using chloroform/hexanes/ethyl acetate (1:3:1) as the eluent, and the second major band

was collected (0.051g, yield 35%). But in the ^{1}H NMR spectrum, two impurity triplets showed up at δ 3.9 and 4.7 ppm. Recrystallization from chloroform/methanol did not remove the impurity. Then the product was purified by preparative HPLC (reverse phase octadecyl-silane bonded to LiChrosorb 10 μm; 50 cm; inner diameter 8 mm; eleunt Tetrahydrofuran;water 65:35; UV detection at 415 nm). The relevant fraction was collected, the solvent evaporated.

IR (KBr): 1718 (C=O) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ -2.76 (s, 2H), 2.72 (s, 6H), 2.97 (s, 6H), 3.15 (t, 2H, J=7.1 Hz), 3.82 (t, 2H, J=6.0 Hz), 4.68 (t, 2H, J=7.1 Hz), 4.84 (t, 2H, J=6.0 Hz), 6.80 (d, 2H, J=8.7 Hz), 7.30 (d, 2H, J=8.7 Hz), 7.58 (d, 4H, J=7.8 Hz), 8.11 (d, 4H, J=7.8 Hz), 8.31 (d, 2H, J=5.8 Hz), 8.35 (d, 2H, J=5.8 Hz), 8.46 (d, 2H, J=8.3 Hz), 8.50 (d, 2H, J=8.3 Hz), 8.73-8.93 (m, 8H); ^{13}C NMR: 21.5, 28.9 ($\underline{C}H_2Br$), 34.4 ($\underline{C}H_2C_6H_5$), 40.8 ($N\underline{C}H_3$), 64.6 ($COO\underline{C}H_2CH_2Br$), 66.3 ($COO\underline{C}H_2CH_2C_6H_5$), 113.0 (aromatic $\underline{C}H$), 118.3, 118.7, 121.0, 125.8 ($\underline{C}$), 127.5, 127.9, 128.1, 129.1, 129.7 (aromatic $\underline{C}H$), 131.1, 134.5, 134.6, 137.6, 138.9, 139.0, 146.9, 147.5, 149.7 ($\underline{C}$), 166.3 ($\underline{C}OO$), 166.8 ($\underline{C}OO$). (The chemical shifts which were not assigned were very close to those of **31 a**.)

FAB: $(M+H)^+$, m/z = 984/986.

Anal. Calcd. for $C_{60}H_{50}N_5O_4Br$: C, 73.17; H, 5.08; N, 7.11. Found: C, 69.76; H, 5.26; N, 6.37.

Prepararion of viologen and N,N-dimethylaniline linked porphyrin (22)

A mixture of **37** (0.088 g, 0.1 mmol) and 4,4-dipyridine (0.17 g, 1.1 mmol), which had been previously recrystallized from ethyl acetate, in 7 ml of N,N-dimethylformamide was stirred at 80 °C for 5 days. Most of the solvent was removed with a rotary evaporator and a large volume of ether was added. The solid precipitate was collected and washed well with ether to remove the unreacted 4,4'-dipyridine. The product was

purified by thick layer chromatography, using chloroform as the eluent, and the bottom band was collected (0.019 g, 17.9%). The trace amount of 4,4-dipyridyl left was removed by thick layer chromatography using ethyl acetate as eluent. The above procedure was performed in the dark.

IR (KBr): 1717 (C=O) cm^{-1}.

^1H NMR (DMSO-d_6): δ -2.96 (s, 2H), 2.66 (s, 6H), 2.86 (s, 6H), 3.05 (m, 2H), 4.58 (m, 2H), 5.00 (br, 2H), 5.20 (br, 2H), 6.73 (d, 2H, J=8.2 Hz), 7.24 (d, 2H, J=8.2 Hz), 7.63 (d, 4H, J=8.4 Hz), 8.09 (d, 6H, J=8.4 Hz), 8.36-8.38 (m, 8H), 8.70-8.85 (m, 12H), 9.50 (d, 2H, J=6.6 Hz); ^{13}C NMR: 21.0, 34.2 ($\underline{C}H_2C_6H_5$), 40.8 ($N\underline{C}H_3$), 59.3 ($\underline{C}H_2N$), 63.8 ($COO\underline{C}H_2CH_2N$), 66.0 ($COO\underline{C}H_2CH_2C_6H_5$), 112.6 (aromatic $\underline{C}H$), 118.2, 118.5, 120.6, 121.9 (dipyridyl $\underline{C}H$), 125.3 (dipyridyl $\underline{C}H$), 125.4 (aromatic $\underline{C}$), 127.6, 127.9, 128.6, 129.4 (aromatic $\underline{C}H$), 131.4, 134.1, 134.5, 137.4, 138.1 (dipyridyl $\underline{C}$), 140.7, 146.0 (dipyridyl $\underline{C}H$), 146.4, 149.2 (aromatic $\underline{C}$), 150.9 (dipyridyl $\underline{C}H$), 152.9 (dipyridyl $\underline{C}$), 165.3 ($\underline{C}OO$), 165.8 ($\underline{C}OO$). (The chemical shifts which were not assigned were very close to those of **31 a**.)

FAB: $(M+H)^+$, m/z = 1139/1141; $(M-Br^-)^+$, m/z = 1060.

4. FLUORESCENCE STUDIES

4.1 Theory

Luminescence is the emission of photons from electronically excited states which occur in molecules as a result of a series of physical phenomena, normally beginning with the absorption of light. Luminescence is divided into two types, depending upon the nature of the ground and excited states. In a singlet excited state, the electron in the higher-energy orbital has the opposite spin orientation to the second electron in the lower orbital. These two electrons are said to be paired. In a triplet state these electrons are unpaired, i.e. their spins have the same orientation. The return from an excited singlet state to the ground state does not require an electron to change its spin orientation. A change in spin orientation is needed for a triplet state to return to the singlet ground state. Fluorescence is the emission which results from the transition of an electron from a higher singlet state to a ground singlet state. Such transitions are quantum mechanically "allowed" and the emission rates are typically near 10^8 sec^{-1}. Phosphorescence is the emission which results from transition between states of different multiplicity, generally a triplet excited state returning to a singlet state.[1]

The absorption and emission of light for a luminescent molecule is nicely illustrated by the partial energy level diagram as in Fig. 4-1.[2]

The lowest heavy horizontal line represents the ground state energy of the molecule, which is normally a singlet state and is labeled S_0. The upper heavy lines are energy levels for the ground vibrational states of three excited electronic states. The two lines on the left represent the first (S_1) and second (S_2) electronic singlet states. The one on

the right (T_1) represents the energy of the first electronic triplet state. Numerous vibrational energy levels are associated with each of the four electronic states, as represented by the lighter horizontal lines. The transitions between the various electronic levels are expressed by the vertical lines.

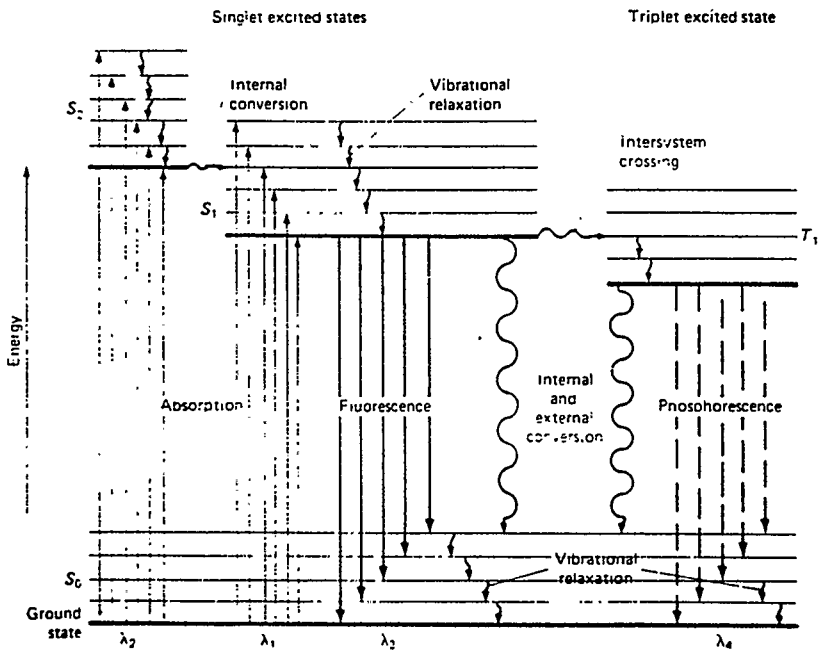


Fig. 4-1 Partial energy diagram for a luminescent system.[2]

Here we focus on the features of fluorescence since we carry out fluorescence spectroscopy study in our research.

The deactivation of porphyrin S_1 state, P^*, may be caused by fluorescence emission, intersystem crossing, internal conversion or photochemical reaction.[3]

$$P \xrightarrow{h\nu} P^*$$
$$P^* \xrightarrow{k_f} P + h\nu$$
$$P^* \xrightarrow{k_{ic}} {}^3P^*$$
$$P^* \xrightarrow{k_r} E$$

where k_f, k_{ic}, and k_r are the rate constant of fluorescence, internal conversion and intersystem crossing, quenching of fluorescence and photochemical reaction. E is the product of the photochemical reaction. P^* can also be quenched by a quencher A.

$$P^* + A \xrightarrow{k_q} P^{+\cdot} + A^{-\cdot}$$

where k_q is the rate constant of fluorescence quenching.

The quantum yields of fluorescence, ϕ_f and ϕ_f^o, in the presence and absence of the quencher, can be expressed in terms of the rates of processes competing for deactivation of the lowest excited singlet state. ϕ_f^o is given by:

$$\phi_f^o = \frac{k_f}{k_f + k_{ic} + k_r} = \frac{k_f}{k_f + \Sigma k_d} \qquad (1)$$

where Σk_d is the sum of the rate constants for deactivation of the lowest excited singlet state by all competitive radiationless processes. In the presence of a quencher, we have

$$\phi_f = \frac{k_f}{k_f + \Sigma k_d + k_q[A]} \qquad (2)$$

Ratioing (2) to (1) yields (3).

$$\frac{\phi_f}{\phi_f^o} = \frac{1}{1 + k_q\tau_o[A]} \qquad (3)$$

where τ_o is the lifetime of the spin allowed excited state in the absence of the quencher, A, and [A] is the concentration of the quencher.

Equations (2) and (3) apply to intermolecular fluorescence quenching. When the quencher, A, is covalently linked to the light absorber and if the concentration is very low so that no intermolecular quenching occurs, the quenching is a unimolecular process and the equation can be rewritten as:

$$\frac{\phi_f}{\phi_f^o} = \frac{1}{1 + k_q\tau_o} \qquad (4)$$

Since the lifetime τ_o can be measured by time-resolved fluorescence spectroscopy, the rate constant k_q could be obtained by measuring τ_o and the ratio of quantum yields of fluorescence in the presence and absence of the quencher. Alternatively, since the lifetimes of the excited state in the absence (τ_o) and presence (τ) of the quencher are given by[1]

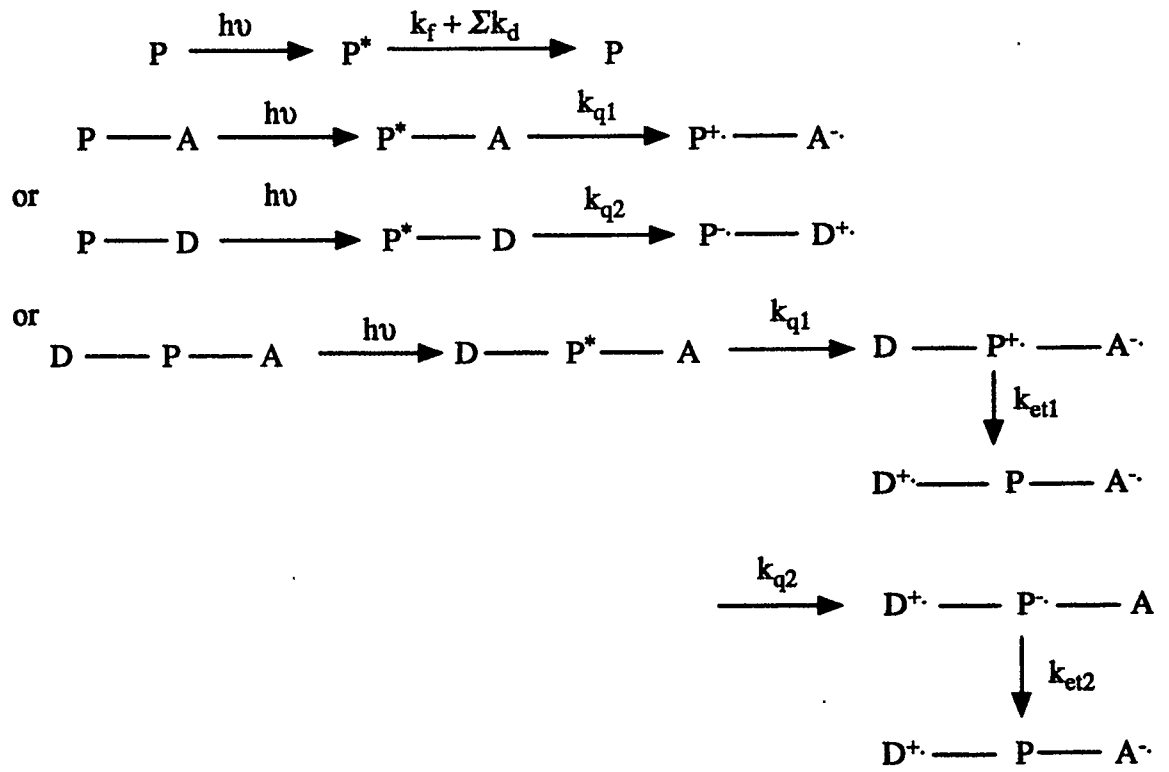
$$\tau_o = \frac{1}{k_f + \Sigma k_d} \qquad (5)$$

$$\tau = \frac{1}{k_f + \Sigma k_d + k_q} \qquad (6)$$

and therefore

$$\frac{\phi_f}{\phi_f^o} = \frac{\tau}{\tau_o} \qquad (7)$$

In our study, we have a linear molecule in which an electron acceptor and an electron donor are covalently linked to the light absorber, and we also have the reference compounds, the light absorber, and the electron acceptor linked light absorber and the electron donor linked light absorber. In this case, the photoinduced electron transfer reactions involved could be illustrated by the scheme as follows:



and

$$\frac{\phi_f}{\phi_f^o} = \frac{1}{1 + k_q\tau_o} \qquad (8)$$

where k_q is the electron transfer rate constant for the linear molecules with either the electron acceptor or/and the electron donor. When both the electron acceptor and the electron donor were bonded to the porphyrin, the k_q observed should be expressed as:

$$k_q = k_{q1} + k_{q2} \qquad (9)$$

based on the assumption that the two quenching processes in D-P-A molecule are independent.

The above equations are derived by assuming that the rotation of chromophores around single bonds is much faster than the rate of electron transfer. Under this assumption, the molecules can adopt all possible conformations during porphyrin excitation lifetime and the rate constant is the time-average k_q (averaged over all possible conformations).

In reality, the rate of electron transfer is comparable to the rate of σ bond rotation. According to the Marcus and Levich theories, the rate of electron transfer (here the k_q) is distance and orientation dependent. The k_q depends on the center-to-center distance of the light absorber and the quencher (the electron acceptor or the electron donor). Also, the k_q is a function of the relative orientation of P and A or P and D. Thus, the rate of electron transfer in such systems can not be described by a single rate constant. The k_q calculated using equation (8) would be the effective quenching rate constant.

4.2 Experimental

The samples for fluorescence study were prepared and purified as described in chapter 3. Dichloromethane used for spectral measurements was purified by washing with concentrated sulfuric acid, water, 5% sodium bicarbonate solution, water again and dried over calcium chloride followed by distillation over calcium hydride. Acetonitrile used was spectrograde as received from BDH. All sample solutions for the static-state

fluorescence measurement were deoxygenated by irrigating with an argon or nitrogen gas stream. Sample solutions for time-resolved fluorescence study were degassed by freeze-pump-thaw, 5 cycles and sealed under vacuum. All the spectroscopic measurements were carried out at room temperature.

UV-visible absorption spectra were recorded on a Perkin-Elmer Array 3840 UV/VIS spectrophotometer.

Fluorescence emission spectra were recorded on a PTI Fluorescence instrument. The fluorescence intensities were obtained by integration along the emission spectrum between 610 and 750 nm and corrected with the absorbance obtained from UV-Vis absorption spectra.

Time-resolved fluorescence measurements were conducted on a PTI LS-100 Luminescence spectrophotometer by the method of time-correlated single photon counting (TCSPC). A hydrogen-discharging lamp was used as the excitation source.

4.3 Results and Discussion

4.3.1 Visible Spectra

The spectral characteristics of six porphyrins in the visible range were studied in acetonitrile solution and exhibit a normal free-base porphyrin pattern[4,5], and showed maxima as in Table 4-1.

The absorption peaks of these porphyrins are interpreted as (π,π^*) in origin.[4] It could be seen that all the visible spectra (Fig.4-2) showed are characteristic of free-base porphyrins. An exceedingly intense band (sometimes called the Soret band) appears at

about 414 nm. It is a B (0,0) band that resulted from S_0 to S_2 transition. Four visible bands are seen between 510 and 700 nm which are D_{2h} Q bands. They resulted from S_0 to S_1 transition. Unlike those metalloporphyrins which have only two Q bands, in free-base porphyrins, the D_{4h} symmetry is broken into D_{2h} symmetry by the actural proton axis.[6] Thus Q(0,0) splits into $Q_x(0,0)$ and $Q_y(0,0)$ for free-base porphyrins. Each band has a vibration overtone, $Q_x(1,0)$ and $Q_y(1,0)$ respectively. We can characterize the visible bands between 500 and 700 nm as follows: 512.4 is a $Q_y(0,0)$ band, 548.5 is a $Q_y(1,0)$ band, 590 is a $Q_x(0,0)$ band and 645 is a $Q_x(1,0)$ band.

Table 4-1. Visible Absorption Maxima of Porphyrins in Acetonitrile

Porphyrin	λ_{max}(nm)				
Porphyrin methyl ester (**31 a**)	414.2	512.9	547.5	588.9	647.2
Porphyrin-donor bromoester(**37**)	416.1	512.9	547.5	589.9	645.2
Porphyrin dimethyl ester(**31 b**)	414.2	512.9	547.5	588.0	645.2
Porphyrin-Donor (**23**)	416.3	513.9	548.5	589.9	646.2
Porphyrin-Acceptor (**24**)	416.1	512.9	548.5	588.9	645.2
Donor-Porphyrin-Acceptor (**22**)	416.1	513.9	548.5	589.9	645.2

From Table 4-1 and Fig. 4-2, it was found that the absorption bands of the porphyrin compounds with covalently linked electron acceptor or electron donor are almost the same except that the Soret bands are red-shifted compared to porphyrin methyl ester and porphyrin dimethyl ester. No band broadening or appearance of new peaks was observed for compounds **22, 23, 24** and **37**, which suggested that no ground-state complexes

between P and D or P and A were formed. This is reasonable considering that the bridging chains (two methylene groups) between P and D or P and A are not long enough to allow D and A groups to fold back on the porphyrin ring.

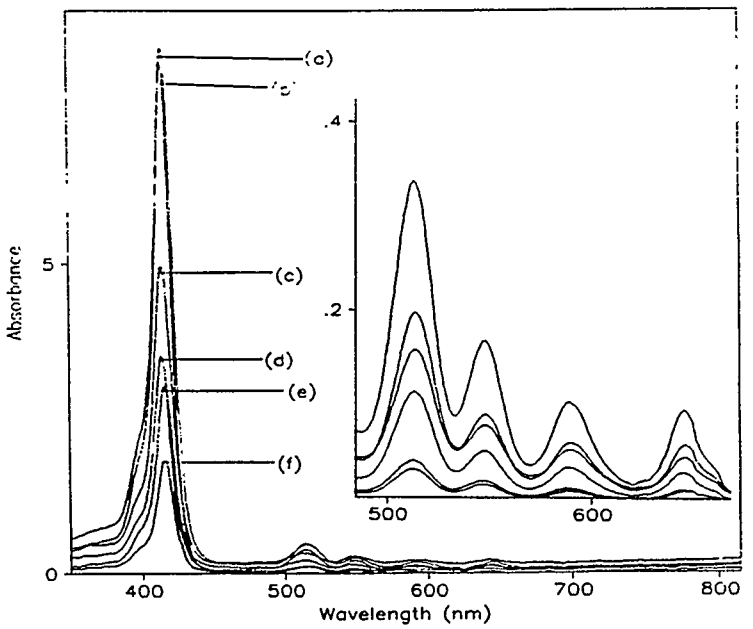


Fig. 4-2 Visible absorption spectra of porphyrins.

(a)P-A (**24**), (b) P-D (**23**), (c) Porphyrin methyl ester (**31 a**), (d) Porphyrin dimethyl ester (**31 b**), (e) Porphyrin-donor bromoethyl ester (**37**), (f) D-P-A (**22**).

4.3.2 Fluorescence Spectra

The fluorescence spectra of porphyrin methyl ester (P), porphyrin-donor (P-D), porphyrin-acceptor (P-A) and donor-porphyrin-acceptor (D-P-A) in acetonitrile were recorded at different excitation wavelengths. The fluorescence spectra of different porphyrins with excitation wavelengths of 590.9 nm are shown in Fig. 4-3. The concentration of the sample solutions for the measurement was adjusted in order to keep the absorbance of the excited wavelength constant for all samples.

From Fig. 4-3, we can see that the fluorescence intensities of P-D, P-A and D-P-A are all

smaller compared to that of the porphyrin without a quencher, indicating that the photoexcited singlet state is quenched by the covalently linked donor or acceptor. The relative fluorescence intensities measured in two solvents at each excitation wavelength corrected by absorbance are shown in Table 4-2. The numbers in the brackets are the relative fluorescence intensities of D-P-A compared to those of compound **31 b**, as two ester groups existed in the D-P-A molecule.

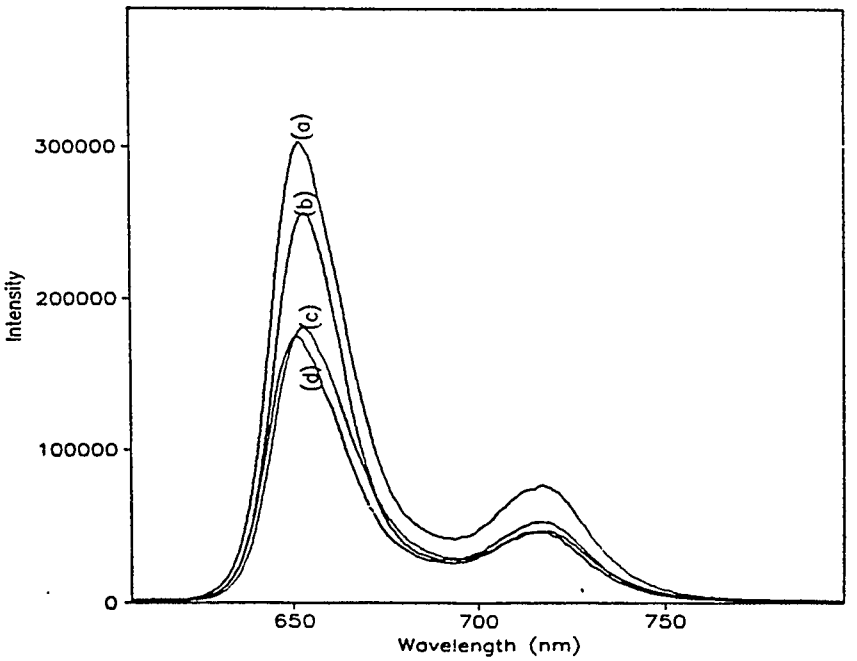


Fig. 4-3 Relative fluorescence spectra of porphyrins excited at 590.9 nm in deoxygenated CH_3CN. (a) P (**31 a**), (b) P-A (**24**), (c) P-D (**23**), (d) D-P-A (**22**)

As shown in Table 4-2, when acetonitrile was used as solvent, the relative intensity of P-D was smaller than that of P-A, indicating that N,N-dimethylaniline was a more efficient quencher than the electron acceptor, viologen. From the data, we can see that reductive quenching is favored in this system in acetonitrile instead of the normally observed oxidative quenching.[7] But the oxidative quenching is favored in

dichloromethane. This could be explained by the free energy change in the electron transfer quenching reaction. (The free energy change of the reaction was calculated as described in chapter 2. The half-wave potentials of the three compounds with acetonitrile as solvent were literature values, while those with dichloromethane as solvent were kindly measured by Dr. A.S. Hinman. For half-wave potential values of different compounds, please refer to Table A-1 in the appendix.)

Table 4-2 Relative intensities of porphyrins

Porphyrin	ϕ_f/ϕ_f^o (%)				
	380.0 nm	415.1 nm	513.9 nm	548.5nm	590.9 nm
in acetonitrile					
P (31 a)		100	100	100	100
P' (31 b)		82	105	117	124
P-D (23)		51	65	76	72
P-A (24)		69	77	91	83
D-P-A (22)		52(63)	71(68)	75(64)	69(56)
in dichloromethane					
P (31 a)	100	100	100	100	100
P' (31 b)	84	82	92	91	95
P-D (23)	69	89	77	80	84
P-A (24)	65	54	72	74	76
D-P-A (22)	64(77)	55(67)	74(80)	77(85)	79(83)

In the donor quenching case, we have the free energy change, $\Delta G_{P\text{-}D}$,

in acetonitrile $\Delta G_{P\text{-}D} = 23.06\ (0.81 + 1.06 - 2.05) = -4.15$ kcal/mol

in dichloromethane $\Delta G_{P\text{-}D} = 23.06\ (0.94 + 1.12 - 2.05) = 0.23$ kcal/mol

In the acceptor quenching case, we have $\Delta G_{P\text{-}A}$,

in acetonitrile $\Delta G_{P\text{-}A} = 23.06\ (1.06 + 0.96 - 2.05) = -0.69$ kcal/mol

in dichloromethane $\Delta G_{P\text{-}A} = 23.06\ (1.10 + 0.80 - 2.05) = -3.46$ kcal/mol

When comparing the relative intensities of P-A and P-D in the two solvents at the same excitation wavelength, it was found that a more negative ΔG led to a higher degree of quenching as expected.

Note that the relative intensity of D-P-A is comparable to that of P-D or P-A with a lower relative intensity. This is quite reasonable when taking the conformation of the D-P-A molecule into account. It is known that the fluorescence quenching is distance and relative orientations dependent. A shorter distance between the quencher and the fluorophore will lead to a higher degree of the fluorescence quenching (lower relative intensity). In P-D or P-A, A or D can get very close to P, but in D-P-A, both D and A may have relatively long distance from P due to the steric repulsion between A and D.

4.3.3 Measurement of Fluorescence Lifetimes

The time-resolved decay of fluorescence of the four porphyrins in acetonitrile was measured by the single-photon-counting method at three different excitation wavelengths and the average fluorescence lifetimes were obtained. Since a double exponential decay was observed for the fluorescence intensity decay of reference compound **31 a**, instead of a single exponential decay as it should be, the data obtained in acetonitrile are

included in Appendix A. The data obtained in dichloromethane at excitation wavelengths of 380.0 nm, 513.9 nm and 548.5 nm are tabulated in Table 4-3.

Table 4-3 Fluorescence lifetimes of porphyrins

Porphyrin	<τ> (ns)		
	380.0 nm	513.9 nm[a]	548.5 nm[a]
P (31 a)	9.3	9.1	9.2
P-A (24)	7.3*	6.7*	7.1*
P-D (23)	8.1*	8.2*	7.8*
D-P-A((22)	6.9*	6.6*	6.8*

* Double-exponential decay was observed and <τ> is calculated as $(A_1\tau_1+ A_2\tau_2)/(A_1+A_2)$. τ_1 and τ_2 are the long and short lifetime measured while A_1 and A_2 are the amplitude coefficients for τ_1 and τ_2.

a. Please refer to reference 14, and these two sets of data were kindly measured by Dr. Guojun Liu.

The fluorescence quantum ratios of the porphyrins obtained by steady-state measurement and those by time-resolved method (τ/τ_o) in dichloromethane are compared in Table 4-4. The rate constants of fluorescence quenching of these compounds calculated with equation (8) are also listed in Table 4-4.

The results from the lifetime measurements are higher than those obtained from intensity measurements at the excitation wavelength of 380 nm. One possible explanation is the formation of nonfluorescent ground-state complex which quench the fluorescence and can not be detected by the TCSPC instrument. But this contradicts to the result from the

absorption spectroscopic study. From Table 4-4, we found that at the excitation wavelength of 513.9 and 548.5 nm, the results for P-A and D-P-A from the lifetime measurement agreed with those from the intensity measurement within experimental error. This also proved that no ground-state complexes were formed. For P-D, at 548.5 nm, the results from the two methods agreed while at 513.9 nm, the result from the intensity method was still higher. The reason for this is unknown.

Table 4-4 Relative fluorescence intensities and rate constants of porphyrins

Porphyrin	ϕ/ϕ_o (%)	$<\tau>/\tau_o$(%)	$k_q \times 10^{-7}$ s^{-1}
λ_{ex}= 380 nm			
P-D (23)	69	85	4.8
P-A (24)	65	72	5.8
D-P-A (22)	64	71	6.0
λ_{ex}= 513.9 nm			
P-D (23)	77	90	3.3
P-A (24)	72	74	4.3
D-P-A (22)	74	72	3.9
λ_{ex}= 548.5 nm			
P-D (23)	80	85	2.7
P-A (24)	74	77	3.9
D-P-A (25)	77	74	3.3

From Table 4-4, we also find that the quantum ratios from the TCSPC method are very close at different excitation wavelengths while those determined by intensity measurement agreed with each other at the wavelengths greater than 500 nm. At the excitation wavelengths of 380 nm and 415 nm (refer to Table 4-2), the quantum ratios are significantly lower than those at the excitation wavelengths greater than 500 nm. This phenomenon can be explained by assuming that the excited states of P formed by exciting P at 380 or 415 nm, and those greater than 500 nm are different. In the case of 380 and 415 nm, P is excited into its S_2 state. The S_2 state relaxes quickly to S_1 and the fluorescence is emitted due to the subsequent S_1 to S_0 transition. In a TCSPC experiment, we study the fluorescence quenching after the formation of S_1 state. In the steady-state measurement, the study of fluorescence quenching starts at the time of light absorption because one must know exactly how much light is absorbed to excite P to its S_2 state. The relative fluorescence efficiency ϕ/ϕ_0 from the intensity measurement is a product of the following two terms:

$$\phi/\phi_0 = (\eta/\eta_0) \times (\zeta/\zeta_0)$$

where η and η_0 are the efficiencies of the S_1 state turnout from S_2 state of a triad or a diad molecule and **31 a**, respectively; and ζ and ζ_0 are the efficiencies of fluorescence emission from a triad or a diad molecule and from **31 a**. In general

$$\zeta/\zeta_0 = \langle\tau\rangle/\tau_0$$

Only at long wavelengths,

$$\phi/\phi_0 = \langle\tau\rangle/\tau_0$$

because $(\eta/\eta_0) = 1$. The fact that ϕ/ϕ_0 is less that $<\tau>/\tau_0$ means that $(\eta/\eta_0)<1$ at the excitation wavelengths of 380 and 415.1 nm. This suggests that there are more mechanisms for the deactivation of S_2 state in P-D, P-A, and D-P-A than in **31 a.** It might be due to the electron transfer quenching. Since the rate of S_2 to S_1 transition is extremely fast, the rate of electron transfer from D to P^{**} or from P^{**} to A, where P^{**} stands for P in its S_2 state, must be extremely fast. This is possible because the energy required for the S_0 to S_2 transition is much larger than $E_{0,0}$ and will lead to a much negative free energy change of electron transfer and then a much larger rate of electron transfer.[8] This represents the first evidence of ultra-electron transfer from fluorescence studies.

The k_q values listed in Table 4-4 were quite close to those obtained in porphyrin-viologen[9] and porphyrin-quinone[10] systems. The k_q of P-A is faster than that of P-D. Recall that $\Delta G_{P\text{-}A} < \Delta G_{P\text{-}D}$, and it is understandable that $k_{q(P\text{-}A)} > k_{q(P\text{-}D)}$. So the result is in agreement with the theoretical prediction. The k_q in D-P-A is comparable to that in the sum of $k_{q(P\text{-}A)}$ and $k_{q(P\text{-}D)}$ as predicted in equation 9, which suggests that the contributions of P-A and P-D are not independent. Although both the oxidative and reductive quenching occurs in the D-P-A molecule, the conformation of the P-A and P-D part in the triad are not the same as those of P-A and P-D molecules. The third component in the triad affects the rate of the electron transfer from P to A, or from D to P as we discussed before. The actual rate constant of electron transfer from P to A and from D to P are not the same as $k_{q(P\text{-}A)}$ and $k_{q(P\text{-}D)}$.

5. CONCLUSIONS

In our study, the concept of designing a photomagnetic molecule has been proposed for the first time. A cyclic photomagnetic molecule containing a $Ru(bpy)_3^{2+}$ light absorber, a viologen electron acceptor and an N,N-diethylaniline electron donor was designed and the synthesis was attempted.

A linear molecule containing a porphyrin light absorber, a viologen electron acceptor and an N,N-dimethylaniline electron donor was synthesized. Two reference compounds, a viologen linked porphyrin and an N,N-dimethylaniline linked porphyrin have also been prepared.

These compounds were studied by UV-vis spectroscopy, steady-state and time-resolved fluorescence spectroscopy. This represents the most systematic studies of electron transfer in a triad molecule. In previous studies, only one of the model compounds, donor-light absorber or light absorber-acceptor was employed as a control for studying electron transfer in triad molecules. It has been assumed that either the oxidative or the reductive quenching occurred in a triad molecule. Our study showed that both the oxidative and reductive quenching could happen at the same time in the triad molecule. The study of excitation wavelength dependence of fluorescence quenching has been carried out. For the first time, the results of fluorescence quenching obtained from the time-correlated single photon counting and those from steady-state study have been correlated and found the S_2 state of P can be quenched by D and A probably via an ultra-fast electron transfer mechanism.

The relative importance of donor and acceptor quenching could be tuned by varying the reaction medium. In acetonitrile, the electron donor was a better quencher than the acceptor. In dichloromethane, the electron acceptor became a better quencher. Those results are in agreement with the theoretical predictions.

For the solvents used, it was observed that the quenching efficiency of the triad molecule is comparable to that of a reference compound with a higher degree of fluorescence quenching at different excitation wavelengths. The rate constants of fluorescence quenching were calculated. The rate constant of the triad molecule was not the sum of those of the porphyrin-donor and porphyrin-acceptor. This suggests that the contribution of fluorescence quenching from the donor and the acceptor are not independent. This is because the two quencher groups are bulky and they repell one another and thus, can not approach porphyrin as close as they can in a diad molecule. This is the first report of examining the co-operative effect of two quenchers both covalently attached to the same chromophore

This study provides insight into the electron migration path in a triad molecule, which will be useful for the electron transfer studies in future cyclic photomagnetic molecules.

6. SUGGESTIONS FOR FUTURE STUDIES

A cyclic molecule should be prepared by modifying the structure of compound **22** and cyclizing it. Since the distance between the light absorber and the quencher plays an important role on the rate constant of electron transfer, we should change the number of methylene groups between the light absorber, and the electron acceptor or the donor to study the distance effect. The other thing we should do is to modify the structure of compound **22** and **24** by adding a methyl group at the open end of the dipyridyl group and to compare the electron transfer behavior to that of the compounds we made. Since the half-wave potentials of the modified compounds will be different, we can compare the experimental result with the theoretical prediction to make this study of electron transfer more complete.

Further study of the electron transfer mechanism by flash photolysis technique is also needed. In a flash photolysis experiment, the porphyrin will be excited by a short light pulse. The absorption spectra of transient species at different times after the pulse are measured. From the changes in the absorption spectra, we can know exactly what species are formed after fluorescence quenching. We will also know the lifetimes of the transient species and their interconversion. Also, we can know the second electron transfer step after the primary oxidative or reductive quenching.

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APPENDIX A

Table A-1 Half-Wave Potentials*

Compound	$E_{1/2}$, V (CH_3CN)	$E_{1/2}$, V (CH_2Cl_2)
N,N-Dimethylaniline	0.81[a]	0.94
Viologen	-0.96[b]	-0.80
Porphyrin (31 a)	1.06[c,d]	1.10
Porphyrin (31 a)	-1.06[c,d]	-1.12

* vs. SCE; a. ref. 29 in Chapter 2; b. ref. 32 in Chapter 2; c. ref 30 in Chapter 2; d. measured in butylnitrile

Table A-2 Fluorescence Lifetimes of Porphyrins (in CH_3CN)

	$\langle\tau\rangle$* (ns)		
Porphyrin	430 nm	514 nm	548 nm
P (31 a)	11.5	11.6	11.0
P-A (24)	9.9	10.8	11.1
P-D (23)	6.6	8.8	9.2
D-P-A (22)	8.3	10.0	9.9

* Double-exponential decay was observed and $\langle\tau\rangle$ is calculated as $(A_1\tau_1+ A_2\tau_2)/(A_1+A_2)$. τ_1 and τ_2 are the long and short lifetime measured while A_1 and A_2 are the amplitude coefficients for τ_1 and τ_2.

Table A-3 Relative fluorescence intensities of porphyrins (in CH_3CN)

	514 nm		548 nm	
Porphyrin	ϕ/ϕ_o (%)	τ/τ_o (%)	ϕ/ϕ_o(%)	τ/τ_o (%)
P-A (24)	77	93	91	101
P-D (23)	65	75	76	83
D-P-A (22)	72	86	75	89

APPENDIX B - NMR Spectra

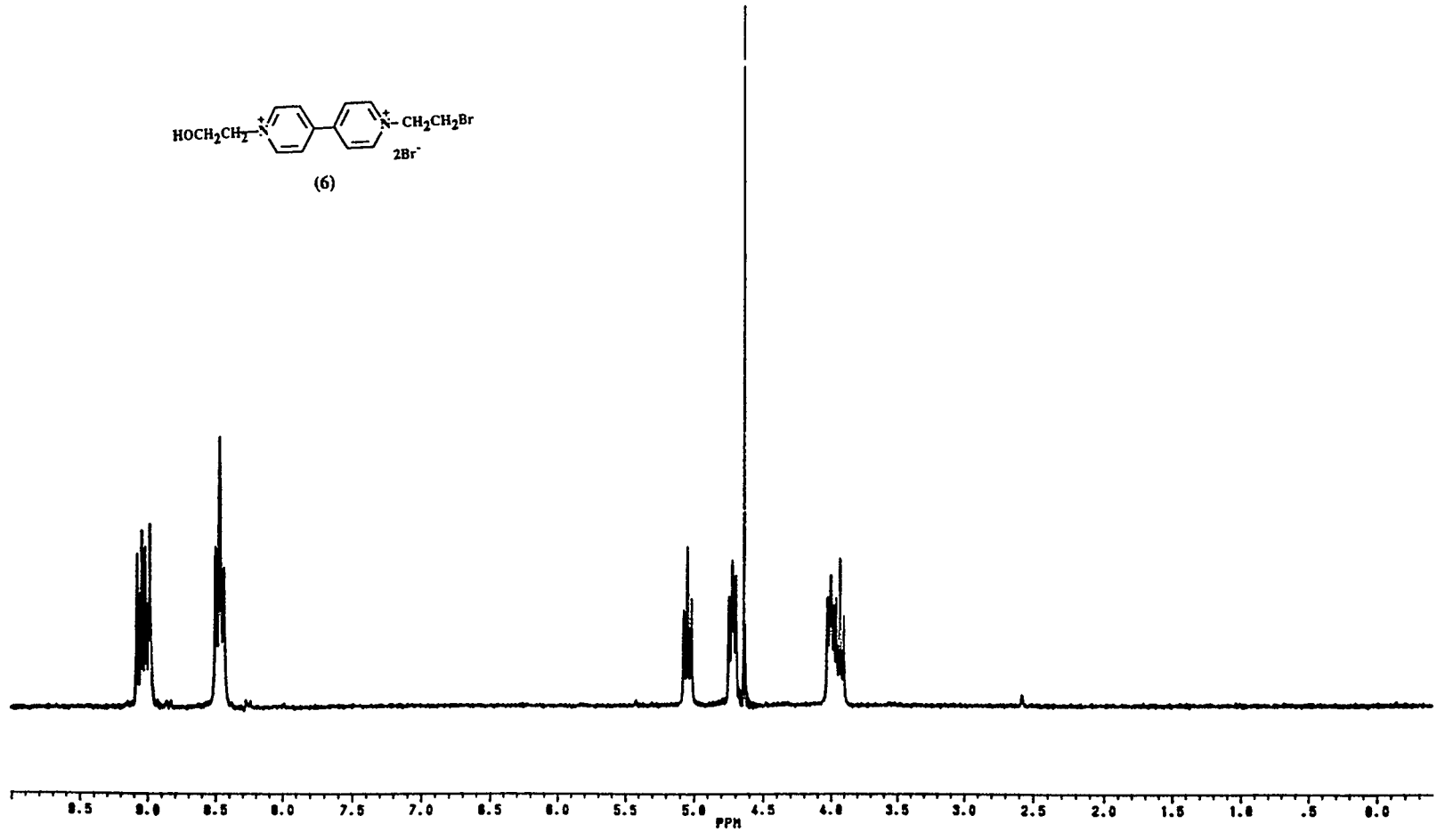


Fig. B-1. ^{1}H NMR spectrum of 1-(2-bromoethyl)-1'-(hydroxyethyl)-4,4'-bipyridinium dibromide **(6)**

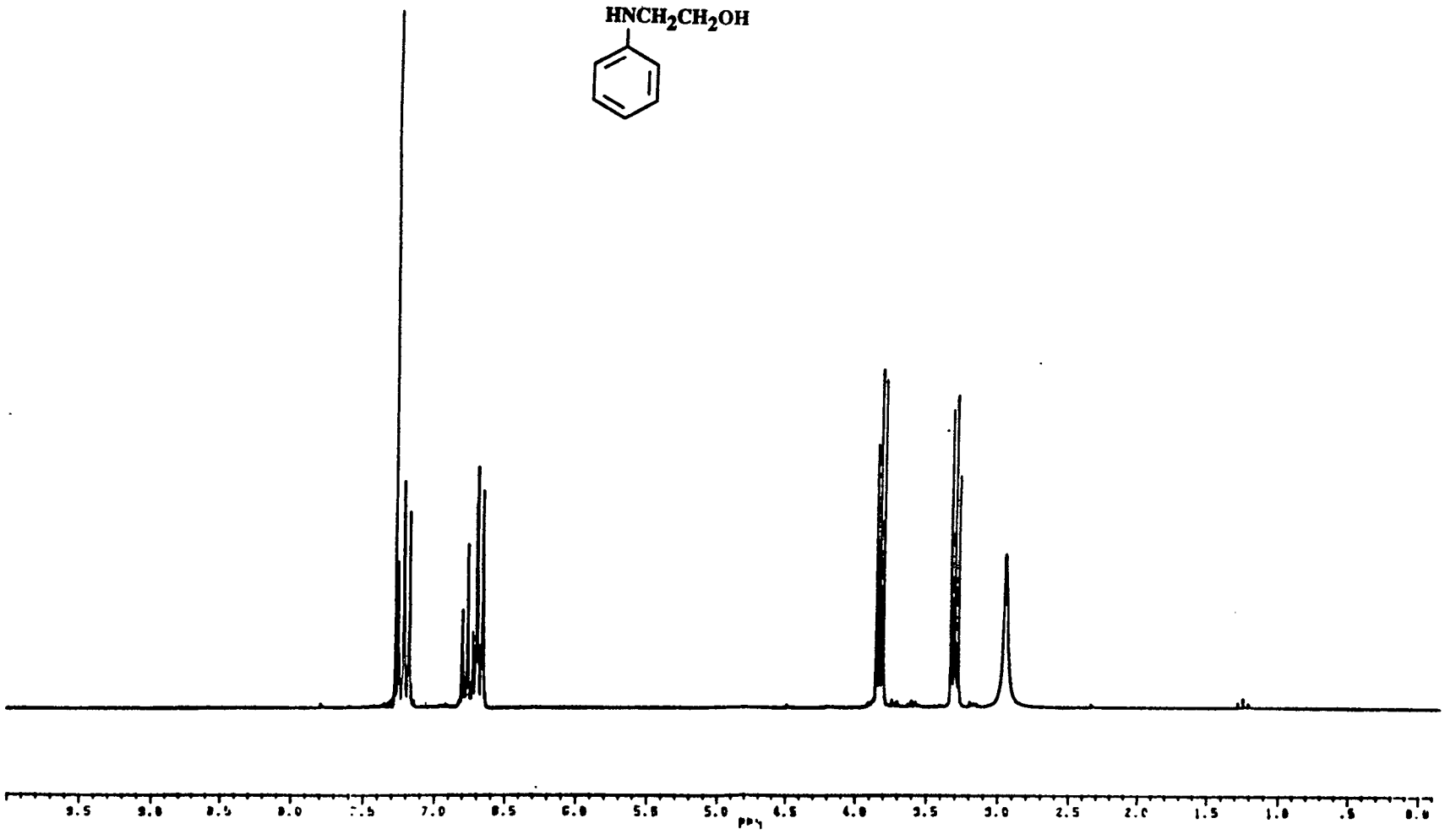


Fig. B-2. ^{1}H NMR spectrum of N-(2-Hydroxyethyl) aniline .

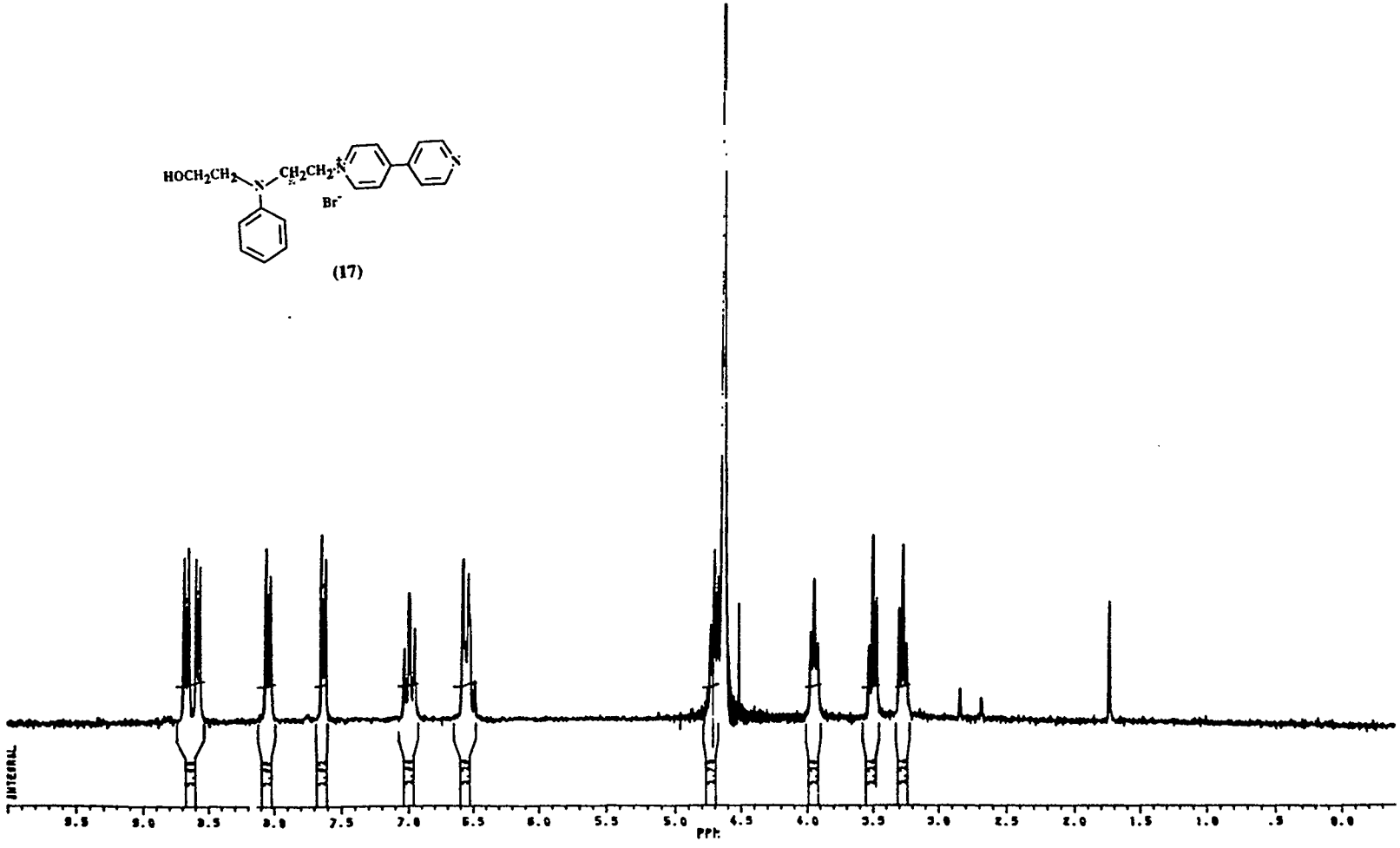


Fig. B-3. ^{1}H NMR of 1-[2-(N-hydroxyethyl-N-phenyl)ethylamino)-4-(4'-pyridyl) pyridinium bromide **(17)**

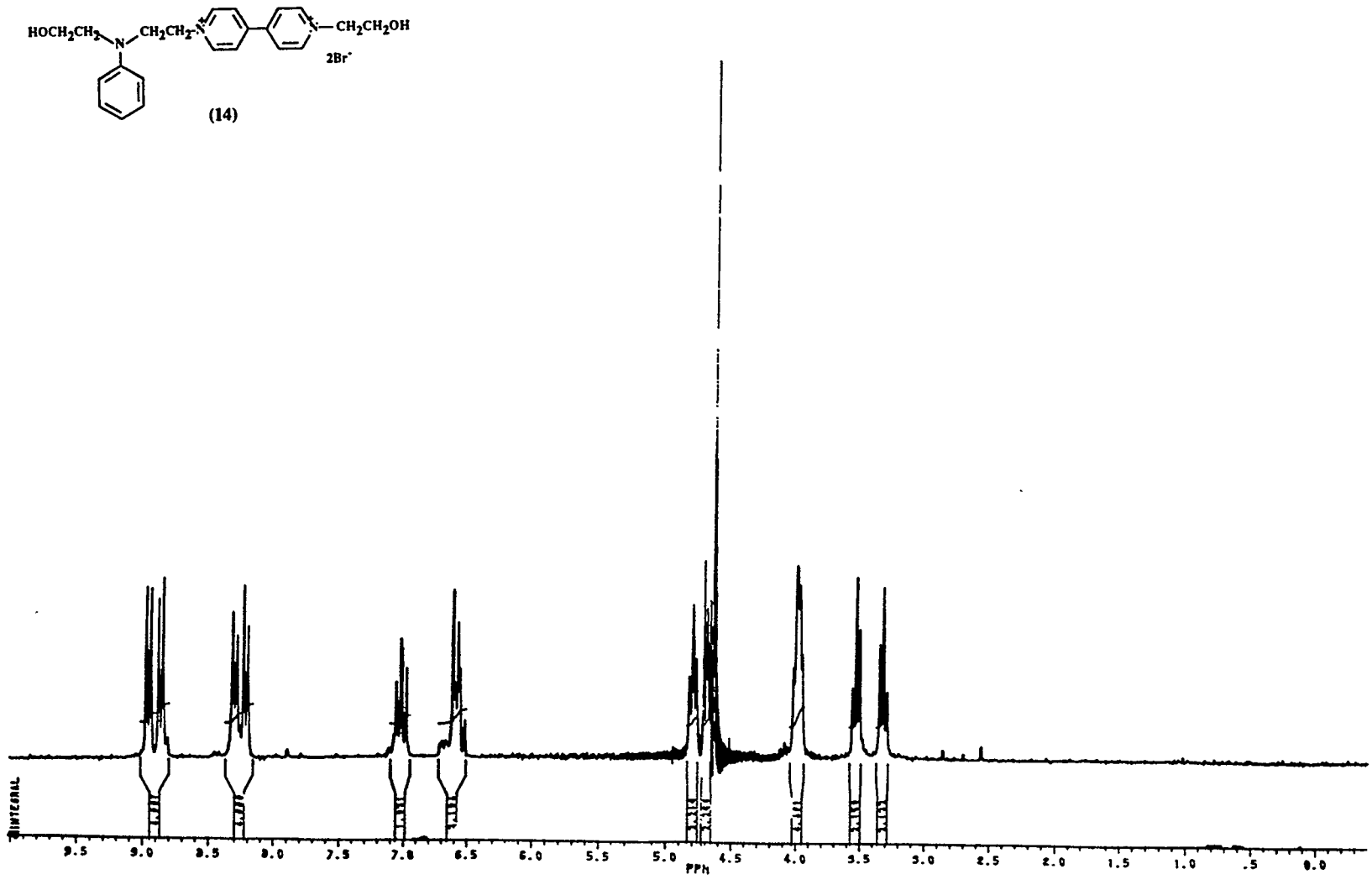


Fig. B-4. ^{1}H NMR spectrum of 1-(2-hydroxyethyl)-1'-[2-(N-hydroxyethyl-N-phenyl)ethylamino]-4,4'-bipyridinium dibromide **(14)**

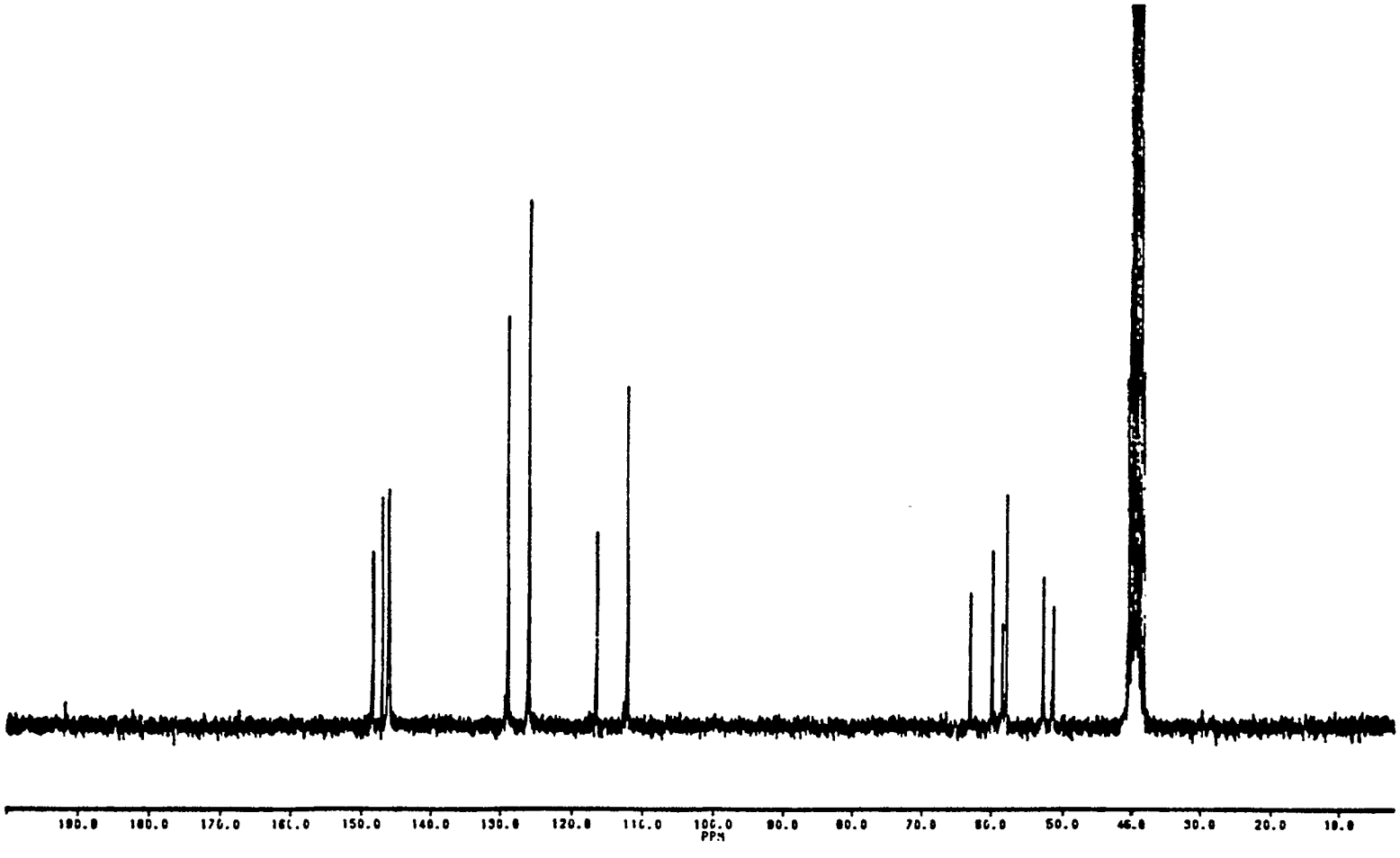


Fig. B-5. ^{13}C NMR spectrum of 1-(2-hydroxyethyl)-1'-[2-(N-hydroxyethyl-N-phenyl)ethylamino]-4,4'-bipyridinium dibromide (**14**)

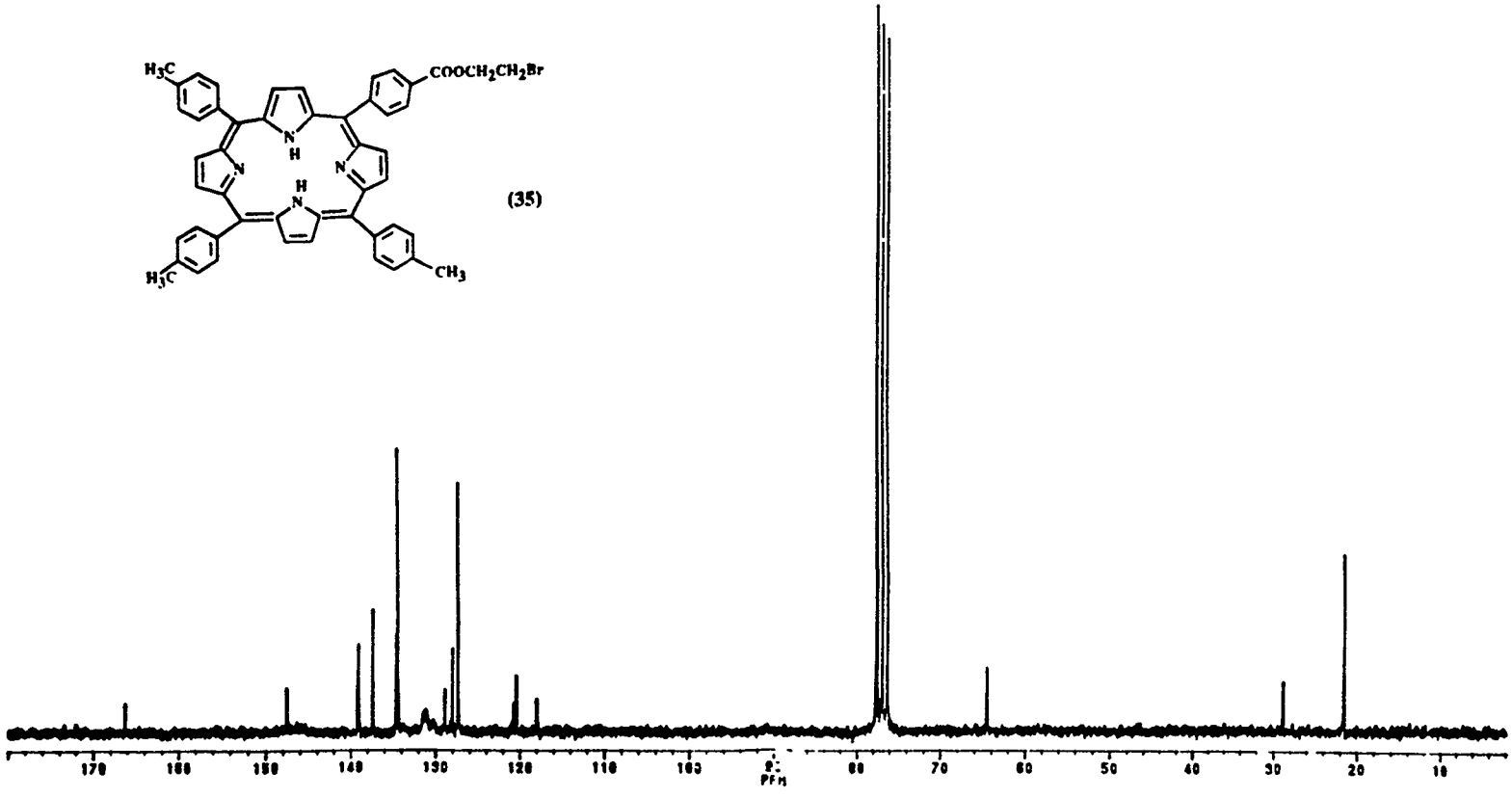
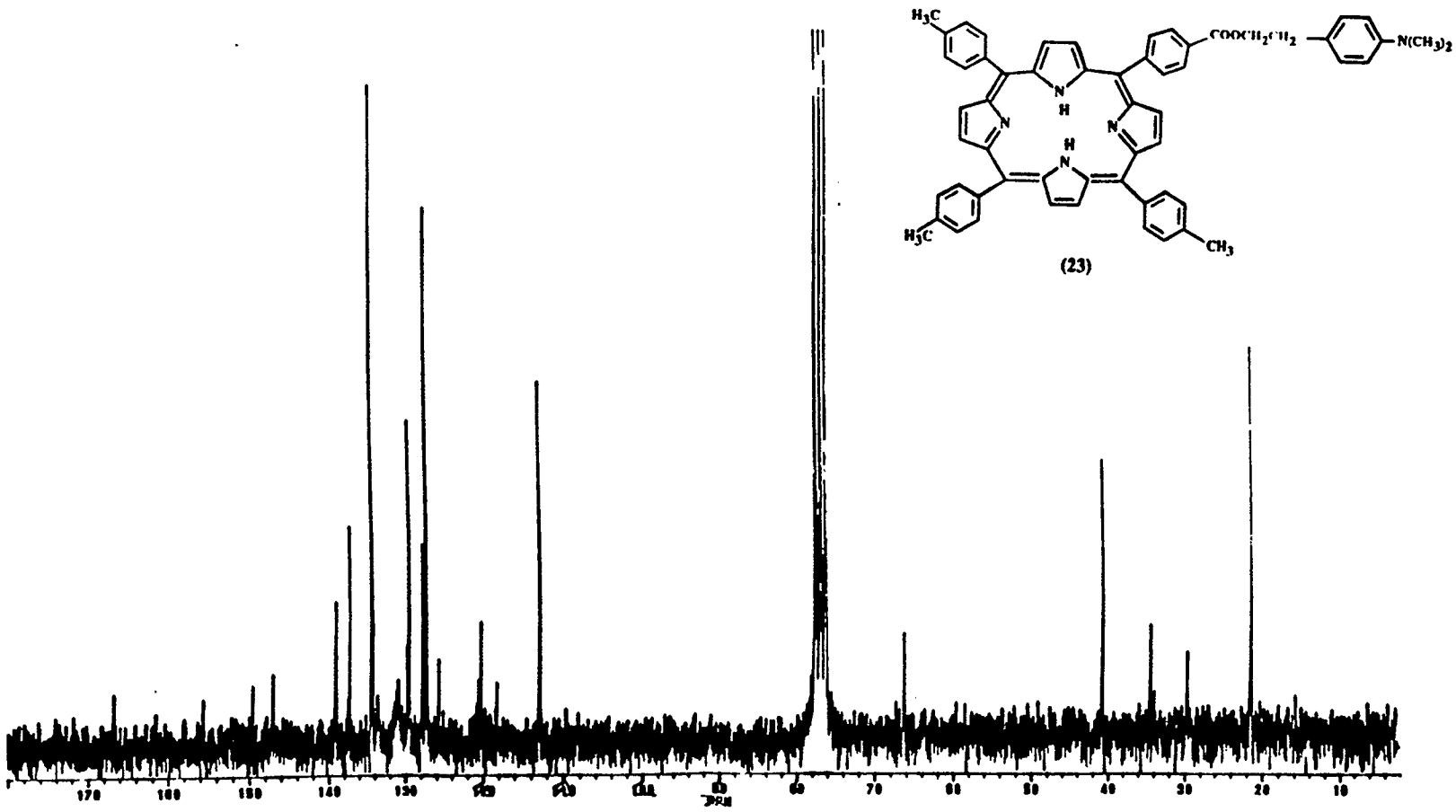


Fig. B-6. ^{13}C NMR spectrum of 5-[4-(2-bromoethyl) toluate]-10,15,20-tritolylporphyrin (35).



(23)

Fig. B-7. ^{13}C NMR of 5-[4-(N,N-dimethyl-4-aminophenethyl) toluate]-10,15,20-tritolylporphyrin. (23)

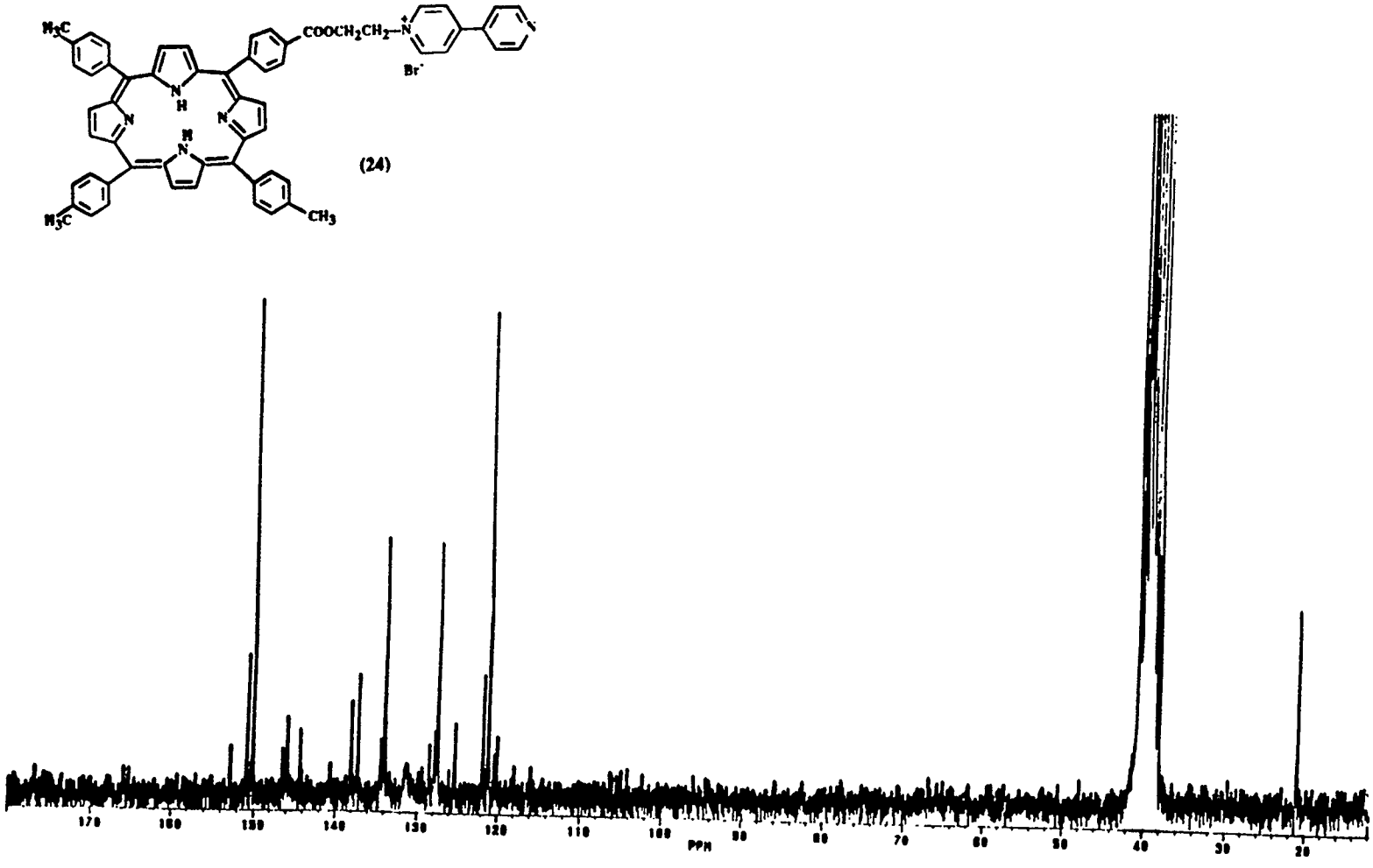


Fig. B-8. ^{13}C NMR spectrum of covalently linked Porphyrin-Acceptor (24).

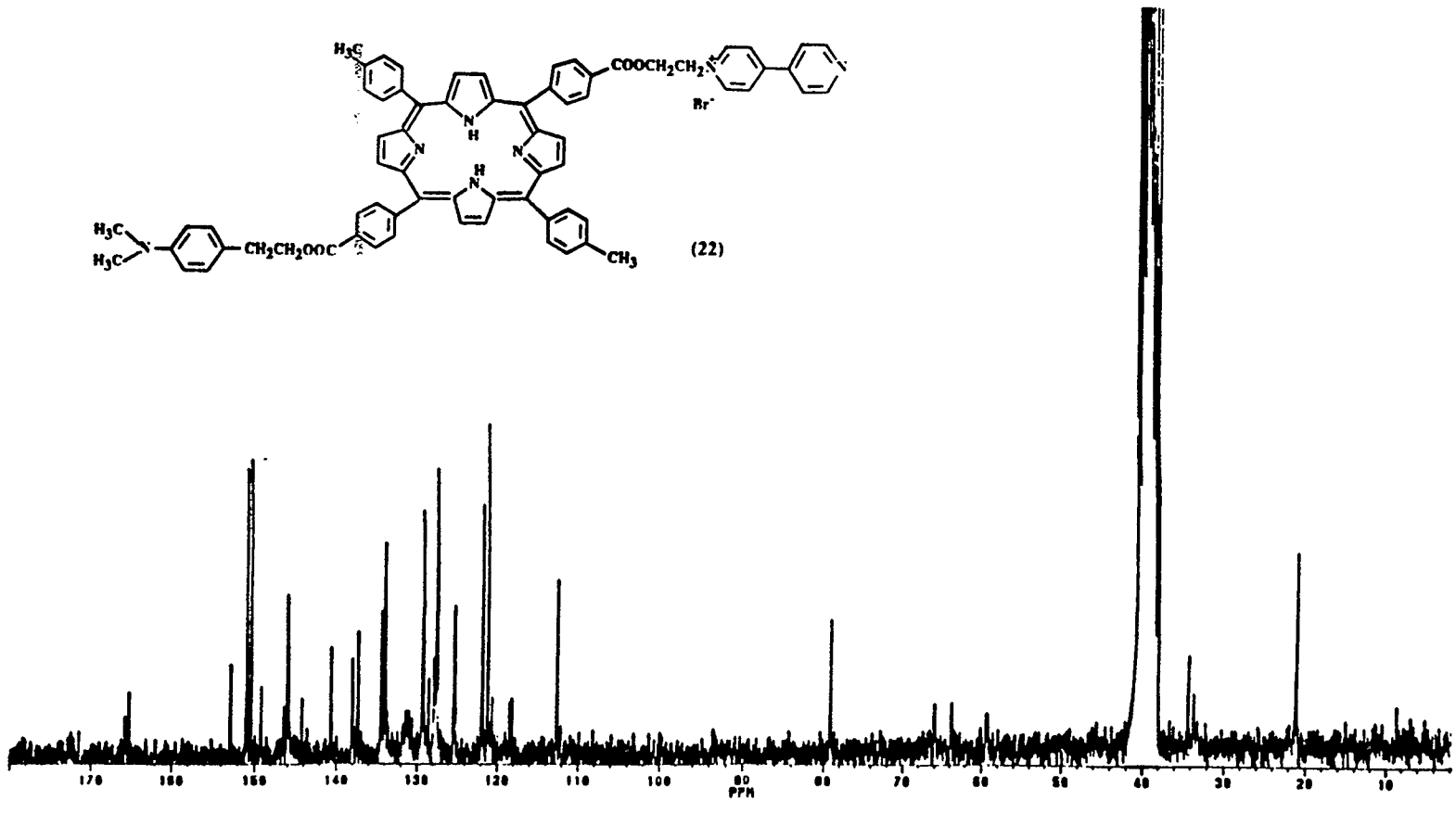


Fig. B-9. ^{13}C NMR spectrum of covalently linked Donor-Porphyrin-Acceptor (22).

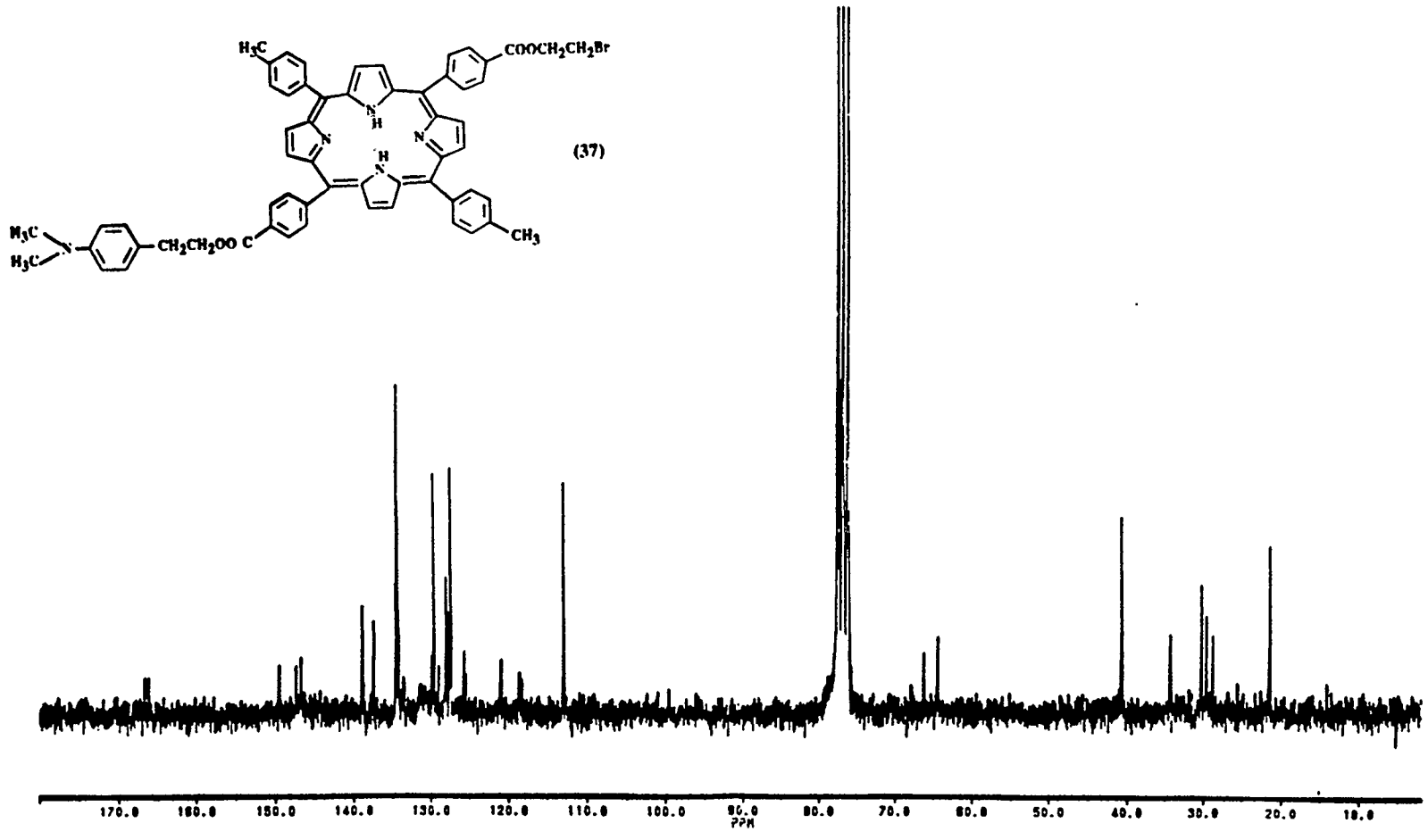


Fig. B-10. ^{13}CNMR spectrum of 5-⟨4-[2-(N,N-dimethyl-4-aminophenyl)]ethoxycarbonylphenyl⟩-15-[4-(2-bromoethyl toluate)]-10,20-ditolylporphyrin (37)