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Preparation of electron donor and acceptor molecules for porphyrin derivatization

Christoph Hoefler
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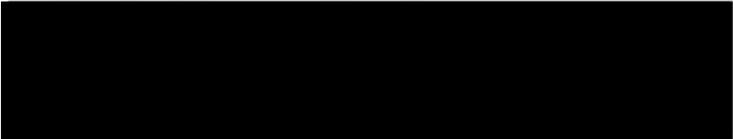
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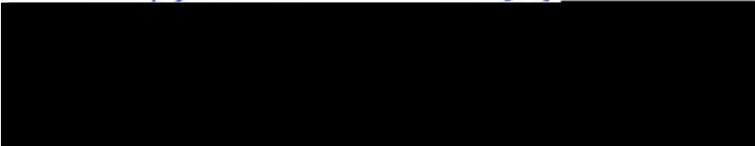
AN ABSTRACT OF THE THESIS OF Christoph Hoefler for the
Master of Science in Chemistry presented in August 5, 1992.

Title: Preparation of Electron Donor and Acceptor
Molecules for Porphyrin Derivatization

APPROVED BY THE MEMBERS OF THE THESIS COMMITTEE:


Carl C. Wamser, Chair


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Porphyrins derivatized with electron donating and
electron withdrawing groups can be used for artificial
photosynthesis. Four new compounds, two electron donors and

two electron acceptors, have been synthesized for prospective porphyrin linkages.

N-[4'-(N',N'-Dimethylamino)phenyl]-4-bromobutanamide (BromoDonor) was synthesized in a substitution reaction of 4-bromobutyryl chloride with N,N-dimethyl-p-phenylene diamine. 4-Bromobutyryl chloride was obtained by refluxing the acid in thionyl chloride. The molecule was characterized by IR and $^1\text{H-NMR}$.

N-[4'-(N',N'-Dimethylamino)phenyl]-4-aminobutanamide (AminoDonor) was prepared in a multi-step synthesis that involved the protection of an amino group. A tert-butoxy carbonyl group (Boc) was attached to 4-aminobutanoic acid as a first step. The amino-protected acid was coupled to N,N-dimethyl-p-phenylenediamine using a carbodiimide under mild reaction conditions. The protection group was cleaved with trifluoroacetic acid. The dihydrochloride was prepared for structural analysis. The compound was identified by elemental analysis, MS, IR and $^1\text{H-NMR}$.

1-(3-Bromopropyl)-1'-phenylmethyl-4,4'-bipyridinium dibromide (BromoViologen) was prepared in a two step synthesis. Benzyl bromide was attached in a nucleophilic substitution to 4,4'-dipyridyl in toluene to give 1-phenylmethyl-4-(4'-pyridyl)pyridinium bromide. 1,3-Dibromopropane was attached in the same reaction type to the monosubstituted salt in acetonitrile yielding the BromoDonor. Disubstitution to 25% of the 1,3-dibromo

propane was observed, as confirmed by elemental analysis, MS, IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.

1-(3-Hydroxypropyl)-1-phenylmethyl-4,4'-bipyridinium dibromide (HydroxyViologen) was prepared in the same manner by nucleophilic substitution of 1-phenylmethyl-4-(4'-pyridyl)pyridinium bromide with 3-bromo-1-propanol in acetonitrile. The structure was confirmed by elemental analysis, MS, IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.

Several unsuccessful attempts have been done to link these donors and acceptors to different porphyrins. It was attempted to link the HydroxyViologen to TCCPP following typical ester formation procedures. Repeated attempts with DMAP as a catalyst and inert atmospheric conditions showed no improvements.

The coupling of AminoDonor to TCCPP was tried in a similar manner without success. No product formation was observed by using a carbodiimide as a coupling agent for AminoDonor and TCCPP.

The attempt to link the BromoViologen in a nucleophilic substitution to THPP in DMF with cesium carbonate as a base failed. Also without success was the attempt to attach the BromoViologen to TCCPP under similar reaction conditions. In all cases, porphyrin reaction products were isolated by chromatography, but none showed the appropriate spectral characteristics.

PREPARATION OF ELECTRON DONOR AND ACCEPTOR MOLECULES
FOR PORPHYRIN DERIVATIZATION

by

CHRISTOPH HOEFLER

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE
in
CHEMISTRY

Portland State University

1992

TO THE OFFICE OF GRADUATE STUDIES:

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CHAPTER I

ARTIFICIAL PHOTOSYNTHESIS

INTRODUCTION

In nature the photosynthesis process is used to convert light into a storable chemical form. This unique system is fairly complex so that many reactions involved in this process are still not completely understood. A great advance, for which the Nobel Prize was awarded in 1988, was the elucidation of the reaction center in purple bacteria,^{1,2} which resembles chlorophyll in its mode of action.

The essence in photosynthesis is that CO₂ and water are used for the buildup of larger molecular compounds using sunlight as the energy supply. Natural photosynthesis has an overall gross efficiency of 9.2%.³ This value is however lowered to 2% if dark reactions and photorespiration are considered.

Different approaches have been made to mimic photosynthesis.⁴⁻⁶ The research in solar energy conversion developed to a fast growing area in the last 15 years. Most photochemistry which has been done so far has focused on sensitizers or light absorbing compounds whose absorption

maxima were in the UV region. Such systems would actually absorb only up to 5% of the sunlight which reaches the earth's surface. A main reason for this low performance is that most of the UV light is filtered out by the ozone layer.

For this reason new sensitizers with absorption maxima in the visible region had to be found and examined. The most obvious step was to use light absorbers that are abundant in nature.

The light absorbing unit in photosynthesis is chlorophyll whose basic structure is derived from a porphyrin molecule. Such porphyrin structures have absorption maxima that range between 400 and 700 nm. The spectral distribution of sunlight reaching the earth surface shows this absorption region to contain almost 50% of the available energy.⁷

In general the sunlight is used as an energy supply for water cleavage, executed by the photosynthesis process. The outcome of the water cleavage reaction is molecular oxygen that reenters the respiration cycle and hydrogen stored in the form of a reducing agent (e.g. NADPH or NADH). Water cleavage requires a minimum energy of 1.23 V which corresponds a wavelength of 509 nm. Since only about 70% of the photon energy contributes to the desired cleavage reaction⁵ the limiting wavelength is further lowered to about 400 nm. Nature avoids using an inefficient photosystem

at 400 nm and adapts to the sun's performance by using two connected photosystems (P680 and P700) to achieve the required potential difference.

An artificial photosystem has the benefit that it can be made much more durable than a natural one. In addition, an artificial photosystem could be optimized for a specific energy conversion problem like fuel generation, water splitting or electricity production. This might lead finally to higher solar efficiencies in comparison to a natural system.

Electron Transfer

The photochemical reaction in the reaction center of photosynthesis is an electron transfer step which leads to charge separation induced by irradiation. The quantum yield for this simple photochemical reaction is almost unity, which means that every absorbed photon gives rise to an electron transfer.

In a simplified model the chlorophyll containing protein can be seen as an electron donating group attached to a ubiquinone unit that acts as an electron acceptor. Irradiation moves electrons to excited states in the chlorophyll molecule from where they can move to an electron acceptor. In fact many complex mechanisms mediate this electron transfer that leads to an effective charge separation.

A model compound consisting of a porphyrin and a covalently linked electron acceptor (or donor) would be very useful to scrutinize the nature of the electron transfer in such linked systems. Reference (9) gives a survey of the most important achievements in this field so far. An energy level diagram (see Figure 1) displays the competing processes that can occur in a D-A (donor-acceptor) linked system.⁹

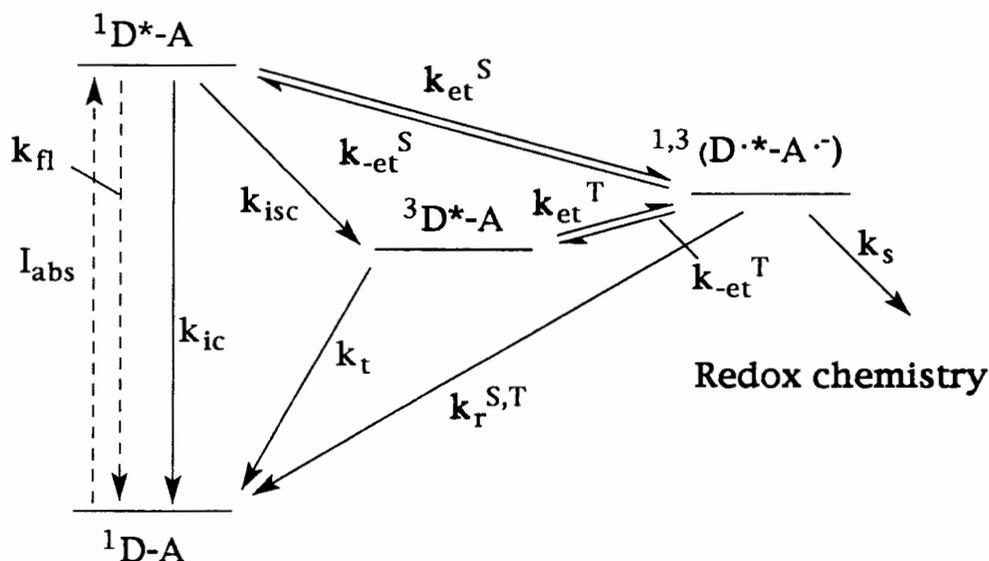


Figure 1. Energy level diagram.

The acceptor group is able to oxidatively quench the excited state of the donor group. This leads to formation of a radical ion pair ($\cdot^+D-A\cdot^-$), which can react in a subsequent redox reaction, e.g. water splitting.

The quenching can occur either from an excited singlet or triplet state of the donor. The transitions are indicated

by the rate constants k_{et}^S and k_{et}^T . Competing processes are fluorescence (k_{fl}), internal conversion (k_{ic}) and intersystem crossing (k_{isc}) from the excited singlet state as well as phosphorescence (k_p) and nonradiative decay (k_{nr}) from the triplet state. Effective charge separation requires that:

$$I-1 \quad k_{et}^S \gg (k_{fl} + k_{ic} + k_{isc})$$

$$I-2 \quad k_s \gg (k_r^S + k_{-et}^S + k_{-et}^T)$$

A model compound has a well defined structure and environment, which consequently simplifies studies on intramolecular electron transfer. The general photoinduced electron transfer reaction is then



The electron transfer step can occur in two different ways. Either the acceptor is reductively quenched from its excited state by the donor or the donor is oxidatively quenched from its excited state by the acceptor. In most covalently linked porphyrin acceptor systems the latter is the case and the following reaction scheme can be applied:

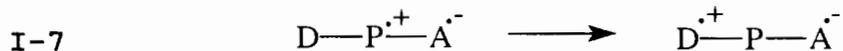
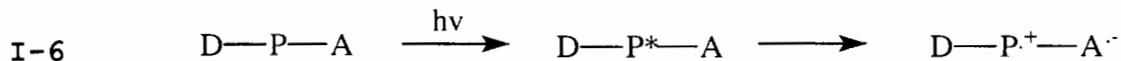
Effective charge separation is limited by the competing back reaction that leads to recombination of the positive and negative charge.



It is therefore desirable to find systems that have reverse electron transfer rates. Studies on covalent linked systems where the donor is a porphyrin and the acceptor is a viologen (disubstituted dipyridinium compound) have been done extensively.¹⁰⁻¹⁹ In most cases a meso-tetraphenylporphyrin was used as donor, but porphyrins with one pyridine ring have also been used. The studies focused on how geometry affects the electron transfer kinetics. This was done by varying the spacer groups between porphyrin and viologen and/or by changing the attachment position (ortho, meta and para) of the spacer to the tetraphenylporphyrin.

Charge separation can further be improved by covalently linking another donor molecule to the D-A linked system. Since 1985, studies²⁰⁻²⁸ have been made on so-called triad and related molecules (tri for three subunits).

In these systems electron transfer proceeds in sequential steps. The porphyrin in the excited state is oxidatively quenched by the acceptor followed by an electron transfer from the donor molecule to the porphyrin. The process is depicted in Equations I-6 and I-7.



Such systems can be extended by addition of further electron donor and acceptor groups (tetrad, pentad etc.). Advantageous in multi-linked systems is that a sequential electron transfer process occurs, similar to nature, which prevents charge recombination. The most prominent example is the tetrad molecule²⁹⁻³¹ (see Figure 2) that consists of a porphyrin with a covalently linked carotenoid polyene as a donor and a diquinone species as acceptor attached in trans configuration. Quantum yields of up to 0.83 and lifetimes up to 340 μs could be achieved with such systems depending on the solvent.

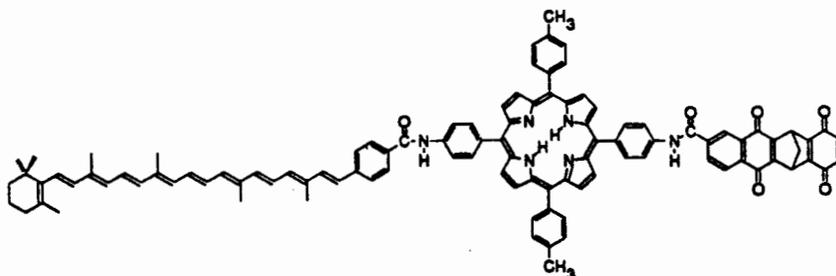


Figure 2. Picture of the Tetrad Molecule.

Porphyrin Films

Thin films of photoactive material like porphyrins can be used to convert solar energy into electrical or chemical energy. Such films have been prepared by interfacial polymerization.³²⁻³⁴ Hereby two reactive monomers dissolved in two immiscible solutions are constrained to react only at the interface of these solutions.

Thin polymeric porphyrin films have been prepared using tetra(p-hydroxyphenyl)porphyrin (THPP) in aqueous base with tetra(p-chlorocarbonylphenyl)porphyrin (TCCPP) in chloroform or dichloromethane and tetra(p-aminophenyl) porphyrin (TAPP) in DMSO with TCCPP in ethyl acetate.³² A picture of these porphyrins is given in Figure 3.

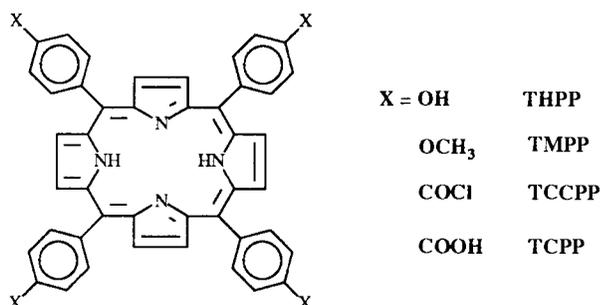


Figure 3. Picture of Porphyrins used for Interfacial Polymerization.

The diffusion of the porphyrins through the membrane is hindered by their size so that the polymerization process stops at an early stage to yield films that are extremely fragile and thin (~ 0.01 μm). Rinsing the film pieces in

various solvents and water removes traces of monomers and low oligomers, and hydrolyzes unreacted acid chloride. This leads to two distinct sides of each polymer film, one that is abundant in carboxylic acid groups (C side) and the other containing hydroxy (H side) or amino (N side) groups. A picture of the film is given in Figure 4.

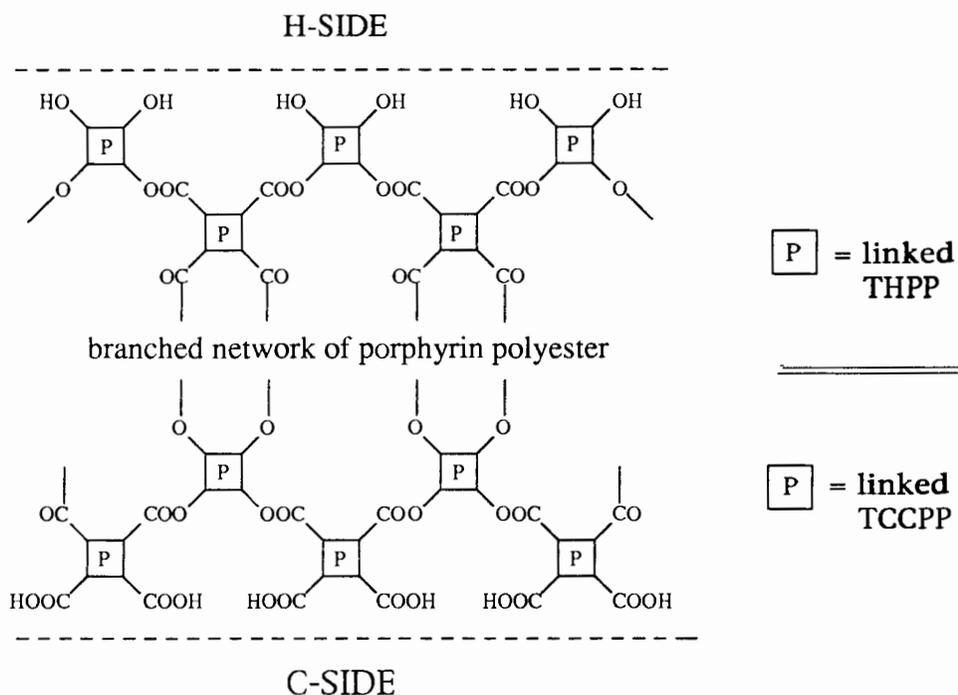


Figure 4. Picture of an idealized film structure after hydrolysis of the acid chlorides.

It is assumed that the actual surface is much more irregular than represented in the idealized figure. The film displays a structural asymmetry in functional groups across the membrane due to this limited degree of order. Presumably this structural asymmetry is responsible for a redox

asymmetry that leads to charge separation upon irradiation. According to this model the smallest degree of linkages is found in close proximity to the surface, whereas inside the membrane the linkage of up to four functional groups may occur. Consequently eight different substitution patterns are conceivable along the membrane [C₁ through C₄ and H₁ through H₄; where X_n (n= 1-4) is a TCCPP or THPP monomer with linkage to n other porphyrins].³³

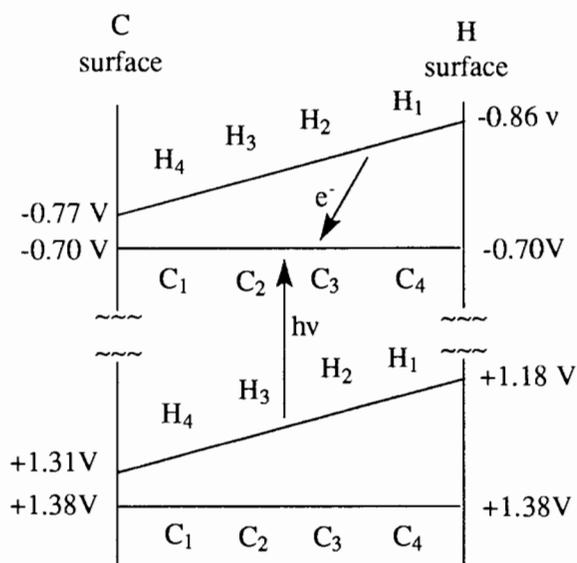


Figure 5. Model of the Redox Potential Gradient across an Artificial Membrane.

Electron transport within the film occurs from the H-side towards the C side leading to an accumulation of electrons on the C side and holes on the H side. The electrons are transported along a redox gradient through the membrane. Figure 5 shows a model for this redox

gradient.^{33,34} The redox potentials were calculated by earlier studies.^{34,35} This can be compared with the natural photosynthesis process where electrons are also moved along a redox gradient.

Electron Donors And Acceptors

Electron donating and electron accepting groups might be attached in different combinations on the film surfaces. Since electrons are moved to the C-side of the film upon irradiation, linking an electron acceptor on the C-side and an electron donor group on the H-side should lead to longer charge separation times. Such an arrangement would correspond a multiad (derived from the previously mentioned triad molecule). The opposite combination, with a donor at the electron rich C-side and an acceptor at the H-side should shorten charge separation times.

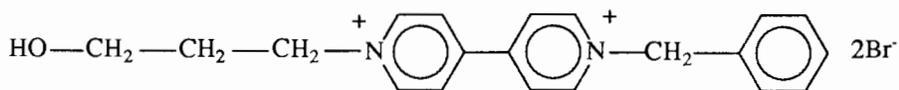
Since the films are so fragile and sensitive to mechanical force, mild reaction conditions are required for these final couplings to the film. To study the effects of the substituted groups, linkages on the monomer compounds should be done first.

Electron donating groups include alkylated amines, carotenoids, aromatics (substituted), polyaromatics and porphyrins.³⁶ N,N-Dimethyl-p-phenylenediamine has been chosen as an electron donating group. The diamine was

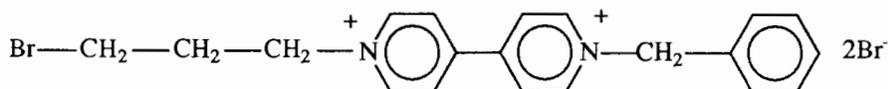
covalently linked to a propyl group that contained the corresponding functional group in the terminal position.

Electron accepting groups include quinones, geminal unsaturated dicyano compounds, aromatics substituted with electron withdrawing groups, ammonium compounds and viologens.³⁷ The most widespread examples that appear in nature are quinones. Viologens have found industrial application as herbicides. The synthesis of an asymmetric viologen has been chosen as electron acceptor. Again the acceptor moiety is separated by a propyl group spacer.

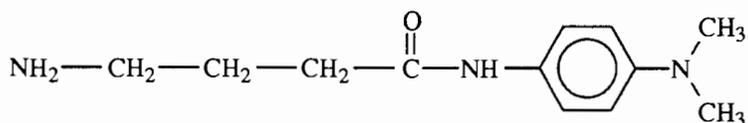
The attachment of the electron acceptor as well as the electron donor on both sides is desired to study its effects. Therefore functional groups at the other end of the spacer had to be chosen so that all different combinations are possible. The donor has been synthesized with an amino or a bromo group at its end. The viologen has been synthesized with a hydroxy and bromo group as functional group. An overview of all four target molecules is given in Figures 6 and 7. All four target molecules are new compounds. This was verified by an online literature research at Chemical Abstracts on 23 June 1992. The research was done by formula index and nomenclature of the compounds.



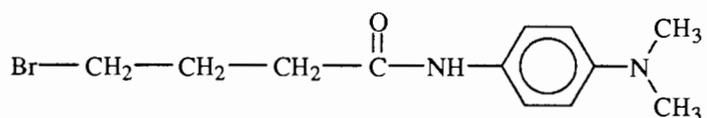
HydroxyViologen



BromoViologen

Figure 6. Structures of Acceptor Target Molecules.

AminoDonor



BromoDonor

Figure 7. Structures of Donor Target Molecules.

The C-side offers either an acid chloride or a carboxylic acid (after hydrolysis) as functional group. The HydroxyViologen can react in a substitution reaction with the acid chloride to form an ester. The AminoDonor can react in the same reaction type to form an amide bond. The

AminoDonor could also be attached to a carboxylic acid under milder reaction conditions using a carbodiimide as a coupling agent. Also conceivable is a nucleophilic substitution of a BromoViologen or BromoDonor with a carboxylic acid.

The H-side has an phenol as functional group. The BromoViologen as well as the BromoDonor should react in a nucleophilic substitution with the hydroxy group. An overview of all different combinations is illustrated in Figure 8.

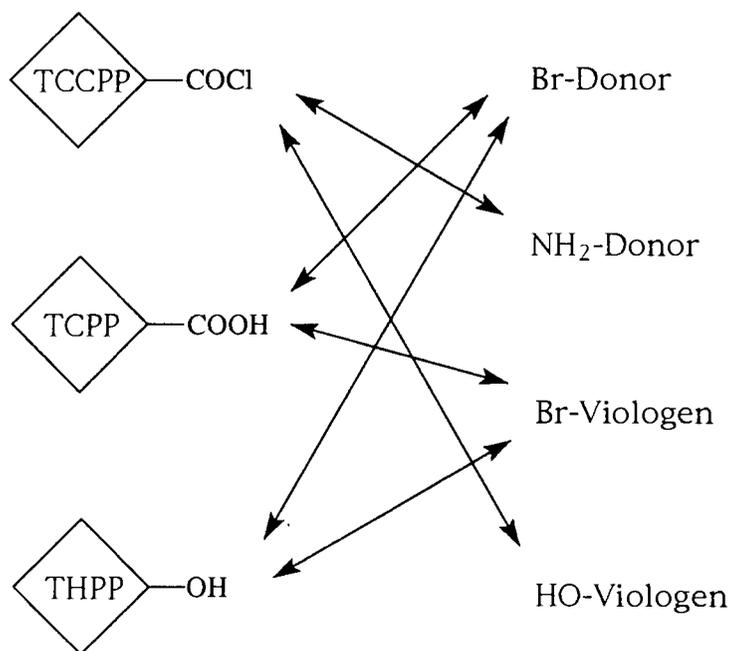


Figure 8. Overview of possible Linkages between Porphyrins, Donors and Acceptors.

Summary

Porphyrin films can be used for solar energy conversion. Upon irradiation they separate charge for a limited time. The attachment of donor and acceptor molecules on opposite sides of the film might improve charge separation times. The intent of the work was to synthesize new donor and acceptor molecules and to attach them to the same porphyrins that are used for the film synthesis. Preferentially mild reaction conditions were chosen for the final couplings due to the sensitivity of the films to mechanical force and hydrolysis.

CHAPTER II

INSTRUMENTAL METHODS

EXPERIMENTAL

Physical Methods

Fractional Distillation. Purification of liquid products was achieved by distillation using a fractionation column. For vacuum distillations the apparatus was connected to a cooling trap of acetone/dry ice to protect the pump.

Elemental Analysis. Elemental analysis was performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

Melting Points. Melting points of solid phase compounds were determined using sealed capillary tubes in a Mel-Temp apparatus. Melting points could be determined to a limit of 300°C.

Infrared Spectra. The infrared spectra were recorded on a FTIR Perkin-Elmer spectrophotometer having a range of 4000-500 cm^{-1} . Spectra of solids were obtained from KBr pellets. Spectra of liquids were obtained between NaCl plates. All spectra were calibrated using a polystyrene film. The following abbreviations were used for the description of the spectra: sh = sharp, br = broad, s =

strong, m = middle, w = weak, as = asymmetric, sm = symmetric.

Nuclear Magnetic Resonance Spectra. 90 MHz proton NMR spectra were recorded on a Varian Model EM-390 spectrometer. 400 MHz proton and 100 MHz carbon-13 spectra were recorded on a Bruker AMX-400 spectrometer. Chemical shifts were reported relative to TMS or DSS for proton and carbon-13 spectra and are given in units of ppm.

Mass Spectra. Mass spectra were performed at Oregon Graduate Institute on a fast atom bombardment (FAB) mass spectrometer. The peak units are given by the m/z (mass/charge) ratio.

Reagents

Acetonitrile. Analytical reagent grade CH_3CN was purchased from Aldrich and further purified. CH_3CN was refluxed over phosphorous pentoxide for several hours then distilled. The distillate was redistilled again from potassium carbonate (anhydrous) using a fractionating column.

Benzyl bromide. Analytical reagent grade $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ was purchased from American Tokyo Kasei, Inc. (TCI) and used without further purification.

Benzyl chloride. $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ was purchased from Aldrich and distilled before using.

3-Bromo-1-propanol. Analytical reagent grade Br-(CH₂)₃-OH was purchased from TCI and used without further purification.

4-Bromobutanoic acid. 4-Bromobutanoic acid was purchased from Aldrich and used without further purification.

4-Bromobutyryl chloride. Analytical grade Br(CH₂)₃COCl was purchased from Aldrich and used without further purification.

Cesium carbonate. Analytical reagent grade Cs₂CO₃ was purchased from Aldrich and used without further purification.

Chloroform. Analytical reagent grade CHCl₃ was purchased from Aldrich and further purified. CHCl₃ was dried over calcium chloride (anhydrous) and distilled using a fractionating column. The distillate was stored over molecular sieve 4 Å.

Cyclohexane. Analytical reagent grade cyclohexane was purchased from Aldrich and used without further purification.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). Analytical reagent grade DBU was purchased from Aldrich and used without further purification.

1,3-Dibromopropane. Analytical reagent grade Br-(CH₂)₃-Br was purchased from TCI and used without further purification.

Dichloromethane. HPLC grade CH_2Cl_2 was purchased from J.T. Baker and dried over molecular sieve 4Å.

1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride. Analytical reagent grade was purchased from Aldrich and used without further purification.

Dimethylformamide. Analytical grade $(\text{CH}_3)_2\text{NCHO}$ was purchased from Aldrich and used without further purification.

Dimethylsulfoxide. Analytical reagent grade DMSO was purchased from Mallinckrodt and used without further purification.

Dioxane. Analytical grade p-dioxane was purchased from Aldrich and used without further purification.

4,4'-Dipyridyl. Analytical reagent grade 4,4'-dipyridyl was purchased from TCI and used without further purification.

Ethyl acetate. HPLC grade ethyl acetate was purchased from J.T. Baker and used without further purification.

Hydrochloric acid. Analytical grade HCl was purchased from J.T. Baker and used without further purification.

Iodotrimethylsilane. $(\text{CH}_3)_3\text{SiI}$ was purchased from Aldrich and used without further purification.

Magnesium sulfate. Analytical grade MgSO_4 was purchased from Mallinckrodt and used without further purification.

N,N-Dimethyl-p-phenylenediamine. Analytical grade $\text{NH}_2\text{-C}_6\text{H}_4\text{-N(CH}_3)_2$ was purchased from TCI and distilled in vacuum before using.

Phosphomolybdic acid. A 20 % solution in ethanol of phosphomolybdic acid was purchased from Aldrich and used without further purification.

Pyridine. Analytical reagent grade $\text{C}_5\text{H}_5\text{N}$ was purchased from Aldrich and further purified. Pyridine was kept over potassium hydroxide overnight and distilled using a fractionating column. The distillate was stored over molecular sieve 4 Å.

Pyridinium chloride. $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ was purchased from Aldrich and used without further purification.

Silica gel. Silica gel grade 60, 60 Å 230-400 mesh was purchased from Aldrich and used without further purification.

Sodium bicarbonate. Analytical grade NaHCO_3 was purchased from Mallinckrodt and used without further purification.

Sodium bisulfite. Analytical grade NaHSO_3 was purchased from Aldrich and used without further purification.

Sodium hydroxide. Analytical grade NaOH was purchased from Matheson, Coleman & Bell and used without further purification.

Sodium sulfate. Analytical grade Na_2SO_4 was purchased from Matheson, Coleman & Bell and used without further purification.

Sodium dithionite. Analytical grade $\text{Na}_2\text{S}_2\text{O}_4$ was purchased from Aldrich and used without further purification.

2-(Tert-butoxycarbonyloxyimino)-2-phenylacetonitrile. Boc-on was purchased from Aldrich and used without further purification.

5,10,15,20-Tetrakis(4-methoxyphenyl)-21H,23H-porphine. TMPP was purchased from Aldrich and used without further purification.

5,10,15,20-Tetrakis-(4-carboxyphenyl)-porphine. TCPP was purchased from Porphyrin Products Inc. and used without further purification.

Thionyl chloride. SOCl_2 was purchased from Aldrich and distilled before using.

Triethylamine. Analytical reagent grade Et_3N was purchased from Aldrich and further purified through distillation.

Trifluoroacetic acid. CF_3COOH was purchased from Aldrich and used without further purification.

CHAPTER III

SYNTHESIS OF PORPHYRINS

INTRODUCTION

Tetrakis-(4-hydroxyphenyl)porphyrin (THPP) and tetrakis-(4-chlorocarbonylphenyl)porphyrin (TCCPP) were prepared by modifying functional groups of the commercially available tetrakis-(4-methoxyphenyl)porphyrin (TMPP) and tetrakis-(4-carboxyphenyl) porphyrin (TCPP), respectively. THPP was prepared by an ether cleavage of TMPP according to reference (38) with slight modifications. The TMPP as delivered from Aldrich showed significant impurities. Concluding from a $^1\text{H-NMR}$ that was taken of this material the impurities could be mainly ethylbenzene and one or more further compounds in minute concentration. A chromatographic purification of TMPP before the ether cleavage was not done, because it was assumed from previous references³⁸ that the ether cleavage would not be complete and lead to hydroxy- methoxy-porphyrin mixtures. Such a mixture would have required a subsequent chromatography to obtain pure materials.

To simplify the usual procedure for preparation of THPP from TMPP with pyridinium chloride, and to promote

cleavage of all four ether groups an alternative method¹¹ was attempted using iodotrimethylsilane as cleaving agent. However, no cleavage was observed for TMPP.

The synthesis of TCCPP was done following a typical preparation method for acid chlorides from acids.³⁹ A structural overview for THPP and TCCPP synthesis are given in Figure 9 and Figure 10.

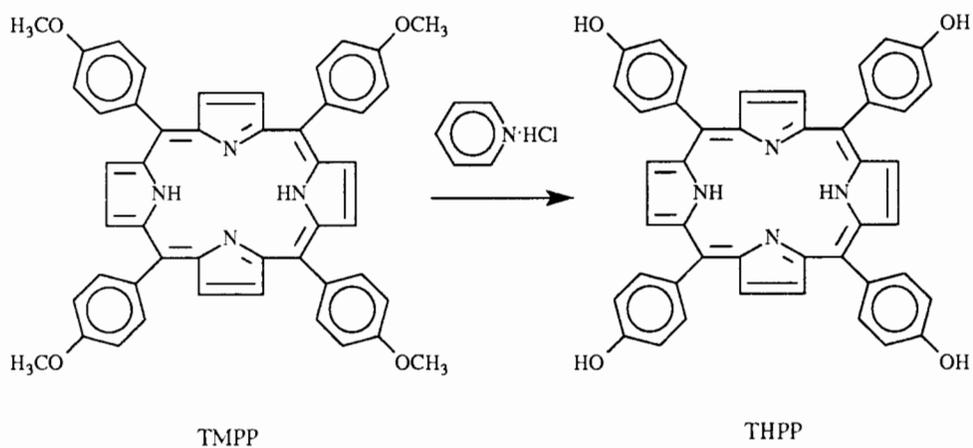


Figure 9. Synthesis of THPP.

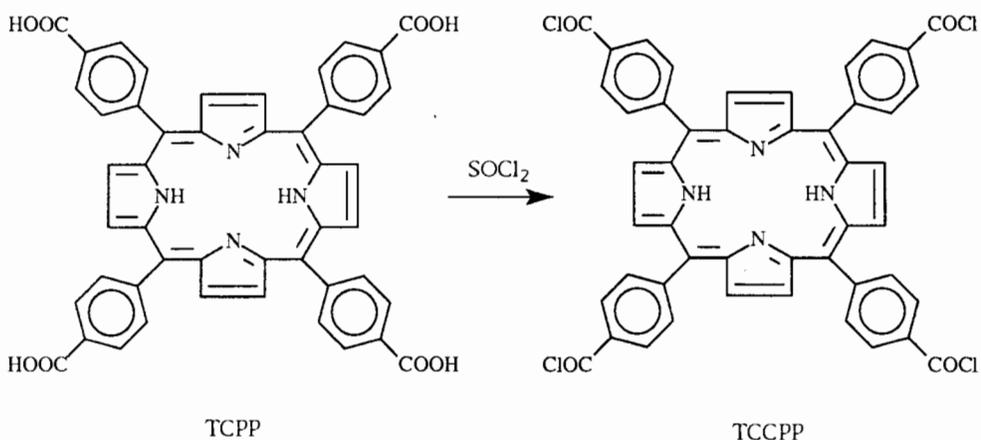


Figure 10. Synthesis of TCCPP.

Experimental

5,10,15,20-Tetrakis-(4-hydroxyphenyl)-21H,23H-porphine (THPP). Tetrakis-(4-methoxyphenyl)porphine (TMPP) (5.0 g, 6.8 mmol) and pyridinium chloride (100.0 g, 864 mmol) were refluxed in a 250 ml 3-neck round-bottom flask with reflux condenser, drying tube and thermometer. The solution was heated to 210°C and magnetically stirred. After 6 hours, an additional 25 g (216 mmol) of pyridinium chloride were added and the solution refluxed for 2 more hours.

The hot, green fluid was poured into 1.5 l ice-cold water. Ethyl acetate (500 ml) was poured into this solution and the pH adjusted to 13 by addition of 6 M NaOH. The color changed from green to purple. The layers were separated and the water phase extracted three more times with 200 ml of ethyl acetate. The combined organic layers were dried over Na₂SO₄, filtered and evaporated off to dryness on a rotovap. The purple crude material obtained was further dried on the oil pump [crude yield: 5.3 g (78 mmol) = 114%].

A portion of this crude product (1.52 g) was purified by column chromatography over silica gel with MeOH as the solvent (30 cm height, 4.5 cm diameter column). This resulted in 1.1 g recovery. The yield was 3.86 g (5.7 mmol) = 84% (calculated for whole charge).

Nuclear Magnetic Resonance Spectroscopy. The spectrum was taken on a 400 MHz NMR. The chemical shifts are listed in Table I. The THPP was dissolved in methanol- d_4 using TMS as a standard. The spectrum consists of a singlet for the pyrrole protons and an AA'BB' pattern for the p-substituted phenol. The phenol proton is exchanged with the solvent and doesn't show up. No peak for the methoxy protons is observed in the 3-4 ppm region which indicates that the cleavage was successful on all four ether bonds. The integration corresponds with the ratio of protons.

TABLE I
 $^1\text{H-NMR}$ CHEMICAL SHIFTS FOR THPP

ppm	Rel. Int.	Splitting	Assignment
8.90	3.9	broad	pyrrole- <u>H</u>
8.03	4.0	doublet	aromat- <u>H</u>
7.24	4.0	doublet	aromat- <u>H</u>

5,10,15,20-Tetrakis-[4-(chlorocarbonyl)phenyl]-21H, 23H-porphine (TCCPP). Tetrakis-(4-carboxyphenyl) porphine (TCPP) (500 mg, 0.63 mmol) was refluxed with 10 ml (137 mmol) of freshly distilled thionyl chloride in a 100 ml round-bottom flask with reflux condenser and drying tube for 6 hours. Excess thionyl chloride was distilled off, finally in vacuum. The blue residue was

further dried on the oil pump. The yield was 528 mg (0.61-mmol) = 97 %.

Infrared Spectroscopy. The infrared absorptions are tabulated in Table II and the spectrum is shown in the Appendix. The spectrum was taken from an earlier TCCPP preparation, which was stored for 7 months in a dessicator. The acid chloride got partly hydrolyzed during that time, but still shows a strongly shifted carbonyl stretch vibration at 1778 cm^{-1} . This indicates that the acid chloride is quite stable to hydrolysis and can be temporarily stored under dessication. The carboxyl group gives rise to broad H-O stretching at 3448 cm^{-1} and a second carbonyl stretching at 1731 cm^{-1} .

TABLE II
INFRARED ABSORPTION BANDS FOR TCCPP

3448 (br)	3036 (m)
2966 (m)	2872 (m)
1778 (vs)	1731 (s)
1601 (m)	1560 (w)
1537 (w)	1490 (m)
1401 (m)	1307 (w)
1240 (w)	1202 (s)

CHAPTER IV

SYNTHESIS OF BROMOVILOGEN

INTRODUCTION

Asymmetric 4,4'-bipyridinium salts have already been prepared in various combinations.⁴⁰ The crucial step is to prevent disubstitution after the monosubstitution, which would lead to a viologen. A structural overview is illustrated in Figure 11. The principle is to use a very nonpolar solvent like toluene or cyclohexane. The monosubstitution leads to formation of a salt, which immediately precipitates out due to its low solubility in the nonpolar solvent. The 1-phenylmethyl-4-(4'-pyridyl) pyridinium bromide as well as the chloride has been prepared. It was found that the bromide salt formation occurs much faster and in higher yield.

The presence of viologen can be detected by a simple test. Sodium dithionite can reduce the viologen to a radical ion. This radical ion is a chromophore, since charge delocalization is possible over the whole ring system. The formation can easily be detected as a strong blue color.

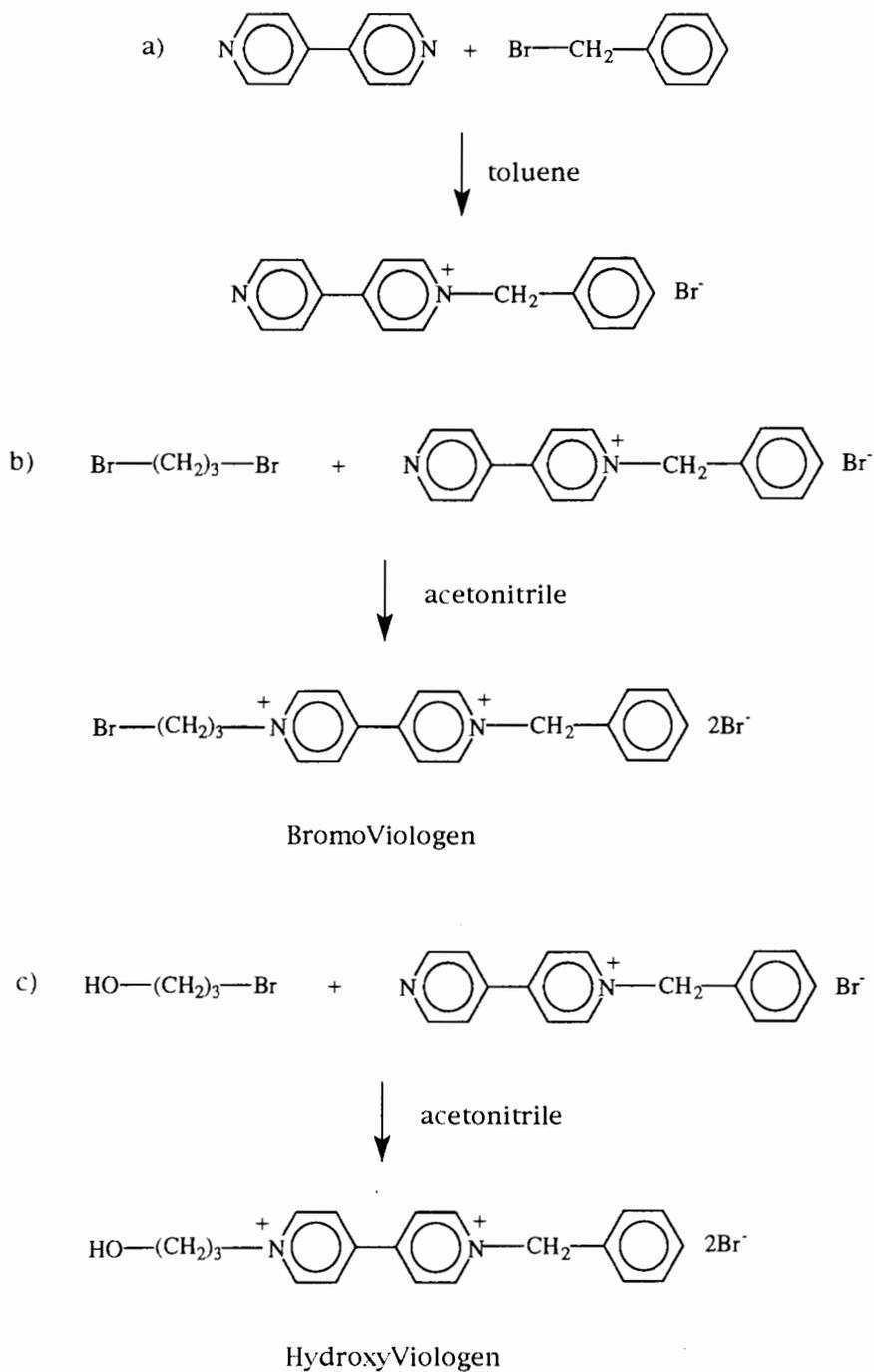


Figure 11. Syntheses of BromoViologen and HydroxyViologen.

The viologens were only synthesized from the bromide to increase the solubility of the viologen for subsequent reactions. A problem in the synthesis of the BromoViologen is that both bromides in 1,3-dibromopropane can be replaced by the monosubstituted bipyridinium salt. To prevent this a solvent must be used that dissolves the monosubstituted dipyridyl but not the formed viologen. The doubly positive-charged viologen should precipitate out of solution and is thereby protected from a subsequent substitution. Polar aprotic solvents that can be used for this reaction are acetonitrile, dimethylformamide and dimethylsulfoxide. Solubility tests indicated that acetonitrile is most suitable in this sequence, since it has the lowest dielectric constant and is still able to dissolve the monosubstituted bromide. DMF and DMSO are too polar and dissolve viologen readily. The viologen product has a limited solubility in acetonitrile so that the formation of disubstituted product was observed only to 4%. In the second substitution the undesired disubstituted viologen is formed that immediately precipitates out of solution. That way the equilibrium is shifted favorably for a new disubstitution. The long reaction time enhances this byproduct. Formation of this product was prevented by increasing the amount of 1,3-dibromopropane for monosubstitution.

1-Phenylmethyl-4-(4'-pyridyl)pyridinium chloride

The reaction was done following similar procedures of a previous reference.¹³ 4,4'-Dipyridyl (20.0 g, 128 mmol) was dissolved in 300 ml toluene by slightly heating in a 1000 ml 3-neck round-bottom flask equipped with reflux condenser and addition funnel. Freshly distilled benzyl chloride (13.2 ml, 115 mmol) was added dropwise within 20 minutes. The first precipitate was formed after two hours. The solution was allowed to cool to room temperature after 28 hours. The white precipitate was filtered off, washed with diethyl ether and dried in oil pump vacuum. The dithionite test applied on the crude product was negative, indicating absence of viologen. The yield was 2.74 g (9 mmol) = 8%. The melting point was determined to be 235-236°C.

Structural Analysis

Infrared Spectroscopy. The infrared absorptions are tabulated in Table III and the spectrum is shown in the Appendix. The characteristic feature of the spectrum is a very strong absorption at 1637 cm^{-1} due to C=N stretching. The ring "breathing" modes can clearly be distinguished at 1595 cm^{-1} and 1495 cm^{-1} with the lower range frequency typically stronger than the first. The out-of-plane vibrations of the monosubstituted phenyl ring appear in the expected region at 690 cm^{-1} and 720 cm^{-1} .

TABLE III
 INFRARED ABSORPTION BANDS FOR
 1-PHENYLMETHYL-4-(4'-PYRIDYL)PYRIDINIUM CHLORIDE

3424 (br, m)	3107 (w)
3025 (s)	2978 (m)
2931 (m)	2884 (w)
1637 (vs)	1595 (m)
1548 (m)	1531 (m)
1495 (m)	1454 (m)
1413 (m)	1360 (w)
1343 (w)	1290 (w)
1225 (m)	1202 (w)
1178 (m)	1161 (m)
1078 (w)	720 (m)
690 (w)	620 (w)

Nuclear Magnetic Resonance Spectroscopy. The spectrum was recorded on the 90 MHz spectrometer. The material was dissolved in D₂O with DSS as a standard. The molecule has a symmetry plane, which leads to chemically equivalent protons on either side. The monosubstitution splits the pyridyl resonances in two AA'BB' pattern.⁴¹ The AA'BB' pattern at lower field can be assigned to the substituted pyridyl ring due to deshielding of the positive charge. The benzyl protons appear in the expected

region. All peak integral ratios are as expected. The chemical shifts are presented in Table IV.

TABLE IV

¹H-NMR CHEMICAL SHIFTS FOR
1-PHENYLMETHYL-4-(4'-PYRIDYL)PYRIDINIUM CHLORIDE

Chem. Shift	Rel. Int.	Splitting	Assignment
5.80	2	singlet	-CH ₂ -ph
7.50	5	singlet	-CH ₂ -aromat-H
7.83	2	doublet	pyridyl-H
8.36	2	doublet	pyridyl-H
8.73	2	doublet	pyridinium-H
9.03	2	doublet	pyridinium-H

1-Phenylmethyl-4-(4'-pyridyl)pyridinium bromide
(PreViologen)

The reaction was done following procedures of previously described viologen syntheses.⁴² 4,4'-Dipyridyl (10.0 g, 64 mmol) was dissolved in 300 ml toluene in a 1000 ml 3-neck round-bottom flask equipped with reflux condenser and addition funnel. The solution was heated to 100°C. Benzyl bromide (8.7 ml, 73 mmol) was added within 60 minutes. The first product precipitated out after 1-2 minutes.

After 2 hours an additional 50 mmol of benzyl bromide was added, because TLC showed the presence of unreacted 4,4'-dipyridyl. The heating was removed after a total of

3.5 hours and the solution allowed to cool overnight. The yellowish precipitate was isolated by filtration, washed with diethyl ether and dried in oil pump vacuum.

The dithionite test applied on this obtained salt gave no blue color, indicating no viologen formation. The yield was 6.7 g (20 mmol) = 32%. The melting point was determined to be 228-230°C.

Structural Analysis

Infrared Spectroscopy. The frequencies are tabulated in Table V and the spectrum is displayed in the Appendix.

TABLE V
INFRARED ABSORPTION BANDS FOR PREVIOLOGEN

3424 (br,m)	3095 (w)
3025 (m)	2978 (m)
2919 (w)	1631 (s)
1590 (s)	1531 (m)
1490 (m)	1454 (m)
1219 (m)	1155 (m)
802 (s)	608 (s)

The main feature is the strong absorption at 1631 cm^{-1} due to C=N vibration mode. The phenyl ring "breathing"

modes are at 1590 cm^{-1} and 1490 cm^{-1} . A weak C-H stretching of the phenyl ring can be seen at 3095 cm^{-1} .

Nuclear Magnetic Resonance Spectroscopy. The spectrum was recorded on the 90 MHz spectrometer. The material was dissolved in D_2O with DSS as a standard. All peaks appear as expected in the aromatic region except for the benzyl protons. The pyridyl portion of the spectrum consists of two shifted AA'BB' patterns.⁴³ The lower field pattern can be assigned to substituted pyridyl ring due to the deshielding effect of the positive charge. Integration ratios were in agreement with the expected proton distribution. The chemical shifts are reported in Table VI.

TABLE VI
 $^1\text{H-NMR}$ CHEMICAL SHIFTS FOR PREVIOLOGEN

ppm	Rel. Int.	Splitting	Assignment
5.83	2	singlet	$\text{CH}_2\text{-ph}$
7.50	5	singlet	$\text{CH}_2\text{-ph-H}$
7.86	2	doublet	aromat-H
8.38	2	doublet	aromat-H
8.73	2	doublet	aromat-H
9.06	2	doublet	aromat-H

BromoViologen

1-Phenylmethyl-4-(4'-pyridyl)pyridinium (2.6 g, 7.9 mmol) was dissolved in 300 ml acetonitrile by heating to 80°C in a 1000 ml 3-neck round-bottom flask with reflux condenser. 1,3-Dibromopropane (8.1 ml, 79 mmol) was added at once after all of the monosubstituted bipyridinium salt had dissolved. The solution was refluxed for 9 days. The first yellow precipitate was observed after 1.5 days. The solution was allowed to cool to room temperature overnight. The yellow precipitate was filtered off and dried in oil pump vacuum (2.36 g).

The acetonitrile phase was dried by rotary evaporation to give a yellow substance, which was further dried in oil pump vacuum. It remained a yellow substance. The dithionite test on both fractions were positive. ¹H-NMR and TLC showed that only the first obtained precipitate was the desired product. The yield was 2.36 g (4.4 mmol) = 56%. The substance decomposes by heating above 300°C.

Structural Analysis

Infrared Spectroscopy. The infrared absorptions are tabulated in Table VII and the spectrum is shown in the Appendix. The most striking feature in the spectrum is the strong, sharp absorption at 1631 cm⁻¹ due to C=N stretching vibrations. One of two double bond stretches

for indicating the phenyl ring can't be seen on the spectrum, but the second is present at 1495 cm^{-1} . As an explanation the first vibration is either low and hidden under the strong C=N double bond vibration or the adjacent positive charge shifts the two bands to lower frequencies. The "breathing" modes can then be assigned to the absorptions at 1554 cm^{-1} and 1448 cm^{-1} which are in the anticipated range. This set of assignments corresponds well with the anticipated intensities of the absorption. The aromatic C-H stretching can be seen at 3095 cm^{-1} . No specific C-Br vibration between 680 and 500 cm^{-1} can be assigned, because the vibrations in this region are poorly resolved.

TABLE VII
INFRARED ABSORPTION BANDS FOR BROMOVILOGEN

3436 (s)	3095 (w)
3025 (m)	2989 (m)
2860 (w)	1631 (s)
1554 (w)	1507 (w)
1495 (w)	1448 (m)
1360 (w)	1270 (w)
1208 (w)	1172 (w)
826 (m)	737 (w)

Nuclear Magnetic Resonance Spectroscopy. The $^1\text{H-NMR}$ spectrum was recorded on the 400 MHz spectrometer and is shown in the Appendix. The viologen was dissolved in methanol- d_4 , and TMS was the standard. The assignment in table form can be seen in Table VIII.

TABLE VIII
 $^1\text{H-NMR}$ CHEMICAL SHIFTS FOR BROMOVIOLAGEN

Chem. Shifts	Rel. Int.	Splitting	Assignment
2.70	1.18	quint	Br-CH ₂ -CH ₂ -
3.61	1.21	triplet	Br-CH ₂ -CH ₂ -
4.98	1.21	triplet	CH ₂ -bipyridyl
6.06	1.00	singlet	CH ₂ -ph
7.47	1.50	multiplet	CH ₂ -aromat-H
7.65	1.00	multiplet	CH ₂ -aromat-H
8.74	2.36	multiplet	bipyridyl-H
9.39	2.38	multiplet	bipyridyl-H

The spectrum shows that both the monosubstituted viologen and the disubstituted viologen were formed in the reaction. The ratio could be calculated by peak integration to be about 27:1(mono/di). The BromoViologen contains a propyl group that has a triplet, quintet, and triplet pattern. The methylene protons adjacent to bromide experience a less deshielding influence than the ones in

the neighborhood of the positively charged bipyridinium. Therefore the triplet at lowest field can be assigned to the methylene protons adjacent to the pyridinium ring. The heteroaromatic *p*-substituted dipyriddy displays the typical AA'BB' pattern at very low field due to the positive charge. The benzyl protons show as a singlet, and the phenyl protons give rise to a multiplet in the aromatic region.

TABLE IX

 ^1H -NMR CHEMICAL SHIFTS FOR DISUBSTITUTED VIOLOGEN

ppm	Rel. Int.	Splitting	Assignment
3.01	0.04	quintet	CH ₂ -CH ₂ -CH ₂
5.09	0.10	triplet	CH ₂ -CH ₂ -CH ₂
6.06	1.00*	singlet	CH ₂ -ph
7.47	1.50*	multiplet	CH ₂ -aromat- <u>H</u>
7.65	1.00*	multiplet	CH ₂ -aromat- <u>H</u>
8.74	2.36*	multiplet	bipyridyl- <u>H</u>
9.39	2.38*	multiplet	bipyridyl- <u>H</u>

*peaks in common with BromoViologen (Table VIII)

The disubstituted viologen possesses a vertical symmetry plane in contrast to the BromoViologen. As a consequence the two outside methylene groups are chemically equivalent and have the same chemical shifts. The propyl group with its symmetry plane through the

middle positioned carbon gives rise to a quintet and a triplet pattern. The chemical shifts for the benzyl and the aromatic protons are not affected by the disubstitution and are the same as those of the BromoViologen. For this reason no specific integration could be done for the aromatic protons for the disubstituted viologen. The chemical shifts and the proton assignments are given in Table IX. The spectrum is shown in the Appendix.

¹³C-NMR Spectroscopy. A decoupled carbon-13 NMR spectrum reveals the number of nonequivalent carbons in a compound. The material was dissolved in methanol-d₄ using TMS as a standard. Peak assignments were done by calculations using reference values available in the literature.⁴⁴ No equivalent could be found for the disubstituted dipyridyl unit so that values for a -NR₃⁺ group were taken instead, assuming that the alkylated ammonium group has similar effects as the positively charged bipyridinium group. The BromoViologen has a horizontal symmetry plane. This symmetry property has the consequence that the aromatic *ortho* and *meta* positions are chemically equivalent. Considering these points the spectrum of the BromoViologen should consist of 10 peaks in the aromatic region (above 110 ppm) and 4 peaks in the alkyl region (80-0 ppm), which are both in agreement with the experimental results. The chemical shifts as well as

the assignments are given in Figure 12 and Table X. The spectrum is shown in the Appendix.

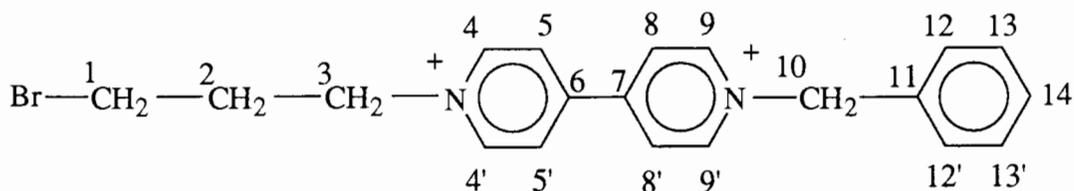


Figure 12. Structure of BromoViologen.

TABLE X

¹³C-NMR CHEMICAL SHIFTS FOR BROMOVIOLAGEN

ppm	assignment	ppm	assignment
29.5	C2	130.7	C8, C8'
34.7	C1	131.1	C14
61.6	C3	134.3	C11
65.7	C10	147.0	C6
128.5	C13, C13'	147.3	C7
128.6	C12, C12'	151.3	C4, C4'
130.5	C5, C5'	151.4	C9, C9'

FAB Mass spectrometry. The results for FAB-MS spectrometry are listed in Table XI. The spectrum is shown in the Appendix. The first striking feature of the spectrum is that the molecular ion peak is missing. This may be due to the fact that the substance is dissolved in

a matrix (in this case glycerol) and the bromide ions are able to dissociate from the molecule. Fragments that leave the matrix upon irradiation are not accompanied by bromide ions for this reason. The backbone structure however can be seen at 370 units. Another assumption that must be made is that the viologen was reduced during the irradiation process. Peak positions are given by the value m/z (mass to charge ratio). Considering that the viologen carries a double positive charge, the peak for the backbone should appear at 185 units. Since this is not the case the viologen must be only a +1 ion. This statement is supported by the fact that viologens are easily reducible and the solvents used for the matrix (glycerol and n-butyl alcohol) are good electron donors. The fragmentation pattern follows expected cleavages. The loss of the phenyl group leads to the monosubstituted dipyridyl. The presence of a bromine in this fragment can be seen in two neighboring lines that represent the ^{79}Br and ^{81}Br isotopes, respectively. Loss of the bromine gives rise to a peak at 197 units. Finally the propyl group is cleaved off to yield dipyridyl which results in a peak at 157 units. The peak at 247 results if the bromopropyl group is cleaved off first from the backbone structure. Additional adduct formations can be observed. Glycerol adds to the monosubstituted dipyridyl (peak 247) to give a peak at 338 units. The disubstitution impurity can be

assigned to a peak at 617 units. This dimer carries one bromide with it, supported by the fact that the isotopic pair of lines is observed. The loss of this bromine gives rise to a small peak at 536 units.

TABLE XI
FAB-MS DATA FOR BROMOVILOGEN

m/z	intensity	fragment assignment
617	17	$\text{CH}_2 \leftarrow \text{CH}_2 - \text{N} \langle \text{C}_6\text{H}_4 \rangle - \langle \text{C}_6\text{H}_4 \rangle \text{N}^+ - \text{CH}_2 - \langle \text{C}_6\text{H}_5 \rangle \cdot \text{Br}^-$
536	2.0	$\text{CH}_2 \leftarrow \text{CH}_2 - \text{N} \langle \text{C}_6\text{H}_4 \rangle - \langle \text{C}_6\text{H}_4 \rangle \text{N}^+ - \text{CH}_2 - \langle \text{C}_6\text{H}_5 \rangle \cdot$
370	57	$\text{Br} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{N} \langle \text{C}_6\text{H}_4 \rangle - \langle \text{C}_6\text{H}_4 \rangle \text{N}^+ - \text{CH}_2 - \langle \text{C}_6\text{H}_5 \rangle$
338	94	glycerol + $\text{N} \langle \text{C}_6\text{H}_4 \rangle - \langle \text{C}_6\text{H}_4 \rangle \text{N}^+ - \text{CH}_2 - \langle \text{C}_6\text{H}_5 \rangle$
279	67	$\text{Br} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{N}^+ \langle \text{C}_6\text{H}_4 \rangle - \langle \text{C}_6\text{H}_4 \rangle \text{N}$
247	100	$\text{N} \langle \text{C}_6\text{H}_4 \rangle - \langle \text{C}_6\text{H}_4 \rangle \text{N}^+ - \text{CH}_2 - \langle \text{C}_6\text{H}_5 \rangle$
197	33	$\cdot \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{N}^+ \langle \text{C}_6\text{H}_4 \rangle - \langle \text{C}_6\text{H}_4 \rangle \text{N}$
157	36	$\text{N} \langle \text{C}_6\text{H}_4 \rangle - \langle \text{C}_6\text{H}_4 \rangle \text{N}^+$

Elemental analysis. The results of the elemental analysis are shown in Table XII. They are in poor agreement with the calculated results. The experimentally obtained values don't add up to 100%. One reason for this could be that the sample still contained water, which is favored by the hygroscopic nature of the BromoViologen. A

calculation for BromoViologen dihydrate was done and showed much better agreement with the experimental results.

TABLE XII

ELEMENTAL ANALYSIS OF BROMOVIOLAGEN AND DISUBSTITUTED VIOLAGEN MIXTURE

	% C	% H	% N	% Br
calc.	45.35	4.09	5.29	45.26
calc.	42.51	4.09	5.29	42.42
dihydrate				
exp.	43.64	4.08	5.24	42.26

CHAPTER V

SYNTHESIS OF HYDROXYVIOLOGEN

INTRODUCTION

Viologens are electron acceptors. The presence of an alcohol group during the HydroxyViologen synthesis presents the risk that the viologen might get reduced during preparation. To prevent this the 3-bromo-1-propanol concentration should be kept low and reaction times kept short. The described synthesis displayed no reduction of the viologen, as indicated by $^1\text{H-NMR}$ and the absence of a blue color.

HydroxyViologen

The synthesis was done similar to previous viologen preparations described in the literature.⁴⁵ 1-Phenylmethyl-4-(4'-pyridyl)pyridinium bromide (2.0 g, 6 mmol) was dissolved in 200 ml anhydrous acetonitrile in a 1000 ml 3-neck round-bottom flask equipped with reflux condenser. 3-Bromo-1-propanol (1.1 ml, 12 mmol) was added at once and the solution refluxed. An additional 1.1 ml (12 mmol) 3-bromo-1-propanol was added after 9 hours. The first precipitate was yellow and observed after 24 hours reaction

time. The solution was allowed to cool after 41 hours. The precipitate was filtered off and dried in oil pump vacuum (1.33 g). A dithionite-test applied on the yellow crude turned out positive. The yield was 1.33 g (2.8 mmol) = 47%. The melting point was determined to be 236-238°C.

Structural Analysis

Infrared Spectroscopy. All absorption frequencies are tabulated in Table XIII and the spectrum is included in the Appendix. The O-H stretch vibration can be observed at 3330 cm^{-1} as a broad band due to intermolecular hydrogen bonding. The C-O stretching is difficult to assign in the fingerprint region. Saturated primary alcohols absorb in the region between 1085 and 1030 cm^{-1} so that the absorption band at 1072 cm^{-1} could be the C-O stretching. The in-plane O-H deformation vibration can be assigned to the absorption at 1366 cm^{-1} . The strongest band in the spectrum is the C=N stretching vibration at 1637 cm^{-1} . The shorter wavelength C=C stretching vibration for the phenyl ring is not observed, maybe for the same reasons as mentioned for the BromoViologen. However, the weak C-H stretching vibration at 3107 cm^{-1} and the moderately strong absorptions at 732 cm^{-1} and 690 cm^{-1} clearly indicate the phenyl ring presence. This is also supported by the observation of characteristic weak overtone bands in the region 1660-2000 cm^{-1} .

TABLE XIII
INFRARED ABSORPTION BANDS FOR HYDROXYVIOLOGEN

3330 (br)	3107 (w)
3025 (s)	2989 (s)
2872 (m)	1637 (vs)
1554 (m)	1507 (m)
1495 (m)	1448 (s)
1366 (m)	1325 (w)
1172 (m)	1072 (m)
873 (m)	732 (m)
690 (w)	614 (w)

Nuclear Magnetic Resonance Spectroscopy. The proton chemical shifts for the HydroxyViologen, acquired at 400 MHz, are listed in Table XIV. The spectrum is shown in the Appendix. The material was dissolved in methanol-d₄ using TMS as a standard. The propyl chain gives rise to a triplet, quintet and triplet pattern. The methylene protons adjacent to the hydroxy group are deshielded and show up at lower field than the quintet pattern. The triplet pattern of the methylene protons adjacent to the dipyridyl unit appear at lowest field in the propyl pattern, since they are strongly deshielded by the positive charge. The disubstituted dipyridyl displays the expected AA'BB' patterns of a 1,4-disubstituted aromatic compound. Due to

the deshielding of the positive charges the pattern is shifted downfield to 9.03 ppm. The benzyl protons appear as a singlet, and the phenyl protons appear as a multiplet in the aromatic region. All integrated peaks are in accordance with the expected proton ratio.

TABLE XIV
 ^1H -NMR CHEMICAL SHIFTS FOR HYDROXYVIOLOGEN

ppm	Rel. Int.	Splitting	Assignment
2.30	1.00	quintet	HO-CH ₂ -CH ₂
3.68	1.00	triplet	HO-CH ₂ -CH ₂ -
4.90	1.00	triplet	CH ₂ -bipyridyl
6.03	1.00	singlet	CH ₂ -ph
7.47	1.51	multiplet	ph- <u>H</u> (m+p)
7.63	1.00	multiplet	ph- <u>H</u> (o)
8.72	1.98	multiplet	bipyridyl- <u>H</u>
9.34	1.99	multiplet	bipyridyl- <u>H</u>

^{13}C -NMR Spectroscopy. The pure material was dissolved in methanol-d₄ using TMS as a standard. The spectrum is shown in the Appendix. Peak assignments were done using a -NR₃⁺ group for the calculations as substitute for the bipyridinium assuming similar effects.⁴⁶ The HydroxyViologen has a horizontal symmetry plane. For this reason the *ortho* positions and *meta* positions give rise to only one peak each. The total number of nonequivalent

aromatic carbons is 10 and the number of nonequivalent alkyl carbons is 4, which are both in agreement with the experimental results. The specific assignments of the peaks is given in Table XV and Figure 13.

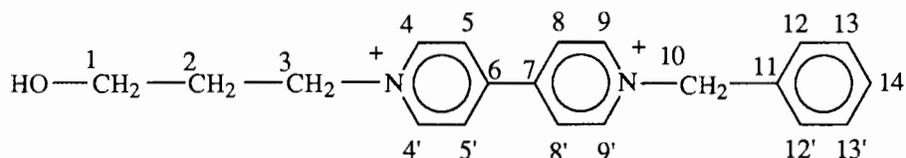


Figure 13. Structure of Hydroxyviologen.

TABLE XV

^{13}C -NMR CHEMICAL SHIFTS FOR HYDROXYVIOLOGEN

ppm	assignment	ppm	assignment
34.5	C2	130.8	C8, C8'
59.0	C3	131.2	C14
60.9	C1	134.3	C11
65.8	C10	147.0	C6
128.3	C13, C13'	147.4	C7
128.6	C12, C12'	151.1	C4, C4'
130.5	C5, C5'	151.7	C9, C9'

FAB Mass spectrometry. The results for FAB mass spectrometry are listed in Table XVI. The spectrum is shown in the Appendix. As in the BromoViologen spectrum it can be observed that the molecular ion peak is missing.

TABLE XVI
 FAB-MS DATA FOR HYDROXYVIOLOGEN

m/z	intensity	fragment assignment
397	4	$\text{HO}-(\text{CH}_2)_3-\text{N}^+\text{C}_5\text{H}_4-\text{C}_5\text{H}_4\text{N}^+-\text{CH}_2-\text{C}_6\text{H}_5 +$
338	11	$\text{HOCH}_2\text{CHOHCH}_2\text{O}^-$ $\text{N}^+\text{C}_5\text{H}_4-\text{C}_5\text{H}_4\text{N}^+-\text{CH}_2-\text{C}_6\text{H}_5 + \text{glycerol}$
306	100	$\text{HO}-(\text{CH}_2)_3-\text{N}^+\text{C}_5\text{H}_4-\text{C}_5\text{H}_4\text{N}^+-\text{CH}_2-\text{C}_6\text{H}_5$
247	14	$\text{N}^+\text{C}_5\text{H}_4-\text{C}_5\text{H}_4\text{N}^+-\text{CH}_2-\text{C}_6\text{H}_5$
215	69	$\text{HO}-(\text{CH}_2)_3-\text{N}^+\text{C}_5\text{H}_4-\text{C}_5\text{H}_4\text{N}^+$
157	17	$\text{N}^+\text{C}_5\text{H}_4-\text{C}_5\text{H}_4\text{N}^+$

The backbone structure can be seen at 306 units. Again it must be assumed that the viologen was reduced in the ionization process. The splitting off of the propyl group is responsible for the peak at 247 units. Preferred is however the loss of the benzyl group, which can be concluded from the higher peak intensity at 215 units. The further loss of the propyl group leads to 4,4'-dipyridyl, which can be seen as the peak at 157 units. The observed peak at 185 units is due to the solvent glycerol, which was confirmed by a blank sample. In addition to the fragments, some adduct formations are observable. The first one is a combination of glycerol and benzylbipyridyl at peak 247.

The second at 397 is due to adduct formation of the HydroxyViologen and a glycerol alkoxide.

Elemental Analysis. The data for elemental analysis are listed in Table XVI. The calculated values are in agreement with the experimentally obtained results. The maximum deviation is 0.25%.

TABLE XVII
ELEMENTAL ANALYSIS OF HYDROXYVIOLOGEN

	% C	% H	% N	% Br
calc.	51.53	4.76	6.01	34.28
exp.	51.28	4.84	5.89	34.36

CHAPTER VI

SYNTHESIS OF AMINODONOR

INTRODUCTION

The synthesis of the AminoDonor involves the coupling of an amino group with a carboxylic acid. The formation of an amide bond can usually be done by reaction of the corresponding acid chloride with an amine. In this case the starting material (4-aminobutanoic acid) contained both an amine group as well as a carboxylic acid group, so that the acid chloride would lead to polymer formation.

The approach for the synthesis was derived from peptide synthesis.⁴⁷ Hereby the amino group of the bifunctional starting material was protected by a tert-butoxycarbonyl group (Boc). The amino protected acid was then coupled with the donor amine using a carbodiimide as a coupling agent. The last step was the removal of the Boc protecting group with a strong acid.

The free amine is very sensitive towards oxidation. Exposure of the free amine to air leads to darkening within hours. Therefore for each use small amounts were prepared right away to keep exposure to air as low as possible. The

amine dihydrochloride was prepared for structural analysis.
A structural overview is illustrated in Figure 14.

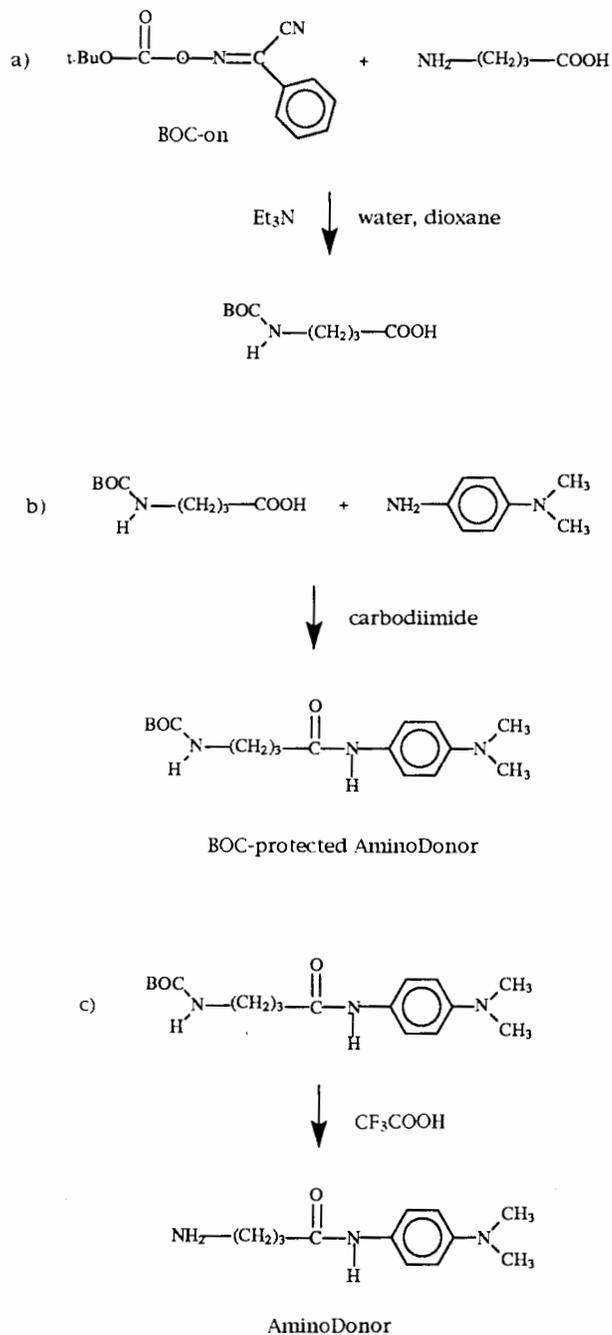


Figure 14. Synthesis of AminoDonor.

N-(Tert-butoxycarbonyl)-4-aminobutanoic acid

The synthesis was done according to the literature.⁴⁸ 4-Aminobutanoic acid (8.0 g, 77 mmol) and 16.2 ml (116 mmol) of triethylamine were dissolved in a mixture of 70 ml water and 50 ml dioxane. 2-(Tert-butoxycarbonyloxyimino)-2-phenylacetonitrile (Boc-on) (21.0 g, 85.3 mmol) was added to this solution, whereby a slight yellow colorization was observed. This mixture was stirred for 24 hours. Water (50-ml) and 100 ml of ethyl acetate were added and the layers separated. The water phase was acidified to pH 3 and extracted three times with 100 ml of ethyl acetate. The combined organic phases were evaporated off on a rotovap to give a yellowish high viscosity oil. Yellow-white crystals were obtained from this oil after storage in the refrigerator for one night.

For further purification the crystals were dissolved in ether and extracted two times with 0.5 N NaHCO₃ solution. The combined aqueous layers were acidified with 5% citric acid and extracted three times with 100 ml of ether. The combined organic layers were dried over MgSO₄, filtered and evaporated off on the rotovap. It remained a slightly colored oil. Cooling of this oil in the refrigerator led to formation of white crystals.

The yield was 12.22 g (64 mmol) = 83%. The melting point was found to be 54-55°C.

Structural Analysis

Infrared Spectroscopy. The infrared absorptions are tabulated in Table XVIII and the spectrum is shown in the Appendix. Characteristic functional groups in the molecule are a carboxylic acid and an amide. In the solid state, a hydrogen bonded hydroxy group exhibits a typical broad absorption at 3365-3324 cm^{-1} . The carboxyl C=O stretching vibration is observed at 1725 cm^{-1} . Assignments of C-O stretching and O-H deformation vibrations can't be made, since many other absorptions are observed in this region like $-\text{CH}_2\text{CO}-$ deformation vibration and C-N stretching vibration. The N-H stretching vibration of the amide overlaps with the broad band of the hydroxy group.

TABLE XVIII

INFRARED ABSORPTION BANDS FOR
N-(TERT-BUTOXYCARBONYL)-4-AMINOBUTANOIC ACID

3365 (br)	3224 (br)
2978 (s)	2931 (m)
2860 (m)	2813 (w)
1725 (s)	1678 (s)
1542 (s)	1454 (m)
1366 (m)	1278 (m)
1166 (m)	1014 (m)
861 (w)	661 (m)

Nuclear Magnetic Resonance Spectroscopy. The spectrum was recorded on the 90 MHz instrument. The material was dissolved in CDCl_3 using TMS as a standard. The chemical shifts and the assignments are tabulated in Table XIX. The three methyl groups of the Boc protecting group can freely rotate and appear therefore as a singlet. The propyl group of the aliphatic acid gives rise to the expected triplet, quintet, triplet pattern. The methylene protons adjacent to the nitrogen experience the biggest shift to low field followed by the triplet from the methylene protons next to the carboxylic group. The proton attached to the nitrogen shows up as a broad peak at 4.85 ppm due to the quadrupole moment of the nitrogen.⁴⁹ The integration of the peaks is in agreement with the expected hydrogen ratio.

TABLE XIX

¹H-NMR CHEMICAL SHIFTS FOR N` (TERT-BUTOXYCARBONYL)`4-AMINOBUTANOIC ACID

ppm	Rel. Int.	Splitting	Assignment
1.43	9	singlet	(CH ₃) ₃ -O
1.83	2	quintet	CH ₂ -CH ₂ -CH ₂ -
2.35	2	triplet	CH ₂ -CH ₂ -COOH
3.18	2	triplet	-HN-CH ₂ -CH ₂ -
4.85	1	singlet	NH-CH ₂

Boc-protected AminoDonor

The coupling of the amine with an acid was done according to reference.⁴⁸ The *N,N*-dimethyl-*p*-phenylene diamine was distilled in vacuum before using. *N*-(Tert-butoxycarbonyl)-4-aminobutanoic acid (6.05 g, 32 mmol) and 4.4 ml (31.7 mmol) of triethylamine were dissolved in 50 ml dichloromethane in a 250 ml round-bottom flask. *N,N*-dimethyl-*p*-phenylenediamine (4.3 g, 31.7 mmol) and 6.1 g (32 mmol) of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride were added to this solution. The solution turned slightly brown. This mixture was stirred at room temperature for 16 hours. The solution was washed with 80 ml water, 80 ml 50% citric acid, 80 ml water, 80 ml saturated NaHCO₃ solution and 80 ml water again. The organic phase was dried over MgSO₄, filtered and evaporated off on a rotovap. A white-brown solid was obtained, then recrystallized from cyclohexane/dioxane (v:v, 16:3). This gave white crystals, which were then dried on the oil pump. The yield was 7.25 g (22.9 mmol) = 74%. The melting point was found to be 117°C.

Structural Analysis

Infrared Spectroscopy. The infrared absorptions are tabulated in Table XX and the spectrum is shown in the Appendix. The important functional groups are two secondary amide bonds and a para substituted phenyl ring. Two sharp

N-H stretching vibrations are observed at 3342 cm^{-1} and 3307 cm^{-1} . The bands are slightly shifted to lower frequencies due to the solid state. The amide I band as a consequence of the C=O stretching vibration can be seen at 1684 cm^{-1} . The amide II band indicates N-H deformation and C-N stretching vibrations. They appear as strong absorptions at 1648 cm^{-1} (C-N) and 1531 cm^{-1} (N-H). The two medium strong bands at 1272 cm^{-1} and 1166 cm^{-1} can be assigned to a asymmetric and symmetric C-O-C stretching vibration, respectively. The para substituted phenyl ring gives rise to characteristic medium absorption at 808 cm^{-1} . The "breathing" modes are present at 1595 cm^{-1} and 1443 cm^{-1} .

TABLE XX

INFRARED ABSORPTION BANDS FOR BOC-PROTECTED AMINODONOR

3342 (sh, s)	3307 (sh, s)
3177 (w)	2978 (m)
2931 (m)	2872 (m)
2790 (m)	1684 (s)
1648 (s)	1607 (m)
1595 (m)	1531 (s)
1443 (m)	1272 (m)
1166 (m)	808 (m)

Nuclear Magnetic Resonance Spectroscopy. The spectrum was recorded on the 90 MHz NMR spectrometer and it is shown in the Appendix. The material was dissolved in CDCl_3 using TMS as a standard. The chemical shifts are tabulated in Table XXI.

TABLE XXI

 ^1H -NMR CHEMICAL SHIFTS FOR BOC-PROTECTED AMINODONOR

ppm	Rel. Int.	Splitting	Assignment
1.50	9	singlet	(CH_3) ₃ -O
1.90	2	quintet	NH- CH_2 - CH_2 -
2.40	2	triplet	CH_2 -CO
2.93	6	singlet	N(CH_3) ₂
3.25	2	triplet	NH- CH_2 - CH_2 -
4.91	1	singlet	NH- CH_2 - CH_2 -
6.81	2	doublet	aromat- H
7.56	2	doublet	aromat- H
8.28	1	singlet	NH-aromat

The methyl hydrogens of the Boc protection group are chemically equivalent and appear as a singlet. The propyl group gives rise to the expected triplet, quintet, triplet splitting. The methylene protons adjacent to the nitrogen experience the strongest deshielding effect and show up at lowest field. The hydrogens from the amide bond appear as

singlets. The one in proximity to the phenyl ring is deshielded and is shifted to lower field for this reason. Both peaks are broadened due to the quadrupole moment of the nitrogen.⁵⁸ The para-substituted phenyl ring exhibits the classical AA'BB' splitting pattern. Integration is in agreement with the expected hydrogen ratio.

FAB Mass spectrometry. The results for FAB mass spectrometry are listed in Table XXII. The spectrum is shown in the Appendix. The molecular ion peak, which indicates the molecular weight of the compound, is observable with the highest intensity at 321 units. One property of the FAB method is that a proton is added to each fragment or the original compound. So in fact the molecular ion peak was expected at 322 units. As an explanation it could be conceived that the AminoDonor preferentially gets oxidized to form a radical cation instead of accepting a proton. The dimer of BOC-AminoDonor is protonated in contrast to the monomer and the corresponding peak at 643 units can be clearly observed in weaker intensity. The remaining peaks are in agreement with the expected fragmentation pattern. The tertiary-butyl group is cleaved off first to yield a fragment that gives rise to a peak at 266 units. The further loss of CO₂ is responsible for a peak at 222 units. Theoretically it also could be possible that a N(CH₃) radical is cleaved off, which is unlikely in comparison to the competitive CO₂

Elemental analysis. The results for elemental analysis are shown in Table XXIII. The calculated values are in agreement with the experimentally obtained results.

TABLE XXIII
ELEMENTAL ANALYSIS OF BOC-PROTECTED AMINODONOR

	% C	% H	% N
calc.	63.53	8.47	13.09
exp.	63.47	8.44	12.99

AminoDonor

The removal of the Boc amino protecting group was done according to reference.⁵⁰ Boc-protected AminoDonor (250 mg, 0.81 mmol) was stirred at room temperature with 1.5 ml (19.4 mmol) of trifluoroacetic acid in a 25 ml round-bottom flask for 15 minutes. Immediate gas evolution and a very slight color change to purple were observed. The solution was cooled down in an ice bath and adjusted to pH 13 by addition of 6 M NaOH. The purple color disappeared at basic pH. The aqueous solution was extracted three times with 25 ml dichloromethane. The combined organic layers were dried over Na₂SO₄, filtered and evaporated off on the rotovap. The crude was further dried on the oil pump. The yield was 177 mg (0.8 mmol) = 99%. The amine dihydrochloride was prepared for structural analysis, since the free amine is sensitive to oxidation. Thus 3 M HCl

(0.25 ml) was added to 50 mg of the free amine. The excess water and hydrochloric acid were evaporated off in vacuum.

Structural Analysis

Infrared Spectroscopy. The infrared absorptions of the free amine are tabulated in Table XXIV, and the infrared absorptions of the dihydrochloride are tabulated in Table XXV. The spectra are shown in the Appendix.

AminoDonor. Characteristic groups are primary and tertiary amines as well as a secondary amide. The N-H stretching vibration of the primary amine appears as a broad band of medium intensity. Two absorption bands at 3424 cm^{-1} and 3295 cm^{-1} are sticking out of this broad band indicating the asymmetric and symmetric vibrations. The N-H deformation vibration can be observed at 1631 cm^{-1} . It is not possible to identify unambiguously the C-N stretching vibration in the fingerprint region due to its common weak absorption. The amide I band (C=O stretching vibration) appears as a strong absorption at 1654 cm^{-1} . The amide II band is observed as a strong absorption at 1519 cm^{-1} . The para-substituted phenyl ring gives rise to two characteristic C=C stretching modes. The higher wavenumber one is observed at 1601 cm^{-1} , the lower wavenumber one is hidden by the amide II band. The benzene para substitution pattern can clearly be determined by a single medium absorption at 814 cm^{-1} .

TABLE XXIV

INFRARED ABSORPTION BANDS FOR
 N-[4'-(N',N'-DIMETHYLAMINOPHENYL)]-4-AMINOBUTANAMIDE

3424 (br)	3295 (s)
3107 (m)	2954 (m)
2884 (m)	2790 (m)
1654 (s)	1631 (m)
1601 (s)	1519 (vs)
1478 (m)	1443 (m)
1319 (m)	1161 (w)
814 (m)	520 (w)

AminoDonor Dihydrochloride. The spectrum displays all important absorption bands like amide I and II. A detailed description is redundant, since it was done for the free amine, so that just the hydrohalide absorptions are described. The N-H⁺ stretching vibrations of the NH₃⁺ group can be viewed as a number of broad bands⁵¹ with medium intensity from 3436 cm⁻¹ to 3048 cm⁻¹. The N-H⁺ stretching vibrations from the R₃NH⁺ group are shifted in correct manner to lower frequencies and appear as a bundle of peaks with medium intensity from 2684 cm⁻¹ to 2496 cm⁻¹.

TABLE XXV

INFRARED ABSORPTION BANDS FOR
 N-[4'-(N',N'-DIMETHYLAMINOPHENYL)]-4-AMINOBTANAMIDE
 DIHYDROCHLORIDE

3436 (br)	3283 (m)
3236 (m)	3189 (m)
3048 (s)	2966 (s)
2884 (m)	2684 (m)
2637 (m)	2578 (m)
2496 (m)	2449 (m)
1684 (vs)	1601 (m)
1548 (s)	1519 (s)
1478 (m)	1313 (m)
1137 (m)	849 (m)

Nuclear Magnetic Resonance Spectroscopy. The spectrum was recorded on the 90 MHz instrument. The spectrum of the is shown in the Appendix. The dihydrochloride (to avoid oxidation) was dissolved in D₂O using DSS as a standard. The chemical shifts are tabulated in Table XXVI. The amine protons as well as the amide proton are exchanged with the solvent and don't appear in the spectrum. The propyl group gives rise to a triplet, quintet, triplet pattern with the triplet adjacent to the nitrogen at lowest field. The two methyl groups attached to the diamine are chemically equivalent and give rise to a

singlet. The aromatic protons don't appear in an expected AA'BB' pattern but as a multiplet in the aromatic region. Since the spectrum was taken in acidic medium it could be assumed that both nitrogens on the benzene ring can get protonated creating a similar environment on both sides. In this case the AA'BB' splitting pattern can't be observed.

TABLE XXVI

¹H-NMR CHEMICAL SHIFTS FOR
N-[4'-(N',N'-DIMETHYLAMINOPHENYL)]-4-AMINOBUTANAMIDE

ppm	Rel. Int.	Splitting	Assignment
2.08	2	quintet	⁺ H ₃ N-CH ₂ -CH ₂ -
2.66	2	triplet	CH ₂ -CO
3.16	2	triplet	⁺ H ₃ N-CH ₂ -CH ₂ -
3.33	6	singlet	N(CH ₃) ₂
7.78	4	multiplet	aromat- <u>H</u>

CHAPTER VII

SYNTHESIS OF BROMODONOR

INTRODUCTION

The BromoDonor synthesis involves an amide bond formation in its final step. The procedure was to form the 4-bromobutyryl chloride first, which is then allowed to react with N,N dimethyl-p-phenylenediamine. Although straightforward looking, this synthesis was troublesome. The formation of side products in large scale was observed each time the coupling was attempted. Changing the base from pyridine to triethylamine and varying the reaction time increased the yield only little.

The attempt to synthesize the BromoDonor under milder reaction conditions using the carboxylic acid and the amine as starting materials and a carbodiimide as coupling agent failed. Product formation of less than 1% was observed by this method.

Furthermore it turned out that the BromoDonor is sensitive to light exposure and heat. A structural overview of the synthesis is given in Figure 15.

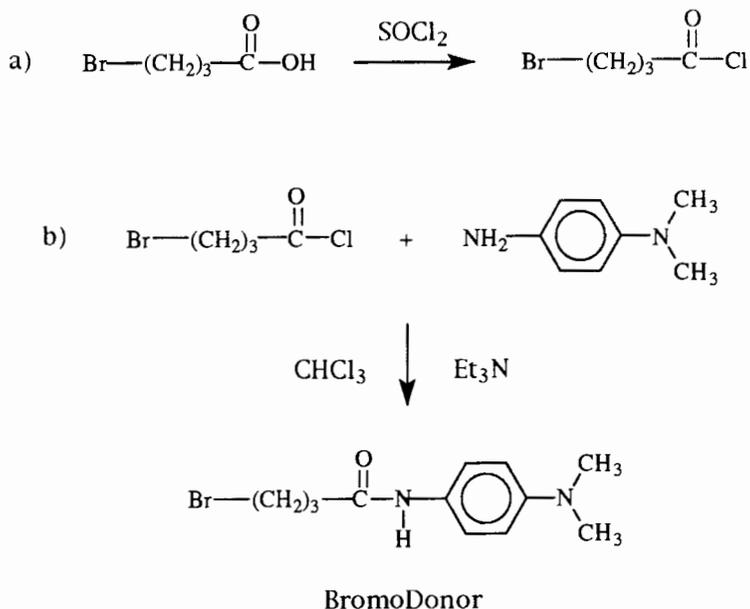


Figure 15. Synthesis of BromoDonor.

4-Bromobutyryl chloride

The acid chloride is prepared by the common known procedure of refluxing the acid in thionyl chloride. 4-Bromobutyric acid (11.98 g, 71 mmol) and 10 ml (137 mmol) thionyl chloride were refluxed in a 25 ml round-bottom flask equipped with reflux condenser and drying tube for 2 hours. The thionyl chloride was distilled before using. Excessive thionyl chloride was subsequently distilled off. The acid chloride was distilled in vacuum (bp 106°C at 4.3 Torr). A colorless oil was obtained. The yield was 12.58 g (68 mmol) = 95%.

Structural Analysis

Infrared Spectroscopy. The infrared absorption bands are listed in Table XXVII and the spectrum is shown in the Appendix. The C=O stretching vibration of the acid chloride is shifted in typical manner to higher frequency and appears at 1789 cm^{-1} . The very weak absorption band at 3565 cm^{-1} suggests that the acid chloride was hydrolyzed only to a small degree during the sample preparation.

TABLE XXVII
INFRARED ABSORPTION BANDS FOR 4-BROMOBUTYRYL CHLORIDE

3565 (w)	2966 (m)
2907 (m)	1789 (s)
1437 (m)	973 (m)

BromoDonor

The coupling of the amine with the acid chloride is carried out in a typical preparation method using triethylamine as a base. 4-Bromobutyryl chloride (5.93 g, 32 mmol) was dissolved in 25 ml DMF and stirred in a 500 ml Erlenmeyer flask. Pyridine (3.3 ml, 41.6 mmol) and 4.22 g (31 mmol) N,N-dimethyl-p-phenylenediamine were added. The solution was stirred at room temperature overnight. To this solution 40 ml of 1 M NaOH were added and the pH verified as basic. The brown solution was extracted with 100 ml of ether, twice with 50 ml of 1 M HCl and once with 60 ml of

water. Since all product seemed to be in the water phase, the solution was neutralized with NaHCO_3 and extracted two times with 100 ml of ether. The combined organic layers were dried for 2 hours over Na_2SO_4 and the ether evaporated off on the rotovap. The residue was very impure. Therefore it was dissolved in ether again and the product precipitated out by addition of cyclohexane. The precipitate was filtered, recrystallized from cyclohexane and dried in vacuum. The yield was 0.42 g (1.4 mmol) = 5%. The melting point was determined to be 114-116°C.

Structural Analysis

Infrared Spectroscopy. The infrared absorption bands are listed in Table XXIX and the spectrum in shown is the Appendix. The main characteristic group is a secondary amide. The N-H stretching vibration can be seen at 3260 cm^{-1} , indicating trans configuration. The amide I band (C=O stretching vibration) is observed at 1648 cm^{-1} . The amide II band (N-H deformation and C-N stretching vibration) shows up as a strong absorption band at 1525 cm^{-1} . The breathing modes of the benzene ring can be seen at 1590 cm^{-1} and 1495 cm^{-1} . A single strong absorption at 814 cm^{-1} clearly indicates the para-substitution of the benzene ring.

Nuclear Magnetic Resonance Spectroscopy. The spectrum was recorded on the 90 MHz spectrometer and is

shown in the Appendix. The chemical shifts are tabulated in Table XXVIII. The material was dissolved in CDCl_3 using TMS as a standard. The propyl group gives rise to a triplet, quintet, triplet splitting pattern. The methylene protons adjacent to the bromide can be assigned to the triplet at lowest field due the deshielding effect of the bromide. The para-substituted benzene ring displays the expected AA'BB' splitting pattern. The amide proton is hidden under the doublet of the aromatic pattern at 7.41 ppm. The deshielding effect of the nitrogen and the benzene ring move the chemical shift to such low field but within range of the literature values. The two methyl groups can freely rotate and appear as a singlet.

TABLE XXVIII

^1H -NMR CHEMICAL SHIFTS FOR
N-[4'-(N',N'-DIMETHYLAMINOPHENYL)]-4-BROMOBUTANAMIDE

ppm	Rel. Int.	Splitting	Assignment
2.26	2	quintet	$\text{CH}_2\text{-CH}_2\text{-CH}_2$
2.56	2	triplet	CO-CH_2
3.03	6	singlet	$\text{N}(\text{CH}_3)_2$
3.73	2	triplet	$\text{CH}_2\text{-Br}$
6.81	2	doublet	aromat- <u>H</u>
7.41	2	doublet	aromat- <u>H</u>

TABLE XXIX
INFRARED ABSORPTION BANDS FOR
N-[4'-(N',N'-DIMETHYLAMINOPHENYL)]-4-BROMOBUTANAMIDE

3260 (s)	3166 (m)
3107 (m)	3048 (m)
2907 (m)	2801 (m)
1648 (s)	1613 (m)
1590 (m)	1525 (vs)
1437 (m)	1260 (m)
1260 (m)	1161 (m)
814 (s)	520 (w)

CHAPTER VIII

COUPLING ATTEMPTS OF ACCEPTORS AND DONORS TO THE PORPHYRINS

INTRODUCTION

It was first attempted to couple the HydroxyViologen in a substitution reaction with TCCPP. The first experiment was done following typical procedures⁵² using triethylamine as a base. Since the coupling was unsuccessful the experiment was repeated using N,N-dimethylaminopyridine (DMAP)⁵³ as a catalyst. The catalytic activity of DMAP has been found to increase the yield tremendously in this type of reaction.⁵⁴ Even with this catalyst a coupling couldn't be achieved. An assumption was that traces of water would hydrolyze the acid chloride before the linkage could occur. To exclude this possibility the experiment was repeated with both triethylamine as base and DMAP as catalyst under inert atmosphere. All solvents had been dried again before using. The experiment did not result in the desired linkage. It can be concluded that moisture was not the reason for the failure of the coupling. These three experiments are described under sections a₁ to a₃ below.

In the same type of reaction it was attempted to link the AminoDonor to TCCPP. The AminoDonor was prepared

separately before the experiment, dried in vacuum for one or two days and used right away so that contact with air was minimized. The experiment was done twice. One attempt was made following typical procedures using triethylamine as base, and the other with DMAP as an additional catalyst. In both cases no linkage could be observed by ^1H NMR. These experiments are described under sections b₁ and b₂.

A further possibility to couple an amine and a carboxylic acid is using a coupling agent like a carbodiimide. The attempt to link TCPP and AminoDonor in the same manner as done before for the AminoDonor synthesis was not successful. The experimental description is described in section b₃.

A further attempt was to attach the BromoViologen to THPP. The reaction is a nucleophilic substitution following the $\text{S}_{\text{N}}2$ mechanism. Polar aprotic solvents are suitable for this reaction type since they solvate only the cations leading to 'naked anions' with much higher nucleophilicity. Such solvents are DMF, DMSO or HMPA. HMPA shows significantly higher reaction rates in comparison to other aprotic solvents. It was attempted to couple TCPP as nucleophile with BromoViologen in HMPA according to previously described esterifications.^{55,56} Surprisingly the solubility of the porphyrin in HMPA is very low. The limited solubility made the coupling reaction impossible. The reaction of the phenol group with BromoViologen was

carried out using DMF as solvent and cesium carbonate as base.⁵⁷ Methyl iodide was added to the solution at its final stage to methylate the unreacted phenol groups. This was done to decrease the polarity of the molecule so that a subsequent chromatography could be carried out easier. The linkage was unsuccessful even under refluxing and 24 hours reaction time, although the methylation was found to be complete within 30 minutes to yield TMPP. The experiment is described in section c.

A further attempt was to couple the BromoViologen in a nucleophilic substitution to TCPP. The synthesis was done according to reference (58) using cesium carbonate as a base. Also in this case no product formation could be detected by NMR. The experiment is described in section d.

TCCPP and HydroxyViologen (a1)

TCCPP (446 mg, 0.51 mmol) was dissolved in 20 ml anhydrous DMF and cooled in an ice bath. HydroxyViologen (240 mg, 0.51 mmol) and 0.86 ml (6.1 mmol) triethylamine were dissolved in 50 ml anhydrous DMF and added to this solution. Heat evolution and brown colorization was observed at this step. The solution was stirred for 10 minutes at 0°C and for 20 more minutes at room temperature. Water (10 ml) was added to stop the reaction whereby heat evolution was also observed. The DMF/water phase was evaporated off to dryness in vacuum. The brown-purple crude

was dissolved in methanol with a little 3 M HCl addition and chromatographed on a silica gel column (100 g silica gel, height 15 cm, diameter 4.5 cm, eluent MeOH/3 M HCl v:v; 9:1). No product formation could be observed by ^1H -NMR.

TCCPP and HydroxyViologen (a₂)

HydroxyViologen (73 mg, 0.16 mmol) and 0.88 ml (6.3 mmol) triethylamine were dissolved in 200 ml DMF (anhydrous). 4-Dimethylaminopyridine (DMAP) (7 mg) was added whereby the color changed slightly from yellow to green-yellow. TCCPP (137 mg, 0.16 mmol) was dissolved in 100 ml DMF (anhydrous) and added at once. The solution turned brown in color. Weak heat evolution was observed. The organic phase was distilled off in vacuum after 18 hours reaction time. The remaining crude was dissolved in a little DMF and chromatographed on a column (150 g silica gel, eluent first DMF then MeOH). The top of the column was sliced off and extracted with MeOH (acidified), since it contained porphyrin. However, ^1H -NMR analysis of each fraction displayed no product formation.

TCCPP and HydroxyViologen (a₃)

HydroxyViologen (593 mg, 1.27 mmol) and 621 mg (5.08 mmol) DMAP were dissolved in 100 ml DMF (anhydrous) in a 250 ml 3-neck flask with addition funnel and two gas

tube adapters. The setup was flushed with N₂ for 10 minutes. Triethylamine (7.09 ml, 5.08 mmol) was added to this solution. The color changed from yellow to green-yellow. TCCPP (1.1 mg, 0.13 mmol) was dissolved in 50 ml DMF (anhydrous) and added immediately via an addition funnel. The color changed from brown to purple with time. The solution was stirred under N₂ atmosphere for 24 hours. Water (3 ml) was added and the solution stirred for 30 more minutes. The DMF phase was distilled off in vacuum and the crude material rinsed thoroughly with water and CH₂Cl₂ to remove unreacted viologen and DMAP. ¹H-NMR of this crude showed that there could be no coupling product in there.

TCCPP and AminoDonor(b₁)

AminoDonor (177 mg, 0.8 mmol) was dissolved in 30 ml anhydrous dichloromethane. The solution was cooled down in an ice bath. TCCPP (171 mg, 0.2 mmol) dissolved in 20 ml anhydrous dichloromethane was added at once to this solution. Brown colorization was observed. Triethylamine (0.33 ml, 2.39 mmol) was added after 3 minutes and the solution stirred at room temperature. The reaction was stopped after 45 minutes by addition of 2 ml water and vigorous stirring. The organic phase was evaporated off on the rotovap. The crude mixture was dissolved in methanol with a small amount of 3 M HCl and chromatographed on a column (100 g silica gel, height 35 cm, diameter 2 cm,

eluent MeOH/3 M HCl v:v; 25:1). No product formation could be detected by $^1\text{H-NMR}$.

TCCPP and AminoDonor (b2)

AminoDonor (61 mg, 0.27 mmol), 8 mg (0.065 mmol) DMAP and 1.53 ml (11.0 mmol) triethylamine were dissolved in 40 ml anhydrous dichloromethane. TCCPP (238 mg, 0.27 mmol) was dissolved in 25 ml anhydrous dichloromethane and added at once via an addition funnel. Heat evolution and brown colorization was observed. The organic phase was evaporated off after 18 hours to dryness. The remaining crude material was dissolved in 5 ml DMF and chromatographed on a column (100 g silica gel, eluent acetone). The upper part of the column was sliced off and extracted with MeOH (acidified). $^1\text{H-NMR}$ analysis of each fraction showed no product formation.

TCCP and AminoDonor (b3)

TCCP (100 mg, 0.13 mmol) and 138 mg (0.47 mmol) of AminoDonor dihydrochloride were dissolved in 20 ml dichloromethane. Triethylamine (0.44 ml, 0.6 mmol) and 98 mg (5.11 mmol) of 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide hydrochloride were added and the solution stirred at room temperature for 24 hours. The organic phase was extracted with 5% citric acid, washed with water, dried over Na_2SO_4 , filtered and further dried on the oil pump. NMR analysis of the crude indicated no product formation.

THPP and BromoViologen (c)

Cesium carbonate (1.43 g, 0.44 mmol) and BromoViologen (116 mg, 0.22 mmol) were dissolved in 150 ml DMF and stirred. The solution turned black. THPP (150 mg, 0.22 mmol) was added and the solution stirred at room temperature for 20 hours. The color changed to green. Methyl iodide (0.2 ml, 3.3 mmol) was added and the solution stirred until the methylation was found to be complete after 30 minutes. The organic phase was distilled off to dryness and the purple remaining crude material chromatographed on a silica gel column (150 g silica gel, height 30 cm, diameter 4.5 cm, eluent first chloroform then methanol). Different fractions were obtained, whereby the main product was TMPP. The desired coupling product could not be detected by $^1\text{H-NMR}$ analysis.

TCPP and BromoViologen (d)

TCPP (200 mg, 0.25 mmol) was partly dissolved in deionized water. The pH of this solution was 4.75. A 20% Cs_2CO_3 solution was added to the TCPP solution until the pH reached 9. The aqueous solution was evaporated off to dryness and the crude product dissolved in 35 ml DMSO, giving it a purple color. BromoViologen (134 mg, 0.25 mmol) was added and the solution refluxed for 16 hours. An additional 325 mg (1.0 mmol) Cs_2CO_3 was added, since a

control TLC showed no product formation (no additional spot and no quenching of the red porphyrin fluorescence was observed in comparison with the starting material).

Although the solution was refluxed for 30 more hours, no product formation could be seen by TLC. Therefore 74 mg (0.48 mmol) of DBU were added as another base. The DMSO was distilled off to dryness after 80 hours reaction time and the crude dissolved in 6 ml MeOH. The crude was chromatographed on a silica gel column (30 g silica gel, height 22 cm, diameter 2 cm, eluent MeOH). None of the fractions contained the desired product, as tested by ^1H NMR spectroscopy.

CONCLUSION

Four new molecules have been synthesized, two electron donors and two electron acceptors. Each compound has a specific functional group attached, so that covalent linkages to other molecules are possible. The molecules can be used for artificial photosynthesis due to their electron donating or electron accepting properties.

The attempt to couple these compounds to porphyrins was unsuccessful. The reaction conditions for the couplings were chosen to be mild in the first instance, e.g., room temperature without acidic or basic conditions. This approach was taken for prospective linkages to the porphyrin film, because mild reaction conditions would have

been necessary to avoid destroying the sensitive film. The typical reaction conditions were scrutinized for the various linkages and were found not to be applicable for these specific porphyrins, electron donors and acceptors.

Further research could be done to make these linkages possible. One possibility might be to synthesize donors and acceptors with better leaving groups. Studies could be done on an IodoViologen, a TosylateViologen or an IodoDonor for nucleophilic substitutions with THPP or TCPP.

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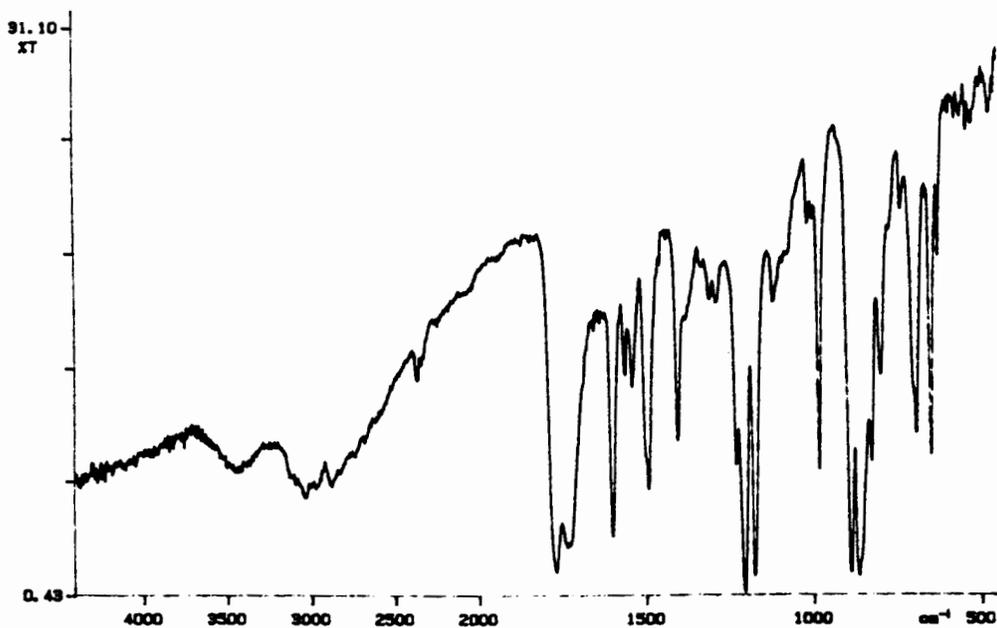
APPENDIX

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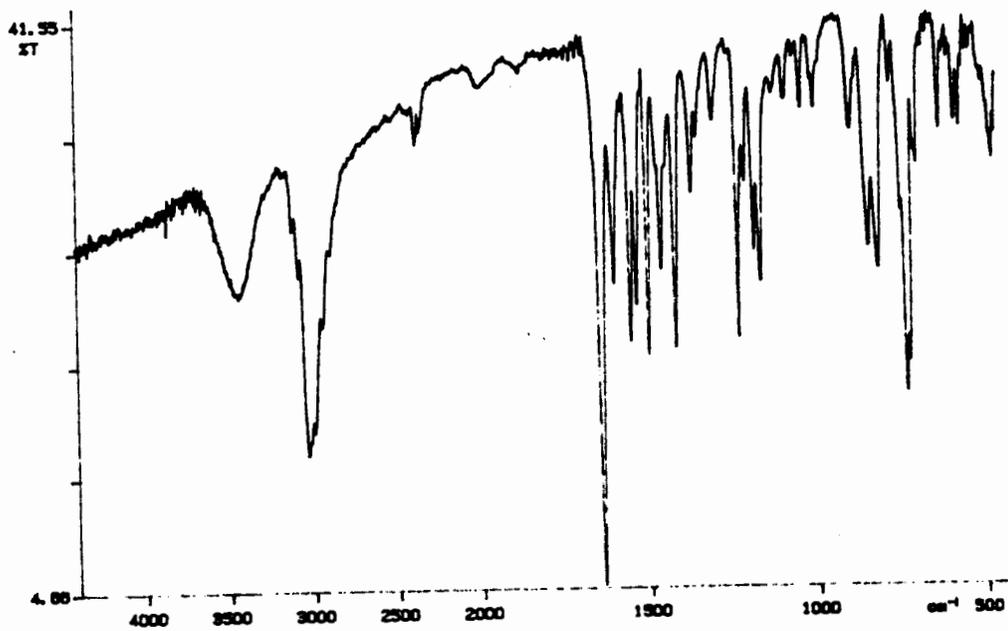
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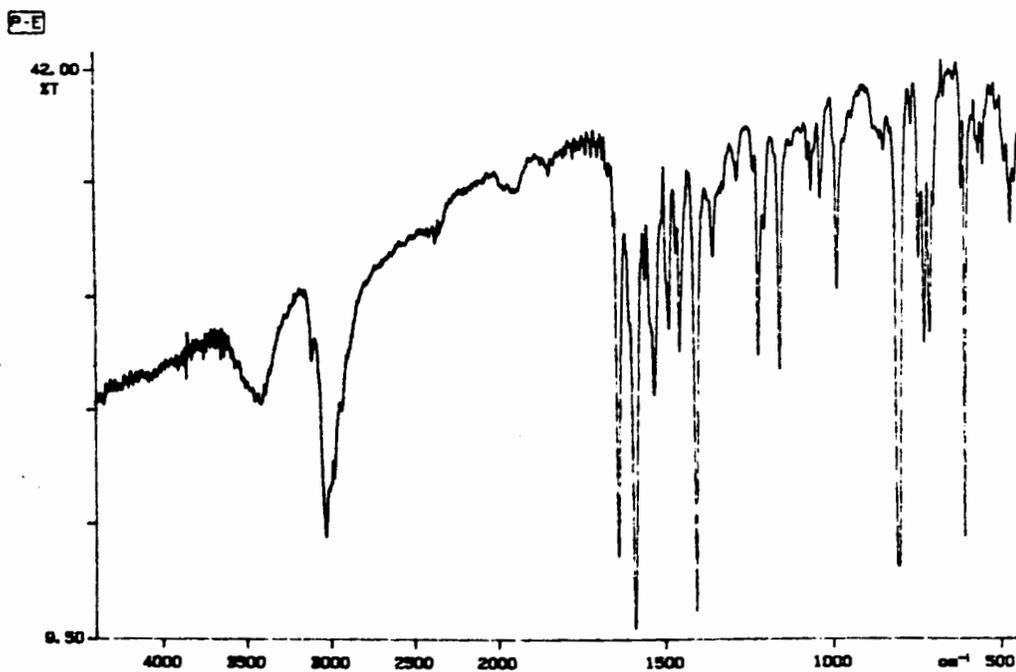
P-E



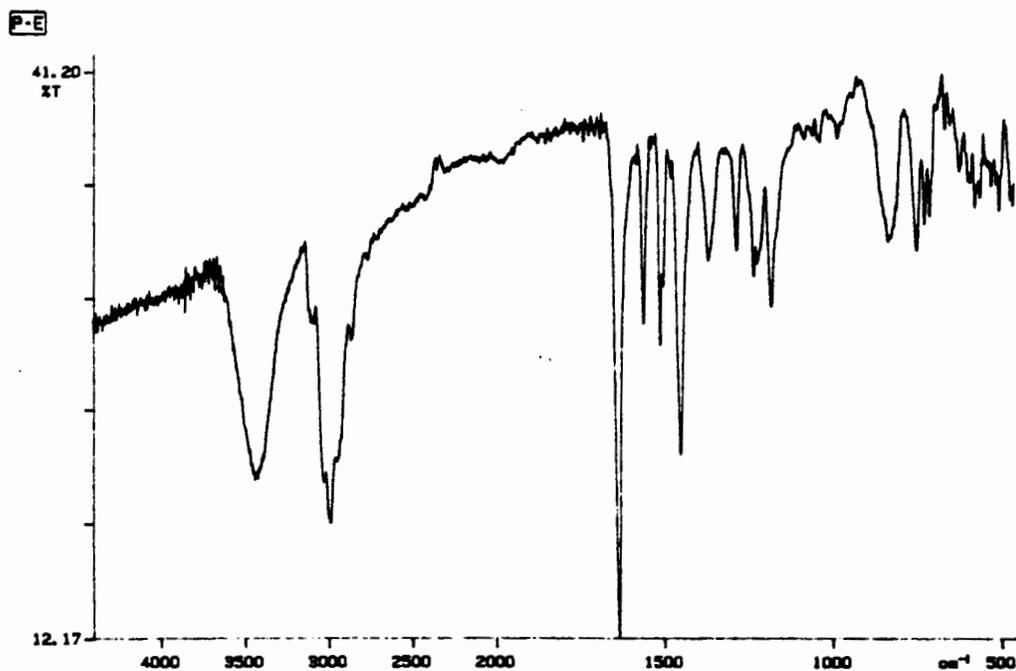
Infrared spectrum of TCCPP

P-E

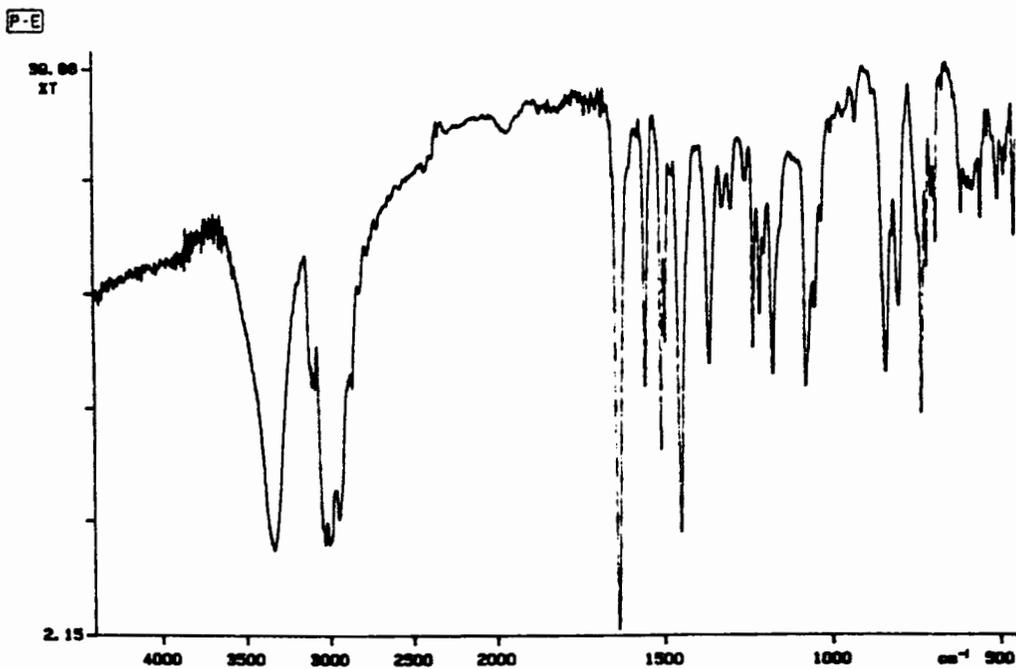
Infrared spectrum of 1-Phenylmethyl-
4-(4'-pyridyl)pyridinium chloride



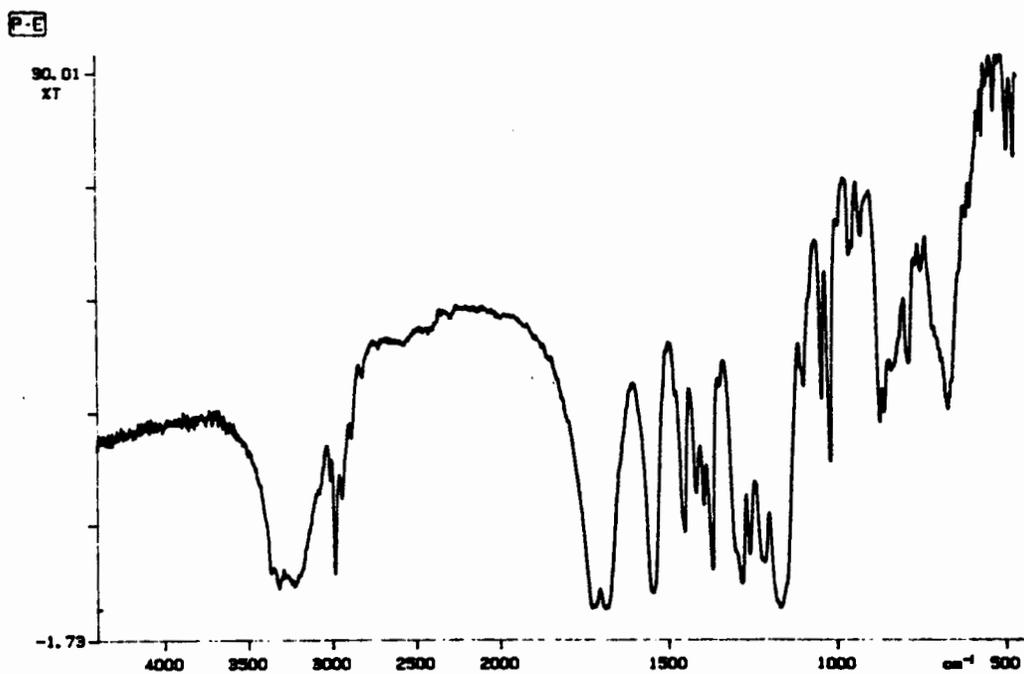
Infrared spectrum of PreViologen



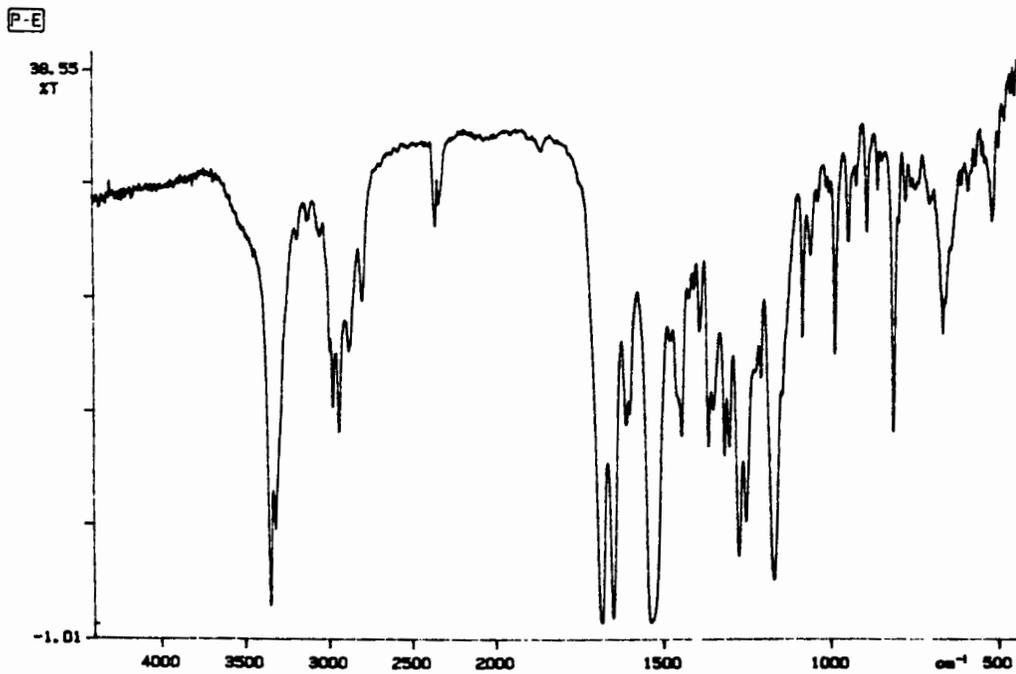
Infrared spectrum of BromoViologen



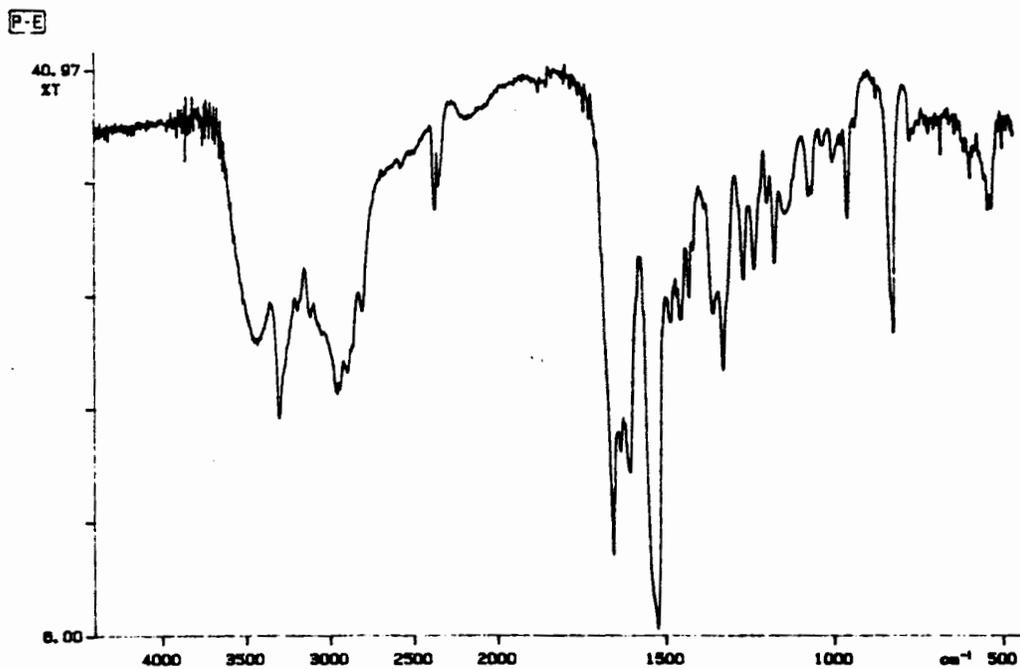
Infrared spectrum of HydroxyViologen



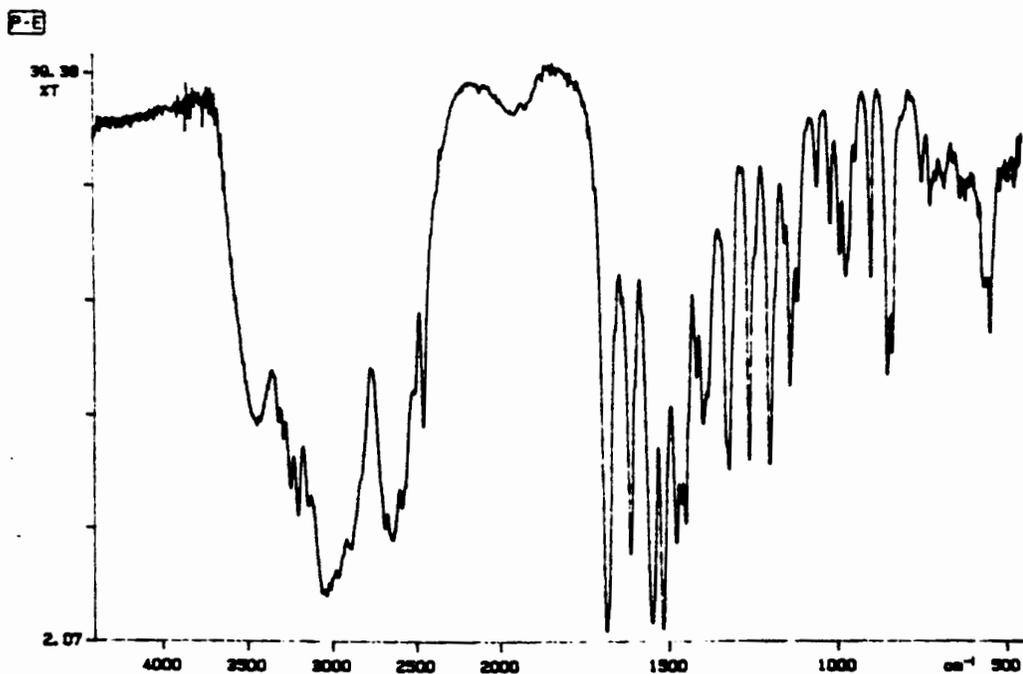
Infrared spectrum of N-(Tert-butoxycarbonyl)-4-aminobutanoic acid



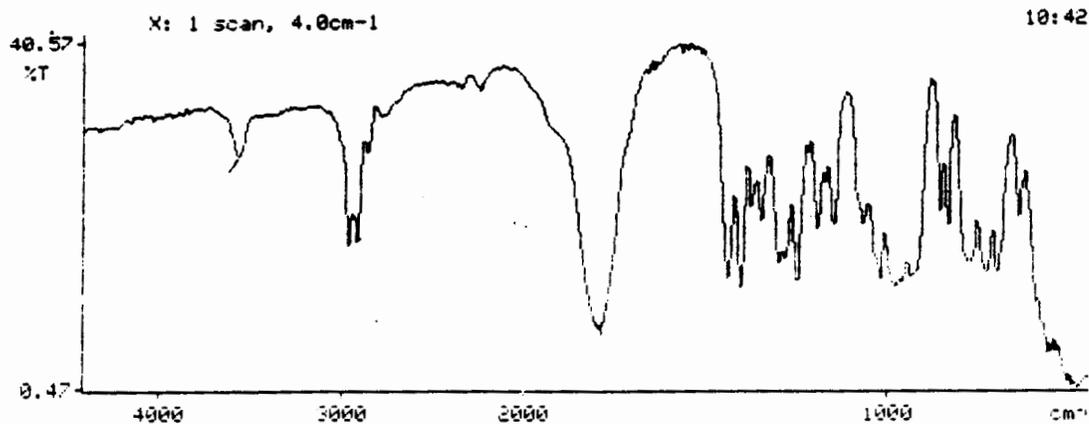
Infrared spectrum of BOC-protected AminoDonor



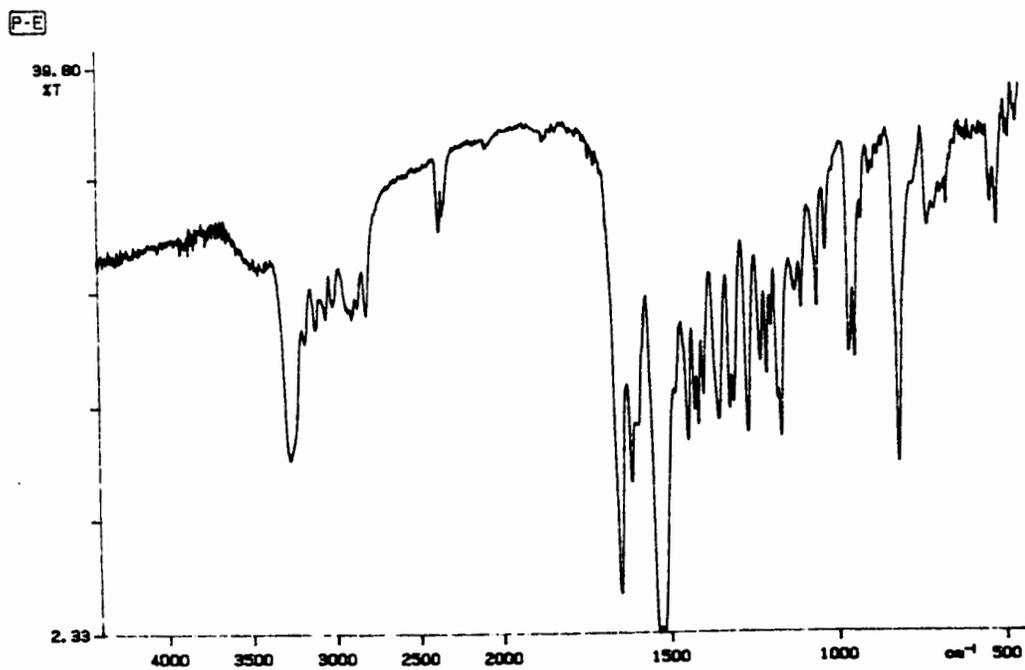
Infrared spectrum of AminoDonor



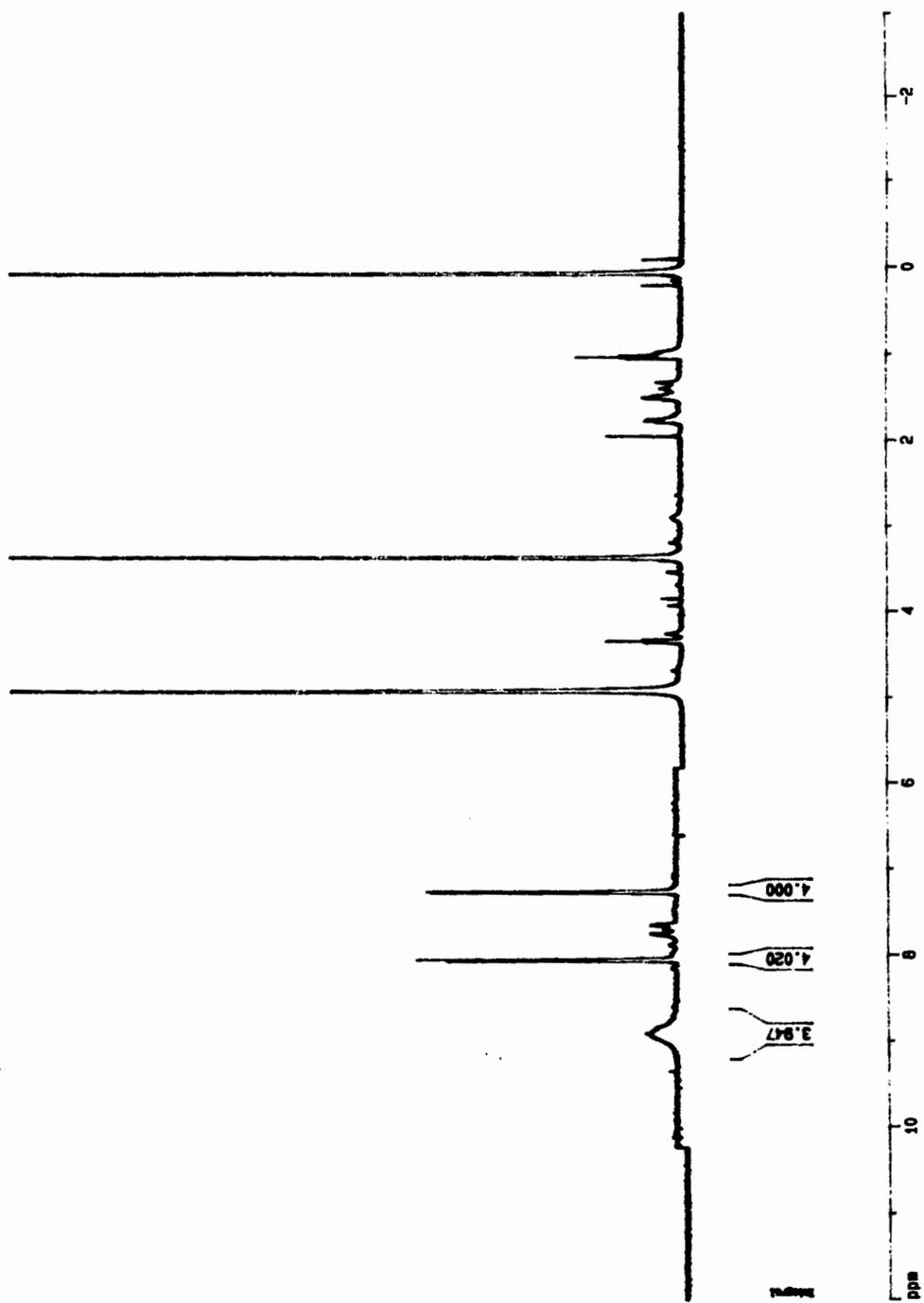
Infrared spectrum of AminoDonor dihydrochloride

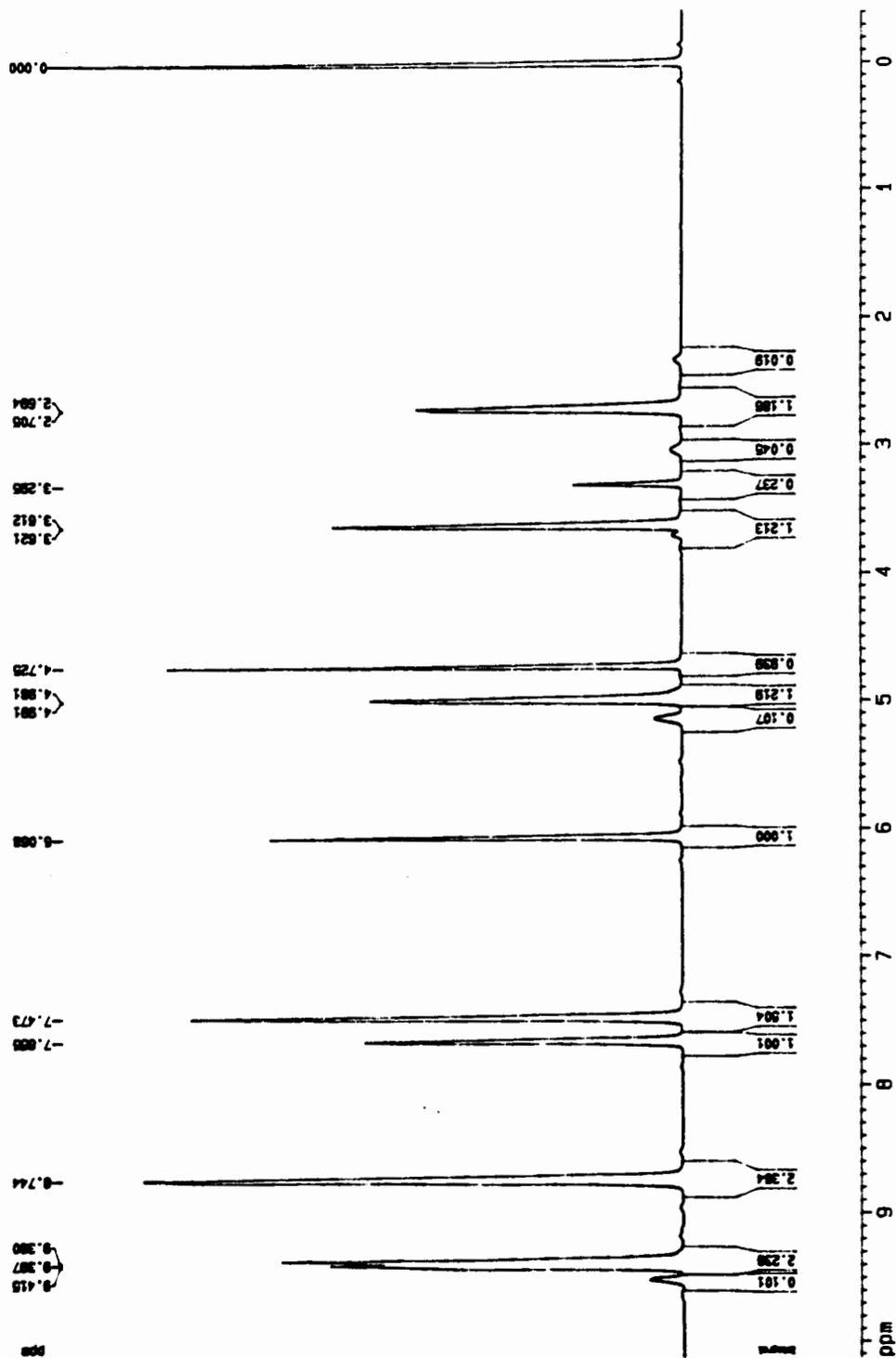


Infrared spectrum of 4-Bromobutyryl chloride

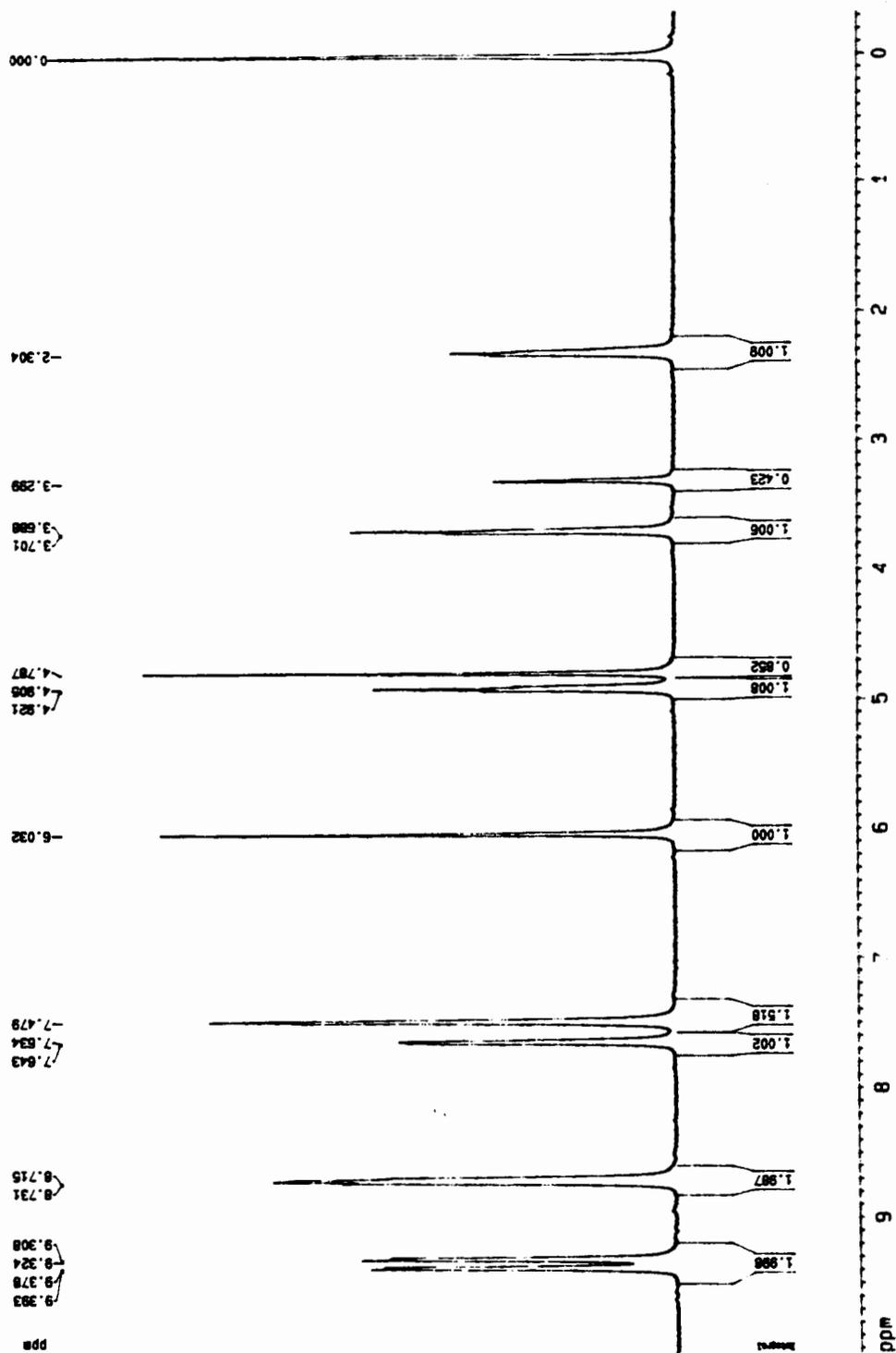


Infrared spectrum of BromoDonor

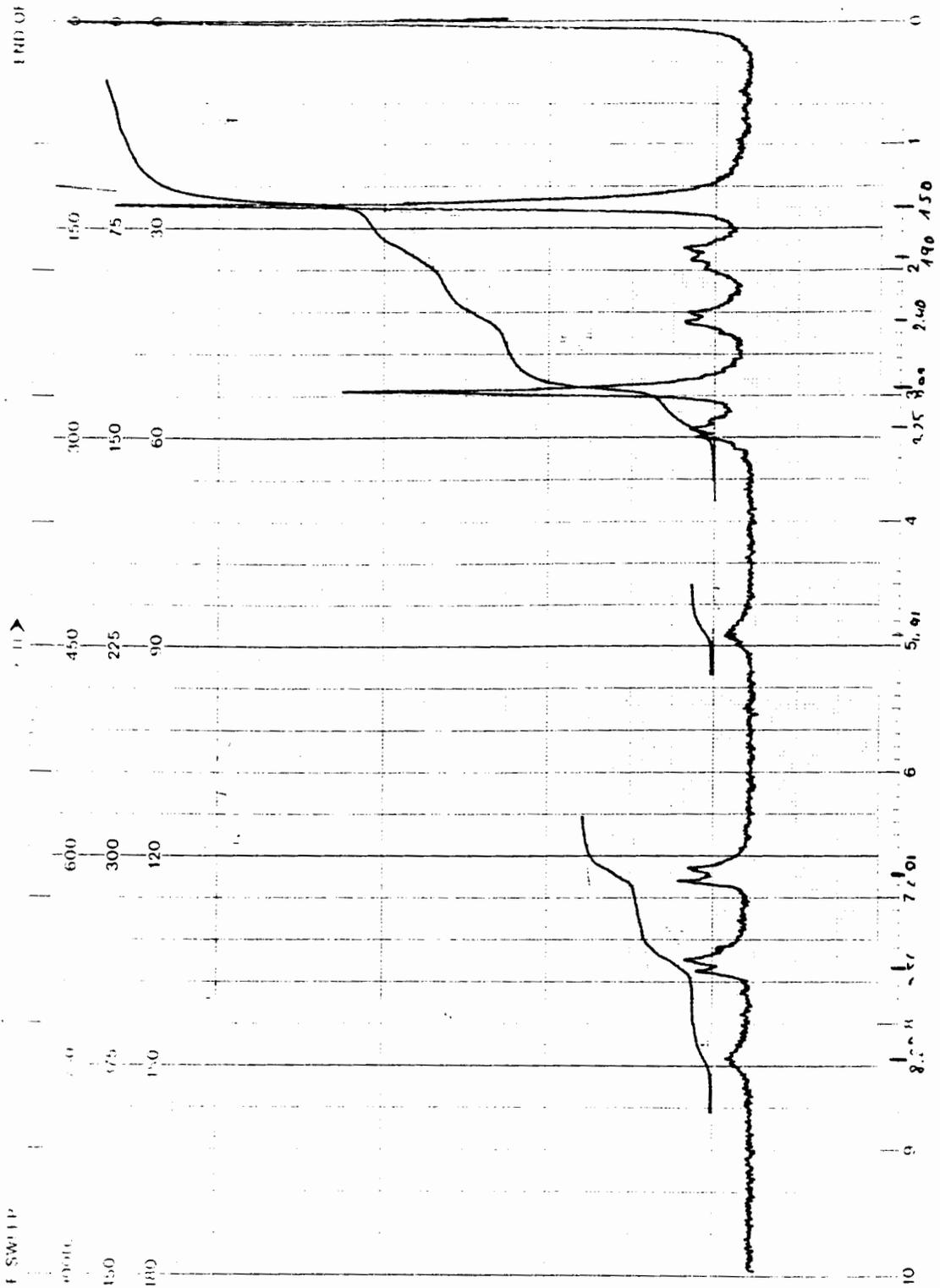
 $^1\text{H-NMR}$ of THPP



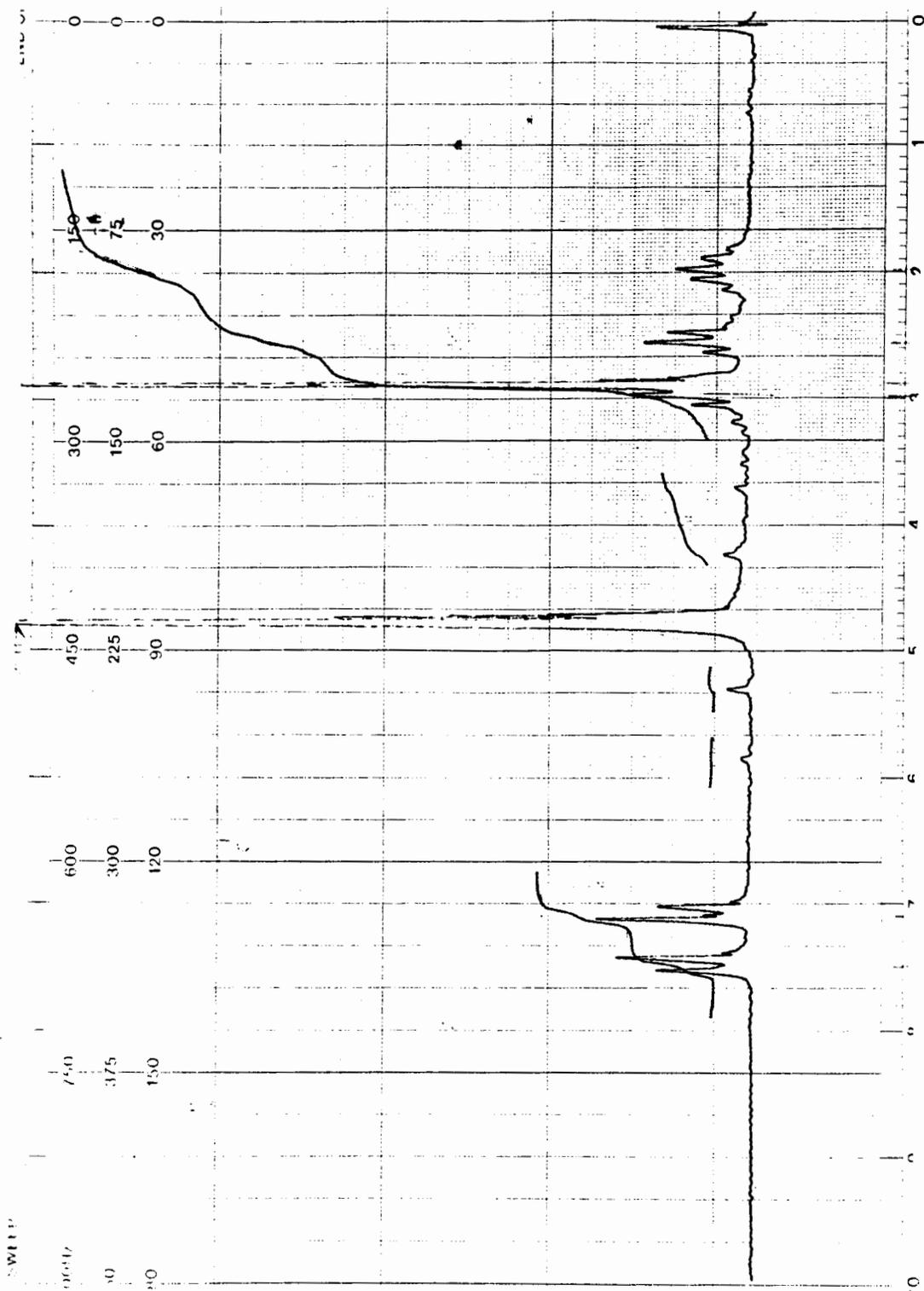
$^1\text{H-NMR}$ of BromoViologen



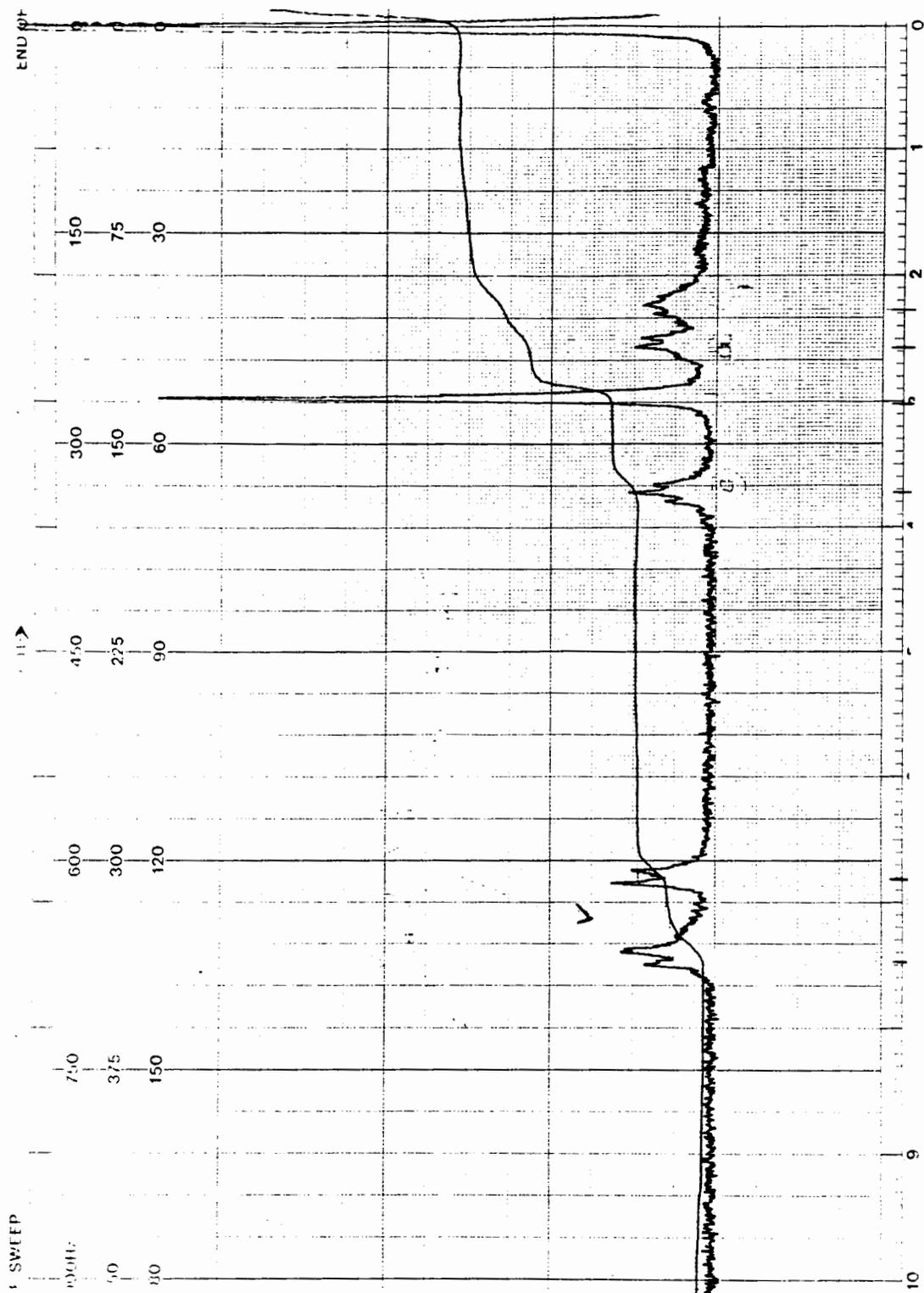
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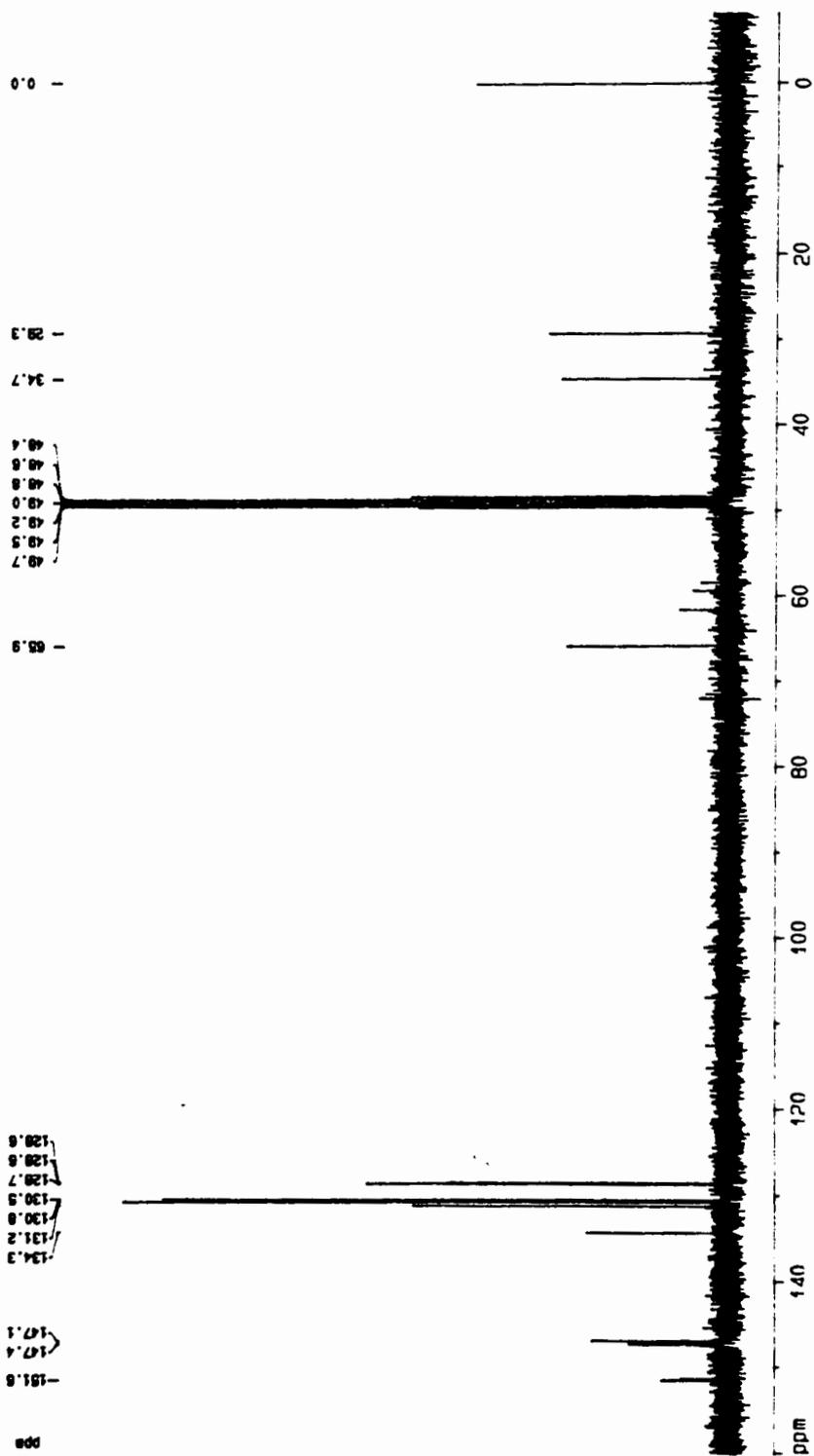
$^1\text{H-NMR}$ of BOC-AminoDonor



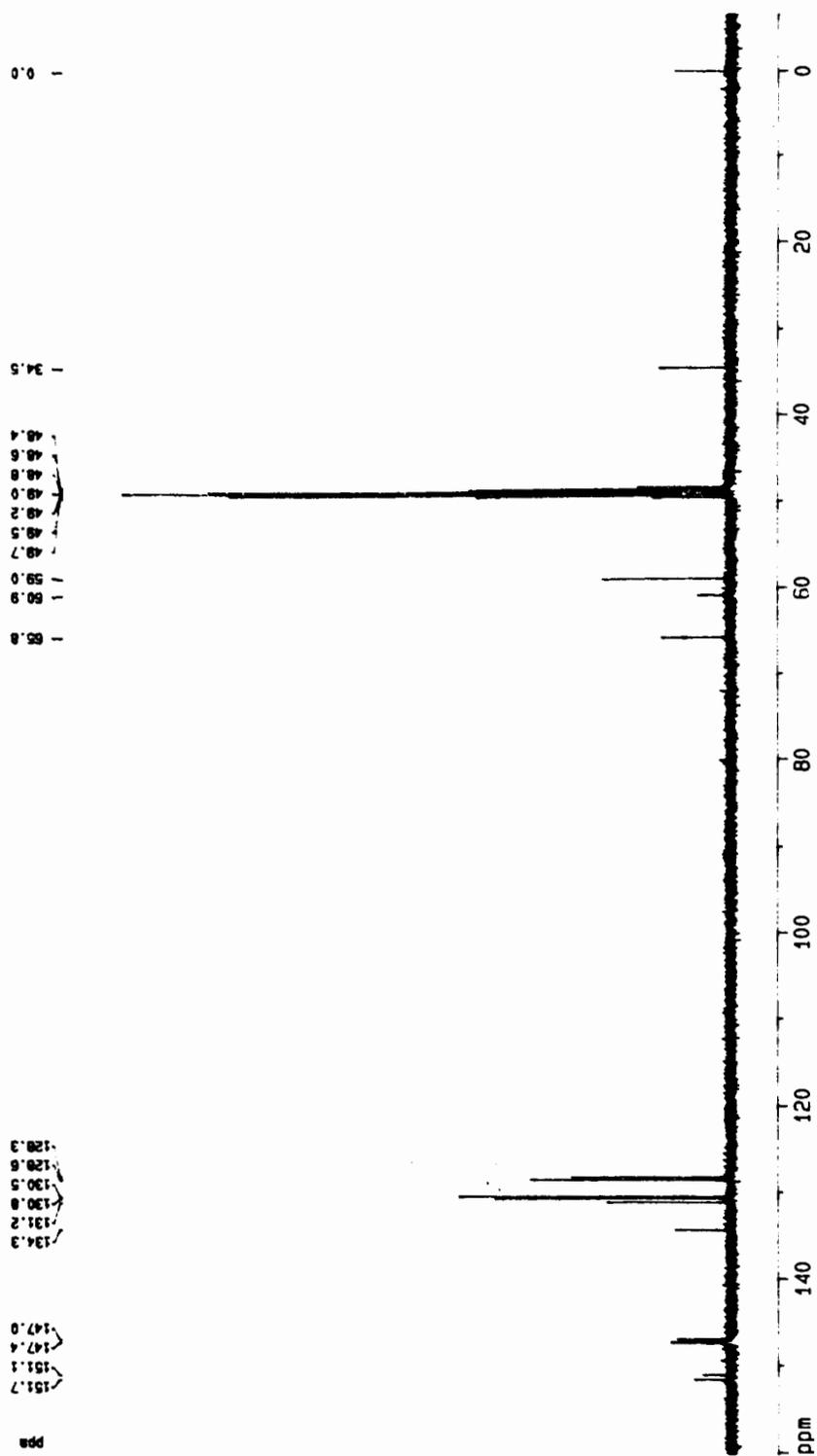
$^1\text{H-NMR}$ of AminoDonor dihydrochloride



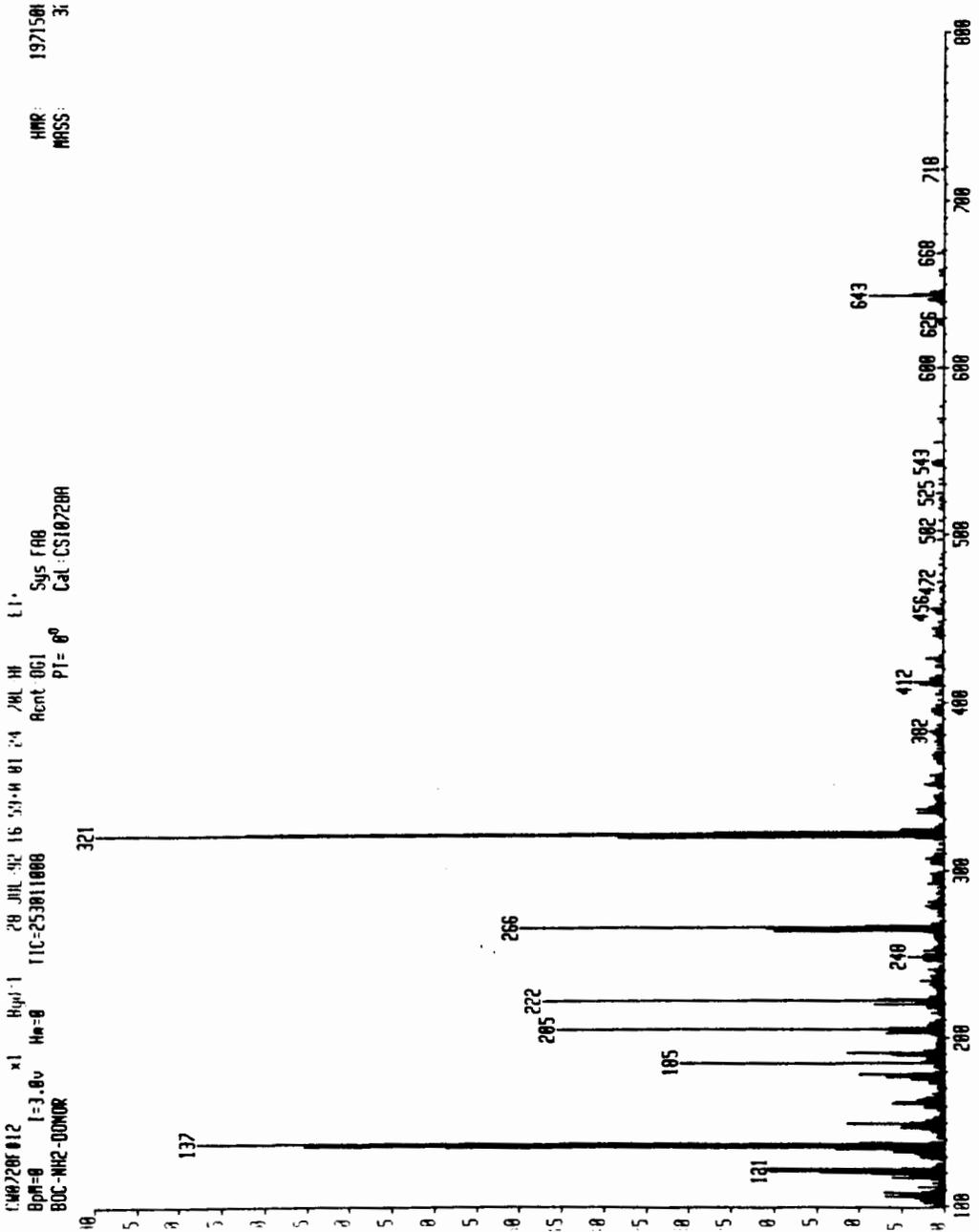
$^1\text{H-NMR}$ of BromoDonor



^{13}C -NMR of BromoViologen



^{13}C -NMR of HydroxyViologen

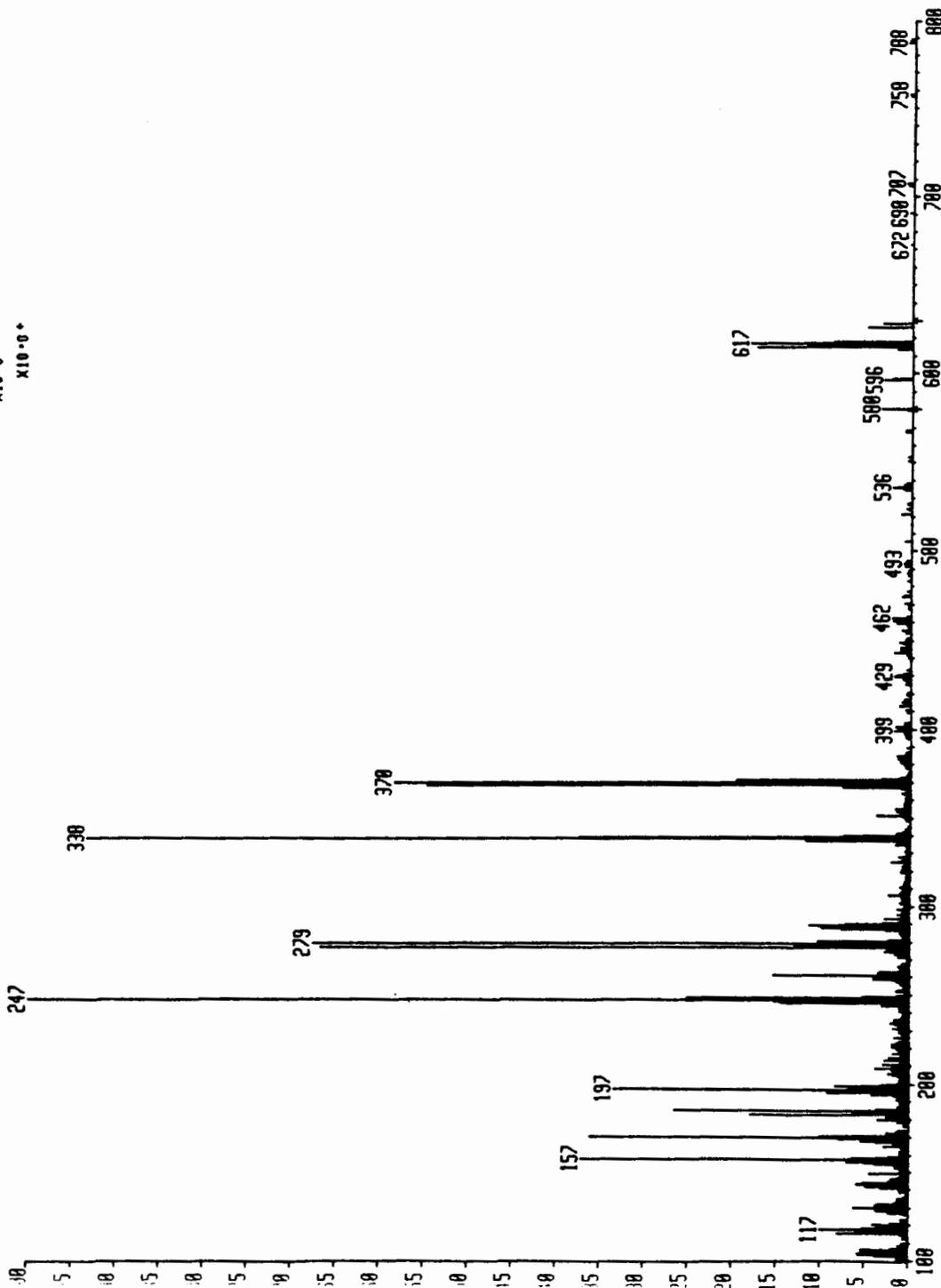


FAB-MS of spectrum of AminoDonor

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 BR-VIODOGEN IN GLYCEROL

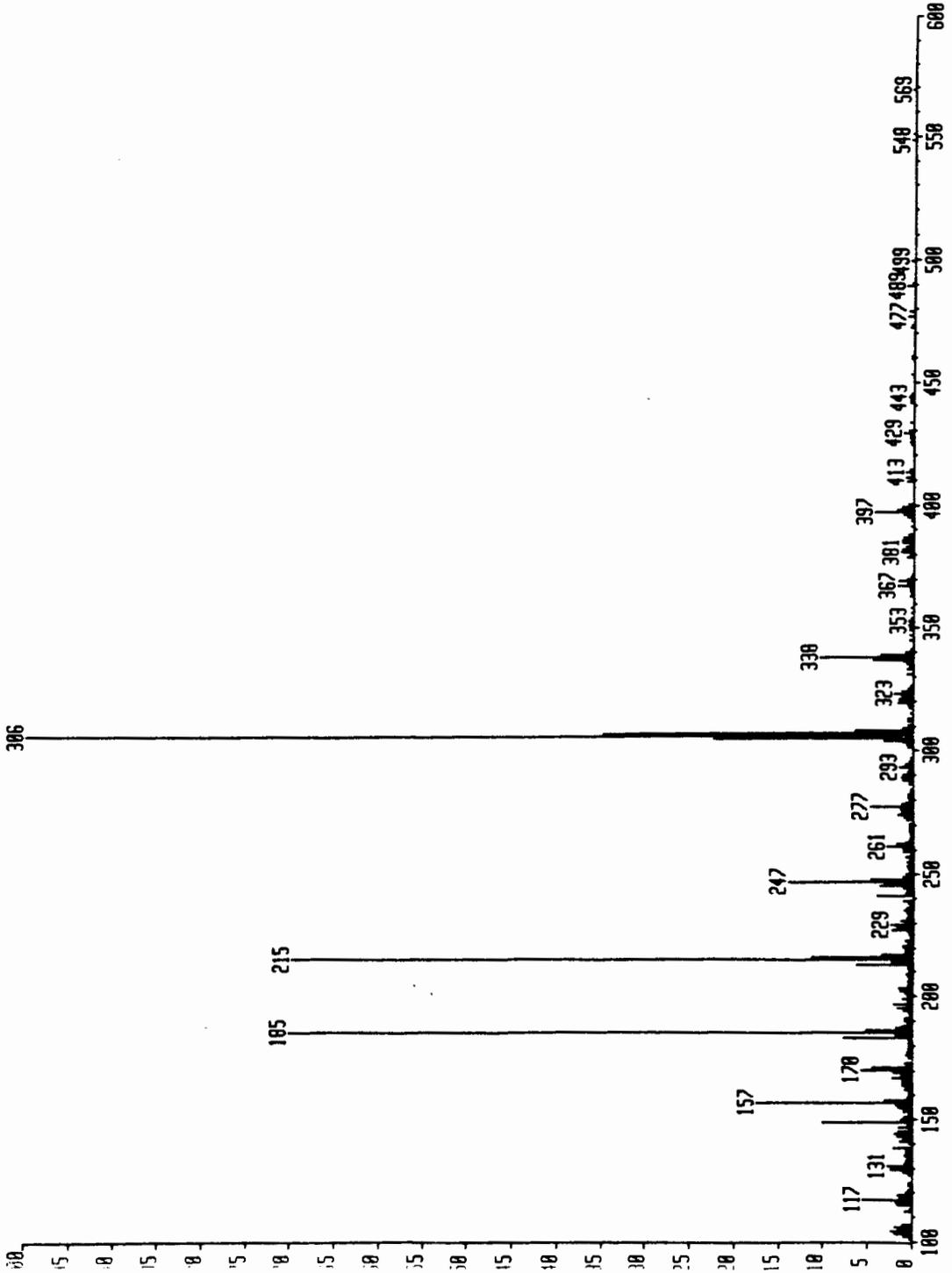
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 X10.0*



FAB-MS spectrum of BromoViologen

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H0-VIOL0GEN IN GLYCEROL PT= 0° Cal: CS107200



FAB-MS spectrum of HydroxyViologen