TETRAPHENYLPORPHYRIN DIMERS AND THEIR DERIVATIVES

by

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ABSTRACT

Tetraphenylporphine (TPP) and its *para*-methyl derivative have been synthesized by direct reaction of pyrrole with the corresponding aldehyde. The synthesis of two unsymmetrically substituted tetraarylporphyrins is reported. The compounds prepared are 5-(4-hydroxyphenyl) -10,15,20-tritolylporphyrin and 5-(4-hydroxyphenyl)-10, 15,20-triphenylporphyrin.

The sythesis of covalently linked porphyrin dimers, joined *via* ether linkages, is described. High yields of the tetraarylporphyrin dimers were obtained by the reaction of the bi-functionall,6-ditosyloxyhexane with phenolic porphyrins such as 5-(4-hydroxyphenyl)-10,15,20-tritolyl-porphyrin. The dimeric porphyrins were then chromatographically separated from the unreacted monomericporphyrins.

The reduction of the porphyrins (monomers and dimers) has been carried out using the standard diimide precursor, *p*-toluenesulfonylhydrazine. We have been able to demonstrate that the most efficient chlorin preparation involves the diimide reduction of a tetraarylporphyrin to the corresponding bacteriochlorin, followed by the addition of the "high potential quinone" DDQ, to dehydrogenate the bacteriochlorin. A detailed study of the absorption spectra of these chlorins and bacteriochlorins was undertaken. Zinc metallo-derivatives of the porphyrins, chlorins and bacteriochlorins were prepared by the reaction of the free bases with zinc acetate in dry pyridine.

An attempt was made to synthesize tetra-*meso*-[*p*, *p*'-(3,3'-phenoxypropoxyphenyl)]-*strati-bis*porphyrin (Compound XX), a novel cyclophane system composed of two opposed, co-axial porphyrin rings, rigidly held together by peripheral ether linkages. The synthesis was attempted by construction of a second porphyrin ring on top of a pre-existing one, by way of the condensation of four pyrroles with a tetraaldehyde, derivative of tetraphenyl-porphyrin, under high dilution conditions. The last reaction step was unsuccessful. The structures and purity of the intermediate compounds leading to the *strati-bis*-porphyrin were established by mass spectroscopy and proton n.m.r. spectroscopy.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my Research Advisor, Professor David Dolphin, for introducing me to the very important field of Porphyrin Chemistry. I would also like to thank all the students I know, who have been or are in Dr. Dolphin's research laboratories, for the useful chemical discussions we have engaged in.

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Barb, my wife, deserves special appreciation for general support and encouragements.

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ABBREVIATIONS

In this work the terms porphyrin, porphine and porphin are used interchangeably. Abbreviations which may occur without definition include:

Abs. = Absorbance

ATP = Adenosine Triphosphate

DDQ = 2,3-Dichloro-5,6-dicyanobenzoquinone

DMF = N,N-dimethylformamide

EPR = Electron Paramagnetic Resonance

Hz = Hertz (cycles per second)

I = Intensity

Lit. = Literature

M.W. = Molecular Weight

Ref. = Reference

TFA = Trifluoroacetic acid

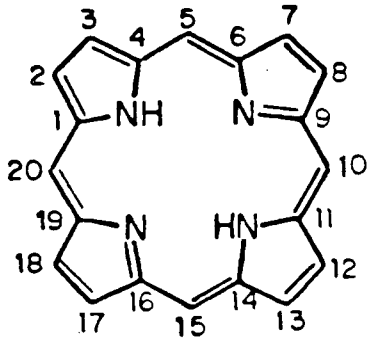
TPBC = *meso*-Tetraphenylbacteriochlorin

TPC = *meso*-Tetraphenylchlorin

TPP = *meso*-Tetraphenylporphyrin

STRUCTURE AND NOMENCLATURE

The nomenclature (a) is that recommended for tetrapyrrolic macrocycles by IUPAC rules for nomenclature, *J. Amer. Chem. Soc.* 82, 5582 (1960).



(a)

In this thesis the protons 2,3,7,8,12,13,17,18 are referred to as the β-pyrrole protons. The carbons 1,4, 6,9,11,14,16,19 are the α-carbons. The positions 5,10, 15,20 are the *meso*-positions.

INTRODUCTION

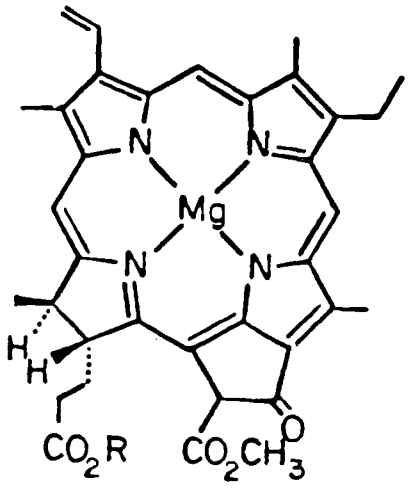
(a) Natural occurence and importance of porphyrin dimers and aggregates.

Porphyrin aggregates play an important role in both photosynthetic and metabolic processes.[1,2]

The biosphere depends upon photosynthesis to carry out the conversion of photonic into chemical energy as well as to maintain an oxidizing atmosphere for catabolism (conversion of organic compounds to CO_2) which provides the energy necessary to drive endergonic biochemical processes. The classical reaction of photosynthesis requiring chlorophyll-a (2) involves CO_2 fixation, namely

$$CO_2 + H_2O \xrightarrow[\text{(light, chlorophyll)}]{} [CH_2O] + O_2 \qquad (1)$$

where $[CH_2O]$ is a carbohydrate and water serves as the oxidizable hydrogen donor.



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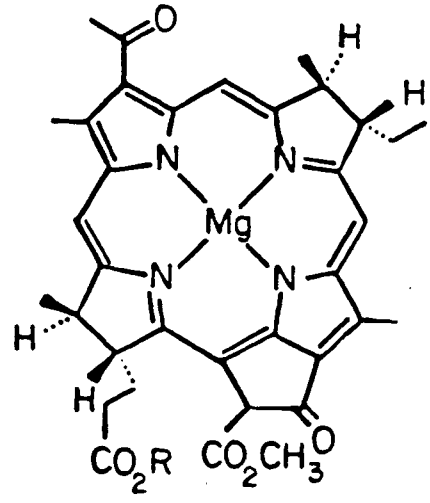


(3)

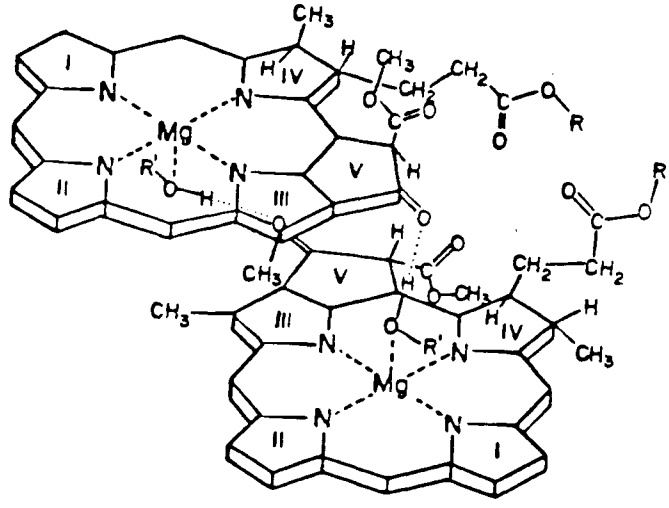
A reaction similar to (1) occurs in photosynthetic bacteria which utilize bacteriochlorophyll (3) and hydrogen

donors other than water.[1]

The photosynthetic process divides naturally into light-driven primary reactions [3,4] and the subsequent CO_2 reduction steps studied by Calvin, Bassham, and coworkers.[5] Under the title of primary reaction is included the conversion of light energy into reductants and oxidants and, in the case of green plants and blue-green algae, the chemical and physical states involved in the oxygen-evolving apparatus.

The primary events of photosynthesis take place in a photosynthetic unit where a large number of chlorophyll (Chl) molecules act cooperatively as an antenna to absorb visible light and to transfer the electronic excitation, so produced to a photoreaction centre or trap.[6] In the excited trap, an electron is ejected from a special pair of chlorophyll molecules,[7] Chl_{sp}, thereby creating a radical, $Chl_{sp}^{\cdot}$, in which the unpaired electron is delocalized over the π-systems of both macrocycles. The Chl_{sp} of photosystem I in green plants (*i.e.* the radical of P700) has a characteristic Gaussian electron spin resonance (ESR) signal with a free-electron g-value of 2.0025 and a signal width (*i.e.* twice the Gaussian standard deviation) of 7 gauss (1 gauss = 10^{-4} tesla)[8]. Evidence for the participation of just two chlorophyll molecules in sharing the *in vivo* unpaired electron comes from ESR[8] and electron nuclear double resonance (ENDOR) spectroscopy. A comparison of the signal width for the monomeric Chl radical *in vitro* with that of P700 *in vivo*

radical shows that the latter is reduced relative to the former by a factor of approximately $1/\sqrt{2}$. Theory predicts that the signal should be narrowed by a factor of approximately $1/\sqrt{N}$ when an unpaired electron is spread equally over N Chl molecules.[8] Both *in vivo* ESR[8] and ENDOR evidence[9] supports a two-molecule species for the *in vivo* P700 radical.



SCHEMATIC REPRESENTATION OF THE PROPOSED STRUCTURE OF SPECIAL-PAIR CHLOROPHYLL-**a**. FOR CLARITY THE GROUPS ATTACHED TO RINGS I AND II ARE NOT SHOWN. R = PHYTYL AND R′ IS H, ETHYL, OR PROTEIN. (REF. 55)

The primary events in photosynthesis may be viewed schematically as[10]:

$$P_1\square P_2 + h\nu \longrightarrow P_1\square{}^*P_2 \longrightarrow P_1{}^*\square P_2 \longrightarrow P_1{}^{+\cdot}\square P_2{}^{-\cdot}$$

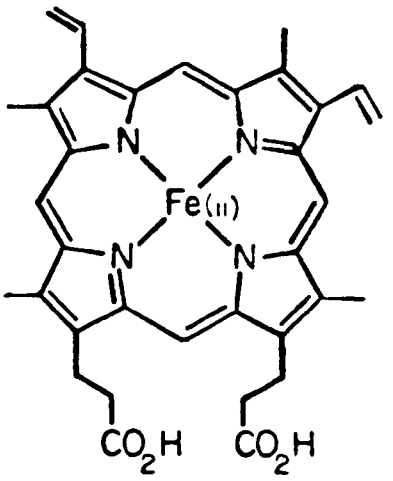
where P_1 represents the primary electron donor (the first stable species which has lost an electron after the absorption of a quantum of light energy), P_2 is the

primary electron acceptor (the first stable species which has gained an electron after the absorption of a quantum of light energy), and the box represents the antenna pigments, protein and whatever other material is necessary for a functioning phototrap. The part of the primary photochemistry which is best understood is the primary electron donor unit. In bacterial photosynthesis, which is the best characterized of all photosynthetic systems, P_1 is a bacteriochlorophyll aggregate which consists of four separate but interacting molecules specifically boung by a protein.[4,11-13] When this aggregate is excited, and an electron is subsequently lost, the cation radical thus formed is apparently shared equally over at least two of the bacteriochlorophyll molecules.[8,14-16] This spin delocalization is probably important in both stabilizing the oxidized species and also in providing for the secondary oxidation of cytochrome c_2 at some distance from the location of the reduced primary species, perhaps on the opposite side of the membrane.

There are other biological systems that also function through multiple porphyrin centres. For example, it is assumed that electron transport reactions from one heme protein (*eg.*; cytochrome oxidase) involve a close approach of iron porphyrin centres either through a shared ligand or of the porphyrin edges.[10]

Heme protein participation[17] in oxygen transport, peroxide reduction and disproportionation, the mitochondrial electron transport chain, and drug metabolism (cyto-

chrome P450) stresses the biological importance and diverse roles of the iron porphyrins. Iron protoporphyrin IX (4) (heme) is the prosthetic group of hemoglobin (Hb), myoglobin (Mb), catalase, peroxidase, and many of the cytochromes.[18]



(4)

The respiratory pigment hemoglobin contains four heme prosthetic groups and is distributed in red blood cells; myoglobin is a monomer found in muscle cells. Both pigments reversibly bind oxygen for use in cellular catabolism. Hydroperoxidases are hemiproteins (iron is present as Fe^{3+} in the resting enzyme) which serve to catalyze the reaction

$$2H_2O_2 \xrightarrow{\text{catalase}} 2H_2O + O_2 \qquad (2)$$

in the case of catalase or a peroxidative reaction

$$ROOH + H_2A \xrightarrow{\text{peroxidase}} ROH + H_2O + A \qquad (3)$$

The reaction pathways by which these enzymes act are complex.

When nature uses chlorophyll as a source of electrons it is not too surprising that it is the dihydroporphyrin ring rather than the divalent magnesium ion which supplies them. With iron porphyrins, however, it has generally been assumed that the iron atom itself is the entity which undergoes the redox reaction, and in the cytochromes which function *via* an Fe (II) $\rightleftharpoons$ Fe(III) couple, there is no doubt that it is the metal which is the *eventual* site of electron capture or release.[18]

There are two closely related series of iron porphyrin containing enzymes, the catalases[19] (Cat) and the peroxidases[20] (which are typified by horseradish peroxidase (HRP)). The resting enzymes both contain trivalent iron and are oxidized by the hydrogen peroxide. The first intermediate observed spectrophotometrically during this oxidation is the so-called primary compound (Cat I or HRP I) which has two electrons less than the parent ferrihemoprotein. A one-electron reduction of the green primary compound forms the brown-red secondary compound (Cat II or HRP II). While the first step in the catalytic cycle of these two enzymes is the same, *i.e.*; a two-electron oxidation, by hydrogen peroxide, to their primary compounds, the two enzymes then perform different functions. Cat I oxidizes a second molecule of hydrogen peroxide to molecular oxygen and is itself reduced back to the ferrihemoprotein, while HRP I reacts with a hydrogen donor AH_2 to give a free radical and the secondary compound of the enzyme HRP II (eq. 4) which can in turn

oxidize a second donor molecule with the formation of the ferrihemoprotein (eq. 5).[18]

$$HRP\ I + AH_2 \longrightarrow HRP\ II + AH^{\cdot} + H^{+} \qquad (4)$$

$$HRP\ II + AH_2 \longrightarrow HRP + AH^{\cdot} + H^{+} \qquad (5)$$

In the 1961 Report of the Commission on Enzymes of the International Union of Biochemistry (*c.f.* also the Enzyme Nomenclature Recommendations, 1965) cytochromes are defined as "hemoproteins whose principal biological function is electron and/or hydrogen trasport by virtue of a reversible valency change of their heme iron". A discussion of this definition is given by Lembert and Barrett.[21] Cytochromes P-450, first detected in mammalian microsomes, are a class of hemoproteins concerned with enzymic hydroxylation, demethylation, N-oxidation, and possibly also the anaerobic reduction of azo and nitro compounds.[22] Before hydroxylation can occur, P-450 has the probable multiple tasks of substrate recognition and binding, electron acceptance, then O_2 binding and activation.[23] During the enzymic cycle of cytochrome P-450 ferric cytochrome P-450 first combines with a substrate, followed by one-electron reduction to form a ferrous cytochrome P-450-substrate complex which can bind either oxygen or CO reversibly.[24-26] It is suggested that the "activated" oxygen, formed after the addition of the second electron to the O_2-P-450 complex, interacts with the substrate to give rise to hydroxylated product, water, and ferric cytochrome P-450. Thus, cytochrome P-450 not only functions as an electron transporter but resembles the oxygen

carriers hemoglobin and myoglobin, in terms of its capability toward O_2 binding.[27]

The axial ligands of the heme iron in cytochrome P-450 are of great interest, since they hold the key to our understanding of the enzymic function and the underlying principles that enable the single complex protoheme to perform various functions ranging from oxygen transport, oxidation catalysis, to electron transport. The possibility of axial sulfur ligation in cytochrome P-450 has been repeatedly expressed in the literature based on EPR evidence.[26,28-29]

Cytochrome c was named and described in the classical work of D. Keilin (1925, 1926)[30-31] which established its wide occurence in cells from mammals to invertebrates and yeast. The biological role of cytochromes in cellular respiration was established by Keilin (in 1966),[32] but today we know that it is not restricted to processes of cellular respiration. Cytochromes c play also an important role in photosynthetic processes and in anaerobic dark processes of bacteria such as nitrate and sulphate reduction. A short summary of the occurence and of some of the properties of the cytochromes of type c is given by Lembert and Barrett (see Ref. 21, pp. 124-125).

Cytochrome oxidase is a very important part of the mitochondrial respiratory chain. It is responsible for both electron transport leading to the reduction of O_2 to water, namely[33-35]

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad (6)$$

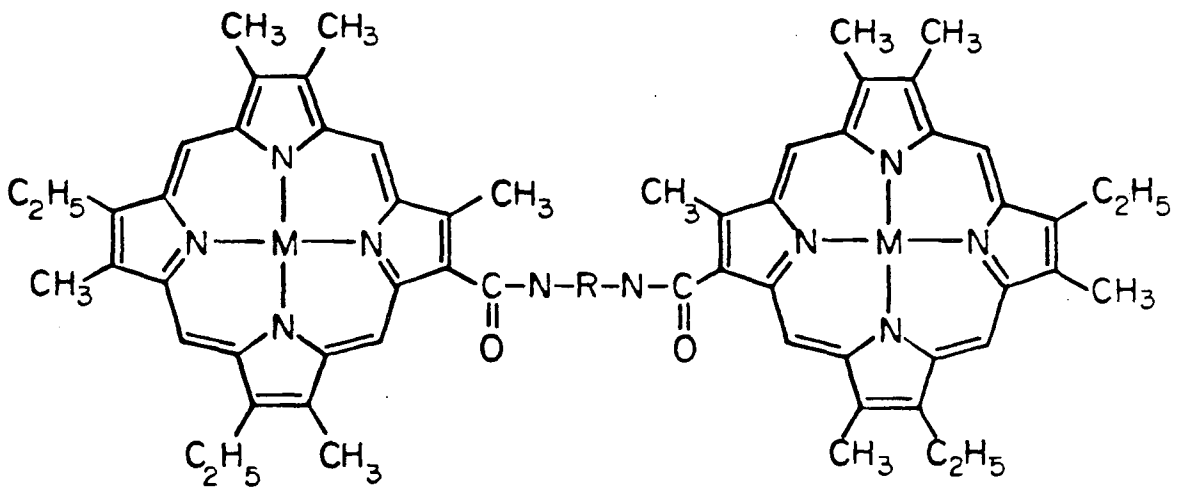
and the conservation of the energy required for ATP synthesis.[36-38] Cytochrome oxidase contains two copper ions and two heme groups (a and a_3) per subunit. When the reaction with O_2 is carried out at 25° , the measured rates are such that Greenwood and Gibson,[39] conclude that any intermediates must have half-lives of less than 10 μ sec. Several mono- and dioxygenases (metalloenzymes), which reduce oxygen with concomitant oxidation of organic substrates, also contain more than one functional metal ion. These include the monooxygenases laccase (mono-phenol monooxygenase, 4Cu), and ascorbate oxidase (8Cu) as well as the dioxygenase L-tryptophane oxygenase (2 hemes and 2Cu).

In contrast to the large number of biological systems that reduce O_2, evolutionary processes appear to have developed only a single dinitrogen fixing system, nitrogenase.[40] Although the molecular mechanism has not yet been elucidated, a binuclear metal site for dinitrogen reduction has been proposed.[41]

(b) Synthetic porphyrin dimers, their syntheses and the uses to which they have been put.

The study of electron transfer within naturally occuring porphyrin aggregates is difficult because of the complexity of the systems in which they occur and would be greatly aided if simple dimeric and polymeric porphyrin molecules were available.

Dolphin *et al.*;[42] were the first to report the synthesis of covalently-linked dimeric porphyrins, joined by amide linkages, CO-NH-R-NH-CO, where R is either an ethylene or *p*-phenelene group, as shown (5),



(5)

Electronic energy transfer between non-conjugated covalently-linked chromophores has been demonstrated in a variety of cases.[43] The problem is intermediate between studies of electronic relaxation within a single molecule.[42] A covalent linkage has several inherent advantages: (a) The distance between the chromophores can be known and varied from several to many Ångstroms. (b) The orientation of one chromophore with respect to the other may sometimes be rigidly fixed whereas intermolecular energy transfer in solutions involves randomly oriented molecules. (c) Since the energy is transferred within the molecule, the role of the environ-

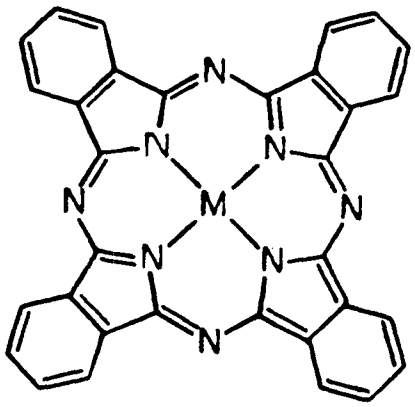
ment is minimal.

In their study, Dolphin *et al.;* investigated intramolecular energy transfer in a series of double porphyrin molecules. The two 12,17-diethyl-3,7,8,13,18-pentamethylporphyrin carboxamide molecules (5), were structurally identical except for the metals M and M', which were either Zn, Cu or Co.[42] Their choice of metals was based on the energy levels and luminescence characteristics. Zn fluoresces and phosphoresces,[44] Cu luminescences from the tripdoublet or quartet,[45] while Co has no emission.[46] The Cu phosphorescence has a far shorter lifetime than the Zn.[47]

Since the first report by Dolphin *et al.;* [42] of covalently-linked dimeric porphyrins, joined by amide linkages (5), a number of similar dimeric porphyrins with amide, ester, or ether linkages have been reported.[48-57]

The development of efficient catalysts for the reversible multielectron reduction of O_2 and N_2 would have great significance. Such catlysts are essential to the oxygen cathode of an air-powered fuel cell and to electrochemical nitrogen fixation. Many monometallic macrocyclic complexes adsorbed on graphite have been examined as catalysts for oxygen reduction.[58] The most effective macrocycles have four nitrogen donor atoms. In the phthalocyanine series (6), the order of reactivity is Fe > Co > Ni > Cu > Mn. However, such studies have failed to reveal any catalyst that is capable of reversible reduction of O_2 to water, possibly because with a single

metal centre, initial $2e^-$ reduction to H_2O_2 is always dominant.



(6)

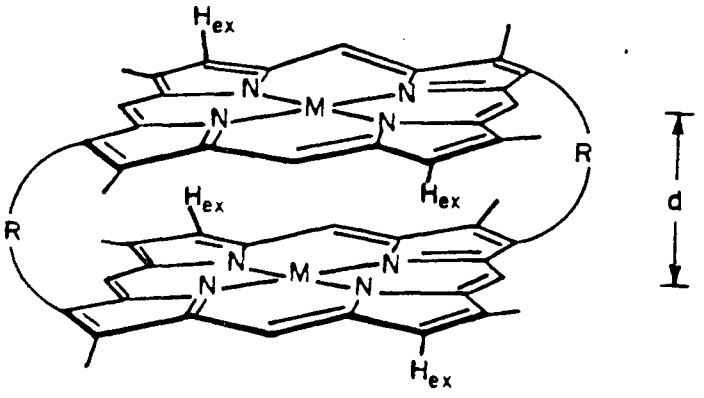
Collman *et al.*,[52] have approached this problem, of the development of efficient catalysts for the reversible multielectron reduction of O_2 and N_2, by constructing a new class of so-called "face-to-face porphyrins" in which two porphyrin rings are held in parallel conformation. Thus, two metal atoms might act in concert to bind and reduce dioxygen (or dinitrogen) in the gap between the porphyrin rings. Eventually these binuclear, cyclophane porphyrin complexes are to be attached to graphite to be tested as electrode catalysts.

Chang *et al.*,[50] have synthesized three homologous cofacial diporphyrins (7) that have interplanar distances ranging from 6.4Å to 4.2Å.

These cofacial diporphyrins have great sigificance in many branches of chemistry. As organic molecules, in addition to being challenging synthetic targets,

they may present a multitude of properties by the mere token of their size and the resulting interaction of the two 18π-electron porphyrin rings.[59] As inorganic molecules, they have the unusual capability of constraining two metal ions at selected distances and thus, may display interesting properties arising from metal-metal interactions. Furthermore, from the point of view of biochemistry, they represent a class of elaborately designed bioinorganic models for many essential biological systems; *eg.* (a) the cytochrome oxidase model capable of multi-electron reduction of oxygen; (b) the monooxygenase model by which molecular oxygen can be "activated" *via* two-electron transfer; (c) polynuclear complexes with certain catalytic activity, among these we may cite: Mn-Mn dimer for oxidation of water and decomposition of superoxide, Ru-Ru and Mo-Mo dimer for binding and reduction of dinitrogen, also Rh-Rh systems for formation of organometallic compounds (*eg.* Rh-CH=CH-Rh); (d) the "special pair" chlorophyll model in photosynthetic units; and (e) chlorophyll aggregates model for studying excitation energy transfer processes. Appropriate models are essential to our complete understanding of the mechanism of trapping of the absorbed light energy during the primary photochemistry in photosynthesis. When it becomes possible to reproduce in model systems the high efficiency for converting light energy into chemical potential that is exhibited by the *in vivo* system, it may then be possible to construct solar cells of high

efficiency and possibly at low cost.



(7)

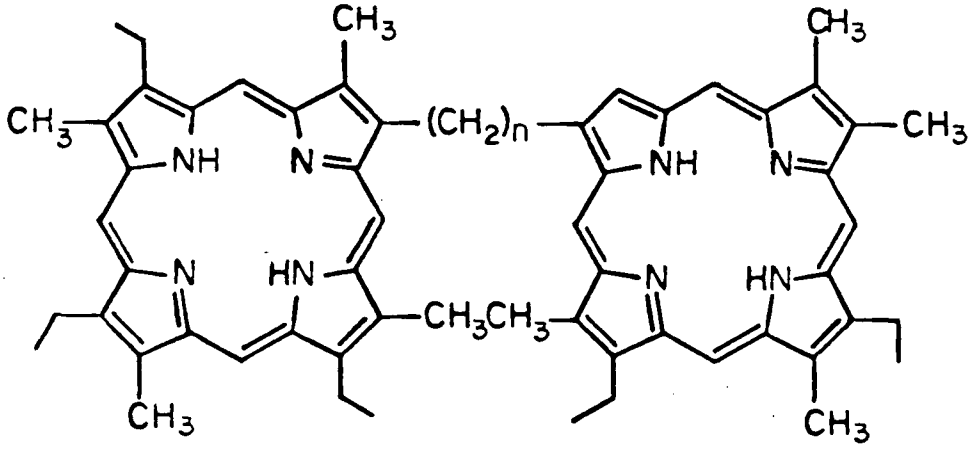
R = $-CH_2CH_2CON(N\text{-}Bu)CH_2CH_2CH_2-$, d = 6.4Å
R = $-CH_2CON(N\text{-}Bu)CH_2CH_2CH_2-$, d = 5.4Å
R = $-CH_2CON(N\text{-}Bu)CH_2CH_2-$, d = 4.2Å

(REF. 50)

All the covalently-linked dimeric porphyrins reported so far (see Refs. 42,48-57), are joined by amide, ester or ether linkages. That all of these systems employed the coupling of porphyrins, through these functional groups, results from the 'ready' availability of the porphyrin precursors and the ease of formation of amide, ester and ether linkages. However, once formed, such linkages have numerous disadvantages in that they generally lower the solubility (of systems which naturally

have low solubilities), and increase the reactivity and thereby decrease the stability. In addition the presence of extraneous functional groups complicates mechanistic and spectral studies on such systems.

Dolphin and Paine, in our laboratory, recently reported[60] the synthesis of dimer porphyrins (8).



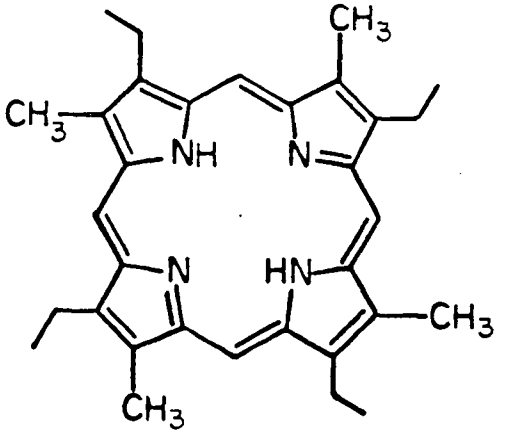
(8)

Whereas all previous syntheses of dimeric porphyrins[42,48-57] consist of joining two preformed porphyrin entities in the final steps, the approach by Dolphin and Paine consists of constructing the covalent link *first*, and then building a porphyrin onto either end. To avoid the disadvantages of the linkages discussed above, the synthesis of dimer porphyrins (8) has been developed where the hydrocarbon chain plays a passive role both chemically and electronically.

The various dimeric porphyrins covalently joined *via* amide, ester or ether linkages have been studied spectroscopically. The electronic absorption spectra of these various dimers show a variety of changes in

in their electronic transitions, compared to the corresponding monomeric species, which are related to small changes in their conformations. Thus a blue shift in the Soret band of the cofacial porphyrin dimers has been observed by Chang *et al.*[50] and Collman *et al.*[52] whereas Kagan *et al.*[53] saw no change in the Soret region but a considerable red shift in the visible region.

Dolphin *et al.*,[61] have studied the interactions between the dimeric porphyrins (8) using their electronic absorption spectra and ^{13}C n.m.r. spectra. The electronic spectra for the free bases n = 0, 1 and 8 have been compared with those for monomeric etioporphyrin I (9),



(9)

The spectra of the same four species in their protonated forms (each porphyrin ring is an N,N-diprotonated dication) are also discussed. For the dimer (8) (n = 8) no changes are observed between its spectra, of both the free base and protonated cations, and those of etioporphyrin I (9),

suggesting that the two porphyrin rings in this dimer (whose centres could be greater than 15Å apart) do not interact. But in the n = 1 and n = 0 dimers, a significant effect of the Soret band is observed, including the appearance of two resolved bands in the dication case.[61]

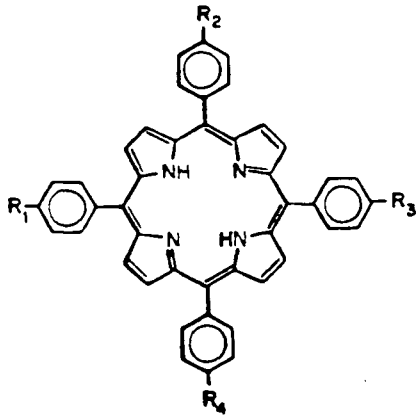
The electronic interaction between the two porphyrin rings in the dimers (8) is also evident when examining their ^{13}C magnetic resonance spectra. The spectra were obtained from deuteriochloroform solutions containing an excess of trifluoroacetic acid, to increase the solubility and allow the observation of α carbons by eliminating NH tautomerization.[62] For chain length ≥ 3, the porphyrin nuclei are largely pseudosymmetrical, as the charge-repulsion entailed by diprotonation of each macrocycle should tend to minimise the interaction. The *meso* carbons give only a single broad peak for all n *greater* than 2, but resolve into four well-defined peaks for n *less* than 2.[61]

(c) The advantages of the porphyrin dimers we synthesized, with respect to the other dimers.

Because of their ease of preparation tetraarylporphyrins have been widely used as models for the naturally occuring porphyrins.[63]

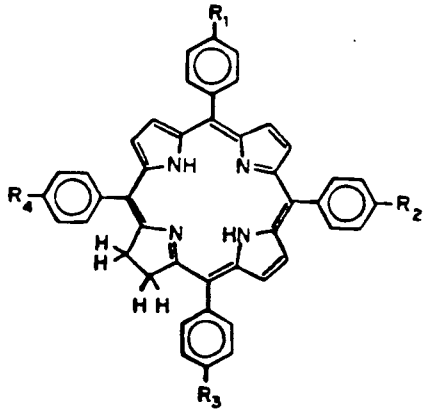
The reaction between pyrrole and aldehydes represents one of the first syntheses of *meso*-substituted porphyrins,[64] and at the present time affords the most convenient route to the large scale preparation of synthetic porphyrins. In 1939, Rothemund[65] isolated *meso*-tetraphenylporphyrin (TPP) (10) from a sealed tube re-

action of pyrrole and benzaldehyde in pyridine at 150°. It was later found[66] that the addition of zinc acetate to the reaction improved the yield of porphyrin, and these conditions have been widely used in the preparation of a variety of *meso*-substituted porphyrins.[67] Under these reaction conditions yields rarely exceed 10%, and the porphyrin is invariably contaminated with the corresponding chlorin (11).



(10)

R_1-R_4=H



(11)

R_1-R_4=H

An examination of the stoichiometry of the reaction shows that the formation of a mole of TPP, from four moles of pyrrole and four of benzaldehyde, requires six oxidizing equivalents. Accordingly the yield of porphyrin increased from 10 to 40% when the Rothemund reaction was carried out in refluxing acetic acid, rather than under the anaerobic conditions of the sealed tube.[68] Dolphin[69] has reported a detailed study of the mechanism of the Rothemund reaction and has isolated some reaction intermediates in the synthesis of *meso*-tetraphenylporphyrins from pyrroles and benzaldehyde. Briefly the formation

of *meso*-substituted porphyrins from pyrroles and benzaldehyde can be summarized as follows:[69]

4 Pyrrole + 4 Benzaldehyde ⟶ Porphyrinogen (12) + $4H_2O$

↓

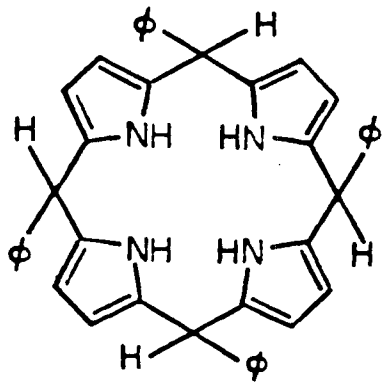
Porphomethene (13)

↓

Porphodimethene (14)

↓

Porphyrin (10)



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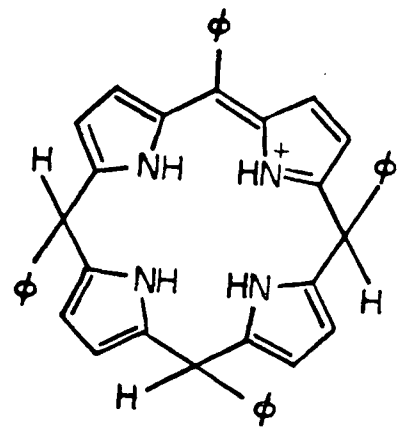
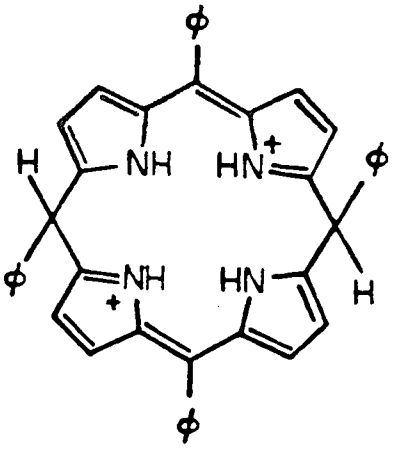


(13)

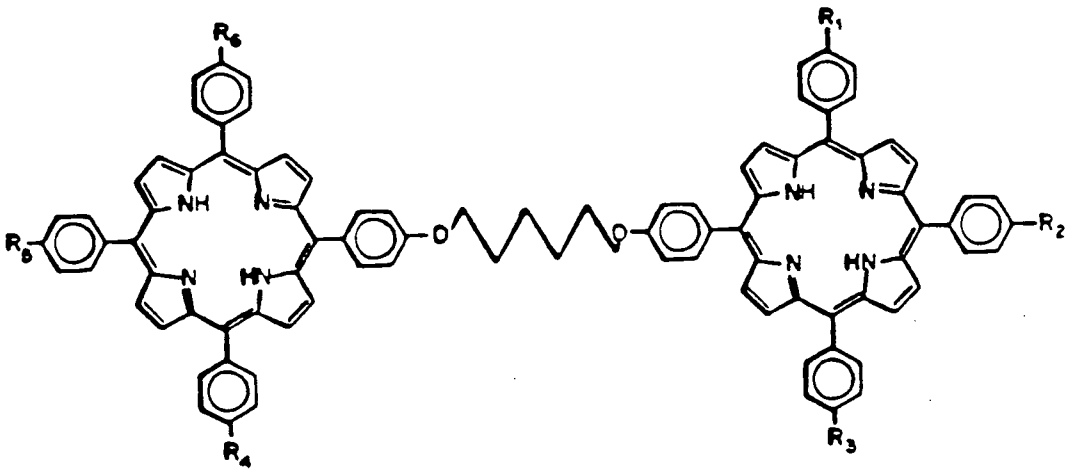
In this work, we have synthesized *meso*-tetraphenylporphyrin and other *meso*-substituted tetraarylporphyrins following the procedure developed by Adler *et al.*[70] The yield and rate of the condensation of pyrrole and benzaldehyde to TPP have been found to depend on the acidity, the solvent, the temperature, the availability of atmospheric oxygen, and the initial concentration of the reagents.[68] The procedure where equimolar amounts of pyrrole and benzaldehyde are refluxed in propionic acid solvent represents the most convenient method for rapidly and reproducibly obtaining a 20 ± 3% yield of crystalline TPP of high purity.

The central role played by oxidation/reduction



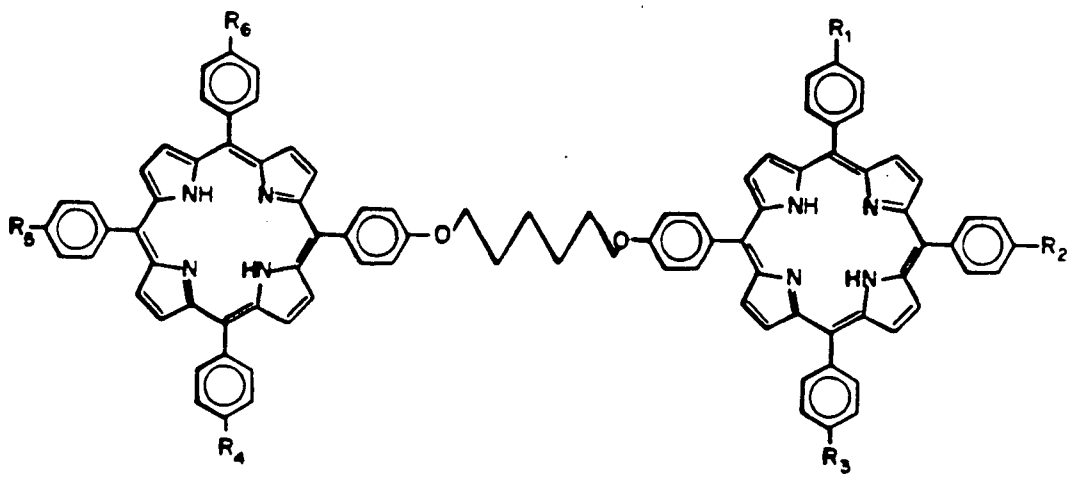
(14)

reactions of porphyrins in photosynthesis and electron transport mechanisms coupled with the well-recognized cryptoolefinic nature of the peripheral double bonds in porphyrins[71-74] has prompted us to investigate the diimide reduction of the *meso*-tetraarylporphyrin dimers (15) and (16). The porphyrin dimers 5,10,15-triphenyl-20-[4-[6-(10,15,20-triphenyl-5-porphinyl)-phenoxy]hexoxy] phenyl]porphine (15) and 5,10,15-tri-*p*-tolyl-20-[4-[6-[*p*-tolyl-5-porphinyl)-phenoxy]hexoxy]phenyl]porphine (16) were synthesized and characterized as described in the Experimental Section.



(15)

R_1-R_6=H



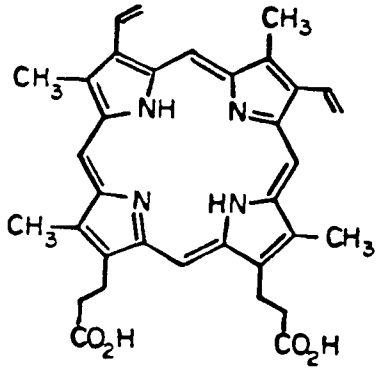
(16)

R_1-R_6=-CH_3

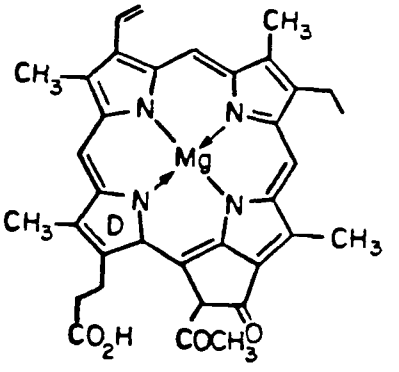
We have been able to demonstrate that porphyrins and chlorins are indeed readily reduced by diimide produced from the standard diimide precursor *p*-toluenesulfonylhydrazine[75] and that diimide reduction is the best synthetic procedure for preparing reduced derivatives of the tetraphenylporphyrin ring system. To date no synthetic method has been devised in which the chlorin, and almost any other hydroporphyrin macrocycle, is built in the rational step-by-step fashion now commonly employed in porphyrin synthesis. Chlorins are usually found as the undesired by-products in *meso*-tetraarylporphyrins.[69,75] The general synthetic approach to chlorins involves first the synthesis of the respective porphyrin and then its subsequent reduction to chlorin. It is noteworthy that the same approach is used in the biosynthesis of chlorophylls, too.[77]

A full investigation of the late stages of biosynthesis of the chlorophylls has been hindered by the insolubility of the intermediates and the relevant enzymes. The pathway was first outlined by Granick[78] on the basis of the intermediates which accumulate in mutants of *Chlorella vulgaris* which are unable to make chlorophyll itself. Protoporphyrin-IX (17) is considered to be the last metal-free precursor of chlorophyll-a and bacteriochlorophyll.[79] In green plants, chlorins are generated only in light. Etiolated seedlings accumulate the porphyrin protochlorophyllide (18), and so the formal *trans*-hydrogenation of ring D, to give chlorophyllide-a (19),

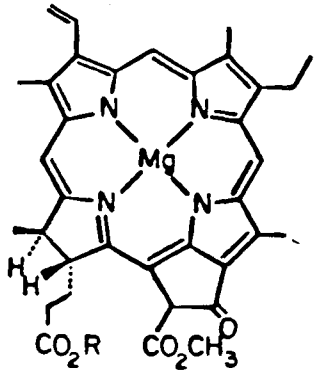
could be a photochemical reduction[80] or one switched on by light. The reaction has been extensively studied[80] and it is found that the protochlorophyllide is bound to a protein forming a so-called holochrome. After the reduction of ring D, all that remains for the formation of chlorophyll-a (2) from chlorophyllide-a (19) is the esterification of the propionate carboxyl group with the C_{20} alcohol phytol (20).[81]



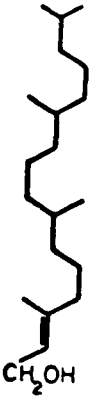
(17)



(18)



(19)

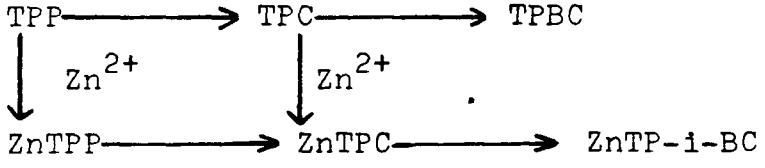


(20)

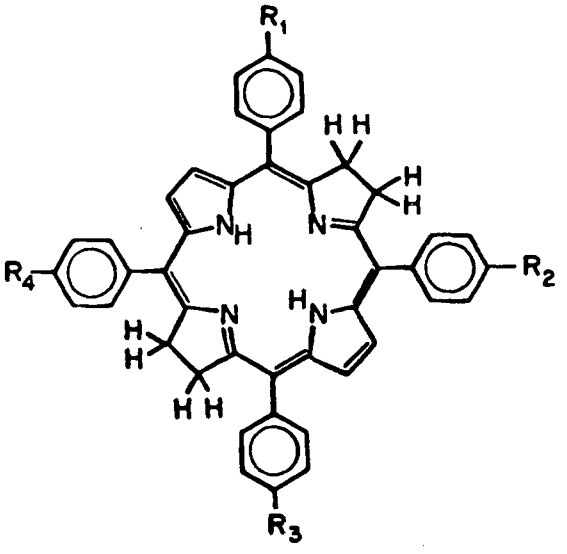
The best approach to the etio-type chlorins is the treatment of porphyrins with reagents typical for the hydrogenation of isolated double bonds. Reactions of this type support an electronic structure of the porphyrin macrocycle in which at least two of the peripheral double bonds do not fully participate with the 18 π aromatic

conjugation system. The behaviour of tetraphenylporphyrin (10), tetraphenylchlorin (11), zinc tetraphenylporphyrin and zinc tetraphenylchlorin toward *p*-toluenesulfonylhydrazine in pyridine is summarized in Scheme I.

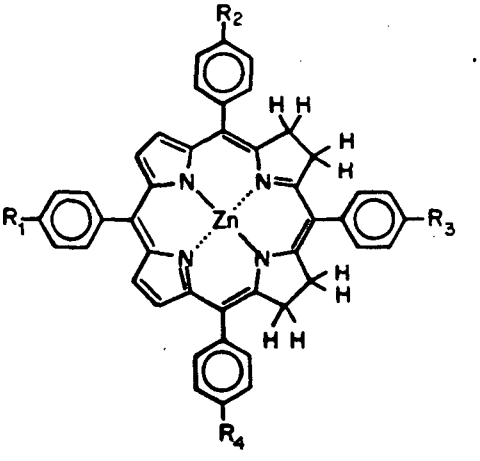
SCHEME I. Reduction of Tetraphenylporphyrin (TPP), Tetraphenylchlorin (TPC), Zinc TPP (ZnTPP) and Zinc TPC (ZnTPC), with Diimide in Pyridine.*



* TPBC = tetraphenylbacteriochlorin (21), ZnTP-i-BC = zinc tetraphenylisobacteriochlorin (22).



(21) R_1-R_4=H

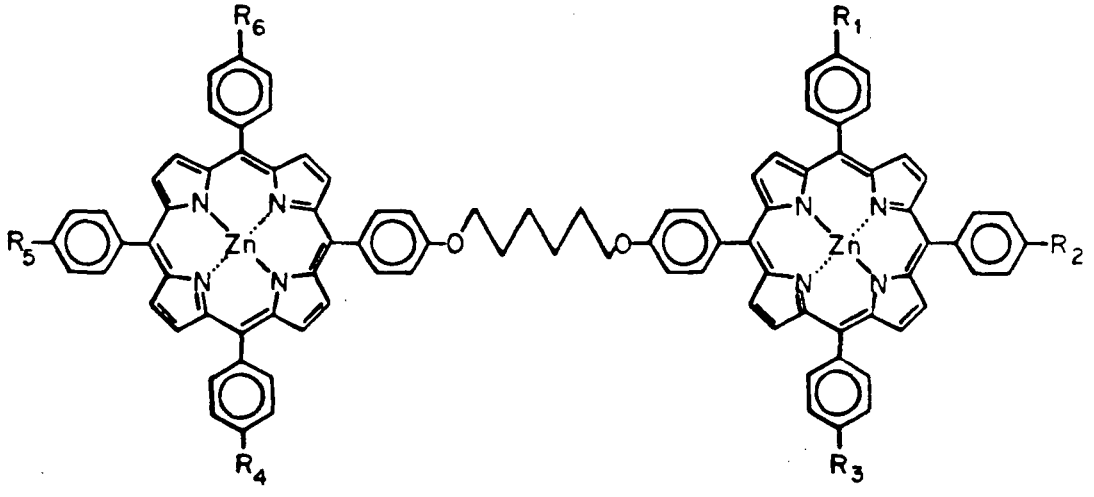


(22) R_1-R_4=H

A remarkable feature of these reductions is the influence on the course of the reaction of metal-free tetraphenylchlorin (11) affords tetraphenylbacteriochlorin (21) contaminated by no more than 2-4% of tetraphenylisobacteriochlorin (TP-i-BC) as determined by its uv-visible spectrum. Reduction of zinc tetraphenylchlorin affords

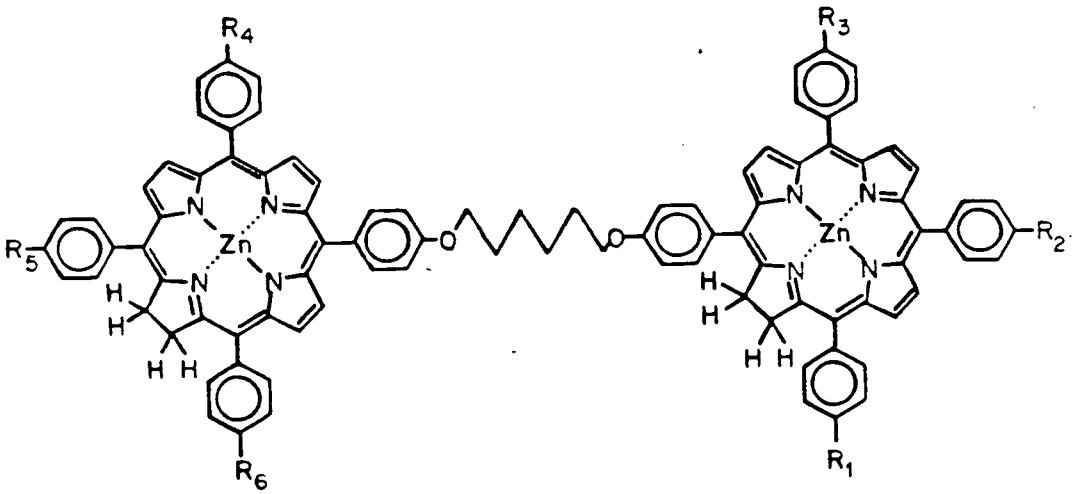
the zinc complex of tetraphenylisobacteriochlorin with a similar degree of selectivity.[82]

In this thesis, we report the syntheses of zinc complexes of dimeric pophyrin, chlorin and bacteriochlorin molecules. We have made the zinc complexes of 5,10,15-triphenyl-20-[4-[6-(10,15,20-triphenyl-5-porphinyl)-phenoxy]hexoxy]phenyl]porphine (23) as well as the chlorin (24) and bacteriochlorin (25) derivatives. For convenience the covalently linked triphenylporphyrins, chlorins, and bacteriochlorins discussed in this thesis will be referred to by the following system of nomenclature; TPC-O-C_n-O-TPC refers to a TPC dimer in which the two chlorins are linked together by an n-carbon alkyl chain *via* ether linkages at the *para* positions of the phenyl groups of the first and second porphyrins. Thus TTP-O-C_6-O-TTP is 5,10,15-tri-*p*-tolyl-20-[4-[6-[*p*-(10,15,20-tri-*p*-tolyl-5-porphinyl)-phenoxy]hexoxy]phenyl]porhine (16).



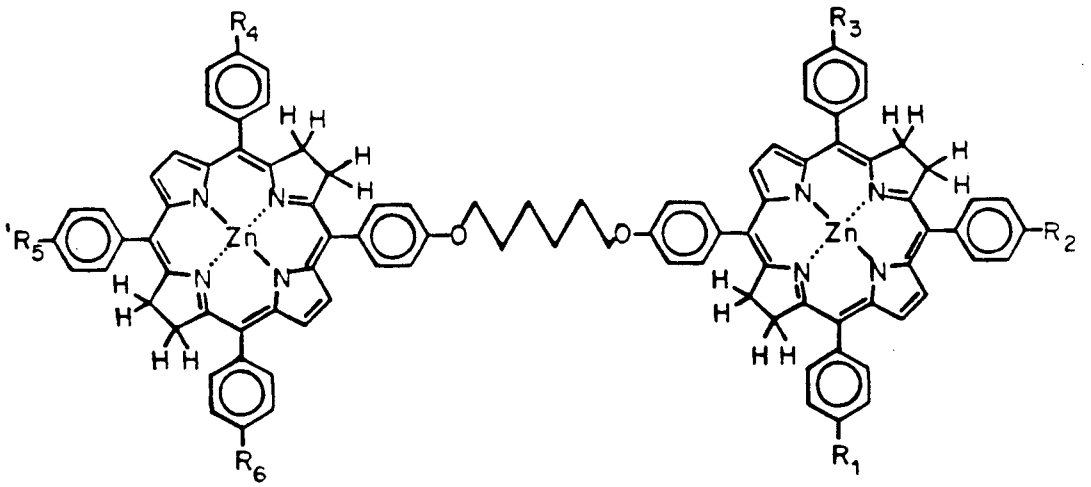
(23)

R_1-R_6=H



(24)

R_1-R_6=H



(25)

R_1-R_6=H

We have synthesized the zinc complexes of dimeric porphyrins (23), chlorins (24) and bacteriochlorins (25) because luminescence properties are well studied in zinc monomers. A discussion of the photochemistry of porphyrins and metalloporphyrins is probably best begun with a consideration of the properties of the excited states involved. It is generally accepted that the prominent electronic transition of porphyrins and their metal complexes are $\pi \longrightarrow \pi^*$ transitions associated with the porphyrin ring. Most of the luminescence and photochemistry observed from these compounds is also associated with the porphyrin π,π^* states even though the lifetimes and reactivities of these states depend strongly on the metal ion incorporated.

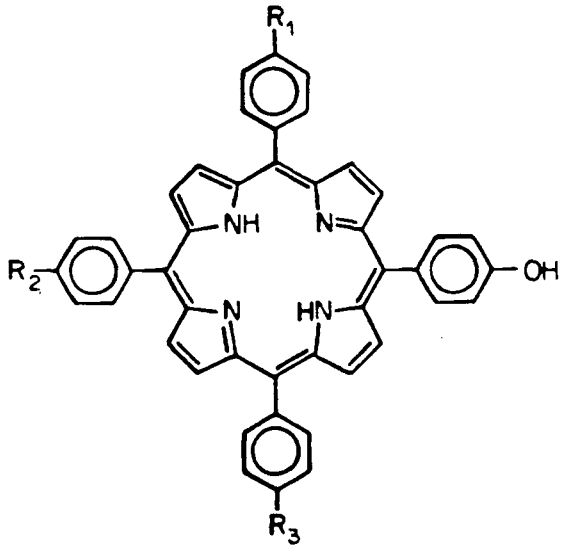
Although luminescence was early recognized as characteristic of several porphyrins and their metal complexes[83] and even used in many cases as an analytical technique, the first systematic study of the influence of different metals on porphyrin fluorescence and phosphorescence was by Becker and Kasha in 1955.[84] A discussion of the emission properties of free base and metallo-porphyrins reported to date at room temperature in fluid medium and in liquid nitrogen temperature (77°K), is given by Hopf and Whitten.[85] In general most free base porphyrins, chlorins and related compounds show strong fluorescence at room temperature and both fluorescence and phosphorescence in rigid glasses. Metalloporphyrin luminescence falls into several categories, dependent largely on the electronic structure of the metal.[85]

The other reason we sythesized the zinc complexes (23), (24) and (25) is that the redox chemistry of zinc monomeric porphyrins (and the corresponding reduced porphyrins) is well studied. In 1937, Rabinowitch and Weiss[86] treated chlorophyll-a (2) with ferric chloride, thereby obtaining a chemically oxidized species whose optical spectrum was similar to that produced by photooxidation. Although the product was not fully characterized, this reaction is possibly the earliest preparation of a π-cation radical of a porphyrin derivative. In 1957, George *et al.*,[87] advanced the suggestion that π-cation radicals were formed by electron abstraction from the porphyrin π-system without interruption of the π-conjugation. It was not until 1964 when Closs and Closs[88] isolated and characterized the π-anion and π-dianion of 5,10,15,20-tetraphenylporphinato-Zn (II) (ZnTPP) that the ability of the porphyrin π-system to undergo redox reactions was generally appreciated. Felton[89] gives a detailed discussion where attention is directed toward reversible electron transfer reactions of metalloporphyrins and cites selected examples in which the oxidized or reduced complexes have been shown to play a biochemical role.

In the Experimental Section of this thesis we report the syntheses of porphyrin, chlorin, and bacteriochlorin dimers because we view them as appropriate models in the study of the role of porphyrin aggregates in both photosynthetic and metabolic processes.

DISCUSSION

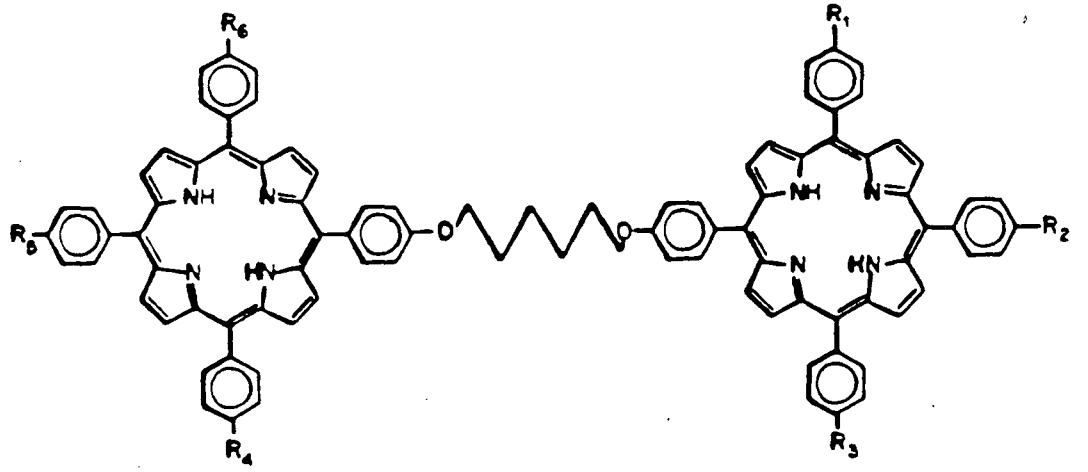
The synthesis of the mono-substituted porphrins (26) and (27) was accomplished by means of a mixed-aldehyde approach. One equivalent of a substituted aldehyde (*p*-hydroxybenzaldehyde) and three equivalents of benzaldehyde or *p*-tolylaldehyde were condensed with four equivalents of pyrrole. The resulting mono-substituted porphyrin crystallized from the reaction mixture along with the corresponding tetraarylporphyrin. The two pophyrins along with small amounts of polysubstituted tetraarylporphyrins, were then separated by "dry-column" chromatography.[90] The separation was facilitated by the strongly basic nature of the hydroxy substituents. The synthetic procedure used is a modification of that initially developed by Rothemund[64] and refined by Adler *et al.*[70] to synthesize tetrasubstituted porphyrins



(26) R_1-R_3=H

(27) R_1-R_3=-CH_3

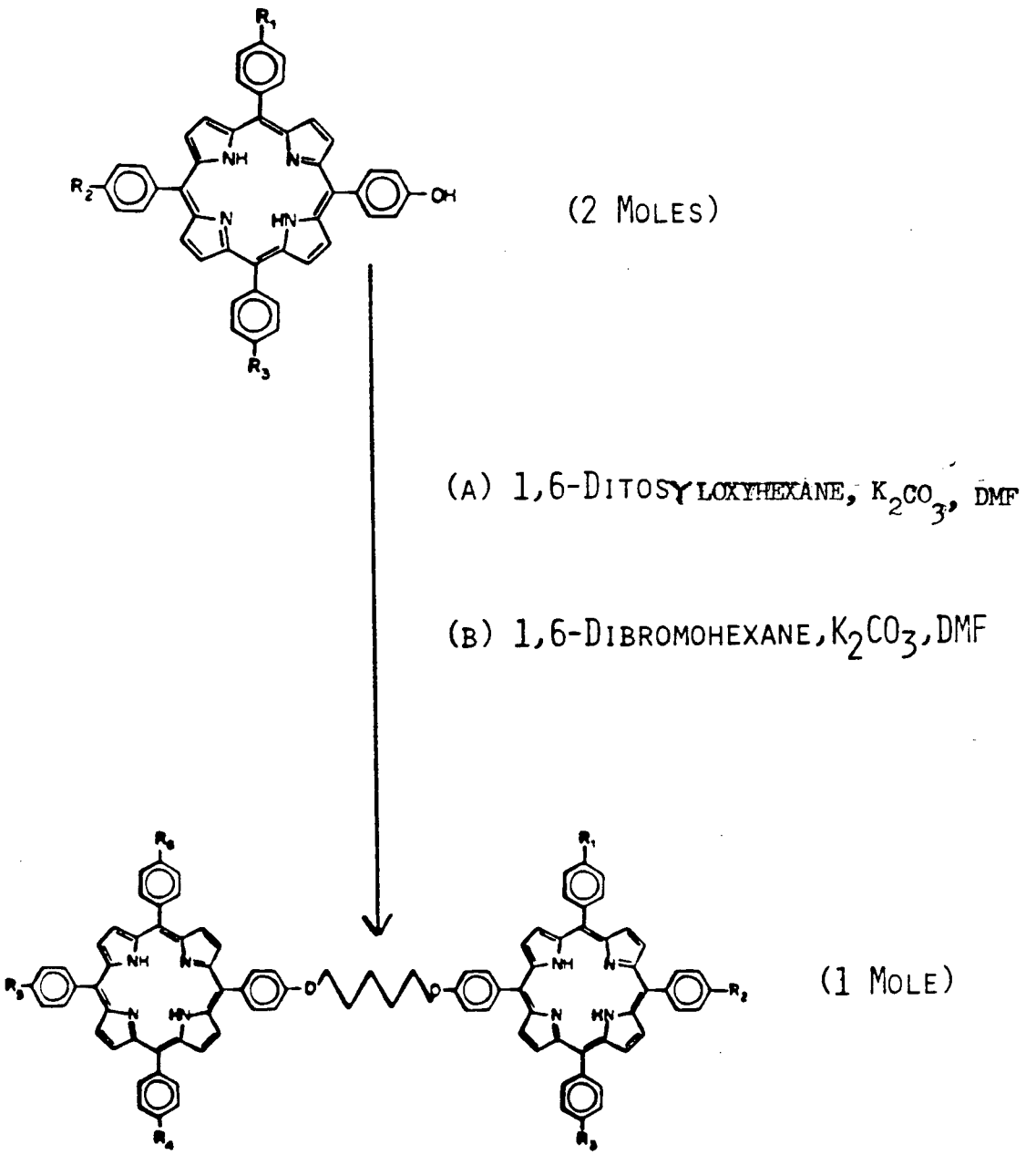
The synthetic route used in the synthesis of porphyrin dimers is illustrated in Scheme II where the syntheses of TPP-O-C_6-O-TPP (15) and TTP-O-C_6-O-TTP (16) are shown. This *one*-step synthesis of porphyrins gives yields of up to 77%. The reaction of two moles of (26) with one mole of 1,6-ditosyloxyhexane gives the porphyrin dimer (15) in 77% yield. After work-up the latter compound is easily separated from the starting materials by chromatography since it is relatively non-polar. We have also synthesized the porphyrin dimer TTP-O-C_6-O-TTP (16) by coupling two moles of TTP-OH (27) using one mole of 1,6-dibromohexane instead of 1,6-ditosylhexane with slightly lower yields (72%).



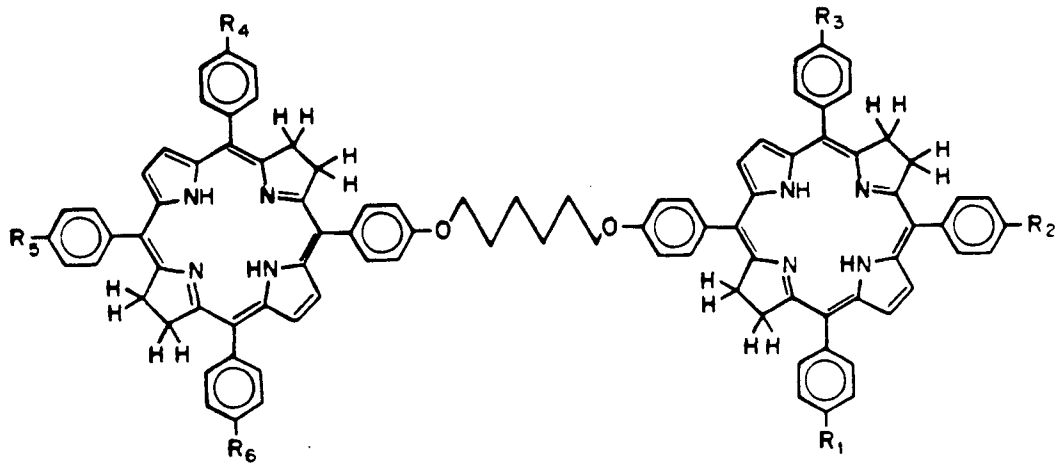
(15) R_1-R_6=H

(16) R_1-R_6=-CH_3

SCHEME II

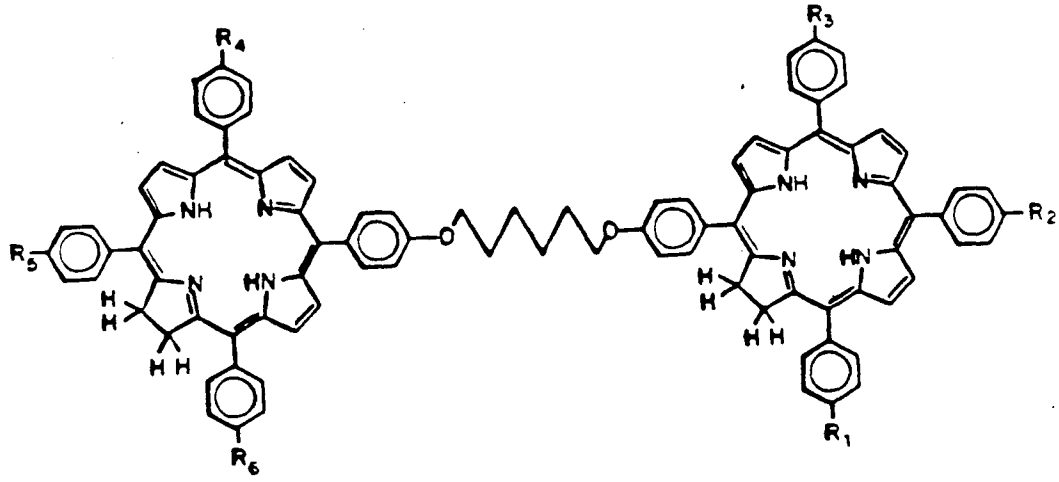

(2 MOLES)
(A) 1,6-DITOSYLOXYHEXANE, K_2CO_3, DMF
(B) 1,6-DIBROMOHEXANE, K_2CO_3, DMF
(1 MOLE)

Diimide reduction of the porphyrins (monomers and dimers) has been carried out using *p*-toluenesulfonylhydrazine. There is one noteworthy feature of the preparative aspects of diimide reduction of these tetraarylporphyrin derivatives. DDQ dehydrogenation of tetraphenylbacteriochlorin is sufficiently faster than dehydrogenation of the chlorin that the most efficient chlorin preparation involves reduction of tetraphenylporphyrin to a chlorin-bacteriochlorin mixture followed by addition of DDQ to dehydrogenate the bacteriochlorin. We synthesized TTBC-O-C_6-O-TTBC (28) and TTC-O-C_6-O-TTC (29) with yields of 65% and 60% respectively. There are three possible isomers for (29) depending on which of the peripheral double bonds in the two covalently linked macrocycles are reduced.



(28)

R_1-R_6=-CH_3



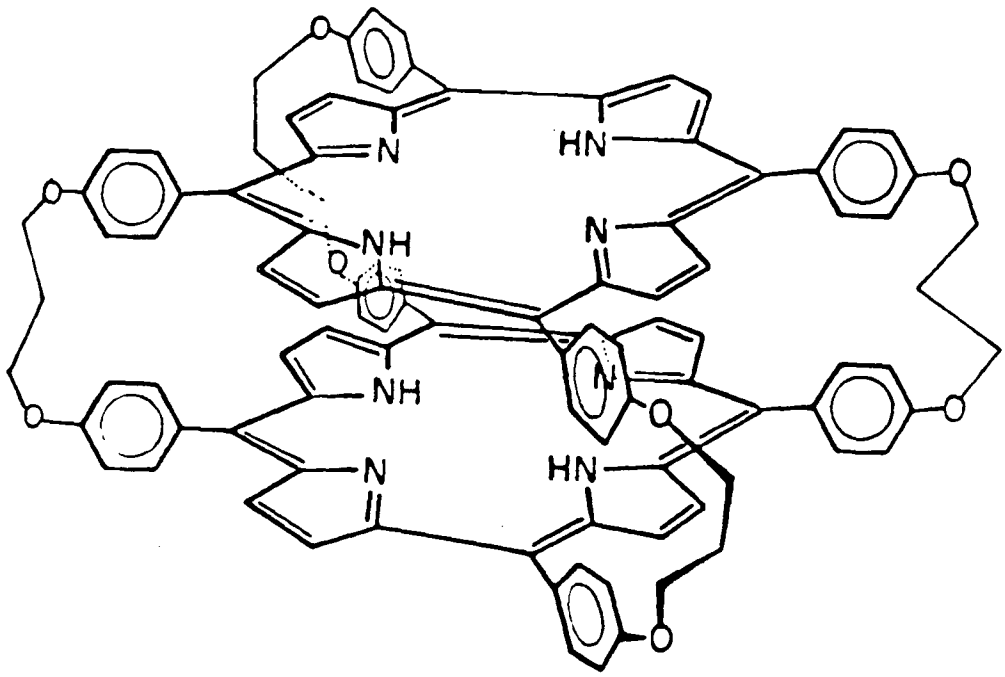
(29)

R_1-R_6=-CH_3

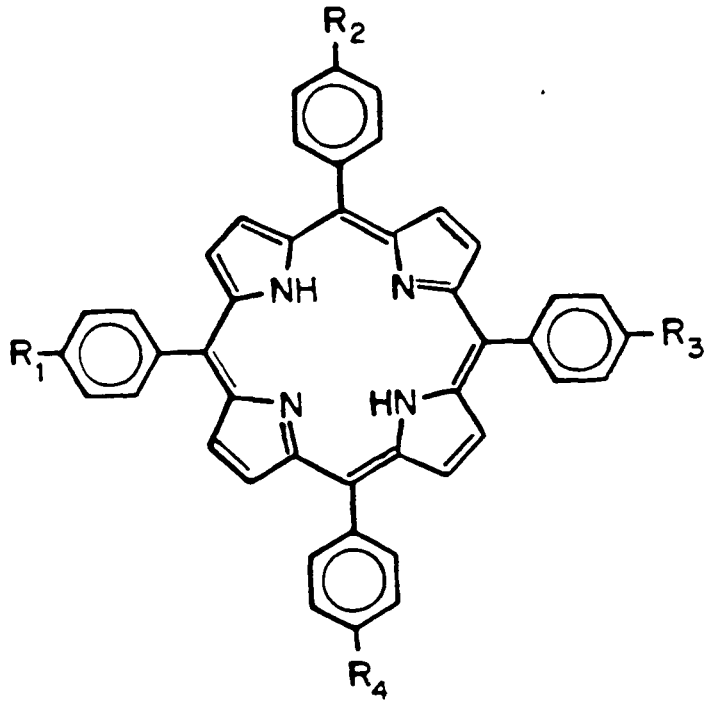
Zinc metal insertion into the porphyrins, chlorins and bacteriochlorins was accomplished by the "acetate method". Under the term "acetate method" are those metalation reactions where the N-H protons of the porphyrins (or reduced derivatives) to be metalated are transferred to the acetate ions.[91] All metalloporphyrins, metallochlorins and metallobacteriochlorins reported in this study were prepared from reacting the free bases with zinc acetate in dry pyridine solvent. The conversion to the metallo-derivatives was monitored using visible spectroscopy. It should be noted that nearly all metallochlorins (and metallobacteriochlorins) are unstable with respect to light-induced oxidations by molecular oxygen in some solvents, and some are even unstable in the solid state. The product of these photooxidations is seldom a single product such as the corresponding porphine, but usually is a mixture of the porphine and various compounds

resulting from cleavage of the ring(s).[92] Since the preparative methods given for the metallochlorins and metallobacteriochlorins involve several solvents, it is necessary to carry out the preparations (and storage) in the minimum of light and oxygen. In our study all the solvents used for these preparations were deoxygenated by bubbling nitrogen through the solvents for at least half and hour.

We attempted to synthesize tetra-*meso*-[*p*,*p*'-(3,3'-phenoxypropoxyphenyl)]-*strati-bis*porphyrin (32). The attempted synthesis of *strati-bis*porphyrin was approached by application of the tetraaldehyde modification[93] of the Adler-Longo porphyrin condensation prodedure.[70]



(32)



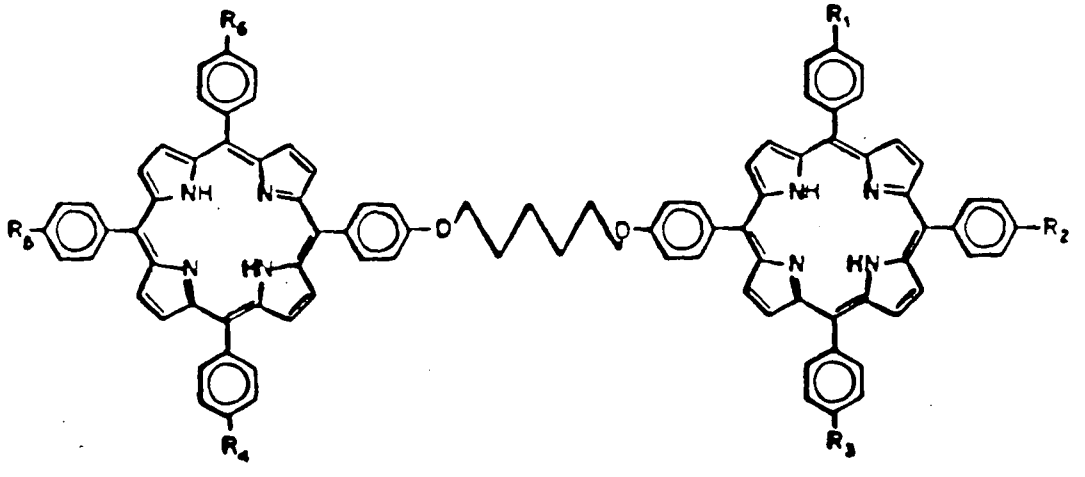
(30) R_1-R_4=-O-$CH_2CH_2CH_2$-Br

(31) R_1-R_4=-O-$CH_2CH_2CH_2$-O-Ph-CHO, Ph=Phenyl

Tetra-*meso*-[*p*-(3-bromopropoxy)phenyl]porphyrin (30) was synthesized by the reaction of pyrrole with *p*-3-bromopropoxybenzaldehyde in refluxing propionic acid. Tetra-*meso*-[(*p*'-formyl-3-phenoxy-*p*-propoxy)phenyl]porphyrin (31) was prepared by reacting (30) with an excess of *p*-hydroxybenzaldehyde in dry DMF solvent in the presence of anhydrous potassium carbonate. The synthesis of *strati-bis*porphyrin (32) was unsuccessful following the addition of (31) and pyrrole (4 equivalents) to refluxing propionic acid-ethylbenzene (1:1) [0.4mM in (31)]. We believe that attempts to sythesize the *strati-bis*porphyrin (32) (with a

3 carbon linkage) were unsuccessful because of the steric strain arising from such a system. We postulate that such a system of co-axial porphyrin rings held together by peripheral linkages, (with 4 carbons or more) could be made. Molecular model studies confirmed this assertion.

The proton n.m.r. spectra of compounds prepared in this study clearly indicate the structures of the compounds. Except in the case of TTP-O-C_6-O-TTP (16), the ratio of the integrated areas for the peaks is as expected in all cases. Initially, we synthesized (16) because the different chemical shifts of the totyl methyls could provide a convenient way of determining stoichiometry *via* n.m.r. However, it turned out that the ratio of the integrated areas corresponding to the tolyl methyl protons and those of the hexyl protons adjacent to the ether linkages was *not* as expected. This anomaly arose due to the differences in the spin relaxation times of the two sets of magnetically non-equivalent protons, a phenomenon frequently encountered in F.T. proton n.m.r. spectroscopy.[94]



(16) R_1-R_6=-CH_3

The rapid development of proton nuclear magnetic resonance (n.m.r.) spectroscopy since about 1960 has had a strong influence on the study of almost all classes of organic compounds. There are, however, few categories of compounds for which such a wealth of information can be obtained by n.m.r. as for porphyrins. This circumstance arises for the most part from the large magnetic anisotropy (ring current) of the aromatic macrocycle of these compounds. The ring current functions as a built-in chemical shift reagent, and spreads the proton n.m.r. spectrum of porphyrins over the unusually large range of more than 15 p.p.m.[95] This in consequence generally simplifies interpretation and assignment, and makes proton n.m.r. a very sensitive probe of structural modifications. The ring current effects, in addition, allow detailed studies of molecular interactions in solution.

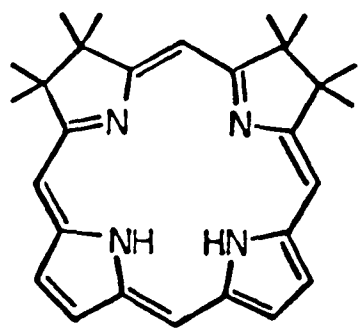
The proton n.m.r. spectra of porphyrins, especially some of the metalloporphyrins, are strongly solvent, concentration and temperature dependent.[95] This is due to the tendency of porphyrins to experience self-aggregation, and this, in combination with the strong magnetic anisotropy of the porphyrins has major consequences for the proton n.m.r. spectra. In the free porphyrin bases, aggregation is weak, and parallels the π-π aggregation behaviour generally observed in aromatic molecules.[96] Under aggregating conditions the accurate determination and assignment of chemical shifts becomes especially important, as aggregation shifts of more than 2 p.p.m. may occur

for the resonances of particular protons as a result of close proximity to the ring current of another macrocycle. A rigorous approach to the problems proposed by aggregation requires mapping the concentration-dependence of the chemical shifts and extrapolation to infinite dilution, but this procedure is really practical only for certain important compounds. The aggregation problem in the assignment of chemical shifts can in general be circumvented by recording the spectra in trifluoroacetic acid (TFA), in which both π-π and coordination-aggregates are broken down by dication formation or by preferential ligation of the metal axial coordination sites with TFA. For sufficiently stable compounds this is a very useful approach, particularly because TFA is an excellent solvent even for otherwise only poorly soluble free base pophyrins.

meso-Tetraphenylporphyrin (TPP) (10) is the parent of a variety of compounds not related structurally to the naturally-occuring porphyrins. The proton n.m.r. spectrum of *meso*-tetraphenylporphyrin shows two resonances (β-pyrrole H,N-H) for the macrocyclic protons, and two signals for the three phenyl protons well separated from the first two. Due to steric hindrance, the phenyl rings in TPP are out of the plane of the macrocycle, they do not rotate freely, and mesomeric interactions between the four phenyl groups and the macrocycle are efficiently reduced. The very similar chemical shifts for the *m*- and *p*-protons of the phenyl groups can be explained on this basis. Although the *m*-protons are closer to the macrocycle, they are

out of its plane, and thus positioned in a less deshielded region. The N-H tautomerism is rapid at ambient temperature on the proton n.m.r. time scale, but has been studied at low temperatures.[97]

As in proton n.m.r. spectra of porphyrins, the spectra of the chlorins and bacteriochlorins are dominated by the ring-current-induced shifts (RIS)[95] of the aromatic macrocycle. In chlorins and bacteriochlorins one or two of the macrocycle peripheral double bonds are reduced without loss of the macrocyclic ring current. Removal of one of the peripheral double bonds leads to a decrease in the ring current, as indicated by the upfield shift of the peripheral proton signals and a downfield shift of the N-H signals. The decrease is moderate in chlorins and bacteriochlorins, but very pronounced in isobacteriochlorins (33). In the latter compounds, the two N-H protons are for the most part located at the two neighbouring (non-reduced) pyrrole rings, a structure which is unfavourable for a large ring current for both steric and electronic reasons.



(33)

Quantities of materials available in natural product chemistry are often minute, and the technique of mass spectrometry has the advantage that, using only dimunitive samples, it can provide accurate information, not only on molecular weights and elemental compositions of compounds, but also details of the nature of some of the functions within complex molecules. Both of these factors are of obvious utility in structural investigations of porphyrins and metalloporphyrins. The major breakthrough in porphyrin mass spectrometry came about 1964 with the introduction of 'direct' insertion probes; before that time it had been virtually impossible to measure the spectra of involatile substances, though using extreme measures, some macrocycles had been examined.[98]

The physical appearance of the molecular ion enables one to ascertain the presence of halogens, metals, *etc.* in compounds. This is of great help in identification of unknown metalloporphyrins because of the general tendency for metal ions not to be lost in fragmentation processes and because the precise isotopic compositions of metals are known. Metal-free porphyrin mass spectra almost invariably possess a cluster of peaks to higher mass than the molecular ion. The explanation of the high mass peaks is that there is scavenging of metal ions by the porphyrin in the source of the spectrometer; it may even be that each instrument has a 'fingerprint' of metal ions which is unique, depending upon the parameters and the construction of the ionization source. In the examples we studied

the metal ions scavenged were copper ions.

A characteristic feature of the mass spectra of porphyrinic compounds is the way in which the ions are split into at least two separate groups. The highest mass group contains the molecular ion and its fragmentation products. After a relatively bare region the doubly charged series of ions is observed. Below about $\frac{m}{e}$ 200 there are several peaks, in all the cases we studied, indicating that there is extensive cleavage of the macrocyclic nucleus. In organic mass specrometry, a major driving force and stabilizing effect for fragmentation is usually the formation of even-electron ions.[99] This principle holds firm in the mass spectra of porphyrinic compounds for both the singly and doubly charged ions; the stability difference between even and odd electron ions is even accentuated by the macro-ring.[100] Features of the spectra of the tetraarylporphyrins we studied are well in accord with the stability of the aromatic nucleus, which allows wide delocalization of the positive charges.

Metal complexes of porphyrins undergo fragmentation in a similar manner to the free bases, the only difference being in the physical appearance of ions owing to the isotopic compositions of the metals. Except in very unusual cases, the metal atom is not lost in any fragmentation process, and this might be expected because of the stability of the macrocyclic nucleus towards cleavage.[101] Most chlorin mass spectra are broadly similar to those of their porphyrin counterparts, 'benzylic' cleavages predominating. Thus, the whole substituent is usally

lost from the reduced ring.[101] *meso*-Tetraphenylchlorin (TPC) (11) gives a mass spectrum which corresponds to that of the porphyrin analogue (10); this novel dehydrogenation is due to electron-impact excitation and not thermal effects in the source of the spectrometer.[102] In almost all the dimers we studied there was strong evidence for the cleavage of the ether linkages leading to the observation of ions such as TPP-OH^{+}, TPC-O^{+} *etc;* and similar ions corresponding to the zinc metallo-derivatives. For a detailed discussion on mass spectrometry of porphyrins and metalloporphyrins the interested reader is advised to see the review by Smith.[101]

Electronic absorption spectroscopy can be used to elucidate the gross structure of porphyrins and their derivatives, such as whether the nucleus is reduced (as in chlorins and bacteriochlorins) or whether certain metals are chelated in the macrocycle.

In 1883, an intense absorption band at about 400 nm was discovered in hemoglobin by Soret;[103] this was later observed in porphyrins by Gamgee.[104] This "Soret" band is the most intense band in the porphyrins and their derivatives, molar extinction coefficients, ε, around 400,000 often being recorded. The Soret band is the band of choice for spectrophotometric determinations; commercial samples of porphyrins often have their purity expressed in terms of the extinction coefficient of the Soret band.

The ultraviolet and visible absorption spectra of tetraphenylporphyrin (10), its *p*-methyl and methoxy de-

rivatives in benzene have been reported.[105] The spectra have been divided into two groups, the first in the region of 700 to about 450 nm, and the second from 450 to 350 nm. The absorption bands in the 700-450 nm region can be regarded as vibrational terms of a common electronic transition,[105] while the intense band in the near ultraviolet region, the so-called "Soret" band, is found in all tetrapyrroles in which the nucleus is fully conjugated and can therefore be regarded as a characteristic of this macrocyclic conjugation. Many of the absorption bands of the *para*-substituted derivatives exhibit small shifts to longer wavelengths as compared to the etio-type spectrum of tetraphenylporphyrin TPP (10), (see Optical Spectral Appendix), while other bands showed no change in position.[105] The intensity of the Soret band is weaker in chlorins and metallochlorins.

Ultraviolet-visible spectroscopy is by far the most widely applied spectroscopic method in hydroporphyrin (chlorins and bacteriochlorins) chemistry and biochemistry. Due to the characteristic and intense absorptions of many hydroporphyrins and the large number of known spectra, the method is sensitive and selective. Considerable effort has also gone in a theoretical interpretation of the uv-vis spectra of hydroporphyrins.

Among the hydroporphyrins, the chlorins and bacteriochlorins as well as their metal complexes, have characteristic absorption bands in the ranges between 350 and 450 nm (Soret or B-band), and 600-900 nm (red or

Q-band). In these cases, the assignment of a certain chromophoric system by uv-vis measurements is relatively safe even in reaction mixtures and biological systems. It should be noted that, in most hydroporphyrins, the intensity of the "Soret" band is no longer an order of magnitude greater than the red band(s), but, rather, of comparable intensity. This is certainly due to the reduced symmetry in the hydroporphyrins and is especially pronounced for unsymmetric substitution.[106]

Chlorins have an intense narrow red band around 660 nm ($\varepsilon \approx 70{,}000$), and a Soret band of about threefold intensity around 400 nm. A double band in the region of 500 nm ($\varepsilon \approx 15{,}000$) is typical for free-base chlorins. Upon metalation, the disappearance of this band is the most characteristic spectral change. The red band of metallochlorins is increased in intensity, and increasingly blue-shifted with increasing electronegativity of the central metal.[106]

Bacteriochlorins have a narrow absorption ($\varepsilon \approx 80{,}000$) at about 750 nm, a split Soret band, and an absorption of intermediate intensity at about 540 nm. As compared to the free bases, the spectra of the metal complexes are red-shifted.[106] As in chlorins, the intensity of the red band increases and that of the Soret band decreases upon metalations. The uv-vis spectra of isobacteriochlorins are in the red region similar to those of the chlorins, but blue-shifted by about 30 nm for similarly substituted compounds. The Soret band of isobacteriochlorins is

split as in bacteriochlorins.[106]

Elemental analyses were performed on purified compounds. The molar ratios C:H:N and the percentages of C,H and N were consistent with the assigned structures. The tetraarylporphyrins we prepared had melting points greater than 360°. The melting point of tetraphenylporphine was reported as 450° by Rothemund.[107] Generally porphyrins have very high melting points, Dolphin *et al.*;[42] in their syntheses of porphyrin dimers, covalently linked *via* amide groups, frequently reported melting points greater than 300°.

CONCLUSIONS

Singlet energy transfer is known to occur between chlorophyll, Chl, molecules.[108,109] Presumably the Chl molecules are arranged in planar, parallel arrays in the chloroplasts[110] in order to facilitate energy transfer. It was therefore of interest to examine the absorption spectra of the porphyrin and metalloporphyrin dimers (as well as the corresponding hydroporphyrins) prepared in this study. The data in the Experimental Section show that the visible absorption bands have positions which are essentially identical to those of the corresponding monomers. The intensities are those that would be expected for a molecule containing two non-interacting molecules. In the Soret region the intensities of the dimers are as expected. There is no splitting of the 420 nm bands into two or more components.

A splitting of the Soret absorption has been reported by Leonard and Longo.[111] The authors reported the results of a study of matrix-isolated tetraphenylporphines (TPP) in matrices of n-octane, argon and sulfur hexafluoride. For TPP in octane with mole ratios less than 500:1 they observed a red shift as the concentration of TPP increases, TPP-TPP interactions become stronger and cause the red shift, as observed in the thin film spectrum. Two bands in the Soret region of the TPP and TPC matrix-isolated spectra, at about 420 and 400 nm, were observed in both cases. In a previous study, Leonard and Longo[112] had observed a splitting of the Soret absorption of matrix-isolated porphine.

They had concluded that the porphine was trapped as pairs or "dimers" in the matrix and that the splitting was due to Davydov splitting of molecular states in pairs. The theory of spectral shifts and splitting of the Soret absorption is quite complicated. Leonard and Longo [111,112] have made pair potential calculations which correlate with the observed experimental results. The absorption spectrum of matrix-isolated porphine shows a greater splitting of the Soret absorption than that of TPP. In the case of TPP and its metal derivatives, the bulky phenyl groups are appreciably twisted with respect to the porphine plane and make guest-host interactions much more significant. Thus, less pairing occurs as compared to the porphine case where there are no bulky phenyl groups. Theoretical calculations of the Davydov splitting were made[111,112] and are, qualitatively, in agreement with the observed matrix-isolated spectra for the porphine and TPP cases. Gouterman *et al.*,[113] have observed a similar temperature dependent splitting of the Soret band in μ-oxometalloporphyrin dimers.

The electronic absorption spectra of the various dimers[42,48-57] show a variety of changes in their electronic transitions. Dolphin *et al.*,[42] in their study of covalently linked octaalkylporphyrins did not study free-base dimers. Instead, they prepared mixed metalloporphyrin dimers. The compounds did not show a splitting of the Soret band. Little,[57] has recently reported the synthesis of covalently linked tetraarylporphyrin dimers that did show a splitting of the Soret band.

The covalently linked tetraarylporphyrins we prepared did *not* show a splitting of the Soret band. Our results may be compared to those of Dolphin *et al.*[61] For their dimer (8) (n=8) no changes were observed between its spectra, of both the free base and protonated cations; and those of the corresponding monomer, suggesting that the two porphyrin rings in this dimer (whose centres could be greater than 15Å apart) do not interact.[61]

The electronic interaction between the two porphyrin rings in the dimers can be studied by examining their proton magnetic resonance spectra. The chemical shifts for the tolyl methyls of 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin (TTP-OH) (27) were found to be δ = 2.68 p.p.m. while those for the dimer TTP-O-C_6-O-TTP (16) were between the ranges δ = 2.63-2.65 p.p.m., in other words, the tolyl methyls of the monomer (27) are *more* shielded than those of the dimer (16). Examination of the proton magnetic resonance spectra shows that the chemical shifts for the pyrrole N-H protons of the porphyrin monomers, *eg.* TPP, are essentially the same as those of the corresponding dimers. Thus as would be expected by considering the steric restraints for the dimer molecules which were constructed with a long (6-carbon) linkage, there is no evidence from the n.m.r. for porphyrin-porphyrin interaction due to the molecule folding back on itself. In contrast to the generally straightforward interpretation of proton magnetic resonance (p.m.r.) spectra in porphyrins the p.m.r. spectra of chlorins and bacteriochlorins are

often very complex. One reason is the reduced ring current shifts. An additional complicating factor in these compounds is the possibility of long-range spin-spin coupling of the protons on the reduced ring(s) with the pyrrole N-H.[95] Due to the complicated p.m.r. spectra for the dimeric chlorins and bacteriochlorins, there is no clear-cut evidence for chlorin-chlorin or bacteriochlorin-bacteriochlorin interaction due to the molecule(s) folding back on themselves.

There are other experiments that could be done to increase porphyrin-porphyrin interaction in the dimers. We could have done low temperature experiments similar to those of Leonard and Longo[111,112] in which they studied matrix-isolated porphyrins. Our compounds have a good deal of conformational freedom and this apparently leads to a decrease in porphyrin-porphyrin interaction. Our singly-linked metalloporphyrin dimers, perhaps, could be constrained to a face-to-face conformation using chelating ligands. Thus, a suitable axial ligand bridge between the two zinc ions could be found that could bring about the required face-to-face conformation. Tsutsui and Taylor[114] discuss some axial ligand bridges in model compounds that can be considered relevant to the cytochrome oxidase system. Among them we may cite the azide, oxygen, halide and imidazolate bridging species.

EXPERIMENTAL

Electronic spectroscopy

Visible spectra were obtained on a Cary 17 recording spectrophotometer. Dichloromethane spectro-grade was used as solvent, unless otherwise specified. Units for the molar extinction coeffient, ε, are $mol^{-1} mm^{4}$.

Nuclear Magnetic Resonance

Nuclear magnetic resonance Fourier-transform spectra were taken at either 100 MHz or 270 MHz with a Varian XL-100 or Nicolet Model NIC-80 spectrometer. Deuteriochloroform ($CDCl_3$) was the solvent used. Resonances are quoted on the delta, δ, scale relative to tetramethylsilane (TMS) (δ=0).

Mass Spectroscopy

Mass spectra were recorded in an Atlas CH-4 spectrometer or an A.E.I. MS-902 spectrometer.

Melting Point Determination

Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Analysis

Elemental analysis for carbon, hydrogen and nitrogen were determined by Mr. P. Borda of the Microanalytical Laboratory, U.B.C.

Chromatography

The chromatographic separations were effected by the "dry column" procedure;[90] using either alumina (Fisher Scientific

A-540 or A-950) or silica gel (Woelm-Activity I) purchased from the ICN Pharmaceuticals, Inc.*

Thin-layer chromatography (TLC) was performed using Silica Gel GF precoated plates (Analtech-Uniplate, 250μ).

CHEMICALS

All chemicals were reagent grade unless otherwise specified.

Pyridine

Dry pyridine was obtained by refluxing reagent grade pyridine over barium oxide for four days and then distilling the solvent from the drying agent.

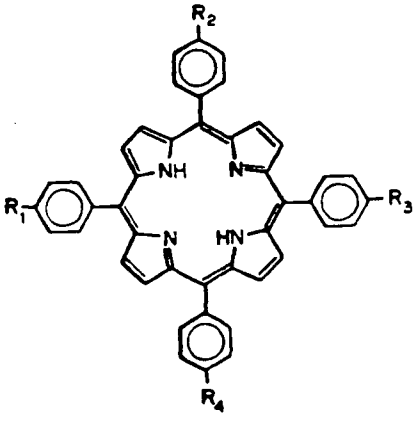
DMF

Dry DMF was obtained by refluxing reagent grade DMF over anhydrous $CuSO_4$, and distilling under reduced pressure.

* The chromatographic column was filled with dry adsorbent (alumina or silica gel). The material to be chromatographed was dissolved in a minimum amount of solvent and then applied on top of the column. The less polar fraction was eluted from the column using less polar solvent. The solvent system was made more polar in order to elute the more polar fractions. In all cases the solvent was applied on top of the "dry column" and solvent added until the product was eluted from the column.

PART (A) - SUBSTITUTED TETRAPHENYLPORPHINES - (MONOMERS AND DIMERS)

Synthesis of *meso*-Tetraphenylporphin (Compound Ia)



R_1-R_4=H

Freshly distilled pyrrole (8 ml, 0.1 mole) and 10 ml (0.1 mole) reagent grade benzaldehyde were added to 300 ml refluxing reagent grade propionic acid. After refluxing for half an hour the solution was cooled to room temperature and filtered. The filter cake was washed with propionic acid, hot water and finally with methanol. The puplish crystals were air dried. The yield of the *meso*-tetraphenylporphin (TPP) was 2.5g (16% yield).

The TPP was recrystallized from methylene chloride and methanol to give 1.8g of purple needles.

Absorption Characteristics of TPP

(Dichloromethane)		(Pyridine)	
λmax, nm	ε x 10^{-3}	λmax, nm	ε x 10^{-3}
647	3.3	647	3.9
592	5.3	592	5.4
548	8.0	550	8.6
515	18.6	515	18.7
485	3.4	485	3.8
419	478	420	468

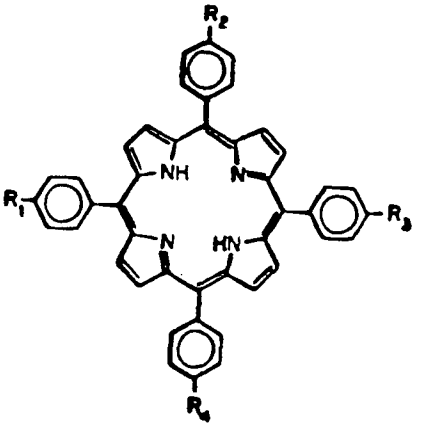
Lit.[115] λmax, nm (ε x 10^{-3}) (Benzene)

420(450) 484(5.0) 516(20.7) 550(8.5) 592(5.8) 646(3.8)

M.p. > 360°, Lit.[107] 450°

Synthesis of *meso*-Tetratolylporphin (TTP)

(Compound Ib)



R_1-R_4=-CH_3

Freshly distilled pyrrole (6.7g, 0.1 mole) and 12.0g (0.1 mole) *p*-tolualdehyde were added to 300 ml refluxing

reagent grade propionic acid. The reaction mixture was refluxed for 30 minutes, cooled to room temperature and filtered. The procedure adopted was that of Adler *et al.*[70] No attempt was made to remove the *meso*-tetratolylchlorin (TTC) impurity. The crude porphin was then recrystallised from methylene chloride and methanol to yield 2.4g of purple needles (14% yield).

NMR Data ($CDCl_3$)

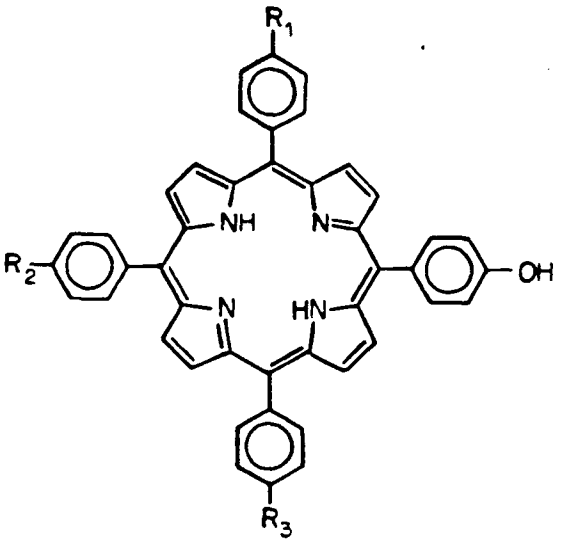
Delta, ppm	# H	J, Hz
2.68	12, methyl (s)	
7.82	8, tolyl-2,6-(d)	7.1
8.35	8, tolyl-3,5-(d)	7.1
8.63	8, β-pyrrole (s)	

Absorption Characteristics of TTP (Dichloromethane)

λmax, nm	650	592	550	516	485	420
$\varepsilon \times 10^{-3}$	4.0	5.4	8.1	18.8	3.6	490
Lit.[115] (Benzene) λmax, nm	649	594	551	516	483	420
$\varepsilon \times 10^{-3}$	5.8	6.9	12.1	23.0	6.0	558

Synthesis of 5-(4-Hydroxyphenyl)-10,15,20-tritolylporphyrin

M.W. 672.8 (Compound IIa)



R_1-R_3=-CH_3

para-Hydroxybenzaldehyde (4.6g, 0.038 mole) and 13.5g (0.112 mole) of *para*-tolualdehyde were mixed with 500 ml of hot propionic acid. Pyrrole (10.1g, 0.15 mole) was added and the reaction mixture refluxed for one hour. The reaction mixture was cooled, filtered and the purple crystals washed with methanol. The yield of the crude porphyrins was 4.3g.

Thin-layer chromatography (Tlc) showed the presence of *meso*-tetratolylporphin (R_f 1) and the mono-substituted porphin (R_f 0.3). There were traces of the di-, tri-, and tetra-substituted porphins. The crude porphyrins were dissolved in 750 ml of methylene chloride and chromatographed on a 60 x 5 cm column of alumina using methylene chloride as the eluant. The chromatographic separations were effected using the dry column procedure.[90] The first band eluted from the column was TTP. It was followed by

a green band of chlorin impurity. A third band which moved very slowly was spread out over the top 15 cm of the column. This band was eluted with 1:1:10 methanol-ethyl acetate-methylene chloride and then taken to dryness under vacuum on a rotary evaporator. This material was redissolved in reagent grade methylene chloride and chromatographed on a 40 x 2 cm column of silica gel using methylene chloride as the eluant. The elution pattern is similar to that of the alumina column except that a dark brown band sticks at the top of the column and a second band separates slowly from the tail of the main porphyrin band. The yield was 1.5g (5.9%).

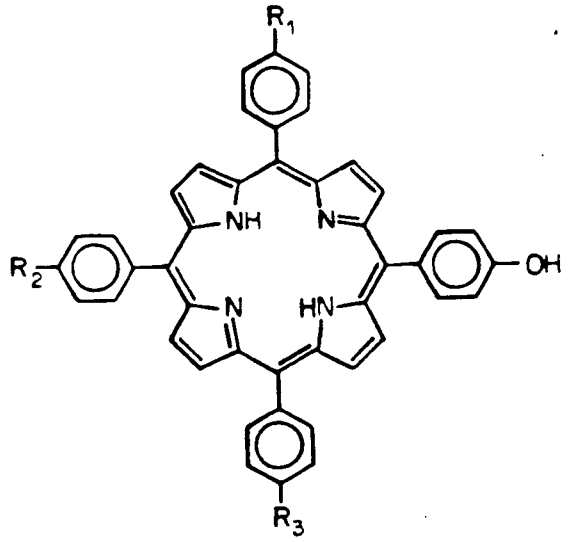
Mass Spectral Data

M/e	I	M/e	I	
672	100 (parent)	505	9	
655	11	455	13	
605	12	405	16	
555	12	343	27	
		336	32	(m/2e)
		331	30	

NMR Data ($CDCl_3$)

Delta, ppm	# H	J,Hz
2.68	9,methyl (s)	
7.48	6, tolyl-3,5-(d)	8.0
8.05	6, tolyl-2,6-(d)	8.0
8.83	8, β-pyrrole (s)	

Synthesis of 5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin (M.W. 630) (Compound IIb)



R_1-R_3=H

The procedure followed was basically the same as that described for 5-(4-hydroxyphenyl)-10,15,20-tritolyl-porphyrin.[116] 6.1g (0.05 mole) *para*-Hydroxybenzaldehyde and 17.5g benzaldehyde (0.17 mole) were used. Pyrrole (14.7g, 0.22 mole) was then added to the reaction mixture.

The reaction mixture was cooled and all the propionic acid solvent removed using a rotary evaporator to leave a tarry residue. The residue was redissolved in boiling methanol and then stood at -10°C overnight. The next day the crude porphyrins were filtered and washed several times with methanol, and then air dried to give 4.3g of shiny purple crystals.

The chromatographic separations were effected as described before.[90] After recrystallisation from methylene chloride-ethanol, 0.6g (7.6%) of the mono-hydroxyporphin was obtained.

Empirical formula: $C_{44}N_4H_{30}O$

M.W. = 630.76

	Calc.	Found	Difference
C	83.79	83.86	+0.07
H	4.79	4.52	-0.27
N	8.88	8.95	+0.07
O	2.54	-	-

Preparation of 1,6-Ditosyloxyhexane.

(Compound III)

A solution of 5.0g (0.04 mole) 1,6-hexanediol in 60ml dry pyridine in a 125 ml glass-stoppered Erlenmeyer was cooled to 0°C and treated with 33.6g (1 molar excess) of tosyl chloride.[117] Dry pyridine was obtained by refluxing reagent grade pyridine over barium oxide for four days and then distilling the solvent from the drying agent.

The Erlenmeyer flask was placed in a refrigerator for 24 hours. The reaction can be followed by the development of a yellow colour, followed by separation of pyridine hydrochloride as long needles. When the reaction was judged complete, the entire mixture was poured with stirring into 400g of ice and water. The tosylate crystallised after 15 minutes additional stirring. The product was filtered, washed with water, dried *in vacuo* at room temperature.

For purification, the tosylate was dissolved in a minimum quantity of methylene chloride-petroleum ether (30°-60°) at room temperature. After stirring with Norit,

the mixture was filtered through filter aid (Celite) and washed. The clean, colourless solution was cooled slowly to -75° in a dry ice-acetone bath with scratching to induce crystallisation and to avoid oiling out. The cooling to -75° was completed and the precipitate filtered. The precipitate was not sucked completely dry but rather transferred to a vial for drying *in vacuo* at room temperature. The ditosylate came out as white needle-like crystals. Yield 7.1g (39%). M.p. 71°-72°.

NMR Data ($CDCl_3$)

Delta, ppm	# H	J,Hz
1.26	4, hexyl-3,4-(tt)	
1.59	4, hexyl-2,5-(t)	
2.45	6, methyl (s)	
3.99	4, hexyl-1,6-(t)	
7.35	4, tolyl-3,5-(d)	8.8
7.79	4, tolyl-2,6-(d)	8.8

Mass Spectral Data

M/e	I	M/e	I
426	100 (parent)	171	32
344	13	155	99
326	17	154	57
255	68	109	14
213	34 (m/2e)	108	60
190	24		

Preparation of 1,6-*Bis*-*para*-formylphenoxyhexane

(Compound IV)

Sodium hydride suspension in oil was washed with anhydrous ether until it was free of the oil. *p*-Hydroxybenzaldehyde (16.2g, 2 fold excess) was dissolved in dry, reagent grade DMF (40 ml). Sodium hydride (6.4g, 0.26 mole) was then added. The reaction mixture was gently warmed until the evolution of hydrogen was complete, and then cooled.

1,6-Ditosyloxyhexane (13.2g, 0.03 mole) was then added to the reaction mixture. The reaction was allowed to proceed with stirring, at room temperature, for 24 hours.

The following day, the whole reaction was poured into a 1 litre separatory funnel. Methylene chloride (400ml) was added, and the mixture extracted twice with 150 ml portions of 10% sodium hydroxide solution to remove excess *p*-hydroxybenzaldehyde. The methylene chloride extract was washed twice with 3N hydrochloric acid to remove the DMF, and finally washed with water. It was dried over a mixture of anhydrous potassium carbonate and sodium sulphate.

On removing all methylene chloride solvent an off-white residue was left behind. The material was recrystallised from ethyl ether-hexane to give 5.5g (54%) off-white chunky crystals. M.p. 93°-94°.

NMR Data ($CDCl_3$)

Delta, ppm	# H	J,Hz
1.57	4;hexyl-3,4-(m)	
1.87	4;hexyl-2,5-(m)	
4.09	4;hexyl-1,6-(t)	
7.00	4;phenoxy-2,6-(d)	8.3
7.84	4;phenoxy-3,5-(d)	8.3
9.40	2;formyl (s)	

Empirical formula: $C_{20}H_{22}O_4$

M.W. = 326.40

	Calc.	Found	Difference
C	73.60	73.69	+0.09
H	6.79	6.74	-0.05
O	19.61	-	-

Preparation of 1-Hydroxy-6-*para*-formylphenoxyhexane

(MW 222)

(Compound V)

p-Hydroxybenzaldehyde (6.1g, 0.05 mole) was dissolved in dry DMF (15 ml). Sodium hydride (1.2g, 10% excess) was added. The sodium hydride was allowed to react with the hydroxybenzaldehyde, (gentle heating), until the evolution of hydrogen was complete.

6-Chlorohexanol (6.83g, 0.05 mole) was then added and the mixture stirred at room temperature for 24 hours. A catalytic amount of potassium iodide was used. The reaction

was protected from moisture by the use of a calcium chloride drying tube.

The whole reaction mixture was then poured into a 1 litre separatory funnel and 350 ml methylene chloride added. The rest of the isolation procedure was similar to that already described for 1,6-*bis*-*para*-formylphenoxyhexane.

On evaporating off the solvent, a yellowish oil was obtained. Yield 9.8g (88%). No attempt was made to purify the oil further.

NMR Data ($CDCl_3$, 60 MHz)

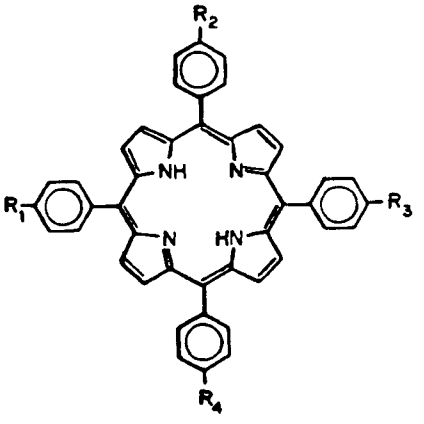
Delta, ppm	# H	J, Hz
1.48	8;hexyl-2,3,4,5-(m)	
3.63	2;α-hydroxy (t)	
3.97	2;α-phenoxy (t)	
6.86	2;phenoxy-3,5-(d)	8.3
7.69	2;phenoxy-2,6-(d)	8.3
9.68	1;formyl (s)	

Mass Spectral Data

M/e	I		M/e	I	
224	6		113	8	
223	11		112	8	
222	40	(parent)	111	17	(m/2e)
204	13		110	7	
123	50		55	100	
122	69		31	25	
121	76				

Synthesis of 5-[(4-(6-Hydroxy-1-hexoxy)phenyl]-10,15,20-tritolylporphyrin (MW 773)

(Compound VI)



R_1-R_3=-CH_3, R_4=-O-$(CH_2)_6$-OH

1-Hydroxy-6-*para*-formylphenoxyhexane, (9.3g, 0.04 mole) and 14.2g *p*-tolualdehyde (0.12 mole) were mixed with 500 ml of hot propionic acid. Pyrrole (10.9g, 0.16 mole) was added and the reaction mixture refluxed for one hour. After cooling the reaction mixture was filtered and the purple crystals washed with methanol.

The isolation procedure followed was that already described for 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin. Tlc showed the porphin to have an R_f value of 0.11. On recrystallisation from methylene chloride-ethanol, the porphin came out as shiny purple needles. Yield 1.4g (4.5%).

NMR Data ($CDCl_3$)

Delta, ppm	# H	J, Hz
1.25	8;hexyl-2,3,4,5-(m)	
2.49	9;tolyl (methyl) (s)	
3.36	2;α-hydroxy (t)	
3.71	2;α-phenoxy (t)	
6.93	4;phenoxy-2,3,5,6-AB quartet	
7.32	6;tolyl-3,5-(d)	7.4
8.01	6;tolyl-2,6-(d)	7.4
8.85	8;β-pyrrole (s)	

Empirical formula: $C_{53}N_4H_{48}O_2$

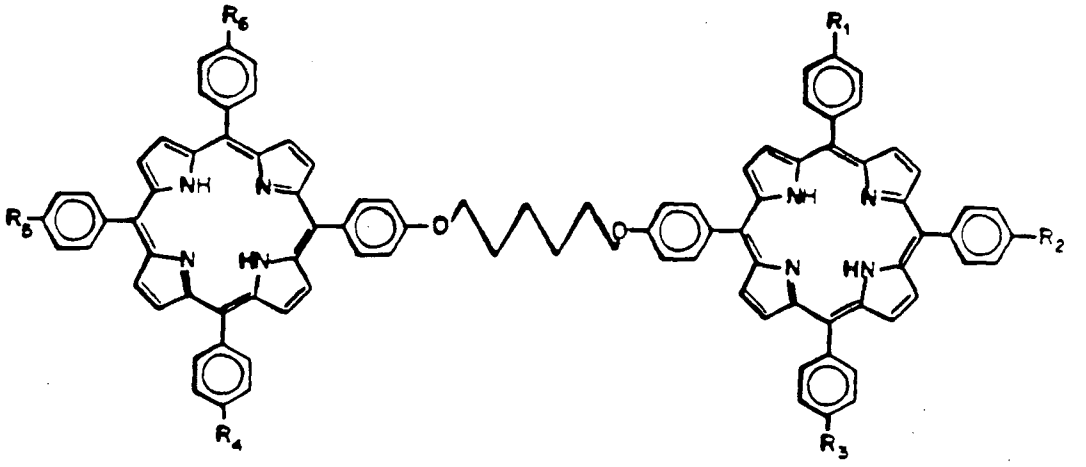
M.W. = 773.00

	Calc.	Found	Difference
C	82.35	82.09	-0.26
H	6.26	6.31	+0.05
N	7.25	7.51	+0.26
O	4.14	-	-

Mass Spectral Data

M/e	I	M/e	I
834	26 (P+Cu)	605	62
775	8	556	16
774	23	555	63
773	42 (parent)	505	68
767	8	455	81
755	29	405	57
705	28	387	100
655	39	331	96

Synthesis of 5,10,15-Tri-*p*-anisyl-20-[4-[6-[*p*-(10,15,20-tri-*p*-anisyl-5-porphinyl)-phenoxy]hexoxy]phenyl]porphine (M.W. = 1524) (Compound VII) .



R_1-R_6=-O-CH_3

1,6-*Bis*-*para*-formylphenoxyhexane (0.8g, 0.002 mole) and *p*-anisaldehyde (5.0g, 0.036 mole) were mixed with 100 ml of 1:1 propionic acid-ethylbenzene. Pyrrole (3.3g, 0.05 mole) was added and the reaction mixture refluxed for one hour, and then taken to dryness under vacuum by means of a rotary evaporator. The resulting black tar was washed briefly with water, and then with dilute ammonium hydroxide. The slightly wet material was triturated with a minimum amount of methanol on a steam bath until the purple crystals of the porphyrins were free from tar. The slurry was then stored overnight in a freezer. The purple solid was filtered off and washed with methanol and then dried. Yield of crude porphyrins was 1.5g. Tlc of the porphyrins showed two spots, tetraanisylporphin (R_f 0.56) and the dimeric porphin (R_f 0.31).

The material was dissolved in a minimal amount of methylene chloride and chromatographed on a 60 x 5 cm column of alumina using methylene chloride as the eluant. The first band eluted from the column was the tetraanisylporphin. The dimeric porphin took 6 hours to be eluted from the column. This fraction containing the dimer was recrystallised from methylene chloride-ethanol to give 41 mg (1.1%) of the porphyrin.

NMR Data ($CDCl_3$)

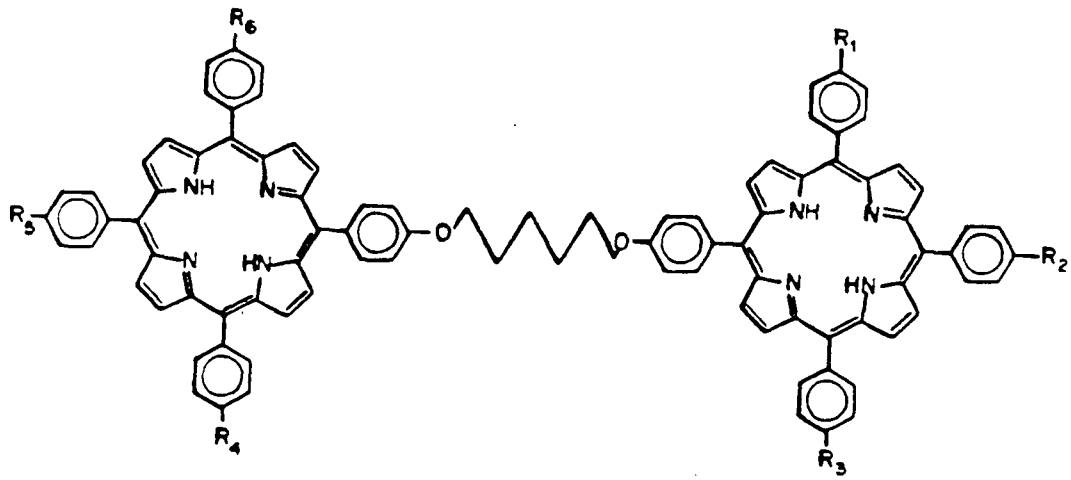
Delta, ppm	# H	J, Hz
1.54	4;hexyl-3,4-(m)	
2.02	4;hexyl-2,5-(m)	
4.12	18;methoxy (s)	
4.34	4;hexyl-1,6-(t)	
7.34	16;anisyl-2,6-(d)	8.1
8.17	16;anisyl-3,5-(d)	8.1
8.90	16;β-pyrrole (s)	

Mass Spectral Data

M/e		I	M/e	I
1528		3	635	10
1527		5	548	12
1526		6	484	10
1525		6	387	26
1524	(parent)	3	357	19
1523		3	342	10
920		4	268	11
852		3		
851		4		
798		13		
786		46		
785		100		
778		35		
764		11		
763		9		
762	(m/2e)	13		
724		44		

Synthesis of 5,10,15-Tri-p-tolyl-20-[4-[6-[p-(10,15,20-tri-p-tolyl-5-porphinyl)-phenoxy]hexoxy]phenyl]porphine. ($TTP\text{-}O\text{-}C_6\text{-}O\text{-}TTP$)

(Compound VIIIa)



$R_1\text{-}R_6 = -CH_3$

A mixture of 1.00g (1.49 mmoles) of 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin (TTP-OH), 3.0g crushed anhydrous potassium carbonate and 341 mg (0.8 mmole) 1,6-ditosyloxy-hexane was stirred magnetically with 25ml of DMF for 24 hours at room temperature. The reaction mixture was then filtered to remove potassium carbonate. Water (10ml) was added to the filtrate. The water-DMF solvent was removed with the aid of a rotary evaporator to leave a purple precipitate.

Tlc of the precipitate showed three spots. The most intense spot moving with the solvent front contained the dimer ($TTP\text{-}O\text{-}C_6\text{-}O\text{-}TTP$). Two less intense spots (R_f values 0.11 and 0.31) were due to the hydroxylated porphins, $TTP\text{-}O\text{-}C_6\text{-}OH$ and TTP-OH respectively.

The precipitate was dissolved in 200 ml methylene chloride and chromatographed on a 25 x 2 cm alumina column using methylene chloride as the eluant. The major band which moved with the solvent front contained the dimer. This band was collected, and after recrystallisation from methylene chloride-ethanol 807 mg (76%) of shiny purple crystals were obtained.

NMR Data ($CDCl_3$)

Delta, ppm	# H	J, Hz
-2.71	4;pyrrole N-H (s)	
1.75	4;hexyl-3,4-(m)	
2.02	4;hexyl-2,5-(m)	
2.63-2.65	18;methyl (2s)	
4.21	4;hexyl-1,6-(t)	
7.54	16;tolyl-2,6-(2d)	3.1, 4.0
8.14	16;tolyl-3,5-(2d)	3.1, 4.0
8.84	16;β-pyrrole (s)	

Mass Spectral Data

M/e	I		M/e	I
1550	11	(P+2Cu)	554	22
1489	13	(P+Cu)	553	28
1430	9		552	32
1429	11		551	42
1428	10	(parent)	550	21
819	15		367	23
818	21		366	26
817	16		315	25
816	10		314	22
815	17		306	36
775	33		305	40
744	91		290	39
734	89		149	67
733	90		91	100
726	94			
714	88	(m/2e)		
673	13			
672	82			
641	55			
627	61			
626	39			
625	58			

Alternative Synthesis of 5,10,15-Tri-*p*-tolyl-20-[4-[6-[*p*-(10,15,20-tri-*p*-tolyl-5-porphinyl)phenoxy]hexoxy]phenyl] porphine.

(TTP-O-C_6-O-TTP)

A mixture of 1.0g (1.49 mmole) of 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin and 0.35g sodium hydride (14.5 mmole) was allowed to react until the evolution of hydrogen was complete (the mixture turned green). The reaction was carried out in 25 ml of dry DMF. 1,6-Dibromohexane (181 mg, 0.74 mmole) was then added. The reaction mixture was stirred for 48 hours at room temperature. The product was precipitated by pouring the reaction mixture into 100 ml of a 10% aqueous methanol solution, and then heating the mixture to coagulate the porphyrin. The product was filtered off, dried at 100°C and then chromatographed on a 20 x 2 cm alumina column using methylene chloride as the eluant. The major band which moved with the solvent front contained the dimer. This band was collected and recrystallised from methylene chloride-ethanol to yield 765 mg (72%) of the porphyrin dimer. **Nmr and mass spectral data were identical to that already reported.**

Empirical formula: $C_{100}N_8O_2H_{82}$

M.W. = 1427.82

	Calc.	Found	Difference
C	84.12	84.10	-0.02
H	5.78	5.56	-0.22
N	7.85	8.20	+0.35
O	2.25	-	-

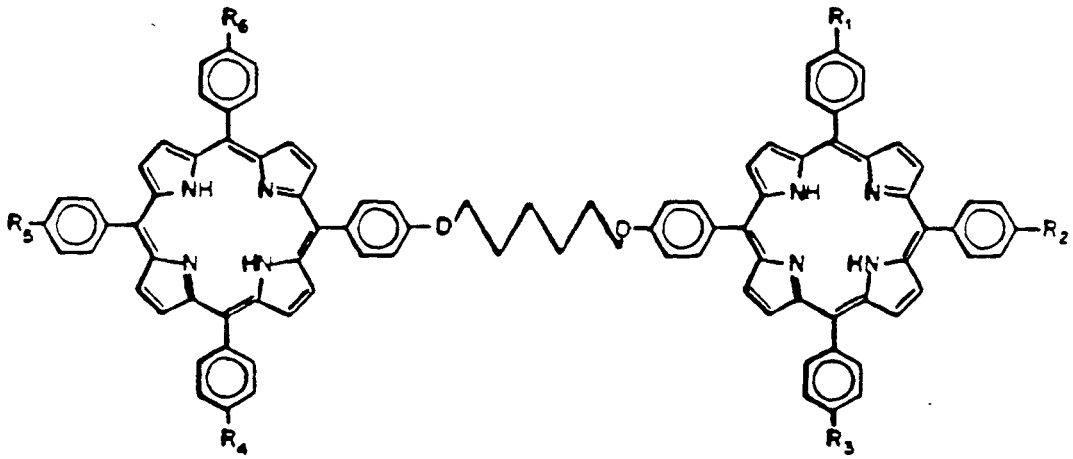
Absorption Characteristics of TTP-O-C_6-O-TTP

λmax, nm (ε x 10^{-3})			
419(712)	487(7.0)sh	518(34.2)	552(16.5)
593(10.6)	649(9.5)		

sh=shoulder

Synthesis of 5,10,15-Triphenyl-20-[4-[6-(10,15,20-triphenyl-5-porphinyl)phenoxy]hexoxy]phenyl]porphine (TPP-O-C_6-O-TPP)

(Compound VIIIb)



R_1-R_6=H

A mixture of 5-(4-hydroxyphenyl)-10,15,20-triphenyl-porphyrin (1.1g, 1.74 mmoles), 400 mg (0.93 mmoles) 1,6-ditosyloxyhexane were stirred for 48 hours in the presence of 1.2g crushed anhydrous potassium carbonate in 20 ml of dry DMF.

The rest of the isolation procedure was similar to that already described for TTP-O-C_6-O-TTP.

On recrystallisation from methylene chloride-ethanol, the dimeric tetraphenylporphyrin came out as a purple, micro-crystalline solid. Yield 903 mg (77%).

Empirical formula: $C_{94}N_8O_2H_{70}$

M.W. = 1343.66

	Calc.	Found	Difference
C	84.03	83.91	-0.12
H	5.25	5.27	+0.02
N	8.34	8.22	-0.12
O	2.38	-	-

NMR Data ($CDCl_3$)

Delta, ppm	# H
-2.74	4;pyrrole N-H (s)
1.80	4;hexyl-3,4-(m)
1.98	4;hexyl-2,5-(m)
4.28	4;hexyl-1,6-(t)
7.73	16;phenyl-2,6-(m)
8.15	16;phenyl-3,5-(m)
8.86	16;β-pyrrole (m)

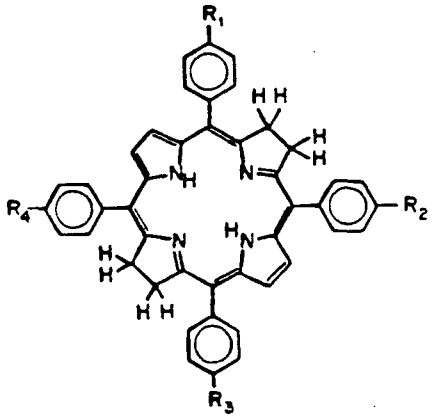
Mass Spectral Data

M/e	I		M/e	I
1466	16	(P+2Cu)	618	29
1405	15	(P+Cu)	616	31
1404	14		615	37
1403	15		614	13
1402	13		613	15
1347	15		589	30
1346	14		543	32
1345	15		511	24
1344	14	(parent)	433	18
1272	12		432	17
1271	13		355	19
1270	12		342	26
1269	13		341	28
838	14		316	64
837	13		293	33
836	14		256	37
835	14		149	83
779	8		108	80
733	9		107	100
717	16			
716	16			
703	17			
693	22			
672	15	(m/2e)		
671	18			
642	23			
630	53			

PART (B) - TETRAPHENYLBACTERIOCHLORINS AND CHLORINS (MONOMERS AND DIMERS)

Synthesis of *meso*-Tetraphenylbacteriochlorin

(Compound IXa)



R_1-R_4=H

A mixture of 1g (1.6 mmoles) of *meso*-tetraphenylporphyrin, 0.6g of *p*-toluenesulfonylhydrazine, 2.0g of anhydrous potassium carbonate, and 75 ml of dry pyridine was heated with stirring at 105°C, under nitrogen and in the dark. Heating and stirring was continued for 12 hours, 0.3g of *p*-toluenesulfonylhydrazine being added every hour. Analysis of a sample of the reaction mixture showed the absence of any tetraphenylchlorin (no 652 nm band, in the visible spectrum). There was a strong band at 742 nm due to the bacteriochlorin.

The reaction mixture was allowed to stand under nitrogen at room temperature for an extra 8 hours. The whole reaction mixture was then added to a mixture of 500 ml of

benzene and 300 ml of 10% aqueous sodium hydroxide and the mixture was digested for 2 hours on a steam bath. After cooling, the benzene layer was washed thrice with a total of 500 ml of cold 3N hydrochloric acid, aqueous sodium bicarbonate solution and then with water. The benzene extract was then dried over anhydrous sodium sulphate for two hours (in the dark). After filtration to remove the sodium sulphate, the benzene extract was then evaporated. The residue was recrystallised from deoxygenated toluene to afford 0.47g (47%) of reddish-purple bacteriochlorin crystals.

Absorption Characteristics of TPBC (Monomer)

λmax, nm	356	378	418	522	740
Ratios	2.6	3.3	1.0	1.4	2.7

Conc. 4.6×10^{-5} M.

Lit.[82] (Benzene)

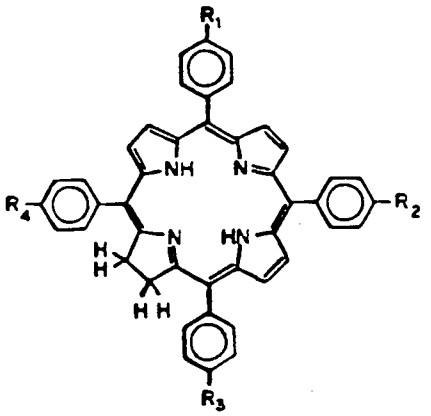
λmax, nm	356	378	520	742
$\varepsilon \times 10^{-3}$	130	160	60	120

NMR Data ($CDCl_3$)

Delta, ppm	# H	J, Hz
-1.30	2;pyrrole N-H (s)	
3.92	8;$-CH_2CH_2-$(s)	
7.52	20;ArH (m)	
7.85	4;β-pyrrole (d)	2.0

Synthesis of *meso*-Tetraphenylchlorin

(Compound IXb)



R_1-R_4=H

meso-Tetraphenylbacteriochlorin, 400 mg (0.65 mmoles), and 147 mg (0.65 mmoles) 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) were stirred together in 300 ml of benzene at room temperature for one hour. The benzene solution was then washed with 5% aqueous sodium bisulphite solution, 5% aqueous sodium hydroxide solution, saturated aqueous sodium bicarbonate solution, water, and was dried over anhydrous sodium sulphate. Removal of solvent gave 350 mg of a residue that was recrystallised from 30 ml of deoxygenated benzene to afford 310 mg (78% yield) of tetraphenylchlorin.

Absorption Characteristics of TPC (Monomer)

λmax, nm	418	518	542	598	651
Ratios	30	2.2	1.6	1.0	4.6

Conc. 4.9×10^{-5} M.

Lit.[82] (Benzene)

λmax, nm	419	517	541	598	652
$\varepsilon \times 10^{-3}$	190	16	12	6.1	42

NMR Data ($CDCl_3$)

Delta, ppm	# H
-1.30	2;pyrrole N-H (s)
4.10	4;$-CH_2CH_2-$(s)
7.6-8.5	26;ArH, β-pyrrole (m)

The band (δ=7.6 - 8.5 p.p.m.) could be resolved into a singlet, area 2H at δ 8.34 p.p.m. and AB quartet of area 4H (δ_A 8.10, δ_B 8.49, J_{AB}=4.5 Hz) assigned to the chlorin ring protons.

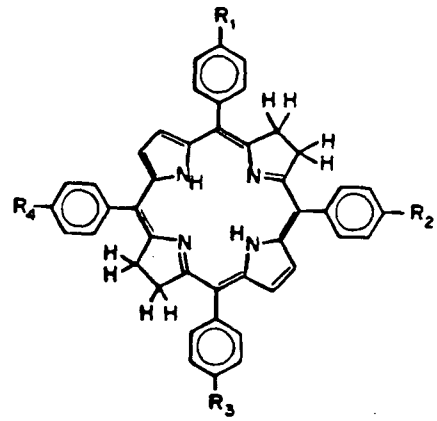
Alternative Synthesis of *meso*-Tetraphenylchlorin

meso-Tetraphenylbacteriochlorin 400 mg, (0.65 mmole) was chromatographed on a 60 x 5 cm column of alumina using dichloromethane as the eluant. The bacteriochlorin moved down the column slowly and was being oxidized to the chlorin (green colouration on the column). The chlorin was then eluted from the column using 20:1 methylene chloride-methanol. A visible spectrum of the eluate indicated that all the bacteriochlorin had been oxidized to the chlorin (no 742 nm band). The solvent was then removed and the residue recrystallised from 25 ml of

deoxygenated benzene to afford 290 mg (73% yield) tetraphenylchlorin. The absorption spectrum in methylene chloride was identical to that already reported.

Synthesis of 5-[4-(6-Hydroxy-1-hexoxy)phenyl]-10,15,20-tritolylbacteriochlorin (M.W. 777)

(Compound Xa)



R_1-R_3=-CH_3, R_4=-O-$(CH_2)_6$-OH

5-[4-(6-Hydroxy-1-hexoxy)phenyl]-10,15,20-tritolylporphyrin (500mg, 0.65 mmole) was reduced to the corresponding bacteriochlorin using *p*-toluenesulfonyhydrazine in a procedure similar to that already described for the preparation of *meso*-tetraphenylbacteriochlorin.

This bacteriochlorin was recrystallised from deoxygenated toluene to yield 376 mg (75% yield) of reddish-purple shiny crystals.

NMR Data ($CDCl_3$)

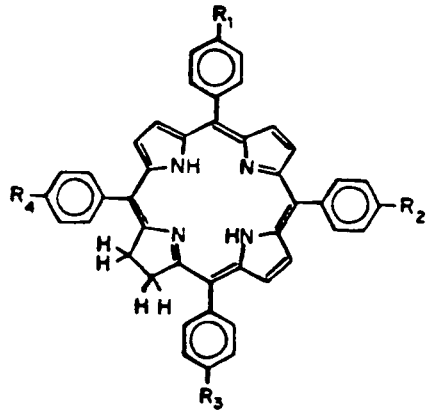
Delta, ppm	# H
-1.31	2;pyrrole N-H (s)
1.53	8;hexyl-2,3,4,5-(m)
2.68	9;tolyl (methyl) (2s)
3.72	2;α-hydroxy-(t)
4.14	2;α-phenoxy-(t)
4.30	8;-CH_2-CH_2-(s)
7.51	8;tolyl-3,5-(m)
8.10	8;tolyl-2,6-(m)
8.55	4;β-pyrrole (s)

Mass Spectral Data

M/e	I		M/e	I
843	9		655	12
842	10		605	13
841	10		555	10
840	14		505	13
839	13		455	17
838	15	(P+Cu)	405	16
837	21		391	11
836	6		386	9
777	5	(parent)	385	10
774	63		381	19
773	100		343	25
772	12		331	27
755	16			
754	17			
743	13			
672	20			

Synthesis of 5-[4-(6-Hydroxy-1-hexoxy)phenyl]-10,15,20-tritolylchlorin (M.W. 775)

(Compound Xb)



R_1-R_3=-CH_3, R_4=-O-$(CH_2)_6$-OH

5-[4-(6-Hydroxy-1-hexoxy)phenyl]-10,15,20-tritolylbacteriochlorin (300 mg, 0.38 mmole) was oxidized to the chlorin using 86 mg (0.38 mmole) of DDQ following a procedure similar to that already described for the preparation of *meso*-tetraphenylchlorin. This chlorin was recrystallised from deoxygenated toluene to afford 193 mg (64% yield) of shiny purplish crystals.

When dissolved in methylene chloride this chlorin was green. Tlc on silica gel plates using methylene chloride as eluant showed two spots (R_f values 0.12 and 0.15) corresponding to the two isomers possible for this chlorin. It was not possible to separate the two isomers on a chromatographic column (alumina or silica gel), due to the oxidation of the chlorins on chromatographic columns.

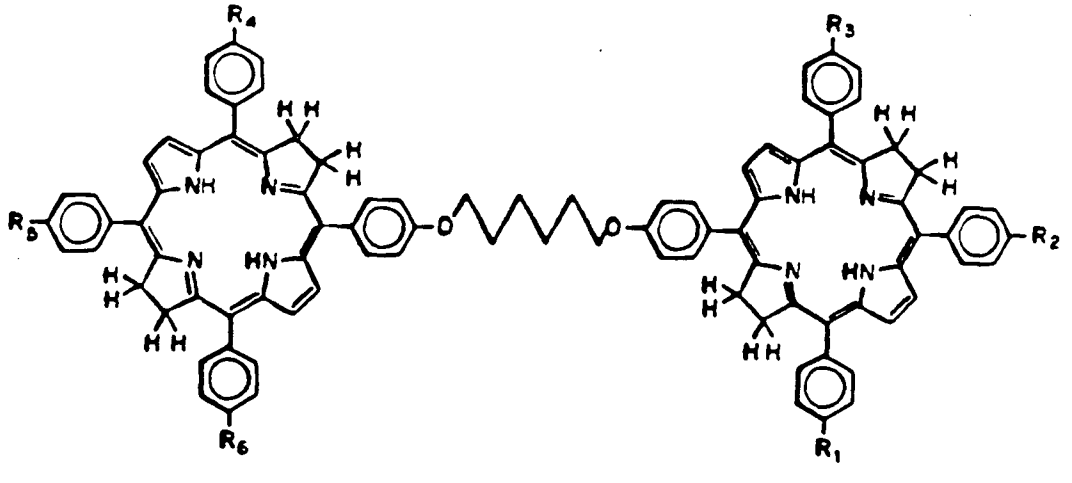
NMR Data $CDCl_3$)

Delta, ppm	# H
-1.32,-1.41	2;pyrrole N-H (2s)
1.56	8;hexyl-2,3,4,5-(m)
2.59	9;tolyl(methyl) (3s)
3.68	2;α-hydroxy-(t)
3.95	2;α-phenoxy-(t)
4.12	4;$-CH_2CH_2-$(s)
7.45-7.64	8;tolyl-3,5-(m)
7.98-8.18	8;tolyl-2,6-(m)
8.43-8.56	6;β-pyrrole (3s)

Dimeric bacteriochlorins, and chlorins were all synthesized in the same manner as the monomeric bacteriochlorins and chlorins. The reducing agent was *p*-toluenesulfonylhydrazine and the oxidizing agent was 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).

Synthesis of 5,10,15-Tri-*p*-tolyl-20-[4-[6-[*p*-(10,15,20-tri-*p*-tolyl-5-bacteriochlorinyl)phenoxy]hexoxy]phenyl]bacteriochlorin (M.W. 1436)

(Compound XIa)



R_1-R_6=$-CH_3$

Recrystallised from deoxygenated toluene-hexane, and dried *in vacuo* at 120°C for 12 hours. Yield 246 mg (65%).

NMR Data ($CDCl_3$)

Delta, ppm	# H
-1.32	4;pyrrole N-H (s)
1.73-2.02	8;hexyl-2,3,4,5-(m)
2.57,2.63	18;tolyl(methyl) (2s)
3.27	4;-O-CH_2-(bt)
4.08-4.16	16;bact.-CH_2-CH_2-(bs)
7.43	16;tolyl-3,5-(m)
7.68-7.94	16;tolyl-2,6-(m)
8.44-8.58	8;β-pyrrole (bs)

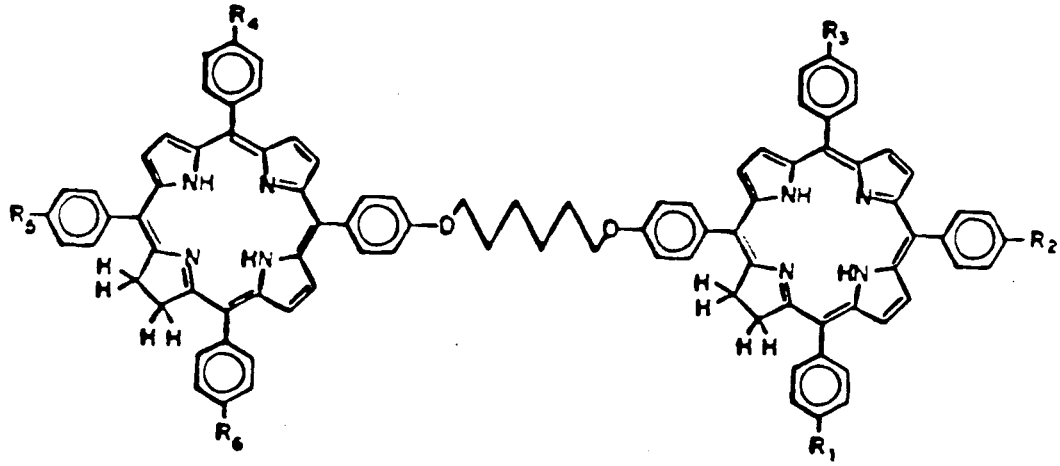
Empirical formula: $C_{100}H_{90}N_8O_2$

M.W. = 1435.88

	Calc.	Found	Difference
C	83.65	83.85	+0.20
H	6.32	6.19	-0.13
N	7.80	7.86	+0.06
O	2.23	-	-

Synthesis of 5,10,15-Tri-*p*-tolyl-20-[4-[6-[*p*-(10,15,20-tri-*p*-tolyl-5-chlorinyl)phenoxy]hexoxy]phenyl]chlorin (M.W. 1432)

(Compound XIb)



R_1-R_6=-CH_3

5,10,15-Tri-*p*-tolyl-20-[4-[6-[*p*-(10,15,20-tri-*p*-tolyl-5-bacteriochlorinyl)phenoxy]hexoxy]phenyl]bacteriochlorin, 200 mg (0.14 mmole) was oxidized using 31 mg (0.14 mmole) of DDQ following the standard procedure. The yield of the chlorin dimer after recrystallisation from deoxygenated toluene-hexane was 121 mg (60%).

When dissolved in methylene chloride this chlorin was greenish. Tlc on silica gel plates with methylene chloride as the eluant showed three spots of approximately equal intensity (R_f values 0.45, 0.55 and 0.75) corresponding to the three possible isomers. The isomers were not separable on any chromatographic column (alumina or silica gel). The absorption spectrum of this mixture of chlorins showed the complete absence of any bacteriochlorin. As expected, the proton magnetic resonance spectrum was complex.

NMR Data ($CDCl_3$)

Delta, ppm	# H
-1.41,-1.76	4;pyrrole N-H (2s)
2.03,2.37	8;hexyl-2,3,4,5-(bm)
2.60	18;methyl (3s)
4.13	8;chlorin-CH_2-CH_2-(2s)
4.40	4;-CH_2-O-(bt)
7.46-7.70	16;tolyl-3,5-(bm)
7.97-8.54	16;tolyl-2,6-(bm)
8.65-8.86	12;β-pyrrole (bs)

Empirical formula: $C_{100}H_{86}N_8O_2$

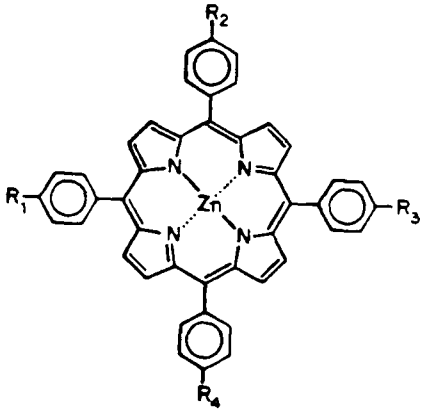
M.W. = 1431.85

	Calc.	Found	Difference
C	83.89	83.70	-0.19
H	6.05	5.98	-0.07
N	7.83	7.99	+0.16
O	2.23	-	-

PART (C) - ZINC METALLO-DERIVATIVES OF THE *MESO*-TETRAPHENYLPORPHYRINS, CHLORINS AND BACTERIOCHLORINS (MONOMERS AND DIMERS)

Synthesis of Zinc *meso*-Tetraphenylporphin (ZnTPP)

(Compound XIIa)



R_1-R_4=H

A mixture of 0.6g (0.98 mmole) of TPP, and 0.6g (2.7 mmole) zinc acetate dihydrate was boiled gently in 75ml of dry pyridine. After conversion to the zinc metalloporphine was complete (approximately 15 minutes), as indicated by the absence of free base absorption bands in the visible spectrum, the solution was transferred to a separatory funnel with 80ml of benzene. Water was added to the separatory funnel, and the resulting benzene layer was washed several times with water to completely remove the pyridine and inorganic salts. A final wash with 1M ammonium chloride was necessary to break the emulsions. The benzene layer was dried over anhydrous sodium sulphate. The resulting benzene solution was

evaporated to dryness under vacuum to yield the solid metalloporphine. Recrystallisation of the of the solid was accomplished by slowly adding methanol to a concentrated methylene chloride solution of the metalloporphine. Purple, shiny crystals of ZnTPP were obtained. Yield 490 mg (74%).

Absorption Characteristics of ZnTPP (Monomer)

λmax, nm	418	548	587	
Ratios	146	5.5	1.0	Conc. 2.8×10^{-5} M.
Lit.[118] (Benzene)				
λmax, nm	419	550	587	
$\varepsilon \times 10^{-3}$	590	23	3.5	

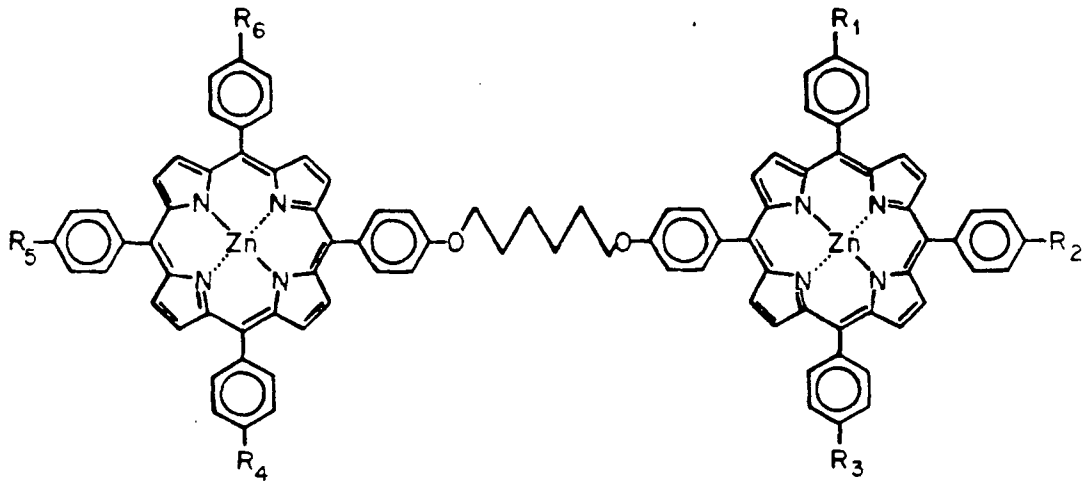
Empirical formula: $C_{44}N_4H_{28}Zn$

M.W. = 678.11

	Calc.	Found	Difference
C	77.94	77.80	-0.14
H	4.16	4.39	+0.23
N	8.26	8.39	+0.13
Zn	9.64	-	-

Synthesis of Zinc Tetraphenylporphin Dimer (M.W. 1470.4)

(Compound XIIb)



R_1-R_6=H

The compound was synthesized as described above for zinc *meso*-tetraphenylporphin. 15 mg (0.01 mmole) of the free base porphyrin dimer (Compound VIIIb) was used initially. Purple, shiny crystals of the zinc porphine cimer were obtained. Yield 10 mg (61%).

Absorption Characteristics of ZnTPP (Dimer)

λmax, nm	419	547	586
Ratios	141	5.2	1.0

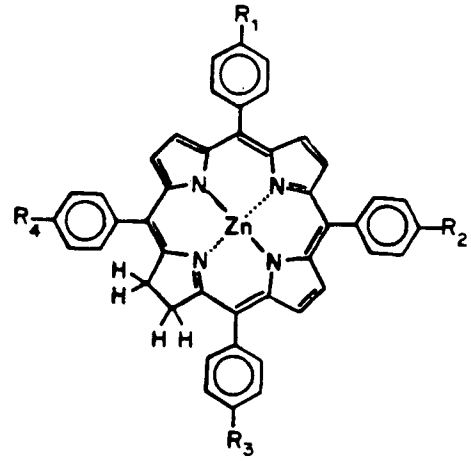
Conc. 3.6×10^{-5} M.

Mass Spectral Data

M/e	I		M/e	I
1476	9		1352	17
1475	11		1060	36
1474	12		793	18
1473	14		735	4
1472	14		694	81
1471	9	(parent)	488	76
1411	15		310	96
1410	8		221	100

Synthesis of Zinc *meso*-Tetraphenylchlorin (ZnTPC)

(Compound XIIIa)[119]



R_1-R_4=H

A mixture of *meso*-tetraphenylchlorin (TPC), 240 mg (0.39 mmole), and 240 mg (1.1 mmole) zinc acetate dihydrate was boiled gently, with stirring under nitrogen, in complete darkness, in 35 ml of dry pyridine. After conversion

to the zinc metallochlorin was complete (approximately 25 minutes), as indicated by the absence of free base absorption bands in the visible spectrum, the solution was transferred to a separatory funnel with about 40 ml of deoxygenated benzene. (Solvent deoxygenation was effected by bubbling nitrogen through the solvent for at least 30 minutes). Water was added to the separatory funnel, and the resulting benzene layer was washed several times with water to completely remove the pyridine and inorganic salts. A final wash with 1M ammonium chloride was necessary to break emulsions. The benzene layer was dried over anhydrous sodium sulphate. The resulting benzene solution was evaporated to dryness under vacuum to yield the solid metallochlorin. The solid was recrystallised from deoxygenated benzene. The yield of the ZnTPC was 226 mg (85%).

Absorption Characteristics of ZnTPC (Monomer)

λmax, nm	424	521	569	593	628
Ratios	540	1.0	1.1	1.8	9.3
		Conc. 2.9×10^{-5} M.			
Lit.[119] (Benzene)					
λmax, nm	422	522	568	590	630
$\varepsilon \times 10^{-3}$	326	6.1	6.9	10.5	57.0

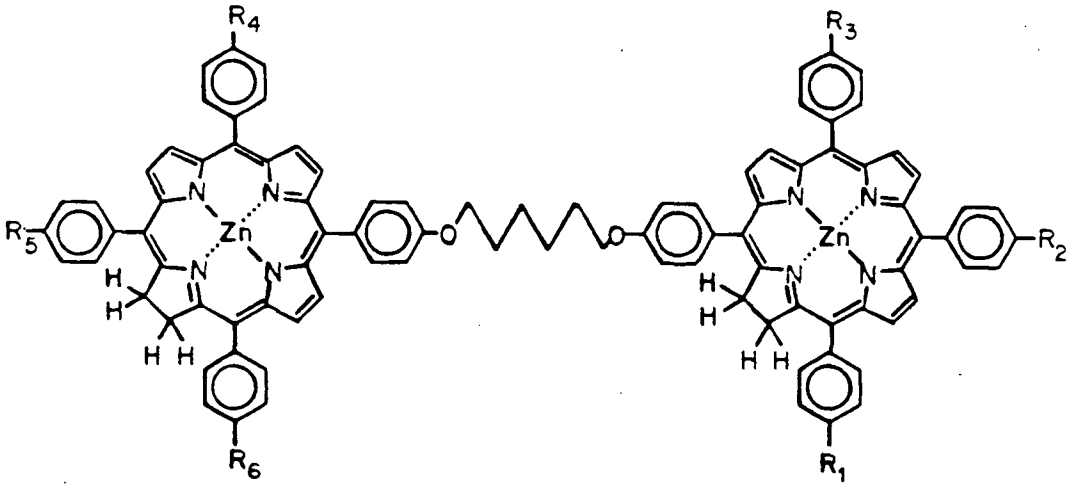
Empirical formula: $C_{44}N_4H_{30}Zn$

M.W. = 680.13

	Calc.	Found	Difference
C	77.70	77.46	-0.24
H	4.45	4.60	+0.15
N	8.24	8.29	+0.05
Zn	9.61	-	-

Synthesis of Zinc Tetraphenylchlorin Dimer (M.W. 1474.4)

(Compound XIIIb)



R_1-R_6=H

The free base chlorin dimer, 5,10,15-triphenyl-20-[4-[6-(10,15,20-triphenyl-5-chlorinyl)phenoxy]hexoxy]phenyl] chlorin, was prepared as described for its tolyl analogue (Compound XIb). The zinc (II) complex was prepared using the standard procedure[119]. The yield was 23 mg (72%) (based on the free base chlorin dimer). No attempt was made to separate the three (zinc tetraphenylchlorin dimer) isomers. Tlc on silica gel plates, using methylene chloride as the eluant, showed 3 green spots (R_f values 0.59,

0.71 and 0.81).

Absorption Characteristics of Zinc TPC (Dimer)

λmax, nm	423	522	569	595	628
Ratios	51.9	1.0	1.2	2.0	9.5

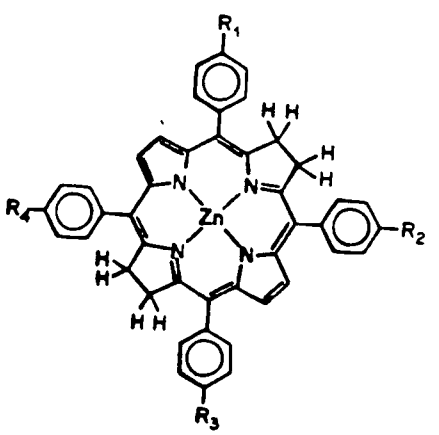
Conc. 5.6×10^{-5} M.

Mass Spectral Data

M/e	I	M/e	I	
1476	10	1061	36	
1475	11	1060	32	
1474	13 (parent)	793	44	
1473	14	792	36	
1472	13	737	6	(m/2e)
1471	10	694	78	
1353	18	488	76	
1352	17	310	98	
1351	8	221	100	

Synthesis of Zinc *meso*-Tetraphenylbacteriochlorin (ZnTPBC)

(Compound XIVa)



R_1-R_4=H

A mixture of *meso*-tetraphenylbacteriochlorin (TPBC),° 60 mg (0.097 mmole), and 60 mg (0.28 mmole) zinc acetate dihydrate, was boiled gently, with stirring under nitrogen, in complete darkness in 20 ml of dry pyridine. The complete conversion to the zinc metallobacteriochlorin took about 30 minutes. The work-up procedure was essentially the same as that described for ZnTPC.

The crude ZnTPBC mixture showed two spots on tlc, using benzene as eluant. The more intense spot moving with the solvent front was that due to ZnTPBC. The less intense green spot (R_f value 0.87) was due to ZnTPC.

The ZnTPBC mixture was quickly chromatographed on a 10 x 5 cm alumina chromatographic column using benzene as eluant. The major band which moved with the solvent front was collected and evaporated. The zinc metallobacteriochlorin solid was recrystallised from deoxygenated benzene to yield 56 mg (85%) of shiny purplish-red crystals.

Absorption Characteristics of Zinc TPBC (Monomer)

λmax, nm	357	378	523	741
Ratios	2.2	5.1	1.0	2.1

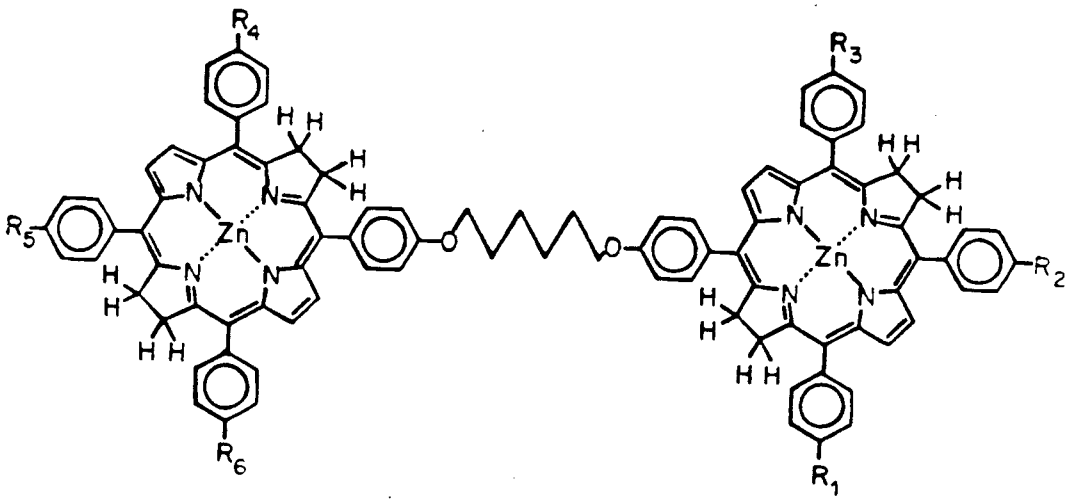
Conc. 1.5×10^{-4} M.

NMR Data ($CDCl_3$)

Delta, ppm	# H	J, Hz
4.12	8;$-CH_2CH_2-$(s)	
7.54	12;phenyl-3,4,5-(m)	
7.86	8;phenyl-2,6-(m)	
8.49	4;β-pyrrole (d)	2.0

Synthesis of Zinc Tetraphenylbacteriochlorin Dimer (M.W. 1478.4)

(Compound XIVb)



R_1-R_6=H

The free base bacteriochlorin dimer, 5,10,15-triphenyl-20-[4-[6-(10,15,20-triphenyl-5-bacteriochlorinyl)-phenoxy]hexoxy]phenyl]bacteriochlorin was prepared as described for its tolyl analogue (Compound XIa). The zinc (II) complex was prepared following the procedure described for the preparation of ZnTPBC. The yield was 47 mg (70%) (based on the free base bacteriochlorin dimer).

Absorption Characteristics of Zinc TPBC (Dimer)

λmax, nm	356	378	522	741
Ratios	2.3	5.2	1.0	2.0

Conc. 1.3×10^{-4} M.

Mass Spectral Data

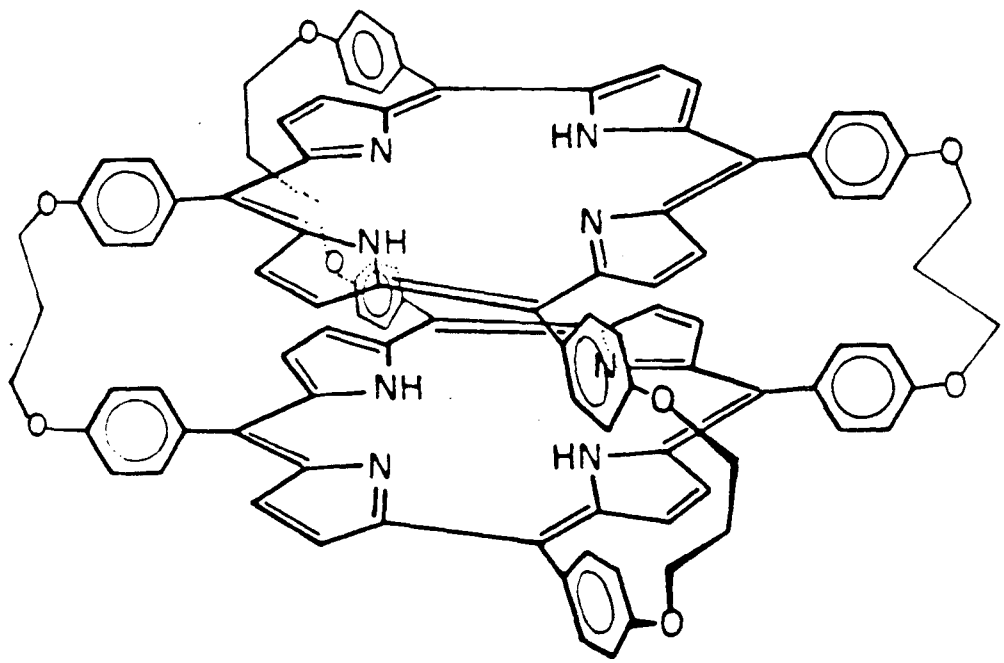
M/e	I	M/e	I
1478	5 (parent)	1060	42
1477	7	793	32
1476	9	739	36 (m/2e)
1475	13	694	76
1474	17	489	79
1354	10	488	68
1061	41	310	100

PART (D) - ATTEMPTED SYNTHESIS OF TETRA-*MESO*-[p,p'-(3,3'-PHENOXYPROPOXYPHENYL)]-*STRATI-BIS*PORPHYRIN

Molecular formula = $C_{100}H_{76}N_8O_8$

(Compound XX)

In a recent paper[53], Kagan *et al.* reported the synthesis of a novel *strati-bis*porphyrin. We set out to synthesize a very similar *strati-bis*porphyrin.



(Compound XX)

Synthesis of *p*-3-Bromopropoxybenzaldehyde

(Compound XV)

A mixture of *p*-hydroxybenzaldehyde, 27.7g (0.23 moles), 5.0g of anhydrous potassium carbonate and 68.8g (0.34 moles) of 1,3-dibromopropane was stirred in a mini-

mum volume (about 20 ml) of reagent grade acetone, at room temperature for 48 hours. The reaction mixture was poured into a 1 litre separatory funnel and 400 ml of methylene chloride added. The mixture was extracted twice with a total of 500 ml of 5% aqueous sodium hydroxide to remove unreacted hydroxybenzaldehyde. The methylene chloride extract was washed twice with water and dried over anhydrous sodium sulphate. The solvents were removed using a vacuum pump at 65°C, to leave behind a yellowish oil. 1,3-Dibromopropane is fairly volatile and was thus removed with the aid of a vacuum pump. The yellowish oil was then dried at 60° *in vacuo*. The yield was 28.1g (51%) of *p*-3-bromopropoxybenzaldehyde.

NMR Data ($CDCl_3$)

Delta, ppm	# H	J, Hz
2.35	2;propyl-2 (tt)	
3.62	2;-CH_2-Br (t)	
4.21	2;-CH_2-O-(t)	
7.03	2;phenoxy-2,6-(d)	8.6
7.85	2;phenoxy-3,5-(d)	8.6
9.89	1;formyl (s)	

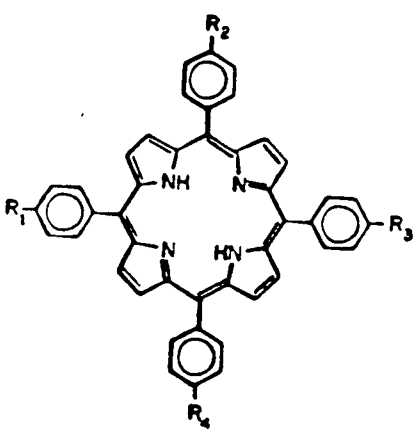
Mass Spectral Data

M/e	I	M/e	I
246	3	122	21
245	9	121	38
244	16	120	6
243	7 (parent)	105	7
242	18	94	6
241	5	93	10
165	2	41	18
164	3	38	13
163	6	32	29
162	10	28	100
161	5		
123	12		

Synthesis of 5,10,15,20-Tetra-[p-(3-bromopropoxy)phenyl]porphyrin

(M.W. 1162.7)

(Compound XVI)



R_1-R_4=-O-$CH_2CH_2CH_2$-Br

p-3-Bromopropoxybenzaldehyde (18.5g, 0.076 mole) and 5.2g (0.077 mole) of pyrrole were added to 270 ml of propionic acid that was near boiling temperature. The reaction was refluxed for one hour and then taken to dryness under vacuum by means of a rotary evaporator. The resulting black tar was washed briefly with water, and then with dilute ammonium hydroxide. The slightly wet material was triturated with a minimum amount of methanol on a steam bath until the purple crystals of the porphyrin were free from tar. The slurry was then stored overnight in a freezer at -5°C. The purple solid was filtered off and washed with a minimal amount of methanol and then dried.

The material was dissolved in 300 ml of methylene chloride and chromatographed on a 60 x 5 cm column of alumina using methylene chloride as the eluant. The porphyrin band moved with the solvent front while a brown impurity stuck on top of the column. The porphyrin was recrystallised from methylene chloride-methanol to yield 1.4g (6.3%) of shiny purple needle-like crystals.

NMR Data ($CDCl_3$)

Delta, ppm	# H	J, Hz
-2.50	2;pyrrole N-H (s)	
2.74	8;propyl-2-(tt)	
4.01	8;-CH_2-Br (t)	
4.61	8;-CH_2-O-(t)	
7.50	8;phenoxy-2,6-(d)	2.9
8.35	8;phenoxy-3,5-(d)	2.9
9.10	8;β-pyrrole (s)	

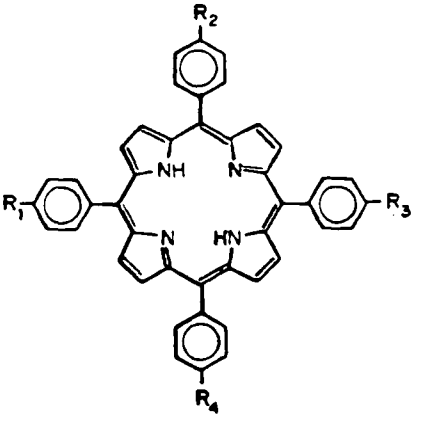
Mass Spectral Data

M/e	I	M/e	I
1224	4	169	27
1223	5(P+Cu)	168	35
1222	6	167	31
1221	5	149	79
1162	15 (parent)	141	27
1161	18	121	33
1080	22	107	65
1067	38	94	76
1065	36	91	63
854	9	80	99
800	13	49	87
743	15	44	100
581	29		
213	31		
212	34		
173	24		
172	41		

A method was worked out for synthesizing 5,10,15,20-tetra-[*p*-(3-bromopropoxy)phenyl]porphyrin starting from 5,10,15,20-tetra-(4-hydroxyphenyl)porphyrin. The procedure is as described below.

Synthesis of 5,10,15,20-Tetra-(4-propionylphenyl)porphyrin (M.W. = 903.1)

(Compound XVII)



R_1-R_4=-O_2C-CH_2CH_3

para-Hydroxybenzaldehyde (17.1g, 0.14 mole) was added to a mixture of 100 ml of propionic anhydride and 350 ml of propionic acid; and the mixture was refluxed. Pyrrole (9.4g, 0.14 mole) was then added. The reaction mixture was refluxed for one hour and then stood overnight at -5°C. The crude porphyrin (purple needles) was filtered off and repeatedly washed with cold ethanol. The yield was 6.7g (21.2%).

NMR Data ($CDCl_3$)

Delta, ppm	# H	J, Hz
1.41	12;β-propionyl (t)	7.1
2.79	8;α-propionyl (q)	7.1
7.51	8;phenoxy-2,6-(d)	8.2
8.22	8;phenoxy-3,5-(d)	8.2
8.88	8;β-pyrrole (s)	

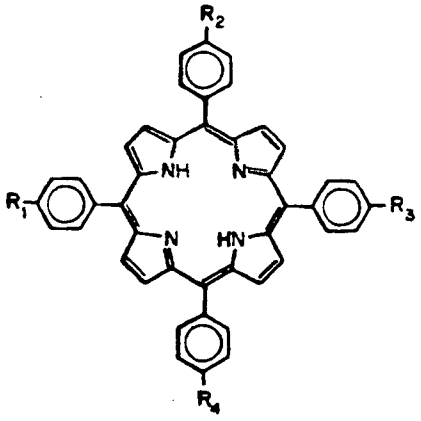
Mass Spectral Data

M/e	I	M/e	I
906	6	649	11
905	10	575	12
904	14	465	2
903	18 (parent)	464	3
902	25	463	2
889	2	462	3
849	10	452	11
791	29	169	19
733	29	149	55
681	11	74	100

Synthesis of 5,10,15,20-Tetra-(4-hydroxyphenyl)porphyrin[116]

(M.W. 678.8)

(Compound XVIII)



R_1-R_4=-OH

5,10,15,20-Tetra-(4-propionylphenyl)porphyrin (6.5g, 7.1 mmoles) was refluxed for 20 hours in 95% ethanol containing 4 g of potassium hydroxide. The resulting green solution was filtered, acidified with acetic acid, and then taken to dryness, yielding an amorphous purple solid which was very soluble in ethanol and aqueous alkaline solution. The solid was taken up in methylene chloride, filtered and evaporated to dryness. It was recrystallised from ethanol-water with a yield of 3.47g (71%).

Empirical formula: $C_{44}N_4H_{30}O_4$

M.W. = 678.75

	Calc.	Found	Difference
C	77.86	78.01	+0.15
H	4.46	4.41	-0.05
N	8.25	8.09	-0.16
O	9.43	-	-

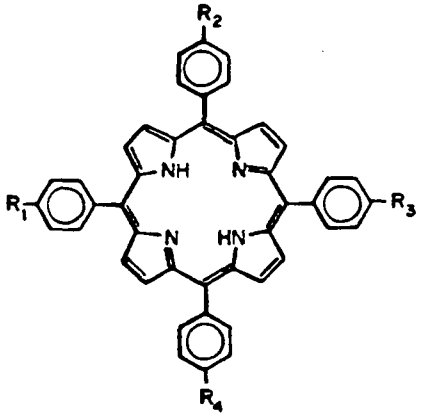
Synthesis of 5,10,15,20-Tetra-[*p*-(3-bromopropoxy)phenyl]porphyrin

(Compound XVI)

5,10,15,20-Tetra-(4-hydroxyphenyl)porphyrin (3.0g, 4.4 mmoles) was stirred in 35 ml of DMF with 1.8g of crushed sodium hydroxide. 1,3-Dibromopropane (17.8g, 88 mmoles) was then added quickly and the reaction mixture stirred for 36 hours at room temperature. Ethanol (50 ml) was added to the green solution followed by 600 ml of water. The purple product was filtered off and washed with absolute ethanol and then dried. It was chromatographed on alumina with methylene chloride as the eluant. The porphyrin moved with the solvent front and separated easily from any unreacted starting material and from two slowly moving green and brown bands near the top of the column. After recrystallisation from methylene chloride-ethanol a very small crop of shiny purple crystals was obtained. Yield 87.4 mg (1.7%). The nmr spectrum was identical to that already reported.

Synthesis of 5,10,15,20-Tetra-[(*p*'-formyl-3-phenoxy-*p*-propoxy)-phenyl]porphyrin (M.W. = 1327.6)

(Compound XIX)



R_1-R_4=-O-$CH_2CH_2CH_2$O-Ph-CHO, Ph=Phenyl

A mixture of 1.4g (1.2 mmoles) of 5,10,15,20-tetra-[*p*-(3-bromopropoxy)phenyl]porphyrin, 1.2g anhydrous potassium carbonate, 2.19g (24 mmoles) of *p*-hydroxybenzaldehyde were stirred for 48 hours in 15 ml of DMF at room temperature. The product was precipitated by pouring the reaction mixture into 100 ml of a 10% aqueous sodium hydroxide, and then heating the mixture to coagulate the porphyrin. The product was filtered off and washed thoroughly with water, then briefly with methanol. The porphyrin was recrystallised from methylene chloride-ethanol. Purple, shiny crystals of the porphyrin were obtained. The yield was 1.21g (76%).

NMR Data ($CDCl_3$/TFA)

Delta, ppm	# H	J, Hz
2.60	8;propyl-2-(tt)	
3.54	16;propyl-1,3-(m)	
7.23	8;β-phenoxy-3,5-(d)	8.6
7.62	8;α-phenoxy-3,5-(d)	7.9
8.04	8;β-phenoxy-2,6-(d)	8.6
8.50	8;α-phenoxy-2,6-(d)	7.9
8.62	8;β-pyrrole (s)	
9.76	4;formyl (s)	

The mass spectrum showed the molecular ion at m/e = 1328, and the doubly charged ion m/2e = 664 as expected.

Attempted Synthesis of Tetra-*meso*-[*p*,*p*'-(3,3'-phenoxypropoxyphenyl)]-*strati-bis*porphyrin.

(Compound XX)

5,10,15,20-Tetra-[(*p*'-formyl-3-phenoxy-*p*-propoxy)-phenyl]porphyrin 0.6g (0.45 mmoles) was refluxed in 1130 ml (0.4 mM concentration) of propionic acid-ethylbenzene (1:1). Pyrrole 0.12g (4 equivalents) was added, and the mixture refluxed for 1.5 hours. The solvent was removed under vacuum by means of a rotary evaporator. The methylene chloride-soluble products were collected. They could not be eluted off any chromatographic column (alumina or silica gel) using methylene chloride as the eluant. The *strati-bis*porphyrin could not be characterized.

We believe that attempts to synthesize the *strati-bis*porphyrin (with a 3-carbon linkage) were unsuccessful because of the steric strain arising from such a system. We postulate that such a system of co-axial porphyrin rings held together by peripheral linkages, (with 4 carbons or more), could be made. Molecular model studies confirmed this assertion.

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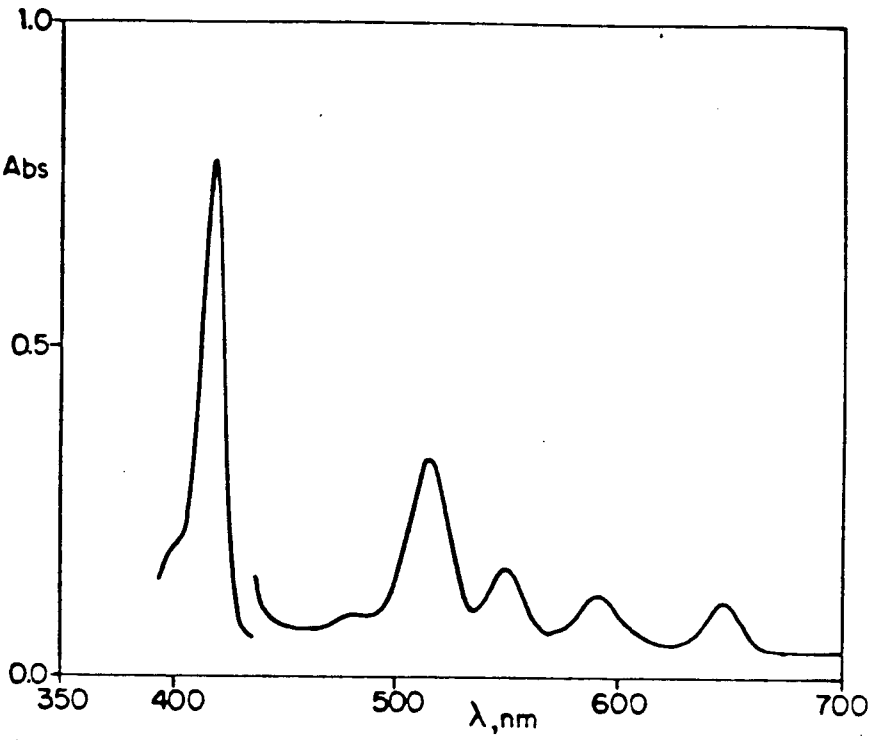
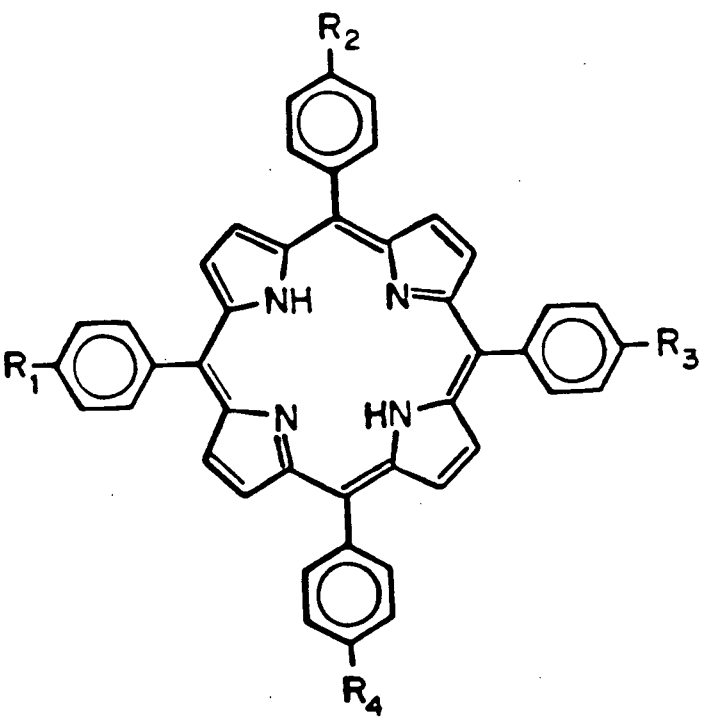
OPTICAL SPECTRAL APPENDIX

Absorption spectra of solutions of tetraarylporphin and tetraarylchlorin (monomers and dimers) were measured in the visible region (700-450 nm) in 10mm quartz cells, and in the 'Soret' region (450-350 nm) in 1mm quartz cells. The absorption spectra of solutions of tetraarylbacteriochlorin (monomers and dimers) were measured in 10mm quartz cells.

The structures of the compounds are as shown below each absorption spectrum. Unless otherwise specified, the groups R_1-R_4 = H (for the monomers) and the groups R_1-R_6 = H (for the dimers).





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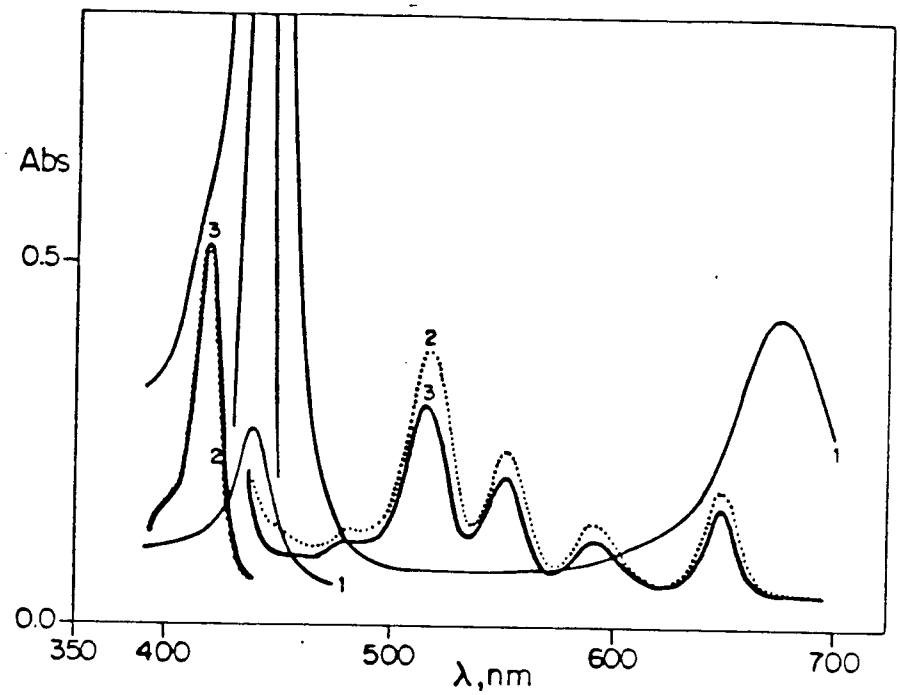
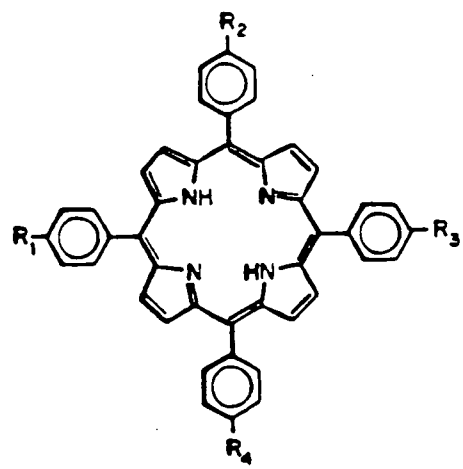


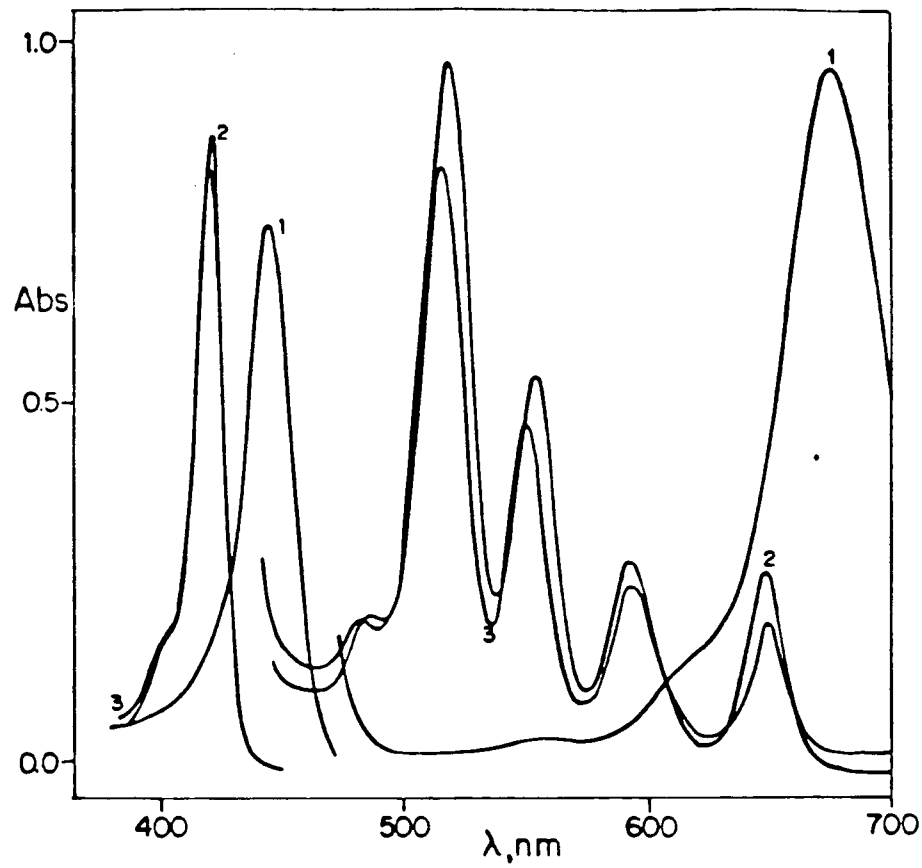


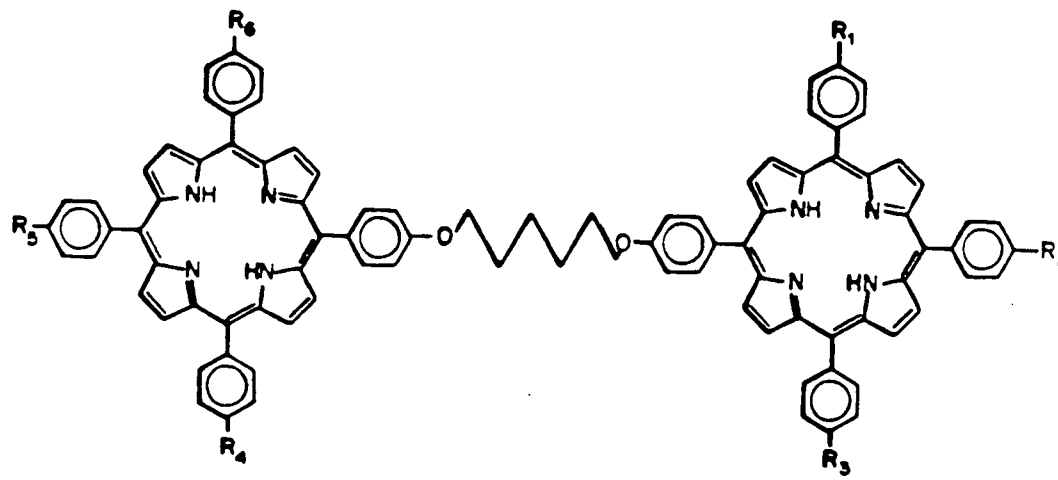
R_1-R_3=-CH_3, R_4=-O-$(CH_2)_6$-OH

Solvent 1 = Dichloromethane/TFA

Solvent 2 = DMF

Solvent 3 = Dichloromethane



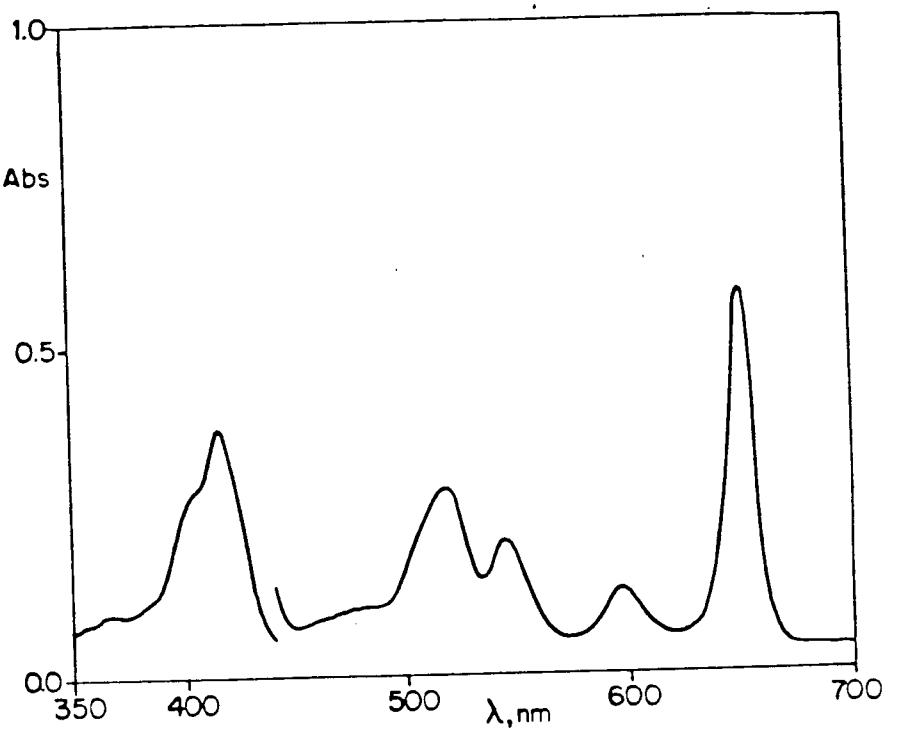


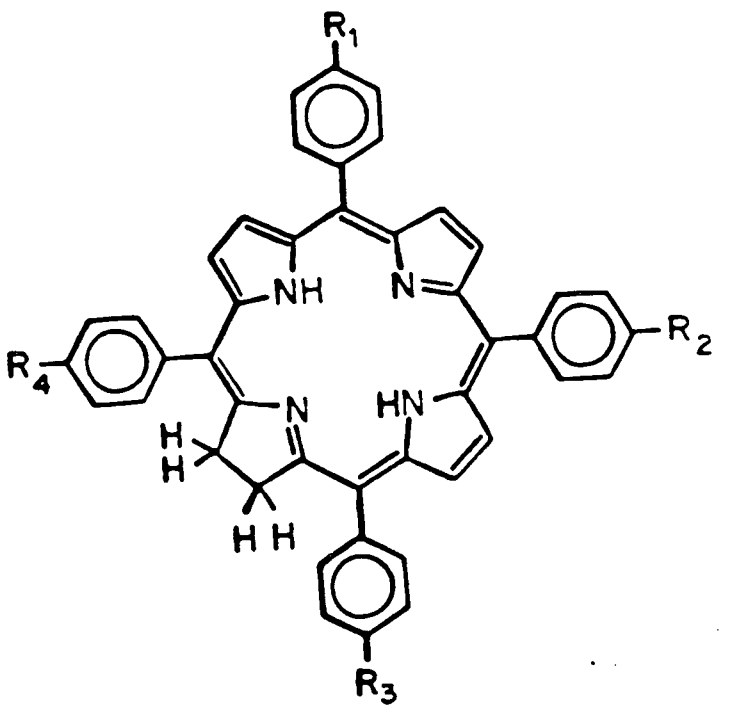
(TPP Dimer)

Solvent 1 = Dichloromethane/TFA

Solvent 2 = DMF

Solvent 3 = Dichloromethane





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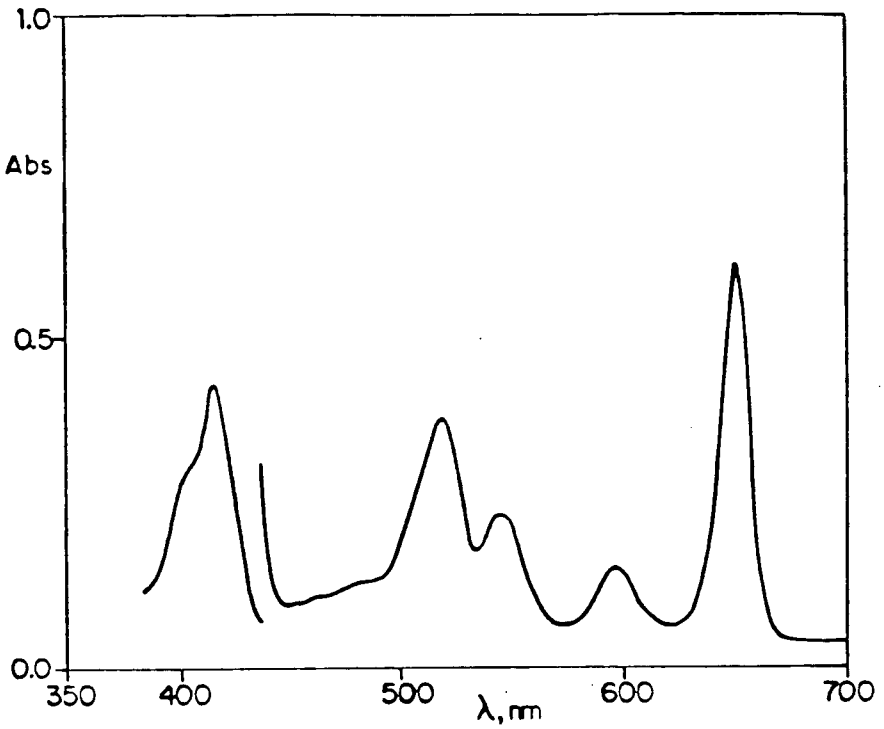
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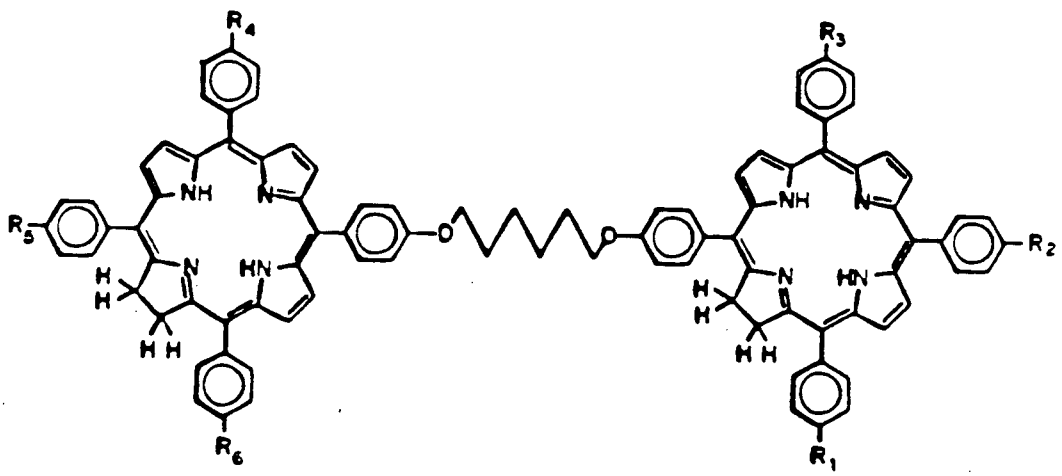
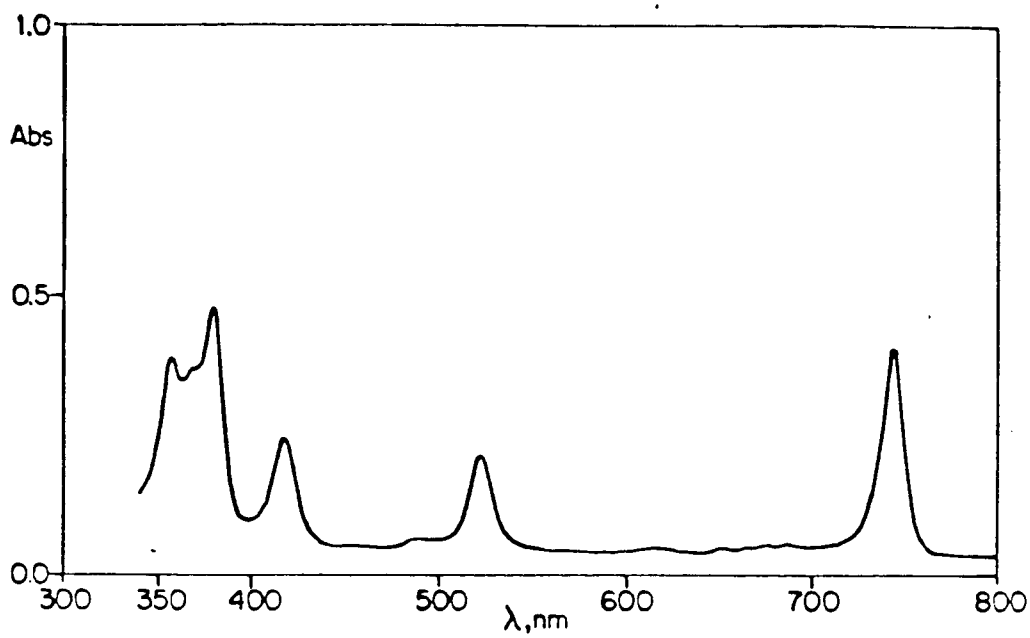
Abs
0.5
0.0
350
400
500
600
700
λ, nm


R4
R5
R6
R3
R2
R1
NH
N
HN
H
H
H H
O
O

(TPC Dimer)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Abs
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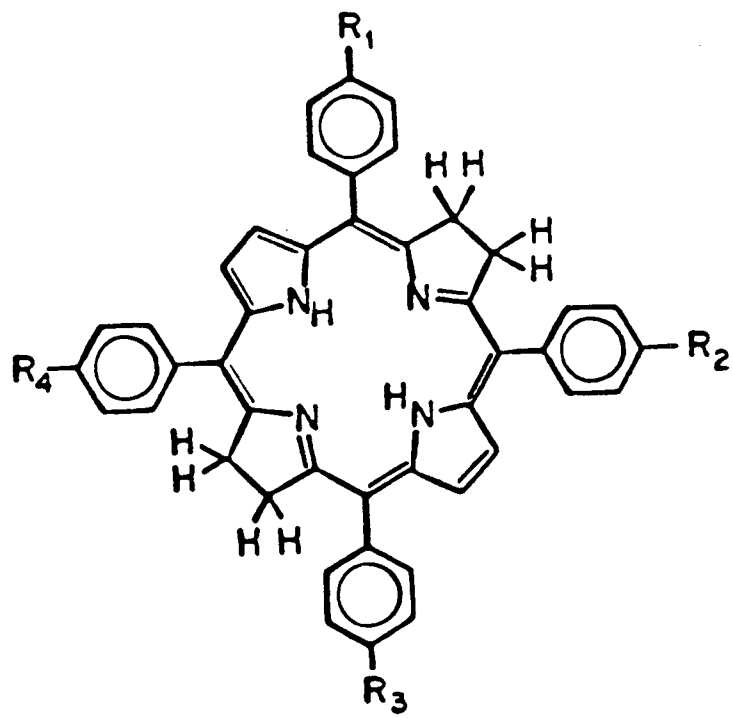
0.0
300
350
400
500
600
700
800
λ,nm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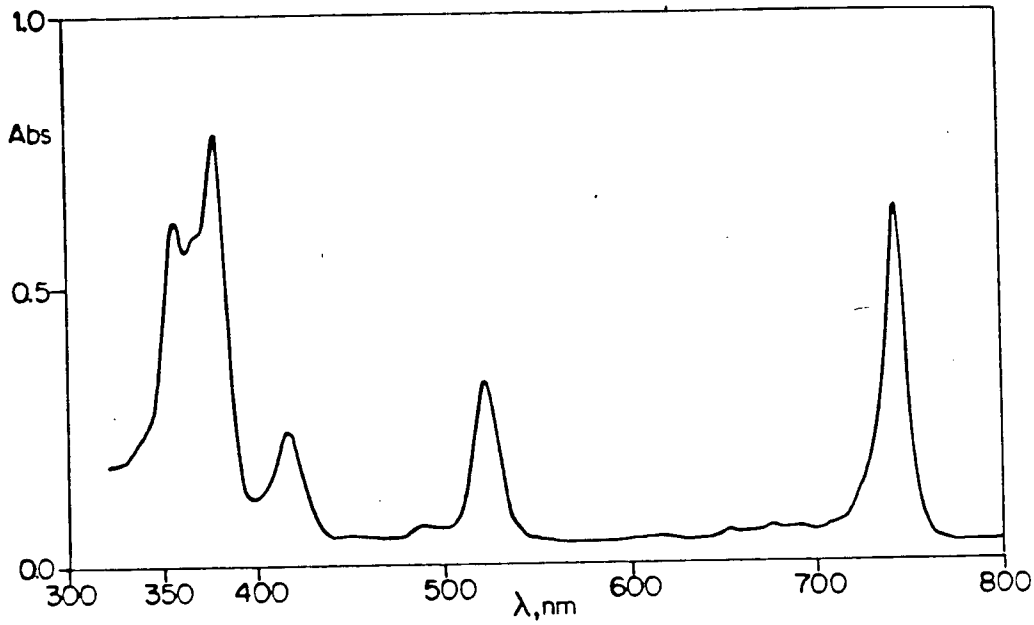
H H
H
H
NH
N
R4
R2
HN
N
H
H
H H
R3

(TPBC)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Abs
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0.0
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350
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600
700
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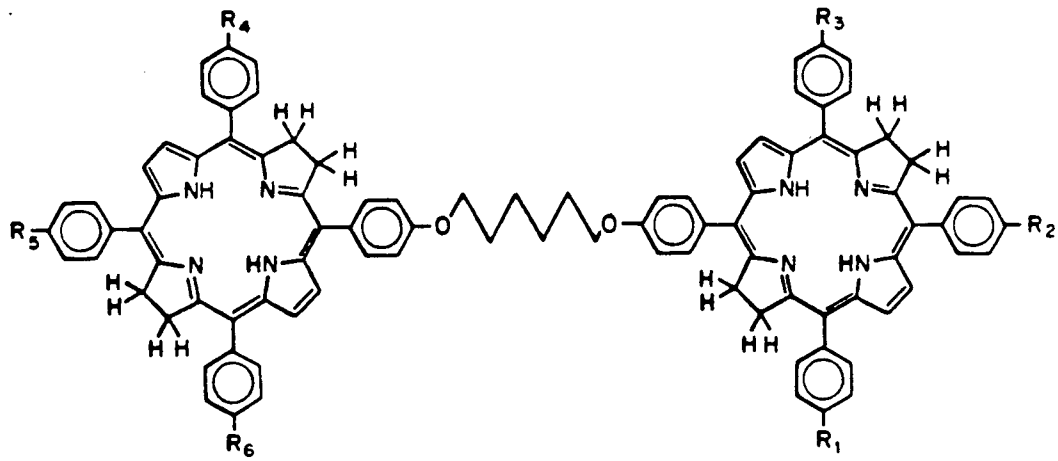
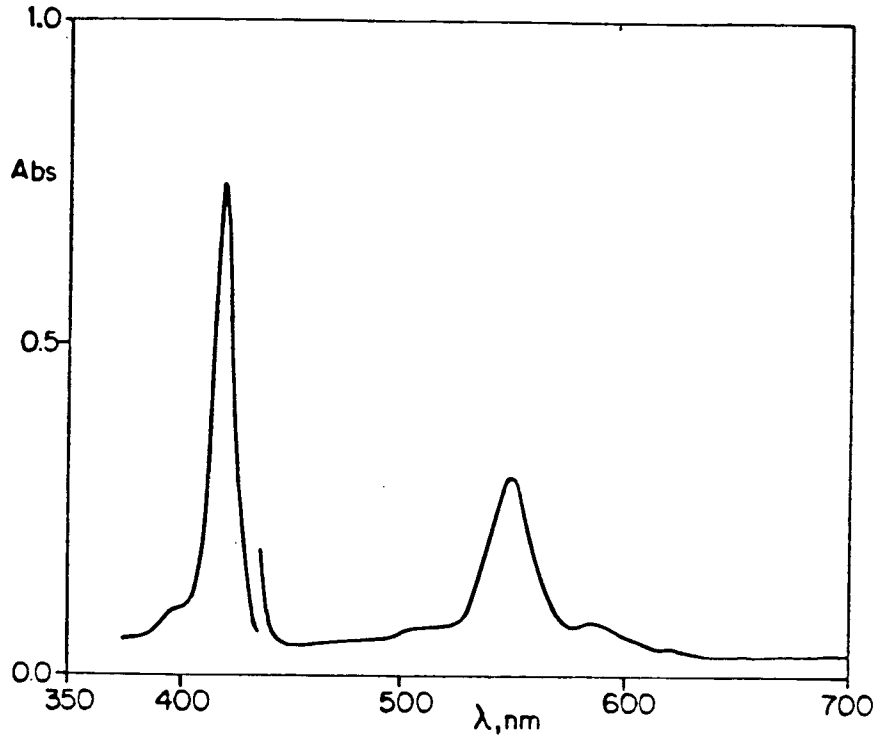
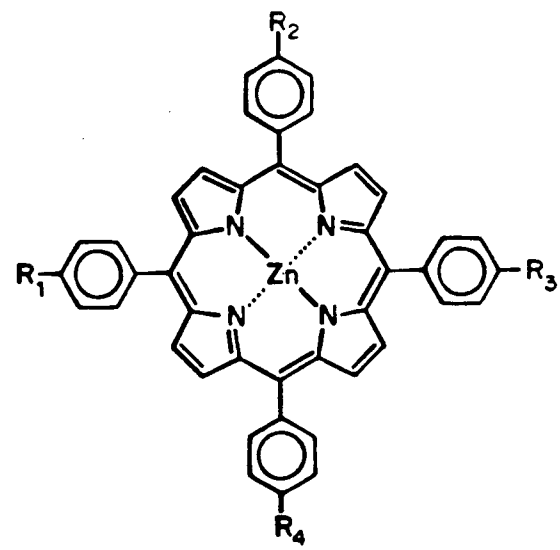
λ,nm


R4
R3
R5
R2
R6
R1
NH
N
HN
O
O

(TPBC Dimer)





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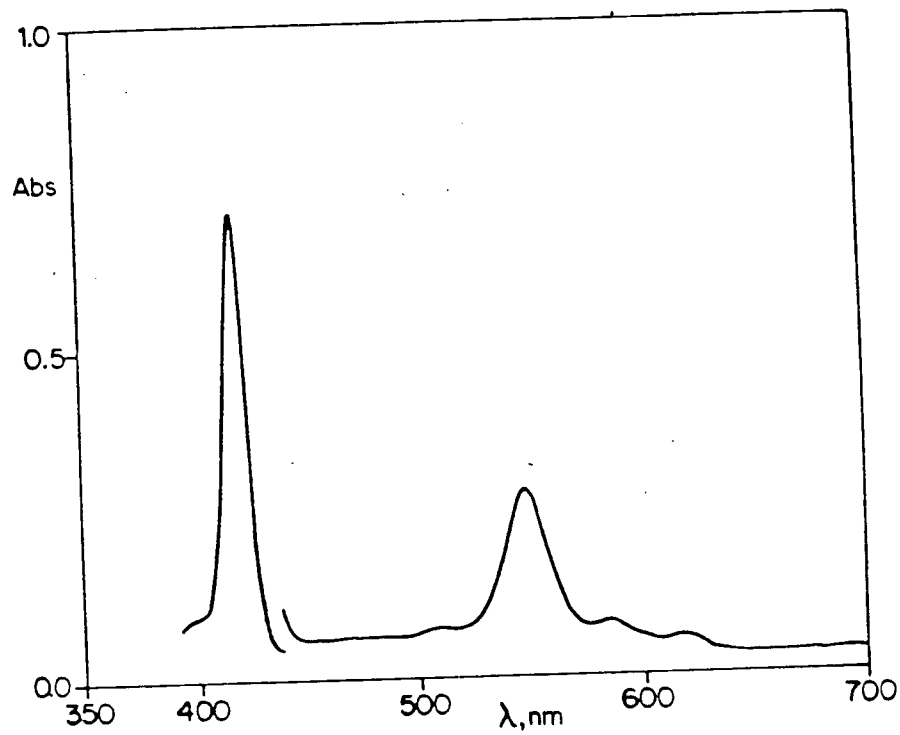

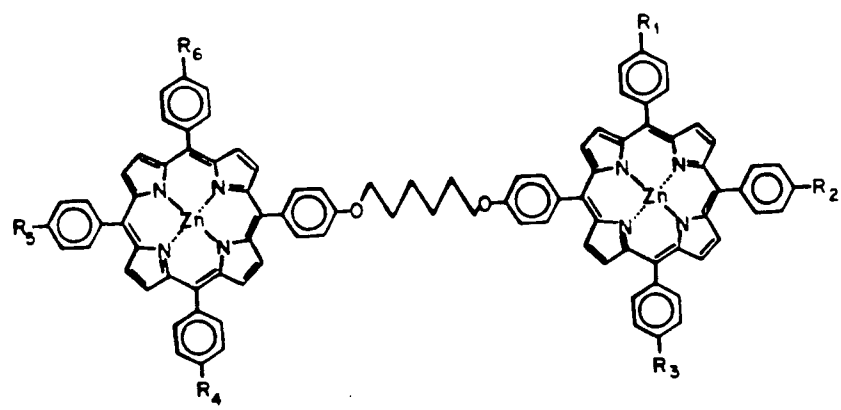

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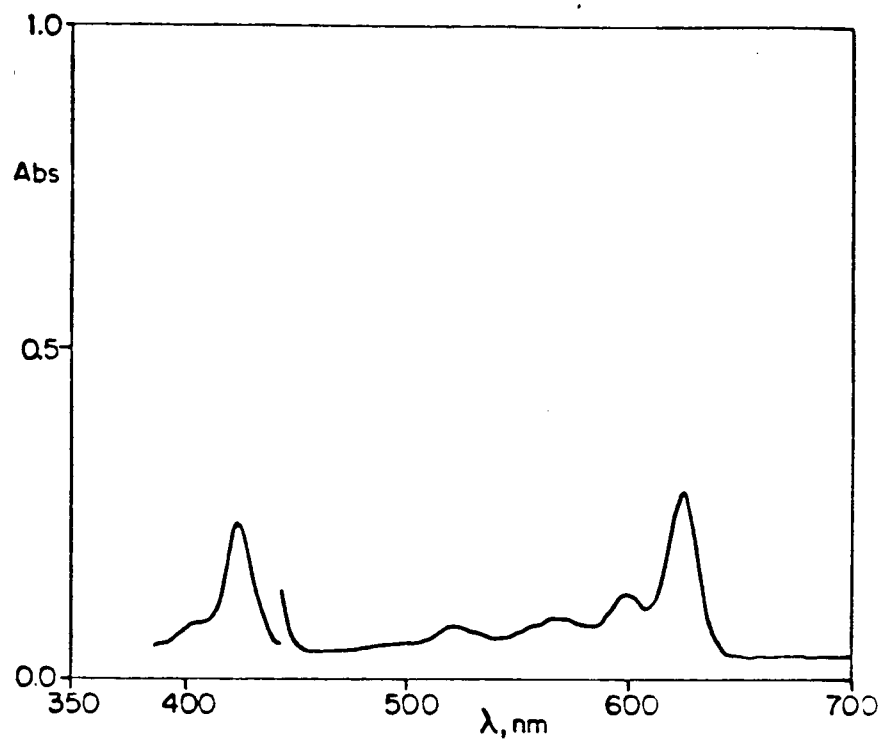

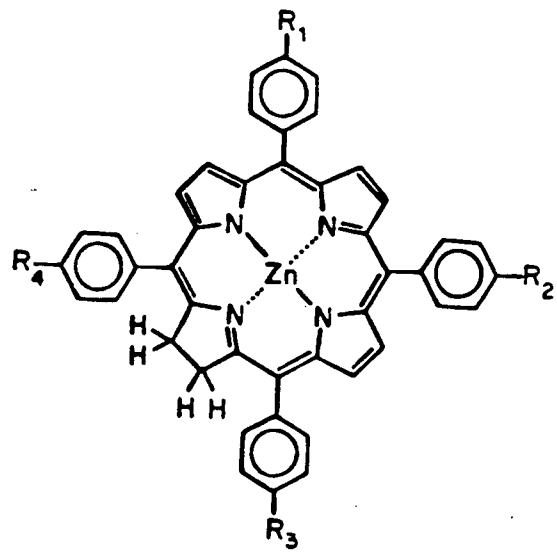

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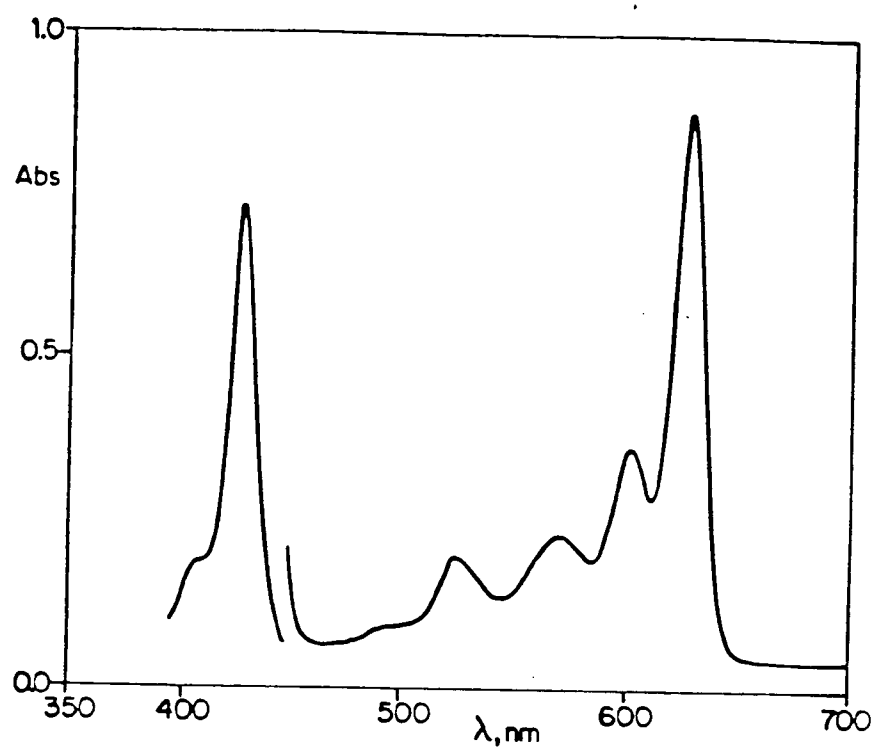
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Abs
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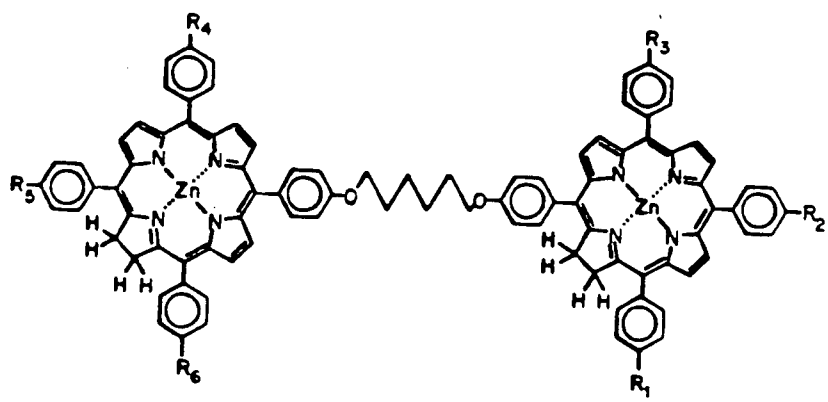
500
λ, nm
600
700


R4
R3
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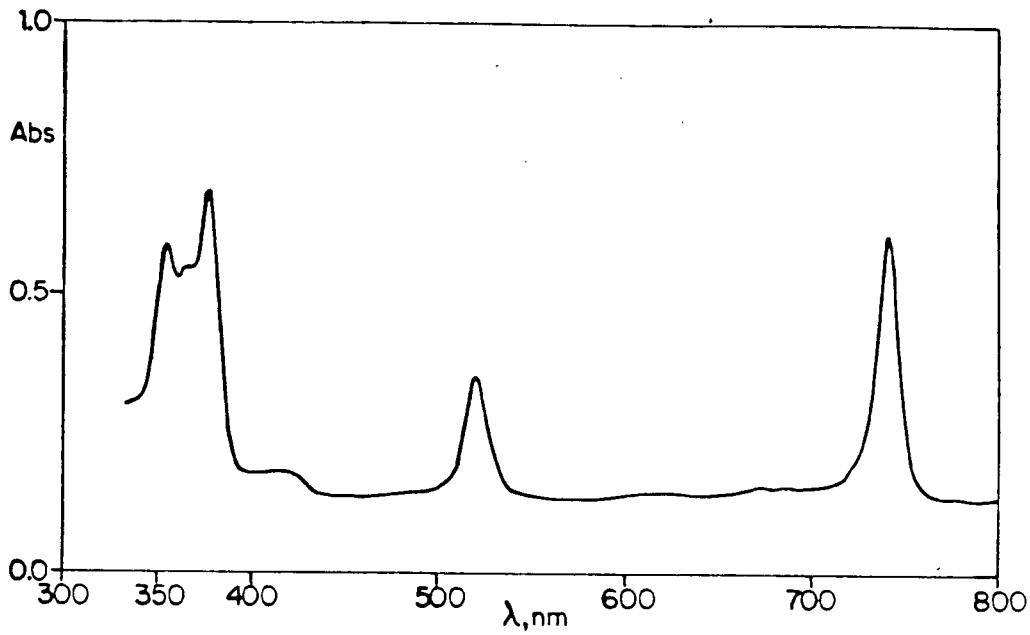
R2
R6
R1
Zn
Zn
N
H
H H
H H
O
O

(ZnTPC Dimer)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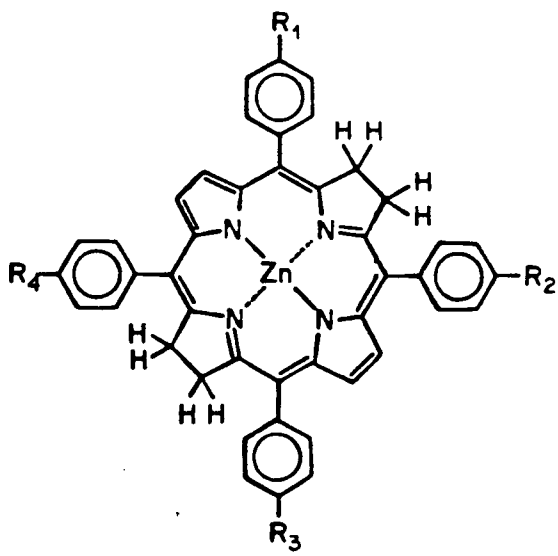
λ,nm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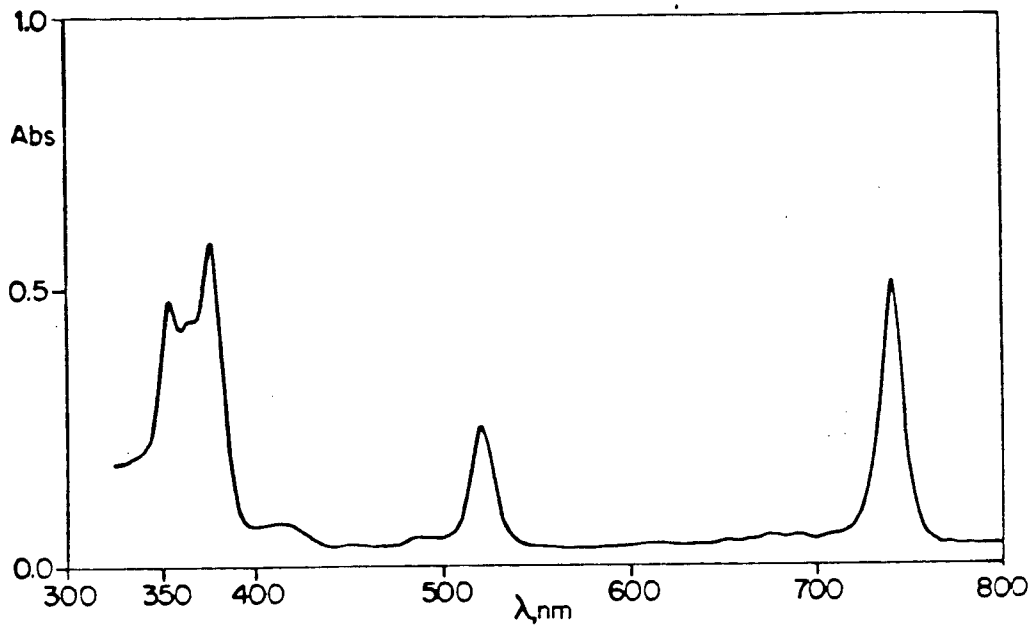
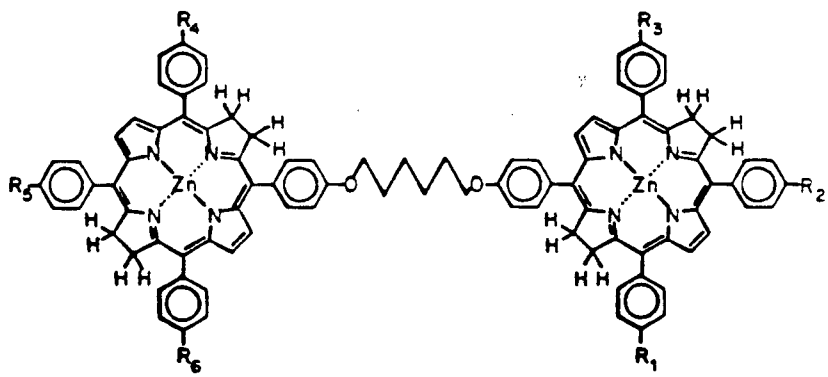
N
N
Zn
N
N
R4
R2
H
H
H H
R3

(ZnTPBC)





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