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**PHOTOCHEMICAL TRANSFORMATIONS INVOLVING PORPHYRINS AND
PHTHALOCYANINES**

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1. Introduction

Photochemistry of the porphyrins and their relatives has been largely inspired by photosynthetic processes in nature. As a result of this, most current studies generally utilize the chemistry of magnesium and zinc porphyrin analogues. Especially, magnesium tetrapyrrole chelates, i.e. magnesium porphyrins and phthalocyanines have found wide interest. This is primarily related to the biological relevance of magnesium porphyrins in nature, notably in photosynthesis and electron transfer (ET), and thus we will focus on this aspect in this review. Outside these areas not many "true" photochemical studies have been performed with magnesium tetrapyrroles.

Although porphyrins and especially phthalocyanines are stable compounds, both will undergo photooxidative degradation or photoexcited ET reactions. An additional problem of magnesium complexes is their low stability in aqueous solution, as they are prone to demetallation. As a result of this, many photochemical studies targeted at modeling the natural situation use the more stable zinc complexes. Zinc derivatives exhibit photochemical properties similar to the natural magnesium derivatives while being more stable and easier to synthesize (Li et al. 1997). Secondly, the propensity of zinc to act as an acceptor atom is used in many supramolecular approaches and/or for the modulation of chromophore properties *via* axial ligand binding. Thus, due to their biological relevance, technical importance and good stability, substituted zinc tetrapyrrole have found significant use as industrial pigments, electron transfer components, for photochemical transformations and in photobiotechnology. Likewise, industrial attention has been given to the stable copper derivatives and copper tetrapyrroles have found industrial uses for oil desulfurization, as photoconducting agents in photocopiers, deodorants, germicides, optical computer disks, semiconductor devices, photovoltaic cells, optical and electrochemical sensing, and as molecular electronic materials.

However, even in this area the body of the available literature is overwhelming and we will only use selected examples to highlight the state of the art of this field. A description of syntheses, methodology, or electron transfer reactions with the various associated model systems is outside the purview of this work and the present work aims to give a broad overview and highlights selected examples in this area.

2. Basic Photochemistry of Porphyrins and Phthalocyanines

2.1 General Concepts and Theoretical Background

Tetrapyrroles are heteroaromatic macrocycles, where the aromatic character of the tetrapyrrole moiety, the central metal, and the reactivity of the functional groups in the side chains govern their chemistry. The tetrapyrrole ligands coordinate almost any known metal with the core nitrogen atoms. Together with the conformational flexibility of the macrocycle and the variability of its side chains, this accounts for their unique role in photosynthesis, medicine, biochemistry and other applications (Senge 1992, Kadish et al. 2000, Kadish et al. 2003).

Porphyrins and phthalocyanines **1-3** are well-known representatives of the tetrapyrrole class of heteroaromatic compounds and they are closely related. Tetraazaporphyrin (or porphyrazine) **2** is the first member of the phthalocyanine class. In phthalocyanines, the carbon atoms of the methine bridges (positions: 5, 10, 15 and 20 in **1**) are replaced by four nitrogen atoms and the parent structure of a phthalocyanine is structure **3**, formally a tetrabenzotetraazaporphyrin.

<Chemical Structure 1>

Tetrapyrroles contain an extended π -conjugated system, which is responsible for their use in many applications ranging from technical (pigments, catalysts, photoconductors) to medicinal (photodynamic therapy) uses. The electronic absorption spectra are controlled by the aromatic 18 π -electron system and typically consist of two main bands. In phthalocyanines the Q band

around 660-680 nm is the intensest one and accompanied by a weaker Soret band near 340 nm (Nyokong and Isago 2004). In porphyrins the situation is reversed with an intense Soret band around 380-410 nm and weaker Q bands in the 550-650 nm region. The position and intensity of the absorption bands are affected by the central metal, axial ligands, solvation, substituents and their regiochemical arrangement, and aggregation. The theoretical background has been widely reviewed and established in pioneering works by Gouterman and Stillman (Gouterman 1978, Mack and Stillman 2003). The spectral characteristics strongly depend on the substituent pattern. By now almost all possible combinations of electron donating, electron withdrawing or sterically demanding groups have been prepared. Tetrapyrroles behave like most other organic chromophores. The absorption of light results in the rapid formation of the lowest excited singlet state *via* promotion of an electron from the HOMO to the LUMO. The excited state can then either relax to the ground state *via* radiative (fluorescence) or nonradiative processes (internal conversion of vibrational relaxation). Another possibility is intersystem crossing to form a triplet state, which again can relax either *via* radiative (phosphorescence) or nonradiative processes. In our context, both types of excited states can take part in photochemical reactions and, in the presence of donor or acceptor units, energy or electron transfer between the chromophores can compete with these processes (Gust and Moore 2000). In addition, metalloporphyrins and phthalocyanines may form ions upon illumination. These are either anion or π -cation radicals and can undergo further photochemical reactions (Senge and Sergeeva 2006, 2008). Numerous reviews have been published in this area, the most comprehensive ones being by Wasielewski (1992) and by Gust et al. (2001). Recent studies have addressed questions of regiochemistry, theoretical calculations, solubility, and the influence of sterically demanding or heteroatom containing substituents (Flamigni 2007, Lo et al. 2007, Takagi et al. 2006).

2.2 Photophysics of Metallated Tetrapyrroles

The basic photochemical behavior of magnesium tetrapyrroles is similar to that of other metallo tetrapyrroles. Magnesium porphyrins (Fajer et al. 1970, Smalley et al. 1983, Slota and Dyrda 2003) and phthalocyanines (van Willigen and Ebersole 1987, Bobrovskii and Kholmogorov 1973, Ough et al. 1991, Kim 1986) may form cation radicals and ions via the triplet state upon illumination. For (phthalocyaninato)magnesium both photochemical oxidations and reductions have been shown to occur. In the presence of carbon tetrabromide as an irreversible electron acceptor the mechanism proceeds via the radical cation (Stiel et al. 1994). The suggested mechanism for the photochemical oxidation is through the lowest lying triplet state of the phthalocyanine and is thought to be similar to that of porphyrins such as (2,3,7,8,12,13,17,18-octaethylporphyrinato)magnesium and (5,10,15,20-tetraphenylporphyrinato)magnesium.

Copper ions are known to be excited state quenchers with the partially filled d orbitals. Copper(II) ions are capable of fluorescence quenching through electron or energy transfer. Furthermore, Cu(II), with its d^9 valence electron configuration, is paramagnetic. These special features have a strong influence on the subsequently discussed photochemical tetrapyrrole transformations. Copper(II) porphyrins are interesting complexes from both a theoretical and experimental point of view. The unpaired electron in the $d_{x^2-y^2}$ orbital couples with the normal porphyrin (π , π^*) excited states to form the singdoublet [$^2S(\pi, \pi^*)$], tripdoublet [$^2T(\pi, \pi^*)$] and quartet [$^4T(\pi, \pi^*)$] states (Kim et al. 1984). These complexes do not exhibit the typical fluorescence of closed-shell metalloporphyrins, but rather show moderately strong phosphorescence from the tripdoublet-quartet manifold (Smith and Gouterman 1968, Gouterman et al. 1970, Eastwood and Gouterman 1969, Bohandy and Kim 1983, van Dijk et al. 1981). The relaxation processes in excited Cu-porphyrins have been extensively studied by picosecond

transient absorption spectroscopy (Kruglik et al. 1995, Hilinski et al. 1984, Serpone et al. 1984). It was found that photoexcitation of a CuP in the $^2S_0 \rightarrow ^2S_n$ channel was followed by an extremely fast (1 ps) intersystem crossing to the excited 2T_1 state, thus suppressing porphyrin fluorescence. The equilibrium formation between the 2T_1 and 4T_1 states proceeds within hundreds of picoseconds. The splitting between the excited 2T_1 and 4T_1 states for different Cu-porphyrins varies, depending on the porphyrin macrocycle structure.

Similar to metalloporphyrins the central metal in metallophthalocyanines has a significant effect on the nature and the lifetime of the excited states. An interesting feature of metallophthalocyanines is their ability to participate in stacked assemblies with others or with metalloporphyrins. Investigations of these assemblies have shown that metallophthalocyanines with transition metals often display an excited-state relaxation pathway associated with the interactions of the macrocyclic π -system and d-orbitals of the central metal. Although H₂Pc and Zn(II)Pc are both strongly fluorescent probes in room-temperature emission experiments, neither fluorescence nor phosphorescence was observed for Cu(II)Pc. Implicit in the fluorescence silence is an ultrafast deactivation of the initially excited state of this paramagnetic compound with a d₉-metal center. A similar mechanism has been proposed for the analogous copper porphyrin (CuP), which showed, however, activation of moderately strong and long-lived phosphorescence as a result of thermally equilibrated triplet-doublet/triplet-quartet states (Sergeeva and Senge 2010). Due to the comparable nature of the porphyrin and phthalocyanine macrocycles and binding of the transition-metal center (i.e., Cu-N), it is likely that a similar ultrafast deactivation pattern governs the photophysics of CuPc.

Many spectroscopic studies provide details on magnetic interactions and spin dynamics of states with different multiplicities, such as doublets, triplets, and charge-transfer states. The communication between these states strongly depends on the temperature and the solvent, and the spectroscopic studies established the existence of radical species deduced through ps optical experiments and the corresponding theoretical calculations.

3. Photosynthesis

The natural photosynthetic process is a rather complex biochemical system that primarily relies on the light absorption by organic chromophores, followed by generation of reduction equivalents and ATP. The main photosynthetic pigments are chlorophylls or bacteriochlorophylls that have very strong absorption bands in the visible region of the spectrum. Together with accessory pigments (carotenoids and open-chain tetrapyrroles) the various photosynthetic pigments complement each other in absorbing sunlight. Photosynthetic bacteria mostly contain bacteriochlorophylls with absorption maxima shifted towards the bathochromic region compared to the chlorin-based pigments.

In its simplest form photosynthesis can be described as the absorption of light through pigments arranged in a light-harvesting complex. These antenna systems permit an organism to increase greatly the absorption cross section for light and the use of light harvesting complexes with different pigments allows for a more efficient process through absorption of more photons and a more efficient use of the whole visible spectrum. The antenna pigments funnel the excitation energy through exciton transfer to a closely coupled pair of (b)chl molecules in the photochemical reaction center (Figure 1). The reaction center is an integral membrane pigment-protein that carries out light-driven electron transfer reactions. The excited (bacterio)chlorophyll molecule transfers an electron to a nearby acceptor molecule, thereby creating a charge separated state consisting of the oxidized chlorophyll and reduced acceptor.

<Figure 1>

After the initial electron transfer event, a series of electron transfer reactions takes place that eventually stabilizes the stored energy in reduction equivalents and ATP. Higher plants have two different reaction center complexes that work together in sequence, with the reduced acceptors of one photoreaction (photosystem II) serving as the electron donor for photosystem I. Here, the ultimate electron donor is water, liberating molecular oxygen, and the final electron acceptor is carbon dioxide, which is reduced to carbohydrates. More simple and evolutionary older types of photosynthetic organisms contain only a single photosystem, either similar to photosystem II or photosystem I (Kadish et al. 2000, Raghavendra 1998, van Grondelle and Novoderezhkin 2006). A simplified scheme of the complex photosynthetic apparatus is shown in an adaptation of the Z-scheme in Figure 2. The Z-scheme illustrates the two light-dependent reactions in photosynthetic systems of higher plants and exemplifies that two photosystems function in sequence to convert solar energy into chemical energy.

<Figure 2>

In chemical terms the photo-induced electron transfer results in transfer of an electron across the photosynthetic membrane in a complex sequence that involves several donor-acceptor molecules. Finally, a quinone acceptor is reduced to a semiquinone and subsequently to a hydroquinone. This process is accompanied by the uptake of two protons from the cytoplasm. The hydroquinone then migrates to a cytochrome *bc* complex, a proton pump, where the hydroquinone is reoxidized and a proton gradient is established via transmembrane proton translocation. Finally, an ATP synthase utilizes the proton gradient to generate chemical energy. Due to the function of tetrapyrrole based pigments as electron donors and quinones as electron acceptors most biomimetic systems utilize donor-acceptor constructs to model the natural photosynthetic process (Figure 3). Variation of the components (donor, bridge, linking group, acceptor), their spatial relationship, solvents and environmental factors then serves to modulate and optimize the physicochemical properties. Several thousand systems of this general type have been prepared and used for investigation of the photoinduced electron transfer (PET) and numerous reviews have been published in this area (Gust and Moore 2000, Wasielewski 1992). Most of the available literature on ET studies in donor-acceptor compounds focuses on porphyrins. Phthalocyanine building blocks have been used more rarely, a result of their low solubility and the lack of appropriate synthetic methodologies to selectively introduce functional groups or for the synthesis of unsymmetrically substituted derivatives. However, this situation is rapidly changing with the renewed interest in solar energy conversion systems. An overview of the various synthetic and structural principles to model the components of the photosynthetic apparatus has been given in the relevant chapter on zinc(II) porphyrins (Senge and Sergeeva 2006).

<Figure 3>

3.1 Chlorophylls and Related Pigments

Chlorophylls (chl) and bacteriochlorophylls (bchl) are the ubiquitous pigments of photosynthetic organisms and the predominant class of magnesium tetrapyrroles in nature. As such they share common structural principles and functions. They are either involved in light harvesting (exciton transfer) as antenna pigments or charge separation (electron transfer) as reaction center pigments. The best-known pigment is chl *a* **4** which occurs in all organisms with oxygenic photosynthesis. In higher plants it is accompanied in a 3:1 ratio by chl *b* **6**, where the 7-methyl group has been oxidized to a formyl group. Both compounds typically consist of the tetrapyrrole moiety and a C-20 terpenoid alcohol, phytol. Most compounds are magnesium chelates, but the free base of chl *a*, pheo *a* **5**, is also active in electron transfer. Chl *a* and *b* can be obtained easily from plants or

algae and their synthetic chemistry has mainly targeted total syntheses and medicinal application in photodynamic therapy (PDT) (Scheer 1991, Senge 1992).

<Chemical Structure 2>

However, many other similar photosynthetic pigments occur in nature (Scheer 1991, Senge 1992, Sergeeva and Senge 2008, Senge and Richter 2006). All share either a phytychlorin **7** or a 7,8-dihydrophytychlorin framework and more than one hundred related pigments have been isolated (Senge et al. 2006.) For example, these compounds include chl *d* **8** from Rhodophytes, the bchls *c* **9**, *d*, and *e* (which are chlorins **12** and show significant variability in their peripheral groups) from Chlorobiaceae and Chloroflexaceae, and bchl *a* **10** and *b* (true bacteriochlorins **13**) found in Rhodospirillales. Other natural pigments are chl *c*, bchl *g* and many of these are esterified with different isoprenoid alcohols. Chemically related chlorins have also been found in many oxidoreductases, marine sponges, tunicates, and in *Bonella viridis*. The deep-sea dragon fish *Malacosteus niger* utilizes a chl derivative as a visual pigment (Douglas et al. 1998). These compounds are derived from chl and then processed by the plant or animal.

Photosynthetic organisms that utilize chls or bchls containing metals other than Mg were unknown for a long time (Hiraishi and Shimada 2001). Past years have seen increasing evidence that both Mg and Zn chlorophylls do exist in nature. By now it has been satisfactorily demonstrated that a purple pigment occurring in a group of obligatory aerobic bacteria is in fact a zinc-chelated-bchl (Zn-bchl) (Hiraishi et al. 1998, Wakao 1996, 1999). The natural occurrence of Zn-bchl *a* has been proven for a limited group of aerobic acidophilic proteobacteria, including species of the genus *Acidiphilium*. The major photopigment in *Acidiphilium* was first identified tentatively as Mg-bchl *a* on the basis of preliminary spectral analyses (Wakao 1993, Kishimoto 1995). However, more detailed studies revealed that all previously known species of *Acidiphilium* contained Zn-BChl *a* as the major photopigment and showed *Acidiphilium* to be a photosynthetic organism (Hiraishi et al. 1998, Wakao 1996).

The naturally occurring Zn-bchl *a* and Mg-bchl *a* show large structural similarities and have very similar physico-chemical characteristics (Scheer and Hartwich 1995). Likewise, Zn-chl *a* exhibits features similar to Mg-chl *a* with regard to redox potential and absorption maxima in organic solvents. The light-harvesting efficiency of Zn-chl *a* and Mg-chl *a* are very similar, although the fluorescence quantum yield of the former is lower than the latter. Compared to other chlorophyll-type pigments Zn-bchl *a* is much more stable towards acid. For example, the rate of pheophytinization for Zn-bchl *a* is 10⁶-fold slower than for Mg-bchl *a* (Kobayashi 1998). In fact, it is difficult to fully demetallate Zn-bchl *a* to bacteriopheophytin (BPhe) by treatment with 1N HCl, which is commonly used for pheophytinization of Mg-bchl and Mg-chl. Due to the chemical stability of Zn-(b)chl *a* and their photo- and electrochemical similarities with Mg-(b)chl *a*, Zn-(b)chl's are an alternative pigment for photosynthetic studies. Thus, it is not surprising that they have been used along with magnesium porphyrins in studies on artificial photosynthetic systems (Osuka 1993, Wasielewski 1984).

3.2 Light-harvesting Complexes and Reaction Center Models

The propensity of metal tetrapyrroles for aggregation has been widely used to mimic natural antenna systems of photosynthesis. The best studied system is the chlorosome, where bacteriochlorophylls self-organize *without* the use of a protein scaffold. Depending on the light conditions these require constructing arrays with as many chromophores as possible. Thus, many studies on the self-assembly of bacteriochlorophyll model compounds or dendritic/polymeric approaches have been performed (Haycock et al 2000, Ikeda et al. 2001). Current studies focus

on large aggregates and chirality effects (Balaban et al. 2003). A typical example involves perylene monoimide donors that have been used to construct antenna models in which up to eight perylene units were covalently bound to a zinc(II) porphyrin (Tomizaki et al. 2002). Osuka and coworkers' windmill porphyrins also present excellent antenna complex building blocks (*vide infra*) (Nakano et al. 2001). In addition, several "porphyrin wheel" antenna complexes were prepared by template assisted synthesis (Tomizaki et al. 2003, Yu and Lindsey 2001) or self-aggregation (Kuramochi et al. 2004). Intramolecular cyclization of porphyrin dodecamers to a porphyrin wheel has also been achieved (Peng et al. 2004).

Classic examples for structural models of the photosynthetic reaction center are the cofacial bisporphyrins or bischlorins (Kalish et al. 1998), which model the structural arrangement of the special pair in the reaction center (Brettar et al. 2001, Pascard et al. 1993, Fletcher and Therien 2002). Zinc(II) bisporphyrins with various other geometrical arrangements, e.g., skewed (Shultz et al. 1999), have been prepared as well, including those bearing C₆₀ acceptor groups (Liddell et al. 2004). The important two-tetrapyrrole-unit found in the special pair has by now been realized in a multitude of different geometrical arrangements. Depending on the porphyrin-porphyrin or porphyrin-acceptor linkage meso-meso, meso-β (Senge et al. 2004), and β-β (Deng et al. 2000) linked systems have been prepared. Similar arrangements are also possible using noncovalent self-assembly. Noncovalent binding of substrates at the zinc(II) center can be used to control the PET in such systems (Yagi et al. 2003)

Today, most reaction center models carry suitable antenna pigments and acceptor groups and in effect are photosystem models. A typical example for a state of the art system that incorporates many aspects of a photosystem consisted of a boron dipyrrole covalently linked to a zinc(II) porphyrin, which carried a suitably modified C₆₀ derivative as axial ligand. Selective excitation of the boron dipyrrole as antenna pigment resulted in energy transfer to a zinc(II) porphyrin followed by electron transfer to the C₆₀ acceptor (D'Souza et al. 2004). These and other photoactive complexes will be discussed in more details later in the section on electron transfer systems.

4. Electron Transfer Systems and Photochemical Reactions

4.1 Introduction

Studies on photoinduced energy- and electron transfer in supramolecular assemblies have witnessed a rapid growth in the past decade. Most of these studies focused on the mechanistic details of light-induced chemical processes. Researchers attempt to generate systems with ultra fast charge transfer and charge recombination applicable as light-induced switches or with long lived charge-separated states to mimic the photosynthesis or for solar energy conversion (Iseki and Inoue 1994). The development of novel photochemically active systems has focused on polychromophoric, dendritic, supramolecular systems, and novel materials. These endeavors have produced an expanding body of information on porphyrin/phthalocyanine dyads, their design, and energy, exciton, and charge transfer properties. Incorporation of these systems into larger architectures now offers the possibility for applications in molecular photonics, electronics, solar energy conversion, nanomaterials and quantum optics.

Most electron transfer studies are aimed at the synthesis and investigation of donor-acceptor complexes that mimic the natural processes. Typically, this involves the construction of systems consisting of donor(s), a covalent or noncovalent bridging unit, and acceptor(s) (Figure 4). In an ideal situation all requirements of the natural system would be modeled. These include: (A) unidirectional electron transfer → redox gradient in subunits; (B) rigid linker groups which do

not play a role in ET → no heteroatoms, conjugated systems, etc.; (C) defined overall geometry with correct relative orientation of the subunits → e.g., special pair model with cofacial orientation of the macrocycles → use of coupling reactions which give products with defined geometry; (D) modeling the protein environment → scaffold, electronic, and steric effects / reconstituted pigment-protein systems.

<Figure 4>

4.2 Donor-Acceptor Electron Transfer Compounds

Most of the available literature on ET studies in donor-acceptor compounds focuses on porphyrins. Phthalocyanine building blocks have been used less often, a result of their low solubility and (until recently) the lack of appropriate synthetic methodologies to selectively introduce functional groups or for the synthesis of unsymmetrically substituted derivatives.

The simplest covalently linked systems consist of porphyrin linked to electron acceptor or donor moiety with appropriate redox properties as outlined in Figure 3. Most of these studies have employed free base, zinc and magnesium tetrapyrroles because the first excited singlet state is relatively long-lived, so that electron transfer can compete with other decay pathways. Additionally, these pigments have relatively high fluorescence quantum yields. These tetrapyrroles are typically linked to electron-acceptors such as quinones, perylenes (Yang 2001, Yang 2001b, Fukuzumi 2005), fullerenes (El-Khouly 2005, D'Souza 2005), acetylenic fragments (**11**, **12**), aromatic spacers (Mitzel 2003, Chandra 2003, Li 1997, Youngblood et al. 2002) and other tetrapyrroles (e.g., boxes and arrays).

<Chemical Structure 3>

Biomimetic systems comprised of porphyrins and quinones have been studied extensively with regard to their electron transfer and charge transfer properties. Porphyrin-quinone (PQ) model systems in which the quinone is fused directly to the porphyrin periphery therefore have a special relevance for the fundamental understanding of rapid biological electron transfer reactions as they are related to photosynthesis and solar energy conversion. In many cases, the magnitude of the reduction potentials of quinones covalently linked to porphyrins suggests light-induced radical-pair generation. However, use of quinones as acceptors decreases the energy that can be stored in the photoinduced radical pair, thus diminishing the likelihood of a mechanism via radical-pair generation (Connolly 1982). Many artificial systems with wide range of functionalized quinone-units have been synthesized and extensively studied (Gust and Moore 2000). Here we will only highlight selected recent works.

A series of “black” (tris- and tetra- β -quinonoporphyrinato)zinc(II) chelates was prepared via thermolysis of a tetra- β -sulfolenoporphyrin in the presence of excess benzoquinone followed by oxidation with dicyanodichlorobenzoquinone in up to 86 % yield. Surprisingly, the absorption spectra of these tetrapyrroles represent broad and intense electronic transitions covering the whole range of visible wavelengths region (Banala et al. 2009).

<Chemical Structure 4>

While most studies utilized quinones as acceptor compounds, these studies almost exclusively used *p*-quinones. Nevertheless, the isomeric, but synthetically less accessible porphyrin-*o*-quinones are much better electron acceptors (Giangiacomo and Dutton 1989). This results in a higher ΔG_{ET} and thus in a higher efficiency of the electron transfer and several *o*-quinone containing zinc(II) porphyrin dyads (e.g., **14-16**), triads and tetrads have been prepared by us (Speck et al. 1997, Speck et al. 2000, Senge et al. 2003). In order to achieve a variation of ΔG_{ET} the general strategy in electron transfer studies generally involves the synthesis of different models via chemical modification of the porphyrin donor or the quinone acceptor. However, this

also leads to changes in a number of other variables such as distance, solvent term, and electronic matrix element resulting in altered electron transfer rates. Here the utilization of porphyrin-*o*-quinones as electron transfer systems offers an attractive alternative. With them a facile and simple variation of ΔG_{ET} can be achieved by using the *in situ* formed semiquinones for metal chelation (Figure 5) (Speck et al. 2002). Some of the sterically hindered parent free-base systems (e.g., free base of **6**) can undergo photochemical degradation reactions. However, such side reactions were not observed with the zinc(II) complexes (Speck. et al. 1997, Speck et al. 2000).

<Figure 5

Although the importance of these compounds as structurally simple models with large electronic donor-acceptor coupling has long been recognized, only few examples of magnesium containing systems have been reported so far. For mechanistic studies, it is essential to have acceptor moieties other than quinones with systematically variable reduction potentials so that the energy of P^+-A^- falls between the energies of the excited singlet and triplet states and beyond. CuP and CuPc play a very important role in the electron transfer processes. One example for alternatives to porphyrin-quinone model systems are the copper picryl porphyrins **17** (Maiya 1985). Here, the interaction between the porphyrin and trinitroaryl group is relatively stronger than in porphyrin-quinone systems (Yamada et al. 1983).

<Chemical Structure 5>

Novel systems of zinc porphyrin containing fluorescent dyes attached to the surface of bacteriophage MS2 enabled energy transfer and sensitization of the porphyrin at previously unavailable wavelengths and participated in the photocatalytic reduction reactions at multiple excitation wavelengths (Stephanopoulos et al. 2009).

Viologen (4,4'-bipyridyl) derivatives are attractive electron-accepting units for tetrapyrrole-containing dyads and more complex donor-acceptor systems as they can be easily reduced, conveniently linked to other molecules via *N*-alkylation of precursors, and can be used to vary the solubility in polar solvents by virtue of their charged nature. Based on the fact that the viologen radical monocation absorbs in the visible region they can be used as convenient charge separation indicators. As a result, a number of magnesium porphyrins (Szulbinski 1995, Zakrzewski and Giannotti 1995) and phthalocyanine (Harriman et al. 1981, Ohtani et al. 1984) –viologen systems have been studied. Typically, excitation of a porphyrin-viologen dyad **18** leads to the porphyrin first excited singlet state, which can then induce photoelectron transfer to the viologen or undergo intersystem crossing to yield the porphyrin triplet state. As viologen is easily reduced, the porphyrin triplet state may also act as an electron donor in these systems.

<Chemical Structure 6>

A different strategy involves using a transition metal center linked to an organic chromophore. This greatly expands the number of electron/energy transfer reactions that can take place within the assembly compared to pure organic or inorganic-organometallic systems. Covalently linking metal complexes to porphyrins yields a cornucopia of candidates for photosynthesis related studies. Again, only a few examples of photoinduced processes based on magnesium phthalocyanine (Kobyshev et al. 1963) and porphyrins (Monnereau et al. 2005, Gabrielsson et al. 2006) have been reported so far (e.g., compounds **19** and **20**).

<Chemical Structure 7>

For example, in 1963, the photochemistry of magnesium phthalocyanine with coordinated uranium cations was studied in pyridine and ethanol and indicated the occurrence of PET to the uranium complex (Kobyshev et al. 1963). A rapid photoinduced electron transfer (2-20 ps)

followed by an ultra fast charge recombination was shown for various zinc and magnesium porphyrins linked to a platinum terpyridine acetylide complex (Monnereau et al. 2005). The results indicated the electronic interactions between the porphyrin subunit and the platinum complex, and underscored the potential of the linking *p*-phenylene bisacetylene bridge to mediate a rapid electron transfer over a long donor-acceptor distance.

Complexes of rhenium(bipyridine)(tricarbonyl)(picoline) units linked covalently to magnesium tetraphenylporphyrins via an amide bond between the bipyridine and one phenyl substituent of the porphyrin **20** exhibited no signs of electronic interaction between the $\text{Re}(\text{CO})_3(\text{bpy})$ units and the metalloporphyrin units in their ground states. However, emission spectroscopy revealed a solvent-dependent quenching of porphyrin emission upon irradiation into the long-wavelength absorption bands localized on the porphyrin. The presence of the charge-separated state involving electron transfer from $\text{Mg}(\text{II})\text{TPP}$ to $\text{Re}(\text{bpy})$ was shown by time-resolved IR spectroscopy (Gabrielsson et al. 2006).

The system is reversible in the absence of an added electron donor but undergoes irreversible reaction at the reduced rhenium bipyridine center in the presence of added triethylamine. The observation of reaction at the rhenium site upon excitation in the absorption band of the metalloporphyrin site is compatible with an ultra fast back electron transfer provided that the triethylamine coordinated to the magnesium prior to absorption and that the electron transfer from the metalloporphyrin to the bipyridine was followed rapidly by irreversible electron transfer from the triethylamine to the metalloporphyrin. The experiments graphically demonstrated the benefits of the incorporation of carbonyl ligands at the electron acceptor as they allowed a tracking of the sequence of charge separation and back electron transfer via time-resolved IR data (Gabrielsson et al. 2006).

Applications of fullerenes in photoinduced electron-transfer studies derive from the fact that back electron transfer is inhibited in donor-acceptor systems incorporating [60]fullerene (C_{60}). Fullerenes can accept up to six electrons and exhibit small reorganization energies while the photoinduced charge-separation is accelerated and charge recombination is slowed. The effect of the introduction of C_{60} as an electron acceptor into tetrapyrrole molecules should enhance our knowledge of the dependence of photoinduced electron transfer dynamics on molecular topology. Thus, relatively long-lived charge-separated states are obtained without a special environment such as an apoprotein (Imahori et al. 2002). Several self-assembled donor-acceptor systems containing fullerenes as three-dimensional electron acceptors and porphyrins as electron donors have been described. A recent system consisting of a ferrocene, two porphyrins and one C_{60} unit exhibited a life-time of 1.6 s (!), comparable to bacterial photosynthetic reactions centers. The quantum yields for charge separation in complex biomimetic systems can reach unity. Recent advances in their synthetic methodologies allow the functionalisation of fullerenes and linking them to other pigments.

Fullerenes (mostly C_{60} but also C_{70} (Kesti et al. 2003)) have been incorporated into multi-component systems with step-wise charge separation (Imahori 2004, Imahori et al. 2002, Imahori and Fukuzumi 2004, Kesti et al. 2003, Imahori, et al. 2002b, Bell et al. 2002, Imahori et al. 2004) and used as core groups for dendrimers with zinc(II) porphyrin donors (Camps et al. 1999). By now C_{60} has also been linked to chlorins and phytychlorin derivatives (Fukuzumi et al. 2001, Helaja et al. 1999) and carotenoid-porphyrin- C_{60} systems are under investigation (Kodis et al. 2004). Many of these systems utilize a pyrrolidine linkage, but bislactone (Montforts et al. 2003), or Diels-Alder derived cyclohexene-linked systems (Bell et al. 2002, Fukuzumi et al 2001) have also found wide applications. Currently, nanostructured systems are emerging (Yamaguchi et al.

2003) and new attention has been focused on combining the utility of fullerene acceptor groups with rotaxane systems (Watanabe et al. 2003, Schuster et al. 2004, Li et al. 2004, Li et al. 2004b). Zinc(II) porphyrins have been used in many systems for complexation studies (Guldi et al. 2001) and to modulate the ET properties by using axial coordination effects (D'Souza et al. 2001, 2002, 2002b) or to construct self-assembled donor-acceptor systems (D'Souza, et al. 2002, 2003, 2004b).

For example, pyridinofullerenes were used as axial ligands for Zn(II)TPP or Zn(II)OEP and the formation of the non-covalent porphyrin-fullerene dyads was indicated by fluorescence quenching of Zn(II)TPP (Wilson et al. 2004). This photoinduced electron transfer is an exergonic process (D'Souza et al. 1999). Photoinduced electron transfer in nonpolar media was reported for porphyrin tripod fullerene systems synthesized via "click" chemistry (Takai et al. 2010). Likewise, a photoactive [2]catenane containing zinc(II)-porphyrin (ZnP) and/or [60]fullerene (C_{60}) as appended groups also prepared via "click" chemistry was described as well (Megiatto et al. 2010). For a related triad ($C_{60} + 2$ Zn(II) porphyrins) it was shown that the main quenching pathway involved charge-separation from the excited singlet state Zn(II)TPP to the C_{60} unit in noncoordinating solvents and from the triplet excited state of Zn(II)TPP in coordinating solvents (El-Khouly et al. 2003). Porphyrin-fullerene dyads with an azobenzene linker were synthesized, and the photophysical properties were investigated using steady-state and time-resolved spectroscopic methods (Schuster et al. 2007). Photosynthetic models containing dendritic C_{60} - H_2P -(ZnP)₃ conjugates were analyzed in relation to the primary events in photosynthesis, i.e., light harvesting, unidirectional energy transfer, charge transfer, and charge-shift reactions. (Schludt et al. 2009). Similar approaches have been used with zinc(II) phthalocyanines (Guldi et al. 2002). Some of the characteristics of fullerene containing systems, e.g., recombination to the triplet state, were also observed with specifically designed triads without a fullerene unit (Gould, et al. 2004).

In line with the general development in the field non-covalently and covalently linked Mg porphyrin-fullerene dyads have been synthesized and investigated spectroscopically (El-Khouly 2005, D'Souza 2005). For example, a covalently linked magnesium porphyrin-fullerene (MgP- C_{60}) dyad with a flexible ethylene dioxide bridge (El-Khouly 2005) was compared to a self-assembled non-covalently linked dyad (MgP••• C_{60} Im, **21**). In the latter, axial coordination of an imidazole (Im) functionalized fullerene (D'Souza 2005) to the magnesium porphyrin was used for bonding. Significant increases in the lifetime of the charge separated states were observed upon coordinating nitrogenous axial ligands to the latter.

<Chemical Structure 8>

Likewise, different types of non-covalently and covalently linked copper phthalocyanine-fullerene dyads have been prepared (Li et al. 2004b, Nierengarten et al. 2000, El-Khouly et al. 2002). An example is a series of fulleropyrrolidinophthalocyanines containing free base, Zn and Cu used as electron-donating building blocks in fullerene dyes of type **22** (Guldi et al. 2004). These experiments support the view that the $C_{60}/C_{60}^{\bullet-}$ couple exhibits the strongest electron affinity, while the different Pc/Pc^{•+} couples play the role of electron donors.

<Chemical Structure 9>

Further investigations showed that the donor ability increases in the following order: CuPc < H_2Pc < ZnPc. In other words, starting from the free base (H_2Pc) addition of either Cu (CuPc) or Zn (ZnPc) increases or decreases the electron density on the phthalocyanine, respectively. Similarly, the energy for the radical ion pair $CuPc^{\bullet-}-C_{60}^{\bullet+}$ formed in a photoinduced electron-

transfer reaction (*vide infra*), decreases in the following order: (1.40 eV) > H₂Pc-C₆₀ (1.36 eV) > ZnPc-C₆₀ (1.23 eV).

Many other building blocks have been developed for use in photochemically active compounds. Perylene units have attracted attention as energy transfer donors, as they increase the light-harvesting efficiency in the green spectral region (where porphyrins are relatively transparent). Classic cases of magnesium porphyrins are **23** and **25**. They represent a family of closely related bichromophoric systems with properties designed to utilize PET strategies (Yang et al. 2001, Yang et al. 2001b, Fukuzumi et al. 2005). A typical example for zinc tetrapyrroles is **23** (Prathapan et al. 2001) but larger arrays including some with phthalocyanine units have been described as well and perylene units have been used as bridging units in D-B-A systems (Hayes et al. 2000, You and Würthner 2004).

<Chemical Structure 10>

4.3 Heteroligand Systems

The photoinduced electron transfer (PET) between metalloporphyrins and free bases in dimeric, trimeric, and oligomeric porphyrin systems has been studied extensively. Depending on the choice of the donor and acceptor unit, electron transfer from either singlet or triplet states may be observed. Electron transfer studies in systems based on heterodimers with covalent or electrostatic bonds is of particular interest as it relates directly to the natural photosynthetic process.

For systems such as the magnesium – free base porphyrin heterodimer **26** EPR spectroscopy is an essential analytical tool that provides information not available from optical studies. It provides details on the magnetic interactions and spin dynamics of states with different multiplicities, such as doublets, triplets, and charge-transfer states. The communication between these states strongly depends on the temperature and the solvent, and the EPR results established the existence of the radical species deduced in ps optical experiments and the corresponding theoretical calculations (Levanon et al. 1993, Zhang et al. 1995, Zaleski 1993).

<Chemical Structure 11>

A series of conformationally restricted magnesium-free-base hybrid arrays bridged linearly via aryl-spacers to form di- (**27**) or trimeric porphyrins was used to study the intramolecular electron-transfer reactions from the singlet excited state of the remote doubly strapped free-base porphyrin to the pyromellitimide acceptor by time-resolved ps fluorescence and transient absorption spectroscopy (Osuka, et al. 1993b, 1994b, 1994c). The electron transfer was more effective in magnesium-porphyrin bridged models than in the related zinc-porphyrin bridged ones, indicating that the past reliance on the use of zinc-based biomimetic models is not always sufficient. Remarkably, the electron transfer rates over two porphyrins were almost similar to those for the ET over one porphyrin independent of the bridging metalloporphyrin. Compound **28** is an example of multichromophoric systems which now more frequently used to study the intramolecular electronic communications between chromophore subunits (Youngblood et al. 2002, Li et al. 1997).

<Chemical Structure 12>

Another example involving dimeric systems linked through non-covalent bonds used (5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrinato)zinc(II) and (5,10,15,20-tetrakis(4-*N,N,N*-trimethylanilinium)porphyrinato)magnesium(II) with complementary charge results in dimerization in solution. Continuous wave time-resolved EPR spectroscopy demonstrated that intramolecular electron and/or energy transfer in electrostatically bound metalloporphyrin dimers can be controlled via simple metal and substituent effects. Although the metal constituents were

identical in these two dimers, the peripheral charged substituents governed the fate of the electron transfer, whereas the energy transfer is controlled via the metal substituents (Murov 1993, Berg et al. 1996).

ET from CuP to its free-base partner was observed in the CuP-H₂P hybrid dimer **29** (Asano-Someda et al. 1994). Clearly, the advantage of a hybrid system is that the energy donor and an acceptor are distinct. The lowest excited singlet and triplet states of the free-base porphyrin monomer are lower than those of the copper porphyrin. Based on T-T transient absorption spectra, the triplet yield of the free-base porphyrin was found to be increased in the hybrid dimer compared to a monomeric free-base porphyrin. Time-resolved ESR showed that the intermolecular energy transfer occurs between the triplets. The lowest excited triplet state of the CuP-H₂P dimer is generated both by energy transfer processes from the triplet manifolds in the copper porphyrin moiety and by intersystem crossing from the lowest excited singlet state of the free-base moiety. As a result of the paramagnetic perturbation, intersystem crossing in CuP is remarkably accelerated and seems to prevent singlet-singlet energy transfer to another porphyrin moiety.

<Chemical Structure 13>

Electrostatically linked dimers can easily be produced by a coupling of two monomers with oppositely charged substituents in the liquid phase. An example of such systems has been illustrated by Tran-Thi et al. (1992), where Zn-porphyrin units were linked with Cu-phthalocyanines. Drastic changes in the ground-state absorption of the electrostatically linked dimer compared to the corresponding monomers indicate a strong interaction between the two chromophores. According to femto- and nano-second absorption spectroscopy, very efficient intersystem conversion takes place in the excited ZnP-CuPc, leading to the final 'triplet' state. In contrast, excitation of a ZnP-AlPc dimer led to an electron transfer from the porphyrin to the phthalocyanine moiety. The different behavior in ET can be explained by the peculiar properties of the paramagnetic CuPc.

For systems such as the copper – copper dibenzofuran-bridged co-facial bisporphyrins **30** and **31** EPR spectroscopy has been shown to be an essential analytical tool that provides information not available from optical studies. It also complements crystallographic studies by probing intramolecular metal-metal arrangements in frozen solution (Chang et al. 2002).

<Chemical Structure 14>

Mixed cyclization of porphyrin containing phthalonitrile compounds with an europium(III) half-sandwich phthalocyanine complex in the presence DBU gave a series of porphyrin-appended europium(III)bis(phthalocyaninato)complexes. These mixed tetrapyrrole triads and tetrad were spectroscopically characterized with steady-state and transient spectroscopic methods. The porphyrin fluorescence was effectively quenched by the double-decker unit through an intramolecular photoinduced electron transfer process. Both the photoinduced electron transfer and recombination of the charge-separated state depended on the number and position of the porphyrin units attached to phthalocyanines (Bian et al. 2007).

Many systems were prepared and detailed photophysical analyses were carried out for zinc tetrapyrrole systems (Senge and Sergeeva 2006). Other examples for hybrid systems are slipped-cofacial dimers consisting of directly linked zinc porphyrin - zinc phthalocyanine units (Ito et al. 2006).

5. Photochemical Reactions

5.1. Porphyrins

Photoinduced metallation of porphyrin was reported first in the seventies of the last century (Bluestein and Sugihara 1973). Various porphyrins, geoporphyrins and Cu(II) 1,3-diketonates underwent a quantitative conversion into Cu(II) porphyrins in a short period of time (depending on the light intensity) upon light irradiation (~400 nm). Dark experiments required several hours or days to achieve a comparable conversion. Since the photochemical reaction occurred upon irradiation by light (~400 nm) in the Soret band, the formation of a porphyrin excited form may be assumed.

Another examples for photochemical transformations involved the copper(II) porphyrins **32** and **33**. These compounds were shown to undergo an unusual self-sensitized photo-oxygenation reaction (Jiao et al. 2006). While stable in the dark under inert gas, they were rapidly transformed into oxygenated adducts upon exposure to both light and air. Compound **33** was less stable and its major photooxygenation product was the α,β -unsaturated ketone **34** (52 %). In contrast the co-facial bis-porphyrin **35** was isolated from the reaction of **32** in the presence of DBU in good yield (60 %) and its structure was confirmed by X-ray analysis

<Chemical Structure 15>

One of the few true photochemical reactions described for Mg(II) phthalocyanines involved a wavelength dependent photocyclization of **36** to **37**. Together with the back reaction this system was developed as a photochromic readout system (Luo et al. 2007). A related example involving molecular motion used a “scissor”-like porphyrin dyad with flexible ferrocene-azabenzene-linkers where light-induced change in conformation of the host molecule forced a non-covalently bound guest to change its conformation as well (Muraoka et al. 2006).

5.2 Photoinduced Ring-Opening Reactions

The photochemistry of chlorophylls is one of the oldest photochemical topics involving tetrapyrroles. The formation of long-lived excited states of chlorophyll and its function as energy-storage and catalytic material in photosensitization reactions has been postulated for some time on the basis of indirect evidence. For example, in the 1930s Rabinowitch and Weiss performed spectrophotoelectrochemical studies on the reversible oxidation and reduction of chl (Rabinowitch and Weiss 1936, 1937). An ethyl chlorophyllide solution was reversibly oxidized by FeCl₃ to a yellow, unstable intermediate from which the green solution was regenerated by reduction with FeCl₂. The oxidation was greatly favored by illumination and the equilibrium was shifted by light towards the yellow form. The nature of the reversible reaction with Fe³⁺ was considered to be an oxidation in which Fe³⁺ was reduced to Fe²⁺ and chlorophyll was oxidized to a chl cation or a dehydrochlorophyll species.

About a decade later Calvin and co-workers reported photochemical reactions of simple chlorins and either oxygen or various *ortho/para* quinones that led to the corresponding porphyrins and unidentified products. Based on kinetic experiments, they proposed a mechanism for the photochemical oxidation of 5,10,15,20-tetraphenylchlorin (H₂TPC) and β -naphthoquinone involving the triplet state of the chlorin molecule as an intermediate (Calvin and Dorough, 1948). The production of P⁺ and P⁻ ions from the first excited triplet state (**T**) of Mg(II)OEP (**P**) predominantly involves triplet-triplet annihilation. Evidence indicated that the reaction of T with ground-state P is not a significant source of ions. On the other hand the two triplets initially can combine to form an excited charge-transfer complex. Less extensive experiments were carried out with Mg(II)TPC due to its instability. However, the data obtained confirmed the existence of a phosphorescence state (Huennekens and Calvin, 1949). The photooxidation rates for the magnesium chlorins were significantly lower (~8 times) than for the corresponding zinc complexes.

The magnesium and zinc complexes of TPC can also be photooxidized using quinones as hydrogen acceptors. More detailed studies showed that the reaction between quinones and Zn(II)TPC resulted in the formation of Zn(II)TPP (Huennekens and Calvin, 1949). Subsequent work showed that Mg(II)TPC and Zn(II)TPC can be photooxidized by molecular oxygen and *o/p*-quinones. Oxygen is reduced to hydrogen peroxide with a concomitant reduction of quinones to hydroquinones. However, oxygen differs from quinones, as the primary formation of oxidation to porphyrins here is followed by secondary reactions. This second reaction involves H₂O₂ that can react either directly or as an initiator of Haber-Weiss processes and resulted in the formation of unidentified products (Huennekens and Calvin 1949b) similar to those obtained by “bleaching” of chlorophyll in the presence of oxygen (Rabinowitch and Weiss 1936, 1937). Subsequent work in this area clarified some aspects of the photo-oxidation of magnesium porphyrins. Barrett found no alteration in the spectral and chromatographic properties of non-fluorescent protoporphyrin complexes of Fe, Ni, Co, Cu and Ag upon irradiation (Barrett 1967). However, irradiation of (protoporphyrinato dimethyl ester)magnesium(II) **38** in various organic solvents resulted in rapid photooxygenation to green-brown products that did not contain magnesium. Moreover, spectroscopic data indicated an interruption of the aromatic ring system, showed no fluorescence and the appearance of a strong band at 1680 cm⁻¹ (CCl₄) in the IR spectrum of the newly formed compound. This green pigment was very photolabile and quickly decomposed to yield 15,16-hydrobiliverdin **39**. Magnesium porphyrins without vinyl side-chains were photooxidized to similar green compounds with the band at 1680 cm⁻¹, confirming no oxidation of the vinyl group. The UV/vis spectra of these green products were similar to those of the phlorins obtained by photoreduction of uro-, copro- and hematoporphyrins (Mauzerall 1962). Thus, photooxidation of magnesium protoporphyrins resulted in the formation of 15,16-hydrobiliverdins upon ring cleavage. This is in contrast to the enzymatic breakdown of heme which proceeds through biochemical transformations *via* biliverdin **40** towards the phycobilins (Beale and Cornejo 1991, 1991b, 1991c).

<Chemical Structure 16>

The reaction of porphyrin ligands with molecular oxygen is related to catabolic processes of naturally occurring porphyrins and drugs and is of a great medical relevance. Various metalloporphyrins, particularly the chlorophylls present in photosynthetic organisms, can be rapidly destroyed by light and oxygen. In fact, without the presence of photoprotective pigments such as carotenes, no natural chlorophyll based photosynthetic system would be stable. Initial studies on the photooxygenation of Mg(II)OEP (**41**) (Fuhrhop and Mauzerall 1971, Fuhrhop 1974, Fuhrhop et al. 1974), Mg(II)TPP (Matsuura et al. 1980, Smith et al. 1980) and Mg(II)protoporphyrin and Mg(II)(tetrabenzoporphyrin) (Goedheer and Siero 1967, Goedheer 1967) were reported in the 1970s and 1980s.

For example, exposure of Mg(II)OEP to visible light in the presence of air in benzene solution, resulted in the quantitative conversion of the porphyrin into a chromophore with an intense absorption band above 800 nm. This reaction proceeded uniformly and no intermediates with lifetimes of more than 10 s were observed. The primary product was an open-chain magnesium formylbiliverdin complex **42** that can be easily demetallated to the formylbiliverdin. A similar photooxidation pathway was found for Mg(II)TPP. It reacted readily with molecular oxygen to yield the corresponding 15,16-dihydrobiliverdin similar to the one shown for Mg(II)OEP in Scheme 1. Further studies have proposed that the photooxygenation of metallo-*meso*-tetrasubstituted porphyrins proceeds *via* a one-molecule mechanism involving only one oxygen molecule. Most likely, the first intermediates formed upon photooxygenation are short-lived

peroxides. Such compounds are very instable and a possible dioxetane structure is shown in formula **43**.

<Scheme 1>

5.3 Reactions of Chlorophyll

The most obvious chemical reaction involving chlorophyll is the chlorophyll breakdown in fall during senescence. This process involves annually more than 10^9 tons of chlorophyll and despite its obvious prominence in the natural beauty of the fall season remained unknown until about 20 years ago (Hendry et al. 1987). Different groups have shown that the central step is a ring-opening reaction at the 5-position (Kräutler and Matile 1999, Gossauer and Engel 1996, Iturraspe et al. 1995).

This is in contrast to the situation encountered for heme, which is oxidatively cleaved at the 20-position. As shown in Scheme 2, the crucial steps during chl degradation are the conversion of chl *a* into pheophorbide *a* **5**, followed by enzymatic transformation into the bilinone **44**. During this step the macrocycle undergoes oxidative C5 ring-opening, incorporates two oxygen atoms (the CHO one from O₂) and is saturated at the 10-position. This reaction is catalyzed by a monooxygenase and the red compound **44** is further converted to the still fluorescing compound **45**, and finally into the nonfluorescing derivative **46**; along with some changes in the side chains directed to increase the hydrophilicity of the breakdown products. Chl *b* **6** is first converted into chl *a* **4** and then subjected to the same reactions. Note that this is an enzymatic process not a simple photochemical reaction and should not be confused with the photooxidative ring-opening reactions.

<Scheme 2>

A second reaction involves the classic chlorin to porphyrin conversion. Any chlorin which has hydrogen atoms at the sp³-hybridized centers of the reduced ring can be oxidized to the respective porphyrin. Oxidation may be achieved by various oxidants including oxygen (Inhoffen 1968). Likewise, reductions to hydroporphyrins and other reactions of the macrocycle are possible. However, most of these are of interest only for the specialist. The best known reaction is probably the Krasnovskii photoreduction to **47** (Scheer and Katz 1974).

Similar to porphyrins chl's undergo photooxygenation (Hynninen 1991, Gurinovich and Tsvirko 2001). Chlorophylls are potent photosensitizers and will produce singlet oxygen in the presence of air or triplet oxygen (Inhoffen 1968). Thus, chls can undergo self-destruction. The chemistry of this photooxygenation is heavily involved and differs somewhat for individual types of (b)chls. (Iturraspe et al. 1995, Inhoffen 1968, Troxler et al. 1980, Llewellyn et al. 1990, Llewellyn et al. 1990b). While being partially responsible for the low stability of chls in solution (Peled et al. 2000) and for unwanted side reactions in food stuff (Min and Boff 2002) the same reaction also offers potential for future applications. Chl and derivatives thereof may be used as photosensitizers to affect desired chemical transformations and they have been utilized for applications in photodynamic therapy (PDT) (Nyman and Hynninen 2004).

As lipophilic pigments where the (b)chl's are embedded in natural systems in apoproteins, photosynthesis in general is a transmembrane process. Thus, PET reactions in lipid membranes have been investigated extensively. Many reports have been published on photo-initiated (i.e. the photo-initiated species acts as a catalysts to mediate thermodynamically favored reactions) and photo-driven (i.e. some of the light energy is converted into the products) processes (Tunuli and Fendler 1981). Typical examples are Mg(II)OEP sensitized electron transfer reactions across lipid bilayer membranes (Ilani et al. 1989). The reaction mechanism involves a reduction of photoexcited Mg(II)OEP at the reducing (ascorbate) side of the bilayer with the charge carrier

most likely being a neutral protonated Mg(II)OEP anion. Thus, the magnesium porphyrin participated as a sensitizer and a transmembrane redox mediator.

A well studied system is a Mg-substituted horseradish peroxidase. This system can form stable porphyrin π -cation radicals in the presence of oxidants (Kuwahara et al. 1982, Deguchi et al. 1985) and photooxidation and -reduction occur through direct reaction of the excited-state porphyrins with oxidants and reductants, respectively. In general, porphyrins appear to be photooxidized both via electron transfer and $^1\text{O}_2$ mechanisms. Thus, photoirradiation of the Mg-substituted horseradish peroxidase under aerobic conditions results in two simultaneously occurring reactions. A porphyrin π -cation radical is generated through electron transfer from excited porphyrin to O_2 and a so-called the 448-nm compound via a singlet oxygen mechanism. A species with an absorption band at 448 nm was first formed upon irradiation and was then converted in the dark to a final product with a band at 489 nm, probably via an isomerization reaction.

6. Photoinduced Electron Transfer in Applied Photochemistry

Tetrapyrroles have found applications in the different areas of the current research targeting highly interesting topics of organic and medicinal chemistry, material and nanoscience. They have shown to be effective photocatalysts for aquatic wastes and organic pollutants degradation in green chemistry. On the other hand, they can also be used as efficient stabilizing agents for polymers and dyes.

The search for alternative energy sources is one of the most important aims of the present century that has found renewed attention after a lack of interest for several decades. Solar energy conversion, electrophotography, hydrogen production and photocatalysis are the most popular topics involving tetrapyrroles. Photoenergy conversion systems have been designed using donor-acceptor molecules, polymers, and carbon nanotubes. The mechanism of photoinduced electron transfer (PET) is extensively studied and a variety of the artificial systems applying PET are examined for use as molecular devices. Here we will highlight the future potential of these materials as molecular devices in emerging areas of nanoscience, especially in the utilization as prospective (photo)catalysts in areas of green chemistry and hydrogen production, and in solar energy as photovoltaic cells and junctions.

6.1 Nanomaterials – Molecular Electronic Devices

The discovery of charge transfer across donor-acceptor systems opened an effective way to improve the photooptical response of organic materials. Here the development and use of organic ultra-thin monolayers as potential models for optoelectronic devices and catalysts in solid photochemistry has attracted great attention. Some studies focused on the fabrication of CuPc and CuP thin films using photoinduced deposition methodologies (Yamanouchi and Saji 1996, Hoshino et al. 1996, Bearinger et al. 2008) and investigated their optical (Yamada et al. 1995), optical memory and photoswitching (Liu et al. 1994) and xerographic properties (Xu et al. 2002). Many memory and switching phenomena in organic solid films have been described as prototypical candidates for molecular electronic devices and photogeneration in these organic superlattices under an applied electric field may play a fundamental role. Some work has been reported on PET and back electron transfer (charge recombination) of hetero-Langmuir-Blodgett films with phthalocyanines as a sensitizer. For example, a transient electric current was observed upon the selective photoexcitation of CuPc and the resulting charge separated state in the device survived for a few minutes. Applying electric biases and/or lowering temperatures caused the charge-separated state to last much longer (Naito and Miura 1993).

Disk-shaped like monomers can form rod-like aggregates (discotic mesophase materials) and they exhibit long-range order, large electrical anisotropies. The high interest in these materials stems from their promise as organic electronic devices requiring high charge mobility and dense integration (e.g., organic field effect transistors, organic light-emitting diodes, and photovoltaic cells).

Tetrapyrroles, especially with flexible hydrocarbon chains, exhibit a remarkable feature to form discotic mesophase architectures. An example are the octa-substituted phthalocyanines **48–50** with and without polymerizable styryl side chains: CuPc(OC₂H₄OCH=CHPh)₈ (**49**) with styryl groups at the termini on the side chains, or with one alkoxy group removed CuPc(OC₂H₄CH=CHPh)₈ (**50**) (Dragger et al. 2001) and CuPc(OCH₂)₂OBz)₈ (**49**). The latter compound **49** formed highly coherent rodlike aggregates in Langmuir-Blodgett films with excellent control of rod orientation (Smolenyak et al. 1999, Zangmeister et al. 2001). Irradiation of the styryl π - π^* absorbance bands with $\lambda \sim 254$ nm for horizontally transferred LB films of **48** and **50** resulted in a stabilization of their rodlike aggregates, through formation of cyclobutane links between adjacent side chains (through common [2+2] cycloaddition (Donley et al. 2003)). Polymerized thin films have shown a long-range order that was confirmed by atomic force microscopy and X-ray reflectometry. The differences in the orientation of individual Pc's, between films of **48** and **49**, were determined by transmission and reflectance. Higher dark photoconductivities and electrical anisotropies were observed in films of **48** after annealing and polymerization, compared with those found for films of **49**.

<Chemical Structure 17>

Several studies were aimed at the fabrication of molecular-based photoelectrodes and special attention has been given to the efficient uptake of visible light and conversion into output of the photosystems. Typical examples are the construction, determination of photoelectric characteristics, and an evaluation of the photoelectrodes (Meshitsuka and Tamaru 1977, Ichikawa et al. 1994). For example, photoelectrode devices constructed from CuPc as a p-type semiconductor in combination with *N,N*-diphenylglyoxaline-3,4,9,10-perylenetetracarboxylic acid bisbenzimidazole as n-type semiconductor in the water phase were investigated in terms of kinetics. Each film of the p/n bilayer presents a photoanode, where the photoinduced oxidation of thiol occurs. The holes originate on account of the photophysical events in the p/n interior, involving the charge separation of excitons at the p/n interface (Abe et al. 2008).

Gas sensitive electrodes can be fabricated by use of CuPc incorporation into a polypyrrole backbone. The photoresponse in electrochemical mode increases due to the presence of phthalocyanine in the films and enhanced sensitivity towards nitrogen gas as compared to pure polypyrrole film was observed (Radhakrishnan and Deshpande 2001).

Molecular conductance junctions (Nitzan and Ratner 2003) are another important utilization of phthalocyanines. Here a molecule or a small cluster of molecules conduct electrical current between two electrodes. Copper phthalocyanine (CuPc) has been used in silicon-based molecular nanotechnology to integrate molecular electronic function with silicon surfaces (Hersan et al. 2000). The knowledge about the mechanisms of charge transfer and the role of the outer phenyl ring is important to understand the interaction with the surrounding substrate when the CuPs molecule is bound to the surface via its central copper atom (Abramczyk et al. 2006). One example is the intercalation of CuPc pyridinium complex and iron phthalocyanine into two layered titanates from Na₂Ti₃O₇ to study the microstructure control (Kaito et al. 2002).

6.2 Solar Energy

The current targets in solar energy conversion are reaching 10 % conversion efficiency. This is within reach and has caused an intensive development of organic and hybrid thin film photovoltaics (third generation solar cells). Substantial improvements have been made resulting in new device concepts and improved understanding of energy conversion processes. Films of tetrapyrrole semiconductors are promising candidates for stable and low cost electrode materials that can be used for solar energy conversion. Various copper phthalocyanines have been investigated as thin-film electrodes in photoelectrochemical cells (Yangi et al. 1993, Osada and Mizumoto 1986). Most likely, due to their stability this field will be dominated by phthalocyanine derivatives although porphyrin systems are continuously advancing (Yamashita et al. 1989).

Zinc porphyrin dimers have been incorporated into solar cells to improve their light harvesting efficiency to yield enhanced performance. Such materials have potential in next generation solar energy conversion systems as 3-dimensional light harvesting arrays (Mozer et al. 2009). Photochemical solar cells constructed from organized assemblies of single-walled carbon nanotubes and a protonated porphyrin on nanostructured SnO₂ electrodes, are photoactive and absorbed in the entire visible region (Hasobe et al. 2006). Organic–inorganic hybrid cells also demonstrated enhanced performance through use of nanoporous Si as *n*-type and CuPc.

Other studies reported the construction and analysis of photovoltaic cells fabricated with CuPc and TiO₂ (Ding et al. 2005, Arbour et al. 1990, Grätzel and Halmann 1990, Doherty et al. 2007) or ZnS (Zhang et al. 2005) nanoparticles. The dye-sensitized TiO₂ solar cell showed conversion efficiencies of 7-10 % under standard solar conditions. These high efficiencies are associated with ultrafast charge transfer from the dye to TiO₂, the high internal surface area of the TiO₂ films, the broad absorption of the dye, and the efficient separation of opposite charges between the domains. Recently, some attention has been given to composites of metal phthalocyanines and carbon nanotubes due to their high quantum efficiency facilitated by charge transfer between them and the complementary properties of the composites. These are regarded as promising candidates for the fabrication of donor–acceptor heterojunction diodes and photovoltaic devices. An example of such constructions has been reported recently for a copper phthalocyanine with long dodecyl chains covalently attached to modified multi-walled carbon nanotubes (Wang et al. 2005).

6.3 Hydrogen Production

Photochemical processes capable of the evolution of molecular hydrogen are one of the most important areas of current research. Considerable interest has followed after Fujishima and Honda reported the photoelectrochemical water splitting using a UV-responsive TiO₂ electrode (Fujishima and Honda 1972). At present, dihydrogen (H₂) energy is attracting significant attention as a “clean energy” source with water photolysis being one of the most promising procedures to produce H₂. Some of the strategies are based on the development of the an efficient solid/water interface to achieve the (photo)chemical energy conversion under solar irradiation.

A number of photosensitization reactions have been described that offer potential use in chemical applications or are of fundamental interest. One of the oldest photochemical reactions involves tetrapyrrole photosensitizers is the photoreduction of methyl viologen. Being *p*-type of semiconductors, CuPcs can be used to construct *p/n* type of organic bilayers as photoelectrodes and used in water phase (Abe and Nagai 2007). Copper tetrapyrroles can be used in aqueous solution to reduce methyl viologen (MV) from MV²⁺ to MV^{•+} which is capable of decomposing water in the presence of a catalyst. Three-component system [chromophore/donor/MV] for

hydrogen production was analyzed using CuPc as a chromophore (Yarnaguchi et al. 1986). However, sulfonated phthalocyanines compared unfavorably to metalloporphyrins (Harrimana and Reichoux 1980). Some studies were carried out on the photodynamics of these systems for future applications (Ichikawa, et al. 1995). In addition, studies on the photoexcitation of zinc porphyrin-viologen systems showed their potential use in hydrogen production (Petersson et al. 2009).

Another approach used hydrogenase active site models and metalloporphyrins. Visible light-driven hydrogen generation was observed from non-covalent assembly of a pyridyl-functionalized hydrogenase active-site model complex and zinc tetraphenylporphyrin (Li et al. 2008). Other examples included two kinds of light-sensitive, electro- and enzyme-active electrodes modified with zinc porphyrins, hydrogenase, and viologen triad multilayers. Here, the first zinc porphyrin or viologen layer was covalently immobilized on the substrate surfaces followed by hydrogenase and polyviologen layers or electrostatically adsorbed positively charged porphyrin (Liu et al. 2008).

6.4 Dye Industry

Improvements in the lightfastness of disperse dyes is a major goal in dye industry. The relationship between chemical structure and lightfastness of dispersed dyes and complete determination of the reaction mechanisms that characterize the photofading of disperse dyes on polyamide and PET substrates is of great interest. Many studies have been focused on investigating the light-induced reduction, photo-oxidation by singlet oxygen and wavelength-dependent of photo-reduction in various organic solvents, to name a few.

Himeno et al. (2000) reported that reductive fading of monoazo disperse dyes combined with vinylsulfonyl copper-phthalocyanine on nylon or polyester substrates was decreased compared to the rate of reductive fading of disperse dyes without the CuPc dye. Singlet oxygen generated by the photosensitization of CuPc dyes suppressed the reductive fading of disperse dyes. Nylon had a greater tendency to give light-induced reduction and oxidation of disperse dyes than polyester, depending upon the properties of the adsorbed dye. Some investigations were carried out purely on CuPc dyes. Examples are the photosensitized oxidation of copper phthalocyanine (CuPc) reactive dye on cellulose under different conditions (Okada 1992, Okada et al. 1990, Okada, et al. 1990b) and additives (Hihara et al. 2001), and photochemical reduction of tetrasodium salt of copper tetrasulphonatophthalocyanines with amines (Kaneko et al. 1995, 1996).

Dyes are utilized in polymer materials to enhance their color-changing properties. However, these additives can affect considerably the polymer stability towards degradation. Interestingly, CuPc can play the role of a polymer stabilizer against degradation as well as in some cases to be its trigger. The interaction mechanism of dyes can occur via two pathways (Sánchez et al. 2004, Allen 1994, Bamford and Dewar 1949). In one pathway, after the light absorption in oxygen containing media, the dye produces chemical species such as singlet oxygen and superoxide anions. These reactive species then accelerate polymer degradation. In the other pathway, the dye reaches excited singlet (S_1 , S_2) and triplet (T_1 , T_2) states. The energy absorbed is then transferred to the chemical groups in the polymeric chain via intermolecular energy transference.

For example, CuPc incorporated into polycarbonate resulted in accelerated degradation under UV-radiation. As a strong sensitizer, CuPc very likely enhances the formation of reactive species in polycarbonate. Excited states of CuPc may increase the formation of free radicals, which is the beginning for the sequential photo-oxidation processes leading to the degradation of a polycarbonate. Alternatively, photodegradation of polycarbonate triggered by CuPc may proceed via electron transfer sensitization (Saron et al. 2006). In contrast, a three component system

involving hindered piperidine (known to be effective photostabilizers for some polymers), antioxidant and CuPc have shown synergistic effects. Interestingly, CuPc alone, offered little photoprotection and some enhanced photoprotection was observed for antioxidant-CuPc. These results indicate that CuPc and a hindered piperidine exhibit a highly favorable interaction for photostabilization (Allen and Parkinson 1983). Finally, CuPc dyes can also be used as heterogeneous sensitizers to induce the photopolymerization of trimethylolpropane triacrylate (Rosche et al. 1997).

7. Green Chemistry of Tetrapyrrole Based Dyes – Photodegradation, Stabilization and Photocatalysis

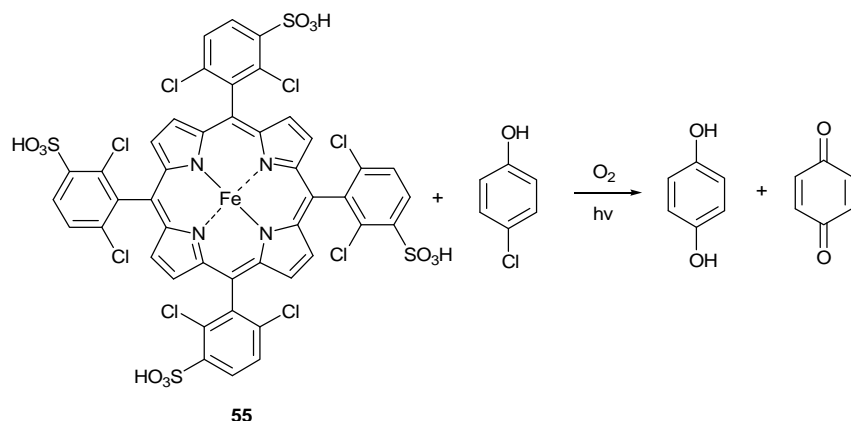
High levels of environmental contamination have been associated with dye wastewater contents from textile dyeing and finishing industry. Various types of synthetic dyes are used in textile industry including azo, anthraquinone, triarylmethane and phthalocyanines designed to be highly robust. Moreover, due to the complexity and variety of the dyes used for different purposes, as well as their non-biodegradability, it is rather difficult to find unique treatment methods that would result in effective degradation of all types of dyes. Azo dyes are the largest class of commercially used colorants, while phthalocyanines are mainly utilized as blue and green dyes. Copper phthalocyanines (**51–54**, **56** are examples of the commercially used CuPc dyes) are the most important derivatives of the phthalocyanine pigment class (Gordon and Gregory 1983). Their commercial success is based on three features: beautiful bright blue to green shades and strength, remarkable chemical stability and excellent fastness to light. Due to their low tendency to migrate in materials, CuPc are used in inks and printing, coatings, some plastics, textile and leather. However, environmentally, these advantages as robust and efficient colorants decrease the efficiency of convenient treatment technologies. Additional contamination associates with metals such as copper released during the process from the metallized dyes.

<Chemical Structure 18>

7.1 Tetrapyrrole-Based Photocatalysts

Tetrapyrroles are suitable candidates for use in (photo)catalysis, an advanced oxidation process which is used to eliminate organic pollution. The oxidation rates depend strongly on the oxidation potential of the central metal, and thus zinc(II) derivatives typically take up a central position. Some selected examples for the use of zinc(II) tetrapyrroles as photosensitizers are the oxidation of isopropyl alcohol (Uchida et al. 1977) or water (Gerasimov et al. 1991), the photochemical dediazonation of arene diazonium salts with a zinc(II) phthalocyanine derivative (Becker et al. 1986), the photocatalytic decomposition of CCl₄ (Khairutdinov et al. 1982), trichlorophenol (Kasuga et al. 2000), amino acids (Spikes et al. 1995, Zhang and Xu 1994) and of atrazine (Héquet et al. 2000). Likewise reactions with hydroquinone (Fan and Bard 1979), cellulose (Thomas and Allen 2002) and the photocatalytic destruction of organic matter in effluents from paper industry (Machado et al. 2003) were studied and a variety of antimony porphyrin based photocatalysts were prepared and analyzed (Shiragami et al. 2005).

Phenol photooxidation can also be performed by an iron porphyrin in the presence of oxygen. The main photooxidation product was *p*-benzoquinone (33 %, λ_{\max} 245 nm), although some *p*-hydroquinone (6 %, λ_{\max} 288 nm) was also observed. This is similar to reports for the degradation of phenols in the presence of phthalocyanines and other photosensitizers.



<Scheme 3>

5,10,15,20-Tetrakis(2,6-dichloro-3-chlorosulfophenyl)porphyrin and its Sn and Zn complexes were also successfully used in the photodegradation of 4-chlorophenol and 2,6-dimethylphenol (Monteiro et al. 2005). Likewise, silica microspheres functionalized with 5-(4-allyloxy)phenyl-10,15,20-tri(2,6-dichlorophenyl)porphyrin were used to oxidize 1,5-dihydroxynaphthalene under visible light irradiation in aerated aqueous solution (Cai et al. 2009). Visible light photocatalysis using SiO₂ immobilized water-soluble and -insoluble tin porphyrins degraded 4-chlorophenol and Acid Orange 7 in water. Interestingly, the visible light activity of the porphyrin photocatalyst was enhanced by increasing the loading of insoluble tin porphyrin (Kim et al. 2008).

Photocatalysts prepared *in situ* by CuPc immobilization on Al and encapsulated inside zeolite-X showed a remarkable affinity towards CN⁻. Here, photooxidation is based on transferring electrons from the zeolite to cyanide ions in solution (Mohamed and Mohamed 2008). Mesoporous catalysts prepared from 3-aminopropyltrimethoxysilane and (hexadecafluorophthalocyaninato)copper(II), followed by co-condensation of tetraethylorthosilicate around a micelle formed by *n*-dodecylamine demonstrated efficacy for photodegradation of organochloride compounds, industrial dyes and pesticides with unproblematic recuperation from the reaction medium (DeOliveira et al. 2008).

7.2 Tetrapyrrole Photocatalysts Based on Titanium Dioxide

TiO₂-based photocatalysts are being used in photocatalytic technologies for the degradation of organic compounds in water. In past decades, interest has focused on the development of economically and environmentally friendly catalytic systems with enhanced activity of TiO₂-based catalysts for use in the oxidative degradation of various organic pollutants. Several studies have been also carried out to investigate the influence of different semiconductor types such as Al₂O₃ or WO₃ and phthalocyanine complexes on the photoactivity. For example, it was found that the photocatalytic activity of the phthalocyanine complexes, supported on TiO₂ or WO₃ was much higher compared to dielectric Al₂O₃.

Thus, titanium dioxide (TiO₂) is one of the most popular materials to be used as a photocatalyst for air treatment and degradation of organic pollutants in water. Having a large band gap (3.2 eV with $\lambda \leq 385$ nm), TiO₂ can consume only about 5 % (with energy above 3.0 eV, $\lambda \leq 410$ nm) of solar light reaching the earth surface. Thus, to increase the efficiency of solar energy utilization through TiO₂, it is often doped with transition metal ions or organic dyes to shift the photoresponse of the catalyst into the visible region. In view of its low cost and feasibility, dye sensitization is considered to be an effective method to modify the photochemical properties of TiO₂ particles. Mechanistically, the photosensitization of TiO₂ proceeds via initial excitation of

the dye. A photoinduced electron transfer from excited dye to TiO_2 and the surface reaction of TiO_2 conductive band electron were suggested as the key processes.

Systematic investigations demonstrated the existence of an optimum photoreactivity depending on the amount of impregnated porphyrin. It was shown that TiO_2 impregnated with Cu-based sensitizers is beneficial for the photoactivation of TiO_2 , and CuP's (Mele et al. 2003, 2005, Wang et al. 2007) and CuPc's have shown to improve the photocatalytic activities of these photocatalysts.

Comparative studies showed that TiO_2 samples doped with CuP and FeP are more photoactive than simple TiO_2 (anatase), whereas samples including MnP showed less photoreactivity (Mele et al. 2007). Free-base porphyrins have shown slightly higher photoactivity than TiO_2 , suggesting that the porphyrin macrocycle is photocatalytic as well. However, samples impregnated with CuP exhibited the highest photoactivity. These results, related to the photodegradation of 4-nitrophenol (4-NP) in an aqueous heterogeneous environment, suggest that the Cu(II)-Cu(I) photocatalytic redox cycle plays the main role in the process.

Similar results were shown for a series of TiO_2 -CuPc's systems where different Cu(II)Pc (TiO_2 -CuPc) were examined for their photocatalytic degradation of 4-NP (Mele et al. 2002). The high photocatalytic activity was explained by an electron transfer from the conduction band of the excited Pc to the conduction band of a semiconductor. Recent studies have shown that the photocatalytic activity of polycrystalline TiO_2 samples impregnated with rare-earth-metal diphthalocyanines in the 4-NP photocatalytic degradation show better photoactivity for the complexes of lanthanide metals, such as Nd, Sm and Ho (Mele et al. 2007b). Improved photocatalytic activity was observed in the decomposition rates of 4-NP for TiO_2 -lanthanide diphthalocyanines over those impregnated with Cu(II)P's.

Plastic is widely used all over the world and its waste as the so-called "white pollution" has been recognized as one of the central environmental problems. Heterogeneous photocatalytic oxidation can occur under moderate conditions, such as room temperature, atmospheric pressure, and molecular oxygen as the only oxidant. Recently, studies of the solid phase photodegradation of TiO_2 -embedded plastic upon irradiating the composite film for 300 h under air have shown reduction of its average molecular weight by two-thirds and weight by 27 % (Cho and Choi 2001). Comparative studies have been carried out on polystyrene incorporated in (TiO_2 /CuPc) and TiO_2 alone. Faster photocatalytic degradation of polystyrene was observed in polystyrene- TiO_2 /CuPc than in polystyrene- TiO_2 . During photocatalytic degradation, activation of polystyrene by the reactive oxygen species attacking neighboring polymer chains leads to chain cleavage and production of new reactive radicals. The higher charge separation efficiency of TiO_2 /CuPc photocatalyst results in more effective generation of reactive oxygen species both on surface and inside thin film, polystyrene undergoes faster and completer mineralization over TiO_2 /CuPc than over TiO_2 photocatalyst (Shang et al. 2003).

Another serious environmental problem is caused by azo dyes from textile industry. Here, methyl orange is often selected as a reliable model to investigate decolorization and decomposition of azo dyes using photocatalysts. Photo-stable copper 2,9,16,23-tetracarboxyl phthalocyanine (CuTcPc) doped with amorphous TiO_2 (am- TiO_2) hybriide photocatalyst exhibits excellent photocatalytic activity towards methyl orange under visible irradiation ($\lambda > 550$ nm) (Chen et al. 2005). In contrast, no photobleaching of methyl orange was observed with bare am- TiO_2 at $\lambda > 550$ nm. Degradation of acid chrome blue K was achieved with TiO_2 based photocatalysts containing carboxy and nitroporphyrins. Here, the photoexcited sensitizer had remarkable effects on the photodegradation of the dye under natural sunlight (Li et al. 2008b).

7.3 Photodegradation of CuP and CuPc Dyes

Although porphyrins and especially phthalocyanines are stable compounds, both will undergo photooxidative degradation or photoexcited ET reactions. The phthalocyanine systems are very stable even in advanced catalytic processes such as photocatalytic oxidation. Photoelectrocatalytic oxidation attracts considerable attention as a way to increase the photocatalytic efficiency in degradation of organic pollutants and studies have been carried on to apply this methodology for decolorization of Pc systems.

For example, the decolorization of commercially relevant reactive CuPc-dyes – e.g., the *Remazol Turquoise Dyes* family - was studied in aqueous solutions under different conditions. For example, *Remazol Turquoise Blue 15 (56)* was investigated by direct cathodic reduction on platinum electrode and photoelectrocatalytic oxidation on Ti/TiO₂ as nanostructured semiconductor thin-film electrodes with higher efficiency for combined processes of photoelectrocatalytic oxidation and electrochemical reduction (Osugi et al. 2006).

<Chemical Structure 19>

Some studies on photostable CuPc sulfonates sodium salts were carried out under UV ($\lambda > 320$ nm) or visible light ($\lambda > 450$ nm) in the presence of a TiO₂ semiconductor in an aqueous medium. They underwent photobleaching in the presence of TiO₂. The spectral analysis showed that the dye photobleaching led to complete destruction of the phthalocyanine ring. In addition, the stability of the dye towards visible light was greatly affected by the physical properties of TiO₂ semiconductors, and the dye photostability could be improved through addition of electron sacrificers such as 4-chlorophenol (Sun et al. 2005).

Another example of photodegradation catalyzed by titanium dioxide is illustrated for the CuPc dye **54** (*Alcian Blue 8 GX*) (Caliman et al. 2007). This dye is one of the so-called biological stains, such as *Eosin Y*, *Auramine O*, *Hematoxylin*, or *Rose Bengal* etc. which are widely used in biomedical research laboratories and for diagnostic purposes. Some of them are known to be toxic or mutagenic to humans and animals, highly resistant to microorganisms such that biological wastewater treatment processes are very inefficient in treating of these dyes. Decolorization and mineralization of phthalocyanine dye **51** (*C.I. Direct Blue 199*) has been studied using an advanced oxidation process. Decolorization was found to be more difficult than that of an azo dye (*C.I. Acid Black 1*) under the same operating conditions (Shu and Chang 2005).

8. Photomedicine

8.1 Photodynamic Therapy and Singlet Oxygen Production

The interaction of tetrapyrrole derivatives with oxygen under the influence of light, and their photostability, has been a matter of great interest due to its medicinal relevance. Photodynamic therapy (PDT) presents the only one clearly established medicinal application of porphyrins and relies on the selective accumulation of a tetrapyrrole photosensitizer in target tissue where it can be activated with light to produce toxic singlet oxygen resulting in e.g. tumor necrosis. Typically, two different photosensitization processes are discussed. Type I reactions include charge transfer, whereas the type II pathway involves transfer of excitation energy from porphyrin to triplet oxygen. Several porphyrin-based compounds have been approved for medicinal applications and others are in Phase-2 trials. (Spikes and Bommer 1991, Bonnett 2000, Wiehe et al. 2005, Dougherty et al. 1998, Shumov et al. 1978, Kessel and Dougherty 1999, O'Connor, et al. 2009). Amongst these tetrapyrroles, chlorophyll derivatives are currently under active investigation and show some promise (Nyman and Hynninen 2004). The use of chlorophyll derivatives in technical applications is still in the early developmental stage.

Although many different derivatives are under investigation the majority of compounds are free base derivatives. The situation is different for zinc(II) phthalocyanines. A classic study on zinc(II)phthalocyanine of type **3** showed that it is an efficient photosensitizer for singlet oxygen with a quantum yield of *ca* 0.4 (Valduga et al. 1995). The efficiency of the photosensitization reaction strongly depends on the macrocycle conformation and substituent pattern (Weitman et al. 2001). Thus, the quantum yield for singlet oxygen generation for tetrasulfonated zinc(II) phthalocyanines (0.7) is almost three times that of the zinc(II) naphthalocyanines (0.25) (Spikes et al. 1995). Phthalocyanine derivatives exhibit some photophysical advantages compared to porphyrins: increased Q-band absorption coefficient, red-shifted absorption bands resulting in deeper light tissue penetration (Ochsner 1996), high triplet quantum yields, long triplet lifetimes and high singlet oxygen and fluorescence yields (Rosenthal 1991). For specific substituents pattern this can result in improved photodynamic activities compared to commercial photosensitizers (Ochsner 1996, Ball et al. 1998).

A few current examples are shown below and include unsymmetrically substituted derivatives **57** (Kudrevich et al. 1997), the cationic derivative **58** (Fernández et al. 1997), the neutral derivative **59** (Ball et al. 1998) and the classic anionic derivative **60** (Griffiths et al. 1994, 1997). "(Tetrabenzoporphyrinato)zinc(II)", an intermediate structure between that of porphyrins and phthalocyanines, has also been investigated in this respect. However, its quantum yield for singlet oxygen generation in liposomes (0.023) is much lower than that of Photofrin (0.19) (Gross et al. 1993). Other examples are zinc, palladium, copper and free-base porphyrin complexes of 5-(4-(trimethylammonium)phenyl)-10,15,20-tris(2,4,6-trimethoxyphenyl)porphyrin iodide (Milanesio et al. 2008) or compounds with photocleavable linkers as photodynamic prodrug systems (Bakar et al. 2009, Jiang and Dolphin 2008). Note, that zinc derivatives are not necessarily the best metal derivatives of phthalocyanines for use in PDT (Canti et al. 1992). Taking aspects like tissue clearance and target specific localization into account, porphyrin derivatives will most likely carry the field in this application. In addition, many of these systems are under scrutiny for their antibacterial action (Segalla, et al. 2002).

<Chemical Structure 20>

A series of meso substituted tetracationic porphyrins have been synthesized and the role of amphiphilicity and zinc insertion in photodynamic therapy efficacy (such as fluorescence and singlet oxygen quantum yields, uptake by vesicles, mitochondria and HeLa cells, dark and phototoxicity in HeLa cells) were studied (Pavani et al. 2009). Some studies have been carried out to investigate copper tetrapyrroles with regard to singlet oxygen production for use in PDT. For example, the iminium salt of octaethylbenzochlorin copper complex **61** was tested for its tumoricidal effects on the AY-27 N-[4-(5-nitro-2-furyl)-2-thiazolyl] formamide tumor line and was found to be an effective photosensitizer *in vivo* in combination with non-coherent light sources. Skin photosensitization was found to be minimal when drug-injected mice were illuminated in a solar simulator (Selman et al. 1993). As expected, the photodynamic ability of this complex required the presence of molecular oxygen in order to generate reactive species upon light activation (Hampton et al. 1993, Cavaleiro et al. 2001).

Sometimes, the efficacy of one-photon PDT is limited by hypoxia, which can prevent the production of the cytotoxic singlet oxygen species, leading to tumor resistance for PDT. To solve this problem, two-photon excitation of the photosensitizer can be employed. Excitation of the CuPc triplet state leads to an upper excited triplet state with distinct photochemical properties, which could inflict biological damage independently from the presence of molecular oxygen (Fournier et al. 2004). The potential of a two-photon excitation process was investigated on

Jurkat cells incubated with copper phthalocyanine tetrasulfonate (Mir et al. 2008). Significant advances can be expected from this line of research.

Tetrapyrroles have also found wide use in DNA binding and intercalation studies (Meunier 1992) and type II photosensitized reactions (Foote 1991) offer an intriguing possibility for site-specific photoinduced oxidation of DNA. Most studies were performed with free base porphyrins (Caminos and Durantini 2008) but a recent example is the use of a tetraruthenated zinc(II) porphyrin (Adam et al. 1997) for the specific photooxidation of 2-deoxyguanosine bases to form 8-oxo-2-deoxyguanosines (Araki et al. 2000).

Other studies showed that copper-based tetrapyrroles can exhibit photonucleolytic activity and may be used for the DNA cleavage. Many copper complexes have been shown to exhibit nuclease activity in the presence of external co-oxidants (Borah et al. 1998, Hegg and Burstyn 1996, Baudoin et al. 1998, Itoh et al. 1997, Dhar and Chakravarty 2003, Melvin et al. 2000). Only few reports are available where copper-(II) complexes promote DNA cleavage on their own (Reddy et al. 2004, Verma et al. 2004). For example, hexaporphyrin dyads were synthesized from *n*-butyl stannonic acid and 5-(4-carboxyphenyl)-10,15,20-tritolyldiporphyrin (H₂TTP-CO₂H) followed by copper insertion as artificial nucleases (Chandrasekhar et al. 2005) The Cu-hexaporphyrin **62** showed high nuclease activity towards DNA supercoils. Interestingly, DNA cleavage did not occur in the presence of the free base hexaporphyrin alone and a monomeric CuP complex also failed to cleave it. Considerable inhibition of DNA cleavage in the presence of singlet oxygen quencher NaN₃ suggests the involvement of reactive oxygen species for cleavage.

<Chemical Structure 21>

Another example of potentially useful biomolecules is presented by the porphyrin **63** (Chandra et al. 2003) units. Enediynes (Golik et al. 1987, Lee, 1987) themselves are known to undergo rearrangements to form diradicals upon photoactivation leading to H-abstraction from DNA and cell death (Smith and Nicolaou 1996). It is interestingly to note, that "doubly N-confused" copper porphyrins have also been synthesized and investigated in terms of their singlet oxygen production. The free base "doubly N-confused" porphyrin complex **64** exhibits a low fluorescence quantum yield of 9.1×10^{-3} , which is completely suppressed in the Cu(III)P complex **65**. However, a high singlet oxygen quantum yield ($\phi_{\Delta}=0.66$) was observed for the Cu(III). These results were explained in terms of enhanced intersystem crossing rates, induced by a heavy atom effect, rather than a redox quenching involving the metal ions in an unusually high oxidation state. The "confused porphyrins" are photochemically stable in oxygen-free solution but are bleached more or less rapidly by photogenerated singlet oxygen in the absence of other quenchers (Engelmann, et al. 2004).

Phthalocyanines act as photosensitizers for the production of singlet oxygen in a similar manner to the porphyrins. Besides their catalytic properties, as discussed above, TiO₂ can be used to kill bacteria under UV irradiation. For instance, *Lactobacillus acidophilus*, *Saccharomyces cerevisiae*, and *Escherichia coli* can be completely sterilized when incubated with platinum-loaded TiO₂. TiO₂ photocatalysis is known to generate various active oxygen species, such as hydroxyl radicals and peroxide, and superoxide radical anions under UV irradiation. These properties can be used to develop disinfection materials and self-disinfecting thin films particularly attractive in places such as hospitals or for emergency medicine in disaster zones. Dye-sensitized TiO₂ films prepared with CuPc as sensitizers have shown bactericidal activities. E.g., such films can kill *E. coli* DH5 α bacteria under visible light irradiation ($\lambda > 420$ nm) and the bactericidal activity is related to the adsorption amount of the dye on film (Yu et al. 2003).

Dyes can also be attached to polymers soluble in water or/and in polar solvents, or to the insoluble polymer supports for recovery from the reaction medium for further reuse. CuPc can be easily functionalized for preparation of polymer hybrid thin films (Choe et al. 2004). For example; CuPc was linked to an amino group of *Amberlite IRA-93* and is strongly fluorescent in the solid state and in DMF suspension. Singlet oxygen quantum yields were determined in suspension by monitoring the photooxidation of diphenylisobenzofuran. Fluorescence and singlet oxygen production are environmentally depended on dye aggregation (Bourdelande et al. 1997). The degree of aggregation plays an important role in the photochemical mechanisms of photooxidation. Singlet oxygen production in these systems is expected to be different for monomers (Abramczyk et al. 2004).

Currently, photodynamic antimicrobial treatment is gaining more interest. Although photosensitizing agents and light have been used for medical purposes for a very long time, only little information is available about the exact mechanism of PDI for bacteria. Some studies have been carried on Gram negative bacteria involved in chronic infections such as cystic fibrosis and also one of the common causes of hospital acquired infections. Recent examples are studies of the phototoxic effects of the (acridyl)bis(arginyl)porphyrin on the sensitivity of *Pseudomonas aeruginosa* (Steenkeste et al. 2010). The photodynamic inactivation efficiency of *Escherichia coli* was investigated in bacteria treated with 5,10,15-tris[4-(3-N,N,N-trimethylammoniumpropoxy)phenyl]-20-(4-trifluoromethylphenyl)porphyrin iodide. Here photosensitization activity of the porphyrin such as damage of plasmid and genomic DNA was compared with other porphyrin based active tetracationic sensitizers (Caminos et al. 2008).

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Legends to Figures:

Figure 1. Cartoon scheme of a photosynthetic system. (RC = reaction center, DA = donor acceptor complex, LHC = light harvesting complex)

Figure 2. Simplified Z-scheme of the photosynthetic apparatus in Higher Plants.

Figure 3. Schematic view of a biomimetic electron transfer compound.

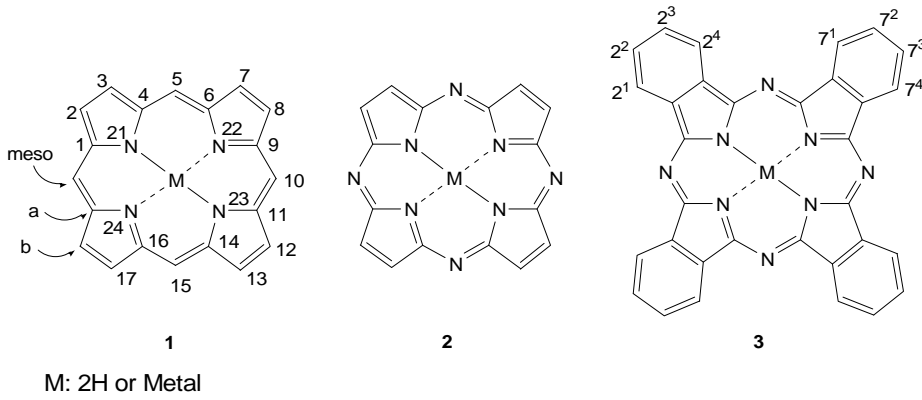
Figure 4. Synthetic model of a natural photosynthetic system.

Figure 5. Porphyrin-*o*-quinone systems.

Scheme 1. Photochemical ring-opening reactions of Mg(II)OEP.

Scheme 2. Photochemical reactions of chlorophyll

Scheme 3. Photooxidation of phenols.



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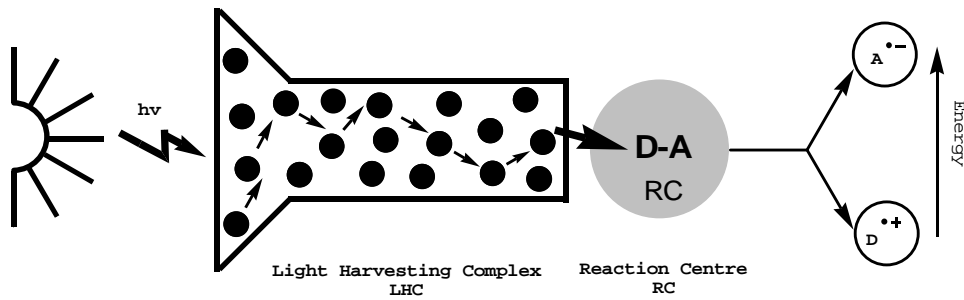


Figure 1. General scheme of a photosynthetic system. (RC = reaction center, DA = donor acceptor complex, LHC = light harvesting complex)

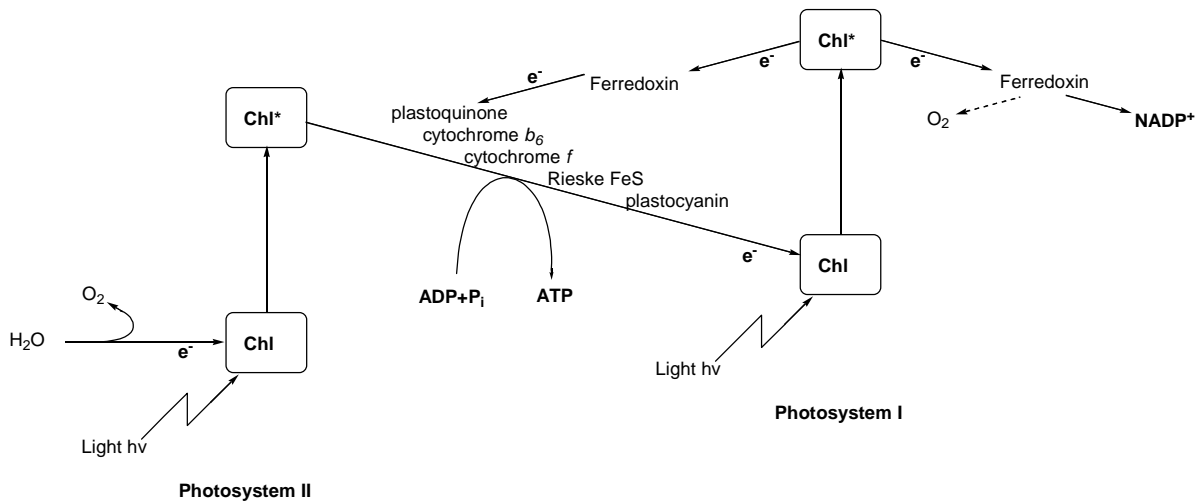


Figure 2. Simplified Z-scheme of the photosynthetic apparatus in Higher Plants.

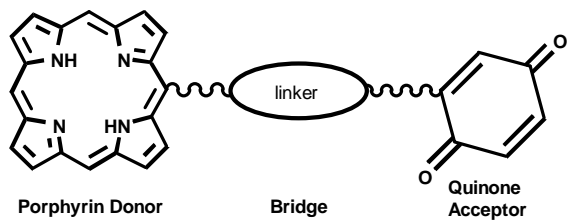
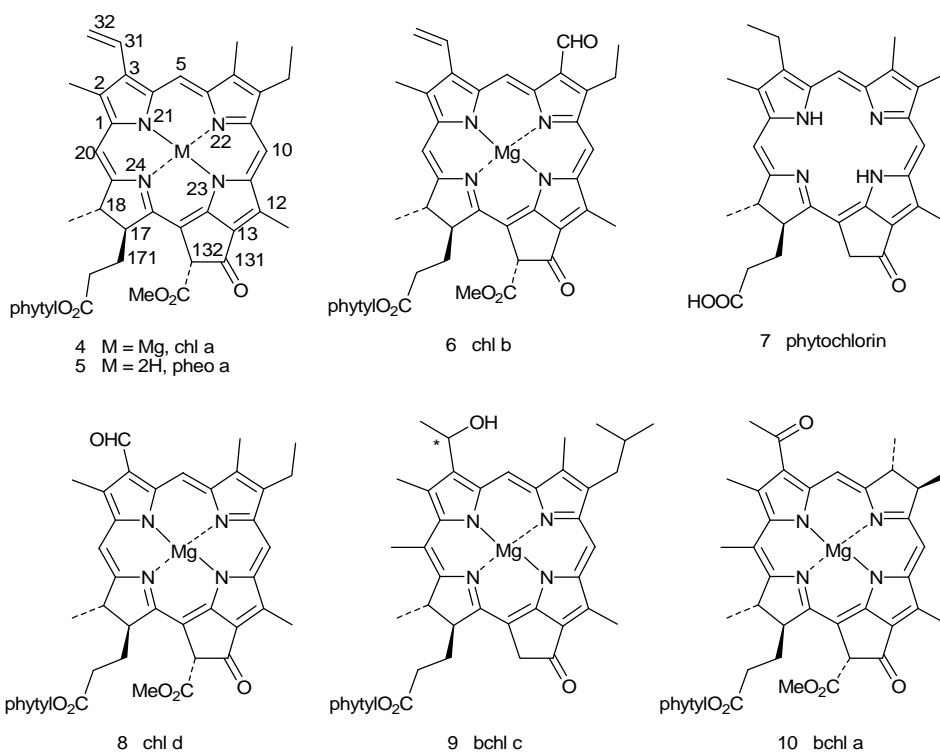


Figure 3. Schematic view of a biomimetic electron transfer compound.



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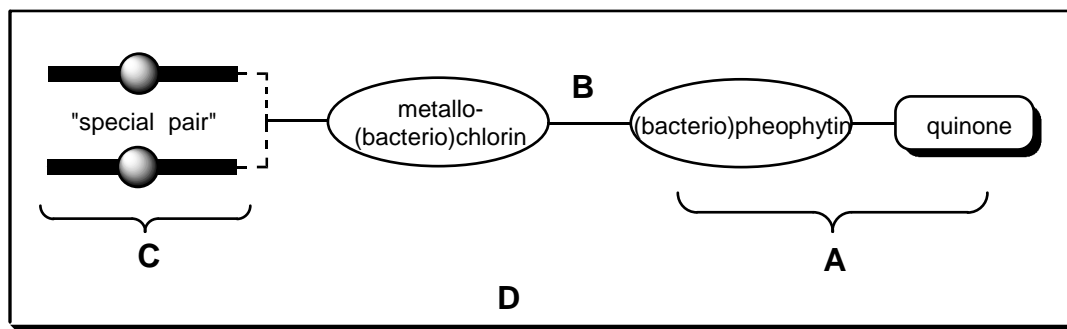
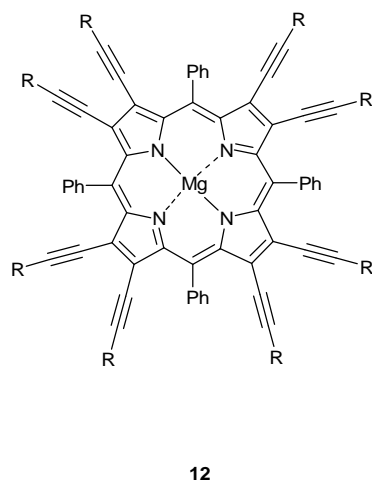
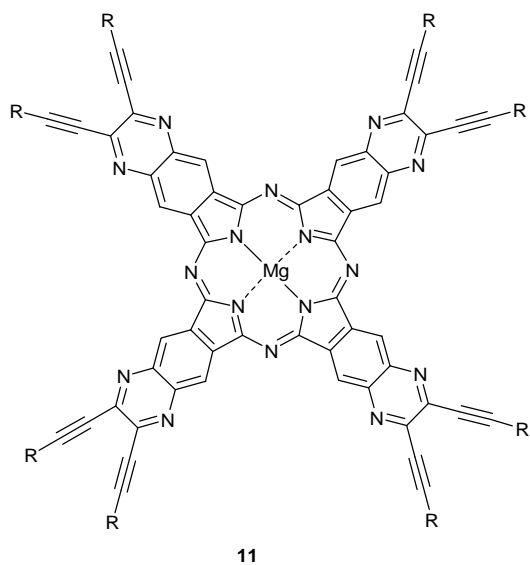
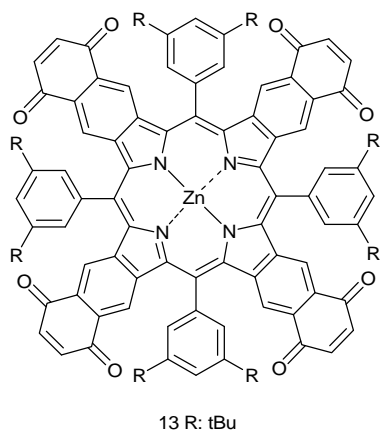


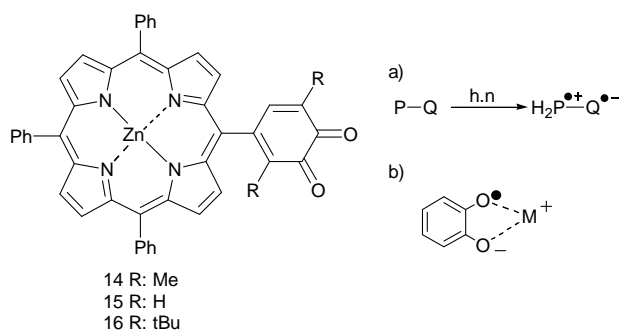
Figure 4. Synthetic model of a natural photosynthetic system.



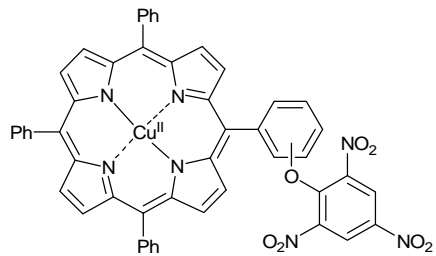
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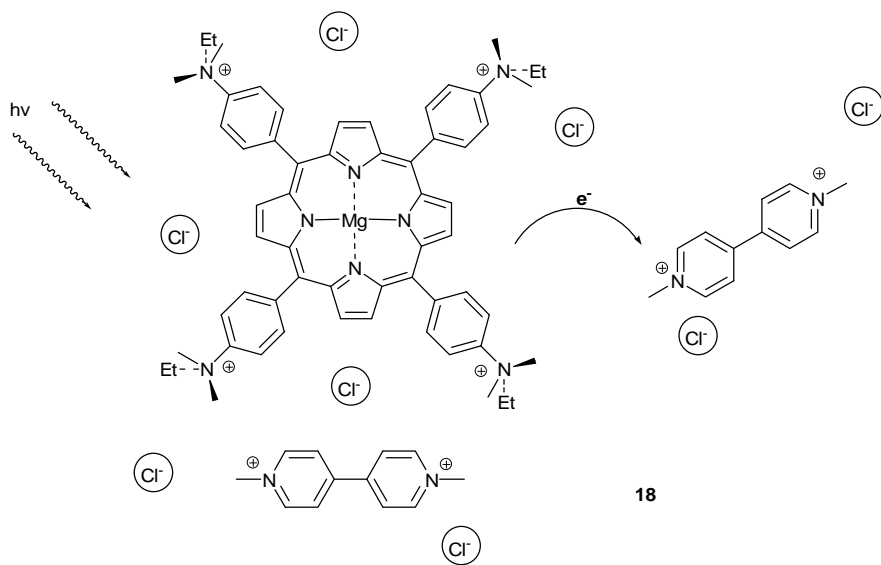


<Figure 5> Porphyrin-*o*-quinone systems.



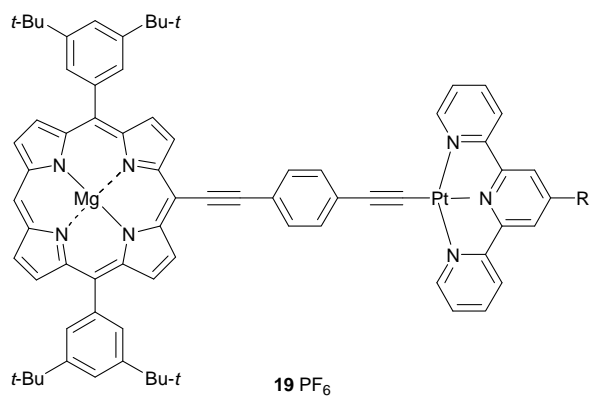
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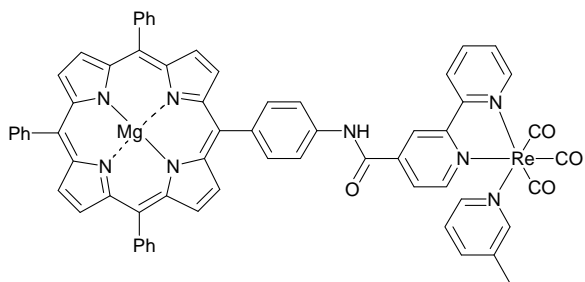


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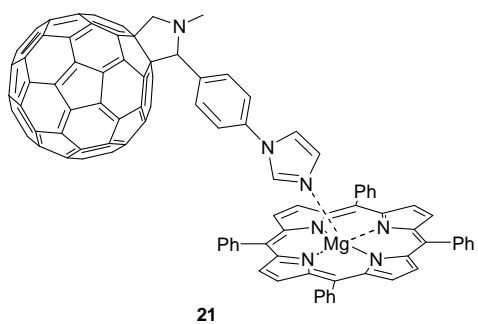


19 PF₆

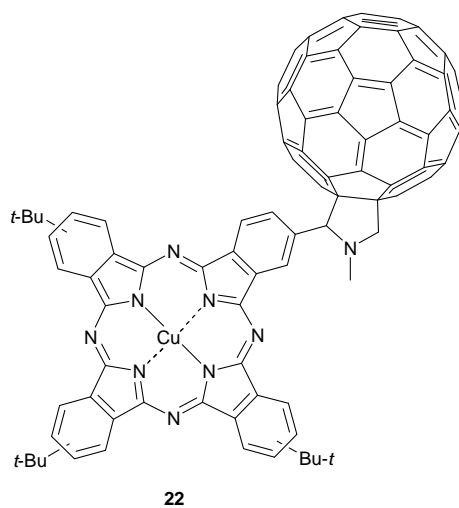


20 PF₆

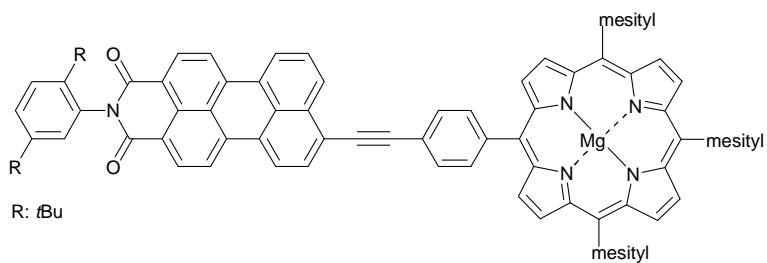
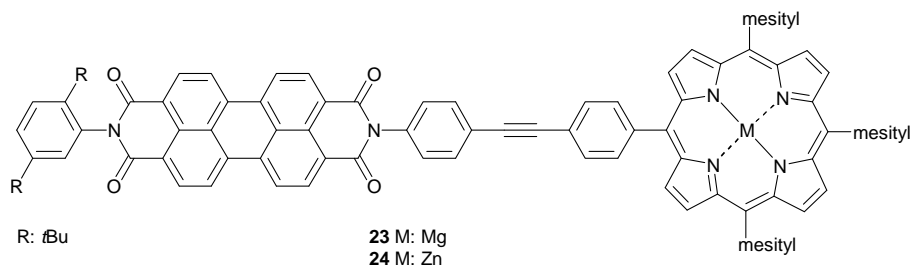
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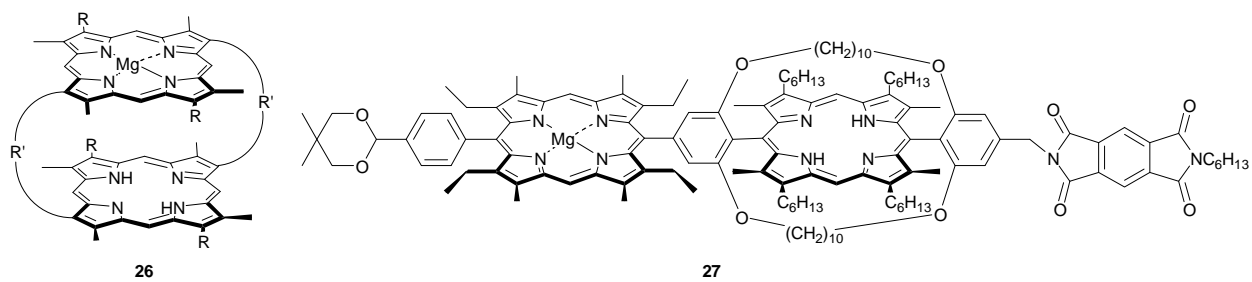


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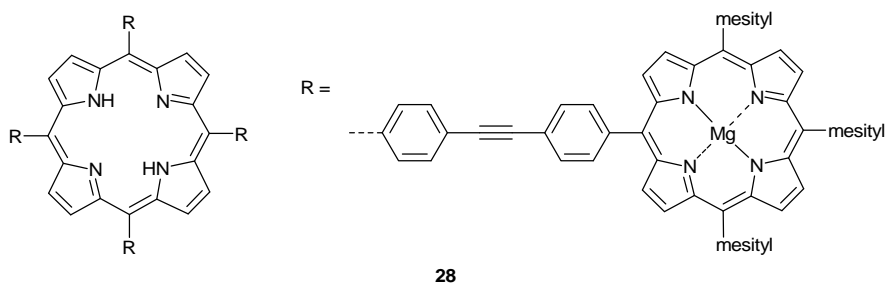
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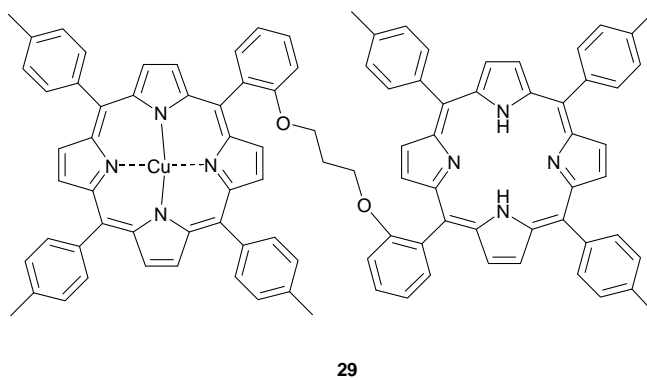


R: $n\text{-C}_8\text{H}_{17}$, R': $\text{CH}_2\text{CON}(n\text{-Bu})\text{CH}_2\text{CH}_2$

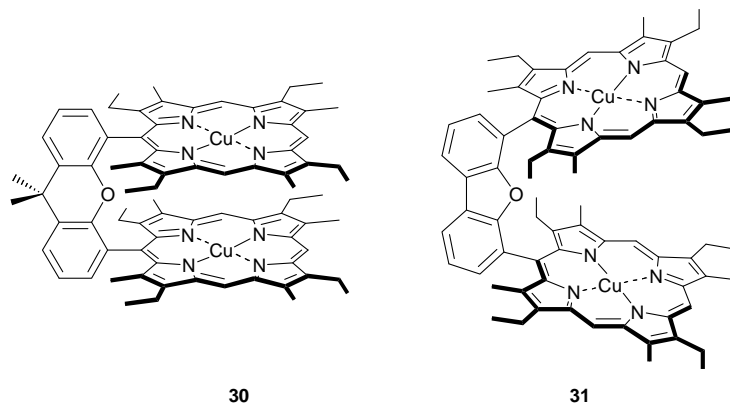
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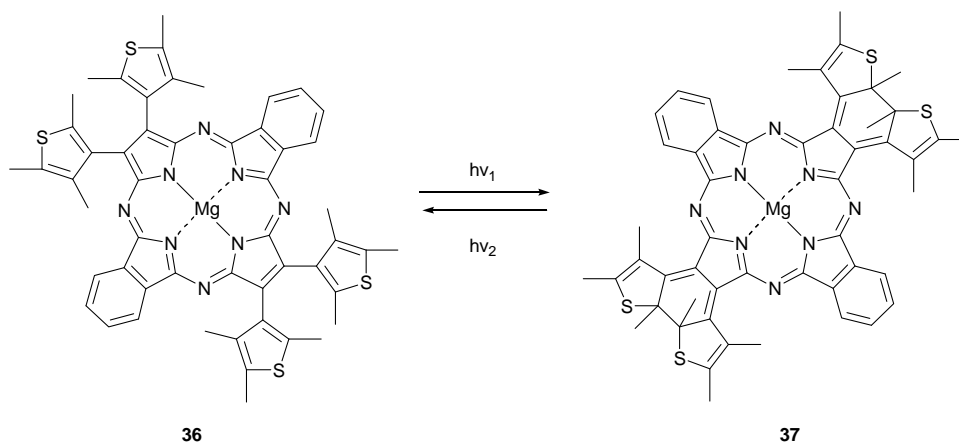
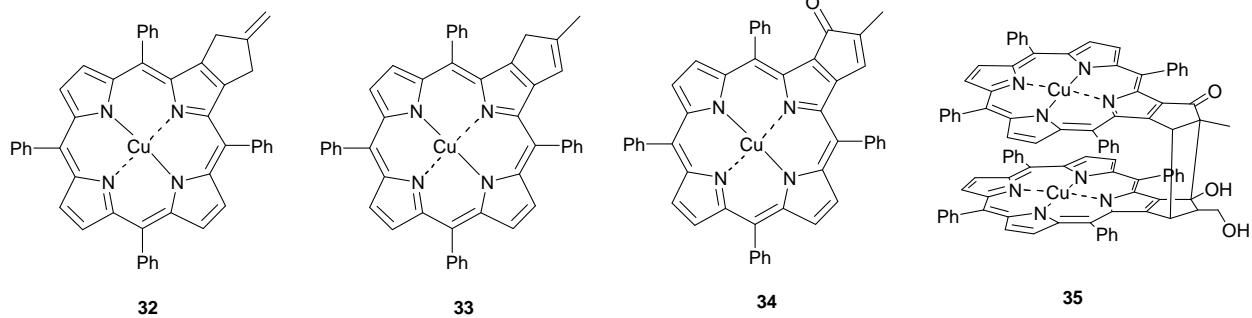
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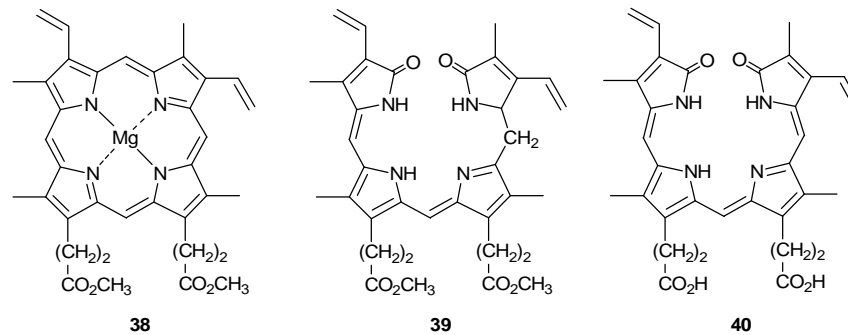
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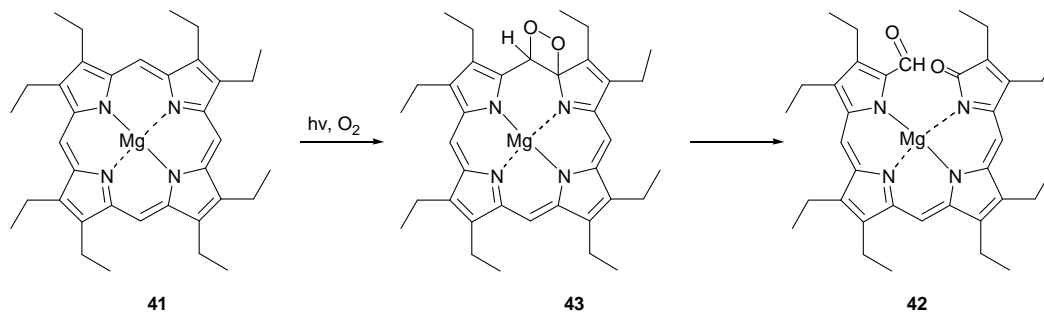
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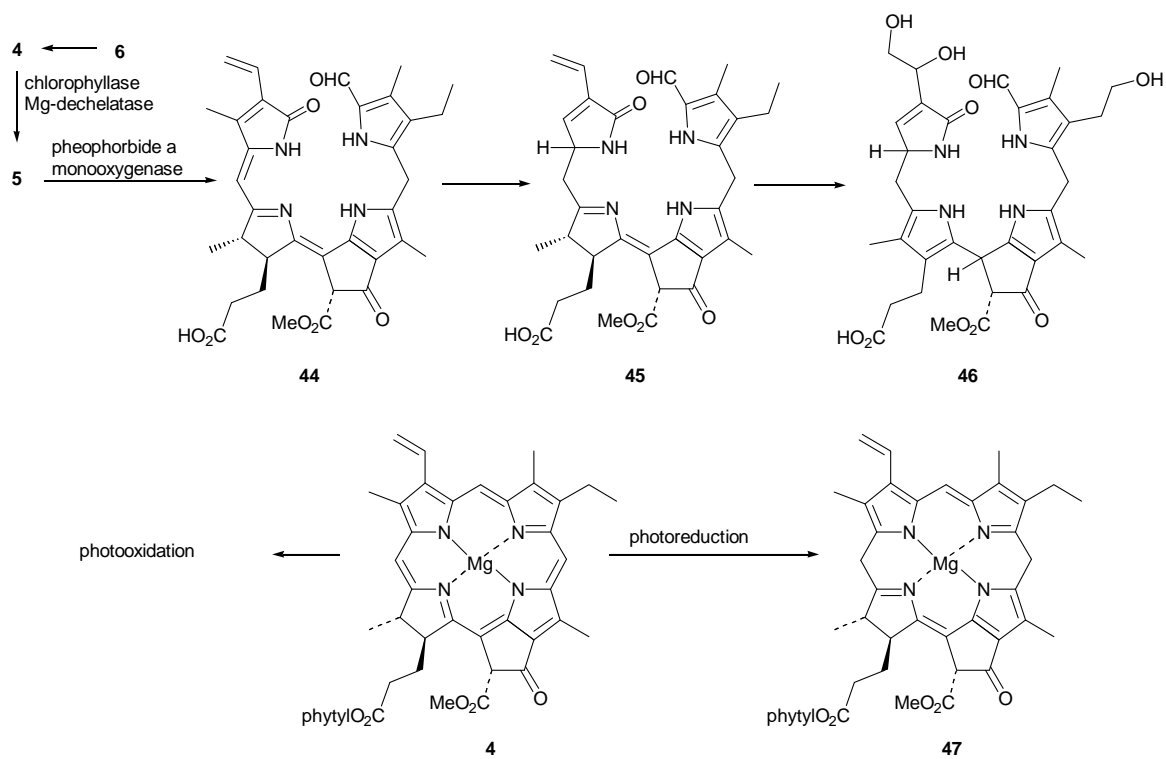
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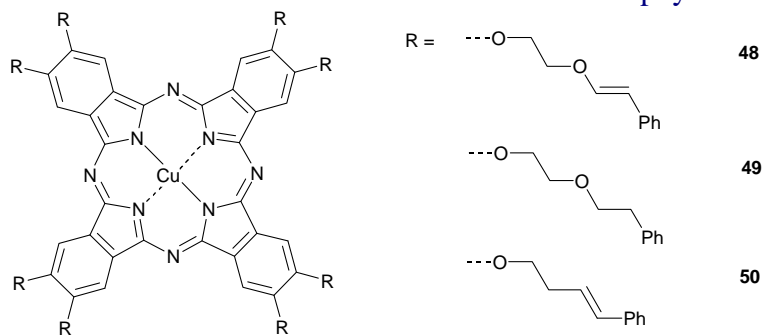
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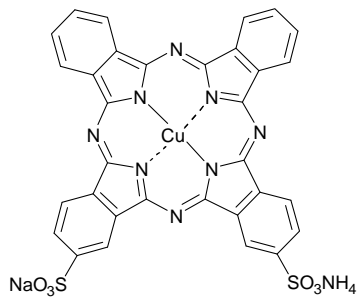
Scheme 1. Photochemical ring-opening reactions of Mg(II)OEP.



Scheme 2. Photochemical reactions of chlorophyll.

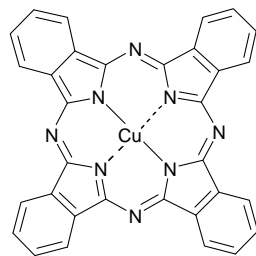


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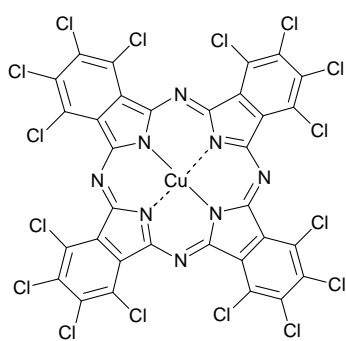
C.I. Direct Blue 199

51



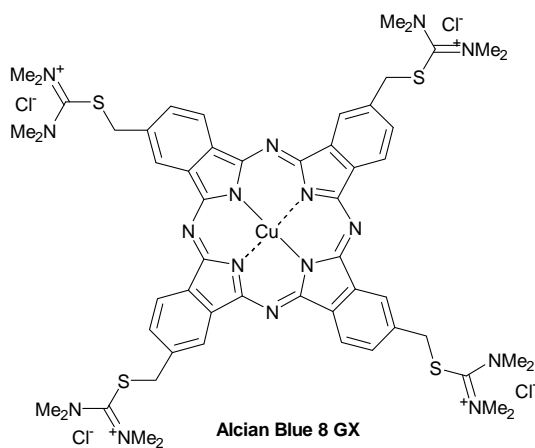
Phthalocyanine Blue BN

52



Phthalocyanine Green G

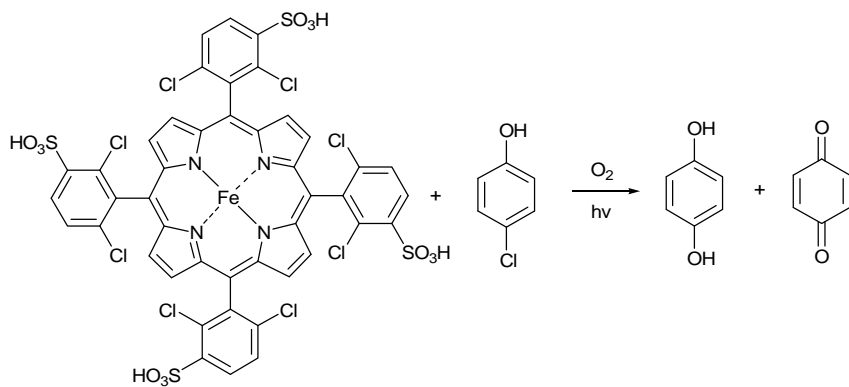
53



Alcian Blue 8 GX

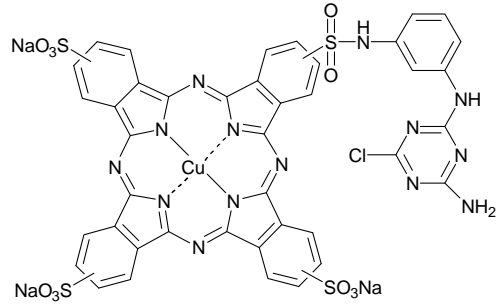
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<Chemical Structure 18>



55

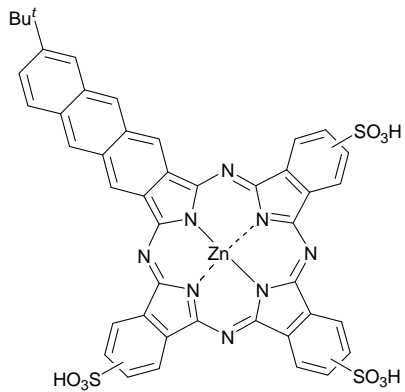
Scheme 3. Photooxidation of phenols.



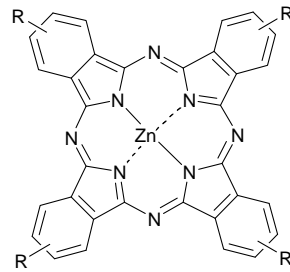
Remazol Turquoise Blue 15

56

<Chemical Structure 19>



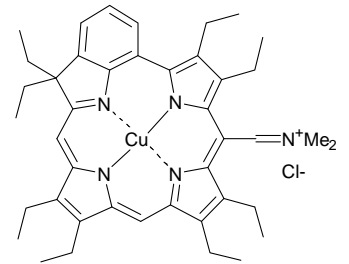
57



58 R = C(CH₃)₂CH₂N⁺

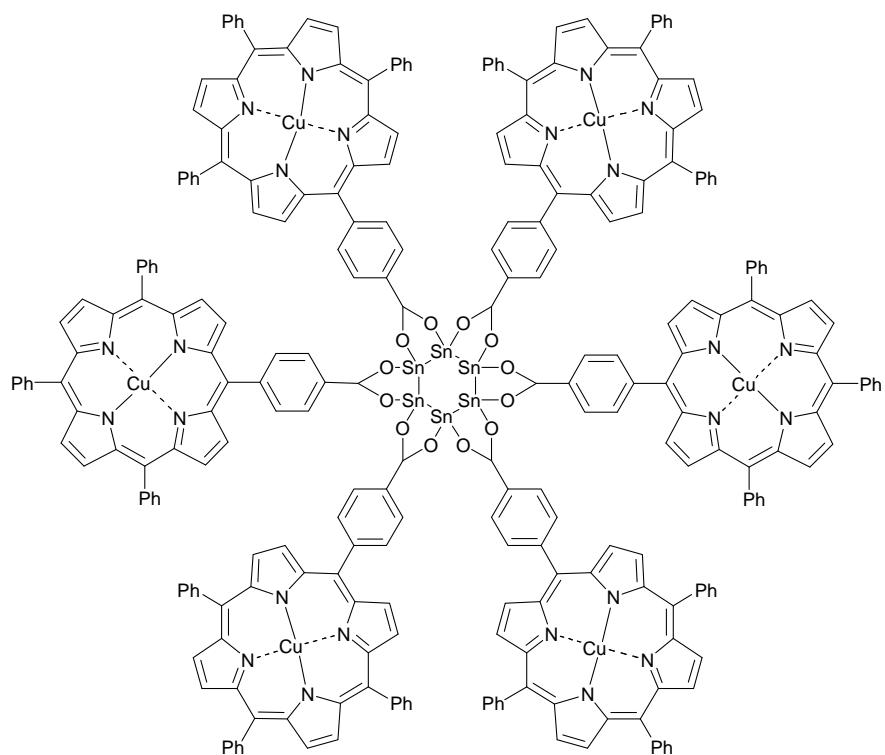
59 R = SO₂N(C₈H₁₇)₂

60 R = SO₃⁻

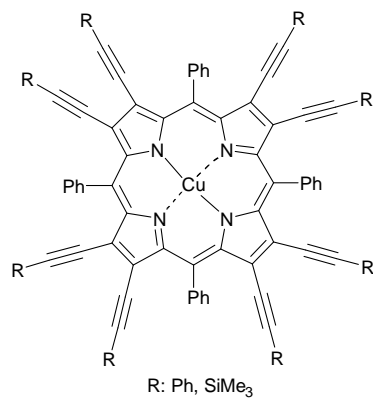


61

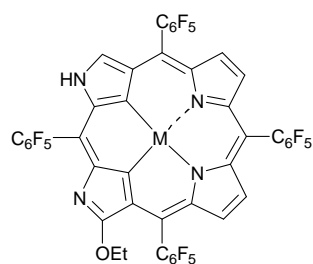
<Chemical Structure 20>



62



63



64 M: 2H

65 M: Cu(III)

<Chemical Structure 21>