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METALLOPHTHALOCYANINES: SYNTHESIS, PROPERTIES AND APPLICATIONS – A REVIEW

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Abstract: Phthalocyanines (Pcs) are an exciting class of molecules that exhibit appreciable physical and chemical stabilities. The Pc macrocycle can host most metal ions in its cavity; hence numerous metallophthalocyanines (MPcs) have been synthesized, characterized, studied and assessed for their potential applicabilities in diverse areas of mankind. The nature of the metal ion encapsulatede within the Pc cavity plays a crucial role in the properties, reactions and of course, applications of the resulting MPc. MPcs exhibit a wide range of applications ranging from industrial, technological to medical, especially in oncology. . A review of the chemistry of MPcs (synthesis, properties and applications) is hereby presented.

Keywords: Metallophthalocyanine, synthesis, electronic spectra, solvents, reactions, singlet oxygen

Introduction

The chemistry of phthalocyanines (Pcs, Fig. 1) has continued to gain popularity in the last few decades because of the extensive application of these compounds in man's everyday life. The robust chemistry of Pcs is exploited in their use as electrocatalysts and photocatalysts. However, not many Pc derivatives can play both roles efficiently. While electrocatalysis requires the central metal in the metallophthalocyanine (MPc) to be electroactive, the existence of a transient but relatively long-lived excited state is vital for photocatalysis. Such a metastable state could be rapidly "quenched" in the presence of features which promote energy and charge (electron) transfer. This excludes Pcs containing electroactive transition metal centres from photocatalytic activity. A diamagnetic metal centre is neither electroactive nor does it rapidly quench the metastable excited state.

Aluminium phthalocyanine derivatives have been successfully used in the photodynamic therapy (PDT) of cancer (Kuznetsova *et al*., 1990; Edrei *et al*., 1998), and there is an on-going aggressive effort to use the zinc analogue for the same purpose. It is believed that zinc would have some advantages over aluminium, as it is not alien to the animal body system. Zinc is an essential nutrient for the functioning of a large number of enzymes involved in the growth of animals.

The chemistry of phthalocyanines is not only of academic interest. The application of Pcs in man's everyday life and the industry cannot be overemphasized. Again, because of the similarity of the Pc structure to that of porphyrin (Fig. 1), which is the core framework in hemoglobin and chlorophyll, Pcs have attracted much attention as replicates of such vital biological systems.

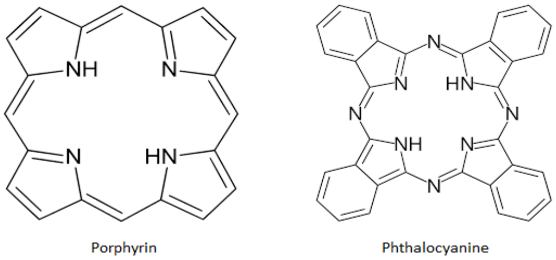


Fig. 1: Molecular structures of porphyrin and phthalocyanine

General applications of phthalocyanines

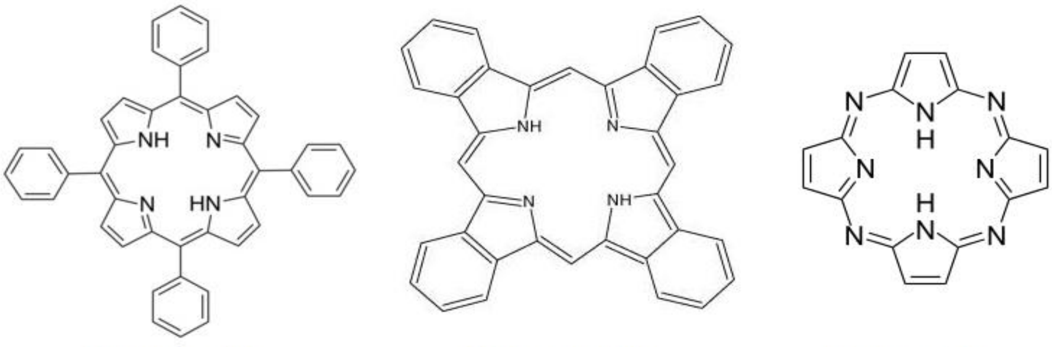
The substituted Pc derivatives function as active components in various processes driven by visible light (Lim *et al*., 1999). In this respect, they find applications in photoredox reactions, photooxidations in solution (Leznoff and Lever, 1989-1993), photochemical cells and photovoltaic cells (Wöhrle and Meissner, 1991). Pcs also possess electronic and morphological characteristics that are especially favourable for semiconductive or conductive properties (Lim *et al*., 1999). Pcs also find use as light absorbing layers in rewritable optical media (CD-RW) (Gan, 2000), photoconducting materials in laser printers, non-linear optics (optical communication), chemical sensors (Radhakrishnann and Deshpande, 2002), Langmuir-Blodgett (LB) films (Robert *et al*., 1985), and as conventional dyestuffs. In fact, the Royal Mint uses the popular copper substituted variety as a blue dye in 5 pound notes.

Worth stressing is the use of phthalocyanines in oncology, particularly PDT (Rosenthal, 1991; Bonnett, 2000). For this purpose, transition metal Pcs are not applicable, and so attention is focused on phthalocyanines containing non-transition metal centres. For PDT action, it is necessary that the drug be easy to administer via injection into the blood stream. As the blood itself is a water-based system, water solubility then becomes an essential requirement for a PDT drug. Additionally, the drug will have to traverse lipid membranes – consequently, it should also be sufficiently lipophilic. One should then speak of a water-soluble lipophilic drug. The Pc macrocycle itself is lipophilic, and water solubility could be achieved by introducing sulphonate ions as ring substituents. Mixed-sulphonated aluminium phthalocyanine ($AlPcS_{mix}$) commercially known as Photosens® has been developed as a PDT drug in Russia, and has been used in hospitals with a fair measure of success (Bonnett, 2000).

In summary, the potential industrial applications of Pcs can be represented by Fig. 2, with some overlaps among the various categories.

Electronic structure and spectroscopy of phthalocyanines

The phthalocyanine molecule contains four isoindole groups, linked by four nitrogen atoms to form a symmetrical 18π electron conjugated aromatic macrocycle which is related to the naturally occurring porphyrins and possessing very high thermal and chemical stability. Pc is known systematically as tetraazatetrabenzoporphyrin (TABP) (Fig. 1). Other related synthetic porphyrins include tetraphenylporphyrin (TPP), tetrabenzoporphyrin (TBP) and tetraazaporphyrin (TAP) (Fig. 2). Pc was discovered accidentally in 1907 by Braun and Tcherniac, as a by-product during the synthesis of o-cyanobenzamide (Braun and Cherniac, 1907).



Tetraphenylporphyrin

Tetrabenzoporphyrin

Tetraazaporphyrin

Fig. 2: Molecular structures of synthetic porphyrins

The phthalocyanine structure was only determined about two decades later by independent efforts of Linstead (Linstead and Lowe, 1934; Byrne *et al*., 1934; Robertson, 1935). The X-ray diffraction analyses of Robertson also suggested the structure of metallophthalocyanine (MPc) (Fig. 3).

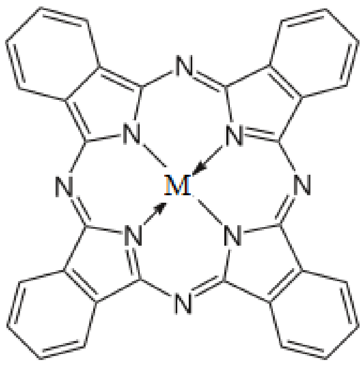
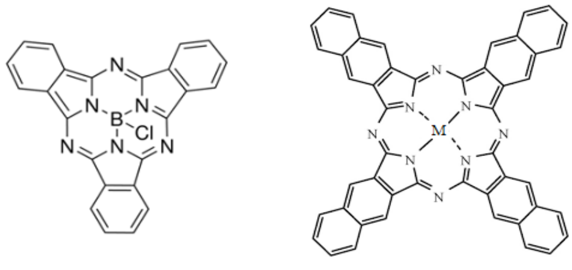


Fig. 3: Molecular structure of metallophthalocyanines



Subphthalocyanine

Metallonaphthalocyanine

Fig. 4: Molecular structures of subphthalocyanine and metallonaphthalocyanine

The four pyrrole nitrogens in the phthalocyanine structure form a cavity into which metal ions can bind by coordinate-covalent bonds between the metal and the nitrogens. Like the porphyrins, the Pc macrocycle can play host to over seventy different metal ions in its central cavity. In the absence of a metal ion, protons may bind to the negatively charged nitrogens, forming the so-called free base phthalocyanine (H_2Pc or Pc), Fig. 1. Other phthalocyanine analogues include subphthalocyanine and naphthalocyanine (Fig. 4).

The geometry of the nuclear skeleton is almost perfectly square planar with a π-electron system of D_{2h} symmetry and C_2 axes in the x, y and z directions. The insertion of a metal into the cavity of the free-base phthalocyanine, while still maintaining the planarity of the molecules increases the symmetry from D_{2h} of H_2Pc to D_{4h} of MPc, which comprises of a C_4 principal axis of rotation, four perpendicular C_2 axes and a horizontal mirror (σ_h) plane; this should confer an almost zero dipole moment on the molecule.. The increase in symmetry is also reflected in the reduction in number of allowed electronic transitions within the molecule, resulting in spectra shown in Fig. 5.

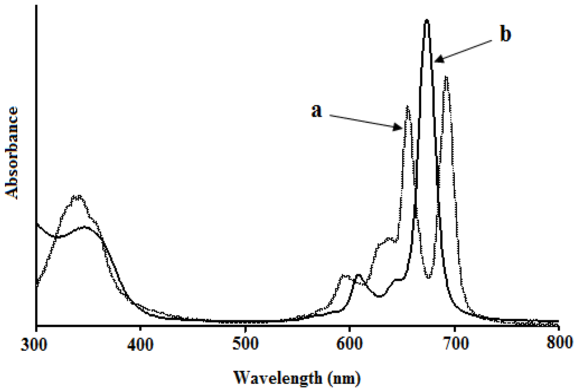


Fig. 5: Ground state electronic absorption spectra of free-base phthalocyanine (a) and metallated phthalocyanine (b)

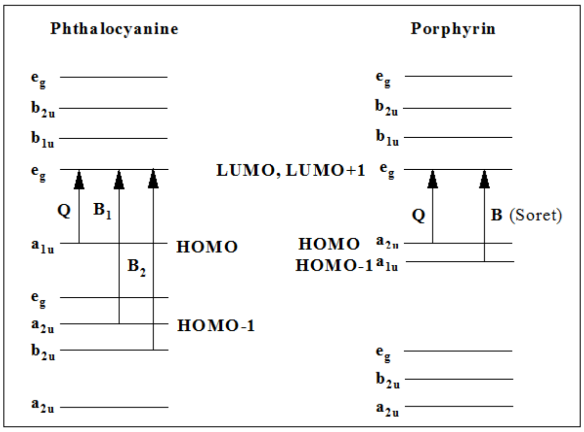


Fig. 6: Electronic transitions in phthalocyanines and porphyrins – Origin of Q and B absorption bands

There have been several meticulous theoretical calculations and experimental data for the molecular orbitals of phthalocyanines; however, it is convenient to use the four-orbital model proposed by Gouterman's group (1972, 1978). Gouterman proposed that the spectral properties of porphyrin analogues may be understood qualitatively by considering four frontier orbitals: the HOMO-1, HOMO, LUMO and LUMO+1 orbitals. The first two are occupied (and nearly degenerate in porphyrins) while the last two are unoccupied and degenerate when the macrocycle is perfectly square planar. The introduction of an aza or benzo group into the porphyrin skeleton (resulting in an MPc) destroys the accidental degeneracy of the HOMO-1 and HOMO in the porphyrin (Gouterman 1978; McHugh *et al*., 1972; Lee *et al*., 1982) (Fig. 6).

The assignment of the ground state electronic absorption bands in MPcs may be done qualitatively on the basis of the Gouterman's model. The Q and B (Soret) bands both arise from π-π* transitions and can be explained in terms of linear combination of transitions from a_{1u} and a_{2u} HOMO orbitals to the doubly degenerate e_g (LUMO) orbitals.

The accidental degeneracy of the a_{1u} and a_{2u} orbitals of porphyrins is expected to lead to almost coincident absorption bands due to $e_g \leftarrow a_{1u}$ and $e_g \leftarrow a_{2u}$ transitions, but in fact these two transitions mix together by a process known as "configurational interaction", resulting in two bands with very different intensities and wavelengths (Fig. 7). Constructive interference leads to the intense high-energy B band, while the weak low-energy Q band is a result of destructive interference.

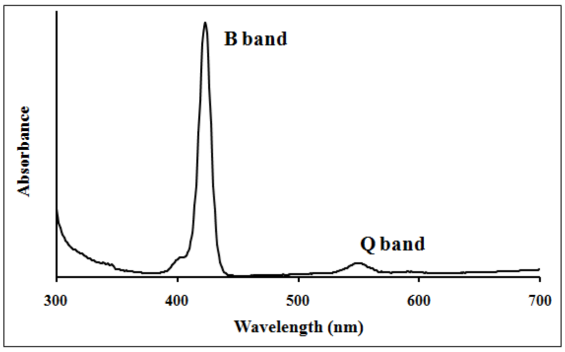


Fig. 7: Ground state electronic absorption spectrum of *tetra*phenylzinc porphyrin (ZnTPP) in DMSO

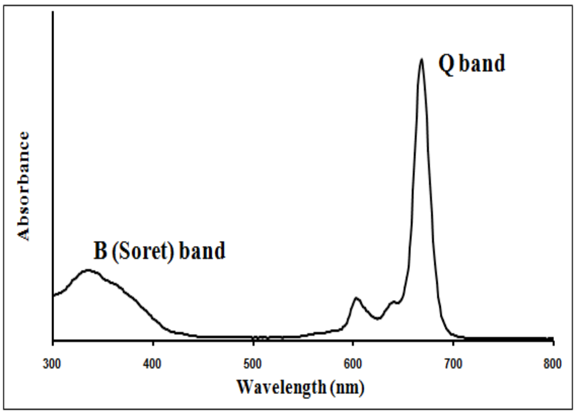


Fig. 8: Ground state electronic absorption spectrum of zinc phthalocyanine (ZnPc) in DMF

On the contrary in phthalocyanines, the a_{1u} and a_{2u} orbitals are widely separated, giving no room for configurational interaction. The Q and B bands are ~ 320 nm apart (Fig. 8).

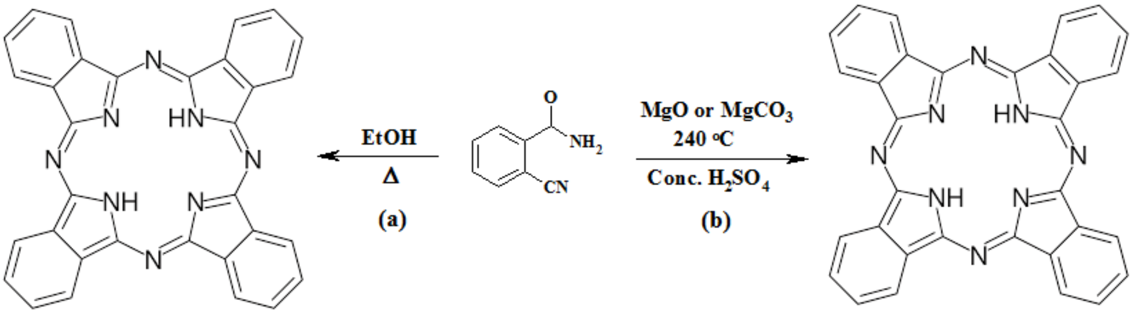
The UV/vis spectrum of an MPc typically has a Q band near 670 nm with extinction coefficient greater than 10^5 L mol^{-1} cm^{-1}, and accompanied by a series of vibrational bands. It has been evidenced (Nyokong *et al*., 1987) that the Soret of MPcs is a superimposition of two bands B_1 and B_2 in the 350 nm expanse, especially in the absence of strong axial ligands. Additionally, three other transitions could be observed below 300 nm in the ground state electronic absorption spectra of diamagnetic MPcs such as ZnPc and MgPc (Mack and Stillman 1994). These give rise to the N, L and C bands in order of increasing energy, respectively.

A tricky situation is also observed in the optical spectra of MPcs, which is due to the presence of non-bonding electrons on the azomethine nitrogens of the macrocycle. The n orbitals are proximal in energy to the π orbitals (HOMO) and consequently, the π* ← n transition is expected to be coupled with π* ← π transition. Huang *et al.* (1982) proposed that the band around 605 in the optical spectra of MPcs could have a partial contribution from the π* ← n transition. This idea was supported by the clear observance of the 605 nm band in the spectra of oxidized and reduced MPc ions, in which case the normal π* ← π (Q and Q_{vib}) transition probabilities are drastically weakened around the 605 and 670 nm regions (Stillman, 1993), but the 605 nm band does not change.

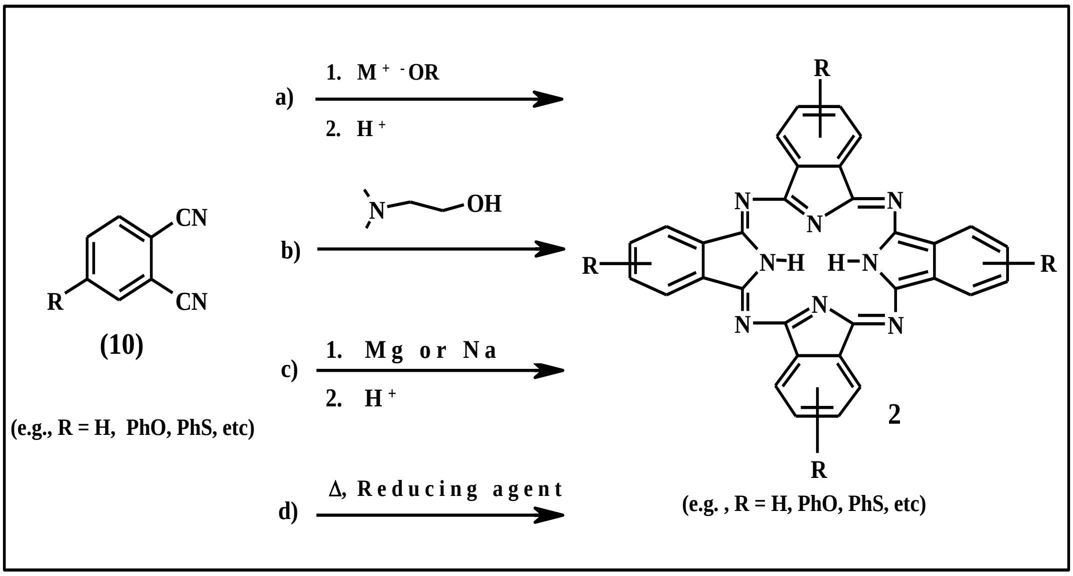
Methods of Phthalocyanine synthesis

Metal-free phthalocyanines

The earliest synthesis of phthalocyanine (Pc) was achieved by heating *o*-cyanobenzamide in ethanol under reflux (Braun and Cherniac, 1907), to yield the blue product in low yield (Scheme 1a). Linstead and co-workers (1934a) later showed that better yields could be obtained if Mg^{2+} ions are mixed with *o*-cyanobenzamide, the reaction mixture heated above 230^0C and the resultant metallophthalocyanine demetalated with conc. H_2SO_4 (Scheme 1b). However, an attempt to synthesize substituted phthalocyanine using this method was unsuccessful.



Scheme 1: Synthesis of metal-free phthalocyanines from *o*-cyanobenzamide



Scheme 2: Synthesis of metal-free phthalocyanine derivatives from substituted phthalonitrile

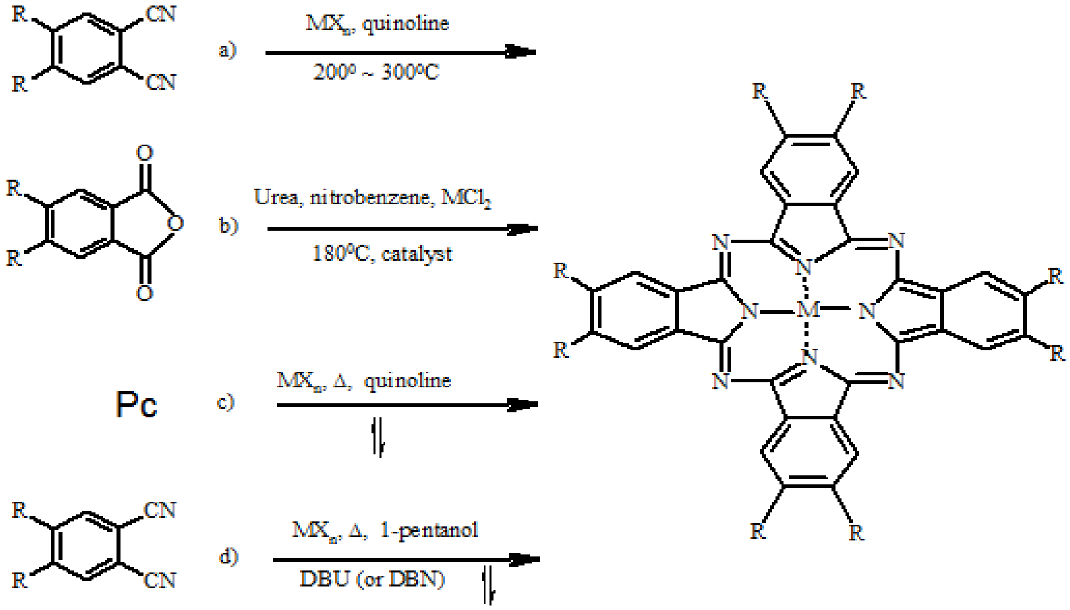
Later studies showed that Pc can be synthesized by treating phthalonitrile with an alkali metal *n*-pentoxide in alcoholic solutions at 140°C (Scheme 2a). This reaction gave the alkali metal phthalocyanine, which was then demetalated to Pc with conc. H_2SO_4 (Listead and Lowe, 1934). A simpler method involved the treatment of phthalonitrile with ammonia gas in 2-*N,N'*-dimethylaminoethanol to give Pc in very good yield (Brach *et al*., 1970) (Scheme 2b) . Phthalonitrile can be fused with magnesium or sodium metal above 200^{0}C to give metallophthalocyanines (Listead and Lowe, 1934; Barrett, 1936), from which Pc can be obtained by acid treatment (Scheme 2c). In the presence of a reducing agent like hydroquinone, substituted phthalonitriles can be fused at 180°C to give the corresponding substituted phthalocyanine in good yield, Scheme 2d.

Unsubstituted metallophthalocyanines

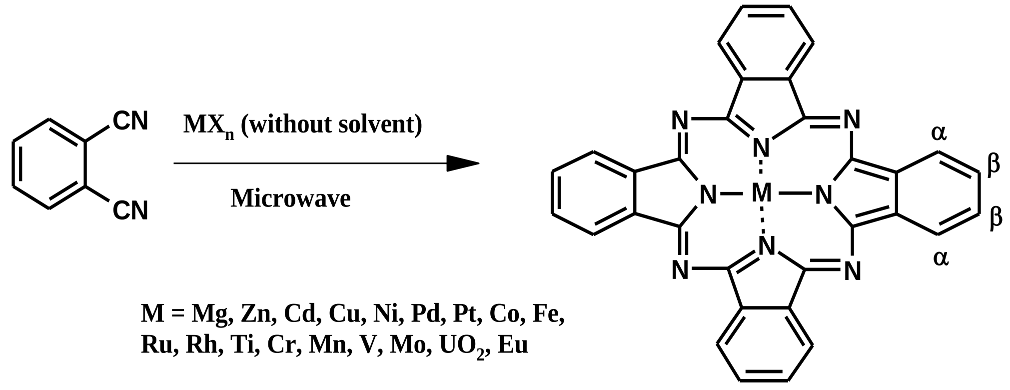
Linstead and co-workers (1934b, 1936) first described the synthesis of metallophthalocyanines(MPcs) by heating a metallic salt with phthalodinitrile in a high boiling solvent (Scheme 3a). This reaction was used for the synthesis of phthalocyanine pigments like copper phthalocyanine in industry. Phthalic anhydride (or related compounds like phthalic acid, phthalimide and phthalamide) has been used extensively in the preparation of metallophthalocyanines (Lever, 1965; Moser and Thomas, 1963) (Scheme 3b). Alternatively, MPc could be prepared by refluxing Pc in the presence of a metal ion in organic solvents such as quinoline (Tomoda *et al*., 1983) (Scheme 3c). Tomoda *et al*. (1983) reported that a variety of MPcs could be prepared under mild conditions with strong organic bases such as 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) or 1,5-diazabicyclo [4.3.0] non-5-ene (DBN). The reaction involves heating to reflux a mixture of phthalonitrile and a metal salt in the presence of DBU or DBN as catalyst, in a primary alcohol such as 1-pentanol (Scheme 3d).

However, the products of these reactions usually lack purity, which calls for a vigorous purification procedure.

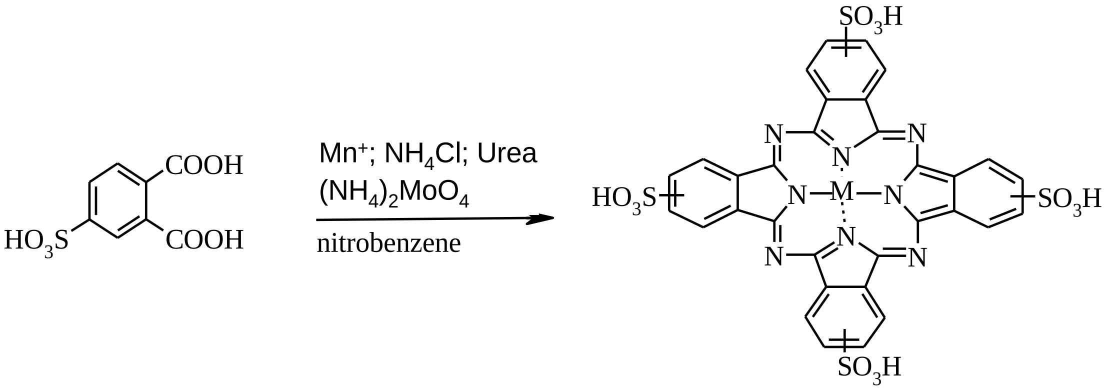
MPcs have also been prepared quickly and efficiently by the reaction of phthalonitrile with hydrated metal salts without solvents and under microwave irradiation (Villemin *et al*., 2001) (Scheme 4).



Scheme 3: Synthesis of metallophthalocyanines from phthalic anhydride and related compounds



Scheme 4: Microwave synthesis of metallophthalocyanines

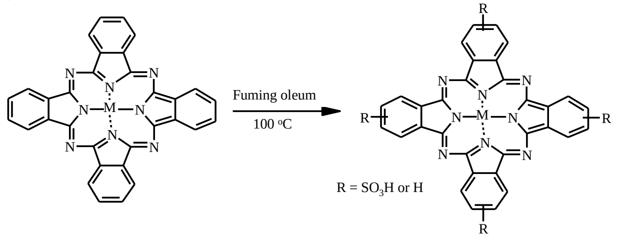


Scheme 5: Synthesis of tetrasulphonated MPc

Ring-substituted MPcs

The most usual method of synthesizing ring-substituted Pcs is by cyclotetramerization of substituted phthalonitriles (Foley *et al.*, 1997; Torre and Torres, 1997) (Scheme 3 a,d). If monosubstituted phthalonitriles are employed, tetrasubstituted Pcs are obtained, with the drawback of a mixture of positional isomers (Foley *et al.*, 1997; Wöhrle *et al.*, 1993). 4,5-Disubstituted phthalonitriles are used as starting materials for octasubstituted Pcs, with no problem of isomerism if the phthalonitrile substituents are similar (Foley *et al.* 1997; Wöhrle *et al.*, 1993; Ozoemena and Nyokong, 2002). The tetra- or octa-substituted Pc can now be metalated as described above (Scheme 3c). Weber and Busch (1985) synthesized tetrasulphonated metallophthalocyanine complexes by reacting 4-sulphophthalic acid and a metal salt in the presence of ammonium chloride, urea and ammonium molybdate, in nitrobenzene (Scheme 5).

The reaction of an unsubstituted MPc with fuming sulphuric acid or oleum at 100 ^{0}C gave a mixture of differently sulphonated MPcs (Ambroz *et al.*, 1991). The mixture was shown to contain mono-, di-, tri- and tetra-sulphonated MPc (Scheme 6).



Scheme 6: Synthesis of mixture of differently sulphonated MPc (MPcS$_n$; n = 1, 2, 3, or 4)

Metallophthalocyanine aggregation

MPc aggregation is recognized by broadening and/or splitting of Q band, indicating the presence of additional electronic levels of the aggregates. The overlapping of energy levels leads to radiationless excited state deactivation, thus making aggregates photo-inactive. The aggregation behaviour of MPcs is well documented (Dhami and Phillips, 1996; Choi *et al.*, 2000). MPc aggregates could be formed in a number of ways, which include the following: (a) Direct linkage or bridge between two or more Pc rings, where the rings are close enough in space to allow intramolecular association (Nevin *et al.*, 1987); (b) Covalent bonding involving the metal as μ oxo links, especially for iron, manganese and silicon-containing Pcs (Lever *et al.*, 1986); (c) Sandwitch-type complex formation, whereby two Pc rings share one central metal (Nensala and Nyokong, 1998); (d) Weak association in which peripheral substituents hold two Pc rings that are adjacent in space (Sielcken *et al.*, 1987; Szymczyk and Abramczyk, 2004).

The degree of aggregation strongly depends on the metal inside the ring and the peripheral substitution at the benzo group (Szymczyk and Abramczyk, 2004). For example, Pcs containing Si or Ge are not expected to form aggregates due to the presence of axial ligands on the metal, which tend to prevent π-π stacking between adjacent rings. It has been suggested (Abramczyk *et al.*, 2004) that π-π interactions between adjacent molecular rings stabilize columnar aggregates.

Aggregation tendency has been observed to be large in aqueous solutions for MPcs that contain substituents that impart water solubility, e.g., sulphonated derivatives (Kuznetsova *et al.*, 2003; Edrei *et al.*, 1998). However, aggregation in aqueous solution is very similar to that observed in the solid phase of tetrasulphonated copper(II)phthalocyanine (Szymczyk and Abramczyk, 2004). In contrast, non-substituted copper(II)phthalocyanine molecules do not form dimers even in the solid phase (Szymczyk and Abramczyk, 2004). In view of these results, it is obvious that the hydrophylic groups at the benzo group must play a crucial role in the aggregation.

MPc aggregation has a great influence on the intermolecular photoinduced processes, and it is easily characterised by a broadening and diminishing of the red absorption band, coupled with a blue shift of the band by 30 to 50 nm (Van Lier and Spikes, 1989). Aggregation can be overcome by either, synthesizing metallophthalocyanines in which the metal has an axial ligand such as chlorine, or by adding bulky peripheral substitution to prevent the phthalocyanine macrocycle aggregating by simple steric hindrance. Bulky peripheral groups prevent an effective π-π interaction between the phthalocyanine subunits (Sastre *et al.*, 1999). Alpha substitution (see Scheme 4 for notation) has also been shown to hinder phthalocyanine aggregation (George *et al.*, 1998). Bulky α-substituents impose a steric constraint on the molecule, thereby restricting conformational freedom and consequently, obstructing the approach of a second molecule to form a coplanar dimer.

Reactions of metallophthalocyanines

Unsubstituted MPcs are generally impervious to chemical treatment. For example, heating to very high temperatures (> 500^{0}C) would not lead to the macrocycle's decomposition, with only a change of state (sublimation) being observed. Metal chelation with the four pyrrole nitrogen atoms of the macrocycle stabilizes the complex. Hence, metallophthalocyanines are more stable than their metal-free counterparts. However, a few reactions of MPcs have been observed and documented:

Redox reactions

These are the most notable of all MPc reactions. Oxidation and reduction can be achieved in three principal ways viz: electrochemical, photochemical and chemical. The Pc ring has a great propensity to undergo redox reactions and its redox behaviour dominates the redox chemistry of the complex, especially if the central metal is not electroactive, e.g. zinc. With electroactive metals like the transition metals, the redox chemistry of the complex becomes complicated, as there is need to distinguish the redox attributes of the metal centre from those of the ring. The redox activity of the Pc ring is directly associated with the frontier orbitals (HOMO and LUMO) in the molecule. Oxidation implies the removal of electron(s) from the HOMO while reduction means the addition of electron(s) to the LUMO. In the light of this, it is logical to think that there is a correlation between HOMO energy and the ease of oxidation; and the LUMO energy and the ease of reduction. The Pc skeleton exists as a dianion Pc(-2), and the removal of one and two electrons from the HOMO (a_{1u}) results in the formation of Pc(-1) and Pc(0), respectively. For Pc reduction, up to four electrons can be added to the LUMO, terminating in Pc(-6) species (Table 1), since the e_g orbital is degenerate.

Table 1: Electronic description of phthalocyanine oxidation states

Species	Pc(0)	Pc(-1)	Pc(-2)	Pc(-3)	Pc(-4)	Pc(-5)	Pc(-6)
G.E.C	$(a1_u)^0(e_g)^0$	$(a1_u)^1(e_g)^0$	$(a1_u)^2(e_g)^0$	$(a1_u)^2(e_g)^1$	$(a1_u)^2(e_g)^2$	$(a1_u)^2(e_g)^3$	$(a1_u)^2(e_g)^4$

G.E.C = Ground state electronic configuration

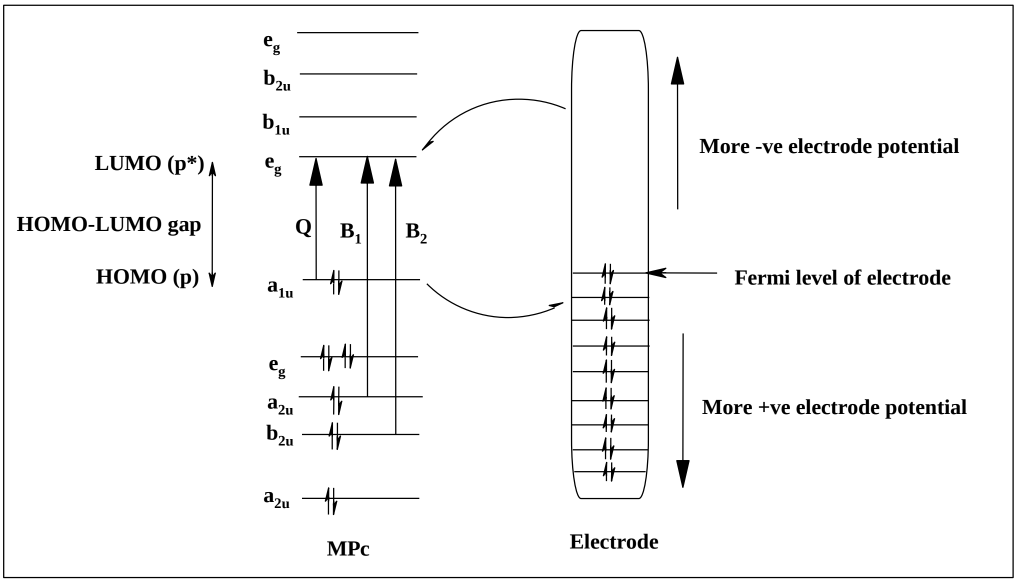


Fig. 9: Relation between redox potentials and frontier orbitals

Electrochemical oxidation/reduction of the Pcs involves the deliberate application of potential to the electrode. Electrodes used in electrochemistry are composed of metals, or metal-like materials. In these materials there are no distinct orbitals, but continuous bands of energy that the electrons can occupy. Like the HOMO in a molecule, there is a Fermi level in a metal. All the energy levels below the Fermi level are occupied at O K. When one applies a negative potential to the electrode, the Fermi level moves to higher energy (higher tendency to reduce the analyte). On the other hand, application of a positive potential moves the Fermi level to lower energy (higher tendency to oxidize the analyte) (Fig. 9). If the HOMO energy of the Pc molecule is increased, oxidation is favoured, while a lowering of the LUMO energy favours reduction. The literature on electrochemical redox processes of Pc is robust (Lever *et al.*, 1986, 1989) and the rich electrochemistry of Pcs is exploited in many applications.

Photochemical redox reactions of Pcs are carried out at room temperature using visible-wavelength light and an electron donor or acceptor. In the photo-assisted reduction, Stillman's group used hydrazine as the electron donor and CBr_4 as electron acceptor in organic solvents (Mach and Stillman, 1994; Gasyna and Stillman, 1990; Nyokong *et al*., 1986). However, it was very difficult to obtain stable solutions of the oxidized and reduced species despite degassing the solutions before the experiments. Chemical reduction of MPcs has been achieved by direct reaction with a strong reducing agent (alkali metal film in an air-free vial) to give the reduced species (Clark and Yandle, 1972; Felton and Linschitz, 1966).

Decolouration and destruction in aqueous solutions

The destruction of MPcs (M = Co, Fe) in aqueous solutions has been reported (Borisenkova *et al*., 2000). These reactions take place in the presence of an alkali and a stream of oxygen, and are oxidative in nature.

Reaction with ligating agents

Most MPc complexes interact with a variety of molecules such as pyridine (Pennesi *et al*., 1985a), cyanide (Nyokong and Guthrie-Stratchan, 1993), carbon monoxide (Pennesi *et al*., 1985b) and imidazole (Jones and Twigg, 1969), to form axially coordinated species. Axial ligand displacements have also been reported, and are known to be dissociative and occur in stepwise manner (Penessi *et al*., 1985 a,b; Jones and Twigg, 1969).

Reaction with acids

The reaction of MPcs with acids leads to a successive protonation of the azomethine nitrogens. These reactions have been studied using dilute or concentrated sulphuric acid, HCOOH, HSO_3Cl (Gaspard *et al*., 1972, 1979; Borokov and Akopov, 1986) and CF_3COOH (Bernstein and Lever, 1992). MPc protonation has also been observed from reaction with Lewis acids (Freyer and Ming, 1997; Graczyk and Bialkpwska, 1978) in organic solvents. A harsh acid treatment on MPcs leads to substitution reactions at the benzo rings. For example, sulphonated MPcs are usually synthesized by heating the MPc in oleum or fuming sulphuric acid at 100^0C (Ambroz *et al*., 1991) (Scheme 6). The stepwise protonation of the MPc ring gives rise to characteristic successive bathochromic shifts of the Q band (Beeby *et al*., 2001), with the tetra-protonated species absorbing about 170 nm to the red of the unprotonated Pc (Beeby *et al*., 2001). These protonated species have been found to be fluorescent and their emission spectra are also red shifted, compared with those of the unprotonated Pcs (Beeby *et al*., 2001). However, the fluorescence quantum yield and lifetime are reduced on protonation (Beeby *et al*., 2001). An interesting feature in the spectra of the protonated species is the change in symmetry accompanying consecutive protonation. Theoretical investigations of the Pc (Bernstein and Lever, 1992) using a four orbital model, describe the spectral changes upon protonation. It has been shown that monoprotonation leads to a reduction in symmetry from D_{4h} to C_{2v}, resulting in a splitting of the Q band. Di (*trans*)- and tri-protonation results in a splitting of the Q band due to C_{2v} or D_{2h} symmetry while the Q band of the diprotonated *cis* form is not expected to split (Freyer and Ming 1997). Tetraprotonation reverts back to the D_{4h} symmetry and only one Q band is predicted.

Apart from input by Beeby's group and a few others (Beeby *et al*., 2001; Weitman *et al*., 2001; Lang *et al*., 1992; Ogunsipe and Nyokong, 2003), literature is very sparse on the effects of protonation on the photophysicochemical properties of MPcs. Beeby *et al.* (2001) demonstrated that protonation reduces the energy of the excited states and their lifetimes. In particular, the triplet energy is lowered to a value where energy transfer to ground state oxygen is no longer favourable. The effects of substituents, solvents and acid strength on the ease of protonation of MPcs bearing various ring substituents and axial ligands; as well as the effects of protonation on the photophysicochemical properties (e.g. fluorescence quantum yield, Φ_F; singlet oxygen quantum yield, Φ_Δ; and photodegradation quantum yield, Φ_{Pd}) of the complexes, have also been reported (Ogunsipe and Nyokong, 2003; Ogunsipe *et al*., 2012).

Solvent effects on MPc spectra

The wavelength and intensity of absorption bands are both affected when a molecule is in a solvent environment compared with its spectrum in the gas phase. This is due to the unequal perturbation of the ground and excited electronic states of the molecule, which depends on the nature of the solvent-solute interactions in the two states. Solvent effects on spectra of organic molecules have been linked with a range of solute and solvent properties. For example, solvents effects were used to distinguish between $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions (Calvert and Pitt, 1966; McConnell, 1952); changing from a non-polar solvent (e.g., hexane) to a polar solvent (ethanol) results is a shift of the ($\pi^* \leftarrow n$) band to shorter wavelengths (blue shift), and the ($\pi^* \leftarrow \pi$) band to longer wavelengths (red shift) (Calvert and Pitt, 1966). The observed solvent shifts in the aromatics were also attributed to hydrogen bonding, which tends to cause electron migration in the solute molecule. Solvent effects have also been ascribed to the stabilization of preferred resonance structures in the solute by certain solvents due to their dielectric constants and their acid-base properties (Brooker *et al*., 1951).

The shifts in the absorption wavelength are often interpreted in terms of the dielectric constant (relative permittivity) and refractive index of the solvent. A qualitative account of these effects in terms of dipole, polarization and hydrogen-bonding forces has been given (Bayliss and McRae, 1954).

The interpretation of solvent effects is difficult because they are often small and not easy to measure precisely and also because they are often the result of several individual effects which sometimes reinforce one another and sometimes cancel out. All organic solution spectra are subject to a general polarization red shift. The electromagnetic field of the absorbed light induces in the solute molecules an electric dipole moment, which oscillates at the same frequency of the incident field; the 'transition dipole' thereby formed induces a momentary polarization in the solvent molecules. The solute's excited state, now polar, experiences a greater stabilization from the solvent than the ground state, the result being a red shift in the spectrum.

Superimposed on the polarization red shift are other shifts due to the fact that the solute molecule, in accordance with the Franck-Condon principle, at the instant of excitation is not in equilibrium and is therefore in a state of strain with respect to its environment. This Franck-Condon strain can be related partly to the polarity of the solute and solvent molecules and the changes in dipole moment of the solute during the transition (orientation strain); and partly due to parking strain arising from changes in the dimensions of the solute due to the excitation.

It has been suggested (Law *et al*., 1997) that the interaction between coordinating solvents with Pc molecules stabilizes the LUMO of the complexes. The band positions in titanium(IV) phthalocyanine (Ti(IV)Pc) complexes were red shifted as the polarity of the solvent increased for non-coordinating solvents, with the magnitude of the red shift following the order hexane < toluene < chloroform < 1-chloronaphthalene. The electronic absorption spectra of MPc complexes in various organic solvents have been analysed using the method originally described by Bayliss (1950) (Equation 1),

$$F = \frac{n^2 - 1}{2n^2 + 1} \qquad \text{(Equation 1)}$$

F is the polarizability function and n, the solvent's refractive index.

The positions of the Q band absorption of Ti(IV)Pc complexes showed a linear dependence on the function F in Equation 1, suggesting that the shifts were caused mainly by solvation (Law *et al*., 1997).

The effect of solvents and the environment on MPc fluorescence spectra are complex, and there is no simple theory which can account for all these effects. Spectral shifts result from the general effects of solvent polarity whereby the energy of the excited MPc decreases with increasing solvent polarity. This effect is usually accounted for by the Lippert equation (Equation 2) (Lakowicz, 1999).

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right)\frac{(\mu_E-\mu_G)^2}{a^3} + \text{constant}$$

(Equation 2)

Where $\bar{V}_A$ and $\bar{V}_F$ are the wavenumbers (cm^{-1}) of the absorption and emission, respectively; h, the Planck's constant; c, the speed of light; and a, the radius of the cavity in which the absorbing molecule resides. ε, n and µ are solvent parameters – dielectric constant, refractive index and dipole moment, respectively while the subscripts 'E' and 'G' denote the excited state and ground states respectively.

Spectral shift can also occur due to specific fluorophore-solvent interactions and due to charge separations in the excited state, as polar solvents are expected to support charge separation while non-polar solvents are not. Absorption spectra are generally less sensitive to solvent polarity than emission spectra. This is because absorption of light occurs in about 10^{-15} s, a time which is too short for motion of the absorbing molecule or solvent. Absorption spectra are not affected by the post-absorption decrease in the excited-state energy. Solvents effects on the photophysical and photochemical properties of selected MPc complexes have been studied extensively by Ogunsipe and co-workers (Ogunsipe *et al*., 2003; Ogunsipe and Nyokong, 2011).

Photophysics and photochemistry of MPcs

The literature on photophysics and photochemistry of MPcs is very extensive. As earlier stated, MPc species show a strong absorption in the red region (Q band) of the solar spectrum (ε ~ 10^5 M^{-1} cm^{-1}) and a moderately intense (broader) one in the near-UV region (Soret or B band). When an MPc molecule is irradiated at its Q band maximum, the excited triplet state is populated (as a result of intersystem crossing from the excited singlet state). The efficiency of this intersystem crossing is quantified by the triplet quantum yield (Φ_T), which in turn is determined by flash photolysis. The T_1(MPc) state absorbs in the region 450-500 nm, with ε values of ~ 10^4 M^{-1} cm^{-1}. Both the S_1(MPc) and T_1(MPc) states undergo radiative and non-radiative deactivation processes and fall back to the ground state (S_0).

Fluorescence and triplet lifetimes (and quantum yields) of MPcs

The lifetime of an excited state is defined as the time taken for the concentration of the molecules in that state to decrease to 1/e of its original value. The usual lifetime of the first singlet excited (S_1) state of MPcs is of the order a few nanoseconds (ns), and is strongly dependent of factors which include: (i) the nature of the central metal ion, (ii) nature of peripheral and/or non peripheral substituents, (iii) nature of the solvent and (iv) the presence of other species interacting with the molecule in the S_1 state. The typical lifetime a T_1(MPc) state ranges between the microsecond (µs) and millisecond (ms). This longer lifetime is due to the forbiddance of the $T_1 \rightarrow S_0$ transition. The metastable nature of the T_1 state makes it a good candidate for sensitization and photochemistry. The S_1(MPc) state is deemed too short-lived for any substantial sensitization or chemical reaction. During the lifetime of the T_1 state, the molecule is more susceptible to non-radiative deactivation or quenching than luminescence. As a result, MPc phosphorescence is not readily observed in solution at room temperature. MPc phosphorescence can mainly be observed by trapping the T_1 state in a rigid glass (matrix) Mack and Stillman, 1994).

Fluorescence and intersystem crossing are two complementary photophysical processes. Hence in Table 2, high Φ_F values are accompanied by low Φ_T values for the MPc complexes. The nature of the central metal ion has a great effect on Φ_F and Φ_T values; heavy metal ions and paramagnetic metal ions enhance the yield of the triplet state. The paramagnetic effect, as anticipated, shortens the lifetime of the triplet excited state (τ_T), due to the presence of low-lying d-orbitals, which promote the quenching of the T_1 state by charge transfer processes; the same features that promote $T_1 \leftarrow S_1$ transition, would also promote the $S_0 \leftarrow T_1$ transition. In particular, MPcs in which M is a paramagnetic transition metal ion (e.g. Cu^{2+}, Cr^{2+}) posses very short τ_T values (Table 2).

MPcs show higher Φ_T values than the metal-free Pc. Apart from the heavy atom effect, other factors like molecular rigidity and solvent type have also been reported to influence MPc fluorescence and intersystem crossing. For instance, solvents like chloroform and carbon tetrachloride, which contain heavy Cl atoms, tend to promote intersystem crossing; hence fluorescence would be weak in such solvents.

Again, features that impart greater rigidity on the macrocycle, are expected to make it more fluorescent, as there exists a less likelihood of electronic energy 'leaking out' non-radiatively. This explains why the Φ_F value of silicon naphthalocyanine (SiNPc, 0.38) is higher than that of silicon phthalocyanine (SiPc, 0.18) (Boguta *et al*., 2003). The fusion of an extra benzo group in SiNPc makes the molecule more rigid.

Table 2: Photophysical properties of some metallophthalocyanines (Darwent *et al*., 1982)

Compound	τ_S (ns)	Φ_F	τ_T (µs)	Φ_T
H_2Pc	6.0	0.70	140	0.14
H_2TSPc	9.8	0.62	170	0.22
ZnPc	3.8	0.30	-	-
ZnTSPc	2.9	0.32	245	0.56
AlClPc	6.8	0.58	500	0.40
AlTSPc	5.3	-	500	-
CuPc	-	-	0.035	> 0.70
CuTSPc	-	< 10^{-4}	0.065	0.92
CrPc	-		0.02	-

Much has been reported on the photophysics and photochemistry of MPc derivatives (Ogunsipe *et al*., 2004; Maree *et al*., 2001; Ogunsipe and Nyokong, 2005), however there is still ample room for literature expansion in this area.

UV (versus visible) irradiation of MPcs - Photophysical and photochemical consequences

The photophysicochemical consequences of UV irradiation of MPc complexes were well reviewed by Tokumaru (2001). Red visible light irradiation of MPc complexes leads to the population of the S_1(MPc) state, while UV irradiation populates higher excited states (S_2 and higher). UV light irradiation is known to result in more efficient reactions than red light irradiation (Tokumaru and Kaneko, 1997; Tokumaru, 1997). For example, it was found that red light irradiation of copper(II) tetrakis(*N*-octyldecylsulfamoyl)phthalocyanine in chloroform did not give any product but UV irradiation led to substitution of the $CHCl_2$ group (from the solvent) on to the Pc ring (Prasad and Farraudi, 1982). Also, rhodium(III) acidophthalocyanine ($Rh^{III}Pc(CH_3OH)X$; X = halide) in acetonitrile, in the presence of 2-propanol under UV irradiation and xenon flash light (~ 600 nm) oxidized 2-propanol to acetone more efficiently than when red light was used (Muralidharan and Ferraudi, 1983; Ferraudi and

Muralidharan, 1983). It was also found that zinc(II) tetrasulphophthalocyanine (ZnTSPc) was stable towards visible light but degraded under strong UV irradiation (Kaneko *et al*. 1994). A lot more has been reported on the photochemical behaviour of ZnTSPc; for example, Nishimura *et al*. (1990) observed no result when an acetonitrile solution of ZnTSPc was irradiated with red light in the presence of triethanolamine; but ZnTSPc was reduced when UV irradiation was used. Transient absorption showed that the T_1(ZnTSPc) state was not quenched by the amine, and so the reactive species was presumed to be a higher excited singlet state. Kaneko *et al*. (1996) also observed similar results for ZnTSPc and CuTSPc in aqueous acetonitrile and in the presence of amines (triethanolamine, triethylamine and ethylenediaminetetraacetic acid). Irradiation of ZnTSPc and CuTSPc at 365 nm resulted in the macrocycles' reduction. 656 nm irradiation did not induce such a reaction, and the mechanism of the reaction was discussed in terms of the participation of a higher excited singlet state of the macrocycles. In a similar manner, □-octabutoxyphthalocyanine (□-$H_2(OBu)_8Pc$) was reduced by triethanolamine under UV irradiation, but not with red light (Kaneko *et al*., 1996).

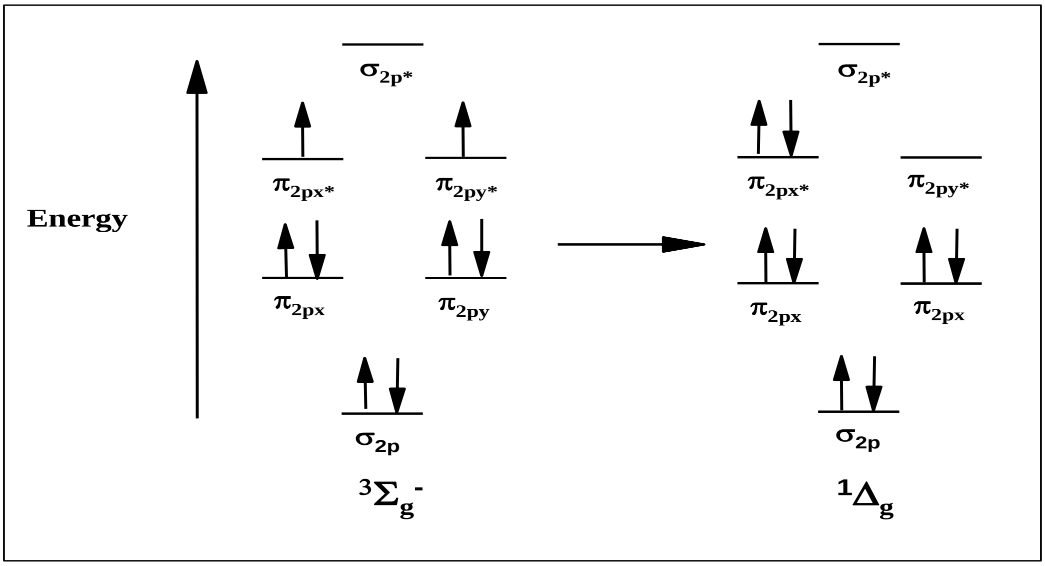
With UV excitation, ZnTSPc (in aqueous acetonitrile) and □-$H_2(OBu)_8Pc$ (in ethanol) fluoresce at 450 nm and 440 nm, respectively and with quantum yields of 0.038 and 0.013 respectively. Whereas with red excitation, their fluorescence occurred at 680 nm (Φ_F = 0.31) and 788 nm (Φ_F = 0.19), respectively (Kaneko *et al*., 1997). There is also a report (Rückmann *et al*., 1997) that □-octaalkoxyphthalocyanines (□-$H_2(OR)_8Pc$, where R = OC_2H_5, OC_3H_7, OC_4H_9, OC_5H_{11} and $OC_{10}H_{21}$), on UV excitation in ethanol, fluoresce at ~ 420 nm, but with considerably lower quantum yields than those of red fluorescence. The triplet quantum yields with UV- and red-excitations were found to be 0.53 and 0.44, respectively, for the (□-$H_2(OR)_8Pc$ molecules. The higher Φ_T value with UV excitation was ascribed to the presence of an additional pathway for intersystem crossing from the higher excited singlet state. Accordingly, this state rapidly undergoes intersystem crossing to a higher triplet state at a higher rate than the competing internal conversion to the S_1 state. This also explains the observed lower Φ_F values with UV excitation than those with red excitation.

Generally, an increase of energy gap between the lowest and a higher excited state tends to reduce the rate constant of deactivation from the higher to the lower state; this lengthens the lifetime of the higher state, therefore making the state more susceptible to reactions with other species (Tokumaru, 2001). Photochemical irradiation of MPcs with UV light populates their higher excited states, which rapidly dissipate in a unique manner different from the lowest excited states (populated under visible light irradiation of the Q band). The higher excited states often exhibit characteristic emission and enhanced reactivity via electron transfer, energy transfer, etc, competing with rapid fluorescence. This is an exception to the Kasha-Vavilov rule, which states that the quantum yield of luminescence is independent of the excitation wavelength. In almost every case in which an MPc has been used to sensitize a photo-reaction, it is the excited triplet state that is active (Howe and Zhang, 1997). The longer lifetime of the T_1(MPc) state compared with that of the S_1(MPc) or S_n(MPc) state is a significant advantage since at a given concentration of quencher the number of diffusional encounters between a molecule in an excited state and a quencher molecule increases as the lifetime of the excited state increases.

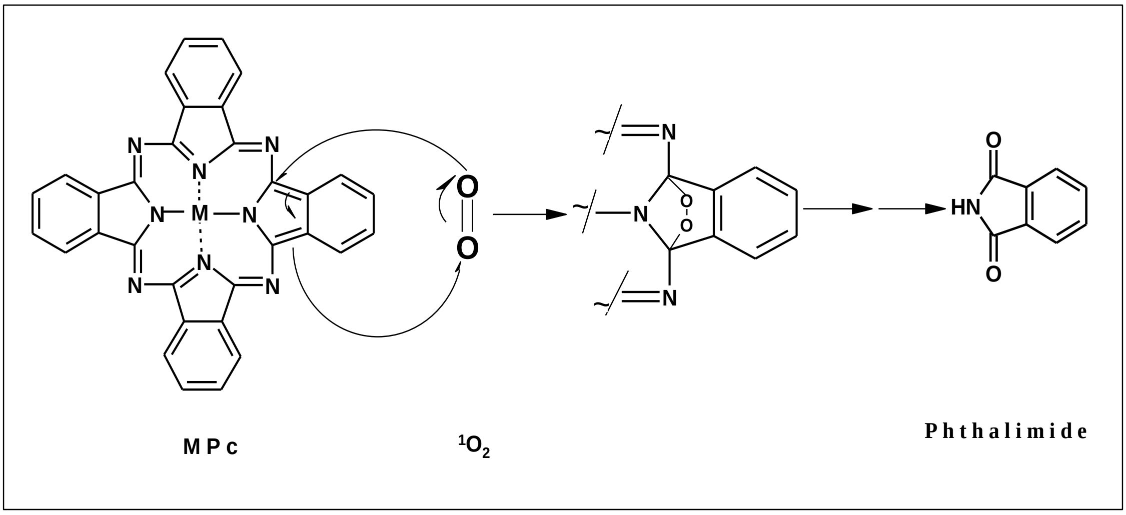
Photosensitized singlet oxygen production by MPcs

Photosensitization is the process by which a photochemical or photophysical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called a photosensitizer. MPcs have proved to be efficient photosensitizers, essentially due to their strong light absorption and also due to the relatively long lifetime of their excited triplet state. Oxygen is a potent quencher of the excited states of molecules. When the quenching of an excited state takes place, the excitation energy may be transferred to the oxygen molecule, generating the first excited state of the oxygen molecule known as singlet oxygen. Oxygen is unusual in that it has a triplet ground state, and hence relaxation of the singlet state to the ground state is spin forbidden, resulting in a long lifetime for singlet oxygen. Singlet oxygen is a highly reactive species and is responsible for oxidative damage in a number of systems (Rosentha, 1991; Wagner *et al*., 1998; McDonald and Dougherty, 2001; Gilbert and Baggott, 1991).

In the ground state, the outermost electrons are distributed according to Hund's of maximum multiplicity, in the π_{2px^*} and π_{2py^*} antibonding orbitals [96,97]. The extreme reactivity of $(O_2)^1\Delta_g$ arises from the pairing of two electrons into one of the π_{2p^*} antibonding orbitals (Scheme 7).



Scheme 7: Molecular orbital diagrams showing the electron distribution in triplet triplet and singlet oxygen



Scheme 8: [4+2] cycloaddition reaction of MPc with singlet oxygen

Photodegradation of MPcs by singlet oxygen

Photodegradation is the photochemical transformation of a molecule into lower molecular weight fragments, usually in an oxidation process. The ability of singlet oxygen to react with macrocyclic metal complexes has been documented (Schnurpfeil *et al*. 1997; Sobbi *et al*., 1993). Singlet oxygen reacts with tetra-azaporphyrin derivatives in a Diels-Alder [4+2]-cycloaddition, with the MPc ring acting as a diene and singlet oxygen as the dienophile. For MPcs, phthalimide was found to be the photo-oxidation product (Sobbi *et al*. 1993) (Scheme 8).

Photodegradation (photobleaching) studies are undertaken in order to determine the stability of the MPcs towards photo-irradiation. As stated above, it is widely believed that photodegradation is a singlet oxygen-mediated process and so its efficiency should depend on the concentration of singlet oxygen.

The presence of electron-donating substituents on the MPc ring was reported (Ogunsipe *et al*., 2003) to bring about rapid photodegradation, which is attributed to the ease of oxidation of the ring due to the presence of these substituents.

On the other hand, electron-withdrawing substituents tend to stabilize the ring in the presence of light; therefore, complexes containing electron-withdrawing groups are more difficult to oxidize and hence more resistant to oxidative degradation. Experiments performed in deuterated solvents gave enhanced photodegradation (Maree *et al*., 2001). It is known that singlet oxygen has a longer lifetime in deuterated solvents; therefore, the probability of its reaction with the MPc ring is increased, giving rise to enhanced degradation. In the presence of diazabicyclooctane (DABCO), a singlet oxygen scavenger, photodegradation rate was found to decrease (Maree *et al*., 2001). This observation further supports the suggestion that singlet oxygen is actually involved in the photodegradation process. In aqueous solutions, photobleaching rate is low, presumably due to aggregation. Singlet oxygen generation is low for the aggregated species; hence photodegradation rate is expected to be low.

Conclusion

In conclusion, this review has described the applications (actual and potential), synthesis, spectral, photophysical and photochemical properties of metallophthalocyanines. The most usual method of synthesizing ring-substituted MPcs is by cyclotetramerization of substituted phthalonitriles in the presence of a metal salt; this can also be achieved in solvent-free microwave-assisted synthesis. Oxidation and reduction are the most notable of all MPc reactions, and can be achieved in three principal ways viz: electrochemical, photochemical and chemical. An interesting feature in the spectra of the protonated species is the change in symmetry accompanying consecutive protonation. It has been shown that monoprotonation leads to a reduction in symmetry from D_{4h} to C_{2v}, resulting in a splitting of the Q band. Di (*trans*)- and tri-protonation results in a splitting of the Q band due to C_{2v} or D_{2h} symmetry while the Q band of the diprotonated *cis* form is not expected to split. Tetraprotonation reverts to the D_{4h} symmetry and only one Q band is predicted. The interpretation of solvent effects is difficult because they are often small and not easy to measure precisely and also because they are often the result of several individual effects which sometimes reinforce one another and sometimes cancel out.

Oxygen is a potent quencher of the excited states of molecules. When an excited MPc molecule is, the excitation energy may be transferred to nearby oxygen molecules, generating the first excited state of the oxygen molecule known as singlet oxygen. Ironically, singlet oxygen is implicated in the photodegradation of MPcs; hence MPcs with singlet-oxygen-quenching features are more photostable.

References

Abramczyk H, Szymczyk I, Waliszewska G & Lebioda A 2004. Photoinduced redox processes in phthalocyanine derivatives by resonance raman spectroscopy. *J. Phys. Chem.*, 108: 264-274.

Ambroz M, Beeby A, MacRobert AJ, Simpson MSC, Svensen RK & Phillips D 1991. Preparative, analytical and fluorescence spectroscopic studies of sulphonated aluminium phthalocyanine photosensitizers. *J. Photochem. Photobiol. B: Biol.*, 9: 87-95.

Barrett PA, Dent CE & Linstead RP 1936. Phthalocyanines, Part VII: Phthalocyanine as a co-ordinating group. A general investigation of the metallic derivatives. J. Chem. Soc., 1719-1736.

Bayliss NS 1950. The effect of the electrostatic polarization of the solvent on electronic absorption spectra in solution. *J. Chem. Phys.*, 18: 292-296.

Bayliss NS & McRae EG 1954. Solvent effects in organic spectra: Dipole Forces and the Franck–Condon Principle. *J. Chem. Phys.*, 58: 1002-1006.

Beeby A, FitzGerald S & Stanley CF 2001. A photophysical study of protonated (tetra-*tert*-butylphthalocyaninato)zinc. *J. Chem. Soc. Perkin Trans.*, 2 1978-1982.

Bernstein PA & Lever ABP 1992. Protonation of cobalt tetraneopentoxyphthalocyanine as a function of oxidation state. *Inorg. Chim. Acta*., 198: 543-555.

Boguta A, Wrobel D, Hoffmann TJ & Mazurkiewicz P 2003. Mixtures of organic macrocycles for applications in solar cell devices. *Cryst. Res. Technol.*, 38: 267-274.

Bonnett R 2000. Chemical Aspects of Photodynamic Therapy. Gordon and Breach Science Publishers, Amsterdam.

Borisenkova SA, Denisova EP, Batanova EA, Girenko EG, Kaliya OL, Lukyanets EA & Vorozhtsov GN 2000. Kinetics and mechanism of destruction of cobalt phthalocyanine derivatives in aqueous solutions. *J. Porphyrins Phthalocyanines*, 4: 684-688.

Borokov NY & Akopov AS 1986. Acid-base characteristies and kinetic stability of tetra-4-tertiary-butylphthalocyanine and its complexes in buffer solutions, *Zh. Fiz. Khim.*, 60: 750-752.

Brach PJ, Grammatica SJ, Ossana OA & Weinberger L 1970. Improved synthesis of metal-free phthalocyanines. *J. Hetero. Chem.*, 7: 1403-1405.

Braun A & Cherniac J 1907. Über die produkte der einwirkung von acetanhydrid auf phthalamid. *Ber. Deut. Chem. Ges.*, 40: 2709-2714.

Brooker LGS, Keyes GH, Sprague, RH, VanDyke RH, VanLare E, VanZandt G, White FL, Cressman HWJ & Dent SG 1951. Color and constitution. X: Absorption of the merocyanines. *J. Am. Chem. Soc*., 73: 5332-5350.

Byrne GT, Linstead RP & Lowe A 1934. Phthalocyanines: Part II - The preparation of phthalocyanine and some metallic derivatives from *o*-cyanobenzamide and phthalimide. *J. Chem. Soc*., 1017-1022.

Calvert JG & Pitts JN 1966. Photochemistry. John Wiley & Sons Inc, New York, p. 255.

Choi MT, Li, PP & Ng DK 2000. A direct comparison of the aggregation behavior of phthalocyanines and 2,3-Naphthalocyanines. *Tetrahedron*, 56: 3881-3887.

Clark DW & Yandle JR 1972. Electronic spectra of the negative ions of some metal phthalocyanines. *Inorg. Chem.*, 11: 1738-1742.

Darwent JR, Douglas P, Harriman A, Porter G & Richoux M-C 1982. Metal phthalocyanines and porphyrins as photosensitizers for reduction of water to hydrogen. *Coord. Chem. Rev*., 44: 83-126.

Dhami S & Phillips D 1996. Comparison of the photophysics of an aggregating and non-aggregating aluminium phthalocyanine system incorporated into unilamellar vesicles. *J. Photochem. Photobiol. A: Chem*., 100: 77-84.

Edrei R, Gottfried V, Van Lier JE & Kimel S 1998. Sulfonated phthalocyanines: Photophysical properties, in vitro cell uptake and structure–activity relationships. *J. Porphyrins Phthalocyanines*, 2: 191-199.

Felton RH & Linschitz H 1966. Polarographic reduction of porphyrins and electron spin resonance of porphyrin anions. *J. Am. Chem. Soc*., 88: 1113-1116.

Ferraudi G & Muralidharan S 1983. Photochemistry of transition-metal phthalocyanines. Analysis of the photochemical and photophysical properties of the acido(phthalocyaninato)rhodium(III) complexes. *Inorg. Chem*., 22: 1369-1374.

Foley S, Jones Gurnos, Luizzi R, McGarvey DJ, Perry M & Truscott TG 1997. The synthesis and photophysical properties of polyether substituted phthalocyanines of potential use in photodynamic therapy. *J. Chem. Soc. Perkin Trans.* 2: 1725-1730.

Freyer W & Minh LQ 1997. Interaction of acenannulated metallotetraazaporphyrins with the Lewis acid aluminum bromide. *J. Porphyrins Phthalocyanines*, 1: 287-295.

Gan F 2000. Some considerations of organic materials for high density optical disk data storage. *Chinese Sci. Bull*., 45: 572-576.

Gaspard S, Verdaguer M & Viovy R 1972. Protonation de la phtalocyanine de cuivre(II) et de son dérivé 4-4'-4"-4''' tétracarboxylé. *J. Chim. Phys. Phys.-Chim. Biol.*, 69: 1740-1747.

Gaspard S, Verdaguer M, Viovy R 1979. Protonation of phthalocyani-nes. Part I. Effect of substituents on the acid-base properties of copper deri-vatives; spectroscopic studies. *J. Chem. Res*., 3072-3096.

Gasyna Z & Stillman MJ 1990. Absorption and magnetic circular dichroism spectroscopy of metal- and ring-oxidized porphyrins. Spectral characteristics of the one- and two-electron oxidation products of cobalt octaethylporphyrin. *Inorg. Chem*., 29: 5101-5109.

George RE, Snow AW, Shirk JS & Barger WR 1998. The alpha substitution effect on phthalocyanine aggregation. *J. Porphyrins Phthalocyanines*, 2: 1-7.

Gilbert A & Baggott J 1991. Photo-oxidation Reactions, Essentials of Molecular Photochemistry. CRC Press: Boca Raton, pp. 501-525.

Gouterman M 1978. In: Physical Chemistry. Dolphin D (ed.), Vol. 3, Part A. Academic Press, New York, pp. 1-165.

Graczyk A & Bialkowska E 1978. Magnetic properties of oxidation products of phthalocyanine complexes with metal chlorides with electron acceptor properties. *Tetrahedron*, 34: 3505-3509.

Howe I & Zhang JZ 1997. Ultrafast studies of excited-state dynamics of phthalocyanine and zinc phthalocyanine tetrasulfonate in solution. *J. Phys. Chem. A*, 101: 3207-3213.

Huang TH, Reickhoff KE & Voight EM 1982. Shpol'skii effect and vibronic spectra of the phthalocyanines. *J. Chem. Phys.*, 77: 3424-3441.

Jones GJ & Twigg MV 1969. Axial ligand exchange reactions of ferrous phthalocyanine. Exchange of imidazole for dimethyl sulfoxide. *Inorg. Chem.*, 8: 2120-2123.

Kaneko Y, Arai T, Sakuragi H, Tokumaru K & Pac C 1996. Effect of excitation wavelength on photoreduction of metal-free and copper(II) 1,4,8,11,15,18,22,25-octabutoxyphthalocyanines with triethanolamine. *J. Photochem. Photobiol. A: Chem*., 97: 155-216.

Kaneko Y, Nishimura Y, Arai T, Sakuragi H, Tokumaru K, Umeda M, Yamamura S & Matsunaga D 1994. Suppression of UV light-induced fading of color filters of zinc(ii) tetrasulfonatophthalocyanine by introduction of a nitrophenyloxy- or a cyanophenyloy-sulfonyl group. *J. Photopolym. Sci. Technol*., 7: 151-158.

Kaneko Y, Nishimura Y, Takane N, Arai T, Sakuragi H, Kobayashi N, Matsunaga D, Pac C & Tokumaru K 1997. Violet emission observed from phthalocyanines. *J. Photochem. Photobiol. A: Chem.*, 106: 177-183.

Kuznetsova NA, Gretsova NS, Derkacheva VM, Kaliya OL & Lukyanets EA 2003. Sulfonated phthalocyannes: aggregation and singlet oxygen quantum yield in aqueous solutions. *J. Porphyrins Phthalocyanines*, 7: 147-154.

Lakowicz JR 1999. Principles of fluorescence spectroscopy. Kluwer Academic/Plenum Publishers, New York, pp. 184-210.

Lang K, Wagnerova DM, Engst P & Kubat P 1992. Influence of protonation on the reactions of triplet-state sulfonated chloro-aluminium(III) phthalocyanine with dioxygen. *J. Chem. Soc. Faraday Trans.*, 88: 677-680.

Law W-F, Liu RCW, Jiang J & Ng DKP 1997. Synthesis and spectroscopic properties of octasubstituted (phthalocyaninato)titanium(IV) complexes. *Inorg. Chim. Acta.*, 256: 147-150.

Lee LK, Sabelli NH & LeBreton PR 1982. Theoretical characterization of phthalocyanine, tetraazaporphyrin, tetrabenzoporphyrin, and porphyrin electronic spectra. *J. Phys. Chem.*, 86: 3926-3931.

Lever ABP 1965. The phthalocyanines. *Adv. Inorg. Chem. Radiochem*., 7: 27-114.

Lever ABP, Hemstead MR, Leznoff CC, Liu W, Melnik M, Nevin WA & Seymour P 1986. Recent studies in phthalocyanine chemistry. *Pure Appl. Chem.*, 58: 1467-1476.

Lever ABP, Milaeva ER & Speier G 1989. In: Phthalocyanines: Properties and Applications. Leznoff CC & Lever ABP (eds.) Vol. 3, VCH, New York, p. 55.

Leznoff CC & Lever ABP 1989-1993. Phthalocyanines, Properties and Apllications, Vols. 1-3. VCH, New York.

Lim YM, Park SH, Song SH, Park CJ, Ryu H, Jee JG & Yang HS 1999. Synthesis and characterization of phthalocyaninatometal (PcM, M = Fe^{2+}, Co^{2+}) complexes with monodentate aromatic isocyanide ligands. *Bull. Korean Chem. Soc*., 20: 701-704.

Linstead RP & Lowe AR 1934. Phthalocyanines: Part III - Preliminary experiments on the preparation of phthalocyanines from phthalonitrile. *J. Chem. Soc.*, 1022-1027.

MacDonald IJ & Dougherty TJ 2001. Basic principles of photodynamic therapy. *J. Porphyrins Phthalocyanines*, 5: 105-129.

Mack J & Stillman MJ 1994. Photochemical formation of the anion radical of zinc phthalocyanine and analysis of the absorption and magnetic circular dichroism spectral data. Assignment of the optical spectrum of [ZnPc(-3)]-. *J. Am. Chem. Soc.*, 116: 1292-1304.

Maree MD, Kuznetsova N & Nyokong T 2001. Silicon octaphenoxyphthalocyanines: photostability and singlet oxygen quantum yields. *J. Photochem. Photobiol. A: Chem*., 140: 117-125.

McConnell H 1952. Effect of polar solvents on the absorption frequency of n→π electronic transitions. *J. Chem. Phys.*, 20: 700-704.

McHugh AJ & Gouterman M, Weiss C 1972. Porphyrins XXIV: Energy, oscillator strength, and Zeeman splitting calculations (SCMO-CI) for phthalocyanine, porphyrins, and related ring systems. *Theoret. Chim. Acta*, 24: 346-370.

Moser FH & Thomas AL 1963. In: Phthalocyanine Compounds, Reinhold, New York.

Muralidharan S & Ferraudi G 1983. Sequential biphotonic processes in rhodium(III) phthalocyanines. *J. Phys. Chem.*, 87: 4877-4881.

Nensala N & Nyokong T 1998. Photoassisted reduction of thionyl chloride using lanthanide diphthalocyanine complexes. *Polyhedron*, 17: 3467-3475.

Nevin WA, Liu W, Greenberg S, Hempstead MR, Maruccio SM, Melnik MM, Leznoff CC & Lever ABP 1987. Synthesis, aggregation, electrocatalytic activity, and redox properties of a tetranuclear cobalt phthalocyanine. *Inorg. Chem*., 2: 891-899.

Nishimura Y, Kaneko Y, Arai T, Sakuragi H, Tokumaru K, Kiten M, Yamamura S & Matsunaga D 1990. Wavelength-dependent photofading of zinc phthalocyanin in the presence of an electron donor. *Chem. Lett*., 19: 1935-1936.

Nyokong T, Gasyna Z & Stillman MJ 1986. Photooxidation of phthalocyanines. Photoinduced reactivity of the triplet state. *ACS Symp. Ser.*, 321: 309-327.

Nyokong T, Gasyna Z & Stillman MJ 1987. Phthalocyanine π-cation-radical species: photochemical and electrochemical preparation of [ZnPc(-1).+ in solution. *Inorg. Chem.*, 26: 548-553.

Nyokong T & Guthrie-Stratchan J 1993. Kinetics of the reaction of cyanide with ruthenium phthalocyanine complexes. *Inorg. Chim. Acta*, 208: 239-242.

Ogunsipe A, Maree D & Nyokong T 2003. Solvent effects on the photochemical and fluorescence properties of zinc phthalocyanine derivatives. *J. Mol. Struc*., 650: 131-140.

Ogunsipe A & Nyokong T 2005. Photophysical and photochemical studies of sulphonated non-transition metal phthalocyanines in aqueous and non-aqueous media. *J. Photochem. Photobiol. A: Chem.*, 173: 211–220.

Ogunsipe A & Nyokong T 2011. Solvent Effects on the Photophysicochemical Properties of Tetra(*tert*-butylphenoxy)phthalocyaninato Zinc(II). *Acta Phys-Chim. Sin.*, 27: 1045-1052.

Ogunsipe AO, Chen J-Y & Myokong T 2004. Photophysical and photochemical studies of zinc(II) phthalocyanine derivatives - effects of substituents and solvents. *New J. Chem.*, 28: 822-827.

Ogunsipe AO, Idowu MA, Ogunbayo TB & Akinbulu IA 2012. Protonation of some non-transition metal phthalocyanines - spectral and photophysicochemical Conseq & Nyokong T 2003. Effects of substituents and solvents on the photochemical properties of zinc phthalocyanine complexes and their protonated derivatives. *J. Mol. Struc.,* 689: 89-97.

Ozoemena K & Nyokong T 2002. Octabutylthiophthalocyaninatoiron(II): electrochemical properties and interaction with cyanide. *J. Chem. Soc. Dalton Trans*., 1806-1811.

Pennesi G, Ercolani C, Ascenzi P, Brunori M & Monacelli F 1985. Equilibrium and kinetic study of pyridine binding to phthalocyaninatoiron(II) in dimethyl sulphoxide. *J. Chem. Soc. Dalton Trans*., 1107-1111.

Pennesi G, Ercolani C, Rossi G, Ascenzi P, Brunori, M & Monacelli F 1985. Equilibrium and kinetic study of the reaction between phthalocyaninatoiron(II) and carbon monoxide in dimethyl sulphoxide in the presence of pyridine. Evidence for the formation of a transient. *J. Chem. Soc. Dalton Trans*., 1113-1118.

Prasad QR & Ferraudi G 1982. Photochemistry of transition-metal phthalocyanines. Monophotonic and sequential biphotonic photochemical processes of copper(II) tetrakis(N-octadecylsulfamoyl)phthalocyanine in nonaqueous media. *Inorg. Chem*., 21: 2967-2971.

Radhakrishnann S & Deshpande SD 2002. Conducting polymers functionalized with phthalocyanine as nitrogen dioxide sensors. *Sensors*, 2: 185-194.

Robert GG, Petty MC, Baker S, Flowler MT & Thomas NJ 1985. Electronic devices incorporating stable phthalocyanine Langmuir-Blodgett films. *Thin Solid films*, 132: 113-123.

Robertson JM 1935. An *X*-ray study of the structure of the phthalocyanines: Part I - The metal-free, nickel, copper, and platinum compounds. *J. Chem. Soc*., 615-621.

Rosenthal I 1991. Phthalocyanines as photodynamic sensitizers. *Photochem. Photobiol*., 53: 859-870.

Rückmann I, Zeug A, Herter R & Röder B 1997. On the influence of higher excited states on the ISC quantum yield of Octa-aL-alkyloxy-substituted Zn-phthalocyanine molecules studied by nonlinear absorption. *Photochem. Photobiol*., 66: 576-584.

Sastre A, Gouloumis A, Va´zquez P, Torres T, Doan V, Schwartz BJ, Wudl F, Echegoyen L & Rivera J 1999. Phthalocyanine−azacrown−fullerene multicomponent system: synthesis, photoinduced processes, and electrochemistry. *Org. Lett*., 1: 1807-1810.

Schnurpfeil G, Sobbi AK, Spiller W, Kliesch H & Wöhrle D 1997. Photo-oxidative stability and its correlation with semi-empirical MO calculations of various tetraazaporphyrin derivatives in solution. *J. Porphyrins Phthalocyanines,* 1: 159-167.

Sielcken OTE, van Tilborg MM, Rocks MFM, Hendricks R, Drenth W & Nolte RJM 1987. Synthesis and aggregation behavior of hosts containing. Phthalocyanine and crown ether subunits. *J. Am. Chem. Soc*., 109: 4261-4265.

Sobbi AK, Wöhrle D & Schlettwein D 1993. Photochemical stability of various porphyrins in solution and as thin film electrodes. *J. Chem. Soc. Perkin Trans.*, 2: 481-488.

Stillman MJ 1993. Absorption and magnetic circular dichroism spectral properties of phthalocyanines. Part 2: Ring-oxidized and ring-reduced. In: Phthalocyanines. Principles and Properties. Lever ABP & Leznoff CC (eds.)VC .H Publications, New York, pp. 227-296.

Szymczyk I & Abramczyk H 2004. Peripheral substituent and solvent effects on the aggregation and photochemical properties of copper(II)phthalocyanine and copper(II)phthalocyanine-3,4',4'',4'''-tetrasulfonic anion. *Pure Appl. Chem.*, 76: 183-187.

Tokumaru K 1997. In: Phthalocyanines. Shirai H &Kobayashi N (eds.). IPC, Tokyo, p. 170.

Tokumaru K 2001. Photochemical and photophysical behaviour of porphyrins and phthalocyanines irradiated with violet or ultraviolet light. *J. Porphyrins Phthalocyanines,* 5: 77-86.

Tokumaru K & Kaneko Y 1997. In: Phthalocyanines. Shirai H, Kobayashi, N (eds.). IPC, Tokyo, p. 224.

Tomoda H, Saito S & Shiaishi S 1983. Synthesis of metallophthalocyanines from phthalonitrile with strong organic bases. *Chem. Lett*., 313-316.

Torre G & Torres AT 1997. Synthesis and characterization of highly conjugated unsymmetrically substituted phthalocyanines. *J. Prophyrins Phthalocyanines,* 1: 221-226.

Van Lier JE & Spikes JD 1989. In: Photosensitizinig Compounds: Their Chemistry, Biology and Clinical Use. Bock GS & Harnett S (eds.). John Wiley and Sons, Chichester, pp. 17-32.

Villemin D, Hammadi M, Hachemi M & Bar N 2001. Applications of microwave in organic synthesis: An improved one-step synthesis of metallophthalocyanines and a new modified microwave oven for dry reactions. *Molecules,* 6: 831-844.

Wagner SJ, Skripchenko A, Robinette D, Foley JW & Cincotta L 1998. Factors affecting virus photoinactivation by a series of phenothiazine dyes. *Photochem. Photobiol*. 67: 343-349.

Weber JH & Busch DH 1965. Complexes derived from strong field ligands. XIX. Magnetic properties of transition metal derivatives of 4,4',4'',4'''-Tetrasulfophthalocyanine. *Inorg. Chem*., 4: 469-471.

Weitman H, Schatz S, Gottlieb HE & Kobayashi N 2001. Ehrenberg spectroscopic probing of the acid-base properties and photosensitization of a fluorinated phthalocyanine in organic solutions and liposomes. *Photochem. Photobiol*., 73: 473-481.

Wöhrle D, Eskes M, Shigehara K, & Yamada A 1993. A simple synthesis of 4,5-disubstitutted 1,2-dicyanobenzenes and 2,3,9,10,16,17,23,24-octaasubstituted phthalocyanines. *Synthesis*, 194-196.

Wöhrle D & Meissner D 1991. Organic solar cells. *Adv. Mater*., 3: 129-138.