A Brief Review on Synthesis and Studies of Symmetrically Tetra Substituted Metal Phthalocyanines

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Abstract: This review paper gives an overview on the accidental discovery of phthalocyanine, its structural similarity with bio molecules, various methods of synthesis and structural investigations of symmetrically tetra substituted metal phthalocyanine. It also summarizes recent applications and advancements in the use of phthalocyanines and related compounds in various fields such as colorants like dyes and pigments, coating materials and non-colorants such as catalysts, electrochemical sensors, semiconducting materials, photo conductors, as nonlinear optical devices, solar cell functioning materials and use of substituted phthalocyanines in medicinal field. And also, this review article includes research carried out in our laboratory since last two decades. Some literature on the electrochemical studies of phthalocyanines is also reported.

Keywords: Substituted; Phthalocyanines; Applications

History and discovery

Phthalocyanines are a class of organic compounds accidentally discovered as highly colored byproducts of industrial chemical reactions of ortho-(l, 2)-di-substituted benzene derivatives in the beginning of twentieth century. Braun and Tcheranic (1907), working at South Metropolitan Gas Company (London), observed a dark insoluble compound during the preparation of 2-cyanobenzamide from phthalimide and acetic acid. In 1927, Diesbach and Von der Weid, while attempting to synthesize dinitriles of benzene by the corresponding di-bromides and cuprous cyanide in pyridine obtained a blue colored product with 23% yield with formula $C_{32}H_{18}N_8Cu$ and was found to be copper phthalocyanine.

In 1928, the structural elucidation of phthalocyanine was started at Grange mouth plant of Scottish Dyes Ltd. A group of chemists (Dandridge, Drescher, Dunwirth and Thomas) at Scottish Dyes Ltd., noticed the formation of insoluble blue colored impurities during the manufacture of phthalimide from phthalic anhydride and ammonia in the glass lined iron vessel. The colored product on analysis was found to be iron phthalocyanine by Linstead at Imperial College. Iron phthalocyanine was formed by the reaction of phthalimide and metal iron of the vessel. Linstead proposed a structure, which was further confirmed by Robertson using X-ray diffraction studies and was patented in 1928. In 1933, Linstead used the term phthalocyanine for the blue product. The word phthalocyanine was derived from Greek, -"naphtha" means rock oil and "cyanine" means dark blue during the year 1933-1934. The first series of academic reports on metal phthalocyanines were published by Linstead and his coworkers at the University of London in 1934 and are characterized them by the available physiochemical techniques.

Structure of phthalocyanine and its similarity with bio molecules

Phthalocyanines offer a great structural flexibility and can host approximately 70 different elements in the central part of phthalocyanine cavity. Moreover, a

large range of peripheral substituents of phthalocyanines are known, in general which were introduced in order to improve the poor solubility of unsubstituted phthalocyanine.

Structural similarity of phthalocyanine with naturally occurring porphyrins are given in Figure (1). Four isoindole units join through a conjugated system to give the structure of phthalocyanine molecule (Fig-1b). This is a planar tetra dentate (coordination number is four) molecule and was found to form a number of complexes with metals and metalloids by replacing the two hydrogen atoms present at the center of the phthalocyanine molecule (Fig-1a - shows phthalocyanine numbering system). The structural similarity of phthalocyanine with biologically important molecules like Chlorophyll (Fig-1c) and Hemin (Fig-1d) forced the host of scientists to focus their attention on the synthesis and study of physico-chemical properties associated with phthalocyanine class of compounds. During 1930s, metal phthalocyanines emerged as major colorants in the market. The Imperial Chemical Industry and I. G. Farben industry started manufacturing copper phthalocyanine in 1936.

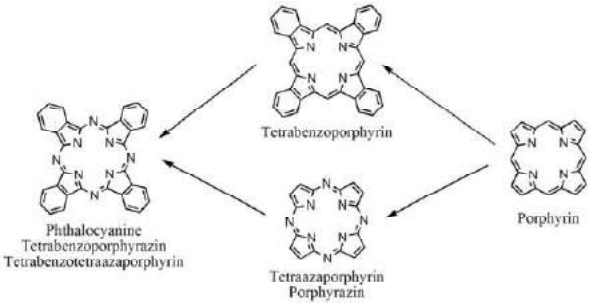
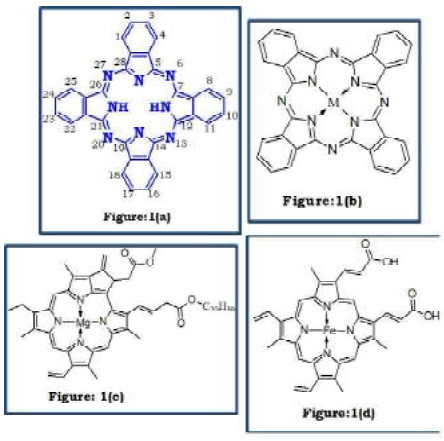


Figure -1: Structural similarity of phthalocyanine with naturally occurring porphyrin.



General methods of synthesis of phthalocyanines

From the literature survey it is clear that, there is no single general method is applicable for the preparation of metal phthalocyanines. The various methods used for the synthesis of metal phthalocyanines are described in figure-2.

We have discussed six important methods of preparations of unsubstituted metal phthalocyanine. However, the substituted metal (II) phthalocyanines can be prepared by using suitable substituted starting materials at the desired positions.

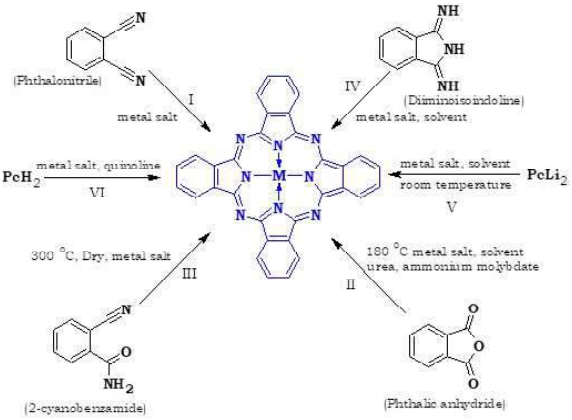


Figure -2: Various methods of synthesis of metal phthalocyanines

Phthalocyanines of cobalt, nickel, chromium, iron, vanadium, lead and titanium have been prepared by method I, in which one mole of phthalonitrile was heated with stoichiometric amount of metal chloride for two hours in quinoline or a mixture of quinoline and trichlorobenzene as solvent. The reaction may also take place in the presence of urea instead of quinoline.

In the second method (II), reaction completes after four hours of heating phthalic anhydride at a relatively high temperature. Trichlorobenzene, nitro benzene or chloro naphthalene is generally used as a reaction medium (solvent). Copper, cobalt, nickel, zinc, iron and tin phthalocyanines have been prepared by adopting the above procedure in the presence of any one of these catalysts like ammonium molybdate, arsenic pentoxide, ferric chloride or zirconium tetrachloride etc.

Methods III and IV involve the heating of o-cyanobenzamide and diiminophthalamide respectively with a suitable metal or metal salt for 4-6 hours. The impurity of phthalimide, o-cyanobenzamide and their derivatives present in the reaction mixture could be removed by repeated heating with sodium hydroxide solution. Iron, nickel, cobalt, magnesium and copper phthalocyanines have been synthesized by these methods.

The method V involves the heating of metal free phthalocyanine and metal salt in quinoline or benzophenone solvent. In the last method (VI), a labile metal phthalocyanine was subjected to demetallation with a salt of less labile metal. This method was generally used to prepare highly stable metal phthalocyanines from dilithium phthalocyanine, which are much more useful in color technology and ink formulations. Because of the solubility of dilithium phthalocyanine in alcohol, it was extensively exploited for the preparation of metal phthalocyanines [**17**]. These reactions involved double decomposition of dilithium phthalocyanine with less labile metal salts in the presence of suitable solvents. Heavy metal phthalocyanine complexes of uranium, lead, thorium, lanthanum, neodymium, samarium, europium, gadolinium, holmium, erbium, thulium, ytterbium, lutetium, dysprosium and hafnium have been synthesized by this method.

The chemistry of formation of phthalocyanines

Synthesis of phthalocyanine class of compounds was started with metal phthalocyanines. The synthesis of phthalocyanine and phthalocyanine complexes has been described at length by Linstead and his co-workers during 1930s. The specific feature of synthesizing phthalocyanine complexes is that they are seldom obtained from an available phthalocyanine ligand. They suggested two general methods for the preparation of metal free phthalocyanine. The first method involves the use of phthalonitriles or o-cyanobenzamide as starting material for the synthesis of metal phthalocyanines, whereas the second method was from a labile metal phthalocyanine. According to the second method, metal free pthhalocyanine can be prepared by boiling oxide-free lithium, sodium, calcium or magnesium phthalocyanines with concentrated sulphuric acid or hydrochloric acid followed by pouring the mixture slowly into the crushed ice. Metal-free phthalocyanine can also be prepared by decomposition of the following metal phthalocyanine derivatives: beryllium, sodium, magnesium, potassium, calcium, manganese, cadmium, tin, barium and lead in acids. Most of these procedures were scaled up and employed for the manufacture of metal-free phthalocyanine. Phthalocyanine forms complexes with a wide variety of metals and metalloids from every group in the periodic table. Most of the reported preparative methods and procedures have been reviewed by earlier workers.

The mechanism of formation of phthalocyanine involves the union of four isoindole units symmetrically around a central metal atom in one reaction system (template synthesis). In the formation of copper phthalocyanine using phthalic anhydride, urea, copper (II) acetate and ammonium molybdate catalyst, the phthalic anhydride is converted into phthalimide, which in turn is converted into monoiminophthalimide and diimino phthalimide. The reaction sequence starting from phthalic acid or anhydride involves the addition of nitrogen atoms to the carbon atoms of the maleic anhydride residue of phthalic anhydride. Urea present in the reaction medium provides the nitrogen atoms but at the temperature of formation of metal phthalocyanines, urea molecules are believed to decompose and polymerize. Therefore, the source of nitrogen is probably the mixture of urea, urea decomposition products and urea polymers.

If the phthalic acid is used as a starting material for the preparation of phthalocyanine, the most probable reaction intermediates formed prior to the formation of metal phthalocyanine are phthalic anhydride, phthalimide, monoiminophthalimide and diiminophthalamide. Structures of these reaction intermediates are shown in figure.3.

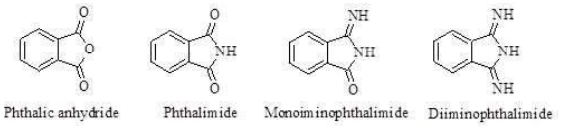
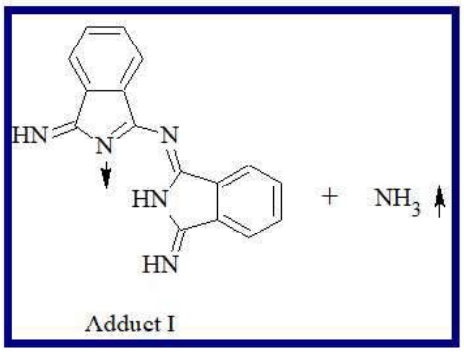
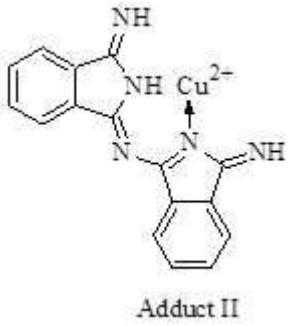


Figure-3: Probable intermediates formed during the synthesis of phthalocyanine.

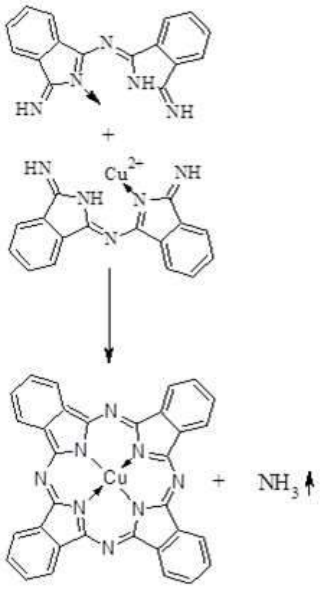
The most accepted generalized mechanism of formation of metal (II) phthalocyanine is either monoiminophthalimide molecule or diimino phthalamide molecule condenses with itself to form an adduct (I), as shown below:



At the same time, either monoiminophthalimide molecule or
diiminophthalamide molecule reacts with copper (II) acetate to give a metallated adduct (II) as shown below:



Consequently, condensation of adducts (I) and (II) takes place to form copper (II) phthalocyanine molecule with the liberation of ammonia molecule.



Industrially, phthalocyanines were produced by using inexpensive materials like phthalic anhydride and urea which is more useful and cheaper than phthalonitrile route to produce higher volume with lower cost applications as shown in figure 4.

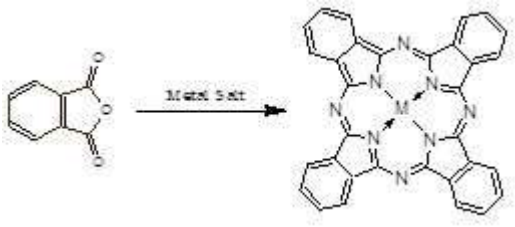


Figure-4: Synthesis of phthalocyanine from phthalic anhydride

Applications of phthalocyanines

Phthalocyanines having wide range of applications in various fields, a concise review of applications were highlighted by different side headings as colorant applications, non colorant applications, new phthalocyanine materials and medicinal applications (Fig. 5).

Colorant Applications

Even though numerous phthalocyanines have been reported since the last hundred years, only copper phthalocyanine, copper polychloro phthalocyanine and their analogues have triggered wide spread applications as colorants. The phthalocyanines have enjoyed popularity as dyes and pigments because of their powerful tinctorial property, excellent fastness, cleanliness and intensity. The phthalocyanines are used as colored stuff in textile industries, printing inks and writing inks, paints, casein finish for leather, coloring plastic goods, etc. Large numbers of reviews and monographs have been documented in the literature regarding the importance and use of the phthalocyanine compounds as valuable paints and pigments. The phthalocyanines are highly useful as inks, especially for security documents and offset inks with minimum reflectance (maximum absorbance) at 720 or 715 nm [1]. Alkyl amido copper phthalocyanines are used for paints, as they improve dispersion power and coloring strength than that of other metal phthalocyanine dyes [2-3]. Reports are documented in the literature regarding the use of metal phthalocyanine derivatives as textile inks in the form of paste or pulp with 20% pigment or an aqueous

dispersion of phthalocyanine pigments have also been used in pad dying along with resin emulsion [4-6]. Phthalocyanines have found extensive use in modern high technology like cyano dyes for inkjet printing, electro photography, in xerography as charge generation materials for laser printers and as colorants for cyano toner. Phthalocyanine pigments have good resistance towards acids, alkali solvents and this property was exploited in the applications of coloring polyvinylchloride fibers, cuproamonium cellulose, viscous nylon fibers, etc.[7]. Phthalocyanine green (copper phthalocyanines with 14-16 chlorine atoms) and phthalocyanine blue (copper phthalocyanine with TTP-355) have been used in almost all types of paints, enamels, emulsions and automotive finishes. Electrochemical syntheses of phthalocyanines have also been used for direct coating of the material on the metal surface. Because of better flow and improved texture, phthalocyanine class of compounds have also found wide spectrum of uses as leather varnishes, heat set varnishes, flexographic ink vehicles and glass varnishes [8-11].

The phthalocyanines were used to color rubber foams, polyurethane foams, styrene polymer foams, polyesters, cellulose acetate sheetings and vinyl chloride polymers, in spite of their weak dispersion. This problem was overcome by using stearic acid and some plasticizers like dioctyle phthalates. The copper phthalocyanine, magnesium phthalocyanine and copper chloro phthalocyanine were also used as stabilizers to enhance the properties like tensile strength and percent elongation of the silicone rubber. The nitro or chloro iron phthalocyanines were used as peptizer for natural and synthetic rubbers.

Non-Colorant applications

A non colorant application of phthalocyanines was graphically shown in figure 4. Phthalocyanines along with their coloring applications have also been used as catalysts and most of them were patented. In the polymerization reactions of drying oils [12-13], iron and cobalt phthalocyanines were used as catalysts. Cobalt phthalocyanine and its derivatives were used as catalysts for the oxidation of mercaptans and active catalyst in the sweetening process of C_4 and C_5 fuel gases, pyrolysis of naphthal and kerosene [14]. Stearically hindered metal phthalocyanines were used as a catalyst for thiol oxidation in the presence of oxygen and showed high stability of the catalytic site with respect to cobalt phthalocyanine [15]. Metal (II) phthalocyanines were used as catalysts in the oxidation of p-nitrotoluene to p-nitrobenzoic acid [16]. Metal phthalocyanines were used as catalysts in the synthesis of cyclic carbonates from carbon dioxide and epoxide [17] and for the polymerization of alkenes [18].

Phthalocyanines were used as catalysts for the aerobic synthesis of meso substituted porphyrins. Slota and Dyrda studied the UV Photo stability of metal phthalocyanines in organic solvents through kinetic studies of photochemical reactions induced by UV radiations [19-20]. Bayer and co-workers synthesized metal (Co, Ni and Zn) phthalocyanines containing eight hydroxy methyl mercapto groups at the periphery positions from 1, 2-bis-(hydroxy ethyl mercato)-4, 5, dicyano benzene and investigated their conductivity behaviour [21]. Renjie Li et.al.[22] synthesized metal free phthalocyanines and studied their electron donating and electron withdrawing nature. Also, they have synthesized 1, 8, 15, 22-tetrasubstituted lead phthalocyanine complexes and exploited their electrochemical properties [23-24]. The phthalocyanines have been used as heat shields for plasma display devices [25]. The metal phthalocyanines are used as photosensitizers and radio sensitizers [26-27]. Nickel (II)-tetra-halo substituted phthalocyanines are used as synthetic metals having increased electrical conductivity [28]. Santigo et. al.[29] synthesized 2, 3, 9, 10, 16, 17, 23, 24-octakis (n-octadecylthio) - phthalocyaninato oxo titanium (IV) and developed it as a liquid crystalline photoconductor [29]. Sulphur containing metal phthalocyanine complexes are used as additives for metal working lubricants and lubricating greases [30].

Kobayashi studied the metal-ligand interactions in the divalent metal phthalocyanine on the basis of their IR, Raman and other relevant spectroscopic methods [31-32]. In 2005, Liao et.al. [33] explained the effect of peripheral substituents on the electronic structure and properties of ligated and un-ligated metal phthalocyanines. Rosa and Baerends [34] explained the interaction of metal with phthalocyanine molecule by the density functional approach method. In addition, they have also satisfactorily explained the bonding in the metal phthalocyanines including the

percent covalence, relative strength of π and σ bonds, interplay of d, s, and p orbitals in the relation between the electronic features, structure and coordination property.

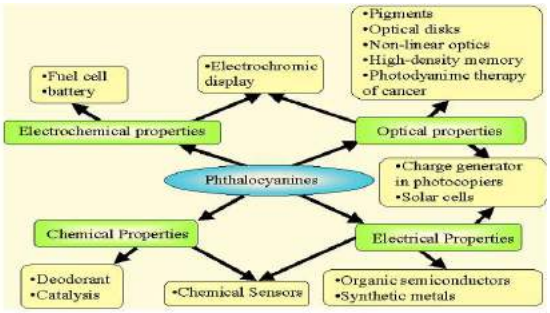


Figure -5: Applications of metal phthalocyanines

Material science applications

Phthalocyanine classes of compounds are considered to be interesting materials with unconventional and unique properties. Discovery of new routes and modifying the existing synthetic routes provided new dimensions for synthesizing these classes of compounds as catalysts, sensitizers, sensors, electro-catalysts, display devices and information storage devices. Though, these properties were identified in the monomeric phthalocyanines, material scientists throughout the world planned to immobilize these materials particularly for the applications like catalysts, sensors, electro-catalysts and display devices. The incorporation of phthalocyanine units in the polymer matrix, combination of phthalocyanines with traditional polymer led to a powerful tool for designing new materials with special properties [35-37]. The special properties associated with new materials were governed solely by the nature of ligand, metal ion and polymer. Whorle et. al., studied the phthalocyanine polymers and according to him polymer with phthalocyanine ligands as a part of new work were insoluble in most of the solvents, which invariably exhibits high thermal stability, good catalytic and excellent electrochemical properties [38-40]. The conductivity behavior of polymer based phthalocyanines was reviewed by Venkatachalam and Krishnamurthy [41].

The literature survey revealed that some of the polymers exhibited electronic conductivity in polycrystalline pressed pellet [42-43] form and in thin films apart from their photoconductivity and dielectric properties. The thin films of polymeric phthalocyanines obtained from 1, 2, 4, 5-tetracyanobenzene with titanium sheets or copper films on pyrolytic graphite were found to exhibit various electrochemical and electro catalytic properties [44-45].

Medicinal Applications

Many uses of metal Phthalocyanines were reported in literature in the field of medicine. The barium and sodium salts of copper phthalocyanine trisulphonic acids "Monsol Blue" 2G and 2GS were employed to stain the plant tissues *in-vivo* because of their non-toxic property. The phthalocyanine based dyes were used to stain virulent germs and specifically stained lipids containing chorine. Derivatives of cobalt phthalocyanines were used as antagonist to inactive hydrogen peroxide and iso-nicotinoyl hydrazide, so that tubercle bacteria from the sputum of patients being treated with iso-nicotinoyl hydrazine may be cultured. Copper poly chloro phthalocyanines had been used as component of an ointment used against mustard gas. Photodynamic therapy is a binary treatment now accepted in clinic for various malignancies in several countries around the world. Phthalocyanine molecules are second-generation photosensitizers with enhanced photophysical and photochemical properties over those of porphyrins. They have been shown to be phototoxic against a number of cell types and tumour models. Cook et. al., explained clearly the photodynamic therapy (PDT) of tumors by substituted metal phthalocyanines. The zinc phthalocyanine with 10 mg/L exposed to 12 J/cm^2 red light killed over 90% tumor cells [46-50]. Current status of phthalocyanines in the photodynamic therapy of cancer was well studied by Cynthia M. Allen et.al in 2001.

Since last two decades, in our research laboratory researchers are involved in extensive investigations on synthesis and studies of substituted metal phthalocyanines, and reported more than twenty research papers are reported in journal of good repute. We have utilized phthalic acid, 3 and (or) 4 - substituted phthalic acid and trimellitic anhydride (1,2,4 – benzene tricarboxylic anhydride) as a starting material for the preparation of respective phthalocyanine, tetra and (or) 3 and (or) 4 –

substituted phthalocyanine and tetra amido phthalocyanine. This will be modified further in order to obtain respective phthalocyanine precursors for the preparation of desired compounds. Some of the synthesized molecules are screened for their biological activity, biosensing ability and conducting ability etc. some of the selected reported research was discussed below.

M.P. Somashekarappa et al reported synthesis and spectroscopic investigations of Iron (III) phthalocyanine complexes [shown in figure 6a and 6b] with chlorides and dianionic, symmetrically halogen substituted phthalocyanine as ligands and about synthesis, spectral and magnetic susceptibility studies on tetrachloro metal phthalocyanines of copper, cobalt, nickel and zinc. [51-52]

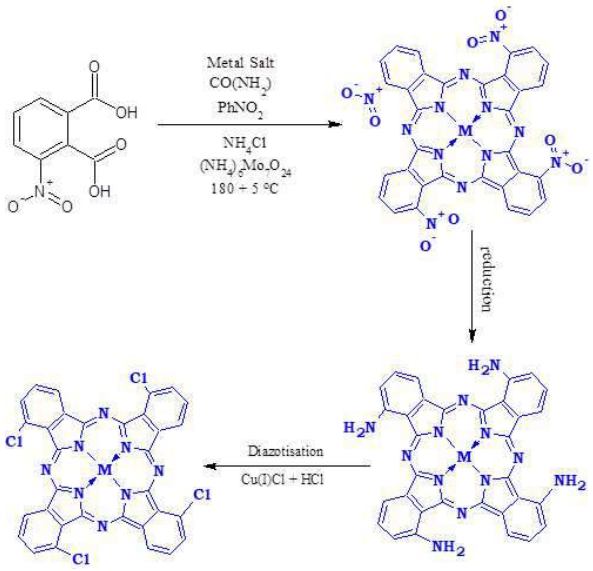
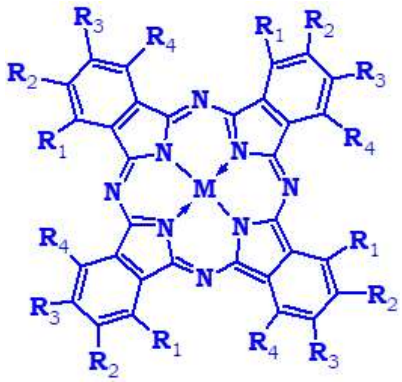


Figure 6a: Synthetic route of tetrachloro copper phthalocyanine



Substituents	Product
R_1 =R_2 = R_3 = R_4 = H	FeCl(pc)
R_2 =Cl; R_1 = R_3 = R_4 = H	FeCl(4-Clpc)
R_1 =Cl; R_2 = R_3 = R_4 = H	FeCl(3-Clpc)
R_2 =Br; R_1 = R_3 = R_4 = H	FeCl(4-Brpc)
R_1 =Br; R_2 = R_3 = R_4 = H	FeCl(3-Brpc)
R_2 =I; R_1 = R_3 = R_4 = H	FeCl(4-Ipc)
R_1 =I; R_2 = R_3 = R_4 = H	FeCl(3-Ipc)

Figure -6b: Derivatives of Iron (IIII) phthalocyanines

K R Venugopala reddy and co workers prepared symmetrically substituted octabromo phthalocyanine pigments of Co (II), Cu (II), Ni (II) and Zinc (II). Which were prepared via the sandmayer's reaction of octamine metal (II) phthalocyanine, shown in figure-7, octa-amine metal (II) phthalocyanine was prepared by the reduction of octa-nitro metal (II) phthalocyanine in turn octa-nitro metal (II) phthalocyanine was prepared from the template synthesis of the starting material 3,5 dinitro phallic acid with divalent metal in presence of suitable solvents and catalyst, synthetic path was displayed in figure-8 and characterized by various spectral and other techniques **[53]**.

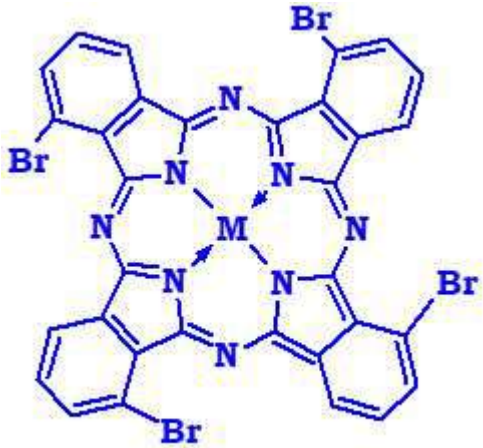
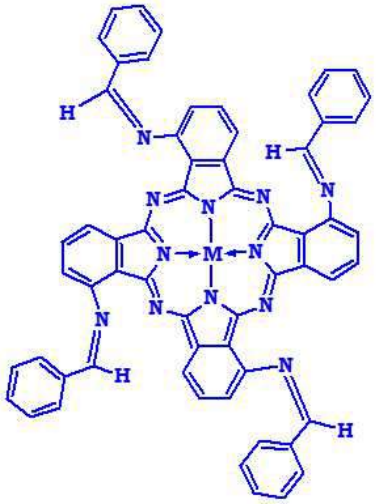


Figure 7: Synthetic route of Octabromo copper phthalocyanines

Moin Khan et al synthesized 2,9,16,23 and 1,8,15,22 tetra imino metal phthalocyanine by the

condensations of terta amino metal phthalocyanine with various carbonyl compounds like aromatic aldehydes such as benzaldehyde, 4-nitro benzaldehyde, 4- methyl benzaldehyde etc. terta amino metal phthalocyanine was prepared from the reduction of 2,9,16,23 and 1,8,15,22 tetra nitro metal phthalocyanine, in turn they will be prepared from 4-nitro phthalic acid and 3-nitro phthalic acid respectively. And all the synthesized compounds were characterized various available techniques like IR, UV-Vis, powder XRD and magnetic susceptibility studies and selected compounds are screened for their biological activities like antifungal and antibacterial. Electro chemical investigations/ redox behavior of molecules was also monitored by various techniques [54-55].



Fasiulla et al[56] prepared 1,2,8,9,15,16,22,23 octa imino metal (II) phthalocyanine by the condensation reactions of octa amino metal (II) phthalocyanine with various aromatic aldehydes such as 4-nitro benzaldehyde, 4- methyl benzaldehyde and 4-methoxy benzaldehyde etc. Octa amino metal phthalocyanine was prepared from the reduction of 1,2,8,9,15,16,22,23 octa nitro metal phthalocyanine, in turn they will be prepared from 3,5 - dinitro phthalic acid. And all the synthesized compounds were characterized various available techniques like IR, UV-Vis, powder XRD and magnetic susceptibility studies [56]

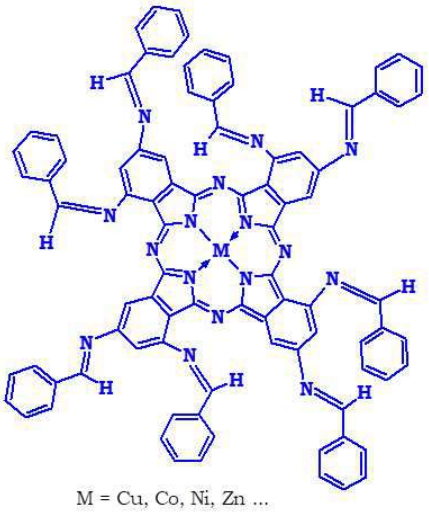


Figure -8: Synthesis of Octa imino metal phthalocyanines

Harish M N K et al[57] decorated nickel (II) phthalocyanine periphery by aryl, 4-subsituted aryl oxadiazole pendants and in continuation introduced soft alkyl chains by varying chain length. He prepared title compounds by the one pot condensations of 2,9,16,23 tetra carboxy nickel (II) phthalocyanine with various aromatic and long chain aliphatic carboxylic acid hydrazides in presence of suitable cyclising agents like phosphorous oxy chloride and poly phosphoric acid in an experimentally optimized reaction condition. Inturn tetra carboxy nickel (II) phthalocyanine was prepared starting from trimellitc anhydride (1,2,4-benzene tri carboxylic anhydride). Further he carriedout DC-conductivity studies and biosensing studies for synthesized complexes. And in continued part of the work 2,9,16,23 tetra [1,3,4] oxadiazole substituted phthalocyanine of copper, cobalt is prepared and characterized. Via electro chemical investigations, bio sensor ability of phthalocyanines was also reported by MNK Harish. Shoukat ali et al studied on the synthesis naphthoxy methylene [1,3,4] oxadiazole substituted and furan and naphthofuran substituted copper, cobalt and nickel phthalocyanine and characterized by available physicochemical techniques like IR, electronic spectral and NMR techniques. Further X-ray diffraction studies and thermal studies were also carried to know the relative crystallinty and thermal stability of the synthesized complexes [57-58].

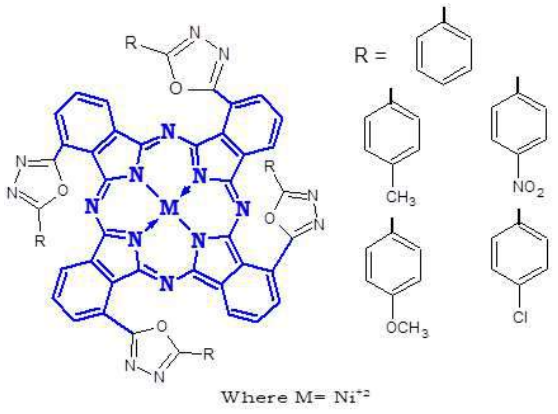


Figure -9a: Aromatic Oxadiazole substituted phthalocyanines

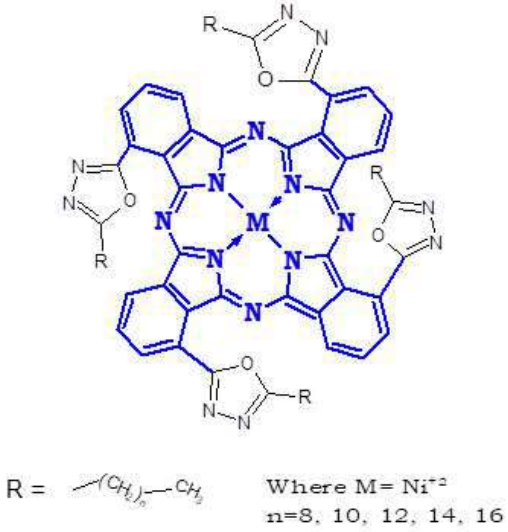


Figure -9b: Aliphatic Oxadiazole substituted phthalocyanines

Rajesh T N et al. [59, 60] synthesized and characterized suphur and nitrogen containing heterocyclic substituted metal phthalocyanine, like benzothiazole [1,3,4]-oxadiazole, 2–amino, 5-phenyl [1,3,4]-oxadiazole substituted phthalocyanines of cobalt, copper and nickel shown in figures 9 and 10 respectively. Along with the characterization by various techniques, some interesting photo physical studies have been reported [**59-60**].

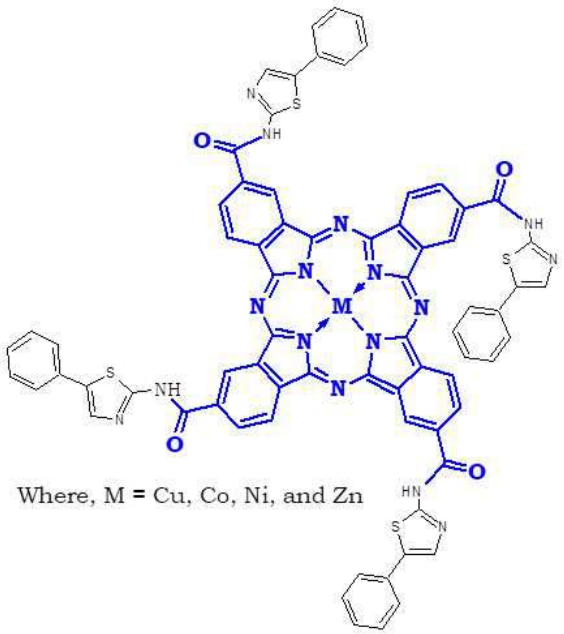


Figure -10: Tetra benzothiazole substituted metal phthalocyanines via amide linkage

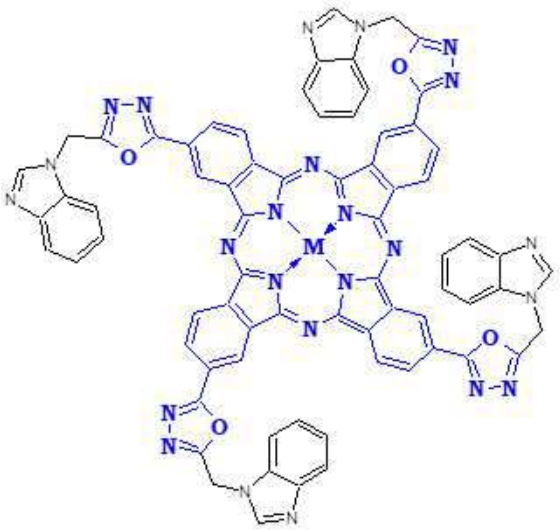


Figure -11: Tetra substituted metal phthalocyanines via oxadiazole ring.

Shoukat Ali et al [61, 62] reported various derivatives of phthalocyanines naphthoxy methylene and furan/ benzo furan [1,3,4]-oxadiazole substituted metal (II) phthalocyanine of copper, cobalt and nickel and are shown in figure-12. Effect of substitution over phthalocyanine periphery in the synthesized compounds compared to tetra carboxy metal (II) phthalocyanine was monitored by spectral techniques

like IR, UV-Vis, ^{13}C-NMR etc. Auxiliary X-ray diffraction studies and thermal studies were also carried to make out average crystallinity and thermal behavior of compounds. Electrochemical investigations were also done with the help of various phthalocyanines. Some neurotransmitters like dopamine and ascorbic acid were also identified by phthalocyanine modified carbon paste electrode by Cyclic voltametric studies.

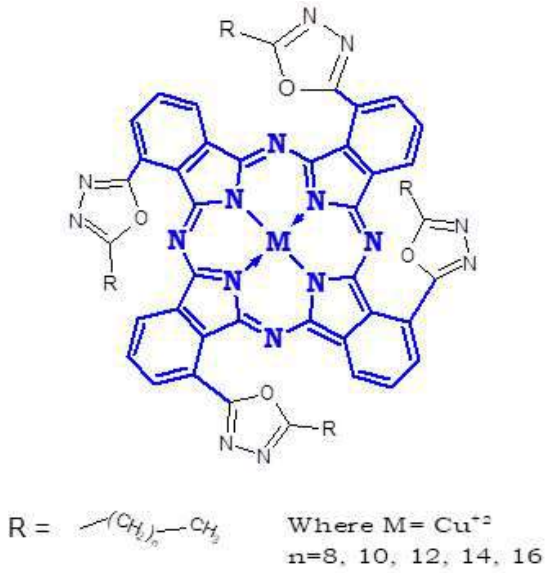


Figure -12b: Aliphatic oxadiazole substituted copper phthalocyanine

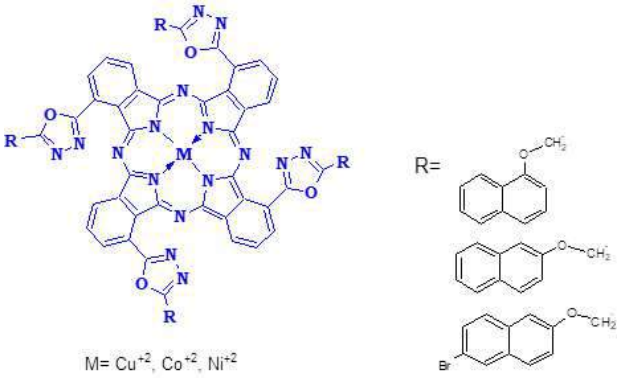


Figure -12b: Tetra naphthoxy methylene substituted metal phthalocyanines via oxadiazole ring

Electrochemical studies of phthalocyanines

As phthalocyanines are supramolecular pi-conjugated electron rich species they are the materials of electrochemical interest. In metal-phthalocyanines, even metal can also act as an active redox center for analytical applications. Electrochemical and spectroelectrochemical characterization of newly synthesized manganese, cobalt, iron and copper phthalocyanines are reported by Mursel Arici and his co-workers from Turkey **[63]**. Leonardo N.Furini from Brazil and co workers extensively studied electrochemical properties of nickel phthalocyanine and the effect of thin film morphology tuned by deposition techniques. **[64]**. As phthalocyanines can be easily used as a co-material with the carbon paste in different proportions, preparation and exploration of phthalocyanine modified carbon paste electrode in analytical applications is of new research interest. Ersin Demir and co-workers from Turkey, explored Phthalocyanine Modified Electrodes in Electrochemical Analysis **[65]** Synthesis and effect of substituent position, metal type on the electrochemical properties of (3-morpholin-4-ylpropoxy) groups substituted cobalt, manganese phthalocyanines was effectively reviewed by Zekeriya from Turkey **[66]**. Poor solubility of phthalocyanine as of high molecular weight and increasing of molecular weight upon substitution is also considered as an advantage of phthalocyanine in electrochemical aspects in the current literature.

Conclusions

The synthesis and characterization of substituted metal (II) phthalocyanine, its versatile applications from colorant textile dyeing to non-colorant including electrochemical sensor applications and material science to biological/medical science has been reviewed. It is hoped that this review article will contribute much more to chemistry literature, young researchers will get better information on phthalocyanine chemistry and thereby one can design their own research for future prospects.

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