Phthalocyanines: Structure, Synthesis, Purification and Applications

Sönmez ARSLAN[1],
Batman Üniversitesi Fen Edebiyat Fakültesi Kimya Bölümü, Batman.
**sonmez.arslan@batman.edu.tr*

Abstract

Phthalocyanines (Pcs) are introduced with its derivates. Their structures were highlighted with their types. Their synthesis and purification methods were given and finally their applications were stated.
Keywords: Phthalocyanine, Structure, Synthesis, Purification and Applications

Özet

Ftalosiyaninler türevleri ile birlikte tanıtıldı Onların çeşitleri ile birlikte yapıları vurgulandı. Sentez ve saflaştırma metodları verildi. Son olarak onların uygulamaları belirtildi.
Anahtar Kelimeler: Ftalosiyanin, Yapısı, Sentezi, Saflaştırma ve Uygulamaları

1. Introduction

Phthalocyanine derivatives, which have a similar structure to porphyrin, have been utilized in important functional materials in many fields. Their useful properties are attributed to their efficient electron transfer abilities. The central cavity of phthalocyanines is known to be capable of accommodating 63 different elemental ions, including hydrogens (metal-free phthalocyanine, H_2-Pc). A phthalocyanine containing one or two metal ions is called a metal phthalocyanine (M-Pc)[1]. Between the time frame of the years 1930-1950, the full elucidation of the Pc chemical structure was determined and its X-ray spectra, absorption spectra oxidation and reduction, catalytic properties, magnetic properties, photoconductivity, and many more physical properties were investigated. As a result of these studies, it was concluded that Pcs are highly colored, planar 18 π-electron aromatic ring systems similar to porphyrins [2,3].

2. Structure of Phthalocyanines

2.1 Tetrapyrolle Macrocycles

Like the porphyrins as in Figure 1, Pcs are a class of macrocyclic compounds have bivalent, tetradentade, planar, 18 π-conjugated electron aromatic ring systems. In contrast, Pcs are composed of four pyrrole units linked by four aza (—N=C—) groups at the α-carbon of pyrrole unit and they have four aza bridges and four phenylene rings [2,3].

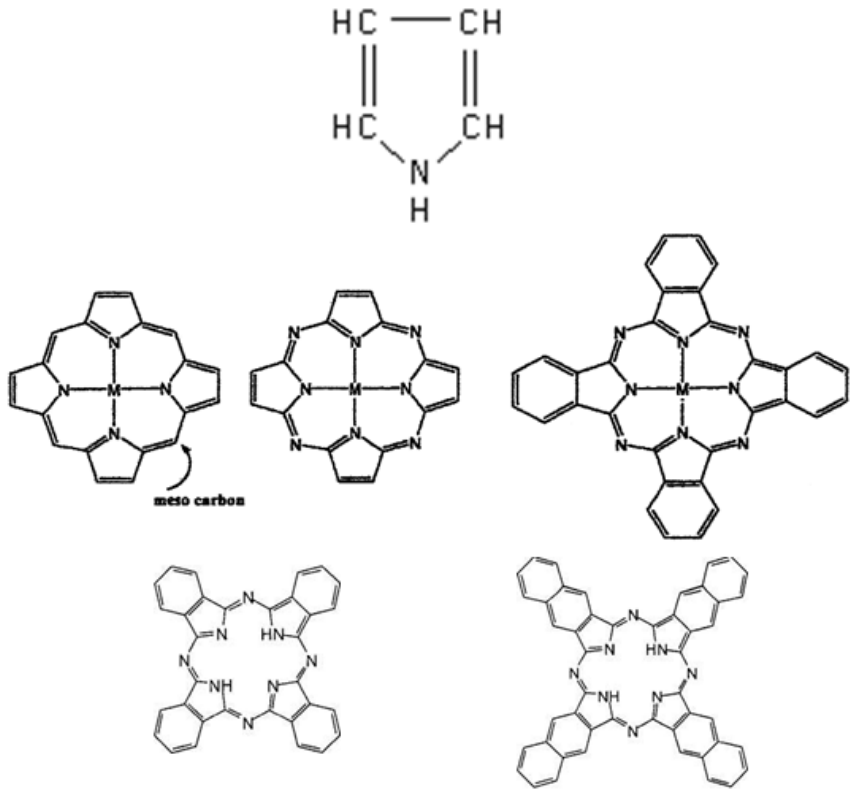

Figure 1: TP macrocycles; pyrrole unit, unsubstituted porphyrine, porphyrazine, MPc , H_2Pc, and NPc.

There are various metal-free (H_2TP) and metallo-tetrapyrolles (MTPs) as in Figure 1. MTPs are highly stable macrocyclic π-systems that display interesting properties that make them potential candidates for various applications.

2.2 Nomenclature of Pcs and Numbering of the benzene carbons on Pcs

Pcs are highly colored, planar 18 π-electron aromatic ring systems similar to porphyrins as in Figure 1. Notation and naming of Pcs are shown in Figure 2.

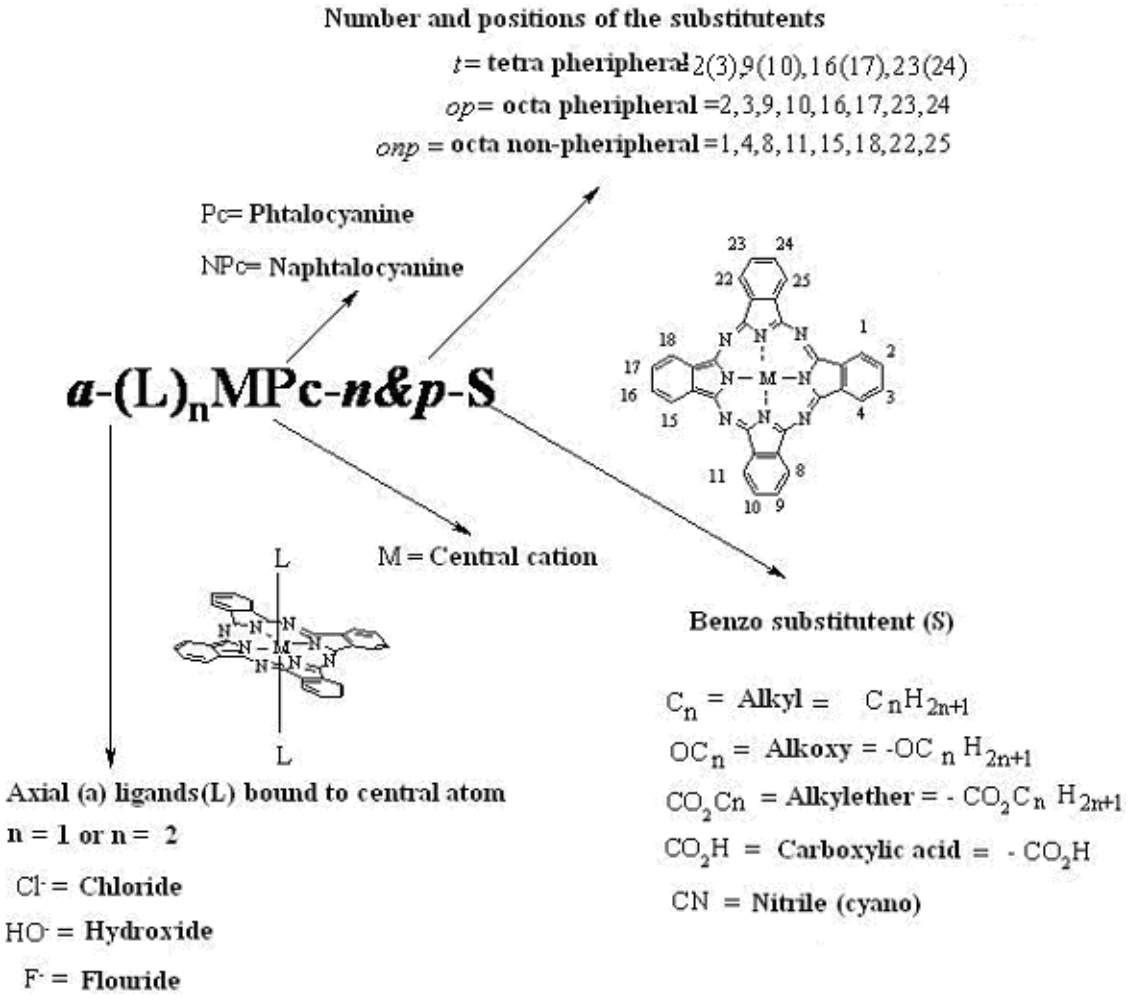

Figure 2: Notation and naming of Pcs.

3. Synthesis and Purification of Phthalocyanines

3.1 Phthalocyanine Synthesis

3.1.1. Synthetic routes to H_2Pcs

Since their discovery in 1907, there have been numerous attempts to improve the synthetic procedures for the preparation of Pc compounds. These attempts were aimed at lowering the reaction temperatures required and obtaining higher yields as well as using starting materials that were easy to prepare or commercially available. An important milestone occurred when Linstead and Lowe reported the use of phthalonitrile as the starting material shown in Figure 3. Unsubstituted H_2Pc can be prepared from phthalonitrile (1) or 1,3-diiminoisoindoline (2) as shown in Figure 3. The compound is virtually insoluble in most organic solvents. It can only be dissolved slightly in high boiling solvents such as 1 -chloronaphthalene, quinoline, etc. In most

laboratory syntheses, various derivatives of o-disubstituted benzene were used extensively for the preparation of H_2Pc. The most commonly used synthetic method is the cyclotetramerization of (1), (1,2-dicyanobenzene) to form H_2Pc, which can be achieved using several different methods, Figure 3. Reaction of (1) with ammonia forms (2) (1,2- diiminoisoindoline) which further condenses under relatively mild conditions to form the desired H_2Pc [4], Figure 3.

The cyclotetramerization reaction proceeds in the presence of either a reducing agent such as hydroquinone or a non-nucleophilic hindered base such as 1,8-diazobicyclo[4.3.0]non-5-ene (DBN) in a melt or in pentanol solution, without the presence of any metal ions that might be incorporated into the product as MPc impurities [2,4], Figure 3. In addition to that H_2Pc can be prepared by refluxing (1) in the presence of lithium metal dissolved in pentanol to form Li_2Pc, which further undergoes demetallation using dilute aqueous acid in Figure 3. [2,3].

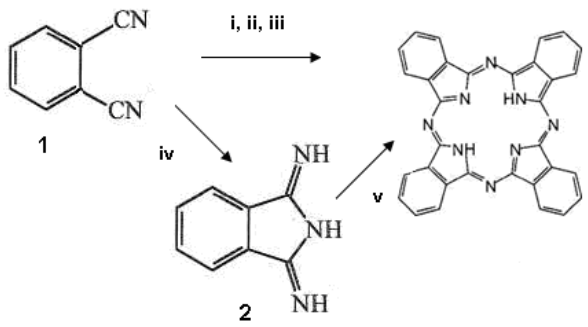

Figure 3: Synthetic routes to H_2Pc; reagents and conditions. i. Lithium, boiling pentanol, followed by aqueous hydrolysis. ii. Fuse with hydroquinone. iii. Heat with DBN/DBU in pentanol solution. iv. Ammonia, boiling methanol, sodium methoxide v. A high boiling point alcohol under reflux.

A Pc molecule consists of a central cavity that can accommodate different metal ions. Introduction of metal cations (e.g. Fe^{2+}, Zn^{2+}, Co^{2+} etc.) into the central cavity of Pc molecule influences its physical properties greatly. For example, when a metal cation is introduced to the Pc molecule, the macrocycle exists as dianion (Pc^{2-}) and can be oxidized or reduced to different oxidation states [5,6].

Many metal atoms can fit exactly into the central cavity without destruction of the planar structure of the Pc; however, some metal ions are too large to be accommodated in the central cavity of the Pc, causing distortion of the planar structure of the macrocycle. The

nature of the chemical bonding between the central metal ion and the four nitrogen atoms of the (2) groups is of interest.

There are two types of possible bonding: electrovalent and covalent [5,9]. According to X-ray analysis, the central metal atom with a +2 oxidation state is bonded to two nitrogen atoms by covalent bonds and to the other two nitrogen atoms by coordinate covalent bonds, Figure 4.

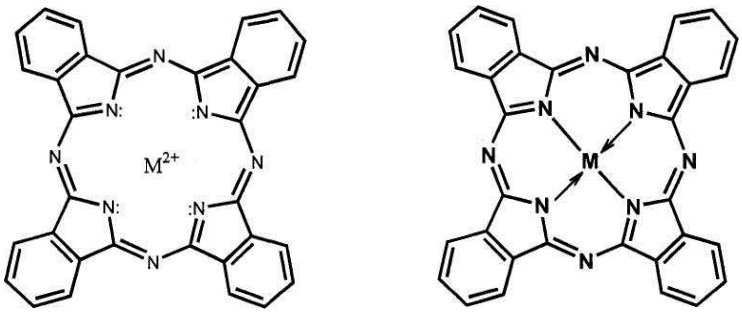

Figure 4: Central metal atom (M)-ligand bonding in Pc

Metal cations with an oxidation state of +1 can also be incorporated into the central cavity. The bonding between the central metal atom with a +1 oxidation state (Li^+, K^+, Na^+ etc.) and the four nitrogen atoms of the macrocycle is considered to be electrovalent in nature, characterized by its ionic character and relative weakness. The central nitrogen atoms can ligate two M^+ atoms, as in Figure 2.5 However; in this case, the central nitrogen atoms ligate two ions. Since both of these cations cannot be accommodated in the central cavity, the metal ions protrude from the plane of the Pc ring. Pc and other alkali metal derivatives possess high solubility in polar organic solvents [5,6].

Due to the strong covalent and coordinate covalent bonding between the Pc and the metal ion, the metal cations cannot be removed without destruction of the macrocycle.

3.1.2 Synthetic routes to MPcs

The first method involves the cyclotetramerization reaction of (1) in the presence of any metal atom or its salt. In this reaction, four moles of (1) is reacted with one mole of metal salt at 180-190°C in the presence of quinoline.

Approximately seventy different elemental ions can be placed in the central cavity of Pcs and their physical properties are greatly influenced by the choice of the central metal.

Pcs usually exist as a (Pc^{2-}) which tightly holds many ions with an oxidation state of +2 such as Cu^{2+}, Co^{2+} and Fe^{2+}. It is difficult to remove most metals from the central cavity of Pcs without destroying the macrocycle [6], Figure 4.

Most MPcs are prepared directly from (1) or (2) using the metal ion as a template for the cyclotetramerization, Figure 5. o-cyanobenzamide (3), phthalimide (4) or phthalic anhydride (5) can be used as a precursor in the presence of a metal salt such as copper(II)acetate or nickel(II)chloride and a source of nitrogen (urea). Also, the reaction between H_2Pc or Li_2Pc and an appropriate metal salt produces most MPcs, as shown in Figure 5. The insolubility of H_2Pcs in most organic solvents requires the use of an aromatic solvent having a high boiling point, such as 1-chloronapthalene or quinoline, to ensure complete metallation. The use of the Li_2Pc as the precursor is easier due to the solubility of this complex in acetone and ethanol, in which the insoluble MPc product is collected on completion of the metal-ion exchange reaction [7].

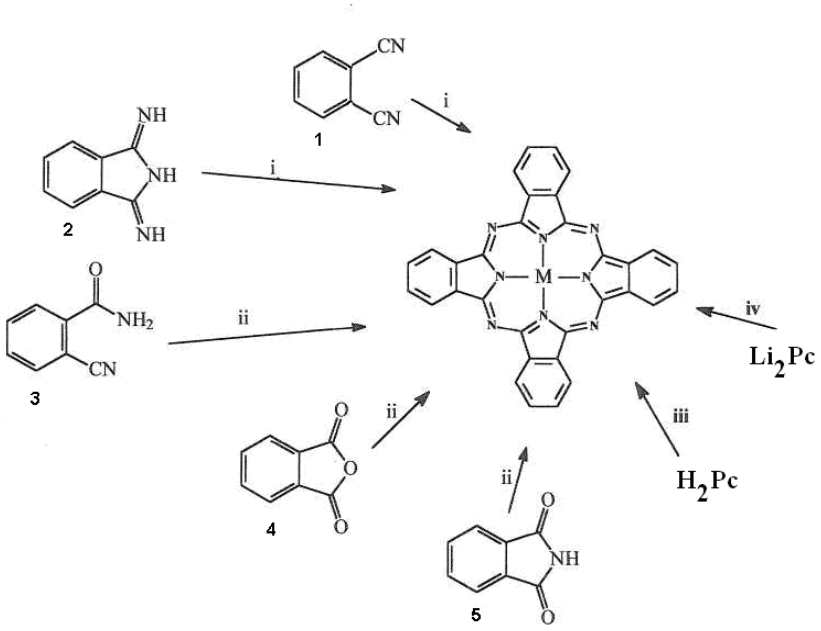

Figure 5: Synthetic routes to MPc; reagents and conditions. i.Heat in a high-boiling-point solvent (hydroquinone) with metal salts. ii. Heat in a high boiling-point solvent with urea and metal salt. iii. Lithium, boiling pentanol, followed by aqueous hydrolysis. iv. Heat in ethanol with a metal salt.

3.2 Purification Methods of Pcs

Methods of purification of substituted Pcs are stated here under nine headings from a to i. Thus substituted Pcs can be purified by a) dissolution in concentrated sulphuric acid,

followed by precipitation in cold water or ice, b) dissolution in concentrated hydrochloric acid, followed by precipitation in aqueous base, for amino-substituted Pcs, c) column chromatography on alumina and solvent evaporation or recrystallization, d) column chromatography on silica gel using normal, flash, or vacuum methods followed by solvent evaporation or recrystallization, e) gel permeation chromatography, f) washing insoluble substituted Pcs with a variety of solvents to remove impurities leaving a purified residue, g) extracting soluble substituted Pcs from insoluble impurities with a variety of solvents and evaporation of the solvent or recrystallization of the extracted substituted Pc, h) sublimation methods and i) other methods, including thin layer chromatography (TLC) and high performance liquid chromatography (HPLC). [2,5].

A few comments should be mentioned concerning problems associated with purification of substituted by purification methods a-i. For method b, the main difficulty is that unwanted amino impurities could be both solubilised and reprecipitated by the given method.

Chromatographic methods c and d can provide excellent separation of soluble substituted Pcs but a word of caution is advised. As all Pcs exhibit strong aggregation effects, it often happens that bands, eluting from a column or spots on TLC that supposedly represent a pure substituted Pc, can incorporate unsubstituted Pc or other Pcs and thus a pure band on column chromatography or a single spot on TLC is by itself an insufficient criterion of purity and should be accompanied by, particularly, mass spectral and other spectroscopic data.

Gel permeation chromatography (Method e) can separate molecules according to size. By this method binuclear Pcs, existing in extended conformations, can be separated from mononuclear Pcs but not those binuclear Pcs that exist in folded conformations. Very insoluble substituted Pcs can be separated from soluble impurities by washing with solvents (method f), but this method leaves other insoluble impurities behind.

It was found that if any solvent, even dimethylformamide, quinoline, dimethyl sulfoxide, methanol, or other unusual solvents could solubilise the Pc to some extend, a rapid filtration through silica gel or alumina may remove polymeric and even more insoluble impurities. On the other hand, relying solely on solvent extraction (method g)

to isolate soluble, substituted Pcs can give mixtures of Pcs or Pcs containing impurities [2,5].

Therefore, method g is the best coupled with chromatographic methods between c-e. Preparative TLC (method i) can be used to separate small quantities of Pcs, but recoveries from TLC are often low and aggregation phenomena discussed above may still give incomplete separations as shown in Figure 5**.**

4. Applications of Phthalocyanines

As a result of their high electron transfer abilities, MPcs have been utilized in many fields such as molecular electronics, optoelectronics, photonics, etc [8-13]. The functions of MPcs are almost universally based on electron transfer reactions because of the 18 π electron conjugated ring system found in their molecular structure. Typical function of phthalocyanine derivatives: Photosensitization, Photovoltaic Light absorption, Photoconductivity, Conductivity, Electronic sensors, Solar cells, Photodynamic therapy, Optical disks, Synthetic metals, Catalysts, Optoelectronics, Liquid crystals. Further, particular derivatives are known to have potential as second-generation photosensitisers for photodynamic therapy (PDT) of cancer [14] because they show strong absorption of the far-red light between the wavelengths of 600 and 850 nm, which has greater tissue penetration properties [15], and satisfactory photosensitization of singlet oxygen [16]. For some applications, the lower solubility of unsubstituted M-Pcs can present problems, but low solubility in common organic solvents can be overcome by the introduction of appropriate substituents onto the ring system. In this context M-Pc analogues containing a pyridine (Py) ring in place of one or more of the benzenoid rings are particularly interesting compounds because quaternization of the pyridine nitrogen is expected to confer solubility in aqueous media. Tetrapyridoporphyrazine M-Pc analogues in which all four benzenoid rings are replaced by pyridinoid rings were first synthesized by Linstead and his co-workers in 1937 [17]. They obtained an insoluble product from the self-condensation of 3,4-dicyanopyridine which was presumably a mixture of ‘positional isomers’ or regioisomers. Subsequently, Yokote and Shibamiya reported the synthesis and dying properties of some unsubstituted benzopyridopyridoporphyrazines [18,19] and the ring system attracted the attention of other groups, resulting in a substantial increase in the

number of known derivatives [20,21]. Yokote and Shibamiya also reported the synthesis of unsubstituted benzopyridoporphyrazines containing a mixture of benzenoid and pyridinoid rings by cross cyclotetramerization of phthalic anhydride and pyridine carboxylic anhydride [22]. For many applications the absorption maxima of M-Pcs are best if moved near the infrared region. The strongest absorption of M-Pcs in the visible region, the so-called Q band, can be attributed to the allowed highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) (π–π^*) transition. The Q-band of M-Pcs can be moved by bathochromic effects through extension of the π conjugation system such as seen in naphthalocyanines and anthracyanines, but yields of naphthalocyanines and anthracyanines are however usually low. M-PCs having substituents have been used to solve the solubility problem.

Kaynakça

[1] Sakamoto K., Ohno-Okumura E., 2009. Syntheses and Functional Properties of Phthalocyanines, *Materials*,1127-1174.

[2] De Diesbach H., Von der Weid E., 1927. Quelques Sels Complexes des o-dinitriles avec le cuivre et la pyridine, *Helvetica Chimica Acta*, 10: 886-888.

[3] Dandridge A.G., Drescher H.A.E., Thomas J., 1929. *Dyes British Patent*, No: 322169.

[4] Elvidge J.A., Linstead R.P., 1955. Conjugated macrocycles. Part XXVII. The formation of tetrazaporphins from imidines. Tribenzotetrazaporphin, *Journal of the Chemical Society*, 3536-3544.

[5] Linstead, R.P., Lowe A.R**.,** 1934. Phthalocyanines Part III:Preliminary experiments on the preparation of phthalocyanines from phthalonitrile, *Journal of the American Chemical Society*, 1022-1027.

[6] Robertson J. M., 1936. *Journal of the Chemical Society*, 1195-1205.

[7] Robertson J.M., Woodward J., 1937. *Journal of the Chemical Society*, 219-230.

[8] Sakamoto K., Okumura E., Hirohashi R. 2004. *Phthalocyanine as Functional Dyes*. IPC: Tokyo, Japan.

[9] de la Torre G., Vazquez P., Torres T., 2004. Role of structural factors in the nonlinear optical properties of phthalocyanines and related compounds, *Chemical Reviews*, 104: 3723-3750.

[10] Cid J.J., Yum J.H., Jang S.R., Nazeeruddin M.K., Martinez-Ferrero E., Palomares E., Ko J., Graetzel M., Torres T., 2007. Molecular cosensitization for efficient panchromatic dye-sensitized solar cells. *Angewandte Chemie International Edition*, 46: 8358-8362.

[11] Kadish K.M., Smith K.M., Guilard R., 2003. *The Porphyrin Handbook*, Volumes 15-20. Academic Press: San Diego, CA, USA.

[12] Pinzon J.R., Plonska-Brzezinska M.E., Cadona C.M., Athans A.J., Gayathri S.S., Guldi D.M., Herranz M.A., Martin N., Torres T. Echegoyen L., 2008. $Sc_3N@C_{80}$-ferrocene electrondonor/acceptor

conjugates as promising materials for photovoltaic applications, *Angewandte Chemie International Edition*, 47: 4173-4176.

[13] Campidelli S., Ballesteros B., Filoramo A., Diaz D., de la Torre G., Torres T., Rahman G.M.A., Aminur E.C., Kiessling D., Werner F., Sgobba V., Guldi D.M., Cioffi C., Prato M., Bourgoin J-P., 2008. Facile decoration of functionalized single-wall carbon nanotubes with phthalocyanines via "Click Chemistry", *Journal of the American Chemical Society*, 130: 11503-11509.

[14] Dougherty T.J., 1993. Photodynamic Therapy, *Phtotochemistry and Phthobiology*, 58: 895.

[15] Moan J., 1990. Properties for optimal PDT sensitizers, *Journal of Photochemistry and Photobiology B: Biology*, 5: 521-524.

[16] Cook M.J., Chambrier I., Cracknell S.J., Mayes D.A., Russell D.A., 1995. Octa-alkyl zinc phthalocyanines: Potential photosensitizers dor use in the photodynamic therapy of cancer. *Phtotochemistry and Phthobiology*, 62: 542-545.

[17] Linstead R.P., Noble E.G., Wright J.M., 1937. Phthalocyanines IX. Derivatives of thiophene thionaphthene, pyridine and pyrazine, and a note on the nomencleature. *Journal of the Chemical Society*, 911-921.

[18] Yokote M., Shibamiya F, Shoji S., 1964. Copper tetra-3,4-pyridinoporphyrazine from pyridine-3,4-dicarboxylic acid. *Journal of The Chemical Society of Japan, Chemistry and Industrial Chemistry,* 67: 166-168.

[19] Yokote M., Shibamiya F, Hayakawa H., 1965. Aza compounds XXIX, *Journal Synthetic Organic Chemistry Japan*, 23: 151-155.

[20] de la Torre G., Claessens C.G., Torres T., 2007. Phthalocyanines: Old dyes, new materials. Putting color in nanothechnology. *Chemical Communications*, 2000-2015.

[21] Tokita S., Kojima M., Kai N., Kuroki K., Nishi H., Tomoda H., Saitoh S., Shiraishi S., 1990. Synthesis and properties of 2,3,9,10,16,17,23,24-octaalkyl tetrpyrazinoporphyrazine, *Journal of The Chemical Society of Japan*, 219-224.

[22] Yokote M. Shibamiya F., 1959. Cu Bz-azaphthalocyanines. *Journal of The Chemical Society of Japan, Chemistry and Industrial Chemistry,* 62: 224-227.