Journal of Chemical Reviews

2024, Volume 6, Issue 1

Review Article: Recent Developments in Synthesize, Properties, Characterization, and Application of Phthalocyanine and Metal Phthalocyanine

Othman Abdulrahman Hamad[1], **Rebaz Obaid Kareem**[2,*], **Peshang Khdir Omer**[1]

[1]*Chemistry Department, College of Science, University of Raparin, Al Sulaymaniah, 46012 Ranya, Iraq*
[2]*Physics Department, College of Science, University of Halabja, 46018, Halabja, Iraq*

Use yor device to scan and read the article online

Citation: O.A. Hamad, R.O. Kareem*, P.K. Omer, **Recent Developments in Synthesize, Properties, Characterization, and Application of Phthalocyanine and Metal Phthalocyanine.** *J. Chem. Rev.,* **2024,** *6*(1), 39-75.

https://doi.org/10.48309/JCR.2024.412899.1250

Article info:
Received: 26 August 2023
Accepted: 10 October 2023
Available Online: 31 October 2023
ID: JCR-2308-1250
Checked for Plagiarism: Yes
Language Editor: Dr. Fatimah Ramezani
Editor who Approved Publication: Prof. Dr. Ghasem Rezanejade Bardajee

Keywords:
Phthalocyanines, Properties, Syntheses, Variety applications, Characterization, Photodynamic therapy

ABSTRACT

Phthalocyanines (Pcs) are macrocyclic chemical compounds that have attracted a lot of attention in the last decade due to their varied properties. Over time, the extensive utilization of PCs has been justified due to their exceptional nature, with their numerous desirable qualities stemming from the straightforward and adaptable methods for altering their structure. These modifications have enabled a wide range of applications, including photodynamic therapy for cancer treatment, chemical sensing, solar cells, nonlinear optics, and, most recently, photoinitiator systems for various polymerization processes, including free radical, cationic, and controlled radical polymerizations. Pcs distinctive electrochemical, photochemical, and photophysical properties have made all of these advancements possible. Our motivation to emphasize the significance of phthalocyanines in chemical science is driven by their remarkable success story. This study commences with an exploration of the design and synthesis of Pcs tailored for specific applications, followed by a spotlight on innovative research that harnesses the diverse activation capabilities of these macrocycles to initiate various types and also describes characterization.

Othman Abdulrahman Hamad: He is originally from the north of Iraq (Kurdistan) Al-Sulaymaniah. He has BS.c. degree in general chemistry from the University of Salahaddin University-Erbil in 2004, and received MSc. degree in chemistry in 2014 at Kahramanmaraş - Sütçü İmam University in Türkiye. He is studying PhD. in Inorganic Chemistry at Firat University in Türkiye.

***Corresponding Author: Rebaz Obaid Kareem** (obedrebaz9@gmail.com)

Rebaz Obaid Kareem: He earned the BS.c. degree from the Department of Physics in 2018 at Halabja University, College of Science, Halabja, Iraq. He also received the M.Sc. degree in General Physics in 2023 from Firat University, Turkey. His research interests include Bioceramics and Metal Oxide Structures.

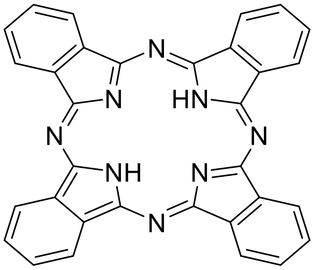
Peshang Khdir Omer: Peshang studied for undergraduate degree in Chemistry at Koya University-Koya between 2008 and 2012. After a year, he got a position at Raparin University as assistant Chemistry. In 2021, he obtained MSc. degree in Inorganic Chemistry at Firat University, Turkey, at the same year; he got a position as an assistant lecturer and started his PhD. degree at Koya University in Iraq.

Content

1. Introduction

Coordination chemistry is a branch of chemistry that focuses on the study of coordination compounds. It involves the examination of compounds in which a central metal atom is encompassed by one or more anions and molecules, with potential direct connections to the metal. These connections may or may not result in a charge within the complex. When a complex carries an electrical charge, its stability is maintained by counter-ions in its immediate vicinity. The central metal ions serve as the central structural elements of these complexes, and they are surrounded by a diverse assortment of neutral molecules and/or ions. While it is tempting to assume that coordinating covalent bonds solely link these elements to the central ion, the actual bonding in coordination compounds is typically more intricate. The molecules or ions forming the outer layer around the metal ion are referred to as ligands [1].

Phthalocyanines are indeed part of coordination chemistry. They are a class of coordination compounds that consist of a central metal atom or ion coordinated with phthalocyanine ligands. In this context, they are a specific example of compounds studied within coordination chemistry, where the focus is on



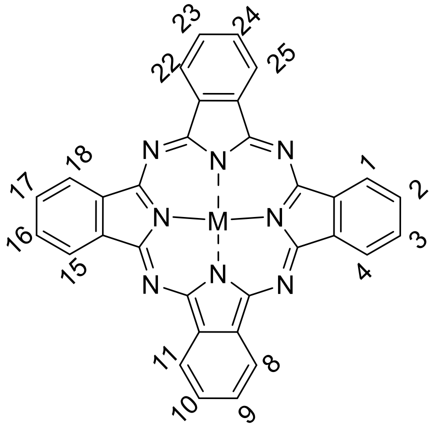
(**1**)

Scheme 1. Phthalocyanine structure (**1**)

understanding the interactions and properties of such coordination complexes [2].

Phthalocyanines (Pcs) are organic or organometallic compounds owning the basic porphyrin ring structure of formula ($C_{32}H_{18}N_8$), shown in **Scheme 1** [3]. Phthalocyanines are planar and macro-heterocyclic compounds [4,5] and solid at room temperature [6]. The molecule of Pcs has an aromatic structure and possesses exceptional stability due to its conjugation. Pcs are macrocycle compounds having an 18π-electrons system [7,8]. Pcs compounds are obtained from about seventy different metals and could have been prepared [4].

The chemical formula for phthalocyanine is 29*H*, 31*H*- tetrabenzo [*b*,*g*,*l*,*q*]- 5, 10, 15, 20-tetraazaporphine. According to the Hückel rule (4n+2), when n = 10, the dianionic ligand with 42 electrons displays pronounced aromaticity, as displayed in **Scheme 2** [9], as well as center metal atoms [10].



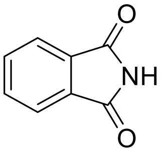
(**2**)

Scheme 2. Metal phthalocynine structure (**2**)

Phthalocyanines, unearthed during the early 19th century, are one of the few types of colorants still in use today, The discovery and synthesized of phthalocyanines was a complete accidentally, also in 1907, Von Braun produced a phthalocyanine that included no metals [11], and de Diesbach prepared Cu-Pcs in 1927 [12]. Although they failed to define their findings, chemists at Scottish Dyes Ltd are credited with discovering phthalocyanines when they synthesized and analyzed Fe- Pcs. According to the generally accepted account of their discovery, four chemists named Dandridge, Drescher, Dunworth, and Thomas came upon an insoluble blue substance during the regular production of phthalimide from phthalic anhydride, both of which are white and solids. A registered application was filed in 1928 [13]. The product, which was collected as phthalimide, was discovered to be tainted with a dark-colored impurity. The impurity remained in the Phthalimide despite heating or dissolving in the water and most reagents [14]. Phthalimide structure is shown in **Scheme 3**. This compound was created by reacting phthalic anhydride with ammonia in a glass-lined iron kettle [15]

The phthalimide and impurity were separated and examined [16]. When cuprous chloride was introduced into molten phthalimide, a vigorous reaction occurred, resulting in the formation of a colored product [17]. The metals had to be a key part of the structure of this new compound. This structure was later confirmed by X-ray diagrams [18].

The name of "phthalocyanine" contained from the Greek words for "rock oil" (naphtha) and "dark blue" (cyanine). This term was originally coined by Sir Reginald Linstead in 1934 to describe these macrocyclic molecules [19].



(**3**)

Scheme 3. Phthalinide structure (**3**)

However, Pc is the first name of a particular compound that represents substituted and unsubstituted Pcs [20].

In 1934, Linstead and his colleagues conducted experiments that clarified the structure of metal- Pc [21,22]. Many different physical features of Pc were studied between the 1930s and the 1950s, including its X-ray spectrum, reduction, oxidation, and absorption spectra, in other words, Pcs possess various attributes such as their ability to act as catalysts, exhibit magnetic characteristics, and numerous other properties. As a result, Pcs can be described as flat aromatic ring compounds composed of 18-electron atoms and displaying a wide range of colors, reminiscent of porphyrins [23,24]. Prior to 1960, there existed highly conjugated phthalocyanines were already in existence, and these derivatives of Pcs exhibited a robust structural framework. Their valuable chemical and physical characteristics, such as vibrant colors and conductivity, along with their exceptional chemical and thermal stability, gave them a considerable edge. This led to their extensive adoption in a variety of applications [25].

Metal phthalocyanines (M-Pcs) are identified with over 70 distinct elemental ions, including hydrogen without metal phthalocyanine (H_2-Pc) [26]. The molecules have been given bonding between the center atom (its metals) with a great organic ring structure surrounding it. The central metal atom is surrounded by four nitrogen atoms like a square. It has two kinds of bonding possibly covalent and electrovalent bond [27]. Besides these have found widespread use in electronics, electrophotography, solar cells, liquid crystals, chemical sensors, and Langmuir-Blodgett films [28,29]. When the core metal or the pivot or permutation rings of phthalocyanines are altered, they find applications in a wide range of disciplines [30]. Metal-free organic sensitizers can shift the Soret and Q bands toward lower energy absorption by employing porphyrins and phthalocyanines compounds, while others use strong electron donating or withdrawing moieties to tune the optical band gap [31].

1.1 Typical properties of phthalocyanines

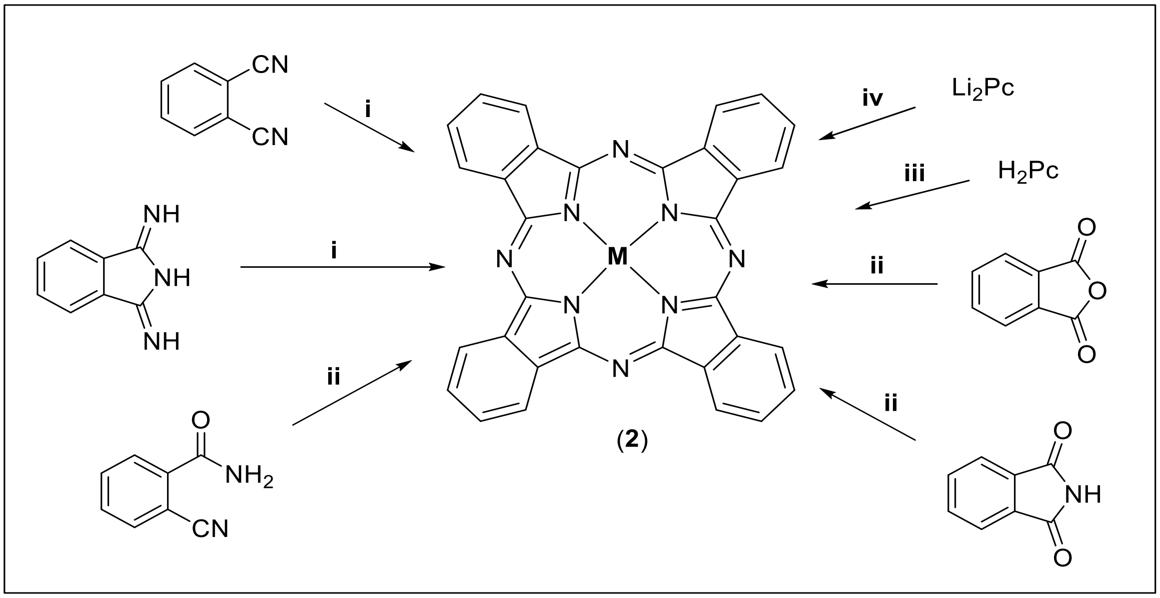
Pcs are thermally stable, resistant to strong acids and bases [6], that have been effectively used as working parts in semiconductor and electrochromic gadgets [32]. However, phthalocyanine has low solubility and limited solubility in DMSO and other polar chemical solvents [33].

Pcs exhibit high absorption in the red (700 nm) portion of the visible spectrum [34]. Pcs have great promise as photosensitizers for use in photodynamic therapy (PDT) of cancer [35,36], they are ideal candidates for PDT because of their numerous benefits [37,38]. However, they have been used successfully implemented as active components in semiconductor and electrochromic devices [32].

Purification of substituted Pcs might be accomplished by soluble in strong sulphuric acid, then precipitating in cold water or ice, for amino-substituted Pcs, dissolving in concentrated hydrochloric acid, then precipitating in water. Therefore, alumina column chromatography with evaporation or recrystallization of the solvent and conventional, flash, or vacuum column chromatography on silica gel, then the solvent is evaporated or the crystals are reformed [23,39]. Gel chromatography can separate molecules based on their size, but it cannot differentiate mononuclear Pcs from those in folded conformations. Washing with solvents can remove very insoluble substituted Pcs from soluble impurities, but this process leaves other insoluble impurities behind [40], as shown in **Scheme 4.**

2. Synthesis of Phthalocyanines

Metal-substituted or non-substituted phthalocyanines might be produced that have not been replaced and can be employed as a stable colorant [41]. These issues are solved by phthalocyanine, which includes dendrimers and polymers. Aside from that, Phthalocyanine is made up of polymers with different names depending on their side groups and the main chain of the polymeric cycle. Organic solvents do not dissolve polymerics or macrocyclic



Scheme 4. Reagents and conditions for MPc synthesis (**2**): i. Mix metal salts with a solvent that has a high boiling point (hydroquinone). ii. Mix the urea and metal salt in a solvent with a high boiling point. Iii. Lithium, then pentanol aqueous hydrolysis at high temperature. iv. Warm a metal salt dissolved in alcohol.

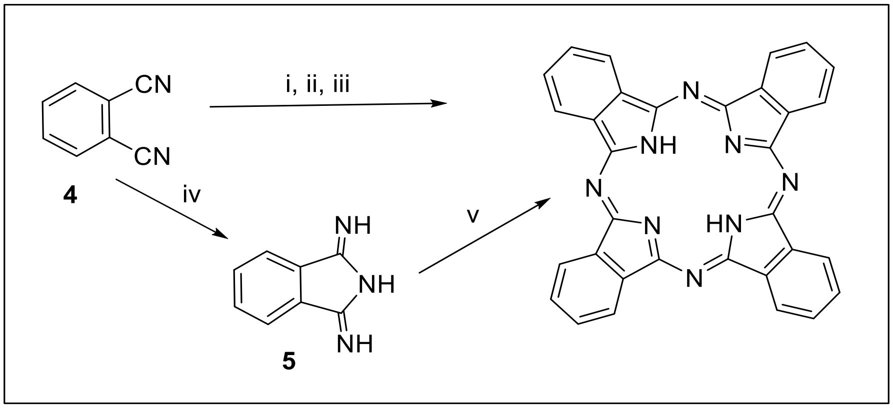
phthalocyanines. It takes a lot of effort to achieve utility and Efficiency [42].

Phthalocyanines may exhibit varying properties in both their solid and solution phases, particularly in terms of nonlinear optical properties. The excitonic effect, which is linked to intermolecular interactions, might explain this discrepancy [43].

2.1. Synthesis of hydrogen substituted phthalocyanines

As demonstrated in **Scheme 5**, unsubstituted H_2Pc may be made from phthalonitrile (1) or 1,3-diiminoisoindoline (**5**). In most organic solvents, the molecule is almost insoluble. In high boiling solvents like 1 -chloronaphthalene, quinoline, and others, it can only be minimally dissolved. The most frequent technique for forming H_2Pc is (**4**) (1,2-dicyanobenzene), which may be done in various ways. (1) reacts with ammonia to generate (**5**) (1,2-diiminoisoindoline), which then reacts in a milder condition to form H_2Pc [44].

One example of a reducing agent is 1,8-diazobicyclo(4.3.0)non-5-ene (DBN), which



Scheme 5. Regaents and conditions for H_2Pc synthesis: i. Lithium, followed by aqueous hydrolysis of boiling pentanol. Ii. Add hydroquinone to the mix. iii. Heat in a pentanol solution containing DBN/DBU. v. Reflux of alcohol with a high boiling point. iv. Ammonia, boiling methanol, sodium methoxide

may be used as a melt or a pentanol solution, with free ion and metal, is used in the cyclotetramerization procedure, with the result as M-Pc impurities [45, 39].

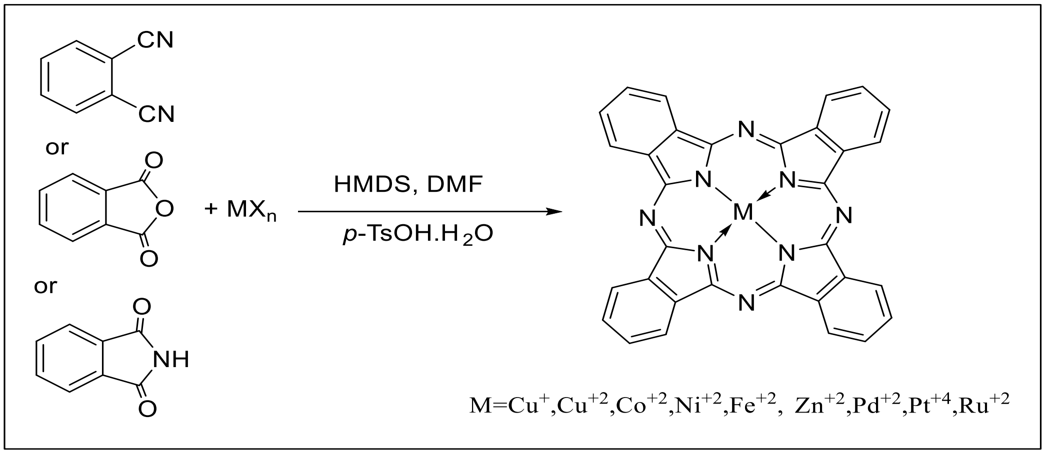
Many papers on the synthesis and research of heterocyclic substituted metal phthalocyanine have been published in recent years [46]. The physical and chemical characteristics of the Pc macrocycle are greatly influenced by the substituents and metal atoms introduced, allowing it to be used in a variety of applications [47].

Metal halides (MXn) or/and phthalonitrile (PN), phthalic anhydride (PA), and phthalimide (PI) were used to optimize the reaction conditions. The CuCl: phthalonitrile: hexamethyldisilazane (HMDS): dimethyl formamide (DMF): para toluene sulphonic acid (*p*-TsOH.H_2O) molar ratio of 1:4:4:1:0.41 produced the greatest results. In a typical experiment, PN, PA, or PI was mixed with HMDS, Metal halides (MXn), p-TsOH, and DMF in a glass tube and swirled for 20 minutes [45], refluxing with more metal solution [23], under a nitrogen environment. After that, the tube was sealed and the mixture was microwaved for 10-15 minutes. To further investigate the breadth and limits of this reaction, we used various raw materials and metal salts, including $Cu(OAc)_2.H_2O$, $CuCl_2.2H_2O$, $CoCl_2$, $NiCl_2$, $FeCl_2.4H_2O$, $ZnCl_2$, $PdCl_2$, $PtCl_4$, and $RuCl_3$, as can be seen from **Table 1** [45].

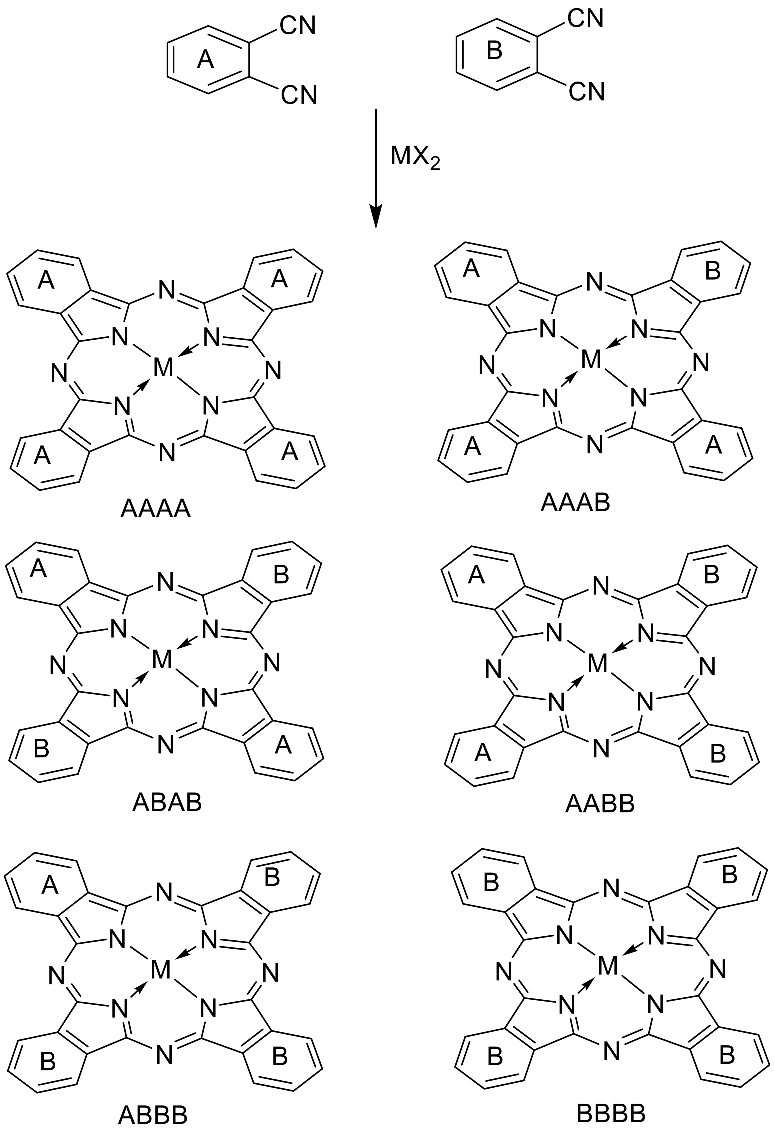
After several minutes, various starting materials such as PN, PA, and PI are transformed into MPcs with good yields. It's worth noting that in the absence of HMDS and *p*-TsOH.H_2O as a catalyst, the reaction yields plummeted, and in the case of the PN, the process was totally halted. Furthermore, no reaction has happened with any of the raw ingredients in the absence of DMF [45]. The Pcs with various central metals and peripheral substituents were found to have heavier central metals [48] , as showed in **Scheme 6**.

Table 1. MPc synthesis by the reaction of PN, PI, or PA under microwave irradiation [49]

Entry	MXn	Yield (%)/time (min)		
		PN	PI	PA
1	CuCl	78(7)	75(7)	50(8)
2	$Cu(OAc)_2.H_2O$	55(7)	68(8)	35(8)
3	$CuCl_2.2H_2O$	88(7)	50(8)	62(8)
4	$CoCl_2$	86(7)	48(9)	48(8)
5	$NiCl_2$	50(7)	45(9)	30(8)
6	$FeCl_2.4H_2O$	78(7)	44(9)	40(8)
7	$ZnCl_2$	69(7)	40(10)	33(8)
8	$PdCl_2$	87(7)	68(9)	72(8)
9	$PtCl_4$	76(15)	0 (15)	17(12)
10	$RuCl_3$	65(15)	18(12)	0(12)



Scheme 6. Microwave-irritated hexamethyl dislazane to create phthalocyanines

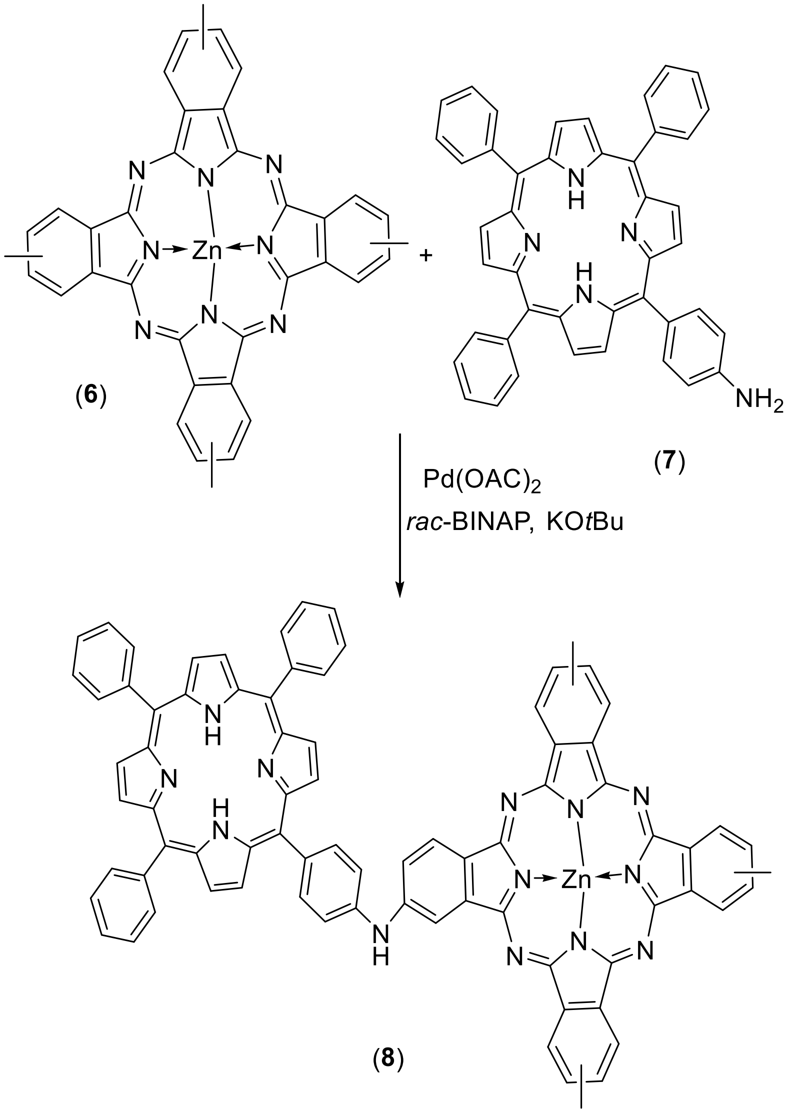


Scheme 7. Concentration of twice PNS, A and B to yield the following products

2.2. Synthesis of peripheral substitution and fused ring (Mixed and cross-condensations)

M-Pc analogs and related systems [50] have been made, going back to Linstead and co-workers' investigations in the 1930s, by condensation operations employing various methodologies to make compounds having AAAA, AAAB, AABB, ABAB, ABBB, and BBBB structures. In this review, we use Leznoff's phrase [51], which refers to the total separation of the various structures [52,53]. Prepare the replies that have been well reviewed [54].

There are four items available [55]. Even so, Recent research on low symmetry Pc has centered on the readily distinguishable AAAB product produced by porphyrazine (Pz), naphthalocyanine (Nc), unsubstituted Pc, R-substituted Pc, [56] instead of tetrapyrazo porphyrazine,-substituted Pc, [57] and R,-instead of Pc [58] AAAA parent chemical substance, as well as Pc, a partially fused Pc,[59] R-substituted Pc [60] Pc AAAA parent compounds with R,-substituted [61], as shown in **Scheme 7.**

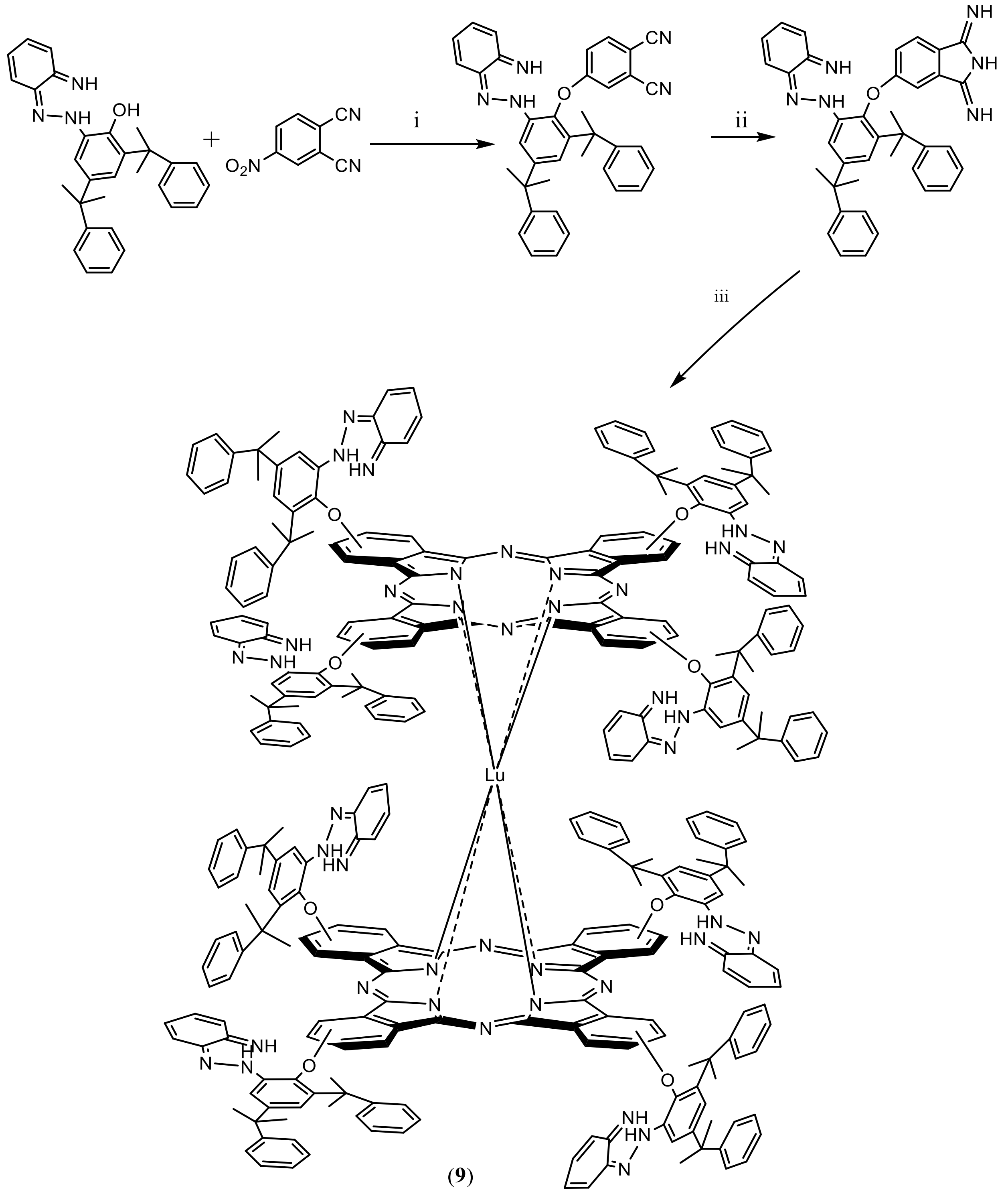


Scheme 8. Construction of Pc-porphyrins with an NH-linkage with a *meso*-phenyl group replaced

Since the late 1980s, various selective techniques for the synthesis of particular low-symmetry Pc have been established [62]. The production of poor symmetry free base AAAB complexes was highlighted by Kobayashi *et al*. in 1990 [63]. Hoffman and Barrett used this strategy to a limited extent [64]. In recent years, Several selective techniques for the synthesis of targeted low symmetry Pc compounds have been developed since the late 1980s [62,65].

2.3 Phthalocyanine-porpherene linkage synthesis

The Sonogashira cross coupling reaction proved effective in creating more plural structural systems of Pc with sub Pc [66]. The electron transport mechanisms in highly conjugated systems were then explored. In addition, NH-linked Zn-Pc was prepared [67]. In the presence of potassium tert-butoxide, Under the Buchwald-Hartwig amination conditions utilizing Pd(OAc)/*rac*-BINAP as the catalytic system, the interaction between amino-functionalized porphyrin 8 and 4-iodophthalonitrile resulted in the formation of interconnected entities. These entities were linked to the meso-phenyl group [67], as shown in **Scheme 8.**



Scheme 9. Synthesis and Purification of product 7 with a yield of 25%; (i) K_2CO_3, DMF, Ar; (ii) NH_3, CH_3ONa; (iii) $Lu(CH_3COO)_3 \cdot H_2O$,1,8- diazabicyclo(5,4,0) undec-7-en (DBU), octanol, Argon atmosphere

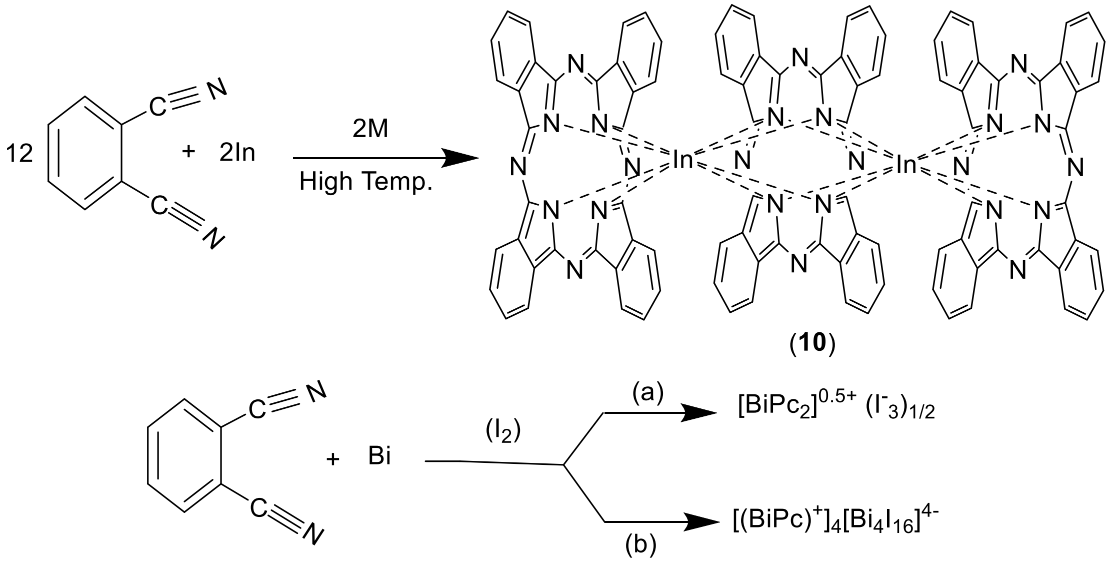
2.4 Double-deckers phthalocyanines synthesis

Lutetium $(C_{30}H_{28}N_{30})_4$ [Double Deakers] The Z-scan process was used to produce 2Lu. From the nonlinear absorber 4-Nitro phthalonitrile, this product might be obtained by a base-catalyzed nucleophilic nitro group displacement method. To make 4-[2-(2*H*-1,2,3-Benzotriazol-2-yl)-4,6-*bis*(2-phenylpropan-2-yl) phenoxy] phthalonitrile, a single-step reaction was performed at 70-90 °C in dry DMF in an argon atmosphere. 5-[2-(2*H*-1,2-Benzotriazol-2-yl)-4,6-bis(2-phenylpropan-2-yl) phenoxy] To get bis(phthalocyaninato) lutetium(III) complex, 1,3-diiminoisoindoline was reacted with lutetium(III) acetate monohydrate in octanol under the catalytic influence of DBU for 12 hours at high temperature in an argon atmosphere. Next, a precipitate (250 mL) was made by dissolving the mixture in water. The solution was diluted to a volume of 250 mL with water and allowed to precipitate. Using silica gel column chromatography (THF/methanol, 10:1), product **9** was synthesized and purified with a yield of 25% [68], as shown in **Scheme 9.**

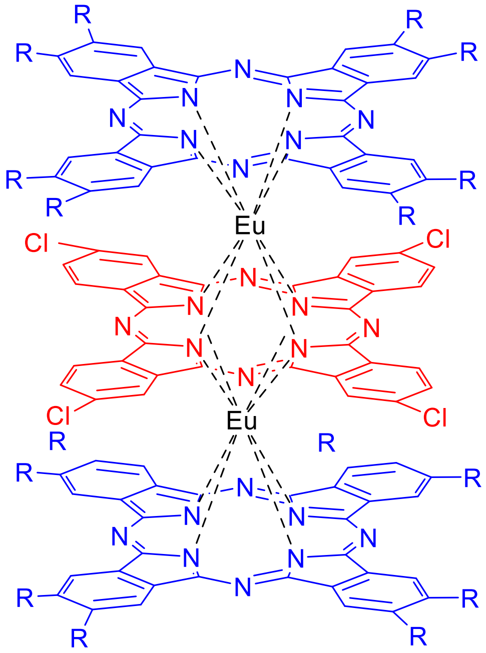
2.5 Triple-deckers phthalocyanines synthesis

The triple deckers are a range of products, in connection with the product distribution varying based on reaction circumstances, metal type, and macrocycle substituents. One of the main goals of this research was to see if triple-decker compounds could be manufactured and connected into arrays in the same way as monomeric porphyrin building blocks could [69]. The nature of the tetrapyrrole macrocycles itself may also be used to check the optical characteristics of triple decker compounds with porphyrins, phthalocyanines [70]. The Bi_2Pc_3 combination is generated using the procedure outlined without the use of iodine $Bi_2Se_3 + 12\ o\text{-}DCB \rightarrow Bi_2Pc_3 + 3Se\ 0$, In a 1:12 molar ratio, powdered Bi_2Se_3 (0.64 g) and o-DCB (1.54 g) were combined. And it was heated at 220 °C for 24 hours after being evacuated and sealed. The liquid o-DCB undergoes catalytic tetramerization at this temperature [71].

Bismuth (III) triple-decker phthalocyanine, Bi_2Pc_3, $Pc=C_{32}H_{16}N_8^{2-}$, is obtained via the reaction of Bi_2Se_3 with 1,2-dicyanobenzene at 220 °C, and the resulting crystals have a triclinic crystal structure. Each bismuth (III) ion has four *N*-isoindole atoms connecting it to the center Pc ring and four *N*-isoindole atoms connecting it to the outer Pc ring. It is possible to characterize the structure of metal(III)-phthalocyanines using the general equations M_2Pc_3 or MPc_2 with a single monooxidized phthalocyaninato ring. The same method used to create bismuth(III) phthalocyanine complexes yields two distinct forms, but in an iodine environment is different [71], as shown in **Scheme 10.**



Scheme 10. Synthesis triple deckers phthalocyanines (**10**)



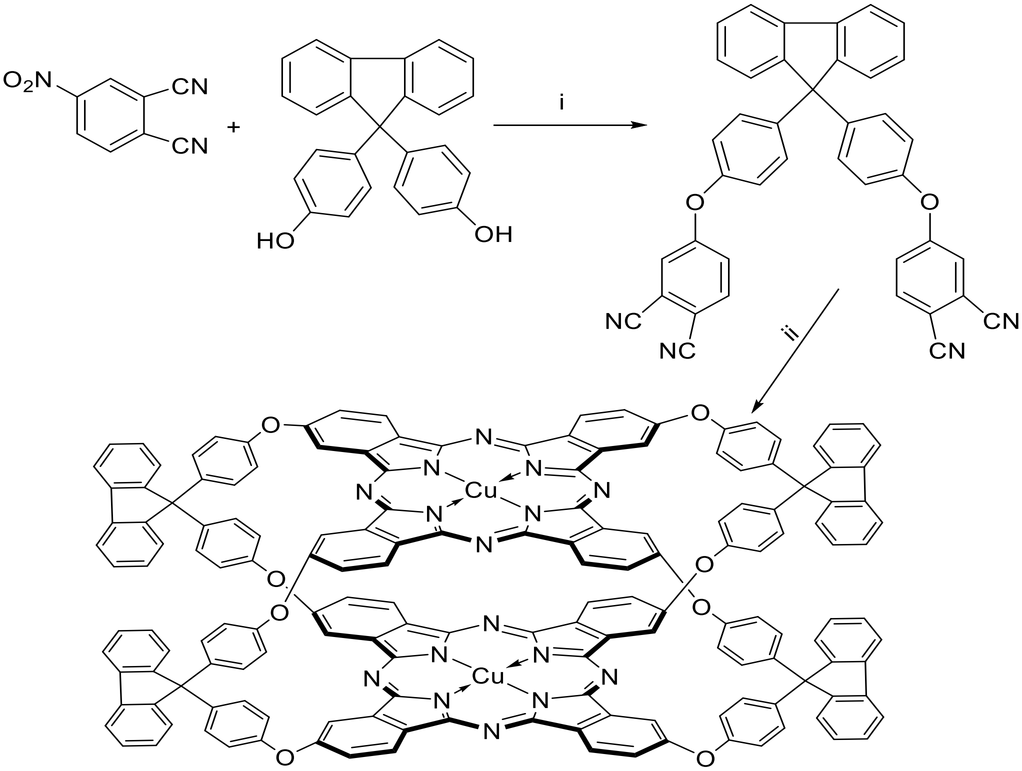
(**11**)

Scheme 11. Heteroleptic corrolee phthalocyannine europium triple-decker complexes $Eu_2[Pc(R)_8]_2[Cor(C1Ph)_3]$schematic molecular structure (**11**)

These triple-decker complexes are air-stable in the most popular solvents contained $CHCl_3$ and CH_2Cl_2 and include up to eight individual one-electron redox processes [72], as shown in **Scheme 11.**

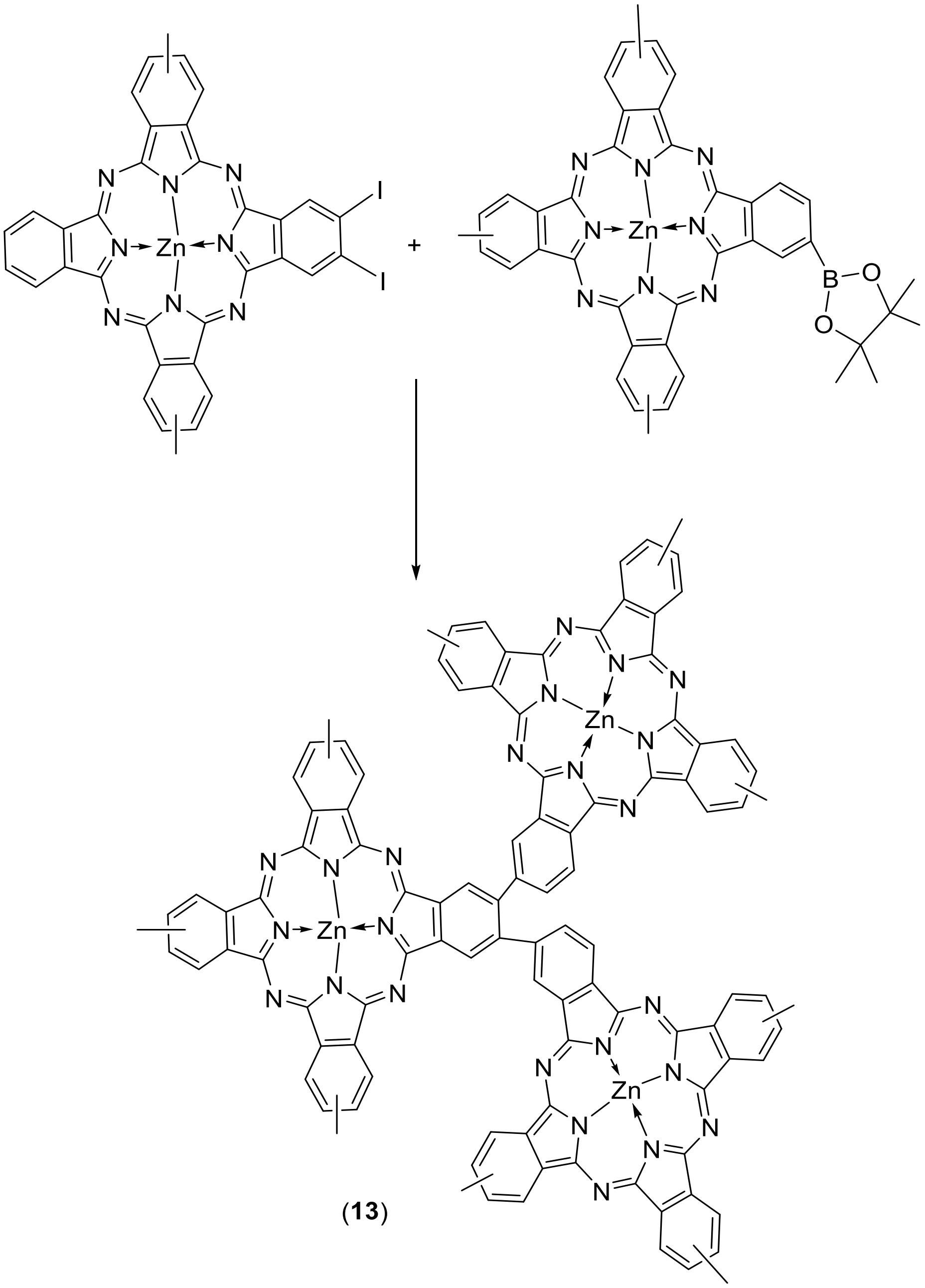
2.6 Synthesis of ball-type metallophthalocyanines

This type of Phthalocyanine was obtained by combining 4-nitrophthalonitrile and 9,9-bis(4-hydroxtphenyl) fluorine at high temperature using dry DMF and K_2CO_3, in this way [4,4-9,9-bis(4-oxyphenyl) fluorene di phthalonitrile was formed by adding $CuCl_2$ in the presence of N_2 atmosphere, ball type (9,9-tetrakis-bis (2,10,16,24)-CuPc(II) 4-oxyphenylfluorene) was discovered, as shown in **Scheme 12.** Conditions and reagents: i: K_2CO_3, DMF, N_2, 24 h, rt; ii: $CuCl_2$, N_2, 360 °C for compound $CuCl_2$ [73].



(**12**)

Scheme 12. Conditions and reagents: i: K_2CO_3, DMF, N_2, 24 h, rt; ii for compound $CuCl_2$, N_2, 360 °C



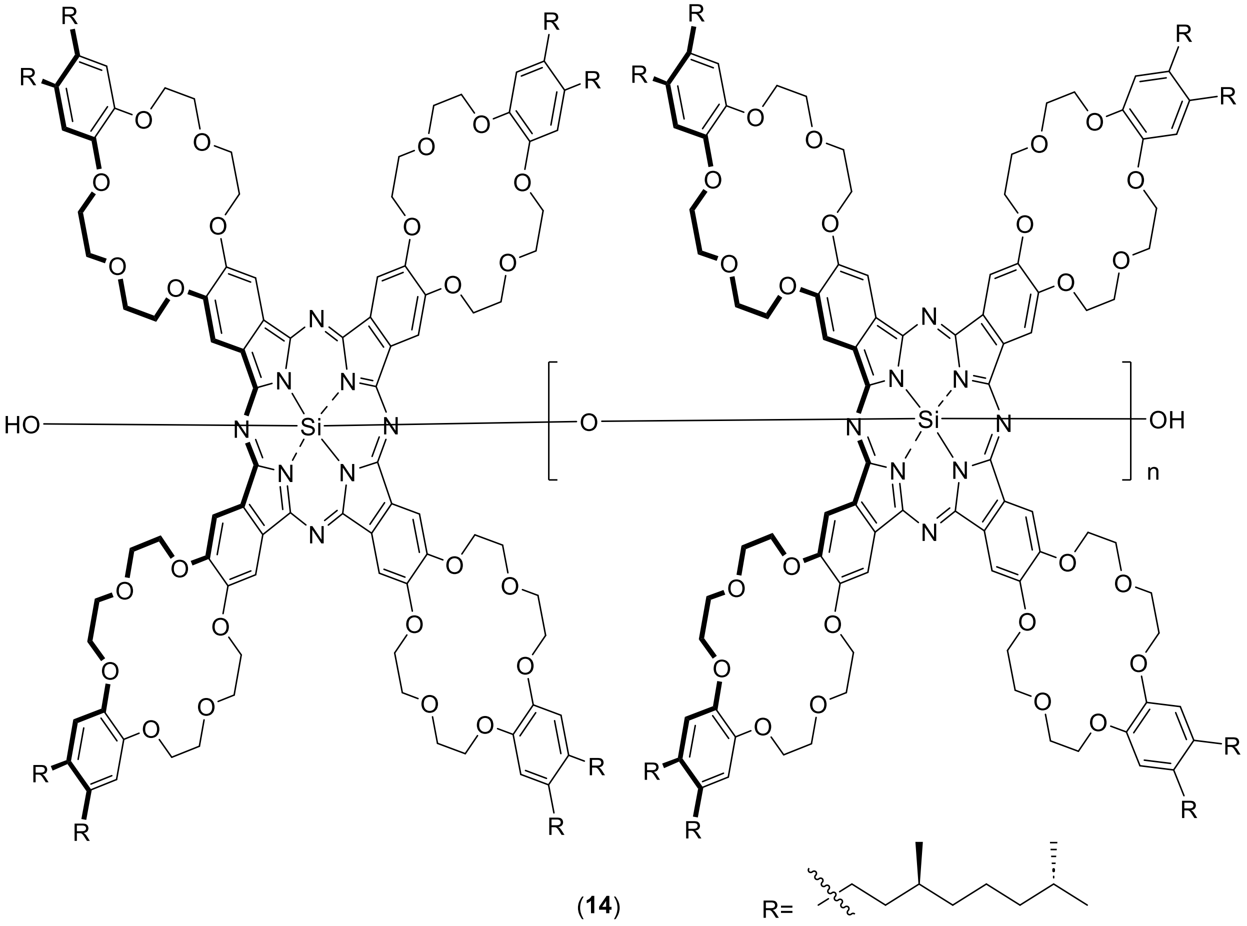
Scheme 13. Suzuki coupling conditions used to create a Pc homotriad (**13**)

2.7 Synthesis of triad phthalocyanines

One of the most beneficial cross-coupling processes is known as the Suzuki coupling reaction [74]. It is coupling has also been used to make covalently heterodyne pairs, or Pc-Pc couples, the Pc–$(Pc)_2$ homotriad, and Pc–porphyrin heterodyads that are directly conjugated through carbon-carbon bonds [75]. The molecules are made using a simple one-step process [74], as shown in **Scheme 13**.

2.8 Synthesis of polymer phthalocyanines

Hanack and colleagues produced and developed main-chain-type Pcs polymers, which depend on connecting the metal ions inside the core with proper bivalent bridges [76]. This method establishes a canonical configuration for the Pc



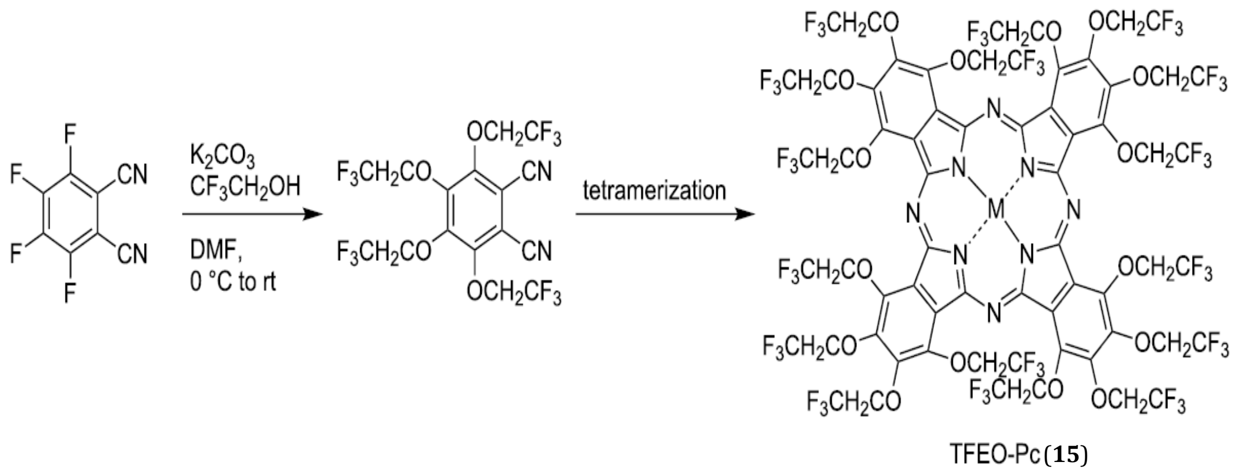
(**14**)

Scheme 14. Pc polymer as a main-chain polysiloxane (**14**)

molecules inside it, this arrangement within the so-called "shish-kebab" polymer. This method yields compounds with good solubility and up to 200 macrocyclic units [77]. As the polysiloxane backbone passes through the middle of the Pc rings, the Pc molecules are able to stack closely together, with just 0.34 nm of clearance between them. Kobayashi *et al.* reported a different structured phthalocyaninato-polysiloxane system, in which rod-like Pc polymers were placed into organized hexagonal channels using a sol-gel method to create organic-inorganic composites [78], as shown in **Scheme 14.** The development of porous organic polymers (POPs) based on pc has been swift and multifaceted. POPs are built from a wide variety of organic monomers to create their highly polymerized framework. POPs may have their molecular structures and characteristics engineered and manipulated to suit certain purposes [79].

2.9 Phthalocyanines synthesis with a trifluoroethoxy group

Because of the repulsion of the trifluoroethoxy group, it is well-documented that aggregation may be prevented using trifluoroethoxy-substituted phthalocyanines. Furthermore, fluorine's high electronegativity altered these features. As a result, as compared to non-fluorinated molecules, many fluorine-containing substances are resistant to oxidation and metabolism. In the disciplines of medicinal and agricultural chemistry, fluorine is also a vital component. It's hard to dissolve Pc in conventional organic solvents because it is very symmetrical due to its conjugate planar



Scheme 15. Tetramerization use to induce TFEO-Pc

structure. They are chemically and thermally stable because of the strong bond between carbon and fluorine [80]. Tri fluoro ethoxy the phthalocyanines with substitutes (TFEO-Pcs) with tri fluoro ethoxy group (-OCH_2CF_3) presence of phthalocyanine periphery may be easily produced from trifluoroethanol, as can other fluorine-containing phthalocyanines (CF_3CH_2OH). To begin, with tetrafluorophthalonitrile that is readily accessible to the public (1) and combined with trifluoroethanol to make tetrakis (trifluoroethoxy)phthalonitrile (2). After that, tetramerization is used to induce TFEO-Pc as part of a broad phthalocyanine synthesis, shown in **Scheme 15**. Because TFEO-Pcs compounds have a significant proportion of fluorine atoms, they are very soluble in organic solvents [80].

3. Applications of Phthalocyanines

M-Pcs have a critical part in human life applications, due to the fact their various construction chemistry, electrical, with optical characteristics, and they have a wide range of applications [81,82].

Three reasons account for the majority of phthalocyanine's commercial impact: the initial characteristic is their striking and vibrant shades spanning from blue to green, coupled with their remarkable coloring strength. The second feature is a subsequent attribute that pertains to their robust chemical stability. For instance, copper phthalocyanine can sublime at an exceedingly high temperature of 5800°C and can also dissolve in pure sulfuric acid without undergoing disintegration. The third has exceptional light fastness. It's exceedingly tough to find a property combination like this [83]. This part of a research looks at how phthalocyanines have advanced as contrast agents in different varieties in the last several years [84].

3.1 Traditional applications

By far the most important is the copper derivative. It's incredibly stable and produces bright, crisp cyan hues. Because the Sort band absorption tails into the visible area some other metal phthalocyanines aren't as stable, and/or they are a duller green. As a result, copper phthalocyanines will be the focus. Copper phthalocyanines are pigments as well as dyes [85].

3.1.1 Copper phthalocyanine pigments

The majority of pigments made of phthalocyanine molecules, (copper phthalocyanine) such as CI Pigment Blue 15- can exist in several crystalline forms. The α--form is more environmentally friendly so greener, and more stable β--form are the two primary polymorphs of copper phthalocyanine. When it comes to charge generating materials for laser printers, polymorphism is critical.

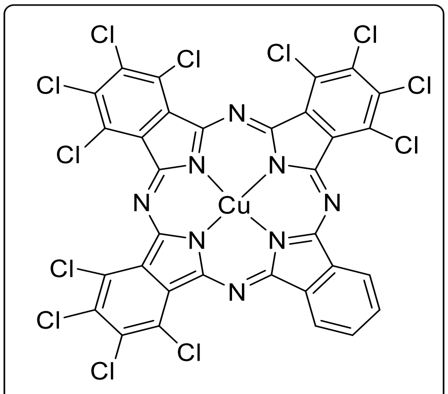
Copper phthalocyanine is produced in a variety of ways, but all of them result in coarse crystal form, which cannot be used as dyes. In this way, the metastable, tiny particulate-form may be created, which is excellent for, using a variety of processes (for example, sulfuric acid precipitation or sodium chloride grinding) [85].

The effects of organic pigment's molecular structure, the kind of dispersion agent used, and the length of the ball milling process were examined. Comparing Cl Pigment Green 7 to other pigments, the results indicated that it had higher dispersion stability over time [86].

One of the most significant families of colorants among them is copper phthalocyanine, which has exceptional qualities including light resistance, tinting strength, covering power, and resistance to alkalis and acids. As previously stated, depending on the level of substitution, colors move from blue to green due to the presence of halogen substituents like chlorine and bromine, which also serve to stabilize the form. Printing inks are the most common use for the greener version of copper phthalocyanine, and CI Pigment Green 7 is a prominent example of this kind of pigment [87], as shown in **Scheme 16.**

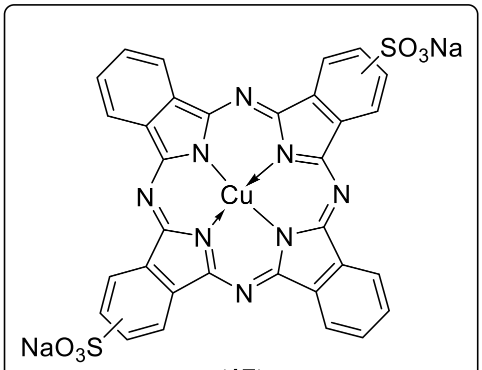
3.1.2 Copper phthalocyanine dyes

The lower relevance when phthalocyanine pigments are compared to phthalocyanine dyes is due to the enormous size and stiffness of the molecules. It's too big to dye polyester and polyacrylonitrile synthetic fibers, and it's only useful for nylon. As a result, it is nearly solely employed to color Cotton and paper are examples of cellulosic substrates. Copper phthalocyanine derivatives are also used to make significant ink jet printers' cyan dyes. It is well knowledge that CI Direct Blue 86 is a kind of phthalocyanine cyan dye. It is the first commercially available phthalocyanine dye [83], as shown in **Scheme 17.**



(**16**)

Scheme 16. CI Pigment Green 7



(**17**)

Scheme 17. CI Direct Blue 86

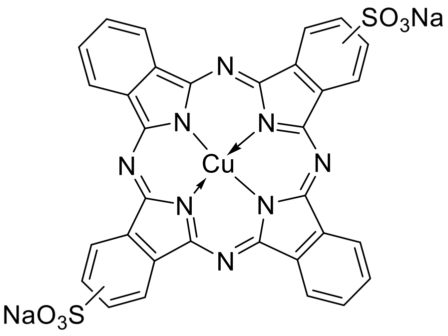
3.2 High-technology applications

The unique chemical and physical features of phthalocyanines make them ideal for a variety of applications, including effective color, chemical, and thermal stability [88], and high conductivity, also used in organic light emitting devices and printers [41].

3.2.1 Ink jet printing

Over the last decade, inkjet printing has advanced dramatically [89,90], with developments in colorant importance and ink technology using a key role. Copper phthalocyanine dyes stand out as the preferred cyan dyes for nearly all inkjet printers due to their unique combination of characteristics (mentioned previously).

Early ink jet printers, which initially debuted by the end of the 1980s, had to rely on generic coloring agents that had been cleaned up to a considerably higher quality for ink jet use. CI Direct Blue 199 as shown in **Scheme 18** was the cyan dye of choice at the time, and it is still commonly utilized in today's ink jet printers.



(**18**)

Scheme 18. CI Direct Blue 199 (**18**)

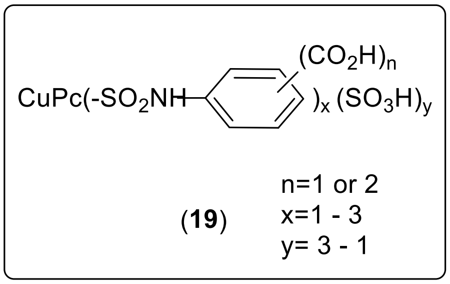
This dye has excellent all-around qualities. However, it is particularly water-soluble in most situations [91].

Avecia's research [92] resulted in a dye with significantly improved water fastness, yet it was still far from flawless. The theory of differential solubility was applied to create this dye as shown in **Scheme 19.** Most ink jet inks have a pH between 7.5 and 10, making them alkaline, while the majority of paper surfaces are somewhat acidic to neutral (*p*H 4.5-7.0). The Carbonyl (C=O) group possesses the right pKa to present in the ink in its ionized, water-soluble state, but to transform, upon contact with the paper, into the free acid, water-insoluble form.

Ink jet printing is also starting to employ CI Pigment Blue 15, especially when great endurance is required, such as in many outdoor applications.

3.2.2 Electrophotography

Photocopying and laser printing are two common examples of electrophotography. Titanyloxy phthalocyanine type IV polymorph [93] is the best material for generating latent images in current laser printers. It has a high photoinduced discharge speed and is compatible with semiconductor infrared lasers [89]. The utilization of CI Pigment Blue 15, commonly known as copper phthalocyanine pigment, in the cyan toner is an anticipated choice. Hexadecafluoro copper phthalocyanine stands as a prominent material for facilitating electron transport within organic semiconductors [94]. Additionally, blue and green phthalocyanine pigments serve as the primary color agents employed in the fabrication of color filters for liquid crystal displays [95].



(**19**)

Scheme 19. Avecia dye production (**19**)

3.3 Flow-injection analysis (FIA)

The use of MPs and Pc have been clear to be useful in flow injection, sequential injection analysis, and microfluidic systems have been proven to be effective.

3.3.1 Phthalocyanine liquid chromatography flow injection analyzer (FIA)

Phthalocyanines were most likely initially utilized with the advent of FIA in 1984 for use in liquid chromatography's flow-injection analysis (FIA), phthalocyanine-containing chemically modified electrodes for electrochemical detection in LC/FI systems became commonplace [96]. The quantification of captopril, thiopronine, and penicillamine was accomplished using a combination of liquid chromatography and flow-injection analysis. This approach involved utilizing electrochemical detection in conjunction with an electrode that incorporated a conductive carbon cement (CCC) matrix. This electrode had undergone chemical modification with cobalt phthalocyanine. The procedure was extensively elucidated in the research conducted by Favaro and Fiorani [97].

3.3.2 Electrochemical methods/ phthalocyanines

Electrochemical sensors and biosensors rely heavily on Pcs and M-Pcs containing cobalt (II) phthalocyanines (CoPcs). Data and information regarding the use of Flow-Injection-Analysis (FIA) with phthalocyanine-modified electrodes make up the vast bulk of what is currently available [98].

The Pc family's significance in various applications has been firmly established, thanks to its structural adaptability and distinctive characteristics arising from the integration of diverse inorganic and organic elements into its structure [99].

3.3.3 Modified carbon-paste electrodes

The electro-oxidation of organic peroxides was facilitated using cobalt-phthalocyanine modified carbon-paste electrodes, as demonstrated by Joseph Wang and coworkers [100]. It is impossible to reverse the oxidation process. The use of a cobalt-phthalocyanine-modified carbon paste electrode for the detection and determination of amitrole in flow injection analysis demonstrates the usefulness of such electrodes as indicators for electrocatalytic amperometry measurements of triazolic herbicides like amitrole at low oxidation potentials (+0.40 V) [101].

3.3.4 Electrodes made of modified glassy carbon

The oxidation of the antioxidant tart was the subject of research conducted by Pingarrón, who examined the behavior of a nickel phthalocyanine (Ni(II)-4,9,16,23-tetraaminophthalocyanine) polymer covered glassy carbon electrode.BHA, or –butylhydroxyanisole [98].

In two papers, Shaidarova *et al.* changed glassy carbon electrodes. The first study used a glassy carbon electrode's electrocatalytic reaction after having a polyaniline layer deposited on it and then having copper (II) tetrasulfo phthalocyanine to determine dopamine under static circumstances and with FIA. Dopamine oxidation was mediatized using a polyaniline composite film containing copper (II) tetrasulfophthalocyanine and applied to a glassy-carbon electrode (GC) in both acidic and neutral environments [102]. In their second work, they described the electrocatalytic oxidation of sulfur amino acids and flow-injection measurements at a glassy carbon electrode modified with a nickel (II) polytetrasulfophthalocyanine screen [103].

The electrode, made of glassy carbon with copper modifications, Maria Sotomayor and colleagues [104] developed a bio-inspired sensor for monitoring sodium diclofenac (II). In recovery investigations, the usage of a sensor For pharmaceutical preparations as well as biological blood samples, the findings were remarkably similar to those obtained by HPLC [103].

3.3.5 Modified graphite electrodes

The measurement of N-acetylcysteine (NAC) in pharmaceutical formulations was done using flow injection analysis (FIA) with amperometric detection, using an ordinary pyrolytic graphite (OPG) electrode modified with cobalt phthalocyanine (CoPc). In preliminary research, cyclic voltammetry was utilized to determine the optimal conditions for NAC analysis. For the voltammetric measurements, in this technique, used a three-electrode cell with a pyrolytic carbon electrode, a platinum wire electrode, and a calomel electrode [98, 105].

3.3.6 Boron-doped diamond electrodes with modifications

To achieve highly sensitive detection of hydrogen peroxide, a modified electrode consisting of cobalt phthalocyanine on boron-doped diamond (CoPc-BDD) was developed. The process involved the photochemical transformation of the hydrogen-terminated surface of the BDD electrode using 4-vinylpyridine, resulting in the introduction of pyridine groups. Subsequently, these pyridine moieties were immobilized on the electrode surface by immersing it in a solution containing cobalt phthalocyanine. Through cyclic voltammetry, it was demonstrated that the CoPc-BDD electrode exhibited catalytic activity for the electrochemical oxidation of hydrogen peroxide. This modified electrode, referred to as CoPc-BDD, it was demonstrated as an appropriate selection for hydrogen peroxide detection when incorporated into a flow-injection analysis-electrochemical detection (FIAECD) system [106].

3.3.7 Modified screen-printed electrodes

Various M-Pcs were used to modify screen-printed carbon electrodes and use them as sensors in FIA applications. In 1997, Rippeth and colleagues released a paper detailing the development of a wall-jet flow cell equipped with a screen-printed amperometric pesticide biosensor and a complete flow-injection system. The first biosensor was made by using the technique of encapsulating the enzyme acetylcholinesterase (AChE) on a cobalt phthalocyanine screen-printed carbon electrode [107].

3.3.8 Membrane matrices made from modified poly (vinyl chloride) PVC

Two new potentiometric azide membrane sensors were documented, with one of them employing manganese(III) porphyrin [Mn(III)P] ionophores dispersed in plasticized poly(vinyl chloride) PVC matrix membranes and the other using cobalt(II) phthalocyanine [Co(II)Pc] ionophores distributed in the same way [108]. The near- and sub-Nernstian membrane sensor responses based on Mn(III)P and Co(II)Pc in batch mode were -56.3 and -48.5 mV/decade, respectively. The pH of the environment did not affect the sensors' responses, so the range of 3.9 to 6.5 was steady within 0.9 mV for at least 8 weeks. Most typical anions that are commonly connected with azide ions did not create any interference. The growth of a groundbreaking FIA automated potentiometric method for measuring selenium as well as was discussed, along with its applications in pharmaceuticals and the analysis of anodic slime [109].

3.4 Photodynamic therapy (PDT)

In general, new cancer medications and clinical trials have resulted in very minor improvements in treatment results [110]. The number of new clinically authorized medications is modest [111]. Photodynamic therapy refers to a series of cancer treatment techniques depending on the exposure to light of photosensitizers (PS) (PDT). PDT is a highly selective and less invasive anticancer treatment method [112, 113]. Photosensitizer (PS), light, and oxygen are the three necessary components [114]. Phthalocyanines (PCs) are ingested orally or intravenously, and when the photoexcitation which results in the formation of reactive oxygen species (ROS), is produced, causing irreparable damage to cancer tissue. Among the photosensitizers used in PDT, the porphyrin derivatives and Pcs family organic dyes have garnered a great deal of interest [115].

Because of its considerable Photodynamic efficacy and a notably high molar absorption coefficient (ε⍰⍰⍰$10^5 M^{-1} cm^{-1}$) within the red region of the spectrum (approximately 630-730 nm), which facilitates deeper tissue penetration of the activating light [116], zinc phthalocyanine (ZnPc) emerges as a prospective category of photosensitizers in the field of Photodynamic Therapy (PDT) [117]. These macrocycles may engage with one another via attractive stacking interactions, resulting in aggregation in solution, owing to their wide flat hydrophobic aromatic surface [118].

3.5 Organometallic phthalocyanine solar cells

Organic solar cells were made, described, and characterized, employing various pc compounds including poly (CuPc), copper tetrakis(4-cumylphenoxy) phthalocyanine, copper phthalocyanine, and titanyl phthalocyanine. These phthalocyanines demonstrated absorption of light with wavelengths exceeding 500 nm. Cu-Pc is one of the most widely studied Pcs for organic solar cell applications. It has a high absorption coefficient in the visible range of the spectrum, making it efficient at capturing sunlight. CuPc can be used as an electron donor material in organic solar cells [119]. Also, the conductivity of poly (copper phthalocyanine) (PolyCuPc) is quite high [120]. Because of their low cost and simple production technique, so many attempts have been made to develop solar cells using organic semiconductors. Pcs have several advantages to solar cells [121], including resistance to heat, mild steadiness, with a high degree of visible-range and solar cells. ZnPc is another commonly used Pc in organic solar cells. It has good electron mobility, which is important for efficient charge transport within the device [122]. The developed method for fabricating organic photovoltaic cells that use PolyCuPc, copper tetrakis (4- cumylphenoxy) phthalocyanine (Tc-CuPc), (CuPc), and titanium indium phthalocyanine (TiOPc) as donors and 6,6-phenyl-C61-butyric acid methyl ester (PCBM) as acceptors [123]. The studies will provide a method for improving the photovoltaic characteristics of inverted organic solar cells by combining PCBM with Pcs [93, 124]. TiO_XPc has been studied for its potential application in solar cells, particularly in organic and dye-sensitized solar cells. It is primarily used as a light-absorbing and electron-transporting material in these types of solar cells [125].

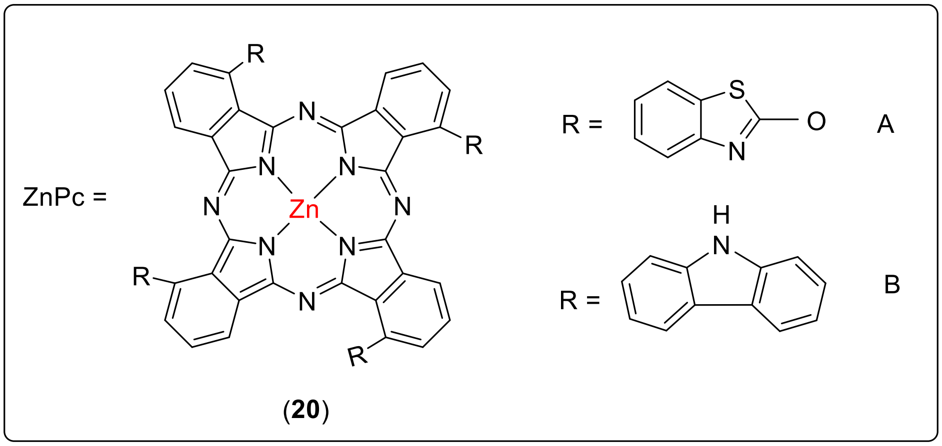
It has been observed that organic solar cells are unstable due to photo-induced O_2 migration into C60 or due to the interaction of Al electrodes with oxygen and water [126]. To solve this problem, non-corrosive Au electrode solar cells have been developed lately [127].

4. Typical Characterizations of Phthalocyanines

Pcs compounds have a broad variety of unique characteristics, CuPCs, and ZnPCs compounds were chosen and employed, as described earlier. The electrical and steric impacts of surrounding groups may change the nature of the aggregative interaction with a complex ion in the cavity. The concentration, temperature, and solvent type all have a role as well. Solvents that compete with the aggregative interaction will have the greatest noticeable influence on decreasing aggregation. When the concentration of PC is raised, the molecules tend to cluster together, leading to a narrowing of the Q band and a hypsochromic shift [128].

4.1 Zinc phthalocyanine derivatized with benzothiazole or carbazole

Most organic solvents are incompatible with metallophthalocyanines however, adding substituents to the ring system makes them more soluble. Both Complex **A** and Complex **B** shown in **Scheme 20** were very well readily soluble in several different types of organic solvents. Pyridine exhibited a noticeable red shift in **Figures 1** and **2**. Since the Q-band of phthalocyanine moves toward the red end of the spectrum as the solute's refractive index increases, a red shift is seen in pyridine **Table 2**, **Figures 1** and **2**. Ground-state absorption spectra for both A and B. **Figures 1** and **2** revealed the behavior of monomers, as demonstrated with a single Q band characteristic of phthalocyanines with metal ions. Pc ring HOMO-LUMO and π-π* transitions are responsible for the visible Q band (670-700 nm) in the visible spectrum [129]. Also, in the visible spectrum, unsubstituted MPcs have a strong absorption peak between 600 and 700 nm, giving it a bluish-green hue. Substituted MPcs, on the other hand, show this absorption at longer wavelengths, and it depends on the metal ion size, core modification, and metal ions [130].



Scheme 20. Oxybenzothiazole (**A**), oxycarbazole (**B**), phthalocyanine (**20**)

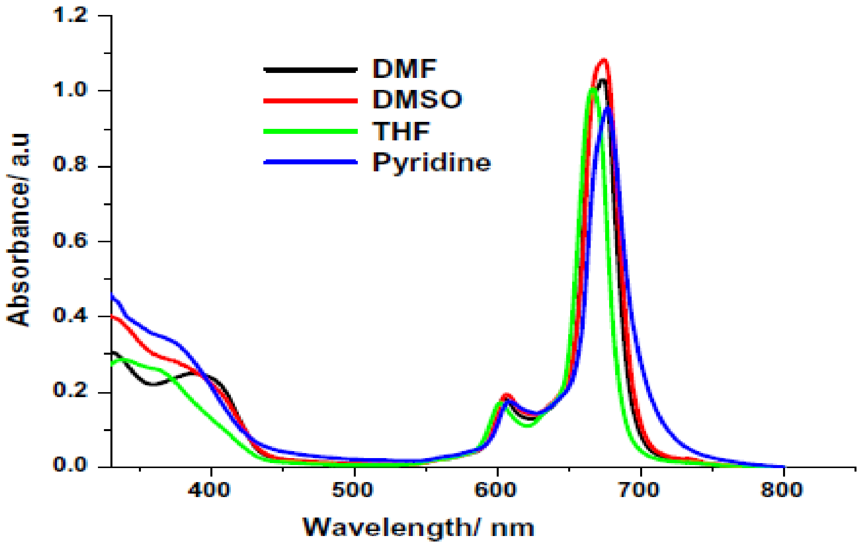


Figure 1. Spectra of compound A absorption in various solvents

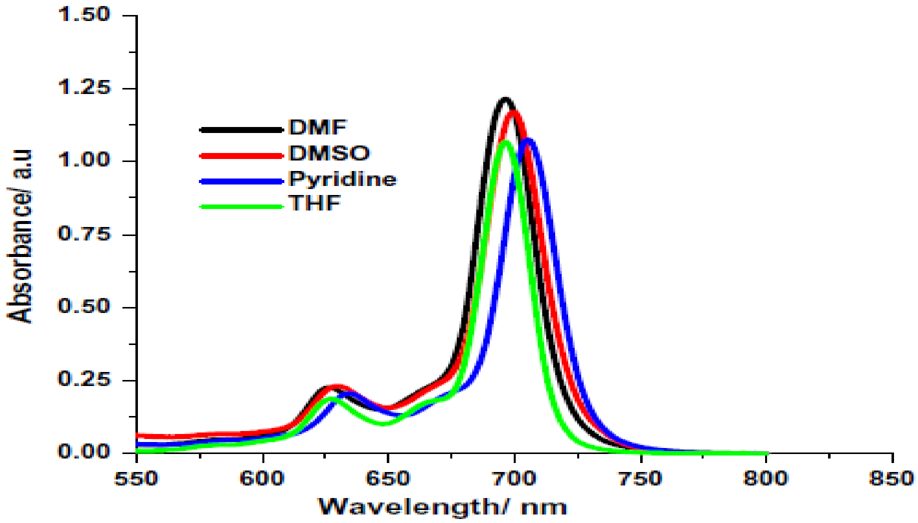


Figure 2. Spectrum of complex B absorption in various solvents

UV-Vis (DMSO)A: λ_{max} nm (log ε); 672 (5.29), 606 (4.59), 337 (4.79). FT-IR: (υ_{max}/ cm^{-1}): 3018 (Ar–H), 1598 (C=C), C=N (1560), 1288, 1120 (C–O–C), 940 (C–S–C), 730, 714, 760, and 830 (C–H).

UV–Vis (DMSO)B: λ_{max} nm (log ε); 700 (5.12), 630 (4.59), FT-IR: (υ_{max} /cm^{-1}): 3200 (NH), 3161 (Ar–H), 1576, 1077, 1110 (C–O–C), 1559 (C=N), and 1412 (C=C).

It can be shown from **Table 2** that compound A absorbs most strongly between 669 and 677 nm in the Q band (in different solvents), whereas the B band absorbs across a wider range of wavelengths (336-337) owing to the overlap between the B1 and B2 bands. Q band absorption in DMSO for unsubstituted ZnPc is at 672 nm, while for benzothiazole derivatized ZnPc it is at the same wavelength. Red shift is more pronounced in the oxycarbazole substituted ZnPc complex B than in the benzothiazoles derivatized Pc or the unsubstituted ZnPc. There is evidence that phthalocyanine deforms significantly when large, central groups (like phenyl groups) overlap with smaller, peripheral groups. As a

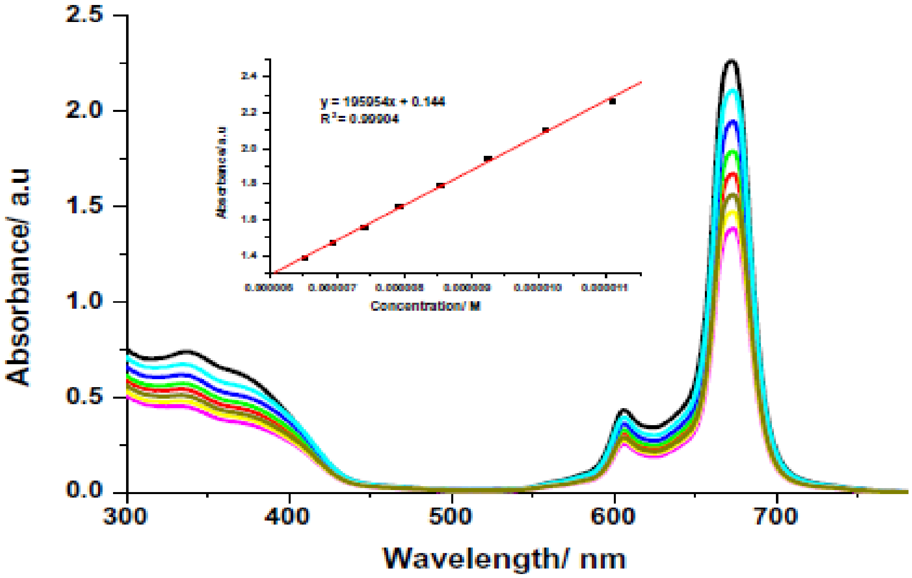


Figure 3. Complex A absorption spectra in dimethyl sulfoxide (DMSO). Place a plot of concentration vs. absorbance (demonstrating compliance with the Lambert-Beer law) here [119].

Table 2. Different solvent spectra for the compounds A and B

Complexexs	Solvent	Q band λ_{max} nm	Excitation λ_{exc} nm
1	DMSO	672	673
	DMF	671	672
	Pyriden	677	676
	THF	669	668
2	DMSO	700	702
	DMF	694	697
	Pyriden	705	706
	THF	697	698

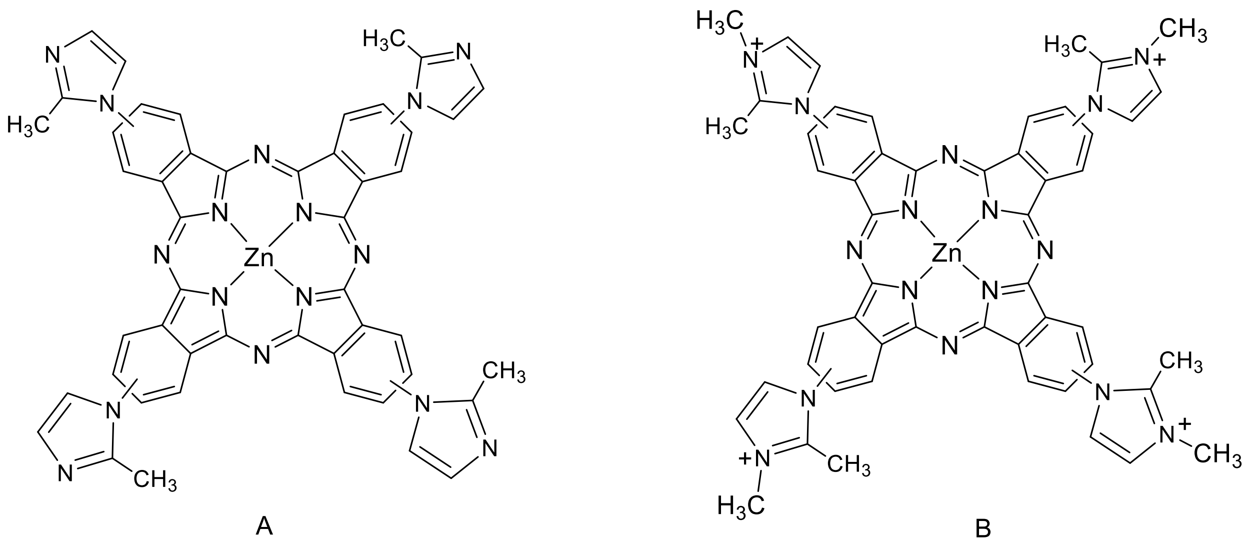
consequence, the Q band splits and red shifts. Since the oxycarbazole substituent B is more massive than the benzothiazole, it may account for the red shift seen in compound B relative to A. As may be seen in **Figure 3** below 1.1×10^{-5} M, complex 1 complied with Beer-Lambert's law. Similar results were seen for complex B [129].

4.2 A conducting polymer and zinc phthalocyanine Zn(II)Pc

Zinc phthalocyanine Zn(II)Pc is characterized as having four quaternizedimidazolyl moieties **Scheme 21** (A, B). To characterize Zn(II)Pc, ^{1}H NMR spectra at 400 MHz were obtained using a Bruker AC-400. An Analytic JENA S 600 used a UV-Vis spectrophotometer to get the UV-Vis spectra. Zn(II)Pc (21 B) was easily resolved in a ^{1}H NMR spectrum in **Figure 4** using the polar coordinating solvent d-DMSO, with the protons in the Pc macrocycle and aromatic protons in the imidazole fragment placed in the 9.7-8.1 ppm region. The presence of methyl (N-CH_3) groups may also be seen in the spectra, peaking at around 4.1 ppm.

^{1}H-NMR (CD_3OD/with drop of TFA, 400 MHz) A: δ (ppm) = 9.5-9.1(m, 6H), 9.09-8.8 (m, 2H), 8.5-8.1 (m, 8H), 7.9-7.8 (m, 4H), 2.95 (d, J = 4 Hz, 6H), and 2.88 (d, J = 4 Hz, 6H). A

^{1}H-NMR (DMSO-d6, 400 MHz) B: δ (ppm) = 9.7-9.2 (m, 8H), 8.8-8.4(m, 8H), 8.16 (d, J = 8 Hz, 4H). 4.11 (d, J = 8 Hz, 12H), and 2.95 (s, 12H). B



Zinc (II) 2(3),9(10),16(17),23(24)-tetra-(2-methyl-1*H*-imidazol-1-yl)-phthalocyaninato (2-)-N29, N30, N31, N32. 21A

Zinc (II) 2(3,4),9(10,11),16(17,18),23(24,25)-Octa-(2-methyl-1H-imidazol-1-yl)-phthalocyaninato (2)-N29, N30, N31, N32. 21B

Scheme 21. Zinc phthalocyanine Zn(II)Pc (**21**)

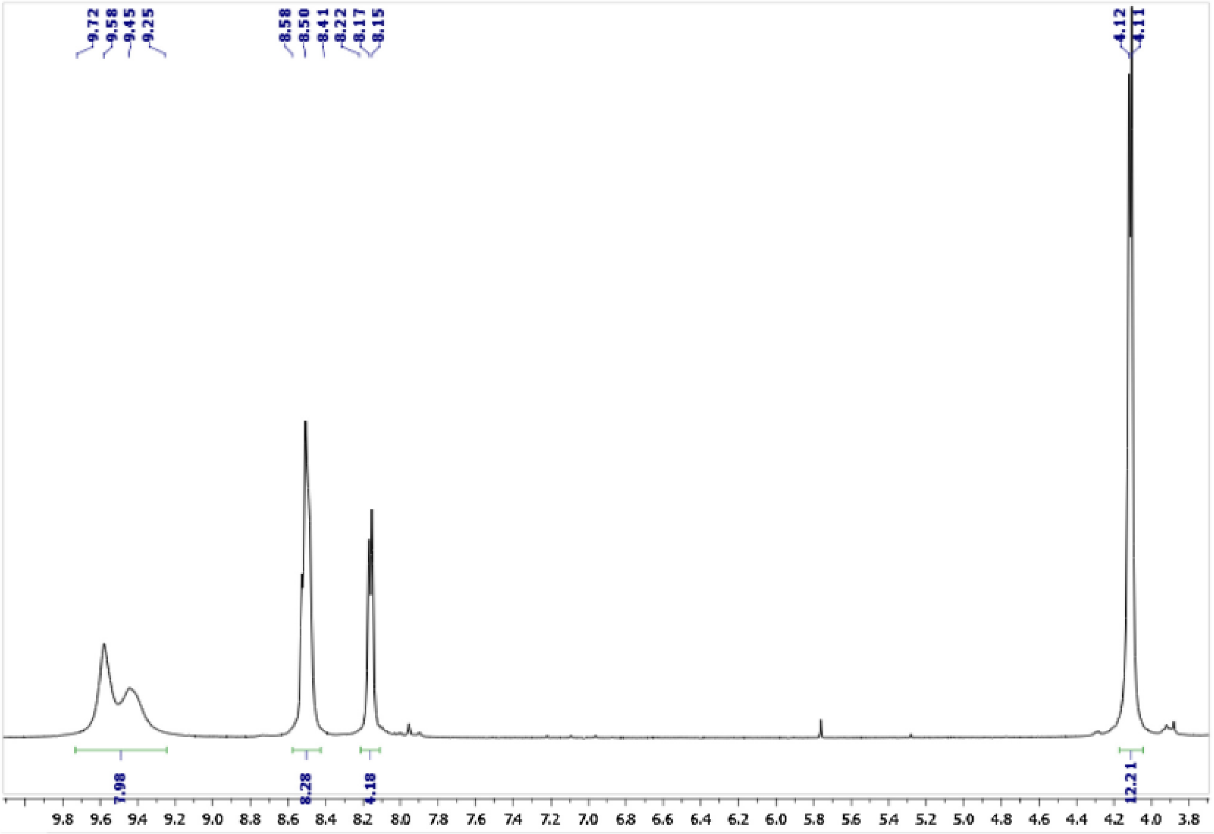


Figure 4. Zn(II)Pc (A, B).^{1}H-NMR (DMSO-d6) spectra

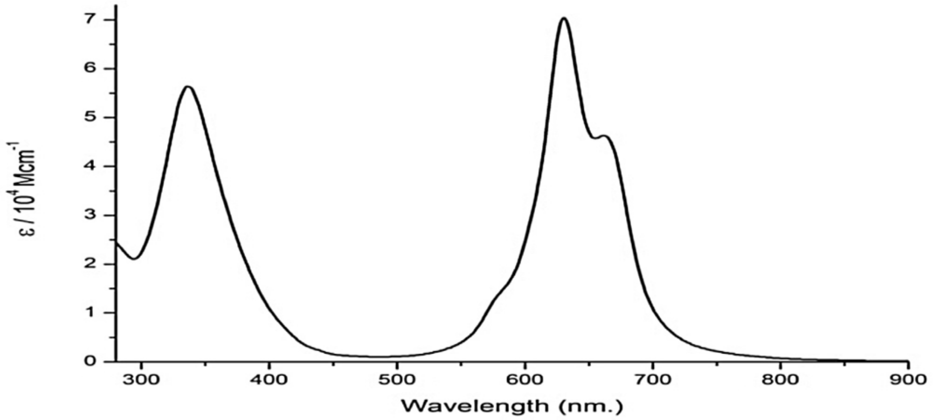


Figure 5. Zn(II)Pc UV-Vis spectra (B), in water ~ 1 × 10^{-5} M [120]

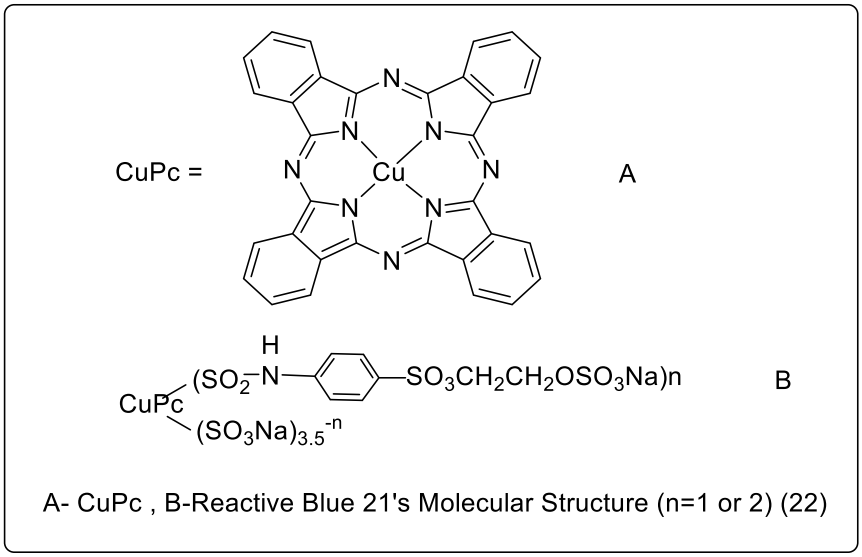
Zn(II)Pc spectra in the UV-vis range, (23), the Q-band can be detected, with its center at 631 nm see **Figure 5**. Aggregation of Zn(II)Pc (23) is shown by a broadening of the Q band when the compound is dissolved in water.

UV-Vis (H_2O): λ_{max}(log ε) = 663 (4.66), 631 (4.84), and 337 (4.75). B

UV-Vis (DMSO): λ_{max}, nm (log ε): 676 (5.32), 610 (4.53), and 350(4.72). A [131].

4.3 Phthalocyanine derivatives-reactive Blue 21

Scheme 22 depicts the radiation pattern for Reactive Blue 21, while **Figure 6** illustrates its UV-Visible radiation pattern. The chemical contains two prominent absorption bands in its UV-Vis spectra. Electronic transitions between the π-highest (HOMO) and π*-lowest (LUMO) energy levels cause absorption in the ultraviolet (UV) range of around 300 to 400 nm (B-band). The other may be seen between 550 and 700 nm (Q- band) and is caused by π- HOMO to π* LUMO energy level transitions. The results also show that the chemical has a strong absorption between 200 and 250 nm. Absorption spectra in the UV-Visible band, from 200 to 800 nm, were captured using a Hitachi U-3310 spectrophotometer (Hitachi Co., Japan) [131].



Scheme 22. Radiation pattern for Reactive Blue 21

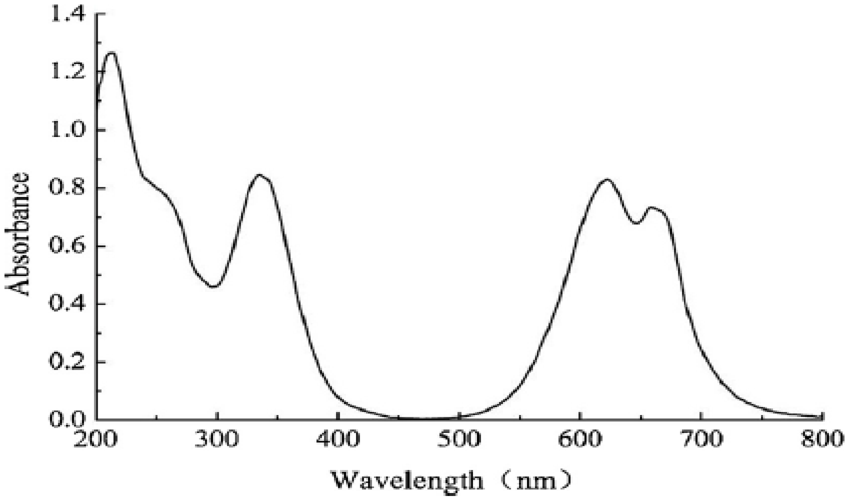


Figure 6. UV-Vis spectrum of Reactive Blue 21

The changed textiles had significantly lower reflectance than the unmodified sample over the spectrum from 550 to 700 nm. The significant absorbance of Reactive Blue 21 between 550 and 700 nm is responsible for this drop. It proves that Reactive Blue 21 can be successfully dyed into cellulose fibers. **Figure 7** displays the FT-IR spectra of both the grafted and ungrafted textiles. The -C=N- group stretching vibrations and the Cu-N ligand group stretching vibrations on the modified cellulose fabric were responsible for the shoulder detected at 1595 cm^{-1} and 697 cm^{-1}, respectively [132].

4.4 Powder to thin film processing of copper phthalocyanine semiconductors

The depicted molecular structure of CuPc is shown in **Figure 8** (a). Different polymorphic forms of CuPc are known to exist, with α -phase and β phase being the most often seen. As can be seen in **Figure 8** (b), in CuPc molecules with the *α* phase, the planar molecules form an angle of approximately 65° with the b axis. Molecules of CuPc in the *β*-phase arrange themselves in a herringbone configuration,

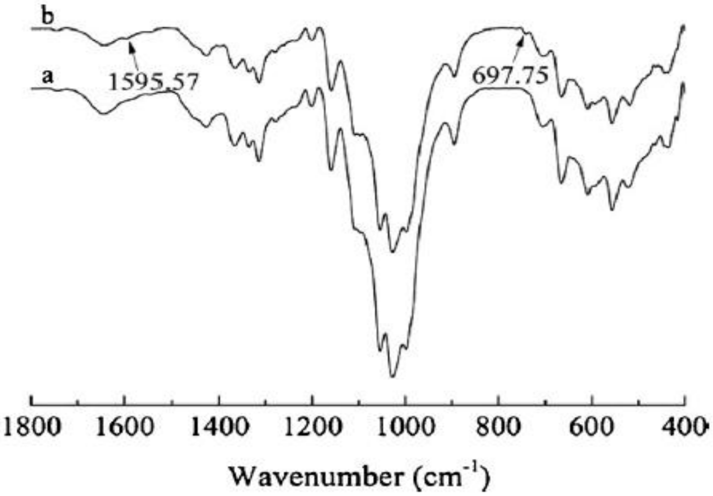


Figure 7. Comparison of the FT-IR spectra of the original cloth (a) and the altered fabric (8%) (b) [121].

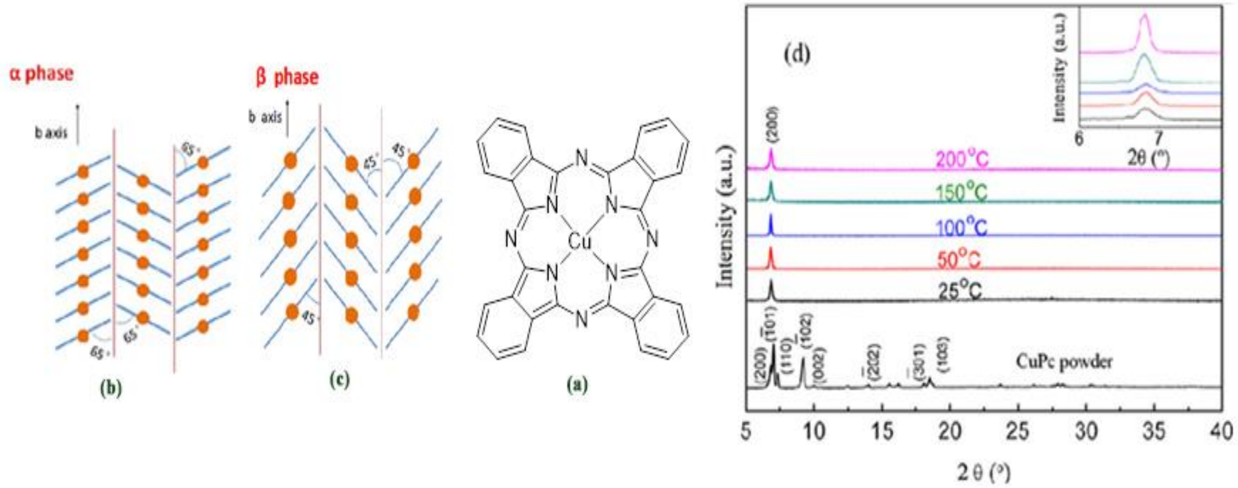


Figure 8. The CuPc molecular structure (a), the layered architectures of -phase (b), phase (c), and X-ray diffraction (XRD) patterns of CuPc powders and films deposited at various temperatures for the substrate (d).

indicating an almost 45° angle with the b axis **Figure 8** (c). Higher conductance for the α-phase crystal may be explained by the fact that the π electron overlap is greater in it than in the β-phase crystal, which results from the change in tilt angle. In **Figure 8** (d), we see the XRD patterns for the current CuPc powder and films. The XRD pattern of CuPc powder showed a typical characteristic of polycrystalline containing both α and β- phases, which is a succession of peaks. CuPc films, on the other hand, show just a single diffraction peak at 6.84. This peak is congruent with that described in the kinds of literature, coming from the (200) orientation of the α-phase. In addition, the good texture of the α-phase in the CuPc films is shown by a single peak along the (200) orientation for all of the films made at various substrate temperatures (25 °C, 50 °C, 100 °C, 150 °C, and 200 °C). As indicated in the inset of **Figure 8** (d), the full width of half maximum (200) peaks decreases steadily as the substrate temperature rises.

CuPc powder and film UV-Vis absorption spectra are shown in **Figure 9**. The absorption is caused by the overlap of molecular orbitals inside the aromatic 18 π-electron system with orbitals on the core metal atom. Also comparing the films' optical absorbance to that of CuPc powder reveals a striking difference see **Figure 7**, which is likely due to the phase transition. The region ultraviolet spectrum of (B band) and the visible region (Q band) (π - π * transition), CuPc films' spectra display two prominent distinctive bands. There are two primary absorption peaks inside the Q band, one at 620 nm due to the dimer and the other at 680 nm due to the monomer. Typical of *α*-CuPc films, two peaks can be seen in the Q band about the sample with a 25 °C substrate temperature: one at 622 nm and another at 696 nm in the present films. Peaking at around 622 nm, moves toward longer wavelengths as soon as the substrate heats is raised. This peak of the Q band moves redward by 8 nm, to a wavelength of 630 nm, when the temperature of the substrate reaches 200 °C. The peak originates from the oscillation of free electrons inside metal ions. It is likely that, the free electron oscillation around the Cu center is affected by the growth in particle size as the substrate temperature rises, leading to a red shift in light absorption. Q band's other peak, at 696 nm, is insensitive to changes in substrate temperature. Using data from the literature, we calculated the direct energy gap (Eg) in today's α-CuPc films. For a film made at

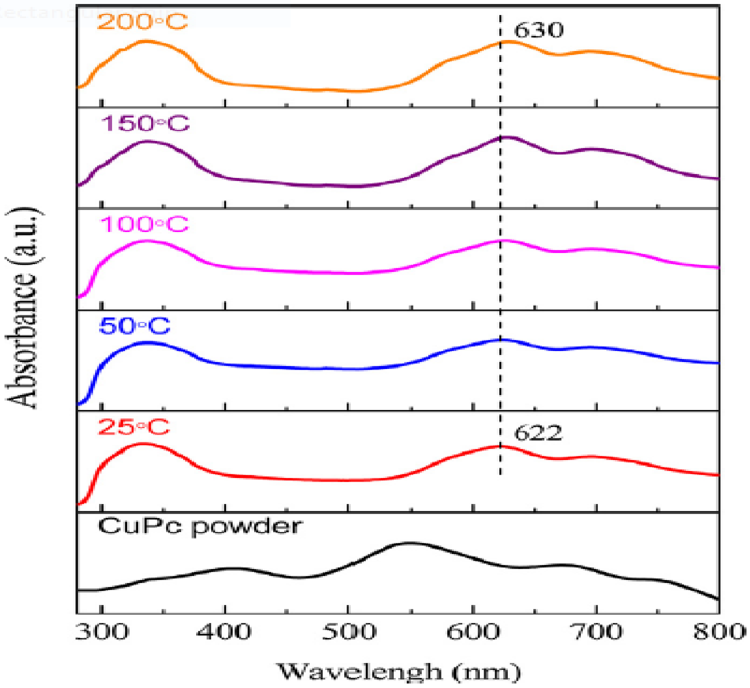


Figure 9. CuPc powder and films are made at different substrate temperatures, as shown in UV-Vis spectroscopy. The highest point of the CuPcfilms is shown by the dotted line [122].

25 °C and 200 °C, the computed values for Eg are 1.525 eV and 1.609 eV, respectively. According to the stated Eg (1.5 1.7 eV), these numbers are in agreement [133].

4.5 Copper phthalocyanine derivatives

The UV-Vis Spectral comparison of new emerging materials and recycled CuPc catalysts shown in **Figure 10** confirms the catalyst's stability throughout the process. There is a prominent absorption peak of about 650 nm in these spectra, and this is the Q-band, which is shared by all metallophthalocyanines and is associated with the $a_{1u}(\pi)$ $eg(\pi^*)$ transition. Parameters such as symmetry, center metal, etc. all of these factors contribute to the exact location of the Q band. It is worth noting that although non-metallated phthalocyanines exhibit a double-peaked Q band, the CuPc has only displayed a single-peaked Q band.

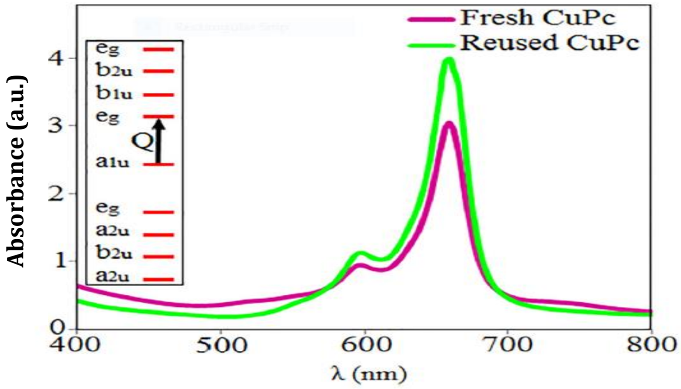


Figure 10. UV-Vis spectra of fresh and reused CuPc

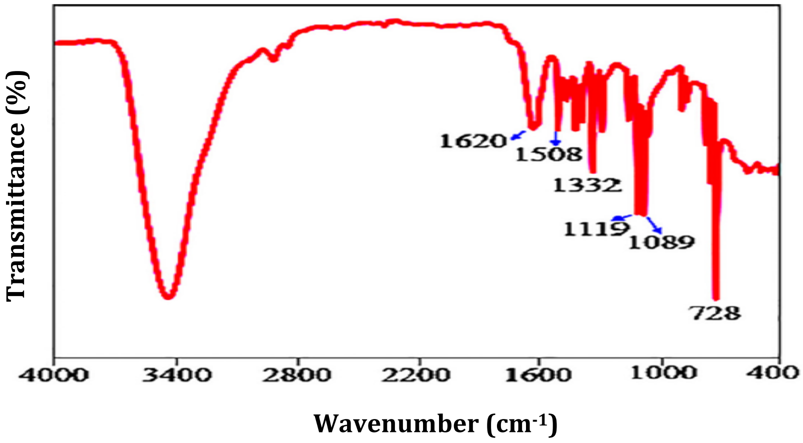


Figure 11. FT-IR spectrum of CuPc **[**123**]**

In **Figure 11,** we see the FT-IR spectra of CuPc. The C=N and C=C vibrations in this spectra were seen at 1620 cm^{-1} and 1508 cm^{-1}, respectively. Isoindole was initially seen to exhibit C-N and C-C stretching at 1332 and 1119 cm^{-1}, respectively. Peaks at 1600 and 1470 cm^{-1} are associated with aromatic ring breathing vibrations; peaks at 1089 cm^{-1} are attributable to CH in plan deformation, while peaks at 728 cm^{-1} are attributable to CH out of plane deformation of the phenyl ring [134].

4.6 Complexes of metallophthalocyanines containing thiazole groups

The phthalocyanine system's UV-Vis absorption spectra displayed signature Q and B bands. Two prominent absorption bands were seen in the spectra of phthalocyanines. The −π-π* transition from the phthalocyanine rings of (HOMO) to its (LUMO) causes one of these to occur in the visible area between 600 and 700 nm (Q band). The other band, the B band, lies in the ultraviolet spectrum between 300 and 400 nm and results from the LUMO transition at deeper energy π levels. All of the phthalocyanines (a-c) may be best characterized by their electronic spectra. The monomeric characteristic derivatives of the tetrasubstituted compounds of phthalocyanine

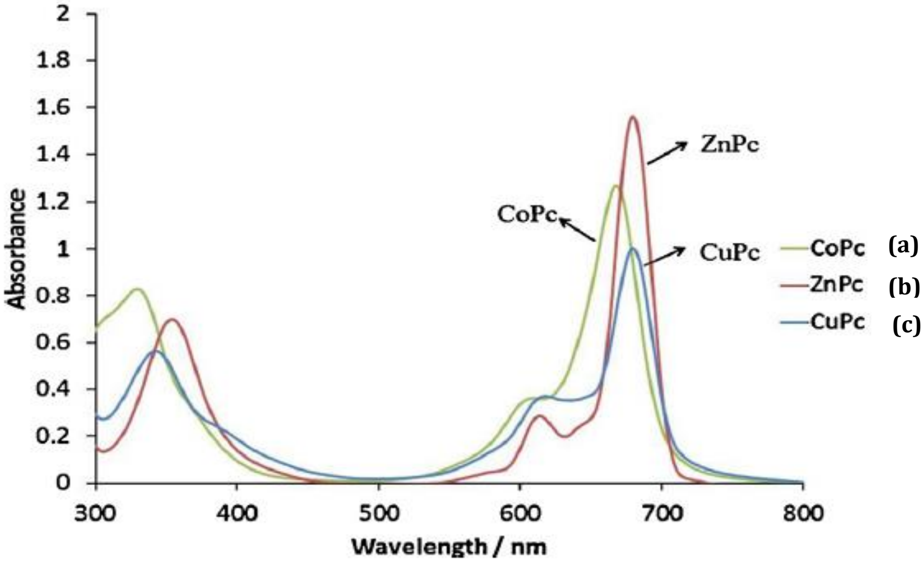


Figure 12. The spectra of electronic absorption in (DMF) show a range of 4-6. Concentration: 6.00 × 10^{-6} M [118]

complexes (a and c) were indicated by a single (narrow) Qband in their electronic absorption spectra, as is typical of metallated phthalocyanine complexes. There was a characteristic B-band at 329, 344 nm and a Q band at 668, 680 nm in the UV-Vis spectra of CoPc (a) and CuPc (c) in DMF. ZnPc (b) displayed a B band at 354 nm in its UV-Vis spectrum when dissolved in DMF, as well as a strong Q band at 679 nm and a faint band at 614 nm. Compounds (a)-(c)'s UV-Vis spectra in DMF are shown in **Figure 12** [128].

5. Conclusion

Pcs are chemical substances, organic or inorganic macromolecule compounds that were accidentally discovered more than one century ago. This study, work presents the successful results of several derivatives of Pcs with a wide range of applications that have been produced and are improving. New types of Pcs compounds show interesting development potential in electrical, electrochemical, and photosensitizers for photodynamic therapy of cancer treatments. Application and characterization of different compounds and functionalized with the synthesized variant of PCs, MPCs, exhibited monomeric behavior in solution and demonstrated increased solubility in common organic solvents. The arrival of these reviews comprising so many diverse knowledge substituents prompted us to provide this comprehensive summary of the current state and future directions of research in this area. The Pcs compounds have undergone a full structural investigation for the first time. This method has been used to examine the salient molecular interactions within the produced crystal structure. In addition, pc photochemistry and photophysics were investigated. The results showed that the produced PCs may be utilized as a photosensitizer for treating cancer and that compounds with a heavy central atom had better therapeutic effects.

Acknowledgments

To the Chemistry Department of Firat University, the authors would like to express their gratitude for providing research and technical assistance.

Orcid:

Othman Abdulrahman Hamad
https://orcid.org/0000-0001-8170-9094

Rebaz Obaid Kareem
https://orcid.org/0000-0001-6273-1309

Peshang Khdir Omer
https://orcid.org/0000-0002-6965-1843

References

[1]. R. Mukherjee, Coordination chemistry with pyrazole-based chelating ligands: molecular structural aspects, *Coordination Chemistry Reviews*, **2000**, *203*, 151-218. [Crossref], [Google Scholar], [Publisher]

[2]. M. Gottfried, H. Marbach, Surface-confined coordination chemistry with porphyrins and phthalocyanines: aspects of formation, electronic structure, and reactivity, *Zeitschrift für Physikalische Chemie*, **2009**, *223*, 53-74. [Crossref], [Google Scholar], [Publisher]

[3]. F.H. Moser, A.L. Thomas, The Phthalocyanines, Manufacture and applications, **1983**. [Crossref], [Google Scholar], [Publisher]

[4]. Ü. Demirbaş, *et al.,* Electrochemical and spectroelectrochemical study on novel non-peripherally tetra 1, 2, 4-triazole substituted phthalocyanines, *Journal of Molecular Structure*, **2018**, *1155*, 380-388. [Crossref], [Google Scholar], [Publisher]

[5]. Y. Gao, *et al.,* Theoretical insights into photocatalytic CO_2 reduction on Palladium phthalocyanine, *Chemical Physics Letters*, **2022**, *803*, 139812. [Crossref], [Google Scholar], [Publisher]

[6]. J.R. Miles, M.R. Willis, R.P. Jones, Photoconduction properties of some monomeric phthalocyanines and dibromoanthrone. *Materials science in semiconductor processing*, **2012**, *15*, 61-72. [Crossref], [Google Scholar], [Publisher]

[7]. C.G. Claessens, U. Hahn, T. Torres, Phthalocyanines: From outstanding electronic properties to emerging applications, **2008**, *8*, 75-97. [Crossref], [Google Scholar], [Publisher]

[8]. E.S. Dodsworth, *et al.,* Intramolecular coupling in metal-free binuclear phthalocyanines, *The Journal of Physical Chemistry*, **1985**, *89*, 5698-5705. [Crossref], [Google Scholar], [Publisher]

[9]. D. Wöhrle, *et al.,* Practical applications of phthalocyanines–from dyes and pigments to materials for optical, electronic and photo-electronic devices, *Macroheterocycles*, **2012**, *5*, 191-202. [Crossref], [Google Scholar], [Publisher]

[10]. R. Bechara, *et al.,* PEDOT: PSS-free organic solar cells using tetrasulfonic copper phthalocyanine as buffer layer, *Solar Energy Materials and Solar Cells*, **2012**, *98*, 482-485. [Crossref], [Google Scholar], [Publisher]

[11]. P. Gregory, Steamrollers, sports cars and security: phthalocyanine progress through the ages, *Journal of Porphyrins and Phthalocyanines*, **1999**, *3*, 468-476. [Crossref], [Google Scholar], [Publisher]

[12]. R.B. Short, Phthalocyanine dimers and PIMs based on hexaphenylbenzene, Cardiff University (United Kingdom), **2011**. [Google Scholar], [Publisher]

[13]. M.K. Engel, K.R.K. Hokoku, Single-crystal and solid-state molecular structures of phthalocyanine complexes, **2003**, *34*, 1-246. [Crossref], [Google Scholar], [Publisher]

[14]. M. Mayukh, Near-IR absorbing phthalocyanine derivatives as materials for organic solar cells, **2011**. [Crossref], [Google Scholar]

[15]. J.B. Crawford, *et al.,* AMD070, a CXCR4 chemokine receptor antagonist: practical large-scale laboratory synthesis, *Organic Process Research & Development*, **2008**, *12*, 823-830. [Crossref], [Google Scholar], [Publisher]

[16]. P. ERKa, H. Hengelsberg, Phthalocyanine Dyes and 1 1 9 Pigments, **2003**. [Google Scholar]

[17]. A. Varotto, *et al.,* Phthalocyanine blends improve bulk heterojunction solar cells, *Journal of the American Chemical Society*, **2010**, *132*, 2552-2554. [Crossref], [Google Scholar], [Publisher]

[18]. H. Uchida, *et al.,* Novel efficient preparative method for phthalocyanines from phthalimides and phthalic anhydride with HMDS, *The Journal of Organic Chemistry*, **2003**, *68*, 8736-8738. [Crossref], [Google Scholar], [Publisher]

[19]. C. Dent, R. Linstead, A.J. Lowe, 217. Phthalocyanines. Part VI. The structure of the phthalocyanines. *Journal of the Chemical Society (Resumed),* **1934**, 1033-1039. [Crossref], [Google Scholar], [Publisher]

[20]. D. Dini, M. Hanack, Physical properties of 107 phthalocyanine-based materials, **2003**, *11*, 1. [Crossref], [Google Scholar]

[21]. G.V. Kuvshinov, *et al.,* СИНТЕЗ И ОПТИЧЕСКИЕ СВОЙСТВА КАМФОРАЗАМЕЩЕННЫХ ТЕТРАПИРАЗ ИНОПОРФИРАЗИНОВ, **2017**, *60*, 60-67. [Google Scholar]

[22]. G. Byrne, R. Linstead, A. Lowe, 213. Phthalocyanines. Part II. The preparation of phthalocyanine and some metallic derivatives from *o*-cyanobenzamide and phthalimide. **1934**, 1017-1022. [Crossref], [Google Scholar], [Publisher]

[23]. S. Arslan, Phthalocyanines: Structure, synthesis, purification and applications, *Journal of Life Sciences*, **2016**, *6*, 188-197. [Crossref], [Google Scholar]

[24]. Z. Zamiraei, M. Golzar, H. Hamidi, Reviewing of metalloporphyrins as novel catalysts for synthesis of conducting and water-soluble polymers, *Advanced Journal of Chemistry, Section A*, **2018**, *1*, 105-116. [Crossref], [Google Scholar], [Publisher]

[25]. A. Nas, *et al.,* Unmetallated and metallated phthalocyanines bearing oxadiazole groups: synthesis, photophysical and photochemical studies, *Journal of luminescence*, **2014**, *154*, 15-21. [Crossref], [Google Scholar], [Publisher]

[26]. K. Sakamoto, E. Ohno-Okumura, Syntheses and functional properties of phthalocyanines. *Materials*, **2009**, *2*, 1127-1179. [Crossref], [Google Scholar], [Publisher]

[27]. H. Salavati, A. Teimouri, S. Kazemi, Synthesis and characterization of novel composite-based phthalocyanine used as efficient photocatalyst for the degradation of methyl orange, *Chemical Methodologies*, **2017**, *1*, 12-27. [Crossref], [Google Scholar], [Publisher]

[28]. K. Kadish, K.M. Smith, R. Guilard, The porphyrin handbook: Phthalocyanines: synthesis, Academic Press, **2000**, *15*. [Crossref], [Google Scholar], [Publisher]

[29]. X. Shen, *et al.,* Efficient photoelectrochemical water oxidation of cobalt phthalocyanine decorated $BiVO_4$ photoanode by improving kinetics, *Applied Surface Science*, **2021**, *564*, 150463. [Crossref], [Google Scholar], [Publisher]

[30]. S.-H. Kim, Functional dyes, Elsevier, **2006**. [Crossref], [Google Scholar], [Publisher]

[31]. O. Opeyemi, Porphyrin and phthalocyanines-based solar cells: fundamental mechanisms and recent advances, *Advanced Journal of Chemistry, Section A*, **2019**, *2*, 21-44. [Crossref], [Google Scholar], [Publisher]

[32]. G. de la Torre, C.G. Claessens, T. Torres, Phthalocyanines: old dyes, new materials. Putting color in nanotechnology, *Chemical communications*, **2007**, 2000-2015. [Crossref], [Google Scholar], [Publisher]

[33]. N.S. Lebedeva, *et al.,* Investigation of interaction between alkoxy substituted phthalocyanines with different lengths of alkyl residue and bovine serum albumin, *Journal of Luminescence*, **2015**, *166*, 71-76. [Crossref], [Google Scholar], [Publisher]

[34]. M. Miretti, *et al.,* Photodynamic inactivation of multiresistant bacteria (KPC) using zinc (II) phthalocyanines, *Bioorganic & Medicinal Chemistry Letters*, **2017**, *27*, 4341-4344. [Crossref], [Google Scholar], [Publisher]

[35]. H. Li, F.R. Fronczek, M.G.H. Vicente, Pegylated phthalocyanines: synthesis and spectroscopic properties, *Tetrahedron Letters*, **2011**, *52*, 6675-6678. [Crossref], [Google Scholar], [Publisher]

[36]. X.-S. Li, *et al.,* Highly positive-charged zinc (II) phthalocyanine as non-aggregated and efficient antifungal photosensitizer, *Bioorganic & Medicinal Chemistry Letters*, **2015**, *25*, 2386-2389. [Crossref], [Google Scholar], [Publisher]

[37]. E. Güzel, *et al.,* Synthesis and photophysicochemical properties of novel thiadiazole-substituted zinc (II), gallium (III) and silicon (IV) phthalocyanines for photodynamic therapy, *Inorganica Chimica Acta*, **2017**, *467*, 169-176. [Crossref], [Google Scholar], [Publisher]

[38]. L. Freitas, *et al.,* Zinc phthalocyanines attached to gold nanorods for simultaneous hyperthermic and photodynamic therapies against melanoma in vitro, *Journal of Photochemistry and Photobiology B: Biology*, **2017**, *173*, 181-186. [Crossref], [Google Scholar], [Publisher]

[39]. H. De Diesbach, E. Von der Weid, Quelques sels complexes des o-dinitriles avec le cuivre et la pyridine, **1927**, *10*, 886-888. [Crossref], [Google Scholar], [Publisher]

[40]. B. Kaboré, *et. al.,* High-performance thin-layer chromatography phytochemical profiling, antioxidant activities, and acute toxicity of leaves extracts of lannea velutina A. rich, *Journal of Medicinal and Chemical Sciences*, **2023**, *6*, 410-423. [Crossref], [Google Scholar], [Publisher]

[41]. D. Hohnholz, S. Steinbrecher, M. Hanack, Applications of phthalocyanines in organic light emitting devices, *Journal of Molecular Structure*, **2000**, *521*, 231-237. [Crossref], [Google Scholar], [Publisher]

[42]. Ö. Bekaroğlu, Functional phthalocyanine molecular materials, Springer Science & Business Media, **2010**, *135*. [Crossref], [Google Scholar]

[43]. N.B. McKeown, Phthalocyanine-containing dendrimers, *Advanced Materials*, **1999**, *11*, 67-69. [Crossref], [Google Scholar], [Publisher]

[44]. J.A. Elvidge, R.P. Linstead, Conjugated macrocycles. Part XXVII. The formation of tetrazaporphins from imidines. Tribenzotetrazaporphin, *Journal of the Chemical Society (Resumed)*, **1955**, 3536-3544. [Crossref], [Google Scholar], [Publisher]

[45]. A. Zare, M. Mirzaei, M. Rostami, E. Jafari, Photosensitization of phthalocyanine for singlet oxygen generation in photodynamic therapy applications, *Journal of Medicinal and Chemical Sciences*, **2020**, *3*, 55-59. [Crossref], [Google Scholar], [Publisher]

[46]. K. Geetha, S.S. Lakshmi, Synthesis, Characterisation and Antimicrobial studies of Dinuclear copper (II) complexes derived from Pentadentate Schiff base ligand, *Research Journal of Chemical Sciences*, **2014**, *4*, 68-75. [Crossref], [Google Scholar]

[47]. P., Sen, M. Managa, T. Nyokong, New type of metal-free and Zinc (II), In (III), Ga (III) phthalocyanines carrying biologically active substituents: synthesis and photophysicochemical properties and photodynamic therapy activity, *Inorganica Chimica Acta*, **2019**, *491*, 1-8. [Crossref], [Google Scholar], [Publisher]

[48]. N. Jia, *et al.,* Effect of central metals and peripheral substituents on the third-order nonlinear optical properties of tetra-benzimidazole and benzothiazole substituted phthalocyanines, *Optical Materials*, **2018**. *76*, 81-89. [Crossref], [Google Scholar], [Publisher]

[49]. M.R. Reddy, *et al.,* Synthesis and spectral properties of a deoxyribose-phthalocyanine conjugate using a sonogashira coupling reaction, **2007**, *2007*, 0628-0632. [Crossref], [Google Scholar], [Publisher]

[50]. O. S. Hashim, Synthesis, characterization of nickel (II) phthalocynine, and screening of its potential antibacterial activity, *Journal of Medicinal and Chemical Sciences*, **2022**, *5*, 1242-1246. [Crossref], [Publisher]

[51]. M. Durmuş, S. Yeşilot, V. Ahsen, Separation and mesogenic properties of tetraalkoxy-substituted phthalocyanine isomers, *New Journal of Chemistry*, **2006**, *30*, 675-678. [Crossref], [Google Scholar], [Publisher]

[52]. T.E. Youssef, *et al.,* Phthalocyaninatoindium (III) acetylacetonates for nonlinear optics, *European Journal of Organic Chemistry*, **2004**, *2004*, 101-108. [Crossref], [Google Scholar], [Publisher]

[53]. T. Kimura, *et al.,* Preparation and electrochemical and optical properties of *α*-octaalkylphthalocyanines with four fused TTF units, *Journal of Porphyrins and Phthalocyanines*, **2011**, *15*, 547-554. [Crossref], [Google Scholar], [Publisher]

[54]. N.B. Mckeown, The Synthesis of symmetrical 98 phthalocyanines, The porphyrin handbook: Phthalocyanines: Synthesis, **2000**, *15*, 61. [Crossref], [Google Scholar]

[55]. K. Sakamoto, *et al.,* Photosensitizer efficacy of non-peripheral substituted alkylbenzopyridoporphyrazines for photodynamic therapy of cancer, *Journal of Photochemistry and Photobiology A: Chemistry*, **2002**, *153*, 245-253. [Crossref], [Google Scholar], [Publisher]

[56]. M.J. Fuchter, *et al.,* Synthesis of porphyrazine-octaamine, hexamine and diamine derivatives, *Tetrahedron*, **2005**, *61*, 6115-6130. [Crossref], [Google Scholar], [Publisher]

[57]. Y. Chen, *et al.,* Supramolecular zinc phthalocyanine− perylene bisimide triad: synthesis and photophysical properties, **2007**, *111*, 16096-16099. [Crossref], [Google Scholar], [Publisher]

[58]. M.R. Reddy, *et al.,* Design, synthesis, and spectroscopic investigation of zinc dodecakis (trifluoroethoxy) phthalocyanines conjugated with deoxyribonucleosides, **2006**, *45*, 8163-8166. [Crossref], [Google Scholar], [Publisher]

[59]. S.J. Lange, *et al.,* Synthesis and coordination chemistry of unsymmetrical tetraazaporphyrins containing single oxathia-

and thiacrown substituents, **2000**, *56*, 7371-7377. [Crossref], [Google Scholar], [Publisher]

[60]. V. Novakova, *et al.,* A phthalocyanine–mestranol conjugate for photodynamic therapy prepared via click chemistry, *Tetrahedron Letters*, **2010**, *51*, 1016-1018. [Crossref], [Google Scholar], [Publisher]

[61]. T.V. Dubinina, *et al.,* Synthesis and investigation of spectral and electrochemical properties of alkyl-substituted planar binuclear phthalocyanine complexes sharing a common naphthalene ring, *Inorganica Chimica Acta*, **2010**, *363*, 1869-1878. [Crossref], [Google Scholar], [Publisher]

[62]. C.G. Claessens, D. González-Rodríguez, T. Torres, Subphthalocyanines: singular nonplanar aromatic compounds synthesis, reactivity, and physical properties, *Chemical reviews*, **2002**, *102*, 835-854. [Crossref], [Google Scholar], [Publisher]

[63]. N. Kobayashi, *et al.,* Synthesis, spectroscopy, and molecular orbital calculations of subazaporphyrins, subphthalocyanines, subnaphthalocyanines, and compounds derived therefrom by ring expansion, *Journal of the American Chemical Society,* **1999**, *121*, 9096-9110. [Crossref], [Google Scholar], [Publisher]

[64]. M.J. Fuchter, *et al.,* ROM polymerization-capture-release strategy for the chromatography-free synthesis of novel unsymmetrical porphyrazines, *The Journal of Organic Chemistry*, **2005**, *70*, 2793-2802. [Crossref], [Google Scholar], [Publisher]

[65]. S.S. Erdem, *et al.,* Solid-phase synthesis of asymmetrically substituted "AB3-type" phthalocyanines. *The Journal of Organic Chemistry*, **2008**, *73*, 5003-5007. [Crossref], [Google Scholar], [Publisher]

[66]. J.R. Pinzón, *et al.,* Metal nitride cluster fullerene $M_3N@ C_{80}$ (M= Y, Sc) based dyads: Synthesis, and electrochemical, theoretical and photophysical studies, *Chemistry – A European Journal*, **2009**, *15*, 864-877. [Crossref], [Google Scholar], [Publisher]

[67]. A.M. Pereira, *et al.,* Recent developments in the synthesis of homo-and heteroarrays of porphyrins and phthalocyanines, *Journal of Porphyrins and Phthalocyanines*, **2009**, *13*, 419-428. [Crossref], [Google Scholar], [Publisher]

[68]. S. Saydam, *et al.,* Synthesis, Characterization, Electrochemical, and Optic Limiting Properties of Novel CoII, CuII, and Double-Decker LuIII Phthalocyanines, *European Journal of Inorganic Chemistry*, **2009**, *2009*, 2096-2103. [Crossref], [Google Scholar], [Publisher]

[69]. J. Li, *et al.,* Synthesis of thiol-derivatized europium porphyrinic triple-decker sandwich complexes for multibit molecular information storage, *The Journal of Organic Chemistry*, **2000**, *65*, 7379-7390. [Crossref], [Google Scholar], [Publisher]

[70]. G. Lu, *et al.,* Europium triple-decker complexes containing phthalocyanine and nitrophenyl–corrole macrocycles, *Inorganic Chemistry*, **2015**, *54*, 9211-9222. [Crossref], [Google Scholar], [Publisher]

[71]. J. Janczak, *et al.,* Bismuth triple-decker phthalocyanine: synthesis and structure, *Polyhedron*, **1999**, *18*, 2775-2780. [Crossref], [Google Scholar], [Publisher]

[72]. G. Lu, *et al.,* Self-assembled organic nanostructures and nonlinear optical properties of heteroleptic corrole–phthalocyanine europium triple-decker complexes, *Dyes and Pigments*, **2015**, *121*, 38-45. [Crossref], [Google Scholar], [Publisher]

[73]. M.S. Ağırtaş, *et al.,* Synthesis, characterization, and electrochemical and electrical properties of novel mono and ball-type metallophthalocyanines with four 9, 9-*bis* (4-hydroxyphenyl) fluorine, *Dalton Transactions*, **2011**, *40*, 3315-3324. [Crossref], [Google Scholar], [Publisher]

[74]. S.S. Gujral, *et al.,* Suzuki cross coupling reaction-a review, *Indo Global Journal of Pharmaceutical Sciences*, **2012**, *2*, 351-367. [Crossref], [Google Scholar]

[75]. H. Ali, J.E. van Lier, Phthalocyanine-boronates: a synthon for the preparation of

molecular assemblies, *Tetrahedron Letters*, **2009**, *50*, 337-339. [Crossref], [Google Scholar], [Publisher]

[76]. M. Hanack, M. Lang, Conducting stacked metallophthalocyanines and related compounds, *Advanced Materials*, **1994**, *6*, 819-833. [Crossref], [Google Scholar], [Publisher]

[77]. P. Samorí, *et al.,* Self-organization of semiconducting polysiloxane-phthalocyanine on a graphite surface, *Advanced Materials*, **2005**. 17, 1265-1268. [Crossref], [Google Scholar], [Publisher]

[78]. M. Kimura, *et al.,* Preparation of organic–inorganic composites containing rod-like phthalocyanine polymers, *Chemical Communications*, **2003**, 2504-2505. [Crossref], [Google Scholar], [Publisher]

[79]. W. Ji, *et al.,* Porphyrin-and phthalocyanine-based porous organic polymers: From synthesis to application, *Coordination Chemistry Reviews*, **2021**, *439*, 213875. [Crossref], [Google Scholar], [Publisher]

[80]. S. Mori, N. Shibata, Synthesis and application of trifluoroethoxy-substituted phthalocyanines and subphthalocyanines, *Beilstein Journal of Organic Chemistry*, **2017**, *13*, 2273-2296. [Crossref], [Google Scholar], [Publisher]

[81]. B. Zhu, *et al.*, Novel planar binuclear zinc phthalocyanine sensitizer for dye-sensitized solar cells: Synthesis and spectral, electrochemical, and photovoltaic properties, *Journal of Molecular Structure*, **2015**, *1079*, 61-66. [Crossref], [Google Scholar], [Publisher]

[82]. T. Sizun, *et al.,* Microstructured electrodeposited polypyrrole–phthalocyanine hybrid material, from morphology to ammonia sensing, *Journal of Materials Chemistry*, **2012**, *22*, 25246-25253. [Crossref], [Google Scholar], [Publisher]

[83]. G.R. Nagargoje, A.S. Bondge, P.D. Kadam, K.I. Momin, S.B. Zangade, D.D. Kadam, S.P. Panchgalle, V. More, Quantification of langlois reagent by ^{19}F-NMR spectroscopy, *Journal of Applied Organometallic Chemistry*, **2023**, *3*, 213-223. [Crossref], [Publisher]

[84]. B.-D. Zheng, *et al.,* Phthalocyanines as contrast agents for photothermal therapy, *Coordination Chemistry Reviews*, **2021**, *426*, 213548. [Crossref], [Google Scholar], [Publisher]

[85]. S. Simovic, P. Heard, C. Prestidge, Hybrid lipid–silica microcapsules engineered by phase coacervation of Pickering emulsions to enhance lipid hydrolysis, *Physical Chemistry Chemical Physics*, **2010**, *12*, 7162-7170. [Crossref], [Google Scholar], [Publisher]

[86]. O. Hakeim, *et al.,* UV-curable encapsulation of surface-Modified organic pigments for inkjet printing of textiles, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2014**, *447*, 172-182. [Crossref], [Google Scholar], [Publisher]

[87]. B.B. Topuz, *et al.,* Synthesis and characterization of copper phthalocyanine and tetracarboxamide copper phthalocyanine deposited mica-titania pigments, *Dyes and Pigments*, **2013**, *96*, 31-37. [Crossref], [Google Scholar], [Publisher]

[88]. N. Kobayashi, *et al.,* Substituent-induced circular dichroism in phthalocyanines. *Journal of the American Chemical Society*, **1999**, *121*, 12018-12028. [Crossref], [Google Scholar], [Publisher]

[89]. P. Gregory, High-technology applications of organic colorants, Springer, **1991**, 175-205. [Crossref], [Google Scholar]

[90]. P. Gregory, Chemistry and technology of printing and imaging systems, **1996**, 113-138. [Google Scholar], [Publisher]

[91]. P. Gregory, Industrial applications of phthalocyanines. *Journal of porphyrins and phthalocyanines*, **2012**. [Crossref], [Google Scholar], [Publisher]

[92]. M.L. Jackson, *et al.,* Wet-on-wet primer with low film build UV light protection. **2000**, Google Patents. [Google Scholar], [Publisher]

[93]. P.M. Borsenberger, D.S. Weiss, Photoreceptors: organic photoconductors, Handbook of Imaging Materials, CRC Press, **2001**, 387-442. [Google Scholar], [Publisher]

[94]. K.R. Brown, M.J. Natan, Hydroxylamine seeding of colloidal Au nanoparticles in solution and on surfaces, *Langmuir*, **1998**, *14*, 726-728. [Crossref], [Google Scholar], [Publisher]

[95]. P. Gregory, High-technology applications of organic colorants, Springer Science & Business Media, **2012**. [Crossref], [Google Scholar]

[96]. K.M. Korfhage, K. Ravichandran, R. Baldwin, Phthalocyanine-containing chemically modified electrodes for electrochemical detection in liquid chromatography/flow injection systems, *Analytical Chemistry*, **1984**, *56*, 1514-1517. [Crossref], [Google Scholar], [Publisher]

[97]. G. Favaro, M. Fiorani, Determination of pharmaceutical thiols by liquid chromatography with electrochemical detection: Use of an electrode with a conductive carbon cement matrix, chemically modified with cobalt phthalocyanine, *Analytica Chimica Acta*, **1996**, *332*, 249-255. [Crossref], [Google Scholar], [Publisher]

[98]. J.K.F. van Staden, Application of phthalocyanines in flow-and sequential-injection analysis and microfluidics systems: A review, *Talanta*, **2015**, *139*, 75-88. [Crossref], [Google Scholar], [Publisher]

[99]. D. Gounden, N. Nombona, W.E. Van Zyl, Recent advances in phthalocyanines for chemical sensor, non-linear optics (NLO) and energy storage applications, *Coordination Chemistry Reviews*, **2020**, *420*, 213359. [Crossref], [Google Scholar], [Publisher]

[100]. J. Wang, *et al.,* Electrocatalysis and amperometric detection of organic peroxides at modified carbon-paste electrodes, *Talanta*, **1991**, *38*, 1077-1081. [Crossref], [Google Scholar], [Publisher]

[101]. B.R. Kozub, R.G. Compton, Voltammetric studies of the redox mediator, cobalt phthalocyanine, with regard to its claimed electrocatalytic properties, *Sensors and Actuators B: Chemical*, **2010**, *147*, 350-358. [Crossref], [Google Scholar], [Publisher]

[102]. L. Shaidarova, *et al.,* Voltammetry determination of dopamine by the electrocatalytic response of an electrode modified by a polyaniline film with an inclusion of copper (II) tetrasulfophthalocyanine, *Journal of Analytical Chemistry*, **2013**, *68*, 516-524. [Crossref], [Google Scholar], [Publisher]

[103]. L. Shaidarova, *et al.,* Electrocatalytic oxidation and flow-injection determination of sulfur amino acids on a glassy carbon electrode modified by a nickel (II) polytetrasulfophthalocyanine film, **2013**, *68*, 536-544. [Crossref], [Google Scholar], [Publisher]

[104]. A. Wong, L.D. Marestoni, M.D.P.T. Sotomayor, Monitoring of diclofenac with biomimetic sensor in batch and FIA systems, *Journal of the Brazilian Chemical Society*, **2014**, *25*, 1283-1291. [Crossref], [Google Scholar], [Publisher]

[105]. F.I. Ahmadi, R. Fathollahi, D. Dastan, Phytochemical constituents and biological properties of scutellaria condensata subsp. pycnotricha, *Journal of Applied Organometallic Chemistry*, **2022**, *2*, 119-128. [Crossref], [Google Scholar], [Publisher]

[106]. T. Kondo, A. Tamura, T. Kawai, Cobalt phthalocyanine-modified boron-doped diamond electrode for highly sensitive detection of hydrogen peroxide, *Journal of the Electrochemical Society*, **2009**, *156*, F145. [Crossref], [Google Scholar], [Publisher]

[107]. J.J. Pancrazio, *et al.,* Development and application of cell-based biosensors, *Annals of Biomedical Engineering*, **1999**, *27*, 697-711. [Crossref], [Google Scholar], [Publisher]

[108]. S.S. Hassan, *et al.,* Novel polymeric membrane sensors based on Mn (III) porphyrin and Co (II) phthalocyanine ionophores for batch and flow injection determination of azide, *Electroanalysis*, **2008**, *20*, 438-443. [Crossref], [Google Scholar], [Publisher]

[109]. A.H. Kamel, *et al.,* Development of a novel automatic potentiometric system for determination of selenium and its application in pharmaceutical formulations and anodic slime,

2008, *20*, 1016-1023. [Crossref], [Google Scholar], [Publisher]

[110]. S. Şener, *et al.,* Synthesis, characterization, and DFT study of novel metallo phtalocyanines with four carboranyl clusters as photosensitisers for the photodynamic therapy of breast cancer cells, **2019**, *129*, 124-131. [Crossref], [Google Scholar], [Publisher]

[111]. T. Hampton, Targeted cancer therapies lagging, *Medical News & Perspectives*, **2006**, *296*, 1951-1952. [Crossref], [Google Scholar], [Publisher]

[112]. D. Grose, W. Anseline, P. Smith, Photodynamic therapy for the prevention of skin cancer, *Dermatologic Surgery*, **2014**, 40, 1441-1442. [Crossref], [Google Scholar], [Publisher]

[113]. B.-D. Zheng, *et al.,* Recent advances in supramolecular activatable phthalocyanine-based photosensitizers for anti-cancer therapy, *Coordination Chemistry Reviews*, **2021**, *447*, 214155. [Crossref], [Google Scholar], [Publisher]

[114]. T.J. Dougherty, *et al.,* Photodynamic therapy, *Journal of the National Cancer Institute*, **1998**, *90*, 889-905. [Crossref], [Google Scholar], [Publisher]

[115]. M. Ascencio, *et al.,* Protoporphyrin IX fluorescence photobleaching is a useful tool to predict the response of rat ovarian cancer following hexaminolevulinate photodynamic therapy, *Lasers in Surgery and Medicine*, **2008**, *40*, 332-341. [Crossref], [Google Scholar], [Publisher]

[116]. A. Zielichowska, *et al.,* The photodynamic effect of far-red range phthalocyanines (AlPc and Pc green) supported by electropermeabilization in human gastric adenocarcinoma cells of sensitive and resistant type, *Biomedicine & Pharmacotherapy*, **2015**, *69*, 145-152. [Crossref], [Google Scholar], [Publisher]

[117]. G.A. Gauna, *et al.,* Synthesis and comparative photodynamic properties of two isosteric alkyl substituted zinc (II) phthalocyanines, *European Journal of Medicinal Chemistry*, **2011**, *46*, 5532-5539. [Crossref], [Google Scholar], [Publisher]

[118]. C.A. Hunter, J.K.M. Sanders, The nature of. pi.-. pi. Interactions, *Journal of the American Chemical Society*, **1990**, *112*, 5525-5534. [Crossref], [Google Scholar], [Publisher]

[119]. M. Iwase, *et al.,* Fabrication and characterization of phthalocyanine-based organic solar cells, *Materials Sciences and Applications*, **2014**, *5*, 278. [Crossref], [Google Scholar], [Publisher]

[120]. N. Obata, *et al.,* Small-molecule-based organic photovoltaic devices covering visible and near-infrared absorption through phase transition of titanylphthalocyanine induced by solvent exposure, *Japanese Journal of Applied Physics*, **2011**, *50*, 121603. [Crossref], [Google Scholar], [Publisher]

[121]. T. Hori, *et al.,* Bulk heterojunction organic solar cells utilizing 1, 4, 8, 11, 15, 18, 22, 25-octahexylphthalocyanine, *Solar Energy Materials and Solar Cells*, **2011**, *95*, 3087-3092. [Crossref], [Google Scholar], [Publisher]

[122]. T. Oku, *et al.,* Microstructures and photovoltaic properties of C60 based solar cells with copper oxides, CuInS2, phthalocyanines, porphyrin, PVK, nanodiamond, germanium and exciton diffusion blocking layers, *Energy Materials*, **2013**, *28*, 21-39. [Crossref], [Google Scholar], [Publisher]

[123]. A. Kawashima, *et al.,* Microstructures and photovoltaic properties of polysilane/C_{60}-based solar cells, *Materials Sciences and Applications*, **2012**, *3*, 557. [Crossref], [Google Scholar], [Publisher]

[124]. S. Sekar, *et al.,* Copper phthalocyanine conjugated graphitic carbon nitride nanosheets as an efficient electrocatalyst for simultaneous detection of natural antioxidants, *Electrochimica Acta*, **2022**, *413*, 140150. [Crossref], [Google Scholar], [Publisher]

[125]. M. Brumbach, D. Placencia, N.R. Armstrong, Titanyl phthalocyanine/C_{60} heterojunctions: Band-edge offsets and photovoltaic device performance, *The Journal of*

Physical Chemistry C, **2008**, *112*, 3142-3151. [Crossref], [Google Scholar], [Publisher]

[126]. K. Yoshida, *et al.,* Fabrication and characterization of phthalocyanine/C60 solar cells with inverted structure, **2012**, *2*, 461. [Crossref], [Google Scholar], [Publisher]

[127]. T. Kuwabara, *et al.,* Highly durable inverted-type organic solar cell using amorphous titanium oxide as electron collection electrode inserted between ITO and organic layer, *Solar Energy Materials and Solar Cells*, **2008**, *92*, 1476-1482. [Crossref], [Google Scholar], [Publisher]

[128]. H.Y. Yenilmez, A.M. Sevim, Z.A. Bayır, Synthesis and photophysics of new metallo phthalocyanine complexes with thiazole groups and their fluorescence quenching studies with benzoquinone, *Synthetic Metals*, **2013**, *176*, 11-17. [Crossref], [Google Scholar], [Publisher]

[129]. P. Khoza, E. Antunes, T. Nyokong, Synthesis and photophysicochemical properties of zinc phthalocyanine derivatized with benzothiazole or carbazole photosensitizers, *Polyhedron*, **2013**, *61*, 119-125. [Crossref], [Google Scholar], [Publisher]

[130]. A. Kumar, V.K. Vashistha, D.K. Das, Recent development on metal phthalocyanines based materials for energy conversion and storage applications, *Coordination Chemistry Reviews*, **2021**, *431*, 213678. [Crossref], [Google Scholar], [Publisher]

[131]. E. Buber, *et al.,* Construction and amperometric biosensing performance of a novel platform containing carbon nanotubes-zinc phthalocyanine and a conducting polymer, *International Journal of Biological Macromolecules*, **2017**, *96*, 61-69. [Crossref], [Google Scholar], [Publisher]

[132]. L. Hu, *et al.,* Functional modification of cellulose fabrics with phthalocyanine derivatives and the UV light-induced antibacterial performance, *Carbohydrate Polymers*, **2018**, *201*, 382-386. [Crossref], [Google Scholar], [Publisher]

[133]. X. Ai, *et al.,* Phase modification of copper phthalocyanine semiconductor by converting powder to thin film, *Applied Surface Science*, **2018**, *428*, 788-792. [Crossref], [Google Scholar], [Publisher]

[134]. S. Farahmand, M. Ghiaci, J.S. Razavizadeh, Copper phthalocyanine as an efficient and reusable heterogeneous catalyst for direct hydroxylation of benzene to phenol under mild conditions, *Inorganica Chimica Acta*, **2019**, *484*, 174-179. [Crossref], [Google Scholar], [Publisher]
