# CHEMICAL MODIFICATION OF PHTHALOCYANINES AND THEIR APPLICATION IN THE SYNTHESIS OF PHTHALOCYANINE PIGMENTS

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**Abstract:** In this article, we solved the problem chemical modification of phthalocyanines and their application in the synthesis of phthalocyanine pigments and a the time in the world a lot of about this problem and in general, the synthesis of the basic structure of Pc requires the presence of phthalogene for the construction of isoindole fragments and a nitrogen source for the formation of azomethine bridges.

**Keywords:** Pigment, exothermic reaction, method, phthalonitrile, atoms, earth metals, molecules, sulfamides

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## INTRODUCTION

Despite the very large number of Pc derivatives obtained in recent decades, several representatives of this class of compounds discovered back in the 30s of the last century continue to have the greatest industrial value: metalless H2Pc, CuPc copper complex and chlorinated CuPc-Cln derivatives (n = 1-15) [8]. Approaches to obtaining them are well studied and debugged in the industry, which ensures their low cost (7-15 € for CuPc) [1]. The main ways of synthesis of these pigments are shown in Figure 1.1.

In general, the synthesis of the basic structure of Pc requires the presence of phthalogene for the construction of isoindole fragments and a nitrogen source for the formation of azomethine bridges between them. Cyclic tetramerization of phthalogens is accelerated in the presence of metal ions performing a coordinating function [2]. Most world manufacturers produce CuPc (1.2) by heating to 200 °C a mixture of phthalic anhydride (1.6), urea (1.8), copper chloride and a catalyst (usually ammonium molybdate or molybdenum oxide) in a high-boiling (>180°C) solvent (most often in kerosene, trichlorobenzene or nitrobenzene). The highly exothermic reaction of the aromatic macrocycle formation proceeds from 2 to 8 hours with a yield of up to 90%. This process can also be carried out without the use of a solvent: by "dry sintering" of the same components at an elevated temperature of 200-300 °C. In this case, the reaction proceeds faster, eco-logical and technologically simpler, but the resulting product requires additional cleaning[12]. To obtain phthalocyanines of higher purity, phthalonitrile is used as a phthalogene, which also contains a sufficient number of nitrogen atoms for the formation of a macrocycle. As with the use of phthalic anhydride, the process can be carried out in a solvent medium or during fusion using the same catalysts. A distinctive feature of this method is the formation, along with the main product, of partially chlorinated CuPc (when using copper chlorides as a source of metal ions), which, nevertheless, can be useful for obtaining a phase transition-resistant α-form of the pigment. Chlorination is suppressed in the presence of ammonium salts or urea. The industrial production of phthalocyanine pigments from phthalonitrile is severely limited by its inaccessibility [10].

## EXPERIMENTAL METHOD

Green polyhalogenated pigments can be obtained in a similar way to CuPc synthesis-on the basis of halogenated phthalic anhydride (1.9) or phthalonitrile (1.10) [4], but, due to the high cost of substituted phthalogens, the main industrial way of their synthesis is gas-phase chlorination (bromination) of CuPc in a eutectic mixture of NaCl/AlCl3 at 200 ° C in the presence of a catalyst (for example, FeCl3). The hue of such pigments depends on the ratio of Cl and Br atoms in the molecule, as well as the total number of halogen atoms (it is not economically feasible to introduce more than 14-15 substituents, as well as to obtain exclusively brominated or fluorinated derivatives) [8].

## RESULTS AND DISCUSSION

Synthetic ways of obtaining metal-free Pcs (1.1) usually pass through the formation of unstable phthalocyanates of alkaline or alkaline earth metals (Na, Li,Ca), which are easily demetallized in the presence of mineral acids or alcohols [2, 3], although the production of H2Pc is also possible by direct synthesis methods from phthalic anhydride or phthalonitrile [8, 10].

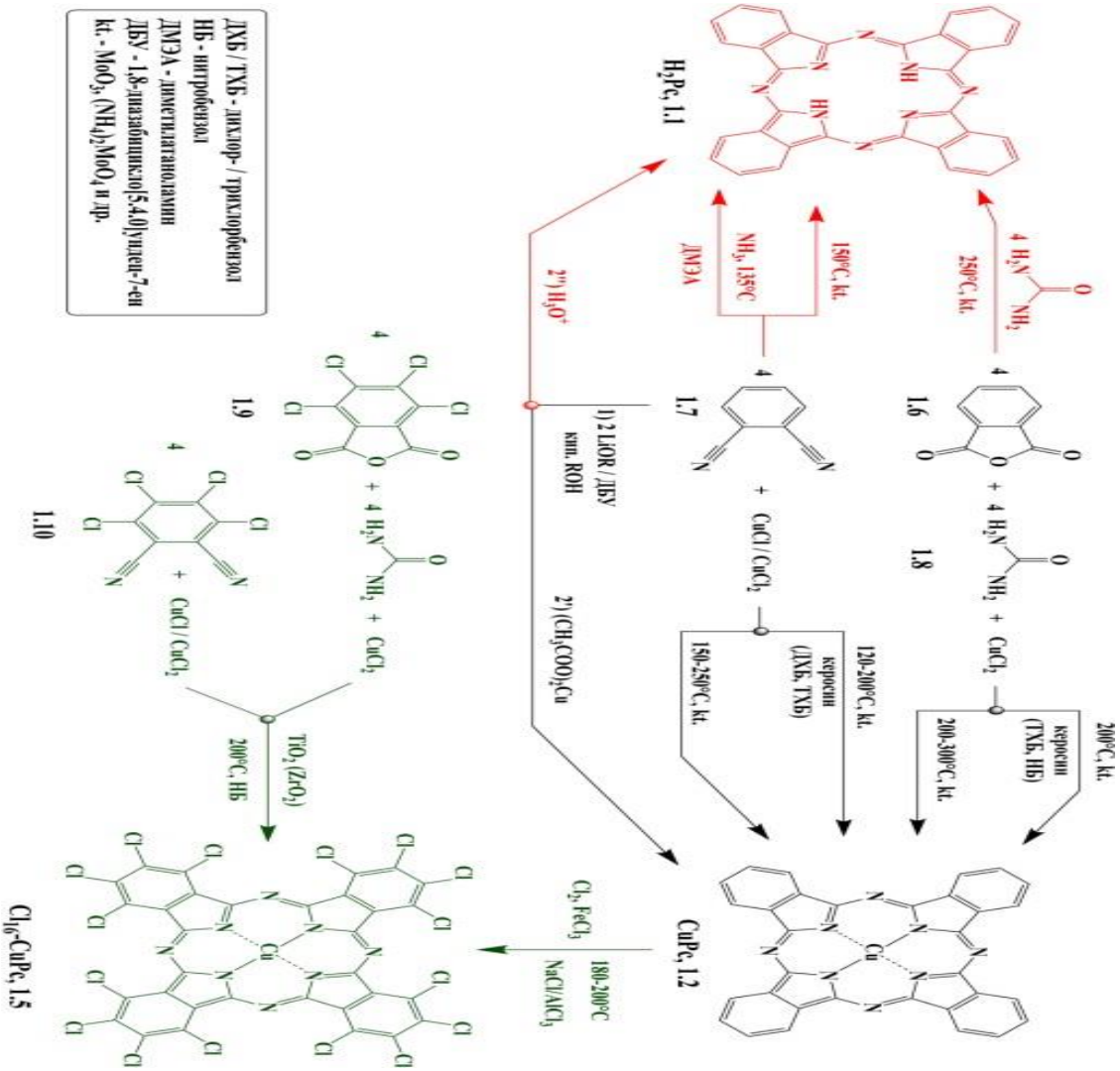


**Figure 1.1. The main ways of synthesis of phthalocyanine pigments.**

To obtain very pure phthalocyanines in laboratory practice, phthalonitriles and metal acetates are usually used as starting materials, and synthesis is carried out in high– boiling alcohols in the presence of a strong base - lithium alcoholate or 1,8-diazabicyclo undec-7-ene (DBU) [1]. Using this method, it is possible to obtain both metal-free Pcs [6] and their metal complexes [7].

Aluminum and cobalt complexes are also commercially available, used as pigments [4] and obtained similarly to CuPc, as well as water-soluble Pcs forms used as dyes, the methods of obtaining which are discussed in the Section

Regardless of the method of preparation, phthalocyanine pigments are subjected to post-synthetic processing to impart the shade, dispersion, stability, etc. required for a particular graduation form.

These characteristics usually depend on the crystalline modification of the pigment. Almost always, high-temperature ways of Pcs synthesis lead to the formation of large particles (1-100 μm) of the most thermodynamically stable β- form, into which other crystalline forms also pass at a temperature of 200-400 ° C. Highly dispersed particles (~50 nm) of the α-form are formed when Pcs is treated with sulfuric acid (conc. 60-100%), followed by hydrolysis of the resulting sulfates (using dilute solutions) or precipitation on ice (from a solution in

concentrated acid). The grinding of β-form particles in a bead mill in the presence of NaCl also leads to a β→α phase transition, and further abrasion with the addition of an organic solvent leads to an α→ε transition (with particle size). The preparation of other crystalline forms of phthalocyanine pigments is described in [10]. The grinding of pigments is carried out even if it does not lead to a change in their crystal modification (as, for example, for halogenated Pcs derivatives). The necessary stabilization of the obtained highly dispersed particles is carried out by various methods.

A variety of applications of phthalocyanines have determined the need to develop approaches to the modification of basic molecules with the introduction of various functional fragments into their structure or onto the surface of the particles formed by them. The structure of Pcs molecules (the presence of a coordination center and reactive fragments on the periphery) provides greater variability in its chemical modification (Figure 1.2): a) by introducing substituents into benzene rings; b) by replacing or annelating benzene fragments, including heteroaromatic structures; c) a variation of the central ion with the production of molecular ensembles and extracomplexes of different geometries.

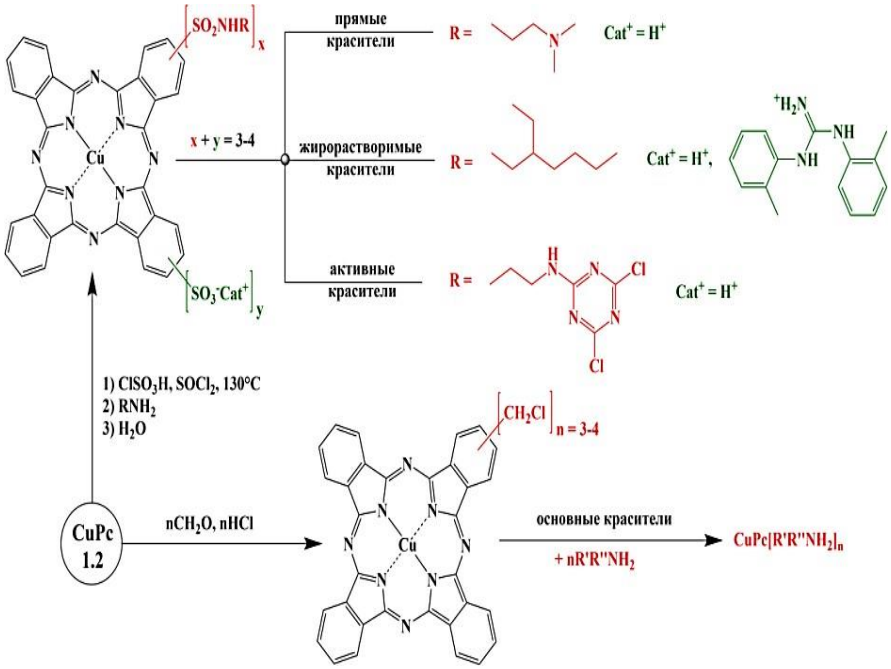


**Figure 1.2. Variants of chemical modification of the structure of phthalocyanines.**

The simplest and most effective way of modification is the introduction of substituents into the peripheral positions of Pcs by electrophilic aromatic substitution reactions. All 16 positions of 4 benzene rings can be replaced, but the most reactive positions are spatially uncomplicated [1]. In addition to the halogenated MPc obtained in this way, used as green pigments, MPc sulfonic acids are of the greatest industrial importance.

Most often, sulfogroups are introduced into the structure of dyes to increase their solubility in water, which depends on the number of such groups in the molecule. Thus, the presence of one sulfogroup in the CoPc molecule does not provide dissolution in water, but allows the use of this compound as a cube dye (C.I. Vat Blue 29), since its leukoform obtained by reduction has sufficient solubility. The introduction of 2 to 4 sulfogroups into the CuPc molecule leads to the production of water-soluble dyes (C.I. Direct Blue 86 and 87, C.I. Acid Blue 249) [8]. Most often, Pcs sulfonation is carried out by heating in oleum (with a wide range of reaction conditions), although other methods have been described, for example, using sulfur anhydride [9]. Of great industrial importance is the process of sulfochlorination of phthalocyanines with further production of sulfamides, which open up opportunities for the synthesis of direct [8], fat-soluble [9] and active [5] dyes (Figure 1.3).

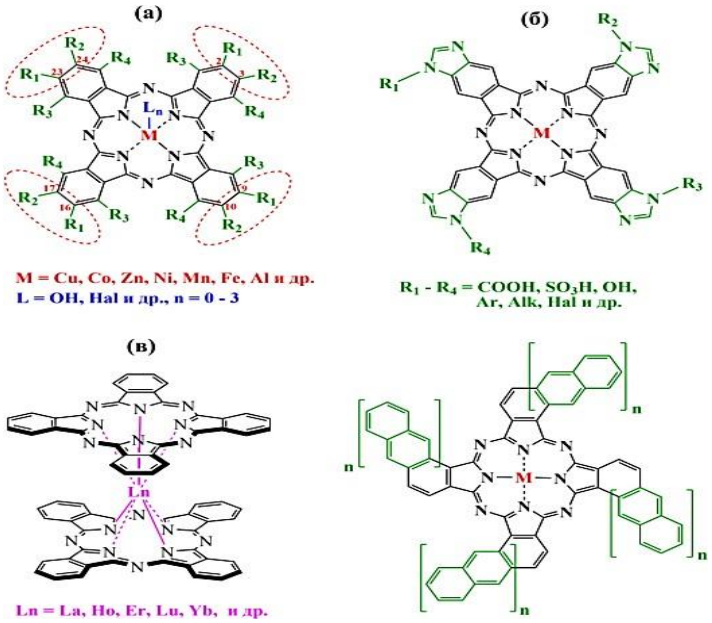


**Figure 1.3. Dyes based on sulfamido- and aminomethyl-CuPc [4-5].**

Also widely used are methods of direct chemical treatment of phthalocyanine pigments (Figure 1.3) by hydroxymethylation [8], halomethylation followed by amination and the production of dyes of the basic type [10].

The paper [4] presents a method for modifying polyhalogenated phthalocyanine Pigment Green 36 using a salt of 4-mercaptobenzenesulfonic acid (Figure 1.4). The introduction of a small amount of sulfogroups into molecules located on the surface of crystalline aggregates of pigment does not lead to solubility in water, but the stability of aqueous suspensions of such Pc increases due to ionization of SO3Na groups. A less common, but rather promising method of processing pigments is the reaction with aryldiazonium salts, which allows various functional fragments to be introduced onto the surface of their particles. The effectiveness of such surface treatment of organic pigments has been noted, for example, in reviews [4, 5].

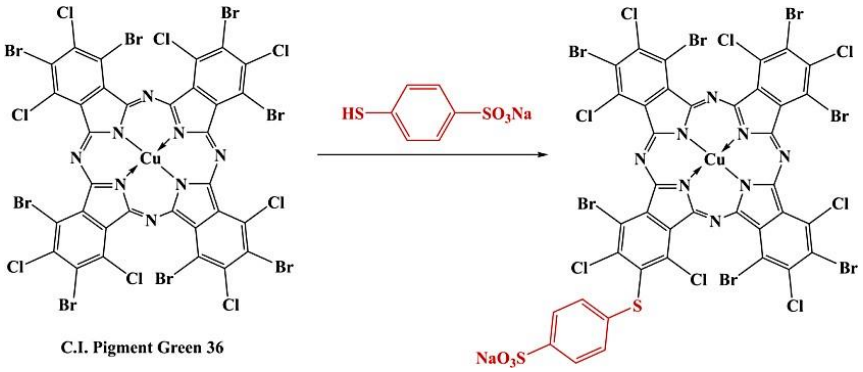


**Figure 1.4. Chemical surface treatment of P.G. pigment [7].**

The reaction proceeds between aromatic fragments (functional groups) located on the surface of pigment aggregates and substituted aryldiazonium molecules under fairly mild conditions: in water, alcohol or a mixture thereof and at a temperature of about 80 ° C. The intermediate link between the surface of the pigment and the injected group is usually a phenyl fragment, while the possibility of changing the position, number and structure of functional groups in the ring provides flexibility of the approach (Figure 1.5). By introducing sulfo- and carboxygroups in this way, pigments with high colloidal stability and low interfacial tension in aqueous media are obtained [6].

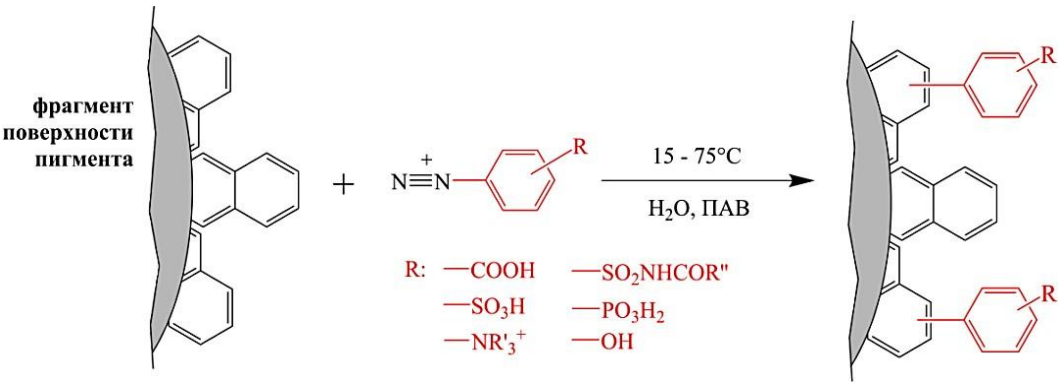


**Figure 1.5. Modification of the pigment surface with aryldiazonium salts [5].**

Similarly, by modifying phosphinate functional fragments capable of specific binding of calcium ions, pigments with increased adhesion to paper are obtained [6]. Heteroaromatic diazonium salts can also act as donors of functional groups [7].

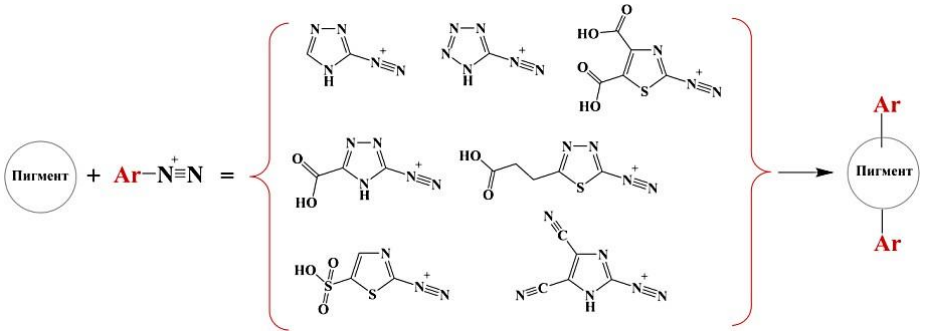


**Figure 1.6. Heteroaromatic surface modifiers of pigments [7].**

Basically, studies of the "diazonium" method of surface modification are carried out on the example of carbon nanomaterials [3]: soot – the most common black pigment, carbon nanotubes, graphene particles and others. The surface of the particles of polycyclic organic pigments (phthalocyanines, quinacridones, cube dyes, etc.), whose crystals are also formed by extended aromatic structures, should also be successfully treated with aryl diazonium modifiers. In the report [2], however, it is noted that, depending on the type of pigment, the effectiveness of such treatment can be significantly different: the representative of azopigments, for the most part, did not enter into the target reaction at all, while for quinacridone pigments, the efficiency of modification depended on the degree of their crystallinity. In addition to the published results of this dissertation [8-10], there are practically no descriptions of the use of diazonium treatment on the example of phthalocyanine pigments in the literature.

The above-described methods of chemical modification of phthalocyanines are the most attractive from the point of view of industrial implementation due to their cheapness and relative technological simplicity. However, their significant disadvantage is often statistical substitution in a relatively small number of product molecules. In turn, modern applications of phthalocyanines require their high purity and, most often, a strictly defined design of molecules.

In this regard, modified phthalocyanines used in promising developments are obtained using pre-substituted phthalogens. By changing the ratio of phthalogens with different substituents, it is possible to obtain asymmetrically substituted macrocycles with the required number of functional groups in each Pc molecule.

The monograph [9] discusses in detail the issues of obtaining sulfo-, carboxy-, halogen-, bifunctional- and asymmetrically substituted, areno- and heteroannelated phthalocyanines and their structural analogues based on respectively substituted phthalogens (more often, phthalonitriles 1.11 or 1,3-diimino-isoindolenines 1.12),

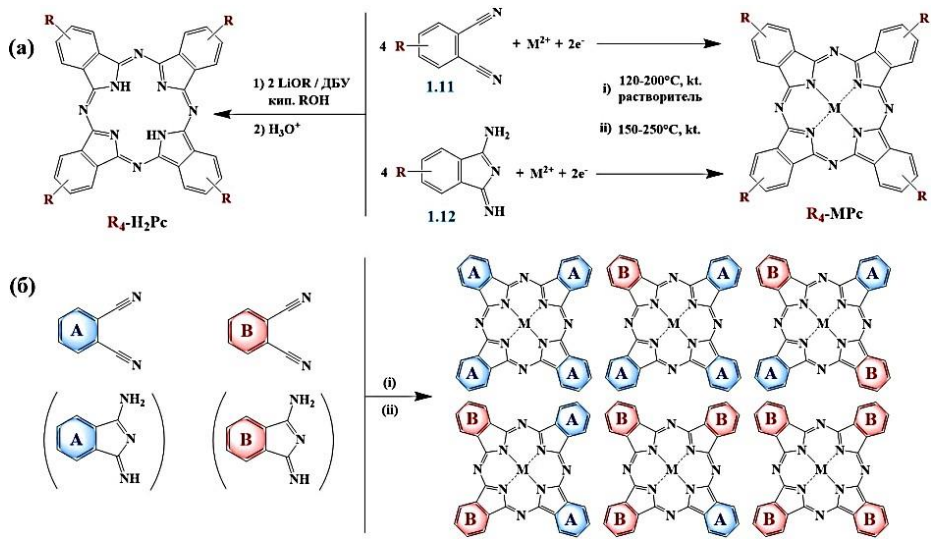


**Figure 1.7. General scheme of synthesis of a) symmetrically and b) asymmetrically substituted Pcs.**

Substituted Pcs can also be obtained by reaction of the initial components in a high-boiling solvent, or by fusion at temperatures from 150 ° C, in the presence of metal ions or strong bases [6]. The variation of the production conditions is due to the reactivity and stability of specific substituted phthalogens. A number of new approaches to the synthesis of Pcs derivatives, for example, under microwave exposure or in the medium of ionic liquids, are reflected in the review [5]. With mixed condensation of phthalogens (Figure 1.7 b), differing in the structure of the aromatic fragment and/or the type and number of substituents, a difficult-to-separate statistical mixture of asymmetrically substituted phthalocyanines is formed. Selective synthesis of Pcs of this type requires additional selection of conditions (the use of non-stoichiometric ratios of phthalogens, the introduction of pre-organizing substituents, etc. [6]), or is possible, for example, with the expansion of the cycle of substituted subphthalocyanines [4].

The number of phthalocyanine derivatives obtained in the last two decades is huge, however, the most popular structures include: branched alkyl substituents [5, 6] to increase solubility in nonpolar organic media; cationic [7-10] or anionic [9] groups to impart water solubility; electron-donating and/or electron acceptors, substituents to increase the efficiency of charge transfer in the molecule.

To create additional coordination centers, as well as opportunities for self- organization, more complex substituents are introduced into Pcs molecules. For example, in [8], methods for the synthesis of new functionalized derivatives of divalent metal phthalocyanates containing benzo-15-crown 5 fragments, phosphoryl and pyridinium groups as peripheral substituents are presented (Figure 1.8).

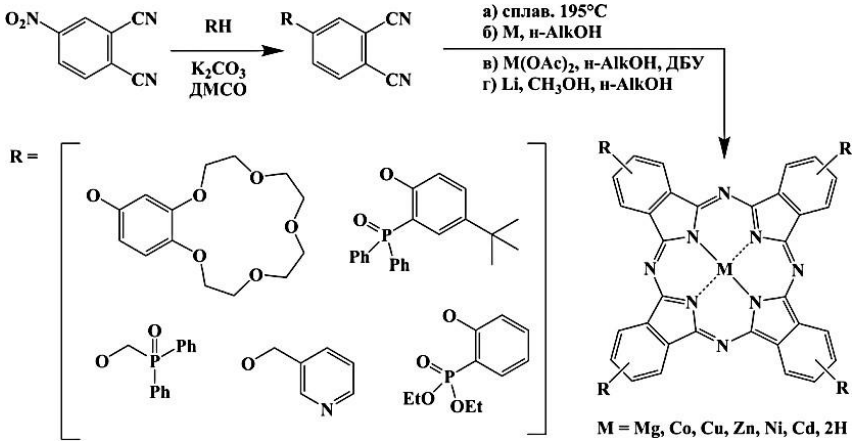


**Figure 1.8. An example of the synthesis of new tetrasubstituted Pcs [8].**

The chemistry of sandwich compounds based on phthalocyanine complexes with rare earth elements is actively developing. The ability of supramolecular complexes of this type to reversible oxidative-reducing transformations determines the prospects for their use as components of electrochromic systems, sensory and conductive materials [7]. Two- and three-deck compounds were obtained (Figure 1.8) with a wide range of ions (lanthanides, actinoids, some elements of the main groups) and with the variation of peripheral substituents in the macroligand, including Pcs complexes with crown-5 fragments [7-9].

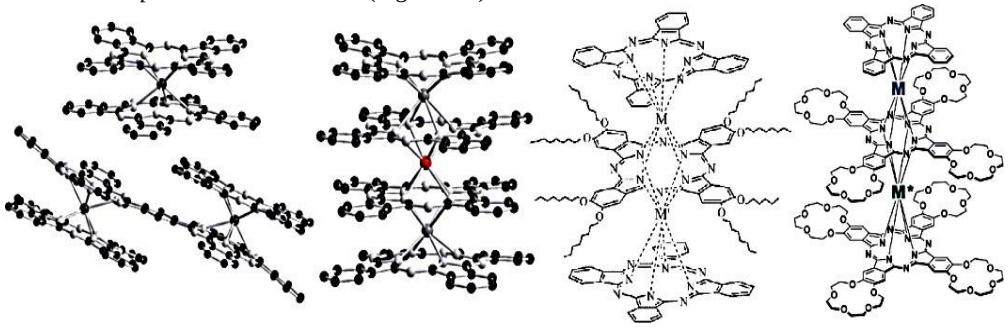


**Figure 1.9. Examples of the structures of sandwich Pcs complexes.**

## CONCLUSIONS

The synthesis of homoleptic (with the same ligands) sandwich complexes is usually carried out either similarly to the production of MPc (Figures 1.1, 1.7), but in the presence of ions capable of octacoordination, or by the interaction of these ions with Li2Pc (H2Pc) in a high-boiling solvent. Mixed condensation of phthalogens, mixed complexation in solution, or tetramerization of phthalogens of a new ligand in the presence of an existing complex is used to obtain heteroleptic (with different ligands) compounds [8].

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