

Synthesis and selected properties of metallo and metal-free 2,3,9,10,16,17,23,24–octacarboxyphthalocyanines

Joanna Nackiewicz* and Marta Kliber

Department of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland

E-mail: Joanna.Nackiewicz@uni.opole.pl

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Abstract

This review article reports methods of synthesis and selected physicochemical properties of metallo and metal-free 2,3,9,10,16,17,23,24–octacarboxyphthalocyanines. The most frequently used methods of synthesis for this class of compounds are described in this article. Moreover, aggregation, catalytic and photocatalytic properties of these complexes are presented. Potential applications of metallo and metal-free 2,3,9,10,16,17,23,24–octacarboxyphthalocyanines are also given.

Keywords: Metallo and metal-free 2,3,9,10,16,17,23,24–octacarboxyphthalocyanines, synthesis, absorption spectra, aggregation, catalytic and photocatalytic activity, applications

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1. Introduction

Phthalocyanines (Pc) are a group of chemical compounds which are structurally analogous to naturally occurring porphyrins. Phthalocyanines do not occur in nature – they are obtained by

synthesis. Initially, these compounds were used as dyes and pigments.^{1,2} Annually, around 50 000 t of phthalocyanines are produced per year.³ Due to their numerous and interesting photophysical and photochemical properties phthalocyanines are increasingly applied in electronics and nonlinear optics and they can also be used as catalysts.^{1,4-9} Recently much attention has been paid to new types of well soluble and asymmetric phthalocyanines.¹⁰⁻¹³ Because of their similar structure to porphyrins, they can be used as models of biologically active compounds.¹⁴ On account of these properties, phthalocyanines are studied as second generation photosensitizers which can find use in photodynamic therapy (PDT).^{4,15-21}

A phthalocyanine molecule can be modified using many different ways, *i.a.* by adding eight carboxylic substituents to a benzene ring obtaining a compound which is well water-soluble in contrast to unsubstituted phthalocyanines. This fact significantly broadens the research range for these compounds, *e.g.* in biological systems which is important as far as practical application is concerned.

The paper reviews literature on methods of synthesis and selected properties of metallo (MPcOC) and metal-free (H₂PcOC) 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines.

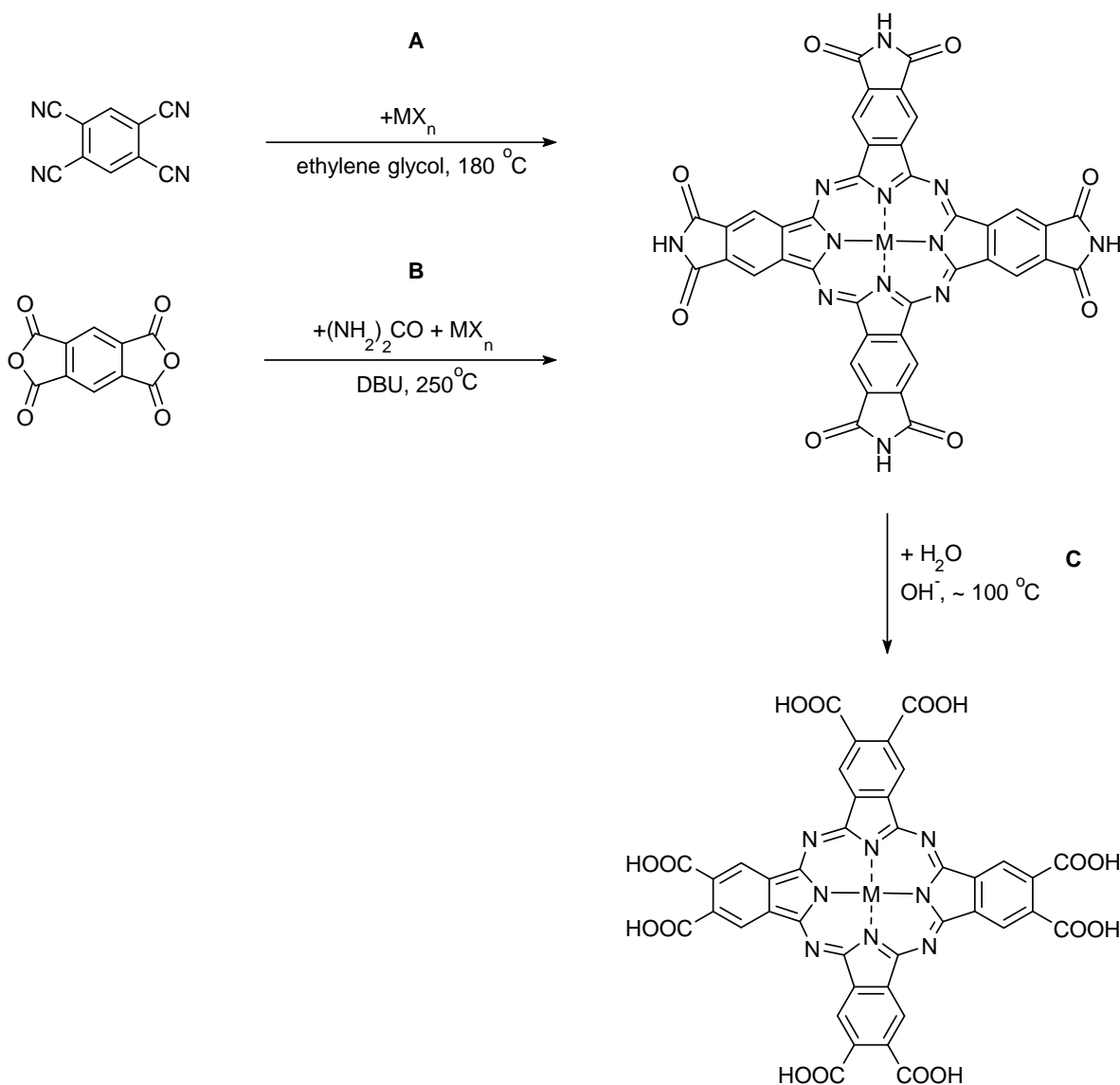
2. Methods of Synthesis of Octacarboxyphthalocyanine

One of the first methods of synthesis of octacarboxyphthalocyanines was proposed by Boston and Bailar.²² Essentially it consists of two steps (Scheme 1). In the first step of synthesis a tetraimide derivative of metallo phthalocyanine is obtained as a result of cyclical tetramerization of 1,2,4,5-tetracyanobenzene in the presence of the respective metal salt in ethylene glycol (Scheme 1A). An analysis of the product obtained after this step shows that a monomeric form of phthalocyanine, and not a polymer of phthalocyanine as it was suggested by Inoue *et al.*,²³ has been obtained. In the second step of the synthesis an alkaline hydrolysis of the obtained tetraimide to carboxylic derivative takes place (Scheme 1C). The hydrolysis was conducted at the temperature about 100 °C (8-10 h) using about 50% KOH solution. The product precipitates from the solution (at about pH 2) using HCl, thus it is possible to obtain the monomeric form of copper octacarboxyphthalocyanine.

Sakamoto and Ohno²⁴ obtained a phthalocyanine tetraimide as a result of the reaction between an pyromellitic dianhydride with a metal halide of respective metal in the presence of urea and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as a catalyst (Scheme 1B). Afterwards they have also conducted an alkaline hydrolysis, similarly to Boston and Bailar²² and they have precipitated the product with concentrated HCl. According to Sakamoto and Ohno²⁴ if a synthesis is conducted using this method it is possible to obtain octacarboxyphthalocyanine acid of a respective metal.

The heating of pyromellitic dianhydride and urea with a metal salt and ammonium molybdate as a catalyst is generally based on fusion yet it is preferred to heat also with high-boiling solvents, *e.g.* sulfolane. The product obtained after this step can undergo acid hydrolysis using

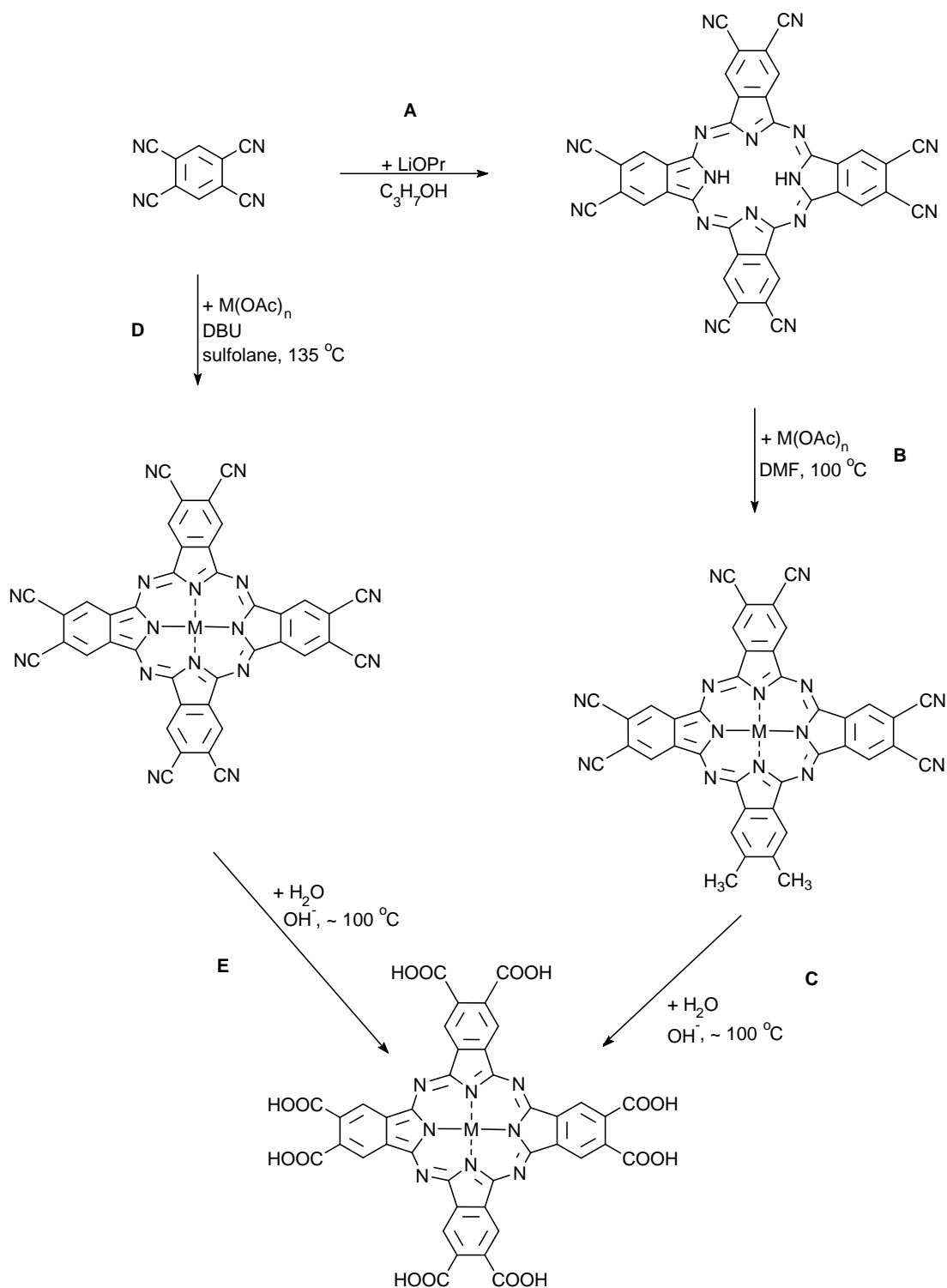
about 15% sulfuric acid and 2,3,9,10,16,17,23,24-metallo-octacarboxyphthalocyanines, *e.g.* CuPcOC can be prepared.^{25,26}



Scheme 1. Synthesis of metallo-octacarboxyphthalocyanine from phthalocyanine imides according to Boston and Bailar.²²

Metallo-octacarboxyphthalocyanines can be obtained also in a three-step synthesis.²⁷ In the first step starting with 1,2,4,5-tetracyanobenzene metal-free octacyanophthalocyanine is obtained as a result of heating with lithium propoxide in anhydrous *n*-propanol. In the second step metallation of metal-free octacyanophthalocyanine occurs due to the introduction of a respective metal salt into the mixture containing metal-free octacyanophthalocyanine. After this step metallo octacyanophthalocyanine is created. The third step of the synthesis is based on an alkaline hydrolysis of nitrile into carboxylic derivatives (Scheme 2A – 2C and 2E). It is also

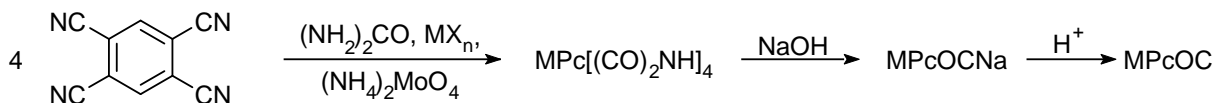
possible to hydrolyze nitrile derivative, which was obtained in the first step, that is metal-free octacyanophthalocyanine and as a result metal-free octacarboxyphthalocyanine is obtained.



Scheme 2. Synthesis of metallo-octacarboxyphthalocyanines from octacyanophthalocyanines according to Wöhrle *et al.*²⁷

Starting from 1,2,4,5-tetracyanobenzene in the presence of solid sodium methoxide in THF (tetrahydrofuran) Nemyklin *et al.* obtained metal-free octacyanophthalocyanine at room temperature. Metallo-octacyanophthalocyanine can also be obtained by adding a respective metal salts after formation of metal free octacyanophthalocyanine.²⁸

It is also possible to get metal-free octacyanophthalocyanine by conducting a reaction of 1,2,4,5-tetracyanobenzene with anhydrous salt of a respective metal (Scheme 2D).²⁹ In this reaction it is necessary to use a polar aprotic environment that is sulfolane and a strong aprotic base, *e.g.* DBU, since using protic solvents like alcohols or DMF leads to obtaining a contaminated mixture in which CN groups hydrolyze into amide groups. However, a new method of synthesis of metallo 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines (Co, Cu, Zn, Al, Cr) with the use of DMF as a solvent has appeared. The mixture of 1,2,4,5-tetracyanobenzene and salt of a respective metal was heated in DMF in the presence of urea and ammonium molybdate as a catalyst. The amide derivative, which is received after this step, undergoes an alkaline hydrolysis and the obtained sodium salt of octacarboxyphthalocyanine acid is transformed into carboxylic acid. Moreover, the obtained product was purified with chromatography on silica gel and chromatographic analysis showed that the metallo-2,3,9,10,16,17,23,24-octacarboxyphthalocyanines occur as a single isomer.

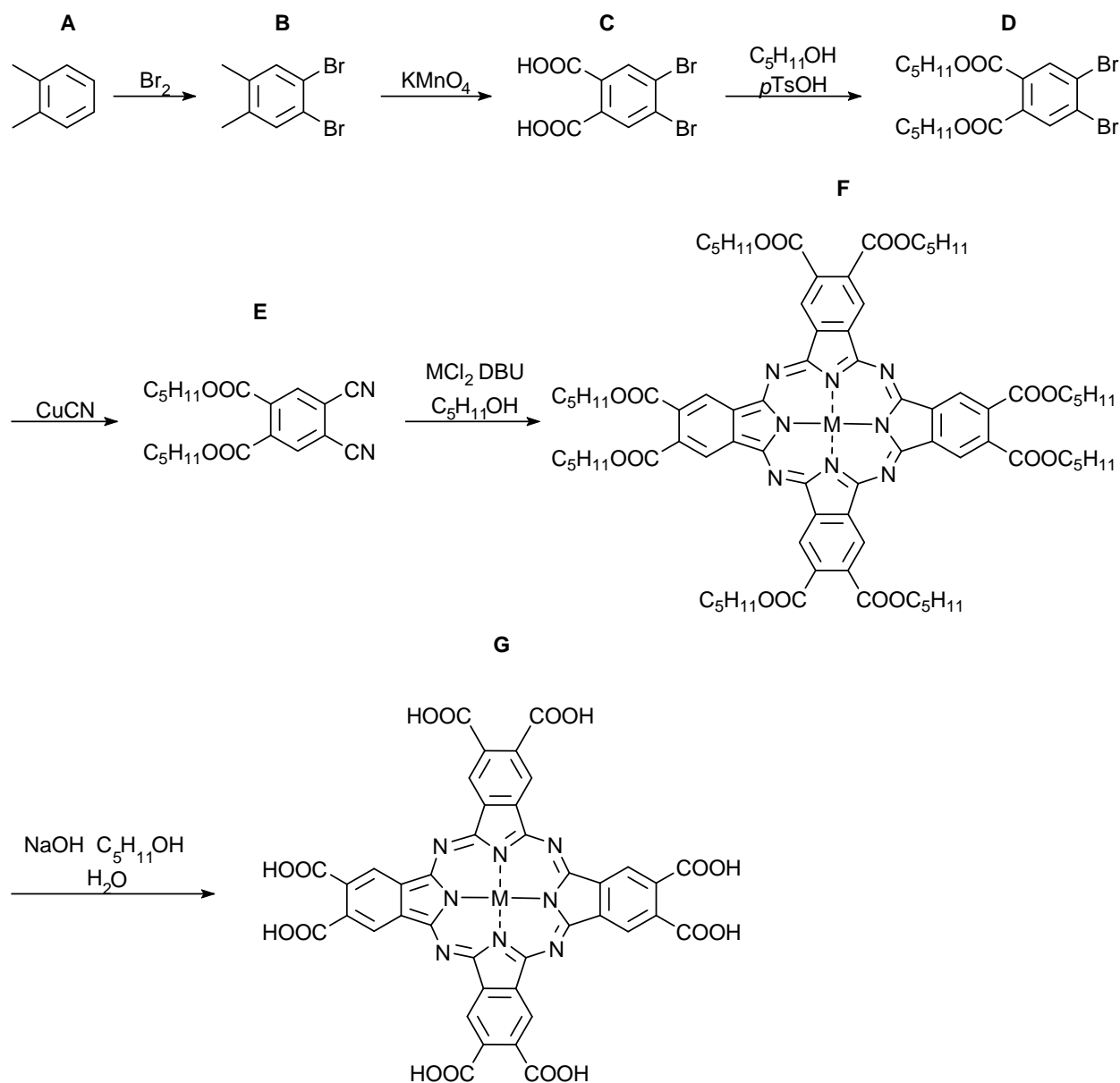


Scheme 3

Synthesis of metallo octacarboxyphthalocyanines from phthalocyanine imides according to Shaposhnikov *et al.*³⁰ MX_n- metal chloride.

A six-step synthesis of metallo 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines has been proposed, starting from *o*-xylene,³¹ (Scheme 4A) or using 4,5-dibromobenzene-1,2-dicarboxylic acid,³² (Scheme 4C).

Further synthetic procedures are based on esterification, the Rosenmund von Braun reaction, and a highly reactive product E (Scheme 4E) is obtained which undergoes a cyclotetramerization into compound F. The alkaline hydrolysis of the ester derivative leads to obtaining a carboxylic derivative (Scheme 4G).



Scheme 4. Synthesis of metallo octacarboxyphthalocyanines.^{31,32} according to Opris *et al.*³¹, Nemykin and Lukyanets.³²

3. Physical Properties

The presence of eight carboxylic groups in the benzene rings significantly improves the solubility of these complexes in polar solvents. Metallo and metal-free 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines dissolve well in water with pH above 7,³³ also such complexes as CoPcOC, ZnPcOC, Al(OH)PcOC and Cr(OH)PcOC are water soluble but they do better in alkaline solutions.³⁰ Moreover metal-free 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine is

soluble in DMSO,³⁴ whereas according to authors solubility in water is limited. The hydroxy aluminium octacarboxyphthalocyanine (Al(OH)PcOC) conjugated with diammine platinum give water- soluble complexes at pH > 8.2.³⁵ Generally octacarboxyphthalocyanines are very stable compounds,³⁶ especially the complexation of metal helps to increase the stability of these complexes.³⁷ These compounds have a relatively high thermal stability.^{14,27,38,39} According to Opris *et al.*³¹ the heating of CuPcOC in the temperature up to 250 °C leads to a 13.5% loss of the total mass which indicates the loss of water whereas the decomposition of phthalocyanine molecules starts in the temperature of about 330 °C. Also for the series of complexes like CoPcOC, CuPcOC, ZnPcOC, Al(OH)PcOC and Cr(OH)PcOC in the temperatures from 120 °C to 150 °C the change in mass is caused only by the loss of adsorbed and crystallization water,³⁰ and if the heating process is continued anhydride fragments are created.

Octacarboxyphthalocyanines show also resistance to light, many acids and bases. However, some, *e.g.* metal-free octacarboxyphthalocyanine, undergo decomposition under the influence of light, oxygen in an alkaline environment, or in concentrated H₂SO₄. Using an inert gas atmosphere and leaving it in the dark does not cause the decomposition of this compound.³³

4. Spectral Properties of Octacarboxyphthalocyanines: Absorption and Emission Spectra

In UV-vis absorption spectra two absorption regions are distinguished: the B band (approx. 300-400 nm) and the Q band (approx. 550-750 nm). The common feature of spectra of metallo phthalocyanines (MPc) which have a D_{4h} symmetry is one intensive and narrow band which occurs in the Q region at λ_{\max} = 650-750 nm. Spectra of free-base phthalocyanines (H₂Pc) differ substantially in the Q region from the spectra of metallo phthalocyanines (Figure 1). In the case of metal-free phthalocyanines (D_{2h} symmetry) the LUMO orbital is split into two levels: Q_x and Q_y, so in the UV-vis spectrum (the Q band) two intensive peaks called Q_x and Q_y (ϵ Q_x > ϵ Q_y) are visible, instead of one as it happens in the case of metal complex. On the hypsochromic side those bands are accompanied by vibronic bands which are much less intensive (Q_{vib, x} and Q_{vib, y}).⁴⁰

Fluorescence spectroscopy has been used in studies of phthalocyanines and porphyrins for years. As far as phthalocyanines are concerned S₁ as well as S₂ emissions are known. In the literature there are cases of phthalocyanine complexes which show the weak violet emission (S₂) in addition to the strong red emission from the lowest singlet excited state (S₁).^{41,42} The emission spectrum for ZnPcOC is shifted in relation to the absorption spectrum in the direction of longer waves and its shape is a mirror image of the absorption spectrum (Figure 2).

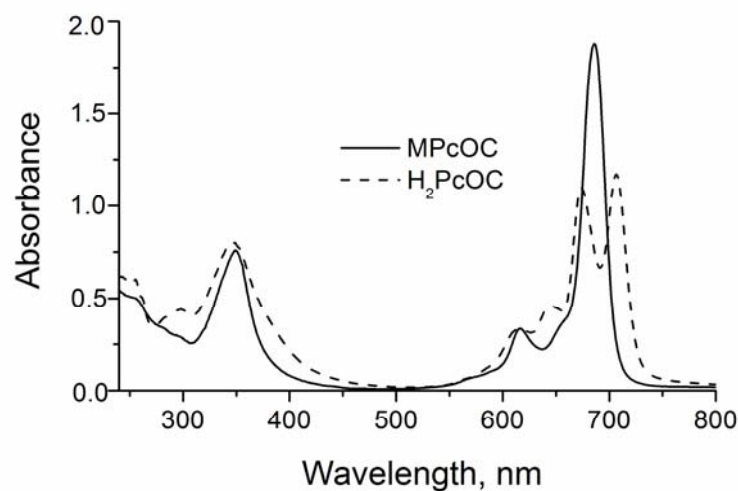


Figure 1. UV-vis spectra of CuPcOC(—) and H₂PcOC (- - -) in aqueous solution at pH 7.5.

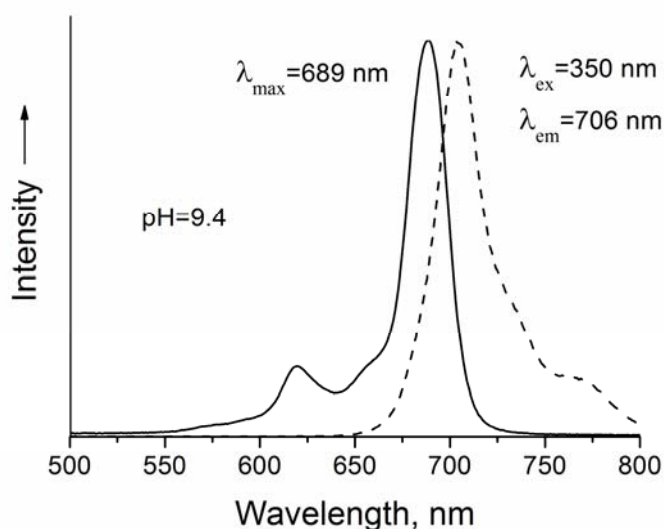


Figure 2. Normalized absorption and emission spectra of ZnPcOC in a solution at pH=9.4; $c_{\text{ZnPcOC}} = 5 \cdot 10^{-6} \text{ mol/dm}^3$.⁴³

The absorption spectra of phthalocyanines in concentrated H₂SO₄ are frequently described in literature. In this solution a protonation of bridging nitrogen atoms takes place which strongly polarizes the phthalocyanine molecule. This polarization decreases the energy of all electron transition of the macrocycle. Spectral data for phthalocyanines in concentrated H₂SO₄ has been shown in Table 1. In longer wavelengths of the Q band metal-free phthalocyanine with

carboxylic substituents (H_2PcOC) has a band shape analogical to metallo phthalocyanines with the same substituents (MPcOC - D_{4h} symmetry) which indicates equivalence of the four inner nitrogen atoms in H_2PcOC . The data presented in the Table suggests that, in comparison to unsubstituted phthalocyanines, those which have carboxylic substituents absorb at shorter wavelengths (in the Q and B region) whereas in the case of N and L bands – at longer ones. Electron- withdrawing substituents decrease the basicity of meso-nitrogen atoms and a λ_{max} shift occurs in the direction of shorter wavelengths.³³

Table 1. Spectral data of phthalocyanine in concentrated sulfuric acid

Complex	Q				B		N	L		References
	λ_{max} , nm									
H ₂ Pc	835	773	746	692	440	303	-	230	203	
H ₂ PcOC	754	702	671	640	390	335	295	230	-	
CuPc	790	745sh	698	634	438	303	254	222	210	33 ^a
CuPcOC	745	702	666	640	390	335	295	230	210-200	
	750									31
ZnPcOC	750									31

^aspectra were recorded 1 h after dissolving

The effect of the solvent on the location of the Q bands for MPcOC and H_2PcOC complexes is presented in Table 2.

Table 2. Spectral parameters for MOCpC complexes

Complex	Solvent ^a	Q band		Refs.
		λ_{abs} , nm	λ_{em} , nm	
CuPcOC	DMF	690	-	30
		690; 645		27
	DMSO	694	-	30
	H_2SO_4	746	-	30
ZnPcOC	pH 7.4 (PBS)	693	702	46
	pH 10	689	699	47
	(0.1M KOH)	690		93
	DMSO	700	708	72
	Pyridine-water	700	712	43
	DMF-water	698	713	43,44
	DMSO-water	700	716	43,44

Table 2. Continued

Complex	Solvent ^a	Q band		Refs.
		λ_{abs} , nm	λ_{em} , nm	
Al(OH)PcOC	Ethanol-water	694	708	43,44
	Redist. water	689	703	43,44
	pH 9.4 (BRB)	689	706	43,44
	pH 7.4 (PBS)	689	694	46
	DMSO	704	711	71
	DMSO	699		30
	DMF	693		30
Al(OH)PcOC	H ₂ SO ₄	753		30
	water	696	706	71
	pH 8.2 (PBS)	689	696	94
AlPcOC	pH 10 (0.1M KOH)	689		93
	DMSO	707	714	72
(OH) ₂ SiPcOC	pH 7.4 (PBS)	691	703	46
	pH 10	693	700	47
	DMSO	703		73
SiPcOC	pH 10 (0.1M KOH)	690		93
	pH 7.4 (PBS)	697	704	46
(OH) ₂ GePcOC	DMSO	700		73
OTiPcOC	pH 10	693	700	47
(OH)GaPcOC	pH 11 (PBS)	688	699	74
CoPcOC	DMF	687		30
	DMSO	689		30
	H ₂ SO ₄	751		30
	DMF	704		30
Cr(OH)PcOC	DMSO	702		30
	H ₂ SO ₄	762		30
	DMF	714, 683, 652, 622		27
H ₂ PcOC	pH 7.12	706, 674		44
	pH > 10	690		44
	MTOACl	722		44

^a DMF: dimethylformamide, DMSO: dimethylsulfoxide, PBS: phosphate buffer saline, BRB: Britton-Robinson buffer, MTOACl: methyltriocetylammmonium chloride

The locations of bands are typical for monomeric species of octacarboxyphthalocyanines. Moreover intermolecular hydrogen bonding may occur which inhibit aggregation thus a monomeric band appears in the spectrum. Bands for MPcOC in such solvents like: DMF, DMSO or pyridine are clearly shifted bathochromically in relation to *e.g.* the location of those bands in aqueous solutions with $\text{pH} > 7$. The location of the bands of octacarboxyphthalocyanine can be caused by many factors *e.g.* the type of complexed metal ion to ligand, solvation of molecules, a different degree of dissociation which depends on the type of solvent, the ability of the solvent to establish hydrogen bonds with octacarboxyphthalocyanine molecules and a coordination of solvent molecules into the central metal of those complexes.⁴³ Also when a concentrated H_2SO_4 is used the locations of bands with a strong bathochromic shift are obtained because of the protonation of meso-nitrogen atoms.³⁰

The locations of the bands in UV-Vis absorption spectra for H_2PcOC , i.a. in aqueous solutions, in solutions with different pH values, in mixed solutions (water-ethanol, water-methanol) and in solutions containing surfactants are presented by Suchan *et al.*⁴⁴ In water the location of the Q and B bands changes and the concentration of the studied phthalocyanine has a strong effect on the location. In solutions with pH of 7.12 the following λ_{max} (the Q band) for H_2PcOC have been obtained: 674; 706 nm. When pH was > 10 only one band has been obtained at 690 nm in the Q band instead of two. Such a change in the Q band is connected to the change of symmetry from $\text{D}_{2\text{h}}$ to $\text{D}_{4\text{h}}$. Moreover, in solutions containing a surfactant (methyltriethylammonium chloride) a band with a strong bathochromic shift was obtained (722 nm). The cationic surfactant interacts with H_2PcOC molecule and this leads to the enrichment of the chromophoric system.⁴⁴

UV-Vis absorption spectra for ZnPcOC , Al(OH)PcOC , $(\text{OH})_2\text{SiPcOC}$ and $(\text{OH})_2\text{GePcOC}$ in the phosphate buffer with pH of 7.4 and solution with pH of 10 have been shown by Idowu and Nyokong.^{45,46} Those complexes show a characteristic absorption with the Q band at the wavelength of about 690 nm (Table 2). The obtained spectra are typical monomeric spectra with a narrow single Q band typical for metallo phthalocyanine complexes. The increase of mass of the central metal causes the bathochromic shift of the Q band.

Solvents have an effect on the locations of bands not only in the absorption spectra but also in emission spectra of octacarboxyphthalocyanines. The effect of pH on the absorption or emission spectra depends on the kind of the complexed metal ion (Table 2).⁴⁷ In aqueous solutions with $\text{pH} > 7$ λ_{em} occurs usually from 694 to 706 nm. The λ_{em} was significantly higher in solutions containing aprotic or weakly protic organic solvents than in solutions containing protogenic solvents.⁴³

The location of the bands in UV-vis absorption spectra of octacarboxyphthalocyanines may change in time by *e.g.* the presence of substances which interact with phthalocyanine ligand. During studying the catalytic activity of FePcOC and CoPcOC complexes in the oxidation of 2-mercaptoethanol spectral changes were shown which were caused by the presence of thiol in the solution of cobalt octacarboxyphthalocyanine. In time, the shape and location of bands in the Q region changed significantly. CoPcOC complex in aqueous solution with pH of 7.0 containing 2-

mercaptoethanol (time $t=0$) has two bands at $\lambda_{\text{max}} = 630$ and 680 nm. The band at 680 nm was assigned to $\text{O}_2^- \text{CoPcOC}$ adduct. In time, the spectrum in the Q region changes and two new bands at 450 and 730 nm appear. The band at 490 nm was assigned to Co(I) .⁴⁸

5. Aggregation of Octacarboxyphthalocyanines

The properties of phthalocyanines to a large extent depend on their degree of aggregation; this is fairly common for this class of compound. Both metal-free and metallo phthalocyanines connected and make dimers or even higher associated molecules. Many factors influence aggregation, *i.a.* concentration of phthalocyanine, solvents, peripheral substituents, the type of complexed metal ion, ionic strength of the solution and temperature.⁴⁹⁻⁵¹ Aggregation usually influences application properties of these compounds negatively. Aggregated compounds develop mainly due to interactions of delocalized π electrons of macrocycles.⁵² However, the functional groups as well as by oxygen atom (the creation of μ -oxo or μ -peroxo connections). The arrangement of the phthalocyanine macrocycles in the crystalline state in liquid crystal mesophases, in polymers which were created by the covalent bonds along the axis which connect the centers of macrocycles and in the associated compounds which occur in solutions is similar. This arrangement in all cases is stacking.⁵²

In UV-vis spectra it is possible to trace the changes of the aggregation process, which are visible in the B band as well as the Q band. In the UV-vis spectrum of dimer complexes in solutions an intensive and broad band occurs in the Q band at about $\lambda_{\text{max}} = 630$ nm (Figure 3). Along with the intensity of aggregation this band and the B band to a lesser extent undergo a hypsochromic shift. The λ_{max} position of trimer band and higher aggregated compounds occur usually between 600 and 630 nm.^{53,54} Whereas the intensive band at 660-700 nm, typical for the monomeric form, is bathochromically shifted about 30-70 nm against the λ_{max} of the dimer band. The B band also undergoes a bathochromic shift but to a much lesser extent. (Figure 3).^{40,54} For FePcOC in a solution with pH of 7.0 a dimer band and a monomer band can be seen at 634 nm and at 680 nm respectively. However, regardless of the presence in the spectrum of dimer band, iron octacarboxyphthalocyanine occurs mainly in the monomeric form due to the electrostatic repulsion of negatively charged carboxylic groups (dissociation of eight carboxyl groups at this pH value).⁵⁵

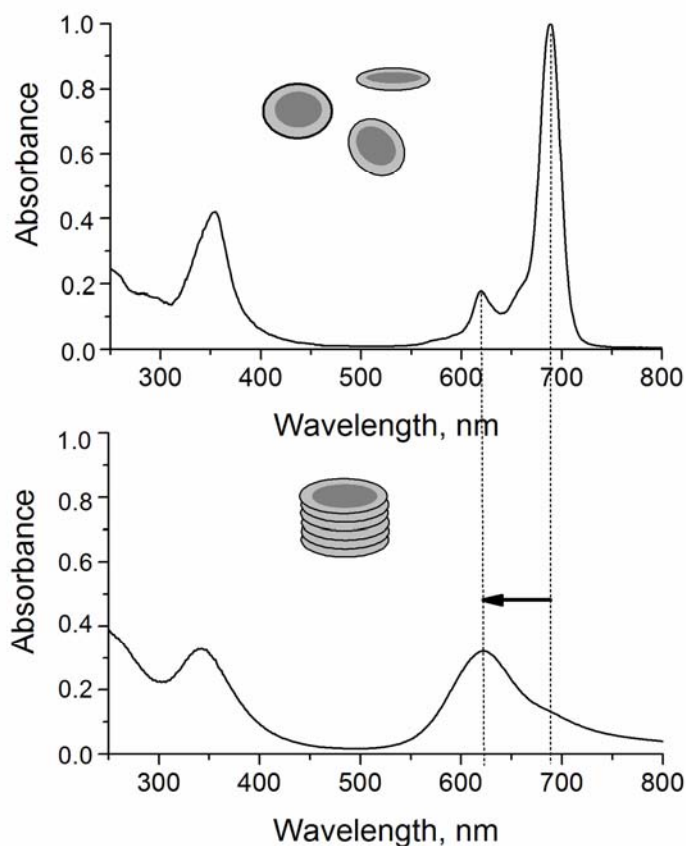


Figure 3. The effect of aggregation on MPcOC spectrum.

The aggregation of phthalocyanines is usually a result of π - π interactions between π electron clouds of adjacent macrocycles. However, in the case of compounds with carboxylic substituents interaction with hydrogen bonds can be additionally expected. Usoltseva *et al.*⁵⁶ claim that the creation of liquid crystal columnar structures in solutions by carboxylic phthalocyanines is conditioned by a mutual interaction of macrocycles and additionally by hydrogen bonds between carboxylic groups. Yet, as the authors suggest, the location of carboxylic groups in a molecule is significant. The occurrence of hydrogen bonds between molecules has also been proposed for CuPcOC in solid state.⁵⁷ From STM images the distance between two adjacent Pc units in a two-dimensional network arrangement of molecules on a graphite surface has been estimated at 1.82 ± 0.05 nm. The arrangement model of CuPcOC molecules implies the presence of hydrogen bonds between carboxylic groups. In this model the distance between adjacent Pc units is 1.71 nm. This value is compatible with the one obtained from an analysis of STM images. The arrangement of CuPc on the graphite surface differs from the arrangement of CuPcOC molecules significantly. CuPc molecules are tilted at a certain angle and closely packed in contrast to CuPcOC units which are connected by hydrogen bonds.⁵⁷

As far as the assessment of the effect of hydrogen bonds in stabilization of stacking arrangement is concerned, the values of aggregation constants of octacarboxyphthalocyanines provide valuable information. The aggregation of copper octacarboxyphthalocyanine in aqueous solutions was studied and described by Suchan *et al.*⁵⁸ The location of the band at $\lambda_{\text{max}} = 685 \text{ nm}$ was assigned to the monomeric form and around 640 nm to the aggregated form. For this complex in the concentration range of $0.5\text{--}5.0 \cdot 10^{-6} \text{ mol/dm}^3$, the absorbance of the main band at $\lambda_{\text{max}} = 685 \text{ nm}$ shows some deviation from the Beer law. In this concentration range monomers and dimers dominate in the solution and the obtained constant value of dimerization is $10^6 \text{ dm}^3/\text{mol}$ in the temperature of $25 \text{ }^\circ\text{C}$. The theory of interaction in phthalocyanine aggregates is generally based on molecular exciton coupling.^{52,59,60} The hypsochromic spectra shift for the dimer 1164 cm^{-1} ($688 \text{ nm} \rightarrow 637 \text{ nm}$) indicates a stack-like aggregation of molecules and suggests π – π interactions between Pc macrocycles in dimer and higher aggregates. The authors suggest that a hydrogen bonding between carboxylic groups is most likely of less importance in CuPcOC dimer formation and stability.⁵⁸ The effect of pH on aggregation was tested for the same complex.⁶¹ CuPcOC strongly associates at $\text{pH} < 5.5$ whereas in solutions with $\text{pH} \geq 6.2$ monomers mainly dominate. The studied compound shows a strong tendency for aggregation in the phosphate buffer and the degree of aggregation is 3 (the value of average assembling number $n=3$) in the studied range of concentration ($1\text{--}12 \cdot 10^{-5} \text{ mol/dm}^3$) in solutions with pH of 5.6–6.0. At pH of 6.0 an cumulative aggregation constant of $10^9 (\text{dm}^3/\text{mol})^2$ was obtained and at pH of 5.9 it is $10^{10} (\text{dm}^3/\text{mol})^2$. The obtained results lead to a conclusion that a strong tendency to aggregation in the studied range of pH is a result of not only π – π interactions between Pc macrocycles but in this case also of occurrence of hydrogen bonding between the studied phthalocyanine molecules. The locations of monomeric band at $\lambda_{\text{max}} 687 \text{ nm}$, dimeric band at about 630 nm and trimeric band at about 600 nm were obtained.⁶¹

Aggregation of water-soluble ZnPcOC was studied by analyzing the UV-vis absorption spectra and fluorescence emission spectroscopy.⁴³ ZnPcOC aggregates in aqueous solutions and the degree of aggregation depends on the concentration of the solution. In the studied range of concentration ($0.5\text{--}50 \cdot 10^{-6} \text{ mol/dm}^3$) in the temperature of $25 \text{ }^\circ\text{C}$ the values of assembling number $n=2$ and $K_n=5 \cdot 10^6 \text{ dm}^3/\text{mol}$ were obtained. The maximum of dimeric band for this complex was obtained at $\lambda_{\text{max}}= 636\text{--}8 \text{ nm}$ and the maximum of monomeric band at $\lambda_{\text{max}} = 689 \text{ nm}$. Moreover, the obtained value of the spectral shift is 1185 cm^{-1} . The spectral shift as well as the value of dimerization constant suggest strong interactions between Pc molecules in this complex. In order to study aggregation it is possible to use data obtained from measurements of fluorescent spectra in different solvents and on this basis it can be concluded that the fluorescent form is the monomeric form of phthalocyanine. Dimerization and further multimerization causes very strong quenching of this fluorescence.⁴³

Many different factors influence aggregation *e.g.* the concentration of the complex, pH , temperature, the presence of cationic surfactants and alcohols.⁴⁴ A gradual decomposition of associated compounds in the case of metal-free octacarboxyphthalocyanine is caused by such factors like *e.g.* a rise of temperature, pH , a decrease of concentration, an addition of methanol,

ethanol cationic surfactant into an aqueous solution of this phthalocyanine. In acid solutions H_2PcOC undergoes strong aggregation which leads to a complete disappearance of the monomeric form. Researching the aggregation equilibrium in the case of H_2PcOC causes some difficulties since, except the spectral shifts connected with aggregation, H_2PcOC monomer can occur in two forms of different D_{2h} and D_{4h} symmetries.

6. Catalytic and Photocatalytic Activity of Octacarboxyphthalocyanine

Metallo phthalocyanine complexes are also interesting as oxidation catalysts of *e.g.* compounds containing sulfur *e.g.* cysteines, thiols, sulfides and other environmentally hazardous compounds.^{62,63,64} These studies are significant not only for their basic reasons but also for their ecological aspect.

The aggregation of octacarboxyphthalocyanine influences its catalytic and photocatalytic activity. The process causes a decrease of the number of active center thus the reaction rate decreases. Water-soluble $CoPcOC$ shows a very strong catalytic activity in oxidation of mercaptoethanol in the presence of 2,4-ionene (poly(quaternary ammonium salts)) in a solution. In the presence of 2,4-ionene $CoPcOC$ does not aggregate and does not create a μ -peroxo complex.⁶⁵

Iron octacarboxyphthalocyanine shows catalytic activity in the decomposition of hydrogen peroxide which can be defined by measuring the initial rate of the reaction (V_0) against the increasing concentration of oxygen.⁵⁵ The reaction proceeds according to the catalase-like mechanism. The rate of decomposition depends on the central metal of octacarboxyphthalocyanine. In the case of $FePcOC$ the initial rate of decomposition of hydrogen peroxide is about 30 times faster than for $CoPcOC$. The V_0 value is significantly influenced by pH. At $pH > 7$ the reaction rate increases because the concentration of monomers in the solution increases. The catalytic activity in this reaction is due to the monomeric form of $FePcOC$.⁵⁵ At $pH 6.5$ OOH^- is formed by dissociation of H_2O_2 and the formation of OOH^- appears to be favored in the decomposition of H_2O_2 .

Oxidation of 2-mercaptoethanol (RSH) is catalyzed by homogenous polymer complexes of iron (III) and cobalt (II) octacarboxyphthalocyanines which turned out to be efficient catalysts in aerobic oxidation of 2-mercaptoethanol.⁴⁸ RSH oxidation in the presence of $CoPcOC$ or $FePcOC$ complexes occurs according to Michaelis-Menten mechanism and the catalytic activity in this reaction changed in the series $CoPcOC > Fe(III)PcOC$. A ternary activated complex is created where RS^- and O_2 reversibly coordinate with the central metal on the phthalocyanine ring. Conducting a reaction in aqueous solution with pH of 7.0 is due to the fact that at this pH value the studied complexes occur mainly as catalytically active monomers. Table 3 shows kinetic parameters of 2-mercaptoethanol oxidation which was catalyzed by metallo-octacarboxyphthalocyanines. In this case $Co(II)PcOC$ proved to be a more effective catalyst.

Table 3. Kinetic parameters for the oxidation of 2-mercaptoethanol catalyzed by MPcOC

Complex	V_{\max} mol/Lmin ⁻¹	K_B , mol/L	k , min ⁻¹
Fe(III)PcOC ^a	$7.2 \cdot 10^{-5}$	$2.47 \cdot 10^{-3}$	720
Co(II)PcOC ^a	$8.4 \cdot 10^{-3}$	$5.05 \cdot 10^{-3}$	840

^a [MPcOC] = $1.00 \cdot 10^{-7}$ mol/L, pH=7.0, temp. 25 °C; K_B – the Michaelis constant;
 k - the rate-controlling step

Cobalt octacarboxyphthalocyanine was also applied to oxidize the ascorbic acid. The first step is the creation of a catalyst-oxygen complex and the limiting step is the reaction of dioxygen with the ascorbate monoanion (AH^-). The maximum rate (V_{\max}) of this reaction is obtained at the pH of about 6.5. Moreover, albumin (BSA) influences the reaction rate of oxidation of ascorbic acid catalyzed by CoPcOC. In the presence of proteins cobalt octacarboxyphthalocyanine loses its catalytic activity in this reaction.⁶⁶ In UV-vis absorption spectra no changes are observed which could indicate mutual CoPcOC-BSA interaction, however such an interaction can occur and not show in the absorption spectra. Moreover, an attempt has been made to identify the products of oxidation of ascorbic acid in the presence of CoPcOC and they are ascorbate radical (A^{\bullet}), hydroxyl radical (OH^{\bullet}) and hydrogen peroxide (H_2O_2).⁶⁷

Metallo-octacarboxyphthalocyanines (Fe, Mn, Co) can serve as catalysts in oxidizing 2,4,6-trichlorophenol (TCP) into compounds which could be less hazardous for the environment (mainly into formic or oxalic acid). FePcOC shows the strongest activity. Its activity in oxidative decomposition of TCP in an aqueous solution is little but its activity is exceptionally high in the presence of water-soluble cationic polymers which have pyridinium side chain. The presence of such a polymer improves solubility of phthalocyanine, creates a propitious micro environment which surrounds the phthalocyanine catalyst and also prevents the inactive aggregates.⁶⁸

Photochemical properties include singlet-oxygen quantum yield (Φ_A) and photodegradation, whereas photophysical properties include fluorescence lifetimes and triplet state quantum yields (Φ_T) and lifetimes (τ_T).³ The photochemical properties of phthalocyanines are tested in regard to their possible use in photodynamic therapy (PDT). Photodynamic therapy (PDT) is a very dynamically developing neoplasm treatment method which is a form of light therapy that incorporates visible light and a photosensitizer. The search for new photosensitizers with better clinical parameters imposed their classification into generations where every next one is better than the previous. Among the most promising second generation photosensitizers are phthalocyanines which contain diamagnetic metals such as zinc, aluminium, gallium or silicon into the phthalocyanine macrocycle. These complexes have long triplet lifetimes and high triplet state quantum yields, followed by oxygen quenching of their triplet states to produce singlet oxygen (1O_2), which is one of the reactive oxygen species, that has an important function in many photosensitization reactions *e.g.* in PDT.^{3,4,69,70} Thus, high triplet state quantum yields and lifetimes condition high singlet oxygen quantum yields. The triplet quantum yield and triplet

lifetimes of phthalocyanine determine its efficiency as a photosensitizer. Moreover, the efficacy of phthalocyanines complexes as PDT agents is due to their strong absorption in the phototherapeutic window (600–800 nm).⁷¹

The photophysical and photochemical parameters of metallo octacarboxyphthalocyanines are shown in Table 4. The values of fluorescence quantum yields are lower for the ZnPcOC complex than for the AlPcOC, yet triplet quantum yields values are higher for the zinc-complexed species than for the aluminum-complexed species. It is due to a stronger coupling with spin-orbit (SOC) caused by Zn(II) in comparison to Al(III) (Table 4). As far as the relative masses of the central metal ions are concerned, Zn(II) will lead to a stronger spin orbit coupling than Al(III), thereby increasing the possibility of the hitherto spin-forbidden transition and diminishing that for spin-allowed fluorescence. In turn shorter triplet lifetimes for ZnPcOC complex, as opposed to AlPcOC complex, can be explained by the fact that $S_1 \rightarrow T_1$ intersystem crossing is more promoted in the ZnPcOC should also suffice in clarifying the shorter triplet lifetimes of these complexes. High yields of the metastable excited state of the tested complexes make it possible for zinc and aluminum octacarboxyphthalocyanines to be used as photosensitizers in photodynamic therapy PDT.⁷²

MPc derivatives containing silicon or germanium metals present efficient intersystem crossing to the triplet state which results in high triplet state yields that are necessary for photosensitized reactions. The $(OH)_2GePcOC$ demonstrated high triplet quantum yields in comparison to Φ_T for $(OH)_2SiPcOC$. It is supposed on the basis of spin-orbit coupling because Ge (IV) as a heavier atom will cause a stronger SOC than Si (IV) by that increasing the probability of the spin-forbidden transition and reducing spin-allowed fluorescence. The triplet lifetimes of both octasubstituted complexes are long enough for photosensitized reactions to take place. Furthermore, the studied singlet oxygen quantum yields values of these germanium and silicon phthalocyanine complexes indicate that these complexes will be relevant for use in photochemical reactions requiring singlet oxygen such as PDT. Photophysical parameters for MPcOC complexes in DMSO are presented in Table 4. Germanium and silicon octacarboxyphthalocyanines show high yields of the metastable excited state and that should make them applicable in areas involving photosensitizers.⁷³ Gallium octacarboxyphthalocyanine $((OH)GaPcOC)$ is characterized also by a high triplet yield and a good solubility of this complex in aqueous solution is also an additional asset which according to the authors puts this compound into the group of promising photosensitizers.⁷⁴

Table 4. The photophysical and photochemical parameters for MPcOC complexes

Complex	Solvent	Φ_F^a	Φ_T	Φ_Δ	Φ_{IC}	τ_T (μs)	Refs.
ZnPcOC	water	0.23	0.50 ^b	0.32 ^c	-	160	45,46
	pH 10	0.18	0.48 ^b	0.52 ^d	0.34	130	3,47
	DMSO	0.24	0.62 ^e	-	0.14	480	72
AlPcOC	DMSO	0.44	0.34 ^e		0.22	1270	72
(OH)AlPcOC	DMSO	-	-	0.12	-	-	3
(OH)AlPcOC	DMSO	0.23	0.20 ^e	0.15 ^f	-	756	71
(OH) ₂ SiPcOC	water	0.27	0.32 ^{b,e}	0.12 ^{cf}	-	450	71,45,46
	pH 8.2	0.12	0.28 ^g	0.12 ^h	-	25	94
	pH 10	0.06	0.30 ^b	0.33 ^d	0.64	70	47
	DMSO	0.27	0.48 ^e	0.33 ⁱ	0.25	760	73
(OH) ₂ GePcOC	water	0.24	0.34 ^b	0.22 ^c	-	90	45,46
	DMSO	0.19	0.79 ^e	0.63 ⁱ	0.02	480	73
	water	0.13	0.62 ^b	0.31 ^c	-	240	45,46
OTiPcOC	pH 10	0.07	0.20 ^b	0.24 ^d	0.73	70	47
(OH)GaPcOC	pH 11	0.21	0.67 ^j	-	0.12	80	74

As standards the following were used:

^a ZnPc in DMSO, $\Phi_F = 0.2$.

^b ZnTSPc in aqueous solution; $\Phi_T^{Std} = 0.56$.

^c ZnPcS_{mix} in aqueous solution, $\Phi_\Delta^{Std} = 0.45$.

^d ZnTSPc in aqueous solution in the presence of Triton X, $\Phi_\Delta^{Std} = 0.3$.

^e ZnPc ($\Phi_T^{Std} = 0.65$ in DMSO); ^f ZnPc in DMSO ($\Phi_\Delta^{Std} = 0.67$) or AlPcS_{mix} in water ($\Phi_\Delta^{Std} = 0.34$).

^g AlPcS_{mix} in PBS ($\Phi_\Delta^{Std} = 0.44$); ^h AlPcS_{mix} in PBS ($\Phi_\Delta^{Std} = 0.34$); ⁱ ZnPc in DMSO ($\Phi_\Delta^{Std} = 0.67$).

^j ZnTSPc in aqueous solution, $\Phi_T^{Std} = 0.56$, ZnPc in DMSO, $\Phi_T^{Std} = 0.65$ and ZnPc in DMF $\Phi_T^{Std} = 0.58$.

The singlet-oxygen quantum yield by AlPcOC in a solution of pH=7.4 is much lower than of those presented in the studies for other monomeric aluminum phthalocyanines. Such a low singlet-oxygen quantum yield can be explained by the creation of some sort of associates which are not observed in the UV-Vis absorption spectra. These associates develop through hydrogen bonds between two axial hydroxyl ligands (Figure 4).⁷⁵

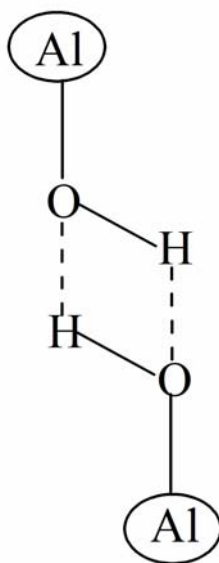


Figure 4. Proposed dimerization in (OH)AlPcOC.⁷⁵

The heavy atom effect as well as aggregation have an influence on the fluorescence quantum yields, Φ_F .³ The values of the fluorescence quantum yields diminish together with the rise of the atomic number of the central metal in octacarboxyphthalocyanine complexes and this is consistent with the strengths of spin-orbit coupling induced by the respective central metals based on their relative atomic numbers. A decrease in probability of fluorescence is a result of an increase in SO coupling. From the point of view of PDT therapy a photosensitizer should have the lowest possible fluorescence quantum yield which increases the probability of intersystem crossings and a result of more effective intersystem crossings is a higher triplet oxygen quantum yield.

The singlet oxygen quantum yields and lifetimes for respective metallo octacarboxyphthalocyanines are higher in DMSO than in water. This is connected to the fact that DMSO as an organic solvent prevents the process of aggregation. In photodynamic therapy, aggregation is a negative phenomenon, since it has an adverse effect on the physicochemical properties of photosensitizers and it decreases the singlet oxygen quantum yield which in turn causes a significant weakening of the cytotoxicity of the photosensitizer.^{43,76,77}

The degradation of phthalocyanine particles under the influence of radiation was studied because it makes it possible to determine the stability of these complexes.⁴⁶ During radiation, the (OH)₂SiPcOC complex was the least stable whereas aluminum octacarboxyphthalocyanine (OH)AlPcOC was the most stable. Low Φ_Δ values correspond with low values of (OH)AlPcOC and (OH)₂GePcOC photodegradation. This may have been possible due to the fact that photodegradation process is considered to be singlet oxygen mediated. Yet the (OH)₂SiPcOC

complex reacted differently because its photodegradation rate did not correlate with its singlet oxygen quantum yield.

ZnPcOC combinations with quantum dots (QDs) could be possible candidates to be used as photosensitizers in the photodynamic therapy PDT. They are a relatively new class of compound of unique properties and find use in many fields including applications for example in tagging of biological molecules, in light emitting diodes and in photodynamic therapy.⁷⁸ Greater ZnPcOC triplet lifetime values in the presence of QDs, correlates adequately with a reduction of ZnPcOC triplet quantum yield values in the presence of QDs. Idowu and Nyokong⁴⁵ described photophysical properties of Zn, Al, Si and Ge octacarboxyphthalocyanine complexes in the presence of water-soluble CdTe quantum dots capped with L-cysteine (QDs-CYS). In the presence of QDs-Cys there was an increase of triplet quantum yields and triplet lifetimes of the MPcOC in comparison to Pc without QDs (Table 5).⁴⁵

Table 5. The photophysical and photochemical parameters for MPcOC complexes in aqueous solution

Complex	Φ_F	Φ_T^b	Φ_Δ^c	τ_T (μ s)	Refs.
(OH)AlPcOC	0.27 ^a	0.32	0.12	450	71,45,46
(OH)AlPcOC + BSA ^d	0.25 ^a	0.28	0.29	580	46
(OH)AlPcOC-QDs	0.25 ^e	0.40	0.31	495	45
ZnPcOC	0.23 ^a	0.50	0.32	160	45,46
ZnPcOC + BSA ^d	0.21 ^a	0.43	0.40	280	46
ZnPcOC-QDs	0.21 ^e	0.55	0.60	190	45
(OH) ₂ Si PcOC	0.24 ^a	0.34	0.22	90	45,46
(OH) ₂ SiPcOC + BSA ^d	0.21 ^a	0.36	0.26	110	46
(OH) ₂ SiPcOC-QDs	0.18 ^e	0.32	0.21	130	45
(OH) ₂ GePcOC	0.13 ^a	0.62	0.31	240	45,46
(OH) ₂ GePcOC + BSA ^d	0.12 ^a	0.58	0.40	300	46
(OH) ₂ GePcOC-QDs	0.12 ^e	0.67	0.66	270	45

^a ZnPc in DMSO was used as a standard, $\Phi_F = 0.2$.

^b ZnTSPc in aqueous solution was used as a standard, $\Phi_T^{\text{Std}} = 0.56$.

^c ZnPcS_{mix} in aqueous solution was used as a standard, $\Phi_\Delta^{\text{Std}} = 0.45$.

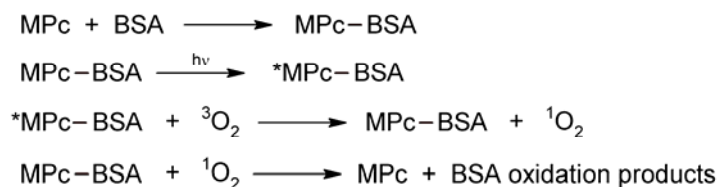
^d BSA:MPcOC (10:1).

^e Rhodamine 6G ($\Phi_F = 0.94$ in ethanol) and ZnPc ($\Phi_F = 0.2$ in DMSO) were employed as standards for QDs and MPcs, respectively.

A limitation of PDT therapy is usually too low selectivity of applied photosensitizers, so an effective transport of the medicine into neoplastic cells plays a significant role.^{79–81} Albumin has an important function in the transport of many exo- and endogenous ligands and in an effective

administration of medication. Due to the possibility of binding dyes, it increases the passive selectivity of photosensitizers through an increase in transmissivity and an effective administration of the medicine in the tumor. Thereupon it is vital for many drugs to bind with serum albumin since it can influence their location and fate in the human body.^{46,82-84} It seems that the destinations of dyes administered in such a way are directly the neoplastic cells.

By contrast, photosensitizers which are in unbound forms cause damage mainly to blood vessels surrounding the tumor.⁷⁹ MPcOC complexes interact strongly with albumin thus they can be easily transported in blood.⁴⁶ In case of germanium octacarboxyphthalocyanine, a bathochromic shift of the monomer band by 3 nm (from $\lambda_{\max} = 687$ nm to $\lambda_{\max} = 700$ nm) has been observed after adding albumin in comparison to the band of phthalocyanine itself and this means there was a binding between metallo phthalocyanine complex and albumin. Moreover, the studied phthalocyanines in the presence of albumin show a rise in the efficiency of singlet oxygen generation. Higher Φ_{Δ} values observed in the presence of albumin can result from an effective quenching of the triplet state by oxygen in the presence of bovine serum albumin (BSA), as a consequence of the enhanced lifetime of the MPcOC triplet state in the presence of BSA. In the presence of albumin metallo-phthalocyanine complexes showed also greater photodegradation. An increase in MPcOC photodegradation in the presence of albumin can be caused by the presence of oxidatively active products generated in the process of albumin photo-oxidation. The diagram of albumin photo-oxidation in the presence of metallo phthalocyanines can be presented as follows⁴⁶



Many drugs applied in the anticancer therapy use platinum complexes. Such a combination of photodynamic activity of phthalocyanine macro-ring and high efficiency of platinum complexes can lead to creation of new effective anticancer drugs.^{85,86} Covalent conjugates of aqua platinum(II) and octacarboxy-substituted ZnPc bearing one, two, three and four aqua platinum fragments have been studied for their potential of being used as sensitizers for PDT. The obtained conjugates show higher photostability in DMSO.⁸⁵ From the chosen photophysical parameters for (OH)AlPcOC(Pt)₃ and (OH)AlPcOC(Pt)₄ complexes and zinc octacarboxyphthalocyanine conjugated with platinum it is clear that they are better photosensitizers because of their higher triplet quantum yields than the complexes without platinum.^{71,85}

In photodynamic therapy PDT a selective accumulation of the photosensitizer in neoplastic cells is required. Many phthalocyanines which for example contain aluminum and zinc as central metals show a high fluorescence quantum yield and due to it the location and distribution of

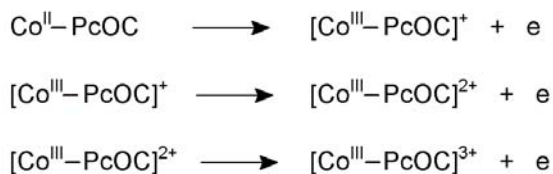
these complexes can be studied with the use of fluorescence imaging methods. Cobalt octacarboxyphthalocyanine is a compound with low fluorescence quantum yield and therefore Raman imaging was used to study the distribution of this compound in K562 cells. The research which was carried out showed that phthalocyanines were very locally present in the cell K562.⁸⁷

Aluminum and zinc octacarboxyphthalocyanines were used in the phototransition of 4-chlorophenol into benzoquinone.^{88,89} A significant activity, as far as 4-chlorophenol photo-oxidation is concerned, was not obtained for AlPcOC complex despite the fact that the compound did not occur in the solution (pH 10) as a monomer and it did not show significant degradation. This can be explained by the creation of a hydrogen bonding between the axial hydroxyl groups (Figure 4).⁷⁵ The zinc complex proved to be the best photocatalyst in this reaction however it undergoes degradation in time, especially the monomer band at λ_{max} 684nm, which is responsible for the activity of the photocatalyst.⁸⁸

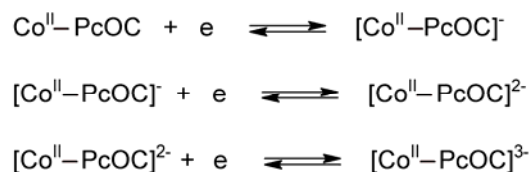
7. Electrochemical Properties

Many applications of metallo phthalocyanines are closely connected to their redox properties. A basic degree of oxidation of their molecules is -2 (Pc(-2)). The phthalocyanine ligand can be oxidized to Pc(-1) or Pc(0) or reduced in terms of electrons to Pc(-3); Pc(-4); Pc(-5); Pc(-6). Whereas centrally coordinated metal ion does not always show the ability to take part in redox processes. It can be observed in the case of *e.g.* most elements from the main groups and some transition elements such as Ni(II) or Cu(II). A metal atom can intercede in the redox processes. The ability of many metallo phthalocyanines to attach one or two axial ligands can have a significant effect on the redox properties of these compounds.⁴⁰

The redox properties of cobalt octacarboxyphthalocyanines were described by Sakamoto and Ohno.²⁴ Three cathodic and six anodic peaks were observed for this complex so three reversible reduction couples (-0.24 ; -0.66 ; -1.39V / vs. Ag/AgCl) and three irreversible oxidation pairs (1.06 ; 0.87 ; 0.67 V / vs. Ag/AgCl) occur. The following oxidation steps were proposed for CoPcOC.



and reduction steps



Whereas for CuPcOC two reversible reduction waves were obtained at $E_{1/2} = -0.91$ and -1.26 V and one reversible oxidative wave at $E_{1/2} = 0.64$ V. The half potentials for ZnPcOC are respectively; -0.81 ; -1.18 ; -1.83 and $+0.56$ V/ vs. ferrocene/ferrocenium.³¹ The presence of electron-withdrawing substituents in benzene rings decreases the density of the charge in the phthalocyanine ring thus the reduction potential shifts to more positive potential in comparison to uncarboxylated phthalocyanine.

The properties of redox-active self-assembled molecular films of novel metallo octacarboxyphthalocyanine (MPcOC, M = Fe, Co and Mn) complexes integrated with cysteamine monolayer on gold electrodes via amide bonds were presented by Agboola and Ozoemena.⁹⁰ The obtained results show that the electron transfer rate constant depends indeed on the central metal in the complex of octacarboxyphthalocyanines (Co > Mn > Fe). A strong dependency on the pH of the solution was showed. When the pH of the solution increased from 2 to 11 clear changes in electron transport were seen, signified by increasing peak-to-peak separation potentials and resistance to charge transport. Octacarboxyphthalocyanine derivatives have been initially used in electrocatalytic analysis for detecting epinephrine (an important neurotransmitter). Initial results show that the complexes of octacarboxyphthalocyanines (especially FePcOC) are sensitive to electrooxidation of epinephrine and they could serve as efficient materials to generate electrochemical sensors in the analysis of epinephrine in the physiological pH. Au-cys-FePcOC qualifies to sensitive indication of epinephrine in the physiological pH (pH 7.4), with excellent sensitivity and very low limit of detection. This work shows that these electrodes have great promise for analytical applications to epinephrine analysis judging by the satisfactory sensitivity, limit of detection, diffusion coefficient and rate constant obtained.⁹¹

Cobalt octacarboxyphthalocyanine (CoPcOC), absorbed onto glassy carbon electrodes (GCE), can be used for the electrocatalytic detection of nitrite, L-cysteine and melatonin. Two redox reactions were observed for this complex in the buffer of pH=4: $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ ($E_{1/2}$ vs Ag/AgCl -0.30 V) and $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ ($E_{1/2}$ vs Ag/AgCl 0.30 V). It was observed that the more carboxylic substituents are attached to the ring the more difficult it is for reduction and easier for oxidation to take place. Cobalt octacarboxyphthalocyanines show good electrocatalytic properties in oxidation of both nitrite and melatonin.⁹²

8. Conclusions

This review article concerning metallo and metal-free 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines reports on the different methods of synthesis of these complexes. It seems that the choice of the appropriate method largely depends on the type of metal. It is vital to sustain appropriate anaerobic conditions and temperature during alkaline hydrolysis of octacyano and imide derivatives to appropriate octacarboxyphthalocyanines. Octacarboxyphthalocyanines of some metals, *e.g.* copper, cobalt, show a high chemical and thermal stability whereas others *e.g.* zinc or metal-free octacarboxyphthalocyanines are relatively less stable compounds. These complexes are soluble in aqueous solutions of pH >7 which is beneficial as far as application of these complexes in biological research is concerned. These complexes show a tendency to aggregate in solutions; however, the appropriate selection of physicochemical conditions enables the occurrence of the appropriate form *e.g.* monomer, dimer or a higher aggregated compound. It seems that in the case of octacarboxyphthalocyanines forces connected to π - π interactions dominate in the aggregated compounds which leads to stacking structures of aggregated compounds and the effect of interaction through the hydrogen group –COOH can be treated as insignificant. Metallo octacarboxyphthalocyanines can be used as photosensitizers in PDT research (zinc, aluminum, gallium complexes); electrocatalysts in many reactions (*e.g.* cobalt, iron complexes).

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Authors' Biographies



Joanna Nackiewicz is a graduate of the Faculty of Mathematics, Physics and Chemistry of Opole University, from which she also took her Ph.D. degree. Currently she works as lecturer in the Division of Physical Chemistry and Molecular Modelling, O.U. Her scientific interests are related to metallo octacarboxylphthalocyanine synthesis and studies of their aggregation.



Marta Kliber, M.Sc. is a graduate of the Faculty of Chemistry of Opole University. Currently she is a Ph.D. student of the Environmental Doctoral Studies of the Opole University and the Wroclaw University of Technology. Research for her Ph.D. studies is currently carried out in the Division of Physical Chemistry and Molecular Modeling, O.U. Her scientific interests are

focused on studies of phthalocyanines, mostly regarding the possibility of their application in photodynamic therapy (PDT).