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Zinc Carboxyphthalocyanines: Synthesis, Properties, Photocatalysis

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Approaches of synthesis of zinc phthalocyanines substituted with different (eight, four and two) numbers of carboxylic groups in the macrocycle are summarized. The influence of structural factors on their physicochemical, photochemical properties and aggregation of differently ionized forms, as well as their functioning in diverse photocatalytic systems has been reported.

Keywords: Zinc carboxyphthalocyanine, synthesis, ionization, aggregation, photochemistry, photocatalysis.

Карбоксифталоцианины цинка: синтез, свойства, фотокатализ

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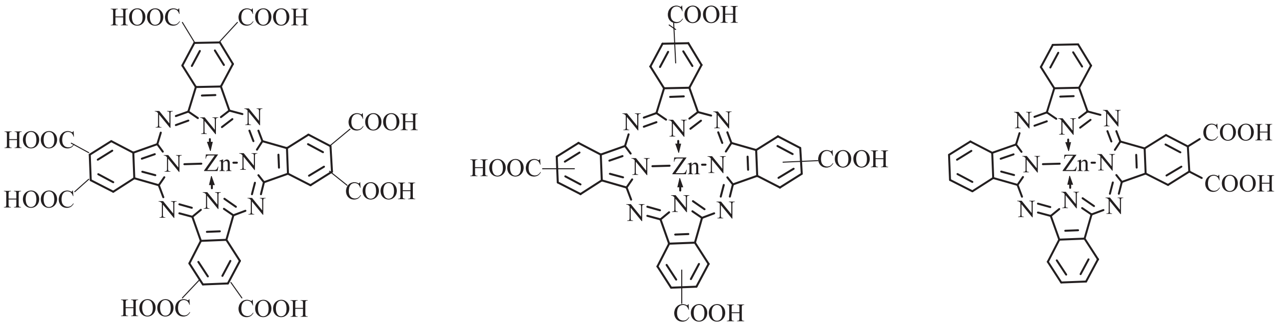
Обобщены подходы к синтезу карбоксизамещенных фталоцианинов цинка с различным (окта-, тетра- и ди-) количеством карбоксильных групп в макроцикле. Рассмотрено влияние структурных факторов на физико-химические и агрегационные свойства их карбокси- (кислотных) и карбоксилатных форм, а также функционирование карбоксифталоцианинов цинка в различных фотокаталитических системах.

Ключевые слова: Карбоксифталоцианин цинка, синтез, ионизация, агрегация, фотохимия, фотокатализ.

Introduction

Phthalocyanines substituted with carboxylic groups have been intensively investigated due to potential use in diverse applications.[1,2] Thus, for example, in form of water-soluble alkali salts they represent interest as photosensitizers for photodynamic therapy, for catalytic therapy of cancer,[3-6] catalysis and photocatalysis of different reactions in organic synthesis.[7-9] The corresponding acids are used for TiO_2 sensitization to the visible region of the spectrum – for photocatalytic water treatment from organic pollutants[10] and in dye-sensitized solar cells.[11,12]

Zinc complexes of phthalocyanine carboxylic acids are of particular interest. Zinc phthalocyanine and its derivatives have high triplet state quantum yields and long triplet lifetimes, which are required for efficient photochemical activity, including function in processes of TiO_2 photosensitization and singlet oxygen ($^1O_2$) generation. There are many studies on the synthesis and investigation of various zinc carboxyphthalocyanines (CZnPc), containing also other



OCZnPc TCZnPc DCZnPc

Figure 1. Structure of zinc carboxyphthalocyanines.

substituents,[12,13] however, systematic analysis of the impact of structural factors on the physicochemical and aggregation properties of CZnPc with different positions of functional groups was not carried out.

In this paper, we report on the study of zinc phthalocyanines substituted with different (2, 4, 8) numbers of carboxylic groups in macrocycle: symmetrical zinc octa-4,5-carboxyphthalocyanine (OCZnPc), zinc tetra-4(5)-carboxyphthalocyanine (TCZnPc, mixture of position isomers) and zinc unsymmetrical di-4,5-carboxyphthalocyanine (DCZnPc) (Figure 1). The most studied in this series is OCZnPc, having due to eight polar carboxylic groups the highest solubility, especially in aqueous alkaline solutions.[14-17] Aggregation, some photophysical and photochemical properties of TCZnPc were reported recently.[4] Properties of unsymmetrical DCZnPc were investigated by us in this work for the first time.

The present paper is a mini review of our recent, mostly unpublished or published in hardly accessible sources, works on the synthesis of CZnPc with different numbers of carboxylic groups in the macrocycle, studies of physicochemical and photochemical properties of their ionized (carboxylate) and unionized (acid) forms, as well as studies of the CZnPc potential as photocatalysts in various processes.

The history of synthesis of zinc carboxyphthalocyanines

The works on the synthesis of phthalocyanines containing in macrocycle carboxylic groups, appeared in 70-ies of the last century. The first information on phthalocyanine carboxylic acids and their functional derivatives is reflected mainly in the patent literature. Their physicochemical properties, including spectral characteristics, were absent, except for the work of Gaspard *et al.* who have studied the spectra of protonated forms of copper tetra-4-carboxyphthalocyanine in sulfuric acid.[18]

The symmetric metal complexes of octa-4,5-carboxyphthalocyanine, including zinc (OCZnPc), the sodium salts of which are easily soluble in water, are of particular interest. These compounds have been prepared by melting pyromellitic acid, its dianhydride or diimide with urea and metals or their salts in the presence of catalysts with subsequent saponification of formed tetraimides.[19-21] A significant disadvantage of this method is formation along with monomer OCMPcs of their dimers and oligomers, involving common benzene fragments. Monomeric OCZnPc was prepared by Wöhrle *et al.* from pyromellitonitrile[22,23] and, later, by us – by interaction of pyromellitic dianhydride with urea and anhydrous zinc acetate in the presence of ammonium molybdate as catalyst in 1-bromonaphthalene with subsequent hydrolysis of imide groups in reaction products.[3,24] For removal of admixtures of corresponding oligomers the purification was carried out by chromatography of aqueous solution of sodium salts on alumina using phosphate buffer as eluent. The approaches to preparation of pure OCMPcs are detailed in the review.[14]

Synthesis of OCMPcs using 4,5-*bis*(alkoxycarbonyl) phthalonitriles as starting compounds is of special interest. We have developed two new synthetic methods of dialkyl 4,5-dicyanophthalates from pyromellitic dianhydride without the use of toxic catalysts.[25-27] The methods of OCZnPc synthesis were also developed using the interaction of 4,5-*bis*(ethoxycarbonyl)phthalonitrile and metal salts in solvents (hexanol or diglyme). Despite the multistage, this method allows preparation of OCMPc with a higher yield. So, the total output for OCZnPc per pyromellitic anhydride amounted to ~ 30 %[13] that fourfold exceeds the yield, obtained directly from pyromellitic anhydride.[3]

The synthesis of TCZnPc does not represent special complexity. It is usually derived from available trimellitic acid or its anhydride by melting with excess urea in the presence of zinc salts in high-boiling solvents following by hydrolysis of the amide groups.[28-30] TCZnPc is a mixture of isomers with different position of carboxyl groups in macrocycle.

DCZnPc refers to the much less accessible non-symmetric 4,5-dicarboxyphthalocyanine of A_3B type. Interest in this group of compounds has increased dramatically in the past two decades owing to their research in solar cells as sensitizers of titanium dioxide to the visible region of the spectrum.[11,12] For this purpose various zinc 4,5-dicarboxyphthalocyanines have been synthesized with sterically hindered electron-donating substituents facilitating electron phototransfer from phthalocyanine into the conduction band of the semiconductor. However, disubstituted DCZnPc has not been yet described. It was recently synthesized by us by statistical condensation of unsubstituted phthalonitrile with 4,5-*bis*(hexoxycarbonyl)phthalonitrile in hexanol, chromatographic isolation of zinc 4,5-*bis*(hexoxycarbonyl) phthalocyanine with further hydrolysis of the ester groups.[31]

Acid forms of carboxyphthalocyanines

Carboxyphthalocyanines in acid form are soluble in aprotic polar solvents, such as dimethylformamide, dimethylsulfoxide (DMSO), *N*-methylpyrrolidone. The UV-Vis spectra of OCZnPc, TCZnPc and DCZnPc acids in DMSO are typical for phthalocyanines and have two main bands, corresponding to π-π^* electronic transitions – Q and Soret bands with maxima in the 670–700 nm and 340–350 nm regions, correspondingly (in the Figure 2 they are shown in comparison with spectrum of unsubstituted ZnPc). One can see (Figure 2) that spectra of CZnPc acids in DMSO are typical for monomeric species – narrow intense Q_{0-0}-band accompanied with well resolved vibrational satellites. Q_{0-0}-bands of symmetrical OCZnPc and ZnPc also are symmetric and have one maximum unlike to split ones for unsymmetrical DCZnPc and TCZnPc. Spectral and photochemical characteristics for acid forms of CZnPc in DMSO are summarized in Table 1, from which it follows, that the increase in the number of carboxyl groups in the molecule leads to the red shift of Q_{0-0}-band – on 15 and 10 nm when going from DCZnPc to TCZnPc and from TCZnPc to OCZnPc, accordingly. The molar extinction coefficients for OCZnPc and DCZnPc as individual compounds are 170000–190000 $M^{-1}\cdot cm^{-1}$. TCZnPc has a much lower ε_{max}=67000 $M^{-1}\cdot cm^{-1}$, which value is well consistent with ε_{max}=54700 $M^{-1}\cdot cm^{-1}$, obtained recently for this compound in the work.[4]

The fluorescence peaks of investigated CZnPc in DMSO are red shifted from the corresponding absorption maximum (Table 1) with Stokes shift of 5–10 nm being typical for phthalocyanines. The measured fluorescence quantum yields (Φ^{fl}) in DMSO for OCZnPc and DCZnPc (0.24 and 0.21, correspondingly) are close to reported for unsubstituted ZnPc (0.20[34]), whereas the fluorescence intensity of a mixture of position isomers TCZnPc is twice less (Table 1).

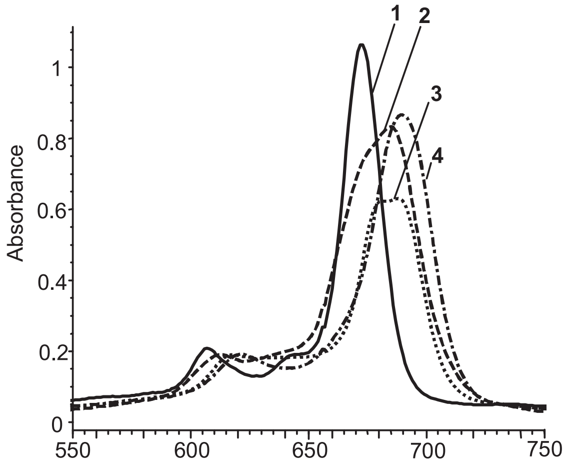


Figure 2. UV-Vis spectra of ZnPc (1), DCZnPc (2), TCZnPc (3) and OCZnPc (4) in DMSO.

The $^1O_2$ quantum yields (Φ_Δ) were obtained in DMSO using the 1,3-diphenylisobenzofuran (DPBF) chemical trapping method, and for OCZnPc and TCZnPc within the accuracy of measurements well coincided with literature data given in Table 1. The value of Φ_Δ=0.56 for DCZnPc was obtained in this work for the first time. In general, all CZnPc in DMSO efficiently, with close Φ_Δ values, generate $^1O_2$ and can be used as sensitizers of its formation.

All of the investigated compounds in aerated DMSO solutions undergo photobleaching upon excitation in the Q-band region, apparently due to oxidative photodegradation of the phthalocyanine ring.[35,36] The photodegradation quantum yields (Φ_d) for CZnPc are about 10^{-6} in aerated DMSO (Table 1), demonstrating their rather high photostability in this solvent. It should be noted that Φ_d values obtained in this study are very close to the Φ_d=1.3·10^{-6} value, reported by us previously for tetra-*tert*-butyl substituted PcZn with laser excitation in DMSO.[37] The Φ_d values for ZnPc derivatives are several orders of magnitude lower in DMSO than in non-coordinating solvents, since coordination of the metal center by DMSO shields the PcZn chromophore from interaction with oxygen.

Carboxyphthalocyanines in acid form exist in water at $pH < 4$.[16] Because of hydrophilic character of unionized carboxyl groups it was reasonable to expect that they are able to ensure CZnPc solubility in water. However, it was found that none of the studied compounds dissolves in water at $pH<4$ at least as aggregates, even OCZnPc with eight hydrophilic unionized carboxyl groups in molecule. Apparently, π-π interactions of neighboring flat aromatic phthalocyanine molecules result in their aggregation. The hydrogen bonds between carboxyl groups of the adjacent molecules also ought to be taken into account.

Solubility and aggregation of zinc carboxyphthalocyanines in carboxylate form

Sodium salts of CZnPc (in carboxylate, fully ionized form) do not dissolve in organic solvents, but they are soluble in water at $pH > 7$.[16] Electronic absorption spectra of OCZnPc, TCZnPc and DCZnPc in alkaline water solutions are shown in Figure 3.

The data of Figure 3 clearly demonstrate that under full ionization of the carboxyl groups the true solutions of the monomers can be obtained only for OCZnPc. Thus, spectra of OCPcZn have narrow and intense Q-band, inher-

Table 1. Spectral and photochemical* parameters of CZnPc in DMSO.

Compound	λ_{max}, nm	ε_{max}, $M^{-1}\cdot cm^{-1}$	λ_{max}^{fl}, nm	Φ^{fl}	Φ_d	Φ_Δ
OCZnPc	698[32]	190000[32]	708[33]	0.24[33]	1.8·10^{-6} [32]	0.56[32]
TCZnPc	690, 682	67000	697[4]	0.11[4]	1.1·10^{-6} [4]	0.62[4]
DCZnPc	685, 677	170000	690	0.21	0.6·10^{-6}	0.56

*Φ^{fl}, Φ_d and Φ_Δ are the fluorescence, photobleaching and $^1O_2$ quantum yields, correspondingly.

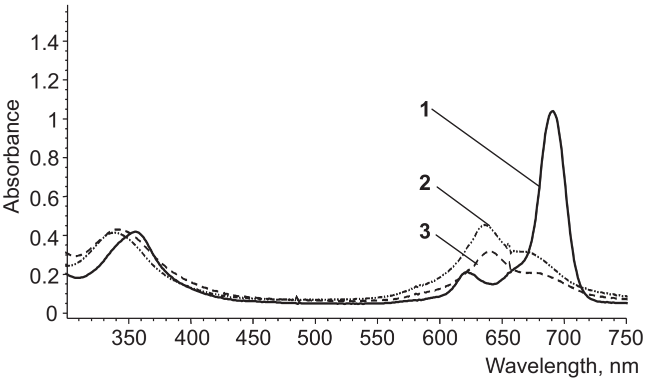


Figure 3. UV-Vis spectra of OCZnPc (1), DCZnPc (2) and TCZnPc (3) in alkaline water solution at p*H*=11.

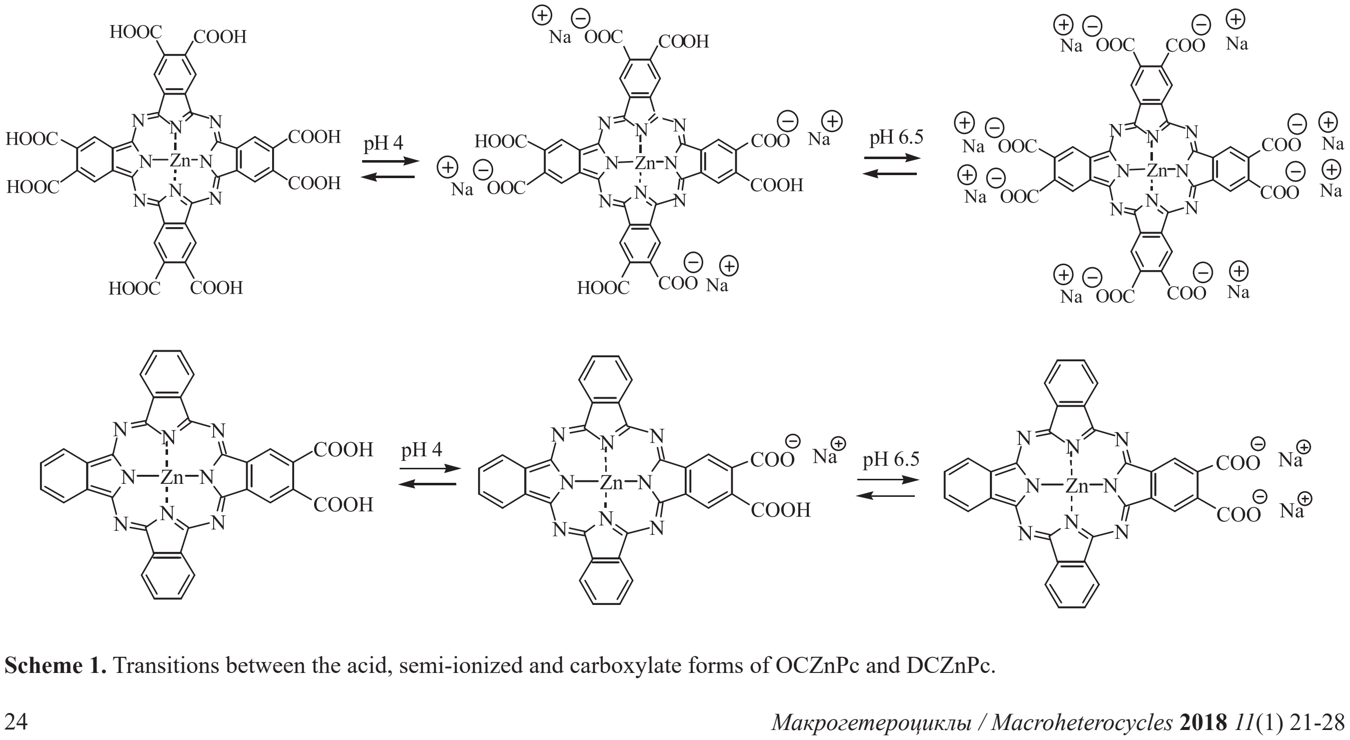
ent in monomeric state. In spite of full at p*H*=11 carboxyl group ionization, spectra of TCZnPc and DCZnPc in these conditions exhibit presence of characteristic broad band with a maximum in the region of 630–640 nm, indicative the aggregation to dimers.[14] It is well known that the dimers are photochemically inactive due to rapid deactivation of the excitation energy. For this reason, TCZnPc and DCZnPc in aqueous media have a high resistance to irradiation and do not generate $^1O_2$. Monomeric in alkaline water solutions ionized OCZnPc generates $^1O_2$ with quantum yield 0.57.[16] Under Q-band excitation, the photobleaching of OCZnPc carboxylate occurs with quantum yield about $1\cdot10^{-4}$. Dependence of the photobleaching rate upon p*H* in the 7–12 p*H* range was not found.[16]

Zinc carboxyphthalocyanines in semi-ionized form

Earlier,[16] we have found for OCMPc that ionization of two adjacent carboxyl groups, connected with the same benzene ring of macrocycle, occurs in two steps due to mutual acceptor impact. One carboxyl group is protonated – deprotonated within 5–6, and another – within 3.5–4 p*H* range with predominant existence of octaanion, intermediate semi-ionized tetraanion and neutral acid at p*H* > 7, about 5 and < 4, respectively. Among CZnPc under investigation the formation of semi-ionized form is possible only for OCZnPc and DCZnPc (Scheme 1); their solubility and aggregation we have studied in the present work.

Electronic absorption spectrum of OCZnPc at p*H*>7 has the intensive $Q_{0\text{-}0}$-band of monomeric octacarboxylate species. Titration of this solution by HCl to semi-ionized tetracarboxylate form (p*H*=5[16]) results at p*H* about 6.5 in the decrease of absorbance and replacement of narrow and intensive $Q_{0\text{-}0}$-band by the broad band of dimers. Thus, tetraanion of OCZnPc in aqueous solution exists in the form of soluble dimers. With the further decrease of the p*H* to <4 the sedimentation of higher aggregates of unionized OCZnPc acid was observed. In the case of DCZnPc, spectrum did not change and was typical of the dimers throughout the whole p*H* range from 11 to about 4. It was found that dimers of dianionic DCZnPc are water soluble, those of monoanionic species (at p*H* 5) are marginally soluble. At p*H*<4 neutral DCZnPc acid precipitated.

TCZnPc behaves differently. During the titration with acid of alkaline water solution (p*H* 10–11) of his fully ionized dimers already at p*H*=5, when semi-ionized DCZnPc and OCZnPc still are in solution, the sedimentation of TCZnPc was observed. These results indicate that transition of TCZnPc tetraanion to unionized acid form occurs at p*H*>5. Indeed, the presence of the adjacent acceptor carboxyl group in DCZnPc and OCZnPc increases the acidity of the carboxyl group as compared to that of TCZnPc without such substituent. On the other hand, in semi-ionized DCZnPc and OCZnPc, neighboring carboxylate (COO^-) group as a donor weakens the acid strength of other. Hence it follows that, if OCZnPc and DCZnPc ionize in two steps (at p*H*~4 and 6.5), the transition between the TCZnPc acid form and tetraanion is at intermediate p*H* (in 5–6 p*H* region), resulting in its full deposition from solution at p*H* 5.



Scheme 1. Transitions between the acid, semi-ionized and carboxylate forms of OCZnPc and DCZnPc.

Photocatalysis with zinc carboxyphthalocyanines

Thanks to the availability and photophysical and physicochemical properties of CZnPc, they are widely researched in the photocatalytic systems of interest for decisions both of purely theoretical tasks, such as modeling of selected stages of plant photosynthesis, as well as for practical use in the power engineering, ecology, medicine and chemical technology. Regarding the principal functioning mechanism these catalytic systems are divided into two groups. The first group consists of photocatalysts of electron transfer from donor to acceptor, the second one – of $^1O_2$ photosensitizers, where CZnPc function is to transfer the absorbed excitation energy to molecular oxygen with the formation of $^1O_2$. The examples of both types of photocatalytic systems are presented below.

The sensitized by OCMPc reduction of methylviologen and tetrazolium salts

Photocatalysis of electron transfer from donor to acceptor was thoroughly investigated in model reactions of methylviologen photoreduction sensitized by substituted ZnPc.[37] It was shown that there is a strong dependence of the sensitizer efficiency on the nature of the substituents, determining both redox and photophysical properties of molecule, with maximum activity found in compounds with neutral substituents containing heavy atoms (zinc tetra-3-phenylthiophthalocyanine).

As part of this work methylviologen diboron fluoride (MV^{2+}) and *p*-nitrotetrazolium chloride (NTC^{2+}) were used as the acceptor in anaerobic process of their reduction with triethanolamine in order to determine the possibility of usage and assess the efficiency of OCZnPc as a sensitizer of electron phototransfer. Irradiation in argon by LED (664 nm) of solution containing OCZnPc ($5\cdot10^{-6}$ M), MV^{2+} ($1\cdot10^{-4}$ M) and triethanolamine (0.1 M) for 20 min led to the formation of methylviologen reduced form, identified in accordance with[37] by intense (A=1.49, l=1 cm) absorption at 399 nm. After the termination of the irradiation the spectrum was restored to its initial state. In the absence of MV^{2+} or triethanolamine these changes do not take place. When using cation NTC^{2+} instead of MV^{2+}, the reaction mixture remained stable after irradiation.

In spectrum of irradiated by LED during 15 min solution containing OCZnPc ($5\cdot10^{-6}$ M), NTC^{2+} ($6\cdot10^{-5}$ M) and triethanolamine (0.1 M) the absorption bands emerged in the red (λ=630 nm) and blue (λ=450 nm) spectral regions due to formation of various forms of formazane.[38] Similar bands have been observed in the product of NTC^{2+} reduction with hydrazine hydrate. In a row of OCMPcs (M=Ni, Pd, AlOH, Zn) OCZnPc has proven to be the most active in the electron transfer process from donor to acceptor, while nickel complex showed practically no activity.

The sensitized by OCMPc charge separation in high energy-gap semiconductors with the generation of reactive oxygen species

This type of photocatalysts such as TiO_2 sensitized by carboxyphthalocyanines was investigated earlier.[10,39] When TiO_2 is sensitized with a dye, the sensitizer absorbs photons followed by electron injection to semiconductor conduction band. As a result phthalocyanine transforms into a cation-radical and the injected in semiconductor electrons diffuse to the surface of TiO_2 particles where they interact with adsorbed O_2 with the formation of such oxidants as superoxide ion $O_2^{\bullet-}$ and radical $OH^{\bullet}$ (review[39] and references therein). Phthalocyanine cation-radical can also oxidize substrates with suitable redox potential with dye regeneration. It was shown[10] that the use of such systems can clear for two hours under visible light the water from such persistent pollutants as 4-chlorophenol, chlorobenzene, 1,2,4-trichlorobenzene. TiO_2 sensitized by TCZnPc is also effective in degradation under the visible light of phenol pollution in water.[39]

The sensitized by CMPc charge separation in high energy-gap semiconductors for solar cells

Carboxyphthalocyanines are among the most promising sensitizers of TiO_2 in DSSC type solar cells (dye-sensitized solar cells).[40,41] The photoanode consists here of a glass with a conductive layer, on which is a thin layer of dye-sensitized TiO_2. The cell is fulfilled with a liquid electrolyte with a redox mediator, I^-/I_3^-, and contains a counter electrode (cathode). The excited dye injects an electron into the TiO_2 and farther to conductive layer and external circuit. Oxidized sensitizer molecule is regenerated *via* reduction by mediator. Diffusion of the oxidized form of the mediator through electrolyte to the cathode completes the circuit. OCZnPcs meet the key requirements to photosensitizers for solar cells, the main of which are the effective absorption in the area of maximum solar radiation, presence of groups, linking sensitizer to TiO_2, and the long lifetimes of excited states.

To study the relative efficacy of CZnPc functioning in solar cells we have constructed according to instructions[42] the experimental solar cells and measured their characteristics – short-circuit current and open circuit voltage (Table 2). The modification of TiO_2 with CZnPcs was produced by their adsorption from alcohol solution in the presence of coadsorbate (3α,7α-dihydroxy-5β-cholic acid), reducing aggregation of dye.

Modified with CZnPc layers of TiO_2 fully absorb light in the areas around 400 nm and 600–700 nm (Figure 4). The main maximum in long wavelength range testifies to the presence of sensitizer in the monomer form that is most promising for efficient electron transfer.

Table 2. Characteristics of solar cells with CZnPc sensitizers, obtained under the solar irradiation during summer in Moscow region.

Sensitizer	TiO_2 layer thickness, μm	I sh.-circ., mA/cm^2	U open circuit, mV
DCZnPc	12	2.4	408
TCZnPc	10	0.18	300
OCZnPc	12	0.70	200

The shown experimental material (Table 2) suggests that presence of two carboxyl groups directly bound to the same benzene ring of phthalocyanine macrocycle

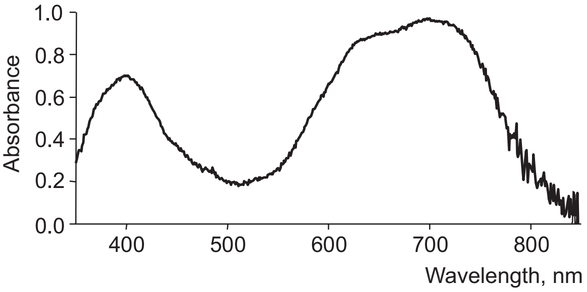


Figure 4. Absorption spectrum of TiO_2 modified with DCZnPc by adsorption from $2\cdot10^{-4}$ M alcohol solution containing $2\cdot10^{-4}$ M 3α,7α-dihydroxy-5β-cholic acid (obtained as the difference spectra of TiO_2 reflection before and after application of sensitizer).

allows achieving the best characteristics of solar cell. Asymmetric configuration provides the necessary orientation of the dye relatively to TiO_2 surface and efficient electron transfer from excited sensitizer molecule into TiO_2 conduction band.[40] TCZnPc and OCZnPc are flat on TiO_2 surface that is unfavorable for electron transfer. It should also be noted that our testing in solar cells of aluminum and silicon OCMPcs as TiO_2 sensitizers revealed their much lower efficiency in comparison with OCZnPc.

CZnPcs as sensitizers of singlet oxygen generation

Reviewed in physicochemical part of this work ability of CZnPc to efficient sensitization of $^1O_2$ generation had served as a basis for their studies in systems where oxidizing properties of $^1O_2$ are of principal importance.

1. Photodynamic therapy (PDT) of cancer

Owing to its efficient generation of $^1O_2$, OCZnPc in the form of sodium salt turned out to be[3] promising photosensitizer for PDT. Proposed in patent[3] photosensitizers OCZnPc and OCAlPc, in addition, have increased selectivity of accumulation in tumor tissue, not inferior to analogs in the effectiveness of PDT.

Photodynamic activity of TCZnPc was demonstrated recently[4] on photooxidation of bovine serum albumin and photo hemolysis of erythrocyte membranes. Despite the fact that TCZnPc is hydrophilic and therefore has a low affinity to membranes, it caused their considerable damage. TCZnPc showed the greatest activity in comparison with non-metal TCH_2Pc and its aluminum complex. The quantum yields of fluorescence, triplet excited states and $^1O_2$ generation clearly demonstrate the potential for its application both for photodiagnostics and PDT.[4]

2. Photocatalytic water purification from toxic organic contaminants

OCZnPc and OCAlPc have been investigated as sensitizers of 4-chlorophenol photooxidation into benzoquinone[7] and of 4-nitrophenol into hydroquinone and 4-nitrocatechol.[43] It has been shown that the rate of photooxidation corresponds to efficacy of photosensitizer in $^1O_2$ generation. Zinc complex showed better activity in this reaction compared to aluminum one, but OCZnPc is subjected to photodegradation.

As an example of a heterogeneous system can also serve immobilized on amberlite IRA 400 carboxysubstituted ZnPc which was tested with a positive result in oxidative degradation of phenols.[44]

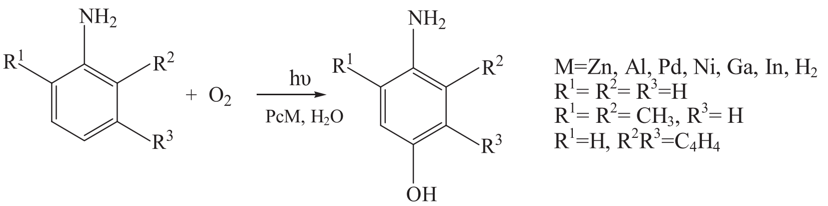
3. The sensitized by OCMPc oxidation of aromatic amines by oxygen

A few years ago, we have first shown that substituted ZnPc and some other MPc are efficient photocatalysts of *para*-hydroxylation by oxygen of aromatic amines of benzene and naphthalene series.[8,9,45] Selectivity of *p*-aminophenols formation in this process is not less than 80 %, and at heterogenization of MPc on mineral carriers and some organic polymers turnover of catalysts exceeds 25000. Special test experiments have shown $^1O_2$ to be oxidizing agent in these processes.

Accordingly, in the present work OCZnPc was investigated as a sensitizer of photooxidation of aromatic amines (aniline, 2,6-xylidine and 1-naphthylamine – Scheme 2) both in solution and adsorbed on the surface of the aminopropylated silica gel (NH_2-SiO_2).

Photooxidation of aromatic amines in solution or in the presence of sensitizers, heterogenized on NH_2-SiO_2, was conducted in a glass reactor with constant stirring and the saturation of the reaction mixture with oxygen. As light sources four LEDs (λ=664 nm) with a capacity of 0.2 W each were used. At regular intervals reaction mixture was sampled, substrate conversion and output of products were determined by HPLC method. The main product of amine oxidation is the corresponding *p*-aminophenol, which selectivity exceeds 80 %.

Kinetic curves of oxidation obey first order equation, at least up to 60 % of amine conversion. The first-order rate constant of 1-naphthylamine oxidation in OCZnPc solution was estimated to be 0.361 min^{-1}. This value exceeded the corresponding values for other OCMPc (M=Ga, Pd, Al, In) which were equal to 0.197, 0.181, 0.111 and 0.078, accordingly. High photocatalytic activity of OCZnPc as compared to other OCMPc is due to the high quantum



Scheme 2. Photooxidation of aromatic amines into *p*-aminophenols.

yield of $^1O_2$ generation and exclusive monomeric state in solution.

Photooxidation rate constant values (k) of different substrates in the presence of OCZnPc are equal for aniline, 2,6-xylidine and 1-naphthylamine to 0.014, 0.019 and 0.361 min^{-1}, respectively. The obtained k values show that the introduction in aniline ring of two methyl groups leads only to a slight increase of reaction rate, whereas expansion of π-conjugation when going from benzene to naphthalene is accompanied by a significant acceleration of substrate photooxidation. These facts are consistent with the electrophilic nature of $^1O_2$ as main oxidizing agent.

Usage of OCMPc/NH_2-SiO_2 led to a decrease of oxidation rate due to the aggregation of OCMPc on the carrier surface, but in this case OCZnPc was also the most active.

Conclusions

The methods of synthesis of CZnPc with a different number of carboxylic groups in the macrocycle – octa-, tetra- and dicarboxy substituted ones – are reviewed.

The influence of structural factors on physicochemical and aggregative properties of CZnPc in various ionization forms has been studied.

It was found that CZnPc in acidic form can be used effectively as sensitizers of $^1O_2$ generation and electron phototransfer reactions in aprotic polar solvents regardless of the degree of substitution, while OCZnPc – also in aqueous solution at p$H>6.5$.

The heterogenization of CZnPc on carrier by adsorption from solution gives stable in the water at p$H<4$ systems with potential as heterogeneous catalysts and photocatalysts, while its chemical grafting to carrier allows preparation of heterogeneous systems, stable in solution for the entire p*H* range.

The functioning of various CZnPc in photocatalytic systems is discussed. Their potential is demonstrated in modeling of selected stages of plant photosynthesis, as well as for practical usage in power engineering, ecology, medicine and chemical technology.

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